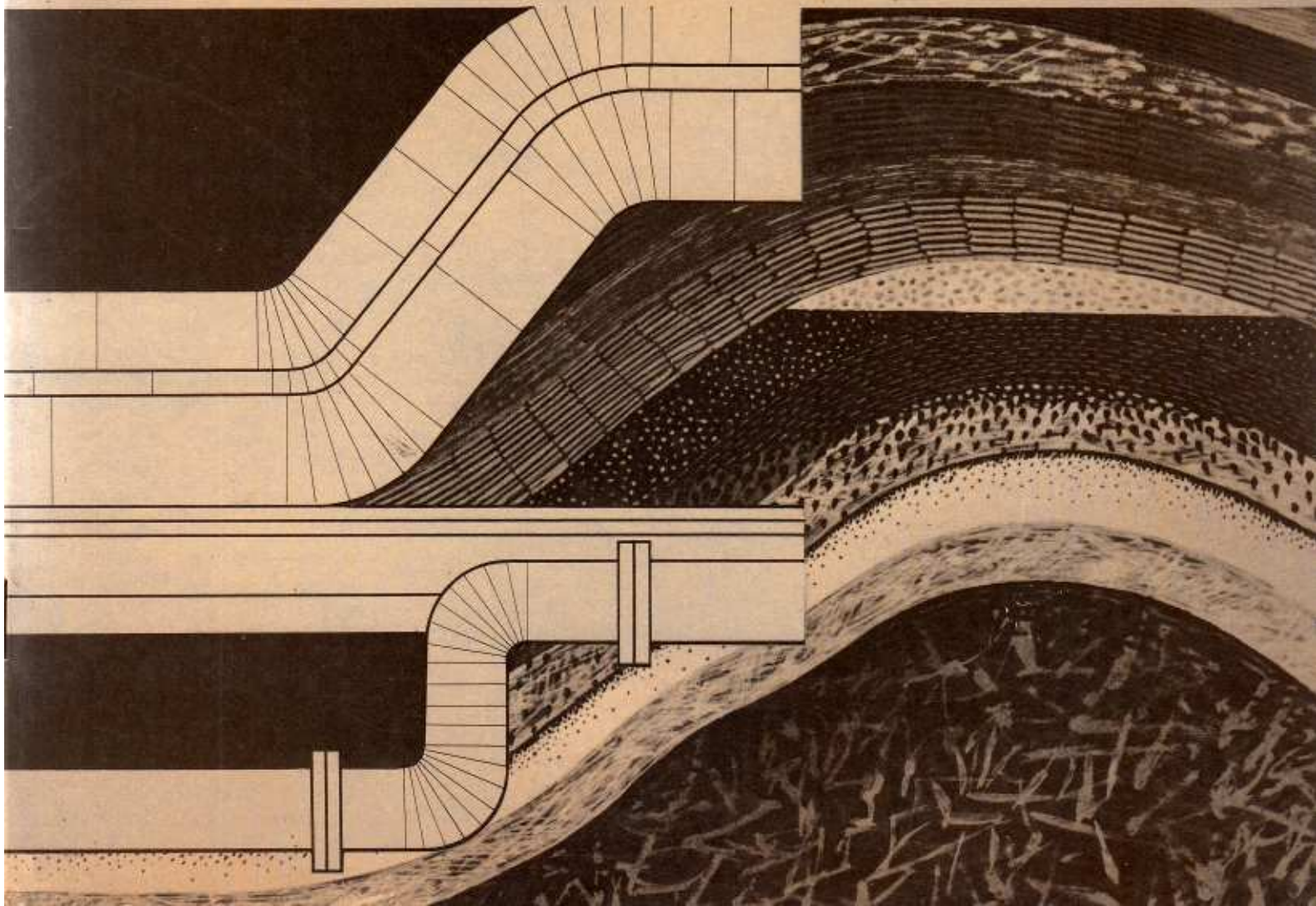




Petroleum





A hundred years of progress.

Part one

Petroleum and where it comes from

A typical section of oil-bearing rock, seen through a microscope.



Over a third of the world's power comes from petroleum. Petroleum also provides more than half the total production of organic chemicals. Where do we find this necessity of modern life? The answer is – almost anywhere: in the middle of a desert, beneath the sea bed, or even in the back garden. The petroleum may be seeping to the surface or buried beneath miles of rock. There may be only a few gallons of it or there may be a vast reservoir. Usually it is very difficult to find. When you do make a find, it may be thousands of miles from where you want to use it. Before you can use it, you have to refine it. All this means a lot of work and costs a lot of money. But, at the end of it all, there are a hundred and one things you can do with the petroleum. As a fuel, you can use it to drive the engines of cars, ships, and aeroplanes. Or you can burn it to keep your house warm. As bitumen, you can use it to cover mud tracks to make roads. As a lubricant, you can use it to keep the moving parts of machinery running smoothly. As a chemical, you can use it to make plastics, solvents, and detergents.

To keep pace with the huge demand for petroleum, there has grown up one of the largest and most scientifically mechanized industries in the world. And all this has come about within the last hundred years.

What is petroleum? – Petroleum is a mineral oil which is often referred to simply as 'oil'. In contrast to oils that come from animals and plants – for example, cod-liver oil and olive oil – it is found in rocks; hence the name petroleum, from the Latin *petra* rock and *oleum* oil. Like animal and vegetable oils, petroleum consists of a complex mixture of hydrocarbons – that is, organic compounds of the two elements hydrogen and carbon. Hydrocarbons are typical of the raw stuff of

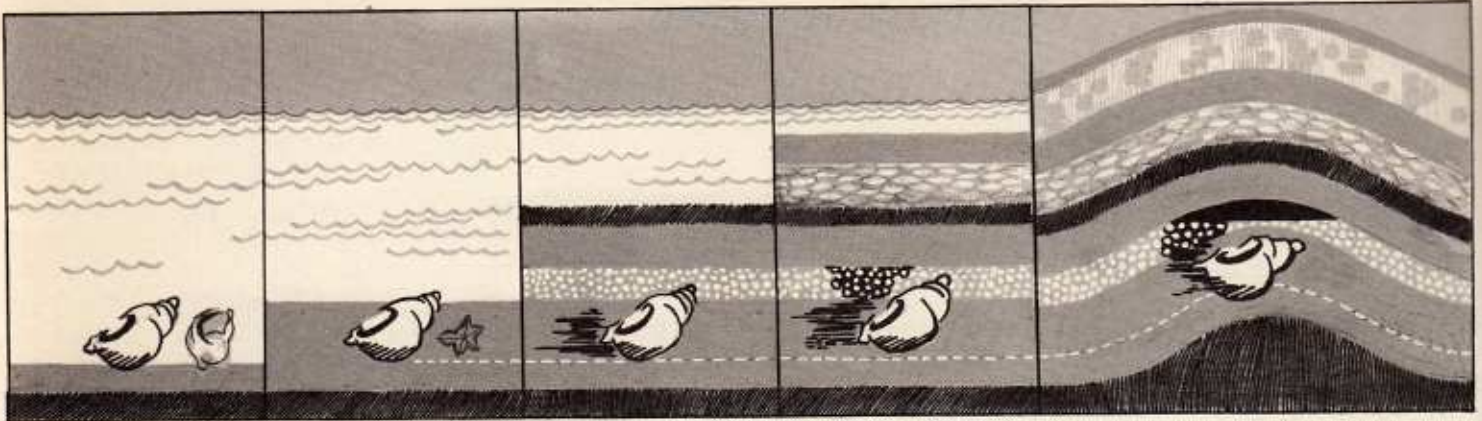
Stages in the formation of oil: Marine life dies and sinks to the mud of the sea bed. This mud has been brought down to the sea by rivers. The dead organisms now buried by another layer of mud, begin to decompose.

Pressure and heat resulting from succeeding layers of mud cause the decomposing matter to ooze from its muddy prison. The granular layer represents a bed of sandstone; the mud on the sea floor has become

first clay, then shale. The formation of these rock strata may take many millions of years.

The fluid, now turned to oil, flows out through cracks in the shale into the pores of the overlying sandstone.

Although the oil sometimes seeps to the surface, it may be halted, as here, by a barrier of non-porous rock. This barrier may trap the oil thousands of feet below ground level. The oil accumulates in the rock pores, like water in a sponge.



which living things are made. What are these organic compounds doing mixed among the inorganic minerals of the rocks?

