(HIGH TEMPERATURE, VAPOR-PHASE CRACKING OF HYDROCARBONS)

Gaseous Product Distribution in Hydrocarbon Pyrolysis

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ARLIER studies of hydrocarbon pyrolysis (12, 14, 46) were usually conducted at temperatures below 650° C. (1202° F.), or, when higher temperatures were used, at extremely short reaction times, to obtain data suitable for kinetic interpretation. Because of the emphasis given to these relatively mild pyrolysis conditions, the interpretation of results generally stressed dissimilarity in the behavior of individual or groups of hydrocarbons. However, except in the production of acetylene, practical operating conditions for hydrocarbon pyrolysis fall in the temperature range of 1200° to 2000° F. at reaction time well above 0.1 second. In this range of pyrolysis conditions the gaseous product distribution for most feed hydrocarbons other than methane shows a striking similarity, only slightly affected by the composition. structure, or molecular weight of the feed hydrocarbon when cracked at equivalent temperatures, reaction times, and partial pressures (14, 28).

In the first part of this study, empirical relationships for the prediction of gaseous product distribution are developed for a wide range of feed hydrocarbons by the use of a simple and general approach to the analysis of the behavior of the complex gaseous reaction systems encountered in high-temperature, vapor-phase cracking.

Pyrolysis data show similiar gaseous product distributions

Previous studies have shown that hydrocarbons of equal carbon-hydrogen weight (C/H) ratio will yield approximately equal quantities of gas of similar composition (26-28, 33) independently of their molecular weight or structure as long as the severity of cracking is sufficient to eliminate the effects of the primary decomposition reactions. The composition, although not the total

yield, of the nongaseous products was shown to be affected by feed hydrocarbon properties other than carbon-hydrogen ratio because of the tendency of feed hydrocarbons of higher molecular weight to form nongaseous cracking products through primary reactions—that is, those specific to the feed hydrocarbons, such as dehydrogenation, cyclization and dehydrocyclization, and polymerization.

As illustrated in Table I, the influence of carbonhydrogen ratio on gaseous product distribution is small for natural gas liquids, and for petroleum and shale oils, so that only minor changes in cracking conditions will compensate for the tendency of hydrocarbons of higher carbon-hydrogen ratio to form gases of higher hydrogen content and higher paraffinolefin ratio (26, 28). This similarity in gaseous product distribution tends to be masked by the relatively slow rates of the primary cracking reactions for hydrocarbons of low molecular weight such as methane, ethane, and ethylene.

From the data on pyrolysis obtained in this and earlier studies, any reaction schemes attempting to interpret gaseous product distributions-by the assumption of dehydrogenation or carbon-carbon bond scission reactions specific to a given hydrocarbon (14, 38) did not appear applicable for reaction temperatures above 1300° F. and reaction times above 1 second. Such reaction schemes could not account for the similarity in gaseous product distribution at equivalent cracking conditions for feed hydrocarbons of such widely varying molecular weights, structures, and compositions. Instead, an exploration of the equilibria and the secondary reactions determining the partial pressures of the species constituting the major portion of the gaseous products of hydrocarbon pyrolysis appeared more suitable.

Gaseous product distributions are interpreted using secondary gas-phase reactions

On the basis of the data obtained in this study it appeared that in the range of pyrolysis conditions where the primary decomposition reactions are essentially completed, the gaseous product distributions could be interpreted using a reaction system consisting of:

1. Hydrogenation of the gaseous olefins to paraffins of equal carbon chain length

2. Slow hydrogenolysis of paraffins with two or more carbon atoms to methane or methane and a higher paraffin

This reaction system can be expressed in generalized form as:

$$C_{i}H_{2i} + H_{2} \rightleftharpoons C_{i}H_{2i+2}$$
(1)

$$U_i H_{2i+2} + H_2 = U H_4 + U_{i-1} H_{2i}$$
(2)

where the carbon numbers of the various hydrocarbons are i = 2, 3, ..., n. The approach of System 1 to equilibrium can then be defined in terms of the mole fractions of the reacting constituents, the reaction temperature, and the total pressure by the function $f_{1(i)}/K_{1(i)}$, where



Figure 2. Effect of reaction time on approach of ethylene-hydrogenethane system to equilibrium

