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# Thermal Treatment of Gaseous Hydrocarbons I. Laboratory Scale Operation

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ONSIDERABLE attention has been given recently to the possibility of utilizing gaseous hydrocarbons, such as natural gases and gases from oil-cracking plants, as sources of motor fuel of high antiknock value. Since the researches of Berthelot (2) which led to the first comprehensive theory of the mechanism of decomposition of hydrocarbons, many workers have demonstrated the conversion of aliphatic hydrocarbons into liquids essentially aromatic in nature. It is now seventy years since Berthelot began his researches on this subject and unproved steps are still to be found in all suggested mechanisms for the changes. Our knowledge of the mode of pyrolysis of even the gaseous hydrocarbons is still imperfect, but certain of the normal changes of these compounds. when subjected to heat, are

A review is presented of the mechanisms of thermal decomposition and polymerization of the gaseous hydrocarbons. Conversions to motor benzene, distilling below 200° C., of 16 to 25 per cent with paraffins (methane excepted) and 25 to 30 per cent with olefins are readily obtained by atmospheric pressure treatment at 750° to 950° C. The gasoline fraction contains benzene, toluene, styrene, m- and p-xylenes, and indene, while the higher boiling products contain naphthalene, anthracene, phenanthrene, and chrysene. By the polymerization of olefins at pressures between 200 and 2000 pounds per square inch (14.05 to 140.5 kg. per sq. cm.) and temperatures 300° to 550° C. conversions into liquids up to 92 per cent are attained. Of the liquid hydrocarbons obtained, 86 per cent is in the gasoline range and has about five-sixths the blending efficiency of benzene. The gasoline fraction contains olefins and paraffins with 3 to 8 carbon atoms to the molecule.

now reasonably clear. Furthermore, in many cases it is possible to forecast with reasonable certainty the nature and the approximate quantities of the products obtained when even complicated gaseous mixtures are decomposed. Investigations on the laboratory scale, using pure single gases and synthetic mixtures, are largely responsible for these advances in knowledge.

From the industrial viewpoint, the production of liquid hydrocarbons from gaseous paraffins and olefins is of considerable importance owing to the vast quantities of these hydrocarbons available for development. In 1929 the quantities of paraffin hydrocarbons available, expressed in millions of cubic feet, were stated (3) to be: methane, 2,015,000; ethane, 336,150; propane, 111,415; and butane, 64,980. The quantities of gaseous olefins available are more difficult to estimate because of the considerable variation in the gases produced in cracking operations. A figure of 275,000 million cubic feet may be taken as the volume of cracker gas produced in 1930, and of this it is estimated that the quantities of gaseous olefin hydrocarbons available from this source, expressed in millions of cubic feet are: ethylene, 16,500; propylene, 22,000; butylenes 11,000.

From these figures it is estimated that the potential yield of benzene from the paraffins and olefins (methane excluded) by pyrolysis is of the order of 4,750,000 tons per year. Al-

ternatively, if quantitative dehydrogenation of the paraffins to olefins and quantitative polymerization of the olefins to lowboiling liquid hydrocarbons are assumed, the potential liquid yield is 17,750,000 tons per year. On the assumption of 60 per cent efficiency for the two processes in combination, the yearly production would be reduced to 10,650,-000 tons, but even this represents a quantity rather more than twice that produced by singlestage pyrolysis for aromatic hydrocarbons. Here, then, are two alternative schemes for the utilization of large quantities of gas with gasoline as the product; of the two, the second method is the more efficient and the more flexible, since by varying operating conditions it is possible to vary the products from butylene to lubricating oils.

The scope of Part I is a general review of work on the labo-

ratory scale on the following processes: (1) pyrolysis for the production of motor benzene, (2) pyrolysis for the production of olefins, and (3) polymerization and condensation of olefins to give low-boiling liquids.

The term "pyrolysis" throughout this paper is confined to thermal treatments above  $600 \,^{\circ}$  C. with the rates of flow used: for, although pyrolysis is a term of general application to the paraffins, with the olefins complications arise. The above operations are covered by patents (1).

While processes 1 and 3 are both of direct application to gas containing olefins such as gas from oil-cracking plants, natural gas must approach process 3 via mild pyrolysis for the production of olefins, or, as an alternative, via process 1. Figure 1 indicates the steps involved in these operations.

### MECHANISM OF DECOMPOSITIONS

PARAFFIN HYDROCARBONS. From their study of the action of heat on the unbranched chain paraffins from ethane to N-hexane the authors conclude that the degradation of these hydrocarbons proceeds by the reversible elimination of a molecule, HX, which may be either a paraffin of smaller molecular weight or, in the limit, hydrogen. The residue from this primary decomposition is an olefin. Thus with ethane, propane, and N-butane the primary decompositions are indicated by:

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Ethane:
 CH_3CH_3 = CH_2: CH_2 + HH
Propane:
 CH_3CH_2CH_3 = CH_2:CH_2 + CH_3H
 CH_{3}CH_{2}CH_{3} = CH_{3}CH:CH_{2} + HH
N-butane:
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With each hydrocarbon the reactions are given in order of their importance. As the series is ascended, the tendency for hydrogen to be eliminated, leaving an olefin with the same number of carbon atoms as the original paraffin, rapidly diminishes.



FIGURE 1. STEPS IN PYROLYSIS AND POLYMERIZATION **Operations** 

Methane requires separate consideration since the absence of a carbon-carbon linkage causes its behavior to be different from that of the higher members of the series. Methane is far more stable than the other paraffins, and on decomposition the main reaction produces carbon and hydrogen. At comparatively low temperatures, however, ethylene is formed and the mechanism of the early decomposition may be expressed by:

 $CH_{2}H \longrightarrow =CH_{2} + HH$ 

two of the CH<sub>2</sub> residues combining to form ethylene.

