The Production of
Polymer and Plastics Intermediates
from Petroleum

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PREFACE

In the last two decades one of the most impressive features of the British economy has been the rate of growth of the production of organic chemicals from petroleum. In 1950, less than 10 per cent of all organic chemicals were produced from petroleum, whilst by 1964 an estimated 2·5 million tons or over 70 per cent of organic chemicals were petroleum based. The importance of this aspect of organic chemistry is not reflected in most textbooks on the subject, and the aim of the present volume is to make available authoritative accounts of some of the processes operated in the Petrochemical Industry.

The first chapter on thermal cracking for olefins is of particular interest in view of the continuing expansion of ethylene capacity, as witness the recent announcement by ICI Ltd. of plans for a single plant to produce 450,000 tons of ethylene from naphtha. Several plants for the production of acetylene from oil are under construction in the United Kingdom, and in the second chapter the process developed by the Badische Anilin- and Soda Fabrik Company is described. Routes to butadiene are critically reviewed in the third chapter.

'Acetylene versus Ethylene', a chapter prepared by the editorial staff of *European Chemical News*, differs from the other contributions in that it focuses attention on economics. The acetylene and ethylene based routes for manufacturing vinyl chloride are given a detailed analysis in which the authors are not subject to the usual inhibitions experienced by the operators of chemical plant concerning cost data.

The fifth chapter on acetic acid directs attention to an area which offers very great potential, namely the direct production from petroleum fractions of relatively sophisticated chemicals without the necessity of first having to prepare the familiar chemical building blocks, such as the olefins.

The trend to replace indirect multistage processes by direct methods of manufacture, which avoid the use of expensive reagents not contributing to the final product, is well illustrated by the demise of the chlorhydrin route; this is described in the sixth chapter dealing with the methods of manufacture of ethylene and propylene oxides and glycols. In chapter seven an account is given

of the OXO process—one of many processes which depend on the catalytic activity of certain compounds of the transition metals.

The last three chapters review methods of manufacture of styrene, phenol and caprolactam respectively.

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THERMAL CRACKING FOR OLEFINS

Colin B. Cotterill

1.1 INTRODUCTION

CRACKING may be defined as the breaking down of large molecules, usually hydrocarbons, into smaller ones by the application of heat. Heat is necessary as the reaction is powerfully endothermic. It can be carried out in the presence or absence of catalysts, and in the presence of additives such as steam or hydrogen. The products are usually unsaturated. Processes for the purely thermal cracking of hydrocarbons are of outstanding importance as the major source of ethylene throughout the world; they are also the major source of propylene and are important producers of butadiene, which are obtained as co-products when sufficiently heavy feedstocks are used. The thermal cracking of feedstocks such as paraffin wax, paraffinic gas oils and catalytic cycle oils, is also used for the production of longer-chain olefins for conversion to plasticizer and detergent alcohols.

The importance of cracking processes for the production of ethylene can be judged from a recent review[1]. This indicates that the non-communist world capacity for ethylene, currently estimated to be in the region of $6\frac{1}{2}$ million tons/year, is likely to reach 11 million tons/year in the next few years when currently planned extensions are installed. These figures reflect the growing importance of ethylene as a key intermediate in the manufacture of polyethylene, ethylene oxide and glycol, ethylene dichloride, vinyl chloride, styrene, ethanol, long-chain alcohols and olefins, elastomers, acetaldehyde and other important products.

1.2 TYPES OF CRACKING OPERATION

In order to show how the thermal processes used for the production of olefins fit into a more general pattern, a very brief review is given of the various types of cracking operation that are used commercially. The types of cracking operation are summarized in *Table* 1.1[2].

