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The Production of Olefine-containing and Fuel Gases

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TRANSLATION EDITOR'S PREFACE

This monograph reviews comprehensively the production processes of gasification of distillate and residual liquid fuels employed both in Western Countries (France, Germany, U.K., U.S.A.) and in Russia itself. Production figures, technological details and gas compositions and flow rates are cited in numerous tables and graphs. The book should be of interest to chemical engineering students and plant engineers, and Pergamon Press are to be congratulated upon their initiative in making this translation available to English-speaking engineers and technologists.

B. P. MULLINS
INTRODUCTION

Hundreds of oil-chemical products, manufactured on a large scale, are produced at the present time from oil and gas. These materials were obtained earlier from coke-chemical production, the wood-chemical industry and the processing of animal and food materials. In recent years in the Soviet Union the oil-chemical industry has rapidly developed. Chemical conversion based on new types of raw materials is of great importance to the U.S.S.R. since our reserves are very extensive.

In the Soviet Union considerable attention is paid to the development of the oil and gas industries. In 1965, 150 thousand million cubic metres of natural gas and 230–240 million tons of oil will be obtained. This must significantly increase the energy reserves of our country and must serve as an inexhaustible source of raw materials for obtaining chemical products.

The manufacture of ethylene and propylene is particularly important for the Russian national economy since they are good raw materials for oil-chemical production of ethyl alcohol and the synthesis of polymers. In the years of Soviet rule, our chemical industry has been extremely successful. In the period from 1913 to 1957 chemical production increased 112 times and from 1937 to 1956, 7 times. At the present time the Soviet Union occupies second place in the world as a manufacturer of chemical products, coming after the U.S.A., and in its rate of growth outstrips all capitalist countries.

The seven year plan opens up wonderful prospects for the Soviet chemical industry. In the resolutions of the 21st Congress of the Russian Communist Party concerned with the planned development of the national economy of the U.S.S.R. for 1959–1965, it was stated that “The overall volume of production of chemical products must be increased approximately three times. A wide development of synthetic materials must be obtained; the production of artificial fibres must be increased 4 times and of these, the most costly — synthetic fibres — 12 to 13 times, and plastics and synthetic resins, more than 7 times”.

Increased production of polymer materials must be carried out
on new raw materials. The large increase and development of the synthetic material industry is visualized on the basis of useful natural gases and gases from oil extraction. The construction of large combines of undertakings for the complex treatment of by-product gases from oil refining, natural gases, gases from oil reprocessing factories and other forms of raw materials are all contemplated.

The resolutions of the 21st Congress also plan the use of by-product gases from oil refining in the production of synthetic rubber instead of alcohol used formerly, which will make it possible in the seven year period to save about 1300 million roubles in capital costs.

The use of crude oil for the production of chemical products will release a large amount of materials which we use for nutritive purposes. Thus, in 1957, the production of ethyl alcohol needed for the manufacture of synthetic rubber and for other technical purposes, consumed many hundred tons of feeding materials.

In 1965 more than 2-5 million tons of hydrocarbon gases are considered necessary for processing into various chemical products.

The realization of the planned programme for the production of synthetic detergents and fat substitutes from crude oil will permit the release of not less than 400,000 tons of edible fats. By catalytic conversion of crude oil with water vapour on special catalysts, hydrogen, necessary for the production of ammonia and nitrogenous fertilizers, will be obtained.

It should be noted that over the last 10–12 years in a number of industrially developed countries (U.S.A., England, France, etc.) where there is a wide use of natural gas for illuminating and energy purposes, synthetic gas from the gasification of crude oil has been used in practice for satisfying peak demands in the localities for natural town's gas, for supplying gas in districts at considerable distances from sources of natural gas and for obtaining chemical raw materials.

In many districts remote from natural gas sources in the Soviet Union, gas obtained from crude oil is also used in the same way.

The present monograph is devoted to the conversion (gasification) of heavy crude oil (mazuts, cracking residues) and also gasoline and light condensing gases containing ethylene, propylene and hydrogen.
CHAPTER I

METHODS OF CHEMICAL TREATMENT
OF GASES AND PRODUCTS FROM THE
PYROLYSIS OF CRUDE OIL

The chemical treatment of oil and oil products may be carried out by following two basic directions—the production of raw materials for oil-chemical synthesis (in particular by gasifying heavy oil residues) and the production of chemical products.

