THE PYROLYSIS OF PLASTICS IN MOLTEN SALTS

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SUMMARY

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A laboratory scale reactor has been built and operated for the pyrolysis of polyethylene in a bath of molten salt between 490 and 700°C. Products of pyrolysis have been identified and measured. The effect of temperature and stirring on pyrolysis products have been investigated. Observations have been made to allow a reasonable description of the mechanism of the pyrolysis process. A theoretical model has been produced by which the process can be compared with conventional naphtha pyrolysis with good agreement. Technical and economic considerations for commercial operation of the process are discussed with examples.

In the experiments, ethylene was a major product of pyrolysis, with a yield from 7 to 14%, which is unlike conventional analytical pyrolyses, but in agreement with some other work on bulk pyrolysis of the plastic. It is estimated that a commercial unit would be self-sufficient in energy if it used one third of the pyrolysate as fuel. A unit dealing with 5 tonnes per day of plastic would probably be economic, but larger sizes are limited by the cost of waste collection to about 30 tonnes per day.

Keywords: pyrolysis, plastic, molten salt, waste.

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OUTLINE

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

ACS	American Chemical Society
AF	across flats (spanner size)
BS	British Standard
E.P.A.	Environmental Protection Agency (U.S.A.)
FID	flame ionization detector
HDPE	high density polyethylene
HTS	heat transfer salt
i.d.	inside diameter
LDPE	low density polyethylene
o.d.	outside diameter
PE	polyethylene
PP	polypropylene
PS	polystyrene
PTFE	polytetrafluorethylene
PVC	polyvinylchloride
r.p.m.	revolutions per minute
SCI	Society of Chemical Industry
S.I.	Systeme Internationale (of units)
TM	trade mark

Symbols

B	constant (from Arrhenius equation)
C	constant (from Arrhenius equation)
c_1	inlet concentration of pentane
c_2	outlet concentration of pentane
d	diameter
h	height
K	reaction velocity constant
K_5	reaction velocity constant for pentane
$K_{5\theta}$	reaction velocity constant for pentane at temperature θ
KSF	Kinetic Severity Function
n	stirrer speed in r.p.m.
P	pressure
r	radius
Re	Reynolds number
T	time
t_b	base thickness
T_e	equivalent time
t_f	flange thickness
t_l	lid thickness
t_w	wall thickness

ΔG	Gibbs Free Energy change
μ	viscosity
ρ	density
θ	temperature of cracker outlet

1 INTRODUCTION

1.1 Origins

This thesis relates the methods and results of a practical project based on the idea of using a bath of liquid at high temperature as a means of breaking down waste plastic into useful chemicals. The project stemmed from a continuing interest in conservation of resources by conversion of waste, but also represented a new field of study for the Department of Chemical Engineering, Aston University, namely molten salt reactors. This project was amongst the first of several molten salt studies, which have now become an important part of the work of the Process Research Group in this Department.

This Group has not been concerned with the uses of molten salts in metallurgy or as indirect heat transfer media in the chemical and nuclear industries. Instead, we have been interested in molten salts as liquids intimately involved in industrial chemical processes. It is our view that the technical problems of using salts as process liquids are solvable, and that molten salts show great promise for a new generation of high temperature liquid chemical plants.

From a unit operation point of view, pyrolysis is one of the simplest uses to which molten salts might be put. One line of research could have been to take an existing process (such as the thermal cracking of petroleum) and construct a molten salt analogue. A difficulty of this approach is that one would be comparing a rudimentary new process with a highly developed technology. Even if the molten salt method were developed to pilot scale, it would need to show very considerable advantages in order to justify its use instead of a tried and trusted design.

By contrast, the thermal breakdown of plastic waste is not a well-established technology. The inherent difficulties of the material are indicated by the variety of methods which have been proposed, and the small scale to which they have been limited. 'Normal' pyrolysis processes utilise material in the form of vapours (as typified by various petroleum conversion processes) or as non-caking solids (as in coal retorts or lime kilns). Plastic waste is difficult because of its tendency to fuse together into a viscous heterogeneous mass. It was felt that the promise of molten salt reactors would be shown if this difficult material could be handled with relative ease. At the same time, many of the practical details of construction and operation would be common to other possible processes.

1.2 Aims and Objectives

The principal objective of this project was to construct a reactor for the pyrolysis of plastics in a bath of molten salt, taking into account the relevant literature, and with a view to possible scale-up for industrial use. The reactor was to be of modest but not tiny dimensions, and was intended to illustrate some of the practical aspects which industrial operation might entail, rather than to examine any fundamental chemistry of the process.

An important difference from many other studies on the pyrolysis of plastic waste was the intention to convert the material into basic chemical feedstocks such as ethylene or benzene. The industrial version of this reactor would not be intended just for the disposal of rubbish, nor to make fuel from waste. Rather, it treats scrap plastic as an important resource within the industrial society.

A secondary but important objective was to produce a survey of the literature relevant to this project. As well as helping certain decisions to be made on the project, the survey was intended to be helpful to the Research School in this Department in developing a new field of research, namely molten salts as high temperature chemical process fluids, particularly for pyrolysis and comparable reactions.

It was realised from the outset that the literature to be examined would be widely scattered, and some compromise would be necessary regarding the thoroughness of the search. Some practical problems such as high temperature seals and pressure venting could be anticipated, but others were bound to arise in the course of the work. Similarly, it was likely that some ideas would be changed by practical experience and examination of the literature, causing problems to be re-assessed.

1.3 Some Definitions

It may be helpful to draw a distinction between certain terms which are sometimes confused, particularly in discussing waste. The following are presented as explanations of some important concepts in this thesis, rather than dictionary definitions.

POLYMER	A chemical compound, the molecular formula of which may be written as a high multiple of some simpler compound, group or a combination of such compounds or groups. In this context, the term mainly refers to synthetic organic polymers.
PLASTIC	The commercial form of a polymer or polymers. It may be almost pure polymer; may contain small additions (colours, stabilizers etc); or may contain large amounts of other substances (plasticizers, fillers etc). It may be an industrial raw material, may be in the form of a product (usually in conjunction with other substances) or may be waste of some sort.

PYROLYSIS	The substantial breakdown of material by heat in the absence of reagents (particularly oxygen or air). The term usually implies fairly rapid processes well above room temperature (say 400 °C or higher). The products of pyrolysis may be classed as vapours (VOLATILES) which come off as gases and condensable liquids, and the remaining material (RESIDUALS) which is normally a solid (ash or char) or semi-solid (tar).
THERMAL DEGRADATION	The general process of breakdown of substances by heat under specified conditions (in air, vacuum, nitrogen etc). The effects range from slight physical changes (discoloration, embrittlement etc) to complete destruction by pyrolysis. The term is quite often used in contrast to pyrolysis for comparatively slow reactions.
THERMOLYSIS	A term sometimes used in contrast to pyrolysis for heat induced reactions at moderate temperatures (30 to 300 °C or so).

COMBUSTION	The burning of material, usually but not necessarily with oxygen (itself or in air) as the oxidant. Flames are often present, but need not be.
INCINERATION	The efficient destruction of material by combustion. The burning process is usually promoted by draughted air (sometimes oxygen). An auxiliary material (fuel) is often burnt simultaneously to provide heat to ensure complete conversion. Waste incineration is essentially a means of disposal, although heat can sometimes be usefully recovered. Occasionally, scrubbing the exit gases may provide HCl or SO_2 in worthwhile amounts.

WASTE	The general term for material which cannot be used conveniently at its point of origin, and is therefore discarded in a more or less organized fashion for disposal or recovery. Generally the greater the degree of organization, the higher the potential value of the material as scrap, or the easier it will be to ensure safe disposal.
RUBBISH	Waste of no value. That is, discarded material which is to be disposed of. Clearly, the decision to designate any particular piece of material 'rubbish' is essentially arbitrary, and depends on volume, available methods, economic and environmental factors, apart from any intrinsic property of the material.
LITTER	Thoughtlessly and indiscriminately discarded material. The cost of collection is usually far more than the possible commercial value, and the volume of any useful substance is economically negligible. Litter is mainly an environmental and social problem rather than a commercial consideration.

REFUSE	Variegated waste which is essentially unsorted before removal from its general area of origin, and which is therefore of variable uniformity and uncertain composition. The high cost of sorting makes the recovery of materials from refuse economically unattractive in most cases.
SCRAP	Waste material which is to be processed for re-use, and therefore becomes a valuable commodity. It is usual to distinguish between waste which is utilized on the plant where it arises (PRIMARY or PROCESS SCRAP) and that which is bought in from outside (SECONDARY or CAPITAL SCRAP). The term is again somewhat arbitrary: the practice of tatting (sorting out material from refuse tips - usually illegal) well shows that one man's rubbish can be another's scrap.

RECYCLING	The general process whereby used material is made use of again, instead of being disposed of. Usually involves several physical and chemical processes.
RE-USE	The simplest form of recycling, in which a used product is not converted (other than being cleaned) before being used for the same or a different purpose. Commonly applied to containers, the milk bottle being a good example.
REPROCESSING	The conversion of waste material into a useful product by physical or chemical means. Examples are the granulation of plastic scrap, pyrolysis, shredding of steel and breaking bottles into glass cullet.
RECOVERY	Getting material or thermal values from waste streams, e.g. heat from flue gases, distilling used solvents.
RECLAMATION	The recovery of material which would otherwise (and normally is) lost, e.g. extracting metals from refuse.

1.4 Plastic Waste

Consumption of plastics in the U.K. is about two million tons per year [1], and in the U.S.A. about fifteen million tons per year [2]. A typical price for the virgin polymer is about £400 per ton at present [2]. More than three-quarters of all plastics used are thermoplastics, and nearly two-thirds of plastics sales is accounted for by five thermoplastics: low density polyethylene, high density polyethylene, polypropylene, polyvinylchloride and polystyrene. See TABLE 1.

Estimates of waste vary, and depend on definition. British municipal refuse has typically 3% plastic by weight [3], amounting to about half a million tons yearly [4]. About half the plastics production goes into packaging, and this by its nature is the major part of plastic waste. The plastics industry does a great deal of internal recycling, but processing typically generates 2 to 5% of non-recovered waste plastic [5, 6]. This material, which is generally too dirty for remoulding goes into municipal refuse. At present some 89% of municipal refuse is tipped, 8.4% incinerated [7], although the portion incinerated is expected to rise. Ways of reclaiming plastic from refuse exist, but are presently not economical because of the low value of the resulting scrap.

TABLE 1

Consumption of major thermoplastics during 1978 as a percentage of total plastics in the U.K.[1] and U.S.A.[2]

Plastic	% (UK)	% (USA)
LDPE	20.1	20.0
HDPE	6.9	11.6
PP	10.1	8.4
PVC	18.5	16.5
PS	8.6	10.9
sum	64.2	67.4
100 %	2187 x 10^3 ton	15901 x 10^3 ton

LEGEND LDPE = low density polyethylene
HDPE = high density polyethylene
PP = polypropylene
PVC = polyvinylchloride
PS = polystyrene

At present plastic is possibly unrealistically cheap [1], and if prices go up, then so will the value of scrap. However, there is still no easy way of taking mixed contaminated plastic waste and converting it into usable plastic, other than of the very lowest grade. Insistence on virgin polymer has in fact proved a major stumbling block for several imaginative reclamation programmes [5].

A general feature of thermoplastics is the way in which they break down when heated. Under suitable conditions, they can be broken down to very simple chemical substances such as ethylene or HCl. If these chemicals were processed to plastic, then essentially virgin polymer could be produced from waste. The process of volatilization itself provides some separation from contaminants, and further refinement by distillation or similar unit operations can give as good purity as is required. Pyrolysis is thus a possible way of converting waste plastic into useful chemicals. These might be used for synthesis, or at the very least provide fuel.

This project therefore examines one possible technical means of pyrolysing waste plastic. The waste would be from industrial or sorted domestic waste: too dirty for traditional reprocessing, but with a high plastic content. The intended products are useful industrial chemicals.

Both technical and social developments could alter the importance of plastic waste. For example, the proportion in Japanese municipal refuse is already 8 to 12%[8]. This level or higher in U.S.A. or U.K. refuse would certainly alter the economic arguments against sorting. Readers of the 'Wizard' and 'Adventure' in the 1950's were rather expecting motor-cars to be made of plastic by now. However, the use of plastics in vehicles is steadily increasing, and there are signs that they will replace metals for major body and fixture components over the next few years[9,10]. This would have a major effect on the scrap car industry, and could provide an interesting source of partially sorted waste in volume by the end of the century.

Kaminsky, Menzel and Sinn[11,12] argue that plastics production will equal that of iron and steel by weight by the year 2010. This is possibly true, but the economic argument to support this conjecture involves an unreasonable extrapolation. Plastic production in West Germany at a level of 6.4 million tonnes per annum in 1973 is projected to 1100 million tonnes in 2010 on the basis of a simple exponential. Even the highest population growth forecast would give each German 10 tonnes of plastic to dispose of each year. Moreover the oil (or its equivalent) required would be 30 times the present total consumption.

It seems to me that a more likely forecast is that the use of plastics will slowly rise. Doubling is certainly possible in the forseeable future. At the same time, however, the cost of both energy and plastics is also likely to rise. Doubling again seems plausible. The combination of increased amounts and increased value will be a considerable incentive for recycling.

1.5 Molten Salt Baths

Inorganic salts are the major class of materials which give a stable liquid phase in the temperature range 200 to 2000 °C. Many of them are relatively cheap, non-volatile and stable in the presence of air. They offer a range of densities, viscosities and surface tensions, but in general their fluid properties are similar to the liquids commonly encountered in chemical engineering. They are mostly very good conductors of heat, and have good surface properties for heat transfer.

A bath of molten salt is therefore a fairly obvious method of providing a substantially inert medium for heat control of chemical processes at high temperature. To a certain extent salts have been used in this way, but they are certainly not a normal fluid for chemical process use. This is for a variety of reasons, of which corrosion and transport problems within the plant are probably the most important.

The attractiveness of a molten salt bath for the pyrolysis of plastic waste lies in the great efficiency of heat transfer and thus temperature control of what are usually endothermic temperature-dependant reactions. Furthermore, salts are cheap materials which are not prone to degrade, and would be easy to separate from the organic products of pyrolysis, which are of a completely different chemical character.

There have been many laboratory studies of molten salts and their chemical properties, most of which have been carried out in quartz apparatus. In this study, however, it was felt more appropriate to utilize materials and methods of fabrication more in line with industrial practice.

1.6 Outline of Experimental Work

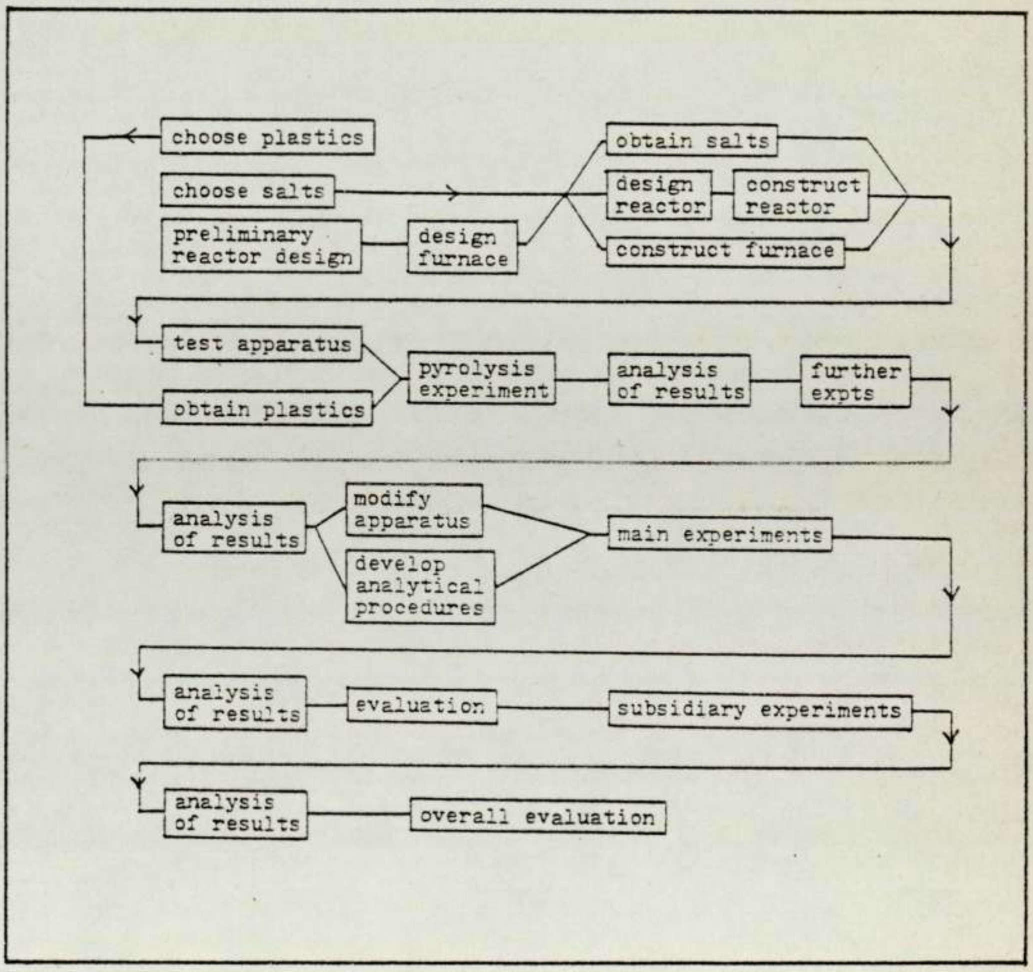
A chart of a proposed schedule of practical work was drawn up at an early date. An abbreviated version of this is given as FIG. 1. The methodology used was that of the Critical Path method, but no time factoring was used, and no dummy activity is shown on the diagram. As well as an aid to scheduling, this plan was helpful in pointing out some of the decisions which were necessary: for example, the salts to be used and the materials of construction are inter-related by the possibility of corrosion.

Some considerable time was spent on a literature search in order to help these decisions, before the first phase of practical work - construction of the apparatus - began. This search continued at a less intensive level throughout the project, and resulted in the literature survey given in section 2 of this thesis.

The design and construction phase of the work is shown as the first horizontal section of FIG. 1. The preliminary experimental work followed. It mainly consisted of checking the apparatus for integrity, safety and basic performance of its components, and will be only briefly mentioned. There then followed a series of dummy runs in which salt was melted and observations made, but no

FIGURE 1

Chart of experimental work



actual pyrolysis was done. The thermal characteristics of the apparatus (warm-up time and so forth) thereby enabled a reasonable plan of operation to be drawn up for the main experiments. Some initial pyrolyses were then carried out, using single granules of plastic in an unstirred bath of salt in the reactor (without a lid, but under a blanket of nitrogen). Observation of these tests proved very helpful in gaining an idea of the processes involved. Progressive additions of larger amounts of plastic were made without difficulty.

Trial pyrolyses in a closed reactor were then carried out with some caution. Minimum salt, maximum headspace, minimum temperature and gentle stirring were used, and the amount of plastic gradually increased from one granule (30 mg) to batches of a few grams. These precautions were in case of any explosive release of vapour, which was not in fact found to occur. It was felt that gentle stirring was safer than unstirred salt, particularly for larger amounts of plastic. The aim of these runs was to develop a method of work with the apparatus, find out the time factors involved and the sort of products which were formed. Methods of sampling and analysis were also tried out, though they were further refined during the course of the main experiments.

The main part of the experiments followed modification of the apparatus and technique to overcome minor problems in the trial runs. The amount of salt was increased to give greater thermal inertia and a smaller headspace. The stirrer was changed from a simple flat paddle to a propeller. Since the reactor was unbaffled, the propeller was intended to give greater vertical mixing.

The main experiments comprised the sampling of the vapours produced at intervals after addition of the plastic, or the sampling of the whole vapour produced. In the first case the time-dependant changes could be observed. In the second case the overall conversion of the plastic could be found. Different temperatures and stirrer speeds were used. The composition of the vapours produced was measured by gas chromatography.

Some subsidiary experiments were done in between the main runs, and also afterwards. They ranged from the very minor (such as a statistical check on the volumes of the sample bottles) to an important test such as the addition of ethylene to check on vapour residence time. The apparatus was itself examined from time to time, to check for corrosion, gas tightness etc.

The apparatus was specially designed for easy modification, and included some features which allowed for possible lines of experiment which were not followed in this study. For example, a third type of stirrer was designed and constructed. This was of the centrifugal vortex type, and performed well with a model system (paraffin and water). It was not used with the molten salt, mainly because it was felt that the propeller was more easily related to industrial practice.

2 LITERATURE SURVEY

2.1 General Comments

The actual literature dealing directly with the pyrolysis of plastic in molten salt is very small indeed. On the other hand, the literature which may be considered relevant is very large. Molten salts, pyrolysis, waste processing, and plastics degradation are all major studies in their own right. Likewise, high temperature chemical engineering and économic considerations both imply another large body of literature.

The aim of this survey is not, therefore, to provide a minute analysis of the few papers directly concerned with the title topic. Nor is it intended to give an exhaustive list of publications in the fields mentioned above. Instead, some important source books and bibliographies will be mentioned: these give access to the appropriate area. Those books and papers which the author has found particularly helpful will be noted with some comments. Papers which make some particular point, or help to place things in context, will also be cited, in an attempt to describe the various areas of information (or lack of it) which are important to this project.

2.2 Waste

2.2.1 Waste Recycling In an ecologically- conscious society, waste recycling has come to be thought of as a virtue, and discussion often becomes moral rather than technical. Like most virtues, however, it is easier to talk about than put fully into practice, and a voluminous literature is accompanied by less real practical success than one might expect. A very readable and often witty introduction to the topic is given by Porteus [4]. Though dealing with world-wide literature, he is particularly concerned with U.K. experience. He is critical of over-simple solutions, showing many examples where the solution has been more expensive than the problem, or where nice ideas (e.g. recovery of heat from refuse) have clouded economic realities (there was no local use for the heat). Nonetheless, it is clear that his book is arguing for both technical and social improvements in the treatment of waste.

By contrast, a Pollution Technology Review by Jackson[13] is primarily a condensation of data, being an excellent summary of recent literature on resource recovery from municipal refuse. The majority of work cited is American, which not only reflects the origin of the book, but also the great efforts which have been made by governement and industry in the U.S.A.. The same author has another compilation on energy recovery from solid waste [14].

A more conventional textbook is that of Baum and Parker[6], which notably includes a chapter on pyrolysis, and another on the re-use, recycling and reclamation of plastic waste. Yen[15] is the editor of a review text on recycling and disposal of solid wastes, which includes papers on fuels from waste[16] (dealing with pyrolysis), plastic waste management[17], and general aspects of plastic disposal and recycling[18]. Waste recycling is now covered in most general handbooks of industrial and municipal waste disposal. For example, that of Pavoni, Heer and Hagerty[19] is a considerable general source.

A quantification of the ease of recycling has been defined as a 'Recycle Index' which is the product of the numerical assessments of the ease of collection and of processing of waste[20]. Such calculations suggest that plastics have a useful potential for profitable recovery operations.

2.2.2 Plastic Waste Some general reviews already cited on waste recycling[4, 6, 13] also have good sections on plastic waste. An SCI monograph by Staudinger[21] makes a good statement of the problems raised by plastic waste. The same author edited a collection of papers concerned with the environmental aspects of plastics[22]. In this, Fergusson[23] argues that the problems are often overstated: plastics can be disposed of without difficulty by modern technology. Staudinger and Bessant[24] say that plastics have contributed much to conservation of resources, and point out that the energy and hydrocarbons required for plastic manufacture account for only 2 % of U.K. oil consumption. Thus even total recovery would have only a marginal effect on energy and resource utilization.

This small percentage, however, amounts to sufficient material to be commercially interesting, as is indicated by Laporte's recent investment of £ 500 000 in a new U.K. plant for making boards from plastic waste[25].

A very important theoretical study was made by Milgrom for the U.S. Environmental Protection Agency[5]. As well as considering economic, social and technical aspects at the moment, he discusses how financial incentives and deliberate design of products could be used to favour recycling.

Baum and Parker have also written a short discussion of the practicalities of plastic recycling[26]. Another review of the same year[27] looks at various possibilities and predicts that pyrolysis has the greatest promise for recovery of chemical or heat values from plastic waste. A similar conclusion is reached by Fergusson in a later well-referenced review concentrating on industrial waste plastic[28]. The extra costs of cleaning and separating are said to mitigate against the process becoming economic. A review by Flintoff[7] favours pyrolysis as being more efficient than direct incineration. Kaminsky, Menzel and Sinn[12, 29] discuss various aspects of plastics recycling and their own work on pyrolysis.

Two Japanese reviews are by Kagiya[30] in 1972 and Muramatsu[8] in 1975. They indicate the enormous attention paid to plastic waste reclamation in Japan. This is partly due to the lack of cheap oil - a situation which is becoming worldwide! The latter review notes that in Tokyo urban refuse, plastic goods are classified along with pianos as 'difficult waste to treat appropriately'.

Most recently, an entire issue of 'Kunststoffe'[31] was devoted to plastic recycling, with papers on measures in Austria, Belgium, France, Germany, Italy and Scandinavia, along with the inevitable review by Fergusson[32] about work in the U.K., U.S.A. and Japan.

2.3 Pyrolysis

2.3.1 Theoretical Considerations

Pyrolysis as an art extends back in history to the invention of cooking. Pre-Roman industries like charcoal and lime manufacture are also pyrolytic processes. It will readily be appreciated, however, that the most relevant body of theory so far as this project is concerned stems from the high temperature processes used in petroleum refining. Any real understanding of such processes depends on the development of Free Radical theory this century. A historical description of the emergence of the theory is given by Rice [33], who may fairly be credited one of the founding fathers of this branch of chemistry. The mechanism he proposed along with Herzfeld [34] is still used as the basis for explanation of many pyrolysis processes, modifications being mainly a matter of detail.

The vapour phase high temperature conversion of hydrocarbons has received much attention since then. The considerable increase in knowledge has been tempered with an appreciation of how much is yet to be discovered. A good source on current knowledge is given by an ACS symposium report [35] published in 1976. Of the 28 papers therein, almost all are concerned with vapour phase cracking of hydrocarbons in tubular reactors. It says much about the complexity of the subject that two papers are entirely devoted to the simplest hydrocarbon, methane, and neither is by any means the final word on the subject.

If it is difficult to explain the thermal decomposition of simple hydrocarbon vapours, then no apology is required for any failure to provide an exact and detailed mechanism for the much more complex situation of a solid polymer being pyrolysed into a vapour mixture. It must be understood, therefore, that such explanations and theoretical discussions advanced in this thesis are necessarily simplifications and of a somewhat tentative nature. A symposium which dealt with more complex pyrolysis situations such as degradation in melts and with more complex materials such as plastics was held in 1970[36]. Many of the contributions have some useful relevance to this project, and will be separately cited.

The vapour phase pyrolysis of hydrocarbon mixtures is relevant in understanding the secondary reactions which may take place in the head-space of a molten salt reactor for the pyrolysis of plastics. Some points which may be mentioned are: consideration of the pyrolysis of ethylene itself[37, 38, 39]; the importance of wall effects[40 - 45]; the fact that the cracking of mixtures is not just the sum of the cracking of the components[46,47]; that hydrogen promotes the formation of ethylene from higher olefins[48,49]; that ethylene requires a higher temperature than other olefins to cyclize into aromatics[50]; that propylene tends to polymerize below 550 °C but decomposition is the main process at 600 °C and above[39]; that the presence of small amounts of oxygen may have significant effects, though these vary with concentration and other factors[40,51]; on the other hand, steam is essentially inert in hydrocarbon cracking[52,53]. An interesting fact is that HCl in small amounts can affect hydrocarbon pyrolyses[54]. Its effect varies, sometimes accelerating, sometimes inhibiting, sometimes having little effect, depending on the precise situation. This has significance in that PVC is a likely contaminant in hydrocarbon plastic waste from many sources, and might have an effect on the main process by generating HCl, this being its principal mode of pyrolysis.

Most of the above studies take the formation of certain radicals as an experimental observation or as a reasonable hypothesis. For considerations as to why certain species should be formed (e.g. molecular orbital approach, symmetry rules) reference is made to standard texts, such as that of DePuy and Chapman[55], or a current awareness paper[56].

2.3.2 Industrial Hydrocarbon Pyrolysis The chemical industry is essentially a pragmatic enterprise, so that the lack of an academically rigorous theory has never been the main obstacle to exploitation of a chemical reaction. Knowledge is however essential for proper development of a commercial plant, in particular the way in which a process responds to different variables. This is usually achieved by a mixture of experimental correlation and as much theory as can usefully be employed. This approach is reflected in technical journals such as 'Hydrocarbon Processing' in which economic factors play as big a role as chemical ones. A useful feature of the journal is its regular publication of Handbook issues, with summaries and flow diagrams for major processes and their commercial applications [57,58,59]. A frequent co-author of papers on ethylene manufacture in this and similar journals is Zdonik [60]. A collection of reprints by Zdonik et al [53] has been found a very useful source of information on cracker practice and theory.

A general overview of the petrochemical industry is given in the text of Goldstein and Waddams [61], which is a standard work on the subject. All aspects - theoretical, descriptive and economic - are covered in a well-balanced, well-referenced, well-indexed and very readable book.

2.3.3 Pyrolysis of Coal Coal is a polymeric organic solid, and there is considerable industrial experience of its conversion to gases and liquids by thermal and allied methods. It is thus peculiarly relevant as a model for pyrolysis of plastic. As a matter of fact, a thermoset plastic has been used as a model for coal in pyrolysis studies [62,63,64]. Coal differs from common plastic waste in its much higher proportion of carbon. For this reason, many coals can be converted to coke by relatively simple methods. A useful summary of coke production technology is given in a monograph by Gibson and Gregory [64].

Pyrolysis and hydrogasification are the two main methods for converting coal to gaseous or liquid fuels, though solvent extraction is increasingly important. A summary of coal liquefaction processes has recently been given by Taupitz [65], including some explanation of the basic reactions during coal pyrolysis. A general overview of coal gasification is given by Verma [66], and an ACS monograph has papers on a variety of studies [67]. 'Chemical Engineering Progress' publishes regular 'capsules' on various processes, including a whole batch of twelve on the general subject of coal processing [68].

2.3.4 Pyrolysis of Waste The purpose of pyrolysing waste is usually to convert it into fuel, and the waste which has been most studied in this respect is municipal refuse. There seem to be innumerable conferences on advanced refuse disposal, at which pyrolysis is a popular topic, but the symposium reports are not always readily available. Papers on 'pyrolysis of waste' in the regular journals usually turn out to be a favourable report on some particular patent process.

'Energy World' had a special incineration supplement in 1974 with a good descriptive review of refuse pyrolysis techniques, though no references[69]. A more satisfying paper, the same year, was by McIntyre and Papic[70], giving a technical and theoretical background, references and a critical description of the state of the art of processes.

Slightly earlier, the U.S.A. National Technical Information Service produced a technical and economic assessment of alternative schemes for refuse pyrolysis[71]. In the U.K. the Warren Spring government laboratories have a long-standing research programme on municipal refuse, and published a review paper on pyrolysis[72].

Most recently Jones [73] has reviewed current technology for the thermal conversion of wastes to fuel. Some 49 processes are listed as being demonstrated or under development, and a further 12 in the laboratory stage. The American Chemical Society held a recent symposium on the thermal conversion of waste, which should be published in the near future [74].

Symposium review papers on the pyrolysis of municipal refuse include those by Lamb [75], Sussman [76] and Wilson [77,78]. An interesting report is that of Houson [79], describing the problems of setting up an actual commercial plant. In contrast to the technical complexities of the more academic papers, and the unbounded optimism of some publications, it is a straightforward but witty record of a series of difficulties overcome. To quote "If we had known all the trouble, we probably would not have started ... Now we're glad we did."

Various commercial enterprises have made in-house design studies for refuse pyrolysis, but these are not publicly available. However, the Battelle Institute published such a design in their final report [80] on a project. In the project a working pilot plant was built and demonstrated, and a fairly detailed scale-up design made and costed for a 100 + ton per day facility for municipal refuse.

If the foregoing suggests that the U.S.A. is the main developer of waste pyrolysis techniques, this impression is correct. There is some European experience, but the other country in which waste pyrolysis is taken very seriously is Japan. The reports which are available to the non-Japanese reader are very impressive. At least a dozen firms are actively involved in various rival projects mainly for the production of fuel oil or gas. Two reviews are cited here [81,82], but the particular expertise of the Japanese in pyrolysing plastic waste will be dealt with later.

2.4 Plastics

2.4.1 General Information There is a wide variety of texts on polymer science at all levels. The 'Polymer Handbook' [83] has been found to give some useful summaries, and has been much used as a main source of data on plastic properties. The 'Encyclopedia of Polymer Science and Technology' [84] has some excellent articles by leading authorities (some of which will be specifically cited) and has proved invaluable for concise summaries and explanations as well as a source of references.

Two journals in particular should be mentioned, namely 'European Plastics News' and 'Modern Plastics International' as a source of statistics on the industry, especially in their annual reviews of production, consumption and market trends [1,2]. Of course, some interesting articles arise in the other polymer journals and in chemical and chemical engineering publications.

2.4.2 Polymer Pyrolysis Mechanisms The thermal breakdown of natural and synthetic polymers covers a wide range of interests. These range from the purely academic (in the insight it gives into bonding and reaction mechanisms) through the utilitarian (such as its use in analysis) to the commercial need to develop polymers which can resist high temperatures.

A text which essentially covers experimental methods, results and conclusions up to 1962 is that of Madorsky[85]. This book contains much data, and the inferences from it, but is not really concerned with applications. Conley[86], in treating thermal stability, is naturally forced to deal mainly with thermal breakdown, in a useful source book. These are the only books I know of to deal solely with thermal degradation of polymers, apart from a report of a symposium[87] held in 1960.

The subject is, however, included as a major item in several texts on the general subject of polymer degradation, the first being the report of a symposium[88] in 1951. A comprehensive monograph was published by Grassie[89] in 1956. With a good balance between explanation, results and references, this book has been much thumbed during the project described in this thesis! The same author has an encyclopaedia entry which covers much the same ground in a similar style[90]. Grassie is also the author of a 1965 current awareness paper[91], and the editor of the first of a series of review texts on developments in polymer degradation[92].

A later book on polymer degradation is that of Reich and Stivala[93], which is particularly strong on kinetic aspects, but also has a substantial section on thermal degradation as an analytical method. The most recent book on the subject (1978) is edited by Jellinek[94]. I have not seen it, but the publishers claim it leans towards topics with practical implications. Jellinek also has an encyclopaedia entry on the subject of depolymerization, which is mainly about thermal breakdown[95].

A 1970 NBS symposium, edited by Wall[36], dealt with the current state of research in vapour and condensed phase pyrolysis of organic material. This notably included a paper by Wall himself on the pyrolysis of polymers[96], and several related papers.

The fact that pyrolysis often produces very complex mixtures can be turned to advantage analytically. The pyrolysis of a small amount of plastic by the inlet of a gas chromatograph produces a complex and characteristic chromatogram which can be used to identify and analyse plastics and certain other materials. This process was first suggested in 1954[97], and described as a general technique in 1960 by Janák[98]. The rapid development of the method is shown by a review in 1966[99] having 200 references. A nice description of the technique, with a practical bias, is that of Lehrle[100]. A comprehensive textbook has recently been published[101].

It is important to realise that the pyrolysis products observed by this technique differ in type and amount from those obtained by the pyrolysis of larger amounts of the same material. The success of pyrolysis gas chromatography depends on the use of very small amounts, of the order of micrograms, in order to obtain reproducibility. With larger quantities secondary reactions can cause considerable variations[99,102]. In discussing a practical process for pyrolysing plastic waste, then naturally these secondary reactions will be of profound importance.

Actually, the advent of such techniques and of super-sensitive instruments such as the mass spectrometer, plus the difficulty of interpreting secondary reactions, has rather lead research away from pyrolysis of bulk polymers. The bulk pyrolysis of rubber goes back more than a century as a chemical study[103]. As an example of the difference between early experiments and those of recent years, the pyrolysis of 200 lb of crepe rubber[104] may be noted. This was necessary to collect sufficient of the various products, well before the machine age of analysis. This particular study is probably also the first observation of catalysis by metals in bulk polymer pyrolysis. It may be noted that Staudinger's first ideas on polymers came from rubber pyrolysis[105]. It was his development of this point, particularly in using polystyrene as a model for rubber[106], which led to the foundation of polymer science and plastics technology.

In recent years, bulk pyrolysis has featured in studies of the burning of plastics, following interest in their role in fires as furnishings or building materials[107,108]. Military and astronautic rocket research has looked at plastics for ablative re-entry heat shields and as a part of solid propellants. Both these applications involve pyrolysis, but the work is usually secret, abstruse or both. A review of part of the field which manages to be of more general interest is that of McAlevy and Blazowski[109].

2.4.3 Pyrolysis of Plastic Waste Industrial interest in pyrolysing plastic waste into useful new materials goes back over twenty years with Union Carbide's screw extruder system[110,111]. This was a continuous system said to produce material like good quality petroleum (no sulphur, no polynuclear aromatics) depending on feed, but nothing seems to have been published lately.

A highly technical but theoretical assessment is that of Banks, Lusk and Ottinger[112], who proposed and costed several thermal degradation schemes. Nitrogen, air and steam were considered for the vapour cover, and waste polystyrene, polyethylene and polyvinylchloride were considered as separate sorted waste or as a mixture of equal parts of all three. The theory was presumably extended to practice, since they are authors of a later patent[113].

General summaries of existing plastic pyrolysis processes are given in some more general reviews already cited on waste recycling[13] and plastic waste[8,12].

An unusual idea was that PVC waste could be used to generate HCl as and where needed by pyrolysis. The PVC being a solid, its transport is both cheaper and safer than for the aqueous acid, which is said to give the method sufficient economic advantage[13].

The U.S. patent of Banks et al.[113] describes the heating of different plastics by a pre-heated countercurrent gas flow to get useful products rather than fuels. The apparatus can process one gram per second of polyethylene, with a mean residence time of 3 000 seconds and principal products being hydrogen, benzene, methane and ethylene. A further statement, however, gives C_4 hydrocarbons as the main product at 437 °C. Polystyrene and PVC have also been processed. There is no real difference in product distribution when steam is used in place of nitrogen as heat carrier.

A Japanese process uses an unspecified but presumably solid catalyst to improve plastic pyrolysis[114]. It is claimed that purely thermal breakdown gives an oil product of too broad a boiling range for easy fuel use, but the catalyst makes the product like a conventional fuel oil. The scale is 1.5 tons per day, and the author says it might be useful for small producers of waste.

A fluidized bed process pioneered by Menzel[115] has now been developed to a 10 kg per hour pilot plant[116]. The Sumitomo fluidized bed process is reported to be at a 3 ton per day level[82].

As at least one reviewer has observed [117], very active technical development of plastic waste pyrolysis methods is rarely followed up by their being taken up by industry. It is reported [21] that a U.S. factory has a unit which converts packaging waste into fuel at a rate of forty tons per day. The Mitsui companies brought a patented [118,119] process on-stream in 1971 for the conversion of by-product low molecular weight polyethylene into fuel at the rate of 36 tons per day [120]. The process uses a bath of product oil as a continuous stirred tank reactor operating at 400 to 450 °C. Conversion is about 90% to oil, 5% gases and 5% carbon sludge which is continuously removed. The firm obviously wish to extend the process to general plastic waste, but state that corrosion problems make it unsuitable for PVC, and that chemical components containing metals could be a problem [120].

A similar method of pyrolysis is reported by Speth [121] at the pilot plant level, with a residence time of 8 hours at 400 °C. One ton per day of polyethylene containing up to 35% water can be processed.

In terms of value of chemicals recovered, PVC seems to be the most promising plastic[18]. As well as the HCl which is easily obtained by almost any pyrolytic method, it is claimed the carbonaceous residue can be activated by steam to make an industrially useful activated carbon[122]. It has been suggested[123,124] that where PVC is a minor component of mixed wastes, a preliminary low temperature dehydrochlorination should precede the main pyrolysis, the HCl being taken off in between stages to limit corrosion.

Polystyrene is unique among the major thermoplastics in the ease with which it can be converted to the monomer. Yields in excess of 70% can be obtained by pyrolysis[11]. It does not, however, occur as collectable waste in the same amounts as the polyolefins. Process scrap can be recovered by other means[125], so pyrolysis processes seem to be mainly theoretical[112] or laboratory scale.

One industrial interest in pyrolysis of hydrocarbon plastic waste is for the production of waxes for polishes etc. The direct product can be used[110,126] or the unsaturated end-group can be modified (e.g. by oxidation) to yield an emulsifiable product[127,128]. In this context it has been noted that the presence of Br_2 or a bromine containing compound can enhance the decomposition of the hydrocarbon plastics, as can azide or peroxide[128,129].

Waste reclamation is a notoriously unstable market, as collectors of newspaper for charity have often found. When added to the normal difficulty of forecasting in the chemical industry, and those economic arguments concerned with energy balances, then any waste conversion process must be questionable. No-one can say for sure how significant the pyrolysis of plastic waste will become. In my view, however, the biggest argument in its favour is the great enthusiasm with which it has been pursued by the Japanese. There are at least a dozen firms involved in a similar number of processes[8,81,123]. Many are said to be at the tons per day level and one is fully industrialized[8].

2.4.4 Pyrolysis of Rubber Waste Fundamentally, there is no real reason to separate rubber from plastics in this context, but for the historical accident of its being available from a natural source. Its technology pre-dates the plastic industry, but it is a hydrocarbon polymer, and much of it is now synthetic. Moreover it depolymerizes fairly readily with heat as was long ago discovered [103]. As a matter of fact, the dry distillation of rubber waste was considered as an industrial process a century ago, but was abandoned because of the smell problem [130].

The real peculiarity of rubber waste lies in its great occurrence as automobile tyres. These are the major product of the rubber industry, and have about two-thirds their original weight when discarded. Moreover, they are of a standard shape and sizes, and mainly arise in specific places in a regular fashion. The problem of collecting and sorting is therefore much easier than plastic waste in general. A rubber reclamation industry largely based on used tyres is therefore of long standing. Its nature is described in a textbook edited by Nourry [130] and a paper by Cheater [131].

Unfortunately, only a limited amount of reclaimed rubber can be used in tyres if they are to meet the ever higher specifications. Furthermore, the technology designed to give strength in use causes difficulty in shredding and suchlike processes. The problems and some of the solutions under development for tyre disposal are discussed by Pincott[132] and Greene[133]. Disposal has been such a problem that Belfast City Council had a special incinerator built to take up to 100 tyres per hour[134].

Several pyrolytic processes for tyres are now quite advanced, and others under consideration. A short study of the basics of tyre pyrolysis is given by Schnecko[135]. Fluidized bed methods have been brought to pilot-plant scale in Germany[116], the U.S.A.[136] and Japan[137]. In the U.K. the Department of Industry has commissioned a study of three competing processes, two originating from the Warren Spring Laboratory, the third being the American Intenco Process[138]. In the U.S.A., Goodyear and Firestone have each tried pilot plants but do not see the process as yet being economic for full scale[133]. The University of Tennessee has an E.P.A. funded project for tyre pyrolysis in molten salt[139], and the reactor described in the present thesis is now being used for a similar purpose.

2.5 Molten Salts

It is perhaps worth noting that the term 'fused salts' is common in the U.S.A. and 'ionic melts' is sometimes used, especially by electrochemists. 'Chemical Abstracts' has recently adopted 'molten salts' as an index term.

2.5.1 Laboratory Studies

Though commonly considered a new and perhaps esoteric study, the intrinsic interest and industrial applications of a range of powerful reaction media have made it a significant field. The Molten Salts Discussion Group is a flourishing Special Interest Group within the Chemical Society of Great Britain, and a Fused Salts Information Service has been set up in the U.S.A.. In the U.S.S.R., a special journal is published entitled 'Ionic Melts' (Ionnye Rasplavy). There is in fact a vast amount of data available, and a stream of publications.

A bibliography compiled by Janz in 1963 [140] contained more than 2 000 references. A bibliography complied for the Fused Salts Information Service covering literature up to 1971 [141] has more than 7 000 references. The best known source book is probably that by Janz [142] which gives physical and chemical data for over 1 000 salts and mixes, with appropriate references. Janz is also co-author of another Fused Salts Information Service Publication, a collection of more than 6 000 data entries with a bibliography of over 4 000 references, concerned with eutectic mixtures [143]. This is intended to be an authoritative compendium of properties such as melting points and compositions, but also giving information on corrosion and hazards.

