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Thermal Cracking of Light Hydrocarbons and Their Mixtures

The kinetics and product distributions of the thermal cracking of binary and ternary mixtures of ethane, propane, n- and i-butane were determined in a pilot plant under conditions of residence time, temperature, total pressure, and dilution as close as possible to those prevailing in industrial operation. The kinetics and yields observed with ternary mixtures were compared with those obtained with binary mixtures and with pure components. The experimental selectivities were compared with those which would be obtained from separate cracking and subsequent addition of the product streams. The deviations between the two can be predicted by means of the so-called global kinetics selectivities, which are based upon the selectivities obtained from the pure components cracking and upon the global rates of cracking of the feed components in the mixture.

The key feedstocks for the petrochemical industry are provided by the thermal cracking of hydrocarbons. The design of new plants and the analysis of existing units require basic information on the kinetics and on the product distribution obtained under varying operation conditions. So far, only fragmentary information is available. This paper focuses on the cracking of mixtures of light

tivities or yields obtained from mixtures requires a set of

rate equations accounting for the detailed radical reac-

tion mechanism. So far this approach, which leads to

serious computational problems, has not been applied

literature, is not adequate for the prediction of the prod-

uct distribution of mixtures cracking. It takes the selec-

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The simple additivity rule (5), used until now in the

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hydrocarbons in the C1-C4 range and particularly aims at providing the basis for deciding whether or not a gas mixture should be separated before cracking to optimize the yield pattern. Further, it investigates how far the cracking rates and the selectivities encountered in mixtures cracking can be predicted from information on the individual cracking of the feed components.

CONCLUSIONS AND SIGNIFICANCE

tivities obtained from the individual components at the desired mixture conversion. Obviously, these would have to be taken at the respective conversions of the feed components, which are generally not identical. These individual conversions can be predicted when the global kinetics of cracking of the components in the mixture are available. The selectivities predicted in this way are called in this paper selectivities based upon global kinetics, G.K.B. selectivities. Even these will not necessarly lead to a satisfactory prediction of the experimental values, since they do not completely account for the interaction between the reacting species. The following phenomenological rule, derived from the present work, may be of help in predicting the selectivities in a semiquantitative way: The selectivities obtained from mixtures cracking deviate from those based upon the additivity rule in the same direction as the G. K. B. selectivities.

to practical operating conditions.

F. Froment.

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Accurate overall kinetic equations and product distributions have been obtained for the cracking of a number of light hydrocarbons and their binary and ternary mixtures. Ethylene and propylene yields from mixtures cracking are compared with those that would be obtained from separate cracking. The rigorous prediction of the selecThe thermal cracking of hydrocarbons has been studied mainly in small scale equipment, often by means of static experiments. The main goal of these investigations was to come to some insight into the radical mechanism of the reaction. The equipment seldom permitted variation of the operating conditions over a range sufficiently wide to come to reliable practical correlations.

Several studies have been published on the thermal cracking on *n*-butane, most of which were carried out at low temperature and low total pressure (Sagert and Laidier, 1963; Torok and Sandler, 1969; Large et al., 1972). The order of the overall reaction is generally found to be 1.5. This value would result from a firstorder initiation producing two ethyl radicals and a termination also involving two ethyl radicals. The activation energy is of the order of 60 000 Kcal/Kmole and the frequency factor 10^{14} s⁻¹. At higher temperatures, Kupperman and Larson (1962) observed first-order kinetics and determined an activation energy of 52 000 Kcal/Kmole and a frequency factor of 1.7.1010. Illès (1969) found an order of 1.6 at 696°C and 1.2 at 802°C, at atmospheric pressure. When first-order kinetics are imposed, the rate coefficients were found to vary with the conversion according to a linear relation: $k = k_o - \beta x$.

The thermal cracking of *i*-butane was also mainly studied in the temperature range 500° to 600°C (Konar et al., 1967, 1968; Paul and Marek, 1934). The order was generally found to be 1; the activation energy varied between 63 500 and 66 000, and the frequency factor between $8 \cdot 10^{13}$ and $7.8 \cdot 10^{14}$. Buekens and Froment 1971 investigated the pyrolysis in a bench scale tubular reactor between 620° and 820° C at atmospheric pressure. They found an order of 1 and observed that the cracking was seriously inhibited by its products. The activation energy was 52 600 Kcal/Kmole. The inhibition was accounted for by a hyperbolic law mentioned later.

Illès (1972) has reported on the cracking of a mixture, 50/50 by weight, of *n*- and *i*-butane. He observed product yields which deviate from those calculated on the basis of a simple additivity rule.

The present paper reports on experiments carried out in a highly instrumented pilot plant, under conditions as close as possible to those prevailing in industry. The equipment permits substantial variation in residence time, temperature level, partial pressure of the hydrocarbon(s) at the inlet, and total pressure. The experimental program covered the cracking of *n*-butane and *i*-butane, of their mixtures, and of binary and ternary mixtures of ethane, propane, and *n*-butane.

PILOT PLANT DESCRIPTION

The pilot plant unit used for the experimental research has been represented schematically before (Van Damme and Froment, 1975). Only a brief description will be given here.

