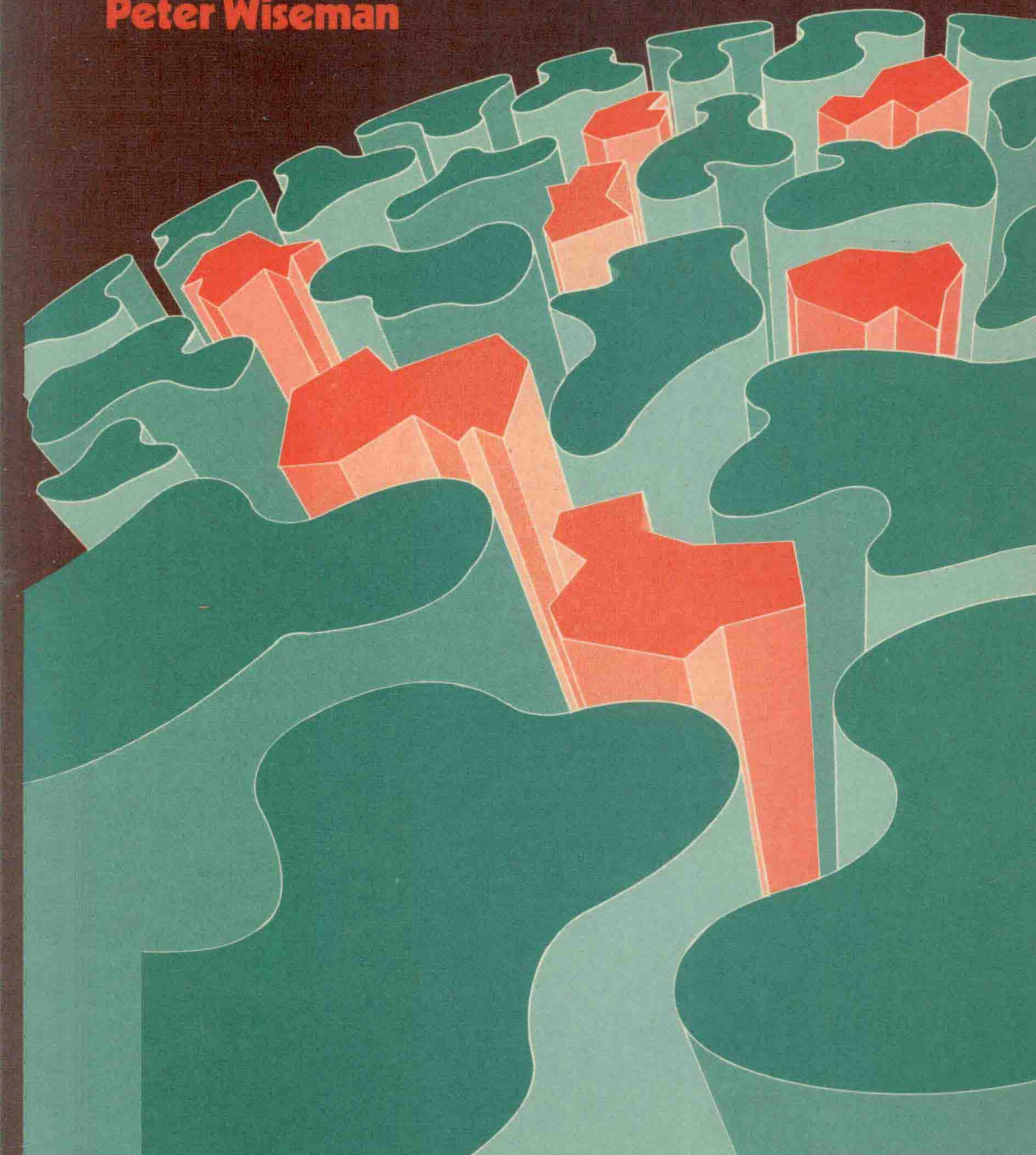
UMIST Series in Science and Technology

PETROCHEMICALS

Peter Wiseman



PETROCHEMICALS

UMIST SERIES IN SCIENCE AND TECHNOLOGY

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Table of Contents

Chapter 5 — Butadiene and Butenes

Chapter 6 — Benzene, Toluene and Xylenes Production

Chapter 7 — Benzene Derivatives

Preface

Petrochemicals can lay two main claims to the attention of those who are interested in chemistry. Firstly, the petrochemical industry is a major industry of great importance in modern society and provides a huge range of useful products, such as plastics, rubbers, fibres, detergents, and solvents, and supplies raw materials for the manufacture of many other chemicals. Secondly, it has a coherent structure made up of an interlocking system of raw materials, processes, and products, which makes it an ideal medium for observing factors that influence the application of chemistry in industry. In this book I have attempted to bring out both of these aspects. Whilst it is written primarily for students and teachers of chemistry and chemical engineering, it should also be useful to practising chemists and chemical engineers as a concise account of what goes on in the petrochemical industry.