Above the range 700° to 750° C. under the conditions of these experiments benzene and other aromatic hydrocarbons are produced from each gas, methane included. Below this temperature range, when the primary reactions are taking place, each hydrocarbon follows its own course, but at the higher temperatures the secondary reactions are similar in all cases. At this stage of the syntheses, ethylene appears to be the starting point. The authors' experiments show that ethylene readily polymerizes to butylene, that butylene by dehydrogenation produces butadiene, that butadiene and ethylene unite in equimolecular proportions to give cyclohexene, and that cyclohexene produces benzene. The mechanism appears to be as follows:

 $\begin{array}{c} 2\mathrm{CH}_2{:}\mathrm{CH}_2 \longrightarrow \mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}{:}\mathrm{CH}_2 \longrightarrow \mathrm{CH}_2{:}\mathrm{CH}\mathrm{CH}{:}\mathrm{CH}_2 + \mathrm{H}_2 \\ \mathrm{CH}_2{:}\mathrm{CH}\mathrm{CH}{:}\mathrm{CH}_2 + \mathrm{CH}_2{:}\mathrm{CH}_2 \longrightarrow \mathrm{CH}_2 & \xrightarrow{\mathrm{CH}_2{:}\mathrm{CH}_2} & \xrightarrow{\mathrm{CH}_2{:}\mathrm{CH}_2{:}\mathrm{CH}_2} & \xrightarrow{\mathrm{CH}_2{:}\mathrm{CH}_2{:}\mathrm{CH}_2} & \xrightarrow{\mathrm{CH}_2{:}\mathrm{CH}_2{:}\mathrm{CH}_2} & \xrightarrow{\mathrm{CH}_2{:}\mathrm{CH}_2{:}\mathrm{CH}_2} & \xrightarrow{\mathrm{CH}_2{:}\mathrm{CH}_2$ CH CH:CH CH

The exact mechanism of the addition of ethylene to butadiene is not clear, but cyclohexene has been shown to be an intermediate in the production of benzene. There are indications that a hexadiene precedes the production of cyclohexene and that a cyclohexadiene precedes the formation of benzene, but of this no satisfactory proof can be advanced as yet.

By analogy with the formation of diphenvl from benzene by condensation, it is reasonable to suppose that butadiene can condense with benzene to form naphthalene, and that anthracene and phenanthrene can be formed from naphthalene in a similar manner. Styrene, a product found in benzene produced by pyrolysis, may similarly be formed by the condensation of benzene and ethylene.

OLEFIN HYDROCARBONS. With the olefins, ethylene, propylene, and the two unbranched chain butylenes, the principal primary changes, common to all, involve the formation of either the two-carbon or the four-carbon (or both) atom members of the olefin series. These reactions may be represented by:

Ethylene:  $2C_2H_4 = C_4H_8$ Propylene:  $2C_8H_8 = C_2H_4 + C_4H_8$ Butylene:  $C_4H_8 = 2C_2H_4$ 

Butylene is not formed from ethylene by condensation to butadiene followed by hydrogenation; the change is a true polymerization. A secondary reaction which follows this polymerization is the elimination of hydrogen and the production of butadiene.

With propylene, an important secondary change, in the presence of hydrogen, is the production of methane and ethylene by scission of the carbon chain at the terminal carbon-carbon bond and subsequent hydrogenation of the radicals, as shown by:

$$CH_3CH:CH_2 + HH \longrightarrow CH_2:CH_2 + CH_3H$$

Of the two butylenes,  $\Delta^{\beta}$ -butylene was found to be more stable than  $\Delta^{\alpha}$ -butylene. Three changes appear to be operative to approximately the same extent at 600° C. with the butylenes: (1) depolymerization to ethylene, followed by secondary hydrogenation of the ethylene to ethane, (2) scission of the carbon chain at the end single linking, with the formation of radicals which by hydrogenation give rise to propylene and methane, and (3) dehydrogenation of butylene to form butadiene.

At higher temperatures hydroaromatic liquid hydrocarbons are produced from the olefins by the general method of addition of butadiene and the olefin. This is followed by the elimination of hydrogen and the production of aromatic hydrocarbons.

PRODUCTION OF AROMATIC HYDROCARBONS FROM PURE PARAFFINS AND OLEFINS ON A LABORATORY SCALE. Under suitable conditions of temperature and contact time all the gaseous hydrocarbons produce quantities of liquid aromatic hydrocarbons. Furthermore, in the approximate temperature range 750° to 1100° C., the factors time and temperature are interdependent so that at the high temperatures it is possible, by adjusting the contact time, to obtain products similar to those at lower temperatures.

The effect of diluents on the production of aromatic hydrocarbons has been studied. Briefly, nitrogen is a true diluent and causes but a slow decrease in the production of aromatics with increasing concentration; oxygen in small quantities improves the yield of liquids, whereas hydrogen causes the formation of aromatics to fall off rapidly.

Some of the results obtained with a rate of flow of 4 liters per hour and a constant temperature reaction space of 52 cc. in a silica tube are given in Table I for the paraffins and in Table II for the olefins.

The pyrolysis of methane is an interesting problem. The conversion into benzene per pass through the reaction tube is low, but it is obvious that, if some economic method of hydrogen-removal could be found, the total conversion into benzene could be increased to perhaps 50 or 60 per cent of the methane supplied. Apart from the liberation of hydrogen and carbon,

any hydrocarbon formed during the pyrolysis of methane would provide useful material for further pyrolysis. Carbon can be reduced to a minimum, and hydrogen-removal and utilization is the remaining problem. On the laboratory scale, hydrogen-removal could be accomplished by the use of copper oxide, but the problem is not solved commercially.