The furnace, built of silica/alumina brick (Li 23), is about 4 m long, 0.7 m wide, and 2.6 m high. It is fired by means of ninety premixed gas burners, mounted with automatic fire checks and arranged on the side walls in such a way as to provide a uniform distribution of heat. The fuel supply system comprises a combustion controller that regulates the ratio of fuel to air and the usual safety devices.

The furnace is divided into seven separate cells, which can be fired independently, to set in any type of temperature profile. Twenty-seven thermocouples are located along the reaction coil, thirteen for measurement of the reacting gas temperature and fourteen for the outside tube wall temperature. A few sampling tubes enable the analysis of the reacting gas at intermediate positions. The reaction section of the tube is about 21.75 m long, made of nickel chromium alloy (Alloy 800, Sandvik Sanicro 31), and has an internal diameter of 10 mm. These dimensions were chosen to achieve turbulent flow condition in the coil with reasonable feed rates.

The first cell generates the dilution steam, while the second preheats the incoming hydrocarbon. The latter is mixed with steam before it enters a mixing chamber which dampens the pressure fluctuations caused by the water pump. The mixture then flows through the reactor coil. The cracked products leaving the furnace are cooled by a spiral quench cooler. A fraction of the product gas mixture is then withdrawn for on-line analysis, while the rest is sent directly to the flare. Nitrogen injection at the reactor outlet provides an internal standard for the online chromatography and contributes to a certain extent to the quenching. The reactor products stream is analyzed by four on-line chromatographs. These chromatographs enable complete analyses of the product streams and complete overall material and carbon balances. The calculations are performed on line by means of a PDP-8E process computer with 16K core memory. Runs for which the carbon balances are off by more than 2% are rejected. Carbon disulfide was added to the water to prevent possible wall effects leading to excessive coke formation. The carbon disulfide concentration in water was 50 p.p.m.

EXPERIMENTAL PROGRAM

Thermal Cracking of n-Butane

The n-butane feed was high purity grade (Air Liquide CH25) and contained less than 0.2 wt % *i*-butane.

The ranges over which the process variables were varied were as follows:

Variable	Range
n-butane flow rate (kg/hr)	0.5-3
Dilution (kg steam/kg hydrocarbon)	0.4-3
Reynolds number	4 500-7 000
Exit temperature (°C)	650-850
Exit pressure (atm abs)	1.2-2.3
Pressure drop (atm)	0.3-0.5

The majority of the experiments, about 150, were grouped into four classes depending upon the partial and total pressure:

Exit pressure (atm abs)	Dilution (kg/kg)	Inlet partial pressure (atm)
1.4	0.4	1.2
1.4	1	0.8
2.0	0.4	1.4
2.0	1	1.0
	Exit pressure (atm abs) 1.4 1.4 2.0 2.0	Exit pressure (atm abs) Dilution (kg/kg) 1.4 0.4 1.4 1 2.0 0.4 2.0 1

To achieve low conversions, even at high temperatures, some

TABLE 1. COMPOSITION OF INVESTIGATED TERNARY MIXTURES, OF ETHANE, PROPANE, AND *n*-BUTANE

Ethane	Propane	<i>n</i> -butane (wt %)
10.80	10.86	78.33
11.40	77.30	10.86
20.81	67.00	11.65
30.63	11.00	58.32
32.09	29.98	37.73
32.20	39.40	28.11
41.39	37.53	20.78
42.23	18.40	39.35
70.61	18.45	10.93

TABLE 2. n-BUTANE CRACKING, CHROMATOGRAPHIC ANALYSIS

Chromatograph	Column material	Carrier gas/flow rate 1/hr	Dimensions, mm	Temp., °C	P roducts analyzed
1) Aerograph 202	Porapack N 80-100 mesh	H ₂ /3.6	$L = 1$ 500, $\phi = 6.3$	35	N ₂ , CH ₄ , C ₂ H ₄ , C ₂ H ₆
2) Packard 419	Durapack 80-100 mesh	H ₂ /3.6	$L = 2\ 000, \phi = 6.3$	35	N ₂ + CH ₄ , C ₂ H ₂ , C ₃ H ₈ , C ₃ H ₆ , <i>i</i> -C ₄ H ₁₀ , <i>n</i> -C ₄ H ₁₀ , 1-C ₄ H ₈ , 2-C ₄ H ₈ , 1,3 C ₄ H ₆
	Durapack <i>n</i> -octane 100-125 mesh				
3) PE 11	Porapack Q 80-100 mesh	N ₂ /2.5	$L = 3000, \phi = 3.2$	45	H ₂ , CH ₄
4) Varian 1200 FID	SE 30, 10% 80-100 mesh	N ₂ /1.5	$L = 3\ 600, \phi = 3.2$	20-130 20°/min	C4, C5, Benz, Tol, Xyl.

