FUELS FROM TYRES BY
PYROLYSIS IN MOLTEN SALTS

A Thesis submitted
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The current annual arisings of used car/van tyres in the U.K. has been found to be around 25m (188,000 tonnes). After the established reuse industries have taken their requirements this leaves 13.5m (102,000 tonnes) waste tyres; a quantity that can no longer be satisfactorily tipped.

Laboratory scale experiments have shown that tyre can be pyrolised, using a molten carbonate system as the reaction medium, at rates corresponding to 14.9 - 42.7 g tyre/min. per litre of melt over the range 475 and 650°C. The product yields by weight of tyre input between the same temperatures are: hydrocarbon oil 23 - 36 wt. %, hydrocarbon gas 7 - 18 wt. %, carbonaceous char 35 - 40 wt. %, steel 16.7 wt. % and inorganics 5.4 wt. %.

The oil and gas evolve from the reactor and can easily be collected by conventional means. The steel and inorganics remain in the reactor although on the commercial scale it is proposed that they would be removed by physical and chemical methods respectively. The char was found to pose considerable handling problems and so a method was devised by which it could be gasified in the reactor. This was best achieved by passing air at a less than stoichiometric rate which gave a gaseous product rich in carbon monoxide. In addition this action provides heat for the system as a whole. The rates at 675 - 900°C were in the range corresponding to 5.6 - 14.8 g char/min. per litre of melt. A process flow chart has been proposed for a continuous operation based on these systems.

Data from theoretical and experimental studies has enabled economic evaluations of several commercial scales to be carried out. These have shown that 4,000 and 10,000 t/yr operations show a DCF rate of return around 30% while a 50,000 t/yr operation shows 60% which would be attractive to an experienced scrap operator.

GASIFICATION MOLTEN SALTS PYROLYSIS TYRES

To

My Father

"Time spent in reconnaissance is seldom wasted"

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CHAPTER
ONE

INTRODUCTION

1 INTRODUCTION

1.1 The Project

It is estimated that something in the region of 200,000 tonnes of used car and van tyres are currently discarded in the U.K. every year.(1) Present reuse patterns suggest that about half of these are not reused in any useful way and have to be tipped. For ecological, conservational and economic reasons this is not a satisfactory state of affairs. The first part of this thesis is concerned with the compilation of a more accurate and specific account of tyre reuse in the U.K. today. It is concerned with both methods and flow volumes. The early parts of the thesis are also concerned with the identification of the best disposal policy and methods for the future.

It has been suggested that pyrolysis of used tyres may provide an answer to the disposal problem.(2) Molten salts as a heat transfer medium for pyrolysis of used tyres have several attractions: they are cheap, thermally stable, have low volatility, show good heat transfer properties, have some useful chemical properties and may be catalytically active. This has been the main area of technical research in the project. It was expected the pyrolysis would produce a range of products including oil, gas and char. Since some of these may have to be used to fuel the process it was suggested that in-situ oxidation of the char would be most appropriate. Not only would this eliminate the need to remove it from the reactor but might also help to circulate/mix the molten salt.

The project was concerned with gathering and interpretation of data on the effects of temperature, salt composition, salt agitation and other parameters on the rates of reaction and the nature of the products. In addition studies of the changes in melt characteristics with the build-up of foreign matter and of its corrosive behaviour were carried out.

Theoretical consideration is given to the design of the process as a whole, proposing larger units and discussing process flows. Such analyses include mass and energy balances which are essential to the design.

Although this work is only intended as a preliminary technical and economic feasibility study a great deal of consideration is given to a final aim of producing a commercial process. At the outset of the project the technical requirements to achieve this were that the process should: i) accept whole tyres without pretreatment, ii) supply its own heat requirements, iii) be stirred by the minimum moving parts, iv) need minimum attention and maintenance and v) pyrolyse tyres rapidly to give a good yield of oil. These considerations were constantly in mind during the project work.

The final intention was to assess the economic viability of this type of tyre pyrolysis as a means of tyre disposal and to make recommendations accordingly. In order to do this it was necessary to make full use of data from both of the earlier two areas of study. Thus data concerning tyre markets as well as information from experimental study of the pyrolysis process was used in the economic evaluation. In this evaluation capital costs were estimated and returns calculated using standard accounting techniques.

1.2 The Thesis

Following this introduction there is a critical survey of the literature on and connected with the subject of the thesis. Effort has been made to achieve a delicate balance between bibliographic listing and technical discussion. The literature survey is split into three sections: 1) Tyre Industry, 2) Pyrolysis and 3) Related Topics

After the literature survey there are two chapters closely dependent on the literature survey. The first makes use of the first chapter of the survey to study the effects of various future disposal strategies and so makes some broad recommendations. The second draws of the later parts of the survey and novel ideas to generate proposals concerning the working concepts of the possible pyrolysis process.

Having some idea or visualization of the final process, some laboratory equipment to test and study the principles involved could be designed and built. This is discussed before the experimental sections which are divided into: 1) Pyrolysis, 2) Char Gasification and 3) Related Studies. This is done because the conceptual process can easily be seen as relating to these three areas.

When all the technical information has been gathered, discussed and interpreted the process concepts can be developed further. This includes rough design concepts for many of the plant process units but is mainly concerned with the production of accurate process flows. This in turn enables sizes or magnitudes of plant units to be estimated. The process flow data and data from as far back as the literature survey has then been used for costing of possible commercial operations and thus to obtain rates of return on various plant options by the DCF method.

Conclusions and recommendations cover the thesis in logical sequence; the used tyre problem being summarized first. Then technical conclusions and recommendations for further development are discussed - from a purely technical point of view. Finally an economic overview is applied before investment recommendations are discussed.

CHAPTER

TWO

LITERATURE SURVEY I - THE TYRE INDUSTRY

2 LITERATURE SURVEY I - THE TYRE INDUSTRY

2.1 Introduction

During the last decade there have been three comprehensive and authoritative reports covering the U.K. and European tyre industry:

(a) "Used Tyre Disposal in Great Britain". Local Government Operational Research Unit commissioned by the Department of the Environment, 1973.

(b) "A Study of the Reclamation and Reuse of Waste Tyres". Rubber and Plastics Research Association commissioned by the Department of Industry, 1976.

(c) "Raw Materials Research and Development Studies on Secondary Raw Materials - Rubber Waste". European Economic Commission, 1979.

The LGORU report (3) is based on a national survey, covering all areas of the used tyre industry. The document sets out the quantities of tyres that are reused in different ways. As might be expected from an early study and the environmental commission the report is mainly concerned with identification of the disadvantages of tipping and pays little attention to current innovative disposal methods. Being survey-based there are one or two numerical and political contradictions but on the whole it is a good report on tyre disposal mechanisms. Norman (4) is clearly impressed by the report as it is the numerical basis for his thesis: "The Scrap Car

Tire Disposal Problem : Alternatives for a Rubber Reclaimer".

The 1976 RAPRA report (1) covers most of the LGORU information in less detail but unlike the LGORU report it also covers less traditional methods of disposal. These, including pyrolysis, are subjected to some technical evaluation and are considered in the overall light of the market situation. The RAPRA report is a useful document and has been used in some detail for this work, but care must be taken (as with the LGORU report) not to confuse apparently contradictory data found in different sections.

The recent EEC report (5) is a very extensive world-wide literature survey. It covers the research and development of new methods of tyre disposal far better than the earlier publications but has little concerning traditional methods. The section concerned with pyrolysis is brief but extremely readable giving information chronologically and by geographical location.

There are no similar documents concerned with the American or Japanese tyre disposal problems but a few academic papers and reports briefly cover these areas(6,7,8). For the American coverage the best publication is probably the Environmental Protection Agency document "Rubber Reuse and Solid Waste Management", 1979 (9) which describes quantities, distribution and collection of used tyres but is poor on technical methods of disposal. A more recent and broader view can be found in the proceedings of the National Scrap Tire Disposal Symposium, 1977 (10).

This chapter is concerned primarily with the U.K. and so draws mainly from the three initially named reports.

2.2 Tyre Manufacture

2.2.1 Production Statistics

Rubber is an unusual commodity in that a large proportion is used in one manufactured product; pneumatic tyres. The British tyre industry produces a wide variety of tyres, ranging from those for private cars to those for earth movers and aircraft. Table 2.1 published in the RAPRA report(11) and based on data from the Rubber Statistical Bulletin(12), gives a good idea of the size of the business and can now be used to estimate the size of the disposal problem.

Tyre type	Car/Van	Truck	Agricultural	Aircraft
Production	23,873,000	3,626,000	1,121,000	84,000
Av. wt. new, kg.	7.8	50	-	-
Production tonnage, t.	186,200	181,300	-	-
Av. wt. worn, kg.	6.8	40	-	-
Tonnage, t.	162,300	145,000	-	-

Table 2.1 Tyre Production in the U.K., 1974 (11)

Clearly the majority are car and van tyres although by weight truck tyres are significant. It might be expected that these figures may have altered since 1974. The increase in registered vehicles from thirteen to fourteen million(13) and the slight increase in usage thereof(14) indicate a higher tyre requirement but these effects are approximately balanced by the increased mileage achieved with modern steel braced radials and so tyre production shows only a slight increase(14). In 1974 some 4,140,000 tyres were retreaded and these are included in the figures just given.(15)

In this project only car/van tyres are considered because not only do these represent the majority but being of almost uniform size can easily be handled in an envisaged process.

2.2.2 Design, Construction and Composition

In order to gain a full appreciation of the problems of recycling tyres it is useful to have a knowledge of their design, construction and composition. There is little information in the general literature although the RAPRA report gives some general formulations. The best data can only be obtained from manufacturers publications,(16,17) or by private communication.

There are basically three types of construction in common use today: cross-ply, fabric-braced radials and steel-braced radials. Typical formulations in terms of rubber compound (rubber, carbon black and additives), fabric (usually rayon, nylons or terylene) and steel are given in Table 2.2.

It is important to note that steel radials have in recent years become far more popular, as is shown by the trends in Table 2.3.

Tyre reinforcement	Rubber compound wt. %	Fabric wt.%	Steel wt.%
Cross-ply	76	21	3
Fabric radial	71	26	3
Steel radial	77	9	14

Table 2.2 Typical Tyre Formulations

It should be realised that used tyre trends are of course several years behind production trends and so the processing difficulty experienced with steel radials by the reclaim industry is likely to become more acute(18). However, efforts are being made to overcome this problem and a cryogenic system(19) is looking promising but to date no reclaimer, with the possible exception of the Michelin Group in France, has established a working plant for the comminution of steel radials.

	Used Tyre Arisings			Percentage		
Tyre reinforcement	1974	1977	1980 proj.	1974	1977	1980 proj.
Cross-ply	10.85m	6.90m	3.35m	55	32	15
Fabric radial	5.92	7.55	7.05	30	35	30
Steel radial	2.96	7.11	12.93	15	33	55
Total	19.73	21.56	23.33	100	100	100

Table 2.3 Used Tyre Arisings by Reinforcement Type

Table 2.2 shows that typically over 70 wt. % of a tyre is rubber compound. Rubber compound may consist of natural and synthetic rubbers, carbon black (reinforcing and abrasive agent), sulphur (main vulcanate), zinc oxide and organic additives such as mercaptobenzothiazoles and thiuram derivatives (accelerator/ curing mixture) and processing oils. A tyre may contain a number of different compounds all of which will be commercially guarded secrets but a typical compound is given in the RAPRA report and reproduced in Table 2.4. In order to obtain the overall percentages in a tyre it is of course necessary to incorporate the percentage of compound in a tyre.

Rubber (Natural/Synthetic)	48 - 55 wt.%
Carbon black (Various grades)	22 - 29
Sulphur	1 - 2
Zinc oxide	2 - 4
Other additives	5 - 8
Process oils	12 - 14

Table 2.4 Typical Rubber Compound, (17, 20)

This section has deliberately concentrated on "typical" and "average" compositions as a commercial process will be faced with a wide variety of tyres. However, in the scientific evaluation of the process that is the aim of this project a specific tyre, the Dunlop SP4 "Worldbeater" steel radial was used. The overall composition data for such a tyre worn to 1 mm remaining tread (the legal limit) is given in Table 2.5. It is shown elsewhere that this tyre is likely to be typical of those in use in the early 1980s. (N.B. Total organic content 53.1 wt.%)

Rubber	Isoprene	26.3 wt.%
	SBR	10.4
	Chlorinated butyl	3.0
	Carbon black	24.7
	Sulphur	1.8
	Zinc oxide	3.6
	Organic additives	9.5
	Fabric	3.9
	Steel	16.8
		100.0

Table 2.5 SP4 Overall Composition, (21)

2.3 The Tyre Cycle

The concept of the tyre cycle which is a crucial aid to understanding tyre reuse was introduced in the LGORU report(3) and has appeared in numerous publications since 1973. The LGORU cycle was perhaps over complicated while that used by RAPRA omitted many crucial flows. The cycle illustrated here is based on data from many sources and is most suitable for use in this chapter.

The central functionaries of tyre reuse in the U.K. are the casing selectors, such as Tyre Disposal Services Ltd., a subsidiary of Dunlop (Holdings) Ltd. The casing selector buys tyres from used tyre outlets; about half of which are resold (at a profit) to retreaders.

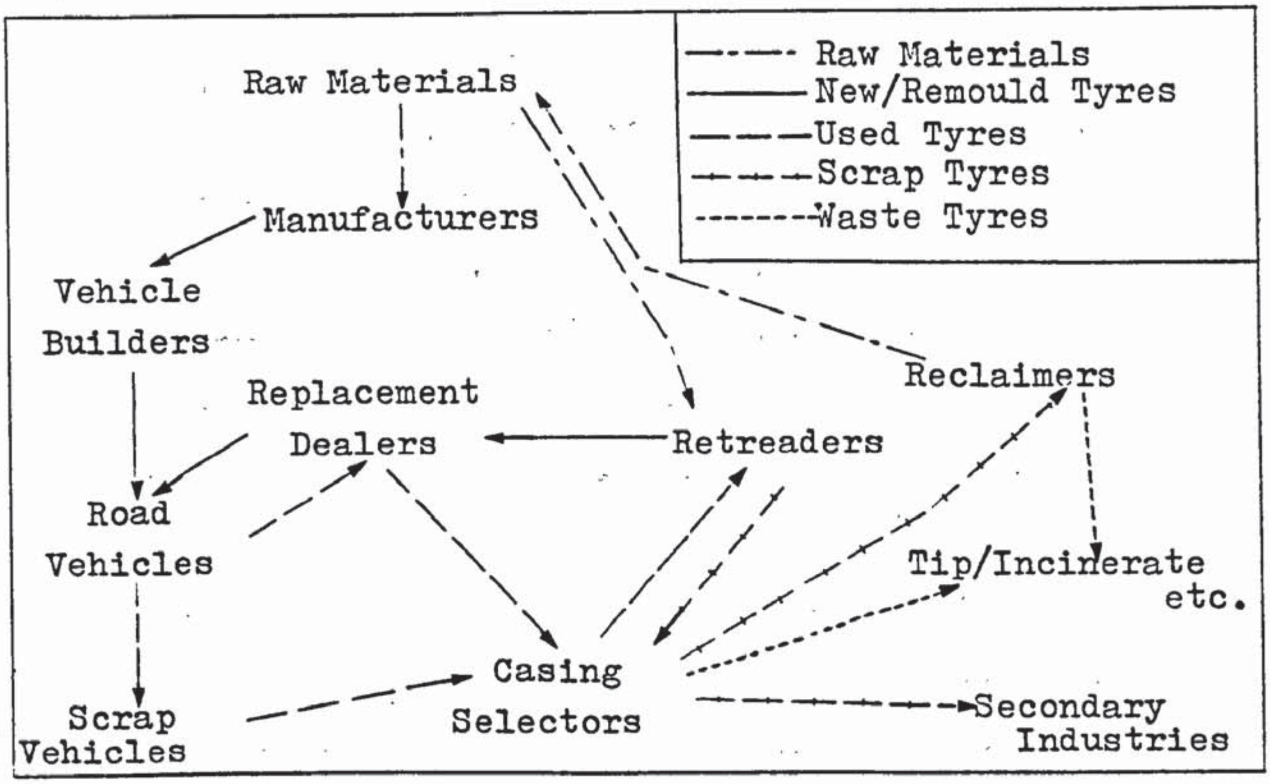


Fig.2.1 The Tyre Cycle

The retreader processes those suitable and then returns the remainder to the casing selector (usually about 30%). Fabric tyres are sold to reclaimers such as United Reclaim Ltd. (usually at a loss; the price not covering transport costs but being more economic than tipping). The reclaimers make a product reusable in new tyre manufacture and a largely useless lint. Some tyres are sold to secondary industries (e.g. splitters) and some are exported but a company the size of Tyre Disposal Services would normally still have to tip some 60,000 tyres per week. These would be readily available for pyrolysis(22).

The tyre cycle illustration is of limited use since it is only qualitative. It is possible to show the flows quantitatively on a scaled Sankey diagram, as in Fig. 2.2. Accurate figures are hard to obtain and there are often discrepancies between sources. However here data and estimates are drawn from a number of sources to give the best possible 1980 projection. The estimated new car/van tyre production for 1980 is 24.5 million to which supply will be added about 1.75 million from stock, making a total of 26.25 million sold. Of these the total commercial export (including those exported on vehicles) will be about 5.00 million while those exported on Government contract will be about 0.30 million(23). This indicates a U.K. supply of 20.95 million, split approximately 7.5 million as original equipment and 13.45 million as replacements. To each of these must be added imports. Tyres on vehicles are not normally quantified alone but the Society of British Motor Manufacturers and Traders in their 1977 report(24) estimate that in 1980 some 750,000 cars/vans will be imported, making 3.75 million tyres as original equipment. In the light of more recent increases in foreign penetration of the U.K. car market this may well be a conservative figure. Western tyre producers generally manufacture in the U.K., eliminating the need for bulk replacement imports, but it is claimed by the British Rubber Manufacturers Association that Comecon sell some 0.60 million in the U.K. annually(25). As is shown in Table 2.6 this indicates a total tyre input to the U.K. market of 25.3 million (190,225 tonnes).

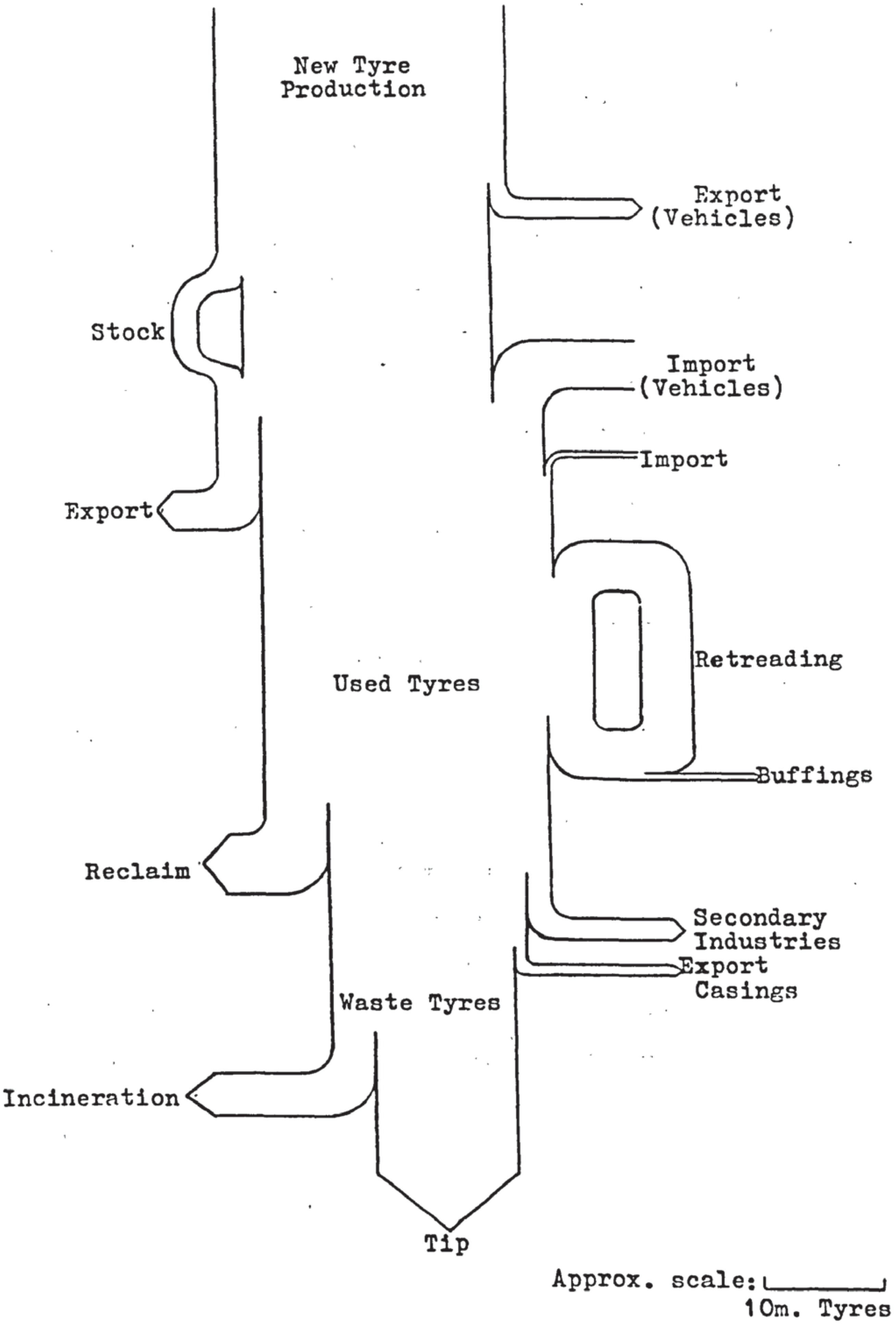


Fig.2.2 U.K. Tyre Flows (Sankey diagram)

	New Car/Van Tyre Production	24.5 m
	Stock additions	1.75m
+ Imports :	Original equipment	3.75m
	Comecon replacements	0.60m
- Exports :	Commercial	5.00m
	Government	0.30m
	Total new introductions	25.3 m
	+ Retreads	3.5 m
	Total Introductions	28.8 m

Table 2.6 Tyre Introductions to U.K. Market, 1980

The RAPRA methodology(1) assumes that used tyre arisings must be equal to the sum of : replacements fitted, retreads fitted and tyes removed from scrapped vehicles. Using the SBMMT 1977 report (24) a figure of 7.38 million tyres were removed from scrapped vehicles (perhaps conservative) the total used tyre arisings are given in Table 2.7.

New replacements	14.05
Retreads fitted	3.50
Vehicle scrap	7.38
Total used arisings	24.93 m

Table 2.7 Estimated Used Tyre Arisings, 1980

This data and that from other sources give a general idea of the reuse patterns and their magnitudes. Assuming reclaim and secondary industries are stable but that retreading declines and incineration increases, the patterns given in Table 2.8 are found. These figures clearly show a worsening waste problem,recent trends show a linear increase of over 0.5m a year. It should also be noted that tipping is a disposal strategy that causes pollution and recovers nothing.

	1974	Est. 1980	Comments
Used Tyre Arisings	20.36m	24.93m	Slight increase
Retread	(4.14m)	(3.50m)	Decline - safety ?
Reclaim	6.00m	6.00m	Stable
Secondary Industries	2.00m	2.00m	Stable
Incineration	2.50m	3.50m	Increasing
Tip	9.86m	13.43m	Increasing

Table 2.8 Tyre Reuse Patterns

2.4 Current Tyre Reuse Patterns

2.4.1 Introduction and Bibliography

The purpose of this section is to explain the current problems and give some idea as to how Table 2.8 is made up.

The literature on tyre reuse is very extensive; a factor that is largely due to repeat publication by the same authors and overlap between authors. The best general U.K. review is probably that by Cheater(26) published in 1973. The afore mentioned LGORU(3) and RAPRA(1) reports are good quantitative sources. Several papers by Beckman et al.(7,8) cover the U.S. market; these usually contain the phrase "Scrap Tire Disposal" in the title. Further U.S. papers can be found in the Proceedings of the 1st National Tire Symposium(10) under a number of authors. Legal restrictions in the U.S. are given in Federal Act DL94-580, 1974(27) but in the U.K. legislation only reached the Green Paper(4) stage.

On a world-wide scale the Franklin Institute's "Scrap Tire Disposal and Utilization Alternatives: A State-of-the-Art Report" covers many methods used in different nations(6). Panske(28) has written a very similar and up-to-date report. Schnecko(29) has covered the situation in West Germany, while Kajdas and Czachowska(30) discuss the problem in Poland.

2.4.2 Tyre Retreading

The technical history from early work to modern methods(31) is well documented. A good summary of present practices is found in the RAPRA report(1).

In the U.K. about half the collected casings pass to retreaders where 50-65% are retreaded for sale(15). The RAPRA report quotes the 1974 retread sales as 3.74 million and the LGORU report(3) while not quantifying reports the Retread Manufacturers Association as expecting a decline. About 14% of U.K. used arisings are finally retreaded.

In the U.S. Sears(32) has estimated 1976 retreading at 36.0 million which according to Crane et al.(8) is 18% of used arisings. Given the higher retreader inspection rate (60%) this compares closely with the U.K. In California the retread sales may be up to 30% of total tyre sales(33).

It should be noted that retreading is controlled by standards and legislation: BS AU 144a in the U.K. and Fed. Spec. 22-T-00441c in the U.S.A.

2.4.3 Crumb and Reclaim

Crumb is usually taken to mean rubber compound comminuted to granules/powder from which reclaim, a sheeted material similar in appearance to unvulcanized rubber compound, is made. The two operating concerns in the U.K., United Reclaim Ltd. and the Rubber Regenerating Co. Ltd., rely on the supply of fabric braced tyres as no comminution process for steel radials is yet operational(4,19).

Reclaim is used in tyre manufacture as a processing aid and often accounts for 12-22% of compound formulations(14). Reclaim is at present far cheaper than new rubber and therefore its usability and price are important market factors.

The reclaim industry is at present faced with the two problems: efficient devulcanization and comminution of steel radials. A patent published by Sear in 1978 introduced the apparently attractive concept of flame devulcanization(34). This was further taken up by Bennett of Dunlop Ltd.(35) and the rights have been a matter of legal conflict. The method, employing extreme thermal shock, may prove to have many technical problems and has faced considerable doubts(36). The problem of steel radials has been largely overcome on the small scale by Union Carbide(37) and United Reclaim(19). Both are based on a cryoginic system, as may be the Michelin process.

The estimates of reclaim volume vary between 5 and 6 million tyres; assuming 70% conversion and working back from the tonnage of reclaim produced the upper limit seems likely. The volume is thought to be steady. In the U.S. Crane et al.(8) put the level at 10m tyres which Hudson and Lake point out is only 5% of used arisings compared with some 24% in the U.K..

2.4.4 Secondary Industries

According to LGORU(3) there is only one organized secondary operation in the U.K., City India Rubber Ltd., but the total secondary usage is put at 2.0 million tyres a year. Beckman et al.(7) and Hudson(38) put the U.S. figure at 3.0 million or 1.5% of used arisings which is low compared to the 8% in the U.K..

2.4.5 Tipping and Landfill

Tipping is normally only carried out after more profitable disposal markets are filled. According to Norman(4) the scarcity of suitable sites and the need to back-fill had increased the 1979 tip cost to £16.00 - 18.50 per tonne.

Landfill is generally unsatisfactory for a number of reasons(39) and in the U.K. is common only in South Wales(3). German research(40) has shown tyres will only decompose in the atmosphere (by ozone attack) over 50 - 80 years. American workers(41) report that micro-organisms can do little to accelerate the process. However an Australian publication (42) claims carefully laid tyres can be used to convert swamp to useful pasture.

In the U.K. the 13.4 million tyres tipped represents some 54% of used arising which must be considered an acute problem, although in the U.S. the figure is 73%.

2.4.6 Combustion and Incineration

Clearly undesirable open burning is declining in favour of incinerators to raise heat; the heating value of tyre being quoted between 33 MJ/kg and 42 MJ/kg(1).

British experience with tyre incinerators is described in the RAPRA report but the account by Stribling(43) is a better source. The first commercial unit was commissioned in 1966 by the Watts Tyre and Rubber Co. incinerating 254 kg/hr to raise 1600 kg of steam at 827 kN/m^2. Modern incinerators by Heenan Environmental Systems Ltd.(44) have ten times this capacity and are claimed(43) to be an economic disposal alternative.

In the U.S. both Goodyear and Firestone now operate tyre incinerators(45,46). It has been reported from Germany that tyres are also used to supplement blast furnace cokes(47) and from the U.S.A. to supplement solid fuels in conventional boilers(48).

The U.K. volume of tyres incinerated was quoted as 2.5 million in 1974 but by 1980 even 3.5 million must be considered a conservative estimate.

2.5 Reuse Alternatives under Study

2.5.1 Structural

The structural uses of worn tyres fall into three categories: marine, transportation and architectural.

Most marine studies have taken place in the U.S. and it appears that apart from disposal there are two advantages: fish breeding grounds and wave reduction. With regard to fish havens, optimistic reviews and successful research have been reported by Myatt(49), Beckman et al.(7), and the Bureau of Sport Fisheries and Wildlife(50). Wave reductions of 70% and 80% have been reported by Kowalski(51) at Rhode Island University and Greene(52) at Rhode Island Yacht Club. The size of reefs appear unlimited as Goodyear have built a reef 300 ft in length(53) and another using 3 million tyres in 400 ft of water(59). They also estimate the U.S. east coast alone could accommodate 1500 million tyres.

Uses in the transportation field are restricted to asphalt components and crash barriers, the best review of which being by the Rubber in Asphalt Committee of the International Institute of Synthetic Rubber Producers(55). In the U.S. crash barriers have been tested by the Texas Transport Institute (56,57). Work by Stokeley and McDonald(58) have found rubberized materials useful in crack repair while in the U.K. Tarmac Roadstone Ltd. have shown an interest in rubberized surfaces(59). Such materials have also been tested for sports applications. Whole tyres are thought to offer a road stabilization preventing creep(60).

Rubberized concrete is reported by Crane et al.(9) to be useful for light weight applications while Firestone have evaluated sound transmission properties and Goodyear non-slip flooring(61). The greatest application may prove to be roofing asphalt but safety and climatic conditions may be problems.

2.5.2 Geophysical Applications

Erosion control research has been carried out in the U.S.(62) and on the Wash in the U.K.(63). Despite the problems associated with their shape(39) a notable amount of research has been completed on ground preparation for road construction (64,65).

The remaining application is in pollution control. Winkler(66) and Kobe Steel Co.(67) have both identified tyre as an oil spill absorber and there is a possibility that the char produced by tyre pyrolysis may absorb metal ions from solution.

2.6 Summary

It is estimated that the current arisings of used car/van tyres are 24.93 million (187,450 tonnes) of which 13.4 million (100,750 tonnes) are currently tipped. Due to the inability of the reclaim industry to deal with steel radials being produced in increasing proportions the problem is likely to increase. As further tip sites cannot be found, alternative disposal must be developed. At present controlled incineration is well under way but other applications are also under evaluation. Of these ocean structures offer the greatest possible volume of disposal. Pyrolysis is evaluated in the next chapter.

It is therefore indicated that at least the 13.4 million tyres tipped and possibly the 3.50 million incinerated are available to a pyrolysis operator; making a total of 16.9 million tyres or 127,000 tonnes.

CHAPTER
THREE

LITERATURE SURVEY II - PYROLYSIS

3 LITERATURE SURVEY II - PYROLYSIS

3.1 Introduction

At an early stage it was obvious that the literature would contain little directly related to this thesis but broadening into allied subject areas a large volume of relevant literature was found. It was clearly desirable to gain knowledge concerning the physical and chemical mechanisms involved in pyrolysis. However, perhaps due to the complex nature of the subject, little is available and so this is left to later chapters. The engineering and experimental aspects of pyrolysis are so well covered that it became necessary to consider information by reactor types and even sub-divide into geographical locations which from a business/market point of view has additional merits. It was also found that useful information could be gained by considering the pyrolysis (strictly non-oxidative) of materials other than tyres.

The search system employed was standard but thorough and extensive, covering: Chemical Abstracts, RAPRA Abstracts, Science Citation Index, U.K. Patents Concordance, Current Contents and Waste Management Information Bulletin. Although the search covered more than a century, most of the effort was concentrated on the high technology boom of the past two decades as this period yielded the most information.

3.2 Mechanisms and Models

3.2.1 Physical Processes

As far as can be ascertained no model fully explaining the physical processes taking place during pyrolysis has yet been proposed in the literature. There are however a number of models that make a partial contribution to the system.

The first usable model is one by Braun and Rothman(68) but this was designed for an isothermal and homogeneous system, the latter being clearly untrue in the case of tyre pyrolysis. The potassium benzoate pyrolysis model proposed by Kulkarne and Doraiswamy(69) incorporates a delayed diffusion factor which is later used by Fan(70) in an oil shale pyrolysis model.

Oil shale has proved a useful area for model comparison as it has many similarities to tyre pyrolysis. Wen and Wei(71), continuing Fan's work, propose a shrinking core of reactive material, all the products being liberated. The final step is taken by Lemcoff and Cunningham(72) whose model is based on a porous particle with a reactive core. A recent model by Fan(73) pulls together a number of features including mass transfer (diffusion), heat transfer, temperature profiles, solid concentration profiles and chemical reactions.

Although no system covers all the needs of tyre pyrolysis many examples partially fit the qualitative model proposed later in which a shrinking reactive core is surrounded by a porous carbon jacket through which heat must pass and out through which products diffuse.

3.2.2 Chemistry of Pyrolysis

Modern rubber compounds are a complex mixture of polymers: polyisoprene, polybutadienes and styrene-butadiene copolymers. The mechanisms of pyrolysis in molten salts can be evaluated at two levels; the first being of general degradative mechanisms such as the terms thermal or catalytic widely used in the petroleum industry and secondly on a more specific level where structure is related to products via a specific chemical mechanism.

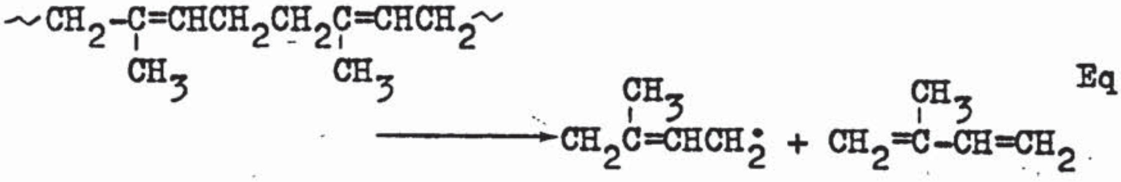
Although most of the specific mechanisms can be "back-related" to classic types of mechanism few background publications are known. However most undergraduate texts(74) refer to thermal and catalytic cracking in the analogous petroleum industry. The thermal mechanism is based on a free radical process while the catalytic, which may possibly contribute in some molten salt systems, is a carbonium ion mechanism. Most texts agree that the stability of carbonium ions and their tendency to rapid rearrangement precludes low molecular weight products but in the case of thermal mechanisms, where fragmentation predominates, small species are formed. Analytical results in the literature(75,76) indicate, even at this stage, that thermal mechanisms dominate in tyre pyrolysis.

It is now possible to be slightly more specific, considering free radical mechanisms in the categories: random scission, chain depolymerization and transfer/elimination. The first is the major mechanism in straight chain saturates; Pitt(77) has found this to be so for pure polyethylene and suggests it may occur in polybutadiene. However Bevilacqua(78) points out that rubber will have weak links due to vulcanates, cross-linking and occasional aldehyde groups and so scission becomes selective. Chain depolymerization or unzipping occurs by free radical initiation and is so favoured where side chains allow charge delocalization leading to radical stabilization. As might be expected this is common in styrene copolymers such as SBR. The zip length may vary, which may help in the understanding of mechanisms. However, as with random scission, increased unsaturation occurs often giving the monomer. The transfer/elimination mechanism occurs where suitable side chains can give up simple molecules. The classic example is hydrogen chloride from PVC or in rubber benzene from styrene copolymers.

There is now just one further useful step; to correlate reaction product with the structure of the source material. In the case of polyisoprene the method dates back to 1826 when Faraday(78) isolated dipentene from rubber and to 1866 when Williams obtained a distillate from rubber identified by Tilden as isoprene(79). It should be noted that the amount of any particular product will vary greatly with the physical conditions which are a key factor in complex thermal degradation. The free radical mechamism proposed by Bevilacqua(78) is, using thermodynamic justifications, written by Bolland and Orr(80) as:

$$RCH{=}CHCH_2{-}CH_2CH{=}CHR' \longrightarrow RCH{=}CHCH_2^{\bullet} + R'CH{=}CHCH_2^{\bullet} \qquad \text{Eq.3.1}$$

which results in little unsaturation loss. The low molecular weight products of Faraday and Williams are also found by Boonsta and van Amerongen(81) who further point out that this is inconsistent with purely random scission and so supporting the weak link theory(78). Furthermore the unzipping of one or two monomer units can be shown to be energetically favourable explaining 19th century observations.

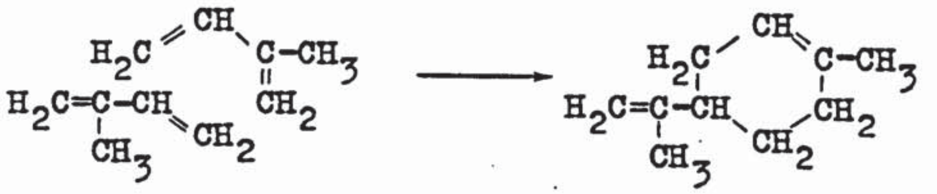


$$\sim CH_2-\underset{CH_3}{C}=CHCH_2CH_2\underset{CH_3}{C}=CHCH_2\sim \longrightarrow CH_2\overset{CH_3}{C}=CHCH_2^{\bullet} + CH_2=\overset{CH_3}{C}-CH=CH_2$$

Eq.3.2

which at lower temperatures may dimerize,

Isoprene (2) Dipentene



Eq.3.3

Most sources, with the exception of Wall(82), agree that relatively low temperature favours these reactions. The additional possibility of hydrogen transfer is put forward by Madorsky(83) but in most cases will be negligible due to the high C-H bond energy compared with weak C-C.

The thermal degradation of synthetic polybutadienes does not generally yield such high proportions of monomer. It is also of interest that many of the fragments further degrade to give carbon and hydrogen. This is particularly evident at temperatures above 450°C.

Although it is clear that some good work in these very general areas has been carried out there is little attempting to unify tyre pyrolysis products with these theoretical mechanisms. It will be seen in the following sections that tyre pyrolysis is viewed in a highly empirical fashion and few attempts at product-mechanism reconcilliation are made.

3.3 Research and Development in Tyre Pyrolysis

3.3.1 Fixed Beds and Rotary Kilns

As is true of most technological histories the early studies of rubber pyrolysis were carried out in 19th century Europe(79). This work was mainly concerned with the Victorian quest for knowledge but soon after the First World War the recycling philosophy emerges with patents by Twiss(84) and Bamber(85). The first pyrolysis process was that patented by Botson and Kamp in 1931 in which solid, liquid and gaseous products are produced for use as fillers, solvents/lubricants and fuels(86). There are a number of good reviews(8,26,87,88) of recent progress from which it is clear that trends in the light of contempory history have been still further towards the recovery of raw materials, energy and fuels.

Recent development of tyre pyrolysis in the U.K. has been carried out by two companies: Batchellor Robinson Metals and Chemicals Ltd.(89-96) and Foster Wheeler Power Products Ltd.(97-99). Both concerns have enlisted the help of the Department of Industry, Warren Spring Laboratory who have experience in domestic refuse pyrolysis.

Batchellor Robinson did not announce their work until a 1977 press release(91) which resulted in national(89) and local(90) press comment. This revealed that a 6 t/d pilot plant was operational at Warren Spring and that it was hoped to build a 50,000 t/y commercial unit by 1979. By 1978(95) a stainless steel vertical kiln reactor operating at 12 t/d was processing shredded tyre to yield 40 wt.% oil, 30 wt.% char, 15 wt.% gas and 15 wt.% steel. The oil and char are quoted as having calorific values of 41.8 MJ/kg and 30.2 MJ/kg respectively. In 1979 the capital investment for the commercial plant was put at £2.5m.

The Foster Wheeler development is based on a 1 t/d cross flow pilot plant in Hartlepool(97). Fletcher and Wilson report(98) that debeaded tyre yielded 50 wt.% oil (42 MJ/kg), 38.2% char (28 MJ/kg) and 11.8 wt.% gas (42 MJ/kg) at 600°C. (One has to be wary of the exclusion of steel and ash from the results inclusion of which reduces the oil yield to 39.4 wt.%) Fletcher and Wilson(98) also observe an increased oil aromaticity with temperature and a Coal Industry patent claims high toluene presence in tyre products(99).

In November 1978 the Department of Industry set up a consultant company, Coal Processing Consultants, as a subsidiary of the National Coal Board and Babcock and Wilcox Ltd.(100,101). Among other duties the company was to evaluate pyrolysis processes developed by Batchellor Robinson, Foster Wheeler/NRDC and Ugland (U.K.) Ltd.. Two have already been discussed and little is known of the third beyond being a subsidiary of a Norwegian shipping line holding a licence to operate a pyrolysis process from Intenco, Houston, Texas who in turn hold a licence from the Duke Energy Co. of Irvine, California. As yet no record of their findings has been seen.

Continental work on kilns and retorts is led by German companies. The first is Herbold Pyrolyse GmbH, Karlsruhe(102,103) whose rotary kiln is capable of processing 600 kg/hr of 30-40 mm scrap at 400 - 800°C to give 40 wt.% oil, 50 wt.% char, 5 wt.% gas and 5 wt.% steel (fabric tyres). The process has been licenced to Albert Miclo, France. The second, Herko Pyrolyse GmbH & Co. (Recycling) KG (Her(bold)-ko?) also operates at 400 - 800°C turning 130-140 mm shredded scrap into 50 wt.% volatiles and 45% solids(104,105). Schaefer(106) and Zeplichal (107-110) operating vertical kilns have also published results. Comment on all these can be found in a review(111) by Sinn.

In France Leyer and Vernaud(112) have pyrolysed powdered rubber while Chapelet and Grand(113) hold a patent claiming 46 wt.% liquid products. Robert and Matthys(114) also hold a patent for tyre pyrolysis. In Poland Besemer(115) has converted shredded tyre at 500°C while some Czech work(116) claims a 37.5% oil yield and a Romanian paper(117) gives detailed oil analyses showing alkyl benzenes, isoprene and methyl styrene. Soviet papers are rarely fully abstracted in English although an interesting Soviet review of tyre disposal in the West has been found(118).

Reviews of developments in the U.S.A. can be found in the recent EEC Retort(5) but trans-Atlantic papers carry more detail (6,7,8). Developments of recent years start with the Firestone -

U.S. Bureau of Mines work(119-124) using the USBM-AGA batch reactor. The temperature was varied but those around 500°C gave (on a steel-free basis) 46 - 48 wt.% oil, 5-7% gas and 42 wt.% solids, the solids increasing with temperature. Various uses are suggested for the highly aromatic oil, the char may be useful as a low grade filler while the gas is a good fuel. Little recent information has been seen; Firestone transferring their activities to depolymerized scrap rubber projects(128). However Marathon Oil(126) have since been using a suspiciously similar technique.

Goodyear's involvement on the U.S. scene is a little less clear but they are known to have operated a 25 tyre/d unit in conjunction with the Tosco Oil Shale Corp.(127,128), although most publications refer to a 15 t/d plant at Rocky Flats. Designated Tosco II this process uses ceramic balls heated to 500-600°C to facilitate heat transfer and help grind the shredded tyre(129,130). The degree of Goodyear involvement is probably limited as it is Tosco who have the background experience gained from shale pyrolysis(131). The pilot programme achieved 50 wt.% oil on a steel-free basis and was due for completion in 1977 when pending an economic evaluation a 100,000 t/yr, $18m plant was planned(132). A further report claimed the project had been shelved(133) despite the encouraging claim(134) of a gross realization of $100/t of tyre processed. Goodyear are also involved in a depolymerized scrap rubber project with Cities Services Co.(135).

DECO Industries Inc., Irvine, California have been active in tyre pyrolysis, patenting(136,137) a process pyrolysing in a triple bank screw conveyor to give 40 wt.% oil (steel-free basis) at 600°C The U.S. patent eliminates shredding (a considerable saving) by introducing a melt chamber in which the steel is retained. A 50 t/d unit is said(138) to exist in Los Angeles and the process has been licenced in the U.S.A. and U.K.(139) while Nippon Oil and Fats Co. are acting as an agent in Japan(140,141).

Thermex operate a conveyor/radiant heated process giving some 45% oil from a fabric tyre(142) and have plans for a 9 t/d plant (143). The Carbon Development Corp.(144) have developed a rotary kiln which operating at 900°C produces a quality carbon black or at 500°C an aromatic oil.

A large number of projects have been reported from Japan; a review by Hirata gives comprehensive coverage(145). Two points must be made in considering Japan: 1) Present law requires pollution-free incineration or 15 cm shredding prior to landfill and ii) Most English language literature is commercial material and so is partial and prone to exaggeration. The technology leaders in Japan are Kobe Steel Ltd., Asahi Carbon Co., the Hyaga Prefecture and Sanyo Electric Co..