A single-author student textbook is that of Bloom [144], which is complete with problems and answers. It has good diagrams and tables, and a useful level of references to other works, reviews etc. Most other texts are edited collections or proceedings of symposia. A research monograph edited by Sundheim [145] covers very similar ground to a collection of reviews edited by Blander [146], both published in 1964. Both are primarily concerned with the physical chemistry of molten salts rather than their use or applications. A later collection of papers edited by Mamantov [147] concentrates on the characterization and analysis of molten salt.

An obvious demand for a regular series of reviews of the subject has been well met by the series 'Advances in Molten Salt Chemistry' which provides quite a good survey of what has recently been established, in well-organized topic sections [148].

Waddington's 'Non-Aqueous Solvent Systems' [149] includes a chapter by Bloom and Hastie on molten salts considered as solvents [150]. The authors clearly set out to prove that molten salts are a good thing, and in a tidy summary of relevant considerations may be thought to have succeeded. Lagowski's 'The Chemistry of Non-Aqueous Solvents' [151] also features molten salts. The chapter authors, Bailey and Janz are also enthusiastic about the subject, but concentrate on experimental techniques [152]. Without trying to note every reported method, they succeed in providing some guidelines for those wishing to do work in the field, with brief but sufficient explanations and of course references to the original work. More recently, Landresse has summarized the methods of many workers [153].

The prime source for the use of salts as reaction media must be that of Sundermeyer in 1965 [154]. With 229 references, it is a comprehensive survey of literature to date, including thumbnail sketches of a vast number of interesting reactions. The same author is a prolific publisher of papers on individual topics. A review of the literature from 1964 to 1972 was made for the Battelle Institute [155]. It is more selective than Sundermeyer, being limited to organic reactions. Kerridge has also surveyed recent advances in molten salts as reaction media, covering selected reactions from 1961 to 1974[156]. A French book on reactions in non-aqueous solvents[157] published in 1963 has a substantial chapter on molten salts. Gordon has given a review of practical techniques and known reactions for the general application of fused salts to organic chemistry[158]. The obvious application of molten salts to catalytic processes was reviewed by Norman and Johnstone in 1951[159]. More recently, Kenney has reviewed the application of molten salts as catalysts for gas reactions, covering literature from 1939 to 1973[160].

Many papers appear each year in various journals on different aspects of molten salts. A general survey in the form of a current awareness paper was published in 1973 by Clarke and Hills[161]. Without wearying the reader with a vast list of works, this paper clearly demonstrates the importance of molten salts, both as a contribution to fundamental chemistry and as a significant component in established and novel technologies.

2.5.2 Industrial Experience There is of course much experience of molten oxides and silicates in the form of slags in smelting, and in the glass industry. The Institution of Chemical Engineers has performed a useful service in publication of a working party report on high temperature chemical reaction engineering[162]. This is an important and critical summary of solids conversion processes in industrial use (in 1969) in the temperature range 600 to 2 000 °C. Most high temperature liquid processes are included. There is a list of then current research projects, and recommendations for areas needing further research. An especially valuable bonus is a section and appendix on containment materials. Molten salts are briefly treated, with recommendations for research to establish their chemical engineering behaviour - e.g. flow in packed beds - to facilitate design procedures.

Slags and glasses tend to be too high melting and too viscous in their lower liquid ranges for suitability as heat transfer liquids below (say) 1 000 °C, so further discussion will now be limited to inorganic salts and hydroxides.

The electrochemical use of molten salts is well-known. A good descriptive text is that of Mantrell[163], who also deals with design methods. The handling of molten salt in electrowinning is generally very simple, however. More advanced methods have been studied as part of the development of nuclear reactors. Molten salts have been used as fuel in nuclear reactors[164,165], and as secondary heat transfer fluids[164], with all the associated problems of pumps, valves, seals and corrosion. According to one source[166], these problems had been so overcome that the reactor was safe and ready for scale-up with no new technology required. Molten salt has also been used for processing nuclear fuel in the fluorination of UF_4 to UF_6 for isotope separation[167], and in solvent extraction of liquid metals[164].

An important but often overlooked industrial application is the use of molten salts for indirect heat transfer. That is, molten salt is circulated to a reactor to control its temperature more effectively than direct application of flame or other heat source. A general text on high temperature heat carriers is that of Chechetkin[168], who describes and compares gases, gas-solid mixtures and liquids (organics, metals and molten salts). Although some use has been made of salts such as aluminium chloride[168], the vast majority of salt used for this purpose is a mixture of 40% $NaNO_2$ 7% $NaNO_3$ 53% KNO_3 commonly known as 'HTS' or Heat Transfer Salt. Its properties were described in a very thorough paper by Kirst, Nagle and Castner [169], which is the prime source of physical and engineering data on the mixture. At the time of this paper (1940) there were several installations with more than a million pounds weight of salt in a single cracker unit. Other information on this salt, and the slightly cheaper nitrate-only mix which is sometimes used, is available from the manufacturers [170]. The working range is 150 to 500 °C (exceptionally 540 °C), it is not normally corrosive to steel, and centrifugal pumps are commercially available for use with it.

A natural development was the use of molten salts for heat treatment of metals, that is: heating, annealing and quenching. Salts for various temperature ranges and purposes have been developed, and surface treatments such as carburizing can be incorporated by the use of salts containing appropriate chemical groups. Full practical details are given in the manufacturer's handbook [171]. This is an important area of practical experience of molten salt.

A number of new processes are at various stages of development. Both current and developing industrial uses are outlined in a very recent paper by Hatt and Kerridge[172]. The Battelle Institute has been notably active, organizing conferences in 1973[173] and 1975[174], and being responsible for a flue gas scrubber[175] and a waste pyrolyser[176], both using molten salt. Warren Spring Laboratory tried molten salt for selectively melting shredded car scrap, though it was not found economically viable[177], and the U.S. Department of Mines tried the separation of copper from tin in a $BaCl_2$ melt[177].

The Transcat Process merits especial mention. This would have been the first full scale commercial plant to use molten salt as a process fluid. A 30 000 tonne per annum unit was scheduled for completion in 1975 for making chlorinated methane derivatives[178]. Unfortunately a world recession in demand for chlorinated hydrocarbons intervened and the plant was never built.[179]

The process uses Cu^+ / Cu^{++} chloride in KCl as a chlorine carrier for the oxychlorination of methane. Depending on the feed and temperature, a distribution of products results. The process is suitable for all chlorinated derivatives of C_1 and C_2 paraffins and olefins. The catalyst in molten form continuously recirculates between two towers by the gas-lift principle. One tower performs the main reaction, while the other regenerates the CuCl with air and some chlorine value. A particular feature of the process is the range of materials it accepts for chlorine values, notably HCl, Cl_2 and unwanted or recycled chlorocarbons. It therefore produces no chlorinated waste, and may be integrated with plants producing waste such as HCl [180,181]. The reactors are constructed of ceramic-lined steel [178].

Baths of molten salt have received serious consideration for coal gasification. Glueck has reviewed such processes, with particular reference to their advantages for control of sulphur emissions [182]. He states that their excellent heat transfer properties are an important advantage, and that corrosion is unlikely to be a great difficulty.

The Kellogg Process involved treating coal with steam in a bath of sodium carbonate, and received intensive laboratory [183] and theoretical [184,185] investigation, but was never brought to commercial use. An alumina-lined steel vessel was used and it was proposed that the 'frozen wall' technique would make cracks self-sealing. This technique involves having the exterior of the vessel below the freezing point of the salt while maintaining the interior molten, usually (as in this case) by an exothermic reaction in the bath or internal electric heating.

A more recent but related process also uses molten sodium carbonate, but uses air to make the product gas by partial combustion of coal [186]. A one ton per hour pilot plant was constructed, also using alumina-lined steel. A simple but elegant overflow device is used to provide a continuous bleed-off of the salt, which is replenished by mixing solid sodium carbonate with the coal feed.

A model process has used phenanthrene in place of, and as a simplified model for, coal [187]. This laboratory study used an alkali metal hydroxide / carbonate melt at around 480 °C for a hydrogenation process. The details were only published in 1978, after completion of my practical work and of course in ignorance of it. It is remarkable to see, however, how similar is the apparatus described to the one I used for the pyrolysis of plastic waste. The main difference was that the hydrogenation operated under pressure, and thus the reactor was made from a commercial autoclave (supplied with a magnetically-coupled stirrer). A removable inner liner of stainless steel was likewise used, though of type 316 for this more caustic environment. No claims for telepathy, plagiarism or incredible coincidence are required to explain this similarity. It is merely reassuring to learn that what seemed to be a logical simple and sensible design has been thought so elsewhere.

There have been a number of patents for molten salt processes, which are cited in some of the reviews given previously[154,155,160]. Worthy of particular mention is a very early patent[188] which essentially tried to patent the entire field of molten salt reactors for the chemical conversion of gaseous material. A German[189] and a French patent[190] both describe the use of combustion to heat the salt internally and also circulate it by the gas-lift pump effect, the molten salt forming a liquid seal between the combustion zone and the pyrolysis zone. A U.S.S.R. patent[191] describes a reactor in two identical parts for pyrolysis of hydrocarbons, in which air is blown into the non-pyrolysis side to regenerate it, and provide heat by combustion of carbon residue. The function of the two sections is regularly switched, and gas-lift again provides circulation.

A notable commercial venture was that of Lessing, reported by Greenberg[192], supplying waste incinerators that used a bath of molten salt - e.g. sodium sulphate at 600 °C. It was stated in 1973 that the system was then commercially available, but that no full-scale units had yet been built; and I have heard nothing of it since. Greenberg was also the inventor of a molten salt heat exchanger for domestic heating boilers, which was claimed to give a 50 % fuel saving[192].

There are several lessons to be learnt from this venture. Firstly, that production of simple technology involving molten salts is not unduly difficult. Secondly, it may be noted that the same idea was independently conceived by myself and my colleagues, and my initial sketches are not dissimilar to Greenberg's test plant. However, just having a good idea is not enough - even producing it in a technically practical form may not be enough to get it into commercial use. Both waste pyrolysis and molten salt reactors seem to have a barrier against moving from pilot plant to commercial operation. Any process involving both these elements might therefore be thought to be doubly handicapped.

2.5.3 Corrosion Data is readily available for many materials under high temperature service, but not when they are subjected to the possible corrosive effects of molten salts. The use of 'frozen wall' techniques or ceramic brick linings would be suitable for the simple containment of salts, but for any more complex plant the use of metals is very desirable.

The literature on corrosion of metals by molten salts is sparse and scattered amongst various special interests. Two fairly general reviews are those of Inman [193] and of Kochergin [194], the latter being particularly concerned with prevention of corrosion. Pizzini [195] has also discussed materials problems. His discussion of corrosion is essentially a restatement of the important thermodynamic explanation advanced by Edeleanu and Littlewood [196] for behaviour in chlorides, along with the observations of Littlewood and Argent [197] on the effect of water as a contaminant in melts.

Oxidative corrosion by oxygen in chloride melts was measured by Seybolt [198] and interpreted by Holmes [199]. The corrosion of a variety of steels and alloys in Na/ K / Mg chlorides has been studied in a wide experimental programme by Stepanov, Kachina-Pulla et al [200,201]. The resistance of stainless steels to Ba / K / Na chloride heat-treatment salt has been extensively investigated by Jackson and LaChance[202]. This is like the mixture which was chosen for the experimental work described in the present thesis. The synergistic effect of sulphate and chloride mixtures has been investigated by Sequeira and Hocking[203].

The use of salts in nuclear engineering has already been referred to, and materials problems have been studied intensively. A good source is Berry[204]. Some interesting insights into experimental methods is given by Grimes and Cuneo[165], although it is pointed out that much of the work is secret. Battelle, for example, are reported[165] to have worked in this area, but their reports are classified. Even apart from the question of secrecy, the peculiar requirements of nuclear technology mean that the information is not easily applicable to a normal industrial situation. For example, the requirement for a low neutron cross-section causes the use of rather outlandish salts such as ZrF_4. The materials used to resist the molten salts also have to resist radiation, and moreover are permitted to be very expensive.

Another particular study arises from modern high performance power generating equipment, involving highly stressed materials at high temperatures, such as turbine blades. When splashes of water deposit salts, or the inorganic components of fuel get onto the surface, they are frequently at such a temperature that they are molten. The studies are predominantly concerned with corrosion by sulphates [205,206,207]. As might be expected, the previous heat-treatment of the metal can have a significant effect on the rate and type of corrosion[208].

Long-term practical experience of corrosion and its prevention of course comes from the heat transfer [169] and heat treatment salt industries [171,202]. Possibly even more important, the latter industry has learned to live with corrosion.

2.6 Pyrolysis of Plastic Waste in Molten Salt

There is one patent[209] on this topic. It describes the thermal breakdown of polytetrafluorethylene into a lower molecular weight waxy product. Sulphate, chloride, nitrate and nitrite melts are suitable, which suggests that the salt exerts little if any useful catalytic effect. Since the plastic is somewhat specialized, and the product even more so, it is difficult to see the process gaining any great commercial significance.

Molten lead baths have been tried in the U.S.A. for pyrolysis of refuse[210]. Pechuro et al in the U.S.S.R. have used lead and salt baths for the pyrolysis of liquid hydrocarbons[211]. Evidently Pechuro has also tried tyre pyrolysis in molten lead[212].

At the University of Tennessee, Larsen has extended his expertise in hydrotreating coal in molten salt to the not very different situation of shredded motor tyres[139], and is also reported to have tried plastics in salt[73]. The apparatus used was a spherical glass flask externally heated by a fluidized sand bath up to 500 °C[139]. It is suggested by Larsen that the most favourable siting of a commercial unit would be adjacent to an ethylene plant, to make immediate use of the products[213]. He comments on the difficulty of separating tyre residues from the salt[214].

At the University of Hamburg, Perkow carried out a study which may be closely compared with mine [215]. His results have been published in a number of papers by Sinn et al [11,12,29,124,216]. The reactor appears to have been a spherical vessel with an electric immersion heater, into which pre-melted plastic was continuously passed to below the surface of the salt, which was stirred. The salt used was a mixture of 35 mole % $MgCl_2$ and 65 mole % KCl. The temperature range was 640 to 850 °C. Polyethylene, polyvinylchloride, polystyrene and a mixture of 60 % polyethylene, 40 % polyvinylchloride were pyrolysed at a rate of 100 grams per hour. A nitrogen atmosphere was maintained by a purge through the plastic inlet.

The results of Perkow's work were compared with an analagous programme by Menzel [115], using a fluidized bed. Although the molten salt reactor was thermally more efficient, it was abandoned in favour of the fluidized bed for larger scale work. This was because of the greater amount of char produced during the salt experiments, and because of corrosion problems [124].

Perkow's work was evidently complete when my work began, and was only discovered after the reactor had been commissioned and experimental work was under way. There is no doubt that the University of Hamburg experiments would have influenced my experimental programme had we known of them earlier. However, the changes would have been mainly in terms of the results to be expected and methods of analysis. Even with hindsight, the reactor design is still preferred and my experiments are perfectly valid. The two projects were very different in character, that of Perkow leaning towards chemists' techniques, whereas mine was intended to be small-scale chemical engineering. The most obvious example is in the choice of a spherical flask by Perkow, and my use of a flange-topped cylindrical vessel. The latter is more easily applied at plant scale, while the former is ubiquitous in chemistry laboratories.

The fact that there is some overlap in our studies is not a disadvantage, especially since my results were partly obtained in ignorance of his. It is therefore gratifying to note that, where comparison can be made, the yields and product distributions found are similar in my work to those reported by Perkow, as were the general trends observed. TABLE 2 gives a comparison.

In reactor design, Perkow's use of a continuous screw feed for plastic is more plausible for industrial scale, and is the method I would have used had finances allowed. On the other hand, my techniques of batch addition

TABLE 2

Comparison of yields in the pyrolysis of polyethylene on molten salt. Results from this project compared with those of Perkow[12] at Hamburg University.

Experimenter	Perkow	Pitt	Pitt
Temperature °C	640	610	650
% Yields			
Hydrogen	0.2	0.2	0.2
Methane	5.6	5.8	8.7
Ethylene	14.0	10.6	13.8
Ethane	4.0	4.2	4.0
Propylene	10.1	9.4	7.1
Propane	1.0	0.9	0.7

permitted some kinetic studies which give some insight into the processes involved. Likewise, I have shown the effect of stirring to be a significant variable. I did not find char formation a problem, and suspect that some of it in Perkow's reactor was caused by wall effects. I do not know the materials of construction he used, so I cannot comment on his corrosion problems, other than to note the higher temperatures and different salt he used.

Also at Hamburg, Krebs [124] studied the pyrolysis of single particles of polyethylene in molten salt, by observing the pressure rise in a sealed container. Although our techniques were vastly different and cannot be compared directly, his observations bear out my own visual and kinetic experiments.

3 MATERIALS AND METHODS

3.1 Materials

3.1.1 Salts The salt used for the main part of the experimental work was a commercial heat treatment salt marketed as "Cassel QS 495" by I.C.I. (Mond Division). According to the manufacturers, it is a mixture of barium, calcium and sodium chlorides used industrially for heat treatment of steels in the range 495 to 700 °C and normally contained in mild steel pots. It was chosen in preference to a single salt or laboratory admixture, because it provides a suitable temperature range in which the salt is stable and can be used safely. Also it is a neutral salt known to be compatible with steels, which presents no particular difficulties with respect to water. The fact that it is already used industrially should reduce problems of scale-up. The redox properties of the components are limited, and the only catalytic effect which could be anticipated arises from the presence of divalent ions.

For the single experiment on a nitrate melt (see 4.12.6) a heat treatment salt from the same source "Cassel TR 150" was used. This is a mixture of KNO_3 and $NaNO_2$ with a working range of 150 to 550 °C.

3.1.2 Plastics The material used in all experiments except those involving comparison between plastics was a proprietry low density polyethylene marketed as moulding granules by I.C.I. (Plastics Division) as "Alkathene WJG47". It is a widely used general purpose grade with no added fillers or colouring. In form it was oblate spheroids each weighing 30 to 40 mg and being of 2 to 4 mm diameter. It was chosen as being representative of the commonest commercial plastic, which is a major part of plastic waste. The use of a single plastic aids interpretation of results. The granular form mimics shredded waste on a scale appropriate to the apparatus, the standard form once again assisting interpretation. It is a linear polyethylene of quoted molecular weight 32 000, crystalline melting point 109 °C and density 0.918 g cm^{-3} at 23 °C.

For the experiments described in sections 4.2 and 4.9, granules of polypropylene (I.C.I. "Propathene" natural, unmodified) of very similar appearance, size and shape to the polyethylene were used. The more spherical granules of approximately equal size were selected from both plastics for the solid residence experiments (4.2) and in all cases badly-shaped particles were not used. The polystyrene granules used in section 4.2 were Shell "Crystal PS" in the form of short rods (length 3.5 mm, diameter 2.5 mm) of unmodified polystyrene.

3.1.3 Purge Gas Nitrogen was used for the purge gas in all experiments. It was supplied by B.O.C. Ltd as oxygen-free "white spot" grade. This has a specified purity of at least 99.9 % and of the impurities, oxygen is less than 10 ppm, water less than 15 ppm, hydrocarbons less than 5 ppm, carbon dioxide less than 5 ppm, hydrogen less than 1 ppm and carbon monoxide less than 1 ppm. No attempt was made to further purify the gas. This was partly because oxygen and water would both be present in the plastic and in the space between granules in the addition tube, but also because any higher purity would be difficult to achieve on an industrial scale. Indeed, the normal grade of nitrogen with an oxygen content of up to 0.5 % would probably be satisfactory.

The same quality of nitrogen was used as the carrier in the gas chromatograph, though here it was passed through molecular sieve to remove water and hydrocarbons and oxygen (for the long-term satisfactory operation of the chromatograph).

3.1.4 Steel Austenitic stainless steel of nominal 18 % chromium, 8 % nickel composition was used for all parts of the reactor in contact with the molten salt or hot vapour. The liner, reactor body and lid were formed and welded from plate corresponding to En 58 M in the old British Standard BS 970:1955. The tubing used for fittings was similar, but titanium-modified for weldability. Stainless steel (18 - 8) was likewise used for the stirrer shaft and paddles.

3.2 Apparatus

3.2.1 General Description A general photograph of the apparatus is given as FIG. 2, and its essential features shown in the functional diagram FIG. 3. The reactor was in the form of a closed, flange-topped cylinder, and the salt was contained in a removable close-fitting liner. The reactor was heated by a specially-constructed vertical tube furnace. All entries and exits into the reactor were made via fittings welded into the removable flat lid. These comprised a gas inlet pipe through which a metered flow of nitrogen was maintained to purge the headspace; a thermowell going down into the molten salt region; a purged bearing for a central stirrer shaft to which various impellers could be attached; and a vent pipe leading via a one-bar bursting disc to a catch-pot part-filled with sand. The vent pipe was purged with nitrogen to prevent it acting as a dead space. The total nitrogen inlet was measured by means of an in-line variable area flowmeter supplied by G. A. Platon Ltd, and covering the range 30 to 600 cm^3 min^{-1} (unit scale calibrated with a soap-bubble flowmeter). The various purge flows were controlled by diaphragm valves against a fixed pressure from a nitrogen cylinder pressure reducer. A small pressure gauge (0 to 1 bar) was fitted on the main purge inlet to the reactor to warn of pressure build-up.

FIGURE 2

General view of experimental apparatus

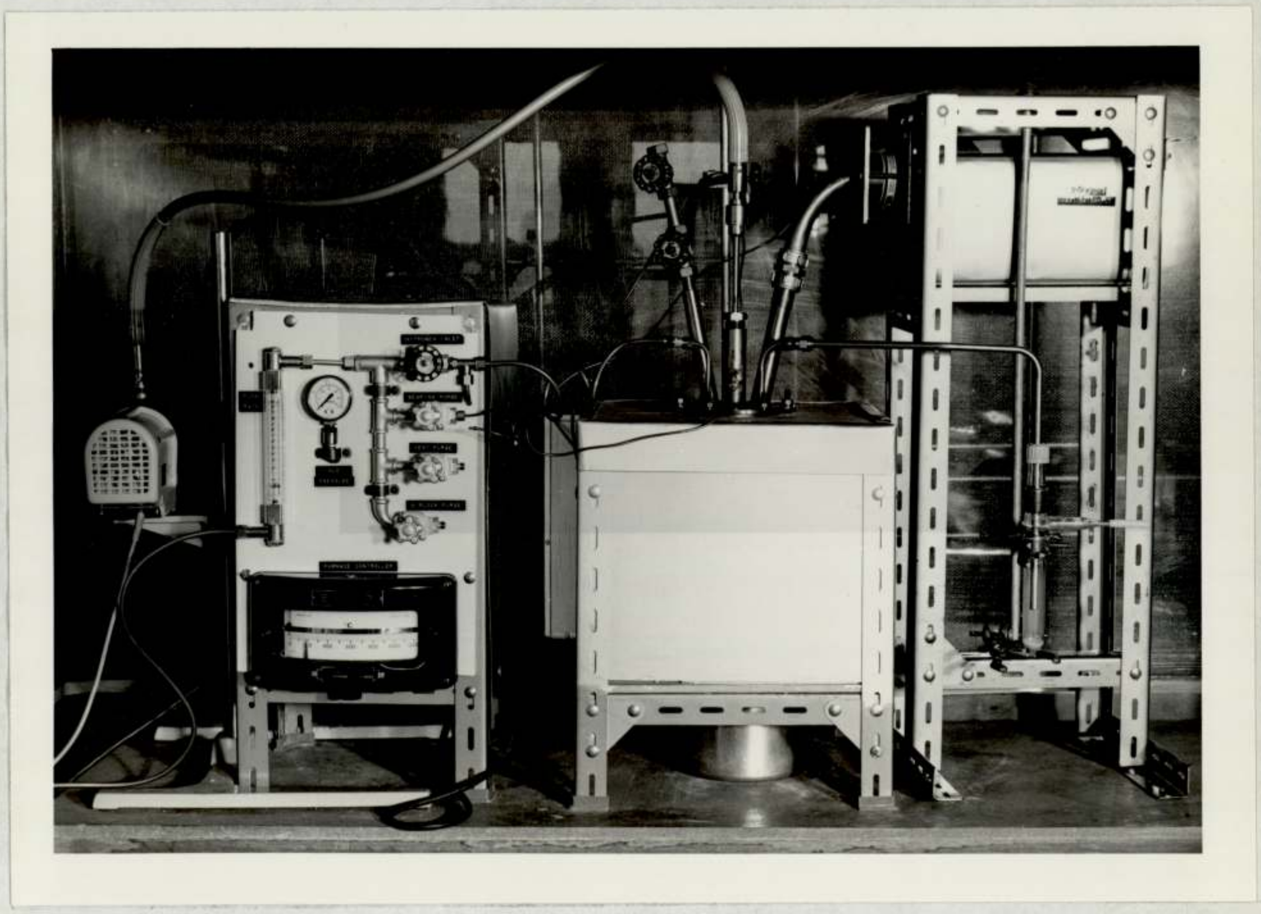
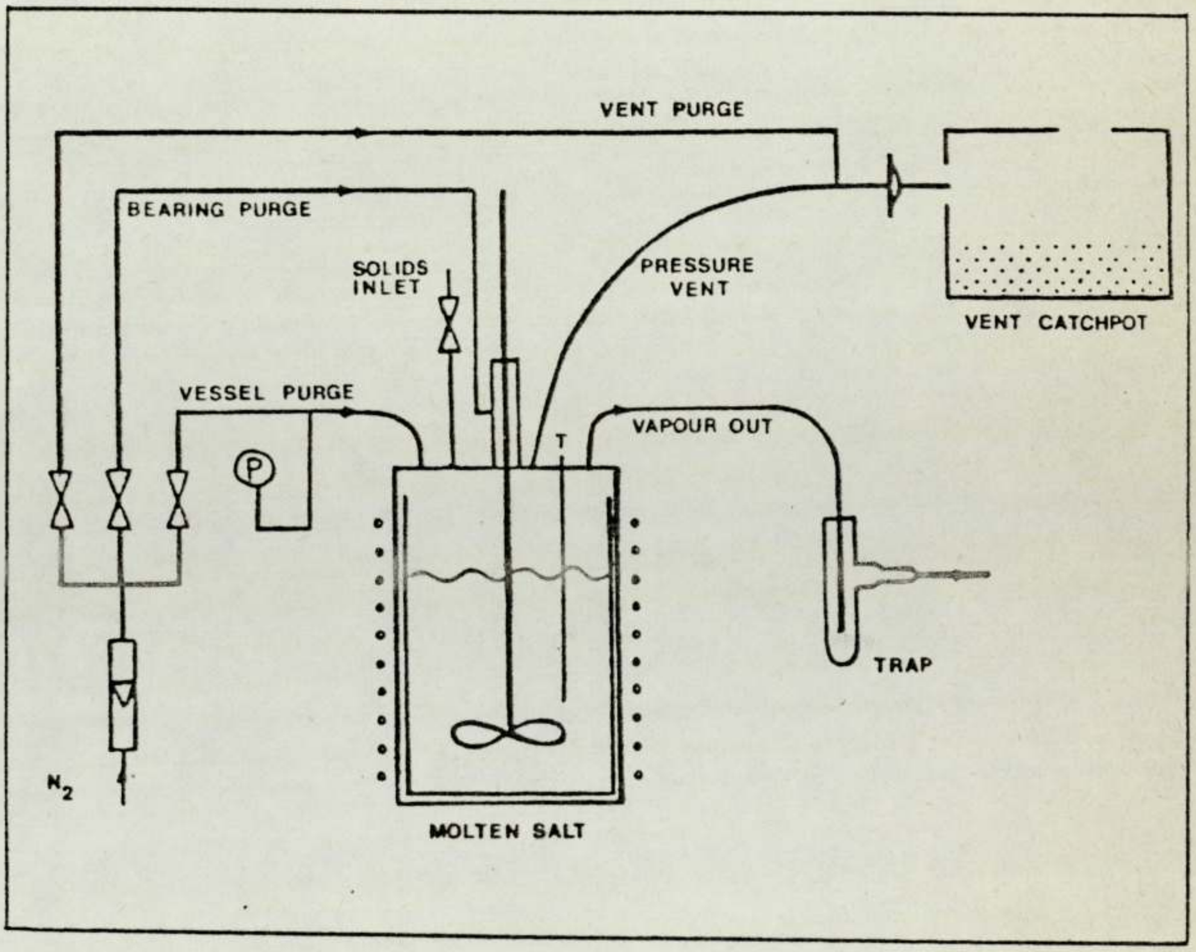


FIGURE 3

Diagram of experimental apparatus



3.2.2 Furnace The furnace was based on a ceramic tube and heating element combined, purchased as a spare part from a commercial (Baird & Tatlock) tube furnace, having a nominal working diameter of 125 mm and overall length 250 mm. It is rated at 1.3 kW at 240 V AC, with a specified maximum working temperature of 1200 °C. This tube was mounted vertically in an insulating box based on an angle-iron ("Handy Angle" TM) box frame, 30 cm high and 38 cm square, raised on four 15 cm legs. The top and base were from 10 mm asbestos-cement composite sheet ("Syndano" TM) with a 125 mm circular hole in the centre, to allow access to the tube. Additional Syndano was used to pack up the tube to a close fit with the top sheet. The main insulation was provided by alumina firebricks crosslaid around the tube. Crushed firebrick was used to fill the space between the bricks and the tube. The sides of the furnace were closed by light gauge, galvanized steel sheet, the exterior of which was painted with temperature resistant aluminium paint. An unsheathed ceramic insulated thermocouple (NiCr - NiAl) was placed adjacent to the middle of the heating coil. A similar thermocouple was placed by one of the steel sides. The thermocouple wires and the element power wires were taken into a 50 mm square electric conduit mounted vertically on one corner of the furnace.

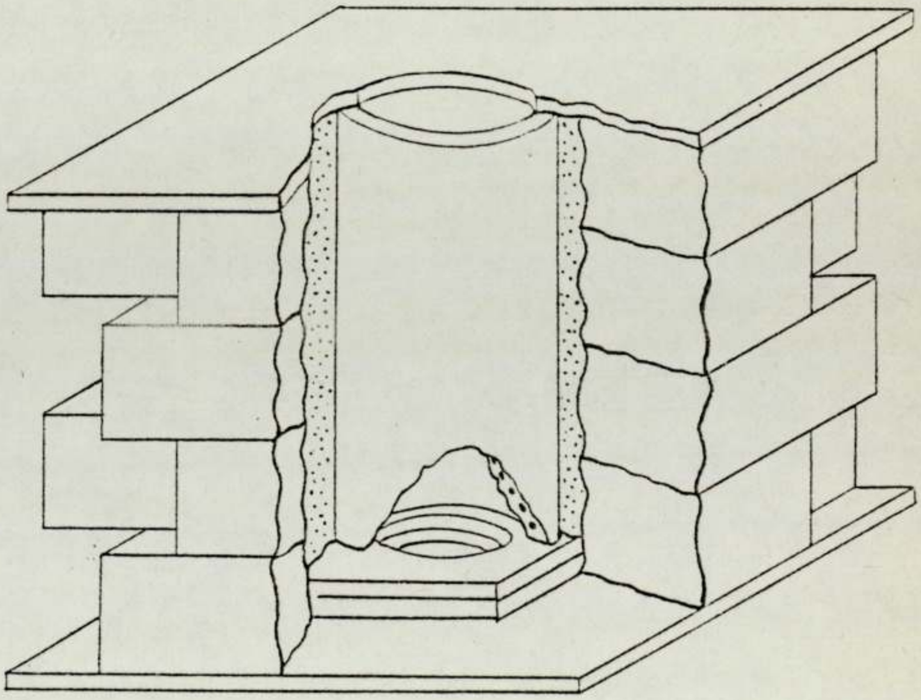
This conduit housed a 'Bulgin' type electric socket for power and earth connections, and a connector block strip for the thermocouples. Wires were laid through grooves cut in the firebricks. Electrical insulation was provided by ceramic sleeves in the interior and by glass fibre sleeves in the outer region of the furnace box. A drawing of the general construction of the furnace is given as FIG. 4.

Two lengths of rectangular tube 25 mm x 50 mm were bolted horizontally to the frame on one side of the furnace box, with the longer faces of the tubes vertical. Holes were drilled through the narrow faces of the upper tube and through the top narrow face of the lower tube, these three holes being accurately aligned vertically. A 12.5 mm aluminium alloy rod was a close fit, and when pushed through the holes formed a vertical support rod for the stirrer chuck mounting.

The furnace temperature was taken from the thermocouple mounted by the heating coil. This was taken to an Ether "Transitrol" temperature regulator which both indicated the temperature and switched electrical power to maintain the furnace at the set temperature. This controller was mounted in a box a short distance from the furnace, the box also supporting the gas controls.

FIGURE 4

Manner of construction of furnace (cabinet projection)



According to the manufacturers, the Ether "Transitrol" controller has on/off points spaced apart 0.2 % of the instrument range, which in this case was 0 to 1200 °C. It is internally compensated, and so no reference cold junction was required. For calibration, the zero was set at the ice point of water, and the calibration was adjusted to give a temperature corresponding to that given by a potentiometer, each in turn being connected to a thermocouple at about 600 °C. Since the controller was only rated at 5 amps, it was used to operate a 10 amp relay which switched both live and neutral power supplies to the furnace. Electrical earth was not switched, being maintained to the furnace box frame all the time when the apparatus was plugged in.

3.2.3 Reactor The reactor was in three main parts: (a) an outer casing in the form of a vertical cylinder 250 mm tall, outside diameter 125 ± 1 mm, of wall thickness 2 mm and a flat base 4 mm thick, fitted with a flange of thickness 2 mm and diameter 166 mm, which had six clearance holes for 3/8 inch bolts. (b) A removable liner in the form of an open topped cylinder 200 mm tall, of outside diameter 118.5 ± 1 mm, wall thickness 2 mm and base 4 mm. (c) A lid of thickness 2 mm to fit the flange on the casing, with the various fittings welded on.

FIG. 5 shows the outer casing, the removable liner and a special tool for lifting the liner out. The tool hooks under two interior studs which can be seen near the top of the liner, and was of mild steel. FIG. 6 shows the lid and its fittings. These comprised a central stirrer gland which will be described separately; a gas inlet pipe of nominal bore 4.0 mm (o.d. ¼ inch); an outlet pipe of nominal bore 6.3 mm (o.d. 3/8 inch); a solids inlet pipe of nominal bore 16 mm (o.d. 20 mm); a vent pipe of nominal bore 20 mm (o.d. 24 mm); and a compression fitting (not visible behind the stirrer gland) for the thermowell. The thermowell was of stainless steel tubing outside diameter 1/8 inch (about 3 mm) and inside diameter 1/16 inch (about 1.6 mm). The solids inlet and the vent pipe were both angled at about 12° from the vertical to prevent

FIGURE 5

Reactor pot, liner and liner removal tool

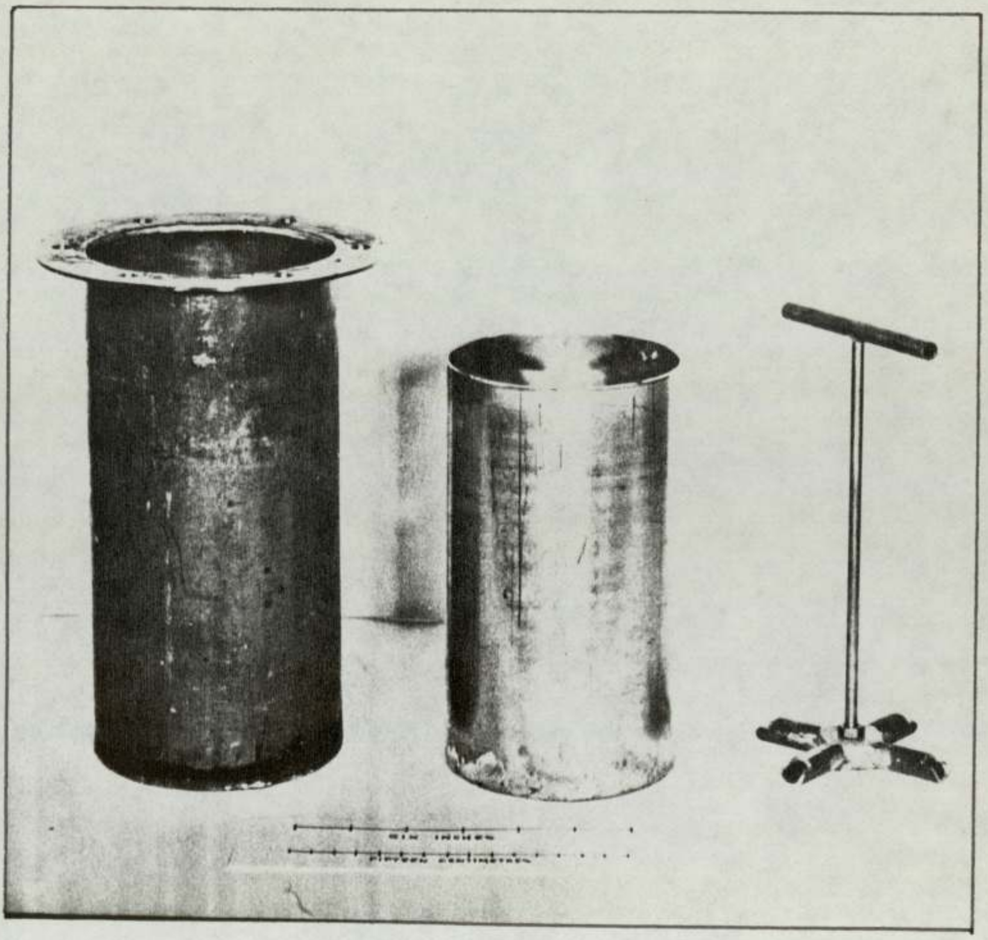
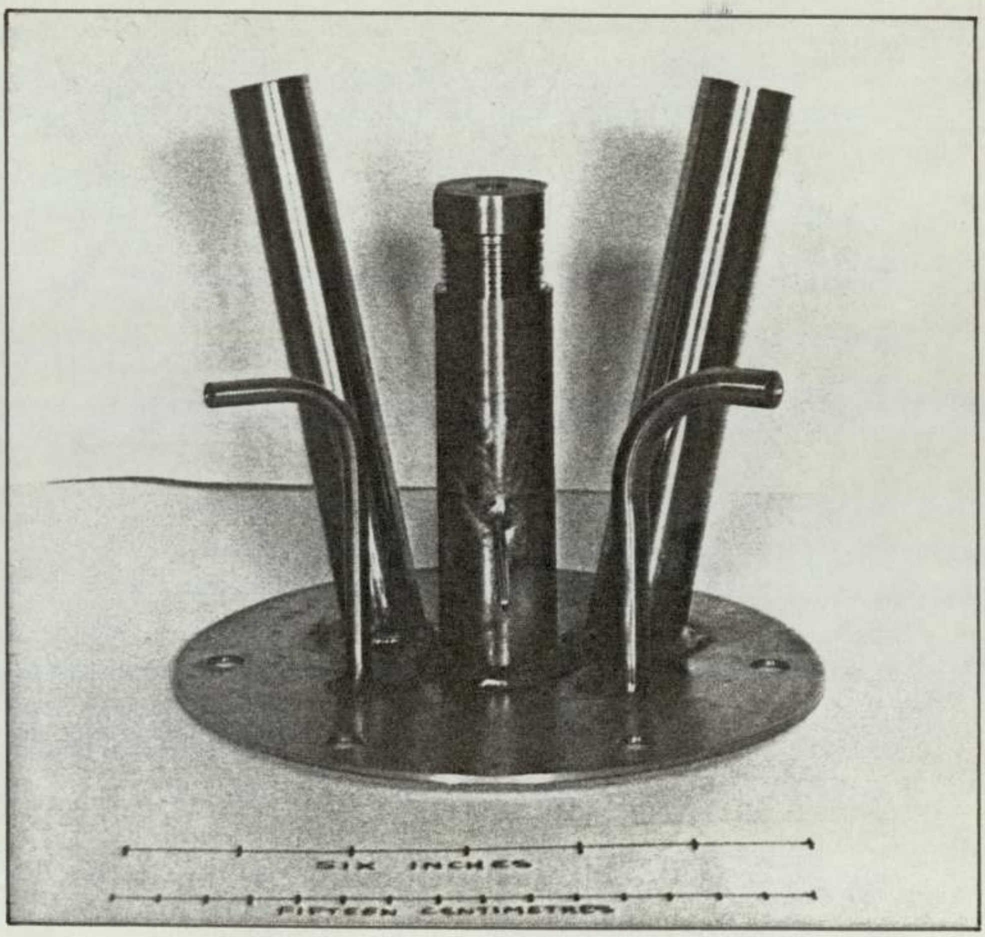


FIGURE 6

Reactor lid and fittings



crowding together of the various fittings in use or assembly. A stub of copper pipe was brazed onto the top of each of these angled pipes to allow the use of standard brass compression fittings - 1/2 inch (12.7 mm) bore on the solids inlet, 1 inch (25.4 mm) bore on the vent pipe. The solids inlet was closed off by means of a brass gate valve (1/2 inch nominal bore - about 13 mm). The vent pipe was continued with copper piping in a gentle curve to a bursting disc (see section 3.2.5). Connections to the gas inlet and outlet pipes were made with stainless steel compression fittings. A proprietry mineral-insulated stainless steel sheathed NiCr - NiAl thermocouple (Electroplan TC-4) fitted smoothly into the thermowell.

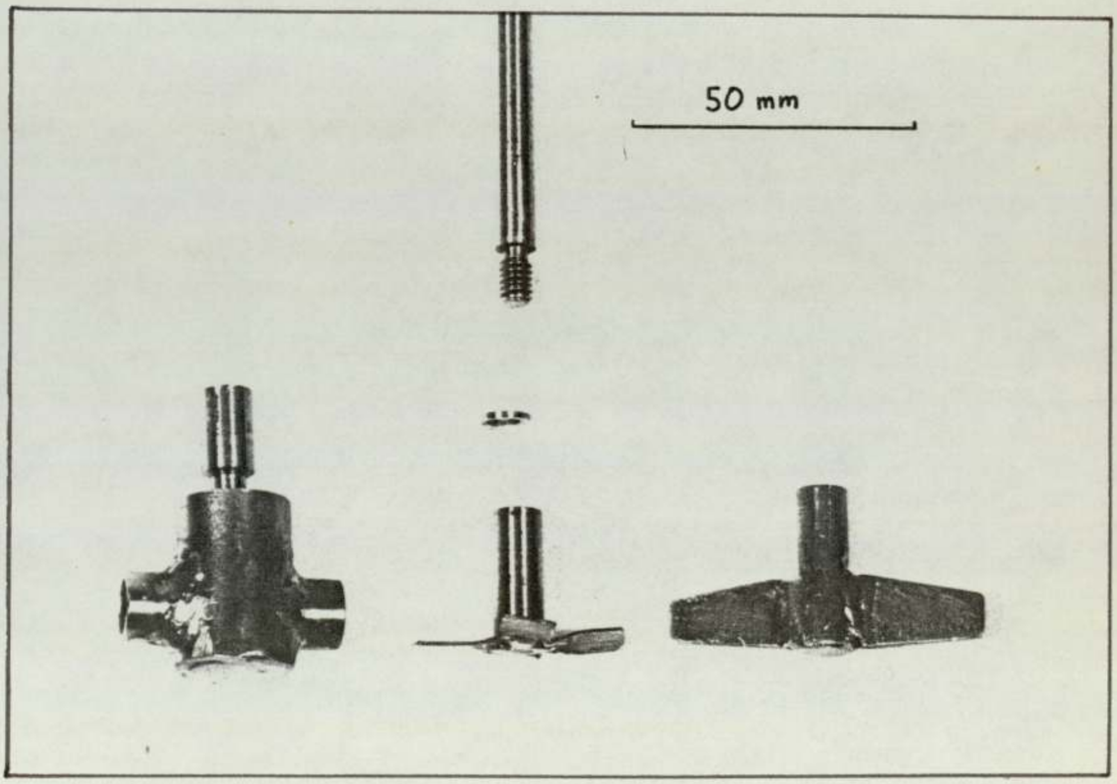
The reactor lid was sealed to the flange by a specially made gasket of 3 mm asbestos board coated with colloidal graphite from an aqueous dispersion (marketed as 'Aquadag'). Backing flanges of 6.5 mm mild steel were used, the upper one being in two halves to allow for the lid fittings. With the top fittings blanked off, no leak could be detected (using soap solution) when the reactor was pressurized to 1.6 bar above ambient with nitrogen.

