# **Pyrolysis of Propane**<sup>1,2</sup>

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HE decomposition of hydrocarbon gases and liquids with associated changes is practiced extensively in industry where it is commonly known as cracking. The general effects of cracking are well known. An understanding of what actually takes place would be of great theoretical and practical interest. The unsaturated compounds and hydrogen obtained by cracking hydrocarbon gas have considerable potential value, and are, in fact, already being used to some extent.

Many investigations of the pyrolysis of hydrocarbon gases have been made. The large amount of published inThe catalytic and non-catalytic decompositions of propane are investigated. The principal products, up to a temperature of intensive decomposition, are found to be hydrogen, methane, ethylene, propylene, and ethane. The net result of the primary decomposition may be represented by equations, but the actual mechanism appears to consist in the inter-reactions, decompositions, hydrogenations, and dehydrogenations of all possible radicals which can be formed by the breaking of the molecule at any point. The belief that the carbon-carbon bond in aliphatic hydrocarbons is weaker than the carbon-hydrogen bond is verified. At temperatures above 700° C., condensation products of an oily aromatic nature are formed by propane decomposition.

Catalysts containing nickel, cobalt, chromium, and iron cause increased yield of hydrogen from the decomposition.

A method is developed for analysis of cracked hydrocarbon gas by low-temperature fractionation supplemented by absorption and combustion methods.

formation dealing with this subject is indicated by the lengthy historical résumé of Egloff, Schaad, and Lowry (3) which appeared recently.

Bone and Coward (1) suggested the formation of residues, such as  $:CH_{2}$ , and  $.CH_{3}$  by the decomposition of hydrocarbons.

Zanetti (6) decomposed a gas consisting of 97 per cent propane and 3 per cent butanes. Unsaturated and saturated gaseous hydrocarbons, aromatic hydrocarbons, and hydrogen were obtained. He also found that iron and nickel gauzes caused a rapid increase in the amount of hydrogen formed.

Pease (5) considered the two principal reactions in the decomposition of propane to be dehydrogenation and demethanation.

Hague and Wheeler (4) found that propane at rest began to decompose at  $460^{\circ}$  C. At higher temperatures the principal products of the decomposition were methane, hydrogen, ethylene, propylene, and ethane.

Davidson (2) investigated the effect of a large number of materials. Nickel, iron, and cobalt markedly decreased the percentages of unsaturates and increased the percentage of hydrogen at all temperatures ( $550^{\circ}$  to  $950^{\circ}$  C.) at which investigations were made.

In all of the investigations mentioned above, there had to be made certain assumptions concerning the composition of the gas resulting from the decomposition. This was necessary because there is no accurate known method of selectively absorbing one of several unsaturated constituents, and not more than two saturated hydrocarbon constituents of a gas mixture can be determined by combustion and absorption methods. Only recently has apparatus been available for analysis by lowtemperature fractionation. Analysis by this method, supplemented by absorption and combustion methods, make unnecessary any assumptions concerning the composition of the gas. This combination of methods was used in the analysis

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of the products of the decomposition of propane herein reported in cases in which it was desired to know rather accurately the composition of the exit gas for the purpose of studying the nature of the decomposition.

The purpose of the present work is to investigate the pyrolysis of propane by analysis of the products by an improved method, and to investigate the catalytic effect of several kinds and forms of catalysts.

## Method of Decomposition

A 20-gallon (75.8-liter) cylinder of commercial liquefied propane under approximately 125 pounds (56.7 kg.) pressure

was obtained from the Skelly Oil Company of Tulsa, Okla. The decomposition of this gas was 97.5 per cent propane, 1.7 per cent ethane, and 0.8 per cent butanes.

Figure 1 is a diagrammatic sketch of the apparatus used in the decomposition of the gas. The method of conducting an experiment depended somewhat upon whether or not the effect of a possible catalyst was being investigated. Gas was released from the cylinder into bottle B, from which it displaced sodium chloride solution. To pass gas through the drying apparatus into the silica reaction tube, saturated sodium chloride solution was allowed to flow into the water jacket G with an overflow at H, thence through a previously calibrated interchangeable tube at I. The exit gas was passed to waste through X or collected at atmospheric pressure in D by controlling the rate at which sodium chloride solution siphoned out. This arrangement gave a constant rate of flow through the furnace. The gas flow was started through the furnace as the desired temperature was nearly reached. When a steady state was attained, the exit gas was collected.