Kobe Steel's UTIFIC system(67,146) involves processing the tyre down to granulated rubber which can be reformed or pyrolysed. The Kobe unit based on a rotary kiln at 500 - 800°C processed 300 kg/hr although the company can now deliver plant of capacities up to 30 t/d. On an oil, char, gas basis the oil yield is in the range 39.5 - 50.0 wt.% but on a steel radial basis this is 31.1 - 42.7 wt.%. Inoue (147,148) has published several papers concerned with this process and patents have also been granted(149,150,151). Recent information indicates that a carbon black may be the primary product(152,153).

Work carried out by Asahi Carbon in conjunction with the Bridgestone Tyre Co. and Osaka Municiple Technical Research Institute (154) is certainly aimed at black production. Char is produced by simple distillation of volatiles before being crushed and treated with steam at 800 - 1000°C. The product is suitable as a black or activated carbon(155).

Sanyo(156) make use of microwaves to convert tyre into oil 10-20%, gas 35-50% and residue 42-44% although the oil yield can be dramatically improved by steam injection(157). From this a vertical steam cyclone reactor was developed to give almost 50% oil from a steel radial.

There is a wide variety of further processes(158-163) mostly aimed at carbon products which is a notable characteristic of Japanese processes. One such process reported by Kokao and Nishida(164) produces a very fine carbon powder in a jet flame at 2000°K.

3.3.2 Fluidized Beds

The theory of fluidized thermal treatments is well explained by Shang and Chronowski(165). The main features related to tyre pyrolysis are improved agitation/mixing and heat transfer.

European research into fluidized bed pyrolysis has been centred on the Institut für Anorganische und Angewante Chemie, University of Hamburg, where work on plastics and tyres has been in progress since 1970(166,167,168). The initial work(169) was funded by Fa. Claudius Peter AG after which, with the aid of the Association of Plastic Producing Industries and the Federal Ministry of Research and Technology, a small pilot unit was built(170,171). The sand bed was fluidized by recycled product gas injected downwards onto an inclined plate. At this stage metal was removed from the reactor bottom but doubts were expressed on char removal(172). At 700°C the unit was capable of pyrolysing 15 kg in pieces up to 30 cm long in just 3 minutes. In cooperation with C. R. Eckelman of Hamburg, a 25 t/d whole tyre plant was built(173). The major innovations were a tilting grate for steel removal and a cyclone arrangement for char and inorganic removals. At 720°C the process yields 27 wt.% liquids, 22 wt.% gases, 39 wt.% char and 12% steel; equivalent to 25.8 wt.% liquids from a 16.5% steel radial. The liquid is highly aromatic and contains only 0.4% sulphur. According to Kaminsky and Sinn (174) an economic evaluation indicates that a 7500 t/a plant "will show a profit of 7%" ! Despite the fact it is unclear what this means, and Schnecko(175) doubts immediate viability, C. R. Eckelman are planning to build such a plant.

The only other fluidized system is that under development by Babcock-Rohrbach(176) which is more accurately considered as a pyrolysis/combustion system. The pilot plant operating at 700°C is capable of processing 100 kg/hr.

In the U.S.A. little attention has been paid to fluidized beds, the exception being the work by the Mitre Corp., Virginia(165). It was claimed in 1977 that this combustive process yielded only char, steel and zinc oxide, all other products being burnt.

In Japan considerable effort has been put into the REPROX system initiated by Japan Gasoline Co. Ltd. and Nippon Zeon Ltd. (177). The Ministry of International Trade and Industry has been involved in the project and the laboratory bench work was performed at the Government Industrial Development Laboratory, Hokkaido(178, 179). In 1974 a 1 t/hr plant was set up at Zeon's Tokuyama site(177). The fluidized medium is product char and the fluidizing agent the product gas giving obvious advantages. Saeki and Suzuki(180) claim that at an optimum 450°C, 52 wt.% oil, 28.1 wt.% char and 14.4 wt.% gas are obtained. In terms of a steel radial the oil yield would be 43.6% which is high but the product contains 1.4% sulphur. The gas is burnt to fuel the system as is part of the char. The remaining char is treated to give fillers and activated carbon. The operators make seven claims

1. Efficient and compact design
2. Limited tyre shredding
3. High value products
4. Economic viability
5. Capable of automation
6. No secondary pollution
7. Safe

The oil is apparently acceptable so it would appear that the value of the solid product is the crucial factor. Scale permitting the process seems viable.

3.3.3 Molten Salts

The use of molten salts as a pyrolysis medium is a relatively new concept and appears to have been the concern of few workers. Molten salts for tyre pyrolysis have only been investigated by: Perkow at Hamburg, Larsen at the University of Tennessee, possibly DECO Energy Inc. and, in passing, the Rockwell Corp.. Very recently a proposal by the CIRTA-EXTRAMET Group, Paris, has been seen.

The molten salt (probably $MgCl_2$-KCl) work at Hamburg by Perkow was not carried beyond the laboratory stage, being dropped in favour of the fluidized bed(168). Using granulated rubber screw fed into an electrically stirred and heated glass flask containing the melt, it appears that only 12.3 - 13.7 wt.% oil was obtained in the region 700-790°C. Although it is a little difficult to interpret the original figures, the char and gas yields are 38-49 wt.% and 20-23 wt.% respectively(169). The products are collected using conventional and electrostatic precipitations. It is suggested by Schnecko(172) that the project was shelved due to melt/solids separation problems. A short report by the Battelle Inst., Geneva also identifies this problem.

The work by Larsen and Chang at Tennessee has been funded by the Rubber Division of the American Chemical Society and the Tennessee

Valley Authority(75), the latter now being the assignee of a Larsen patent(181). The work has been on a bench scale (40g batch) using conventional glassware. The melts have been mainly LiCl-KCl and $ZnCl_2$ although some work has been carried out using $SnCl_2$ and SbI_3(182,183). Further papers published with colleagues detail process flow plans and Larsen has recently claimed to have received an Environmental Protection Agency grant to design a pilot plant(184).

A brief summary of Larsen's results are given in Table 3.1.

Melt	Temp. °C	Oil, wt.%	Gas, wt.%	Char, wt.%
LiCl-KCl	500	47	10	43
$ZnCl_2$	"	43	12	45
None	"	46	10	43

Table 3.1 Results. University of Tennessee (182).

The maximum oil yield in terms of a steel radial would be 39 wt.% It is notable that the $ZnCl_2$ produces a highly aromatic oil (31 vol %) while the LiCl-KCl produces a highly olefinic oil (34 vol %)(75). Larsen attributes the former to Lewis acid behaviour, also noting that this melt remains essentially clean so is proposed for the pilot unit(181). Despite these results the kinetic data indicates thermal rather than catalytic cracking. The only rate data given in these papers is the comment that a 30g batch is pyrolysed in 5 minutes, quickened by Cu^{2+} and Pb^{2+} salt additions(185). The system provides good heat transfer but it was realized that char removal might be a problem.

The involvement of DECO Energy Co. in the molten salt field is not altogether clear. The DECO reactor is apparently a "vertical molten salt unit"(138) but it is not known if the melt is used as a direct or indirect heat transfer medium. The system requires no tyre shredding and after a residence time of 20 minutes (indicating indirect heat transfer) at 480°C gives 49.6 wt.% oil (41% on steel radial basis), 40.0% char and 4.6% gas. The sulphur contents of the oil, char and gas are 0.8 wt.%, 1.8 wt.% and 136 ppm. Little else is known of the DECO molten salt work and the general attitude encountered(139) is one of scepticism. However in mid-1977 it was claimed that a 50 t/d plant was operational in Los Angeles, California (138). Costings from Ugland Management, Norway, put such a plant in 1977 at £1.325m and Marathon Oil valued the liquid product at £63/t (138).

The Rockwell work is, strictly speaking, oxidative gasification but is of interest as it uses Na_2CO_3 at 920°C(186). The laboratory work made use of an alumina-lined, stainless steel reactor which was electrically heated. The pilot unit(187) was designed for general gasifications but tyres were considered as a possible feedstock. The gas contained only 30 ppm sulphur, the rest being retained in the melt as Na_2S.

Reports from the Soviet Union(188) say Pechuro et al. have applied molten lead at 780°C to tyre pyrolysis. The products are 40.5% oil, 9.7% gas and 49.8% char on a steel free basis.

The Cirta-Extramet proposal of December 1979 bears some very close similarities to the original proposal for this project. It is proposed(189) to carry out some tyre pyrolysis/oxidative gasification experiments in molten Na_2CO_3 in the range 500-1000°C. The system would give oil, gas, char, steel and inorganics; the oil and gas values distilling from the reactor, char being skimmed off and sulphur being complexed in the melt. The char will be further treated to give carbon black - a process that is not likely to be successful. The melt is recycled by sulphur removal as H_2S. The proposers have been a little naive as to the problems of char removal and its effective use as a black. Secondly the melt regeneration is concerned only with sulphur and no mention is made of zinc salts or steel. The unrecognised factors will no doubt come to light during the project.

3.4 Pyrolysis of Related Materials

3.4.1 Plastics

An extensive review of plastics has recently been published by Pitt(79), so this treatment will be largely bibliographic. Other reviews are found in "Resource Recovery"(190) and Staudinger's "Plastics and the Environment"(191).

Most concerns involved in tyre pyrolysis have also considered plastics. Sinn et al.(192,193) at Hamburg studied plastic pyrolysis in molten $MgCl_2/KCl$ and fluidized systems, noting that liquid and gaseous products account for 95% of the feed indicating little char formation which has particular advantages in a molten salt system.

When PVC was pyrolysed HCl was produced which is extremely corrosive.

In the U.S.A. plastic pyrolysis is more advanced. The best reviews are a Government Report(194) and a SCI monograph by Staudinger(195). Union Carbide publications by Wall et al. (196) and Potts(197,198) indicate them to be the commercial leaders although a patent for counter-current pyrolysis of PVC and other plastics has been granted to Banks et al.(199). Furthermore it has been reported (200) that a large plant dealing with factory trimmings is operational.

The world leaders in plastic pyrolysis are the Japanese; Pitt cites(77) several dozen companies many of which are mentioned in the Appendices. Mitsui Ltd. operate a 36 t/d plant which recycles hot gas as a pyrolysis medium and has been granted a patent in the U.K. (201). Sumitomo H.I. Ltd. operate a 3 t/d fluidized bed(202), Sanyo a microwave system(203) and the Government Industrial Development Laboratory several small units(204). The involvment of the latter two with tyre pyrolysis is notable. The best English language reviews are the world wide documents by Milgrom(205,206).

Clearly processes for clean factory cut-offs are the primary objective but as the market is small many companies are turning to wider and mixed feedstocks.

3.4.2 Municipal Refuse

Municipal waste represents a large proportion of that turned out by the human race and also the scale of supply is vast as is well reflected by the volume of literature. Again it is only possible to give fleeting coverage to the major processes although many more are recorded in Appendix II. The "Handbook of Solid Waste Disposal" (207) is a useful general review but the critical review by Porteus (208) is more relevant to the U.K.. Wilson(209) and Jackson(210) consider the energy content of municipal waste; Jackson probably taking a high plastic content gives higher values. A particularly interesting review of the acute problem in Japan is given by Joshida and Nishizaki(211).

Research in the U.K. has been headed by the Warren Spring/Foster Wheeler cross-flow development(97). After initial bench work commercial development was undertaken by Foster Wheeler(212) resulting in a process giving up to 50% oil and 20% char/ash (the remainder being gases). It is notable Foster Wheeler have also been involved in tyre pyrolysis(98).

A more advanced European development has been the Danish Destrugas System invented by Borggreen(212) and developed by Pollution Control Ltd.. The Kalundborg, 5 t/d plant feeding crushed refuse into a vertical shaft at 1000°C has been operating for some years and is now under commercial consideration in Germany and Japan. The system produces char and gas, the latter containing 45 vol % hydrogen, <15 ppm SO_x and <150 ppm NO_x (214).

In the U.S.A. there have been numerous developments, the most important of which are: Monsanto's Landgard System, Garrett/Occidental's Flash System and the EPA funded Andco-Torrax Slagging System(215).

The Monsanto system feeds shredded refuse into a rotary kiln through which sufficient air is passed to maintain temperature(216). The gases are burnt and so no fuel product is obtained but the disposal cost of £3/t (1972) was cheaper than incineration. A 100 t/d plant has recently been installed in Baltimore for some £7.0m (217). The Garret Research and Development Co., a subsidiary of Occidental Petroleum Co. have developed a true pyrolysis system which, operating at 500 - 700°C uses a vertical reactor to obtain 40% conversion to a 279 MJ/kg oil (218,219,220). A plant operating in San Diego(221-225) feeds its product oil direct to the generating stations of the San Diego Gas and Electric Co.. The last and highly successful U.S. system, the Andco-Torrax Slagging System, is a two stage pyrolysis/combustion system; the latter part generating heats of up to 1400°C which are used to raise steam(226,227). The system is commercially in use at 200 t/d in Luxembourg and another unit is said to have been ordered for a site in southern France(228). The system accepts tyres as part of the feed but most important is the 97% volume reduction achieved(226).

From Japan, Hamabe reports(229) that Kawasaki H.I. Ltd. have developed the Landgard system to suit local requirements but the stage of development is unknown. Several other Japanese developments are listed in Appendix II.

3.4.3 Hydrocarbons

Pyrolytic treatment has been useful in the treatment of heavy crude oils, tar sands and oil shales. (Coal is considered in Chapter 4.)

The Goodyear-Tosco and Tosco II tyre pyrolysis systems(127) originated from Tosco's oil shale experience. The most recent shale unit employs metal or ceramic balls as a grinding and heat transfer agent(130). Although the main market for this system must be in the U.S.A. and Canada it has been patented in the U.K. (131). Tar sands found in North America can be processed on an air blasted fibrous bed, patents for which have been granted(230) although economic viability is at present uncertain.

In Japan a steam treatment system for low grade crude oil has led to large yields of ethylene and acetylene(231). The U.S.S.R. also processes large deposits of low grade crude in the Baku region. Pechuro et al.(232,233) using the molten lead system previously applied to tyres have been able to obtain 25 wt.% yield in ethylene and a further 25 wt.% in other olefins. The system may not yet be as efficient as catalytic cracking but is certainly cheaper. Molten salts have also been used in this field by Rozhdestvenskii(234) and Aerov(235), the latter incorporating gas-lift melt circulation. Shale has been treated in the U.S.S.R. by Simenov(236) yielding some 65% light oils at 700°C. These systems all bear some relevance to tyre pyrolysis.

Conventional cracking, although in many respects relevant to this thesis, is deliberately not considered here. This is due to the facts that much of these systems are not novel and that they are well documented in numerous texts.

3.5 Conclusions and Summaries

3.5.1 Bases for Evaluation

It appears from the literature that all the pyrolysis work mentioned in this chapter are aimed at the development of commercial plant and processes. It would therefore seem sensible to draw conclusions about these developments on the basis of a few industrial considerations detailed below. It is fairly clear, from general sources, that to be successful a plant must meet basic conditions. For example, the costly process of shredding should be avoided. In addition, an obvious consideration is commercial viability which will in turn be dependent on a number of variable criteria.

In the following sections some of the more important conditions for success are considered with general reference to this chapter. After this a more general summary of plant types is given.

3.5.2 Criteria for Success

3.5.2.1 Pretreatment of Tyre Feed

It appears that all the rotary kiln and fixed bed processes currently under development require some degree of shredding. The reasons for this are usually mechanical and essentially unavoidable but shredding also increases the relative surface area which is important in a system relying on gas for heat transfer. Most quote shredding to less than 15cm although Tosco II makes no mention of pretreatment and larger scale plants generally feed larger material.

In fluidized systems the accepted size is larger, even the Hamburg 15 kg batch unit took 30 cm pieces and it was the Hamburg fluidized plant built by Eckelman that first took whole tyres. Clearly Sinn et al. realized the importance of this requirement at an early stage. The fluidized bed has limited moving features and the heat transfer is far more efficient than in the kiln systems.

The molten salt systems have not as yet reached a scale where whole tyres can even be considered. However from mechanical (reactors are generally simple) and heat transfer (superior to other media) points of view there is no reason for exclusion at a larger scale.

3.5.2.2 Recovery of Valuable Products

All processes mentioned produce the same basic range of products but due to specific conditions quantities and values differ. A general shift from liquid to gas and solid products with increasing temperature is seen in all processes but the maximum yield of oil varies from process to process. The oil is generally more aromatic in fixed and fluidized beds whereas in molten salts there is a marked olefinic content. All processes treat oil as a fuel at about 40 MJ/kg but the molten salt products are usually lower in sulphur. The gases produced are all of similar composition and heating value but those produced by molten salt, especially carbonates, tend to contain less sulphur.

The greatest variation in product value and use is found in the char, covering fuels, activated carbon and carbon black. Carbon black is probably the most valuable but only the Asahi Carbon Co. and the Carbon Development Corp. claim quality black production while Firestone and Kobe Steel suggest possible black production. Nippon Zeon/Japan Gasoline claim to produce activated carbon but all others only consider the char as a fuel. In the fluidized bed and more particularly molten salt processes char presents recovery problems. It has also been suggested that molten salt contact causes considerable deterioration in reinforcing properties.

3.5.2.3 Plant Capacity

Clearly the capacity of a plant can be increased simply by making it larger. However this has obvious disadvantages, pointing to the fact that a small plant with a high capacity is ideal. Unfortunately the literature on pilot and commercial plants is not forthcoming in this area but some conclusions can be drawn from laboratory work.

The faster processes quoting lowest residence are fluidized bed and molten salt systems indicating the rates are at least partially dependent on heat transfer. Of these the fluidized beds are mechanically complex and the molten salt face corrosion problems both adding to costs but since rates are so much higher these may be minor factors.

3.5.2.4 Manning and Maintenance

Very few comments are made concerning manning but Nippon Zeon/

Japan Gasoline's REPROX is said to be "capable of automation". This is probably true of all processes but particularly so of the lower technology types. Maintenance will also be related to plant complexity although molten salt baths will particularly suffer due to corrosion.

3.5.3 Process Type

Although all three types of process produce the same range of products there are differences in reactor performance and product analyses. Here the merits of each type of reactor are given.

The kilns, retorts and fixed beds are generally the simplest reactor type and probably present the lowest costs. The products meet most requirements, the oil being highly aromatic and the char on treatment having multiple uses. However the processes are generally inefficient, having poor heat transfer and long residence times.

The fluidized systems improve the efficiency and thus the throughput. The products are probably slightly more versatile than other systems but a few doubts have been expressed over solids handling. Fluidized beds must also be considered complex technology.

Molten salt systems have the disadvantages of very problematic solids handling and corrosive environments. The possible catalytic activity of the melt produces highly olefinic volatiles but the char can only be considered as a fuel (if it can be recovered). The reactor may be extremely simple in design having virtually no moving parts and is still capable of very high throughput rates.

At this stage no reactor type can be picked out as superior, each having advantages over the other two. The final choice may depend on circumstantial requirements based on the four criteria detailed earlier.

Tabulated summary data for individual processes can be found in Appendices I and II.

CHAPTER

FOUR

LITERATURE SURVEY III - RELATED TOPICS

4 LITERATURE SURVEY III - RELATED TOPICS

4.1 Molten Salts

4.1.1 Introduction and Bibliography

It is not the intention here, and indeed it would not be possible, to cover the entire field of molten salt science and technology; the section has been written with specific reference to the problems of this project.

The most extensive bibliography is the NTIS document by Schalit (237) available in three volumes. A more up to date source is a paper by Janz(238) that is basically a list of references (several hundred). Books by Blander(239) and Sundheim(240) give a good coverage while The Chemists Companion(241) makes a few useful comments. Some of the common problems occurring in molten salt research are outlined by Ishino and Tamupa(242) and a good survey of developments in the early 70s is given by Clarke and Hills(243).

4.1.2 Physical Properties

As it is the melt used in this research, much of this and subsequent sections concentrate on molten carbonates. However a useful source for molten salt physical data in general is the Molten Salt Handbook compiled by Janz(244).

Most of the work measuring physical properties was carried out and published in the 60s. Janz and Lorenz(245) performed multiple measurements, including surface tension, viscosity, conductivity and density on alkali carbonates. They were also responsible for a paper on solid-liquid phase equilibria(246) while the surface tension work was reported by Moiseev and Stepanov(247). Rolin and Recapet (248) made a wide study of the thermodynamics of alkali carbonates and have produced a complete ternary phase diagram for the Na_2CO_3 : Li_2CO_3 : K_2CO_3 system; the eutectic is quoted as 31.5 : 32.5 : 36.0 wt. % melting at 393°C. The eutectic point is close to that of Janz and Lorenz(249) 33.4 : 32.1 : 34.5 wt. % melting at 397°C but criticizes Volkowa's results of 26.6 : 17.9 : 55.5 wt. % (250).

The relevant physical data for the Janz-Lorenz eutectic are given in Table 4.1.

Composition, wt.% ($Na_2CO_3/Li_2CO_3/K_2CO_3$)	31.5/32.5/36.0
Melting Point, °C	393
Density, kg/dm^3	2.28
Viscosity,	54.7 mP at 485°C

Table 4.1 Physical Properties of Triple Carbonate Eutectic

4.1.3 Chemical Properties

There are a number of very general texts concerned with molten salt chemistry, the best examples being Bloom(251) and Blander(239). More up-to-date publications can be found in Advances in Molten Salt Chemistry(252), currently there are three volumes. A number of texts are available in which molten salts are considered as media or solvents for other reactions. Sundermeyer has published a great deal in this area(253-257) although a useful compilation of papers edited by Lagowski(258) is also available. There is, of course, the additional possibility of using molten salts as a homogeneous catalytic system; a number of specific papers can be found but the best general review is Norman and Johnstone(259) who conclude that melts containing metal ions show a similar catalytic effect to the free metal.

The previous paragraph refers to very broad texts but as far as this project is concerned the interest is restricted to a few specific systems in and involving molten carbonates. It is usually accepted that the carbonate melt is not likely to take any part in the pyrolysis reactions although there have been some reports of catalytic activity. Most molten cracking catalysts contain chlorides, zinc being a favourite(260); a point that has been taken up by Larsen for tyre pyrolysis(75). However the carbonate system has been shown during the development of the Kellogg coal gasification process to catalyse the reaction between carbon and steam(261).

It was not surprising to read that where steam is injected into carbonate melts hydrolysis occurs forming corrosive hydroxides(261).

$$CO_3^{2-} + H_2O \rightleftharpoons 2\,OH^- + CO_2 \qquad \text{Eq. 4.1}$$

However since carbon dioxide is already being formed in carbon gasification situations,

$$C + 2H_2O \longrightarrow 2H_2 + CO_2 \qquad \text{Eq. 4.2}$$

$$C + O_2 \longrightarrow CO_2 \qquad \text{Eq. 4.3}$$

there would be a considerable back reaction. The Kellogg workers report a maximum hydroxide concentration of 8% although Hammond and Mudge, working on refuse, report a higher level of 33% (262) as acceptable.

The carbonate melt was chosen partially due to its ability to absorb the sulphur present in tyres thus avoiding secondary pollution. Glueck(263) proposed this could be used to desulphurize coal and enables Kellogg(261) to produce relatively sulphur-free gases. Molten carbonate is capable of absorbing both sulphide and oxide gases:

$$M_2CO_3 + H_2S \longrightarrow M_2S + CO_2 + H_2O \qquad \text{Eq. 4.4}$$

$$M_2CO_3 + SO_2 \longrightarrow M_2SO_3 + CO_2 \qquad \text{Eq. 4.5}$$

$$M_2CO_3 + SO_3 \longrightarrow M_2SO_4 + CO_2 \qquad \text{Eq. 4.6}$$

thus has applications in stack gas scrubbing(264). Reduced to sulphide (by carbon or otherwise) the carbonate can be regenerated, liberating hydrogen sulphide, by the passage of steam and carbon dioxide(265):

$$M_2S + CO_2 + H_2O \longrightarrow M_2CO_3 + H_2S \qquad \text{Eq. 4.7}$$

Little has been published concerning the behaviour of zinc salts in molten carbonates but in the presence of hydroxides it would appear from the aqueous chemistry that zincates can be formed in solution.

4.1.4 Corrosion

Corrosion problems with molten salt systems are generally severe and so restrict many of their industrial applications(266). The processes of corrosion are complex but a general knowledge of the physical and chemical actions involved can be gained from a review by Hoar(267).

The carbonate eutectic is perhaps one of the least harsh systems but has none the less received considerable attention. Janz and Conte using an alumina vessel have studied the effects of this melt on noble metals(268) and stainless steels(269). From potentiostatic polarization studies the anodic corrosion potentials under carbon dioxide / oxygen were found and are given here in Table 4.2..

Metal	Anodic Corrosion Potential, mV	
	600°C	700°C
Pd/Au alloy	- 430	- 485
Au	- 470	- 475
Pt	- 475	- 505
Ag	- 680	-
Ni	-1160	-
SS 304	- 450	-
SS 347	- 450	- 570

Table 4.2 Metal Corrosion Potentials (268, 269)

It can be seen that stainless steels types 304 and 347 have a corrosion resistance comparable with gold and platinum but not as good as the gold/palladium alloy. The values for stainless steels are stabilized in about 12 hours by the formation of $LiFeO_2$. These values translate to an effective corrosion rate of about 0.06 mg/hr/cm^3 for stainless steel 347 at 700°C.

Corrosion problems in nuclear reactors are covered by Berry(270) Tipton(271) and Simons and Stang(272). The latter are concerned with sodium hydroxide cooled reactors reporting severe corrosion especially of moving parts.

A solution to corrosion problems appears to be alumina or magnesia lining of containment vessels. Janz et al.(273) still report around 0.002 mg/hr/cm^2, restricted by the formation of aluminates. It should be noted that this is only true for carbonates; chlorides attack alumina. Another protection measure, reported by Stern(274) is the passivation by galvanic coupling with a more noble metal.

The pyrolysis and oxidation products may also cause corrosion. An analysis of various steels by Fischer(275) report only slight problems. Likewise Clark(276) reports no problem from carbon oxides or hydrocarbons below 550°C but above this carbonization occurs. The reactions are fortunately restricted by steam.

4.1.5 Industrial Applications

The applications mentioned here exclude pyrolysis and coal gasification, as these are major topics elsewhere. There are several good reviews; the survey by Clarke and Hills(243) is very broad, a more specific paper is available by Hatt and Kerridge(277) and the 1974 Battelle publication gives a detailed account of applications in the U.S.A.(278).

The early and still major industrial use for molten salts (commonly nitrates) is heat treatment which was developed by Castner et al.(279) and is now the concern of ICI Cassel(280). Other traditional uses are in electrowinning and metal plating. More modern general uses are in heat exchangers, reactor coolants and fuels, and also in nuclear fuel reprocessing(281).

Molten salts have recently been developed as catalysts for the petroleum industry. Monstanto(282) make use of the Lewis acid Al_2Cl_6 as a dehydrogenation catalyst while it can also be used in the hydrocracking of coal extracts(283). The similar $ZnCl_2$ system has been used in Japan by Nakatsuji(284) to crack anthracene oils and study catalyst poisoning.

Molten carbonate has recently been developed as a scrubbing melt as it removes sulphur from stack gases. The system was developed from Glueck's(285) process to desulphurize coal (useful in Eastern and Central U.S.A. deposits). Most of the development by Rockwell concentrated on absorbing SO_x as SO_3^{2-}/SO_4^{2-} for later regeneration of elemental sulphur. Babcock and Wilcox(286) have published similar work in Europe while Moore(287) at the Battelle

Institute, Geneva, has extended the application to NO_x pollution.

One of the most important events in the field was the development by C. E. Lummus Eng. Co. of the Transcat process(288) which makes use of molten chlorides for catalytic chlorination of hydrocarbons. In 1975 Lummus were ready to build a 30,000 t/a plant but due to a decline in the market the unit was never completed.

4.2 Carbon Oxidation and Coal Gasification

4.2.1 Introduction

It has been established that one of the products of tyre pyrolysis is a carbon char (75,121,148) which in molten salt reactors cannot easily be removed from the reactor(185). The char tends to float on the melt surface or may become entrained in the melt. This has posed a problem to Perkow(168) and Larsen(185), but several methods of separation have been suggested. Most of these are mechanical but some work on gasification of refuse and coal makes use of a pyrolysis/combustion two stage system; the combustor burning char produced in pyrolysis. This system could well be applied to tyre pyrolysis cycling the melt between pyrolysis and oxidation zones:- char produced by pyrolysis being entrained in the melt is circulated to an oxidation zone where it is gasified by air and/or steam leaving a clean melt to be recirculated for further tyre pyrolysis. This concept is introduced here to explain the interest in carbon oxidation and coal gasification literature.

4.2.2 Chemistry of Carbon Oxidation

The simple chemistry can be found in almost any text covering the subject, Walker et al. being a good comprehensive review(289).

The reactions of carbon and oxygen can be written as follows:

$$C + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_{1100} = -394.6 \text{ kJ/mol} \qquad \text{Eq. 4.8}$$

$$C + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad = -112.4 \qquad \text{Eq. 4.9}$$

The heats of reaction given are those measured by Rossini(290) for amorphous carbon at 1100K. Subsequently the following reactions may occur:

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_{1100} = -290.5 \text{ kJ/mol} \qquad \text{Eq. 4.10}$$

$$C + CO_2(g) \longrightarrow 2\,CO(g) \qquad = +169.3 \qquad \text{Eq. 4.11}$$

The respective equilibrium constants at the same temperature quoted by Rossini are:

$$\text{Eq.4.8} \quad Kp = {(CO_2)}/{(O_2)} = 6.3 \times 10^{18}$$

$$\text{Eq.4.9} \quad Kp = {(CO)}/{(O_2)^{0.5}} = 8.8 \times 10^{9}$$

$$\text{Eq.4.10} \quad Kp = {(CO_2)}/{(O_2)^{0.5}(CO)} = 10^{10}$$

$$\text{Eq.4.11} \quad Kp = {(CO)^2}/{(CO_2)} = 1.2 \times 10^{1}$$

all but 4.11 being well displaced to the right.

The reactions occurring between carbon and steam are:

$C + H_2O(g) \longrightarrow CO(g) + H_2(g)$ $\Delta H_{1100} = +136.3$ kJ/mol Eq.4.12

followed by possible subsequent reactions:

$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$ $\Delta H_{1100} = -33.9$ kJ/mol Eq.4.13

$C + 2H_2(g) \longrightarrow CH_4(g)$ $= -89.5$ Eq.4.14

$C + CO_2(g) \longrightarrow 2CO(g)$ $= +169.7$ Eq.4.15

$2CO(g) + 2H_2(g) \longrightarrow CH_4 + CO_2$ $= -269.3$ Eq.4.16

$CO(g) + 3H_2(g) \longrightarrow CH_4(g) + H_2O(g)$ $= -226.1$ Eq.4.17

$CO_2(g) + 4H_2(g) \longrightarrow CH_4(g) + 2H_2O(g)$ $= -191.5$ Eq.4.18

The equilibrium constants for reactions 4.12 to 4.18 are:

Eq.4.12 $K_p = 1.2 \times 10^1$

Eq.4.13 $K_p = 1.0$

Eq.4.14 $K_p = 3.7 \times 10^{-2}$

Eq.4.15 $K_p = 1.2 \times 10^1$

Eq.4.16 K_p = n/a

Eq.4.17 $K_p = 1.2 \times 10^{-2}$

Eq.4.18 K_p = n/a

The reactions 4.12 and 4.13 occur at atmospheric pressure but the reactions 4.14, 4.17 and 4.18 are insignificant giving little methane.

If excess air is present in a simultaneous air/steam gasification (or if the air is moist) another important reaction can occur.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta H_{1100} = -248.3 \text{ kJ/mol} \qquad \text{Eq.4.19}$$

whose equilibrium constant is 7.6×10^8 which approaches that of Eq. 4.8 and 4.9 indicating that much of the hydrogen formed in Eq. 4.12 and 4.13 may not be seen under equilibrium conditions.

4.2.3 Mechanisms

4.2.3.1 Carbon-Oxygen Reactions

The seemingly simple chemistry in fact involves relatively complex mechanisms. Since early investigations(289) it has been questioned whether carbon dioxide is a primary product or formed by monoxide oxidation.

Van der Held(291) proposed that the monoxide was formed at the carbon surface by reaction with oxygen and that the dioxide was formed by further oxidation of part of the monoxide, thus a mixture of the two gases finally escapes. DeGraaf(292) observed that this scheme would mean that the region in which monoxide-to-dioxide oxidation was occurring would naturally be hotter than the carbon surface. This enabled De Graaf to propose a laminar system in which the dioxide formed was the only gas reacting with the carbon after initiation and eliminating the need for oxygen to diffuse (against considerable resistance) to the reactive surface.

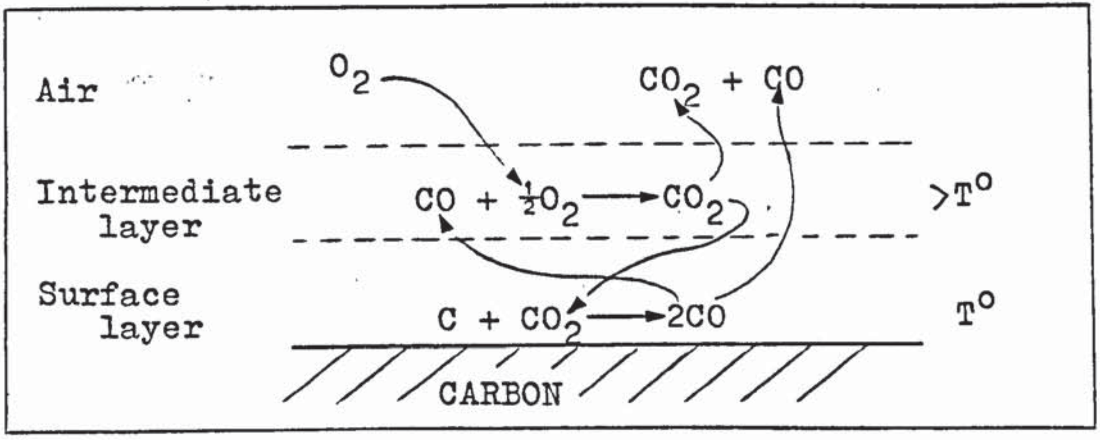


Fig.4.1 De Graaf Mechanism

In de Graaf's system the initiation reaction of oxygen and carbon occurs at 700°C whereafter the cycle described is set up. The presence of monoxide in the surface layer was confirmed spectrophotometrically but at a later date it was pointed out that the detail of the spectrum was characteristic of an oxygen/carbon monoxide mixture rather than the monoxide/dioxide mixture predicted.

Arthur(293) using $POCl_3$ to inhibit the oxidation of monoxide to dioxide indicated that both oxides were primary products whose ratio in the range 460 - 900°C, could be expressed as:

$$(CO)/(CO_2) = 10^{3.4}\, e^{-12{,}400/RT}$$

Rossberg(294) using dry oxygen, again to inhibit oxidation of the monoxide, extended the upper temperature limit to 1420°C. Both

Arthur and Rossberg neglect the reaction of carbon with carbon dioxide as being of any consequence; a direct contradiction of the van der Held hypothesis(291). Lewis(295) confirmed that both oxides were primary products but gives a differing ratio expression. Day(296) extended the theory to show the ratio was largely independent of type of carbon and gas velocity over surface.

In 1961 Fuchs and Bielack(297) put forward the following, temperature dependent, primary product system:

$< 800^\circ C$	CO_2 primary
$800 - 1000^\circ C$	$CO + CO_2$
$> 1000^\circ C$	CO

but there is no clear mention of how or where the temperature is measured.

Using an ^{18}O radio-tracing technique Vaslola et al.(298) were able to show conclusively that both oxides were primary products and that oxidation proceeded via a transient surface intermediate or complex. L'Homme(299) suggests oxygen is chemisorbed onto the carbon surface after which diffusion to a reactive site occurs where the products are formed. Lavrov(300) supports this view, assigning $C_{\overline{x}}CO$ as the surface complex structure.

Recent work by Bukhman and Nurekenov(301) again shows two primary products suggesting a ratio only dependent on temperature:

$$(CO_2)/_{(CO)} = (0.16 \times 10^{-3})^{16,800/_{RT}}$$

This agrees with Arthur(293) and shows that the monoxide predominates except at extremely high temperatures. However it should also be noted that above 1000°C the reaction between carbon dioxide and carbon also becomes significant.

In summary it can be said that:

1) Both carbon monoxide and dioxide are primary products.

2) The ratio is dependent on temperature, the monoxide being favoured at lower temperatures.

3) Secondary reactions do take place.

4.2.3.2 Carbon-Steam Reactions

There are two possible carbon-steam mechanisms; the first involves adsorption of intact water molecules whereas the second is a dissociative process.

The Gadsby and Johnstone(302,303) adsorption mechanism can be written:

$$C + H_2O(g) \longrightarrow C(H_2O) \qquad \text{Eq. 4.20}$$

$$C(H_2O) \longrightarrow H_2(g) + C(O) \qquad \text{Eq. 4.21}$$

$$C(O) \longrightarrow CO(g) \qquad \text{Eq. 4.22}$$

which can be retarded by:

$$C + H_2(g) \longrightarrow C(H_2) \qquad \text{Eq. 4.23}$$

The dissociative mechanism consists of :

$$C + H_2O(g) \longrightarrow C(O) + H_2(g) \qquad \text{Eq. 4.24}$$

$$C(O) \longrightarrow CO(g) \qquad \text{Eq. 4.25}$$

In both mechanisms formation of the dioxide can be accounted for by:

$$C(O) + CO(g) \longrightarrow CO_2(g) + C \qquad \text{Eq. 4.26}$$

Gadsby(302) found that monoxide additions did not retard the reactions which he claims would support the absortive mechanism. The possible dissociation of steam to hydrogen and hydroxyl proposed by Long and Sykes(304) cannot be ignored but would appear to be energetically unfavourable.

4.2.4 Rates and Orders of Reaction

The rates of reactions involving carbon are dependent on the nature of the carbon and reactant gases. In addition mass transfer, reaction retardation and so on will play a role. The rates of all these reactions will also be a function of temperature and pressure.

There is a great deal of data in the literature but, due to differences in variables, comparisons are hard to make; in no case has a comprehensive series of reactions been performed by one group of workers. The rate of carbon-oxygen reaction under various conditions is given in Table 4.3 where the units have been standardized. These give a general magnitude to reaction rates and Fuchs(297) has also quoted a rate constant as 530 s^{-1}. It is clear that the rate increases with temperature and pressure. Further, it has been suggested that the Arrhenius equation is valid up to 700°C whereafter the reaction is diffusion controlled.

Workers	Carbon type	Temp. °C	Pressure, Atm. O_2	Rate, $g/cm^2/s$
Snegireva & Tesner (305)	Black	450	0.4	8.3×10^{-12}
Armington (306)	Black(P-33)	600	0.1	1.1×10^{-11}
Lisyutkina et al. (307)	Black	800	0.2	2.3×10^{-8}
Krivandin & Berner (308)	Black	1050	0.2	4.0×10^{-5}
Lisyutkina (307)	Black	1100	0.2	4.4×10^{-8}
Gulbransen & Andrew (309)	Graphite	575	0.1	2.5×10^{-8}
Earp & Hill (310)	Graphite	500	0.2	8.3×10^{-7}
Earp & Hill (310)	Graphite	700	0.2	2.2×10^{-5}
Armington (306)	Graphite	600	0.1	4.9×10^{-11}

Table 4.3 Rates of Carbon Oxidation with Air/Oxygen

In a heterogeneous system it is difficult to evaluate the true order as bulk mass transfer has an affect on the overall measured order. Most carbon-oxygen reaction orders are quoted at just under unity (suggestive of diffusion control) but there are many contradictions(289).

The rates of carbon-steam reactions are less well documented but it is very clear these are lower than corresponding carbon-oxygen reactions. Some rate data, unfortunately in various units, is given in Table 4.4.

Workers	Carbon type	Temp. °C	Pressure, Atm	Rate
Lisyutkina et al. (307)	Black	1230	na	2.3×10^{-13} g/cm^2/s
Lisyutkina et al. (307)	Black	1730	na	3.9×10^{-11} g/cm^2/s
Goring et al. (311)	na	870	0.1	5.5×10^{-5} s^{-1}
Pilcher et al. (312)	Graphite	1100	1.0	4.8 g/hr

Table 4.4 Rates of Carbon-Steam Reactions

Fortunately the Goring and Fuchs results are comparable units, showing the reaction with steam to be some 10^7 times slower than with air. This is not uncommon but the steam rate is usually quoted(311) as 10^5 times slower. Fuchs and Bielack(297) also point out that rates are proportional to surface area up to 1000°C whereafter they are mass transfer dependent.

The orders in carbon-steam systems are generally found to be between zero and unity varying with temperature(289). Armstrong treated the Johnstone(313) data to show the reaction is expected to be first order above 1370°C (303).

Also occurring in these systems are reactions with carbon dioxide and with hydrogen:

$$C + CO_2 \longrightarrow 2CO \qquad \text{Eq. 4.11}$$

and

$$C + 2H_2 \longrightarrow CH_4 \qquad \text{Eq. 4.14}$$

Goring(311) quotes a rate constant for the latter at $13 \times 10^{-8}\ s^{-1}$ which, especially at low pressures, makes the reaction insignificant. The rates for the former reaction are slower than carbon-oxygen reactions but comparable with carbon-steam reactions.

Workers	Carbon type	Temp. °C	Pressure, Atm.	Rate, g/cm²/s
Armington(306)	Black(P-33)	900	0.1	7.3×10^{-13}
Armington(306)	Graphite	900	0.1	6.2×10^{-12}
Galbransen & Andrew (309)	Graphite	900	0.1	1.1×10^{-9}

Table 4.5 Rates of Carbon-Carbon Dioxide Reactions

Walker et al.(289) reviewing gas reactions of carbon have compiled data from various sources and quote the relative rates of various reactions at 800°C and 0.1 Atm as:

Reaction	Relative Rate
C - O_2	1×10^5
C - H_2O	3
C - CO_2	1
C - H_2	3×10^{-3}

Immediately clear are the summarizing facts that:

1) Carbon-oxygen is by far the fastest reaction.

2) Carbon-steam and carbon-carbon dioxide have similar rates of reaction.

3) Carbon-hydrogen is a negligibly slow reaction under these conditions.

The rates of the various reactions will be reflected in the compositions of the product gases. However it is useful to note that even under equilibrium conditions the monoxide is the dominant product in the carbon-oxygen reaction while in the carbon-steam system hydrogen and carbon monoxide have approximately equal mole fractions while the dioxide fraction is about half this value. These experimental data agree well with theoretical predictions.

4.2.5 Coal Gasification Processes

The chemical processing of coal to yield liquid and gaseous hydrocarbons has, for political and strategic reasons, been an area of intensive research and development for some time. The Fischer-Tropsch/Sasol conversion processes are briefly described in a number of standard texts(74), but detail of modern plants are closely guarded. These processes basically rely on conversion of coal to hydrogen and carbon monoxide by reaction with oxygen and steam at high temperatures followed by treatment over iron and cobalt catalysts to give hydrocarbons. These reactions are:

Eq. 4.9 $C + \frac{1}{2}O_2 \longrightarrow CO$ $\Delta H = -100$ kJ/mol) Producer gas reaction

Eq. 4.8 $C + O_2 \longrightarrow CO_2$ $= -407$ ")

Eq. 4.12 $C + H_2O \longrightarrow CO + H_2$ $\Delta H = +31$ kJ/mol Water gas reaction

Eq. 4.13 $CO + H_2O \longrightarrow CO_2 + H_2$ $= -10$ Shift reaction

followed by

Eq. 4.27 $nCO + 2nH_2 \longrightarrow (CH_2)_n + nH_2O$ $\Delta H = -39.4$ kJ/mol

Eq. 4.28 $nCO + 2nH_2 \longrightarrow H\text{-}(CH_2)_n\text{-}OH + n-1\ H_2O$ $= -59$

This process is currently operated on a large scale in South Africa; the Sasolburg plant converts some 4 million tons of coal to 1 million tons of gasoline, and other products, per annum.

Work on coal gasification can be classified by two different goals. The first is the production of a synthesis gas which by the shift reaction and methanation can be converted to a high calorific value product. The second is merely the production of a more straight forward fuel gas. In 1965 Bituminous Coal Research Inc. produced a listing of a large number of developments(314) since which much further research has taken place. The 1978 Synthetic Fuels Handbook(314) and the ACS Monograph on the subject(315) are the best modern reviews, detailing processes too numerous to mention here.

In Europe work is currently under way with Badische Anilin und Soda Fabrik, Ruhrgas, Central Electricity Generating Board, Lurgi and the Saarbarg-Otto-Rummel consortium. The last mentioned claim to produce a gas of composition; carbon monoxide, 54 V%, hydrogen 31.4 V%, carbon dioxide 13.2 V%, methane 0.2 V% and others 1.2 V% giving a calorific value of 10.4 MJ/m^3.

In the U.S.A. Rockwell, Am Oil, U.S. Bureau of Mines, Occidental Oil and M. W. Kellogg are all known to be involved in this area. The Kellogg process makes use of molten sodium carbonate as a reaction and heat transfer medium and so is of particular interest. Initial laboratory and pilot studies over the period 1964-67 were concerned mainly with the steam gasification of coal at 970 - 1070°C (261). The effects of pressure, gas velocity, ash content and bed height were all evaluated. It was concluded from this work that the rate was largely dependent on surface area, that only some 10% of available steam reacted in one pass and that the reaction followed pseudo-first order kinetics(261). It was found that this reaction left a char that was largely unreactive to steam so in the pilot stage a two-unit system was developed enabling the char to be burnt off with air.