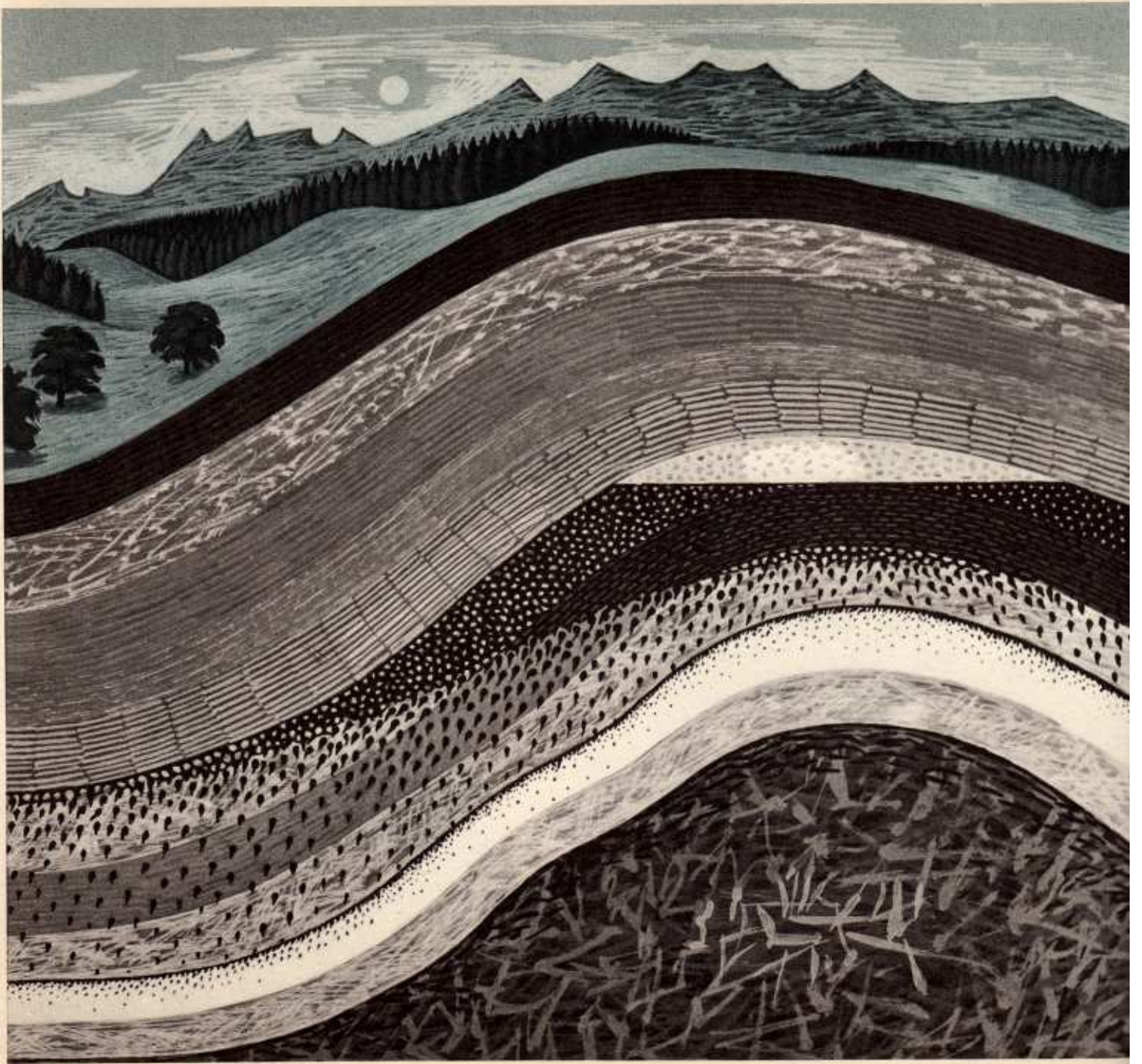
We know that coal, another complex mixture of hydrocarbons, was formed from the breakdown of buried vegetation. Most of this vegetation came from the primeval forests and swamps that flourished many millions of years ago. We are less sure of the origins of petroleum. We believe that most of it has come from the soft bodies of microscopic organisms living in the sea: as these organisms died, so billions of their bodies settled on the sea bed. In the process of time, these accumulations became silted over and, in the absence of oxygen, were eventually transformed into petroleum hydrocarbons. How, we are not sure.

Where is petroleum found? – Petroleum in its natural state is called crude oil and this is to be found in almost every part of the world. The four richest oil-producing areas at present known are the Middle East, the United States, the Caribbean, and Russia. But crude oil is also found in fifty other countries including Borneo, Roumania, Nigeria, the Netherlands,

Oil-bearing areas of the world.

The black dots show where oil is being produced. The areas in the pale tint are those where oil may possibly be found.





Oil trapped in a layer of porous rock that is sandwiched between layers of impermeable rock. The hump in the rock beds is called an anticline, and is one of the commonest of several types of earth trap in which oil may be found.

Scooping up bitumen from the great pitch lake in Trinidad. This lake was formed from natural underground seepage.



Argentina, Japan, and even England. There are also large quantities under the beds of the oceans. In appearance, crude oil is usually a thick dark liquid like black treacle. But the proportions of the different hydrocarbons crude oil contains vary greatly from one area to another or even within the same area.

Crude oil tends to accumulate in beds of porous rocks sandwiched between layers of impermeable rock. The porous rock (for example, sandstone) has a spongelike structure which enables it to hold liquid whereas the impermeable rock (for example, clay) has no spaces into which liquids such as oil can penetrate. Unable to escape either upwards or downwards, the oil is trapped – although often it may migrate along the layers of porous rock to accumulate many miles from where it was originally formed. If the top layer of impermeable rock (called the cap rock) is punctured, the crude oil, because it is under pressure, rises through the hole to the surface. Unless carefully controlled, it can spurt out in a huge gush. This can happen because crude oil contains several ingredients which are liquid under pressure, but which become gases when the pressure is released. Their sudden expansion can drive out the liquid oil with great force.

Sometimes the cap rock may be punctured or cracked naturally – either by the weathering of the rock or by a geological upheaval. This cracking of the cap rock may give rise to seepages of natural oil. Thus in some parts of Texas the water from springs has rainbow smears of oil on the surface. The first prospectors used to rely on these signs in their search for oil before they learned how to detect ‘hidden’ oil. In other parts of the world such as Baku in Russia and Kirkuk in Iraq, petroleum gas, seeping through the ground, burns at the surface. Perhaps the most impressive natural seepage of all is the great pitch lake in Trinidad, consisting of sticky, shining-black bitumen from which all the other components of the original crude oil have evaporated. However, these natural seepages do not happen very often, and in the present search for oil men puncture the top layer artificially by boring down into the rock with drills.

The decision where to drill for oil is usually left to people who have made a careful study of rocks: geologists. Many geologists are continually searching the Earth, often in most out-of-the-way places, for rock formations in which they believe oil may have accumulated. They can find out a great



Burning petroleum gas seeping to the surface in Iraq. This fire is said to have been the 'burning fiery furnace' into which King Nebuchadnezzar ordered Shadrach, Meshach, and Abednego to be cast.

deal from studying the rock surface and the fossils. But what they really need is a third eye with which to peer down deep into the rocks below. Although such an eye does not exist, modern instruments can tell them almost as much.

By burying a few charges of explosive and firing them off, the geologists produce tremors like very small earthquakes. They then study the effects of the explosions with an instrument called a seismometer which, in the laboratory, is used to detect natural earthquakes and underground atomic explosions. With the seismometer, they study the waves reflected from the rocks below and so infer something about what kind of rocks are there and the way in which they lie. Or, using an instrument called a gravimeter, they can study the surface for slight variations in gravity, which, in turn, are influenced by the different densities of the underlying rocks. But, in spite of all the evidence they collect, the geologists cannot be sure whether oil lies below. The only real proof is to bore down into the rock and find out.

Drilling for oil – For hundreds of years, the Chinese have known how to drill deep into the ground in search of water or brine. As long ago as A.D. 1100, they got down to the astonishing depth of 3,500 feet using a heavy plunger, jerked up and down by relays of people jumping on a springboard. The craft of drilling did not reach the West until many centuries later.