THE PRODUCTION OF RAW MATERIALS FOR
OIL-CHEMICAL SYNTHESIS

Hydrocarbon Gases and Hydrogen

The lower olefines (ethylene, propylene, butylene and amylene) are a raw material base for oil-chemical synthesis, gasification of paraffin hydrocarbons, hydrogen, aromatic hydrocarbons, solid paraffins and certain other products.

One of the basic sources of raw materials are hydrocarbon gases: natural, technological and oil refinery gases.

Natural gas, depending on the site from which it is extracted, may consist chiefly of methane (90 per cent) but may also contain a significant amount of ethane, propane and butane (40–50 per cent).

Gases from oil processing plants—with installations for thermal and catalytic cracking, reforming, pyrolysis and coking of oil residues—contain a significant amount of unsaturated hydrocarbons. The composition of various gases obtained during the processing of oil, are given in Table 1.

Cracking gas contains approximately 25 per cent of olefines among which is 2–3 per cent ethylene, 8–10 per cent propylene and 14–16 per cent butylenes.

Ethylene is required in the greatest quantities for chemical processes; however, only an insignificant amount is contained in the gases from cracking. Therefore the requirements for chemical processes may not be satisfied by these gases.
<table>
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<td>mazut</td>
<td>7.6-8.0</td>
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<td>8.3</td>
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<td>water vapour at 800 to 900°C</td>
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</table>

* In volume per cent.
Thus by the thermal cracking of 1 million tons of mazut about 2000 tons of ethylene are obtained but even from this amount a certain part is lost by the evolution of the ethane–ethylene fraction and the chemical processing of the latter. Consequently, ethylene must be obtained by the additional pyrolysis of ethane and propane and the gasification of mazuts with water vapour which is also essentially, a pyrolysis process.

Thus in the U.S.A. only 10 per cent of the ethylene, which is required by undertakings carrying out chemical processing, is obtained from oil refinery gases and 90 per cent is produced by the pyrolysis of ethane, propane and residues—mazuts.

The pyrolysis of ethane, propane and mazuts may be carried out in heat resistant steel tube furnaces or gas generator furnaces with an alternately heated checkered brickwork and by pyrolysis. These processes are carried out at 800–900 °C in the presence of 0.5–2.0 parts of superheated steam in proportion to the raw material (in order to reduce coke formation). The continuous pyrolysis method in a fluidized or moving bed of a heat carrier is well known. The type of plant is selected depending on local productivity capacity and the possibility of capital investment. With insufficient reserves of ethane and propane it is expedient to obtain ethylene by the gasification of mazuts.

The yield of olefines obtained by the gasification of heavy oil residues varies on average from 25 to 35–40 wt. per cent of the raw material. The conversion of mazut into gas consists of 65–86 per cent related to the space velocity.

About 25–30 thousand tons of ethylene and 50 million m³ of gases for energy or illumination may be obtained by the gasification of 100 thousand tons of mazut giving a calorific value of 7000 to 8000 kcal/m³.

In recent years heavy oil residues due to their low cost and wide industrial basis have been continually growing in use in the U.S.A. as an oil chemical raw material. Thus in the U.S.A., by gasifying residual oil fuels about 10 per cent of the total production of ethylene is obtained, i.e. about 150,000 tons in a year, equivalent to 12 million dollars(3).

The gasification of high sulphur mazuts (2–4 per cent S) may give a gas suitable for energy which does not contain sulphur (after desulphurization), which is important for the Martin furnace in metallurgy, where mazut with only a small amount of sulphur may
be used. The manufacture of gas suitable for energy may be combined with the production of ethylene and sulphur.

As distinct from ethylene, propylene and butylene are obtained from cracking gases where they are present in adequate amounts.

At the present time a significant amount of ethylene and propylene are obtained by the pyrolysis of kerosine fractions by direct distillation and cracking at 600–700°C; however this process is not now considered expedient since there are disadvantages with kerosine; consequently other processes are replacing this method.

The production of olefines for chemical processing in the U.S.A. for 1957 was approximately the following (in million tons/year)\(^{(3)}\):

\[
\begin{align*}
C_2H_4 & \quad C_3H_6 & \quad nC_4H_8 + isoC_4H_8 \\
1.64 & \quad 0.77 & \quad \sim 0.5-0.6
\end{align*}
\]

These data testify to the large scale production and chemical processing of gaseous olefines.