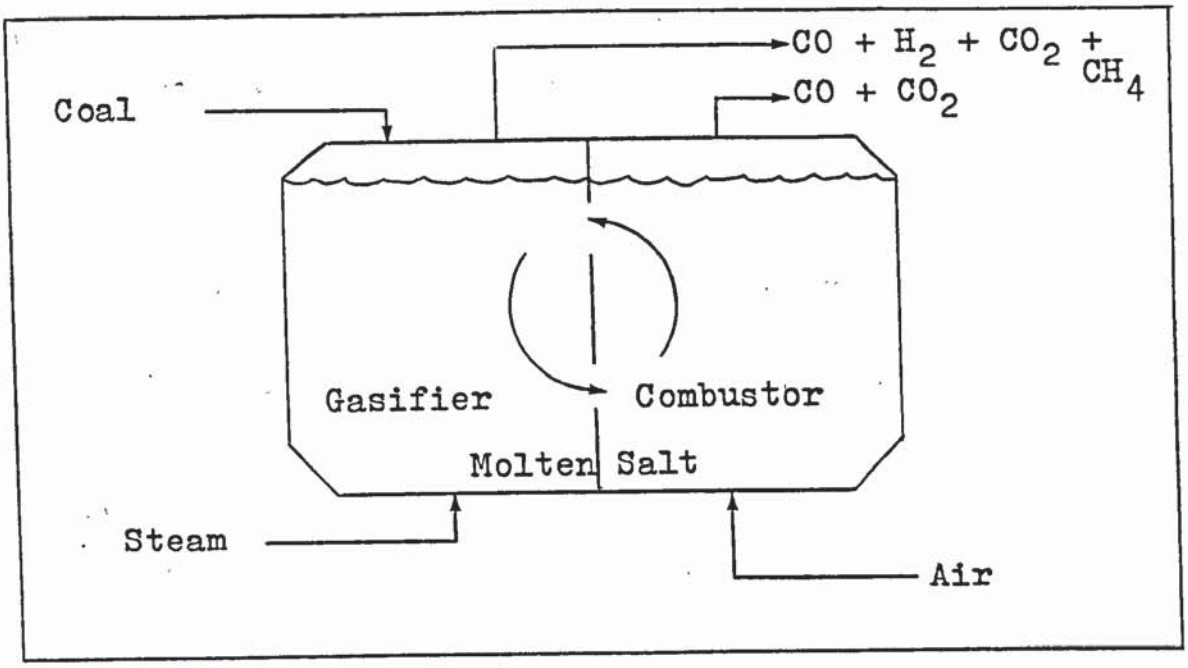


Fig.4.2 Schematic Representation of Kellogg Process

This system had the additional advantage that the combustion reactions were exothermic providing the heat input necessary to maintain gasification. Early reports(316) recognise the problems of the solid-liquid-gas system but the relatively simple design appeared adequate.

A report(317) on the commercial potential of the process was published in 1967 and by 1973 a number of process design papers had appeared. In these, various options including the single vessel gasifier - combustor or separate vessel reactors are discussed but of more note is discussion on the melt chemistry. It was reported that the melt underwent hydrolysis in the gasifier,

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2 \qquad \text{Eq. 4.29}$$

which was recarbonated in the combustor(reverse reaction) but that a hydroxide concentration of 6 mol % was experienced. This caused severe corrosion to steels and led to lining of the vessel with Monofrax A ceramic(317). It was also found that the melt absorbed sulphur present in the coal as sulphide although in the combustor this probably existed as a sulphide/sulphite/sulphate mixture. It was also suggested that sulphur could be removed by,

$$Na_2S + CO_2 + H_2O \longrightarrow Na_2CO_3 + H_2S \qquad \text{Eq. 4.30}$$

regenerating the melt. Finally experiments showed that an ash level of 8 wt. % could be tolerated before removal.

At this stage little was heard from Kellogg and rumours of shelving were heard. However Am Oil Co. were developing a process using FMC's coal pyrolysis process(318) and utilized a low pressure Kellogg process to gasify resulting char. Also at about this time Glueck(319) was suggesting the process might have an application in pollution-free power generation.

The Kellogg principle finally re-emerged in 1976 in a coal processing development by Rockwell(320). A full development unit whose main reactor was some 10 m in height and able to process 1 tonne/hr was commissioned in 1978. The plant included ash removal, sulphur recovery and melt regeneration units. The programme was due for completion in December 1979 and if successful would leave little doubt as to the viability of such processes.

CHAPTER

FIVE

STUDY OF DISPOSAL POLICIES

5 STUDY OF DISPOSAL POLICIES

5.1 Introduction to Model

In the summary to Chapter 2 it is made clear that present disposal strategies cannot be continued. In this and the following chapter some effort was put into identifying the technical alternatives. The strategic policy study is used to evaluate the wider effects of alternative and new disposal methods.

The diagram below illustrates the important patterns in the used tyre disposal industry. The diagram itself is to a certain extent qualitative but detailed values are given in the text. The resource flows are generally considered in terms of energy and materials, although other considerations are mentioned.

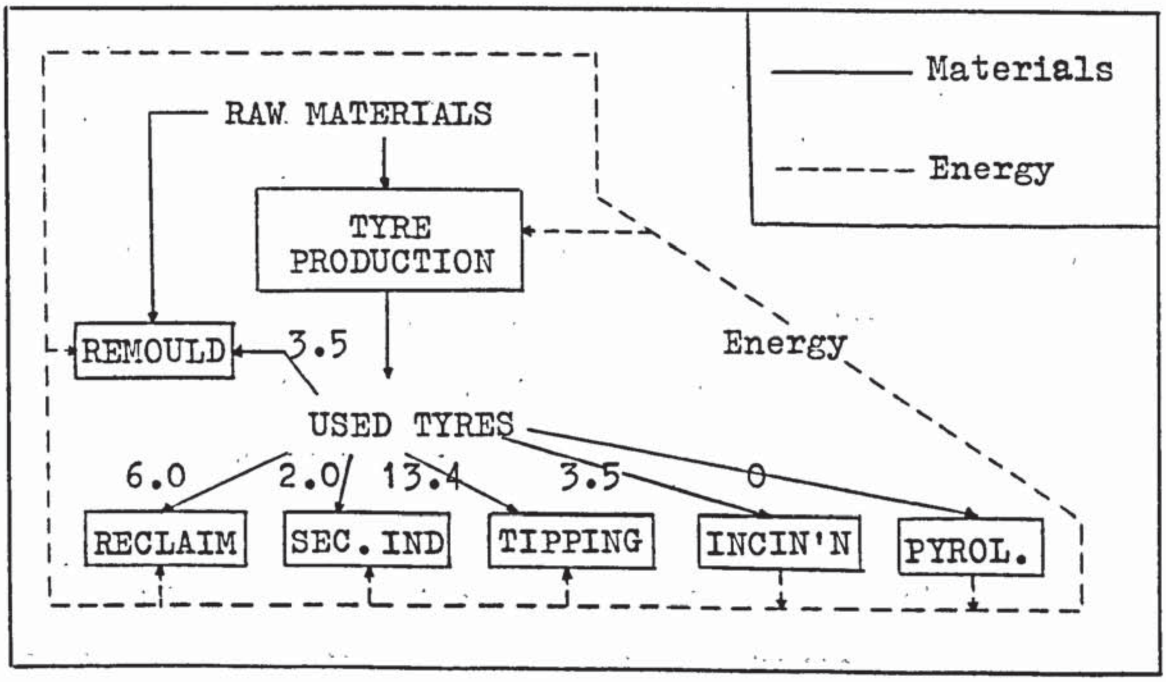


Fig.5.1 Materials and Energy Flow

Of the processes shown only incineration and pyrolysis are net energy producers. All disposal processes will have some detrimental effects on the environment but particularly harmful is the practice of tipping. The model applied to car tyres has the volumetric flows shown in millions of tyres (1980 estimates); notably low are incineration and pyrolysis which can largely be attributed to the state of the technology, collection problems and investment reluctance.

The volumes of each flow are primarily the result of commercial factors but these are of course constantly subject to change. In addition factors such as social pressure and environmental pollution are becoming increasingly important. Although of no direct commercial consequence, these factors can be brought to bear by legislation or financial subsidy. The object of this exercise is to consider, quantitatively where possible, changes in current disposal strategies.

5.2 Alternative Disposal Policies

5.2.1 Tipping

Universal tipping of all used tyres is extremely unlikely to be considered due to the facts that it is costly in terms of materials, energy, space and pollution. It must also be seen that while it is legal, there are many more profitable options.(4)

However a limited increase is not out of the question despite its disadvantages in terms of conservation. To be realistic such an occurrence would only take place if other, more profitable, methods became impossible. If large spaces became available for tipping the likely sufferers in terms of tyre supply must be the new innovative industries.

A reduction in tipping would be highly desirable in environmental and conservation terms but can only be achieved by stimulation of other industries. The most likely areas for stimulating subsidies would be the novel industries of incineration and pyrolysis. These are beneficial in environmental and energy terms but do little to ease pressure on raw materials.

5.2.2 Reclaim

Rubber reclaim is used almost entirely in new tyre production and currently relies on fabric reinforced tyres as a feedstock. Thus the level is essentially fixed by other factors in the market.

If reclaiming were to be increased, by say the development of steel radial comminution processes,(19) there is an immediate problem of finding a use for the product. A certain amount could be absorbed by increase use in new tyre production but some other uses would have to be found. This strategy has its main benefit in raw material conservation although much tyre material is renewable.

A reduction in reclaiming, as occurred in the early 70s, can only add to tipping problems unless new industries can be encouraged to pick up the surplus. On the whole it seems likely that future reclaim will be geared solely to meet the requirement of tyre manufacturers to whom it is essential.

5.2.3 Remould

Remould tyres are in direct competition with new tyres for the replacement market; they are cheaper but less reliable. Remoulds are controlled by law, the severity of which is increasing.

If for any reason, most likely price of the product, remoulding increases, the major sufferer must be new tyres. Being highly profitable an increase in remoulding numbers would poach used tyres from all other reuse industries. The option is environmentally desirable but likely to be socially undesirable in terms of unemployment and product unreliability.

A forced reduction of remoulding by legal restriction of the product would result in increased proportions of scrap steel radials. This may be thought to encourage other industries but at present the secondary industries have a limited market for their products and reclaimers cannot process the steel radials. So again if environmentally undesirable tipping is to be avoided the novel disposal techniques must be encouraged.

5.2.4 Secondary Industries

Secondary industries produce a wide variety of small useful products: fenders, shoes, gaskets, washers, door mats and link belting.

These industries are potentially highly profitable. The supply of used tyres is easily available but the market for the products is currently small.

An increase in the market for these products would help to reduce the amount being tipped. Where the tyres are reused as fenders or barriers whole steel radials may be suitable. However many of the smaller stamped products are most easily made from fabric tyres which are used to produce reclaim which in turn is essential for new tyre production. Despite the great environmental, social and material conservation seen in this strategy the market is very tight.

A drop in secondary activity would give a slight increase to reclaimers but due to distribution problems is also likely to add to tipping volume. The optimum strategy for secondary operators is to concentrate on a small geographical zone making full use of locally contracted supplies.

5.2.5 Incineration

Incineration of tyres is a method by which all tyres may be disposed to raise steam. The advantage of this option is a total destruction of the waste material to yield energy. The method is, disregarding slight secondary pollution, environmentally advantageous but does nothing to recover materials. The major disadvantage of this system is that steam must be used as and when tyres are incinerated; the product is essentially unstorable.

The increased application of incineration would make great inroads into tipping and as such is highly desirable. Although it represents resource loss the heat generated saves on fuel that is approximately equal to the petroleum content of the tyre. It must be said that where incineration meets the specific needs of an operator it has great attractions. Failure of this method to be developed, most likely due to lack of finance for costly capital equipment, can only worsen the tipping problem. Incineration due to debatable return on investment is unlikely to represent a challenge to traditional reuse tyre supplies.

5.2.6 Pyrolysis

Pyrolysis is probably the most novel of disposal techniques under evaluation today. Being a net producer of energy pyrolysis has most of the advantages of incineration and may prove ideal in certain operator circumstances. In addition most systems are pollution free and the heat is produced in the form of storable fuels. This option also poses the possibility of recovery of raw materials such as carbon black and scrap steel; giving the process a considerable conservationary and commercial advantage over incineration. However it is clear that being a high risk technical option finance may only be available from the public sector where cost-benefit accounting is in common use. The commercial risk is probably slightly greater than incineration.

Like incineration this strategy has the potential to considerably reduce the tipping problem (distribution and transport costs permitting).

Its potential to poach established industries is small but due to increased material recovery is slightly superior to incineration. Failure to develop this course will only add to tipping volumes.

5.3 Conclusions

It was made clear in Chapter 2 that tipping is representing an increasing and intolerable problem. Of the alternatives it has been shown that:

1. Reclaim is restricted by the availability of fabric tyres and the demands of the new tyre manufacturers but would otherwise be an advantageous area for development.

2. Remould is controlled by law and social factors making it an unlikely area for development.

3. Secondary industries are in competition with reclaimers for fabric tyres and have currently only a small market for their products.

A summary of the advantages and disadvantages of incineration and pyrolysis are given in Table 5.1.

These disposal strategies generally fall into two categories; the first aimed at recycling materials, while the second is more concerned with energy. In terms of tyre materials only carbon black makes a significant demand on a finite resource, although even this (crude oil) may not be considered particularly acute in the U.K.

Factor	Incineration	Pyrolysis
Capacity	Both systems would, if developed, be capable of processing the quantities of waste likely to be present.	
Environment	Slight secondary pollution.	Pollution free.
Products	Heat/steam and slag.	Oil, gas and steel.
Costs	Both involve high capital costs. Pyrolysis being more complex is probably the more costly.	
Technical Feasibility	Proven	Under development.

Table 5.1 Summary of Incineration and Pyrolysis

The inorganic materials pose only a small demand on their resources while rubber is essentially a renewable resource. However the U.K. is an energy conscious society and so the energy producing strategies must look particularly promising for the future.

CHAPTER

SIX

PROCESS CONCEPTS & RESEARCH OBJECTIVES

6 PROCESS CONCEPTS AND RESEARCH OBJECTIVES

6.1 Requirements of Industrial Process

One of the ultimate aims of this study was to produce the basic information necessary to plan the further development of the process and to see to what extent the process was likely to meet the requirements of an industrial operation. Some of the more general of these requirements are itemised below:

1) The process must be commercially viable showing a good rate of return on capital investment, be in receipt of appropriate grants or satisfy the cost-benefit accounting of a municipal corporation. To achieve this a pyrolysis process may have to satisfy the remaining conditions.

2) The plant should be a net producer of energy, if not in its actual operation, in terms of the energy value of its products against that energy required to obtain them.

3) The plant should be simple enough in its construction and operation to require minimum attention and maintenance. The design of plant should lend itself to automation.

4) Part of the simplicity must be an ability to accept whole tyres with the minimum pretreatment and avoiding altogether shredding or grinding.

5) In connection with the first two conditions the process should yield high value products both in monetary and calorific terms. It should also produce minimum wastes.

6) The plant should have a high throughput for a relatively compact design which will preferably be a low cost design.

7) In order to achieve condition (6) it is almost certain that the design must be one employing the optimum heat transfer efficiency.

These items are basically short summaries; the broader needs are discussed in detail under the appropriate sections.

6.2 Molten Salt Pyrolysis

6.2.1 General Factors

The application of molten salts as a tyre pyrolysis medium may at first appear unusual. However it will be shown here how molten salts meet many of the fundamental needs of a pyrolysis medium and the process requirements of the previous section.

The liquidus range of many eutectic mixtures of salts coincide with the temperatures that are thought to be desirable for tyre pyrolysis. In addition most salts have a high heat capacity, making temperature control easier and have a high thermal stability.(244,245)

The fluid nature itself is also a useful feature. The molten medium can flow into all the irregular cavities of a tyre thus obtaining a large contact area and increasing heat transfer efficiency. The viscosities of most molten salts at operational temperatures are such that reasonably efficient pumping can also be achieved.

For the most part melts do not react with the tyre or the pyrolysis products but act purely as heat transfer media. However some melts have useful chemical properties and some may even act as homogeneous catalysts.(75)

Molten salts do however pose a few problems not found in other systems. There are obvious hazards associated with hot liquid media, as are experienced in the steel industry, but molten salts are also prone to sub-surface vapour explosions if liquids are accidentally introduced. There are similar chemical hazards associated with oxidizing melts and most melts are highly corrosive posing a containment problem. However industrial experience in the areas of nuclear reactor technology (270) and metal heat treatment(280) seem to have overcome these difficulties.

The factors affecting the melt choice can so be summarized in the list below:

1. Liquidus range
2. Viscosity
3. Thermal stability

4. Hazards/safety
5. Chemical properties
6. Industrial experience

6.2.2 Carbonate Eutectic

After extensive consideration of the factors mentioned in the previous section, the triple sodium/potassium/lithium carbonate eutectic was chosen as the salt for this work. The composition of this eutectic is given in Table 6.1 and was found to melt at 395°C (668K) which is in good agreement with the Rolin and Recapet (248) figure of 393°C for the same eutectic. The eutectic composition suggested by Janz and Lorenz(249) which melts at 397°C is sodium carbonate 33.4 wt%, potassium carbonate 34.5wt% and lithium carbonate 32.1 wt%. This is very close to the eutectic used here. That suggested by Volkowa (250), sodium carbonate 26.6 wt%, potassium carbonate 55.5 wt% and lithium carbonate 17.9 wt% which would be

Component	Wt %	Mol %
Na_2CO_3	31.5	30.0
K_2CO_3	36.0	26.0
Li_2CO_3	32.5	44.0

Table 6.1 Triple Carbonate Eutectic (248)

conveniently low in costly lithium carbonate is not confirmed anywhere else in the literature and so ignored. The eutectic used here has been found to be stable in excess of 1050°C.

Janz and Saegusa report(321) the Janz-Lorenz eutectic to have a viscosity of 54.7 millipoise at 485°C. This is between water and a light lubricating oil which agrees with the general melt appearance at this temperature.

Although there is little corrosion work relating specifically to this melt and pyrolysis applications, M. W. Kellogg Co. report(317) that pure sodium carbonate was very corrosive to stainless steels and so used Inconel 600 and Monofrax A for containment. However the Kellogg system was at 900°C and steam was present. Janz and Conte (268,269) put stainless steels 304 and 347 on a par with platinum and gold in the presence of the pure triple eutectic. They further show that under these conditions stainless steels form a passivating oxide layer which in the absence of abrading surfaces may be sufficient protection.

The carbonate eutectic is also able to absorb sulphur(285) as sulphide or sulphate depending on conditions. The sulphur can later be recovered from the melt as hydrogen sulphide. The retention of sulphur in the melt will of course reduce the amounts to be found in the products.

Although carbonates do not usually act as cracking catalysts

(Lewis acids being more suitable) there are reports of its action in carbon-oxygen reactions. Kellogg suggest sodium carbonate catalyses coal gasification but the method of evaluation is unclear.(261) Yosim and Barclay(186) also report sodium carbonate/sulphide mixtures to be effective gasification catalysts.

The only unfortunate chemical feature of the eutectic is that it is hydrolysed by steam to produce the highly corrosive hydroxide,

$$M_2CO_3 + H_2O \longrightarrow 2\,MOH + CO_2 \qquad \text{Eq. 6.1}$$

However in the presence of zinc salts, which are used in tyre manufacture, this hydroxide may form zincates but there is little evidence in the literature. Also notable; the excess carbon dioxide will encourage the reverse carbonation reaction.

In terms of safety the eutectic is the least hazardous of the possible melts. It is not toxic like arsenates and sulphides and it does not take part in oxidative explosions, like nitrates. Chlorides are also a possibility but do not have all of the advantages already discussed.

6.3 Envisaged Two-Stage Process

The literature, as has been seen, shows that molten salt tyre pyrolysis is in principle perfectly feasible. It was shown in many cases that pyrolysis was capable of converting tyres to gaseous, liquid and solid products, the last being a carbonaceous char. The gases and liquids clearly evolve from the reactor at pyrolysis temperatures leaving the solids in the reactor which, especially in the molten salt situation, poses handling problems. Most systems under current evaluation remove the solids by mechanical means to give a full range of products, some of which have to be used to fuel the reactor. The value of the carbonaceous char appears very questionable as uses suggested vary from carbon black to substitute solid fuel; the latter is likely to be the only possible use where molten salt contact has occurred.

During the early evaluation of pyrolysis as a means of tyre disposal in this work it was clear that the most valuable and easily recoverable products were gas, oil and steel. It therefore seemed expedient that the lower value char should be used to fuel the process by combustion. However the handling problem still existed. At this stage the concept of in-situ combustion was put forward which not only eliminated the char handling/removal problem but also, the reactions being exothermic, fueled the process saving the more valuable products and cleaning the melt.

$$C + \tfrac{1}{2} O_2 \longrightarrow CO \qquad \text{Eq. 6.2}$$

$$C + O_2 \longrightarrow CO_2 \qquad \text{Eq. 6.3}$$

$$CO + \tfrac{1}{2} O_2 \longrightarrow CO_2 \qquad \text{Eq. 6.4}$$

An initial calculation showed that in fact this would provide an embarrassing surplus of heat. This, it was suggested, might be corrected by removal through heat exchange and used in say spare heating. An apparently more elegant option was to simultaneously react the char with steam which also gives gaseous products cleaning the melt but is endothermic.

$$C + H_2O \longrightarrow CO + H_2 \qquad \text{Eq. 6.5}$$

$$C + 2H_2O \longrightarrow CO_2 + 2H_2 \qquad \text{Eq. 6.6}$$

Clearly these char gasifying reactions could not be performed simultaneously in the same reactor as pyrolysis as there would be a risk of explosive mixtures of hydrocarbons and air/oxygen arising with disasterous consequences. The first way of avoiding this is to operate a batchwise cycle: tyre pyrolysis - char gasification - tyre pyrolysis - and so on but this would be clearly inefficient. The alternative would be to physically divide the reactor into two areas for pyrolysis and char gasification, perhaps even to the extent of having two separate reactors. Using the second method a continuous process was envisaged in which tyres would be pyrolysed to give (among other products) a char that would be retained with the melt. Then melt plus char would be cycled to a second reactor where the gasification could be performed after which clean melt is returned to the pyrolysis reactor and the cycle recontinued. This option would operate continuously, as is illustrated in Figure 6.1. By careful design of the char gasification reactor it may in addition be possible to use the injected air and steam to achieve a gas-lift circulation of the melt.

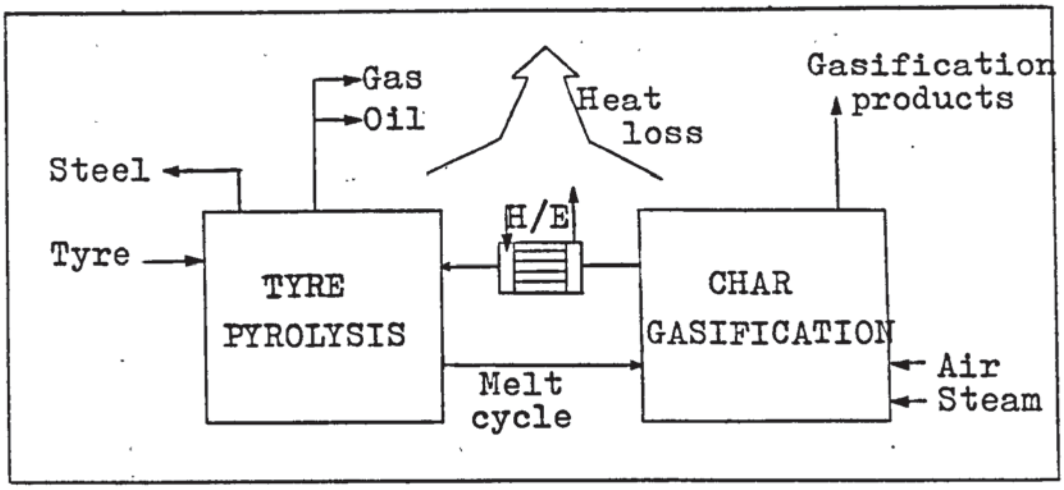


Fig.6.1 Schematic Representation of Two-stage Process

6.4 Feedstock Selection

There are many designs of tyre in use today and so clearly the feedstock for a tyre pyrolysis process would be a mixture of types and brand names. However for the purposes of this study it was essential to select just one type of tyre so as to maintain experimental reproducibility (further comment on experimental reproducibility is given in Chapter 8). In addition it is necessary to ensure that the tyre chosen is typical of that likely to be available when the process matures.

It has already been demonstrated that the current trend of tyre design in the U.K. is towards the steel braced radial. In 1980 this type of tyre will have accounted for some 55-60% of the U.K. market; a figure that is still increasing. Steel radials also pose problems to conventional disposal techniques and so are an even greater proportion of waste tyres.

All major U.K. manufacturers now produce steel braced radials so it would appear that a typical tyre must be chosen from one of the major manufacturers. The market shares are given in Table 6.2.

Michelin	24%
Dunlop	23
Goodyear	21
Firestone	11
Pirelli	9
Avon	7
Uniroyal	5

Table 6.2 Market Shares (322)

The volume steel radials produced by the three market leaders are: the ZX and XZX, SP4 and G 800s respectively. Of these the Dunlop tyre was chosen on the grounds that it is a recent development and has considerable original equipment contracts with vehicle manufacturers.

6.5 Aims of Research

The aim of this research work was to provide and collect data essential to the production of a technical and commercial feasibility report on the pyrolysis of waste tyres in molten salts. The technical data, obtained by experimental work, was an integral part of the data required for commercial evaluation. Given encouraging commercial indicators, the technical data will also be the main basis on which scaling-up recommendations and process flow designs are made.

The objectives of this work can thus be summarized in the following ways:

1) Experimental

(a) To compile rate data relating to tyre pyrolysis such that it may be used in scale-up procedures.

(b) To obtain information with regard to other critical factors affecting scale-up and reactor design.

(c) To understand the effect of physical and chemical conditions on the yields and nature of the products, thus enabling, with rate data, the optimum operational conditions to be determined.

(d) To provide information on reactor materials with particular reference to corrosion.

(e) To obtain experience in the handling and manipulation of molten salt systems and in doing so to identify any particular difficulties and hazards.

2) Commercial

(a) To gain an understanding of the availability and general flow patterns of used tyres.

(b) To identify any effects of alterations to current reuse practices and evaluate their benefits.

(c) To provide an economic evaluation of a molten salt tyre pyrolysis process that may be proposed in the light of experimental results.

CHAPTER

SEVEN

EXPERIMENTAL APPARATUS

7 EXPERIMENTAL APPARATUS

7.1 Simulation of Process Concept

In Chapter 6 it has been shown clearly that the best system for molten salt tyre pyrolysis involves two stages: pyrolysis and char gasification. Therefore the most desirable laboratory system would be a miniature of a full scale plant. However this poses certain difficulties:

1) A continuously operating unit would be costly and complex to construct.

2) A small continuous unit, although giving excellent empirical data, would not facilitate the gathering of data essential to the understanding of tyre pyrolysis. This is particularly true of kinetic data and the understanding of controlling processes.

3) The physical problems of cycling hot molten salt in the laboratory on a small scale make a miniature plant type of unit impractical.

For these reasons it was decided to investigate tyre pyrolysis and char gasification separately using two separate reactor units, thus simulating the continuous concept by working a pseudo-cyclic batch system. This is to say that tyre is pyrolysed in one unit to give its products one of which, char, is transferred, when the experiment is completed, to the second unit where char gasification experiments are performed.

The designed research equipment described is basically two physically separate and independent units. However much of the control and ancilliary equipment is used in common on both units.

7.2 Tyre Pyrolysis Unit

7.2.1 Furnace

The pyrolysis furnace was based on a ready-wound tubular ceramic (Al_2O_3) element of 13.5 cm internal diameter and 30.5 cm in height which was supplied by A. Gallenkamp & Co. Ltd. The immediate surrounds of this heating element were insulated with Triton Kaowool ceramic fibre supplied by Morganite Ceramic Fibres Ltd.. This was contained by industrial firebrick to make up a cube of vertices 38 cm which was covered with Syndanyo asbestos board; circular holes being wet cut in the top and bottom faces to accept the reactor. This was covered in galvanized steel coated in aluminium paint. The whole system was placed on legs raising it 10 cm above bench level, enabling a sand-filled emergency catchpot to be placed under the lower and open end of the furnace tube. (This furnace was largely constructed by Pitt (77)).

7.2.2 Reactor

The pyrolysis reactor was designed to have a molten salt capacity of 1.0 to 1.5 kg although the dimensions of the reactor allows a considerable margin for the violent splashing of the process. This was considered ample to pyrolyse tyre batches of 20 - 40 g. As molten salts are generally corrosive the material used for construction was stainless steel type 321. A diagrammatic representation of the reactor is given in Figure 7.1 and a photograph of the in-situ reactor top is shown in Figure 7.2.

Figure 7.1 shows that the reactor is made up of three main sections: an outer pot 13 cm in diameter and 23 cm in height (a), an easily removable inner liner 12.5 cm in diameter and 19.5 cm in height (b) and a top section (c) through which all the service ports pass.

The tyre is introduced to the reactor through the top section using a sliding immersion rod (d) which passes through a sealing gland (e) clipped to the raised section of the reactor top (f). The products of pyrolysis pass out of the reactor through a 2.2 cm diameter exit port (g) on the side of the raised section and then through a 1.5 cm tube(h) heated by Electrothermal "Heat by the Yard" tape to the condenser system. The pyrolysis gas can form explosive mixtures with air and so the reactor system must at times be purged with nitrogen. Nitrogen purge ports pass through the top of the reactor (i) and into the stirrer (j) and immersion rod (k) glands.

The melt is agitated by a plain feather screw (l) the shaft of which passed through a purpose designed gland (m) in the top of the reactor. Details of this gland which is similar to the immersion rod gland are given in Figure 7.3. The agitator was driven by a 1 m flexible drive (n) from a 150 w electric motor (o). The glands are designed to "leak" inwards.

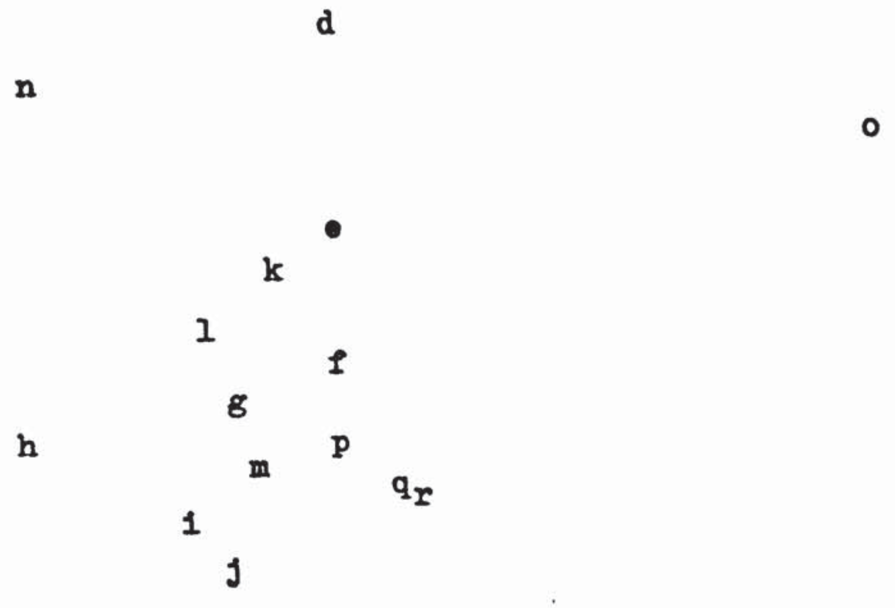
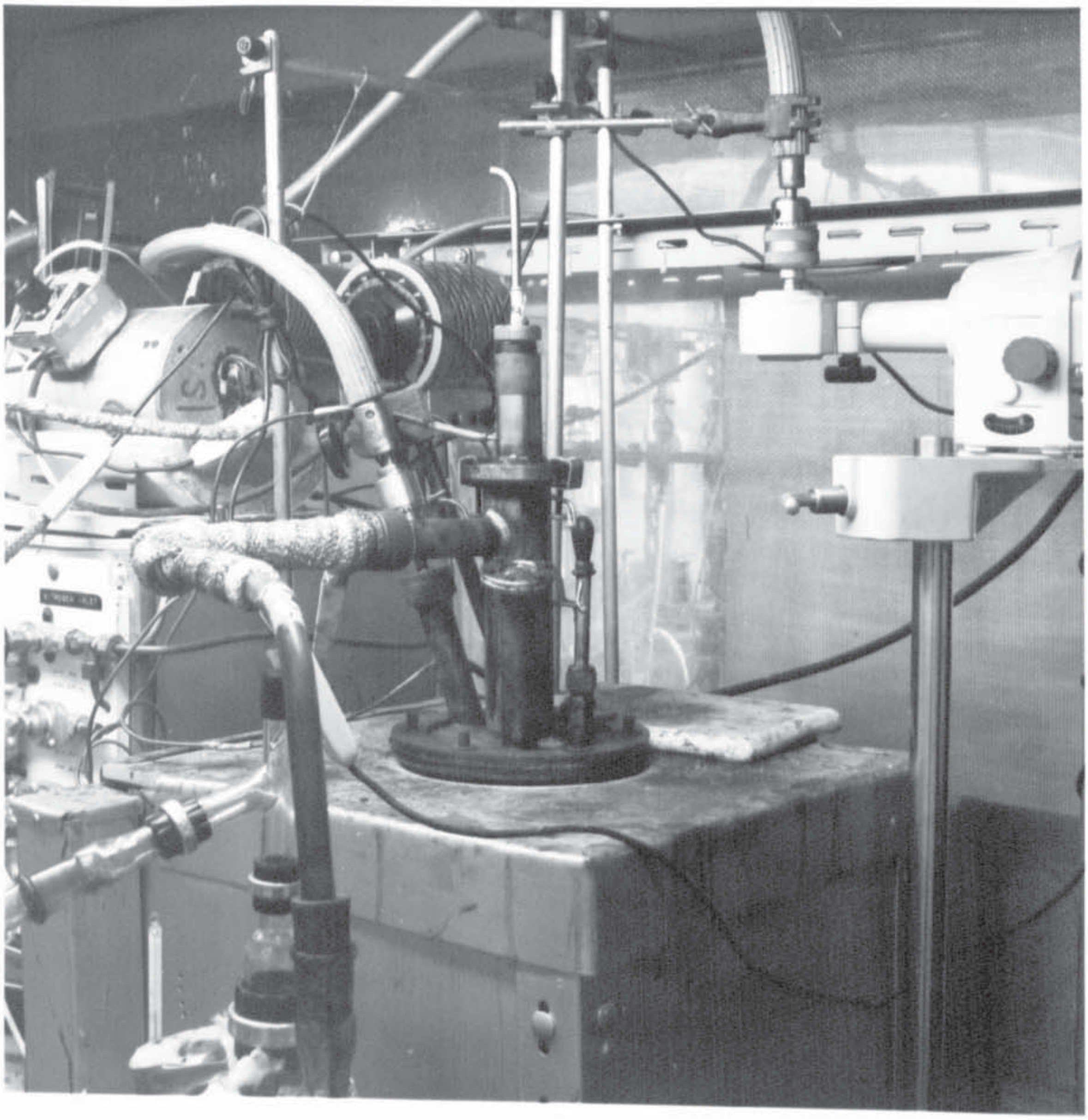


Fig.7.2 Pyrolysis Reactor



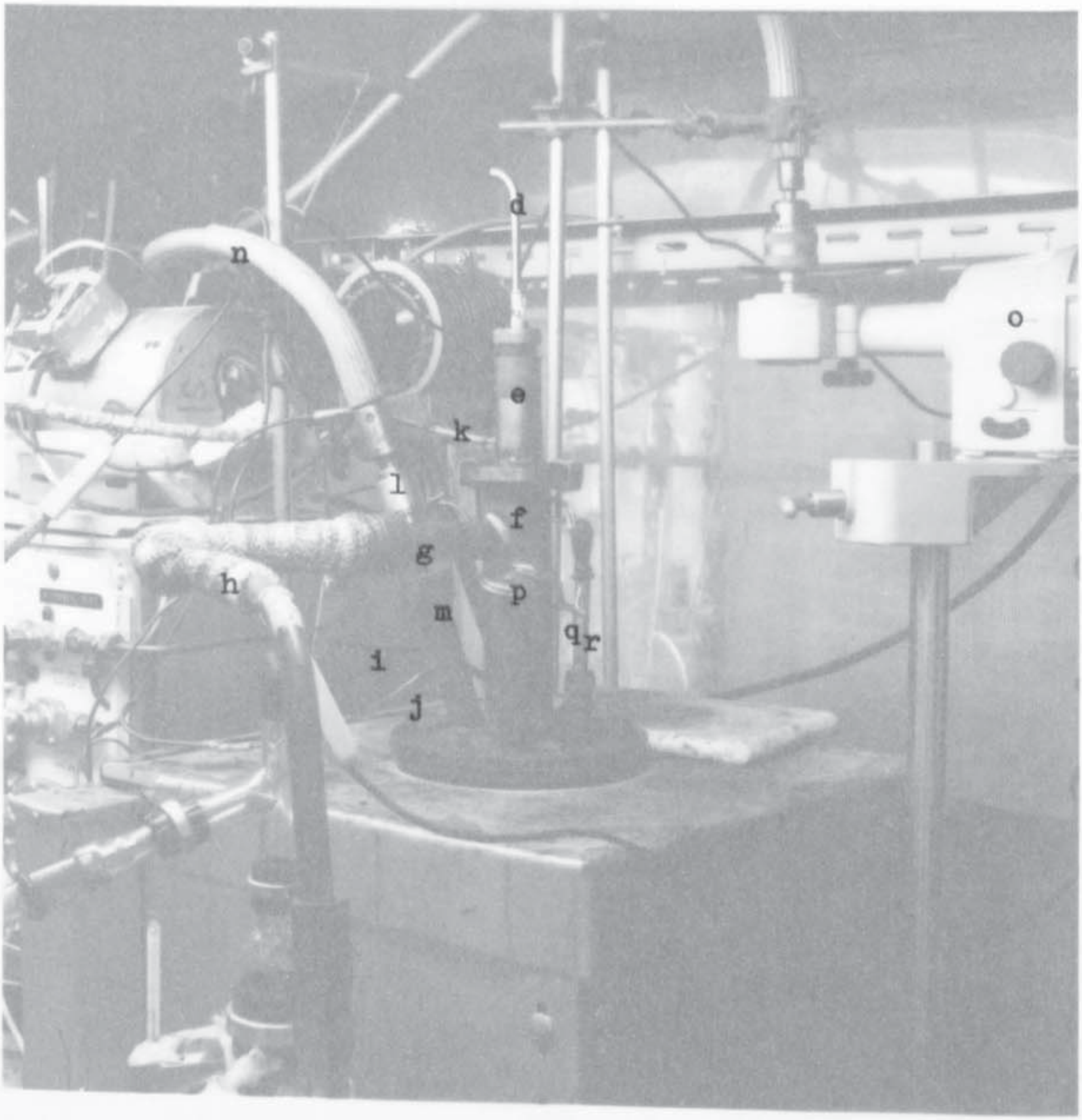


Fig.7.2 Pyrolysis Reactor

Stirrer shaft

Compression nut

Fibre packing space

Washer

Graphite block

Spring

Graphite block

Fig.7.3 Stirrer Shaft Sealing Gland

Stirrer shaft

Compression nut

Fibre packing space

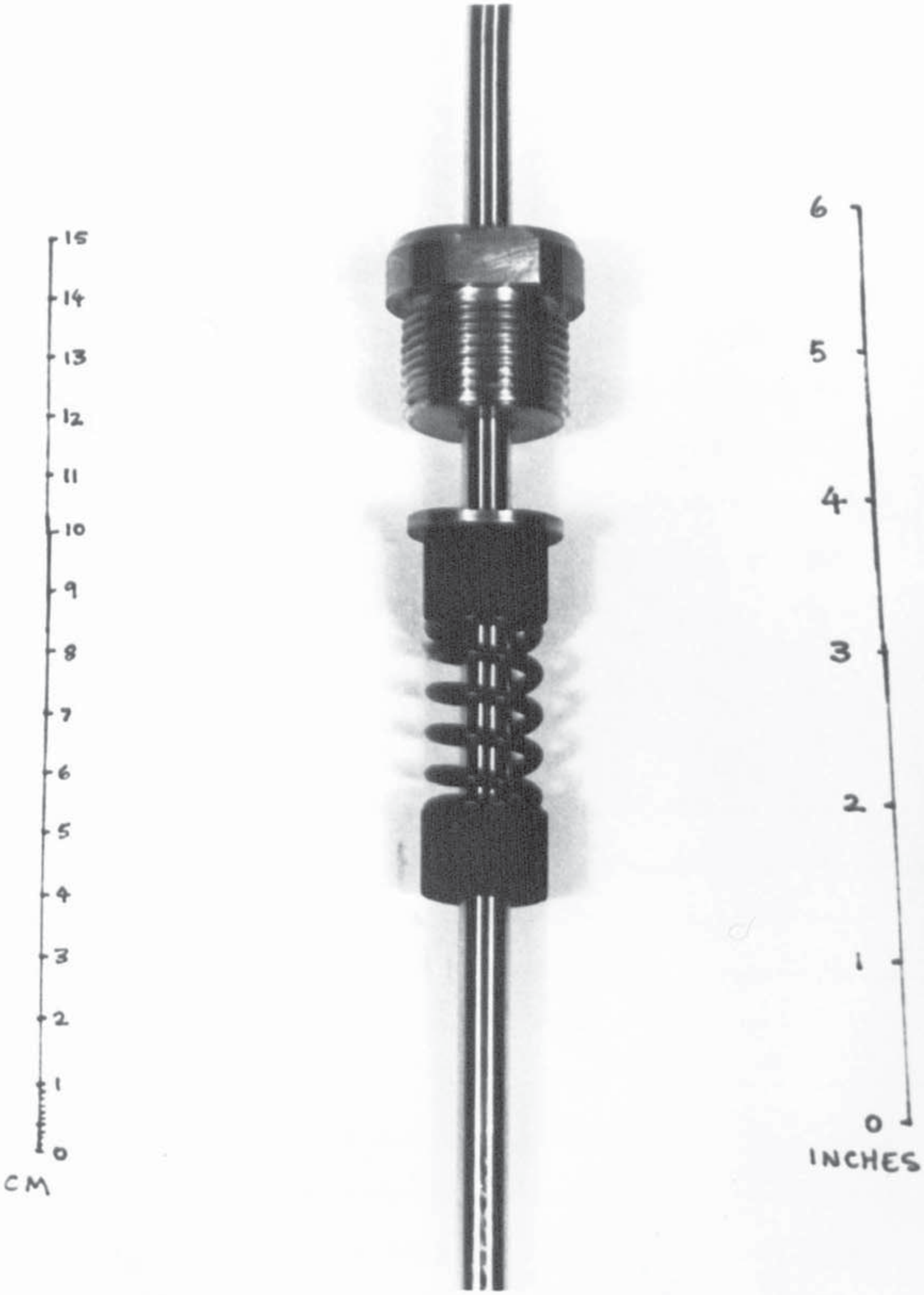
Washer

Graphite block

Spring

Graphite block

Fig.7.3 Stirrer Shaft Sealing Gland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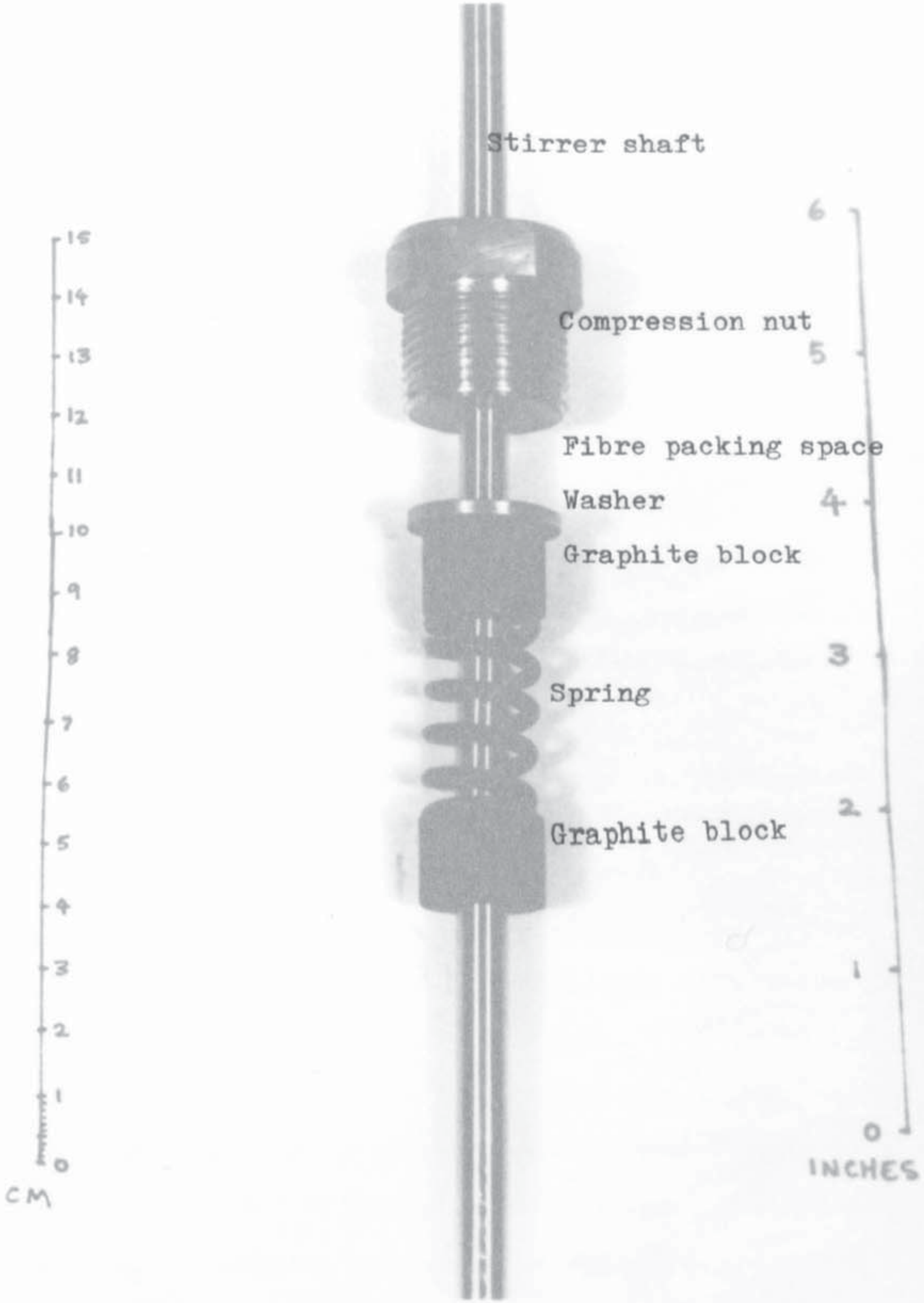


Fig.7.3 Stirrer Shaft Sealing Gland

Also passing through the reactor top were a 2.0 cm diameter explosion port (p), thermocouple well (q) and melt sampling port (r). The explosion port made use of a simple foil disc of 2 cm diameter as the pressure relief material. The bursting pressure was 0.35 - 0.70 N/m^2. The melt sampling port was also used to introduce steam.