The book is based on undergraduate and postgraduate courses given at UMIST for a number of years. After an introductory chapter, the text is structured mainly round the three basic building block petrochemical processes, cracking, catalytic reforming and steam reforming, and the downstream processing of the intermediates that they produce. Reaction mechanisms are discussed where particular points of interest arise, but no attempt is made at a comprehensive discussion of mechanisms: this would have extended the book far

beyond its intended length. Throughout, relationships between process chemistry, technology, and economics have been emphasised. To help develop a feeling for the scale of petrochemical operations, details of US capacities are given for major products. (US data are used because they are much more readily available than those for other countries. As a rough rule of thumb, the total West European petrochemical industry is about the same size as the US industry.) Problems are provided at the end of each chapter; students are strongly recommended to attempt these.

When a book is based on teaching and researches that have been carried out over a substantial period it is inevitable that many people will have made inputs of one sort or another, and it is impossible to acknowledge or even identify all of these. However, I do wish to record my debt to the following students who have carried out research projects on the petrochemical industry and related topics under my supervision, and whose work provided stimulation and information: S. M. Abdul-Hadi, O. M. J. Adams, Zed Alatas, Harout Bronozian, P. J. Campbell, C. Y. Cheung, O. A. Garcia, J. E. Hartley, S. S. Islam, I. P. Kohli, P. A. Obuasi, A. B. Summerscales, and Farouk Warris. To any of these who happen to read this book, best wishes and thanks. I would also like to express my thanks to the series editor Dr R. V. Parish for his encouragement and many helpful comments.

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P. Wiseman
Manchester, July 1985

1

Introduction

1.1 WHAT ARE PETROCHEMICALS?

In a sense, most organic chemical products are petrochemicals. If you take an aspirin tablet it is highly likely that the carbon atoms and some of the hydrogen atoms it contains came originally from petroleum and possibly natural gas. However, the use of the term 'petrochemical' is usually confined to products that are derived from petroleum and natural gas *and* are made on a large scale. Phenol and acetic anhydride are petrochemicals; aspirin, which is derived from them, is not. It is not possible to define precisely what is meant by 'a large scale', but roughly it means products which are made in plants of capacities from about 10 000 tonnes per annum upwards. Most of the processes discussed in this book are operated in plants with capacities in the range 20 000 to 650 000 tonnes per annum.

In terms of tonnage, about 95% of total organic chemical manufacture is at present based on petroleum and natural gas. It is, however, important not to overestimate the importance of the petrochemical industry as a consumer of these materials. In the USA, for instance, only about 5% of petroleum is used as raw material for chemical manufacture. Its main use is as a fuel, as is the main use of natural gas.

It is commonly believed that petrochemicals are made by the oil industry – a 'by-product of refining'. This is a misconception.

The petrochemical industry is a part of the chemical industry, and quite distinct from refining, except in so far as it uses some products of refining as raw materials. Many companies that make petrochemicals do not carry out oil refining, and those oil companies which make petrochemicals tend to have a separate organisation for this part of the business. The oil industry's main business is fuels, with raw materials for petrochemicals as an important sideline. The petrochemical industry's main business is chemicals.

1.2 THE DEVELOPMENT OF THE PETROCHEMICAL INDUSTRY

It is generally agreed that the development of the industry started in 1920, when the Standard Oil Company of New Jersey USA brought a plant into operation for the manufacture of isopropyl alcohol from propylene. The propylene used in this process was a by-product of gasoline production by cracking, a process which had been introduced into the oil industry in 1913. The first petrochemical manufacture based on ethylene was in 1923, when Union Carbide started the production of ethylene chlorohydrin, ethylene glycol and dichloroethane at South Charleston, West Virginia, based on ethylene made by cracking ethane. The industry developed steadily in the USA during the 1920s and 1930s, but was then given an immense stimulus by World War II. By 1945 the petrochemical industry was more or less fully developed in the USA.

Outside the USA, petrochemical manufacture was carried out to only a very limited extent before the 1950s. During that decade petrochemical industries built up, first in the UK and then throughout Western Europe. The 1960s saw the spread of petrochemical manufacture to all developed countries, and massive developments in scale of operation and in process technology. By the end of this decade the petrochemical industry was established on the world scale.