Propane and butane are raw materials for chemical processing. The pyrolysis of propane gives ethylene, the chlorination of propane–halogen derivatives, nitrating-nitroparaffins. The dehydration of n-butane produces butadiene. Large scale production of propane and butane for chemical processing is less than that of olefines. Thus, for example, in the U.S.A. the following natural and oil refinery gases were produced (in million tons/year)\(^{(3)}\):

\[
\begin{align*}
C_3H_8 & \quad nC_4H_{10} & \quad isoC_4H_{10} \\
\sim 0.760 & \quad \sim 0.200 & \quad \sim 0.103
\end{align*}
\]

The other direction to be taken in order to use gaseous raw materials is to use hydrogen obtained by oil conversion and by catalytic conversion of hydrocarbon raw materials with water vapour.

Hydrogen is necessary for the production of ammonia, for conversion into nitric acid and nitrogenous fertilizers. It is obtained by converting gaseous hydrocarbons or a liquid oil raw material (mazuts) at 800–900°C in the presence of catalysts containing nickel and other materials according to the following plan:

\[
\begin{align*}
CH_4 + H_2O & \xrightarrow{800-900^\circ} 3H_2 + CO; \\
C_nH_{2n} + nH_2O & \rightarrow 2nH_2 + nCO.
\end{align*}
\]

The gas has an approximate composition of 50–60 per cent \(H_2\), 20–25 per cent \(CO\), 3–10 per cent \(C_nH_{2n}\), and 5–10 per cent \(CO_2\).
In some countries gaseous hydrocarbons are the basic raw material for obtaining hydrogen.

Thus, the synthetic ammonia industry in the U.S.A. obtains 80–85 per cent of hydrogen from natural gas, the remaining requirements (13 per cent) are guaranteed by coking, electrolysis (4.5 per cent) and other processes. In the U.S.A. a plant has been put into commission for the synthesis of ammonia with a capacity of about 80,000 tons/year using mazuts as the raw material for obtaining hydrogen. The limit of U.S.A. capacity (operating and stand-by plants) for the production of hydrogen and ammonia from mazuts is about 290,000 tons/year.

In the Soviet Union in 1965, 75 per cent of the hydrogen necessary for obtaining ammonia will be derived from crude oil.

_Aromatic Hydrocarbons (Benzene, Toluene, Xylene)_

Raw materials for oil-chemical synthesis are benzene, toluene and xylenes. Coke and oil chemical industries are competing branches in the production of these hydrocarbons.

The following basic methods for obtaining these hydrocarbons are well known:

1. Their separation from narrow fractions of oil, rich in aromatic hydrocarbons.
2. The dehydrogenation of narrow fractions of oil, rich in six membered naphthenic hydrocarbons.

\[
\text{C}_6\text{H}_{12} \rightarrow \text{C}_6\text{H}_6 + 3\text{H}_2 \\
\text{C}_6\text{H}_{12}\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH}_3 + 3\text{H}_2; \\
\]

3. Aromatization (dehydroxylation) of paraffin hydrocarbons

\[
\text{C}_6-\text{C}_8 \rightarrow n\text{C}_7\text{H}_{16} \rightarrow \text{C}_6\text{H}_5\text{CH}_3 + 4\text{H}_2; \\
\]

4. Pyrolysis of kerosine fractions by direct distillation and cracking. (However, under present conditions this process is considered disadvantageous with regard to the use of kerosine fractions in reactive fuels.)

5. The pyrolysis of heavy oil residues with water vapour with the formation of gas and tar rich in aromatic hydrocarbons.

The practicability of using the first method must be decided depending on the hydrocarbon composition of the oil, i.e. on the content of aromatic hydrocarbons in the fractions boiling in the
range 75–150°C. The separation is carried out by means of special methods of distillation and extraction.

Aromatic hydrocarbons are obtained by the dehydrogenation of naphthenes and aromatic paraffins by means of catalytic reforming processes; platforming, hydroforming and their variants.

Benzine fractions are used for catalytic reforming (ligroins by direct distillation and thermal cracking with a boiling point from 65–200°C) or narrower fractions.

During catalytic reforming desulphurization simultaneously occurs (e.g. from 0.5–0.6 per cent S in the original raw material to 0.007 per cent in the benzine from reforming).