The temperature was controlled by a hand-regulated rheostat. The temperatures were read on a calibrated pyrometer connected to a chromel-alumel thermocouple which was placed alongside the silica tube in an ordinary carbon-combustion furnace. The total length of the silica tube was 86 cm., its internal diameter was 1.9 cm., and its heated portion was 28 cm. in length. The volume of the heated portion of the tube was therefore 79 cc.

The carefully prepared sensitive catalysts which were first tried were prepared in general by precipitating the hydroxide from the nitrate with ammonium hydroxide, dehydrating the hydroxide to the oxide, and reducing the oxide *in situ* with hydrogen, where possible to reduce it. These catalysts were held in place near the center of the heated vertical tube by a porcelain plate supported by a glass rod, when experimenting at lower temperatures, and an iron wire support was used at higher temperatures. These materials were found to have no catalytic effect. Nitrogen was passed through the tube to sweep out hydrogen. The hydrogen and nitrogen were allowed to pass into the air through X. Propane gas was passed into the heated tube for a definite period of time, and a sample was then collected for analysis. Blank runs were made under the same conditions.

In later experiments with more rigid catalysts, such as wire gauzes, a sample of gas was taken when a steady state had been reached, the exit-gas flow was diverted to waste, the



Figure 1-Apparatus for Decomposing Propane

stopper was quickly removed from the upper end of a heated silica tube, the catalyst dropped in, the stopper quickly replaced, one minute allowed to pass, and a sample collected in the usual way.

### **Gas** Analysis

In some cases the only analysis made of the gas was that of total unsaturates with bromine water, hydrogen with cupric oxide, and saturated hydrocarbons (where not more than two were present) by combustion. The limitations and inaccuracies of these methods for complex gas mixtures are well known. Complete analyses were made in some cases by lowtemperature fractionation supplemented by absorption and combustion methods.

A diagram of the low-temperature fractionation apparatus is shown in Figure 2. For analysis by this method it was necessary to use a sample of about 20 liters. Liquid air was used as the cooling medium. It was possible to obtain good separation of all the components of the exit gas except propylene and propane. Three fractions were distilled by low-temperature fractionation. The first contained the hydrogen and methane, the second, ethylene and ethane, while the third fraction contained all higher hydrocarbons. Acetylene was not found. These simplified fractions were subjected to supplementary analysis by absorption and combustion.

#### **Results of Decomposition and Analysis**

A series of experiments was made in which the temperature was varied while the rate of flow of gas into the tube was maintained at 7.7 liters per hour. The total unsaturated and hydrogen content of the exit gas was determined. The percentage increase in volume on decomposition was calculated from the volumes of entering and exit gas. These results are shown in Table I.

Table I—Results of Variation	of	Temperature
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Run	TEMP.	UNSATD.	Hydrogen	INCREASE IN VOL.
	° C.	%	%	%
1	600	4.2	2.5	17
2	650	12.0	5.9	30
3	660	25.0	10.7	
4	700	26.0	10.7	45
5	<b>76</b> 0	33.2	15.6	81
6	800	29.0	22.1	105
7	830	22.0	26.5	130

It will be noted that the percentage of hydrogen steadily increases, while the unsaturates increase up to a temperature of about  $770^{\circ}$  C., then decrease.

The results of analysis by low-temperature fractionation were expressed by plotting the curve of the volume distilled as abscissas against the temperature of distillation as ordinates. The values in percentages of each component obtained by low-temperature fractionation supplemented by absorption and combustion are shown in Table II for a series of experiments.

Table	II—Values	of	Components	Obtained	by	Low-Temperature
			Fraction	nation		-

Amount in Exit Gas of: Cal									
Run	TEMP.	$H_2$	CH4	$C_2H_4$	$C_2H_6$	C₃H₀	$C_3H_8$	COMPOSED	
	° C.	%	%	%	%	%	%	%	
8	660	11.0	20.1	15.0	4.7	10.7	40.7	43	
9	760	16.8	35.5	27.1	8.5	6.6	7.3	87	
10	830	26.5	38.4	20.0	12.8	0.0	0.0	100	

The rate of gas flow into the reaction tube was 7.7 liters per hour in each of the three cases given in Table II.