TABLE 3. i-BUTANE AND MIXTURES CRACKING, CHROMATOGRAPHIC ANALYSIS

Chromatograph	Column material	Carrier gas/flow rate 1/hr	Dimensions, mm	Temp., °C	Products analyzed
1) Aerograph 202	Polypropylene- carbonate 100-120 mesh +	H ₂ /6	$L = 8\ 000, \phi = 6.3$	40	$N_2 + CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6 + iC_4H_{10} + nC_4H_{10}, 1C_4H_8, trans 2C_4H_8, iC_4H_8 + 1,3C_4H_6, cis$
	Durapack phenyl- isocyanate 80-100 mesh		$L = 2\ 000, \phi = 6.3$		$2C_4H_8$
2) Packard 419	Durapack n-octane (porasil c) 100-125 mesh	H ₂ /3.6	$L = 4\ 000, \phi = 6.3$	10	N ₂ , CH ₄ , C ₂ H ₄ , C ₂ H ₆ + C ₂ H ₂ , C ₃ H ₈ + C ₃ H ₆ , propyne, propadieen, iC ₄ H ₁₀ , nC ₄ H ₁₀ , 1C ₄ H ₈ + iC ₄ H ₈ + trans 2C ₄ H ₈ , 1.3C ₄ H ₆ , cis 2C ₄ H ₈
3) PE 11	Porapack Q 80-100 mesh	$N_2/2.5$	$L = 3\ 000, \phi = 3.2$	50	H_2, CH_4
4) Varian 1200 FID	SE 30, 10% 80-100 mesh	N ₂ /1.5	$L = 3\ 600, \phi = 3.2$	20-130 20°/min	C4, C5, Benz, Tol, Xyl.

twenty experiments were performed with only the last two cells at high temperature.

Thermal Cracking of *i*-Butane

The *i*-butane feed was also high purity grade and contained less than 0.2 wt % of *n*-butane.

The operating conditions were similar to those described above, except that the hydrocarbon flow rate was varied between 2 and 3.6 kg/hr and the temperature between 575° and 850° C.

Cracking of Mixtures of n- and i-Butane

Binary mixtures of n- and i-butane, containing, respectively, 25, 50, and 75% by weight of i-butane, were investigated under class 1 conditions.

Cracking of Binary Mixtures Ethane-n-Butane and Propane-n-Butane

Binary mixtures containing from 25 to 75 wt % of *n*-butane were investigated under class 1 conditions in a temperature range from 575° to 850° C and with hydrocarbon flow rates ranging from 2 to 3.6 kg/hr.

Cracking of Ternary Mixtures Ethane-Propane-n-Butane

The ternary mixtures mentioned in Table 1 were investigated under the conditions mentioned for binary mixtures.

PRODUCT ANALYSIS

The product analysis involved four on-line gas chromatographs. The columns and operating conditions are given in Table 2 for the analysis of the products of n-butane cracking and in Table 3 for the analysis of the products of i-butane and mixtures cracking.

KINETICS OF PURE COMPONENT CRACKING

n-Butane Cracking

The overall kinetics of the butane disappearance was studied on the basis of conversion vs. V_{eq}/F_o data by means of the integral method of kinetic analysis.

The equivalent reactor volume concept, used in the kinetic analysis, reduces the data to isothermality at a chosen reference temperature and pressure. The concept has been discussed in detail in previous papers (Froment et al., 1961; Van Damme et al. 1975). It was shown to yield the same results as the more complex approach using the nonisothermal, nonisobaric data as such and necessitating numerical, instead of analytical, integration.

The order of the butane cracking was determined from a comparison of experiments yielding equal conversions but differing in butane partial pressure at the inlet. Several sets of such experiments were compared to cover a wide range of conversions and reference temperatures. The order was always found to be 1, with a deviation of less than 0.02. With an order of 1 and accounting for an expansion of 2.4, practically independent of conversion, the frequency factors and activation energies given in Table 4 were obtained.

Again, as with propane and ethane cracking, a slight influence of partial and total pressure is experienced, which is in a sense a contradiction with the first order observed for the overall kinetics. The rate coefficient decreases when the partial pressure and the total pres-

TABLE 4. KINETIC PARAMETERS FOR THE GLOBAL REACTION IN n-BUTANE AND i-BUTANE CRACKING

n-butane		<i>i</i> -buta	ine	
Class	А	E	А	E
1 2	$\begin{array}{cccc} 7.8 & 10^{10} \\ 6.7 & 10^{10} \\ \end{array}$	49 090 48 720	$5.7 \ 10^{10} \\ 8.7 \ 10^{10} \\ 0.1 \ 10^{10}$	48 660 49 450
3 4	$\begin{array}{c} 7.1 & 10^{10} \\ 1.4 & 10^{11} \end{array}$	49 210 50 450	$\begin{array}{c} 6.1 & 10^{10} \\ 7.9 & 10^{10} \end{array}$	48 960 49 380

TABLE 5. VALUES OF k_I^o and a at Different Temperatures

Temp (°C)	750	775	800
k _I °	2.24	4.76	8.29
a	0.47	0.71	0.67

sure are raised. These conclusions are in complete agreement with those arrived at for propane and ethane cracking (Van Damme et al., 1975; Froment et al., 1976).

i-Butane Cracking

For an accurate kinetic analysis of i-butane cracking, it was necessary to account for the dependence of the expansion factor on conversion, partial, and total pressure. A parabolic law was used for the dependence on conversion, so that for class 3 conditions, for example

$$\bullet = 2.07 - 1.38x + 1.74x^2$$

The coefficients were different for each class to account for the effect of total and partial pressure. This function still permits analytical integration of the continuity equation for *i*-butane provided the kinetics follow first order. The values of the rate parameters, obtained by the integral method of kinetic analysis, are also given in Table 4. The rate coefficients are slightly lower than those for *n*-butane cracking, and the influence of partial and total pressure is completely analogous.