	Constan	1 Devel	iny of cluc	King			
Run No.	248	251	239	352	233	446	277
Feedstock	Propane	Butane	12-lb. RVP natural gasoline	Light Diesel oil	Reduced crude	Crude shale oil	Bunker C fuel oil
C/H ratio of feedstock Carrier gas Total pressure of product gas, atm. Partial pressure, atm. ^a Cracking temperature, ° F. Reaction time, sec.	$\begin{array}{r} 4.5\\ \text{None}\\ 0.996\\ 0.982\\ 1500\\ 4.45 \end{array}$	$\begin{array}{r} 4.8 \\ \text{None} \\ 1.02 \\ 1.00 \\ 1500 \\ 4.26 \end{array}$	5.2 None 0.994 0.993 1500 4.19	$\begin{array}{r} 6.39 \\ {\rm Steam} \\ 1.05 \\ 0.756 \\ 1570 \\ 2.56 \end{array}$	$\begin{array}{r} 7.25 \\ N_2 + CO_2 \\ 1.07 \\ 0.924 \\ 1550 \\ 2.36 \end{array}$	7.48 Steam 1.01 0.690 1550 2.47	$\begin{array}{r} 8.51 \\ N_2 \\ 1.00 \\ 0.750 \\ 1550 \\ 1.53 \end{array}$
Wt. % of feed b	80.2	73.4	63.2	54.2	47.7	44.7	34.7
Composition, mole % ^a Hydrogen Methane Ethane Propane Butanes Ethylene Propene Butenes Butadienes Pentadienes Benzene Toluene	24.2 48.3 2.6 0.2 0.1 21.7 1.0 0.1 0.1 0.7 0.1 0.6 Trace	$\begin{array}{c} 22.1\\ 49.4\\ 2.7\\ 0.3\\ 0.3\\ 0.1\\ 21.4\\ 0.9\\ 0.1\\ 0.5\\ 0.1\\ 0.7\\ 0.1\\ \end{array}$	$\begin{array}{c} 22.5\\ 48.3\\ 2.8\\ 0.3\\ 0.2\\\\ 23.5\\ 0.8\\ 0.1\\ 0.6\\ 0.1\\ 0.7\\ 0.1\end{array}$	26.3 44.0 2.4 22.8 1.1 0.2 0.7 0.2 0.7 0.2 1.8 0.1	25.6 43.0 2.7 23.7 2.0 2.0 2.0 0.7 0.2 2.0 0.1	26.3 43.6 2.6 0.1 21.6 1.6 1.0 0.2 2.3 0.2	$\begin{array}{c} 24.7\\ 45.6\\ 3.1\\ \\ \\ 20.3\\ 3.2\\ \\ 0.5\\ 0.9\\ 0.2\\ 1.3\\ 0.1\\ \end{array}$
Acetylene Liquid products Wt. % of feed 6	0,4 19.0	1.3 25.0	 36.3	0.4 42.5	41.8	0.5 49.8	0.1 51.9
Distillation, wt. % 0-200° C. 200-380° C. 300-355° C. Residue by diff. Solid products, wt. %	54.5 19.5 5.9 20.1 0.8	$50.0 \\ 19.8 \\ 7.7 \\ 22.5 \\ 1.6$	52.8 21.1 8.3 17.8 0.5	20.827.28.943.13.3	15.4 17.8 6.7 58.5 10.5	10.4 15.7 8.8 65.1 6.5	7.1 11.2 17.0 64.7 13.4

Table I. Product Distribution for Various Feed Hydrocarbons at Approximately Constant Severity of Cracking

 $\rm H_{2}\text{-}gaseous$ hydrocarbon fraction. Includes small amounts of N₂, CO, CO₂, and sulfur compounds produced from feed. Corrected to 100% material balance.

$$f_{1(i)} = \frac{(C_i H_{2i+2})}{P(C_i H_{2i})(H_2)}$$
(3)

and where $f_{1(i)} = K_{1(i)}$ at equilibrium, assuming the ideal gas state. Similarly, for System 2 the function $f_{2(i)}/K_{2(i)}$ will define the approach to equilibrium, where

$$f_{2(i)} = \frac{(CH_4)(C_{i-1}H_{2i})}{(C_iH_{2i+2})(H_2)}$$
(4)

and where $f_{2(i)} = K_{2(i)}$ at equilibrium.