The main components of the reactor are held together by six ½" AF bolts effecting the seal with gaskets described later. The removable immersion rod gland is also supported on a rubber "o" ring gasket and clipped into place. Most parts of the reactor are adapted from standard fittings; the main reactor dimensions can be taken from Figure 7.1. The index letters refer to both Figures 7.1 and 7.2.

7.2.3 Control and Ancilliary Equipment

The control equipment described here is the nitrogen purging system (Fig. 7.8(c)) and the temperature regulating system (Fig. 7.8(d)). The former is also used on the char gasification unit. Also described is the agitator drive system which is common to the gasification unit.

The nitrogen for purge purposes was supplied from a cylinder fitted with a standard British Oxygen Cº diaphragm reducing valve. The flow was controlled by a series of needle valves which also enabled the gas to be directed as required. The total flow was measured on a simple GAP rotameter. This unit, as shown in Figure 7.8, included a pressure gauge to monitor any dangerous build-up.

The reactor temperature was controlled by a Pye Ether Transitrol 990 thermal controller. The controller was connected to a Cr/Al thermocouple supplied by Electroplan Ltd.. The response from the thermocouple was used to trigger a simple on/off relay through which the furnace current was supplied. The control unit was supported in a purpose constructed steel and wooden control panel.

The agitator was driven by a Heidolph RZR2 electric motor fitted with a RK6, 1 : 0.7 gear head and 1 m flexible drive. The unit can be seen in Figure 7.2. The portable tachometer used to set up the final drive speed was a Venture instrument.

7.2.4 Product Collection and Measurement

Figure 7.4 shows a diagrammatic representation of the product collection and measurement train.

On leaving the reactor the volatile products passed through a 1.5 cm copper tube heated by Electrothermal resistance tape (i). The heating current was controlled by a Cressall Co., 3.7 amp Torrovolt. This led into a Leibig condenser of area 200 cm^2 (ii) followed by a jacketed coil condenser of area 430 cm^2 (iii). Below these the condensates collect in and vapours passed through a bubble column consisting of two concentric tubes of external diameters 10 mm and 17 mm the outer being sealed at the bottom (iv). Thus condensate from the above condensers collects in the outer tube while vapours bubble through aiding nucleation. The remaining vapours leave the bubble column and passed through another identical jacketed

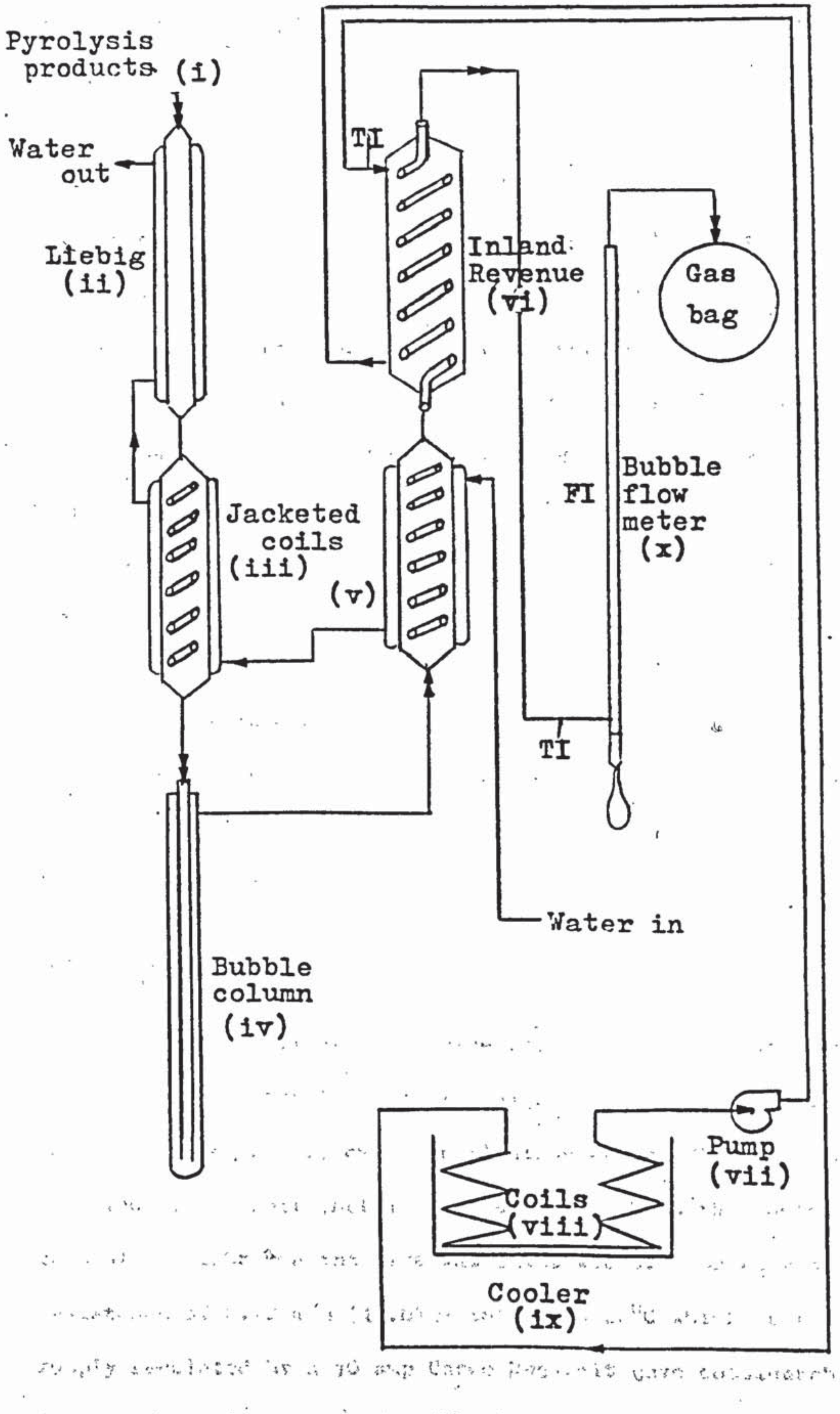


Fig.7.4 Condenser/collection Train

coil(v) followed by an Inland Revenue condenser of area 250 cm^2 (vi) before passing through flow measurement and on to gas collection.

The first three condensers in the described collection train are cooled by water at about 18°C flowing counter-current at about 2.5l/min.. The Inland Revenue gas condenser was cooled by standard ethylene glycol based automotive antifreeze at - 10°C and flowing at 1.5l/min.. This coolant was circulated, by a small Stuart Turner centrifugal pump (vii), through the condenser and a double coil of 9 mm copper tube whose area was about 450 cm^2 (viii). The copper coils were situated in a paraffin bath cooled by a Grant L88 cooler (ix).

The gases leaving the collection train were passed to a simple bubble flow meter (x) and collected in a large, flexible bag (xi).

7.3 Char Gasification Unit

7.3.1 Furnace

The char gasification furnace was designed and built in the laboratory. The tubular ceramic (Al_2O_3) former of dimensions; 10.8 cm external diameter, 9.5 cm internal diameter and 23.0 cm in height was supplied by Beecroft (Metallurgists) Ltd.. Onto the former some 22 m of Fe/Ni/Cr heating wire was lathe wound. The wire had a resistance of 0.72 Ω/m (15.84 Ω total) at 20°C which on the mains supply regulated by a 10 amp Berco Regavolt gave considerably more heat than usually required. The windings were sealed using Purimachos Pyruma fire cement.

The completed winding was placed in a cylindrical aluminium outer shell of 28 cm diameter; the intermediate space was insulated with Triton Kaowool ceramic fibre. The top of the furnace was covered by Pyruma fire cement and the bottom with Syndanyo asbestos compound in such a way as to form a tabular furnace to take the reactor. The entire system was raised 10 cm on legs so an emergency catchpot could be placed underneath.

7.3.2 Reactor

The char gasification reactor was designed along similar lines to the pyrolysis reactor having a heavy stainless steel outer pot 11.5 cm in diameter and 22 cm high (a') into which fitted a light inner liner 9 cm in diameter and 21 cm high (b'). A further vertical section was bolted to the outer pot (c') giving a total height of 35 cm. Fitted to the sides of the extension were ports for a 2 cm diameter char introduction/product exit tube (d') and a pressure sensor (e'). The reactor top (j) contained all the other ports and vents and was bolted in place onto a gasket by six $\frac{3}{8}$" AF bolts. The components of the reactor are shown diagrammatically in Figure 7.5 while Figure 7.6 gives a view of the reactor in-situ.

The main features of the reactor top were : a central stirrer (g'), a 2.8 cm diameter explosion vent (h'), a 0.5 cm diameter purge port (i'), a thermocouple well (j') and the air/steam inlet port (k').

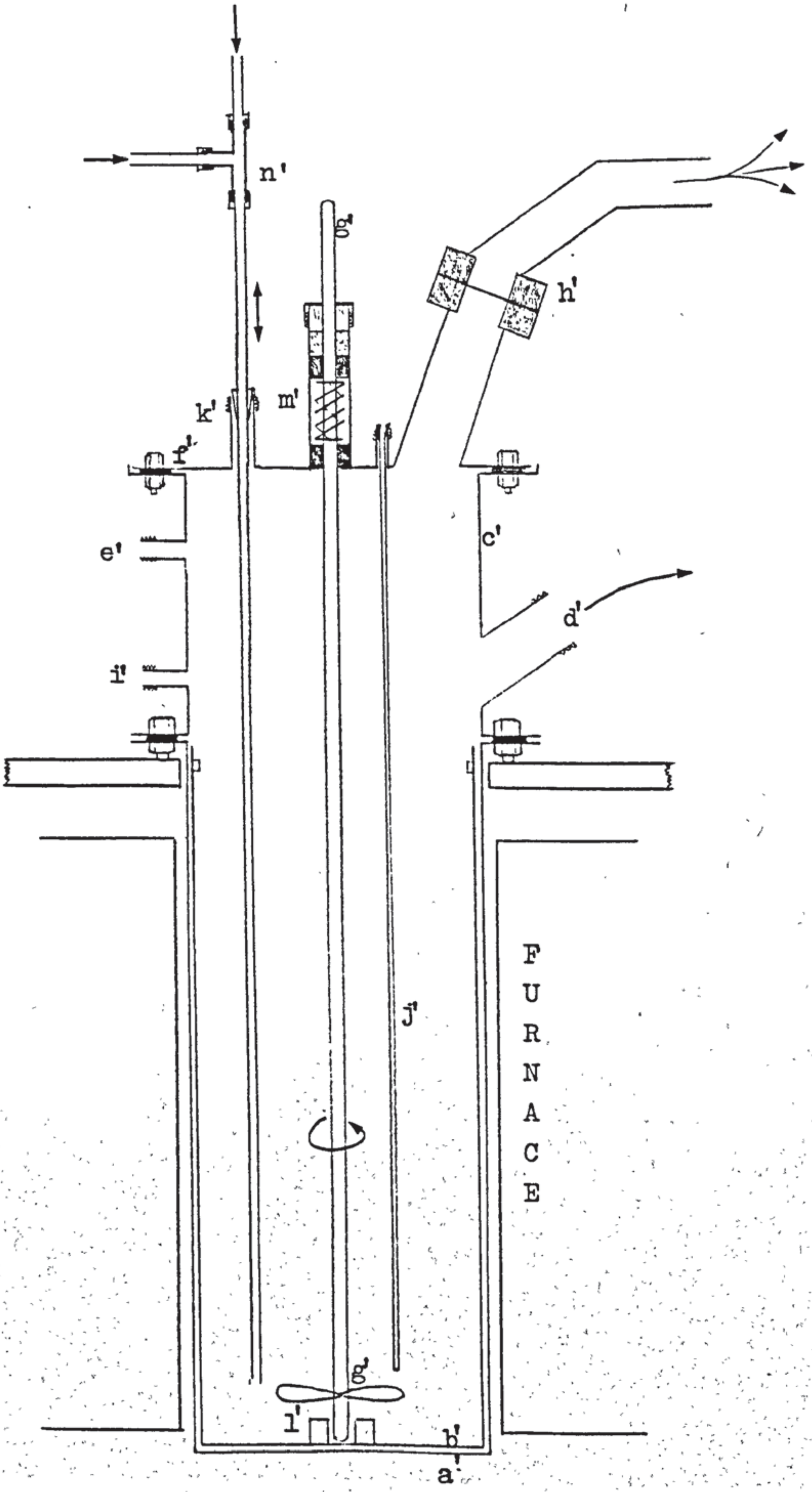


Fig.7.5 Char Gasification Reactor

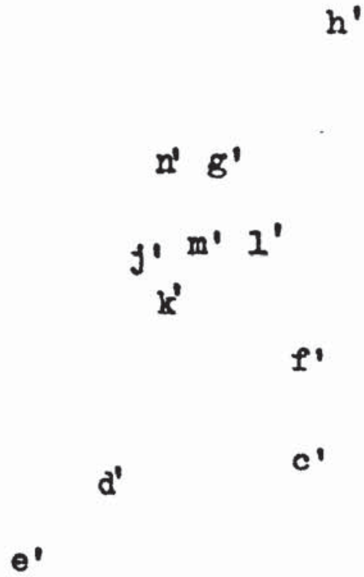
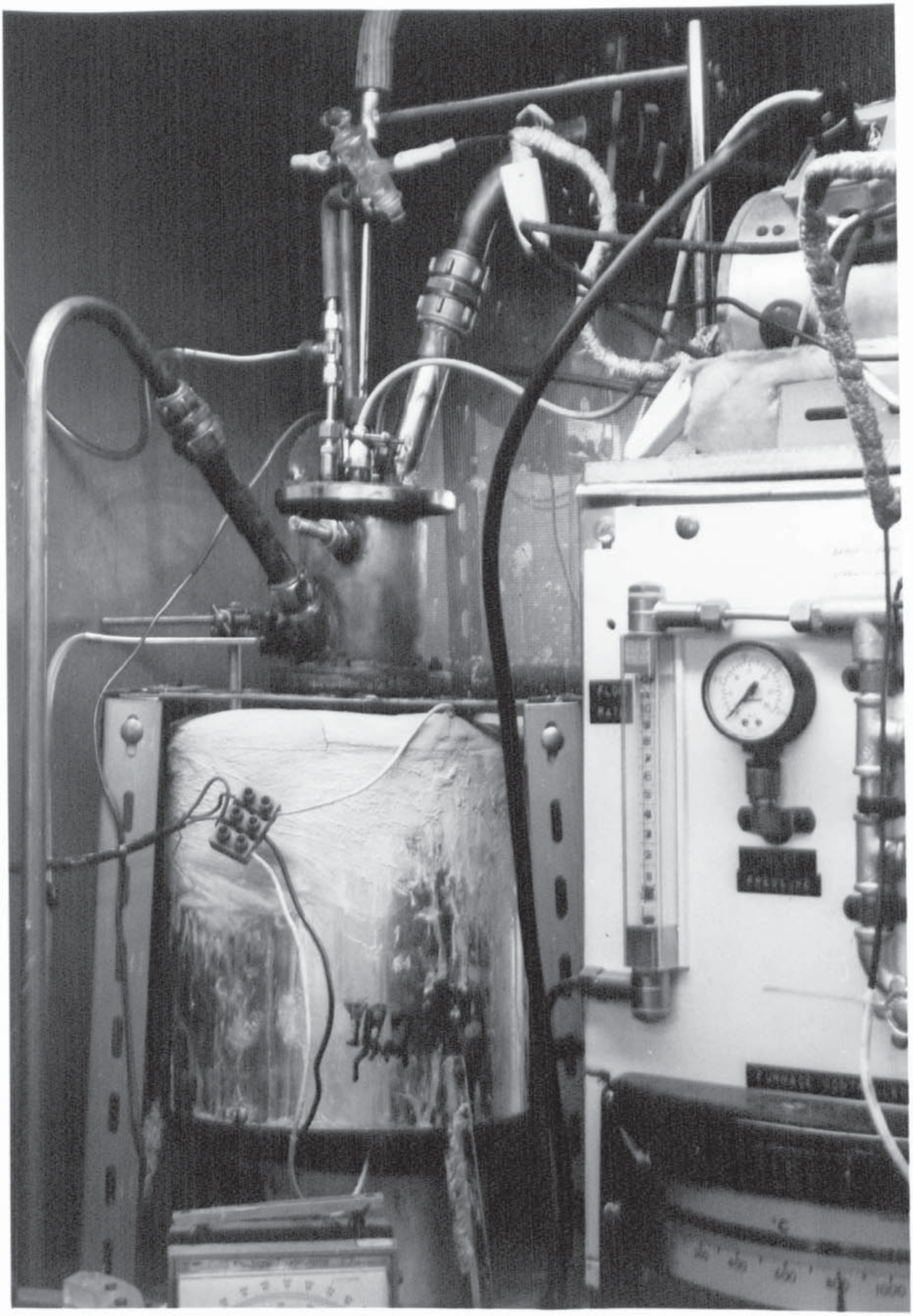


Fig.7.6 Char Gasification Reactor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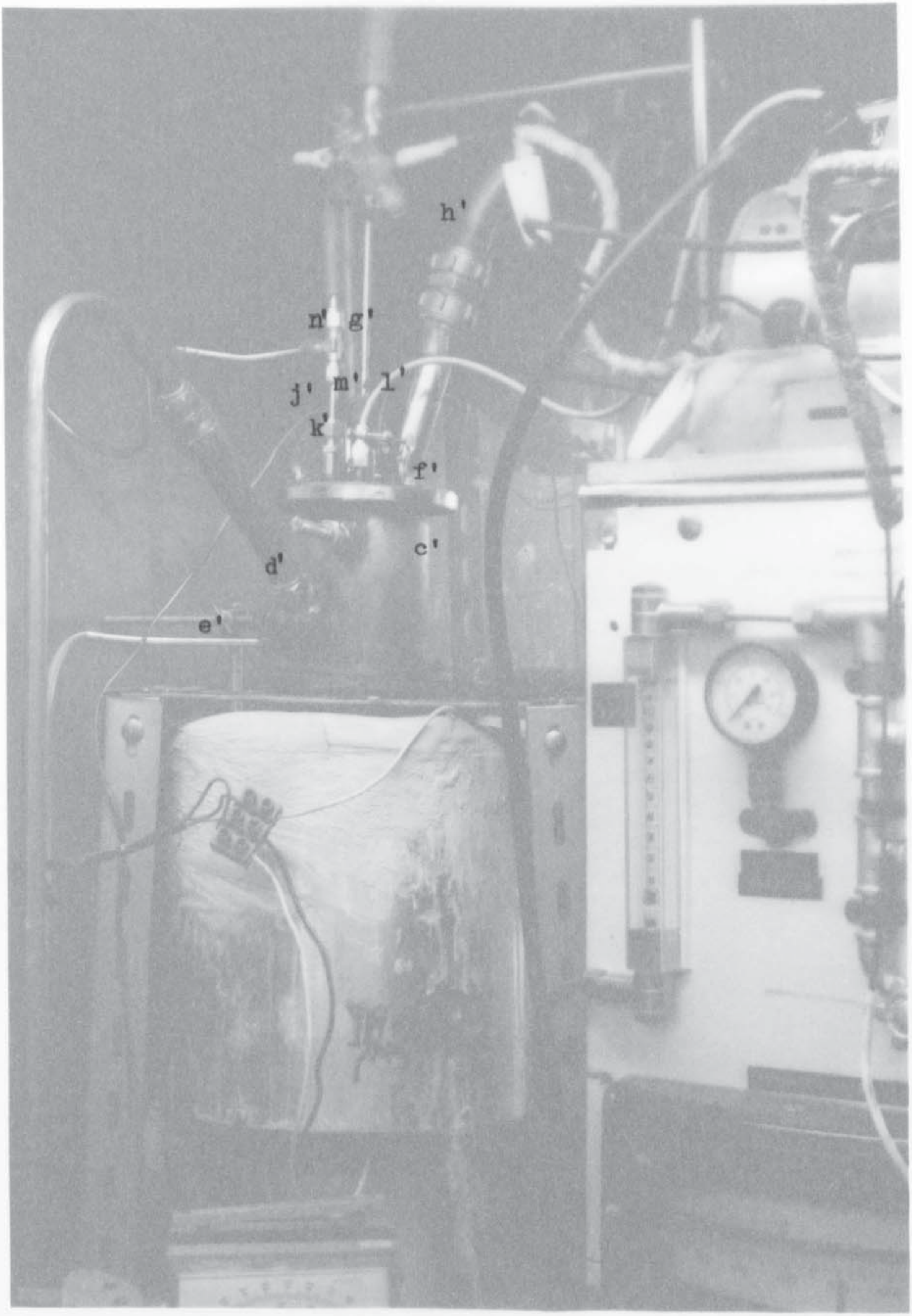


Fig.7.6 Char Gasification Reactor

The stirrer (g') consisted of a plain feather screw about 2.5 cm above the bottom of the shaft that was fitted into a bottom guide (l'). The gland (m') fixed to the reactor top was of very similar construction to that used for the pyrolysis reactor, although slightly smaller in all respects except the ¼" shaft.

The explosion vent (h') was based on a 2.8 cm exit pipe leading to a 5 psi (0.35 N/m^2) explosion disc supported between two carbon blocks and cork gaskets. The pipe from the atmosphere side of the disc was directed away from the reactor in a safe position.

The thermocouple well (j') and nitrogen purge port were made as standard fittings and do not require further comment. The final port, air/steam introduction, was fitted so as to allow retraction of the inlet pipe when desired. The air and steam were mixed in a "T"- joint(n'); the steam being fed vertically from the generator via a two-way tap while the air was introduced horizontally. This arrangement minimized the possibility of plugs of water condensing and being forced into the reactor to cause vapour explosions. These inlets were made from 0.4 cm steel tube.

7.3.3 Control and Ancilliary Equipment

The nitrogen purge flow controls and stirrer controls used in the char gasification were the same as those used for the pyrolysis system.

The temperature of the reactor was controlled in a fundamentally different way to that used for the pyrolysis reactor. Using a 10 amp Berco Regavolt the heat supplied to the reactor was restricted so as to be just capable of steadily maintaining the desired temperature. It was found that with the conventional use of the Pye Ether controller too great a temperature cycle was experienced on this reactor system. The Pye Ether controller was used only to indicate reactor temperature.

The compressed air was supplied as a maintained service at 92 psi. This was reduced to less than 0.35 N/m^2 (5 psi) using a Spirax Sarco MR1 reducing valve and the actual flow controlled by a simple needle valve. The rate of flow was monitored by a standardized rotameter.

The steam used was generated using a purpose-built electrically heated generator. This generator was based on a double parallel tube furnace (Fig. 7.7) each tube being 3.6 cm in diameter. The furnace was wound with about 8 m of 0.72 Ω/m resistance wire as used in the gasification furnace and sealed in the same way with Pyruma fire cement. The casing, about 15 cm in diameter, was made of galvanized steel and Syndanyo compound asbestos and fitted with Kaowool for insulation. The generator tubes were made from $\frac{1}{8}$" stainless steel tube coiled to 2 cm spirals, a total length of some 75 cm; two such tubes were fitted in parallel. A diagram of the steam generator is given in Figure 7.7 and it can also be seen in Figures 7.6 and 7.8. The flow of steam into the reactor was measured (in g/min) from the water fed to the generator. Water was pumped into the generator used either of syringe pump of the Crouzet type or, more often a Cole Palmer WZIR051 peristatic pump which can be seen in Figure 7.8. The temperature in the generator was measured by thermocouple and Comark electronic thermometer while it was controlled by a 5 amp Regavolt.

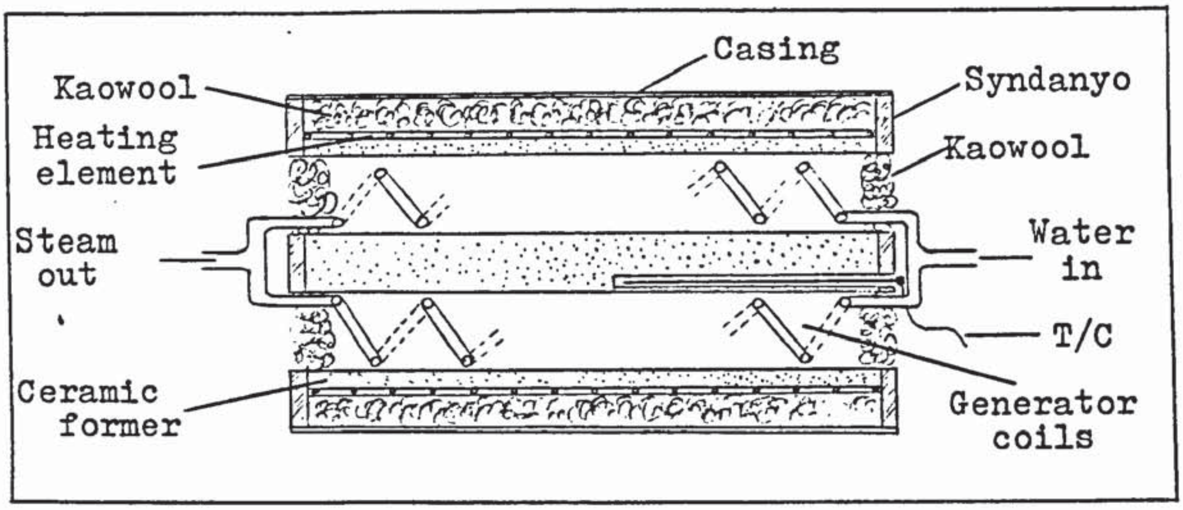


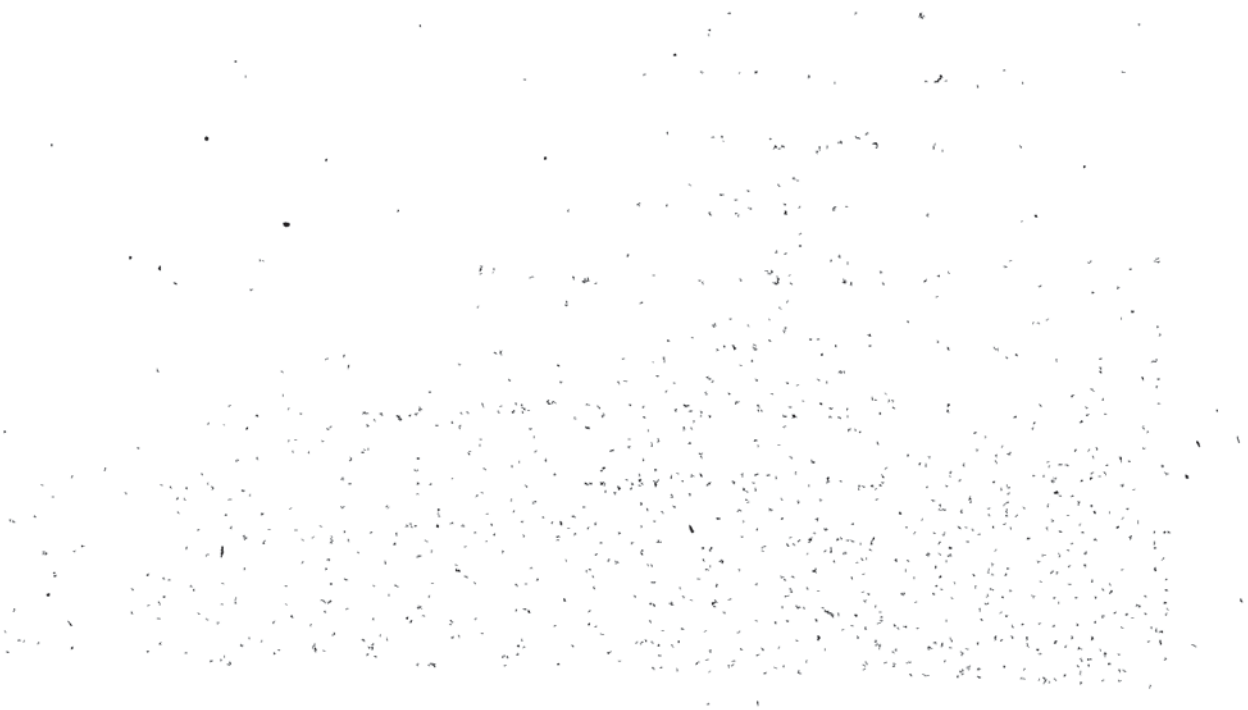
Fig.7.7 Steam Generator

The pressure in the reactor was monitored by a simple water filled monometer. This was coupled to a Fi-monitor so that if the pressure rose above a few psi an alarm was sounded. The Fi-monitor is visible in Figure 7.8.

7.3.4 Product Collection and Measurement

The flow of product gases from the char gasification reactor were measured in two ways. Firstly, if air alone was used and the products are dry, a plain rotameter could often be used. However, more often and always for wet gases the same bubble flow system as was applied to gaseous pyrolysis products was used. The products were not collected in bulk.

Fig.7.8 Experimental Apparatus



Key to Figure 7.8

A. Pyrolysis furnace and reactor

B. Char gasification furnace and reactor

C. Nitrogen purge control panel

D. Temperature controller

E. Paraffin cooler

F. Pyrolysis product condenser train

G. Stirrer motor

H. Flexible stirrer drive

I. Bubble flow meter

J. Steam generator

K. Steam generator supply pump and regulator

L. Fi-monitor

M. Comark electronic thermometer

N. Gasification sample vial

O. M.S. point

P. Condensed steam collection cylinder

Q. Heat wrap controls

R. Safety screw rail

S. Fume hood

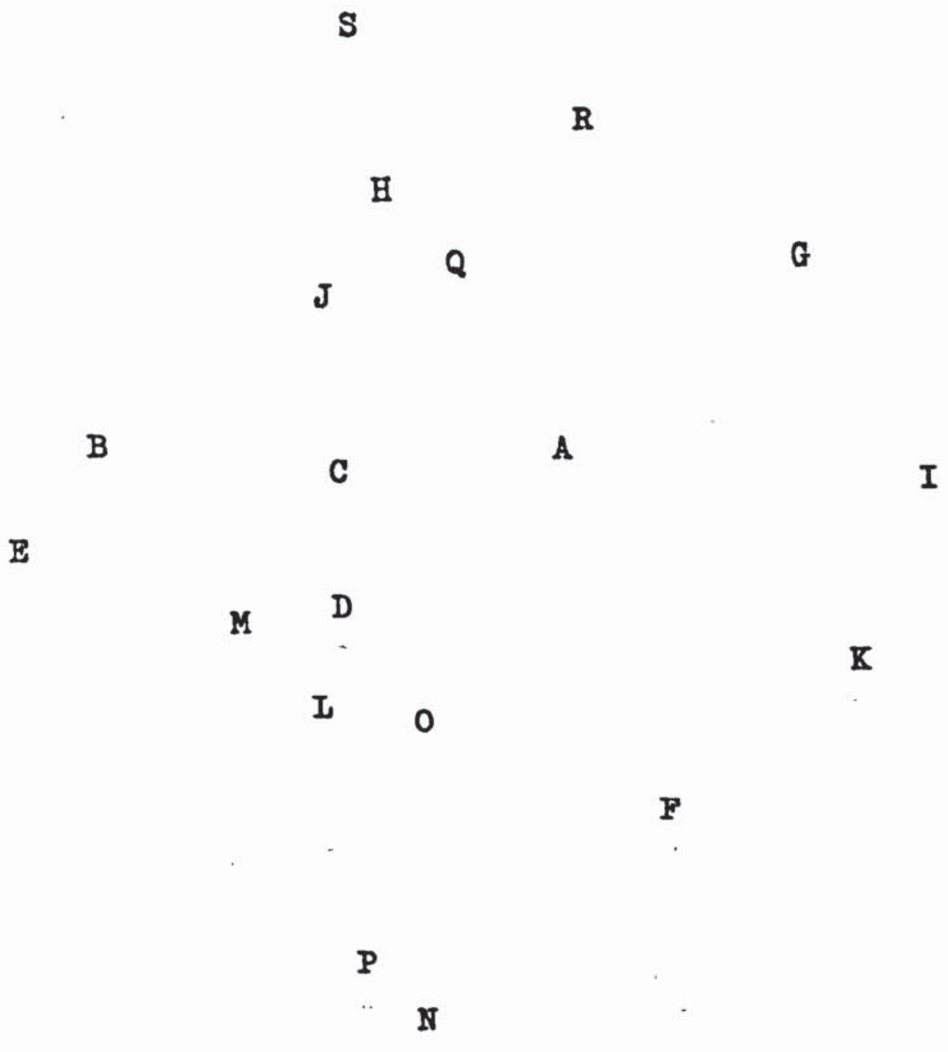
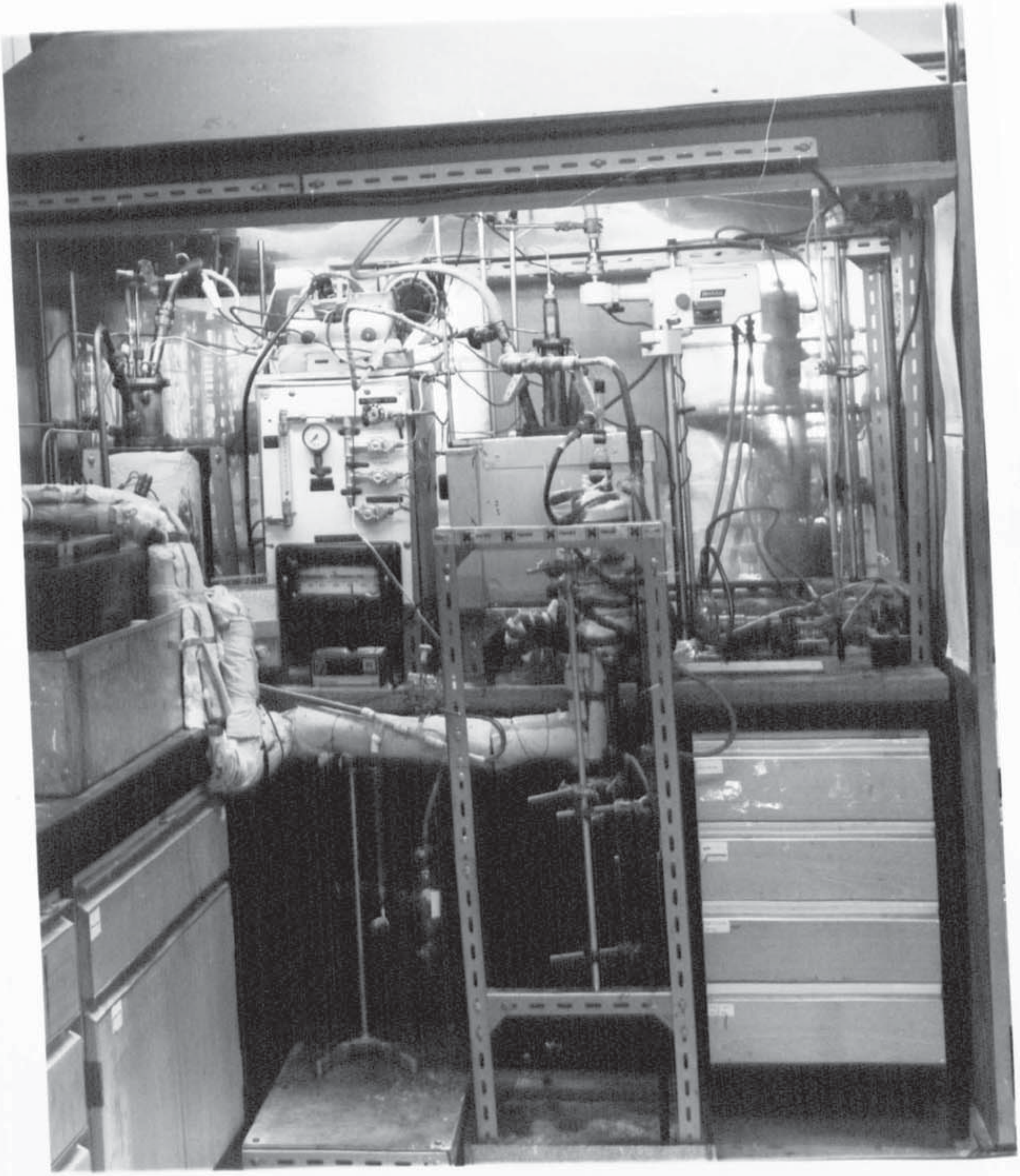


Fig.7.8 Experimental Apparatus



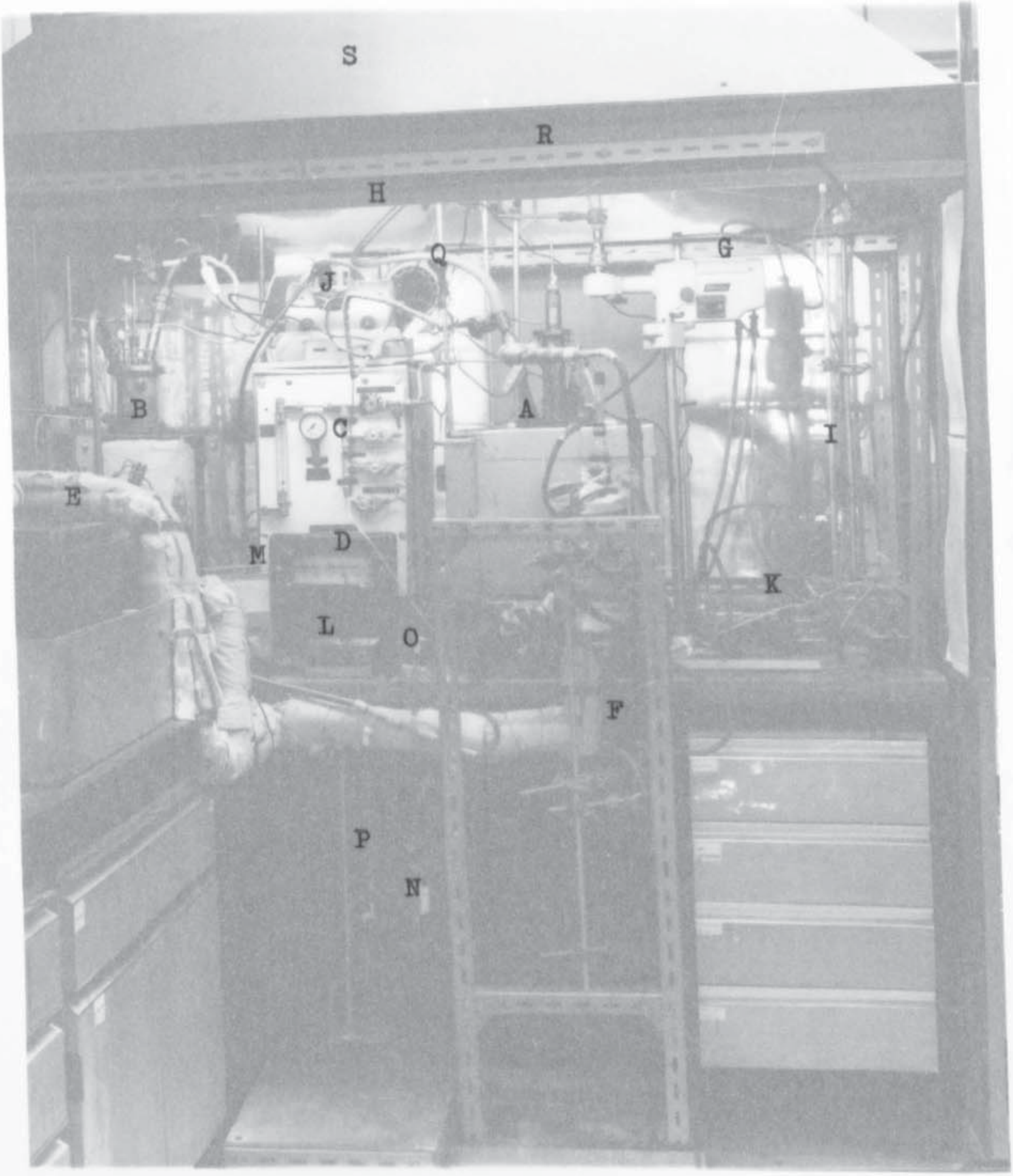


Fig.7.8 Experimental Apparatus

During each run a gas sample was taken in a glass sampling vial by negative displacement of acidified brine. The use of these vials is discussed further in Chapter 11 and can be seen in Figure 7.8. The gas was also continuously analysed by mass spectroscopy from a point near the vial attachment. Between the reactor and these sampling points there was about 1 m of 11 mm copper tube to act as a condenser, the steam being collected later in a graduated cylinder. The constant analysis by mass spectroscopy was also used to measure the gas flow rate by standardization on nitrogen (the method is detailed later).

7.4 Related Test Units

7.4.1 Corrosion Equipment

In order to carry out long corrosion tests a further furnace was designed and built. This was also a tube furnace of tube diameter 8.5 cm. The unit was constructed on exactly the same principles as the char gasification furnace but wrapped in a 12 cm glass fibre pipe insulator. The temperature was monitored by thermocouple and Comark thermometer. The temperature was controlled by a calibrated 10 amp Cressal Torrovolt.

The melt used in corrosion tests was contained in a 50 ml Vitrosil crucible. This was suspended in the furnace by a welded wire frame. During operation the top of the tube furnace was covered by a Synadanyo slab. Safety measures included a light indicating when in use, a steel umbrella preventing access from falling water and a steel catch-tank. The system is shown in Figure 7.9.

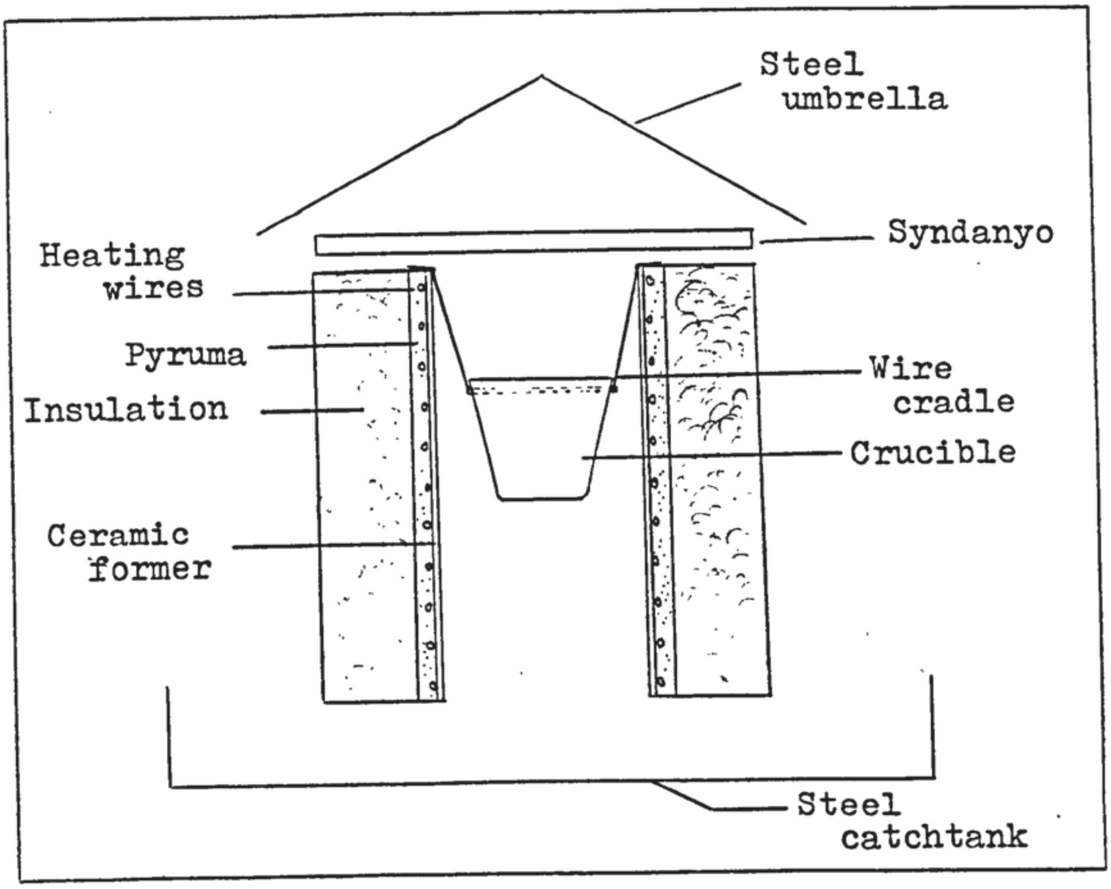


Fig.7.9 Corrosion Test Unit

7.4.2 Bench Equipment

Although the corrosion apparatus was also designed to take a steel beaker, and so could be used for many of the related experiments on the melt described in Chapter 14, much work was carried out on simpler apparatus. For instance many of the melt chemistry experiments could be performed using heavy glassware and electric isomantles.