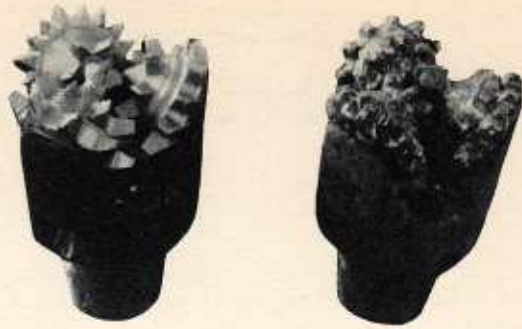
Although people have used oil from natural seepages since the earliest historical times, the petroleum industry is by tradition said to have started in 1859. In that year, near Titusville, Pennsylvania, U.S.A., a top-hatted American by the name of 'Colonel' Drake was the first to use a mechanical drill in search for oil. Drake was employed by a small firm





The top-hatted 'Colonel' Drake – the first man to drill an oil well mechanically. On the extreme right in the background is 'Uncle' Billie Smith, Drake's head driller.

Rock bits :
before and after drilling.



A modern drilling rig.



marketing lamp oil made out of crude oil obtained from natural seepages. He struck oil at 69½ feet down.

Since the time of 'Colonel' Drake, drilling has come a long way. The old-fashioned drills, used up to the turn of the century, pounded a hole in the rock by raising and dropping a pointed plunger, rather like the Chinese drills. They have been replaced by more efficient drills which bite down into the rock with a circular motion, rather like a brace and bit boring a hole into wood. The drill consists of a bit or cutting piece attached to a rotating column of pipe. The pipe is rotated by an engine at the surface. Also at the surface is the derrick, a structure similar in appearance to an electric pylon, from which lengths of pipe are fed in. The bit is kept cool by a current of lubricating mud which flushes out the drill cuttings and helps to prevent a blow-out of oil. The blow-out, as well as being wasteful, can wreck the derrick and set the oil well on fire. With modern methods, holes as deep as five miles have been drilled. Also, using offshore platforms, drilling has been extended to areas under the sea bed and it is now possible to drill in depths of water of more than 600 feet.

When the drill strikes oil, the underground pressure is likely to force the oil up the bore hole and may continue to do so for many years; but if the pressure is not sufficient, or if it falls off, the oil must be pumped. On an average only about one-tenth of the oil below ground can be brought to the surface. New techniques are helping to improve this rate of recovery.

The demand for oil is enormous. In the past twenty-five years, world production has risen, more than threefold, to more than twelve hundred million tons a year. If it were not that new reserves were being discovered even faster, it would soon be running out.

An oil tanker discharging at an ocean berth in Singapore.



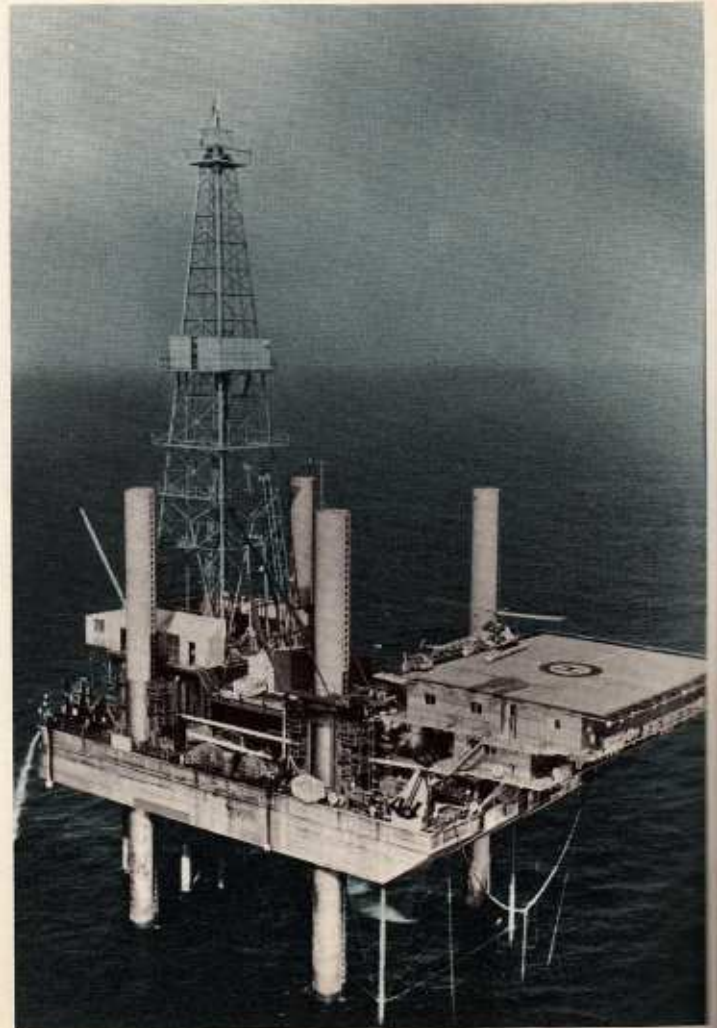
Transporting the oil – Although oil is found in most parts of the world, many of the richest fields outside the U.S.A. are thousands of miles from the industrial centres where oil is most in demand. Getting the oil to where it is wanted involves two journeys. First the crude oil has to be transported from the oilfield to the refinery; then the refined oil products have to be transported from the refinery to the markets where they will be sold. Sometimes refineries are built near the oilfields. More often they are built in the consuming areas.

The oil always starts its journey from the wells by pipeline which may sometimes take it as far as the refinery. But transport by pipeline is usually more expensive than transport by water, and wherever possible tankers are used for moving oil in bulk. Over one third of the world's shipping tonnage is made up of oil tankers, and some of these are among the biggest ships afloat.

Question

You are put in charge of a geological survey party exploring for oil in, say, Nigeria. How would you set about the search? And what kind of information would you need to have before recommending a test drilling? (You will need to find out more about the kinds of rocks in which oil is trapped. Most geology textbooks will tell you.)

An off-shore drilling platform in the North Sea, 22 miles off the Dutch coast. Two drilling crews live on the platform, making a total complement of 38. A helicopter provides communication with the shore.



Part two

Refining the oil and getting the products

Separating the crude oil – A modern oil refinery, with its gleaming metal columns, its miles of intricate piping, and its automatic control panels, looks like something out of science fiction. You would hardly guess it had anything to do with oil because there is not a drop of the stuff to be seen. It is all flowing invisibly through the pipes from one process to the next.

Crude oil is a complex mixture of hydrocarbons which is of little use as it comes out of the ground. The first stage in the refining process is to separate the hydrocarbon mixture into fractions boiling at a similar temperature – that is, into fractions of similar molecular size. It is rather like separating a heap of coal into lumps of similar size by sifting the coal through sieves of finer and finer mesh. This separation is carried out by distilling the crude oil. You have come across distillation several times in the laboratory. Distillation in an oil refinery is essentially similar except that the liquid hydrocarbon mixture is separated not by boiling off the different fractions one after the other but by vaporizing nearly all the crude oil and collecting the separated fractions as the vapours condense back into liquids. Vaporized crude oil is passed into a distillation or fractionating column (which, in a typical oil refinery, may be as high as 200 feet), and the hydrocarbon fractions, boiling at different temperatures and therefore at different heights in the column, are separated and collected.