Thermal reforming, viscosity breaking, catalytic cracking processes, platforming and hydrocracking are typically refinery operations, rather than processes for the production of chemical

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intermediates. Thermal reforming is a mild coil cracking process carried out at fairly high pressures in the liquid phase, and although some gas is produced, the main objective is to obtain motor gasoline from naphthas or heavier crude oil fractions. Viscosity breaking is again a mild thermal cracking operation designed to reduce the viscosity and pour point of heavy straight-run crude oil fractions, for example to render them suitable as feedstock for other types of

Table 1.1. Summary of Types of Cracking Operation

Refining operations
    Thermal reforming (Cracking)
    Viscosity breaking
    Catalytic cracking
    Catalytic reforming (Platforming)
    Hydrocracking

Thermal processes for production of unsaturated hydrocarbons
    (a) Processes operating at $>1,000°C$ (for acetylene)
        Partial combustion
        Electric arc (plasma jet)
        Molten baths

    (b) Processes operating at $<1,000°C$ (for ethylene)
        Processes using solid heat carriers
        High temperature steam pyrolysis
        Coil cracking

cracking process. The catalytic cracking processes, typically carried out in a fluidized bed of silica–alumina catalyst, find wide use in refinery operations for lightening heavy stocks, especially crude oils, with the production of high-octane motor gasolines. Some gas is also produced.

Catalytic reforming is an operation carried out on a straight-run gasoline (i.e. a naphtha) and is not strictly a cracking process. Although some cracking does occur, the main reactions taking place are aromatization of naphthenes and isomerization of paraffins to produce a high-octane gasoline, which can either be used as such or as a source of individual aromatic hydrocarbons. A variety of catalysts is used, including supported platinum in a version of the process known as platforming. Hydrocracking, as the name suggests, is cracking in the presence of hydrogen. It can be done either thermally or catalytically. Cracking occurs by hydrogenolysis, to produce for example a saturated fuel gas from a light feedstock such as naphtha, or a gasoline blending stock or reformer feed from a heavier feedstock.

When production of unsaturated hydrocarbons is the primary objective, cracking is carried out thermally, without catalyst, at

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fairly high temperatures in the gas phase. Processes of this type can be classified into those operating at temperatures above about 1,000°C, and those operating below this temperature. The former are the processes for the production of acetylene or acetylene-ethylene mixtures[3,4]. They can operate on feedstocks ranging from methane to crude oil, and are characterized by very short residence times in the reaction zone (a tenth of a second or less) with rapid quenching of the cracked gas to prevent further reaction of the acetylene. The very high reaction temperatures needed are achieved by passing the preheated cracking stock into the gases produced by burning part of the feedstock or other fuel, as in the BASF process described in detail in Chapter 3, by use of an electric arc[5,6,7], or by introducing the feedstock into a 'plasma jet' obtained by passing an electric discharge through a carrier gas such as hydrogen or argon[8,9]. The use of molten baths has also been claimed[10]. The processes operating at temperatures below about 1,000°C are for the production of ethylene and other olefin co-products, and these are now discussed in more detail.

1.3 THERMAL CRACKING PROCESSES

The objective in the pyrolysis stage of a thermal cracking process is simply to introduce heat into a suitable hydrocarbon feedstock, in an economical manner and in such a way as to give a favourable product spectrum, or cracking pattern. Industrially this is done in three ways. First of all, the feedstock can be contacted with a solid heat carrier, either in a regenerative ('make-and-blow') process operating alternate heating and cracking cycles, or in a moving burden process in which the heat carrier is circulated continuously between a heating and a cracking zone. The heat carrier can be any inert, heat-stable material such as sand, pebbles, coke, etc. Processes of this type are particularly suitable for the cracking of heavy feedstocks that produce a lot of by-product carbon, as the carbon is laid down on the heat carrier and can be burnt off during the heating stage. Second, the vapourized feedstock can be mixed with a hot gaseous heat carrier. Steam is particularly suitable, as it can be separated readily from the cracked gas by condensation. Finally, the feedstock can simply be passed through tubes mounted inside a furnace fired by gas or fuel oil—this is the so-called coil cracking process.

1.3.1 THE LURGI SAND CRACKER

This is an example of a process operating with a continuously circulating solid heat carrier which, as the name of the process

suggests, is finely granular sand[11]. A simplified flowsheet of the pyrolysis section of the process is given in *Figure 1.1*. Almost any feedstock can be used, from ethane to crude oil.