3.2.4 Stirrer Stirring of the salt was achieved by a single impeller mounted on a central vertical 8 mm stainless steel shaft. No baffles were used. This arrangement was chosen for its mechanical stability, and freedom from crevices where corrosion might be accentuated. The combined gland and stirrer bearing will be described separately. The shaft was driven via a flexible drive from an independently mounted, AC single phase electric motor with a variable speed control. (Model RZR-11 made by Heidolph Ltd.) Two gearing heads were used, giving nominal ranges of 70 to 700 r.p.m. or 300 to 3000 r.p.m.. Because of the hollow shaft construction of the head, it was easy to measure the speed of rotation with a portable tachometer applied to the drive head. According to the manufacturers, the power consumption of the motor is 110 W and the available stirring power is 55 W.

The stirrer shaft and the three interchangeable impellers are shown in FIG. 7. As can be seen, the impellers screw on, and a small washer ensures they can be removed without difficulty. Each impeller was formed entirely of 18/8 stainless steel welded together. The finish and dimensioning was not as good as some of those commercially available, but no commercial impeller of

FIGURE 7

Stirrer shaft and impellers



appropriate size could be found of welded construction. (The normal method of joining of commercial impellers was by silver solder. This was felt to be unsuitable, since it has a melting point around 700 °C and might corrode in the salt. The soldered impellers were too thin to dismantle and refabricate by welding.)

A convenient feature of the molten salt used (and which would be substantially true for many other salts) is that, in the working range, its density and viscosity are both close to twice the values for water at ambient. That is to say, the ratio of density to viscosity is virtually the same for the molten salt as it is for water at room temperature. This ratio is the fluid-dependent portion of the tank Reynolds number, so that as far as single phase mixing is concerned, the molten salt can be expected to behave like room temperature water to a first approximation. This assumption was used for the design of the apparatus. No more exact measurements or calculations were made, because of the considerable disturbance from the mixing pattern which would be caused by the pyrolysing plastics.

There is a vast range of possible mixer types and arrangements, which it was beyond the scope of this project to investigate. The three impellers chosen were very simple examples of their classes, i.e. a radial-flow mixer, an axial-flow mixer, and a special two-phase centrifugal dispersing head. The radial-flow mixer was a two-bladed paddle of aspect ratio 1:4 and about half the tank diameter (actually 56 mm) in width. This was used in the initial and kinetic experiments to provide agitation of the salt phase (to aid thermal mixing) without undue disturbance of the top surface of the salt. Some swirl was of course inevitable in an unbaffled tank. The plastic would thus have no positive mixing in the salt, apart from the swirl tending to keep it away from the walls. The rotor speed used (70 r.p.m.) implies a Reynolds number in the vicinity of 3 000 to 4 000, which means a mixed laminar and turbulent regime with some vertical movement as well as rotation.

The other two impellers were of about 0.3 of the tank diameter in width (actually 36 mm). The axial-flow impeller was a four-bladed propeller, each blade being 10 mm across and set at an angle of 10 ° to the horizontal, so that the direction of rotation tended to cause a down-draught. The size implies a Reynolds number of about 20 times the speed of rotation in r.p.m.; that is, a mixed flow regime is expected from the lowest speed used (100 r.p.m., Re = 2 000) up to 500 r.p.m. (Re = 10 000), and a fully turbulent regime thereafter.

In tests with water in a beaker of similar dimensions to the reactor, air entrainment was observed at higher speeds, as the vortex was drawn down into the impeller. At 1 200 r.p.m., the air caused sufficient bumping to greatly upset the stability of the system. This impeller was therefore capable of promoting interaction between the salt and the pyrolysing plastic, possibly up to entraining gas, liquid or solid particles. The propeller was used in the experiments which examined the effect of mixing by varying the speed of the stirrer.

The centrifugal-type impeller was not actually used in molten salt. As is shown in FIGS. 8 and 9, however, it proved efficient in dispersing a light viscous liquid (medicinal paraffin) into water. A thin film could be dispersed without air entrainment and at quite low speeds. Drop sizes were obtained of about 7 mm at 200 r.p.m., 4 mm at 400 r.p.m., 2 mm at 600 r.p.m. and 0.5 mm at 1000 r.p.m.. It would probably have had application for a lower rate of pyrolysis, but for the rapid gasification observed, the drawing of droplets into the salt would probably have caused unacceptably high spattering of the salt, and might even have been dangerous. The latter reason was the most convincing in deciding not to use this stirrer in the molten salt pyrolysis.

FIGURE 8

Centrifugal impeller dispersing paraffin in water at 300 r.p.m.

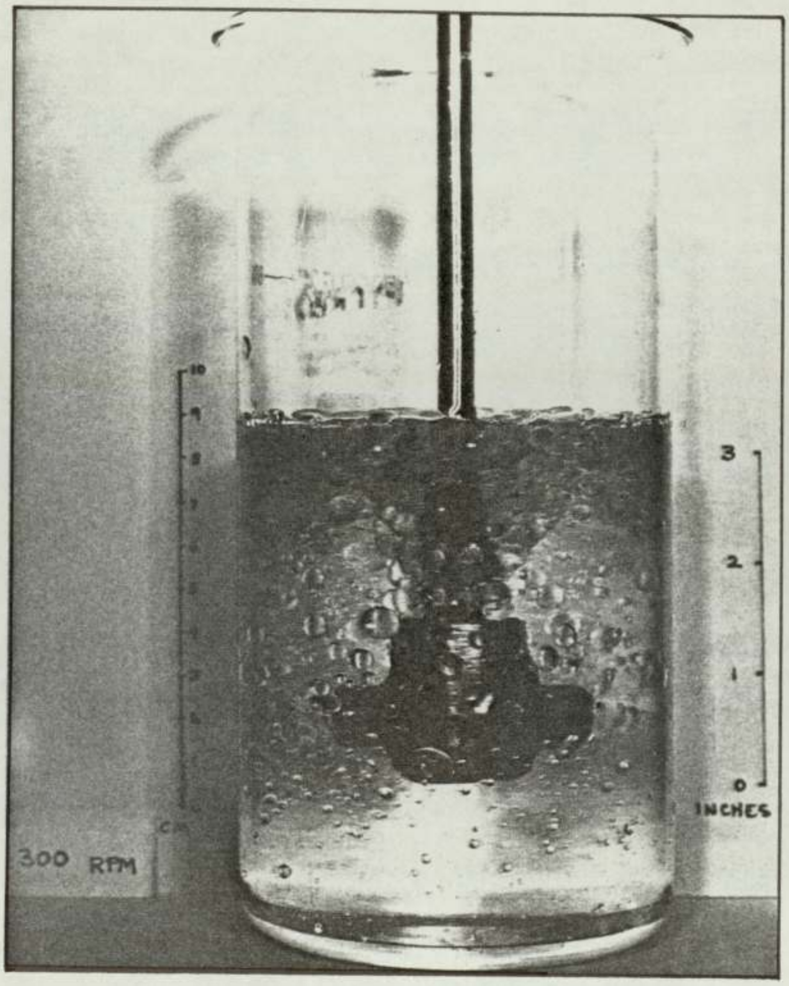
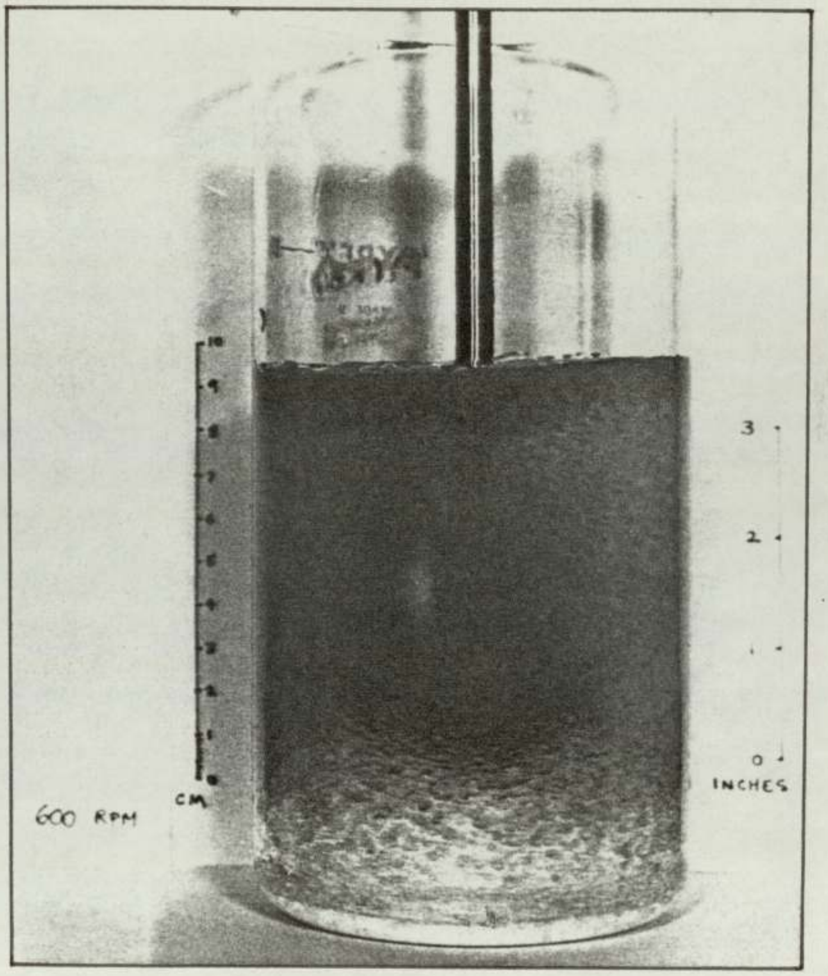


FIGURE 9

Centrifugal impeller dispersing paraffin in water at 600 r.p.m.

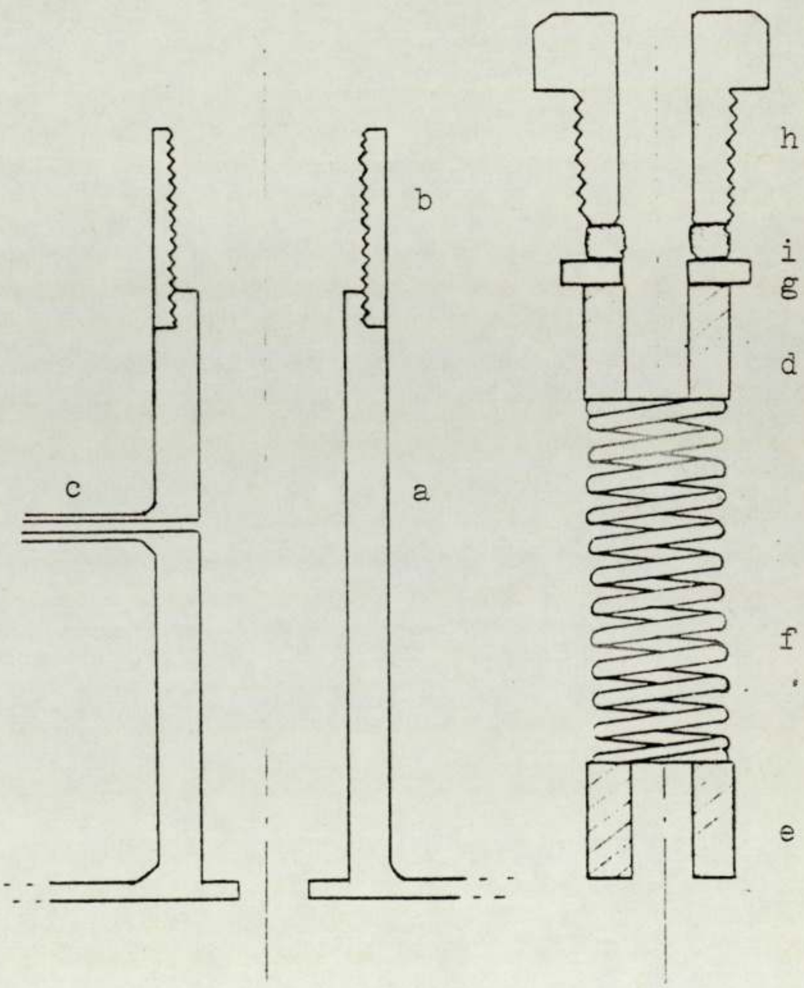


3.2.5 Stirrer Gland The task of sealing a rotating unlubricated shaft at high temperature against leakage of vapour is not an easy one. A leading British manufacturer of shaft seals advised that no product was available to fulfill these requirements under the specified service conditions. A practical solution was found by using a bearing with a relatively efficient upper seal, and a relatively inefficient lower seal. The space between the seals (i.e. the bearing housing) was purged with nitrogen, so that a continuous trickle of nitrogen into the reactor headspace was maintained.

The combined stirrer gland and bearing is shown in FIG. 10. It was sized for an 8 mm stainless steel shaft. The housing comprised a stainless steel tube (a) of o.d. 30 mm, i.d. 19 mm, length 76 mm. This was welded centrally over a 9 mm hole in the reactor lid. A length of internally screwed brass tubing (b) (o.d. 30 mm, i.d. 24 mm, length 26 mm) was screwed onto the top and brazed in place. A side tube (c) for entry of nitrogen was brazed into the housing about 46 mm above the lid. This was stainless steel tubing of o.d. 1/8 inch (about 3 mm) i.d. 1/16 inch (about 1.6 mm). Into the lower part of the housing were fitted an upper (d) and a lower (e) graphite bearing in the form of short tubes 15 mm long, i.d. 8 mm, o.d. just under 19 mm for a smooth fit in the housing. These

FIGURE 10

Manner of construction of combined stirrer gland and bearing (section)



bearings were held apart by a compression spring (f) of o.d. 18 mm, free length 52 mm, compressed to 47 mm. The nitrogen purge therefore enters the space between the bearings. The upper bearing was held in place by a brass washer (o.d. 24 mm, i.d. 8 mm clearance, thickness 3 mm)(g) locating on the lip formed by the end of the tube (a) in the threaded tube (b). The components thus described were constrained by a bored brass plug (h) fitting into the threaded tube (b). The plug had a 9 mm centre hole, a threaded length of 18 mm, a head of thickness 10 mm and o.d. 30 mm, onto which two flats were ground to accomodate a 25 mm AF spanner. Graphited asbestos string was wound around the stirrer shaft above the brass washer (g), and compressed between the washer and the plug (h) to form a dry stuffing box (i). This stuffing box formed an upper reinforcing seal, so that there was more tendency for escape of nitrogen via the lower bearing than via the upper. The brass washer had as a secondary function to provide bearing if the graphite should break up or wear away too quickly. The narrowness of the 9 mm hole in the reactor lid was intended to provide the minimum exposure of the bearing to the reactor envirinment, and limit whip of the shaft should the lower bearing break up. After the initial trials, new bearings were bedded in, and the stirrer height not varied during the rest of the experiments.

3.2.6 Safety Features In designing apparatus for what was essentially an untried operation, it was necessary to make allowance for some of the worst situations which could conceivably occur, and their immediate consequences. The worst unintended occurrences were thought to be: (a) blockage of exits causing overpressure (b) explosive chemical or physical reactions within the vessel (c) sudden massive vessel failure - e.g. the bottom of the reactor falling out (d) failure of temperature-limiting controls (e) products catching fire (f) water coming into contact with the hot apparatus.

As a general precaution, the apparatus was situated on an asbestos-cement topped bench within a PVC fume hood which also prevented direct line of sight with water taps. A transparant screen was hung in front of the apparatus almost all of the time when the furnace was on, working access being possible around the side of the screen. The screen was of wire mesh reinforced PVC. As well as preventing material coming from or onto the apparatus, the screen also improved the effectiveness of the hood ventilation. The control equipment was mounted on a unit separate from the furnace and covered with sheet steel. All the equipment was mounted off the bench (in case of loss of molten salt) and only hardware was kept in the cupboard and drawers underneath the bench.

The furnace base had a hole just slightly smaller than the furnace tube, to allow any leakage of salt to drip freely away. Beneath this hole was placed an aluminium basin half-filled with dry sand, and capable of containing all the salt load. The furnace tube was also mounted a little up off the furnace base so that any sideways seepage of leaking salt would not contact the electrical windings.

A small dial pressure gauge (up to 1 bar over ambient) was attached to the nitrogen purge inlet line, just after the flow controlling valve. The gauge was placed adjacent to the variable area flowmeter reading the total nitrogen inlet. Any partial blockage of the outlet would thus be signified by a reduction in flow rate, and a rise in the gauge reading towards that set on the gas cylinder reducing valve. Vapour generation within the reactor faster than could be emitted through the outlet would be similarly indicated by a rise in pressure above that set on the gas cylinder reducing valve (generally about 0.2 bar). It was intended that the solids inlet gate valve should be used as an emergency vent if such a pressure rise was noted. The gate valve was of wide bore, unlikely to block, and could be opened in a few seconds.

In case the pressure rise was not noticed in time, or was too rapid, a fixed vent line was arranged into a steel catchpot part filled with dry sand, and itself having an opening for gas escape pointing away from the operator. The vent line was of nominal bore 25 mm and closed by a graphite bursting disc (supplied by Graphite Equipment Ltd) made to rupture at an overpressure of 1 bar. From the data given in BS 2915:74 ("Bursting discs and bursting disc assemblies") this size is capable of venting one litre of air in less than 10 milliseconds. The bursting disc was chosen in preference to a relief valve partly because of its simplicity, but also because what was vented might include molten salt (which might freeze and block a valve). The 1 bar rupture pressure of the bursting disc is of course considerably less than the pressure which the apparatus may be expected to withstand (see Appendices).

Venting the gases from the headspace would produce a fire hazard due to the mixing of hot hydrocarbons with room air. Of the gases likely to be present in any amounts, ethylene has the lowest auto-ignition temperature, 450 °C . Since the headspace operates at a lower temperature than the salt, and venting generally has a cooling effect, there is therefore a good chance of the vapours being dispersed by the fume hood ventilation without ignition. If ignition were to occur after venting, then combustion would be as an unconfined vapour cloud away from the operator, and in a region of non-combustible material. On this scale, such a vapour cloud combustion (which the author has seen demonstrated elsewhere) would be dramatic and certainly surprising, but probably not very dangerous. The ignition of small leaks from the apparatus would not cause much of a hazard in the general absence of flammable material and in the presence of a positive pressure of nitrogen in the reactor to prevent propagation of the flame back into the headspace.

The furnace was controlled by the Transitrol unit operating on a thermocouple adjacent to the furnace tube rather than one in the molten salt for several reasons, all concerned with safety. Firstly, this thermocouple was less likely to fail through corrosion. Secondly, the solidified salt is a fair to poor heat conductor, and it would be possible for the electric windings to overheat while the salt thermocouple was still relatively cool. Thirdly, in the event of loss of salt the salt thermocouple would be in a nitrogen-purged vapour space and would thus cool, while the furnace windings would heat up because of the reduced load.

The stirrer motor was connected to the shaft by means of a long flexible drive, which allowed the motor to be situated well away from the furnace. This both protected the motor from heat and accident, and protected the apparatus from vibration. Moreover, the motor is a possible source of ignition for any flammable vapours released.

The spacing out of apparatus was an important design consideration for safe operation. All electricity and nitrogen lines came in on the left of the equipment. The right-hand side was solely for collection of product vapours. Air space was allowed behind the apparatus for free ventilation to avoid any local concentration of vapours and protect the fume hood from working heat. During operation, the furnace bench was kept clear of all equipment not in direct use. Notebooks etc were placed on other nearby benches.

A recognized hazard of molten salts is the expansion of liquid under a solid crust during melting, which can lead to explosion. This effect was deliberately excluded by the basic design in which heat was provided from the sides only and the base was uninsulated (though shielded from convective losses). The furnace tube wattage was fairly low for its size. Experience with metallurgical vertical tube furnaces suggested that uncontrolled heating of a loaded reactor would be unlikely to give a final temperature in excess of 900 °C . This is within the possible static working range for stainless steel, and would not cause breakdown or excessive vapour pressure from the salt used. Because of heat losses from the reactor head, the actual maximum salt temperature turned out to be about 800 °C.

3.3 Method of Addition of Plastic

The original design of apparatus had two gate valves in series on the solids inlet pipe. The space between them was intended to act as an air-lock, into which batches of plastic could be put, and added to the reactor by opening the lower valve. This worked moderately well in the initial proving tests, but gave rise to some difficulties at higher temperature with larger batches of granules. There was some tendency for the granules to jam together in the valves, which was aggravated by the plastic becoming sticky due to transmitted heat. Accordingly, the upper gate valve was removed and the following procedure developed.

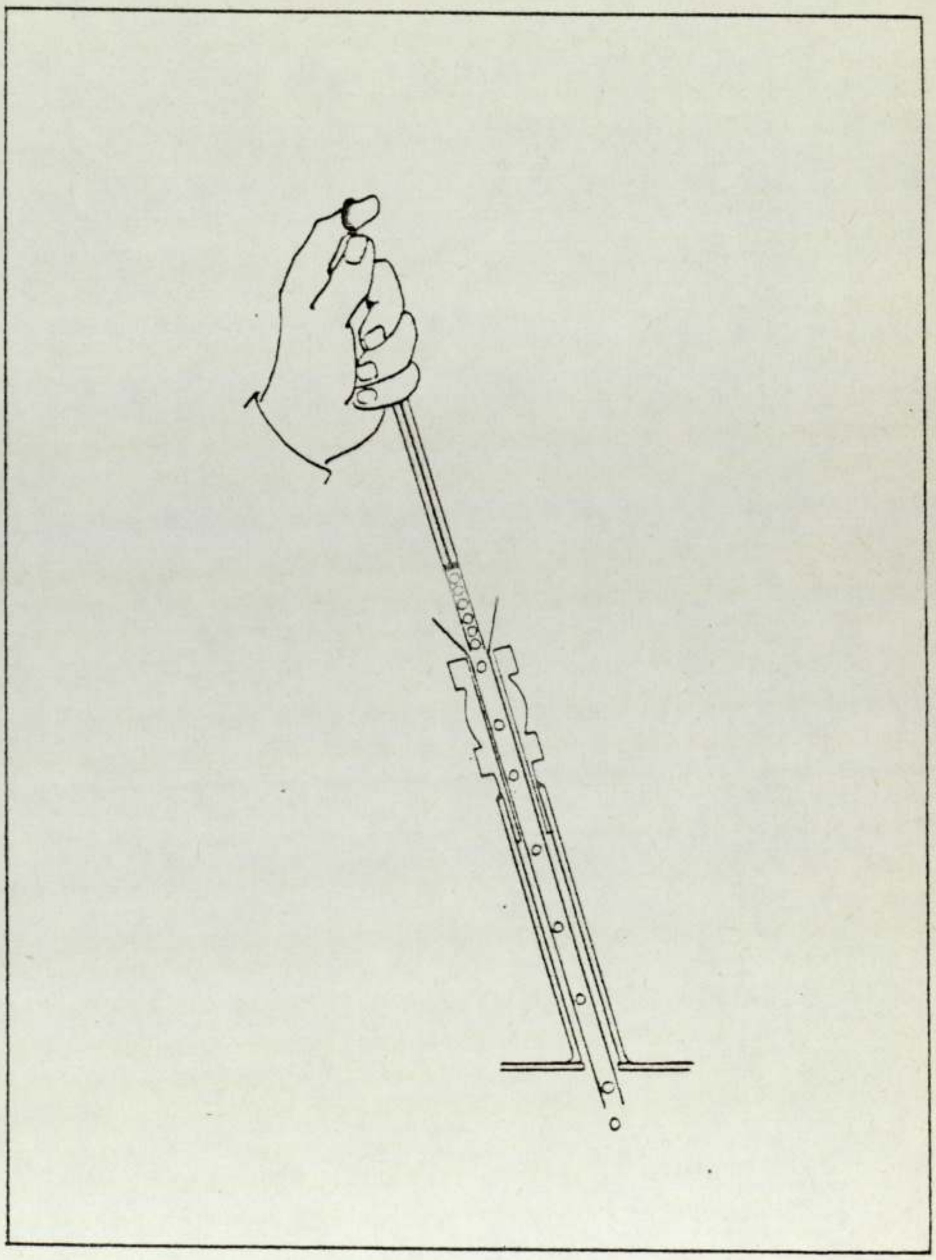
When the reactor headspace had been suitably purged (normally for at least 20 minutes) the gate valve was opened and a glass tube inserted into the inlet pipe. The glass tube had its upper end formed into a funnel, which allowed it to sit on the body of the valve so that its lower end projected just below the lid of the reactor. Its bore was a little larger than the largest granule, so that the plastic particles could slide down freely but did not tend to jam. A pre-weighed portion of plastic granules (1.000 ± 0.004 g) was then passed into the glass tube from a patent syringe system known as a Transfertube (TM). The plastic thereby fell into the reactor. The glass tube was then withdrawn and the gate valve closed. A representation of this procedure is shown in FIG. 11.

After a little practice, the procedure was checked by a colleague with a stop-watch. It was found to take an average of 5.3 seconds for the plastic to be added and the system closed up afterwards. During this short period the glass tube did not heat up sufficiently for the granules to stick to it. Granules of polyethylene were found in separate experiments to have an induction time of about 8 seconds before the onset of gassing, and the shortest time for fumes to be observed at any exit was 12 seconds, so there was little chance of any pyrolysis product being lost during the addition. The slight positive pressure of nitrogen in the reactor prevented the entry of atmospheric air, except possibly some entrained between the granules in the Transfertube.

A Transfertube consists of a polypropylene plunger in a plain 6 mm diameter polypropylene tube, and could comfortably hold one gram of plastic granules. There were plenty of tubes available, so batches of them were loaded in advance. The granules varied sufficiently so that the weight could be adjusted by selecting the last few particles. It was adjusted to within the indicator line on the balance, which has a width equivalent to 6 mg.

FIGURE 11

Method of addition of plastic to reactor



3.4 Method of Sampling Vapour Products

3.4.1 Total Collection In an attempt to collect as near as possible the whole of the vapour products of pyrolysis, a method was developed of great simplicity, but which proved very effective.

The exit vapours were passed out of the apparatus via a downward vertical tube. Just prior to pyrolysis, a 2.5 litre winchester pattern bottle (previously purged with nitrogen) was placed so that the exit tube passed well down into it. Vapours were then collected by upward displacement of nitrogen. Because of the condensables in the vapour, it was visible as a heavy fog gradually filling the bottle rather as a liquid would. During the collection process, the bottle was lowered at intervals so that the level of this fog in the bottle was always below the exit tube (to produce as little disturbance as possible). When the bottle was withdrawn from the tube, it was capped in the face of the exit purge to limit the entry of air. The bottle was shaken, and kept overnight before samples were withdrawn for analysis. This allowed condensable material to deposit on the walls of the bottle, and the vapour to become homogeneous by diffusion.

It will be appreciated that too short a collection time would result in a loss of product as well as perhaps a less correct overall composition. Conversely, an extended collection time produces the risk of material being purged out of the bottle by the continuing flow of nitrogen from the exit tube. Naturally, the bottle must be larger than the volume to be collected.

These factors were examined in preliminary runs (which also served to develop techniques of analysis). Observations of gas production versus time suggested that better than 95% of the yield was collected in 7½ minutes, and that losses due to purging out became significant after 15 minutes. Accordingly, a time period of 7½ to 10 minutes was most generally used. The collection time was supported by direct visual observation of the fog in the bottle.

3.4.2 Time Interval Sampling For studies of gas flow and composition variation with time, a more conventional method of sampling was adapted for the purposes of the work. As sample containers, glass medical-pattern screw-top bottles were used, fitted with polypropylene double-seal caps. These had a nominal (liquid) capacity of 50 cm^3, a total (vapour) capacity of 56 cm^3. As in the total collection method, the bottles were purged with nitrogen before use.

To take samples, a bottle was simply uncapped and placed over the outlet tube so that it was purged by the vapours coming out of the reactor. After preliminary runs had indicated roughly the pattern of flow-rate with time, the sampling time was adjusted so that the bottle would be purged at least twice, but not more than five times. The sampling time thus varied from 10 seconds (during the first surge of a high temperature pyrolysis) to 60 seconds (during the final tail-off of a low-temperature pyrolysis). Generally, however, sampling periods of 15 seconds were used during the initial surge (the first 3 minutes) and periods of 30 seconds during the decay of the hydrocarbon flow. For plotting of results, it was assumed that the vapour composition in the bottle was more representative of the later half of the sampling period than of the first half, so the values could not be taken as average over the collection time. The composition was therefore plotted with a time co-ordinate at two-thirds through the sample time. For example, a sample collected between 60 and 75 seconds after commencement of the run was given a time value of 70 seconds from the start. This was an arbitrary judgment, which however seemed more reasonable than using the middle of the time period, and was consistently used in interpreting experimental results.

As in the total collection method, the exit tube was slowly withdrawn from the bottle, and the bottle promptly but smoothly capped. Analysis was normally carried out on the day following the experiment for the reasons which have already been given. Interestingly, the sample was quite stable in the bottles used: the composition and concentration were very much the same even after several weeks, so it is unlikely there were any serious losses overnight.

3.5 Analytical Methods

3.5.1 Mass Spectrometry The instrument used was a Centronic MGA 200. This is a mobile unit with integral vacuum pumps, which draws vapour samples at a rate of about 20 cm^3 min^{-1} through a flexible capillary inlet. It is a quadrupole system operating up to mass 200 with better than unit resolution. In its normal mode of operation it responds to fixed pre-set masses, but an attachment supplied by the manufacturer was used to give conventional mass spectra, recorded on a Servoscribe 20 cm chart recorder. The mass spectrometer is capable of performing several scans per second, but the time necessary for recording was limited by the speed of response of the chart recorder (0.1 second for full scale deflection). Scans were therefore done no faster than 5 mass units per second.

It had been hoped that this instrument could be used to monitor the reactor outlet continuously. In practice, the capillary inlet became blocked by condensing and polymerizing material from the vapour, despite the traps which were used. Not only was this inconvenient, but it also put an expensive instrument out of commission. Furthermore, the alteration in flow rate caused by a partial blockage would alter the effective sensitivity and hence the calibration of the instrument.

The mass spectrometer was therefore only successfully used to give a mass spectrum from a few samples in 2½ l bottles obtained by the 'total collection' method previously described. Atmospheric air was used for mass calibration: since it is in the nature of quadrupole instruments to give a linear mass output, this was very easy.

To run a spectrum, the bottle was uncapped and the flexible capillary from the spectrometer hung about half-way into the bottle. Reproducible spectra were then obtainable for several minutes before dilution by atmospheric air became significant. Blockages did not occur, because the bottle had been allowed to stand overnight, permitting condensable or unstable material to deposit on the walls.

The principle utility of these spectra was as a check of the identification of components as assigned to peaks on gas chromatograms.

3.5.2 Gas Chromatography The instrument used was a Pye 104 dual column oven with temperature programming control. Flame ionization detectors were used for almost all chromatograms, because of their well-known utility for hydrocarbons. A katharometer (thermal conductivity) detector was used on a few occasions to look for those possible components for which the flame ionization detector is insensitive (H_2 , CO , H_2O , O_2 , CO_2). Chromatograms were recorded on a Kent 10 inch 1 mV chart recorder, and peak areas simultaneously calculated by means of a Kent Chromalog electromechanical integrator in parallel with the recorder.

A variety of columns and conditions were used to study the rather complex vapour from pyrolysis, particularly during the early part of the work when the general nature of the products was being determined. With one exception, all columns were ¼ inch x 5 foot stainless steel. A squalane column at 60 °C isothermal was used in initial tests, clearly showing components up to C_7 and giving a general idea of their distribution, but not fully resolving the C_1 to C_3 gases. An advantage of the flame ionization detector is that its response to hydrocarbons is virtually proportional to the carbon content, so that an estimate of yields could be made without complete resolution of peaks.

Once the decision had been made to concentrate on the C_1 to C_4 hydrocarbons, Poropak 'Q' was used as a column packing. The most usual temperature program was to hold at 80 °C for 4 minutes, to elute methane, ethylene and ethane, then rise at 20 ° per minute to 160 °C , then hold for 20 minutes to purge. In this program, propylene and propane were incompletely resolved, as were C_4 components, though the general ration of the unresolved peaks was visible. On a few occasions the initial hold period was made 60 °C and held for 10 minutes in order to resolve propylene and propane. For those samples with significant amounts of higher molecular weight material, the program was extended to 200 °C and purge time made 30 minutes. A higher starting temperature was used on some occasions to give a sharper benzene peak at the expense of resolution of some lighter components.

A Poropak 'N' column (9 foot glass) was used at 50 °C (then programmed to 150 °C to purge) in a special check for acetylene, which it can separate from other C_2 gases.

In all cases a flow rate of 40 cm^3 min^{-1} of 'white spot' nitrogen was used as eluent (measured by bubble flow-meter). Samples were injected with a Hamilton 0.5 cm^3 gas syringe with a PTFE piston in a glass barrel. Sample sizes from 0.1 to 0.5 cm^3 were used, the standard one being 0.2 cm^3.

3.5.3 Standards Initial identification of peaks on chromatograms and mass spectra was done on the basis of experience and conventional reasoning. The conclusions were checked by performing similar analyses on known compounds. The following materials were available within the Department: air, water, carbon dioxide, hydrogen, methane, ethylene, acetylene, propane, butane, hexane, hex-1-ene, heptane, benzene, toluene. It was discovered that a useful check mixture was readily available in the form of mains (natural) gas. According to the West Midlands Gas Board Regional Laboratory, a typical composition is: CH_4 = 92.5%, C_2H_6 = 3.43%, N_2 = 2.71%, C_3H_8 = 0.93%, C_4H_{10} = 0.23%, CO_2 = 0.13%, C_5 etc 0.07% by volume.

Following the initial identification and approximate quantification of the vapour components, two commercially prepared standard mixtures of hydrocarbons in nitrogen were purchased from Jones Chromatography Ltd. One was 1.05% methane, 0.96% ethane, 1.52% propane and 0.86% n-butane. The other was 1.4% methane, 1.0% ethylene, 0.93% propylene and 1.0% but-1-ene, all by volume. The amount of ethylene in the total collection sample bottles was typically about 2%, so that the standards and the samples were directly comparable with no further preparation. For calibration, therefore, the standards were simply injected as if they were another sample during every series of chromatograms. Usually this was done near the start and near the end of a series, to check that the detector response had not changed. For the kinetic runs, the hydrocarbon concentration in the samples ranged from well above the standards to well below. This was mainly dealt with by altering the attenuation on the gas chromatograph amplifier, but keeping the volume injected the same.

The gas standards were supplied in pressurized cans rather like domestic aerosol sprays. To take a sample of the gas within, the gas syringe was used. Its needle tip was placed just in the can's discharge orifice, and gas slowly drawn into the syringe while the can button was depressed to produce a stream of the gas mixture. Care was taken to flush the syringe and needle with the mixture.

For calculations, the samples were always compared with standards run the same day, although the detector response did not vary by more than a few per cent over the two years in which the standards were in use. The presence of methane in both standards was a particularly useful cross-check. Apparent disagreements between the standards were about the same as the general accuracy of the chromatographic method, i.e. a variation of no more than 5%. The certified composition of the gas cans was consistent with the expected response factors for the components and their peak areas.

3.6 General Description of a Pyrolysis Experimental Run

The nitrogen cylinder pressure regulator and the inlet control valve were adjusted to pass a purge of 200 cm^3 min^{-1} through the reactor. The furnace controller was set to a temperature somewhat higher than was wanted for the salt, and the furnace switched on. The furnace was allowed to come to equilibrium, as indicated by the controller meter, and the stirrer set in motion at about 300 r.p.m.. After 15 minutes the salt temperature was measured, and again after a further 15 minutes. If these readings were the same, the apparatus was judged to be in a steady state. Otherwise, further 15 minute intervals were used.

The nitrogen flow rate was checked and adjusted if necessary, and the stirrer speed set at the required value, using a hand-held tachometer. The sample bottle(s), the funneled glass tube, a stopclock, a notebook and a pre-filled Transfertube containing one gram of plastic, were placed conveniently to hand. The salt temperature was measured with a potentiometer. This, incidentally, is the reason that results are sometimes given at temperatures which are not round figures. The controller did not act directly from the thermocouple in the salt, and in any case was not relied upon for measurement, merely control.

The actual salt temperature was, however, measured by the best available means. Once the system had equilibrated, there was no point in disturbing it merely for the sake of round figures.

Once the apparatus and the operator were prepared, the sample collection bottle was positioned with the reactor outlet tube passing into it. The inlet gate valve was opened, and the glass tube inserted. The Transfertube was put into the top of the glass tube, and the granules expelled. The glass tube was immediately withdrawn. The gate valve was closed, and at the same time the stopclock was started.

The sample collection bottle was watched, and slowly lowered during collection, and after 7½ minutes was removed from the outlet tube and capped. The outlet tube was rotated on its fitting through 180 ° so as to form a chimney venting any excess vapours to the top of the fume hood. The apparatus was purged for at least 10 minutes before adding a further sample of plastic. The first sample of the day was always rejected, and results only counted from subsequent pyrolyses.

For a series of different stirrer speeds at one temperature, the 10 minute purge period was considered sufficient to set up a new equilibrium. For changes of temperature, at least one hour was allowed.

For isothermal experiments with varying stirrer speed, the following procedure was found to be convenient. The stopclock was started (t = 0 min) as a gram of plastic was added, and the vapour sampled for $7\frac{1}{2}$ minutes (from t = 0 to t = $7\frac{1}{2}$ min). This sample was rejected. At the same stirrer speed, a further gram of plastic was added (at t = 20 min) and the vapour collected (from t = 20 to t = $27\frac{1}{2}$ min). The speed was then changed to a new value. A further gram of plastic was added at t = 40 min, and so on. Thus each sample would have the same carry-over (if any) from the previous one. Furthermore, any activation or de-activation of surfaces in the purged reactor was carried out by the first sample. This could be particularly important if the apparatus had not been used for some time, and might render the first sample very anomalous.

For time interval sampling, some dexterity and some concentration were required to take samples as well as to add the plastic. The bottles were pre-labelled and placed in order in groups. The first group (being taken at the shortest intervals) was placed by the outlet tube, with their caps loose but on. The intended sampling times were written down on a piece of paper. These were easy to remember round figures such as 5 - 15, 20 - 30, 40 - 50 seconds.

The clock was started as the gate valve was closed, following addition of plastic. The bottles were then placed on the outlet tube to conform with the intended sampling times. In the event of any fumbling, the programme was simply put back 5 or 10 seconds. After the first few samples, the interval between bottles increased to 15 seconds, allowing time to note down any such change. The final group of bottles was for samples with an interval of a minute or more between them. This could be carried out comparatively leisurely, and allowed the writing down of actual times, or checking of temperature and flow-rate between samples.

4 RESULTS

4.1 General Observations

The cautious addition of increasing amounts of polyethylene granules to a nitrogen-blanketed melt, first in an open bath and later in the closed apparatus, gave a good idea of the pyrolysis behaviour which was to be studied. The following points were noted:

(a) Quantities of up to 5 grams could be added without explosions, violent splashing or other undesired effects.

(b) Copious white fumes were produced. These did not appear to be soluble in water and were very difficult to condense. When allowed to settle, they produced a thin film of waxy grease. A smell reminiscent of various unsaturated volatile hydrocarbons (acetylene, terpenes etc) was quite noticeable.

(c) When the vapours from the pyrolysis region were passed through an acidified solution of aqueous potassium permanganate ($KMnO_4$) the colour was discharged, suggesting the presence of significant amounts of unsaturates.

(d) If the amount and rate of production of the visible fumes could be taken as some indication of the pyrolysis process, then the reaction commenced after a delay of about ten seconds, reached some kind of maximum in about half a minute, and had substantially ceased in ten minutes.

(e) The temperature of the stirred salt did not vary greatly during pyrolysis of the plastic, although there was a noticeable drop in the temperature of the reactor lid, as shown by a contact dial thermometer.

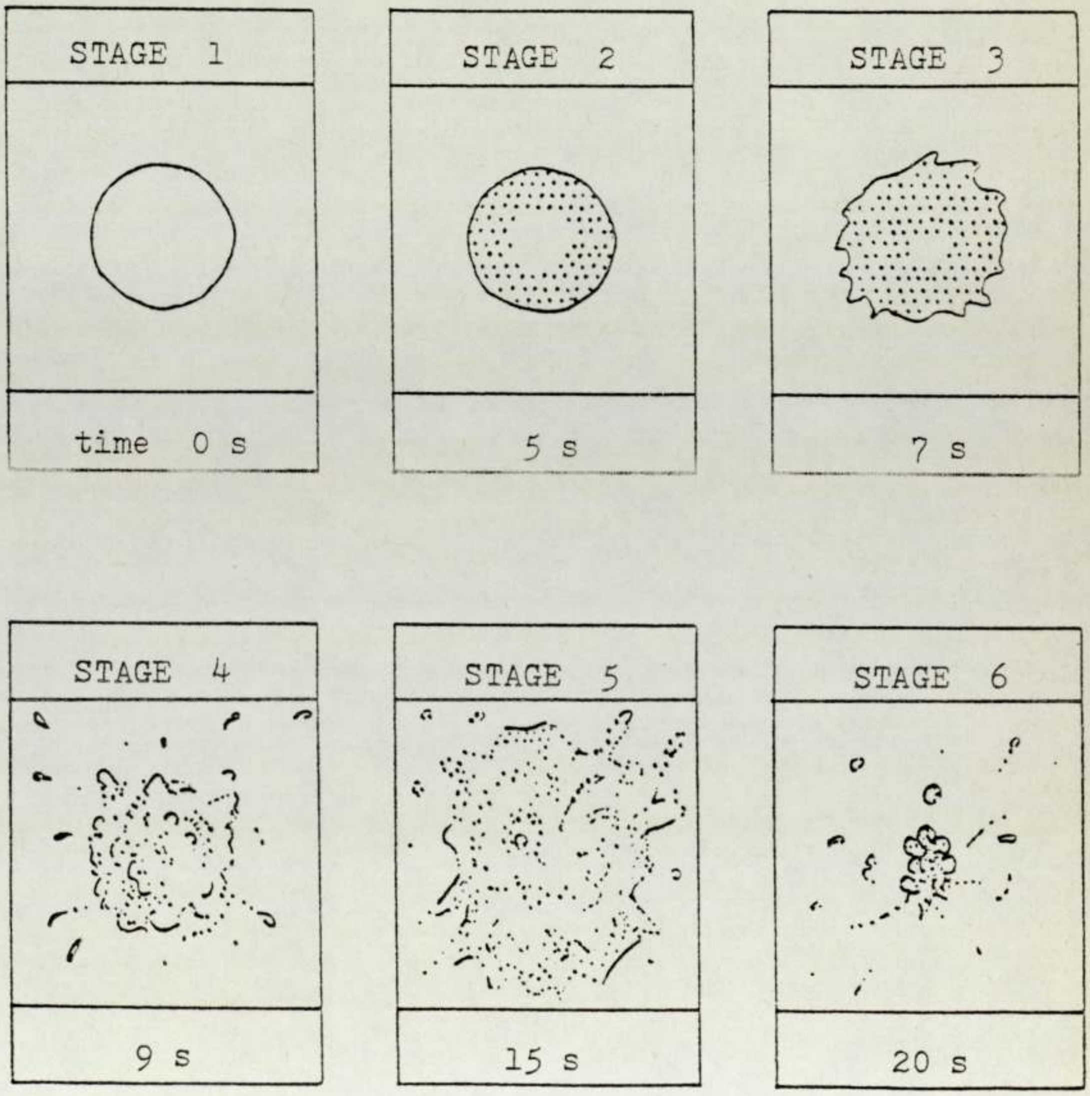
4.2 Residence Times of Solid Particles

The behaviour of single particles of plastic on a static bath of salt at 550 °C under a nitrogen blanket was observed by means of a mirror. A typical sequence is depicted in FIG. 12, and will be described as follows. Stage 1: initially the white opaque particle rests quietly on the melt. Stage 2: after a few seconds, the outer portion of the polyethylene has become hot enough to be transparent, but the centre is still opaque. Stage 3: in a further couple of seconds, the particle loses shape as the outer edge becomes liquid, but a comparatively cool opaque centre is still visible. Stage 4: a second or so later, the centre finally becomes transparent, at about the same time as gassing commences. Stage 5: the particle spreads out to about twice its diameter as a seething shapeless mass for the main pyrolysis stage. Stage 6: by about 20 seconds, this has been reduced to a small bubbling centre which vanishes altogether about 25 seconds after the addition of the granule to the melt.