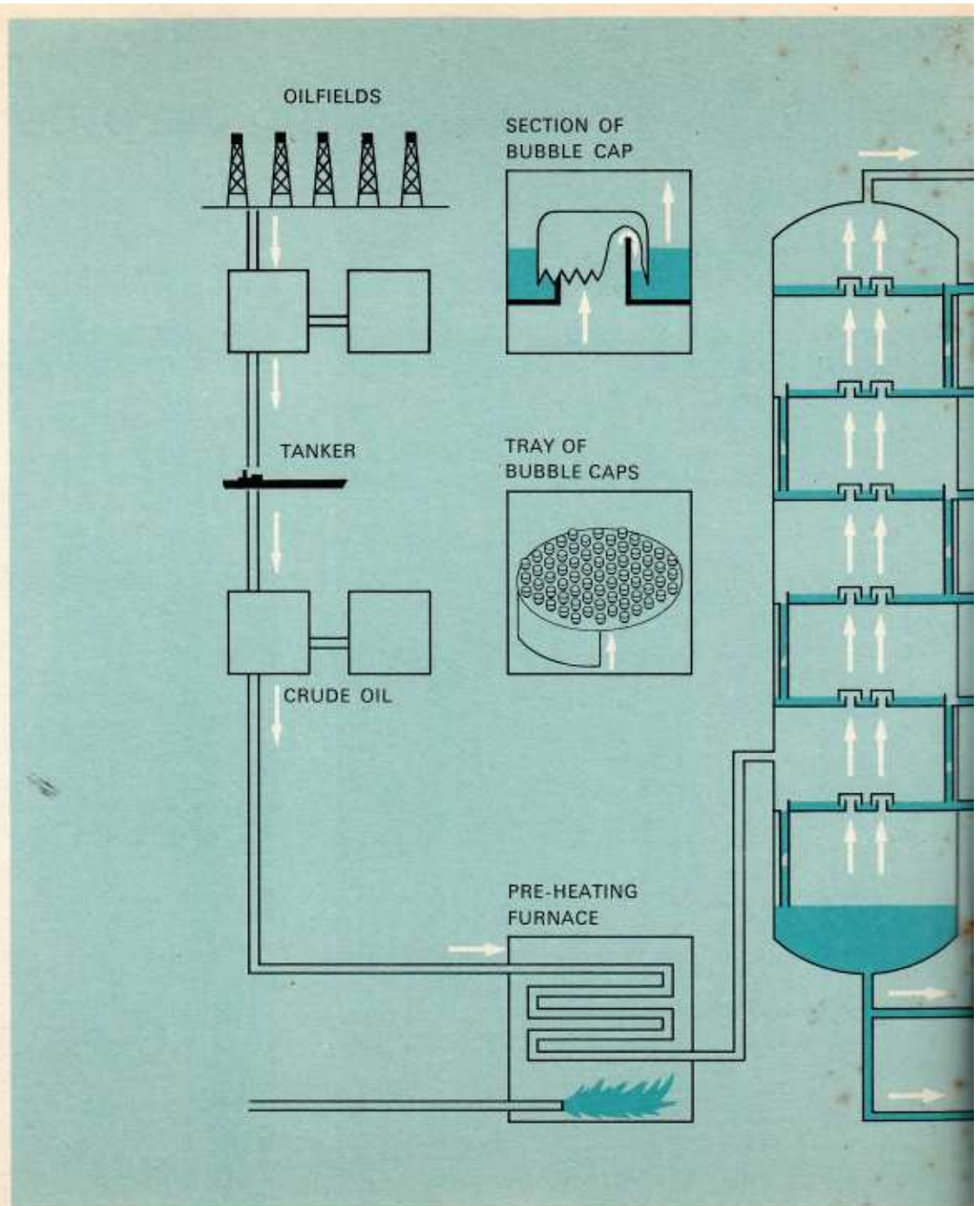
The main fractions into which the crude oil is separated are:

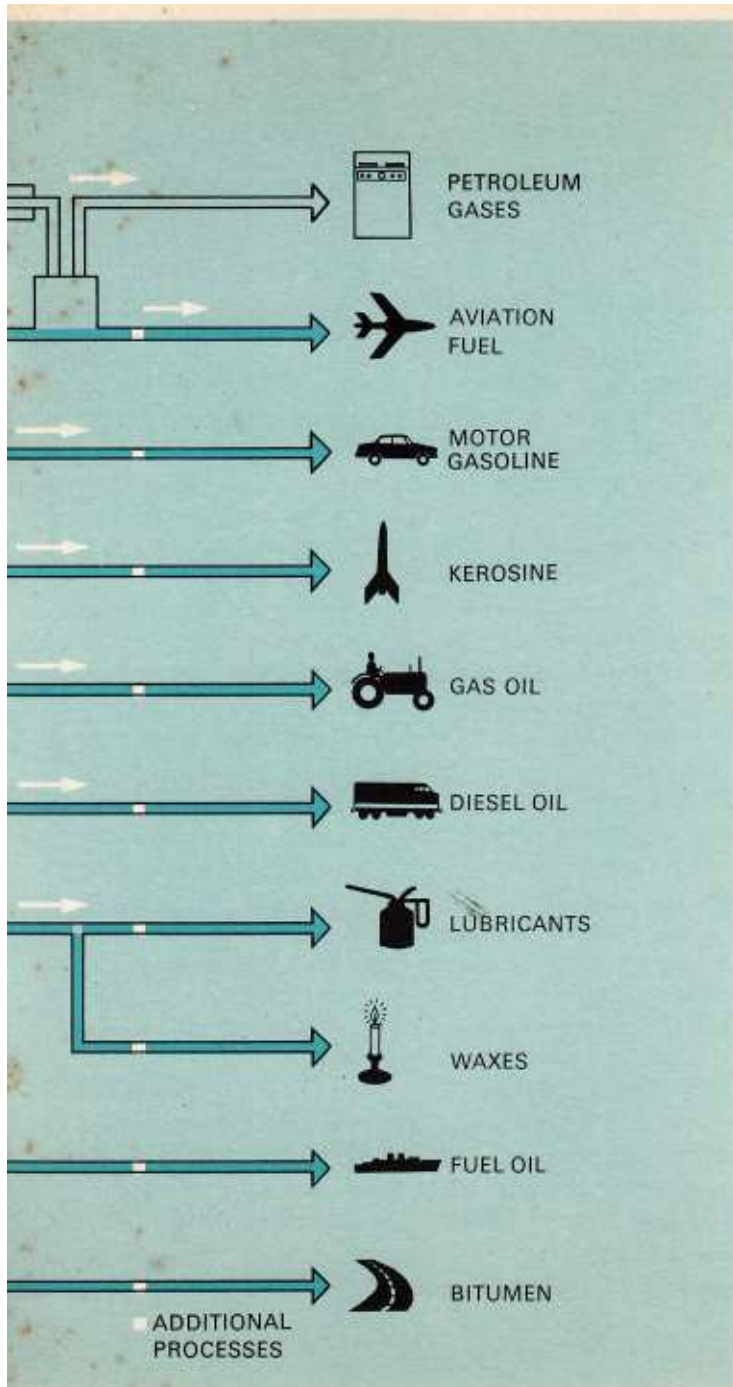
petroleum gases (which are gases at normal temperatures) plus *gasoline* (a colourless liquid boiling between 30°C and 200°C); *kerosine* (a colourless liquid boiling between 140°C and 300°C); *gas oil* (a brown liquid with a boiling range only

Miles of intricate piping –
Stanlow Refinery in Cheshire.



Diagram of a fractionating column in an oil refinery. Vaporized crude oil passes up the column, and separated fractions, as they condense on the trays, are collected off the side. Bubble caps (on each tray there may be many hundreds) help force the rising vapours through the condensed liquids, and so ensure precise separation. The part of the crude oil which does not vaporize is drawn off as a liquid from the base of the column.





slightly above that of kerosine); and a syrupy *residue*. Gasoline is separated from the petroleum gases by cooling, which liquefies the gasoline. The residue can either be used as fuel oil or distilled under vacuum to give lubricating oils, wax, and bitumen.

Conversion – The next stage in the refining process is both the most tricky and the most interesting. It comes about because there is a larger market demand for some oil fractions than for others. Over a period of years, the demand for any particular product can vary a great deal. Take the example of kerosine. At the turn of the century, all that people extracted from the crude oil was the kerosine fraction for lighting, and the rest was wasted. With the invention of the internal combustion engine, the demand for gasoline grew while that for kerosine fell because it was supplanted by electricity for lighting. Then, in the mid-forties, the development of jet engines and rockets called for a fuel based on kerosine.

In a modern oil refinery unwanted fractions are no longer wasted but are converted into those fractions most in demand. On the one hand, large molecules of a heavy fraction such as gas oil can be split to give two small molecules of a lighter fraction such as gasoline. On the other hand, two or more molecules of a light fraction can be joined together (polymerized) to give a larger molecule of a heavier fraction. This playing about with molecules, converting one size into another, is typical of the chemistry of the twentieth century. Yet about fifty years ago it was little more than a chemist's dream.