TABLE I. PYROLYSIS OF PARAFFIN HYDROCARBONS IN SINGLE-STAGE OPERATION FOR PRODUCTION OF AROMATICS AT ATMOS-PHERIC PRESSURE<sup>a</sup>

<b>P</b> . <b>5</b> . 500.00	Timore	Conver- sion to	Conver- sion to Gasoline Boiling Below 170° C.	Conver Per 1000 cu. ft. total	RSION Per 100 cu. m. total	Conve Per 1000 cu. ft. gasoline boiling below	RSION Per 100 cu. m. gasoline boiling below
PARAFFIN	I EMP.	LIQUIDS	(338° F.)	0118	011	338° F.	170° C.
	° C.	% by wt.	%	Imp. gal.	Liters	Imp. gal.	Liters
Methane	1050	8.8	5.0	0.44	7.1	0.25	4.0
Ethane	{ 850 { 900	$\substack{17.93\\21.9}$	$\begin{array}{c}11.2\\10.63\end{array}$	1.7 2.1	$\begin{array}{c} 27.3\\ 33.6 \end{array}$	$\begin{array}{c} 1.1\\ 1.0 \end{array}$	$17.7 \\ 16.0$
Propane	850	23.09	11.65	3.25	52.1	1.6	25.6
Butane	${800 \\ 850}$	$20.4 \\ 24.55$	$12.91 \\ 11.64$	4.0 4.6	$\frac{64.3}{73.8}$	$2.4 \\ 2.35$	38.5 37.8
Pentane	850	26.8	11.87				
Hexane	${800 \\ 850}$	33.7 33.8	19.2 19.0		•••	•••	•••

 $^{a}$  All conversions and yields are calculated on gas input and not on gas decomposed.

Various materials have been tested on the laboratory scale for use in the fabrication of tubes for large-scale pyrolysis. The main points when considering a material are that it (1) must be heat resisting, (2) should not be fragile, (3) should not be porous, (4) should inhibit carbon deposition, and (5) should encourage benzene production. Among the materials tested were silica, porcelain, graphite, copper, aluminum, iron, nickel, fireclay and a number of alloys, but not one of these materials proved perfectly satisfactory.

With the use of various metals and alloys is bound up the question of catalysis, and, in this, two separate factors are involved: (1) benzene formation and (2) carbon deposition.

Generally, these two factors are both unfavorable in a particular alloy or both favorable, but there are exceptions. Two of the best alloys are Ferralloy (14 per cent aluminum, 86 per cent iron) and H. R. 4 (26 per cent chromium, 0.3 per cent nickel, 1.5 per cent manganese, 0.9 per cent silicon, and 0.15 per cent carbon); the former is better than silica in inhibiting carbon deposition and encouraging benzene formation. There are indications to show that carburization takes place in a number of alloys and the catalytic properties may be affected.

TABLE II. PYROLYSIS OF OLEFIN HYDROCARBONS IN SINGLE-STAGE OPERATION FOR PRODUCTION OF AROMATICS AT ATMOS-PHERIC PRESSURE<sup>6</sup>

						Conve	DRSION
						Per	Per
				Con	VERSION	1000	100
				Per	Per	cu, ft.	cu.m.
		CONVER-	CONVER-	1000	100	gasoline	gasoline
		SION	SION	cu. ft.	cu, m.	boiling	boiling
		то	TO	total	total	below	below
Olefin	Темр.	Liquids	GASOLINE	oils	oils	338° F.	170° C.
		% by	% by	Imp.		Imp.	
	° C.	wt.	wt.	gal.	Liters	gal.	Liters
Ethylene	800	36.1	17.7	3.15	50.5	1.6	25.6
Propulana	<i>§</i> 750	35.6	20.4	4.7	75.4	2.75	44.1
riopytene	1800	40.6	19.0	5.32	85.4	2.5	40.1
Ag-Butylene	<b>§</b> 700	35.8	23.6	6.25	100.2	4.1	65.8
Da-Daty lene	1750	39.6	22.45	6.85	110.0	3.95	63.4
A & Butylene	₹700	37.0	25.8	6.4	102.8	4.45	71.4
ap-patylene	₹750	39.6	23.2	6.85	110.0	4.1	65.8
a All convers	ione on	d wielde e	ro coloulo	tod on	des innu	t and no	t on goe

" All conversions and yields are calculated on gas input and not on gas decomposed.

With the exception of the liquids from methane, it is found that 50 to 60 per cent of the total liquid hydrocarbons produced boil below  $170^{\circ}$  C., the chief constituent of this spirit being benzene. With methane, about 80 per cent of the liquid produced is benzene. When considering these figures, account must be taken of the small quantities of liquid treated and of the necessarily high handling losses. The spirit figures are, therefore, conservative estimates. Recent work has demonstrated that the term "spirit up to  $200^{\circ}$  C." means in practice 75 to 80 per cent of the "total liquids" recorded in the tables. On this basis, allowing 75 per cent, the figures become:

	CRUDE G UP TO 2	ASOLINE 200° C.		CRUDE UP TO	GASOLINE 200° C.
	Imp. gal./ 1000 cu. ft.	Liters/ 100 cu. m.	I : 10	mp. gal./ 200 cu, fi	/ Liters/ t. 100 cu. m.
Methane Ethane Propane N-butane	$0.3 \\ 1.5 \\ 2.4 \\ 3.4$	$\begin{array}{r} 4.8\\ 24.0\\ 38.5\\ 54.5\end{array}$	Ethylene Propylene Δα-Butylene Δβ-Butylene	$2.4 \\ 3.9 \\ 5.1 \\ 5.1$	38.5 62.5 80.7 80.7

The experimental data are best indicated in graphical form (Figures 2 and 3). For one rate of flow—namely, 4 liters of gas per hour—the yields are expressed in liters of liquids per 100

cubic meters and Imperial gallons per 1000 cubic feet against the temperature of operation. This method of plotting has been adopted to present the results in a form directly comparable with largescale operation. From Figures 2 and 3, and the corrected table of yields given, it is possible to calculate the approximate benzene production from a gas



FIGURE 2. PRODUCTION OF LIQUID Hydrocarbons from Gaseous Paraffins

of known constitution. Thus, a gas obtained during the removal of gasoline, containing:



was expected to yield 2.7 Imperial gallons per 1000 cubic feet (43.3 liters per 100 cubic meters). In practice, on a semicommercial scale, the figure realized was 2.6 Imperial gallons per 1000 cubic feet (41.7 liters per 100 cubic meters).