Platforming is carried out on a catalyst consisting of activated aluminium oxide containing about 10 per cent platinum, at 440 to 510°C and 14–50 atm. Aromatic hydrocarbons and high octane benzine with an octane number of 75–85 without tetraethyl lead (original octane number 40–50) are obtained.

Hydroforming is carried out on a catalyst consisting of about 25 per cent MoO₃ deposited on aluminium oxide at a temperature of approximately 500°C and a pressure of 10 atm in a hydrogen medium.

The pyrolysis of kerosine fractions for the production of aromatic hydrocarbons and gaseous olefines even at the present time is still carried out on a considerable scale although this method does not appear to be the most efficient and rational.

In conjunction with the fact that in recent years heavy oil residues have been used as chemical raw materials, it is quite possible that a certain amount of aromatic hydrocarbons will be obtained from tars during the gasification of mazuts and other types of raw material. Up to the second world war aromatic hydrocarbons were obtained only in the coking chemical industry.

Thus in the U.S.A. in 1937–1940 about 70,000 tons of toluene were made; in 1944 its production increased there to 435,000 whilst 310,000 tons were obtained from crude oil.

At the present time in the U.S.A. the main amount of toluene is produced by the oil industry which is responsible for 75–80 per cent of its overall production. Thus in 1955, 470,000 tons of toluene were obtained from crude oil (with an overall production of 608,000 tons) and in 1956 726,000 tons. (In the U.S.A., apart from the further chemical processing of toluene, it is also used for increasing the octane number of the benzenes.)
The total share of production by the American oil industry of benzene in 1955 consisted of less than one third (about 32 per cent) or about 320,000 tons, i.e. coke-chemical production of benzene was still important. American manufacture of benzene in 1957 was about 1 thousand million tons.

Xylenes are extensively used as initial raw materials for the production of intermediate products, necessary for plastics, synthetic fibres and other products. About 89 per cent of the total manufactured in America is from the oil industry. In 1955 the U.S.A. production of xylenes from crude oil was about 318,000 tons; in 1957 about 450,000 tons were obtained from oil-chemical and coke-chemical raw materials.

**Production of Oil-chemical Products**

The Production of Chlorine Derivatives

(Synthesis of solvents, intermediate products and insecticides)

Many products may be obtained by chlorinating paraffins, olefins and aromatic hydrocarbons, using cheap crude oil.

Synthesis on the basis of ethylene

On the basis of ethylene, dichloroethane, ethyl chloride and ethylene hydrochloride are obtained which are subsequently converted into ethylene glycol or ethylene oxide.

The production of dichloroethane and ethylene glycol is of considerable interest.

The production of dichloroethane is mainly associated with the industrial manufacture of anti-knock compounds, i.e. tetraethyl-lead. Dichloroethane is obtained by passing ethylene and chlorine into dichloroethane (solvent) in which a catalyst is suspended.

Ethylene hydrochloride is an intermediate product in the manufacture of ethylene glycol and ethylene oxide. It is obtained by passing ethylene and chlorine into water at a temperature of 10° or 50°C. Ethylene glycol and ethylene oxide are obtained by heating ethylene hydrochloride with alkali under different conditions. Ethylene glycol is used for obtaining diethylene glycol; from the latter dinitrodiethylene glycol explosive is obtained.
A large part of ethylene glycol is manufactured from ethylene oxide which is mainly obtained by alkaline hydrolysis of ethylene hydrochloride. There are however industrial plants for direct oxidation of ethylene by the oxygen in air into ethylene oxide at 270 to 300 °C in the presence of silver oxide.

The total output possible in 1958 in plants producing ethylene glycol in the U.S.A. was 590,000 tons, whilst in fact 520,000 tons of this product was produced that year (more than 80 per cent was the oil-chemical ethylene glycol$^{(6,7)}$).

Trichloro- and tetrachloro-ethylene solvents are valuable ethylene chloro derivatives, but they are obtained from acetylene$^{(6,7)}$.