On the other hand, Figure 1 shows that although first order is strictly obeyed, as is evidenced by the influence of the partial pressure on the cracking rate, the rate coefficient decreases with conversion. This is ascribed to inhibition by reaction products. Negligible in *n*-butane cracking, this effect is very pronounced in iso-butane cracking, as observed already by Buekens and Froment (1971) who proposed the following hyperbolic law to account for it:

$$k_I = \frac{k_I^o}{1+ax} \tag{1}$$



Fig. 1. Effect of inhibition on *i*-butane cracking.

This means that the rate coefficient given in Table 4 is really an integral value over the investigated range of conversion. Substitution of (1) into the continuity equation for iso-butane still permits analytical integration. The parameters $k_{1^{0}}$ and *a* were determined by minimizing $\sum (x^{-x}_{calc})^{2}$ using a Marquardt search routine. The results are shown in Table 5.

From these values, an activation energy of 56 820 Kcal/Kmole is found for $k_{I^{\circ}}$ and a frequency factor of $3.51 \cdot 10^{12}$. These values are definitely less reliable than those given in Table 4 for the integral rate parameters. For the sake of comparison, the values obtained at 800°C by Buekens and Froment (1971) by bench scale experiments may be of interest: $k_{I^{\circ}} = 10.91$ and a = 1.09. From this, a point value of the rate coefficient of 7.06 is calculated at 800°C and x = 0.5 and of 5.50 at x = 0.9, whereas the present results lead to 6.21 and 5.17, respectively. Figure 1 also contains the point rate coefficients k_{I} calculated from (1) and the corresponding V_{eq}/F_{o} . The point values are lower than the integral values, of course.

COMPARISON OF CRACKING RATES OF LIGHT HYDROCARBONS

Figure 2 compares the rate coefficients for the cracking of ethane, propane, *n*- and *i*-butane for class 1 conditions (outlet total pressure: 1.5 atm abs, steam dilution 0.4 kg steam/kg hydrocarbon). Whereas the cracking of ethane has an activation energy of 60 670 Kcal/Kmole,



Fig. 2. Arrhenius diagram for ethane, propane, nC₄H₁₀, and iC₄H₁₀ cracking.

from propane onwards the activation energy is close to 50 000 Kcal/Kmole.

KINETICS OF MIXTURE CRACKING

Binary Mixtures

n- and i-butane

To characterize the cracking rates of mixtures and to permit their comparison with cracking rates of the pure components, kinetic coefficients were defined, $k_{N,I}$ and $k_{I,N}$ for the cracking of, respectively, *n*- and *i*-butane in their mixtures. The concentration of *n*-butane was calculated from

$$C_{\mathrm{N,I}} = \left[\frac{1 - x_{\mathrm{N,I}}}{1 + \delta(1 + \gamma) + \gamma + (\epsilon - 1)(x_{\mathrm{N,I}} + \gamma x_{\mathrm{I,N}})} \right] C_t$$

From the experimental data, the following parabolic relation was found between $x_{I,N}$ and $x_{N,I}$:

$$x_{I,N} = A_1 x_{N,I} + A_2 x_{N,I}^2$$

The coefficients of this relation were practically independent of the feed composition. The continuity equation for n-butane may then be written for plug flow conditions and first-order kinetics:

$$F_{N_o} dx_{N,I} = k_{N,I} \frac{(1 - x_{N,I})C_t}{C_1 + C_2 x_{N,I} + C_3 x_{N,I}^2} dV_{eq}$$
(2)

where

$$C_1 = (1 + \gamma) (1 + \delta)$$

$$C_2 = (\epsilon - 1) (1 + A_1 \gamma)$$

$$C_3 = (\epsilon - 1) A_2 \gamma$$

The activation energy used in the calculation of V_{eq} was a molar average of the activation energies of the pure components. $k_{N,I}$ is calculated from the integrated form of (2). The rate coefficient $k_{I,N}$ may be obtained in a similar way. Figure 3 shows $k_{N,I}$ as a function of the mixture composition. It is seen that k_N is very slightly increased by *i*-butane addition. k_I was shown to slightly decrease, but an exact comparison is rendered difficult because of the effect of inhibition. The activation energy



Fig. 3. n-butane rate coefficient vs. composition of binary mixture.

for the cracking of mixtures, expressed in terms of $k_{N,I}$, is close to 55 000 Kcal/Kmole.