CHAPTER

EIGHT

METHODS & TECHNIQUES IN TYRE PYROLYSIS

8 METHODS AND TECHNIQUES IN TYRE PYROLYSIS

8.1 Reactor Preparation

8.1.1 Melt

The melt used during most experimental work was made up to simulate the likely melt composition of a continuously running process. To this end the required salts were mixed together in the appropriate proportions before charging the reactor. The mixture generally used was:

Na_2CO_3	20.2 wt.%	64.0	CO_3^{2-}	11.4 wt.%	38.3
K_2CO_3	23.0		CO_3^{2-}	10.0	
Li_2CO_3	20.8		CO_3^{2-}	16.9	
NaOH	2.2		OH^-	0.9	3.7
KOH	2.5		OH^-	0.8	
LiOH	2.8		OH^-	2.0	
ZnO	10.5		Zn	8.4	
Na_2S	5.7		S^{2-}	2.3	8.2
K_2S	6.5		S^{2-}	1.9	
Li_2S	5.8		S^{2-}	4.0	
	100.0				

Table 8.1 Melt Composition (Standard Foul Melt)

The sodium, potassium and lithium carbonates represent the triple eutectic that is the basic constituent of the melt. The hydroxides are present to simulate the effect of water entering the reactor, deliberately or otherwise, on the carbonate (261).

$$CO_3^{2-} + H_2O \rightleftharpoons 2OH^- + CO_2 \qquad \text{Eq. 8.1}$$

The zinc salt arrives in the melt as it is the major constituent of the rubber curing accelerator mixture(14,21). The sulphides represent the sulphur vulcanate used in tyre production; the weight of sulphide ions being appropriate to the weight of zinc oxide. This mixture will from now on be referred to as "Standard Fouled Melt".

8.1.2 Reactor

Prior to almost every experiment the reactor inner liner was removed and filled with a fresh charge of Standard Fouled Melt. The weight loaded each time was 1.8 kg which when fused has an approximate volume of 0.75 litre. At this stage the gasket assembly consisting of a 'Klingerite' gasket bounded on both faces by a ring of Klinger Sealex expanded PTFE joint sealant, was renewed. The filled inner liner was then placed in the reactor, the top replaced and sealed by tightening the head bolts.

The reactor was then purged with nitrogen (100 ml min^{-1}), the thermo-controller set to the required temperature and the furnace switched on. Once the charge had been fused and the set temperature achieved, the stirrer was started and its speed set using a portable tachometer.

8.1.3 Tyre

It was important that tyre samples used in this work met two conditions:

1) The samples used must be representative of a whole tyre.
2) The samples must be reproducable from experiment to experiment.

The tyre is made up of a number of different rubber compounds and is in this respect symmetrical. Therefore a half-section cut from bead to the crown of the tread will allow both of these conditions to be satisfied. The weight of a sample can be varied simply by changing the arc width of the section.

8.2 Operations

8.2.1 Scale

At this stage it was necessary to decide what weight of tyre section would, in the 0.75l reactor, realistically represent the whole tyre commercial process. Car and van tyres vary in size but a typical example might be: 13 inch (0.33m) wheel rim, perhaps 23 inch (0.58m) overall diameter by 155mm (0.155m) tread width. (The mixed units used are in accordance with the convention in the industry.) Allowing for larger sizes and estimates of tyre and melt heat capacities it would appear that each tyre requires some 200 litres of melt in appropriate dimensions. A worn tyre of typical size might weigh 7.5kg, giving a tyre-in-melt concentration of $40 \mathrm{g\,l^{-1}}$. So in the experimental work on the 0.75 l reactor initial tyre inputs were kept to within this order.

8.2.2 Procedures

Having achieved the required reactor conditions, the tyre introduction port and immersion rod were removed. A weighed tyre section cut from bead to crown was then attached to the rod using steel wire and the rod retracted so that the tyre was immediately under the introduction port gland. A new Klinger Sealex expanded PTFE ring seal was stuck to the port plate, the assembly replaced on the reactor and clipped in position leaving the tyre inside the reactor but well clear of the melt.

At the start of the run the immersion rod was depressed forcing the tyre down into the melt. Simultaneously, a stop-watch was started and the nitrogen purge turned off. The volatile products of pyrolysis evolved from the reactor through a heated (200°C) exit pipe and into the condenser train described in Section 7.2.4. The cooling water was at approximately 18°C while the ethylene glycol anti-freeze coolant was at -10°C. The gas escaping from the oil collection train was passed through a bubble flow meter where its rate of flow was noted and into the gas collection bag.

At the end of each run the collected oil was measured, the gas volume calculated by flow integration, the steel and inorganic products estimated from the tyre input specification and char calculated by difference. The total time was also noted for rate data calculations. When the product flow subsided the reactor was again purged with nitrogen and the introduction port opened so that the immersion rod could be reloaded and, once the system had stabilized, the cycle repeated.

Generally three such batch runs were performed at each set of physical conditions. (An "experiment" was usually made up of three or four such batches.) At the end of the experiment the furnace was switched off and the reactor opened and the contents of the inner liner removed before solidification. At this stage samples of melt, char and steel were taken for analysis or examination.

8.3 Analytical Methods

8.3.1 Chemical Analyses

8.3.1.1 Melt

a) Carbonate and Hydroxide

The method used to determine the carbonate-to-hydroxide ratios was basically the volumetric method described by Belcher and Nutten(323). However the use of indicators was found to be unsatisfactory and so was replaced by the use of a pH electrode and Corning 119 meter. Plotting pH against volume in the normal way a curve with two inflection points was obtained, these being equivalent to the indicator and points in the Belcher and Nutten method. The error of the method was estimated to be ± 5%.

b) Sulphur

The standard method is by precipitation of barium sulphide(323) but this cannot be used in the presence of large amounts of carbonate. Attempts to remove carbonate as carbon dioxide by acid treatment prior to the precipitation could not be validated. Similarly the available volumetric methods were unsatisfactory in this case.

c) Zinc and other metals

Zinc ions in the melt were determined by atomic adsorption spectroscopy using an IL151 Spectrophotometer. Zinc was present in the feed but iron and chromium were also present due to corrosive attack on the containment vessel.

The sample (0.2g) was prepared by digesting to dryness with concentrated nitric acid (10 ml) and 30 w/w % hydrogen peroxide (0.5 ml). This was followed by partial digestion with water (15 ml) concentrated nitric acid (4 ml) and concentrated hydrochloric acid (1 ml). The resulting solution was made up to 50 ml, filtered and suitably diluted. The standards were prepared in the manner recommended by the instrument manufacturers(324) but in addition carbonate, hydroxide and sulphide were added in the same proportions as present in the sample so as to eliminate interference errors. Samples and standards were aspirated at 5 ml per minute at the appropriate instrument settings given in Table 8.2. The error of the method was estimated at ± 6%.

Metal	Abs Wavelength	Flame	Slit	Current	H.V.
Zn	213.9 nm	Acet./Air	320 µm	5mA	460v
Fe	248.3	"	160	"	620
Cr	357.9	"	160	"	460

Table 8.2 AAS Instrument Data

8.3.1.2 Pyrolysis Gas

The gas was collected in a large gas bag throughout each run. The total quantity of gas was obtained by flow rate integration. The gas was then analysed later by GLC and Mass Spectroscopy.

The GLC method was carried out on a Pye Unicam 104 Gas Chromatograph fitted with a column containing 10% Squalane supported on 100 - 120 mesh acid-washed Diatomite C. Nitrogen was used as the carrier gas flowing at 40 ml min^{-1} and the emerging components were detected by Flame Ionization. A sample of 200 - 300 µl was normally injected with an attenuation of $5 \times 10^2 - 10 \times 10^4$; the resulting output being recorded by a Philips PM 8251 single pen recorder and a Venture Mk 2 digital integrator. The best results were obtained at an oven temperature of 60°C. The peaks were identified using known standards and the quantitative values determined by an area summation technique (this is conveniently quick and gives a reasonable accuracy). The maximum error likely to be incurred was ± 10%.

The mass spectorscopic analyses were performed using a Centronic MGA 200 Quadrupole Mass Spectrometer. The instrument was used in its scanning mode over the range 0 - 75; the output being recorded on a Venture RE 541.20 Potentiometric Recorder. Compounds were identified from their molecular ion peaks. Determination with known standards was only performed for hydrogen. The technique was additionally used to confirm the general distribution of products and occasionally to quantify compounds not separated by GLC while the sense of smell was relied upon to detect hydrogen sulphide.

8.3.1.3 Pyrolysis Oil

The quantity produced was measured by collection. The oil was analysed by GLC using a Pye Unicam 204 Gas Chromatograph. Due to the wide range of molecular weights two columns were used. The first, giving an overall analysis, was 10% OV1 on 100-120 mesh Phasechrom Q, the second, giving greater detail in the lower and aromatic regions, was 10% Squalane on 100-120 mesh acid-washed Diatomite C.

For both columns samples of 0.1 or 0.2 µl were injected at an attenuation of 1×10^4. The best results were obtained by using a temperature programme: initially held at 60°C for 2 minutes, followed by a rate of increase of 20°C min^{-1} up to a held maximum of 150°C for the OV1 and 120°C for the Squalane. This level was held to complete elution, normally about a further 15 minutes.

The recording apparatus was the same as that used for the gas analyses. Identification and measurements were carried out using the same techniques of standards and area summation.

8.3.1.4 Steel and Other Inorganics

The measurement of these components for mass balance purposes was based on the input data supplied by the tyre manufacturers(21). Attempts to confirm the steel values by a gravimetric method were made but problems of separation from the melt precluded accurate results. Some of the inorganic components were measured as detailed in Section 8.3.1.1, so crude evaluations were made.

8.3.1.5 Pyrolysis Char

The quantitative determination of char was generally done by difference. However in some cases char collected from the reactor was measured which together with char-in-melt analyses provided a cross-check.

The char was also subjected to some chemical analyses:

a) Sulphur

Total sulphur was measured using the standard IP solid fuel bomb method(325). This was basically an ignition in the presence of sodium carbonate solution, absorbing the sulphur oxides which can then be precipitated as baruim sulphate. The claimed error for this method is ± 5%.

b) Volatiles

These were determined simply by the exposure of a crushed sample at 1000°C under nitrogen for 6 hours. The weight difference being volatile tars and so on. The estimated error was ± 8%.

c) Total Ash

The total ash was merely taken as the residue remaining after a successful calorific value test of the standard type(325). As such it included salt entrained in the sample; the true ash was much lower in each case. The estimated error of the method was ± 8%.

d) Carbon

The carbon content was evaluated firstly by subtraction of the above quantities from the crude char and secondly by comparison of calorific values with that of pure carbon.

8.3.2 Physical Properties

8.3.2.1 Melt

Physical measurements on the melt, such as viscosity, surface tension and density, are in themselves considerable practical projects. Although some attempts were made to measure these properties they were generally unsuccessful, therefore reliance on the literature and practical judgement had to be accepted. A full evaluation of these properties would involve a great deal of time and expense which could not be justified at this stage of the process development.

8.3.2.2 Pyrolysis Gas

The only determinable physical properties of the pyrolysis gas were density and calorific value, both of which were calculated from the chemical composition.

8.3.2.3 Pyrolysis Oil

The product oil was subjected to the following physical measurements: density, viscosity, surface tension, calorific value and flash point. There are well documented techniques for each of these measurements. The basic test, the method used, the reference and one or two comments are given in Table 8.3.

Test	Method	Comments	Ref.
Density	SG bottle	-	(326)
Viscosity	Capillary flow	Ostwald type	(327)
Surface tension	Tension balance	-	
CV	Bomb	Simultaneous sulphur	
Flash point	Closed cup	Pensky-Martens	(328)

Table 8.3 Oil Characterisation Methods

8.3.2.4 Pyrolysis Char

The only physical measurements made on the char were calorific value and bulk density. The former was measured by a standard bomb technique. The bulk density was calculated by mass/volume means; the volume being measured by liquid immersion. (It is important that the char is not significantly wetted. Here the test, performed quickly, can be done using water.) The errors in this may be considerable but only an approximate value is required.

CHAPTER

NINE

EXPLORATORY INVESTIGATION OF TYRE PYROLYSIS

9 EXPLORATORY INVESTIGATION OF TYRE PYROLYSIS

9.1 Experimental

9.1.1 Introduction

The initial purpose of the exploratory programme of experiments was to establish that the pyrolysis of tyres mentioned in the literature could be carried out in molten carbonate using the apparatus constructed. Beyond this the exploratory programme was also used to establish limits, clarify dangers and identify trends.

9.1.2 Experimental Programme

The limits of the process are mostly connected with scale and methods of operation. These might be determined by factors such as, reactor volume, melt liquidus range, heat transfer, heat capacities, condenser capacities and so on. Experiments to gain such information were normally performed in a scanning manner which also served to obtain familiarity with the apparatus identifying difficulties and dangers. The trend identification experiments were planned as a more specific series. The general parameters to be investigated were: temperature, stirring, feed scale, introduction method and melt composition.

The opening experiments did not follow a strict programme and so are not detailed here. The information gained in these experiments was nevertheless useful and is considered in the results and discussion.

The first effect to be studied in the trend identification series was that of melt composition. This was achieved by comparing results of clean, standard fouled and excess fouled melt; the details below show this, those parameters untouched and the resulting measured variables.

Parameter	Constants	Measured Variables
Clean melt	Tyre size	Pyrolysis rate
St. Foul Melt	Melt volume	Product phase
XS Foul by successive 20g tyre additions	Temperature	Product analyses
	Stirring	

Next the effect of tyre weight was examined:

Parameter	Constants	Measured Variables
	(Melt composition)	Pyrolysis rate
Feed weight 10g,	Melt volume	Product phase
20g, 40g, 80g	(Temperature)	Product analyses
	Stirring	Temperature drop

Likewise temperature and stirring:

Parameter	Constants	Measured Variables
Temperature 450-657°C, several introductions at different temperatures	(Melt composition)	Pyrolysis rate
	Melt volume	Product phase
	Tyre size	Product analyses
	Temperature	

Parameter	Constants	Measured Variables
Stirrer Rate 250, 500 and 1000 rpm	(Melt composition) Melt volume Tyre size Temperature	Pyrolysis rate Product phase Product analyses

This short programme was designed to identify trends but also showed up errors in design of the apparatus, methods of operation and methods of measurement. The results of this programme were a crucial part of the design and planning of the main investigation.

9.2 Results

9.2.1 General Observations

The opening experiments involved gravity fed tyre introduction relying on stirring to draw the tyre into the melt. These experiments started using tyre pieces of only a gram or so but built up to full tyre sections of 40g. Also at this early stage the reactor geometry was developed to the described arrangement and the condenser capacity increased to meet scale requirements.

Throughout these experiments it became obvious that at the temperatures reported in the literature the tyre pyrolysed very rapidly. The products obtained were a hydrocarbon gas, a hydrocarbon oil, a carbonaceous residue, steel wires and inorganic materials. The gas and oil being volatile readily evolved from the reactor. The steel wire and inorganic materials were either absorbed in or sank beneath the melt. The char remained in the reactor and being light floated on the melt.

The flotation of the char indicated that in many cases tyre was not pyrolysing in the melt but on top of it. This was confirmed by density evaluations. Furthermore brief experiments using an ethylene glycol/water mixture to represent the melt and a wood of suitable density difference to represent the tyre showed visually that the stirrer was of dubious value in mixing without re-entrainment of the gaseous products. This led directly to the major innovation of the immersion rod relegating the stirrer to a melt circulating function only.

9.2.2 Effects and Trends

9.2.2.1 Melt Composition

Given below in Tables 9.1 to 9.4 are the effect of melt composition on pyrolysis rate, the phase distribution of the products, the analysis of gases and the anlysis of oils. All experiments were performed at 550°C and 500 rpm stirrer speed.

Fouling beyond SFM is expressed in cummulative weight of tyre pyrolysed. The rate given is an average rate over each batch, the end point being taken as that when the gas flow drops below 50 ml min^{-1}. In the case of the clean melt and SFM experiments the rate given is actually an average of three batches.

The oil and gas volumes were measured during experiments; steel and other inorganics were assumed from the tyre specifications and char calculated by difference. No detailed analyses were performed for clean melt. At this stage the oil was not analysed in detail and most aromatics were calculated by difference. A mixture of product oils gave a calorific value of 40.2 MJ kg^{-1}.

Melt Condition	Pyrolysis rate g/min
Clean melt (Average of 3 batches)	7.4
Standard Foul Melt (Av. 3)	6.1
SFM + 19.4g tyre added	6.0
+ 38.6g	5.4
+ 81.2g	5.1
+ 122.1g	4.5
+ 160.3g	4.1

Table 9.1 Effect of Melt Condition on Pyrolysis Rate

Melt	Oil,wt.%	Char,wt.%	Gas,wt.%	Steel,wt.%	Inorgs.wt.%
Clean(Av.3)	27.0	37.6	13.2	16.8	5.4
SFM	22.5	35.8	19.5	"	"
+ 19.4g	26.0	36.8	15.0	"	"
+ 38.6g	30.0	34.3	13.5	"	"
+ 81.2g	30.5	34.3	13.0	"	"
+ 122.1g	32.0	34.8	13.0	"	"
+ 160.3g	30.5	33.8	13.5	"	"

Table 9.2 Effect of Melt Condition on Product Phase Distribution

The oil and gas volumes were measured during experiments; steel and other inorganics were assumed from the tyre specifications and char calculated by difference. No detailed analyses were performed for clean melt. At this stage the oil was not analysed in detail and most aromatics were calculated by difference. A mixture of product oils gave a calorific value of 40.2 MJ kg^{-1}.

Melt Condition	Pyrolysis rate g/min
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+ 81.2g	5.1
+ 122.1g	4.5
+ 160.3g	4.1

Table 9.1 Effect of Melt Condition on Pyrolysis Rate

Melt	Oil,wt.%	Char,wt.%	Gas,wt.%	Steel,wt.%	Inorgs.wt.%
Clean(Av.3)	27.0	37.6	13.2	16.8	5.4
SFM	22.5	35.8	19.5	"	"
+ 19.4g	26.0	36.8	15.0	"	"
+ 38.6g	30.0	34.3	13.5	"	"
+ 81.2g	30.5	34.3	13.0	"	"
+ 122.1g	32.0	34.8	13.0	"	"
+ 160.3g	30.5	33.8	13.5	"	"

Table 9.2 Effect of Melt Condition on Product Phase Distribution

Melt	H_2	CH_4	C_2	C_3	C_4	C_5 etc.	
SFM	0.5	7.5	9.0	12.5	36.0	34.5	wt.%
+ 19.4g	0.5	7.5	10.5	12.5	34.0	35.0	
+ 38.6g	0.5	8.0	10.5	12.0	35.0	34.0	
+ 81.2g	0.5	9.5	11.0	12.0	30.0	37.0	
+ 122.1g	0.5	8.5	10.5	14.0	36.5	30.0	
+ 160.3g	0.5	8.5	10.0	12.5	34.5	34.0	

Table 9.3 Effect of Melt Condition on Gas Composition

Melt	C_5	C_6	C_{7-12}	C_{12+}	Styrene	Other aromatics	
SFM	0	2.5	20.0	34.0	7.0	36.5	wt.%
+ 19.4g	0	3.0	22.5	31.0	8.0	35.5	
+ 38.6g	0	2.5	19.5	33.5	7.0	37.5	
+ 81.2g	0	2.0	16.0	36.0	7.0	39.0	
+122.1g	0	3.0	19.0	38.0	7.0	33.0	
+160.3g	0	2.5	18.5	37.5	7.5	34.0	

Table 9.4 Effect of Melt Condition on Oil Composition

9.2.2.2 Variable Feed Weight

In varying feed weight the surface area to mass ratio is altered and so would be expected to effect the rate of pyrolysis. The rates given are averages of three batches at each weight. The figures in brackets show the (relative) rates divided by weight. It was also observed that larger sample weights caused appreciable drops in temperature; up to 10°C in the 80g cases.

Sample wt.g	Temp.°C	Stirring, rpm	Av. Rate g. min^{-1}	Peak Rate $g.min^{-1}$
10 g	550	500	4.3 (4.3)	9.3 (9.3)
20	"	"	6.9 (3.5)	15.9 (8.0)
40	"	"	8.4 (2.1)	20.1 (4.0)
80	"	"	9.1 (1.1)	34.8 (4.4)

Table 9.5 Effect of Feed Weight on Pyrolysis Rate

9.2.2.3 Temperature

The effect of temperature on rates and rate constants is given in Table 9.6. Again the rates are average over each batch as described earlier.

Temp.°C	Batch	Rate, $g.min^{-1}$	Av.Rate, $g.min^{-1}$	Av.k	Ln.k	$^{1}/_{T}$
450	1	5.5	5.2	0.26	-1.35	1.38×10^{-3}
	2	5.9				
	3	4.3				
550	1	6.9	6.2	0.31	-1.17	1.22×10^{-3}
	2	6.0				
	3	5.8				
675	1	9.8	9.3	0.47	-0.76	1.05×10^{-3}
	2	9.2				
	3	9.0				

Table 9.6 Effect of Temperature on Rate Data

The effect of temperature on product phase distribution is given in Table 9.7 and plotted in Fig. 9.1.

Temp °C		Oil wt. %		Char wt. %		Gas wt. %		Steel wt.%		Inorgs.wt.%	
450	1	28.5	30.8	36.3	34.6	13.0	12.3	16.8	16.8	5.4	5.4
	2	32.0		34.8		11.0		"		"	
	3	32.0		32.8		13.0		"		"	
550	1	22.5	25.3	35.8	36.3	19.5	16.2	"		"	
	2	26.0		36.8		15.0		"		"	
	3	27.5		36.3		14.0		"		"	
675	1	19.5	21.8	37.8	39.1	20.5	17.0	"		"	
	2	21.0		40.8		16.0		"		"	
	3	25.0		38.3		14.5		"		"	

Table 9.7 Effect of Temperature on Product Phase Distribution

The effect on gas and oil composition (quoted in wt. % for mass balance purposes) are given in Tables 9.8 and 9.9.

Temp. °C	H_2	CH_4	C_2	C_3	C_4	C_5 etc.	
450	0.5	8.7	9.5	12.4	39.7	29.2	wt. %
550	0.5	7.5	10.5	12.5	34.0	35.0	
675	0.5	5.0	11.0	10.3	32.1	41.1	

Table 9.8 Effect of Temperature on Gas Composition, wt.%

The effect of temperature on product phase distribution is given in Table 9.7 and plotted in Fig. 9.1.

Temp °C		Oil wt. %		Char wt. %		Gas wt. %		Steel wt.%		Inorgs.wt.%	
450	1	28.5	30.8	36.3	34.6	13.0	12.3	16.8	16.8	5.4	5.4
	2	32.0		34.8		11.0		"		"	
	3	32.0		32.8		13.0		"		"	
550	1	22.5	25.3	35.8	36.3	19.5	16.2	"		"	
	2	26.0		36.8		15.0		"		"	
	3	27.5		36.3		14.0		"		"	
675	1	19.5	21.8	37.8	39.1	20.5	17.0	"		"	
	2	21.0		40.8		16.0		"		"	
	3	25.0		38.3		14.5		"		"	

Table 9.7 Effect of Temperature on Product Phase Distribution

The effect on gas and oil composition (quoted in wt. % for mass balance purposes) are given in Tables 9.8 and 9.9.

Temp. °C	H_2	CH_4	C_2	C_3	C_4	C_5 etc.	
450	0.5	8.7	9.5	12.4	39.7	29.2	wt. %
550	0.5	7.5	10.5	12.5	34.0	35.0	
675	0.5	5.0	11.0	10.3	32.1	41.1	

Table 9.8 Effect of Temperature on Gas Composition, wt.%

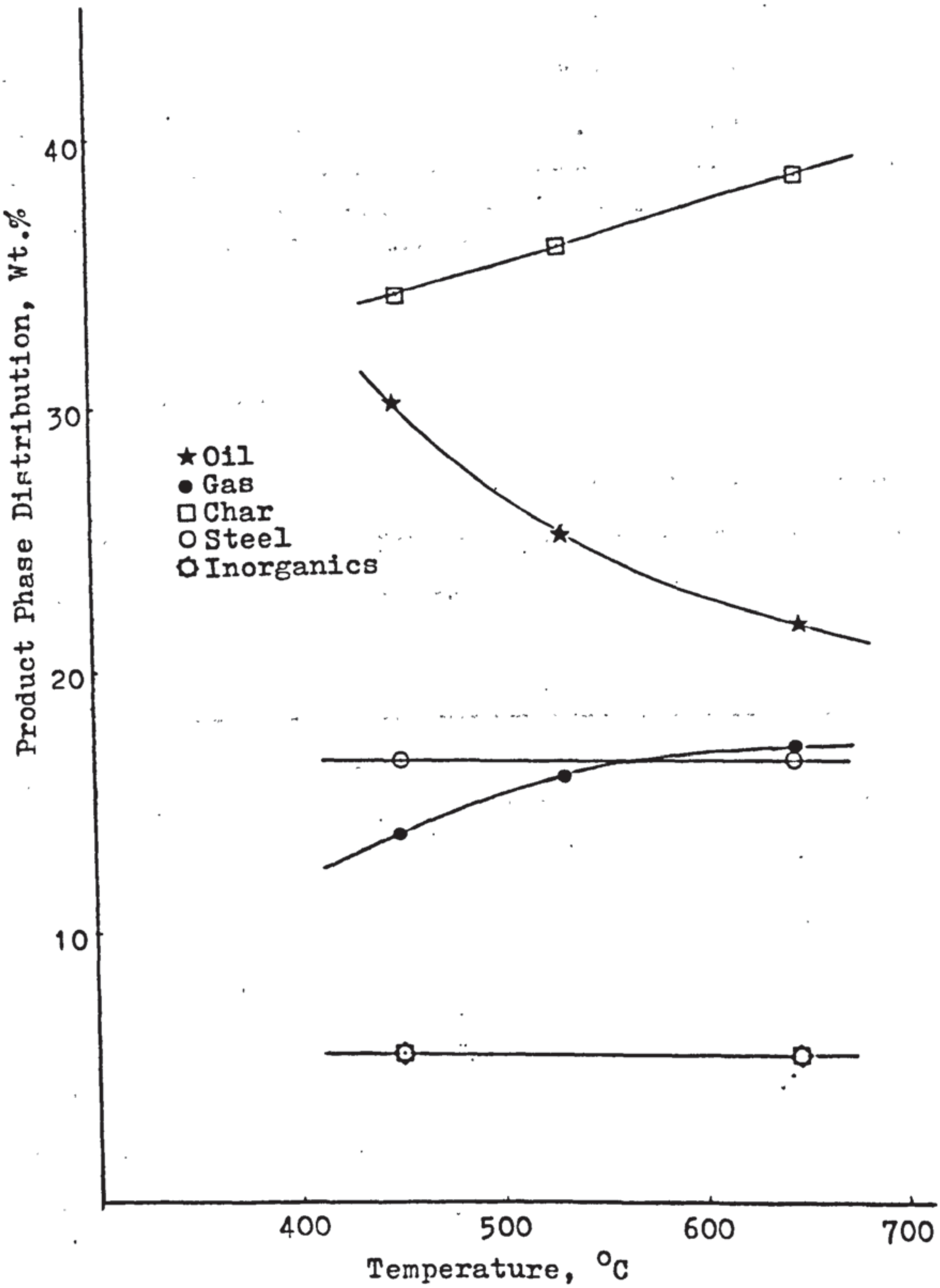


Fig.9.1 Temperature vs. Product Phase Distribution

Temp°C	C_5	C_6	C_{7-12}	C_{12+}	Styrene	Other aromatics
450	1.3	3.6	23.7	32.2	5.0	34.2 by diff.
550	-	3.0	22.5	31.0	8.0	35.5
675	-	1.8	18.7	18.8	4.6	56.1

Table 9.9 Effect of Temperature on on Oil Composition, wt.%

9.2.2.4 Stirring Rate

Using sample sizes of about 20g pyrolysing in Standard Fouled Melt (SFM), the following effects of stirrer speed were noted. The results are also plotted in Figure 9.2.

Temperature, °C	Stirrer rate, rpm	Rate of Pyrolysis $g.min^{-1}$
550	0	3.8
"	250	5.9
Melt change		
550	500	6.8
"	750	7.5
Melt change		
550	1250	8.1
"	250	5.1

Table 9.10 Effect of Stirring on Pyrolysis Rate

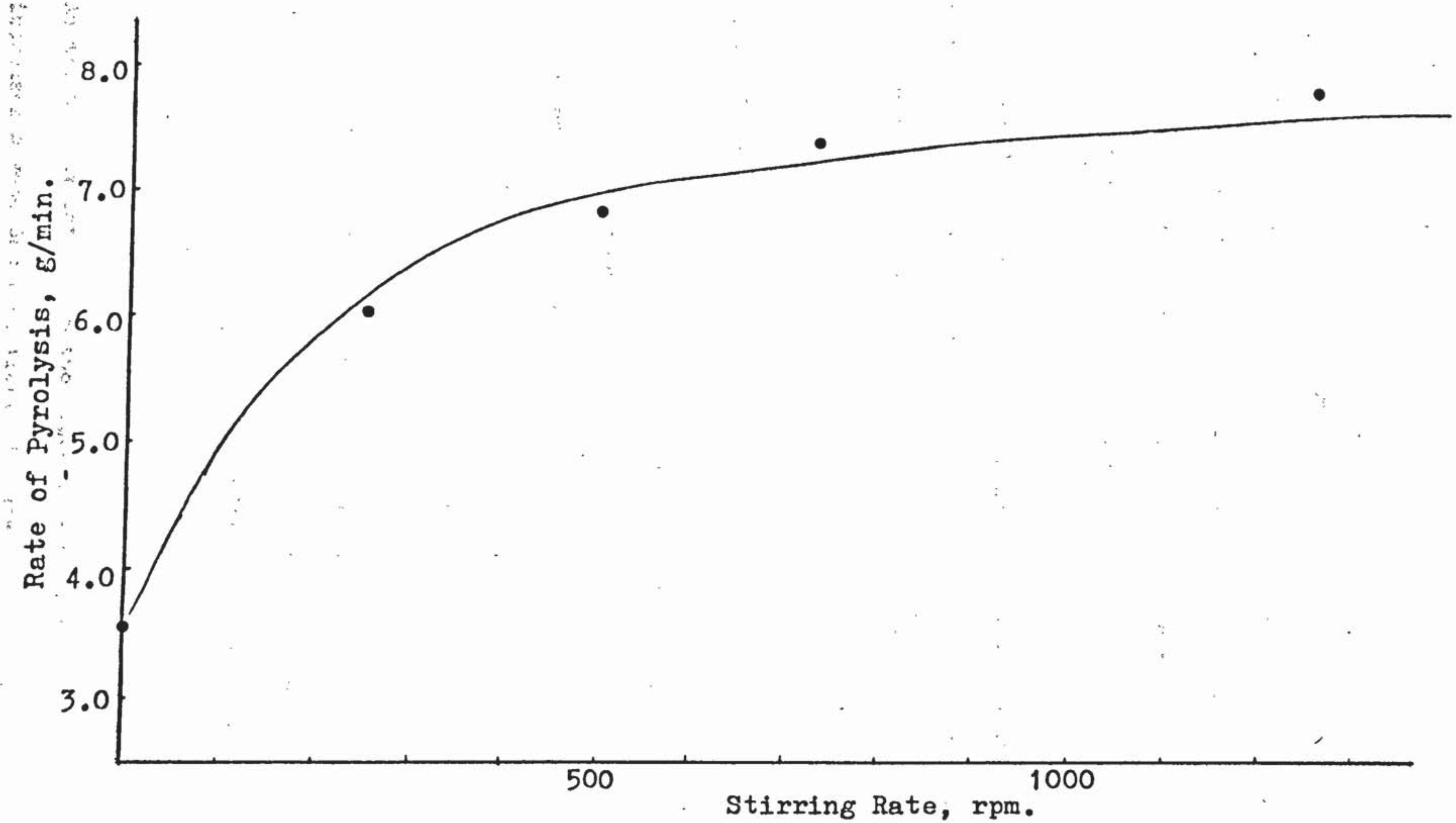


Fig.9.2 Stirring Rate vs. Rate of Pyrolysis

A physical model using wood to simulate tyre, water/glycol to simulate the melt and air to simulate product vapours gave further useful data. (Although wood and the fluid are not similar in density to tyre and melt their differences were almost identical.) The model showed that the solid and liquid of the three phase system were effectively mixed at 600 rpm. Excessive vortex formation and gas entrainment occurred at 1100 rpm.

The effect of stirring rate on product phase distribution and composition was not significant although there was a slight shift to lower molecular weights in the gas fraction at the highest stirring rates.

9.2.3 Trends

During the exploratory experiments, although it was not intended to obtain detailed quantitative results, various trends were observed. The effects of the four parameters evaluated are described below:

- I. Increased melt fouling
  - Reduced rate of pyrolysis.
  - Slight increase in oil yield.
  - Very slight increase in gas yield.
  - Reduced char yield.
  - Shift to higher Mol wt. in oil product.

As might be expected from the degrees of change in fouling the small increases beyond SFM make little difference to the variables.

II. Increased feed weight	Increased rate, g. min^{-1}. Decreased rate constants, min^{-1}. Increased temperature drop on input.

Although the absolute rate increases with feed weight there is an equivalent drop in rate constant.

III. Increased temperature	Increased rate of pyrolysis. Decrease in oil yield. Increase in gas yield. Slight increase in char yield. Increased aromatics in oil. Decreased heavy aliphatics in oil. Increased C_4 in gas.

All variable changes, except char yield, induced by increased temperature are of notable magnitude.

IV. Increase stirring	Increased rate - stabilizing above 750 rpm. Increased mixing - solid/liquid 600 rpm - solid/liquid/gas 1100 rpm

9.3 Discussion, Conclusions and Actions

The exploratory experiments served to identify the importance of the various system parameters. This enabled the design of the main experimental series to make the most efficient use of time, materials and resources.

From the results and trends established in the previous sections it is immediately clear that temperature above all else has the greatest effect on pyrolysis variables. Therefore a temperature based main series was desirable. In Chapter 6 it was established that the process should produce as much oil of high calorific value as reasonably achievable. Given this aim it would appear that a lower temperature of pyrolysis is desirable, as losses in aromaticity are trivial in effect compared with the oil losses at higher temperatures. However to be considered against this is the reduced rate of pyrolysis and hence oil production rate. Clearly there will be some sort of optimum balance; this will be evaluated in later chapters.

If a low temperature is eventually required it would be useful to establish a lower limit for the system. The pure eutectic melts at 397°C and SFM at $\sim$350°C to which must be added allowances for further fouling, viscosity suitability and temperature drop on tyre input. At this stage no accurate quantitative value could be given but it appears that a safe and practical lower limit might be 425°C.

The upper limit of operation was in fact found to be limited to

675°C by the furnace capacity as expected. This was deemed to be adequate given the oil maximization condition. Bearing these factors in mind the range for the main experimental series was set as 450 - 650°C.

The effect of feed weight was important only in confirming that the size chosen, by consideration of other factors, fell within reasonable conditions. The limiting factor here was the cooling of the melt on tyre introduction due to sensible heat exchange. The 80g sample in 0.75 L of melt caused a drop in temperature of 10°C which although not crucial in safety terms makes assigning a temperature to any experiment a little uncertain. This weight is well above the 30g in 0.75 L concentration calculated earlier where no significant drop was recorded. The effects on rate are of interest in developing a physical mechanism for the pyrolysis (as will be seen later), but are of no consequence here since other factors set the limits. No actions were proposed on this parameter at this stage.

The effect of stirring was evaluated on the relative scale of revolutions per minute. The effect of increasing the rate is certainly due to improvements in heat and mass transfer but as is shown in Fig. 9.2 the effect is limited. This is probably due to heat transfer limits within the pyrolysing tyre rather than at the melt-tyre transfer interface.

The intact state of char particles observed after pyrolysis indicates that where the immersion rod was used tyre was held under the melt for most of the time. Using the ethylene glycol/water model it was shown that those pieces that do break away can, to a certain extent, be re-intrained in the melt at relatively low stirrer speeds. Efficient mixing occurs under gentle conditions of agitation. As the immersion rod was used to simulate the commercial operation the stirrer was required only to ensure melt circulation. Therefore it was decided that 600 rpm, using the described stirrer, would be sufficient for a standard mixing condition during the main series of experiments.

The increased degree of melt fouling was noted to reduce the rate of pyrolysis; this is particularly clear in the difference between clean melt and SFM. The most likely explanation is that solid, inorganic, particulate matter restricts the efficiency of heat transfer. It may do this through conductivity/surface contact phenomena or by restricting melt transport. Clearly in a continuous operation build-up would not occur and so in the main experimental series the melt was changed after the addition of three or four tyre batches (i.e. after each experiment). A build-up of loose char on the melt surface may also be a contributory factor but use of the immersion rod will largely eliminate this cause.

The melt condition also appears to alter the product phase distribution; increasing oil yield with fouling. The discrepancy between clean melt and SFM indicates that this may not be a true trend. The increased oil yield can be explained in two ways: firstly, that it may be allied to the rate and thus be an indirect effect. However, more likely it is due to the manner in which batches + 19.4g to + 160.3g were added in short sequence. This means much of the oil from the first batch would be used to wet the apparatus and only emerge as carry-over in the next batch. Looking at the product phase distribution results for temperature variation (Table 9.2) it appears that oil yield is only stabilized after two or three batches. The oil yield for clean melt indicates melt fouling not to be responsible. (The possibility of char build-up on the surface causing oil cracking will be evaluated in the main series.) Since it appears that the increasing oil yield is a carry-over phenomenon the product phase yield will be evaluated as averages over three batches in the main series of experiments.

As well as these actions of fundamental experimental principles the exploratory experiments also enabled inadequacies in the design of the apparatus to be rectified before the main experiments. Most of these changes were of a minor nature having little effect on results but enabling more effective performance of experiments. The apparatus described in Chapter 7 is the final development of the exploratory experiments which was used from here on.

CHAPTER
TEN

PARAMETRIC INVESTIGATION OF TYRE PYROLYSIS

10 PARAMETRIC INVESTIGATION OF TYRE PYROLYSIS

10.1 Experimental Programme

Originally the experimental work was envisaged as a factorial programme varying the parameters of temperature, stirring rate, tyre input, tyre to melt volumes and melt condition. Even if each parameter were only investigated at two or three values the number of experiments would have been impractically large. The exploratory experiments enabled the importance of each parameter to be identified and thus its number of values restricted. Summarizing the exploratory results it was found that the stirring rate could be fixed at a level that gave a well mixed melt, the tyre type was selected on market grounds (Chapters 2 and 6), the input weight was fixed to a likely commercial plant situation and the melt condition was kept within the limits of a likely continuous operation contamination level. This left a programme which was largely based on temperature variation. The first planned programme therefore became:

Temperature	Experiments
475°C	3 or 4 batches each of 20 - 40g
Melt change	
525°C	3 or 4 batches each of 20 - 40g
Melt change	
650°C	3 or 4 batches each of 20 - 40g

These three experiments formed the basis of the experimental runs although in many cases they were repeated and the results given are in fact averages. In every experiment the variables to be measured were rates, melt condition, product phase distribution and product analyses. In addition other variables were occasionally measured.

A second programme of experiments making use of steam was also planned. The aim of steam injection was threefold: to evaluate the effectiveness of steam reforming; to improve oil yield by encouraging nucleation in the condenser; and finally to improve flow characteristics through the reactor. This was done by injecting the steam at different temperatures, points in the reactor, and rates of flow. The steam programme, although again many experiments were repeated, is given below:

Temperature	Injection position	Steam flow rate
475°C	Sub-melt	0.7 g min^{-1}
"	"	1.3 "
"	"	2.3 "
"	"	4.6 "
650°C	Sub-melt	2.3 g min^{-1}
475°C	Reactor head-space	2.3 g min^{-1}
"	Condenser input	2.3 "

The steam was produced using the electric generator described earlier in Chapter 7. The generator was fed by a standardized peristaltic pump and it was this that was used to meter the steam input. The variables measured were the same as in the temperature based series.

In addition a few short series of experiments were performed to answer questions arising from experiments up to this point. Firstly an experiment was performed to evaluate the effect of large amounts of surface char. This was compared directly with a normal SFM experiment:

Temperature	Melt	Experiments
475°C	SFM	3 or 4 batches of 20-40g
475°C	SFM + 100g surface char	"

This experiment together with the head-space injected steam experiment was to help evaluate head-space cracking effects.

The second short programme was one in which the effect of varying degrees of tyre wear were evaluated. Again by including a normal experiment the series became:

Temperature	Tyre wear	Experiments
475°C	1mm tread	3 or 4 batches at 20-40g
475°C	New tyre	3 batches 30g
475°C	Tread only	"

The final experiment was one to test the effect of the melt itself. A four batch (∼30g each) experiment was performed suspending the tyre in the reactor at 475°C containing only nitrogen. The aim was to evaluate the heat transfer and possible catalytic characteristics of the carbonate melt by comparison with a normal experiment.

In these short series the variables measured and analyses performed were the same as in all other series of experiments.

10.2 Results

10.2.1 Rate Data

Detailed rate data are an essential requirement for two reasons: firstly they are needed in estimating the performance of a scaled-up operation and secondly they are useful in interpreting the mechanisms involved in tyre pyrolysis.

It was assumed that all the products of pyrolysis are produced simultaneously throughout the reaction in the same proportions. Therefore the rate of gas production, the only continuously measurable variable, is directly proportional to the rate of pyrolysis. This method enables rates to be calculated and expressed in a number of ways: time averaged over a complete batch, against time or at any particular tyre concentration. The last enables tyre concentration, tyre remaining or tyre pyrolysed to be plotted against time. The general procedure and presentation used here is to give the elapsed time, the rate at each time, the time averaged rate data and the cumulative rate integral (tyre pyrolysed) for each batch. Table 10.1 gives all this data for two experiments (each of three batches) at each of 475°C, 525°C and 650°C.