**Synthesis on the basis of propylene**

In 1936 the high temperature chlorination reaction of propylene in allyl chloride was discovered, from which, by further addition of hypochlorous acid, epichlorohydrin is obtained and by hydrolysing the latter glycerine is formed (with a yield of 75–80 per cent).

\[
\begin{align*}
\text{CH}_2&=\text{CH} \quad \text{CH}_3 & \xrightarrow{\text{Cl}_2} & \xrightarrow{400^\circ} & \text{CH}_2&=\text{CH} \quad \text{CH}_2\text{Cl} & \xrightarrow{\text{HOCl}} & \\
\text{Cl} & \quad \text{OH} & & & & \text{Cl} & & \\
\rightarrow & \quad \text{Cl} & \quad \text{OH} & \quad \text{Cl} & \xrightarrow{\text{C}_\text{at}(\text{OH})_2} & \xrightarrow{60^\circ} & \xrightarrow{\text{O}} & \xrightarrow{\text{NaOH}} & \\
& & & & & & \text{epichlorohydrin} & & \\
& & & & & & \xrightarrow{\text{H}_2\text{O}} & & \\
& & & & & & \text{OH} & \quad \text{OH} & \quad \text{OH} & \\
\rightarrow & & & & & & \text{OH} & \quad \text{OH} & \quad \text{OH} & \\
\end{align*}
\]

Epichlorohydrin is used also for obtaining the valuable epoxy resins.

The first production of synthetic glycerine by this method on an industrial scale was carried out in Germany during the second world war. At the present time there are industrial plants for synthetic glycerine in the U.S.A.

In 1955, in the U.S.A., 40,000 tons of synthetic glycerine were obtained and in 1958 glycerine manufactured was about 135,000 tons, of which about 40 per cent is oil-chemical synthetic glycerine$^{(3)}$.

Recently in the U.S.A. a process was developed for obtaining glycerine by the oxidation of propylene in acrolein with its subsequent conversion by hydrogenation into allyl alcohol. By adding
some molecules of hydrogen peroxide to the allyl alcohol it is converted into glycerine. At the present time one factory in America works on this method.

Another extremely widespread method for obtaining glycerine is the saponification of vegetable and animal fats, which is produced on a large scale during the manufacture of soap.

Obviously, this process, due to the changeover into the manufacture of synthetic soaps has almost completely been eliminated.

*Synthesis of insecticides on the basis of benzene chlorination products*

The insecticides industry is an important consumer of oil-chemical raw material. The most valuable is DDT (\(pp\)'-dichlorodiphenyl trichloroethane) (I) and hexachlorane (II) (gammexane) used for the prevention of agricultural pests.

\[
\begin{align*}
\text{I} & : \quad \text{Cl} \quad \text{Cl} \\
& : \quad \text{H} \quad \text{C} \\
& : \quad \text{CCl}_3
\end{align*}
\]

\[
\begin{align*}
\text{II} & : \quad \text{H} \quad \text{C} \\
& : \quad \text{Cl} \quad \text{H} \\
& : \quad \text{Cl} \quad \text{H} \\
& : \quad \text{Cl} \quad \text{Cl}
\end{align*}
\]

DDT is obtained on the basis of benzene, chlorine and acetaldehyde, but hexachlorane is obtained by adding chlorine to benzene.

The consumption of DDT and hexachlorane in the U.S.A. in 1955 were about 57,000 tons and 77,000 tons respectively. In 1960 the consumption of DDT will be increased there to 73,000 tons.

*The synthesis of other halogen derivatives*

Other halogen derivatives used as intermediate products are obtained by oil-chemical synthesis. We refer here to methane halogen derivatives. The chlorination of methane produces methyl and methylene chlorides.

\[
\begin{align*}
\text{CH}_4 + \text{Cl}_2 & \rightarrow \text{CH}_3\text{Cl} \quad 62\% \\
\text{CH}_4 + 2\text{Cl}_2 & \rightarrow \text{CH}_2\text{Cl}_2 \quad 30\% \\
& \rightarrow \text{CHCl}_3 \text{ and } \text{CCl}_4 \quad 8\%
\end{align*}
\]
The reaction is carried out with excess methane.

Chlorination of methane may occur with a high yield of carbon tetrachloride (about 90 per cent) and chloroform (about 50 per cent): however the principle amount of $\text{CCl}_4$ is obtained by the chlorination of carbon disulphide and $\text{CHCl}_3$ by the chlorination of ethyl alcohol. At the present time the direct manufacture of $\text{CCl}_4$ from methane has been put into production.