The sand circulates between the reactor (1), the lift pipe (2) and a separating bin (3). The sand, together with fuel (for example, recycled heavy oil produced as a by-product in the process) enters the lift pipe at the bottom, and is conveyed pneumatically by means of preheated air into the separating bin. During its passage up the lift pipe, the sand is heated to the temperature required for cracking by combustion of the fuel, and of the carbon which was laid down on the sand during the cracking stage. The flue gases disengage from
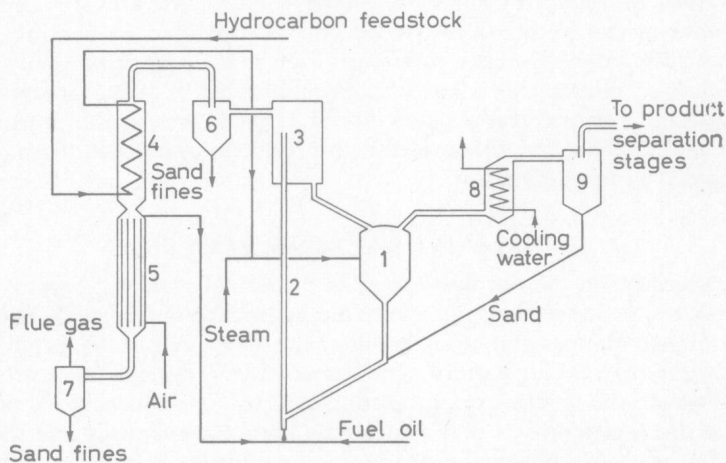

Figure 1.1. The Lurgi–Ruhrgas sand cracker (after Schmalfeld[11]*)*

the sand in the separating bin, and before being vented to stack are passed through a feedstock preheater (4) and an air heater (5) to recover the sensible heat. Sand fines, which are produced by attrition of the sand, become entrained in the flue gas, and are eliminated from the system by cyclones (6) and (7).

The hot sand drops from the separating bin into the reactor where it gives up its heat to the preheated cracking stock, which enters the reactor mixed with superheated steam and fluidizes the sand. The cracked gases enter a cooler (8) which quenches the reaction, and then pass to the product separation stages via a cyclone (9) which returns entrained sand to the main circulation system. The cooled sand drops from the reactor into the bottom of the lift tube, thus completing the cycle.

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1.3.2 THE ONIA–GEGI CYCLIC CRACKING PROCESS

This is an example of a process, recently developed by the Office National Industriel de l'Azote[12,13], which operates on alternate heating and cracking cycles, and is illustrated in *Figure 1.2*. It can cope with a wide range of liquid and gaseous petroleum feedstocks.

The heating cycle is in three phases. First of all, hydrocarbon fuel atomized by steam enters a combustion chamber attached to the pyrolysis reactor, and is burned in a stream of preheated air. The resulting hot flue gases rising through the reactor heat the reactor
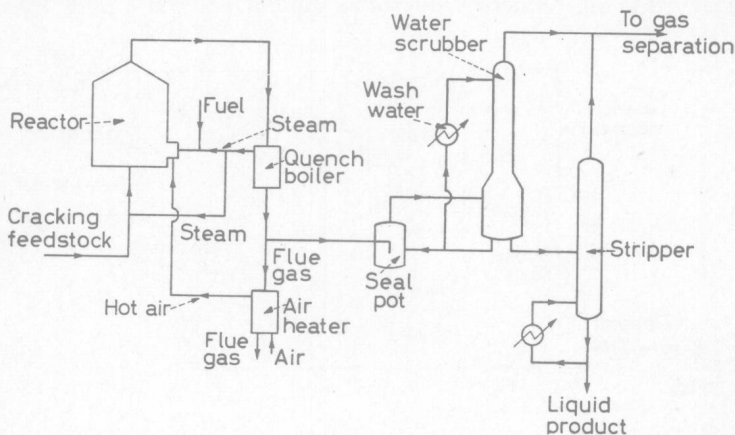

Figure 1.2. ONIA–GEGI cyclic cracking process (after Chopey[12])

bed; they then pass forward to a quench boiler where they raise the steam required, and then on to a heat exchanger for preheating the combustion air. In the second part of the heating cycle, air alone is passed through the now hot reactor bed to burn off carbon deposited during the cracking cycle. Finally, steam is passed for a period to purge combustion products out of the reactor, before commencing the cracking cycle.