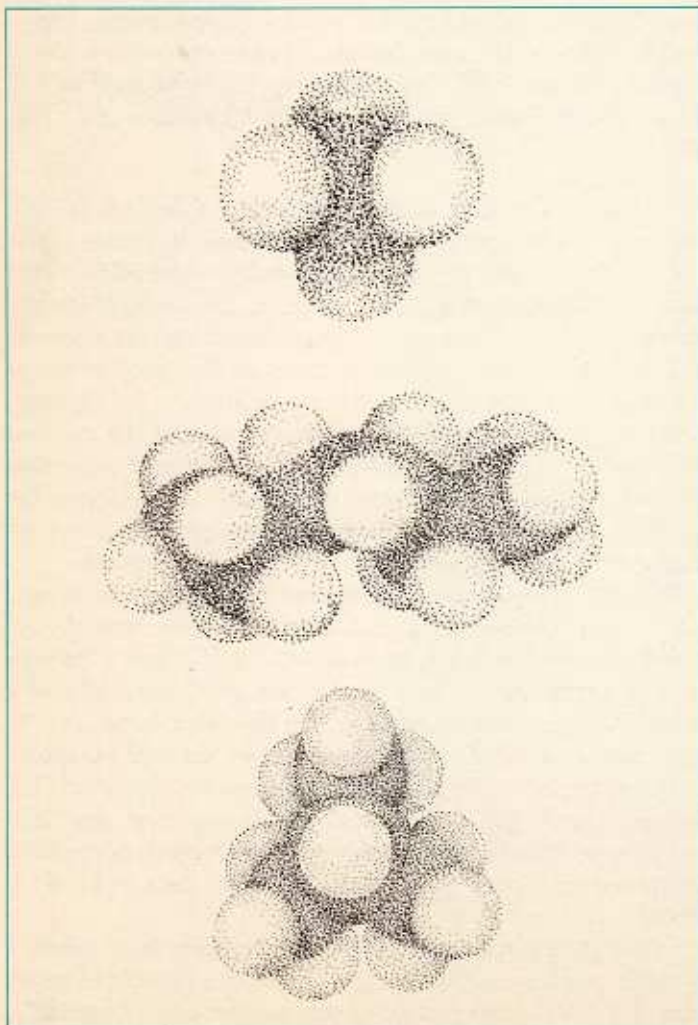
One of the main conversion processes used in an oil refinery is called *cracking*. As the name implies, this process involves breaking down large molecules into smaller ones. Originally,

Hydrocarbon molecules:

methane (CH_4)

hexane (C_6H_{14})

2 methyl propane (isobutane)
(C_4H_{10})

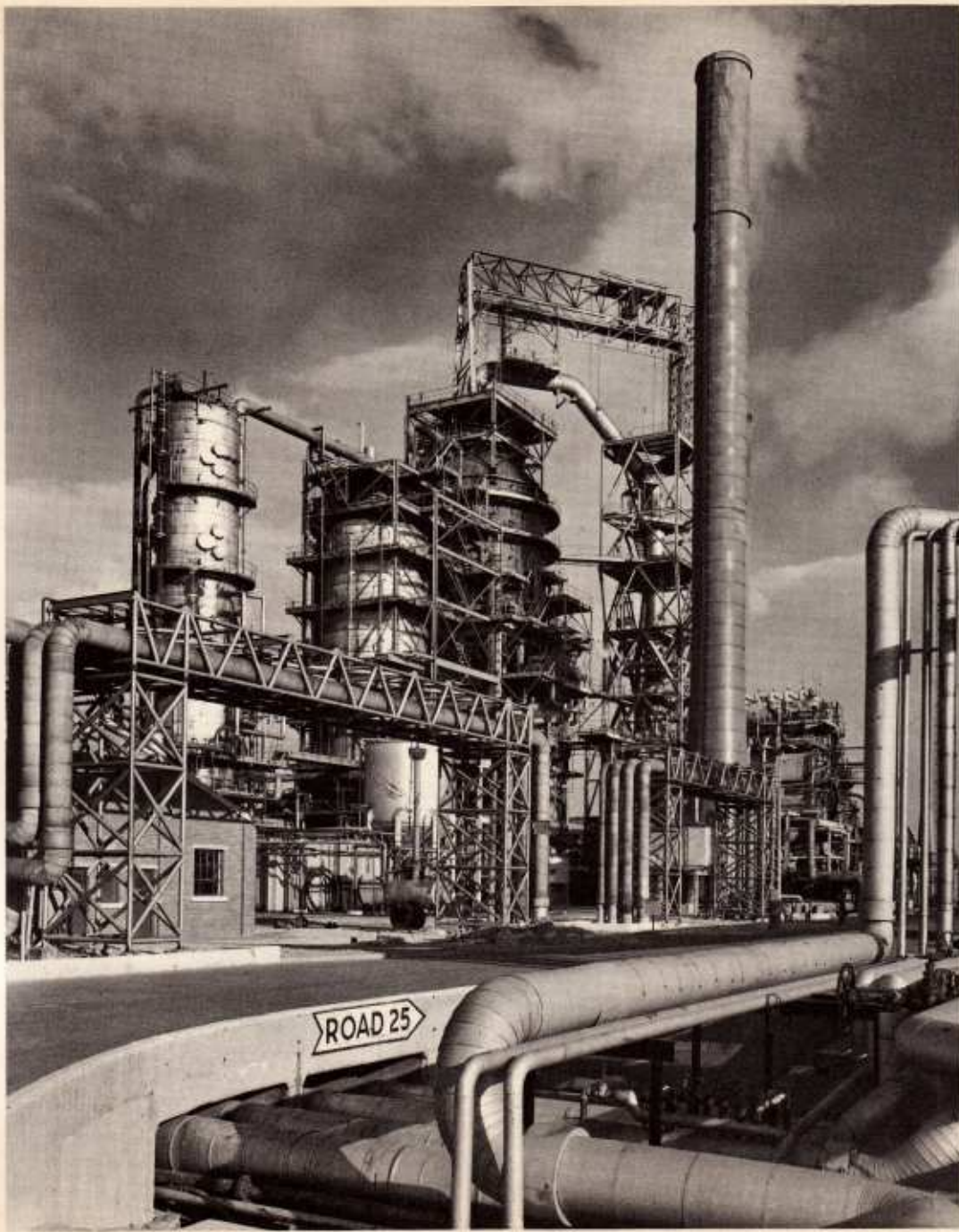


cracking was carried out by heating the heavier oil fractions under pressure: this process is known as 'thermal cracking'. Nowadays it is more usual to crack the oil in the presence of catalysts, for example, silica or alumina. This means that the process - known as 'catalytic cracking' - can be carried out at much lower temperatures and pressures.

As well as breaking down the large molecules, another effect of catalytic cracking is to convert straight-chain hydrocarbons into hydrocarbons with branched side-chains or with ring structures, e.g. aromatic hydrocarbons. When making gasoline, this conversion is especially desirable because both branched and aromatic hydrocarbons function very much more efficiently in engines. The modern internal combustion engine requires gasoline of a very high performance and, in addition to cracking, many refineries operate a reforming process to convert gasoline of poor quality into gasoline with a high aromatic content.

Using conversion processes of this kind, the oil refiner has become a chemical conjurer able, within limits, to draw out of the hat the required fraction with the required properties in the required amount.

Purification - The final stage in the refining process is to remove impurities from the different fractions and so produce finished oil products. Some of the commonest of these impurities are sulphur compounds which tend to give off poisonous fumes of sulphur dioxide when the oil is burnt. The amount of sulphur present depends on where the original crude oil has come from.



A catalytic cracking unit. On the left is the fractionating column reactor.

Oil products – A list of the more important oil products with their uses is given below:

Natural gas is the name given to the gas that comes from an oil well in association with liquid crude oil. The gas consists mostly of methane, the simplest of the hydrocarbons. Some wells produce nothing else but this natural gas. (Natural gas wells in Texas are the main source of helium.)

Natural gas is an excellent fuel and, for a long time, has been extensively used in the United States. But, until recently, it had been little used in other parts of the world because it was too difficult to transport from remote producing areas to the consumer. However, the discovery of natural gas in the Sahara and in Northern Holland, has been followed by the finding of large deposits in the North Sea off the British coast. The exploitation of this new source will possibly lead to great changes in the supplies of energy and in the provision of raw materials for industry.

Petroleum gases consist of ethane, propane, butane, and other very volatile hydrocarbons. They are used to enrich town gas and also to make chemicals. Propane and butane are liquefied under pressure and sold as bottled gas.