The total number of reactive components in the reaction system of Equations 1 and 2 equals 2i + 1 and the sum of the mole fraction of these components, x, is defined as:

$$x = (H_2) + \sum_{1}^{i} (C_i H_{2i+2}) + \sum_{2}^{i+1} (C_i H_{2i}) (5)$$

An analysis of the experimental data obtained in this series of pyrolysis studies indicated that, over a wide range of pyrolysis conditions, apparent chemical equilibria among ethane, ethylene, and hydrogen were established in the cracking products of many types of hydrocarbons and of hydrocarbonhydrogen mixtures (Figure 2 and Table II). At reaction temperatures above 1300° F. and at pressures from 1 to 3 atm., reaction times over 3 seconds permitted attainment of the ethane-ethylene-hydrogen equilibrium for feeds including propane, butane, natural gasoline, residual petroleum oils, and shale oils (Figure 2).

It appeared that the propane-propene-hydrogen equilibrium was approached whenever the ethane-ethylene-hydrogen equilibrium was attained, in spite of considerable scattering of experimental equilibrium constants due to the limited accuracy of the mass spectrometer

analyses for the small concentrations in which the higher molecular weight species were present (9).

Close approach to the ethylene-acetylene-hydrogen equilibrium was also observed under pyrolysis conditions which resulted in the production of significant amounts of acetylene. For example, substantial agreement of calculated and experimental equilibrium constants for the ethylene-acetylene-hydrogen system over a range of reaction times from 0.5 to 5 seconds at reaction temperatures of 1550° and 1700° F. was noted for ethylene-hydrogen and ethane-hydrogen feeds (Table II), in spite of the limited accuracy of the reported values for small ethane and acetylene concentrations

Since the concentrations of the components of the reaction system:



Figure 3. Gaseous product yields from pyrolysis of 2 to 1 mole ratio hydrogen-ethylene mixtures