Temp oC	wt.g	Time mins	Rate $g.min^{-1}$	Av.Rate $g.min^{-1}$	Av.k	∫Rate g
475	22.0	0	6.3			0
		0.5	8.2			4.0
		1.0	9.4			9.0
a		1.5	nt	4.4	0.20	12.0
		2.0	3.8			16.5
		5.0	0.6			21.5
		10.0	0			22.0
475	36.0	0	8.5			0
		0.5	10.1			4.4
		1.0	10.1			8.9
		2.0	8.2			14.3
b		3.5	3.6	4.8	0.13	22.3
		6.0	1.8			27.9
		8.5	0.9			32.9
		11.5	0.6			34.8
		14.0	0			36.0
475	37.5	0	11.2			0
		0.5	15.2			6.8
		1.0	17.7			15.0
		2.0	5.7	6.3	0.17	28.5
c		4.0	2.1			35.5
		5.0	1.6			36.5
		6.0	0.5			37.0
		10.0	0			37.5
475	23.5	0	4.0			0
		0.5	8.0			3.4
		1.0	9.4			7.8
d		2.0	6.4	3.6	0.15	15.8
		4.0	2.4			23.0
		8.5	0.5			23.5
		10.5	0			23.7
475	32.5	0	5.4			0
		0.5	13.2			5.8
		1.0	17.1			13.3
e		2.0	5.8	5.4	0.17	23.3
		4.0	2.1			30.5
		6.0	0.8			32.2
		8.0	0			32.5
475	36.0	0	9.0			0
		0.5	11.0			6.0
		1.0	9.5			14.1
f		1.5	5.3	6.0	0.16	23.5
		4.0	1.2			31.7
		6.0	0.5			34.9
		9.0	0			36.0

Temp oC	wt.g	Time mins	Rate $g.min^{-1}$	Av.Rate $g.min^{-1}$	Av.k	∫Rate g
525	24.5	0.25	24.0			0
		0.5	14.4			8.8
		1.0	9.1			14.0
a		2.0	2.9	4.9	0.20	20.0
		3.5	0.9			23.0
		5.5	0.5			24.0
		7.0	0			24.5
525	26.5	0.25	25.4			0
		0.5	22.5			13.3
		1.0	8.3			21.6
		1.5	5.1	5.3	0.20	24.9
b		2.5	0.8			26.0
		5.0	0.4			26.3
		9.0	0			26.5
525	38.0	0	21.7			0
		0.5	26.0			12.0
		1.0	15.5			21.5
		2.0	7.3	7.6	0.20	34.0
c		2.5	3.6			36.5
		3.0	0.6			37.0
		5.0	0.4			37.5
525	24.0	0	20.5			0
		0.5	23.5			8.4
		1.5	5.0			16.0
d		2.0	1.1	5.3	0.23	19.5
		2.5	0.8			21.5
		5.0	0.3			23.5
		8.0	0			24.0
525	36.5	0	21.0			0
		1.0	17.8			20.0
		2.5	3.4			34.0
e		4.0	1.0	6.1	0.17	36.0
		6.0	0.5			36.4
		8.0	0.3			36.5
		10.0	0			36.6
525	24.5	0.25	24.0			0
		0.5	14.4			12.6
		1.0	9.0			18.4
f		2.0	2.9	4.9	0.20	24.0
		3.5	1.1			24.5
		5.0	0.6			24.7
		7.0	0			24.7

Temp oC	wt.g.	Time mins	Rate $g.min^{-1}$	Av.Rate $g.min^{-1}$	Av.k	∫Rate g
650	26.5	0.25	24.1			0
		0.5	15.2			9.5
		1.0	11.2	7.6	0.29	16.0
a		2.0	3.2			23.0
		3.5	0.5			26.0
		4.5	0			26.5
650	36.0	0.25	30.0			0
		0.5	19.5			16.0
		1.5	4.5			28.5
		2.0	1.5	9.0	0.25	30.0
b		3.0	1.0			32.0
		3.5	1.0			34.5
		4.0	0.5			35.5
650	33.5	0.25	30.6			0
		0.5	20.4			16.7
		1.0	9.6	8.4	0.25	25.3
		2.0	1.9			31.5
c		3.5	0.7			33.0
		4.5	0			33.5
650	31.5	0.25	24.3			0
		0.5	16.7			12.0
		1.0	12.7			20.0
d		1.5	7.0	7.9	0.25	25.5
		2.0	3.4			27.9
		3.5	0.5			30.0
		5.0	0			31.5
650	38.5	0.25	36.2			0
		0.5	18.1			18.0
		1.5	10.0	7.7	0.20	31.1
e		3.0	2.4			38.0
		5.0	0.8			38.3
		7.0	0			38.5
650	34.0	0.25	34.5			0
		1.0	11.5			24.0
		2.0	2.3	8.1	0.24	30.6
f		3.5	1.0			33.1
		5.0	0			34.0

Table 10.1 Tyre Pyrolysis Rate Data

The rate data in Table 10.1 was first plotted as rate vs. time in Fig. 10.1 which by integration gave Fig. 10.2, tyre remaining vs. time. By combination of the two, rates at the fixed concentration of 30g/0.752 can be obtained, as shown in Table 10.2.

Temp. °C	Batch	Rate(30g), g.min	k(30g)	wt. °g	%
475	1 a	-	-	22.0	-
	2 b	11.2	0.37	36.0	83.3
	3 c	14.0	0.47	37.5	80.0
Melt change					
475	1 d	-	-	23.5	-
	2 e	11.0	0.37	32.5	92.3
	3 f	11.5	0.38	36.0	83.3
Melt change					
525	1 a	-	-	24.5	-
	2 b	-	-	26.5	-
	3 c	26.0	0.87	38.0	78.9
Melt change					
525	1 d	-	-	24.0	-
	2 e	23.5	0.78	36.5	82.2
	3 f	-	-	24.5	-
Melt change					
650	1 a	-	-	26.5	-
	2 b	28.5	0.95	36.0	83.3
	3 c	28.0	0.93	33.5	89.6
Melt change					
650	1 d	28.0	0.93	31.5	95.2
	2 e	31.5	1.05	38.5	77.9
	3 f	32.0	1.07	34.0	88.2

Table 10.2 Rate of Pyrolysis with Tyre Concentration

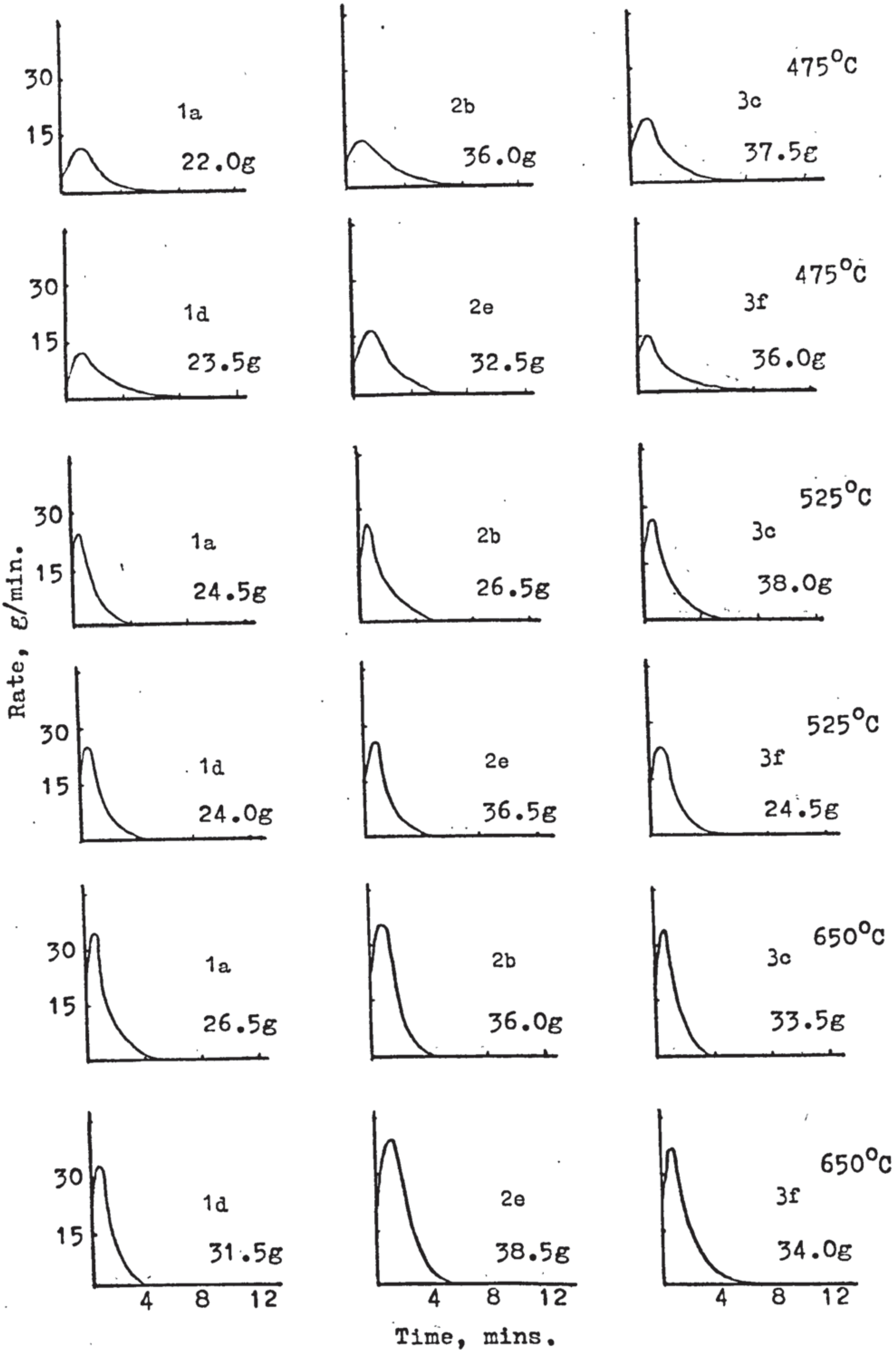


Fig.10.1 Pyrolysis rate vs. Time

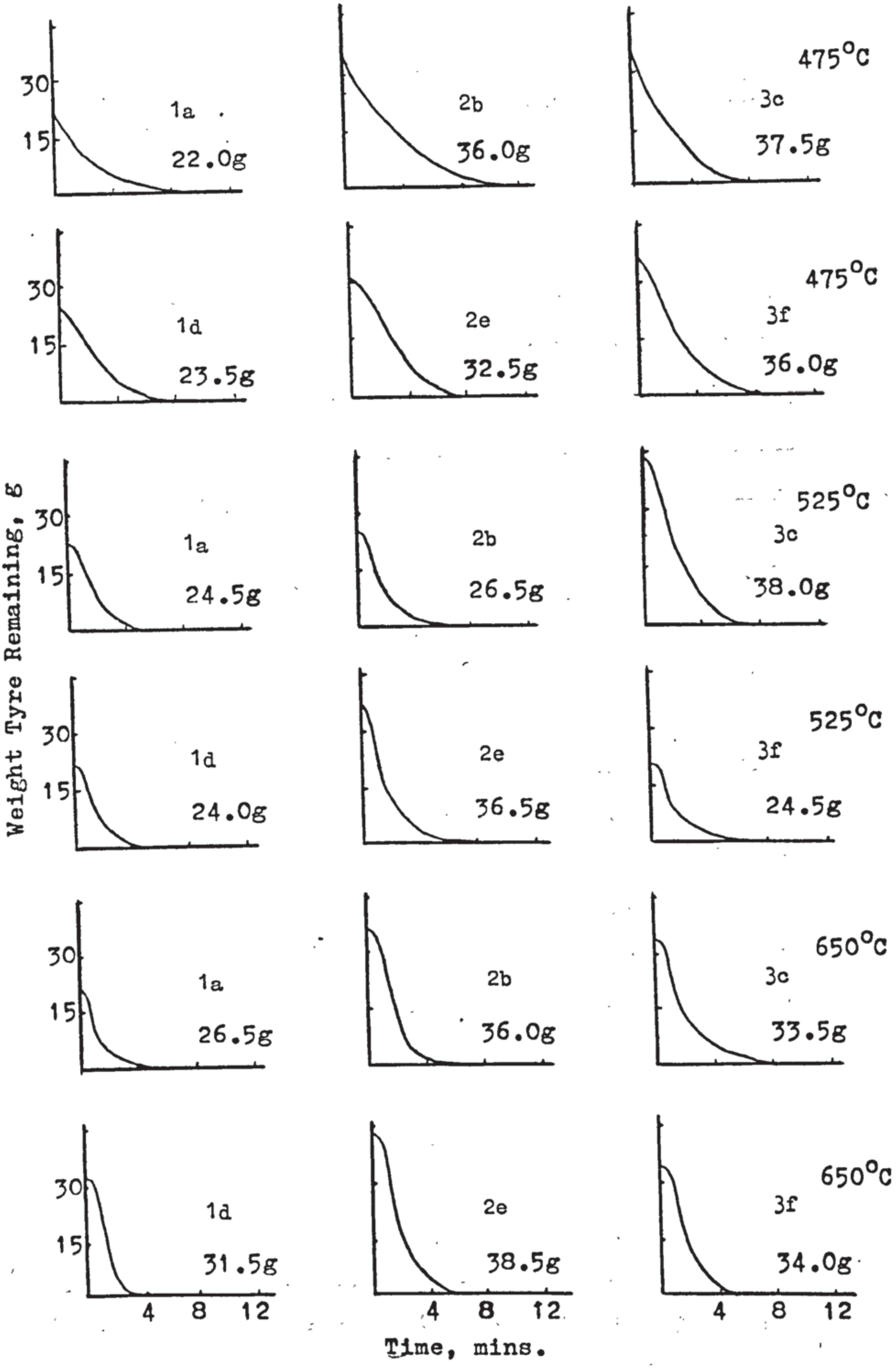


Fig.10.2 Tyre remaining vs. Time

The data given and plotted here was used to obtain information useful to scaling-up and to give an insight into the reaction mechanisms involved.

The rate data from the second series of experiments, using steam, were not treated in such detail. The rate data for sub-melt steam injection is given in Table 10.3

Temp. °C	Steam, g.min^{-1}	Tyre wt.g.	Pyrolysis Rate, g/min	k.av.
475	0.7	37.5	5.8	0.15
	"	35.5	6.2	0.17
	"	35.0	6.1	0.17
	1.3	35.0	4.0	0.12
	"	32.5	4.3	0.14
	"	33.0	4.4	0.14
	2.3	32.0	4.3	0.13
	"	37.0	4.4	0.12
	"	33.5	3.9	0.12
	4.6	29.5	4.4	0.15
	"	31.5	3.2	0.10
	"	33.0	4.0	0.12
650	2.3	30.5	8.2	0.27
	"	33.5	10.4	0.31
	"	31.0	8.4	0.27

Table 10.3 Rate Data for Sub-melt Steam Injection

The rate data obtained when steam was passed only through the reactor head-space are given in Table 10.4 but no sensible data were obtained for the condenser injection of steam due to the back-pressure reducing flow from the reactor.

Temp. ^{o}C	Steam, g/min	Tyre wt.g.	Pyrolysis Rate, g.min	k.av.
475	2.3	32.5	4.3	0.13
	"	30.0	4.0	0.13
	"	31.0	4.9	0.16

Table 10.4 Rate Data for Head Space Steam Injection

The rate data for experiments in which large amounts of char were placed on the melt surface are given in Table 10.5. In this experiment 100g of char was introduced. The rate data for the second short programme, involving tyre wear, are given in Table 10.6.

Temp ^{o}C		Tyre wt.g	Pyrolysis rate, g/min	k
475	1	30.5	4.7	0.15
	2	25.0	4.2	0.17

Table 10.5 Rate Data for Excess Char Presence

Temp^{o}C	Tyre Wear	Tyre wt.g	Rate Pyrolysis g/min	k
475	New	24.1	3.4	0.14
	"	31.4	3.7	0.12
	"	24.8	3.2	0.13
	Tread only	25.3	3.9	0.15
	"	25.1	3.0	0.12
	"	36.0	4.5	0.13

Table 10.6 Rate Data with respect to Tyre Wear

The final experiment; performing the pyrolysis in an empty reactor (N_2 filled), was given the same detailed rate analysis as the initial main series. The rate results are given in Table 10.7. The data for the first two batches are plotted as rate vs time and by integration as weight remaining vs time, both being shown in Fig. 10.3.

To make comparison of the rate data easier, average values for k in the different experimental conditions covered, are given in Table 10.8.

Temp °C	wt.g	Time,mins	Rate,$g.min^{-1}$	Av.Rate g.min	Av.k	$\int$Rate,g
475	21.5	0	0.0	2.9	0.13	0
		0.5	1.0			0.5
		1.0	1.4			0.8
		1.5	3.1			2.2
		2.5	5.0			8.2
		4.0	5.2			15.0
		6.0	0.8			18.7
		8.0	0.3			20.6
		10.0	0			21.5
	22.0	0	0.0	2.6	0.12	0
		0.5	0.5			0.1
		1.0	1.0			0.5
		1.5	1.0			1.0
		2.0	1.3			1.7
		3.5	5.2			9.2
		6.0	2.0			21.7
		8.0	0.5			21.9
		10.0	0			22.0
	36.5	0	0.0	4.5	0.13	0
		1.0	0.8			-
		1.5	1.5			--
		2.5	2.8			-
		4.0	7.0			-
		6.5	2.1			-
		8.0	0.6			-
		12.5	0			36.5
	30.0	0	0.0	4.0	0.13	0
		0.5	0.6			-
		1.0	1.3			-
		1.5	1.5			-
		2.5	2.5			-
		3.5	7.5			-
		5.5	2.0			-
		7.0	0.9			-
		12.0	0			30.0

Table 10.7 Dry Pyrolysis Rate Data

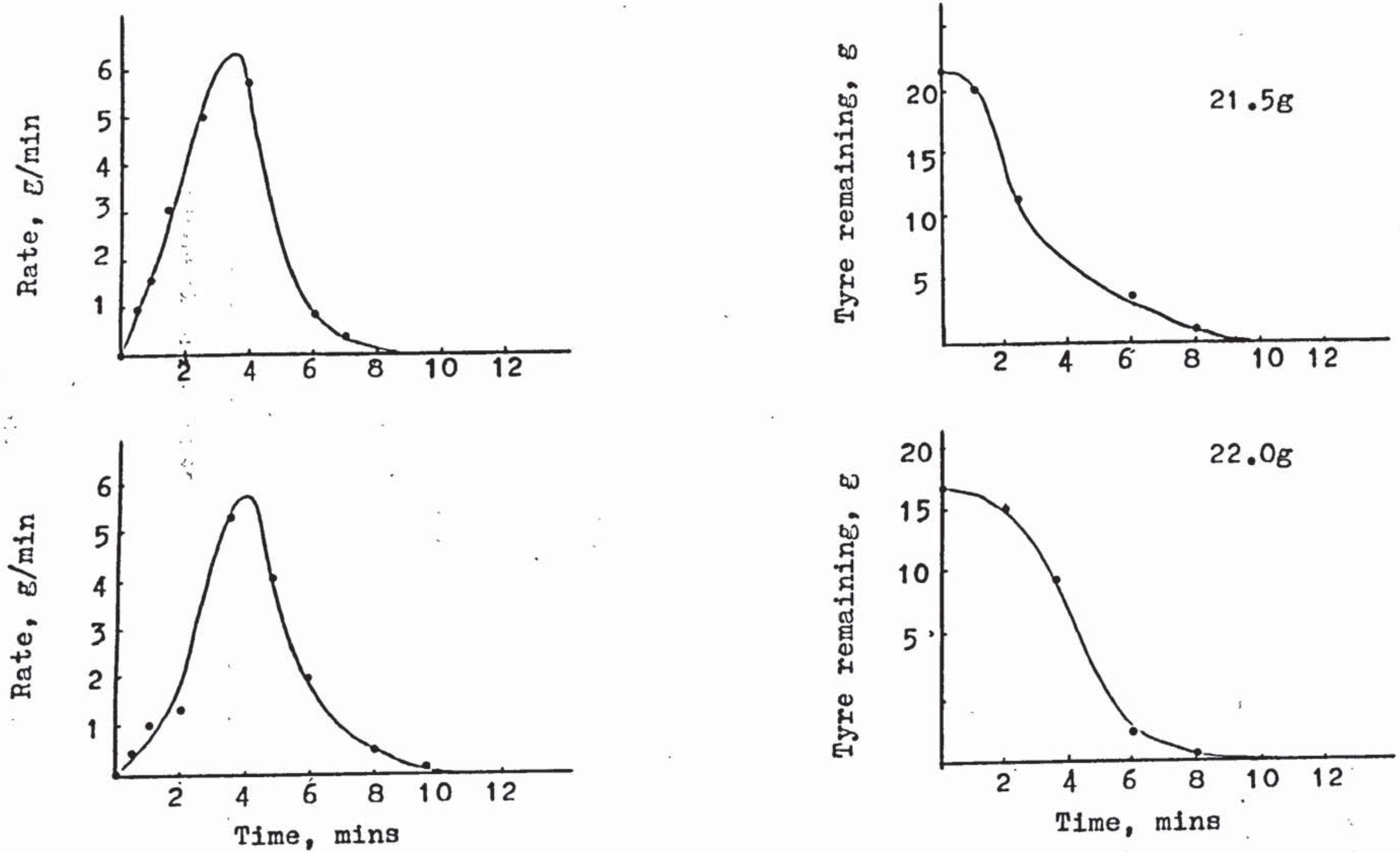


Fig.10.3 Dry Pyrolysis Rate Data

Temp °C	Melt Condition	Tyre Wear	Steam rate, g/min	Steam point	k.min^{-1}
475	SFM	1mm tread	0.0	-	0.16
525	"	"	"	-	0.20
650	"	"	"	-	0.25
475	SFM	1mm tread	0.7	sub-melt	0.16
"	"	"	1.3	"	0.13
"	"	"	2.3	"	0.12
"	"	"	4.6	"	0.12
650	"	"	2.3	"	0.28
475	SFM	1mm tread	2.3	Head-space	-
475	Clean	1mm tread	0.0	-	0.16
"	100g char	"	"	-	0.16
475	SFM	New	0.0	-	0.13
"	"	Tread only	"	-	0.14
475	None	1mm tread	0.0	-	0.13

Table 10.8 Comparison of Rate Constants

The temperature series and the steam series allow k to be plotted against the parameters involved. Fig. 10.4 shows k vs temperature while Fig. 10.5 shows k vs steam rate.

10.2.2 Orders and Kinetic Data

The order of reaction is an empirical concept that can only be determined experimentally and should not be confused with the theoretical concept of molecularity. The order of reaction will be a factor in the proposal of a pyrolysis mechanism.

Studying the plots in Fig. 10.2, tyre remaining vs time, there appear to be linear and exponential sections in each which indicate an order varying from zero to one. However the nature of exponential curves suggest that the orders will be close to one. It is the overall order that is of interest and so no details with respect to time are given.

At this point there are two options in order determination: firstly by attempting to fit the rate data to the first order rate law,

$$\frac{dT_t}{dt} = kT_t$$

T = Tyre

t = Time,

or secondly to calculate the order. As experimental orders are rarely of

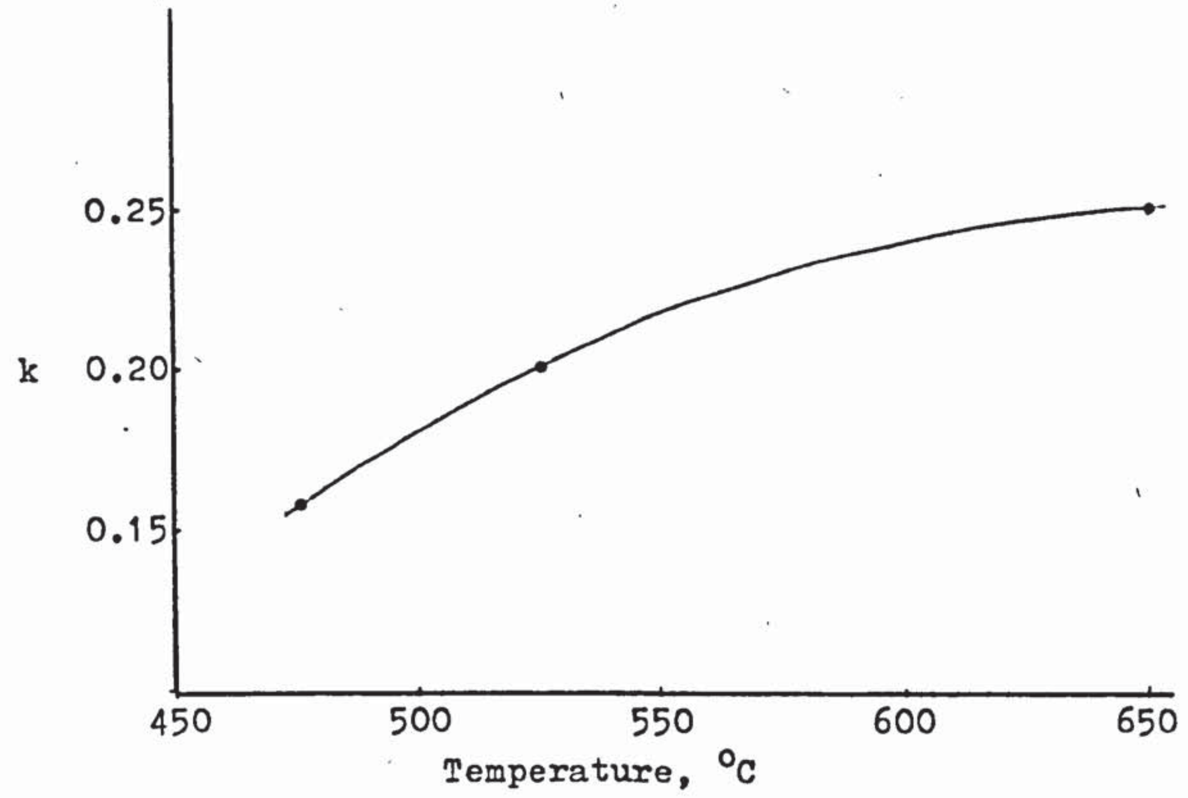


Fig.10.4 Temperature vs. k

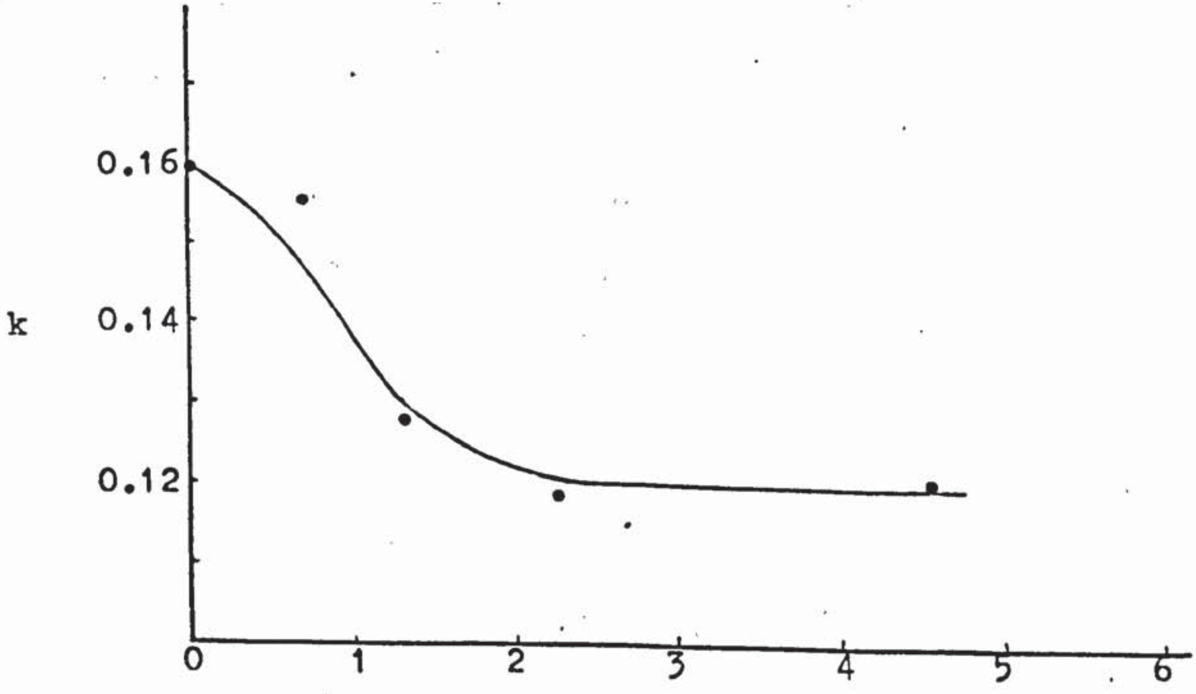


Fig.10.5 Steam flow rate vs. k

precise integer values the latter method was adopted here.

Rate equations are generally of the form,

$$\frac{-d\,T_t}{dt} = k\,T_t^{\,n}$$

n = Order of reaction.

Therefore n can be found from,

$$n = \frac{\mathrm{Log}\left(\frac{-d\,T}{dt}\right)_1 - \mathrm{Log}\left(\frac{-d\,T}{dt}\right)_2}{\mathrm{Log}\ T_1 - \mathrm{Log}\ T_2}$$

or graphically from the gradient of the plot Log $\frac{d\,T}{dt}$ vs Log T which will be -n. The orders of reaction so calculated are set out in Table 10.9.

Temp. °C		Tyre Wt. g.	Order	Av. Order
475	1 a	22.0	1.07	1.05
	2 b	38.0	1.03	
	3 c	37.5	(1.95)	
475	1 d	23.5	0.63	0.97
	2 e	32.5	0.78	
	3 f	36.0	1.50	
525	1 a	24.5	1.15	0.93
	2 b	26.5	0.87	
	3 c	38.0	0.76	
525	1 d	24.0	1.40	1.16
	2 e	36.5	1.32	
	3 f	24.5	0.77	

Continued . . .

650	1 a	26.5	1.18	1.16
	2 b	36.0	1.27	
	3 c	33.5	1.03	
650	1 d	21.5	1.00	0.95
	2 e	38.5	0.81	
	3 f	34.0	1.03	

Table 10.9 Orders of Reaction

10.2.3 Analyses

10.2.3.1 Melt

In the course of the straightforward temperature variant experiments the carbonate to hydroxide ratio remained constant whereas during steam experiments the hydroxide was observed to increase from 3.7 to over 6.0 wt.%. In all experiments the levels of zinc and sulphur were noted to increase slightly. The melt also contained between 0.5 and 2.0 wt.% carbonaceous char after each experiment.

10.2.3.2 Product Phase Distribution

The first and most basic form of product characterization was to categorize products as: oil, gas, char, steel and inorganics. This is given in Table 10.10.

Temp °C		Melt	Tyre	Steam, g/min	Oil, wt.%	Gas, wt.%	Char, wt.%	Steel, wt.%	Inorgs., wt.%
475	1 a	SFM	1 mm T	0.0	24.1	10.9	42.8	16.8	5.4
	2 b	"	"	"	27.0	13.3	37.5	"	"
	3 c	"	"	"	32.0	8.7	37.1	"	"
475	1 d	"	"	"	28.6	10.3	38.9	"	"
	2 e	"	"	"	29.5	9.3	39.0	"	"
	3 f	"	"	"	31.8	12.8	33.2	"	"
525	1 a	"	"	"	26.5	16.2	35.1	"	"
	2 b	"	"	"	27.5	13.5	36.8	"	"
	3 c	"	"	"	29.0	14.8	34.0	"	"
525	1 d	"	"	"	25.6	14.6	37.6	"	"
	2 e	"	"	"	26.1	13.6	38.1	"	"
	3 f	"	"	"	28.5	11.3	38.0	"	"
650	1 a	"	"	"	24.1	19.5	34.2	"	"
	2 b	"	"	"	22.6	18.0	37.2	"	"
	3 c	"	"	"	19.7	16.2	41.9	"	"
650	1 d	SFM			24.1	20.5	33.2		
	2 e	"	"	"	23.5	17.5	36.8	"	"
	3 f	"	"	"	23.8	15.8	38.2	"	"
475	1	SFM	1 mm T	0.7	29.0	6.8	42.0	16.8	5.4
	2	"	"	"	42.8	7.2	27.8	"	"
	3	"	"	"	37.0	6.6	34.3	"	"
475	1	"	"	1.3	30.7	8.6	38.3	16.8	5.4
	2	"	"	"					
	3	"	"	"					
475	1	"	"	2.3	30.5	8.0	39.3	16.8	5.4
	2	"	"	"	34.9	8.9	34.0	"	"
	3	"	"	"	33.6	7.4	36.8	"	"
475	1	"	"	4.6	33.1	7.8	36.9	16.8	5.4
	2	"	"	"					
	3	"	"	"					
650	1	SFM	1 mm T	2.3	23.8	11.5	42.5	16.8	5.4
	2	"	"	"	28.6	8.2	41.0	"	"
	3	"	"	"	30.1	8.2	39.5	"	"
475	1	SFM	1 mm T	2.3HS	31.8	5.6	40.4	16.8	5.4
	2	"	"	"	34.5	9.0	34.3	"	"
	3	"	"	"	35.0	8.0	34.8	"	"
475	1	Clean	1 mm T	0.0	28.5	13.4	38.1	16.8	5.4
	2	"	"	"	26.5	12.9	39.5	"	"
	3	"	"	"	27.0	12.3	38.5	"	"
475	1	S.Char	1 mm T	0.0	30.5	10.1	37.2	"	"
	2	"	"	"	31.5	8.9	37.4	"	"
475	1	SFM	New	0.0	33.6	14.0	34.6	12.8	5.0
	2	"	"	"	26.6	10.8	44.8	"	"
	3	"	"	"	34.4	10.9	36.9	"	"
475	1	SFM	Tr. only	0.0	37.6	15.1	41.9	-	5.4
	2	"	"	"	41.4	11.4	41.8	-	"
	3	"	"	"	38.1	13.6	42.9	-	"
475	1	None	1 mm T	0.0	23.4	18.8	35.6	16.8	5.4
	2	"	"	"	23.6	17.2	37.0	"	"
	3	"	"	"	27.8	12.5	37.5	"	"
	4	"	"	"	26.6	14.6	36.6	"	"

Table 10.10 Product Phase Distribution, Wt.%

In these figures only oil and gas are measured directly from experimental data. Steel and inorganics are taken from the manufacturers specification, leaving char to be calculated by difference (although occasional direct char measurements agreed). Due to the consecutive batch nature of these experiments a clearer view is seen by averaging the results, as is shown in Table 10.11. These results are plotted in Figures 10.6 and 10.7.

10.2.3.3 Chemical Analyses

The chemical analyses of these products were performed using the methods described in Section 8.3.1. The oil analyses are expressed in weight percent of oil and are given in Table 10.12. The chromatographic analysis represents the liquid portion of the oils; it was found by fractionation that oil samples on average contained 8.5 wt. % solid carbon.

The results of pyrolysis gas analysis are given in Table 10.13. The integrator output gives the percentages in weight terms but as gas calorific values are normally given in J/m^3 the figures here are quoted in volume percent. As in the oil analyses no results were obtained for the experiments using clean melt and additional surface char. In most cases no inorganic gases can be present but where steam is passed some carbon oxides may be formed. These cannot be detected due to mass occlusion with nitrogen, ethylene and propane.

The char analyses were not universally carried out but those performed, using methods described in Section 8.3.1 are given in Table 10.14.

Temp ^{o}C	Melt	Tyre	Steam, g/min	Oil, wt.%	Gas, wt.%	Char, wt.%	Steel, wt.%	Inorganics, wt.%
475	SFM	1 mm T	0.0	28.8	10.9	38.0	16.8	5.4
525	"	"	"	27.2	14.0	36.6	"	"
650	"	"	"	23.0	17.9	36.9	"	"
475	SFM	1 mm T	0.7	36.3	6.9	34.7	16.8	5.4
"	"	"	1.3	30.7	8.6	38.3	"	"
"	"	"	2.3	33.0	8.1	36.7	"	"
"	"	"	4.6	33.1	7.8	36.9	"	"
650	"	"	2.3	27.5	9.3	41.0	"	"
475	SFM	1 mm T	2.3HS	33.8	7.5	36.5	16.8	5.4
475	Clean	1 mm T	0.0	27.3	12.9	38.7	16.8	5.4
	S.Char	"	"	31.0	9.5	37.3	"	"
475	SFM	New	0.0	31.5	11.9	38.8	12.8	5.0
	"	Tr.only	"	39.0	13.4	42.2	-	5.4
475	None	1 mm T	0.0	25.4	15.8	36.6	16.8	5.4

Table 10.11 Average Product Phase Distribution

mm T - millimetres tread

HS - Head space (steam injection)

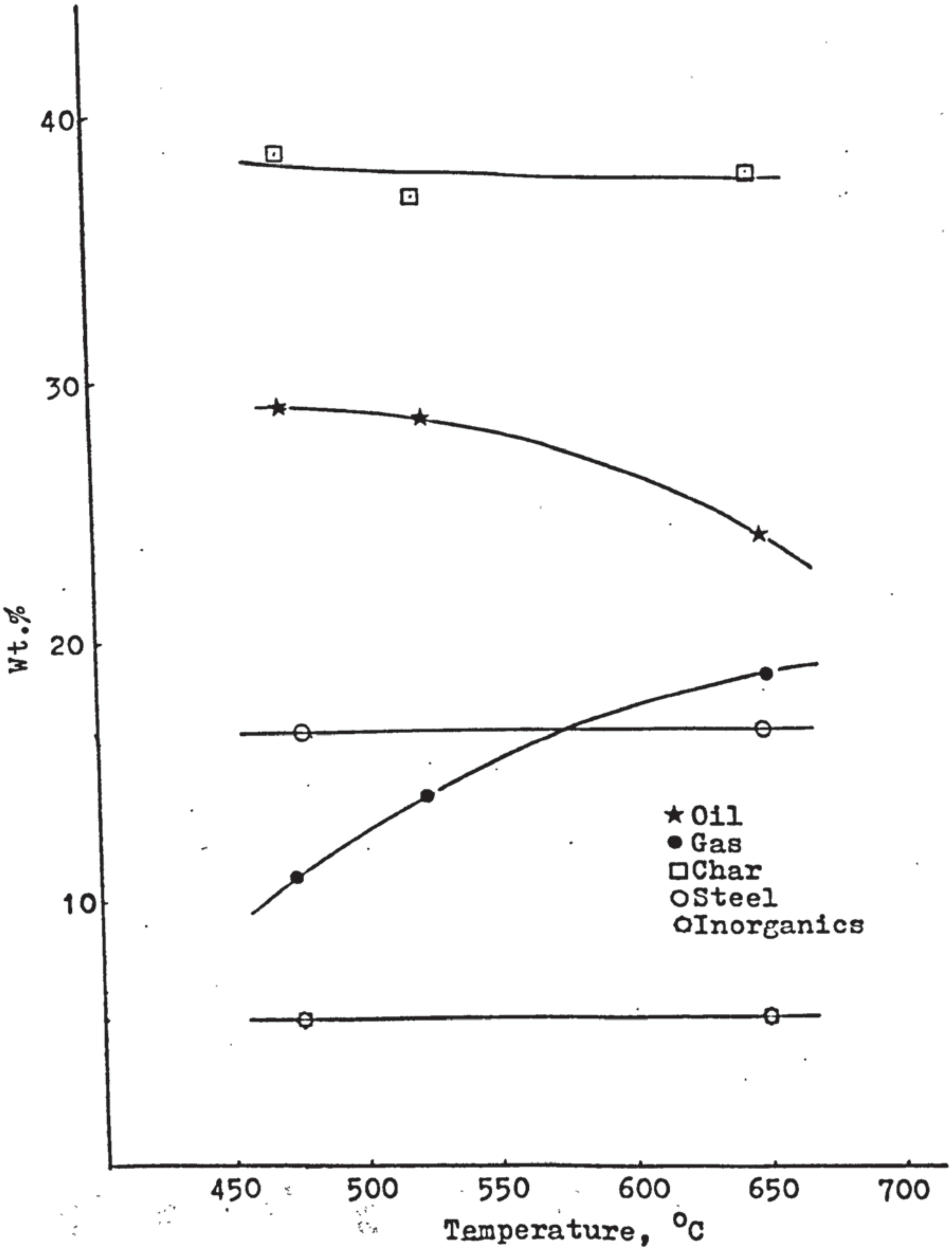


Fig.10.6 Average Product Distribution
(Parametric Investigation)

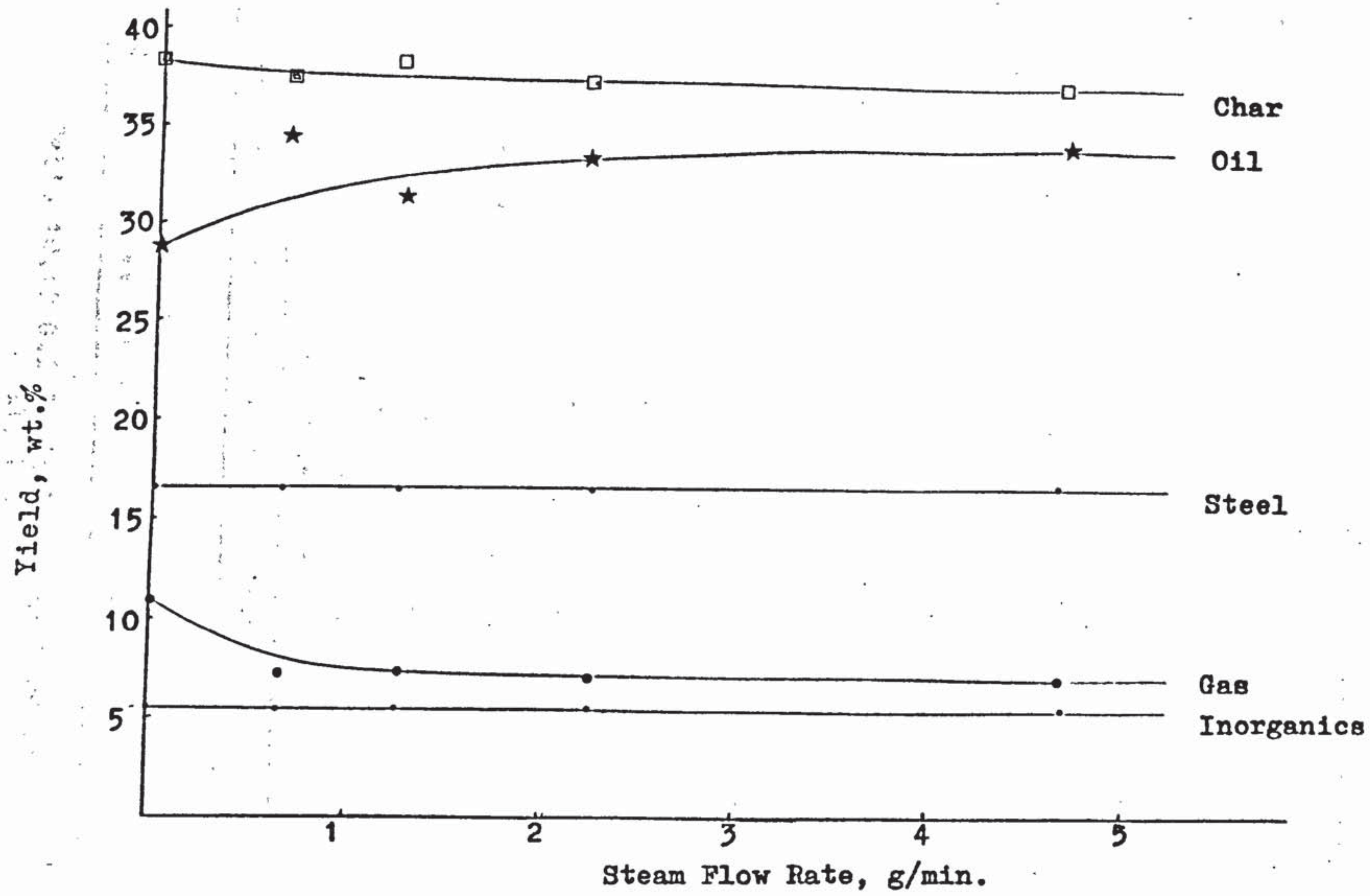


Fig.10.7 Product Yields vs. Steam Flow Rate (475°C)

Temp. °C	475	525	650	475	475	475	475	650	475	475	475	475	475	475
Melt	SFM	SFM	SFM	SFM	SFM	SFM	SFM	SFM	SFM	Clean	S.Char	SFM	SFM	None
Tyre	1mmT	1mmT	1mmT	1mmT	1mmT	1mmT	1mmT	1mmT	1mmT	1mmT	1mmT	New	Tread	1mmT
Steam, g/min	-	-	-	0.7	1.3	2.3	4.6	2.3	2.3HS	-	-	-	-	-
Isoprene	0	0								Na	Na	0	0	1.5
Butadienes	0	0	0.2	0.4	3.7	4.2	4.6	4.8	5.4			0	0	0.1
C_5	0	0	0									0	0	0.2
$n-C_6$	0.2	1.7	0.6	1.2	1.8	1.4	1.9	2.0	1.8			0	0	0.3
C_6	0	0	1.2	0	0	0	0	0	0			0	0	0
$n-C_7$	1.0	1.7	1.3	3.6	2.8	1.8	2.0	1.0	1.3			7.0	3.2	2.2
C_7	0.5	2.3	1.3	1.2	0.9	0.6	1.0	0.5	0.7			0	0	2.5
$n-C_8$	1.8	2.4	1.8	1.9	1.9	1.0	2.0	0.6	2.0			2.4	1.7	2.4
C_8	4.1	3.4	2.4	5.0	4.9	4.0	4.2	1.9	5.0			7.0	3.0	3.8
$n-C_9$	0		0	0	0	0	0	0	0			0	0	0
C_9	0.2	6.9	0.4	0	0.8	0	1.2	0.2	0			0	0.6	6.7
Styrene	5.0		4.6	7.1	6.8	5.7	5.8	4.2	6.0			9.3	8.3	
Benzene	1.4	2.4	5.1	1.8	2.1	1.3	1.7	5.3	1.7			3.1	0.4	2.0
Toluene	8.8	16.0	22.0	9.2	8.9	6.7	6.4	19.1	6.9			11.5	9.5	8.3
Xylenes	10.3	10.1	15.5	4.0	3.6	3.2	3.2	14.9	3.3			4.0	2.7	5.8
E. Benz.	6.8	5.0	5.2	3.2	2.9	2.7	3.0	4.4	3.0			5.0	10.1	5.0
Cumene	2.5	4.3	8.3	2.4	2.6	1.7	2.4	6.7	2.1			2.9	1.7	2.6
P. Benz.	1.0	1.0	0.2											5.0
B. Benz.	10.5	4.1	3.0	10.9	13.6	19.4	18.5	5.5	19.1			3.2	8.9	5.4
C_{10}			3.6											
C_{11}	2.2	2.6	2.8	6.1	5.3	5.6	6.0	5.3	5.4			6.3	1.4	2.4
C_{12}	6.9	4.7	4.6	7.4	4.4	6.1	7.5	5.3	6.2			5.1	7.0	6.1
C_{13}	4.2	2.4	4.8	2.0	2.4	2.2	2.4	2.8	2.0			2.2	2.4	5.0
C_{14}	3.8	5.7	3.3	5.1	5.0	5.1	5.3	7.7	5.3			8.6	9.3	3.8
C_{15}	4.6	4.9	1.8	2.3	3.5	2.2	2.7	1.9	2.1			3.4	3.7	4.6
C_{16}	6.5	5.4	2.8	6.9	5.4	6.8	5.2	3.8	6.8				6.1	6.6
C_{17}	3.8	10.1	1.2	3.5	4.1	3.6	2.0	1.3	3.4			19.0	3.4	3.8
C_{17+}	13.3	5.1	3.0	14.4	11.5	13.6	12.2	1.9	10.2				14.5	13.9
	99.4	102.2	101.0	99.6	98.8	98.9	101.2	101.1	99.7	-	-	100.0	97.9	100.0
Aromatics	35.8 - 46.3	38.8 - 49.8	63.9	30.6 - 38.6	30.5 - 39.5	30.0 - 44.9	27.9 - 41.0	56.0 - 60.1	34.0 - 42.0	-	-	36.5 - 39.0	32.3 - 41.2	28.7 - 40.8

Table 10.12 G.L.C. Analysis of Product Oil, Wt.%

Temp. °C	475	525	650	475	475	475	475	650	475	475	475	475
Melt	SFM	SFM	SFM	SFM	SFM	SFM	SFM	SFM	SFM	SFM	SFM	None
Tyre	1mmT	1mmT	1mmT	1mmT	1mmT	1mmT	1mmT	1mmT	1mmT	New	Tr.only	1mmT
Steam, g/min	0	0	0	0.7	1.3	2.3	4.6	2.3	2.3HS	0	0	0
Hydrogen	5.0	7.0	8.5	6.0	5.2	4.3	4.2	7.9	4.4	5.3	4.8	9.5
Inorganics	0	0	0	$-C_2$	$-C_2$	$-C_2$	$-C_2$	$-C_2$	$-C_2$	0	0	0
Methane	17.4	21.4	17.2	17.9	18.0	19.1	18.8	18.5	33.4	18.6	26.2	47.2
C_2	17.4	14.2	13.4	11.4	11.1	11.0	10.5	10.1	15.4	10.9	18.5	14.6
C_3	14.4	11.5	10.5	10.7	11.5	10.7	10.2	14.4	10.0	10.4	13.8	16.8
Butanes	24.6	3.2	2.5	22.9	25.5	32.1	33.7	2.0	23.5	19.7	20.7	1.6
Butenes		9.9	10.8					10.5				0.7
Isoprene	15.7	16.2	16.3	23.9	22.5	19.9	18.0	19.5	8.1	23.6	5.8	4.3
1,3-Butadiene	4.7	8.3	8.4	6.1	5.0	2.9	2.9	4.5	2.1	8.2	4.2	3.1
Pentanes	3.6	3.6	12.6	1.4	1.0	0	0.5	10.6	2.0	3.8	4.6	1.6
Pentenes		3.6				0						11.1
	102.8	98.9	100.2	100.3	99.8	100.0	98.8	98.0	98.9	100.5	98.6	100.5

Table 10.13 G.L.C./Mass Spectroscopic Analysis of Product Gases, Vol.%

Temp °C	Melt	Tyre	Steam g/min	Carbon wt.%	Volatiles wt. %	Ash wt.%	Sulphur wt. %
475	SFM	1mmT	0	81.6	1.2	15.6	1.6
525	"	"	0	82.6	1.0	15.1	1.3
650	"	"	0	84.5	1.0	14.1	1.4
475	"	"	2.3	83.0	0.8	15.0	1.2
475	None	"	0	90.5	1.6	5.0	2.9

Table 10.14 Pyrolysis Char Analyses, Wt.%

10.2.3.4 Physical Properties

The crude filtered oil was subjected to a number of physical tests detailed in Section 8.3.2. The results of these tests are given in Table 10.15.