ethane-n-butane

The relation between $x_{E,N}$ and $x_{N,E}$, required for the kinetic analysis, was again found to be independent of the feed composition:

$$c_{\rm E,N} = 0.0084 + 0.0125 x_{\rm N,E} + 0.4965 x_{\rm N,E}^2$$

 $k_{\rm E,N}$ and $k_{\rm N,E}$ were found to be independent of conversion, so that the cracking of *n*-butane and ethane in the mixtures is first order, like the pure component cracking, and uninhibited. Figure 4 shows $k_{\rm E,N}$ as a function of $x_{\rm E,N}$ for various mixture compositions and temperatures. The influence of the reversible reaction is only felt, and still very weakly, at the highest temperature, 800°C. The addition of *n*-butane significantly decreases the rate of ethane cracking, while ethane significantly increases the rate of *n*-butane cracking. The kinetic behavior of this binary mixture is very similar to that of ethane-propane mixtures reported earlier (Froment et al., 1976).

propane-n-butane

Again, the relation between $x_{P,N}$ and $x_{N,P}$ was found to be independent of the feed composition:

$$x_{P,N} = A_0 + A_1 x_{N,P} + A_2 x^2_{N,P}$$

 $x_{N,P} = A_3 + \sqrt{A_4 + A_5 x_{P,N}}$

where

$$A_0 = 0.0065; A_1 = 0.6218; A_2 = 0.2974; A_3 = -A_1/2A_0; A_4 = A_2^2 - A_0/A_0; A_5 = 1/A_2$$

With this binary mixture, however, both $k_{N,P}$ and $k_{P,N}$ are lower than the pure component values.

Ternary Mixtures Ethane-Propane-n-Butane

Three rate coefficients can be defined in this case: $k_{E,M}$, $k_{P,M}$, and $k_{N,M}$ to compare cracking rates of ternary and binary mixtures with those of pure components. For the rate coefficient of ethane cracking in the ternary mixture, the formulas are obtained as follows.

The continuity equation for ethane may be written, for plug flow conditions and assuming first-order kinetics, as

 $F_{\rm E_o}dx_{\rm E,M} = k_{\rm E,M}C_{\rm E,M}dV_{\rm eq}$

where



Fig. 4. Ethane rate coefficient vs. conversion.



Fig. 5. Ethane rate coefficient vs. ternary mixtures composition.

Fig. 6. Propane rate coefficient vs. ternary mixtures composition.

$$C_{E,M} = \left[\frac{1 - x_{E,M} + \frac{1}{\gamma_1} y_E + \frac{1}{\gamma_3} y_{E'}}{\left(1 + \frac{1}{\gamma_1} + \frac{1}{\gamma_3}\right) \delta + \frac{1}{\gamma_1} y_E + \frac{1}{\gamma_3} y_{E'} + \left(1 + \frac{1}{\gamma_1} + \frac{1}{\gamma_3}\right) + (\epsilon - 1) \left(x_{E,M} + \frac{1}{\gamma_1} x_{P,M} + \frac{1}{\gamma_3} x_{N,M}\right)} C_{\epsilon} \right]$$

 $x_{P,M}$ and $x_{N,M}$ have to be expressed in terms of $x_{E,M}$. From the experimental data, the following relations were derived:

$$x_{\rm P,M} = A_{13} + \sqrt{A_{14} + A_{15} x_{\rm E,M}}$$
$$x_{\rm N,M} = A_{16} + \sqrt{A_{17} + A_{18} x_{\rm E,M}}$$

The parameters A_{13} ... A_{18} slightly depend upon the feed composition. Substitution of these relations into the continuity equation for ethane and analytical integration yields an expression from which $k_{\rm E,M}$ can be calculated. $k_{\rm E,M}$ is shown as a function of the mixture composition in the tridimensional diagram of Figure 5. The values of $k_{\rm P,M}$ and $k_{\rm N,M}$ are shown in Figures 6 and 7.

When propane is added to a binary mixture of ethane and *n*-butane, the rate coefficient of the cracking of ethane in the ternary mixture $k_{E,M}$ is lower than that of ethane in the original binary mixture $k_{E,N}$. This reflects the effect of propane already noticed in the cracking of binary mixtures. The effect of addition of a third component to the three possible binary mixtures is summarized in Table 6. The effects are always in agreement

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with the observations derived from the cracking of binary mixtures.

Finally, the rate coefficients were fitted as a function of the feed composition for class 1 conditions and $T_R = 800^{\circ}$ C by means of

$$k_{\rm E,M} = P_1 + P_2(1 - \Psi_{\rm E,P}) + P_3(1 - \Psi_{\rm E,N}) + P_4(1 - \Psi_{\rm E,P})(1 - \Psi_{\rm E,N})$$

The following values were obtained for the parameters P_1 , P_2 , P_3 , P_4 , and their 95% confidence intervals by means of a Marquardt search routine:

$$P_1 = 1.93749 \pm 0.20849$$
$$P_2 = -0.75857 \pm 0.55747$$
$$P_3 = -1.54422 \pm 0.66054$$
$$P_4 = 1.28322 \pm 1.91268$$

$$k_{\rm P,M} = P_5 + P_6 (1 - \Psi_{\rm P,E})^2$$

$$+ P_7(1 - \Psi_{P,N}) + P_8(1 - \Psi_{P,N})^2$$

with



 $k_{\rm E,M} < k_{\rm E,P}$

 $k_{\mathrm{P,M}} < k_{\mathrm{P,E}}$

Similar formulas are easily derived for the other temperatures.