Table II. Approach i	to CH	₄-C₂H	${}_{6}-C_{2}H_{4}$	-C₂H₂-	H ₂ Equ	ilibria	in Pyr	olysis	of Hy	drocar	bons o	f Low	Molec	ular W	/eiaht	
Run No.	$285 \mathrm{A}$	285B	285C	264A	264C	264B	290A	287B	310A	305	293A	287A	290B	310B	310C	293B
Feed gas type	М	Methan	e	I	Ethylene					Ho-CoH	or He-(ToHe Mi	vtures			
Feed gas composition, mole %		^									4 01 112-0	J2116 1011.	AUG105			
$\begin{array}{c} H_2\\ CH_4\\ C_2H_6\\ C_3H_4\end{array}$	99 +	99+	99 +	0.0 0.4 3.2 96 4	$0.0 \\ 0.4 \\ 3.2 \\ 96 4$	$0.0 \\ 0.4 \\ 3.2 \\ 96 4$	$\begin{array}{c} 63.6\\0.2\\1.1\\34.8\end{array}$	$ \begin{array}{c} 66.6 \\ 0.1 \\ 1.0 \\ 31.8 \end{array} $	$ \begin{array}{r} 65.2 \\ 0.2 \\ 1.1 \\ 21 \\ 9 \end{array} $	$ \begin{array}{r} 64.8 \\ 0.2 \\ 1.1 \\ 22 5 \end{array} $	$57.3 \\ 0.0 \\ 42.6 \\ 0.0$	$66.6 \\ 0.1 \\ 1.0 \\ 21 \\ 8$	$63.6 \\ 0.2 \\ 1.1 \\ 24.8 \\ 0.2 \\ 0.$	$\begin{array}{c} 65.2 \\ 0.2 \\ 1.1 \end{array}$	$\begin{array}{c} 65.2 \\ 0.2 \\ 1.1 \end{array}$	$57.3 \\ 0.0 \\ 42.6 \\ 0.0 \\ 0.$
Reaction temperature, ° F. Reaction time, sec. Reaction pressure, atm.	$1700 \\ 5.67 \\ 1.01$	$1700 \\ 17.6 \\ 1.01$	$1700 \\ 33.0 \\ 1.01$	$1400 \\ 4.08 \\ 1.01$	$1400 \\ 3.75 \\ 3.09$	$1500 \\ 4.05 \\ 1.01$	$1550 \\ 0.58 \\ 1.04$	$1550 \\ 1.20 \\ 1.02$	1550 3.30 1.01	1550 3.38	1550 3.88	$ \begin{array}{r} 51.8 \\ 1550 \\ 5.00 \\ 1.01 \end{array} $	$ \begin{array}{r} 34.8 \\ 1700 \\ 0.53 \\ 1.04 \end{array} $	$ \begin{array}{r} 31.9 \\ 1700 \\ 1.50 \\ 1.02 \end{array} $	$31.9 \\ 1700 \\ 3.04 \\ 1.01$	1700 3.68
Product/feed gas ratio, moles/ mole	1.032	1.084	1.166	0.932	0.825	0.945	0.947	0.945	0.946	0.939	1.390	0.881	0.983	0.967	0.967	1.413
Product gas composition, mole % H2 CH4 C2H4 C2H4 C4H6 C2H4 C4H6 C2H4 C4H6 C2H2 Partial pressure product/K	$\begin{array}{r} 4.1\\ 93.9\\ 0.0\\ 0.4\\ 0.0\\ 0.2 \end{array}$	13.0 83.6 0.1 1.1 tr. 0.3	$27.7 \\ 69.6 \\ 0.2 \\ 1.2 \\ 0.1 \\ 0.2$	$10,3 \\ 11.6 \\ 5.6 \\ 66.2 \\ 2.4 \\ 0.0$	9.617.511.454.83.50.0	28.229.34.632.11.40.5	$ \begin{array}{r} 62.8 \\ 5.6 \\ 3.7 \\ 24.6 \\ 0.4 \\ 0.7 \\ \end{array} $	$\begin{array}{c} 65.3 \\ 9.9 \\ 3.3 \\ 18.5 \\ 0.2 \\ 0.8 \end{array}$	$\begin{array}{c} 60.5 \\ 16.4 \\ 4.1 \\ 15.0 \\ 0.1 \\ 0.3 \end{array}$	$62.9 \\ 17.9 \\ 3.7 \\ 13.2 \\ 0.1 \\ 0.4$	$ \begin{array}{c} 62.9\\ 20.6\\ 2.8\\ 9.9\\ 0.0\\ 0.3 \end{array} $	$\begin{array}{c} 63.5\\ 21.2\\ 2.0\\ 10.6\\ 0.2\\ 0.5 \end{array}$	$66.5 \\ 12.5 \\ 1.1 \\ 15.3 \\ 0.3 \\ 2.4$	$\begin{array}{c} 65.1 \\ 19.1 \\ 1.2 \\ 10.2 \\ 0.1 \\ 1.1 \end{array}$	$\begin{array}{c} 64.7\\ 24.1\\ 0.9\\ 6.4\\ 0.1\\ 0.7\end{array}$	66.8 26.8 0.6 2.2 0.0 0.5
$\frac{f_1/K_1}{f_2/K_2}$	•••	$\begin{array}{c} 4.3 \\ 4.8 \end{array}$	$\begin{array}{c} 3.8\\ 0.8 \end{array}$	$\begin{array}{c} 0.49 \\ 6.2 \times \\ 10^{-4} \end{array}$	$0.42 \\ 7.5 \times 10^{-4}$	$\begin{smallmatrix}&0.72\\0.0028\end{smallmatrix}$	0.48 6.9×10^{-5}	2.3×10^{-4}	$0.94 \\ 5.5 \times 10^{-4}$	$0.94 \\ 7.1 \times 10^{-4}$	$\begin{array}{c} 0.95 \\ 0.0012 \end{array}$	$\begin{array}{c} 0.62 \\ 0.0018 \end{array}$	$\begin{smallmatrix}&0.65\\0.0019\end{smallmatrix}$	1.11 0.0041	$\begin{smallmatrix}&1.34\\0.0088\end{smallmatrix}$	$\begin{smallmatrix}&2.6\\0.016\end{smallmatrix}$
f_4/K_4 Reaction	3.9 1. C ₂ I	2.3 $\mathbf{f}_4 + \mathbf{F}_2$	1.7 $I_2 \rightleftharpoons C$	2H6. R	eaction 2	2.6 2. C₂H	1,1 6 + H ₂	0.70 → 2CH4	1.7 . Reac	1.1 tion 4.	1.1 C ₂ H ₂ +	0.67 • H₂ ≓	0.75 C₂H₄	1.1	1.1	0.54

Table III. Effects of Pyrolysis Severity on Gaseous Product Composition for Typical Petroleum Oils