The details of the fractionation, performed using simple glassware, are given in Table 10.16. Each fraction was analysed by GLC so that an approximate idea of its components could be gained. Although not as accurate as carefully performed chromatographic analysis the fractionation served to confirm these results. The sample used was a collection of those oils from ordinary experiments at 475 and 525°C. The total input was 175g which gave total products measured of 159.3g indicating a loss (volatiles) of 15.7g. Many of the fractions collected were observed to change colour, usually darkening, if left for several weeks.

Temp°C	475	525	650	475	475	475	475	475	475	475	475
Melt	SFM	SFM	SFM	SFM	SFM	SFM	SFM	SFM	SFM	SFM	None
Tyre	1mmT	1mmT	1mmT	1mmT	1mmT	1mmT	1mmT	1mmT	New	Tr.only	1mmT
Steam, g/min	0	0	0	0.7	1.3	2.3	4.6	23HS	0	0	0
Cal.Val., MJ/kg	41.4	41.4	37.0	42.6	38.3	40.1	38.0	40.0	39.6	40.5	40.0
Flash pt., °C	37	35	35	35	34	35	36	37	36	36	34
Density, kg/dm	0.88	0.87	0.89	0.91	0.91	0.90	0.92	0.91	0.88	0.93	na
Viscosity, cS	4.9	4.1	3.5	7.4	4.2	4.6	3.8	8.2	6.5	11.2	na
S. Tension, N/m	0.0306	0.0304	0.0295	0.0270	0.0297	0.0290	0.0296	0.0305	0.0311	0.0320	na

Table 10.15 Physical Properties of Pyrolysis Oil

Fraction Temp. °C	Wt.	Wt.%	Typical Components
18 - 60	(15.7)	9.0	Isoprenes, butadienes, C_5
60 - 70	9.0	5.1	C_6
70 - 78	-	-	-
78 - 85	6.1	3.5	Benzene
85 - 95	13.5	7.7	C_7
95 - 105	7.9	4.5	H_2O
105 - 115	8.6	4.9	Toluene
115 - 130	8.4	4.8	C_8
130 - 137	14.0	8.0	Ethyl benzene, Xylenes
137 - 144			
144 - 149	4.2	2.4	Styrene
149 - 155	-	-	-
155 - 165	10.9	6.2	C_9, Cumene, Propyl benzenes
165 - 173			
173 - 181	24.6	14.0	C_{10}, Butyl benzenes
181 - 190			
190 - 230	13.3	7.6	C_{11}, C_{12}, C_{13}
230 - 290	11.4	6.5	C_{14}, C_{15}, C_{16}
290 - 340	13.7	7.8	C_{17+}
Residue	15.2	8.7	
	175 g	100.7	

Table 10.16 Fractionation of Pyrolysis Oil
(Samples from 475 & 525°C)

The physical properties of the gas to be evaluated were only calorific value and density. Both were calculated from composition and are given in Table 10.17.

Temp °C	Melt	Tyre	Steam g/min	Calorific Value MJ/m^3	Density, g/dm^3
475	SFM	1mmT	0	82.9	1.65
525	"	"	0	83.2	1.78
650	"	"	0	84.9	1.90
475	"	"	0.7	89.9	1.93
475	"	"	1.3	85.8	1.90
475	"	"	2.3	90.5	1.97
475	"	"	4.6	84.6	1.90
475	"	"	2.3HS	84.0	1.88
475	"	New	0	82.4	2.00
475	"	Tr.only	0	74.0	1.60
475	None	1mmT	0	58.6	1.25

Table 10.17 Physical Properties of Gases

The physical properties of the char are given in Table 10.18. Those properties measured were those that are relevant to the probable use of the char as a fuel. The calorific values given are the bomb values while those in brackets are those calculated from the carbon content which are the relevant values for consideration of in situ combustion.

Temp °C	Melt	Tyre	Steam g/min	C.V.MJ/kg	(Calc.)	Density, kg/dm^3
475	SFM	1mmT	0	20.5-21.5	(25.8)	0.65
475	"	"	2.3	22.0-23.0	(26.2)	0.65
475	None	"	0	24.8	(29.0)	0.60

Table 10.18 Physical Properties of Pyrolysis Char

(In addition it was planned to evaluate the suitability of the pyrolysis char as a rubber reinforcing material. However at the time of writing this data was not available.)

No tests were applied to the steel recovered. Visual evaluation indicates that it is only gradable as a low value scrap.

10.3 Discussion

10.3.1 Introduction

In the discussion comment will be concentrated on the interpretation and meaning of laboratory results. The data will be used to verify physical and chemical models of the system, to make comparisons with other processes and to evaluate the possibilities of process scale-up.

The physical model proposed is discussed at an early stage and although most of the suggestions are based on well documented and common phenomena it is clear that the proposals are put forward in retrospect of the results. The function of the discussion immediately following is to confirm the conjectures put forward (the refutations having already been eliminated).

Comparison with other work and developing processes has been difficult and complicated mainly due to the differing manners in which data have been presented. It has therefore been necessary to, fairly, adjust results to make direct comprisons with worldwide publications. (Much is primarily covered in the Literature Survey.)

The proposals and discussion regarding the chemistry of pyrolysis and the scaling-up of the process are considered independently of published data. This is due to the facts that the work is fundamentally different to most published work and that data with which to make these sorts of comparisons is rare.

10.3.2 Physical Model

It was clear from the outset that quantitative modelling would involve a great deal of work and not be practical on the timescale of this project.

Before discussing the physical mechanisms involved in the pyrolysis model it is necessary to establish the overall thermicity of the pyrolysis reactions. The experimental work was performed in such a way as to make direct heat measurements impossible and so the heat of pyrolysis had to be calculated from the heat values (specific heats) of reactant and products.

The diagram in Fig. 10.8 shows two alternative routes from tyre to the final products of carbon oxides and water. The diagram also shows the heats involved, some of which are known and some of which must be calculated. Fortunately the heat of combustion for worn tyre is well documented varying from 29.1 MJ/kg to 31.4 MJ/kg.(1) This heat must, of course, be equal to the sum of all the heats involved in the pyrolysis route. Here the balance will be performed for the reaction at 475°C using the appropriate yields of products.

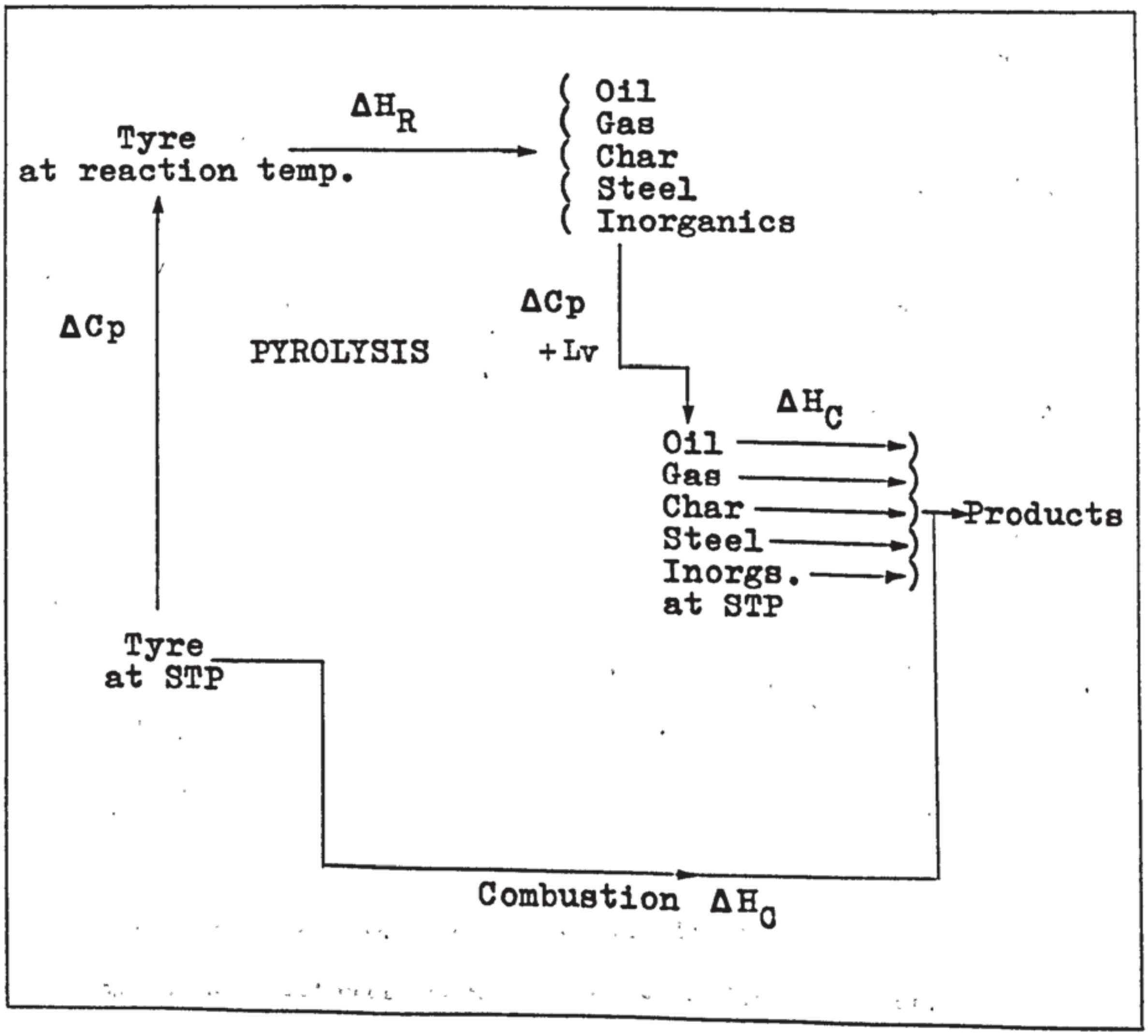


Fig. 10.8 Pyrolysis Heat Diagram

$$\begin{array}{lccccccccc} \text{Tyre} & \xrightarrow{\Delta H_R} & \text{OIL} & + & \text{GAS} & + & \text{CHAR} & + & \text{STEEL} & + \ \text{INORGS.} \\ 1\text{kg} & & 288\text{g} & & 109\text{g} & & 380\text{g} & & 168\text{g} & \ \ 54\text{g} \end{array}$$

The heat capacity of the tyre was calculated from the manufacturers specification, using standard data and found to be 1.11 kJ/kg. Therefore 1kg would require only 0.50 MJ to heat it from 25 to 475°C. Using the yields found experimentally the heat lost in cooling the products can also be calculated. This was found to be 1.33 kJ/kg which over the drop in temperature concerned is 0.60 MJ for 1 kg of tyre fed. The final step in the cycle is the heats of combustion of the products. Here the inorganic materials are taken as incombustible as they are also products of the quoted combustion process. These heats are: oil, 41.4 MJ/kg, gas 50.3 MJ/kg and char 29.0 MJ/kg.

The thermicity of the pyrolysis reaction is given by:

$$\Delta H_R = \Delta H_c\,\text{OIL} + \Delta H_c\,\text{GAS} + \Delta H_c\,\text{CHAR} + (Cp+Lv)\text{PRODS} - \Delta Cp\,\text{TYRE} - \Delta H_c\,\text{TYRE}$$

$$= (41.04 \times 0.288) + (50.3 \times 0.109) + (29.0 \times 0.380) + 0.6 - 0.5 - 29.1$$

$$= 11.92 + 5.48 + 11.02 + 0.6 - 0.5 - 29.1$$

$$= -\ 0.58\ \text{MJ/kg}$$

This shows the pyrolysis reaction to be slightly exothermic. However in terms of heat actually supplied the specific heat capacity requirement for 1 kg of tyre must be re-added, making the process a net supplier of heat by only 0.08 MJ/kg. The pyrolysis is essentially autothermic.

The small exothermic heat of reaction compares closely with - 0.30 MJ/kg obtained by Collins et al.(329) at NASA using Differential Scanning Calorimetry. Larsen(75) using a technique similar to that used here obtained an exothermic value of ca. 3.2 MJ/kg.

The model now proposed is based on an unreacted shrinking core to which mathematical programmes could be applied given time(79). It is assumed that heat transferred from the molten salt initially causes a reaction at the tyre surface one of whose products is a carbonaceous char that remains attached to the unreacted surface. Thus at any subsequent stage the unreacted tyre is surrounded by a porous char jacket. This jacket is not wetted significantly by the melt and so after initial stages there is no direct melt to tyre contact. The basic mechanism proposed is that heat is transferred from the melt to the char jacket through which it is transferred to cause reaction at the unreacted surface. The products produced then diffuse back out through the char jacket. The off-coming vapours may be considered to form a further layer around the char jacket. Fig. 10.9 shows a graphic description of the model based on a spherical particle although in reality most tyre pieces will approximate to cuboids.

The model proposed offers three alternatives for the rate controlling mechanism: heat transfer inwards, mass transfer outwards and chemical reaction. The changes in pyrolysis rate with

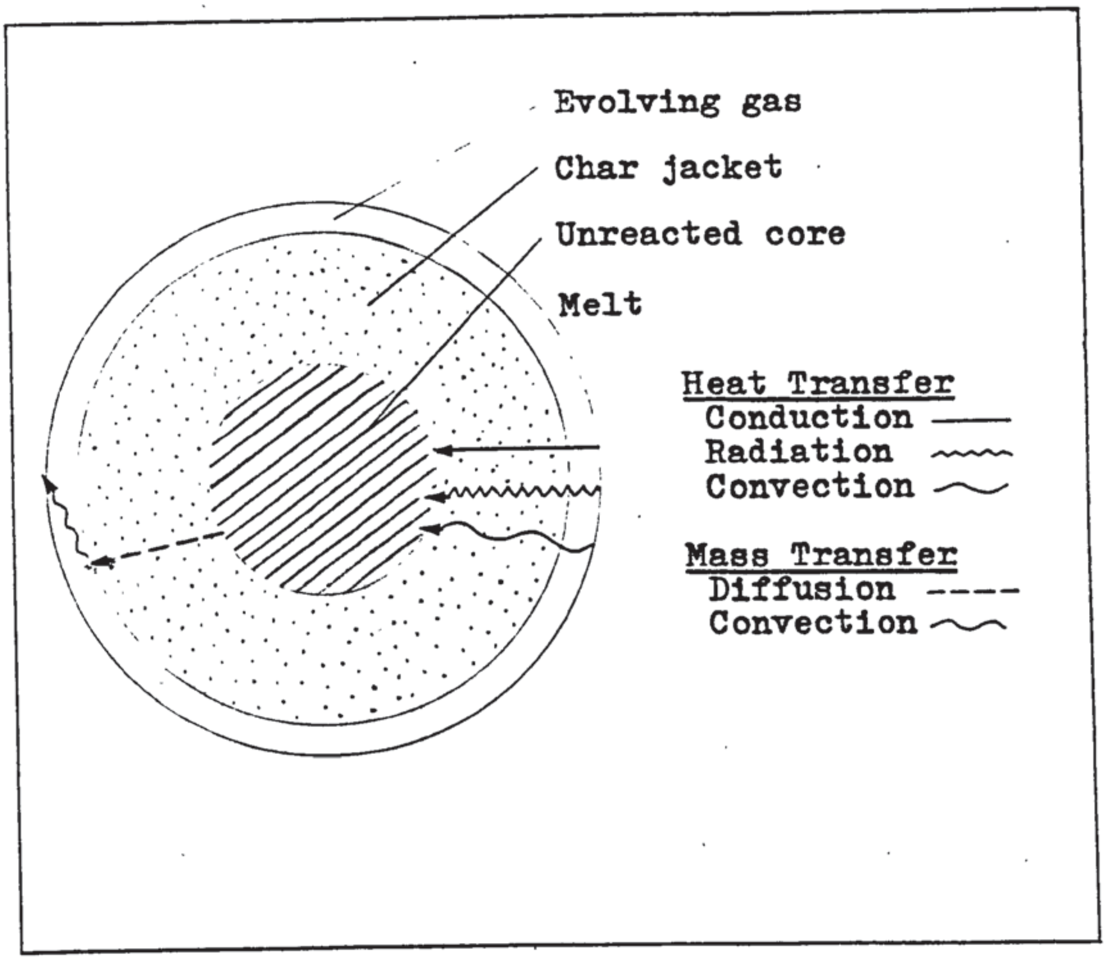


Fig.10.9 Physical Pyrolysis Model

temperature immediately suggest that reaction rate is not the controlling factor which fits with theory regarding heterogeneous systems. The plot of rate vs temperature is seen in Fig. 10.6. Furthermore it can be shown (Fig. 10.10) that the data does not fit the Arrhenius equation for kinetic rates.

It is clear therefore that the rate controlling mechanism must be heat or mass transfer. Dealing first with heat transfer, the reaction thermicity or at any rate the heat requirement is a crucial factor. If the value of ΔCp TYRE + ΔH_R is negative (exothermic)

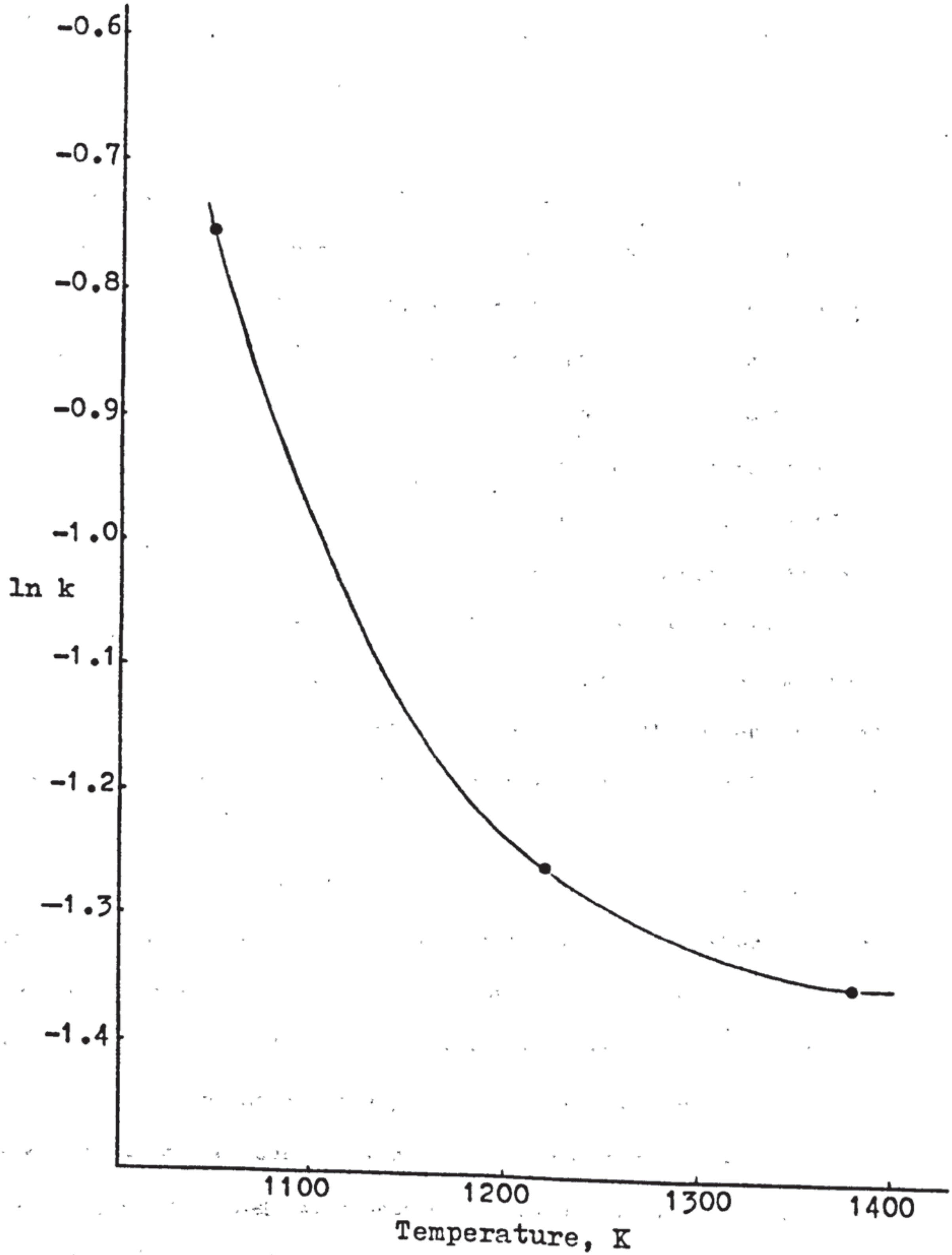


Fig.10.10 Arrhenius plot of pyrolysis rates

then, of course, beyond initiating the reaction, heat transfer is irrelevant. In the exothermic situation the reaction will be self-sustaining in much the same way as combustion. However, since the calculation shows only marginal exothermicity the endothermic case should also be considered.

It is clear that heat transfer within the stirred melt is highly effective but on reaching the gases and char surrounding the tyre particle considerable resistance is experienced. Heat transfer through these layers can be by convection, radiation or conduction: all three directly operate in the gas but there are complications in the char. Convection through the char is limited due to its cellular structure which also limits radiation (although the efficiency of absorption is probably high due to its colour). Conduction through these materials will depend on thermal conductivities but is not likely to be high. A more scientific evaluation is to examine the ways in which these heat transfer methods alter with temperature and attempt to fit the variation to the measured rate data in Fig. 10.4.

Convection is effected primarily by turbulence in the system (obviously limited in the char cellular structure) and should behave in a linear relationship with temperature. Conduction behaves in the same way as it is dependent on a temperature difference ($\propto T_1 - T_2$). Radiation is dependent on absorption and emissivity and is generally proportional to the fourth power of the temperature differences (i.e. is proportionately much greater at higher temperatures). None of the heat transfer phenomena are therefore capable of explaining the falling rate of increase of pyrolysis rate with temperature.

The remaining alternative for rate control is mass transfer of products from the reaction site. Mass transfer out through the carbon jacket will occur by diffusion which is proportional to $(\text{temperature})^{3/2}$. In Table 10.19 are given values for rate and $(\text{temperature})^{3/2}$ which are plotted in Fig. 10.11.

Temp. K	Rate, k	$(\text{Temp})^{3/2}$
748	0.16	20.46×10^3
798	0.20	22.54 "
923	0.25	28.04 "

Table 10.19 Rate vs. $(\text{Temperature})^{3/2}$

The figure based on diffusion theory shows a plot close to linearity indicating the major controlling factor to be diffusion. If the values at 475°C and 650°C are taken the diffusion rate would be expected to increase $(^{923}/_{748})^{3/2}$ times (i.e. 1.37). The experimental rate constant at 475°C is 0.16; using this fact the expected rate constant at 650°C on the diffusion theory is 0.23, which is very close to that experimentally observed. The indication therefore is that the rate of pyrolysis is controlled by the rate at which products can diffuse away from the reaction site.

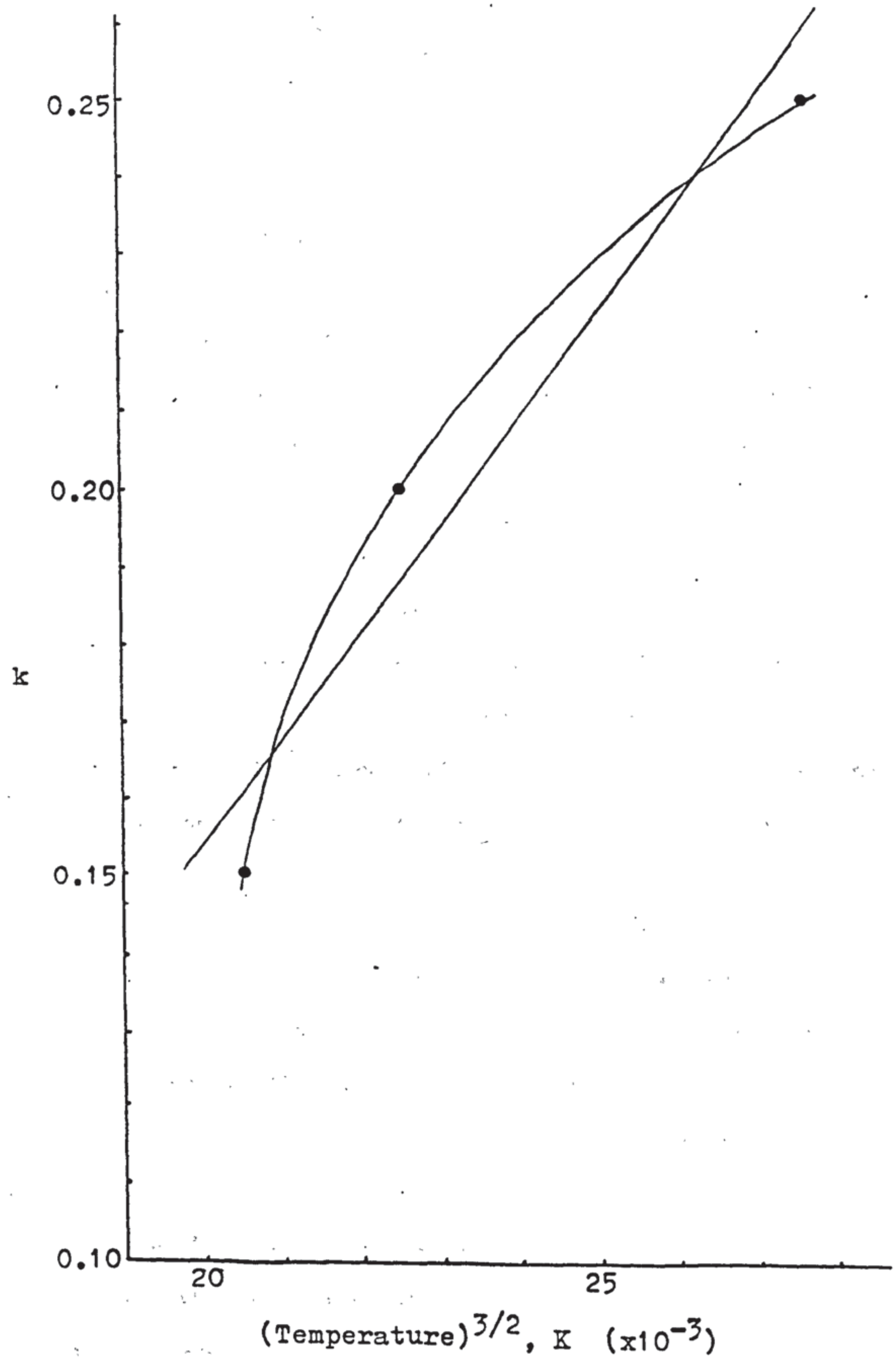


Fig.10.11 Rate vs. (Temperature)$^{3/2}$

10.3.3 Rate Data

The results show that the batch rates averaged over a whole run vary from about 4.5 g/min at 475°C to about 9.5 g/min at 650°C; both from 30g batches in 0.75 litres of melt. The corresponding instantaneous rates for 30g tyre/0.75 l. melt are 11.2 g/min at 475°C and 32.0 g/min at 650°C. Although the rate is a function of (in the extreme) heat supply and more important product removal it is possible to use a residence time expression as the main method of process comparison.

Using Figs. 10.1 and 10.2 together with the known flush-out characteristics of the reactor the residence times for the 30g samples in the 0.75l reactor can be found. These are 2.5 - 3.0 mins at 475°C, about 2.0 mins at 525°C and about 1.5 mins at 650°C. Assuming a linear scale-up for all cut tyres these can be used for direct comparisons.

In early papers(75,182) Larsen makes no statements concerning rates beyond saying "reaction was fast" or "pyrolysis took place rapidly". The first hints come in later papers (184) where pyrolysis of a 2" square portion (40g) is said to be complete within 5 mins, at 450°C. Later in a private communication(185) the residence time under similar circumstances in KCl/LiCl was given as about 3 mins. None of the Rockwell work(186,187) or the Cirta-Extramet proposal(189) make any mention of rate data. Larsen's data are in broad agreement with those obtained here.

The residence times obtained from fluidized beds vary from 1 min for a 5 cm diameter (35g) piece at 600°C in Japan Gasoline/Nippon Zeon's REPROX process(186) to 3 mins for a 700g section in the Hamburg pilot plant(173). Direct comparisons are difficult but it is clear that fluidized beds give rates comparable to or higher than molten salts.

Kobe Steel's rotary kiln (UTIFIC) is quoted(67) as having residence times of 8 mins at 800°C to 18 mins at 500°C which are similar to the Herbold claims(102). These processes rely on heat transfer through the reactor wall and the gases inside and are therefore, not surprisingly, slow. This trend is confirmed by the results in Table 10.7 where the rate in a meltless reactor is shown to be far lower. Tosco II publications(133) are not specific but residence time at 900°C is said to be "very short".

The conclusion at this stage is that molten salts offer a reaction medium capable of very high rates; only fluidized beds can be considered comparable.

The rate data provides a good insight into the physical mechanism controlling pyrolysis, as has been shown in Section 10.3.2 but it also enables some idea of the capacity of scaled-up plant to be obtained. In this section linear scale-up is used to calculate the through-put of a commercial reactor. The process is viewed in two ways: firstly as a batch process and secondly as a continuous process based on a tyre concentration of 40g/l. The capacities per cubic meter of melt are given in two figures, the figure in brackets being one making a linear allowance for the difference in surface areas of cut and whole tyres.

Temp. °C	Batch Capacities, t/m^{3}yr		Continuous Capacities, t/m^{3}yr	
	Linear	(Area)	Linear	(Area)
475	2430	1215	5390	2700
525	3075	1540	11875	5940
650	4495	2250	14200	7100

Table 10.20 Scaled-up Rate Data

The year used here is defined as 6000 working hours. The difference in area to mass ratios is taken as 50% as it is conceivable that the sliced tyre has twice the total surface area of a whole tyre. (The estimate is such as to minimize the estimated capacity.)

The indication is that a 4m^3 reactor operating at 475°C would be capable of pyrolysing some 10,000 tonnes per annum which is the amount likely to be available in a highly populated area such as the West Midlands. The capacity of the plant can be increased by increasing the melt volume or by increasing the temperature of operation. The latter will have an adverse effect on the product phase distribution, the full meaning of which will be discussed later. At this stage it is sufficient to say that a large mass of tyres can be pyrolysed in a relatively small volume of melt.

10.3.4 Analyses and Properties of Products

10.3.4.1 Product Phase Distribution

As will be demonstrated fully at a later stage oil is the favoured pyrolysis product; it has a high calorific value and being liquid is compact and easily storable. The results in Table 10.10 show several clear facts. Firstly oil yields drop with increasing temperature in favour of gas. This trend can be controlled by passing of limited quantities of steam. The second clear trend is that oil is associated with the "fleshy" tread portions of the tyre. This is likely to be beyond the control of the process operator since the degree of wear in the feedstake is a matter of public habit and legal requirements. In these studies a typical steel radial with the present legal minimum tread was used.

The temperature of operation can be controlled so as to optimize the oil yield. Table 10.21 shows the total amounts of oil obtainable per annum at different temperatures and rates (oil yield = rate x proportion realized as oil). In Fig. 10.12 temperature is plotted against total oil showing clearly the immediate increase in realization

Temp. °C	Rate t/m^3/yr	Oil yield, wt.%	Total Oil, t/m^3 melt/yr
475	2700	28.8	778
525	5940	27.2	1605
650	7100	23.0	1635

Table 10.21 Total Oil Realisations

followed by a rapid stabilization. It should be noted that increasing operating temperature will increase the capital cost of plant and probably running costs, but it can be seen that for a small temperature increase say to 500 - 550°C a rate benefit can be gained. A further factor to be considered is tyre availability; the suggested $4m^3$ plant at 525°C would have a capacity over 20,000 tonnes per annum, a quantity unlikely to be collectable over a small region. Since collecting over a larger region would add to running costs (transport) the obvious option is to reduce the melt volume to say $2m^3$ and continue on the 10,000 tonne scale. (The balance here is clearly one of capital cost vs running cost.) The intermediate conclusion, subject to scrutiny in later chapters, is that 525°C offers the greatest rate of oil production but 475°C offers the best yield.

The passing of steam can further increase the oil yield and provided only limited amounts are passed the rate is little changed so the above argument would remain valid. However, steam passage does mean that oil and water are produced in a mixed stream and must be separated. This would probably be relatively simple, although some of the oil gained would be lost in the separation.

The increased oil yield on steam passage could be attributable to three factors: chemical reaction, head-space purging or nucleation in the condenser. The first can be eliminated as the oil composition is in the main unchanged, but the slight increase in lower weight fractions indicates nucleation may be a contributory factor. Experiments purging steam into and above the melt show very similar results

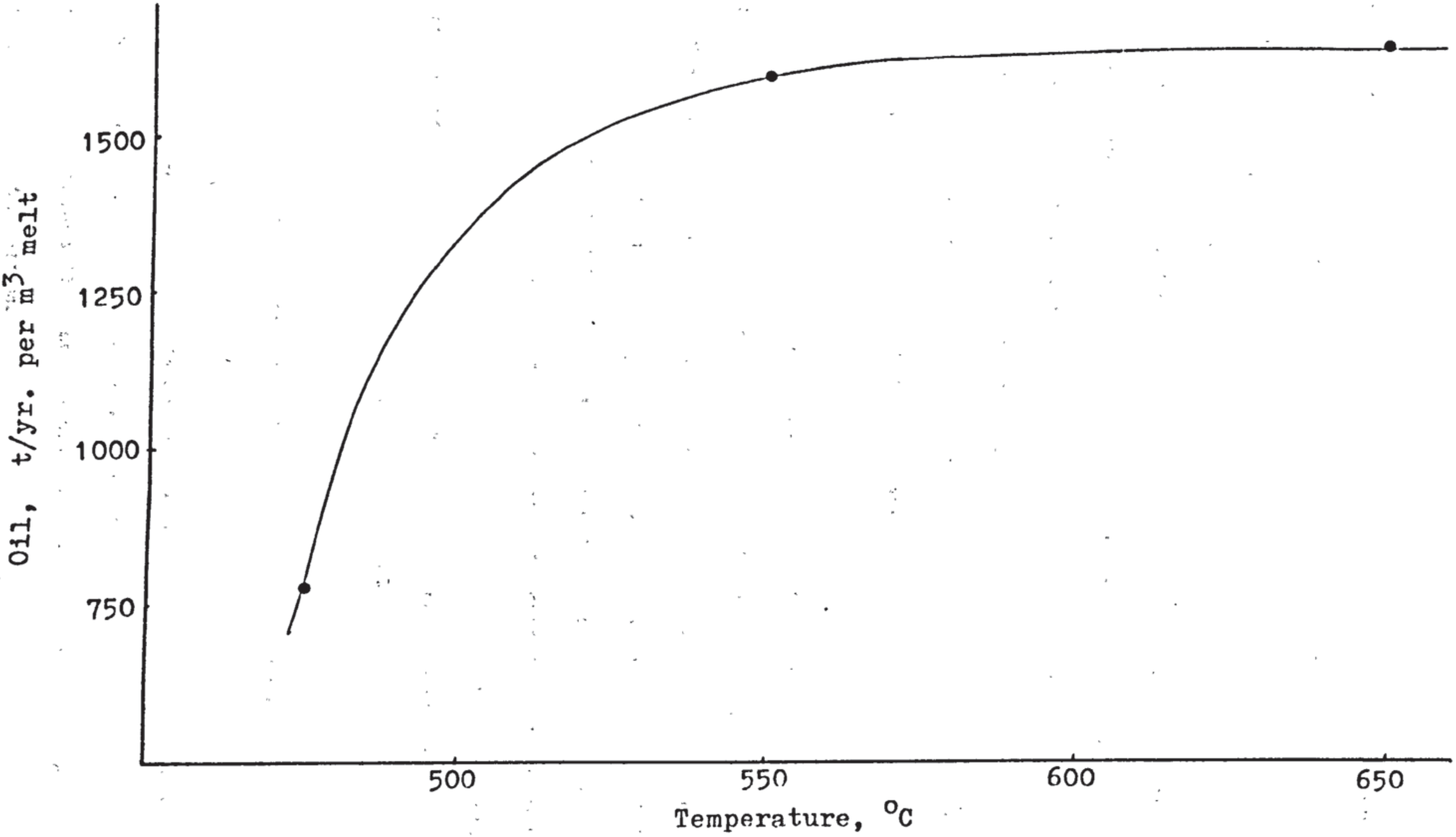


Fig.10.12 Total Oil Production Rate

indicating that the fast clearing of the head-space is the most important factor. Steam immediately condenses in the collection train slowing the volume flow to normal (not achieved at high nitrogen purge rates).

A calculation performed on the products to obtain the total heat recovered from a tyre shows that there is only a slight increase with temperature. This shows that the thermicity of pyrolysis is approximately constant. It also indicates that if external circumstances permit little product energy would be lost by total gasification at high temperatures.

Comparison of the product phase distribution given above with those obtained by other workers is difficult for two main reasons: 1) Feedstocks are not always comparable and 2) results are often presented neglecting one or two products. For example, Larsen(182) uses an unspecified tyre input and presents his results in terms of oil, gas and char only, neglecting steel (if present) and inorganics. Not only is this somewhat simplistic but yields of oil appear higher than in reality. In Table 10.22 the results are compared by subjecting published data to the following conditions:

1) Yields are expressed in terms of wt. % of tyre input.

2) The products are assumed to include 5.4 wt. % inorganics. In molten salt processes inorganics are treated as a separate product but in dry processes they are assumed to be present in the char and are subtracted therefrom.

3) A steel yield of 16.8 wt. % is assumed unless stated otherwise.

Although Table 10.22 does not list all tyre pyrolysis processes (further details are available in the Appendices) the comparable processes giving reasonable details are listed. Bracketed under the process column are indications of the stage of development; laboratory, pilot, etc.

The results given in Section 10.3.2.3 indicate that for worn SP4 radials oil yields from 28.8 wt. % to 36.3 wt. % using steam can be achieved at 475°C. The low figure obtained without steam is clearly attributable to operational procedures and reactor design so may be improved. It should further be noted that the SP4 radial contains some 24.7 wt. % carbon black and so unless char gasification is taking place this must be considered an absolute minimum char yield. Also inconvertible are steel and inorganics, making 53.1 wt. % the maximum total hydrocarbon yield.

The residence time in the head space varies from less than 10 secs at the peak of a batch reaction to several minutes at the end. At the point where the tyre in melt concentration is 40 g / l the residence time is 15-25 secs. Purging with steam at 0.7 g/min (2.5 l/min at 800K) gives a maximum residence time of 30 secs and a great deal less at peak reaction. This steam purge comes close to simulating the residence time in the head-space of the continuous process where tyre concentration is maintained at 40g/l.

Workers	Process	Temp. ^{o}C	Oil, wt.%	Gas, wt.%	Char, wt.%	Steel, wt.%	Inorgs. wt.%	Ref.
Aston Univ.	M.Salt(L)	475	28.8	10.9	38.0	16.8	5.4	-
		525	27.2	14.0	36.6	"	"	-
		650	23.0	17.9	36.9	"	"	-
		475 New	31.5	11.8	38.8	"	"	-
		475 Steam	36.3	6.9	34.7	"	"	-
		650 Steam	27.5	9.3	41.0	"	"	-
Larsen/Tennessee	M.Salt(L)	500	35.5	8.7	34.6	"	"	(181-184)
DECO	M.Salt(?)	480	40.6	4.5	32.7	"	"	(136-138)
	R.Kiln(P)	600	35.2	21.0	25.6	"	"	
Hamburg Univ.	M.Salt(L)	700	18.6	20.9	38.3	"	"	(161)
	(L)	790	6.1	23.1	48.6	"	"	
	F.Bed (P)	720	25.6	21.0	32.2	"	"	(169-175)
Nip.Z/Jap.G.	F.Bed (P)	450	42.6	11.8	27.5	"	"	(178)
Herko	Kiln (P)	600	31.5	11.8	35.5	"	"	(102-105)
Tosco II	C.Balls(P)	900	37.2	18.3	23.3	"	"	(127-130)
USBM	Retort(P)	525	37.3	6.3	34.2	"	"	(119-124)
Kobe Steel	R.Kiln(P)	500	34.4	4.7	42.7	"	"	(146-149)
		700	36.5	12.2	30.1	"	"	
		800	31.2	23.9	23.7	"	"	
Intenco	Kiln (P)	n/a	29.2	9.6	39.0	"	"	(347)

Table 10.22 Pyrolysis Product Comparisons

Taking the oil yield obtained with steam passage at 475°C the results obtained are comparable with most of those quoted in the literature; however the unpurged yields are clearly low by literature standards. None of the literature mentions steam purges but most are continuous processes, explaining the good oil yields. Many processes operated batchwise have high gas purges and/or elaborate collection trains which again would improve oil yields.

Of the mentioned processes only DECO(136) and Nippon Zeon/ Japan Gasoline(177) have inexplicably high oil yields. Little is known of DECO but the latter operate a continuous pilot fluidized bed at 450°C. The type of plant and low temperature undoubtedly aid oil yield but the char yield of 27.5 wt. % is also suggestive of a low carbon black tyre. The oil yields from Kobe Steel(67) show an inexplicable trend and the char yield at 800°C is lower than the carbon black content of an SP4 radial(21). The low oil yield obtained on the Hamburg molten salt laboratory rig(168) are in line with batch non-purged results above. The project was terminated and no work performed on improvement of the yield.

The conclusion at this stage is that the normal results are low due to cracking of the oil in the reactor head-space. When this is eliminated using a fast steam purge the results are mostly comparable with those found in the literature.