Carbon disulphide may be obtained from methane and sulphur.

$$\text{CH}_4 + 4 \text{S} \xrightarrow{500-700^\circ} \text{CS}_2 + 2 \text{H}_2\text{S};$$

$$\text{CS}_2 + 3 \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{S}_2\text{Cl}_2.$$ 

This process is carried out in industry. The chlorination of propane, butane, pentane and other hydrocarbons are also realized on an industrial scale.

The total production of halogen derivatives by oil-chemical synthesis in the U.S.A. was more than 1 million tons in 1958, of which there were 320,000 tons of ethyl chloride. In England, oil-chemical plant capacity for producing halogen derivatives is about 20,000 tons a year.

Alkylation of Benzene, its Homologues and the Chemical Treatment of Benzene Homologues

(The manufacture of phenol, acetone, styrene admixtures)

The alkylation reaction of benzene and its derivatives by olefines may be carried out by various oil-chemical syntheses.

Up to 1945–1946 the alkylation of benzene by olefines (propylene) was mainly used for deriving high octane additions to aviation gasoline.

At the present time this reaction is used for obtaining intermediate products of oil-chemical synthesis.

Alkylation of benzene by propylene\(^{(8-11)}\)

Alkylation of benzene by propylene is carried out in industry by means of three catalysts: phosphoric acid, aluminium chloride and sulphuric acid. The benzene alkylation reaction by propylene, accompanied by the formation of mono-isopropylbenzene, occurs with the formation of di- and tri-isopropylbenzenes as secondary
products, the quantity of which is reduced with increase of excess benzene. From 1.5 to 2 and up to 10 molecules of excess C₆H₆ is taken for one molecule of propylene. The volume and output of the reacting apparatus and also the costs of distilling the excess benzene depend on this ratio.

Different designs of apparatus used for alkylation.

Alkylation with phosphoric acid is carried out with a heterogeneous catalyst in an apparatus similar to that used for polymerization of olefines.

Alkylation in the presence of aluminium chloride is carried out in the liquid phase and in column type apparatuses charged with benzene in which the catalyst is suspended: propylene is passed through the benzene layer. Isopropylbenzene is separated out from the alkylate by fractionating.

In the production of phenol and acetone, the isopropylbenzene in alkaline solution is oxidized by the oxygen in air at 90°C into isopropylbenzene hydroperoxide.

The isopropylbenzene hydroperoxide which is formed is concentrated at reduced pressure (in addition, the unreacted isopropylbenzene is distilled off). Following this, the hydroperoxide is carefully decomposed with a small amount of sulphuric acid into phenol and acetone.

The yields of phenol and acetone are about 80 per cent and 75 per cent of the theoretical, respectively.

This process for the production of phenol and acetone in industry is comparatively new: it has been extensively used in the U.S.S.R.* from 1949 and also in France, England and America.

* The process was developed by Soviet scientists, P.G.Sergeev et al.
Isopropylbenzene is used to obtain methyl styrene for the manufacture of synthetic rubber. Methyl styrene is obtained by the catalytic dehydrogenation of isopropylbenzene in the vapour phase.

\[
\text{H}_3\text{C}-\text{CH}-\text{CH}_3 \xrightarrow{600^\circ \text{C}, \text{ZnO}} \text{H}_3\text{C}-\text{C}==\text{CH}_2
\]

Hydroquinone may be obtained from \( p-p' \)-di-isopropylbenzene, obtained as a secondary product in the alkylation of benzene by propylene, by the following reaction:

\[
\text{H}_3\text{C}-\text{CH}-\text{CH}_3 + \text{H}_3\text{C}-\text{C}-\text{CH}_3 \xrightarrow{2\text{O}_2} \xrightarrow{\text{H}_2\text{SO}_4} + 2\text{CH}_3\text{COCH}_3
\]

However, this method has not yet found an application in industry.

By analogy with the process for producing phenol and acetone, phenol and methyl ethyl ketone may be obtained by alkylation of benzene with \( n \)-butylene, followed by oxidation.

For the last five to seven years alkylation of benzene by propylene and its conversion into phenol and acetone has found extensive application. Thus the production of phenol by this method in the U.S.A. in 1955 was about 120,000 tons out of an overall production of phenol, using various methods, of 235,000 tons. In 1958 about 285,000 tons of phenol were produced by this method.
In France, yearly production is more than 28,000 tons of isopropylbenzene from which 13,000 tons of phenol and 8000 tons of acetone are manufactured.