Two decomposition experiments were made in which the temperature was constant at 830°C., while the rate of flow was changed. The composition of the exit gas is shown in Table III.

Table III—Results of Change in Rate of Flow							
Run	RATE	$H_2$	CH4	$C_2H_4$	C <sub>2</sub> H <sub>6</sub>	CaHe	C₃H
	Liters/hour	%	%	%	%	%	%
10 11	$\begin{array}{r} 7.7\\17.7\end{array}$	$\begin{array}{c} 26.5\\ 20.1 \end{array}$	38.4 34.7	20.0 29.8	$\substack{12.8\\13.6}$	0.0	$\begin{array}{c} 0.0\\ 0.0\end{array}$

In all runs at temperatures above  $600^{\circ}$  C., some carbon was deposited in the reaction tube. In all runs above  $650^{\circ}$  C. a tar fog was seen in the visible exit part of the tube and in the gas-exit line. In a few cases some of this fog was carried into the gas receiver by the gas stream. In such cases drops of oil collected on the surface of the water. The oil which condensed on the tube was of a black tarry nature with an aromatic odor. Not enough of the oil was formed for examination.



A series of experimental decompositions were made with carefully prepared granular catalysts of nickel, iron, chromium, copper, cobalt, aluminum, and magnesium. Runs were made with and without these catalysts under the same conditions of rate of flow and temperature (approximately  $300^{\circ}$  C.). So far as could be determined by analysis of the exit gas for hydrogen and unsaturates, these catalysts had no effect, although in some cases carbon was deposited on them. This seemed to indicate that catalytic effect (if present at all) was inhibited by carbon decomposition. The same iron catalyst had no appreciable effect at 760° C.

A series of runs was made with and without possible catalysts of a more stable and rigid nature. Data from this series are shown in Table IV.

Table IV-Effect of Catalysts

					COMPOSITION	
		FORM OF	PREPARATION OF		of E	XIT GAS
RUN	CATALYST	CATALYST	CATALYST	TEMP.	$H_2$	Unsatd.
				° C.	%	%
12	Iron	Gauze	Reduced with Ha	760	15.1	35.0
13	None			760	15.0	35.0
14	Iron	Gauze	None	830	18.5	30.7
15	Nickel	Gauze	None	830	25.0	21.0
16	None			830	26.5	22.0
17	Nickel	Gauze	Reduced with H <sub>2</sub>	815	27.7	22.1
18	None			815	26.6	22.0
19	Carborundum	Granular	None	840	22.8	25.0
20	None			840	26.6	23.2
21	Calcium carbide	Granular	None	815	24.8	25.2
22	None			815	27.2	23.5
23	Activated alumina	Granular	Used as received	800	21.3	27.4
24	None		·· .	800	21.4	27.6
25	Monel metal	Gauze	None	830	32.2	16.5
26	None			830	26.7	20.4
27	Petroleum coke	Granular	Heated	800	22.2	28.5
28	None			800	24.8	26.2
29	Nickel	Gauze	None	800	36.1	15.4
30	None		· · .	690	34.8	22.0
31	Nichrome	Gauze	None	690	34.8	22.0
32	Monel metal	Gauze	None	830	55.8	3.6
33	Calcium-silicon al-					
	loy	Granular	None	700	20.3	31.8
34	Platinized pumice					
	stone		Used as received	700	17.3	35.0
35	Palladized asbestos		Used as received	700	16.1	32.6
36	None			705	15.0	32.0
37	Reduced vanadium					
	pentoxide	Granular	Reduced with H <sub>2</sub>	705	14.3	34.6
38	Iron	Powder	•••	760	17.3	17.2
39	Nickel	Powder	• • •	760	48.7	13.0
40	Steel	Gauze		800	43.0	11.0

From a comparison of the results at the same temperatures and rates of flow of Table IV, it is seen that catalysts composed of, or containing nickel, cobalt, chromium, and iron decidedly influence the decomposition products. The effect is principally that of increased production of hydrogen and methane. The rate of gas inflow was 7.7 liters per hour in each run of the above series.