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Fig. 10. Ethylene yield from n-butane cracking.

PRODUCT DISTRIBUTIONS

n-Butane Cracking

The product distribution is a function of conversion, total pressure, and partial pressure of the hydrocarbon and temperature. When the yields are plotted vs. conversion, the influence of temperature is found to be negligible in the range investigated. Therefore, the yields of the different products are represented in the Figures 8 to 14 as a function of the *n*-butane conversion, with the *n*-butane partial pressure in the feed and the total pressure as parameters.

The influence of the *n*-butane inlet partial pressure and of the total pressure are summarized in Table 7. Partial and total pressure affect the yields in the same way, except for butadiene. Except for hydrogen and methane, the trends are very similar to those observed in the cracking of ethane and propane (Froment et al., 1976). There is a slight favorable effect of total and partial pressure on the propylene yield, but in the conversion range 50 to 80% only.

i-Butane Cracking

The product yields from *i*-butane cracking are shown in Figures 15 to 21. The ethylene and ethane yields are much lower than those obtained from *n*-butane; the hydrogen yield and the maximum propylene yield (around 80% conversion) are higher; the methane yield is higher in the high conversion range. Iso-butane cracking yields substantial amounts of *i*-butene, so that mixtures appropriate for alkylation can be produced.

The influence of partial and total pressure is shown in Table 7. Again, the effects are very similar, except for



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Fig. 11. Ethane yield from n-butane cracking.

TABLE 7. INFLUENCE OF PARTIAL PRESSURE OF THEHYDROCARBON AND OF TOTAL PRESSURE ON THE PRODUCTYIELDS FOR *n*-BUTANE AND *i*-BUTANE CRACKING

	Increase of C ₄ partial pressure		Increase pres	of total sure
Component	n-butane	<i>i</i> -butane	n-butane	i-butane
H_2	Ļ		Ļ	_
$\overline{CH_4}$	_			
C_2H_4	\downarrow		\downarrow	
C_2H_6	1		↑	
C_3H_6		\downarrow		\downarrow
C_3H_8	↓	↑		↑
$1C_4H_8$	Ļ	\downarrow	\downarrow	Ţ
iC4H8		1		↑
C_4H_6	Ť		\downarrow	ţ
C_5 +	Ť	î	1	1

 $i-C_4H_8$. Compared with *n*-butane cracking, the behavior of the propylene selectivity is reversed.

TABLE 8. PARAMETER VALUES FOR THE HYPERBOL	IC
FITTING OF THE EXPERIMENTAL SELECTIVITIES IN	N
ETHANE- <i>n</i> -BUTANE CRACKING	

	CH_4	C_3H_6
B ₀	0.705	$0.488 - 0.6333 x_{N,E}$
B_1	0.145	0.115
B ₂	-0.79	-0.63



Mixtures Cracking

Selectivities in mixtures cracking

In complete analogy with the definition for the selectivity for a product J in the cracking of a single component, the selectivity for J in the cracking of a mixture of A, B... is defined as follows:

$$y(J) = \frac{\text{moles of } J \text{ formed from } M}{\text{moles of } M \text{ cracked}}$$

This ratio can be written in a more detailed way as

y(J) =

$$\frac{\text{moles of } J \text{ formed from } A + \text{ moles of } J \text{ formed from } B + \dots}{\text{moles of } A \text{ cracked} + \text{ moles of } B \text{ cracked} + \dots}$$
(3)

In the absence of reliable detailed reaction models, the terms in the numerator of (3) cannot be predicted in a rigorous way. The only possibility to estimate these quantities is to take the selectivities obtained from the pure component cracking. The prediction of the terms in the denominator causes less problems, since the kinetics of the global rates of cracking of the components in the mixture are more likely to be available. A reasonable prediction of y(J) may then be written as

$$y(J) \approx \hat{y}(J) = \frac{\Psi_{A}x_{A,M}y_{J,A} + \Psi_{B}x_{B,M}y_{J,B}^{+} \dots}{\Psi_{A}x_{A,M} + \Psi_{B}x_{B,M}^{+} \dots}$$
 (4)

Evidently, the $y_{J,A}$ depend upon the conversion and have to be taken at $x_A = x_{A,M}$, $x_B = x_{B,M} \dots$





The selectivities predicted in this way will be called selectivities based upon global kinetics (GKB selectivities). It is clear that additivity selectivities used until now in the literature and defined by

$$\overline{y}(J) = \Psi_{A}y_{J,A} + \Psi_{B}y_{J,B} + \dots$$
 (5)

are a special case of (4), valid only for $x_{A,M} = x_{B,M} \ldots$. These would be the selectivities obtained from the separate cracking of A,B... to the same conversion, followed by mixing of the effluent streams. They do not account in any way for the interaction between reaction components. The GKB selectivities of (4) partly account for the interaction through $x_{A,M}$, $x_{B,M} \ldots$ which for identical operating conditions may differ from x_A , $x_B \ldots$, but not for the effect of interaction on the selectivities, since $y_{J,A}$, $y_{J,B}$ are taken from single component cracking.

n- and i-butane

Figure 22 shows the selectivities for hydrogen, methane, ethylene, ethane, propylene, and iC_4H_8 as a function of the *i*-butane mole fraction in the feed and for *n*-butane conversion of 96% and an iso-butane conversion of 88%. In the *n*-butane-*i*-butane mixtures, $x_{N,I}$ is not too differ-



Fig. 15. Hydrogen yield from i-butane cracking.

ent from $x_{L,N}$, and indeed the full line representing the additivity selectivities coincides with the dashed lines representing the GKB selectivities.