For granules of similar size, the average time for the onset of gassing was 8.6 seconds for polyethylene, 9.0 for polypropylene and 4.0 for polystyrene. The average time to complete volatilization was about 26 seconds for polyethylene, 32 for polypropylene and 14 for poystyrene. The sessile effect often drove particles to the wall before these processes were completed.

FIGURE 12

Observed changes during the pyrolysis of a single granule of polyethylene on an unstirred salt melt at 550 °C



4.3 Residence Time in the Vapour Phase

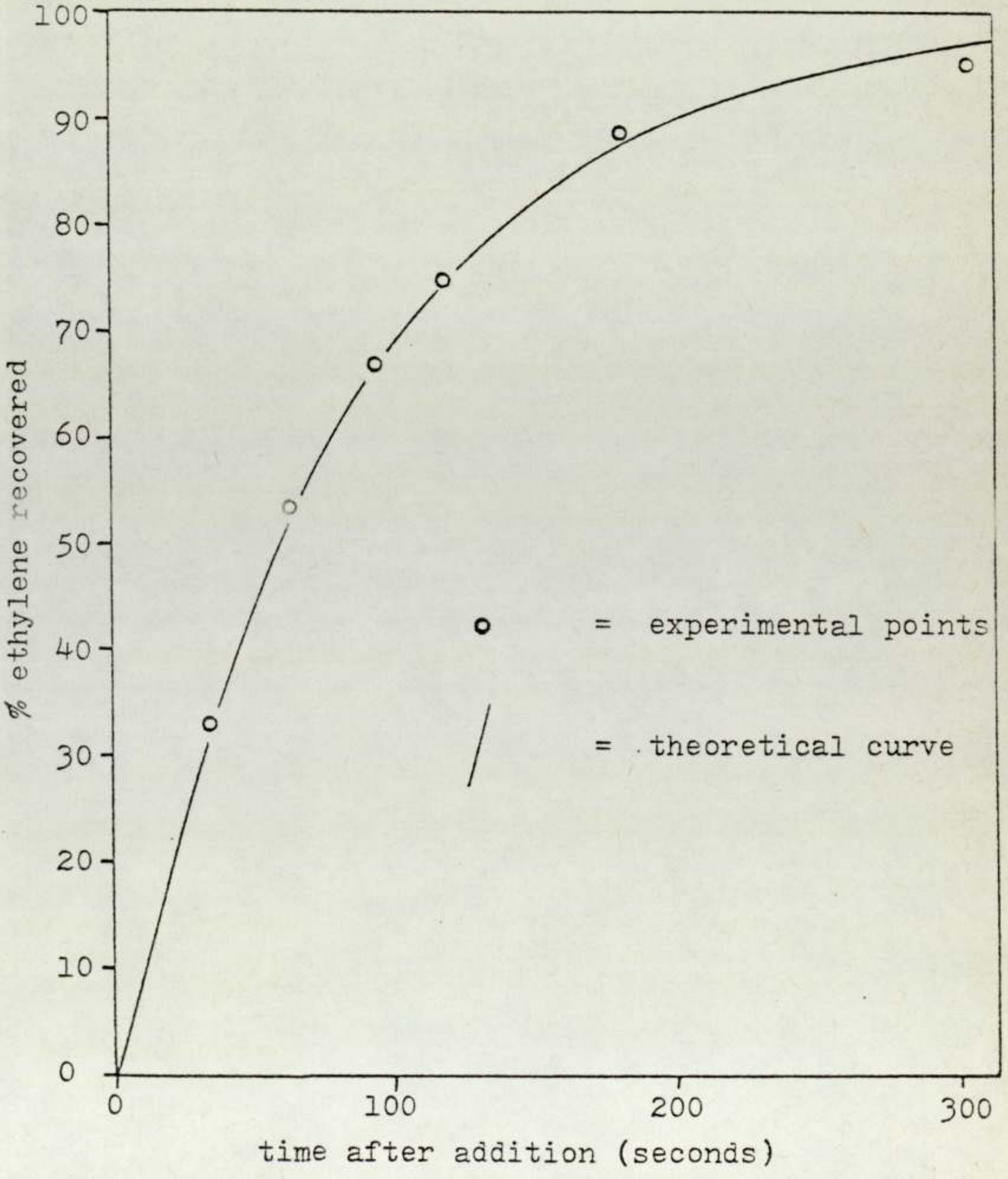
Once the general amounts and types of products, and the time-scale of the pyrolysis process had been found, the residence time of material in the head-space of the reactor was examined. To simulate the production of gas from plastic granules, a 50 cm^3 aliquot of ethylene was injected into the reactor headspace over a period of 15 seconds, via the nitrogen inlet. The general conditions were chosen as those typical of many experimental runs, namely salt temperature 600 °C, stirrer speed 300 r.p.m., nitrogen purge 200 cm^3 min^{-1}.

The gas outflow was then sampled at intervals and analysed by gas chromatography, both exactly as in the other kinetic experiments. The concentration of ethylene in the samples collected was then used to calculate the total amount which had been emitted by the time period represented by each sample. This cumulative emission is shown in FIG. 13 compared with a curve drawn for a 'perfect mixing' model, that is, an exponential curve based on a 'half-life' of 60 seconds. The start time is taken as the middle of the injection period.

As can be seen, there is excellent agreement for the first part of the curve, although the half-life of exactly one minute must be counted rather fortuitous. It will be

FIGURE 13

Test on headspace gas residence: recovery of an added aliquot of ethylene compared with a theoretical model



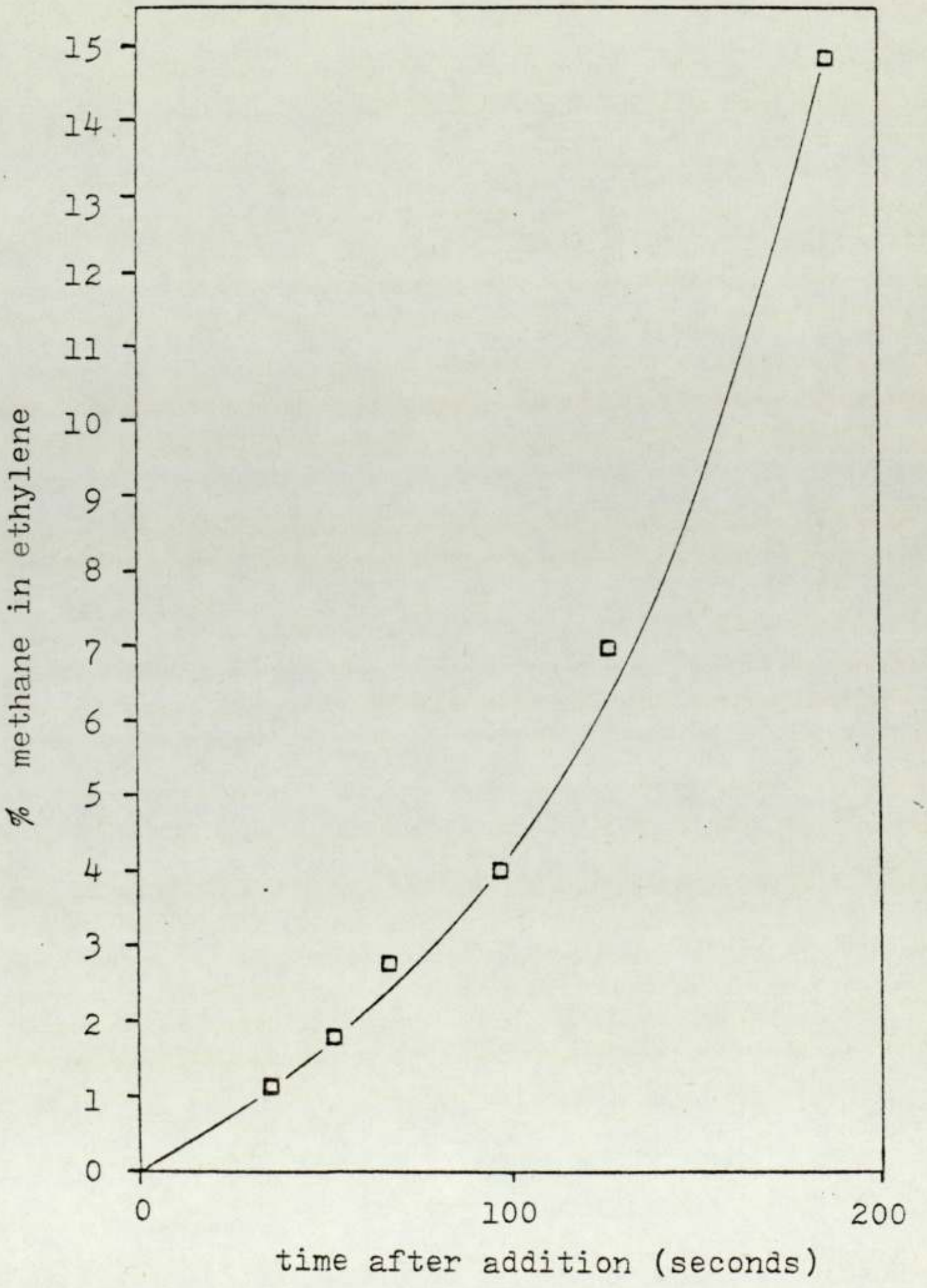
readily appreciated that this is a cumulative graph, in which each experimental observation represents the difference between adjacent points. That is, the amount of ethylene in the samples gets smaller as the total emitted gets larger. The concentration of ethylene in samples subsequent to those shown is so small it is clear that such additions can never bring the cumulative curve to 100 %.

The conversion of ethylene to other materials would account for this loss. Only methane was observed in any quantity, the amount relative to ethylene increasing with time in the reactor, as is shown by FIG. 14. The accumulated ethylene accounts for 95 % of that added. The accumulated methane accounts for a further 3 % if it is assumed that each molecule of ethylene lost gives one molecule of methane (plus hydrogen and carbon), or 2 % if it is assumed that the methane contains all the ethylenic hydrogen (i.e. the ethylene disproportionates to methane and carbon).

Both the addition of the ethylene and the analysis by gas chromatography are subject to errors of the order of 2 %, so the above mass balance is very reasonable. The traces of C_3 hydrocarbons observed were insignificant.

FIGURE 14

Conversion of ethylene to methane with time over a stirred salt melt at 600 °C



4.4 Identification of Products

The feedstock used, polyethylene, contains only the elements carbon and hydrogen, apart from any traces of impurities. Both temperature and pressure were insufficient for any plausible reaction with the nitrogen purge, and air was excluded as much as possible. Hence the only possible products of pyrolysis were carbon, hydrogen and hydrocarbons. Since there are, however, literally millions of different hydrocarbons, the identification of products is at first sight very formidable.

The products naturally fall into three rough groups. Firstly, that material which is involatile and stable at the temperature of the molten salt. This essentially means carbon. It was not practicable with the apparatus and methods adopted to determine the carbon residue from each pyrolysis, only at the end of the experiments to see how much had accumulated. This was not a problem, since it turned out to be a very minor product. Secondly are the substances which have very low vapour pressure at room temperature: the oils and waxes, say C_{10} upwards. Thirdly are those materials which are either gases or liquids with a high vapour pressure at room temperature, namely hydrogen and hydrocarbons to say C_9 . The distinction between the second and third groups is of course far from exact.

Little attempt was made to identify the components of the portion of higher molecular weight material, which appeared as a white wax at lower pyrolysis temperatures and a yellowish grease at higher temperatures. Because of deposition on the interior of the outlet pipe and the small-particle mist which usually appeared, it was not even possible to include this portion in any meaningful mass balance for an individual run.

Similarly, it was not felt worthwhile identifying the more reactive vapour components (polyenes and the like), i.e. those which would polymerize or react in a few hours. This was because for commercial use, only material which can readily be transported is likely to be of interest. As has been mentioned before, the tactic adopted was to leave the samples overnight, to allow any condensation of liquids or reactions to occur, leaving a reasonably stable vapour mixture. Furthermore, the initial experiments suggested that gases such as ethylene might be produced in useful amounts. Any industrial application would almost certainly be concerned with the major rather than the very minor products. Apart from gases such as ethylene, propylene and butadiene, the other commercially significant products which might be expected are the aromatics, which would be detectable in the vapour phase.

Attention was therefore paid to the stable vapour mixtures resulting from pyrolysis, which were examined by gas chromatography and mass spectrometry. Where possible, known substances were used for comparison. In other cases, interpolation was applied, using the known characteristics of the method, and cross-checking between methods.

Up to twenty partially resolved peaks could be observed in some chromatograms, as is illustrated by FIG. 15. It is important to note the change in scale. For example, peaks 'j' and 'n' are of similar size, but 'j' represents a greater mass because 'n' has been amplified five times relative to 'j'. TABLE 3 gives a probable identification of the peaks in the chromatogram, and their relative amounts. This has been based on electronic integration which was not dependent on the chart display, and treated all peaks on a common basis. It is notable that 50% of the vapour is accounted for by C_1 to C_3 gases, 15% by C_4 and 5% by what is probably benzene.

A comparison of a mass spectrum of pyrolysis vapour with known materials is given as FIG, 16, in which the identification of benzene is particularly convincing. By such combinations of techniques, the following were identified as major products: hydrogen, methane, ethylene, ethane, propylene, propane and benzene. The C_4 and C_5

FIGURE 15

Chromatogram of typical pyrolysis vapours

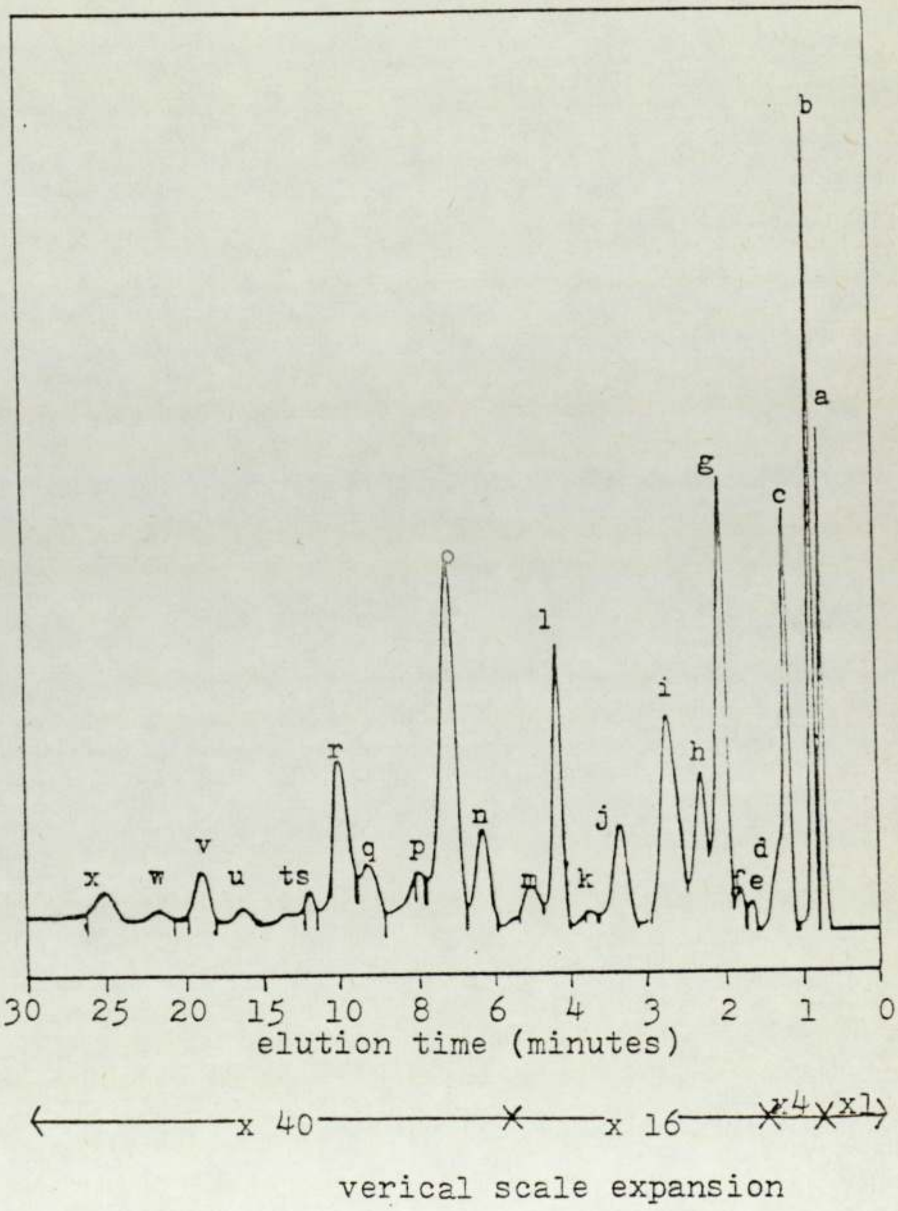


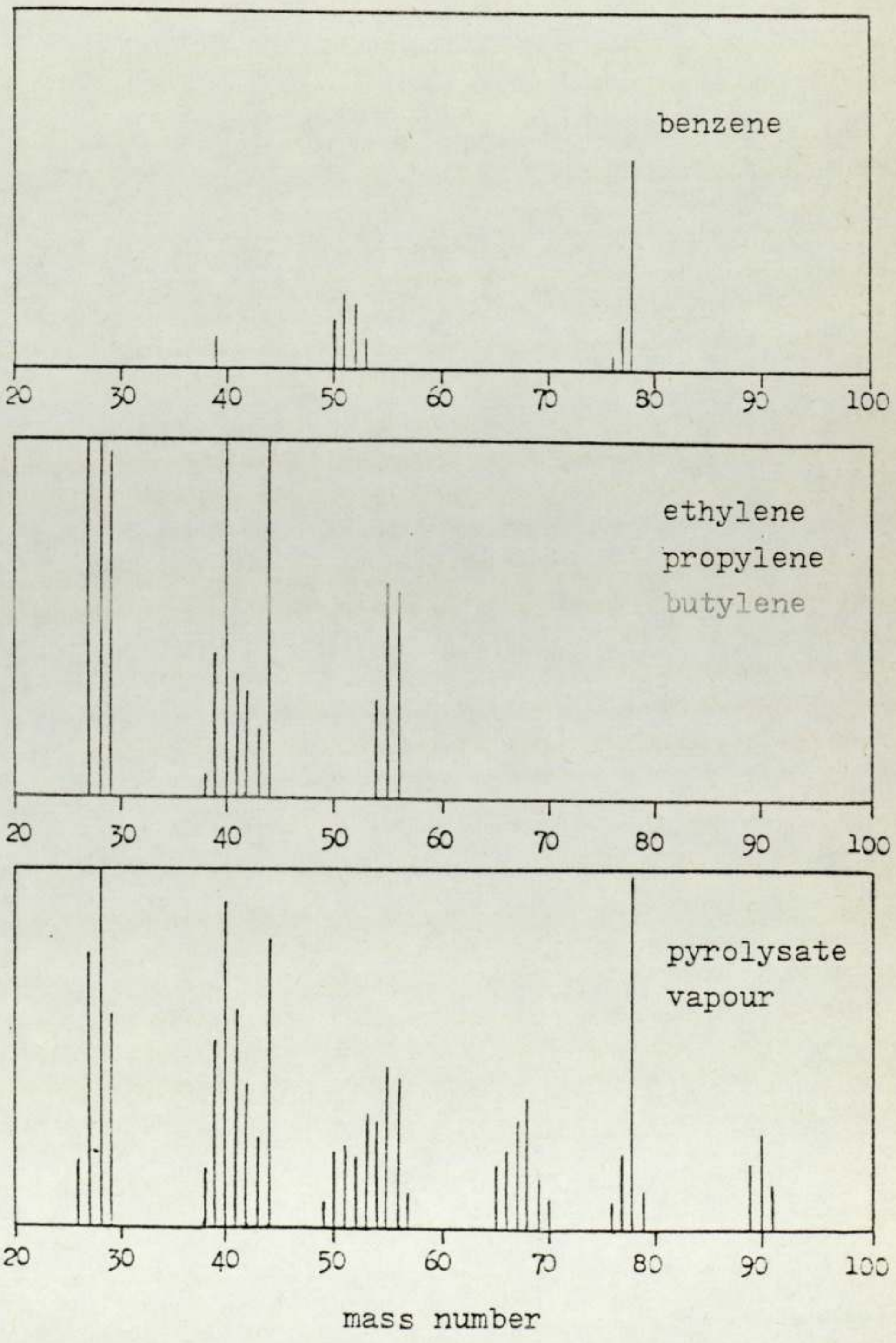
TABLE 3

Probable identification of chromatogram peaks shown in Figure 15 (total peak area = 100)

peak	area	assignment
a	32.1	methane, ethylene, ethane
b	18.9	propylene, propane
c	14.9	1-butene, isobutene, butadiene
d		n-butane
e	0.2	trans-2-butene
f	0.3	cis-2-butene
g	5.3	1,4-pentadiene
h	2.0	1-pentene
i	4.3	isoprene
j	1.8	cyclopentadiene
k	0.05	1,3-pentadiene
l	6.4	cyclopentene
m	1.1	cyclopentane
n	1.1	1,5-hexadiene
o	5.2	benzene, cyclohexene
p	0.05	
q	0.8	
r	1.8	methylcyclohexene
s	0.3	
t	-	
u	-	
v	1.6	heptadiene?
w	1.8	
x		

FIGURE 16

Mass spectrum of pyrolysate vapour compared with spectra of benzene and a mixture of olefins



hydrocarbons were identified as groups, though their exact components were not discriminated. The following were tested for specifically (by gas chromatography) but found to be essentially absent (i.e. less than 1% of the ethylene present): acetylene, carbon monoxide, carbon dioxide, oxygen, water. The single component present in the greatest amount was ethylene by mass.

Because of their predominance, the hydrocarbon gases to C_4 were taken as the main assessment of pyrolyses, and a gas chromatographic technique was adopted to separate and measure these for the main runs.

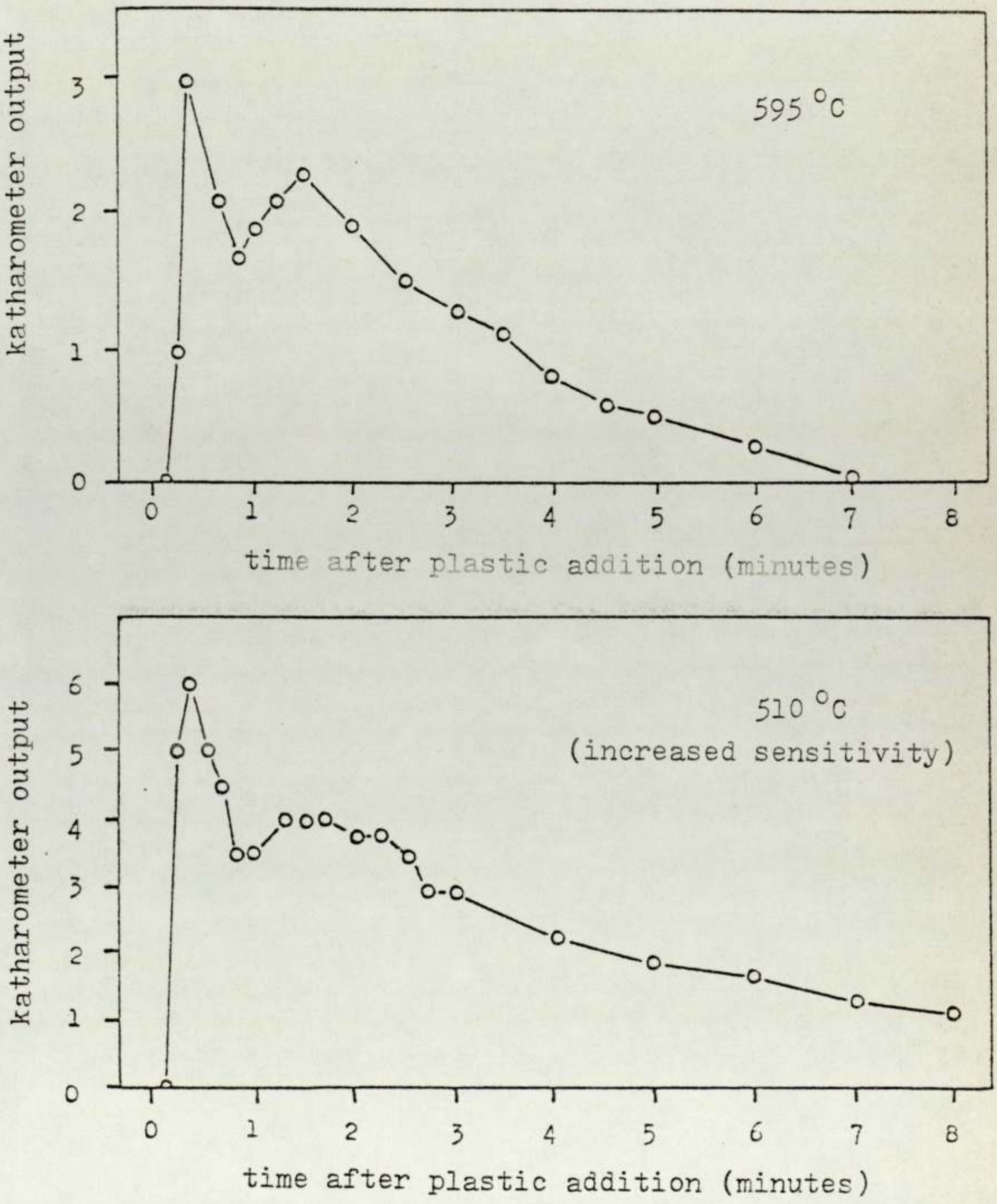
4.5 Changes in Reactor Outflow with Time

One of the earliest experiments utilized a simple katharometer detector in the gas outlet. This reacts to material other than the nitrogen purge, by its different thermal conductivity affecting the cooling and hence the resistance of an electrically heated wire in the gas stream. The measured change is approximately proportional to the amount of material present in the nitrogen. The readings obtained in two runs with this device are shown in FIG. 17.

The sensitivity of the output meter (mirror galvanometer) was increased for the second of the two runs. The failure of this graph to return to the baseline was ascribed to the deposit of high molecular weight material on the wire. Such deposits were clearly visible, and prevented further use of the technique. In both cases, however, it is clear that there is an induction period before any product appears in the outlet tube, the delay being about 10 seconds. There is then an initial surge, followed by a drop in concentration of product before rising to a second maximum, which is followed by decaying in something like an exponential fashion to a negligible amount in about seven minutes. These observations were used to plan the next experiments, in which samples were taken at frequent

FIGURE 17

Changes in hydrocarbon outflow from the reactor with time as indicated by a simple katharometer

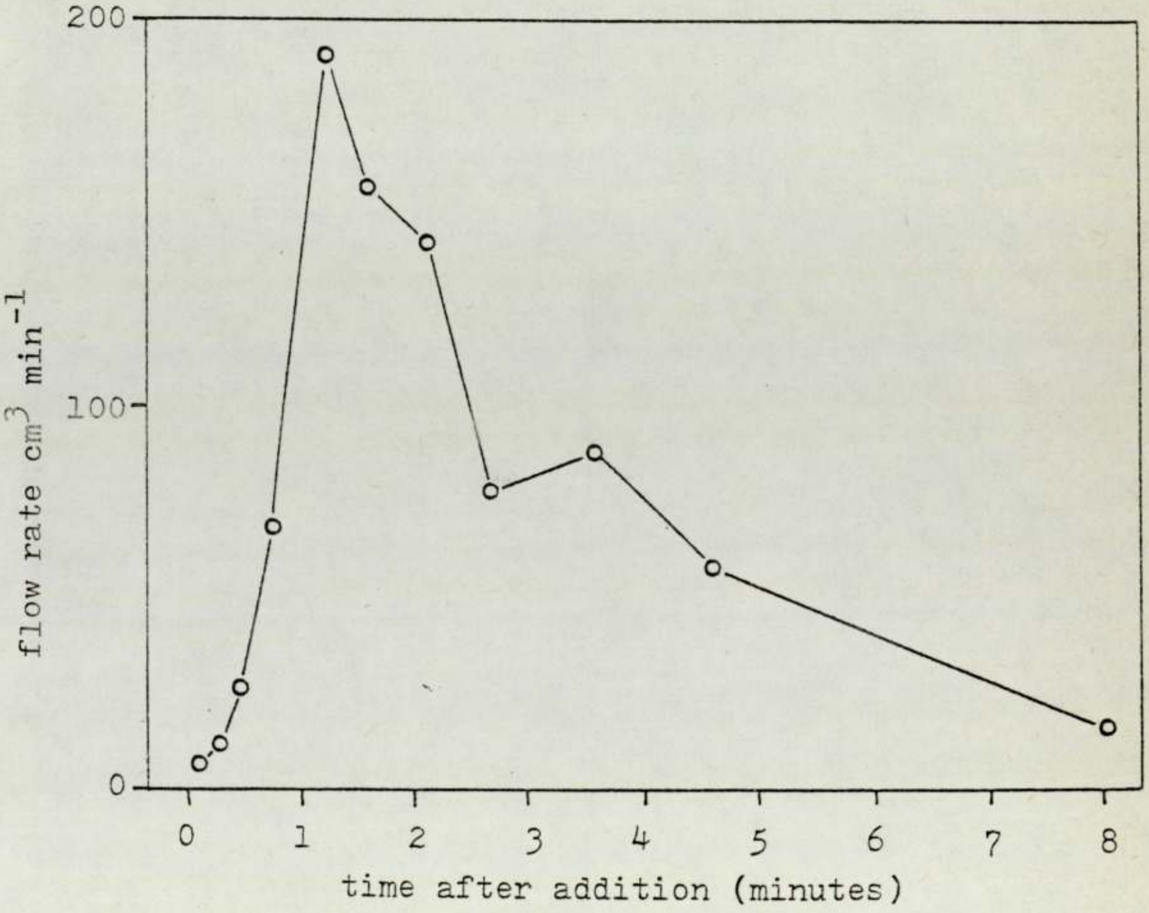


intervals during the initial time period, and less often during the decay period.

The result of one such kinetic experiment is shown in FIG. 18 based on gas chromatographic analysis, by the same technique as is illustrated in FIG. 15. The areas of the peaks were summed and taken as equivalent to ethylene. The flow rate is thus that which would have been observed if ethylene had been the only product. This was very far from the truth, but gave some idea of the magnitude of the actual flow. The fact that methane and hydrogen would give a greater volume per unit mass than ethylene goes some way to compensate for the lower volumes given by the C_3 and higher hydrocarbons.

FIGURE 18

Changes in product flowrate with time. Product vapours as equivalent volume of ethylene.



4.6 Changes in Product Composition with Time

The composition as well as the quantity of outgas was seen to change with time, and can be expressed in a number of ways. TABLE 4 shows the relationship between different carbon number fractions, taken as a percentage of the total detector response up to C_5. It can be seen that after the first half minute, the relative amounts remain approximately constant. It should be noted that because of the lower overall concentrations, the accuracy of the proportions is less as the time elapsed increases. The column used (squalane, 5') did not resolve C_1 to C_2 hydrocarbons.

FIG. 19 shows two partial chromatograms from one of the main series of kinetic runs, using a column (Poropak Q, 5') which did resolve methane, ethylene and ethane. They represent the first two samples, taken 5 to 15 seconds and 20 to 30 seconds after addition of plastic. It can be seen that the first surge of outgas is predominantly ethylene, then the other C_1 to C_4 components increase. Subsequent chromatograms in this run show much smaller relative changes. This behaviour was observed on all kinetic runs.

TABLE 4

Changes in product composition with time. Hydrocarbon fractions as a percentage of total C_1 to C_5.

time seconds	% of total C_1 to C_5			
	$C_1 - C_2$	C_3	C_4	C_5
8	29.8	18.0	18.0	34.2
18	45.3	23.9	21.3	9.2
28	34.3	25.7	21.5	18.5
47	35.8	24.7	21.3	18.3
77	38.2	26.4	22.4	13.0
100	36.8	26.9	22.2	14.1
130	35.6	25.7	20.3	18.4
160	36.7	27.3	20.0	16.0
213	34.6	26.4	18.7	20.3
275	38.3	26.7	17.1	17.9
485	43.6	25.5	13.3	17.6
565	37.9	21.6	12.2	28.3

FIGURE 19

Changes in product composition with time. Comparison of chromatograms for samples after 12 and 27 seconds

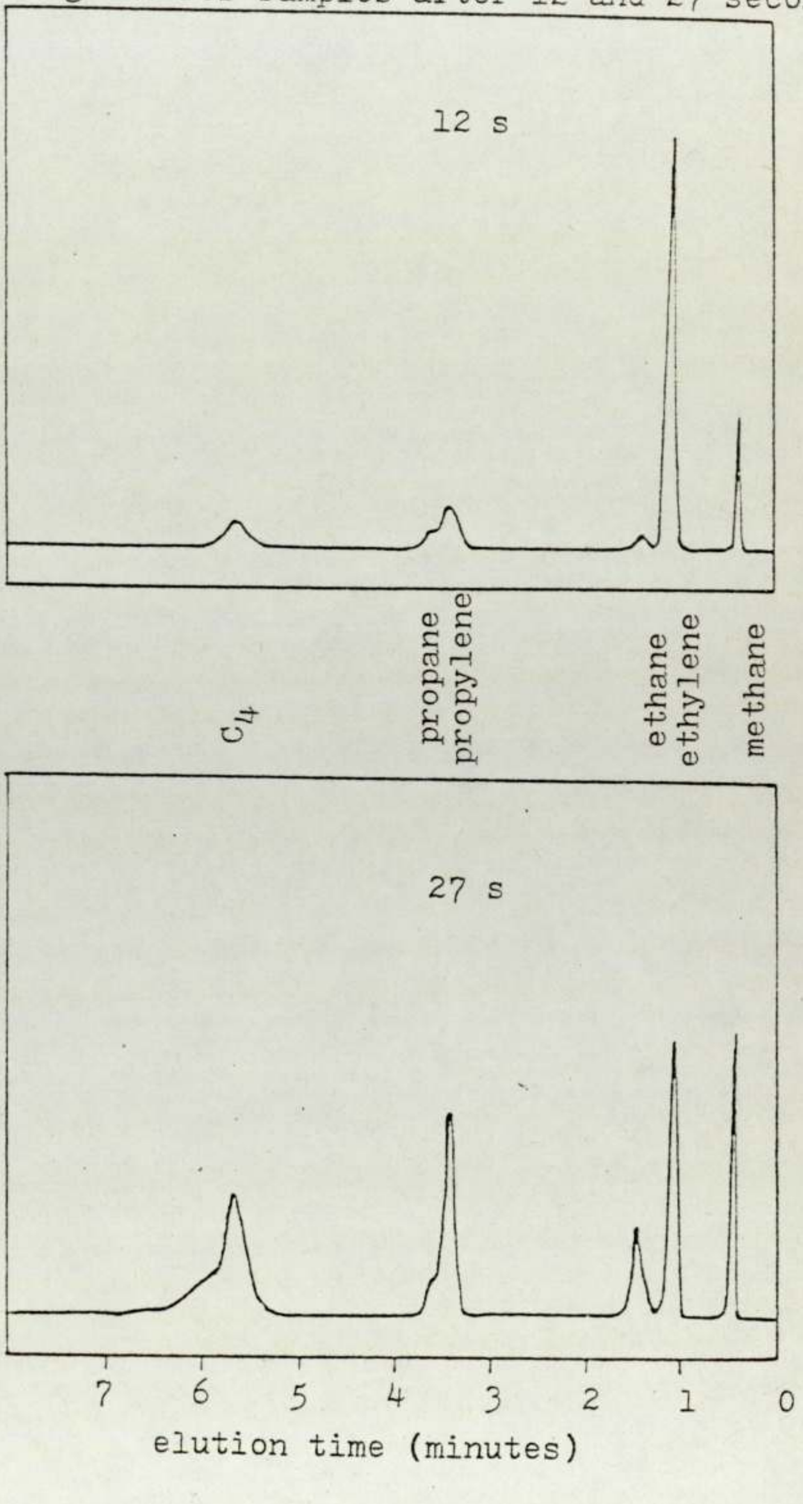


FIG. 20 represents an analysis of results from the same kinetic run, in which the amounts of methane and ethane in the outgas are given as a ratio by volume of the amount of ethylene present. FIGS. 21 and 22 are similar representations from runs at other temperatures. It will be seen that the tendency towards methane increases with both time and temperature, whereas ethane decreases. See also section 4.3 and FIG. 14 for the pyrolysis of ethylene to methane.

FIGURE 20

Changes in product composition with time. Amounts of methane and ethane relative to ethylene in pyrolysate (salt temperature = 608 °C)

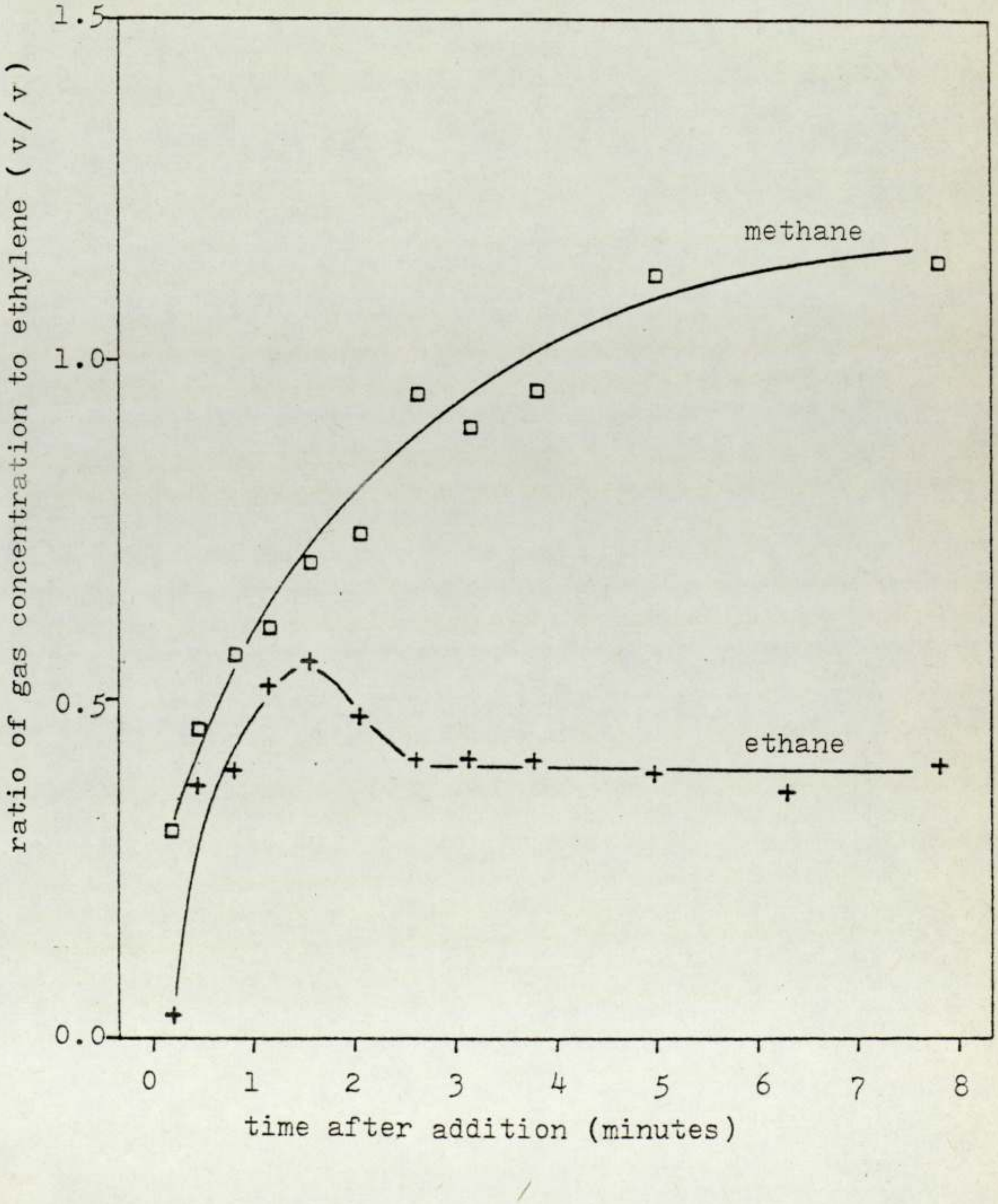


FIGURE 21

Changes in product composition with time. Amounts of methane and ethane relative to ethylene in pyrolysate (salt temperature = 648 °C)

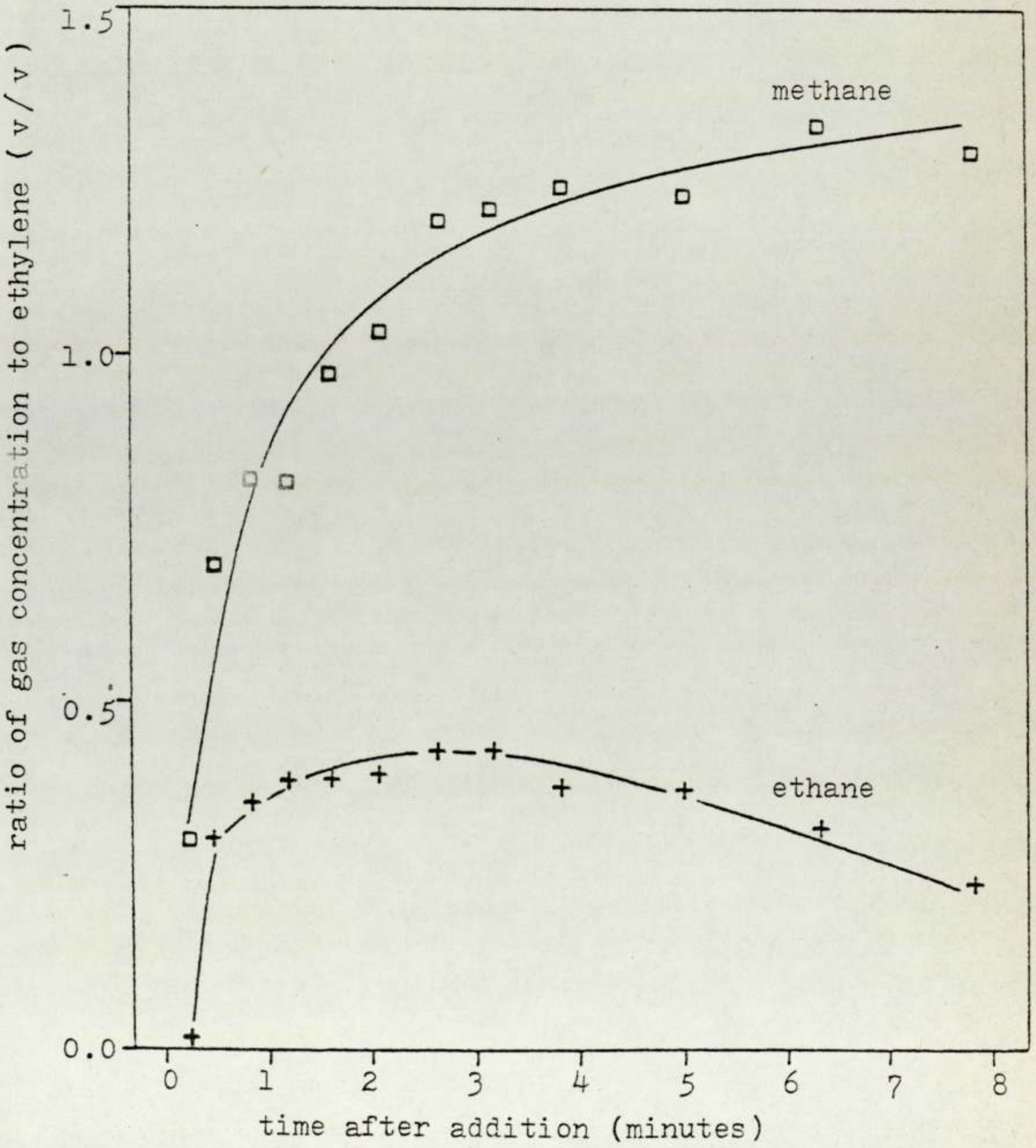
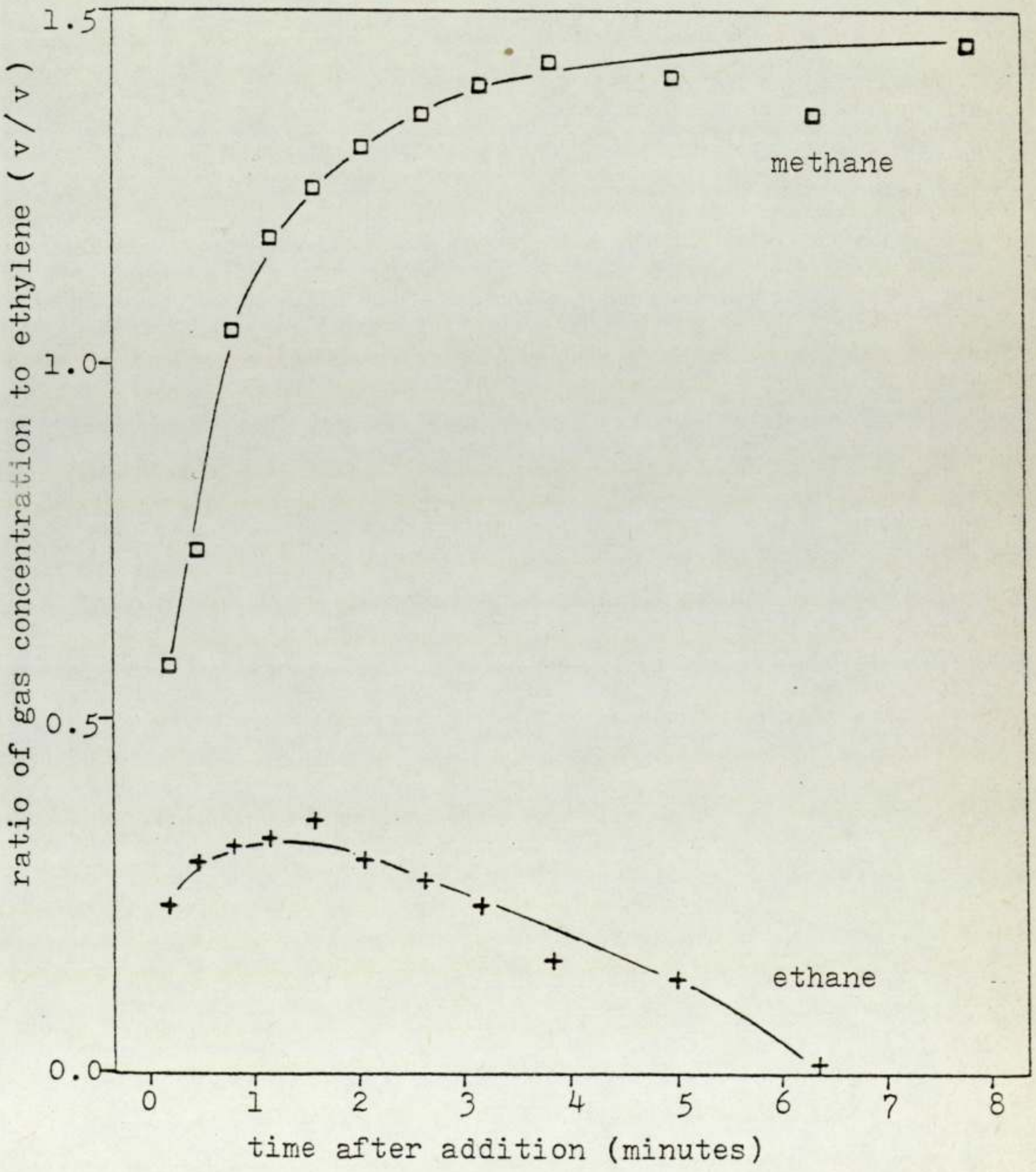


FIGURE 22

Changes in product composition with time. Amounts of methane and ethane relative to ethylene in pyrolysate (salt temperature = 698 °C)



4.7 Effect of Temperature on Pyrolysis

FIGS. 23, 24 and 25 show the mass yield of the different hydrocarbon outgas components to C_3 as a percentage of the polyethylene input, at fixed stirrer speeds. FIG. 26 similarly shows the total gases to C_4 as a function of temperature. These results come from the 'total collection' method of sampling the vapour products.