Run No.	227	272	242	229	245	252	233	257	370	369	356	348	336	357	359	353
Feedstock			R	educed	Crude					Diesel O	il	Red Cru	uced 1de	Diesel oil	Reduced crude	Diesel oil
C/H ratio Carrier gas	7.25 N ₂	$7.25 \\ N_{2}$	$7.25 \\ N_2 + CO_2$	7.25 N_2	7.25 N ₂ +	7.25 N2	$7.25 \\ N_2 + CO_3$	7.25 N2	6.39 Steam	6.39 Steam	6.39 Steam	7.04 Steam	7.04 Steam	6.39 Steam	7.04 Steam	6.39 Steam
Total pressure, atm. Partial pressure of product gas.	1.01	1.01	0.999	0.998	1.00	1.01	1.07	1.01	2,96	3.02	2.95	3.00	2.94	2.96	2.90	2.92
atm. ⁴ Reaction temperature, ° F. Reaction time, sec. Pyrolysis severity function, 10 ^{0.00} Gaseous products, wt. % ^b Gaseous products	$0.745 \\ 1350 \\ 2.42 \\ 1424 \\ 52.2$	$0.743 \\ 1350 \\ 5.29 \\ 1492 \\ 52.1$	$0.765 \\ 1400 \\ 1.27 \\ 1420 \\ 52.6$	$\begin{array}{r} 0.814 \\ 1400 \\ 2.41 \\ 1476 \\ 53.5 \end{array}$	$\begin{array}{c} 0.729 \\ 1400 \\ 5.15 \\ 1545 \\ 52.4 \end{array}$	$0.772 \\ 1550 \\ 1.42 \\ 1583 \\ 51.8$	$0.924 \\ 1550 \\ 2.36 \\ 1632 \\ 47.7$	$0.758 \\ 1550 \\ 4.30 \\ 1692 \\ 47.0$	$2.08 \\ 1350 \\ 1.23 \\ 1367 \\ 46.0$	$2.13 \\ 1370 \\ 3.08 \\ 1466 \\ 54.4$	$2.14 \\ 1440 \\ 2.36 \\ 1516 $	$2.27 \\ 1460 \\ 3.12 \\ 1563 \\ 43.7 \end{cases}$	$2.09 \\ 1470 \\ 6.98 \\ 1651 \\ 43.8$	$2.23 \\ 1480 \\ 8.62 \\ 1684 \\ 4.73$	$2.11 \\ 1540 \\ 2.63 \\ 1632 \\ 45.0$	$2.03 \\ 1550 \\ 2.41 \\ 1634 \\ 47.1$
Composition, mole % ^d H ₂ CH ₄ C ₂ H ₅ C ₃ H ₅ Butanes	$11.5 \\ 31.6 \\ 7.5 \\ 1.0 \\ 0.4$	$14.1 \\ 37.9 \\ 6.4 \\ 0.3 \\ 0.1$	$11.3 \\ 32.2 \\ 6.7 \\ 0.7 \\ 1.2$	$15.1 \\ 35.8 \\ 6.1 \\ 0.6 \\ 0.3$	$17.0 \\ 41.1 \\ 5.1 \\ 0.1$	$19.1 \\ 40.9 \\ 3.7 \\ 0.1 \\ 0.3$	$25.6 \\ 43.0 \\ 2.7 \\$	$30.8 \\ 46.1 \\ 1.7 \\ 0.3 \\ \cdot \cdot \cdot$	$8.8 \\ 33.7 \\ 10.2 \\ 1.2 \\ 0.2$	$11.1 \\ 44.2 \\ 10.1 \\ 0.7 \\ 0.1$	$14.5 \\ 50.1 \\ 7.4 \\ 0.3 \\ 0.1$	$17.2 \\ 49.1 \\ 7.9 \\ 0.4 \\ 0.2$	$22.0 \\ 54.7 \\ 5.8 \\ 0.1 $	$19.7 \\ 60.0 \\ 5.5 \\ 0.2 \\$	$ \begin{array}{c} 19.0 \\ 50.7 \\ 6.5 \\ 0.2 \\ \end{array} $	26.2 53.6 3.5 0.3