Selectivity curves like those of Figure 22 were also drawn for other conversions. The following conclusions were arrived at. The experimental propylene selectivities practically coincide with those calculated from Equation 4. This is not surprising, since the propylene selectivities from the pure components are almost identical.

For conversions above 50% at least, the experimental hydrogen and methane selectivities are lower than those calculated, and the more so the lower the *n*-butane content of the feed. But again, the deviations from GKB values are weak. This could be related to the acceleration of the *n*-butane cracking illustrated in Figure 3.

The ethylene selectivity is markedly higher than the calculated one from 75% iso-butane conversion onwards and again more for the mixture with molar ratio iso to normal of 3, for which the normal butane cracking is accelerated most.

The iso-butene selectivity is lower than the calculated one from about 80% iso-butane conversion onwards. Again, this could be related to the acceleration of the *n*-butane cracking.

ethane-n-butane

Figure 23 shows the effect of ethane addition on the selectivity of *n*-butane cracking. In this case, the deviations with respect to the GKB selectivity lines are more pronounced. The experimental methane and propylene selectivities in terms of the ethane mole fraction Ψ_E were fitted by means of



Fig. 16. Methane yield from i-butane cracking.

$$y = B_0 - \frac{B_1 \Psi_{\rm E}}{1 + B_2 \Psi_{\rm E}}$$

The following values of the parameters were obtained for class 1 conditions by means of a Marquardt search routine. The analogy of the curves for ethylene with those for vapor-liquid equilibria suggested a fit by means of a Margules type of equation:

$y = D_o e^{D_1 (1 - \Psi_E)^2 + D_2 (1 - \Psi_E)^2}$

The parameters D_0 , D_1 and D_2 were independent of conversion. The following values were obtained: $D_0 = 0.900$; $D_1 = -0.905$; $D_2 = 0.825$.

The selectivities for hydrogen and ethylene, which are higher in ethane than in n-butane cracking, are lower than those calculated from Equation (4). This may be related to the slowing down of the rate of ethane cracking by n-butane addition.

The methane and propylene selectivities lie above those corresponding with the GKB selectivity line. They are much higher in *n*-butane than in ethane cracking. It was mentioned already that ethane addition accelerates the *n*-butane cracking.

Propane-n-butane

Again, the selectivities deviate from the GKB selectivity lines, as illustrated by Figure 24. In this case,



Fig. 20. Butadiene yield from *i*-butane cracking.

tane at conversions $x_{E,M} = 40\%$; $x_{P,M} = 73\%$; $x_{N,M} = 88\%$. With ternary mixtures, the additivity, GKB, and experimental lines become surfaces.

The experimental selectivity surfaces were fitted by a polynomial of the second degree. For ethylene:

$$y = P_1 + P_2(1 - \Psi_{\rm E,P}) + P_3(1 - \Psi_{\rm E,P})^2 + P_4(1 - \Psi_{\rm E,N})^2$$

however, the deviations cannot be entirely explained in terms of the rate coefficients of the individual components, because both $k_{P,N}$ and $k_{N,P}$ are lower than k_P and k_N , respectively.

Ternary mixtures

Figures 25 and 26 show the ethylene and propylene selectivities from ternary mixtures ethane-propane-n-bu-



Fig. 21. C₅ + yield from *i*-butane cracking.



Fig. 24. Selectivity for hydrogen, methane, ethylene, propylene, and ethane vs. mole fraction *n*-butane in propane-*n*-butane mixture.

+
$$P_5(1 - \Psi_{\rm E,N})^2$$
 + $P_6(1 - \Psi_{\rm E,P})(1 - \Psi_{\rm E,N})$

The parameters in this model were determined by means of a Marquardt search routine. The following parameter values and 95% confidence intervals were obtained:

$$P_{1} = 0.920369 \pm 0.03145$$

$$P_{2} = -0.43421 \pm 0.14423$$

$$P_{3} = 0.191042 \pm 0.13816$$

$$P_{4} = -0.34040 \pm 0.14715$$

$$P_{5} = 0.24267 \pm 0.13999$$

$$P_{6} = 0.366254 \pm 0.20821$$

For propylene

$$\begin{split} y &= P_7 (1 - \Psi_{\text{E},\text{P}}) + P_8 (1 - \Psi_{\text{E},\text{P}})^2 + P_9 (1 - \Psi_{\text{E},\text{N}}) \\ &+ P_{10} (1 - \Psi_{\text{E},\text{N}})^2 + P_{11} (1 - \Psi_{\text{E},\text{N}}) (1 - \Psi_{\text{E},\text{P}}) \end{split}$$
with







Fig. 23. Selectivity for hydrogen, methane, ethylene, and propylene vs. mole fraction ethane in ethane-*n*-butane mixture.