CONDENSABLE PRODUCTS. The liquid products derived from pyrolysis operations may be conveniently divided into: (1) fraction boiling from 0° to 200° C. and (2) fraction boiling above 200° C.

The nature of the liquid hydrocarbons produced by pyrolysis has been shown to vary somewhat with operating conditions. In the region of optimum production of aromatic liquids, however, the variation is small and a representative example may be taken.

FRACTION BOILING FROM 0° TO 200° C. Up to 75 per cent by volume of this fraction was shown to be benzene itself. Toluene was present to the extent of 5 to 7 per cent. In the boiling range 135° to 150° C. the main constituent was shown to be styrene to the extent of 4 per cent of the gasoline fraction but *m*- and *p*-xylenes were also present. Indene was isolated and identified from the liquids boiling around 180° C. (For analysis made on the liquid product, see Part II, page 319.)

FRACTION BOILING ABOVE  $200^{\circ}$  C. From this fraction naphthalene, anthracene, and phenanthrene were readily isolated and identified, and the presence of chrysene was indicated.

The

paraffins

PRODUCTION OF

GASEOUS OLEFINS

FROM PARAFFIN HY-

present in natural gas

provide a potential

source of olefinic hy-

drocarbons by the ap-

plication of mild

pyrolysis. On the

assumption of quan-

titative dehydrogena-

tion of the paraffins

Egloff, Schaad, and

Lowry (4) have esti-

mated the following

production of olefins

based on figures for

1929 and expressed

in millions of cubic

feet: ethylene, 218,-

700; propylene, 92,-

750; and butylenes,

59,980. This field is

awaiting develop-

ment.

DROCARBONS.

lower



Figure 3. Production of Liquid Hydrocarbons from Gaseous Olefins

Methane as a source of olefins has not been considered here, since in normal pyrolysis the olefin concentration in the exit gas from methane is only from 1 to 4 per cent. With ethane the production of ethylene is a primary reaction, and it is possible by suitable adjustment of the time factor at 900° C. to obtain a conversion into ethylene of 58 per cent (by volume) on the ethane pyrolyzed, or 67 per cent on the ethane decomposed by single-stage operation. Reference may here be made to the results of Cambron (3) which have shown an optimum conversion of 47.2 per cent on the ethane pyrolyzed or 90 per cent on the ethane decomposed.<sup>1</sup> Further development of this treatment is required, but a conversion, in single-stage operation, of 60 per cent by volume of ethane should be readily achieved.

By the mild pyrolysis of propane and butane it is possible to obtain 90 to 100 per cent conversion by volume into gaseous olefins. The increase in volume of the treated gas over the untreated is between 80 and 100 per cent. One experiment with N-butane at 700° C. is as follows:

Inlet gas rate, liters/hour	5.0
Outlet gas rate, liters/hour	9.9
Vol. of tube at reaction temp., cc.	52

Analysis by a Podbielniak gas analysis apparatus combined with separation of unsaturated and saturated components on the Bone and Wheeler gas analysis apparatus gave:

	Per Cent by Volume			
	On exit gas	On inlet gas		
Hydrogen	5.8	11.45		
Methane	27.7	54.8		
Ethane	7.8	15.4		
Butane	11.85	23.4		
Ethvlene	23.5	46.5		
Propylene	18.4	36.4		
Butylenes	4.65	9.2		

The butane used contained 97% by vol. N-butane, 3% propane.

This conversion is 92.1 per cent by volume on the Nbutane passed through, or 120 per cent by volume on the

<sup>1</sup> In a more recent communication [Cambron and Bayley, Can. J. Research, 9, 175 (1933)] the conversion of ethane to olefins has been improved to 59 per cent on the ethane pyrolyzed by the use of baffled tubes. butane decomposed. On a weight basis these conversions are 58 and 76 per cent, respectively.

### INFLUENCE OF PRESSURE ON PYROLYSIS FOR AROMATIC Hydrocarbons

From theoretical considerations the application of pressure to the pyrolysis of paraffin hydrocarbons is not sound, for the initial reaction must involve an increase in volume. This does not apply to the pyrolysis of olefins where, in the early stages, polymerization occurs.

The influence of pressure on the pyrolysis of the paraffins has only been considered experimentally in relation to ethane at pressures up to 150 pounds per square inch (10.5 kg. per sq. cm.) over the temperature range 700° to 800° C. The apparatus used consisted essentially of an electrically heated vertical reaction tube of a Hadfield, Ltd., special steel (H. R. 4) connected at the inlet end to a single-stage compressor capable of operating at pressures up to 200 pounds per square inch (14 kg. per sq. cm.) and at the outlet to three condenser receivers in series. After the condensers, pressure was reduced to atmospheric by means of a loaded ball valve which operated automatically at the set pressure. Gas was metered in and out of the apparatus, and liquid products were weighed and analyzed. The bore of the tube was 2.5 cm., and it was found that a length of 35 cm. was at constant temperature.