In the cracking cycle, the cracking feedstock atomized by steam enters the reactor at the base, and is cracked by contact with the hot reactor bed. Some steam is also introduced into the combustion chamber to prevent feedstock or cracked products entering. The products of cracking pass forward by way of the quench boiler, where again steam is raised, to a water scrubber and stripper where heavy products are separated. The gases pass overhead to the gas separation stage.

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The lengths of the heating and cracking cycles are about the same. The use of two reactors together, one on the heating cycle while the other is on the cracking cycle, ensures a continuous supply of cracked gas to the downstream separation stages.

1.3.3 THE BASF AUTOTHERMAL ETHYLENE PROCESS

This is of interest as a process using a solid heat carrier, which is coke, continuously generated in the process[12]. Coke is thus obtained as a by-product. As the formation of coke can only be sustained by the use of heavy feedstocks, this is essentially a process for the cracking of crude oil, reduced crudes and similar materials. The heating
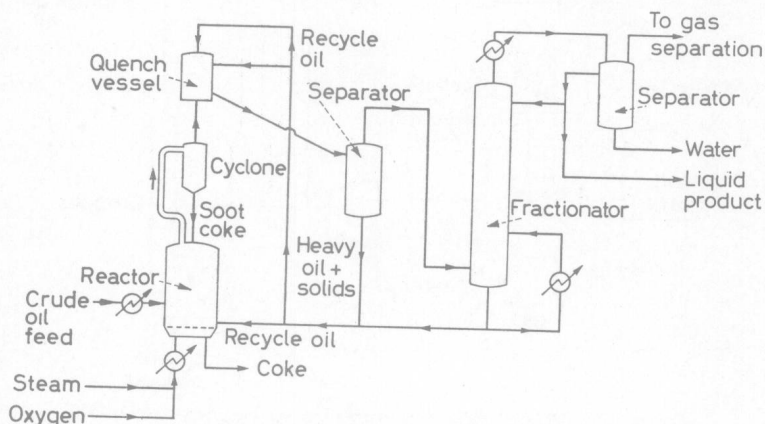

Figure 1.3. The BASF autothermal ethylene process (after Chopey[12])

of the coke, which occurs by burning part of the feedstock and recycled by-product heavy oil in oxygen, and the cracking operation, take place simultaneously in the same vessel. A flowsheet of the process is given in *Figure 1.3*.

A mixture of preheated steam and oxygen is fed under a grid supporting the coke bed in the reactor, and this effects combustion of preheated crude oil and of the recycled heavy oil, which are fed into the bottom of the bed, for heating of the coke. The crude oil cracking stock is introduced into the coke bed, which is fluidized, at a point sufficiently above the grid to avoid undesirable combustion of the cracking products. The latter, containing not only the desired products but also steam, combustion products and entrained solids, leave the reactor overhead and pass through a cyclone, which returns the bulk of the entrained solids to the reactor. They then enter a

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vessel where they are quenched by injection of recycled heavy oil, which not only cools the gases to prevent further reaction, but also washes out residual solids. It is this heavy oil stream, containing carbonaceous solids, which after disengagement from the cracked gases in a separator, is returned to the reactor as fuel. The gases passing overhead from the separator enter a fractionating column, where the remaining heavy oil is separated and recycled for use as quenching oil and as reactor fuel; a heat exchanger on the fraction-ating column base recovers some of the remaining sensible heat as steam. The cracked gases leave the fractionator as overheads, and after cooling enter a second separator, where steam condensate and a light aromatics-rich liquid fraction are run off, and the gases then pass on to gas separation and purification.