 $P_{7} = 0.3398 \pm 0.07261 :$ $P_{8} = -0.09748 \pm 0.08273$ $P_{9} = 0.49485 \pm 0.07286$ $P_{10} = -0.25612 \pm 0.08247$ $P_{11} = -0.60569 \pm 0.11074$

Separate vs. Cocracking

The experimental data presented here permit a comparison of the merits of separate cracking of the components of a mixture vs. cracking the mixture as such. The following conclusions may be drawn:

1. The cocracking of ethane and propane (Froment et al., 1976), ethane and n-butane, propane and n-butane, and ethane, propane, and n-butane leads to lower ethylene than those predicted by the G.K.B. formulas

2. The cocracking of n- and *i*-butane gives rise to higher ethylene and propylene selectivities than the separate cracking. These trends are more pronounced at lower than at high conversions.

Evidently, when separate cracking leads to higher selectivities the benefit would have to be weighed against the cost of separation of the mixture.

TERNARY MIXTURES



Fig. 25. Ethylene selectivity vs. ternary mixtures composition at given conversion.



Fig. 26. Propylene selectivity vs. ternary mixtures composition at given conversion.

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NOTATION

 $a = \text{inhibition constant, s}^{-1}$ A = frequency factor, kcal/kmole $A_{0.5}, A_{13-18} = \text{parameters}$

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 B_{0-2} = parameters

- $C = \text{concentration, kmole/m}^3$
- C_t = concentration, total hydrocarbons, kmole/m³

 $C_{1-3} = \text{parameters}$

- $D_{0-2} = \text{parameters}$
- E = activation energy, kcal/kmole
- F_o = molar flow rate of hydrocarbon at inlet, kmole/s
- \overline{k} = integral rate coefficient, s⁻¹
- $k_{\rm I}$ = point rate coefficient of isobutane, s⁻¹
- $K_{I^{o}}$ = rate coefficient of isobutane at zero conversion, s⁻¹

 $P_{1-12} = \text{parameters}$

- T_R = reference temperature, °K
- V_{eq} = equivalent reactor volume, m³
- x = conversion
- y = selectivity, mole/mole
- $y_{\rm E}$ = moles ethane formed by cracking of 1 mole propane, constant over whole conversion range
- $y'_{\rm E}$ = moles ethane formed by cracking of 1 mole nC_4H_{10} , function of butane conversion

Greek Letters

- γ = mole ratio, *i*-butane/*n*-butane
- γ_1 = mole ratio ethane/propane
- γ_3 = mole ratio ethane/*n*-butane
- δ = dilution ratio, mole steam/mole hydrocarbon at inlet
- e expansion factor, mole products/mole hydrocarbon cracked
- Ψ = mole fraction, mole/mole

Subscripts

- N = normal-butane
- I = iso-butane
- E = ethane
- P = propane
- M = mixture

Superscripts

* = based on global kinetics

- = pure additivity

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Fluid Vortices and Mass Transfer in a Curved Channel Artificial Membrane Lung

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Experimental assessment of theory on the convective dispersion of blood gases by vortices in a curved channel exchanger has demonstrated the impracticality of the proposed design. A nonlinear stability analysis of the fluid dynamics provided an amplitude factor an order of magnitude less than that previously assumed for the system secondary circulations.

SCOPE

For short periods (for example, cardiac surgery), the respiratory function of the natural lung is adequately performed by exchangers in which the blood is in direct contact with the ventilating gas. However, for extended respiratory support, it is necessary to interpose a gas permeable membrane between the blood and gas phases in order to reduce blood trauma caused by direct contact systems (Lee et al., 1961). In the majority of membrane lungs (oxygenators), the blood flow is rectilinear laminar within parallel plate or tubular conduits, and with present membranes the oxygen and carbon dioxide transfers are limited by diffusion through the concentration boundary layer adjacent to the membrane (Mockros and Weissman, 1971). To take advantage of high gas exchange rates offered by ultrathin silicone rubber and hydrophobic microporous membrane technology, and to create compact, economic, and simple oxygenators, development has centered on reducing the fluid phase diffusional resistance by decreasing boundarylayer thickness or generating convective mixing in the blood. These processes may be accomplished by passive or active means. Passive systems utilize the energy of the blood flow coupled with conduit geometry to create mixing, for example, secondary flows in coiled tubes, eddy flows due to surface perturbations and screens (Drinker, 1972). In active units, mixing is generated by external energy, for example, oscillation of curved tubes (Melrose et al., 1972) or toroidal chambers (Drinker, 1972), rotating disks (Hill et al., 1974), rotating cylinders (Smeby and Gaylor, 1974), and flow pulsation across grooved walls (Bellhouse et al., 1973). Generally passive methods are favored owing to ease of operation, simple construction, and the lower blood trauma produced.

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