Pentanes Cell4 Cell6 Butenes Pentenes Butadienes Pentadienes	27.1 11.9 3.2 0.6 2.7 1.1	26.2 9.2 1.6 1.8 0.5	$\begin{array}{c} 0.4 \\ 27.8 \\ 11.0 \\ 2.7 \\ 0.5 \\ 2.9 \\ 1.2 \end{array}$	$27.1 \\ 9.0 \\ 1.1 \\ 0.3 \\ 1.8 \\ 1.0$	27.3 5.6 0.4 0.5 0.5	26.4 4.7 0.8 1.6	23.7 2.0 0.7	17.5 0.7 	$24.3 \\ 14.5 \\ 4.1 \\ 0.7 \\ 1.4 \\ 0.4$	21.5 9.3 1.8 0.1 0.9 0.2	20.3 4.6 1.1 0.1 0.8 0.2	17.4 4.9 1.1 0.7 0.2	14.5 1.8 0.2 0.2 0.1	$ \begin{array}{c} 12.8 \\ 0.9 \\ 0.2 \\ 0.2 \\ 0.2 \end{array} $	18.5 3.4 0.5 0.6 0.1	$14.3 \\ 0.8 \\ 0.2 \\ 0.3$
Acetylene Benzene Toluene	1.1 0.3	1.6 0.3	$1.3 \\ 0.1$	1.5 0.3	$2.1 \\ 0.3$	2.0 0.1	2.0 0.1	$0.4 \\ 2.0 \\ 0.1$	$0.4 \\ 0.1$	0.1	0.5	0.9	0.1 0.5	$\begin{array}{c} 0.1\\ 0.4\\ \end{array}$	0.5	0.2 0.6
Fartial pressure products/ \mathbf{A} f ₁ / \mathbf{K}_1 f ₂ / \mathbf{K}_2 f ₃ / \mathbf{K}_4 Liquid products, wt. % Solid products, wt. %	$\begin{smallmatrix} 1.21 \\ 0.0024 \\ 0.032 \\ 42.8 \\ 5.0 \end{smallmatrix}$	$0.88 \\ 0.0033 \\ 0.039 \\ 41.2 \\ 6.7$	$1.65 \\ 0.0037 \\ 0.043 \\ 42.3 \\ 5.1$	${ \begin{smallmatrix} 1.10 \\ 0.0037 \\ 0.042 \\ 39.5 \\ 7.0 \end{smallmatrix} }$	$0.90 \\ 0.0052 \\ 0.070 \\ 41.4 \\ 6.2$	${ \begin{smallmatrix} 1.97 \\ 0.012 \\ 0.11 \\ 41.9 \\ 6.3 \end{smallmatrix} }$	${ \begin{smallmatrix} 1.00 \\ 0.014 \\ 0.19 \\ 41.8 \\ 10.5 \end{smallmatrix} }$	$0.90 \\ 0.020 \\ 0.37 \\ 41.2 \\ 11.8$	$0.86 \\ 0.0027 \\ 0.033 \\ 53.8 \\ 0.2$	$0.91 \\ 0.0041 \\ 0.050 \\ 45.2 \\ 0.4$	$0.0075 \\ 0.10 \\ \dot{1.5}$	$\begin{smallmatrix}&1.17\\0.0063\\0.074\\50.0\\&6.3\end{smallmatrix}$	$0.96 \\ 0.0086 \\ 0.15 \\ 44.3 \\ 11.9$	${ \begin{smallmatrix} 1.16 \\ 0.013 \\ 0.33 \\ 51.0 \\ 1.7 \end{smallmatrix} }$	$1.72 \\ 0.010 \\ 0.13 \\ 49.0 \\ 6.0$	$0.97 \\ 0.016 \\ 0.34 \\ 48.7 \\ 4.2$