The production of all hydrocarbons shown here increases with temperature up to 600 °C or so. After this, ethylene and methane continue to increase (though tending to level off) while the amounts of ethane and propylene/propane decrease. The fall-off is particularly dramatic in the case of the C_3 fraction (which was several times tested so as to resolve its components and found to be predominantly propylene with around 10 % propane). If ethylene and propylene were to be commercially produced from such a reactor, these graphs suggest the optimum salt temperature would be in the region of 610 °C.

There was a noticeable increase in the amount of benzene formed above 600 °C, but for practical reasons, this was not quantified. Similarly the chromatographic peaks ascribed to cyclic C_5 and C_7 were more pronounced at temperatures approaching 700 °C.

FIGURE 23

Changes in yields of vapour products with temperature (stirrer speed = 333 r.p.m.)

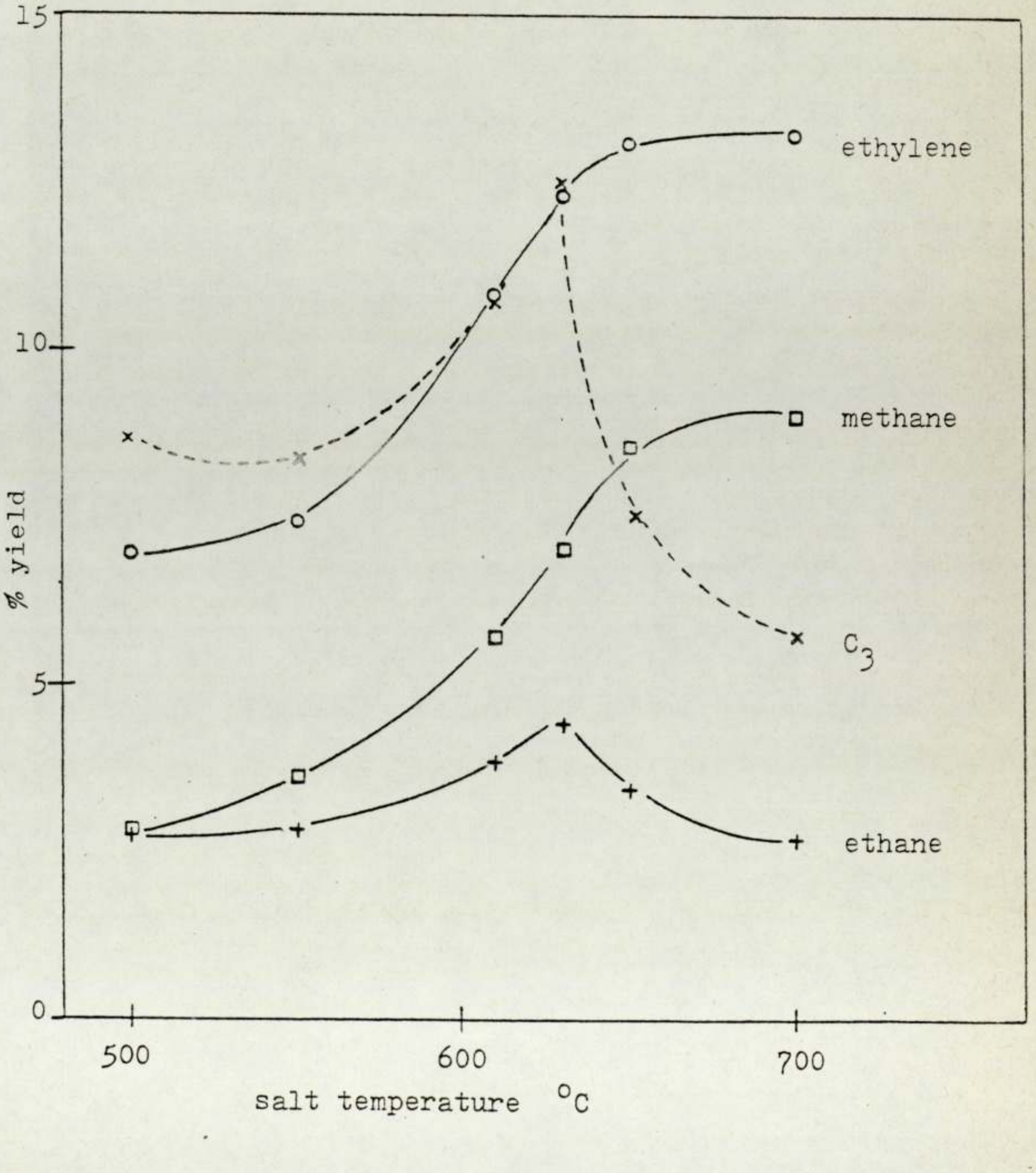


FIGURE 24

Changes in yields of vapour products with temperature
(stirrer speed = 500 r.p.m.)

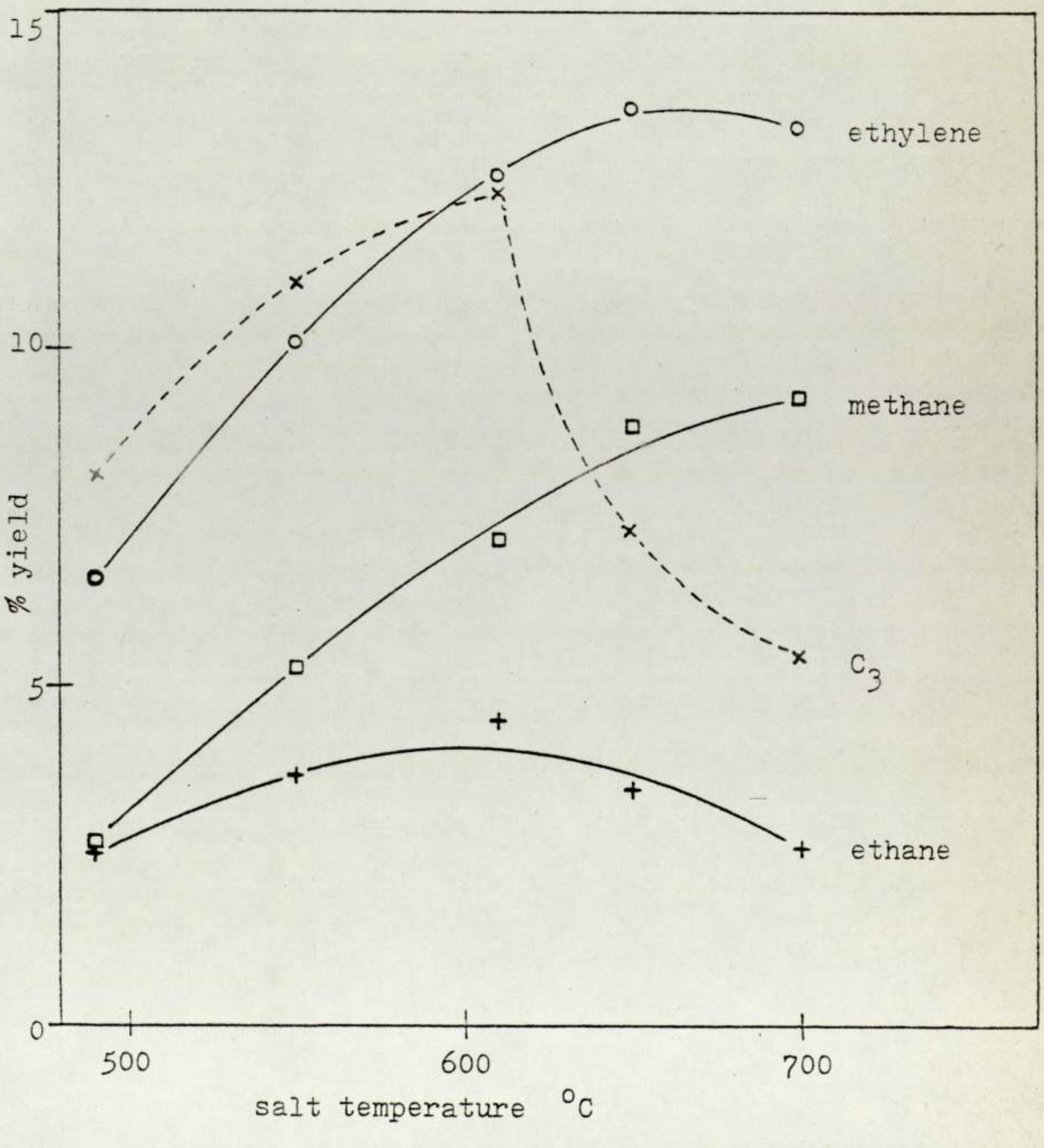


FIGURE 25

Changes in yields of vapour products with temperature
(stirrer speed = 1 000 r.p.m.)

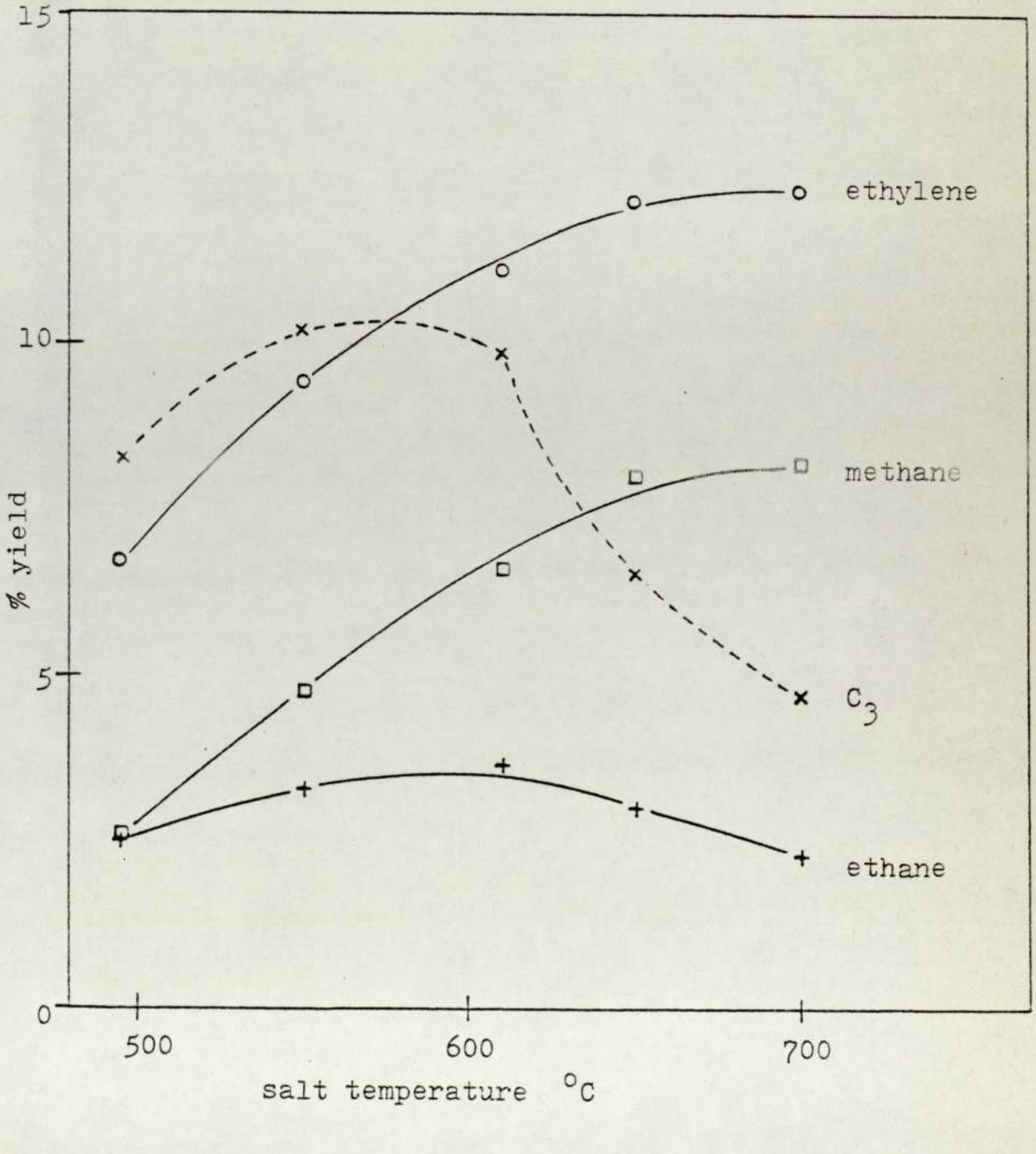
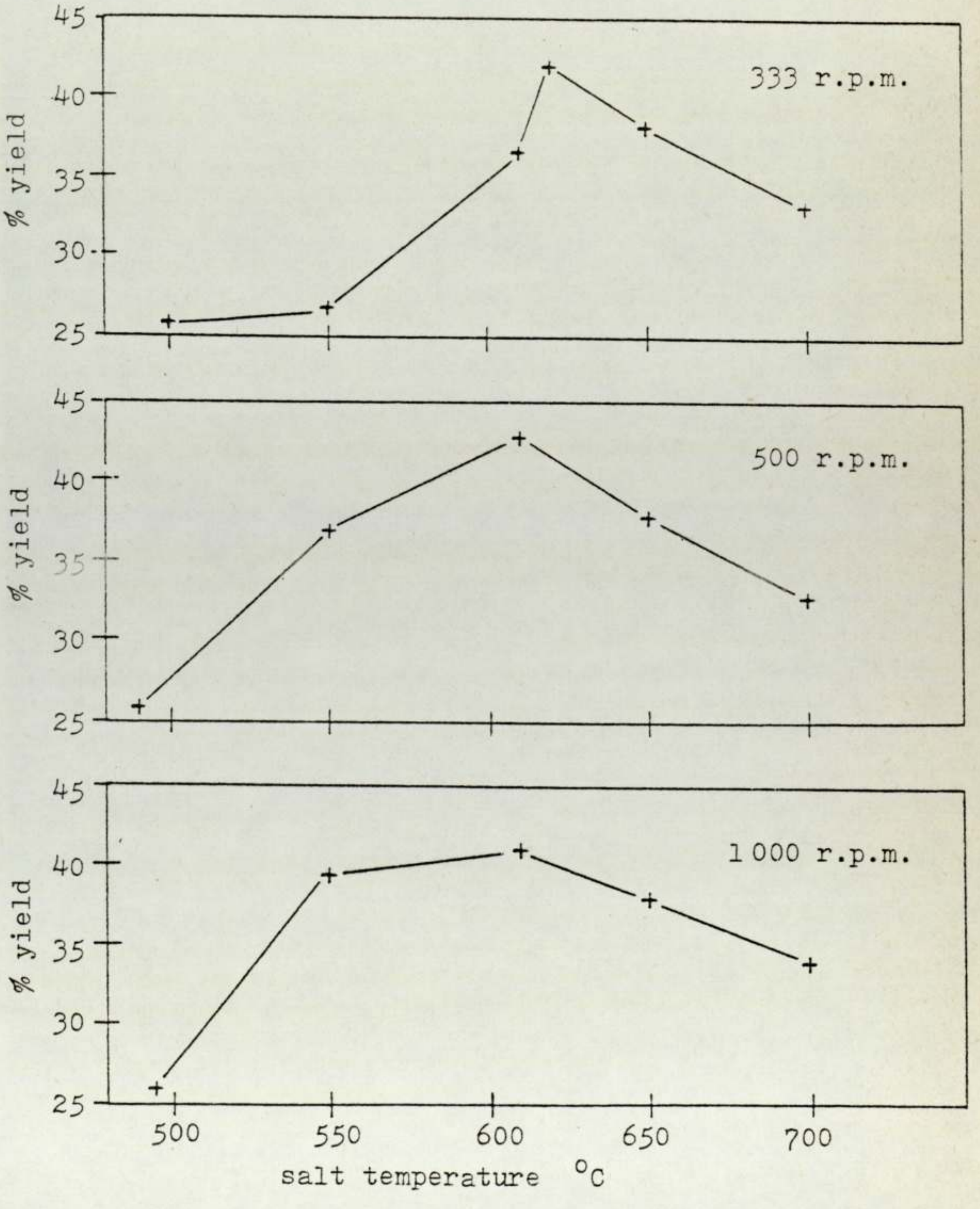


FIGURE 26

Changes in total yield to C_4 with temperature at fixed stirrer speeds



4.8 Effect of Stirrer Speed and Type on Pyrolysis

Two types of stirrer impeller were used. In the kinetic runs a simple two-bladed paddle was used, run at such a speed (320 r.p.m.) that the bath was kept in motion for heat transfer from the walls, but without making sufficient vortex to tend to draw floating material into the body of the melt. This was in order to simplify the situation under which the plastic pyrolysed, so that it could be understood better.

In the total yield runs a four-bladed propellor was used. These experiments were intended to more closely model a practical reactor, in which it might well be advantageous to have forced interaction between floating material and bulk melt. At slow speeds this stirrer would be mainly providing movement of the bulk, while at higher speeds a more turbulent surface and deepening vortex would tend to increase surface action. The depth of the vortex and the onset of vapour entrainment will depend on the viscosity of the salt, which is temperature dependent. The effect of the plastic as it pyrolyses must be considerable.

FIGS. 27 and 28 include some results already given in FIGS. 23, 24 and 25 plus some extra experiments, and show the effects which varying the stirrer speed gave.

FIGURE 27

Changes in yield of ethylene with stirrer speed

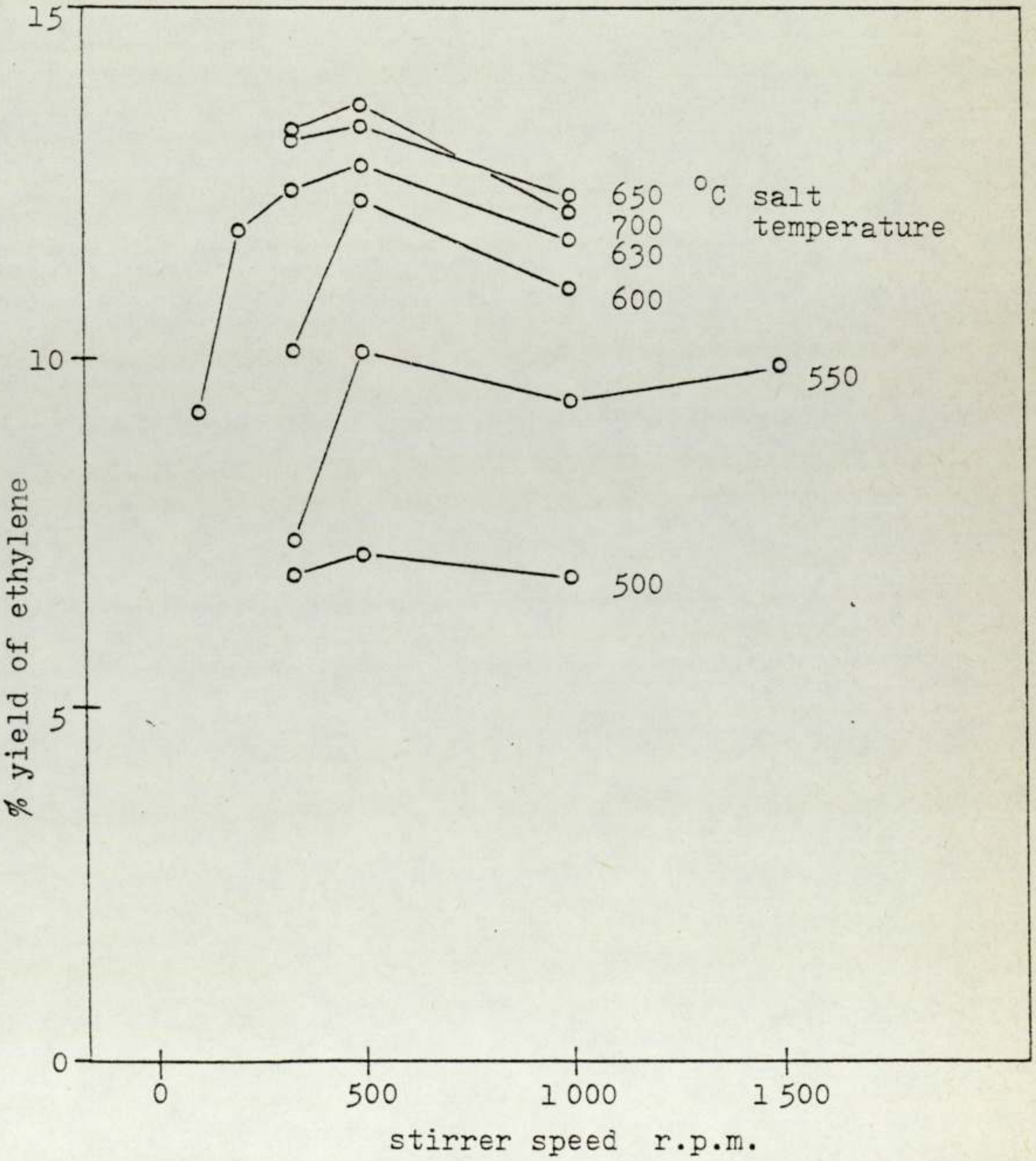
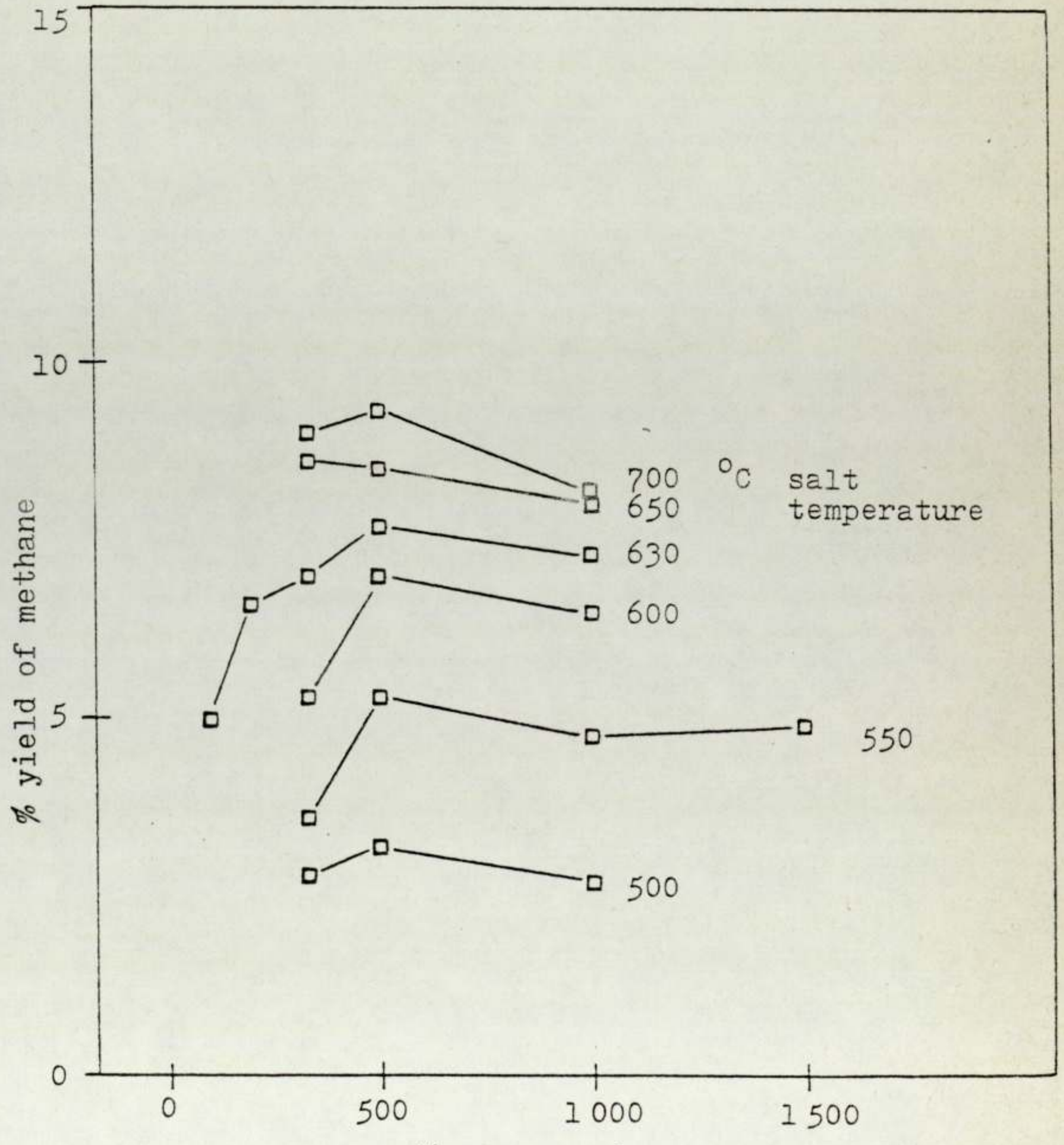


FIGURE 28

Changes in yield of methane with stirrer speed



Evidently the stirrer speed had least effect at the highest and lowest temperatures. This suggests two extremes of mechanism, dependent on the changes in salt viscosity and on plastic breakdown behaviour as a function of temperature. In the region favoured for ethylene and propylene yield (see section 4.7) that is, around 600 °C, the effect is particularly marked. Overall, a speed of 500 r.p.m. seems to give the maximum yield for a given salt temperature. FIGS. 27 and 28 particularly well illustrate the diminishing returns from higher inputs of energy either as stirrer speed or as higher operating temperature.

Pyrolyses without stirring gave non-reproducible results, though often with a higher yield of ethylene than from a bath stirred at moderate speed at the same temperature. This was almost certainly due to pyrolysis occurring on the vessel walls, which were at a higher temperature than the bulk salt, and does not represent a practical situation for an industrial reactor of this design.

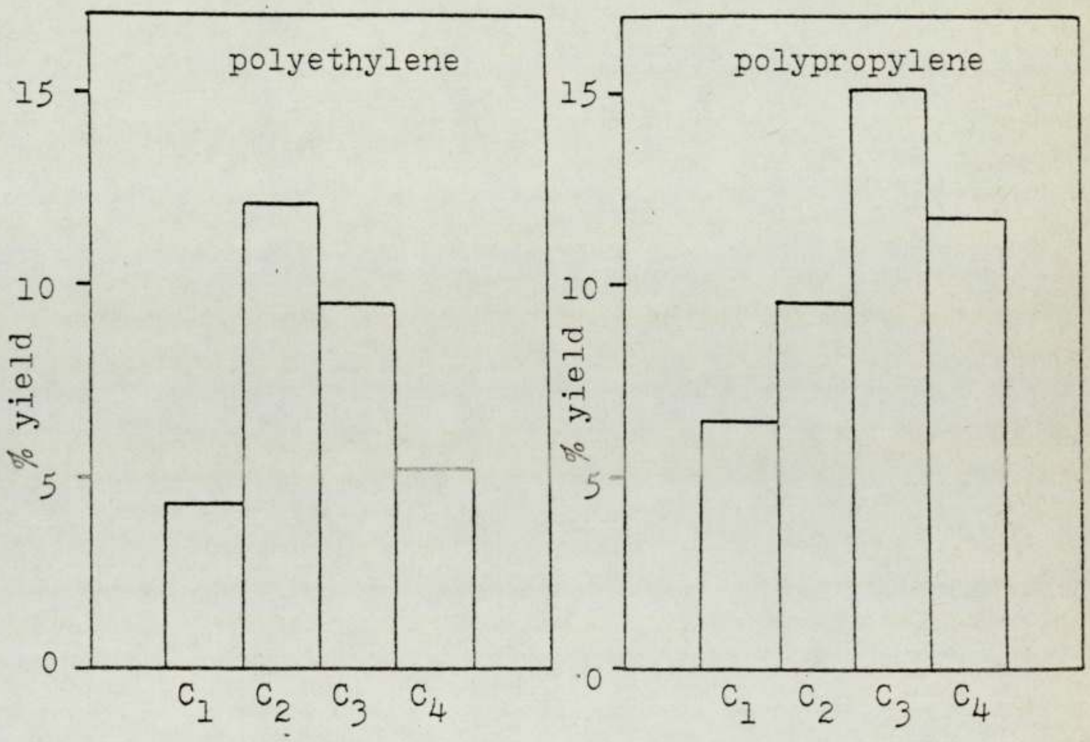
4.9 Comparison of Polyethylene and Polypropylene

Duplicate samples of polyethylene and polypropylene were pyrolysed under identical conditions of stirring and temperature on the same day and analysed in the usual fashion the next day. The conditions were typical of other experimental runs, namely salt temperature 600 °C, stirrer speed 333 r.p.m., nitrogen purge 200 cm^3 min^{-1}.

The results are summarized in FIG. 29 as percentage yield versus carbon number. There was a strong similarity between the two sets of products, except that propylene was the predominant product from the pyrolysis of polypropylene, and the overall yield was greater. The yield to C_4 was 31.0% for polyethylene, and 42.7% for polypropylene.

FIGURE 29

Comparison of the products of pyrolysis of samples of polyethylene and polypropylene under the same conditions



4.10 Test of Gas Collection and Analysis Method

A test of the sampling method for the kinetic runs has already been described in section 4.3. The mass balance of 98 % may be taken as quantitative collection within the limits of experimental error.

In the kinetic runs, the sample bottles were purged by several volumes of the product gas, and it is reasonable to suppose that they contained a representative sample. In the runs to find total yield, however, it had to be assumed that virtually all the product vapour had been collected in the large sample bottle. Yield was calculated from the known volume of the bottle, once the concentration of the gases had been found.

A simple experiment was carried out in which duplicate sample bottles were nitrogen purged, then had a 50 cm^3 aliquot of ethylene injected into them. They were capped and left overnight, then analysed as usual. Ten replicate analyses of each were carried out. This was intended to determine the variability due to the operator and method. Additionally, the dilution by air accompanying the taking of samples could be observed by the reduction in amounts of gases in later analyses. This was important because the results are usually based on two or more chromatograms per total gas sample. The results are shown in TABLE 5.

TABLE 5

Test of analytical procedure. Chromatograph FID responses for replicate injections from duplicate bottles of ethylene in nitrogen.

bottle A		bottle B
250		246
247		244
246		241
235		239
242		247
243		243
236		241
243		239
241		238
238		239
242.3	means	241.9

Overall mean taken = 242

Standard deviation = 3.87 = 1.6 %

Variation between bottles = 0.16 %

The standard deviation of the values recorded was 1.6%. The variation between the bottles was 0.16%. If the first five injections are compared with the second five, there is a mean loss of 1.5%, indicating an average loss of about 0.3% of gas value per injection made. This is also of the order which was observed in replicate analyses of actual samples, though masked by the random variation of duplicates. The calculated volume of ethylene in the bottles was 50.7 cm^3, based on the overall mean of the first five injections from each bottle.

The volumes of all the sample bottles used for the total yield runs were measured by weighing them carefully filled to the brim with water. The largest had a volume of 2755 cm^3, the smallest 2710 cm^3. The mean volume was 2726 cm^3 with a standard deviation of 18.7 cm^3 or 0.7%. Apart from the earliest runs, preference was given to bottles with a volume near 2750 cm^3, and this was taken as the standard volume of the bottle for convenience in calculation.

Although volume did not enter into calculations, the capacities of the bottles used in the kinetic runs were similarly measured, and found to range from 55.0 to 56.3 cm^3. Loss per injection was more serious, initially about 5%, but later improved by technique to between 1 and 1.5 %.

4.11 General Performance of Apparatus

Overall, the apparatus performed as it was intended to do. That is, it pyrolysed batches of plastic granules smoothly and safely, and no problems were experienced with stability, warm-up time, leaks, blockages, explosions etc. The following points were noted.

4.11.1 Thermal Behaviour When loaded with 2.25 kg of salt, the furnace took two hours to bring the salt to a completely molten state at 500 °C , and a further two hours to come to a steady state with the salt in the temperature range 600 to 650 °C . In the stirred steady state, the salt was maintained at temperature if the (nominal) furnace temperature was about 50 K higher. In the range of salt temperatures used (500 to 700 °C) the temperature of the reactor lid varied from 280 to 380 °C and that of the furnace outer skin from 60 to 80 °C . At a salt temperature of 650 °C , electric current was being supplied to the furnace windings for 75 % of the time by the controller, which is equivalent to an average power demand of about 1 kW. It is estimated that the maximum working temperature for such a salt bath in this furnace would be about 750 °C .

4.11.2 Nitrogen Purge Flow rates varying from 50 to 500 cm^3 min^{-1} were used in initial trials, but a flow rate of 200 cm^3 min^{-1} was found to be suitable, and was used for the majority of the runs. This gave a reasonable headspace residence time (see section 4.3) and a convenient volume for collection for analysis. It was found that the stirrer bearing, when finger-tight and running at 320 r.p.m., leaked 50 cm^3 min^{-1} to atmosphere and 250 cm^3 min^{-1} into the reactor for an applied pressure of 0.2 bar. Slightly tightening the stuffing box reduced the leak to atmosphere to less than 5 cm^3 min^{-1} (i.e. not measurable on the flowmeter) without restricting the stirrer speed. For the majority of runs a flow of 50 cm^3 min^{-1} was passed into the stirrer gland, and when checks were made no losses could be measured. The emergency vent line was kept clear by a constant flow of nitrogen of between 10 and 20 cm^3 min^{-1}.

4.11.3 Stirrer Both the flat paddle and the propellor blades ran smoothly and well at speeds up to 600 r.p.m.. Above this, the lack of exact balance in the vanes, and the limited amount of support led to increasing vibration. This was considerable at 1000 r.p.m., and so severe at 1500 r.p.m. that only one test could be made at this speed. Though the stirrer was run for an estimated 72 hours, there was no visible wear in the gland components, and the carbon bushes were intact. The impeller could be unscrewed from the shaft without difficulty.

4.11.4 Salt Of the total of 2250 g of salt which was placed in the reactor, 2239 g was recovered at the end of the experiments, the net loss of 11 g being about 0.5%. Some salt had been lost when changing the stirrer paddle (as material on the stirrer) and it is probable that the original salt had some moisture content because of its high surface area and hygroscopic nature. Hence the losses due to volatilization of the salt were very small. The solidified salt was very faintly grey in colour, presumably due to suspended carbon. Considering the intense colouring power of small amounts of carbon black, the amount of carbon in the salt must be very small. There was no evidence of salt having splashed onto the underside of the lid of the reactor, though some salt had clearly spattered onto the inner walls of the reactor liner, as much as 9 cm above the working salt level.

4.11.5 Corrosion In the course of the experiments, it was estimated that the furnace was in operation for 500 hours; the salt was molten for 370 hours; and the molten salt was stirred for 72 hours. Hydrogen and the hydrocarbon gases were present in significant amounts in the vapour space for an estimated 15 hours, but oxygen was never present other than in very small traces.

A number of features which might be ascribed to corrosion were noted. The interior of the liner had acquired a flakey surface in the region exposed to salt (continuously or by splashing). This scaling is a recognized feature of heat treatment salt baths. Some scales had come off the surface (possibly during the removal and examination of the apparatus rather than during its operation) and fallen to the bottom. The sides and base of the liner interior were scraped to remove all loose material. When this was collected and washed free of salt, it amounted to 71.98 g. Since the available surface area was about 720 cm^3, this represents a loss of 0.1 g cm^{-2} and a penetration of 0.13 mm. On the basis of the time the salt was molten, this gives a corrosion rate of 3 mm per year. It was clear, particularly on cross-sectioning the liner, that the scaling had not reduced the wall thickness to any important extent, and thickness measurements support the weight-loss corrosion rate. It does seem, however, that there was more scaling in the region of the gas-liquid interface, where the corrosion rate is possibly double.

Just toward the end of the experiments, the thermocouple in the salt failed. When the apparatus was opened, it was found (as expected) that the sheath and thermocouple had broken in two, a little above the surface of the salt. It was also found that the stirrer shaft was eroded at a similar level, the 8 mm shaft being reduced to 6.4 mm at its thinnest. No scaling was observed, all surfaces being clean and smooth, particularly the part of the thermowell which would always have been immersed.

From the shape of the thermocouple sheath, and previous experience with a much thinner sheath in the trial experiments, it appears that the thermowell was not sufficiently rigid at higher temperatures and had bent under the force of the stirrer. Corrosion had been concentrated at the bend, which was also in the most violent region where pyrolysis and splashing of salt occur. It also seems plausible that the bent thermowell was rubbing on the shaft, and a portion of the observed erosion was due to wear. It is, however, possible that the erosion was solely due to the high rate of corrosion induced by the speed of rotation and the transition zone in which the surface operated.

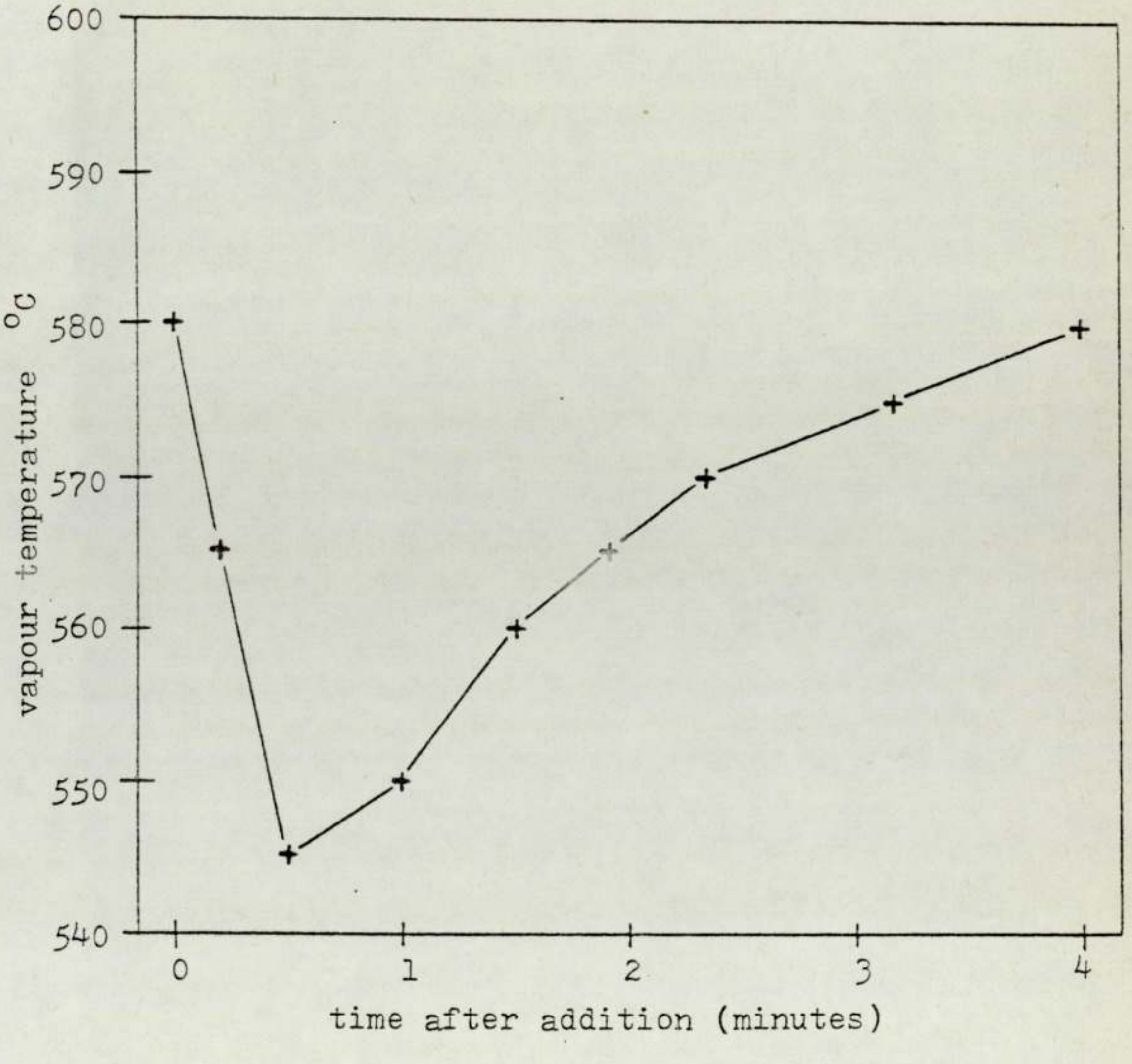
4.12 Miscellaneous Results

A number of observations were made, and single measurements taken, during the course of research which have not yet been noted. They are recorded here as unconfirmed or uncertain results, which do however give some more insight into the processes and problems involved.

4.12.1 Gas Temperature During a couple of pyrolyses, the temperature given by a thermocouple 4 cm above the melt was noted. The combined results are given versus time in FIG. 30. While the interpretation of the graph is open to some doubt, it confirms the endothermic nature of the pyrolysis gasification process and the approximate time-scale noted for single particles and in the kinetic runs.