In West Germany more than 12,000 tons of cumene is produced, from which 8000 tons of phenol and 5000 tons of acetone are obtained.

However up to now, the main amount of phenol is produced by other methods.

More than half the total phenol manufactured is used in the preparation of plastics.

Alkylation of benzene by ethylene and the production of styrene

Styrene is a most important product in the synthesis of rubber. It is obtained from ethyl benzene. The manufacture of styrene is well developed industrially.

The vapour phase alkylation of benzene by ethylene is also well known. It is carried out by using a catalyst of phosphoric acid on kieselguhr at 275°C and a pressure of 60atm.

The dehydrogenation of ethyl benzene is carried out in the vapour phase on activated zinc oxide at 500–600°C. The alkylation of benzene by ethylene is carried out on a large scale required by the continual increase in the use of polystyrene plastics and synthetic rubber.

The production of styrene in 1958 in the U.S.A. was about 570,000 tons, and in England more than 16,000 tons.

Recently in industry, the alkylation of toluene by ethylene has been carried out in order to obtain ethyl toluene. By dehydrogenation it is converted into vinyl toluene which has recently been used in the manufacture of synthetic rubber.

The scope of application for the benzene alkylation reaction with olefines and the various treatments of benzene homologues may be seen from the flow sheet on Fig. 1 (cf. p. 14).

Synthetic Cleansing Materials (Detergents)

The synthetic cleansing materials industry originated during the second world war but its main development has occurred over the last ten years. Thus, in 1945 in the U.S.A. about 4 per cent of cleansing agents (soaps) was obtained by synthetic methods, but
Fig. 1. Flow sheet for the scope of application of the benzene alkylation reaction.
Catalysts: I – $\text{H}_3\text{PO}_4$; $\text{H}_2\text{SO}_4$; $\text{AlCl}_3$; $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n \text{H}_2\text{O}$. II – HF; $\text{H}_3\text{PO}_4 \cdot \text{BF}_3$; $\text{H}_2\text{O} \cdot \text{BF}_3$; $\text{MeX}_n$. 
96 per cent of it was obtained from edible fats. In 1956 a reverse picture was observed: 62.5 per cent of cleansing agents obtained in that country consisted of synthetic soaps and only 37.5 per cent of the total amount was manufactured from edible fats.

In 1957 the U.S.A. made 1,282,000 tons of synthetic cleansing materials, which was 65 per cent of the overall production of cleansing agents.

The most important question for the Russian oil-chemical industry in the next year is to extensively develop the production of synthetic high quality scap substitutes with a view to considerably reducing, and subsequently completely discontinuing, the consumption of edible fats for the production of soap.

In 1965, the realization of this program will permit the saving of 350–400,000 tons of edible fats and 2 thousand million roubles.

Two forms of synthetic cleansing agents are produced in industry: anionic-active and non-ionic. With regard to anionic-active materials sulpho-salts or salts of the sulphur esters are used: with regard to the non-ionic, amides of the fatty acids are used as well as ethers and esters obtained from ethylene oxide.

The most important synthetic cleansing agent is dodecyl benzene sulphonate which is obtained as follows:

Tetrameric propylene–dodecyl and trimeric-nonylene are obtained by the polymerization of propylene on phosphoric acid: this is followed by benzene alkylation with dodecylene which produces dodecyl benzene which after sulphonation gives the sulphonate.

\[
\text{C}_{12}\text{H}_{25} + \text{C}_{12}\text{H}_{24} \rightarrow \text{C}_{12}\text{H}_{25}\text{SO}_3\text{H} \xrightarrow{\text{NaOH}} \text{C}_{12}\text{H}_{25}\text{SO}_3\text{Na}
\]

In Germany polymerization is carried out at 200°C and 40 to 50 atm using liquid phosphoric acid on quartz as the catalyst. In the U.S.A. the process is controlled on solid phosphoric acid (phosphoric acid on kieselguhr) at 170–275°C and with a space velocity of 1–3.8 l. of raw material on 1 kg of catalyst per hour. The polymer which is distilled off as a specific fraction at 176–232°C is dodecylene.

The polymers of propylene are a mixture of branched unsaturated hydrocarbons. Thus in the composition of nonylene 3-ethyl-4-