^a H₂-gaseous hydrocarbon fraction.
^b Includes small amounts of N₂, CO, CO₂ and sulfur compounds produced from feed.
^c Corrected to 100% material balance.

$$C_2H_2 + H_2 \rightleftharpoons C_2H_4$$

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6$$

vary with reaction time, owing to competing pyrolysis reactions, approach to equilibrium indicates high relative reaction rates (5, 44) for the hydrogenation and dehydrogenation reactions between the two-carbon-atom hydrocarbons or related two-carbonatom active species. In contrast, the formation of methane is a relatively slow reaction, as illustrated by the pyrolysis behavior of hydrogen-ethylene mixtures of 2 to 1 mole ratio (Figure 3).

The similarity in gaseous product distribution for all but the thermally most stable feed hydrocarbons under severe pyrolysis conditions must therefore be related to the rapid approach to equilibrium by the two-carbon-atom species and the formation of the other gaseous products via two-carbon-atom intermediates. Support for the formation of these intermediates can be found in

studies of ring formation in hydrocarbon pyrolysis (11, 16, 53) and in the fact that very short reaction times greatly favor the production of ethane, ethylene, and acetylene (19, 48).

The concentrations of methane in pyrolysis products can be related to the function $f_{2(i)}/K_{2(i)}$. The approach of this system to equilibrium is so slow that it has been treated as an apparent stationary state in earlier work (9, 26, 30). However, the rate of approach of the methane-ethane-hydrogen system to equilibrium is well defined as a function of reaction time and temperature for a wide range of feed hydrocarbons (Figure 4). The results for ethane (18, 20) and ethylene (Table II and 54) fall considerably below the data of Figure 4 because of the relative slowness of the primary cracking reactions for these hydrocarbons of low molecular weight. The addition of hydrogen to the feed causes further deviations from the methane-ethane-hydrogen equilibrium (Table II), in contrast to the behavior of the fast-reacting ethane-ethylene-hydrogen and ethylene-acetylene-hydrogen systems.



Figure 4. Effect of reaction time on approach of ethylene-hydrogen-methane system to equilibrium

A significant difference appeared to exist between the behavior of methane and that of other hydrocarbons, probably because of the occurrence of carbon-carbon bond breakage in the initial cracking steps of hydrocarbons with two or more carbon atoms as compared to carbon-hydrogen bond breakage for methane (37, 38, 46). A 1700° F. and a reaction time of approximately 30 seconds, methane cracked into products approaching equilibria among hydrogen, methane, ethane, and ethylene (Table II). This is a general agreement with the pyrolysis data on methane obtained by Hague and Wheeler (18) at 10- to 20-second reaction time.

Reaction	n Temp.	Product Vol	Gas Com ume Frace	$(K_1)(K_2)$			
° F.	° C.	C_2H_4	H_2	CH_4	Exptl.	Calcd.	
$\begin{array}{c} 1652 \\ 1742 \\ 1832 \\ 1922 \end{array}$	900 950 1000 1050	$\begin{array}{c} 0.028 \\ 0.037 \\ 0.028 \\ 0.021 \end{array}$	$\begin{array}{c} 0.140 \\ 0.315 \\ 0.426 \\ 0.543 \end{array}$	$\begin{array}{c} 0.826 \\ 0.639 \\ 0.542 \\ 0.433 \end{array}$	$1240 \\ 111 \\ 58 \\ 30$	$290 \\ 120 \\ 52 \\ 24$	

The behavior of a system of higher molecular weight (i = 3) represented by Equations 2 and 4 is shown in Figure 5. Because of the small concentrations of propane in the high-temperature pyrolysis products of feeds other than propane, and the interference of undecomposed propane when used as a feedstock, the propene-hydrogen-methane-ethylene system was used in preference to the propane-hydrogen-methane-ethane system. The partial pressure product $f_{2(3)}$ based on the reaction scheme of Equations 1 and 2 can be related to the partial pressure product f_s employed in Figure 5, under conditions where equilibrium between olefins and paraffins of equal carbon number is approached $[f_{1(4)} = K_{1(4)}]$:

$$f_3 = \frac{(CH_4)(C_2H_4)}{(C_3H_6)(H_2)} = \frac{f_{2(3)}K_{1(3)}}{K_{1(2)}}$$

It can be seen that the rate of approach of f_3 to its equilibrium

value was much greater than that of $f_{2(2)}$. In spite of considerable scattering of the experimental values of f_s due to the inaccuracy of the propene determinations, a systematic variation of f_s as a function of reaction time and temperature was observed for the wide range of feedstocks investigated.

The equilibrium constants used in Figures 2, 4, and 5 and in the tabulated data were estimated from plots of log K vs. reciprocal absolute temperature. The values of the equilibrium constants were calculated at 100° K. intervals from standard free energies of formation (39).