Gasoline is the stuff that comes out of the petrol pump. Without a volatile fuel like gasoline, the development of the internal combustion engine – and therefore of the car and aeroplane – would have been extremely difficult. The pistons of the internal combustion engine work at such a rate that a fast-burning fuel like gasoline, which will vaporize easily and mix intimately with the air needed for combustion, is required to keep the engine running efficiently.

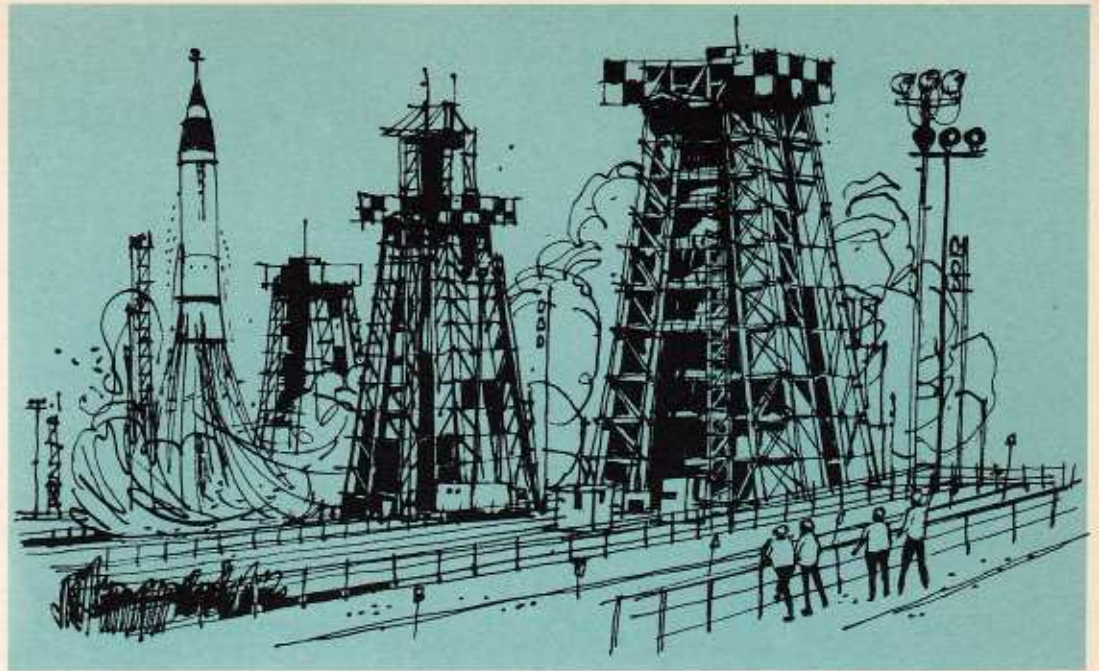
Kerosine, as mentioned before, was once used almost entirely for lighting. In remote farming districts where there is no electricity you may have seen the lamps which burn kerosine for light. Nowadays most of the domestic kerosine goes into heating appliances or cookers.

Mixed with a small quantity of gasoline, kerosine is the standard fuel for jet aircraft and for the first stage of many of the satellite-launching rockets.



The search for natural gas:
a drilling rig in the North Sea.

Kerosine, mixed with a small amount of gasoline, is often used as fuel in the first stages of rockets.



Fuelling a jet aircraft. Aviation fuel has to be of a very high quality and must meet exacting specifications. For example, it must not freeze above minus 60°C.



Gas oil was originally cracked to enrich gas, and hence its name. Nowadays it is chiefly used to make diesel fuel for buses, lorries, and locomotives; though it is also cracked to produce gasoline of high quality.

Fuel oil is burnt to raise steam for ships, locomotives, industrial machinery, and heating plant in general. It is a thick syrupy oil which is difficult to vaporize. To burn it efficiently, it must be broken down or 'atomized' into minute droplets.

Lubricating oils are a blend of specially distilled oil fractions. The most important property of a lubricating oil is its viscosity or the ease with which it flows. Thus the cog wheels of a watch require a much thinner and more mobile lubricating oil than do the moving parts of a ship's engine. The viscosity of the finished lubricating oil depends very largely on the proportions in which the component oil fractions are blended. Greases are liquid lubricants thickened with soaps or other additives.

An interesting new development is that of multigrade oils for cars. An oil becomes less viscous as the temperature rises,



Laying a road with bitumen.

and therefore cars need a thicker oil in summer than in winter. Before the development of multigrade oils, a complete change of oil was needed. Small quantities of a substance containing long-chain molecules are incorporated in multigrades. When cold, the long-chain molecules are tightly coiled and do not affect the viscosity of the oil. When hot, they uncoil to form long strands, thereby increasing the viscosity. Thus they control the viscosity according to the temperature.

Wax is a white solid not found in all crude oils. It is used, among other things, to make candles and polishes and also to impregnate food wrappings.

Bitumen is a black residue which, depending on the distillation process, varies in consistency from a viscous liquid to a brittle solid. Natural deposits of bitumen were used by ancient civilizations for building and for hydraulic works, and bitumen is several times mentioned in the Bible. Nowadays it is used on a very large scale to make roads and aircraft runways. It is also a valuable waterproofing material used to coat roofing felts and to protect underground pipes against corrosion.

Question

In a fractionating column, will oil fractions with the lowest boiling points be at the top or bottom of the column? When the residue from the column is distilled, why is it distilled under vacuum?

Part three

Chemicals from petroleum

It is the exciting new substances that chemists are now able to make which, perhaps more than anything else, distinguish the modern world from Victorian times or even from thirty years ago. An elderly Victorian planted down in presentday surroundings might well look about him in wonder. Polythene – nylon – synthetic rubbers – washing-up liquids – selective weedkillers – all these everyday stuffs would be new to him. He might argue that many of them are mere substitutes for what he knew before and that wool and natural rubber were quite good enough for him. But these new stuffs are not mere substitutes because the chemist is able to endow them with the kind of properties for the jobs they are required to do. He can make textile fibres that are ten times as hard-wearing as wool, that are light, elastic, mothproof, and waterproof, that dry quickly and do not need to be ironed.

Most of these new materials are made from organic chemicals and their manufacture on a large scale requires abundant supplies of an organic starting material. Only two such materials are available in sufficient quantities – petroleum and coal. Both are used extensively, but because petroleum is liquid, it is generally easier to handle in the chemical conversion processes of a modern chemical plant.

A few inorganic chemicals are also made on a large scale from petroleum: sulphur, extracted out of crude oil and oil fractions, is made into sulphuric acid; and hydrogen, from petroleum hydrocarbons, is combined with nitrogen to make ammonia and, ultimately, nitrogenous fertilizers. (See the Background Book, *The Nitrogen Problem*.)

The growth of the industry – Although it is still small compared with the oil industry, the petroleum chemicals industry is growing more quickly than almost any other.