Under the conditions of experiment the maximum conversion into aromatic liquids was found at  $750^{\circ}$  C. and 150 pounds per square inch pressure when aromatic hydrocarbons corresponding to 12.4 per cent of the ethane passed through the reaction tube were obtained. Of these liquids about 50 per cent boiled below 150° C. The conversion at atmospheric pressure—namely, 22 per cent of the ethane pyrolyzed—was therefore not approached under the conditions considered. The formation of ethylene from ethane was apparently inhibited by pressure, and instead more ethane decomposed to methane, hydrogen, and carbon. The approaches the set of the set of



FIGURE 4. POLYMERIZATION OF OLEFINS IN AUTOCLAVES

plication of moderate pressure such as 50 pounds per square inch (3.5 kg. per sq. cm.) is sufficient to reduce considerably the olefin production and the quantity of aromatic hydrocarbons.

The influence of pressure on the production of aromatic hydrocarbons from the olefins cannot immediately be deduced. The influence of pressures up to 150 pounds per square inch on the pyrolysis of ethylene has been studied experimentally over the temperature range  $600^{\circ}$  to  $700^{\circ}$  C. The highest recorded conversion into liquid hydrocarbons in this range is 35 per cent. By a suitable adjustment of the temperature and the time factor this figure may be approached at several pressures. The production of 36.1 per cent of liquid aromatic hydrocarbons at atmospheric pressure has not been improved upon, but the working temperature can be reduced by more than  $100^{\circ}$  C. by the application of pressure, without loss of yield. Increasing the pressure in this temperature region appears to accelerate the deposition of carbon.

## POLYMERIZATION OF OLEFINS

It has been shown that the first stage in the reactions involved when ethylene is heated at atmospheric pressure is a polymerization to butylene. Owing to the decrease in volume which occurs when gaseous olefins polymerize, increase in pressure favors the production of polymers. The case for polymerization and condensation as opposed to pyrolysis for the production of aromatic hydrocarbons is strong and may be indicated as follows:

PYROLYSIS							
(1	) High	te	mperatu	res	(800°	to	
	1100°	<b>C</b> .)	render	nec	essary	the	

- use of expensive special steels.(2) Operation at or near atmospheric pressure is advisable with necessity for large plant.
- (3) Comparative low yields of liquid suitable for motor benzene are obtained.
- (4) Deposition of carbon appears inevitable.
- (5) Production of tar is large.
- (6) Dilution with hydrogen may considerably reduce yields obtainable.
- low (up to 500° C.) Pressures higher than atmospheric are an advantage, and conse-

POLYMERIZATION AND CONDENSATION

Temperatures are comparatively

- quently plant size is reduced. Yields of liquid hydrocarbons approach theoretical (up to 92 per
- cent). Under suitable conditions carbon
- deposition is negligible.
- Tar production is negligible.
- Dilution with hydrogen has no considerable influence on production under suitable conditions.

While this comparison is of direct application to olefins only, it is rendered applicable to natural gas hydrocarbons through the medium of mild pyrolysis. Under conditions less drastic than those necessary for aromatic production by 100° to 150° C., it is possible to achieve high conversions of paraffins into olefinic hydrocarbons with elimination of trouble due to carbon and tar fog formation. To a large extent, also, the steel difficulties are obviated since the temperature range is now reduced to that common in industrial operations such as the methane-steam reaction. The gas produced by the operation of mild pyrolysis resembles gas obtained by the cracking of oil in the vapor phase and contains 40 to 50 per cent by volume of olefins, the rest being saturated hydrocarbons and hydrogen. Under these circumstances it is essential to the application of polymerization that dilution with inert paraffin gases should not interfere considerably with the conversion into liquid polymers. In commercial operation it may be advisable to reduce the load on the plant by elimination of such gases as hydrogen and methane after compression of the mixed gas.

The polymerization of the gaseous olefins has been studied in three different pieces of apparatus: (1) autoclaves, (2) a continuous plant supplied from cylinders of compressed gas, and (3) a continuous plant using a compressor, briefly described previously in the section on the influence of pressure on pyrolysis for aromatic hydrocarbons.

Of these the pressure limit of apparatus 1 and 2 was 2000 pounds per square inch (140.6 kg, per sq. cm.) and of 3, 200 pounds per square inch (14 kg, per sq. cm.).

### Autoclaves

Two mild steel autoclaves were used in this part of the work, one of 500 cc. capacity and the other 750 cc. Of these, the latter was carefully enameled internally so that no steel was presented at operating temperature to the hydrocarbon gas. These autoclaves were heated in a specially designed gas furnace in which the heating gases were circulated by a fan, and it was possible to maintain a steady temperature in the autoclave within  $\pm 2^{\circ}$  C. over long periods of time. Each autoclave had a long tube of small internal diameter supporting the valve, pressure gage, and safety disk at a sufficient.

cient distance from the body of the autoclave to be quite cool. The thermocouple pocket in each autoclave was fitted in the lid. Metal-to-metal joints of the cone type were used throughout, and these could be made and broken usually about fifty times before refacing became necessary.



FIGURE 5. POLYMERIZATION OF OLEFINS IN MILD STEEL Autoclave

The autoclave was filled in the cold with the olefin or gaseous mixture under consideration, and charges were measured by use of a balance weighing to 0.05 gram. Where a mixture was being made up with a saturated gas, such as methane or ethane, the olefin was introduced first and notes were made of the weight added and the pressure when cold. It was then possible, by filling to a calculated pressure, to approach the desired composition of mixture. Finally, this composition was determined accurately by reweighing the autoclave.

The time-pressure curves for ethylene and propylene are shown in Figure 4 and the results summarized in Table III.