The oil crisis of 1973 and the huge increases in the price of oil which followed have had major effects on the industry, and these are still developing. The rate of growth of the petrochemical industry, and of the chemical industry in general, is now much less than it was in the golden days of the 1950s and the 1960s. The technology is changing in response to the increases in price of hydrocarbon raw materials, and of fuel. Possibly the most important effect in the next few years will be a small but significant shift in the geographical centre of gravity of the industry. Many of the oil-producing developing countries are at present setting up major petrochemical developments

based on gas, from oil fields, which would otherwise be wasted. Saudi Arabia, for example, is currently bringing into operation plants which will be able to supply about 3% of total world requirements for ethylene and ethylene derivatives.

1.3 THE RAW MATERIALS – PETROLEUM AND NATURAL GAS

Petroleum, or **crude oil**, occurs underground in reservoirs in porous rock in certain types of geological structures. The oil is recovered from these by drilling oil wells from which it either flows out under the reservoir pressure or is pumped out.

Major deposits of oil occur in only a fairly limited number of regions (see Table 1.1). A notable feature is that more than half the world's known reserves are in the Middle East. Many heavily industrialised countries have only very small reserves of oil. Even the USA, the pioneer of the oil industry and one of the world's major oil producers has to import about half its requirements.

Table 1.1
Distribution of oil and natural gas reserves (%)

	Oil	Natural gas
Africa	9.8	5.9
Asia and Australasia	6.3	5.8
Middle East	54.0	24.2
Latin America	9.5	5.8
North America	7.3	9.1
USSR and Eastern Europe	10.3	44.3
Western Europe	2.8	4.9

Source of data: *Oil and Gas Journal*, **83**, 52, 80–81.

Crude oils vary widely from region to region and from field to field. Some crudes are light-coloured, mobile liquids, others are thick, treacly or tarry materials. Some have quite pleasant smells, others smell quite disgusting. However, all are made up mainly of three types of hydrocarbons, alkanes, cycloalkanes, and aromatics. The differences in character arise from the different proportions of hydrocarbon types, differences in molecular weight range, and differences in the nature and amount of non-hydrocarbon materials.

The alkanes, called *paraffins* in the petroleum industry, range from

methane upwards. Both straight chain and branched chain alkanes are present, in varying proportions depending on the type of crude. The cycloalkanes, called *naphthenes* in the industry, contain five and six membered ring compounds only. The aromatics range from benzene upwards. The proportions of these different types of structures vary over a wide range. Aromatics commonly make up the smallest proportion of the oil.

The molecular weight range covered varies greatly. Oils containing predominantly low molecular weight components are called 'light' oils; those containing a high proportion of high molecular weight materials are called 'heavy' oils.

Oils contain small percentages of sulphur-, oxygen-, and nitrogen-containing organic compounds, and traces of metallic compounds, notably of vanadium.

There are two sources of **natural gas**. It occurs in gas fields, underground reservoirs broadly similar to oil reservoirs, from which it is recovered by drilling gas wells. In addition, large amounts of gas are produced in association with the production of crude oil. We have already seen that oil contains alkanes from methane upwards. In the reservoir the lower gaseous alkanes are often in solution under considerable pressure. When the oil is brought to the surface the pressure is released and a proportion of the C_1 to C_4 alkanes boils off. This is called *associated gas*. In some oil fields, e.g. those in inaccessible regions, this gas is simply burnt. In others it is collected and used.

Natural gas varies widely in composition. Some gases contain only small amounts of alkanes other than methane. These are called *dry natural gas*. This term derives from the fact that if such a gas is compressed at ambient temperature no appreciable amount of liquid is formed. Other gases contain substantial amounts of ethane, propane and butanes, which liquefy if the gas is compressed. These are called *wet natural gas*. Associated gas is invariably wet, whereas gas from gas fields is usually dry. In addition to hydrocarbons, natural gas sometimes contains substantial proportions of other components such as carbon dioxide, nitrogen, hydrogen sulphide and helium. Table 1.2 shows some examples of natural gas compositions.

Dry natural gas is generally used as it stands, except that hydrogen sulphide, if present, would usually be removed, as would most of the carbon dioxide if initially present in large amounts. Wet natural gas is often stripped of propane and butane and most of the ethane, either by scrubbing with a hydrocarbon solvent at about $-45°C$, or by cooling to about $-120°C$ so that the ethane, propane and butanes liquefy. The ethane, propane, and butanes may then be separated by low temperature distillation as required.