In runs 25, 29, and 32 in which 150-mesh gauze was used, the gauze was found to be almost completely disintegrated after a few liters of gas had passed through it. The gauzes used in all other runs were 60 mesh. All gauzes were 6 by 3 inches (15.24 by 7.62 cm.). They were used in concentric roll form.

In one case it was found that by taking samples at 5-minute intervals, the composition of the exit gas varied during the time of catalytic effect. This situation was suspected but not shown to be true in all cases of catalytic effect.

After determination of unsaturates and hydrogen in the exit gas from runs 29, 32, and 39, the residual gas was found by combustion to consist mostly of methane.

#### **Discussion of Results**

Assuming that the two primary decomposition reactions may be represented by the equations,

$$C_{3}H_{8} = CH_{4} + C_{2}H_{4}$$
(1)  

$$C_{3}H_{8} = C_{3}H_{6} + H_{2}$$
(2)

and considering the experimental decomposition at  $760^{\circ}$  C., the results of which are included in Table II, it will be seen that the volumes of methane and ethylene should be equal but are not. The same is true of propylene and hydrogen. Since ethane was found in the exit gas it may be that some of the ethylene produced in the primary decomposition has reacted with some of the hydrogen similarly produced to give ethane. Calculations made on this basis show very good agreement between the volumes of methane and ethylene resulting from primary decomposition by Equation 1. However, there is no definite proof that ethane was formed in this way. In fact, the hydrogenation of ethylene seems very unlikely under the conditions of this experiment. The ethane may be formed by the combination of methyl fragments resulting from the decomposition or by hydrogenation of the ethyl fragments resulting in the same way. After adding the amount of hydrogen which may have combined with ethylene to the amount found, there is still considerable lack of agreement between the amounts of propylene and hydrogen produced by primary reaction (2). Apparently some of the propylene has decomposed in secondary reactions.

Assuming that the methane found in the exit gas is a measure of the extent of Equation 1, the percentage of propane decomposing according to Equation 1 was calculated from the data: 7.2 liters of gas was passed into the reaction tube while the volume of the exit gas was 13.1 liters consisting of 35.5 per cent methane. According to this, 73 per cent of the propane decomposed as represented by Equation 1.

When the experimental decomposition at  $660^{\circ}$  C., results of which are shown in Table II, is considered in the same way as above, it is also impossible to show how the decomposition takes place. In this case 9 liters of propane were passed into the tube while the volume of the exit gas was 12.7 liters containing 20.1 per cent of methane. Calculation indicates that 66 per cent of the propane decomposed follows the course represented by Equation 1. Because of apparently intensive secondary reactions, it is not possible to treat the other decompositions as in the two cases already given.

In any experiment carried out here for which complete analysis of products was made, the proportion of product found could not be accounted for except by reaction or decomposition of radicals resulting from primary decomposition. The net result of the primary decomposition of propane can only be represented by equations showing the formation of compounds. The actual decomposition process of propane appears to consist of formation of fragments, such as methyl, ethyl, and propyl, which undergo changes, such as combination with other radicals, hydrogenation, or further decomposition. This same statement applies, of course, to other hydrocarbons, if true in the case of propane. The final resulting products apparently depended upon inter-reactions, decompositions, hydrogenations, and dehydrogenations of nascent radicals to a much greater extent than have been generally believed. Probably the best way to indicate the primary effect of the decomposition of a hydrocarbon is to represent it as decomposing to all possible radicals. Thus for propane,

$$C_{3}H_{8} \longrightarrow CH_{3} + C_{2}H_{5}$$
$$C_{3}H_{8} \longrightarrow C_{3}H_{7} + H$$

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#### Literature Cited

- (1) Bone, W. A., and Coward, H. F., J. Chem. Soc., 93, 1197 (1908).
- (2) Davidson, J. G., J. IND. ENG. CHEM., 10, 901 (1918).
- (3) Egloff, G., Schaad, R. E., and Lowry, C. D., Jr., J. Phys. Chem., 34, 1617 (1930).
- (4) Hague, E. N., and Wheeler, R. V., Fuel Science Practice, 8, 512, 560 (1929).
- (5) Pease, E. N., J. Am. Chem. Soc., 50, 1779 (1928).
- (6) Zanetti, J. E., J. IND. ENG. CHEM., 8, 674 (1916).