TABLE III. PRODUCTION OF LIQUID HYDROCARBONS FROM OLEFINS

CHAR	ge Pi	VOLUME ROPORTIONS	Темр.	MA: Press	X. URE	Time at Working Temp.	Con- version into Liquids
		%	• <i>C</i> .	Lb./sq. in.	Kg./sq. cm.	Hours	% by wt. on olefin changed
Ethyle Propy	ene lene	••	380–388 400–404	$\begin{array}{c}1410\\1010\end{array}$	$\begin{array}{c} 99.1 \\ 71 \end{array}$	$^{3}_{2.5}$	86.5 80.0
{ Ethyle { Propyl	ene lene	$\left\{ \begin{array}{c} 58\\ 42 \end{array} \right\}$	390-400	1010	71	3.5	87.7
{ Ethyle { Hydro	gen	$\{ 49.2 \\ 50.8 \}$	380-390	1040	73.1	3	65.6
Ethyle   Metha	ene" ine	51.5 48.5	382-390	1390	97.7	3	85.3
Ethyle	ene e	49.21	387 - 392	1220	85.8	2.5	65.1
Ethyle	eneb		385-390	1325	93.1	3	92
<i>a</i> .		1 +		-1 - 1 - 1 - 1			

<sup>a</sup> A possible explanation of the high yield of liquid is that dilution with methane tends to repress the production of methane during reaction. <sup>b</sup> In enameled autoclave.

With olefins alone, or mixed with saturated gases, the pressure increased as heating progressed and attained a maximum in the region  $340^{\circ}$  to  $375^{\circ}$  C.—that is to say, before the reaction temperature was reached. Subsequently, the pressure fell with time when the autoclave was maintained at the reaction temperature, rapidly at first and then more slowly until the pressure drop with time became negligible. The experiment was then stopped and the autoclave allowed to cool.

With ethylene at 400° to 404° C. and pressures of 1200 pounds per square inch (84.4 kg. per sq. cm.) the rate of drop in pressure was very rapid, of the order of 60 pounds per square inch (4.2 kg. per sq. cm.) per minute. In one experiment, under these conditions, a conversion of 73.2 per cent by weight into liquid products was obtained; 39 grams of ethylene produced 28.55 grams of liquid and 6.71 liters of residual gas. The residual gas contained only 15 per cent unsaturated hydrocarbons, and it would appear that these conditions were too drastic for complete conversion to polymers. The temperature range 380° to 392° C. was therefore used in later autoclave work with ethylene. In Figure 4 the differences between a mild steel surface and an enameled surface are clearly seen. The rate of reaction, as indicated by the pressure drop in unit time, was greater with the enameled surface, and the yield of liquid hydrocarbons was the highest reported (92 per cent by weight) and carbon deposition was negligible.

It is of interest that propylene required a temperature approximately 10°C. higher than ethylene to cause polymerization to take place at a comparable rate.



FIGURE 6. POLYMERIZATION APPARATUS

The next step in the development of polymerization work in autoclaves was a consideration of the influence of diluents, including therein other olefins, on the polymerization of ethylene.

The first mixture made up was 1 to 1 by weight of ethylene and propylene, followed by a preliminary investigation of hydrogen, methane, and ethane as diluents. The results are summarized in Table III, and time-pressure curves are given in Figure 5, from which it is obvious that none of the diluents reduced the conversion into liquids below 65.1 per cent by weight. These experiments demonstrated the possibility of treating gas rich in olefins, such as gas from an oil-cracking plant or gas from the mild pyrolysis of natural gas, without previous elimination of hydrogen and saturated hydrocarbons. In practice it would be necessary to consider the economics of such a procedure by balancing the cost of any desired purification against the cost of the extra plant necessary to deal with the whole of the gas.

CONTINUOUS PLANT. For many reasons an autoclave is not a suitable apparatus for effecting the polymerization of olefins; thus, the pressure is not constant and the reaction rate slows up with fall in pressure, while the products remain in the heated zone for a considerable period and suffer change with the deposition of carbon and the production of saturated gases. The next development, therefore, was a simple type of continuous plant with a reactor of tubular form so that lining tubes of different materials could be fitted.

A drawing of the plant is shown in Figure 6. It consisted of a mild steel reaction tube 123.5 cm. long and of 2.5 cm. internal diameter, supported vertically and fitted at the top with an inlet tube and valve and at the bottom with a long axial thermocouple pocket, a gage, and an outlet leading through a condenser to a high-pressure separator of 188 cc. capacity. The tube was electrically heated by a double winding applied to it over mica insulation, giving a distance of 25 cm. at constant temperatures within  $\pm 1.5^{\circ}$  C. Metal temperatures were taken by two thermocouples brazed into small screwed pockets. Ethylene was supplied to the plant from one of two special gas cylinders connected in parallel to a fine adjustment valve at the top of the reaction tube. These cylinders could be warmed in lagged electrical heaters.

Pressures in the tube reactor were controlled by hand adjustment of the valve on the cylinder and the fine adjustment valve at the top of the reaction tube. As the pressure dropped, more gas was admitted from the cylinder to maintain the operating pressure.

From the high-pressure separator, liquid could be withdrawn

to a cooled receiver and gas could be vented through a condenser to a gas meter. Normally it was possible to operate this plant without venting gas—that is to say, without the production of any considerable quantity of saturated gases. In this way gas was taken off at the conclusion of an experiment, measured, and sampled. It was usually sufficient to determine the percentage of olefins using the Bone and Wheeler gas analysis apparatus, but occasionally Podbielniak analyses, accompanied by absorption on the Bone and Wheeler apparatus, were carried out.

The conversion figures were readily determined by weighing the liquid polymers and the gas cylinders before and after an experiment.

Mild Steel Surface. With a surface of mild steel at  $380^{\circ}$  to  $390^{\circ}$  C. and 800 pounds per square inch (56.2 kg. per sq. cm.) pressure the polymerization of ethylene was rapid, and conversions up to 64 per cent on the ethylene supplied were recorded. Unfortunately, it was found that the carbon formation under these conditions represented 6.6 per cent of the weight of the liquids obtained, and, even when the temperature was reduced to  $360^{\circ}$  C., where polymerization was slow, the carbon deposition was not considerably reduced.