1.3.4 HIGH TEMPERATURE STEAM PYROLYSIS AND COIL CRACKING

In the high temperature steam pyrolysis process, superheated steam is used as the heat carrier. The naphtha feedstock is vapour-ized and preheated in an oil heater, consisting of a system of tubes
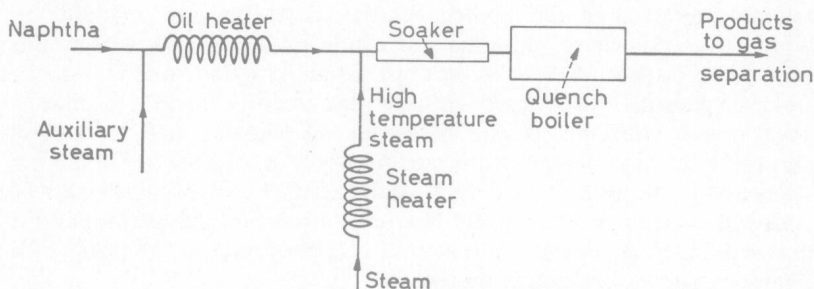

Figure 1.4. Outline of the pyrolysis section of high temperature steam cracking

mounted inside a gas-fired or oil-fired furnace (*Figure 1.4*). As some cracking takes place in the oil heater, a small quantity of steam, called auxiliary steam, is mixed with the feed to minimize carbon deposition. The hot naphtha vapour is then mixed with an excess (about twice the weight of the naphtha) of steam at very high temperature: this is generated by passing low temperature steam through a steam heater analogous to the oil heater, but operating at higher temperatures. Cracking ensues, and is allowed to proceed in a length of empty pipe known as a soaker, after which the gases are cooled rapidly to quench further reaction, usually in a heat exchanger to recover the heat by raising steam.

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In coil cracking, the cracking reaction is caused to occur entirely in a device comparable to the oil heater of the high temperature steam pyrolysis process. However, in order to obtain a high yield of cracked gas, more severe conditions are used than those existing in the oil heater of the steam process.

Unlike the other processes described above, neither high temperature steam pyrolysis nor coil cracking lends itself to the continuous removal of any carbon deposited in the apparatus as a by-product of the cracking reaction. These processes are therefore not suitable for use with very heavy feedstocks. High temperature steam pyrolysis is usually employed for the cracking of naphtha and similar light liquid feeds; coil cracking is also used for cracking naphtha, and for the cracking of gaseous feedstocks such as ethane and propane.

1.4 NAPHTHA CRACKING

As has been indicated above, a wide variety of hydrocarbon feedstocks can be used for the production of ethylene. Propane, and especially ethane, give very high yields of ethylene, and are particularly preferred in the United States where they are available in quantity, and where naphtha and crude oil command a premium for other outlets. However, in the United Kingdom and in Japan, where gaseous hydrocarbons are not readily available, naphtha reigns supreme as the feedstock of choice, and is usually cracked by high temperature steam pyrolysis or the coil cracking process[1]. Naphtha is widely available, it gives fairly high yields of ethylene with a comparatively low level of carbon deposition, and it provides a range of co-products that is appropriate to the needs of a modern petrochemicals complex.

Naphtha is the 'light end' fraction distilled from crude oil. Although the composition of a naphtha depends on the particular crude oil from which it is derived, and on the temperature at which the distillation is cut, naphtha is invariably a complex mixture of many different hydrocarbons. A naphtha from a Middle East crude, for example, cut to an end point of around 165°C, is a mixture of some sixty or more individual hydrocarbons, covering the carbon number range C_4 to about C_9, and containing all types of hydrocarbons—n-paraffins, isoparaffins, naphthenes (cycloalkanes) and aromatics—apart from olefins and acetylenes which are largely absent. Although the cracking pattern obtained from such a naphtha depends on the exact cracking conditions, a typical gas composition obtained by high temperature steam cracking is given in *Table 1.2*[14].