FIGURE 30

Changes in temperature of vapour above molten salt during pyrolysis



4.12.2 Wax Formation It proved very difficult to condense the higher-molecular weight portion of the vapour from pyrolyses, since the oils and waxes appeared as very fine mist particles diluted by non-condensables such as nitrogen and ethylene. During one series of runs at 590 °C and otherwise identical conditions, about 20 % more wax was collected in a trap when the stirrer ran at 500 r.p.m. than when it ran at 320 r.p.m.. There was considerable deposition of greasy material in the reactor outlet pipe, but at no stage was there sufficient to threaten to block the pipe or even substantially restrict the flow of vapour.

4.12.3 Wax Composition The waxy or greasy material which could be condensed from the product vapour varied from a very slightly off-white to a strong yellow colour, the yellow being associated with higher temperature runs. Infra-red and ultra-violet spectra were taken of thin films of wax samples. Spectra for one of the yellowest samples are shown in FIGS. 31 and 32.

The UV spectrum shows a rather lumpy tail down from 190 nm into the visible, which is of course responsible for the yellow colour. A whiter sample gave a similar pattern but of lower intensity. It is reasonable to ascribe this absorption to $\pi - \pi^*$ sort of transitions in mixtures of alkenes and polyenes. The many small shoulders suggest a complex mixture much as was found with the vapour samples. The IR spectrum is typical of predominantly saturated hydrocarbons, and particularly resembles polyethylene film and Nujol (paraffin), both of which will be familiar to spectroscopists. The C-H stretch group just under 3000 cm^{-1} and the methylene/methyl scissor group around 1460 cm^{-1} are fairly typical. Superimposed on this alkane spectrum are smaller indications of unsaturation, particularly extra peaks due to =C-H stretch at 3071 cm^{-1} and C=C stretch at 1639 cm^{-1}. The

FIGURE 31

Ultra-Violet spectrum of waxy portion of pyrolysate

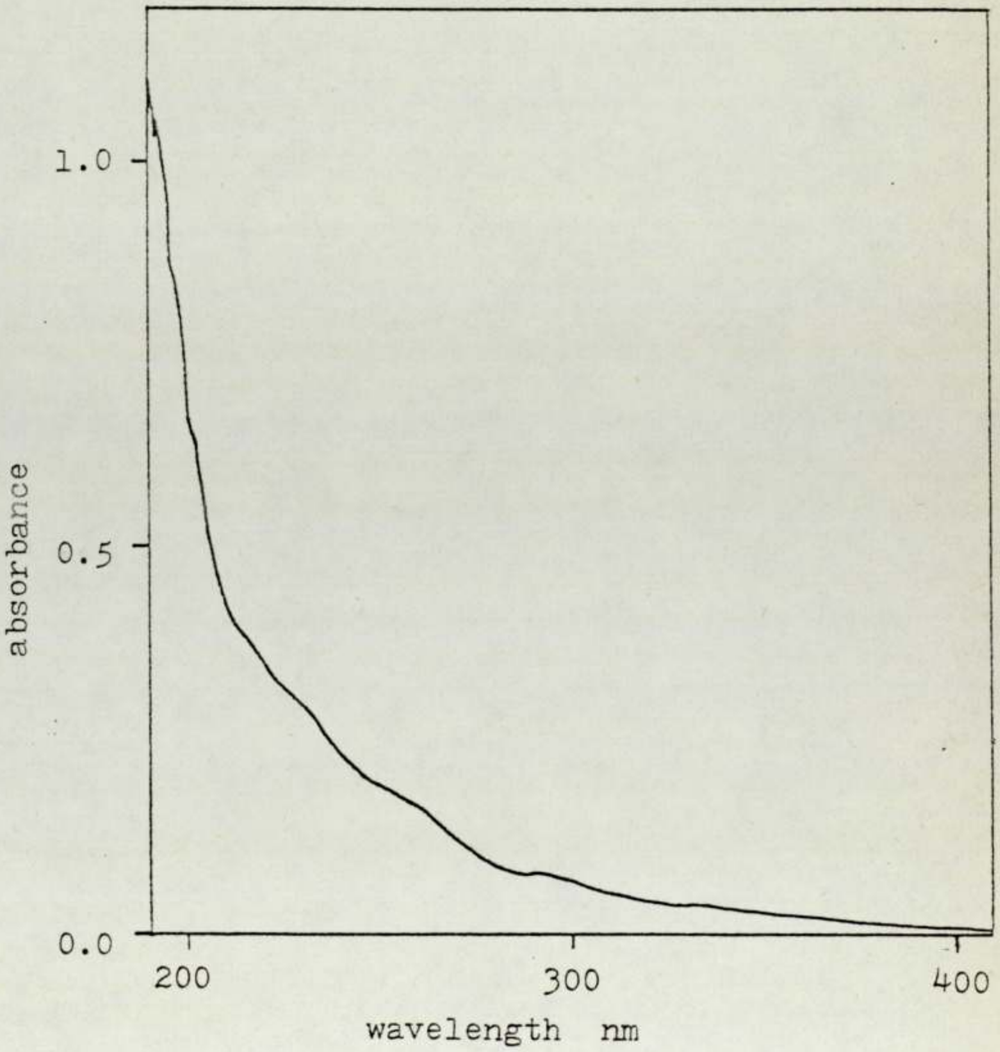
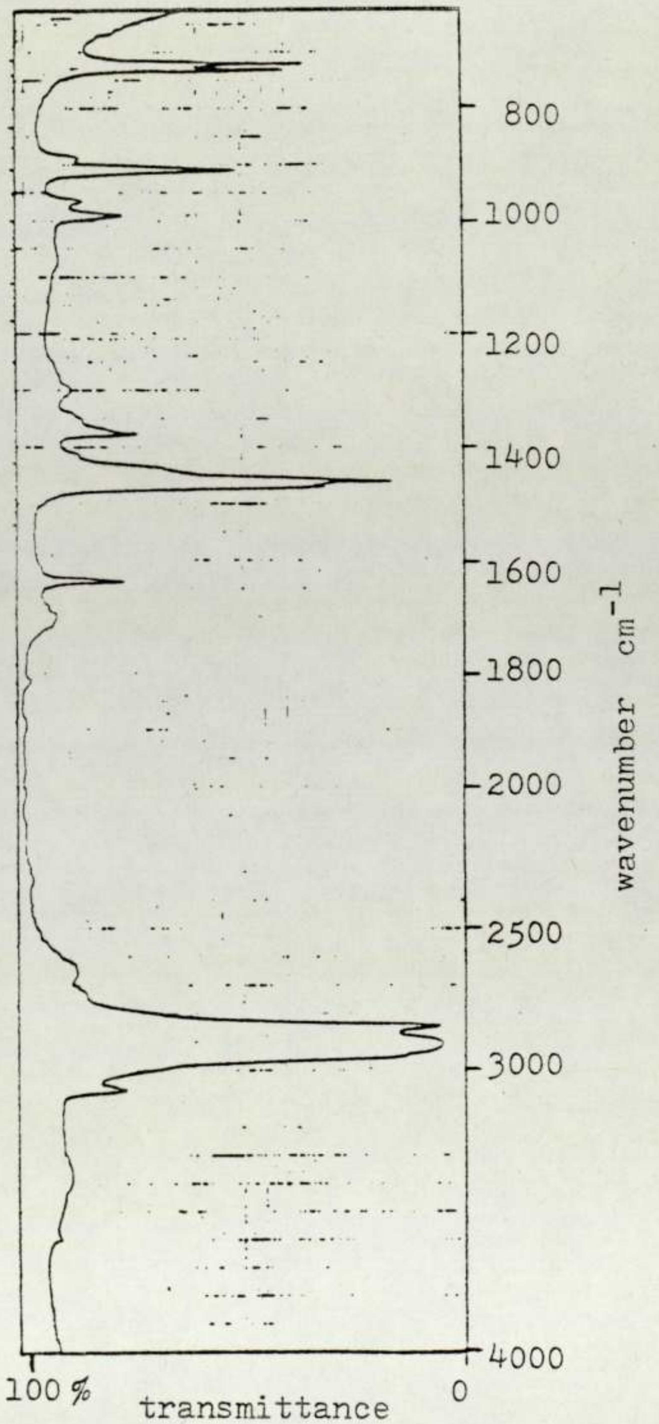


FIGURE 32

Infra-Red spectrum of waxy portion of pyrolysate



latter is particularly diagnostic of unsymmetrical groups around the double bond, as might be expected for double bonds near the end of an alkane chain (from fragmentation of a longer chain). It is tempting to ascribe the double peak around 730 cm^{-1} to aromatics, and there is certainly some suggestion of overtones between 1700 and 2000 cm^{-1}, but it is probably safer just to take this as additional evidence of unsaturation. These additional peaks were smaller in a whiter sample of wax from a pyrolysis at lower temperature, but the spectrum was not qualitatively different. Acetone and carbon tetrachloride extracts from the walls of sample bottles gave similar spectra, making allowance for residual solvent.

4.12.4 Hydrogen Formation The presence of hydrogen was determined in the products of a pyrolysis at 610 °C, in a yield of about 0.2 % of the mass of polyethylene used. This mass is negligible compared with the 10 + % ethylene and with other major components. The volume is not, however, negligible since (on an ideal gas basis) a given mass of hydrogen occupies a volume equivalent to 14 times that mass of ethylene at the same temperature and pressure. The yield of gases is shown in TABLE 6 on a mass and volume basis for 100 g of polyethylene pyrolysed at a salt temperature of 610 °C and a stirrer speed of 500 r.p.m., these being some of the highest yield conditions. It will be seen that the volume of hydrogen is more than a fifth of the volume of ethylene or methane, and about as great as the C_4 hydrocarbon fraction. A commercial reactor would thus be operating under some significant hydrogen partial pressure. This could have some effect on the vapour-phase pyrolysis processes, and on gas and salt corrosion conditions, all of which are discussed elsewhere in this thesis.

TABLE 6

Vapour yields including hydrogen on a volume and mass basis per 100 g polyethylene (610 °C, 500 r.p.m.)

component	mass g	volume dm^3
hydrogen	0.2	2.2
methane	7.2	10.1
ethylene	12.35	9.9
ethane	4.9	3.7
C_3	11.3	6.1
C_4	6.1	2.4
total	42.25	34.3

4.12.5 Carbon Formation Little if any carbon was present in the body of the salt. There was evidence of carbon formation on the walls of the liner, probably where molten plastic had spattered or possibly where vapour had decomposed. Some carbon was evident in the waxy deposit around the outlet pipe inside the reactor. From the amounts recovered (as acid-insoluble portion of the wall scrapings) it is estimated that the overall conversion to carbon did not exceed 2 % of the plastic pyrolysed.

4.12.6 Pyrolysis in Nitrate Melt Individual granules and later quantities of up to 0.5 g of polyethylene were pyrolysed on an unstirred melt of TS 150 quenching salt (KNO_3 + $NaNO_2$) in semi-open conditions under a nitrogen blanket. There was some fear that the nitrate might oxidize the pyrolysis products to give a violent reaction. This was not observed. At 250 °C the plastic melted to a transparent liquid which floated freely on top of the salt. Additions to salt at 500 °C produced some considerable production of vapours, leaving charred fragments behind. These burnt away smoothly when air was admitted, but not under the nitrogen blanket on the salt.

5 DISCUSSION OF EXPERIMENTAL RESULTS

The purpose of this study was to look at the pyrolysis of plastic waste in molten salt as a practical problem in chemical engineering. It is reasonable to postulate some simplified chemical mechanisms to explain the results, but this was not a chemical project on reaction mechanisms, so interpretations must be mainly descriptive and somewhat tentative. In this context, it may be helpful to briefly review some generally accepted pyrolysis mechanisms.

5.1 Pyrolysis of Hydrocarbons

The pyrolysis of petroleum hydrocarbons is well understood in the sense that it can be put to extensive commercial use. On the other hand, there is a continuing stream of papers on the complexities and subtleties of the processes involved. Excluding surface catalysis, the processes are mainly homogeneous vapour phase free-radical ones. Most so-called 'cracking' processes are believed to involve a preliminary fission of a suitable molecule to produce a free-radical species. This is the initiation step. The principal products are then formed by a chain reaction (propagation) which is stopped by the reaction chain meeting another free-radical or a solid surface (termination). This is exemplified by the

Rice-Herzfeld mechanism shown in FIG. 33 for ethane pyrolysis[34], but which can be used with suitable modifications as a model for many other pyrolyses.

FIGURE 33

Rice-Herzfeld mechanism for pyrolysis of ethane[34]

$$C_2H_6 \rightarrow 2\,CH_3^{\bullet} \quad \text{— initiation}$$

$$\left.\begin{array}{rcl} CH_3^{\bullet} + C_2H_6 & \rightarrow & CH_4 + C_2H_5^{\bullet} \\ C_2H_5^{\bullet} & \rightarrow & C_2H_4 + H^{\bullet} \\ H^{\bullet} + C_2H_6 & \rightarrow & H_2 + C_2H_5^{\bullet} \end{array}\right] \text{— propagation}$$

$$\left.\begin{array}{rcl} 2\,C_2H_5^{\bullet} & \rightarrow & C_4H_{10} \\ 2\,C_2H_5^{\bullet} & \rightarrow & C_2H_4 + C_2H_6 \end{array}\right] \text{— termination}$$

Note: The predominant free radical is $C_2H_5^{\bullet}$

The concentrations of $H^{\bullet}$ and $CH_3^{\bullet}$ are so low that termination reactions such as

$$2\,H^{\bullet} \rightarrow H_2$$

are negligible.

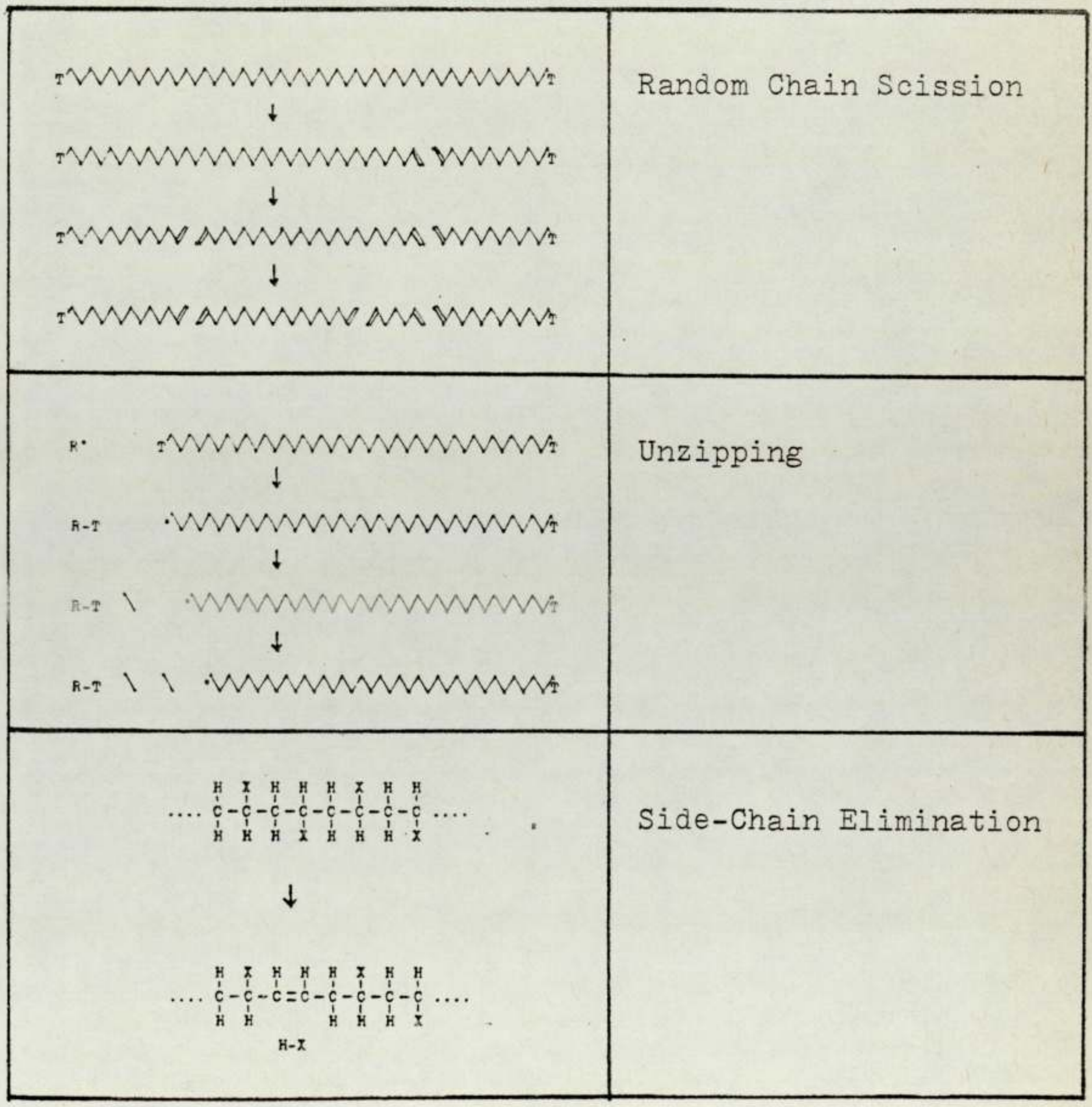
5.2 Pyrolysis of Polymers

Three major mechanisms are generally accepted as providing a simple description of the principal processes involved in the pyrolytic decomposition of commercially important thermoplastic polymers [85-89,93,96,217]. These are shown in FIG. 34.

The simplest of these mechanisms is known as free-radical depolymerization, or more commonly 'unzipping'. In essence it is the reverse of free-radical polymerization. A chain reaction removes monomer units until the end of the chain is reached, or the free-radical is terminated. This mechanism is favoured by those polymers which can give rise to stable free-radicals by delocalization onto side-chain units. It is therefore negligible for polyethylene (which has only protons on the carbon skeleton: these are ineffective for charge delocalization.) Polypropylene may be considered a methyl-substituted form of polyethylene, so unzipping plays a significant part in its pyrolysis. For poystyrene, unzipping is a major mechanism because of the superior charge delocalization offered by the benzene ring. Further substitution, as in polymethylstyrene, produces almost quantitative yields of monomer by efficient unzipping. Unzipping is also a primary mode of pyrolysis for polymethylacrylates and polytetrafluorethylene.

FIGURE 34

Major mechanisms of polymer pyrolysis



T = terminating group
R· = radical initiator
X = electronegative group

One measure of the effectiveness of this process is the 'zip length' or number of monomer units removed from the chain per radical initiation. The zip length is of the order of 0.01 for polyethylene [93], about 5 units for polystyrene [96], and about 1000 for methylmethacrylate and methylstyrene polymers [96]. Polymerization and unzipping are competitive processes for materials with a long zip length, depolymerization being favoured at higher temperatures. For those polymers where this is the prime manner of pyrolysis, a 'ceiling temperature' can be found at which ΔG (polymerization) is zero and forward and backward reactions cancel out [90,93,96]. For polystyrene this temperature is 230 °C [93,96]. Apart from theoretical implications, such figures are of importance in the design of the materials recovery equipment of any commercial reactor for plastic pyrolysis. If the products are kept above the ceiling temperature there is no fear of fouling due to polymerization. Transition to lower temperatures should be made by rapid quenching to a point at which the rate of polymerization will be slow, possibly with the simultaneous use of inhibitors.

The second major pyrolysis mechanism is known as random chain scission (or cleavage or fragmentation). As the name implies, the polymer chain breaks at any point along its length to give two oligomer fragments with unsaturated ends. These fragments may subsequently break into smaller units. For polyethylene this is virtually the only simple mechanism possible, and would ultimately lead to ethylene. The reasons why such a desirable product is not quantitatively produced will be discussed later. Random chain scission often occurs at the same time as most other thermal degradation processes in polymers. It is the predominant mechanism for condensation polymers (such as nylons), the polyolefins and polytetrafluorethylene. For condensation polymers, of course, the monomer is not produced; the elimination of small molecules such as CO_2 often occurs at the scission point.

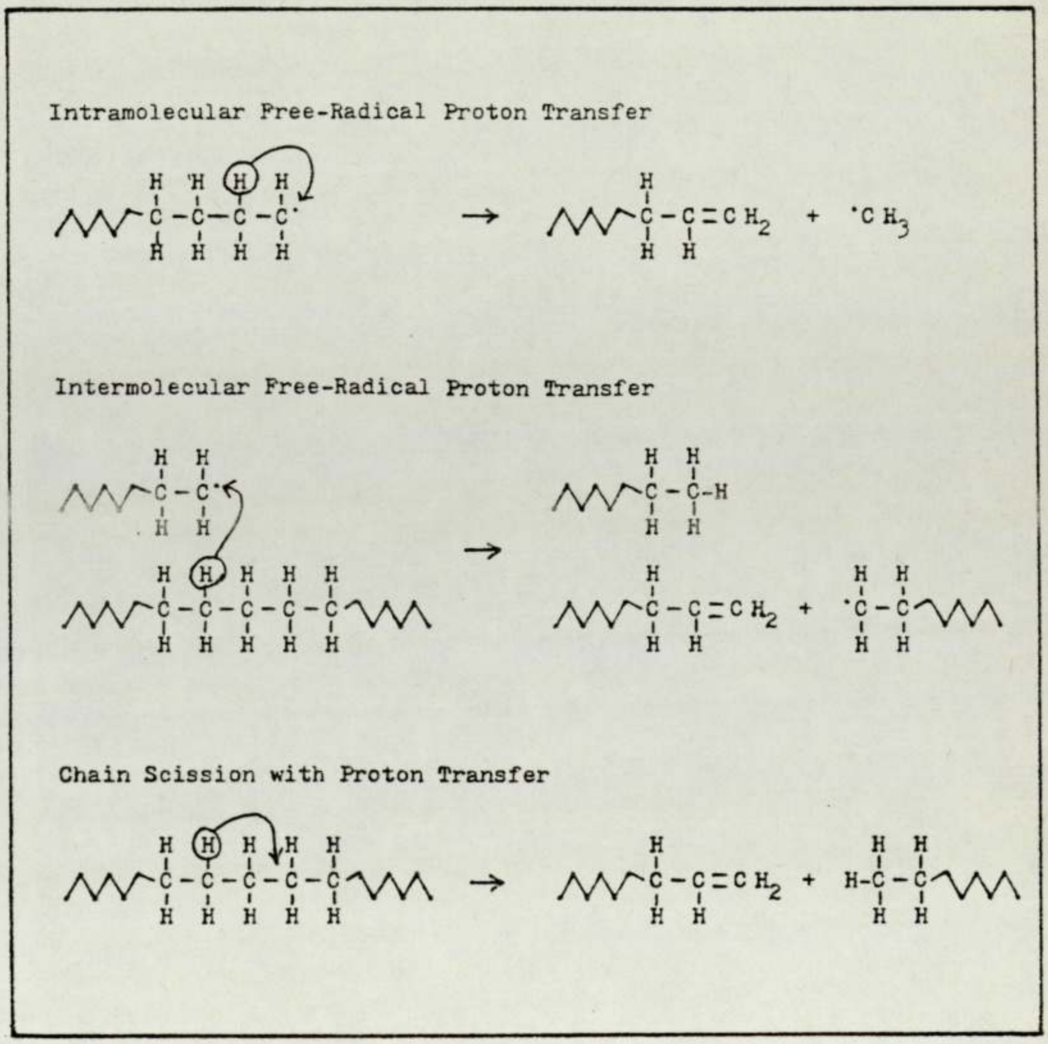
The third type of bulk mechanism commonly encountered applies to those polymers with side groups which can combine to eliminate a small molecule. It is exemplified by the loss of HCl from polyvinylchloride to leave an unsaturated carbonaceous residue. This reaction occurs so readily that considerable amounts of stabilizers are invariably included to make PVC a practical material at ordinary temperatures. Other molecules which can be eliminated from side groups include HF, H_2O and CH_3COOH from polyvinylfluoride, polyvinyl alcohol and polyvinyl acetate respectively.

An important observation is that even carefully prepared samples of polymer tend to decompose at lower temperatures than would be expected from thermodynamic consideration of bond strengths [89,218]. In addition, there are significant differences if the polymer is heated up very slowly (or kept just below its decomposition temperature for some time) compared with rapid pyrolysis[89]. These features may be explained by the presence of impurities or imperfections in the chain structure giving rise to weak links [85,89,93,217,219]. Such weak links are the points at which chain scission first occurs: it is therefore not truly random. These breakdowns may be the initial source of free-radicals for unzipping. Slow heating can break down the impurities without giving radicals of sufficient energy to unzip the chain. Removing this source of free-radicals thereby raises the actual decomposition temperature. Oxygen is a particularly important impurity, occurring as oxo links in the chain, as peroxides or dissolved air or water [89,218,219].

Other reactions which might be expected to occur during pyrolysis include bimolecular reactions such as condensation and proton transfer, and unimolecular rearrangements. Obvious examples of such rearrangements are isomerization of free-radicals or unsaturates (e.g. by proton transfer) and cyclization of C_5, C_6 or C_7 fragments. In the case of polyethylene, it has been suggested[220] that if free-radical fragments are formed by chain scission or external initiator, then a hydrogen abstraction process is favoured rather than unzipping to the monomer. This hydrogen abstraction can be intra- or intermolecular, as is illustrated in FIG. 35. In either case, the new fragments formed include a new free-radical, a new saturated end and a new unsaturated end. It has also been suggested[95] that proton migration could occur during random chain scission instead of forming a pair of free-radicals. Such a process is also shown in FIG. 35, and would give two fragments, one with a saturated and one with an unsaturated end. The process would be hindered by side-groups, and favoured by extra hydrogen on the chain[95]. Since polyethylene has least side-groups and most hydrogen of hydrocarbon polymers, it is plausible to consider this process the most likely manner of chain scission. The production of saturated hydrocarbons during the pyrolysis of polyethylene has been explained by abstraction of

FIGURE 35

Proton transfer reactions during pyrolysis of polyethylene



hydrogen from the polymer by olefins or short-chain free-radicals resulting from chain scission[89].

5.3 Mechanism of Pyrolysis of Polyethylene on Molten Salt

It must be appreciated that the overwhelming majority of studies of the pyrolysis of plastics have dealt with one or other of two special situations. The first is the rather slow low temperature degradation over many hours; aimed at understanding the processes which affect the stability of plastics for higher temperature use. The second is the rapid pyrolysis of very small samples - 10 mg or less - on a heated wire and usually in a vacuum. The lower temperature degradation allows time for relaxation processes and diffusion to occur, and is rarely progressed to substantial breakdown of carbon-carbon bonds. On the other hand, rapid micropyrolysis allows the primary products of pyrolysis to escape from the reaction zone before secondary reactions can occur [98,102], and is thus favoured for structural studies. For example, the pyrolysis of 1 mg of rubber in vacuo gave a yield of 2 % isoprene, as measured by a mass spectrometer. Under the same conditions, the pyrolysis of 10 mg gave a measured yield of 18 % due to vapour phase cracking of the dimer en route to the mass spectrometer inlet [221]. Amounts larger than a few milligrams are also not favoured because of their tendency to sputter off the wire [222].

By contrast, this project has attempted to simulate a hypothetical commercial process involving the rapid pyrolysis of macro amounts of plastic. Sputtering is considered inevitable. Many processes will occur in the condensed phase, and even after volatilization the primary products will pass not into a vacuum, but into a hot and relatively concentrated region near the molten plastic and the salt. Secondary bimolecular reactions will therefore be of major importance in determining the final products.

The most relevant comparison with the pyrolysis conditions occurring in this project is probably the situation encountered when sizeable pieces of plastic are burnt in a self-sustaining manner. The simplest model of a free-burning thermoplastic is where heat is conducted from the burning surface to pyrolyse the bulk, and the volatiles resulting from pyrolysis leave the surface to combust. Unlike lower temperature oxidation, transfer of oxygen into the bulk can be neglected, and the flame would provide an exterior source of heat in much the same way as does a molten salt bath. This simple model has been found to agree with experimental data for polyethylene burning like a candle as a vertical rod [223]. The candle study is particularly comparable with the molten salt project in that the dimensions (3.6 mm diameter rod compared with 3 to 4 mm granules) and temperature(627 °C) were similar .

It has been pointed out [109] that the surface combustion of polymers provides extreme conditions (particularly the very high temperature gradients and heating rates) for which normal thermochemical data is inappropriate. Once again, this could also be said of pyrolysis in molten salt. A number of mathematical models have been proposed for so-called linear pyrolysis (i.e. at a regressing surface) but have not been adequately tested due to lack of data [109]. In summary, however, the process appears to be controlled by a sub-surface thermal degradation, itself dependent on the thermal conductivity of the pyrolysing polymer. In the molten salt bath, the cooling effect of volatilizing products must also be included, along with the insulating effect of the vapour around the particle.

From a practical point of view, it is reasonable to suppose that there will generally be an induction period while the plastic particle heats up, then initial pyrolytic processes involving progressive reduction of average molecular weight will ultimately lead to gas evolution. My visual observations of such an induction period are reported in section 4.2, and it is implied in the various kinetic experiments. At the University of Hamburg, an induction period was also observed, when monitoring the pressure in a sealed vessel containing a single plastic granule on a bed of salt or sand [12,124].

As might be expected, the induction period depends on both temperature and particle size. The time-scales reported for induction and complete gasification are of the same order as was observed in this project.

The decomposition temperature of polyethylene has been reported as 410 °C[96], although slow thermal degradation has been studied by many workers at temperatures starting from 290 °C[85,89]. Grassie states[89] that the production of significant volatiles commences at 360 °C. In the single granule tests at Hamburg, the onset of gassing was associated with a salt temperature of 515 °C and an estimated surface temperature of 375 °C on the polyethylene granule[124]. The induction period was said to be the cube root of the mass. Presumably this applies to small particles only, since for granules more than a few millimetres across, surface gasification could begin before much heat had been transmitted to the centre. For these large particles, the pyrolysis would initially correspond to surface degradation on an effectively infinite bulk polymer, and the onset of gassing would not be delayed by any increase in the size of the bulk material.

It is usually said [89,96] that the pyrolysis of polyethylene produces little or no monomer, yet ethylene was invariably found to be the major product in the molten salt experiments. This shows the difference between conventional pyrolyses of small amounts in vacuum, and pyrolysis of larger amounts on an efficient heat transfer bath of molten salt. The apparent contradiction can be resolved as follows. In either case, ethylene is not a primary product of pyrolysis. In micro studies, fragmenting the polymer chain produces material sufficiently volatile in vacuo (say C_{10} to C_{50}) for it to be removed and examined by mass spectroscopy before further reactions occur. In the macro situation, however, the local vapour concentration limits the mean free path of the molecules, so that many collisions can occur before material escapes from the reaction zone. Moreover, the molten salt is effectively a near-infinite source of heat (due to its much greater thermal capacity than the vapour) and the gases and vapours provide a means of transfer of the heat (which is absent in vacuum studies). The primary products thus pass through a hot concentrated vapour zone. The residence time in this zone allows energy transfer within the molecule to take place, and the many collisions provide activation energy for unimolecular reactions, plus the opportunity for bimolecular reactions. There will thus be a greater tendency for larger molecules to break down into smaller ones. The smaller molecules are thermodynamically favoured at pyrolysis temperatures on entropy grounds. Furthermore, larger molecules will in general spend longer in the reaction zone due to their lower velocities at the same thermodynamic temperature, compared with smaller similar molecules. Proton transfer and isomerization will tend to occur with increased residence time, if they give rise to more stable intermediates or products. My experimental observations are supported by comparable work at the University of Hamburg, where macro amounts of polyethylene pyrolysed to give large amounts of ethylene [12,29,115,124,216].

In the present study, it was noted that the initial surge of gas produced was almost entirely ethylene, but after the first half minute a very different composition resulted, which was then expelled with very little change (see section 4.6). This initial composition may be tentatively explained as follows. The first ruptures of the polymer molecules will occur at the most easily broken points, such as where oxygen is present or near branches. Then there will be a delay until the polymer temperature reaches a level sufficient for true random chain scission.

During the first period the material given off will be fairly small fragments (from chain branches and ends) and will be at low concentration entering the hot zone just by the molten salt. Additionally, breakage of weak points (particularly those associated with oxygen) will give rise to a high proportion of free radicals. The general situation will thus resemble a gas-cracker situation favouring the free-radical formation of ethylene by a Rice-Herzfeld type mechanism.

Once the weak and oxygenated bonds have been broken, and the resulting free-radicals and their products swept away by the purge, breakdown of the polyethylene will follow a slightly different pattern. In this, the main part of the pyrolysis, fission with accompanying proton migration would give non-radical fragments. Under random chain scission, larger fragments would be expected than from breaking branches in the initial pyrolysis phase. Bimolecular collisions involving further fragmentation and proton transfer may then reasonably account for the mixture of alkanes and alkenes which is finally emitted from the reactor.

The formation of other products such as iso-alkenes and cyclic molecules can be understood from the rearrangements commonly recognized in thermal reforming of hydrocarbons at around these temperatures. The absence of acetylene is reasonable, since it is not usually formed from hydrocarbons much below 800 °C , and there is no obvious direct route in such a highly hydrogenated environment[61]. Methane is a favoured product from the cracking of largely saturated gases, being the most stable of all alkanes: demethanation is thermodynamically the most favourable mode of rupture of alkanes[61]. To a lesser extent de-ethanation can occur to give ethane[61]. Ethane can also be formed by the abstraction of hydrogen by ethylene from polymer chain fragments[89] or from various free-radical processes. However, all such processes for ethane formation are much less efficient than the methane, which agrees with the experimental observation that ethane was a minor product. Any ethane formed can itself pyrolyse (this being a major method of ethylene production) which would agree with the lower concentration of ethane found in gas products at higher temperatures. The presence of hydrogen in the product gas is not surprising, since it is a normal product of hydrocarbon pyrolysis.

The conversion of ethylene to methane noted in the vapour residence tests (section 4.3) merits some comment. It is notably different from classical studies of ethylene pyrolysis [39] and also has some implications for operation of commercial versions of the molten salt unit. The pressure of ethylene in the headspace may be estimated as in the range 200 to 20 mbar for the main portion of its residence, with a temperature no more than 600 °C . Both the temperature and pressure are low compared with a normal tubular hydrocarbon cracking unit. A comparable study (temperature 525 - 650 °C , pressure 13 - 360 mbar) of ethylene pyrolysis gave the principal products as propylene, butadiene, but-1-ene, ethane and polymer [37]. Another study at similar temperatures but higher pressure (500 - 600 °C , 200 - 800 mbar) reported only ethane and polymer as products [38]. By contrast, in this molten salt reactor only the faintest trace of ethane was observed, the main product undoubtedly being methane.

A plausible explanation is that vapour phase pyrolysis of ethylene did not occur to any appreciable extent during the vapour residence test. Instead, the methane arose from disproportionation of the ethylene to methane and carbon, this occurring at a hot surface, either the wall of the reactor or the salt surface. Such a reaction is unlikely on the lid, since this was comparatively cool, no more than 380 °C. The disproportionation reaction

$$C_2H_4 \rightarrow CH_4 + C \qquad (1)$$

is thermodynamically favoured at pyrolysis temperatures, so it is normal practice in hydrocarbon cracking to limit the residence time so that thermodynamic equilibrium is not approached. The deposit of carbon on the walls of reactors and production of methane are, however, normal features of hydrocarbon pyrolysis. Steels containing a low proportion of carbon (such as the stainless steel used in the molten salt reactor) are said to promote breakdown of hydrocarbons[41], and nickel (present in the steel) is known to enhance coking in gas crackers[61]. Experimental observations (see section 4.12.5) support the view that breakdown to carbon mainly occurs on the reactor walls. In fact, it is generally true that metal surfaces have undesirable effects in hydrocarbon pyrolysis[40 - 45], and the relatively low metal surface area presented in the molten salt reactor is an important point in its favour.

5.4 The Influence of Temperature

It should be clear from the previous discussion that a complex set of physical and chemical processes are involved in the overall pyrolysis transformation. Many, if not most, of these component reactions are likely to be temperature dependent. Examples are the viscosity of the salt affecting dispersion of plastic in or on the melt; the activation energy for bimolecular reactions; and the kinetics of competing chemical reactions. Since there are a number of phases involved (solid plastic, liquid plastic, molten salt, vapours and reactor wall) and a far from homogeneous vapour, one should be careful of explanations of even the most general kind.

Nevertheless, some kind of knowledge of temperature effects is necessary for design and operation of an industrial unit. A rigorous chemical explanation is not essential, though some kind of understanding is naturally helpful. In practice, pilot scale tests would be used to provide data to produce a satisfactory operating method. Scale is likely to be important, both from a heat transfer and a chemical (wall effects) point of view, and it must be appreciated that this project was necessarily limited in scope. The following is therefore intended as a rationalized description of laboratory scale observations.

At the minimum usable temperature (490 °C) for the chosen salt, there was a substantial conversion of polyethylene to hydrocarbon gases. In general, yields varied by a factor of about two over the temperature range (500 to 700 °C) studied. Methane production consistently increased with temperature, but other components to C_4 showed evidence of maxima on the graphs of yield versus temperature. Although not quantified, the yield of aromatics seemed noticeably greater at higher temperatures, being virtually negligible below 600 °C . The source of the aromatics was almost certainly secondary or tertiary pyrolytic reactions, involving perhaps Diels-Alder cycloaddition followed by dehydrogenation. The increased production of methane at higher temperatures is explicable in terms of its greater thermodynamic stability compared to other hydrocarbons. For other products, the kinetics of the various reactions are probably more important.

Of particular note is the great fall-off in amounts of C_3 hydrocarbons as the salt temperature is increased above 610 °C . One possible explanation is the formation of ring compounds, accounting for the increase in aromatics. It was not practicable to adequately account for the C_5 or C_6 (and to a lesser extent the C_4) fraction because they would occur in both the liquid and vapour portions of the collected pyrolysate. However, the summed yield of C_1 to C_4 hydrocarbons reached a maximum in the region of 610 °C, and it would be surprising if the balance was accounted for by longer chain fragments at higher temperatures. The condensed product also seemed less viscous (i.e. a grease rather than a wax) at higher temperatures, so it is reasonable to suppose that a reduction in C_3 and C_4 at higher temperatures is accounted for by an increase in C_6 to C_8, particularly aromatics. The formation of aromatics is a usual feature of hydrocarbon pyrolysis at higher temperatures [53,61].

Rather than attempt any pat chemical explanation of dubious validity, the following simple model is proposed. The operating region of the reactor may be considered in two parts. The first part is the surface of the molten salt which breaks down the melted polyethylene into a vapour mixture. This vapour mainly consists of straight chain hydrocarbons, with some double bonds, which may broadly be compared to a higher-boiling petroleum fraction. The vapour passes into the second part of the reactor, which is a hot zone near the surface of the salt. In this zone, further breakdown occurs, which may be compared to the vapour phase pyrolysis of naphtha in a conventional tubular cracker. Material is continuously swept away from the vapour pyrolysis region by the nitrogen used as a head-space purge, which simultaneously dilutes and cools the vapours. Further reactions are therefore negligible.

In summary, therefore, the model is as follows.

1) Vaporization of plastic to 'pseudo-naphtha'
2) Pyrolysis of vapours
3) Quench and removal of products.

It is reasonable to suppose that the second stage of pyrolysis principally governs the final products: this is reflected in their similarity to the products of cracking conventional hydrocarbon feedstocks. If this is so, then the product yield and distribution would depend on the temperature and residence time in the hot zone near to the molten salt. The vaporization process would depend on the number of weak links in the polymer chain, and on the volatility of fragments produced by thermal scission. The vaporization stage is thus less temperature-dependent than the vapour pyrolysis stage in the temperature range studied (i.e. well above the degradation temperature for polyethylene, but below the very high temperatures which would volatilize very high molecular weight fragments, and seriously disturb the 'cracker' zone).

In petroleum pyrolysis, increasing the temperature or increasing the residence time has many similar effects. Either is said to increase the 'severity' of cracking. Thus one unit working at a lower temperature with a long residence time may have the same severity as another working at a higher temperature with a short residence time. Other factors are involved in the choice of such combinations, but are outside the scope of the present discussion. A quantitative assessment of the severity of cracking is given by a Kinetic Severity Function (KSF) which combines both time and temperature by means of the reaction velocity constant for a standard compound, n-pentane, and its residence time (actual or hypothetical) in the reactor[53]. For a short explanation see APPENDIX 9. Here, it is only necessary to mention some of its most important properties. Firstly, it can be found for a particular real reactor operating under particular conditions by measurement and calculation. It is then possible to calculate KSF values for other temperatures on the same unit and predict its performance. Furthermore, its performance using a different feedstock can also be predicted. Data from reactors with different geometries but equivalent KSF values can be compared. The logarithm of KSF is inversely proportional to the negative absolute temperature for a fixed 'equivalent time' (a sort of residence time which is effectively a constant for a given unit at a given pressure).

In practice, it is found that conversion of naphtha to propylene is a maximum at about KSF = 1.7, C_4 products have a similar maximum, ethylene yield tends to a plateau in the region KSF = 4 to 6, but methane continues to increase up to the highest KSF values [53]. This is shown in FIG. 36, in which the yields of certain products of naphtha pyrolysis are shown as a function of log KSF [53]. Over the temperature range 500 to 700 °C, negative reciprocal absolute temperature is approximately linearly related to actual temperature, so this graph can be directly compared with FIGS 23 to 26. For convenience, the results at a stirrer speed of 1000 r.p.m. (given in FIG. 25) are given in the same fashion as the naphtha data in FIG. 37.

It would be unwise to interpret the similarity between FIGS 36 and 37 too deeply. Nevertheless, the correlation between a novel experimental reactor and conventional plant is striking, particularly considering the difference in both feedstock and mode of operation. I believe that this correlation provides considerable support for the simple model previously outlined.