Other Surfaces. Various lining materials were tried, including copper, aluminum, stainless steel, and two steels of differing composition which proved reasonably satisfactory namely, Era 131, or containing 0.3 per cent manganese, 0.5 per cent chromium, 0.5 per cent copper, 0.7 per cent molybdenum, 0.1 per cent carbon, and a heat-resisting steel known as H. R. 2, containing 22 per cent chromium, 7 per cent nickel, 1.5 per cent silicon, and 0.15 per cent carbon.



FIGURE 7. INFLUENCE OF PRESSURE ON RATE OF PRO-DUCTION OF LIQUID HYDROCARBONS IN THE POLYMERI-ZATION OF ETHYLENE Lining tubes of copper and Era 131 steel.

Using a lining tube of copper it was found that at a pressure of 800 pounds per square inch it was necessary to operate at 440° C.—that is to say, 50° to 60° C. higher than when using mild steel to obtain comparable reaction rates. The liquid hydrocarbons produced under these conditions gave Engler distillation figures of:



Following this preliminary test of copper as a lining, tests with other materials were carried out at varying temperatures from  $370^{\circ}$  to  $530^{\circ}$  C., and at pressures from 200 to 2000 pounds per square inch (14 to 140.6 kg. per sq. cm.). Some of the results are summarized in Table IV and expressed graphically in Figure 7. As the pressure was increased, the temperature necessary to attain a given rate of production of liquid decreased.

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At pressures of 400 and 600 pounds per square inch (28.1)and 42.2 kg. per sq. cm.) the curves obtained (Figure 7) pass through a maximum point, whereas at pressures above 600 pounds per square inch, such points are not attained with lining tubes of copper. The explanation of this is that at pressures of 800 pounds per square inch (56.2 kg. per sq. cm.) and higher, violent decomposition of the olefin (resembling the flashing of acetylene) occurred, accompanied by a copious deposition of soft carbon. The external evidence of this phenomenon was a rapid rise in temperature accompanied by a very rapid increase in pressure. Thus it is not advisable to employ copper liners in polymerization experiments above a pressure of 600 pounds per square inch unless the temperature is kept low and the attainment of the optimum conversion rate is not attempted. This violent decomposition of ethylene occurred both with an oxidized copper and a cleaned copper surface.

Conversion figures up to 85 per cent were obtained, but this was not a maximum, since it was not possible to account for all the ethylene passed into the apparatus. No material improvement in production is obtained by increasing the copper surface in the reaction zone by packing with Lessing rings.

A Podbielniak analysis of the residual gas after operation at 800 pounds per square inch and 445° to 450° C. gave:

	%
Uncondensed (methane and hydrogen)	5.1
Ethylene	58.4
Propylene	10.0
Butylenes	16.0
Amvlenes	10.0

so that only small amounts of saturated hydrocarbons were being produced under these conditions.

In this continuous plant, the influence of nitrogen as a diluent was considered by first filling the apparatus with nitrogen to a pressure of 400 pounds per square inch (28.1 kg. per sq. cm.). Ethylene was then admitted until the operating pressure of 800 pounds per square inch was attained. No gas was allowed to escape from the system until the conclusion of the experiment. From a series of experiments with nitrogen and ethylene, it was concluded that the partial pressure of the ethylene controlled the rate of production of polymerides.

TABLE IV. POLYMERIZATION OF ETHYLENE

			RATE	
PRESSURE	TEMP. RANGE FOR LIQUID PRODUCTION	Apparent Optimum Temp,	OF Liquid Forma- tion <sup>b</sup>	Remarks
Lb./sq. in. (kg./sq. cm.)	° C.	° C.	Vol./vol. reacti space/hr.	on
	REACTOR W	ITH COPPER	LINING TUBE	
400 (28.1) 600 (42.2) 800 (56.2)	420-540 400-500 390-460	$510 \\ 480 \\ 460^a$	$\begin{array}{c} 0.27 \\ 0.46 \\ 0.53 \end{array}$	Violent decompn.
1200 (84.4)	380-440	$430 - 440^{a}$	0.73	Violent decompn. above 435° C
1600 (112.5)	360 - 415	$410 - 415^{a}$	0.73	Violent decompn. above 415° C.
	REACTOR WIT	H LINING TU	BE OF ERA 13	L
600 (42.2) 1200 (84.4)	$\begin{array}{r} 400-500 \\ 380-500 \end{array}$	480 470	$\substack{\textbf{0.49}\\\textbf{0.79}}$	

<sup>a</sup> These are not true values owing to interference, due to deposition of soft carbon at these temperatures before the maximum conversion is attained. <sup>b</sup> At apparent optimum temperature.

Both the Era 131 and H. R. 2 steels showed distinct advantages over copper as lining tubes.

The results of two series of experiments with Era 131 are given in Table IV for comparison with the results using a copper liner and are indicated graphically in Figure 7. At the lower pressures, copper and Era 131 resemble each other but, at pressures of 800 pounds per square inch and above, no violent decomposition is observed when using Era 131. Thus even at 1200 pounds per square inch pressure it is possible to pass through the maximum conversion rate without interference due to violent decomposition; and, whereas at this pressure the temperature range with copper is limited to  $380^{\circ}$  to  $440^{\circ}$  C., and at the higher temperature violent decomposition occurs, with Era 131 the range is  $380^{\circ}$  to  $500^{\circ}$  C., with maximum conversion rate at  $470^{\circ}$  C. At temperatures above  $470^{\circ}$  C. a surface deposit of hard carbon is formed, but even at  $490^{\circ}$  C. the carbon represents only about 1 per cent of the liquids produced.