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The hydrogen and methane are usually obtained together in a mixture known as tail gas, which can either be used as a source of low grade hydrogen or as fuel. Outlets for ethylene—the major product —have already been mentioned. Propylene is an important intermediate for the manufacture of such products as polypropylene, propylene oxide and glycol, isopropanol, acetone, butanols, etc. The C_4 hydrocarbons, obtained in admixture, provide a useful source

Table 1.2. *Typical Gas Composition from High Temperature Steam Pyrolysis of Middle East Naphtha*

Component	% (w/w)
Hydrogen . . .	1
Methane	16
Ethylene	31
Ethane	8
Propylene . . .	24
Propane	3
Butadiene . . .	5
Butenes	8
Butanes	4

of butadiene (isolated by distillation) and, if desired, of other individual C_4's such as isobutene. Ethane and propane can be further cracked to ethylene, or used as fuel.

1.4.1 REACTION CONDITIONS

In high temperature steam pyrolysis, the naphtha mixed with about 25 per cent of its weight of steam is heated in the oil heater to about 700°C. The high temperature steam is introduced at around 930°C. Cracking in the soaker (contact time of the order of seconds) occurs adiabatically, as although no precautions are taken to avoid heat loss, natural cooling is negligible in comparison with the heat entering; there is however a falling temperature profile in the soaker due to the endothermicity of the reaction. In coil cracking, the naphtha is heated in the coil to temperatures usually above 800°C; rather more steam is mixed with the feed than in the oil heater of the high temperature steam process, to offset the greater tendency for carbon deposition. The contact time in the coil is of the order of a second or less; modern trends are towards high temperatures and short contact times[15]. In order to displace equilibria in the cracked gas in a direction to favour the formation of the desired olefins at the expense of the corresponding alkanes, pressures are kept low;

usually total pressures no higher than those imposed by pressure drop through the pyrolysis section and the quench boilers are used. Steam, which as has already been seen is used to introduce some of the heat (in high temperature steam pyrolysis) and to minimize carbon deposition, serves also as diluent to reduce the hydrocarbon partial pressure further.

The exact cracking conditions used determine, of course, the cracking pattern obtained with any particular feedstock, and there is usually a degree of flexibility. By varying the conditions, within the limitations existing on a given plant, product ratios can be varied to suit the needs of the moment.

1.4.2 CARBON DEPOSITION

The gases produced by the cracking of a liquid feedstock contain a lower ratio of carbon to hydrogen than the starting material. Therefore as cracking proceeds, and more and more gas is produced, the carbon to hydrogen ratio in the residual uncracked or partially cracked liquid (i.e. the material which would be liquid under ordinary conditions of temperature and pressure) progressively increases. A point is thus reached at which, on further cracking, there is no longer sufficient hydrogen relative to carbon in the residual feedstock to sustain the formation entirely of hydrocarbon products, and the excess carbon is deposited as coke. Hence there is a practical limitation to the depth of crack that can be achieved in high temperature steam pyrolysis and coil cracking, using a particular feedstock, beyond which coke deposition becomes a serious problem, necessitating excessive shut-down periods for mechanical removal of carbon from furnace tubes and quench devices. In practice, of course, the onset of carbon deposition is not quite this sharp, and some carbon is laid down before the ultimate limit is reached. The heavier the feedstock, the higher is its initial ratio of carbon to hydrogen, and the lower therefore is the depth of crack at which carbon deposition becomes high. With heavy stocks, a high gas yield can only be obtained in association with high coke formation, and this is why processes have been developed specially for handling this type of material.

The above discussion looks at coke formation from the point of view of the stoichiometry of the reaction, but says nothing about its mechanism. It is now believed[15] that although some carbon may be formed directly on the hot walls of the furnace tubes, the first step in the main process leading to carbon is the formation of condensation products in the gas phase by reaction of intermediates such as dienes. These condensation products—carbon precursors—build up in

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