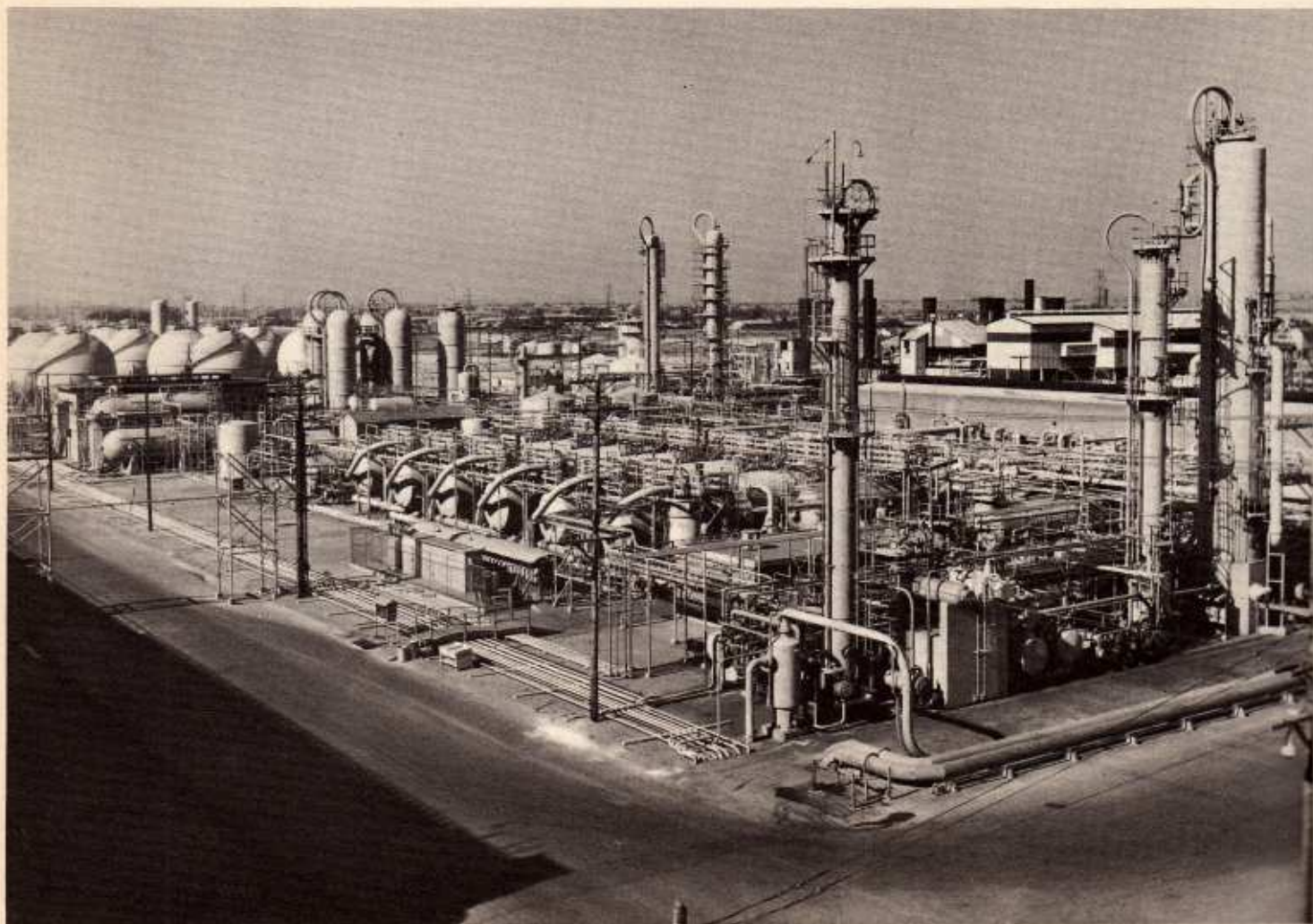
It began in America in 1918 with the manufacture of propan-2-ol from propylene gas derived from petroleum. Other countries, in particular Germany, started up similar manufacturing processes, but it was not until the Second World War and the need to find new sources for strategic materials, that the industry pushed ahead.

After the war, products made from petroleum began to enter the home market. Plastics and washing powders were a great commercial success. Women used to queue for hours to buy a pair of nylons. Since then the demand has risen steadily and the chemical industry has grown in response. In 1950 the British production of organic chemicals from petroleum was 45,000 tons and, only twelve years later, this figure had risen to 1,180,000 tons.

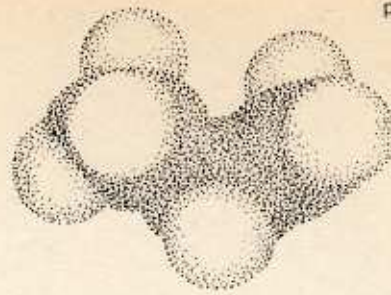
The starting point of the industry is, of course, the chemical laboratory: building new substances and examining their properties to see whether or not they are useful (most of them are not). However, the laboratory synthesis of a few grams of product is one thing, and a day-and-night manufacturing process involving hundreds of tons of product is quite another. Manufacturing chemicals in huge metal plants at high temperatures and high pressures creates problems which belong as much to engineering as they do to chemistry.

Chemical manufacturing – So great is the ingenuity of the present-day organic chemist that it has been said of him that he can synthesize any of the thousands of organic chemicals, starting with methane. However, petroleum contains hydrocarbon building bricks, in particular, the hydrocarbon gases ethylene, propylene, and butylene, which provide a more convenient starting point for synthesis. These gases are chemically very reactive, and can therefore be readily built up into

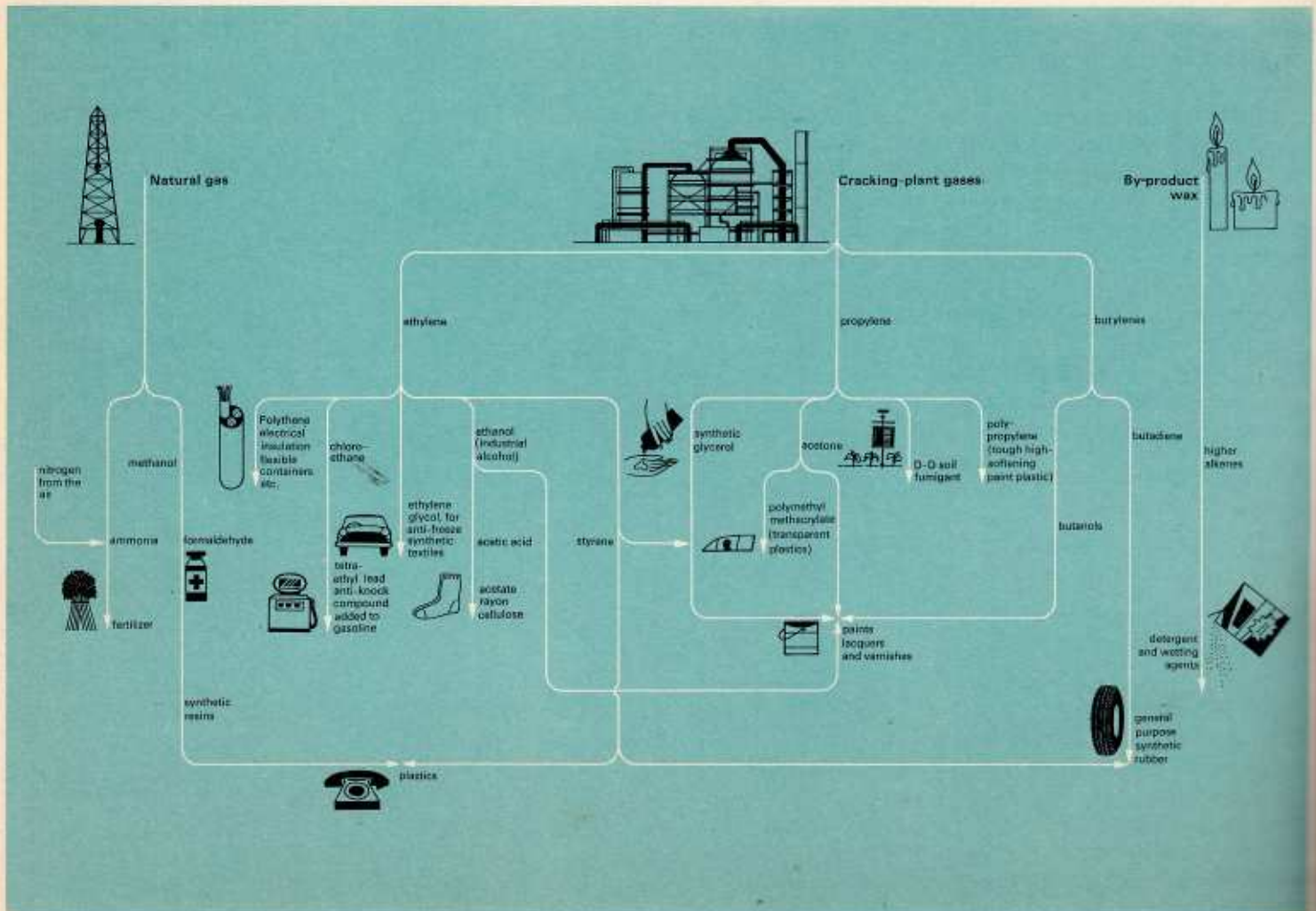
A petroleum-chemicals plant may not look very different from an oil refinery. But, whereas the processes in a refinery are chiefly those of separation, cracking and purification, many of the processes in a chemical plant involve complex chemical reactions. Here is the solvents manufacturing unit in a Cheshire chemical plant. The solvents distillation columns are in the centre of the photograph.



propylene (C₃H₆)



Some of the chemicals and chemical products that can be obtained from petroleum.