FIGURE 36

Products of naphtha pyrolysis in a conventional pyrolyser, as a function of kinetic severity function[60]

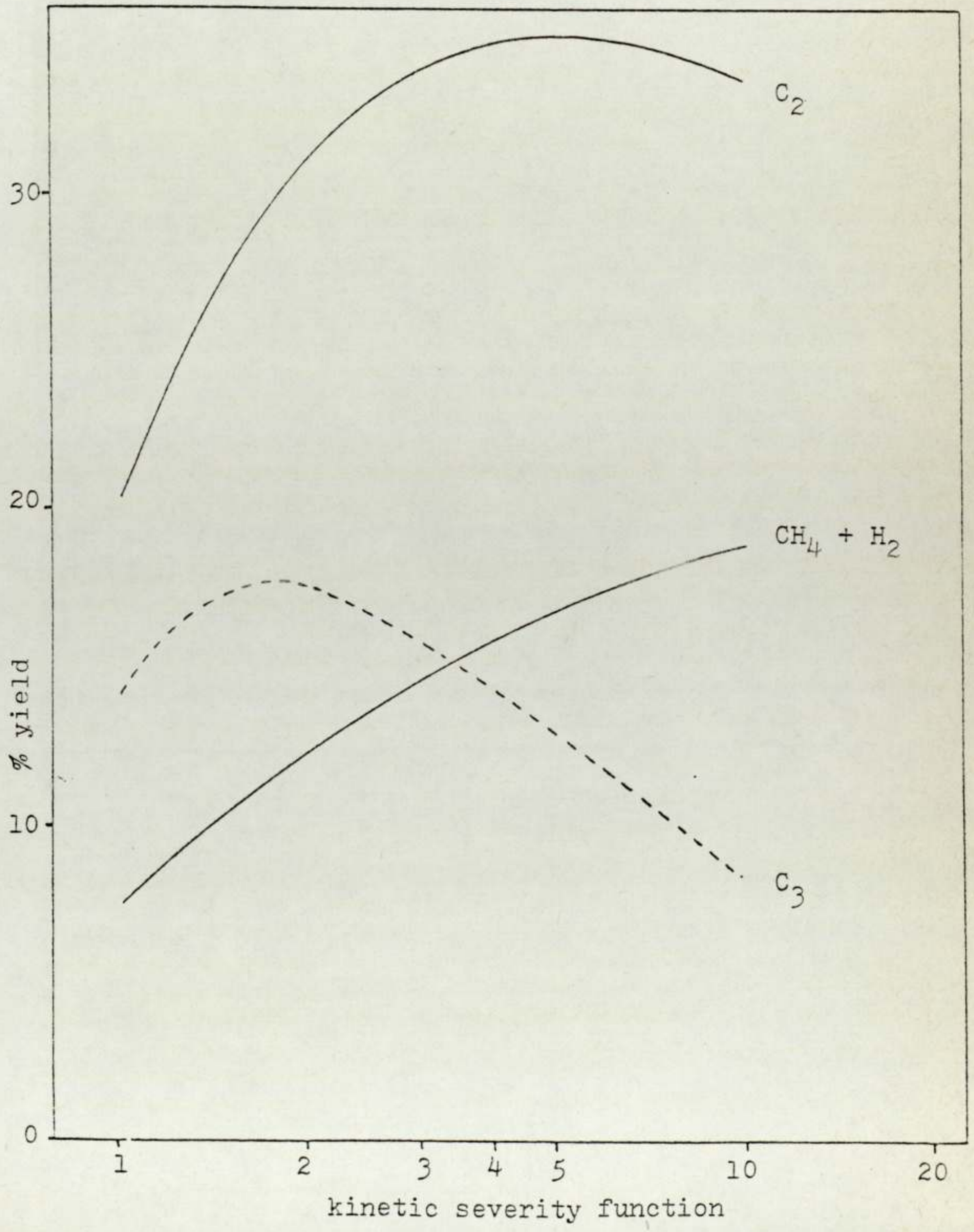
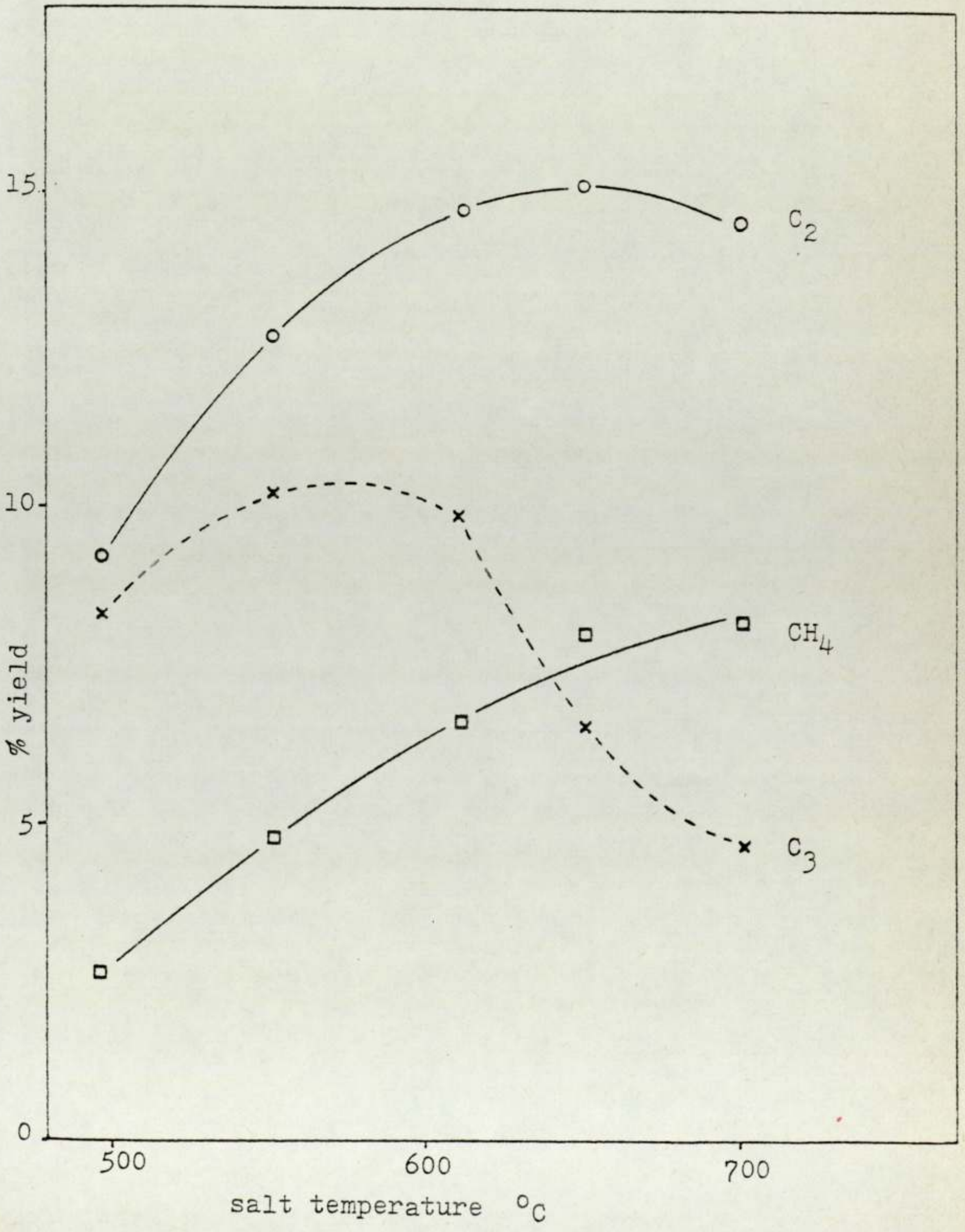


FIGURE 37

Products of polyethylene pyrolysis in the molten salt reactor as a function of temperature (stirrer = 1000 rpm)



A conventional naphtha cracker typically operates at a tube or coil temperature of about 750 °C, and has a residence time in the range 0.1 to 1 second, with a KSF of the order of 1.0. For further comparison, a KSF of (say) 0.7 would be considered 'mild', a value of 2 is 'severe' and 3 would be 'very severe'. The supposed cracker zone in the molten salt unit probably covers a range of KSF values in the range 0.7 to 7, based on the composition changes with temperature. Since these values are for salt temperatures between 490 and 700 °C, which is below the temperature of a conventional cracker, it follows that the residence time in the cracker zone above the salt is probably something more than one second.

The molten salt apparatus at the University of Hamburg was rather different in operation to mine, using a pre-melted plastic feed entering below the salt surface, and temperatures from 640 to 850 °C [11,12,29,124,215,216]. The results are, however, also comparable with the cracker model, since propylene yield from polyethylene was maximum at 640 °C, ethylene levelled off at 790 °C, but methane increased consistently with temperature. Very roughly, these results imply that KSF values were achieved in the Hamburg reactor of a similar range to those in my reactor, but at temperatures typically 50 °C higher. The higher temperature implies a shorter residence time for the same KSF value. The combination of higher temperature and shorter residence time would be expected to give a higher ultimate yield of ethylene [35,53,60,61], as was found to be the case [11,12,29,124,215]. The increased production of carbon and aromatics at these higher temperatures also agree with conventional cracker experience, and support the model.

The fluidized bed pyrolysis of polyethylene by Menzel at Hamburg [11,12,115,124] showed a similar pattern of product composition and yield with temperature, and might also be considered to have a hypothetical internal vapour phase cracker - possibly in the upper region of the fluidized bed.

5.5 Effect of Stirring

The type and degree of stirring would be an important design consideration in any industrial version of the experimental apparatus. Mixing a tank of mobile liquid, to which heat is supplied through the walls, is a conventional enough task not to require further discussion here. On the other hand, the effect of movement of the molten salt on the plastic pyrolysis is less easy to predict, and would certainly require specific attention at pilot plant level. The experiments described in section 4.8 were intended to give some idea of the nature and magnitude of these effects.

As was discussed in section 3.2.4, the propeller used in these experiments was expected to give a mixed flow regime at even the lowest speeds used, and to convert to a fully turbulent regime when the speed was raised to about 500 r.p.m.. The experimental results given in section 4.8 (FIGS 27 and 28) indicate that the yield of desirable products (notably ethylene) is increased by raising the stirrer speed, up to a maximum at about 500 r.p.m.. Increasing the stirrer speed beyond this point does not improve the yield, and actually tended to reduce it slightly.

This observation is most simply explained by supposing that a turbulent liquid is more effective than one with laminar flow, but once full turbulence is achieved no useful change is given by increased stirring. The correlation is intuitively satisfactory, but it is not easy to adequately account for it in terms of the rather complex situation around the salt interface. However, a turbulent surface has both a larger surface area and better heat transfer properties compared with a liquid in a purely laminar flow state. It is reasonable to suppose that turbulence will therefore aid the primary section of the model producing a more dispersed and smoothly vaporizing plastic melt on top of the salt. What is possibly more important is the transfer of heat from the salt to the vapour cracking region just above it. The better heat transfer from a turbulent liquid would allow the cracker zone to operate at a higher temperature, resulting in increased conversion to ethylene. The addition of further kinetic energy to the molten salt in the form of increased stirring would not be expected to greatly improve this heat transfer once the salt was fully turbulent. Violent stirring might have the disadvantage of disturbing the cracker zone and spattering material onto the reactor walls.

It has already been noted that varying the stirrer speed has least effect at the highest and lowest temperatures studied, although a maximum corresponding to the onset of full turbulence is still apparent. At the highest temperatures, the vaporization of the plastic particles will be sufficiently vigorous to disturb the surface in a turbulent manner, to some extent irrespective of the stirrer. The proviso is that the stirrer has to provide effective agitation of the bulk salt. On the other hand, at 500 °C salt temperature there will be little chance for cracking alkanes in the vapour space. That is to say, the hypothetical naphtha cracker in the model virtually becomes ineffective. Instead, one can imagine the reactor headspace being a region in which the unstable fragments and free-radicals directly formed in the polyethylene vaporization interact and rearrange to more stable materials. Stirring the melt would not be expected to have any great effect on such vapour processes, though it could have a marginal change on the plastic vaporization step.

5.6 Kinetics of Pyrolysis of Polyethylene on Molten Salt

It is not proposed here to define an overall mathematical model for the conversion of polyethylene, such as might be attempted for a purely homogeneous or purely surface reaction. There are a number of steps involved, and insufficient data to suggest which are most probably rate-determining. Many processes must be in competition, and their relative effects will depend on temperature. Some comment can however be made on the time element in the pyrolysis process.

The following sequence is suggested as a general description. (See also section 5.3.) A cold granule of plastic dropped onto the molten salt absorbs heat from the salt. Until the plastic becomes completely molten, it maintains a significant temperature gradient, the centre being coolest. When any portion exceeds about 290 °C degradation takes place, and as the exterior reaches 360 to 375 °C gasification commences, continuing until the plastic is completely volatilized. Some heat (enthalpy) is required for the volatilization, and the vapours provide a barrier to heat transfer, so that the vaporization process limits the rate at which heat can be supplied to the body of the granule. The extent of the vapour barrier will depend on its disturbance by movement of the salt or the violence of vapour formation.

The vapour loses contact with a specific plastic granule, and passes into a zone just above the molten salt. This zone is therefore relatively concentrated hydrocarbon vapours and hot, being near to the salt. It is suggested that the principal breakdown of fragments of the polymer chain occurs in this zone, the processes being similar to the pyrolysis of naphtha in a conventional cracker. The endothermic nature of both volatilization and cracking cause a cooling of this vapour zone, as was directly observed in section 4.12.1. The cooling accounts for the dip in flowrate observed after the initial surge of vapour production. (Heat is then transferred to the headspace from the salt and the reactor walls so that it attains its former thermal equilibrium. The expansion of the hydrocarbon gases which results causes the second peak on the graph of outflow against time, e.g. FIG. 17.) The 'naphtha cracker' zone is a limited region close to the melt. Once the vapours pass into the upper portion of the reactor headspace, little further breakdown occurs, this being due to the lower temperature. In fact, the 'naphtha cracker' zone may well be only a very small portion of the headspace, since there is little change in composition of the outflow gases after the first surge.

This is reinforced by the exponential decay type of curve observed for the outflow of hydrocarbons, which closely resembles the physical analogue tested by the sweeping out of ethylene from the headspace. In turn, this agrees with a perfect mixing mathematical model.

Typically, it appears that total vaporization of plastic particles occurs in less than half a minute, and all the major vapour phase reactions are complete by the end of a further half minute. After this time, the main process which occurs is the sweeping out of the reactor headspace by the purge nitrogen. A very small amount of pyrolysis continues on the portions of the vapour which contact the hot zone near the molten salt, or possibly the vessel walls. Thus samples taken near the end of a kinetic run showed slightly more methane than the samples taken after a minute or so, where all components were considered relative to ethylene (i.e. allowing for the dilution by the nitrogen purge).

6 INDUSTRIAL OPERATION OF THE PROCESS

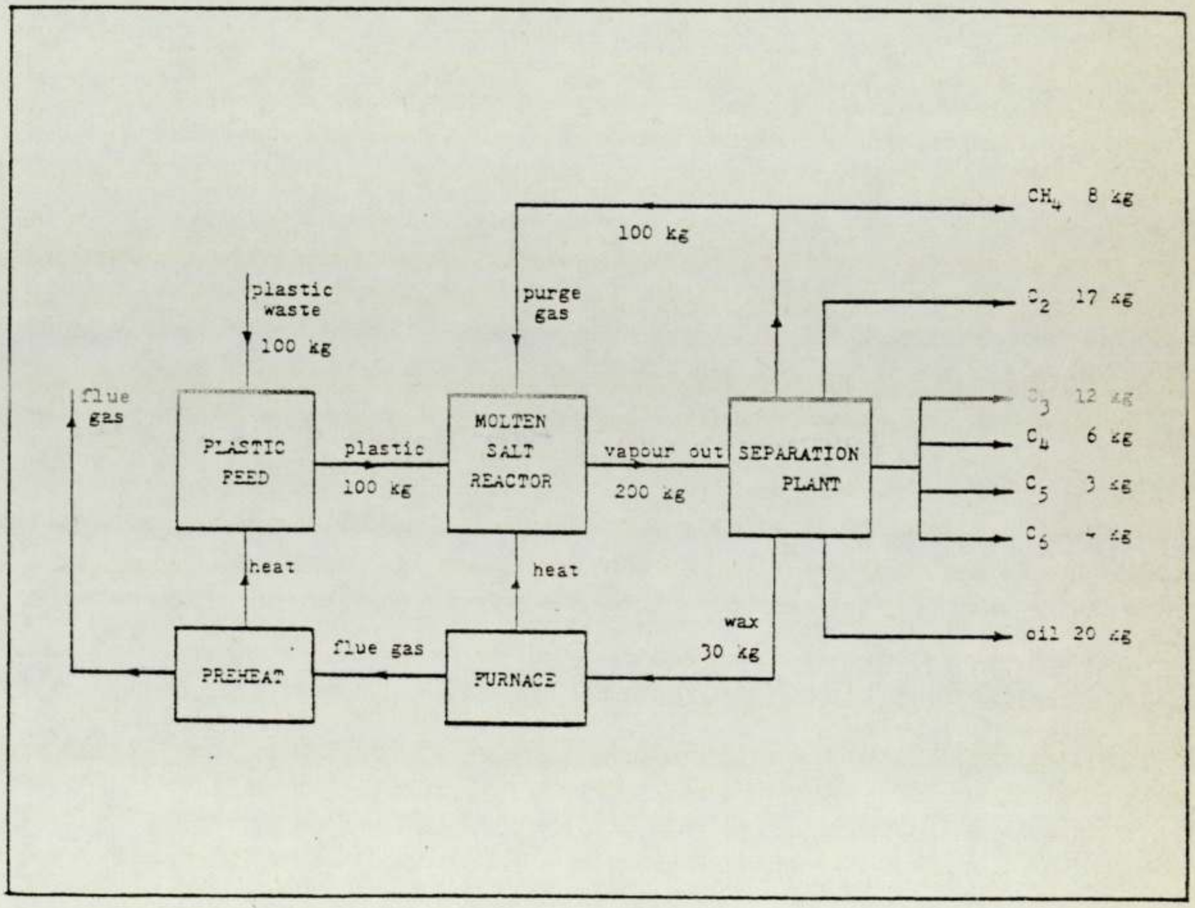
6.1 General Comments

This project has not provided sufficient information for a detailed design or evaluation of a commercial form of the process. Nevertheless, it is possible to make some simple calculations and discuss certain aspects.

FIG. 38 shows a block diagram and mass balance (basis 100 kg plastic) for a plant with similar characteristics to the experimental unit, pyrolysing waste polyethylene at a salt temperature in the region of 600 to 650 °C. Some important differences from the experimental process have been assumed, following conventional chemical plant practice. Firstly, electric heating is replaced by external combustion of fuel derived from the pyrolysis products. The hot flue gases are used to pre-heat the plastic, which is fed in continuously by a screw conveyor, probably in melted form. This use of flue gases conserves energy and also dries the plastic waste. It is here assumed that (except for start-up) the waxy portion of the pyrolysate is used as the prime fuel for the furnace. As a later calculation shows (Appendix A - 6) the reactor should be self-sufficient in energy requirements.

FIGURE 38

Block diagram of an industrial process based on the scale-up of the laboratory molten salt reactor



From experimental results, about half the product will be higher molecular weight material which it is probably uneconomic to separate. The distinction between 'wax' and 'oil' is somewhat arbitrary, and would depend on the cooling and separation processes used. The oil is counted as a product since it may be used as fuel or feed (e.g. to a conventional cracker). Since the wax will arise as a hot fluid adjacent to the molten salt unit, it is suggested that its most effective use is as an immediate fuel. Alternatively, it could be added to the plastic feed, and some other portion used as fuel. A burner system for waxes would be more expensive than one suitable for oil or gas.

Another important difference is that nitrogen is not used as a head-space purge. Instead recycle methane is used. Nitrogen was convenient for laboratory use, but would be much too expensive for plant use. This is partly from its intrinsic cost in large amounts, but also because it would be an extra non-condensable component in the separation stage. In particular, it would not be very easy to separate from methane economically. The amount of methane given in FIG. 38 would produce a gas concentration of C_2 and higher hydrocarbons approximating to that during the initial surge in the kinetic experiments, which are probably most like the conditions under continuous pyrolysis, though some other value might well be found to be optimal.

6.2 Headspace Purge

The function of the headspace purge is primarily to act as a diluent so that desirable products are not broken down by secondary pyrolysis reactions, and is a normal practice in petroleum cracking, particularly for olefin production. There are only two real candidates for a suitable inert gas, methane and steam. Methane would come either from a separation unit attached to the molten salt reactor, or from some general unit on an adjacent plant which utilises products from the plastic pyrolysis. A separator attached to the molten salt unit could then have a less than perfect methane / ethylene separation, so long as the methane was contaminated with ethylene and not the other way about. Since much of the contaminant ethylene will be recycled via the methane purge, the net effect would be to slightly increase the proportion of ethylene in the cracked gases, which would make the separation process easier. A process in which (say) 10 % of the ethylene was carried over into the methane stream would be considerably cheaper than a high efficiency separation, and would probably be worth the loss of ethylene into product methane. Reducing the amount of recycle methane would also have the effect of increasing the ethylene concentration in the product mixture, though such a reduction is limited by the need for a diluent.

The calculated effects of different amounts of methane recycle and of imperfect separation of ethylene are shown in TABLE 7, along with the effect of steam as a purge gas. For the calculation it is assumed that there is no change in product distribution from the pyrolysis stage. It is of course more likely that there will be some undesirable effects which will have to be offset against the advantages of increased concentrations. The table gives the per cent composition of the mixed gas stream after water and all hydrocarbons heavier than C_6 have been condensed out. Hydrogen is ignored, but will be present in the methane streams. On the basis of 100 kg plastic waste, it is assumed that the specified amount of methane is recycled and 8 kg is taken out as product for fuel use. The recycled methane is impure to the extent of the ethylene carried over, and the total loss of ethylene represents that portion which is taken away in the 8 kg of methane which is not recycled.

The other plausible diluent is steam, which is almost invariably employed in modern ethylene production plants. It is generally found to be inert as far as the vapour phase cracking processes are concerned[52,53], but there is no guarantee that it will not affect plastic pyrolysis on a molten salt surface. However, the effects are at least

TABLE 7

Calculated effect of different vapour diluent strategies on the composition of the mixed gaseous products

methane recycle kg	100	100	50	50	steam
C_2 separation loss %	0	10	0	10	-
C_2 total loss %	0	0.1	0	0.7	-
product gas composition					
CH_4 %	72.0	70.7	58.0	56.4	16.0
C_2 %	11.3	12.6	17.0	18.6	34.0
$C_3 - C_6$ %	16.7	16.7	25.0	25.0	50.0

as likely to be good as bad, and would need to be studied experimentally. Banks, Lusk and Ottinger [112,113] claim that steam and nitrogen produce virtually identical products when used to pyrolyse polyethylene in a simple counter-current moving bed reactor. Janning [124] found that steam reduced the amount of char when pyrolysing polyethylene at 800 °C in a fluidized bed. He also reports an increased yield of ethylene compared with systems using nitrogen or recycle gas as fluidizing agent. The use of steam in hydrocarbon crackers is well-known for reducing coke formation on the walls. The high concentration of water would, however, exert a considerable influence on the rate and manner of corrosion of the vessel by the molten salt, which would also require experimental investigation.

The particular advantage of steam is that it is readily condensable, and would thus considerably increase the concentration of ethylene in the mixed product stream (after condensing wax, oil and water) compared with an equivalent headspace concentration for a methane or nitrogen purge. The effect of steam as a diluent is compared with methane in TABLE 7.

6.3 Optimization of Product Distribution

This project has shown that the proportions of the different products depend on the salt temperature, and to a lesser extent on the stirring. It is reasonable to suppose that the feed rate and the amount and type of headspace purge would also affect the outlet composition. Optimization consists of maximizing desirable products and minimizing unwanted ones, the compromise having regard to the capital and running costs, salability of particular products and waste disposal. Experiment and experience would be required to control the operating variables for any particular economic strategy.

During the project, it has generally been assumed that ethylene is a desirable product, that propylene and benzene are probably desirable, and that methane, wax and oil are probably less desirable. It is perfectly conceivable, however, that commercial plants might either operate at relatively low temperatures to maximize oil production at minimum energy cost. At the other extreme, a high temperature and long residence time might be used to get a high conversion to methane. Recycling or a secondary unit might give C_4 to C_9 liquids as preferred products. Another strategy would be to operate so that the fraction used as fuel is exactly sufficient, with no waste or extra fuel used.

6.4 Outlets for Products

Some possible uses for the products of pyrolysis of a waste predominantly comprising polyolefin plastics will be considered. It is assumed that the effects of contaminants can be dealt with effectively on the commercial plant.

6.4.1 Fuel Although the spirit behind this project has been for the conversion of waste plastic into useful chemicals, it has to be admitted that the most economic application might well be the production of hydrocarbon fuel. This might allow the use of lower grade waste, and would probably reduce the need both for pre-treatment of the feed and separation of products. The limitation of scale imposed by the availability of waste means that only one fuel could be produced economically, although in principle several could be made at once. For example, the products would be separated into two streams (apart from recycle) a gas and a liquid. One would be burnt on the molten salt furnace to provide energy for pyrolysis, and the other stream would be the product fuel. This is a case where an appropriate strategy would be to make the non-product stream exactly match the unit's fuel needs.

6.4.2 Ethylene and Propylene It does not seem likely to me that a molten salt unit alone, with a feedstock solely of plastic waste and with refined ethylene as its principal product, can be justified. Firstly, the cost of transport and collection limit its input to perhaps five tonnes per hour at most [11], and hence its output to 10 000 tonnes per year (taking 25% conversion). This level could not compete with the very much larger regular ethylene plants, which commonly produce 100 000 tonnes per year or more. The economies of scale are particularly important in the separation of products such as light hydrocarbon gases. Furthermore, the instability of the waste market means that it is risky to depend on it entirely as a feedstock, particularly if the amounts required are a large portion of that available within reasonable transport distance.

A more reasonable proposal is a molten salt unit providing minor additions to a conventional ethylene unit. In recent years there have been shortfalls in supply of feedstocks to ethylene producers. This has not only led to lower profits from the relative inefficiency of plant running at part capacity, but feedstock prices have increased rapidly. Thus many plants have had to convert at least in part to running on heavier feedstocks [224,225,226].

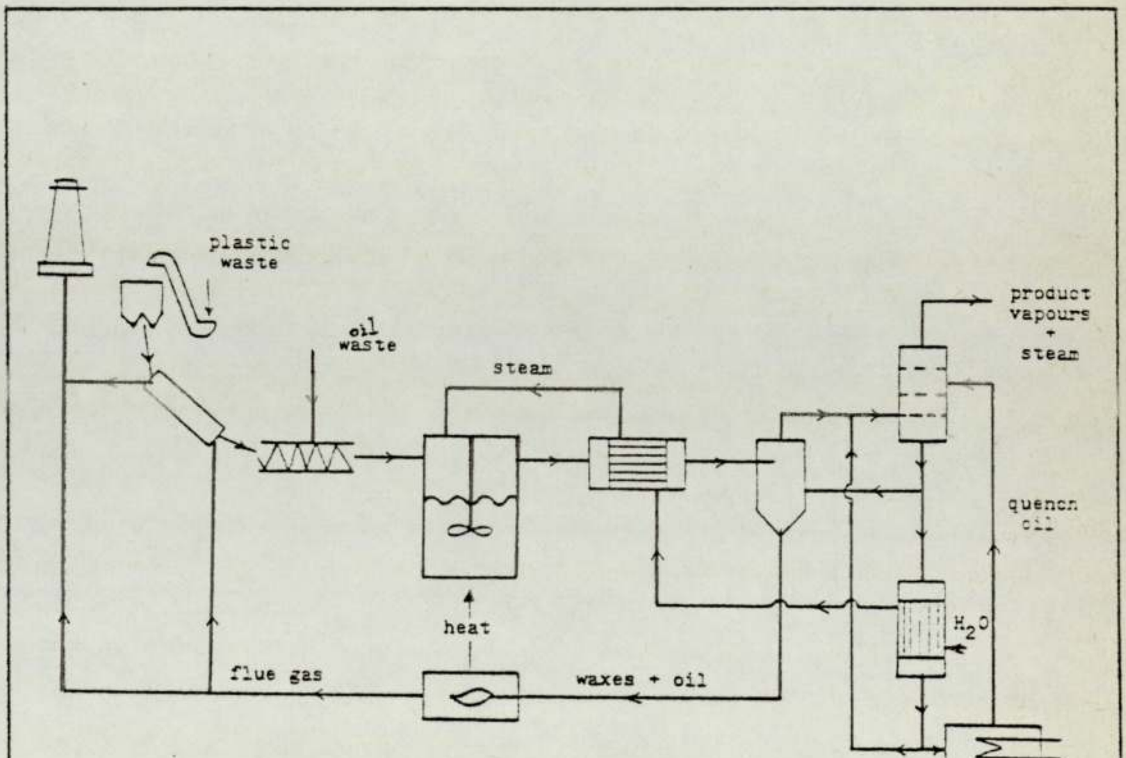
In 1974 the cost of naphtha was already 63 % of the operating costs of a conventional cracker[227], and this percentage has probably increased. Thus any positive contribution to an ethylene production plant might be welcome. Stocks of waste plastic might even be accumulated when naphtha supply is good, and the molten salt unit run as required to make up any shortfalls.

A basic design for such a unit is shown in FIG. 39. It is assumed to be attached to a European-style steam cracker with a naphtha feedstock. The molten salt unit accepts both conventional plastic waste and also lower molecular weight material such as by-product polymer, oils, waxes etc from industrial sources. Minor items such as pumps and controls are not shown, nor are additional fluid circuits for providing fine control of temperatures.

The main input is solid plastic (predominantly the polyolefins) which passes through a rotary kiln, counter to an upward flow of hot flue gases from the salt furnace. This dries and preheats the plastic, which is then passed by a screw conveyor into the molten salt reactor. Also fed into the screw conveyor is any liquid polymer available (waxes, by-product polymer, recycled heavy ends from the molten salt unit) and possibly other hydrocarbon sources such as waste oils. The conveyor is kept at a

FIGURE 39

Functional diagram of hypothetical plastics pyrolysis plant using a molten salt reactor and feeding values to a conventional naphtha cracker plant



temperature of 280 °C by indirect heating from the flue gases (or possibly steam).

The molten salt reactor receives the molten polymer and also steam at 450 °C at a rate equal by weight to the hydrocarbon input. The molten salt is maintained at 650 °C by external combustion, but because the pyrolysis is endothermic, the vapours leave the reactor at 500 °C or so. They are cooled by an in-line heat exchanger to 300 °C, and in so doing raise steam from 120 to 450 °C to feed into the reactor headspace. The vapours then pass into a cyclone where droplets of wax and any solid particles (salt, carbon, fillers and other contaminants from the plastics) are removed. This waxy portion is the primary fuel for the furnace which heats the salt bath, and is made up to the exact amount of fuel required by the controlled addition of oil to the cyclone from a later stage in the plant.

From the cyclone, the vapours pass to an oil quench unit. This is a device for rapidly cooling the vapour by contact with a circulating oil, and is a conventional part of naphtha pyrolysis plant. It works by first adding some quench oil to the vapour stream by means of a special fitting, then passing the vapours into a tower, down which further quench oil flows. Conventionally the quench oil would be separated from the condensed portion of the pyrolysate. In this unit, however, it is proposed that no extra substance be used (except for start-up) and the 'quench oil' is merely the condensed product of the quenching stage. The accumulation of oil in this stage can be used as fuel or recycled to the molten salt reactor. A portion of the hot oil from the base of the quench tower is fed into the cyclone to make up the fuel needs of the furnace. The wetting of the wall of the cyclone also serves to aid condensation of the wax and prevents clogging during start-up and shut-down procedures. The heat absorbed by the quench oil is used to raise low pressure steam at 120 °C, which passes to the reactor outlet heat exchanger and thence to the headspace. The cooled quench oil passes via a tank before being returned to the quench process. The tank is fitted with a coil for heating up during start-up and for temperature control during operation. The gradual removal of oil via the cyclone produces a turnover which prevents the accumulation of polymeric substances in the oil. Excess oil can be used as start-up fuel, or burnt in units elswhere.

The top outlet from the quench tower is maintained above the boiling point of water so that steam does not condense, say at 120 °C. The mixture of hydrocarbons and steam passes to a water quench tower in the main ethylene production plant. This tower follows an oil quench unit and uses water injection to condense out steam and intermediate hydrocarbons. Alternatively the outlet from the plastic pyrolysis oil quench tower could be fed to an intermediate stage in the main plant oil quench unit, but this is more likely to disturb the operating efficiency, particularly if the molten salt unit is in discontinuous operation.

It is considered that the cyclone stage is essential to remove the waxy portion of the pyrolysate, but two other possible methods of dealing with the vapours from the cyclone will be mentioned. The first is where no oil quench is used, and the mixture of hydrocarbons and steam joins the feed to the main cracker unit, adding both chemical and heat values. This is certainly theoretically possible for a unit cracking gas oil, and would probably work on a naphtha unit providing the addition was only a small fraction of the main stream. However, steam cracker units are operated under tightly controlled conditions to optimize their outputs. If (as seems likely) the molten salt unit has an output which is variable in quantity and quality, then its additional values may not be worth the trouble of adjustments to the naphtha pyrolysis unit. On the other hand, the separation stages are more able to tolerate such variations, and it is probably better to pass the plastic pyrolysate to this section of the main ethylene plant.

The second alternative for treating the pyrolysate vapours is to include a water quench tower after the oil quench tower as a part of the molten salt plant. The main reason for not doing this is to keep the molten salt and allied units as simple and cheap as possible. It is, after all, only an adjunct to the main plant. The advantage of a separate water quench would be that the amounts to be transported to the main plant would be much smaller, namely a gas stream and a gasoline stream, the steam having been condensed out. Conversely, there would need to be an extra cooling requirement, and the system is bound to be thermally less efficient than the much larger units employed on the main plant.

Depending on the size and feedstock used for ethylene production, the main plant may have some fraction which it is uneconomic to separate and which is surplus to its own fuel requirements. It could be methane 'tail gas' which would otherwise be flared off, or a C_5 fraction which is too small to bother with. The molten salt unit might be designed to use this fraction as fuel, and to recycle its wax and perhaps oil products.

6.4.3 Synthesis Gas A mixture of carbon monoxide and hydrogen of variable composition is used for a number of chemical syntheses. This mixture is therefore known as synthesis gas, and comes either from a catalysed reaction of hydrocarbons with steam at 800 to 1 000 °C, or from the partial combustion of hydrocarbons. The reactions are exemplified for ethane as follows:

$$C_2H_6 + 2\,H_2O \rightarrow 2\,CO + 5\,H_2 \qquad (2)$$

$$C_2H_6 + O_2 \rightarrow 2\,CO + 3\,H_2 \qquad (3)$$

Gaseous feedstocks such as natural gas, or liquids such as naphtha can be used. Synthesis gas is used for the manufacture of ammonia and methanol, for the Fischer-Tropsch reaction and the Oxo process [61].

In ammonia synthesis, purified nitrogen (from air) and hydrogen (from synthesis gas) are reacted under pressure as follows:

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3 \qquad (4)$$

The air separator which provides the nitrogen also gives the oxygen for the production of synthesis gas by partial combustion.

In methanol synthesis, high pressure and a solid catalyst are used to promote the reaction:

$$CO + 2H_2 \rightarrow CH_3OH \qquad (5)$$

The reaction requires the correct ratio of carbon monoxide and hydrogen, unlike ammmonia synthesis. One method of adjusting the ratio is to have ammonia and methanol manufactured on adjacent plants.

The Fischer-Tropsch reaction is the catalytic condensation of synthesis gas to a hydrocarbon mixture, predominantly normal alkanes and alkenes, essentially thus:

$$CO + 2H_2 \rightarrow (CH_2)_n + H_2O \qquad (6)$$

The usual raw material is coal, and its major application is for synthetic petroleum, though the preponderance of straight chain hydrocarbons gives the product some advantage over cracked petroleum for certain purposes.

The Oxo process produces aldehydes by the addition of synthesis gas to an olefin in solution over a solid catalyst, e.g. for ethylene:

$$CH_2{=}CH_2 + CO + H_2 \rightarrow CH_3CH_2CHO \qquad (7)$$

Variations of the process allow the production of alcohols by hydrogenation of the aldehyde.

It is obvious that at least theoretically the products of plastic pyrolysis are suitable for the manufacture of synthesis gas. As for ethylene production, the safest strategy is probably a molten salt unit making fractional addition to a conventional plant. Waste plastic has the important advantage of a very low sulphur content compared with coal or petroleum feedstocks. To take full advantage of this fact, any unsuitable pyrolysate should be recycled, and the furnace fueled by some more conventional fuel. The hot mixture of steam and hydrocarbons from the cyclone or oil quench could then be fed directly to a synthesis gas unit of the type using reaction (2).

For a synthesis gas unit using partial combustion, the steam would need to be substantially removed by a water quench unit. This would allow more precise control of feed to the synthesizer, but would be energetically less satisfactory. Actually, some steam is commonly added to partial combustion units to a certain extent. It might be that the plastic pyrolysis unit could be used as the source of this steam along with its hydrocarbon and heat values.

If the molten salt unit was attached to a synthesis gas plant based on a liquid feedstock (kerosene, naphtha or gas oil) then then this liquid could be used as the quench for the plastic pyrolysate. The molten salt unit would thus have the effect of enriching and preheating the feed to the synthesis gas unit. The waxy portion of the pyrolysate would be recycled, and the gas portion used as fuel.

If the synthesis gas was used for a Fischer-Tropsch unit, the plastic pyrolysate could either be burnt or reacted with steam to make synthesis gas,or could be fed to the separation side of the unit. Any unwanted hydrocarbons could then be recycled either via the molten salt pyrolyser or via conversion to synthesis gas.

6.4.4 Low Purity Feedstocks The high capital cost of separation plant, and the economies of scale for low temperature distillation, mean that it is unlikely that polymer grade (high purity) ethylene and propylene could be commercially produced solely from plastic waste. There are, however, some processes which will accept a lower purity of olefin. A unit giving substantial separation could probably be constructed at much less cost than one for rigorous purification.

For example, acrylonitrile is made by ammoxidation of propylene by the Sohio process[228] as follows:

$$2\,CH_2{=}CHCH_3 + 3\,O_2 + 2\,NH_3 \rightarrow 2\,CH_2{=}CHCN + 6H_2O \qquad (8)$$

The propylene purity is not critical, between 40 and 90% being suitable. Propane and ethylene are essentially inert, but butenes and higher olefins react. It is important, however, that the feed be sulphur free[228], which the C_3 fraction from polyolefin pyrolysis would be. Not having to separate propane is an advantage, and having ethylene as an allowed contaminant would help to maximize the yield of propylene at minimum cost. Other fractions might be integrated into a synthesis gas process for the production of the ammonia required in this process.

Propylene reacts with benzene much more readily than ethylene does. It is therefore not unusual to use a mixed C_2 / C_3 stream for the vapour phase manufacture of cumene (isopropyl benzene)[61] as follows:

$$CH_3CH{=}CH_2 + C_6H_6 \rightarrow (CH_3)_2CH.C_6H_5 \qquad (9)$$

Ethylene and the alkanes pass through unchanged, and it would then be feasible to add this stream to the feed of a unit making ethyl benzene, for which there are many liquid and vapour phase catalytic processes.

Conversely, ethylene reacts more rapidly in the Wacker-Chemie oxidation to acetaldehyde[61]. This involves the intermediate formation of an adduct of the olefin on palladium chloride in solution. The complex with propylene is less stable than that with ethylene, and is more likely to break down before oxidation occurs. Moreover, the products, acetaldehyde (boiling point 20.8 °C) and propionaldehyde (boiling point 48.8 °C) are readily separated by distillation.

Propylene and ethylene can both be hydrated to propan-2-ol and ethanol respectively by a variety of patent processes[61] . Normally the presence of alkanes does not interfere, nor of course does water. Although production of the two alcohols is normally separate, it is possible that a market could be found for a mixture of them derived from the C_1 to C_3 stream from plastic pyrolysis. The mixed alcohols could be used as an undrinkable solvent, or as a gasoline additive, to improve octane number and prevent icing. The use of these two alcohols is receiving serious attention for octane boosting in the U.S.A. on economic and environmental grounds[229].

There are various other processes in which the mixed products can be used directly, particularly if they are homologues. For example, long chain alcohols from the Oxo process (see section 6.4.3) can be used as mixtures directly as plasticizers, or for the production of emulsifiable waxes or biodegradable detergents[61]. Mixtures of C_6 to C_{12} olefins can be reacted with benzene to form alkylates for the manufacture of sulphonic acid detergent[61].

A broad fraction of pyrolysate could also be fed to a conventional reforming unit. A plausible method would be to pass the vapours from a molten salt unit into a second molten salt unit at higher temperature (800 + °C) to favour the formation of aromatics. The C_6 to C_9 hydrocarbons could then be separated out and transported to a unit dealing with such material from petroleum or coal.

It is also possible to increase the gasoline portion of cracked hydrocarbon gases by catalytic dimerization of C_3 and C_4 olefins: e.g. by the Dimersol process [57]. Possibly a similar process could be carried out on the entire C_3 to C_8 range. This would convert higher olefins and dienes to material which would be left behind as 'bottoms' in a subsequent distillation, producing an olefin-free and hence much more stable gasoline. A feature of the dimerization process is that it tends to produce either branched alkanes or aromatics in preference to normal alkanes. Both of these have high octane numbers.

The olefins could also be converted by hydrogenation to stable alkane mixtures. If the lighter hydrocarbons were used as fuel, the C_4 to C_{12} alkanes and aromatics could be readily stored and transported. They are all liquids at room temperature, except for the C_4 fraction, which would only require moderate pressure or refrigeration. In practice, the C_4 would be sufficiently soluble in a mixture of higher molecular weight hydrocarbons. The mixture could then be used for processes such as the Distillers' oxidation of light naphtha to acetic acid [57,61].

A relatively new method of using naphtha or kerosene feedstocks is the M.B.E. process[57]. The liquid is combined with a hydrogen-rich gas (H_2 about 5% by weight of the hydrocarbon) and thermally hydrocracked to three products: methane (for fuel), ethane (which may be fed to a conventional cracker for ethylene production) and benzene. The products of the molten salt pyrolysis of plastics (apart from wax and oil) may possibly be suitable for feeding to an M.B.E. reactor, providing hydrocarbon, steam and heat values. The molten salt unit would be methane fired, and the waxy portion of the pyrolysate would be recycled.

6.4.5 Carbon Black Good quality carbon black is a useful and salable material with a number of chemical and manufacturing uses. It was formerly produced mainly from natural gas, but currently the major feedstock is oils with a high proportion of aromatics. In either case, the general principle is to decompose the hydrocarbon at high temperatures (around 1500 °C) in a restricted supply of air. This is normally achieved by burning a suitable fuel with excess air, then spraying the aromatic oil into the flue gases [57,61].

Clearly, the oil or gas from plastic pyrolysis could be used for this purpose, either as fuel or hydrocarbon. Conditions would probably be chosen to favour aromatic formation, heavier fractions being recycled and light gases used as fuel. If the plastic waste was rich in styrene plastics then a higher aromatic product would result.

It is theoretically possible that the carbon could be directly formed in the molten salt itself, as has been observed for polyethylene at higher temperatures[11,12, 29, 124,216]. Other types of polymers, notably polystyrene, PVC, nylons, rubbers and thermosets might be expected to give a carbonaceous residue. The recovery of carbon black from the salt is likely to be difficult, however, and makes it difficult to judge the economic viability of the process.

6.4.6 Transcat Process As has been mentioned in section 2.5.2, the Transcat Process is a versatile method for making chlorinated hydrocarbons, notably chlorinated methanes from methane [178], and vinyl chloride from ethane or ethylene or mixtures of the two [230]. Unwanted products can be recycled easily, so that there are effectively no by-products. Various sources of chlorine can be used, notably hydrogen chloride.

It can therefore be imagined that plastics pyrolysis could provide a mixed but suitable hydrocarbon feed for this process. The plastic pyrolyser would be optimized for either methane or ethylene, and sufficient separation plant included to virtually exclude C_4 or higher (which would be recycled or used as fuel). The Transcat recycle would take care of the minor components of the feed.

However, the real possibility for integrating these two molten salt processes lies with the HCl feed. This could be obtained from the pyrolysis of PVC waste, either in a second unit or as a component of mixed plastic waste. One hypothetical method would be to have part of the pyrolysis gas passing counter-current to the incoming plastic waste causing a lower-temperature breakdown of the PVC before the hydrocarbon part of the plastic is decomposed at a higher temperature in the molten salt.

This is undoubtedly the most speculative outlet for the molten salt pyrolysis of plastic waste. However, PVC has already been seriously suggested as a source of industrial HCl [112], and the proposed process has the great advantage that it can use mixed waste. For example, if a substantial amount of plastic became available from a municipal waste separation programme, it could be enriched with industrial PVC waste to the necessary extent. It is likely that other chemical wastes or by-products could be used as part feed.

A most interesting advantage would be the opportunity to integrate two molten salt reactors on the same plant, taking advantage of expertise gained on one to assist in the operation and development of the other.

6.5 Sources of Waste Plastic

6.5.1 General Comments Although virtually all the plastic produced each year will eventually end up as waste, only a fraction of the production can be considered recoverable material. This is for a number of reasons. The lifetime of an individual plastic item may be as low as a few hours for a supermarket meat package, or more than fifty years for the PVC pipe used in buildings. Some plastic occurs in such small quantities and in such intimate mixtures with other materials and becomes waste in such various ways that safe disposal is the best that can be expected. A child's mechanical toy is a good example. Recovery depends on a reasonably large supply and a reasonable concentration of plastic in the waste. Only then is it likely that the process of recovery will be economic. Thus although about two million tonnes of thermoplastics are consumed each year in the U.K. [1], it has been estimated by a large chemical company that only 100 000 tonnes are available for recovery at present.[25]

6.5.2 Municipal Refuse This is a large-scale source of material which is, however, of rather low plastic content, estimated at 1 to 2 % in the U.S.A.[13] and 3 % in the U.K.[3]. In Japan, it may be as high as 8 to 12 %[8]. It has been predicted that Western Europe will produce about 10^8 tonnes of municipal refuse in 1990, of which 10 % will be plastic[231]. Another estimate gives 24 kg per person of plastic collected per year in European municipal refuse by the year 1980[232].

It is probably the main route for disposal of plastic packaging waste, which totals 1.8×10^6 tons per year in the U.S.A.[233], for example. In the U.K. some 55 % of LDPE film produced goes into general packaging, and film is the major (75 %) use of LDPE[1]. About 37 % of polystyrene goes into general packaging[1]. These wastes amount to 181 000 tons per annum of polyethylene and 61 000 tons per annum of polystyrene.

Systems have been devised which are technically capable of producing plastic-rich fractions from refuse[4,11,13,234,235], and even partially sorting it into types[13,232,234,236]. The cost of these processes, however, makes it unlikely that plastic recovery would be viable in isolation. A carefully structured separation facility with plastic as one of several outputs (along with glass, paper and ferrous metal) is an economic possibility, and is presently on trial in Rome[235]. Even if only partial separation was achieved and (say) half the plastic went to landfill or incineration, then refuse could still be a significant source of waste plastic.