With H.R.2 steel, temperatures over 500° C. could be used at 600 pounds per square inch, and, as with Era 131, no violent decomposition of ethylene was observed. The liquid produced at 480° C. and 600 pounds per square inch gave the following Engler distillation test:

Initial boiling point, °C. Volume to 25°C., %	20 Few drops
50	9.2
75	25.5
100	42.5
125	58.0
150	70.0
175	80.0
200	86.0
225	89.5
250	92.0
275	94.0
Final boiling point, ° C.	278

CONTINUOUS PLANT USING COMPRESSOR. This apparatus was designed for operation up to a pressure of 200 pounds per square inch (14 kg. per sq. cm.) for a study of the problem of pressure as applied to pyrolysis, and the plant has been briefly described in the section of this paper dealing with that subject. With ethylene in the pressure region 150 to 200 pounds per square inch (10.5 to 14 kg. per sq. cm.) this plant was useful in indicating that  $550^{\circ}$  to  $600^{\circ}$  C. is a transition region in that, above this range, the liquids produced are largely aromatic in constitution, whereas below this range polymerization occurs and the liquids are largely paraffinic and olefinic in nature.

TIME FACTOR IN POLYMERIZATION OF ETHYLENE. With regard to the time factor in the polymerization of ethylene, a statement of the volume of the reaction space at constant temperature accompanied by the curves in Figure 7 are sufficient for the purpose of transferring these operations to a larger scale. The required volume, after making allowance for the thickness of the lining tube and the cover (of the same material as the liner) placed over the mild steel thermocouple pocket was 68.7 cc. Using a liner of H.R.2 steel at 1100 pounds per square inch (77.3 kg. per sq. cm.) and 470° C., a reaction space of about 0.1 cubic foot is required for the treatment of 50 cubic feet (0.1 cubic meter for 50 cubic meters) of ethylene (measured at normal temperature and pressure) per hour. Expressed in a different manner, it is found that, if the volume of ethylene reacting is corrected by the ordinary gas laws for temperature and pressure and the contact time is taken as the number of minutes required for unit volume of ethylene (so corrected) to pass through unit volume of reaction zone, a figure of about 3 minutes is obtained. The deviations from the gas laws are considerable and no account is taken of volume change during reaction. It is thought that the former method of expression is preferable.

# LIQUID HYDROCARBONS PRODUCED BY POLYMERIZATION AND CONDENSATION

The crude liquid from autoclave operation is turbid and dark in color; 60 to 70 per cent of it boils below 200° C., and 88 to 93 per cent below 300° C., depending upon operating conditions. Engine tests of the liquid boiling below 200° C. indicate that the antiknock value as a fuel is about half that of benzene. The liquids produced in the "dilution" experiments, where the diluent was not another olefin, were invariably lighter in color than those obtained from the olefins alone, and the quantity of carbon was considerably reduced.

The liquid hydrocarbons from the continuous plant possessed a light straw color and were quite transparent. The boiling range of these liquids varied with the conditions of temperature and pressure of their production, but the usual product had a specific gravity of 0.75 to 0.77 at 15° C., and 80 to 86 per cent distilled below 200° C. The liquids obtained



FIGURE 8. FRACTIONAL DISTIL-LATION OF LIQUID BOILING UP TO  $120^{\circ}$ C. IN THE POLYMERIZATION OF ETHYLENE

using a copper lining tube have been fractionated four times through a short but efficient spiral fractionating column, and the distillation curve of the liquids boiling up to 150° C. is given in Figure 8. "Steps" occur at 37° to 39°, 64° to 66°, 94° to 98°, 100°, and 120° C. These steps, together with the evidence supplied by gas analysis,

indicate the presence of olefins or paraffins, or both, containing from 3 to 8 carbon atoms to the molecule. Thus, from gas analyses, propylene, the butylenes, and the amylenes are present. Furthermore, the percentage unsaturation of the liquid fractions has been estimated and it has been found that this decreased with rise in temperature from 75 to 80 per cent in the region of 39° C., to 50 per cent in the 120° C. range. Thus the polymerides are largely olefinic, with an increasing proportion of paraffins as the boiling point increases. All fractions were stable when exposed to sunlight and gave no reaction with maleic anhydride. These facts are taken as evidence that hydrocarbons containing conjugated double bonds in the molecule were absent. There are indications of the presence of naphthenes.



FIGURE 9. RELATIONSHIP BETWEEN SPECIFIC GRAVITY AND BOILING POINT, AND REFRACTIVE INDEX AND BOILING POINT AFTER FRACTIONA-TION INTO  $2^{\circ}$  C. CUTS IN THE POLYMERIZATION OF ETHYLENE

The specific gravities and refractive indices of the 2° C. cuts obtained by fractionation, plotted against boiling point, are shown in Figure 9.

In Figure 10 the results of several experiments on the solubility of ethylene in polymers are indicated graphically. This information was necessary to obtain some idea of the loss of the ethylene due to solubility in the polymers when the



FIGURE 10. SOLUBILITY OF ETHYLENE IN POLY-MERS

Volumes (at normal temperature and pressure) in one vol-ume of solvent per atmosphere of partial pressure; Bun-sen's absorption coefficient, ∞.

latter were withdrawn from the separator, and also to indicate the influence of temperature on this solubility.

### ANTIKNOCK VALUES

It has been stated that engine tests using 30 per cent blends of polymer from autoclave operation with standard stock indicated that the polymer gasoline, up to 200° C., was about half as effective as benzene. The antiknock value of the polymerides is considerably increased by operation in a continuous plant, and in 30 per cent blends the gasoline fraction was five-sixths as good as benzene on a volume relationship. These tests were carried out on the Armstrong engine. The gasoline tested had Engler distillation figures as follows:



When considering the engine test results of the low-boiling polymers from ethylene, attention must be drawn to the specific gravities of the liquid hydrocarbons concerned. On a weight basis it seems reasonable to suppose that the polymers form a rather better antiknock material than benzene.

#### DIESEL FUEL

It will be of interest to produce from the olefin polymers a fraction suitable for use as a diesel fuel. There is reason to suppose that the higher boiling polymerides will constitute a good diesel fuel. Tests are now in progress.

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