Large-scale storage of nitrogenous fertilizer made from petroleum. The 'harvester' machine transfers several hundred tons of fertilizer daily to an overhead conveyor which carries it to a bagging plant.

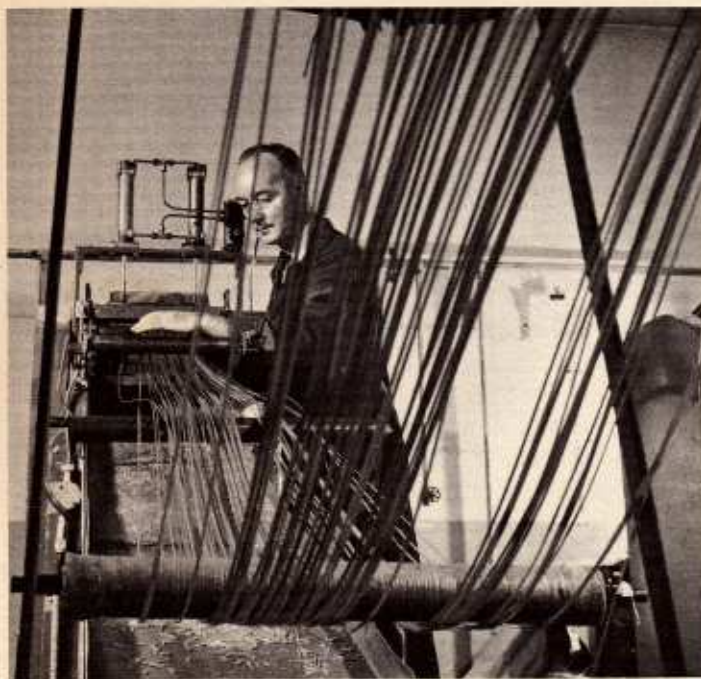
that organic synthesis on a large scale has to offer. Another dream (and one that has already been partially fulfilled) is that before long chemists will be able to make foodstuffs out of petroleum.

With so much starvation in the world, it is a worthwhile goal for any young chemist to aim at.

The petroleum industry and its future – The petroleum industry is composed of a large number of different commercial companies. A few of these are giant concerns. Two of them, Standard Oil of New Jersey and Shell, are, next to General Motors of America, the second and third largest companies in the world. Both of them employ many thousands of people, are involved in all sectors of the industry, including chemicals, and have interests in many countries. There are also a large number of smaller companies which operate either in a single country or in only one sector of the industry.

The industry has grown to its present huge size chiefly by the sale of petroleum as a fuel. Although the supplies of petroleum in the ground will hold out for very many years, there must be a limit to what the Earth contains. Therefore, our descendants may regret that we burnt so much to provide energy instead of leaving it to be used as an organic chemical. With the increasing use of new sources of energy – in particular, of atomic and solar energy – it is to be hoped that the need for petroleum as a fuel may gradually diminish though there is no sign of this as yet. Then it will be splendid if the chemist can use this precious stuff – 'liquid gold' as it is sometimes called – as the raw material with which he shapes his creations as the potter shapes his clay.

Spheres for the storage of liquid butane.



Feeding strands of polystyrene into a chopper machine at a chemical plant. The machine cuts the strands into small chips which are sent to the moulders of plastic articles.

Question

You have seen how, by the addition or taking away of such simple substances as water, oxygen, or hydrogen, one organic chemical can be converted into another. Such reactions are not always easy to bring about in practice and, as you already know, energetics will tell you a great deal about whether or not they will work. Although, at this stage, you will have little idea how to carry out the reactions, suggest how you might make the following substances, starting with ethylene ($\text{CH}_2=\text{CH}_2$)

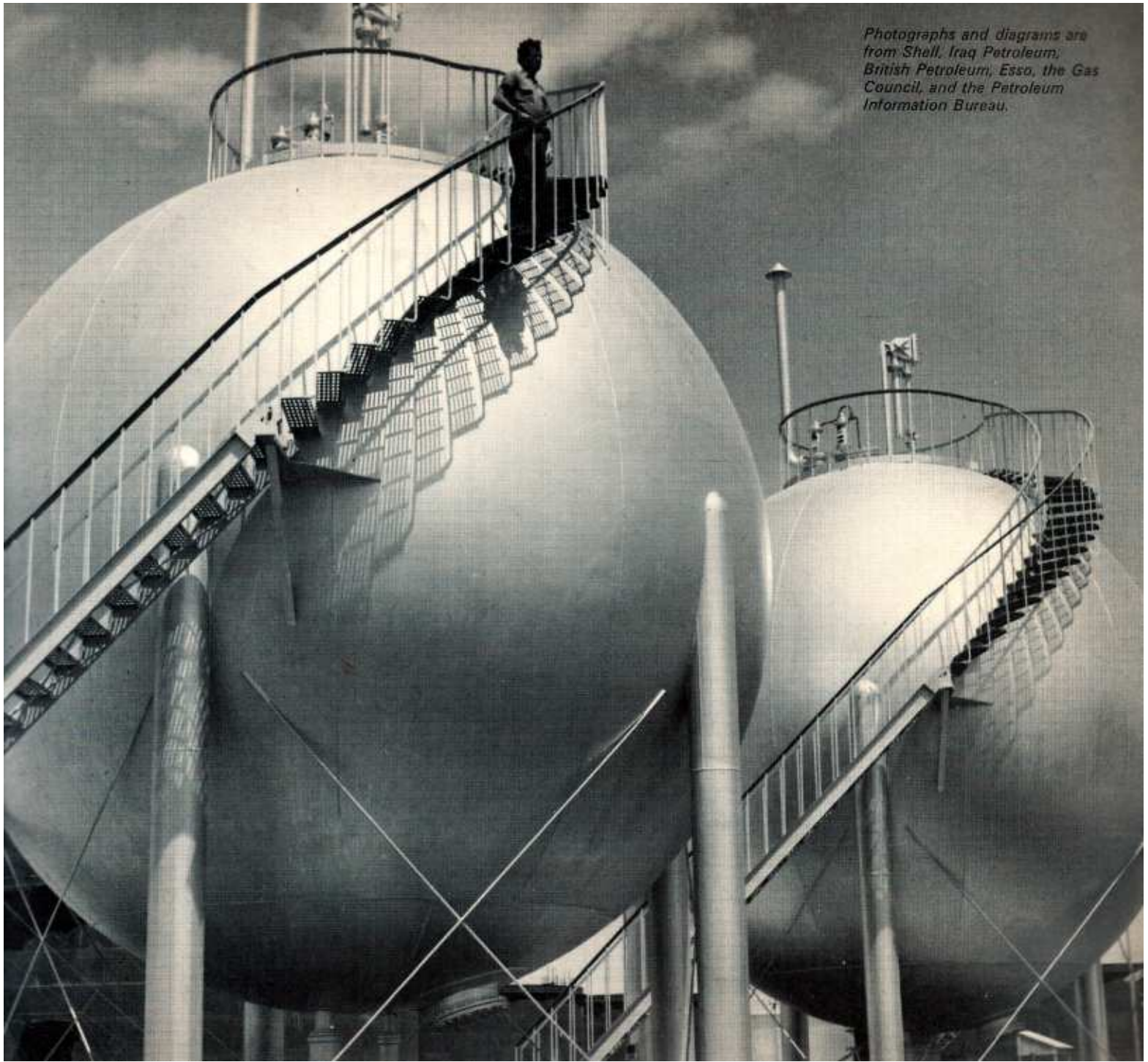
a. ethanol ($\text{CH}_3-\text{CH}_2\text{OH}$)

b. acetaldehyde ($\text{CH}_3\text{C} \begin{array}{l} \text{H} \\ \text{=} \\ \text{O} \end{array}$)

c. acetic acid ($\text{CH}_3\text{C} \begin{array}{l} \text{O} \\ \text{=} \\ \text{OH} \end{array}$)

d. ethyl acetate ($\text{CH}_3 \cdot \overset{\text{O}}{\parallel} \text{CO} \cdot \text{C}_2\text{H}_5$)

You are provided with water and oxygen.



Photographs and diagrams are from Shell, Iraq Petroleum, British Petroleum, Esso, the Gas Council, and the Petroleum Information Bureau.

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