Much industrial waste is disposed of via municipal refuse. For example in the U.S.A. about half a million tonnes per year of plastic industrial waste is disposed of in this way[19]. West German industry in 1973 discarded 24 000 tonnes of plastic waste, much of it via refuse[11]. It would be much more economic if the plastic waste were collected directly from industry, rather than being recovered from mixed refuse, which would depend on economic of legislative incentives giving a value to plastic waste that paper and metal scrap has[5].

6.5.3 The Plastics Industry The prime resin producers and users all produce a certain amount of waste as part of their operations. These arisings have been looked at very carefully by Arthur D. Little Inc.[5]. In the case of polystyrene and the polyolefins it is estimated that about 0.3 % of total production is generated as 'nuisance plastic' which is difficult to dispose of. For PVC the figure is 0.6 %. These figures suggest tens of thousands of tonnes per year in the U.S.A. alone.

The resin compounders and fabricators also generate waste, but unlike the producers it is relatively easy for them to recycle. Nevertheless, about 2.7 % of their production is nuisance plastic. Certain operations give particularly high levels. For example, wire and cable coating generates nuisance plastic at 4 to 5 %, which is equivalent to 20 000 tonnes per year in the U.S.A.. The extrusion coating of paper produces 6 % unusable waste, and the manufacture of foamed plastic articles 9 %. Trimming and cutting processes can produce up to 10 % waste which cannot be recycled by the manufacturer.

The final industrial users (packagers, fabricators) overall generate less than 1 % nuisance plastic, though some instances are particularly high, such as the 6 % typically discarded by users of film for wrapping.

6.5.4 Waste from Other Industries Various service and manufacturing industries generate significant quantities of plastic waste, although they do not primarily deal with plastics. For example, it was reported[21] that a U.S.A. factory has 40 tons per day of packaging waste which is predominantly plastic and which is pyrolysed for fuel. Catering outlets, including airlines and railways, use a lot of disposable ware and pre-packaged units. Distributive trades, such as supermarkets, produce a lot of packaging waste, much of which is plastic. The amounts for an individual supermarket are, however, small - maybe three tons of plastic per year[5], and much the same will apply to other industrial waste. In principle, of course, the amounts and perhaps concentrations could be improved by the operation of scrap merchants, in the same way that metals, paper and rags are collected and sorted.

There is in fact a scrap plastic business in operation, with various small firms competing for scrap which can be ground up and reprocessed. The sources these firms find unacceptable might be candidates for pyrolysis. This would include material which is too badly contaminated for cleaning to be worthwhile, and plastic which has been attached to some other substance such as cloth or metal.

At the moment, those firms dealing in scrap plastic mainly take material which is surplus or off specification, rather than used. Waste merchants deal in used items but regard plastic as a nuisance contaminant in paper, rags or metal. One possibility would be the combination of plastic recovery with the recovery of some other material, thereby giving the merchant further profit from waste which is already worth treating.

As an example, the recovery of copper from wire and cable scrap is an established part of scrap metal markets. The coverings include rubber and cloth, but are nowadays largely plastic, principally PVC. Generally the plastic is burnt off, causing environmental pollution. A molten salt method has already been proposed for stripping plastic from wires [237,238]. The main advantage claimed is a cleaner metal, but the saving in pollution and the possibility of recovery of HCl should also be considered.

Another example is plastic-coated paper and board. Surprisingly, it is considered worthwhile recovering the cellulose portion by pulping, and a largely plastic waste is an unwanted by-product [5]. This waste is presently tipped or burnt, though it is about 10 % of the original scrap.

A down-to-earth idea of the nature of waste recycling is given by an article on the Kabor plant for making boards from waste polyethylene[239]. The £2 million plant can accept plastic with up to 15% contamination. The article is, however, a straight plea for more waste to be supplied, since the owners were having difficulty approaching the 18 000 tons per year capacity. To remedy the deficit, they were starting to operate mobile compactors of 32 cubic yards capacity each. These would greatly reduce the bulk, which is the principal problem in transporting plastic wastes, and would be sited at or near waste arising points. This kind of arrangement is important in getting the maximum supply of concentrated plastic waste at the minimum collection cost. It must be supposed that the problem was not insuperable, since Laporte opened a comparable though smaller plant some three years later[25].

6.5.5 Medical Products A revolution in medical laboratories and treatment units has been the introduction of sterile disposable plastic items such as syringes, Petri dishes, pipettes and specimen containers. Until recently, these were largely made of polystyrene, and last year acccounted for 4% of polystyrene consumption in the U.K., or nearly 7 000 tons [1]. Polypropylene has been increasing its share of the market, and 18 000 tons of polystyrene and 38 000 tons of polypropylene were ascribed to medical use during 1978 in the U.S.A. [2]. These items are either bagged and incinerated on the premises, or autoclaved and passed into municipal waste. Prompt heat treatment is of course required because of the risk of infection.

A small molten salt pyrolyser might therefore be used in a hospital to dispose of such items. It is unlikely that it would be worthwhile collecting chemical products from such a process, though the products might have some minor value as fuel. Polystyrene is a particularly difficult material to incinerate, and has more than once been known to gum up an incinerator designed for human or animal tissue. It is conceivable that bags of autoclaved sterile waste could be collected from hospitals and dealt with in a larger unit, from which chemical values might be derived.

6.5.6 Bottles Plastic bottles deserve special consideration on three counts. Firstly, they are a major and widespread use for plastics and are almost invariably non-returnable. Secondly, their shape and lightness makes them relatively easy to separate from other waste, and to discriminate between full and empty bottles. Thirdly, the consumption is relatively predictable and often waste disposal localized.

In the U.S.A. in 1978, 494 000 tons of high density polyethylene, 46 000 tons of PVC and 28 000 tons of polypropylene were made into bottles [2]. Collections from municipal refuse might be expected to reflect this ratio of plastics. Other collection points, such as catering areas and transport operations might provide a relatively concentrated source of regular composition. A particular source or other changes might alter the relative amounts of the different plastics. For example, it was predicted that 60 % of all bottled beer in Germany would eventually be sold in PVC bottles [21]. The national importance of the drink implies a usage of 4 900 tons of PVC per year per million Germans. Adapting these figure to the U.K. gives 290 000 tons per year of very collectable PVC scrap. It has recently been reported [240] that use of plastic bottles in the U.K. will rise from an annual 10 - 20 million to 120 million by the end of 1979.

There have been a number of tests of collection of plastic bottles, ranging from Boy Scout collections of litter in the U.S.A.[5] to collections from householders in Spain[5] and France[241]. The French currently have PVC bottle collection projects under way in ten towns, and claim a 20 to 47 % recovery of bottles bought[241]. France uses 130 000 tonnes per year of PVC for bottles[241].

6.5.7 Tyres As was mentioned in section 2.4.4, rubber can reasonably be considered along with plastics, and the predominant rubber waste is tyres. In fact, automotive tyres account for 70 % of U.S.A. rubber consumption[13]. The number of tyres discarded annually has been estimated as 200 million in the U.S.A.[133] and 13 million in the U.K.[138] during 1978. By weight, these figures approximate to 24 million tonnes and 1.5 million tonnes respectively. In West Germany 340 000 tonnes were discarded in 1974[124], and in Japan 550 000 tonnes were discarded in 1975[8].

The ready availability of the waste can be seen in the fact that tyre pyrolysis plants are in an advanced state of planning at a level of 100 000 tonnes per year in the U.S.A.[13,242], and 50 000 tonnes per year in the U.K.[243]. Sinn et al.[124] point out that a typical European oil rig produces 22 000 tonnes per year, while American rigs average 1 200 tonnes. Thus a plastic or (more likely) a tyre pyrolysis unit could have an output comparable with an oil well. To take the analogy further, many millions of tyres have been used in land fill and for the construction of artificial reefs[133,244], including one reef of over three million tyres[133]. Goodyear suggest that in future these deposits could be used as rubber 'mines'[133]. The construction of rubber reefs has produced a technology for slashing, compressing, breaking or otherwise reducing the density of bulk tyres [244] which might be of use for a pyrolysis unit.

Although the products of tyre pyrolysis are perhaps not as attractive as those from some plastics, the ready availability of the scrap is a major positive factor. The pyrolysis of tyres in molten salt is under active practical and theoretical investigation at this University, and also the University of Tennessee [139,214].

6.6 Size of Unit

The size of the commercial unit obviously depends on the application. For very special uses, such as the production of HCN from polyurethane, it is conceivable that a very small unit might be useful for dealing with in-house waste. In more general applications, as discussed in 6.4, it seems unlikely that it will be worthwhile processing quantities of less than one tonne of waste per day, though lesser amounts might be dealt with for disposal. The upper limit is defined by the supply of waste in question. The Kabor experience (see section 6.5.4) suggests that 18 000 tonnes per year or 60 tonnes per day is a likely limit [239] for hydrocarbon plastic waste. For tyre pyrolysis plants as large as 100 000 tonnes per year are feasible[13, 242].

Although the process is a continuous one, it need not necessarily operate throughout the year. The unit might be used to feed values to a chemical plant making limited runs and using up accumulated waste. Conversely, it has been suggested that waste pyrolysers could be made portable and taken to accumulations of waste, rather than the other way about [245]. The unit might use pyrolysis gas for fuel and convert bulky solids to transportable liquids.

6.7 Construction of Unit

The design of the furnace and molten salt pot would most sensibly be based on industrial experience of salt baths for metal heat treatment. Standard versions of these are available for salt charges ranging from a few kilograms to about a tonne[171]. There is detailed data on corrosion resistance for the salt mixture $BaCl_2$-KCl-NaCl which is similar to that used on this project[202]. There is of course plentiful experience of design and fabrication of stainless steels for high temperature service.

A large molten salt unit to process 30 tonnes of waste plastic per day would only require about 10 cubic metres of salt, so that a stirrer shaft length of perhaps 2.5 metres would be required. This is not unduly long, even at higher temperatures and without a bottom bearing.

Screw conveyors suitable for plastic waste are available as 'off the shelf' technology. Design of product separation plant and heat recovery systems would come from petrochemical experience. Alloy steel would be needed in the salt reactor, but carbon steel would probably be adequate elsewhere. Special precautions might have to be taken due to the presence of hydrogen, or of course if there was any HCl production from PVC content.

Since PVC is such a likely contaminant, methods of dealing with its HCl production might be considered in slightly more detail. One strategy would be to use corrosion-resistant materials at crucial points and employ some kind of scrubber to remove HCl as soon as possible. Another alternative is to use an alkaline material such as $Ba(OH)_2$ as a 'getter' to absorb acid traces, either in the molten salt reactor or in a unit immediately following it. A method which would deal with even high levels of PVC would be to subject the waste to a lower temperature 'pre-pyrolysis' stage to break down the PVC. This section of the equipment would be vented or purged to remove HCl before the waste passed to the main pyrolyser[123,124].

6.8 Economic Considerations

The use of a plastic pyrolysis unit (whether molten salt or otherwise) will naturally require some economic justification. It may not, however, be strictly necessary for it to make a profit like an ordinary chemical reactor. For example, it may be of very similar cost to dispose of some in-house waste polymer as to convert it by pyrolysis. The pyrolyser may have the advantage that the waste is an assured feedstock which may be valued in times of shortage. On-site treatment removes any dependence on outside contractors, and in any case the cost of disposal may rise.

The capital and running costs of the pyrolyser will depend on how much it is integrated into the main plant: in particular how much labour and equipment is required solely for the feed and separation sections. For example, some suitable separation equipment on a plant may only be running at part capacity for various reasons. Additional feed to this section from a plastic pyrolyser would have effectively no extra capital requirement. Except perhaps in the case of a unit processing mainly PVC, it can be assumed that a plastic pyrolyser is self-sufficient in energy requirements, since some of the product can be used as fuel.

Taking a unit pyrolysing 1 tonne per day of waste which is predominantly olefins, and using 33 % of the product as fuel, on a continuous basis for 300 days per year, the products will amount to 200 tonnes per year. Since the 33 % burnt will be the undesirable portion, it will be assumed that the products have an overall value to the main plant of the equivalent weight of naphtha.

A heat treatment salt bath and control gear for a working salt charge of 590 kg of salt at 650 °C can be bought for about £ 5 000[245]. This is a suitable size for the expected throughput. For the sake of discussion, suppose that this is one quarter of the capital cost, and the capital cost is depreciated over 5 years. The pyrolyser thus has to return £ 4 000 per year to pay off the capital. The main running costs will be the replacement of pot liners (say 8 per year at £ 400 each) and salt (say 2 tonnes at £ 400 per tonne) say overall £ 4 000 per year. If the unit requires the sole attention of one operator or the equivalent on a continuous 3-shift system, then a sum of £ 15 000 per year is required for wages. A further sum of £ 5 000 may be added for overheads and utilities. The total is therefore £ 28 000 per year or £ 140 per tonne, which also happens to be the expected market price for naphtha during 1979[246]. The process would therefore be uneconomic, since there will be an additional cost of collecting and transporting the plastic waste. A further increase in the cost of naphtha might cover this, however. Even so, it is unlikely that such a speculative plant would be built without a bigger profit margin.

It is obvious that the labour cost is the main factor. A plant of five times the capacity would probably not require more than one operator equivalent, and the capital cost of the molten salt unit would probably not be much over twice the cost of the smaller one. This is because the control gear is much the same. No costs are available for a salt bath of such a size, but typically on the smaller units doubling the size increases the price by only 10 %. (Fuel costs to maintain the salt temperature increase by about 50 %, but that is not important here.)

Thus taking a plant of 5 tonnes per day capacity, output 1 000 tonnes per year, the assumed capital cost is £ 40 000 depreciated over 5 years, i.e. £ 8 000 per year. Labour and overheads are £ 20 000 per year. Running costs are 10 tonnes of salt at £ 400 per tonne, and 8 pot liners at £ 1 000 each, which comes to £ 12 000 per year. Total costs are therefore £ 40 000 per year or £ 40 per tonne of product, which would certainly be economic.

7 CONCLUSIONS AND RECOMMENDATIONS

7.1 The Apparatus

A moltens salt reactor has been designed, constructed and operated. Its general performance was in accord with the design intentions. A bath of heat treatment salt could be heated up and melted within a reasonable time, and maintained at a temperature between 490 and 710 °C without difficulty. The molten salt was stirred without problems, and the shaft bearing and seal performed adequately. Corrosion was observed in the reactor, but was not excessive. There were no mishaps, so fortunately the secondary safety features were not used.

In the stirred bath of molten salt, batches of one gram of polyethylene granules were smoothly and rapidly pyrolysed at salt temperatures between 490 and 700 °C. A very simple technique proved effective in sampling the pyrolysis vapours. A test of this technique accounted for 98 % of an added aliquot of ethylene gas. A method of gas chromatography was developed which gave adequate resolution of the product hydrocarbon vapours up to C_6, and this method was cross-checked against standards and mass spectra.

7.2 The Results

Granules of thermoplastic (polyethylene, polypropylene and polystyrene) go through a particular sequence of heating, melting and gasification on the molten salt. For 30 mg particles, this process is complete in about half a minute at 550 °C . For particles of similar size, it was observed that polystyrene is converted in a shorter time than polyethylene, while polypropylene takes longer. No significant amounts of char were observed.

The pyrolysis vapours were gradually displaced from the reactor headspace by a continuous nitrogen purge. This displacement followed the model of a continuous stirred tank reactor with a 'half-life' of about 60 seconds under the flow conditions used for the greatest part of the experimental work.

At least 25 different substances were present in the pyrolysis products of polyethylene, taking hydrocarbons up to C_7. However, ethylene was the predominant product. In the pyrolysis of polypropylene, the principal product was propylene. Substantial amounts of methane were formed in each case, and there was a significant partial pressure of hydrogen. Acetylene could not be detected.

The products of pyrolysis of polyethylene were mostly alkenes, alkanes and dienes. There was a greater proportion of alkanes in products of low molecular weight, whereas products of longer carbon chain length were more commonly dienes. Some cyclization to 5 and 6 membered rings took place, particularly at higher temperatures. Benzene was notably present in the products.

The composition of the pyrolysate was a clear function of temperature, giving a greater proportion of gases at higher temperatures, with correspondingly less wax and oil. The proportion of methane increased continuously with temperature. The production of propylene and propane reached a maximum around 600 °C and fell off sharply at higher temperatures. Ethylene yield reached an apparant plateau at 700 °C. Ethane had a maximum yield around 600 °C. These changes can reasonably be explained by secondary vapour-phase processes acting on the initial products of pyrolysis. The lesser yield of C_2 and C_3 is probably accounted for by increased aromatic production at higher temperature by these secondary reactions.

A simple model is proposed in which the vapours above the molten salt behave as if in a conventional naphtha pyrolysis tube. Use of the Kinetic Severity Function appears to give substantial correlation between the composition of the plastic pyrolysate and the composition of a naphtha pyrolyser. The molten salt unit operates at a lower temperature than the equivalent naphtha pyrolyser, in this model.

Both the composition and overall yield of gases were a function of stirring speed. Yields increased with stirring speed until a fully turbulent regime was achieved. Further increases in stirring rate did not improve yields.

The composition of the pyrolysis vapours varied with time after addition of plastic. The gas collected almost immediately after addition was nearly all ethylene. By the time the particles had been completely gasified, a more complex mixture resulted, which did not vary much in its proportions thereafter. The longer time the vapour spent in the reactor headspace, however, the greater was the conversion of ethylene to methane.

The experiments were carried out independantly of some comparable work at the University of Hamburg by Perkow et al. Many of the Hamburg results were not published until after the equivalent experiments described in this thesis had been carried out. Although the apparatus and experimental programme were very different, where comparisons can be made the general trends and many of the values measured are in good agreement with what was found at Hamburg.

7.3 Industrial Application

The application of the molten salt unit to the conversion of polyethylene waste is technically feasible, and should be economic on a scale of 5 tonnes per day. The problems of collection of waste is the main limitation to the size of the unit: no more than 30 tonnes per day seems likely at present. Changes in the use of, or methods of dealing with waste plastics could well change the situation. In particular, plastic waste might become available in some quantity as a by-product of some other waste recovery programme.

The use of PVC as a feedstock has not been considered in any detail, but its increasing use for bottles could give amounts of waste with some promise for conversion into HCl and char, though corrosion might be a problem. Automotive tyres are a particularly promising alternative to plastic waste as a feedstock for molten salt pyrolysis. This is primarily due to their ready availability on a scale which could feed a plant with tens of thousands of tonnes per year. Considerable further development would, however be required to make a molten salt unit practicable on such a scale.

It is unlikely that a plastics pyrolysis unit would be worthwhile as the sole feed of a particular chemical to a plant. It is more reasonable to consider a waste pyrolyser making useful additions to a plant with other sources of feedstock. A possible exception would be the small-scale generation of reagents such as HCN or HCl.

It is most likely that a plastic pyrolysis unit will be adjacent to, and feed directly to the separation unit on a conventional plant. A possible exception would be the manufacture of carbon black, which is easily stored and transported. It is also possible that relatively small pyrolysis units could be sited near to a source of waste plastic, and producing transportable oil and wax products. This might reduce transport costs.

About one third of the pyrolysate will be required as fuel to supply the energy needed to operate the molten salt pyrolysis unit. The unit can thus be energetically self-sufficient with a yield of about 67% on a dry weight of polyolefin waste. A suitable size would be about 500 kg of salt per tonne of waste to be processed per day.

Use can be made of heat treatment salt technology, and this will be an important body of experience for design considerations. Corrosion will probably be greater than usual on a chemical plant, but can be kept to an acceptable level. The use of renewable linings is a probable method of dealing with corrosion by the molten salt.

7.4 Recommendations for Future Work

Assuming that this work holds some potential for commercial exploitation, future research should be designed to more closely define certain features of the system and to follow up particularly promising areas.

The simplest variation would be to repeat many experiments but using different plastics, in particular polypropylene, polyvinyl chloride and polystyrene. It would probably be of interest to look at the thermosets and the rubbers, since the former are not easily recovered and the latter are available in large quantities. In all cases it would be best to keep to commercial formulations (e.g. moulding granules, reclaim rubber crumb) rather than pure polymer. The co-pyrolysis of a mixture of plastics approximating to that found in municipal refuse would be a useful exercise from several points of view. Firstly, there might be synergistic effects giving unexpected results. These need not necessarily be disadvantageous. For example, PVC might be a promoter for polyolefin pyrolysis, or the presence of other plastics could possibly reduce the char from PVC. Secondly, it would be advantageous to process plastic from refuse without further separation. Thirdly, it would give some idea of the effects of contaminants in supposedly pure industrial plastic waste.

The use of steam as a purge gas is an important alternative to nitrogen which ought to be investigated. As discussed in section 6.2, it has many advantages over nitrogen on an industrial scale. If the pyrolysis results were similar, it would be the most probable choice for commercial pyrolysis of polyolefins. A dry system might have some advantage for PVC pyrolysis to HCl, however. An initial test would be to add a small amount of steam to the nitrogen purge, or even to bubble the nitrogen through water so that it is saturated at room temperature. This would indicate if the presence of water had any special effects.

The addition of a small amount of air would also be interesting, to see if gaseous oxygen has any promoting effect. It would, of course be important to see that the vapours were always on the fuel-rich side of the explosive mixture. After the gasification of the plastic the air addition would be stopped so as to purge out with nitrogen. The most cautious initial test might be to have the purge stream switchable between high purity (oxygen-free) nitrogen and normal industrial grade (up to 0.5 % oxygen).

In a later more advanced reactor, the use of air or air and steam should be considered as a diluent. That is, a small fraction of the pyrolysis products would be combusted in the reactor headspace. The loss of product might be offset by the promoting effect of oxygenated chemical species. Air is of course cheap as a diluent. The next stage of experimental reactor should preferably include facilities for the recycle of the pyrolysis gases. It would be possible to mimic this by using methane as a purge in the present reactor, but special arrangements would have to be made because of the fire risk.

A continuous feed device is probably the single most important addition to the apparatus which can be recommended, since it would then be a more realistic analogy of an industrial unit. Ideally, the feed device should give the option of passing the plastic above or below the surface of the molten salt.

The effect of different types and speeds of stirring will need to be investigated under continuous feed conditions. It is my opinion that drawing much of the plastic below the surface of the salt will give an unacceptable level of splashing due to gas evolution.

The use of other salts would allow the experiments to be carried out at higher or lower temperatures. I think it unlikely that temperatures in excess of 900 °C will be useful, since any gains in yield will be offset by greater energy requirements and difficulties with materials of construction. Similarly, it is my impression that the rate of pyrolysis will be unacceptably slow below 400 °C. It is possible that some salts could exert a useful catalytic effect. For example, if steam were present then carbonates are said [184] to promote the conversion of carbon to CO and H_2, thus preventing the build-up of char.

It was considered by this research group that, apart from polyolefins, the single most promising line of investigation was the pyrolysis of scrap tyre rubber. In fact, a project is already under way, using the apparatus which was built for this thesis, to pyrolyse pieces of tyre on molten salt. A more detailed investigation of the occurrence of plastic wastes and some conversation with industry would be useful. This would seek to identify particular sources of waste which might prove profitable to convert.

It is my belief that only when a particular waste and range of products is decided upon, is it worth looking at corrosion in any detail. Both the salt and the container are variables in this matter, and it would be pointless to fit one to the other, then find a change is required for some other reason. Under continuous pyrolysis, the salt and the vapour space will have rather different properties from those on a simple stirred bath of salt. Similarly, the presence of significant partial pressures of water and hydrogen could have major consequences on corrosion in both vapour and liquid phases.

Finally, it would be of interest to use two molten salt units in sequence. For example, one could be at 500 °C to cause the initial breakdown of the plastic, and the second might be at 750 °C to rationalize the products and eliminate high molecular weight material. The second reactor would probably be in a different form, perhaps in the form of a tower to give good gas - liquid contact. It is in the second reactor that there is the greatest scope for catalytic or scrubbing reactions. Thus it could contain basic salts to remove acid gases, or agents to promote cyclization or other desired reactions.

APPENDICES

Note: The following calculations explain or justify certain numerical assertions in the text. Specialist data is specifically referenced. Standard thermodynamic values and similar data come from standard handbooks[248,249].

A - 1 Vessel overpressure due to polymer gasification with all exits blocked

If a batch of polyethylene (one gram) had gasified in the reactor with all exits blocked the resulting overpressure can be calculated as follows. As a pessimistic assumption suppose that it is totally converted to ethylene at 700 °C. Take the reactor headspace as a volume of 1 dm^3 and assume ideal gas behaviour. The relative molecular mass of ethylene is 28. Therefore 1 g of vapour at 273 K and 1 bar would occupy $(22.4 \div 28)$ dm^3. Therefore:

$$\text{Volume at } 700\,^{\circ}\text{C} = \frac{22.4}{28} \times \frac{973}{273} = 2.85 \text{ dm}^3$$

Since the headspace will already be occupied by 1 dm^3 of purge nitrogen at 1 bar, the total pressure will be 3.85 bar. The vessel overpressure is therefore 2.85 bar.

A - 2 Vessel overpressure due to polymer combustion with all exits blocked

Suppose the reactor headspace has avolume of 1 dm^3, and is filled with air at 1 bar and 800 K. The amount of oxygen will be about:

$$\frac{1}{5} \times \frac{1}{22.4} \times \frac{273}{800} \approx 3 \times 10^{-3} \text{ moles.}$$

The combustion process will therefore be limited by the oxygen, since this quantity could combust only about 40 mg of polyethylene. The reaction

$$(CH_2)_n \text{ (solid)} + O_2 \text{ (gas)} \rightarrow CO(g) + H_2O(g) \qquad (10)$$

implies a volume increase of one volume per volume of oxygen. If isothermal, it would account for a pressure increase of 0.2 bar.

Since combustion is a rapid process in the vapour phase, it may be assumed that the heat of combustion is entirely absorbed in heating up the vapours. (The heat necessary to vaporize the plastic is assumed to come entirely from the molten salt.) The heat of combustion of ethylene at 300 K is 1 330 kJ mol^{-1}, i.e. 665 kJ mol^{-1} for CH_2. Less the heat of combustion of CO, 280 kJ mol^{-1} gives a figure of 385 kJ as the enthalpy released per mole of O_2 involved in the combustion of the vapours to CO and H_2O. In this case, the heat available is therefore 1 155 J.

If it is assumed that the polyethylene has been completely converted to ethylene and then ethylene has combusted to CO and H_2O , the headspace will thus contain (in round figures) 34×10^{-3} mol ethylene, 12×10^{-3} mol N_2, 3×10^{-3} mol CO, and 3×10^{-3} mol H_2O. Assume that the mixture has similar thermal properties to its largest component, ethylene, for which the molar heat capacity at constant volume C_v at 800 K is 76.2 J mol^{-1} K^{-1}. Hence the rise in temperature due to combustion will be:

$$\frac{1155}{76.2 \times 52 \times 10^{-3}} \approx 290 \text{ K}$$

Thus if pyrolysis produced vapours at 500 °C , the effect of combustion would be to raise them the 790 °C . However, taking a very pessimistic view;- Suppose that pyrolysis results in vapours at 700 ° C , then from Appendix A - 1, the headspace pressure due to pyrolysis is 3.85 bar. The effect of combustion will be to increase this to:

$$3.85 \times \frac{1263}{973} = 5.0 \text{ bar}$$

(on an ideal gas basis) or an overpressure of 4 bar

A - 3 Stresses on reactor

The overpressures produced by the unwanted occurrences discussed in Appendices A - 1 and A - 2 may be compared with the pressure at which the reactor would be expected to fail. It should be noted that the reactor was protected by a bursting disc with a rupture pressure of 1 bar. Obviously, the apparatus must not fail below 1 bar. It was considered preferable that if the bursting disc were somehow to be blocked off that the mode of failure should be on the upper end of the apparatus, i.e. venting vapour rather than salt.

The following calculations are estimates of the pressure required for failure of the vessel in the experimental apparatus, and do not follow the methods which would be adopted to design an industrial high temperature reactor. The highest working temperature of the reactor was 700 °C and the highest lid temperature was 380 °C .

At higher temperatures the stress required to produce rupture in a specified lifetime is taken as a more valid criterion than the yield or proof stress. Actually, the reactor would only be required to resist overpressure for a short period, so the lifetime rupture stress is perhaps an unduly pessimistic estimate of failure. On the other hand, sudden pressure rises may generate a greater (temporary) stress than a gradual rise in pressure. The values of stress required to produce rupture in a lifetime of 10 000 hours will therefore be taken as the failure point for the material. Data are taken from Perry[248] and B.S. 1501[250]. To simplify calculations, it will be assumed that steel is exactly half as strong in shear as it is in tension. A shear stress is therefore equivalent to a tensile stress of twice the value. The stress on a body is the applied force divided by the area resisting it. A tensile stress acts perpendicular to the area resisting. A shear stress acts through the plane of the area.

The reactor body may be considered a thin walled cylinder of radius r = 62.5 mm, height h = 250 mm, wall thickness t_w = 2 mm, base thickness t_b = 4 mm. Hence for a pressure P

The stress tending to split the side (tensile)

$$= \frac{P\ r}{t_w} = \frac{62.5\ P}{2} = 31\ P$$

The stress tending to blow the base off (tensile)

$$= \frac{P\ r}{2\ t_w} = \frac{62.5\ P}{2 \times 2} = 16\ P$$

The stress tending to blow the base off (shear)

$$= \frac{P\ r}{2\ t_b} = \frac{62.5\ P}{2 \times 4} = 8\ P$$

However, the base shear stress of 8 P is equivalent to a tensile stress of twice this value, 16 P. Since the base will be subject to both shear and tension at the same time, the total possible stress tending to blow off the base should be taken as the sum (16 + 16) P = 32 P. Therefore rupture of the side and of the base will occur at much the same pressure.

A similar calculation can be applied to the flange welded onto the reactor. However the area resisting shear is half that of the base (flange thickness t_f = 2 mm) so that the total stress would be (16 + 32) = 48 P . In fact, the pressure may act over a larger area: assuming it acts over the whole lid (radius = 83 mm) increases the stress to 85 P. Thus if the whole reactor were at the same temperature and the lid and bolts did not fail, the reactor flange would be the most likely point of failure.

The lid may be assumed to fail as a disc sheared off by the backing flanges. The disc is thus approximately the same diameter as the reactor and the lid is of thickness t_1 = 2 mm. The shear stress is thus

$$= \frac{P\,r}{2\,t_1} = \frac{62.5\ P}{2 \times 2} = 16\ P$$

which is equivalent to a tensile stress of 32 P.

The other part of the system which may fail under excess pressure is the set of bolts holding the flange and lid together. There were 6 bolts each of nominal minimum diameter 7.5 mm, together resisting the pressure applied over the whole reactor lid. Hence the stress on the bolt material is

$$= \frac{P \times (166)^2}{6 \times (7.5)^2} = 82\ P$$

Hence the internal overpressures which could cause failure in these specific ways can be calculated from the supposed failure stress, which is taken to be the rupture stress for a 10 000 hour lifetime. Supposing the body of the reactor is at 700 °C and the lid and fittings are at 500 °C, then as follows:

failure stress for stainless steel at 700 °C = 500 bar
failure stress for stainless steel at 500 °C = 2 500 bar
failure stress for carbon steel at 500 °C = 600 bar

$$\therefore \text{ pressure to split side} = \frac{500}{31} = 16 \text{ bar}$$

$$\text{pressure to blow off base} = \frac{500}{32} = 16 \text{ bar}$$

$$\text{pressure to blow off flange} = \frac{2\,500}{85} = 29 \text{ bar}$$

$$\text{pressure to shear off lid} = \frac{2\,500}{32} = 78 \text{ bar}$$

$$\text{pressure to break bolts} = \frac{600}{82} = 7.3 \text{ bar}$$

There are many assumptions and approximations in this stress analysis. However, two points are clear. The calculated pressures needed to cause vessel failure are all well in excess of the pressures calculated for the disasters considered in appendices A - 1 and A - 2. They are also well in excess of the bursting disc rupture pressure, and would be so even for temperatures 100 K higher.

In conventional design the bolts would be made about as strong as the vessel, in this case either by having twice the number, or having them twice as strong. The use of relatively weak bolts was desirable for the laboratory reactor as a second line of defence should the bursting disc become blocked. At one time, the use of springs was considered to allow for even easier venting, but this would be likely to raise sealing problems unless a very well machined flange and lid were used.

A - 4 Heat required for polyethylene pyrolysis

Suppose that polyethylene at 300 K is completely converted into ethylene at 1 000 K. According to the 'Polymer Handbook'[83] the heat of polymerization of ethylene is 108 kJ mol^{-1} at 300 K. Take the mean specific heat for ethylene in this temperature range as 85 J mol^{-1} K^{-1}. Using a standard (Hess' Law) enthalpy calculation on a basis of 28 grams of polyethylene, the reaction can be written in two stages:

$$\text{PE (300 K solid)} \rightarrow \text{ethylene (300 K gas)} \qquad (11)$$

$$\text{ethylene (300 K)} \rightarrow \text{ethylene (1 000 K)} \qquad (12)$$

Reaction (11) requires 108×10^3 J. Reaction (12) requires $700 \times 85 = 59.5 \times 10^3$ J. Thus the overall conversion of 28 grams of polyethylene requires 167.5 kJ.

A partial breakdown of the polymer to larger fragments would require less energy on account of fewer bonds being broken. On the other hand, greater energy is required to volatilize larger fragments. Calculations on other fragment sizes show only a few per cent decrease in this figure, providing substantial breakdown and complete volatilization is assumed.

A greater reduction in heat requirement is obtained if the resulting vapours leave the reactor at a lower temperature. For example, an exit temperature of 800 K reduces the heat requirement to 150.5 kJ per 28 g polymer. Since the process is endothermic, this lower final vapour temperature is in fact more likely, and was certainly the case with the laboratory reactor.

Perkow[11,12,124] measured the actual heat input for continuous pyrolysis of molten polyethylene in a salt bath at 690 °C to comparable products (partial conversion to ethylene) and found a value equivalent to 130 kJ per 28 g of polyethylene.

Heat recovery techniques could reduce the energy needs of an industrial pyrolysis unit. For example, if waste heat was used to pre-heat the plastic to 120 °C, a saving of 6 kJ per 28 g of plastic would result. On the other hand, sophisticated heat recovery equipment is unlikely to be appropriate for a small unit due to the higher relative capital cost.

Taking the figure of 130 kJ per 28 g of plastic gives 4643×10^3 kJ per tonne. A plant processing 1 tonne of plastic in 24 hours would therefore require a heat input of 54 kW, apart from the energy needed to keep the reactor at temperature without pyrolysis.

A - 5 Size of salt bath required for pyrolysis unit

The size of salt bath appropriate to a particular rate of pyrolysis depends on a number of factors in its design: the shape, stirring and method of heating in particular. The basic requirements of the salt bath are to carry heat from the wall to the plastic pyrolysing on the top surface of the salt. A certain heat capacity is also required to give a thermal inertia to mitigate fluctuations in flow of plastic or fuel.

A unit pyrolysing 1 tonne per day needs to transport heat at about 54 kW. Suppose that in one minute the heat required (3.25×10^3 kJ) were to come from salt cooling from 1 010 to 1 000 K, and the specific heat of the salt is 1.25 kJ kg^{-1} K^{-1}. The salt required would be:

$$\frac{3.25 \times 10^3}{1.25 \times 10} \quad = \quad 260 \text{ kg}$$

That is to say, the stirrer has to transport 260 kg of salt per minute to the surface for the temperature drop to be no more than 10 K. The volumetric flow induced by a turbine in liquid mixing is typically of the order of a few tank volumes per minute, so that a bath of this capacity would probably be adequate from this point of view.

There are recognized methods for calculating heat transfer from the walls of a stirred vessel [248]. A simpler technique is to inspect the manufacturer's data on molten salt baths for heat treatment [171]. Taking the difference between the energy required to maintain a bath at working temperature and that used at its maximum work rate (i.e. when heat is being absorbed by the immersion of objects) an idea of the possible rate of transport of heat through the vessel walls can be obtained. It seems that a bath of 260 kg capacity can just about pass 54 kW at 650 °C .

This is therefore a minimum value of salt requirement. A reasonable estimate might be twice this value, say about 500 kg as the working amount in a pot two-thirds full. The fact that the heat treatment baths are not normally stirred means that this is probably a generous estimate, but worthwhile for the thermal inertia.

A - 6 Fuel requirements for a commercial unit

From previous calculations, take a molten salt unit containing 500 kg of salt, externally fired by the wax and oil part of the pyrolysate, and processing 1 tonne per day of polyethylene. The pyrolysis process requires 54 kW.

Assume the pyrolysate has the same calorific value as a typical fuel oil, say 45 000 kJ kg^{-1}. Since the exit flue gases will be rather hot (over 700 °C) an efficiency of thermal conversion of no more than 50 % is assumed. Hence the fuel requirement is:

$$\frac{54 \times 24 \times 3600}{45\,000 \times 0.5} = 207 \text{ kg per day}$$

According to the manufacturers [171] a salt bath of this size needs about 120 kg of fuel oil per day to maintain it at 650 °C. The total running requirement is therefore 327 kg per day. In round figures, therefore, one third of the pyrolysate is used to fuel the reactor.

Some savings could be effected by using the hot flue gases for other purposes, such as pre-heating or raising steam, so that effectively there are some fuel credits. Nevertheless, this is a reasonable working assumption of the amount needed to run the molten salt reactor.

A - 7 Mixing and the Reynolds number

The two stirrers used in the molten salt were of standard types and sized according to conventional wisdom[248]. Thus the propeller diameter was about 0.3 of the tank diameter, and that of the paddle was about 0.5 of the tank diameter.

The Reynolds number (Re) is a dimensionless group used to quantitatively define a situation involving fluid movement, and is of particular importance in scale-up. Generally, fluid in a large unit will behave similarly to that in a smaller one, providing the Reynolds numbers of the two units are similar. This applies even if the fluids are different. Where gravitational effects are important, another such group - the Froude number - has to be considered, but this can be ignored for the simple stirred tank.

A Reynolds number is made up of the product of two parts, one dependent on the apparatus, the other on the fluid. The fluid-dependent part is the ratio of the density to the viscosity. The apparatus-dependent part involves a dimension and a velocity.

For a cylindrical tank stirred by a conventional impeller, the Reynolds number is defined in American and common British practice as:

$$Re = \frac{n\,d^2}{60}\,\frac{\rho}{\mu} \tag{13}$$

where n is the impeller speed in r.p.m. (the factor of 60 is included to give the unit of second^{-1}) d is the impeller diameter, ρ is the fluid density and μ its viscosity. Care has of course to be taken that the units cancel out correctly.

For the molten salt and temperature range used, both the density and the viscosity were about twice that of water at 20 °C, that is $\rho \approx 2$ g cm^{-3} and $\mu \approx 2$ cP . The diameter of the simple paddle was 56 mm, and it was used at a speed of 70 r.p.m. Thus converting everything to S.I. base units:

$$Re = \frac{70}{60}\,\frac{(56)^2}{10^6}\,\frac{2 \times 10^3}{2 \times 10^{-3}} \qquad s^{-1}\ m^2\ \frac{kg\ m^{-3}}{kg\ m^{-1}\ s^{-1}}$$

That is, Re = 3659.

A similar calculation for the propeller (diameter 36 mm speeds from 100 to 1 500 r.p.m.) gives:

$$Re = 21.6\ n$$

These results are to a much greater precision than can really be justified without more exact data on the dependence of density and viscosity of the salt on temperature. However, they illustrate the principle which could be applied to more exact figures. More importantly, these calculations allow an estimate of the fluid conditions in the reactor.

It is thus probably fair to say that in the runs with the paddle impeller, the Reynolds number was probably between 3 000 and 4 000. For the main runs using the propeller, the Reynolds number was about 20 times the speed in r.p.m.. That is, $Re \approx 2\,000$ at 100 r.p.m., $Re \approx 10\,000$ at 500 r.p.m. etc.

For a stirred tank, it is generally accepted that a Reynolds number below 10 implies a fully laminar flow, and a Re above 10 000 implies a fully turbulent one. Between these values a mixed flow pattern occurs.

A - 8 Calculation of yields of pyrolysis of polyethylene from the chromatogram of the collected vapours

Each resolved peak was assigned an area equivalent by an electro-mechanical integrator. Taking the chromatograph peak due to ethylene in a sample of product vapour, an area of 420 μsV was assigned. An identical volume of a standard mixture containing 1.0 % ethylene gave a peak of 178 μsV.

$$\therefore \text{ product gas contains } \frac{1.0 \times 420}{178} = 2.36\ \%\text{ by volume}$$

Total volume of product (bottle) = 2 750 cm^3

$$\therefore \text{ volume of ethylene } = \frac{2\,750 \times 2.36}{100} = 64.9\ cm^3$$

Density of ethylene at 293 K and 1 bar = 1.17 mg cm^{-3}

$$\therefore \text{ mass of ethylene } = 64.9 \times 1.17 = 75.9\ mg$$

This resulted from the pyrolysis of 1 000 mg of plastic

$$\therefore \text{ yield of ethylene } = \frac{75.9 \times 100}{1\,000} = 7.6\ \%$$

Similarly the yield of other vapour components could be found. Where two adjacent peaks were inadequately resolved, it was assumed that the ratio of the two areas was the same as the ratio of the peak heights, and the area divided accordingly. This applied, for example, to some propylene propane pairs, which are reported as total C_3.

A - 9 The Kinetic Severity Function in hydrocarbon pyrolysis

If a single hydrocarbon were to be instantaneously raised to a pyrolysis temperature, and instantaneously quenched at the end of the pyrolysis period, then the percentage conversion of the hydrocarbon could be predicted from its reaction velocity constant K at that temperature and the time for which it was at the pyrolysis temperature.

In fact, of course, the tube or coil in a conventional cracker has a temperature profile. Since the reaction velocity constant is a function of temperature, it would need to be integrated over the time spent in the pyrolysis region. The temperature profile depends on the feedstock, which is usually a mixture. For the Kinetic Severity Function, suppose that a small amount of pentane is included in the feedstock, but not enough to disturb the temperature profile. The Kinetic Severity Function KSF is defined thus:

$$\mathrm{KSF} \quad = \quad \int K_5 \, d\mathrm{T} \qquad (14)$$

where K_5 is the reaction velocity constant for decomposing pentane, and T is the time spent in the pyrolysis region.

From normal kinetic theory, it can be shown that:

$$KSF = \ln \frac{c_1}{c_2} \approx 2.3 \log \frac{c_1}{c_2} \qquad (15)$$

where c_1 and c_2 are the inlet and outlet concentrations of pentane. For example, if the pentane was 90 % converted to other materials, KSF for the cracker would be 2.3. Hence if pentane is an actual component, the KSF value can be found by analysis.

Since the cracker outlet temperature θ can be measured quite easily, it has proved convenient to define an 'equivalent time' T_e . This is the residence time which would give the same conversion if the entire pyrolysis process had been carried out at the outlet temperature θ and is usually several times the actual residence time, since part of the pyrolysis would have been much hotter. Thus KSF can be equated to:

$$KSF = K_{5\theta} T_e \qquad (16)$$

where $K_{5\theta}$ is the pentane decomposition reaction velocity constant at a temperature θ.

Taking into account the general relationship of reaction velocity constants with temperature (Arrhenius equation) thus:

$$\log K_{5\theta} = B - \frac{C}{\theta} \qquad (17)$$

where B and C are specific constants for the pentane pyrolysis reaction, equations 16 and 17 can be combined:

$$\log KSF = \log T_e - \frac{C}{\theta} + B \qquad (18)$$

The equivalent time depends mainly on the feedstock, pyrolyser geometry and flow rate, plus of course the temperature profile. Since the shape of the temperature profile does not change markedly with temperature (within the operating range of the pyrolyser) the term log T_e is only very weakly dependent on temperature. Thus to a first approximation, log KSF increases linearly with negative reciprocal temperature. In the temperature range 500 to 700 °C the negative reciprocal temperature increases with actual temperature in a fashion not too far removed from linear. It is therefore plausible to compare a graph of yields versus temperature with a graph of yields versus log KSF, as is done with FIGS. 36 and 37

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Notes Abbreviations of titles are mainly taken from the list in the appropriate British Standard [251]. Where an item is in a language other than English, a translation of the title is given, followed by the name of the original language in brackets. For certain minor and / or inaccessible items, information has been taken only or mainly from the Chemical Abstract. In such cases, the Chemical Abstract number follows the reference.

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