Gaseous product distribution can be estimated

It is possible to estimate the distribution of hydrogen and the major olefins and paraffins of low molecular weight obtained in the pyrolysis of natural gas liquids and petroleum and shale oils from Equations 3, 4, and 5 by the use of one additional independent relationship among pyrolysis conditions, feedstock properties, and a parameter of product gas composition. This relationship is required because the reaction system of Equations 1 and 2 rep-



Figure 5. Effect of reaction time on approach of propene-hydrogen-methane-ethylene system to equilibrium



Figure 6. Correlation of gaseous product distribution for petroleum oils and natural gas liquids

resents 2i + 1 components, while Equations 3, 4, and 5 yield only 2i independent relationships. For example, the use of i = 2 will determine the product distribution of the five major components of gaseous pyrolysis products—methane, ethane, ethylene, propene, and hydrogen.

$$\frac{(C_2H_6)}{(C_2H_4)(H_2)} = K_1 \text{ or } f_1(t,\theta) \text{ from Figure 2}$$

$$\frac{(CH_4)^2}{(C_2H_6)(H_2)} = f_2(t,\theta) \text{ from Figure 4}$$

$$\frac{(CH_4)(C_2H_4)}{(C_3H_6)(H_2)} = f_3(t,\theta) \text{ from Figure 5}$$

$$(H_2) + (CH_4) + (C_2H_6) + (C_2H_4) + (C_3H_6) = x$$

To solve this system of equations, an empirical relationship using the paraffin-olefin ratio of the gaseous pyrolysis products was developed in an earlier study (26). This relationship had the form:

$$\frac{\sum_{i=1}^{i} (C_{i}H_{2i+2})}{\sum_{i=1}^{i+1} (C_{i}H_{2i})} = f(t \,\theta, C/H, Px)$$

and introduced the variable of feedstock composition (carbonhydrogen weight ratio). However, the solution of this system of equations is time-consuming, and the accuracy of the results is limited (27). A more practical approach consists of the use of an empirical factor of severity of cracking (43) for correlation of compositions of pyrolysis product gas at various partial pressures (Px) of the reacting system (hydrogen and gaseous hydrocarbons). This procedure is illustrated in Figure 6 with pyrolysis data for 7.04 and 7.25 C/H ratio reduced crudes and for a 6.39 C/H ratio Diesel oil (Table III) and with pyrolysis data for a 5.2 C/H ratio natural gasoline as described below. Data at total pressure levels of approximately 1 and 3 atm. are plotted; for the petroleum oils the partial pressures of the product gas hydrogenhydrocarbon fraction are 0.7 to 0.9 and 2.0 to 2.3 atm., respectively, because of dilution with inert carrier gases. The gaseous product distributions at the two pressure levels are shown to correlate well with the pyrolysis severity function, $t\theta^{0.06}$. The small influence of feed hydrocarbon composition over the 5.2 to 7.25 C/H ratio range is masked by data scattering due to variations in partial pressure, and limitations of the empirical $t\theta^{0.06}$ function in defining severity of pyrolysis over the entire 1.4- to 10.4-second range of reaction time covered by the plots of Figure 6.

If the proposed method for estimating gaseous product distribution is applied to various types of thermal cracking equipment, empirical correlations for correction of differences in measurement of operating conditions will probably be required. This applies particularly to the determination of

effective reaction temperatures and reaction times in cyclic operation or in tube furnaces with extreme temperature gradients. In such cases, the ethane-ethylene-hydrogen equilibrium can be used to correlate the measured with the effective reaction temperatures.

Conclusions

Above reaction temperatures of 1300° F. and reaction times of 1 second, the gaseous product distribution obtained from pyrolysis of natural gas liquids and petroleum and shale oils can be related to apparent equilibria and functions of reaction temperature and reaction time which express the relative approach to equilibrium of various secondary gas-phase reactions.

The variation of the partial pressure products with changes in pyrolysis conditions can be satisfactorily interpreted by two groups of reactions: hydrogenation of the gaseous olefins to paraffins of equal carbon chain length, and hydrogenolysis of paraffins with two or more carbon atoms to methane or methane and a higher paraffin.

The ethylene-hydrogen-ethane system attained equilibrium at reaction times above 3 seconds and rapidly approached equilibrium at reaction times in the order of 1 second. When hydrogen was introduced with the feed hydrocarbon, the olefinhydrogen-paraffin equilibria tended to be maintained. The approach of the ethane-hydrogen-methane system to equilibrium was found to be very slow and independent of feed properties, except when feed hydrocarbons of low molecular weight and with slow rates of primary cracking reactions were used. The behavior of the propene-hydrogen-methane-ethylene system was similar, although the rate of approach to equilibrium was much more rapid.

On the basis of the systematic variation with pyrolysis conditions of gaseous product compositions in vapor-phase cracking of hydrocarbons of all types, a method for predicting the distribution of the major gaseous products from operating variables was developed.