10.3.4.2 Chemical Analyses

The oil produced is clearly a complex mixture of hydrocarbons in which no components dominate to the extent where fractionation would become viable. The aromatic content increases with temperature indicating the possibility that cyclization is occurring in the reactor. High aromatics are here associated with high temperature, long head-space residence, molten salt presence and worn tyres. The aromatic compounds are mostly alkyl benzenes, as mentioned in the literature, many of which are probably reaction products from the styrene-butadiene synthetic rubber. The SBR content of the tyre feed is 10.4 wt. % which can in no way account for all the aromatics found in the products. Details of the formation of many of the compounds in the oil are given in Section 10.3.6.

The only GLC analysis of comparable detail is that given in the USBM papers(119) which although being quoted in vol. % shows many similarities. However a less detailed GLC given by Sinn et al.(169) quoted in wt. % does confirm the quantitative details. The aromatic content is mentioned in passing by other workers and given in Table 10.23. Despite the confusion caused by units it is clear again that high aromatics are universally associated with high pyrolysis temperatures. The data from DECO and Nippon Zeon/Japan Gasoline are given as fractionation results, both having higher solid residues than given in results Table 10.15. It should also be pointed out that due to limited condenser capacity many of the C_5 compounds (including isoprene) tend to be found in the gas rather than oil.

Being a reducing, oxygen free atmosphere the gaseous products consist almost entirely of hydrogen and hydrocarbons. No hydrogen sulphide was detectable as it is absorbed in the melt.

Workers	Process	Temperature, °C	Aromatics
Aston	M. Salt	475	36-46 wt. %
		525	38-50
		650	64
Larsen	M. Salt	500	21-31 v. %
	Dry	500	51
Hamburg	F. Bed	700	58 wt. %
		790	65
USBM	Retort	500	34 v. %
Tosco II	C.Balls	900	95 v. %

Table 10.23 Oil Aromaticity

The gaseous product has a fairly even spread of hydrocarbons in the range $C_1 - C_4$ and, considering its boiling point, a large amount of isoprene vapour. Although not integrated separately $C_2 - C_4$ show a notable portion of olefins which considering conditions of formation and the free hydrogen present may be a little surprising. The isoprene and 1,3-butadiene are clearly a result of the scission of the polymers while the smaller products may be seen as further cracking products. This will be discussed further later.

Hydrogen has clearly presented other workers with a problem: Larsen(181-185) makes no mention of hydrogen. Larsen's methane content is notably higher and he has, probably by efficient condensers, placed isoprene and 1,3-butadiene in the liquid analysis. Hydrogen in the USBM results(119) was calculated via an experimentally measured calorific value and is very high but in other respects is very similar to the results in Table 10.12. Tosco II uses a partially oxidative atmosphere, so carbon oxides are also present but otherwise shows similar trends to other work.

In the analysis of char it is primarily essential only to obtain the carbon and sulphur contents. The carbon content will largely determine the calorific value while the sulphur will determine its acceptability as a fuel. Table 10.13 shows the carbon content to be 80-83 wt. % which is high for carbonaceous fuels. It will be seen in the next section that the measured calorific value does not come up to the level expected from this composition. (Solid fuel bomb determinations are susceptible to incomplete combustion.) The sulphur level is low by coal standards nevertheless care would have to be taken in open combustion but in the melt this is less important. The ash content can be accounted for mostly as entrained salt which would be much higher if the char were fully wetted by the melt. The tyre ash appears, perhaps surprisingly, to be as low as 5 wt. % as is shown by the melt-less experiment.

The carbon content of the char is very similar to that of other publications; Larsen 82 wt. %, USBM 84-86 wt. % and Tosco II 81 wt. %. The sulphur content at 1.4 - 2.5 wt. % is almost identical to Larsen's at 1.7 - 2.1 wt. % although USBM (2.0 - 2.5 wt. %) and Tosco II (2.3 - 2.5 wt. %) average slightly higher. The lowest levels being due to reaction of sulphide with the carbonate melt.

At this point two balances can be performed that help to confirm propositions in this section and verify the chemical analyses. These are aromatic and carbon balances respectively. Dealing with the aromatic balance first, the only aromatic in the tyre is styrene in the SBR. Table 10.24 shows the aromatic input and outputs. As was suggested earlier there are considerably more aromatics in the products than in the tyre feed. Styrene is broadly unaltered indicating that not all the aromatics originate from this source; the chemistry involved is discussed later.

IN	OUT				
TYRE	OIL	GAS	CHAR	STEEL	INORGS
2.4 wt.% as Styrene	Styrene 1.4- 2.6 wt.%	-	-	-	-
	Others 8.9-12.1 wt.%				
	Total 10.3-14.7 wt.%	None	None	None	None

Table 10.24 Aromatic Balance

The carbon balance is given in Table 10.25. Basically the carbon inputs and outputs are in good agreement which serves to confirm the accuracy of the chemical analyses.

IN		OUT				
Tyre		Products				
		Temp °C	475	525	650	475 steam
	wt.%		wt.%	wt.%	wt.%	wt. %
C. Black	23.7	OIL	25.2	23.8	20.1	31.5
Rubber	32.1	GAS	8.8	11.3	14.5	6.9
Organics	7.5	CHAR	30.6	29.9	30.8	28.5
Fabric	3.2	OTHERS	None	None	None	None
TOTAL	66.5	TOTAL	64.6	65.0	65.4	66.9

Table 10.25 Carbon Balance

10.3.4.3 Physical Properties

The physical properties of the products are given in some detail in Section 10.2.3.4, where it can be seen that they vary little with changes in pyrolysis conditions.

In Table 10.26 the oil obtained at 475 - 525°C is compared with the pyrolysis oil from other workers and with a standard fuel oil No. 6. The calorific value of the oil compares well with all other products and would improve after any stripping operations which may be necessary due to its low flash point. The low density indicates that the calorific value in volume terms will be lower but this and its low viscosity will give pumping and burning advantages. A further advantage on combustion is the low sulphur which appears similar to other molten salt oils.

	Aston	Larsen	Hamburg	Kobe	Herko	Tosco II	Nip.Z/J.Gas	No.6
Cal. Value, MJ/kg	41.4	37 - 42	-	41.8	40.0	41.9	39.7	42.5
Flash Pt., ^{o}C	37 PM	-	-	26	-	24 TCC	-	84 TCC
Density, kg/dm^3	0.87	-	-	0.92	-	0.97	0.95	0.97
Visc. $cS^{TEMP.}$	4.9^{20}	-	-	1.5^{50}	-	8.5^{24}	-	1.19^{24}
Sur. Tens., N/m	0.031	-	-	-	-	-	-	-
Residue, wt. %	9.5	-	-	1.0	-	3.4	5.7	10.4
Aromatics, wt. %	39-40	21-31 v %	58	-	-	95 v %	-	-
Sulphur, wt. %	0.5	0.6	0.4	1.0	-	1.0	1.4	1.2

Table 10.26 Comparison of Pyrolysis Oil Properties

Apart from the low flash point (decreased by Pensky Martens) which is mainly a storage problem, the only disadvantage as a fuel is the high solids residue. This is still lower than the No. 6 fuel oil but will restrict burner types, although it may be possible to remove some of these solids.

It is perhaps worth noting at this point that the high aromatic content, low flash point and general properties (excluding the solid residue) could place the oil between gasoline and kerosine in fuel terms. This could make it an extremely valuable product.

The gas produced at 525°C having a calorific value of 83.2 MJ/m^3 would appear far superior to other pyrolysis gases, comparing well with pure butane. Although little has been published concerning gas values Kobe Steel(67) claim 42 MJ/m^3 and Tosco II(134) 36 MJ/m^3, the latter containing notable amounts of carbon oxides. The lack of detectable hydrogen sulphide is in common with Larsen's pyrolysis gas(182) and is a very valuable feature.

The char has been analysed with two possible uses in mind: as a fuel and as a low reinforcing black. As a fuel the important factors are: calorific value, carbon content and sulphur content, which are given and compared with other products in Table 10.27. The calorific value is that calculated from the carbon content and shows a value comparable with the Larsen char but lower than the fluidized bed produced, Nippon Zeon/Japan Gasoline char. The suitability for carbon black use is more complex to assess fully so here is restricted to three standard tests. It is clear that

	Aston	Larsen	Nip.Z/J.Gas	Tosco II	Furnace Coke
Carbon, wt.%	83.2	82.2	86.8	81.5	-
Sulphur, wt.%	2.3	2.1	2.2	2.5	-
Cal.Val., MJ/kg	25.8	25.9	30.9	-	30.7

Table 10.27 Fuel Properties of Pyrolysis Chars

none of the products come up to the desired standard least of all the Larsen (and probably the Aston) product probably due to exposure to the melt. The Kobe product would probably be suitable for reinforcing low stress products such as handle grips. A further option for the char may be as an activated carbon as is detailed in Table 10.28. All the pyrolysis products show reasonable absorption properties but their areas are too low for effective use.

	Aston	Larsen	Kobe	GPF
Strength modules, kg/cm^2	-	21	44	54
Elongation, %	-	530	860	940
Tensile strength, kg/cm^2	-	70	52	55

Table 10.28 Char Reinforcing Properties

	Aston	Larsen	Kobe	GPF
I_2 Abs., mg/g	-	94	77	26
DBP Abs., mg/g	-	78	97	88
Ash, wt. %	10.3	15.1	8.3	0.1
Area, m^2/g	-	8.3	-	27.0

Table 10.29 Char Activation Properties

Note: At the time of reproduction the data for the Aston char was not available.

10.3.4.4 Product Evaluations

In the discussion of the chemical composition of the oil it was made clear that no high value chemical feedstock could be extracted and therefore the oil was only suitable as a fuel. The use of the oil as a fuel was shown in the previous section to be subject to a few improvements. These are: stripping to improve flash point and reduction of residues to widen applications. It is estimated that the bulk loss in stripping would be less than 5% and would be compensated for by an increase in calorific value to over 42 MJ/kg. Having met these conditions and provided the aromatic nature does not pose a severe biohazard, the oil's properties make it suitable for most heating and industrial boiler applications. (The economic value is discussed in a later chapter.)

The gas being essentially sulphur free and of very high calorific value is suitable as a heating fuel. It may also be useful in more specific industrial applications.

As a black or activated carbon the char has no particular value which may be considered fortunate as recovery would be very suspect and the char is a convenient fuel on which to run the process. The calorific value of the char is too low for a marketable fuel but coupled with its tolerable sulphur level it is ideal for in situ burning as was proposed much earlier.

Of the other products the inorganics are of too low a proportion to justify recovery. However the steel which is certainly partially recoverable and would appear to have at least some scrap value.

10.3.5 Orders and Mechanism

The experimental orders of reaction have been given in Table 10.9 and mostly fall in the region 0.80 to 1.30, averaging at 1.04 which can be essentially taken as first order. This justifies the units of time $^{-1}$ used in the presentation of results and earlier parts of the discussion.

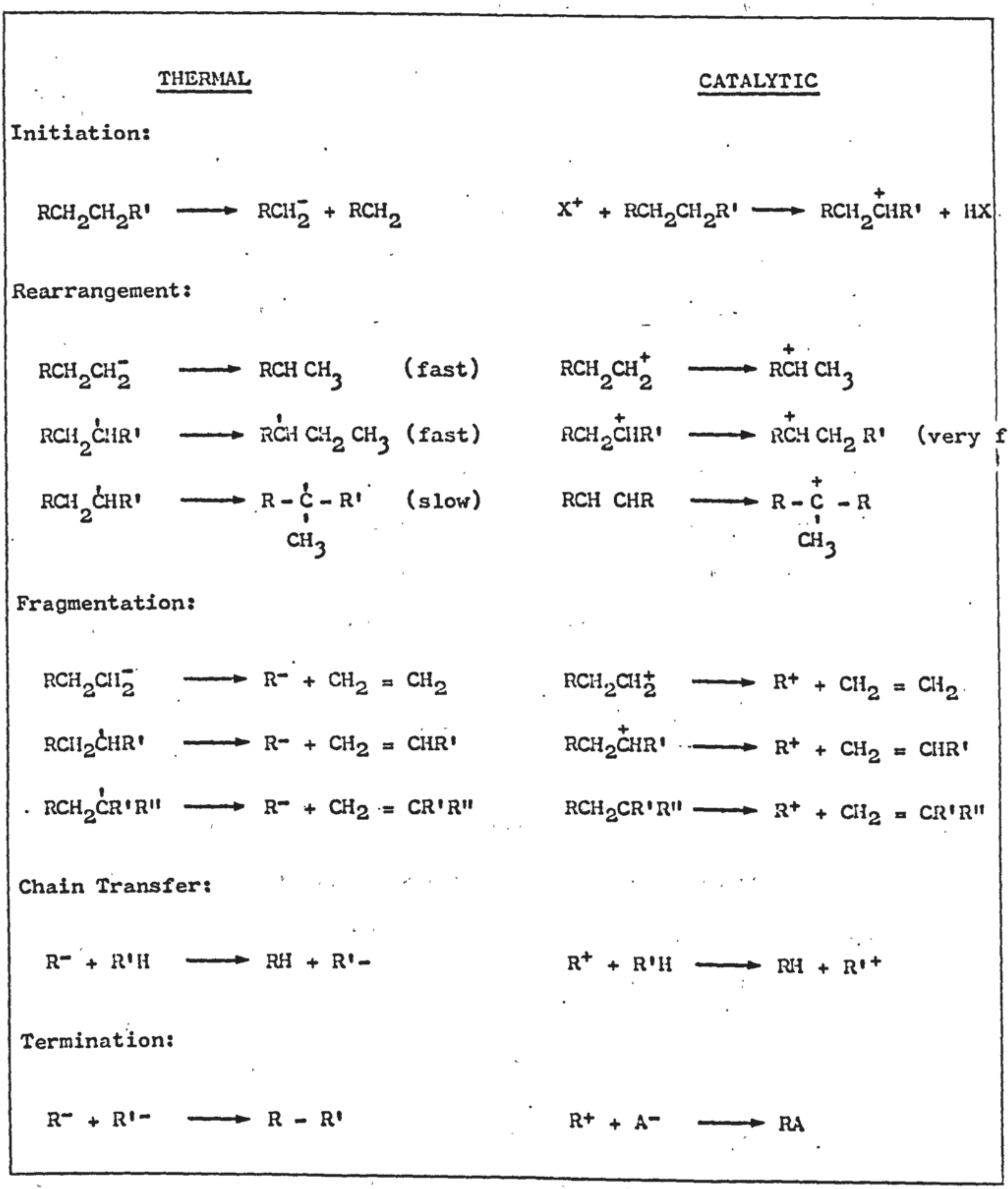
In the proposal of a physical model the conclusion was drawn that the rate of reaction was controlled by a diffusion process. The fact that the order is approximately unity eliminates heat transfer control,which is proportional to temperature gradient, helps to confirm the diffusion process. It may help at this point to imagine the vast (several litres a minute) quantities of vapour being produced over the surface of a relatively small (30g , 15 cm^2) piece of tyre - it seems very likely that vapour escape will (if contained) be restrictive.

Since the rate is not kinetically controlled it is difficult to relate the order to any chemical mechanisms. However unimolecular decomposition reactions of the form,

$$A \longrightarrow B + C$$

do generally follow first order kinetics. A far more meaningful idea of the type of mechanisms involved can be gained from study of the product compositions just given in Section 10.2.3.2.

There are two basic types of mechanism associated with hydrocarbon cracking: thermal and catalytic. In the molten salt pyrolysis system the possibilities of both types arise; thermal through heat supply and catalytic by interaction with melt, impurities and active char. Generally thermal cracking occurs through free radial action while catalytic cracking proceeds via carbonium ion intermediates(74). Typical sequences are shown in Fig. 10.13. The reactions involved in cracking are mostly endothermic (particularly in the case of aromatization) but also show increases in entropy and therefore must be favoured by low reactant pressures and high temperatures. It should be noted that free radicals rearrange and fragment at roughly the same rate but in the case of carbonium ions rearrangement is much faster than fragmentation.



THERMAL	CATALYTIC
Initiation:	
$RCH_2CH_2R' \longrightarrow RCH_2^{-} + RCH_2$	$X^+ + RCH_2CH_2R' \longrightarrow RCH_2\overset{+}{C}HR' + HX$
Rearrangement:	
$RCH_2CH_2^{-} \longrightarrow RCH\,CH_3$ (fast)	$RCH_2CH_2^{+} \longrightarrow R\overset{+}{C}H\,CH_3$
$RCH_2\overset{\cdot}{C}HR' \longrightarrow R\overset{\cdot}{C}H\,CH_2\,CH_3$ (fast)	$RCH_2\overset{+}{C}HR' \longrightarrow R\overset{+}{C}H\,CH_2\,R'$ (very fast)
$RCH_2\overset{\cdot}{C}HR' \longrightarrow R-\underset{CH_3}{\overset{\cdot}{C}}-R'$ (slow)	$RCH\ CHR \longrightarrow R-\underset{CH_3}{\overset{+}{C}}-R$
Fragmentation:	
$RCH_2CH_2^{-} \longrightarrow R^{-} + CH_2 = CH_2$	$RCH_2CH_2^{+} \longrightarrow R^{+} + CH_2 = CH_2$
$RCH_2\overset{\cdot}{C}HR' \longrightarrow R^{-} + CH_2 = CHR'$	$RCH_2\overset{+}{C}HR' \longrightarrow R^{+} + CH_2 = CHR'$
$RCH_2\overset{\cdot}{C}R'R'' \longrightarrow R^{-} + CH_2 = CR'R''$	$RCH_2CR'R'' \longrightarrow R^{+} + CH_2 = CR'R''$
Chain Transfer:	
$R^{-} + R'H \longrightarrow RH + R'-$	$R^{+} + R'H \longrightarrow RH + R'^{+}$
Termination:	
$R^{-} + R'- \longrightarrow R - R'$	$R^{+} + A^{-} \longrightarrow RA$

Fig.10.13 Thermal and Catalytic Cracking Mechanisms

The result is that most thermal products are formed by fragmentation of primary and secondary radicals whereas catalytic products derive from secondary and particularly tertiary ions. (This is due to relative stabilities of primary, secondary and tertiary species.) This hints that thermal cracking is likely to produce the smaller species which can be substantiated further as radical fragmentation energies (75 - 105 kJ/mol) are much lower than those of carbonium ions, permitting the formation of small alkanes.

Looking at the products it is seen that the distribution is fairly typical of thermal mechanisms. The anomally of high butanes in the gaseous phase suggests there may be some catalytic activity but care should be taken here as the reactant is largely made up of C_4 and C_5 polymerized units and so the broad rules for hydrocarbon cracking should not be taken too strictly.

In Larsen's work(181-184) a deliberately chosen Lewis acid type melt was used and would be expected to make a catalytic contribution. It is in fact seen that the gas yield is far lower than in the results shown earlier. This is also observed in the DECO results although less is known of the melt used(139).

On a more general basis it is useful to apply the mechanisms proposed by Pitt(77) to explain the high ethylene production from the pyrolysis of polythene. Proposed are three simple concepts: random scission/fragmentation, monomer unzipping and rearrangement. Taking the simplest mechanism, unzipping, it is clear that this would give rise to butadiene, styrene and isoprene units. All of these are found in considerable amounts in the products; in fact the styrene in the tyre and products balance closely. The scission occurring does not tend to be entirely random as considerable amounts of unsaturated C_8, two butadiene units, are produced. The odd products are, thus, truly representative of random fragmentation.

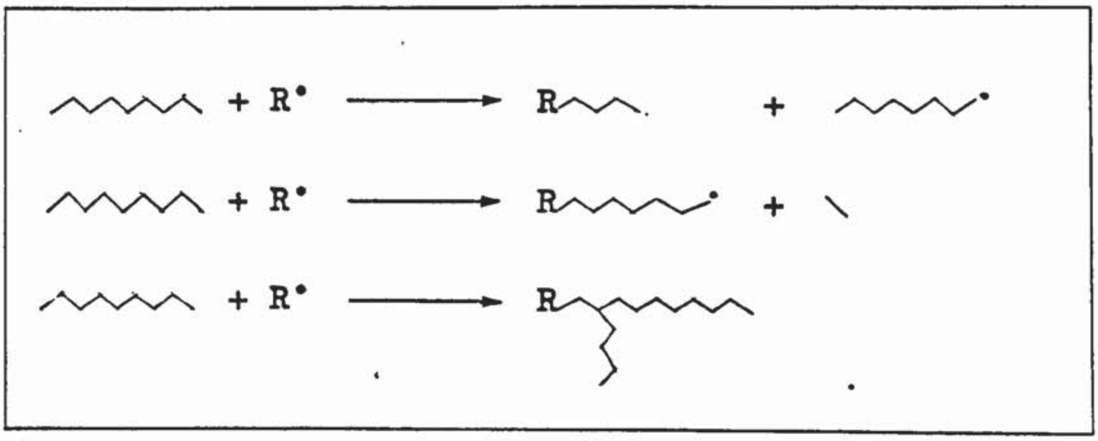


Fig.10.14 Simple Mechanistic Concepts

10.3.6 Chemistry of Tyre Pyrolysis

In this section the suggestions made in the previous section will be taken a little further and applied to specific reactions taking place. It is first necessary to set out a compound mass balance to establish net changes in composition.

The tyre rubber broadly consists of natural, polyisoprene rubber, styrene-butadiene, synthetic rubber and chlorinated butyl rubber. In the chemical conditions of the reactor the halogen of the chlorinated butyl will probably be released as HCl and then be absorbed by the melt making this compound hard to trace. (Here the C_4 products are quoted.) However natural rubber and SBR can be

	TYRE	PRODUCTS	NET CHANGE
Isoprene etc.	26.3 wt. %	1.5 - 2.0 wt. %	
Styrene	2.4	1.4 - 2.6	None/Sl.loss
Butadiene	8.0 +	0.8 - 1.4	Loss
Chlorinated C_4	3.0	-	Loss
Org. oils	9.5 +	-	-
Other Orgs.	-	48.2	-
Total Org.C.	42.8	34.0	Shift from organic to free carbon
Free carbon	23.7	30.6	
Steel	16.8	16.8	None
Inorganics	5.4	-	None

Table 10.30 Compound Mass Balance

shown to be directly responsible for at least part of the isoprene, styrene and butadiene in the products.

In the presence of $H^{\cdot}$ and $CH_3^{\cdot}$ radicals it is not hard to formulate mechanisms by which isoprene and butadiene can give rise to a wide variety of C_1 to C_4 hydrocarbons. If styrene is attacked there are a number of possibilities: attack on the ring-to-vinyl bond would give rise to phenyl radical and hence many of the alkyl

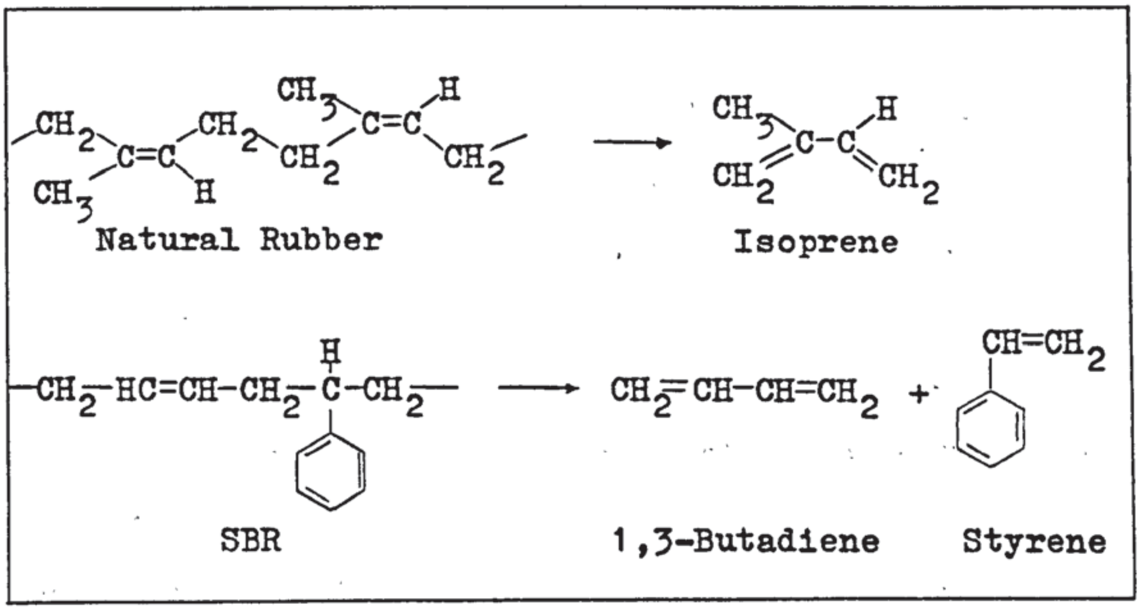


Fig.10.15 Breakdown of Rubber Polymers

benzenes found in the products. The vinyl bond itself offers the possibility of addition followed by further reactions. The ring is of course also open to normal aromatic substitutions.

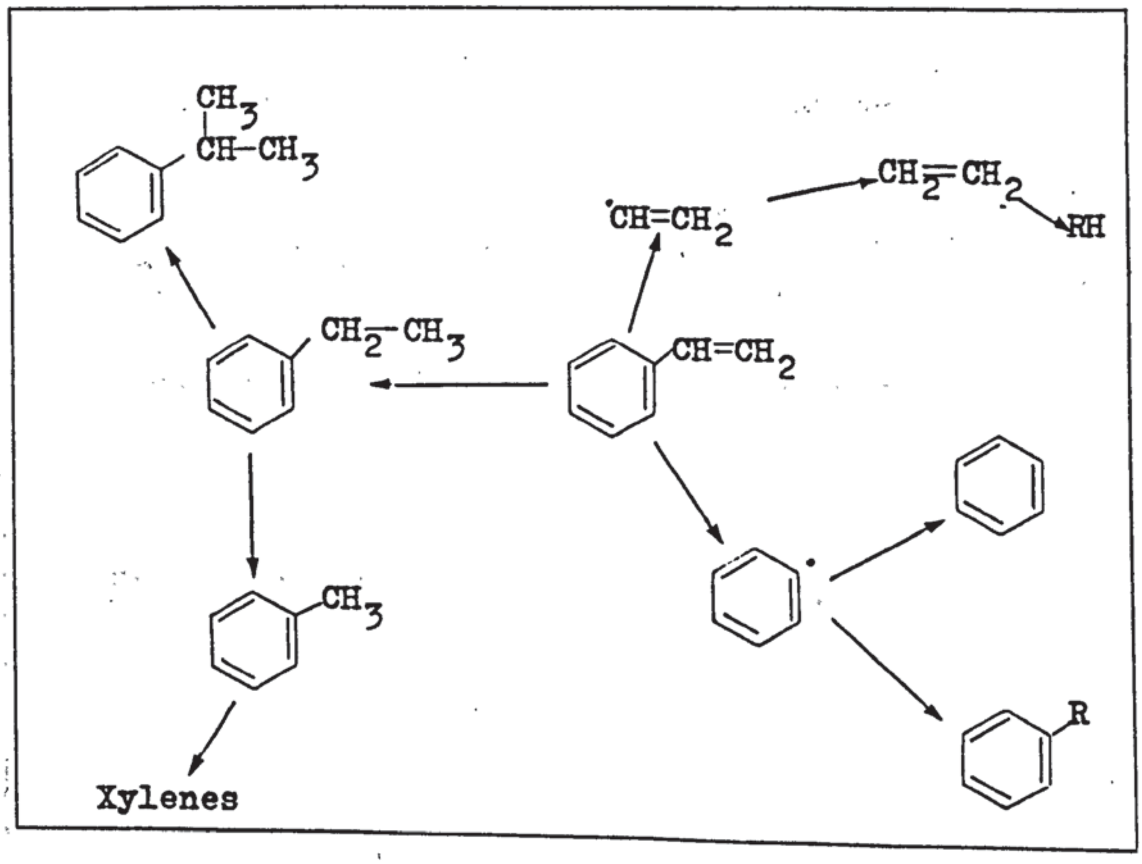


Fig.10.16 Reactions of Styrene

From Table 10.29 it is clear that most if not all the styrene in the tyre (the only aromatic in greater than trace proportions) is accounted for in the oil. This indicates that styrene cannot be the source of all the aromatics present in the products. Even allowing for large errors it is clear that aromatization is occurring in the reactor. There are several classic cyclization reactions, the ones that might be relevant in this case are given in Fig. 10.17. Based on data in Table 10.29 the most likely reactions are those originating from styrene, butadiene and ethylene.

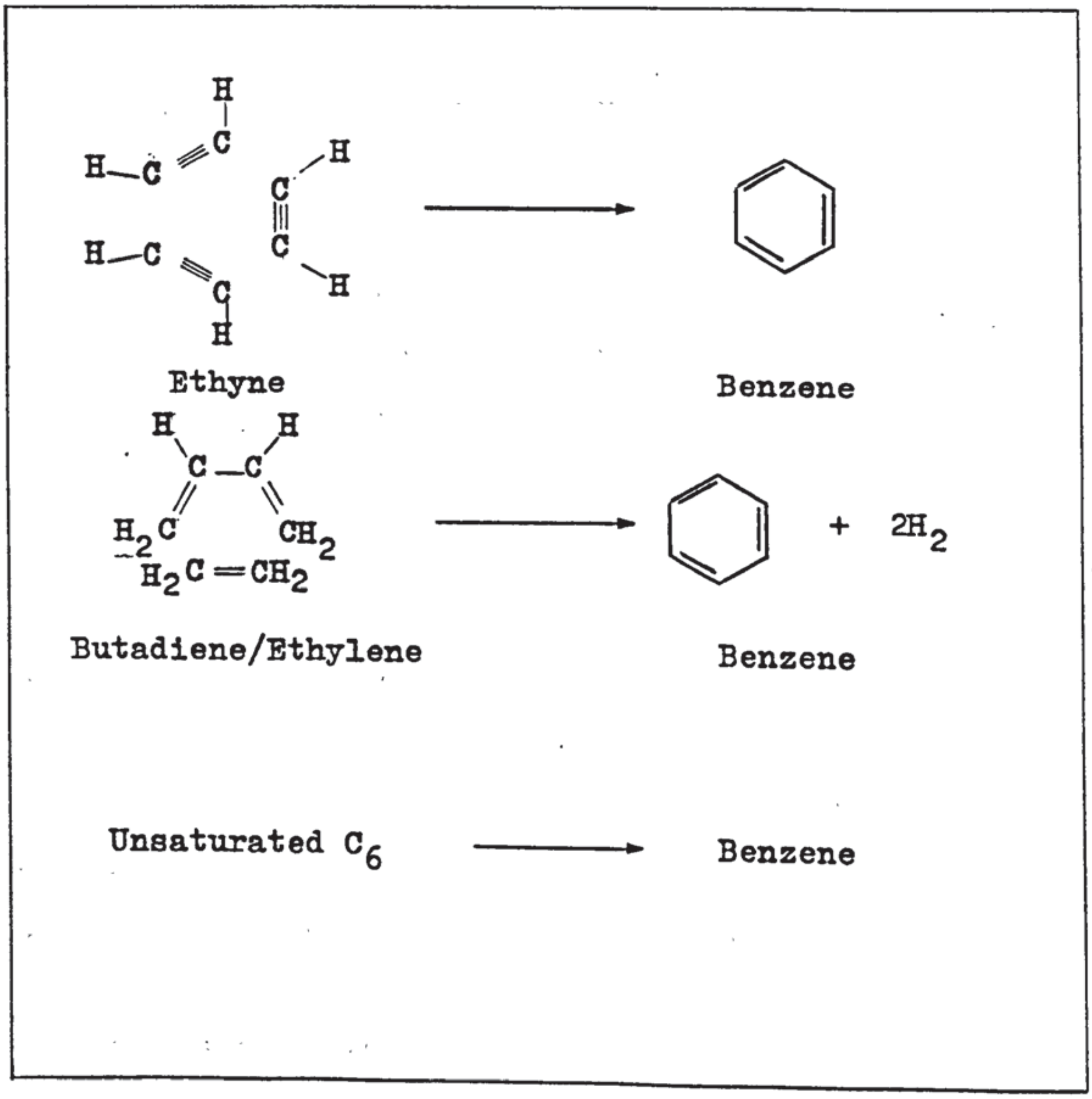


Fig.10.17 Aromatization Reactions

10.3.7 Conclusions

It has been shown that the pyrolysis of used tyres in molten carbonates is capable of disposal of the waste material to realize useful products.

The rate of pyrolysis provides kinetic data that indicates that the reaction is controlled by the rate at which products can escape from the reaction zone. The order of reaction is approximately one and the reaction has been found to be slightly exothermic. The chemical mechanism is evidently a free radical thermal degradation producing a range of products that can be explained in terms of tyre composition. In addition there is considerable evidence that aromatization is taking place.

Increases in temperature cause an increase in rate and shift the product phase distribution from oil to gas. The optimum operating temperature is around 500°C which enables a good yield of oil to be produced at a high rate from a relatively small reactor.

The oil and gas products are both good fuels having high calorific values and low sulphur contents. The oil may require further treatment before use. The char is unlikely to be of any use as a black or activated carbon and would anyway be difficult to remove from the reactor. However it is suitable for in-situ combustion supplying heat for the reactor. The steel may be suitable for sale as scrap.

The experimental results together with those from char removal experiments are used later to design a process flow chart.

CHAPTER
ELEVEN

CHAR GASIFICATION EXPERIMENTAL

11 CHAR GASIFICATION EXPERIMENTAL

11.1 Introduction

It was conclusively shown in Chapter 9 that one of the products of tyre pyrolysis in molten salts is a carbonaceous char that becomes partially entrained in the melt but for the most part floats on the surface. Furthermore it was found that this char presented a considerable handling problem and, even if it could easily be removed from the reactor, it has little value except as a solid fuel.

These were not unexpected results and so it had already been proposed, in Chapter 6, to gasify the char in situ. To avoid mixing combustible gases and oxygen this would be done in a separate reactor to which melt plus char must be transferred. The reactions of carbon with both air and steam yield gaseous products easily removed from the reactor. The reactions with air offer the additional advantage in that being exothermic they will provide heat for the process.

The aims of these experiments were to evaluate: the effectiveness of gasification as a means of char removal, the rates at which it could be achieved and the products obtained.

11.2 Pre-experimental Preparation

11.2.1 Reactor Assembly

Prior to each series of experiments the inner liner of the char gasification reactor, described in Chapter 7, was charged with 1.1 kg of salt (0.5 l melt). In early experiments post-pyrolysis melt was transferred with char from the pyrolysis reactor (to simulate continuously cycling melt) but for safety reasons most experiments were performed using the made-up standard fouled melt. The charged liner was lowered into the reactor after which the head was fitted with a new Klinger Sealex expanded PTFE gasket and secured by tightening the head bolts. At this point the thermocouple, explosion port and purge ports were connected. The Pye Ether temperature controller was now set to a temperature just sufficient to melt the salt and the furnace switched on. When fusion was complete the agitator was lowered into the melt to a level where the blades were about 3 cm from the bottom of the reactor and coupled to the drive unit. Finally the air/steam injection pipe was also lowered into the melt to a level slightly below the agitator blades.

To prepare for an experiment the temperature controller setting was increased to the desired value, the agitator started at the required revolutions (checked by portable tachometer) and the reactor purged with nitrogen. When thermal equilibrium was achieved a weighed char sample was introduced to the reactor through the charging port that after closing doubled as the product exit. Then the nitrogen purge was terminated and the oxidant (air and/or steam) was turned on, initiating the gasification. The procedures from here on are described under Experimental Procedures.

11.2.2 Char Sample

The char used in char gasification experiments was recovered from the pyrolysis reactor whenever the latter reactor was opened. The char thus obtained was not of regular shape or size distribution and so had to be graded using a solids sieving system to achieve samples of reproducible characteristics. In the main, the concern here was to obtain samples of regular surface area-to-weight ratio as this is expected to have an important effect on the reactions.

It was found that the most abundant sizes of char particle removed from the pyrolysis reactor were 2.0 - 3.4 mm and 3.4 - 7.0 mm in the weight ratio of 1 : 1.5 respectively. All experiments were therefore performed using these two grades in these weight ratios.

The analytical characteristics of the char are given in Table 12.1. The methods used to obtain these analyses has already been given in Section 8.3.15. The size of char sample introduced was generally 7.5 g for gasification experiment using air as a partial or only oxidant but 1.0 g where steam alone was used.

11.3 Experimental Procedures

After termination of the nitrogen, the oxidant(s) were introduced; the flow rate of air was controlled and monitored by needle value and rotameter whereas the steam flow rate was controlled by setting of a pre-calibrated syringe pump feeding water to the steam generator.

The progress of the reaction and the composition of the products were both monitored using a calibrated centronic MGA Mass Spectrometer sampling from the product stream. The full method, together with a back-up gas-liquid chromatographic analysis method, are described in Section 11.4.2. In order to follow the course of the reaction the mass spectrum of the products was taken at frequent intervals. This plus knowledge of flow rates in most cases allowed quantification of product flows and hence carbon consumed. When the oxidant appeared to pass through the reactor undepleted the char was clearly all gasified. Where steam alone was used as the oxidant the end of the reaction was determined by passing a short blast of air and checking for signs of further reaction. After passing the sampling points the product gases were allowed to escape to the extraction system.

At the completion of the reaction the oxidant was replaced by nitrogen and the introduction port opened in preparation for the next experiment. A melt sample was taken at this point but the melt was generally not changed until several experiments had been performed.

11.4 Analytical Methods

11.4.1 Feed Char and Melt

The analyses of the feed char that are of importance here are given in Table 12.1 and have to some extent been discussed in earlier sections. The methods used are identical are described in Chapter 9.

Where gasification melts have been analysed the results of interest were:

(a) Char content - to test gasification effectiveness

(b) Carbonate/hydroxide ratio - degree of hydrolysis

These were performed using the methods already described in Section 8.3.11. Occasionally a wet method described by Belcher and Nutten (323) was used to determine the sulphur content.

11.4.2 Gasification Products

11.4.2.1 Mass Spectroscopy

The on-line mass spectroscopic analysis used the Centronic instrument in its external scan mode covering the range 0 - 50 amu. The output was recorded on a Servoscribe 1s Potentiostatic recorder giving peaks whose height could be related to those of standard calibrant gas mixtures (including air) to give quantitative analyses. A complication arises from nitrogen and carbon monoxide's indistinguishable weights but this was solved by applying a mathematical method. However the mathematical method cannot be applied where both air and steam were used as oxidants and so gas-liquid chromatography was also used.

11.4.2.2 Gas-liquid Chromatography

Samples for this technique were collected in glass vials (200 ml) having ground glass taps at each end. These were filled from the product gas stream by negative displacement of acidified brine. The sample for analysis, usually 1 ml, was displaced from the vial by acidified brine onto the chromatograph column through the normal sample loop system.

The instrument used was a Pye Unicam 104 Gas Chromatograph fitted with a katharometer (thermal conductivity) detector. A $\frac{1}{8}$ inch x 9 ft. 80-100 mesh Carbosieve S column, supplied by Jones Chromatography, was used with a helium (occasionally argon) carrier gas at a flow rate of 35 ml/min. The best results were achieved using the temperature programme; 4 mins. held starting temperature (30°C) - climb rate 24°C/min - 175°C maximum temperature and an attenuation of 10 or 100. The output was charted by a Servoscan 1s recorder and integrated by a Kent Chromalog instrument. The results were evaluated using a series of standard gas mixtures.

The calorific values and densities quoted in the results were calculated from these analyses.

11.5 Experimental Programmes

The parameters for gasification experiments were: gasifying agents, char concentration, flow rates of gasifying agent(s), melt agitation and temperature.

In these experiments it was desired to study gasification by air, by steam and by mixtures of the two; that is a complete variation from air alone to steam alone. The temperature was easily varied and was undoubtedly one of the key parameters in the series.

The concentration of char in the melt was restricted by the rates of reaction; fastest with air at high temperatures, slowest with steam at low temperatures. In order to achieve reasonable duration for gasification experiments it was usually the char sample weight and hence char concentration that was adjusted.

The first series of gasification experiments utilized air alone as the gasifying agent at temperatures of 750, 825 and 900°C. At each temperature air flow rates of 1.5, 3.5 and 7.0 l/min. were applied and some variation of agitator revolutions was also introduced. The details of the series are given in Table 11.1. The initial char concentration in each experiment was 15.0 g/l which with the variation of the remaining parameters was thought adequate to evaluate the systems.

The second series was that using steam alone as the gasifying agent. Since the rate of the carbon-steam reaction is far slower than that of the carbon-oxygen reaction(289) the initial char concentration in this series was 2.0 g/l. The steam flow used of 2.1 g/min. was a considerable excess and so was not varied. These conditions gave reasonable duration to experiments. The programme is seen in Figure 11.2.

The final series was aimed at providing a range of oxygen-to-steam mole ratios between the extremes of the first two series. The simplest method of achieving this was to fix the steam flow rate and vary the air flow. The details of this series are given

Reactor Section			
Temp. °C	Air, l/min.	Vel., cm/s	Agitator, rpm
750	1.5	1.87	600
	3.5	4.35	
	7.0	8.70	
825	1.5	2.00	250
			600
			900
	3.5	4.67	250
			600
			900
	7.0	9.33	250
			600
			900
900	1.5	2.13	600
	3.5	4.98	
	7.0	9.98	
600	1.5	1.59	600
675	1.5	1.73	250
			600
			900

Table 11.1 Programme of Air Gasification Experiments

		Reactor Section	
Temp. °C	Steam g/min.	Vel., cm/s	Stirrer, rpm
675	2.1	3.00	600
825		3.49	
900		3.72	

Table 11.2 Programme of Steam Gasification Experiments

in Table 11.3, the agitator and initial char concentration were fixed at 600 rpm and 150 g/l respectively.

Temp.°C	Air, l/min	Steam, g/min	Vel. cm/s	$O_2 : H_2O$ mol. ratio
675	1.0	3.0	5.45	0.056
	2.0		6.60	0.113
	3.5		8.33	0.197
	6.3	0.7	5.30	0.098
825	1.0	3.0	5.63	0.056
	2.0		6.96	0.113
	3.5		9.00	0.197
900	3.5	3.0	9.29	0.197

Table 11.3 Programme of Air/Steam Gasification Experiments

In addition to these planned series a few experiments were performed to answer unexpected questions arising during these series.

CHAPTER

TWELVE

CHAR GASIFICATION RESULTS

12 CHAR GASIFICATION RESULTS

12.1 The Char

Char is one of the major products of tyre pyrolysis. As it is quantified among pyrolysis products it can be considered as almost entirely made up of carbon; involatile tars being the remainder. In a continuously operated process it is this material that can be considered as the feed for the gasification reactor. However in these experiments it has been necessary to remove the pyrolysis product char from the pyrolysis reactor, weigh it and transfer it to the gasification reactor for a gasification experiment. This procedure leads to contamination of the carbon/tar char with melt and other inorganic materials. Clearly the weight of "char" removed from the pyrolysis reactor in this way does not represent the true weight of char as defined in the second sentence of this section; it includes the contaminants. This point is important because one of the methods of calculation of char gasification rate relies on knowledge of the input weight. So in order to know the true input weight of char, as defined in sentence two, it is necessary to have analytical detail of the ex-reactor "char". Table 10.13 shows that the ex-reactor char used in gasification experiments (that obtained by pyrolysis at 475°C) contains some 17.2 wt.% contaminants. Thus a 10g sample of ex-reactor material only contains 8.28g of gasifiable char. In quantifying the feed input for each gasification experiment this was taken into account.

In fact the necessity to perform this correction could be, and usually was, avoided by use of the second, more elegant rate determining method. As will be described fully later this method retrospectively quantifies the carbon input by measurement of carbon in the output. It thus assumes complete reaction and mass balance. Since carbon is 98.5 wt.% of the defined char, this is a valid and accurate method requiring virtually no correcting. Although it might thus be argued that knowledge of the ex-reactor "char" is superfluous, it does act as a good cross-check.

12.2 Rate Determination

It has briefly been mentioned that there were two methods by which the rate of char gasification was determined. Their relative merits have also been commented upon, so here it is only necessary to give a little more detail as to how experimental data was treated to derive results.

1) The first method takes a known weight of ex-reactor char and using the analytical data translates this into the true weight of defined pyrolysis char. It is then placed in the gasification reactor and the experiment carried out. The end of the reaction is taken as the point at which product ceases to flow from the reactor. Thus knowing the weight of input char and the time taken for gasification, a simple average rate can be determined. The disadvantages of this method are that no rate data with respect to char concentration is obtained, occasionally there is a risk of spillage of ex-reactor char after weighing and since the decline in product flow is asymptotic to the time axis it is hard to define the end point of the experiment.

2) The second method measures the composition of the output gas stream with respect to time. Since nitrogen passes through the reactor unchanged the composition of the outcoming reactor gases can, knowing the input rate of nitrogen (which is equal to the output rate), be transformed into quantitative flows. The rates of carbon oxide evolution were then plotted against time. The cumulative integral of these plots gives carbon consumed against time, the point gradients of which are the rates of carbon gasification.

Rates can thus be obtained at two stages in the treatment and by correlation between the two plots the rate of carbon gasification at any particular carbon concentration can be found. The rates so generated can be corrected to read defined char gasification rates (although this would only be a small source of error). This method has the same difficulty in end point determination but, as will be seen later, this is not important as rates at a known char concentration are the prime data.

The mathematical treatments and corresponding graphical plots are not here fully detailed experiment by experiment. However, Figure 12.1 shows examples which will serve to aid the understanding of the method. The plots are typical of results actually obtained.

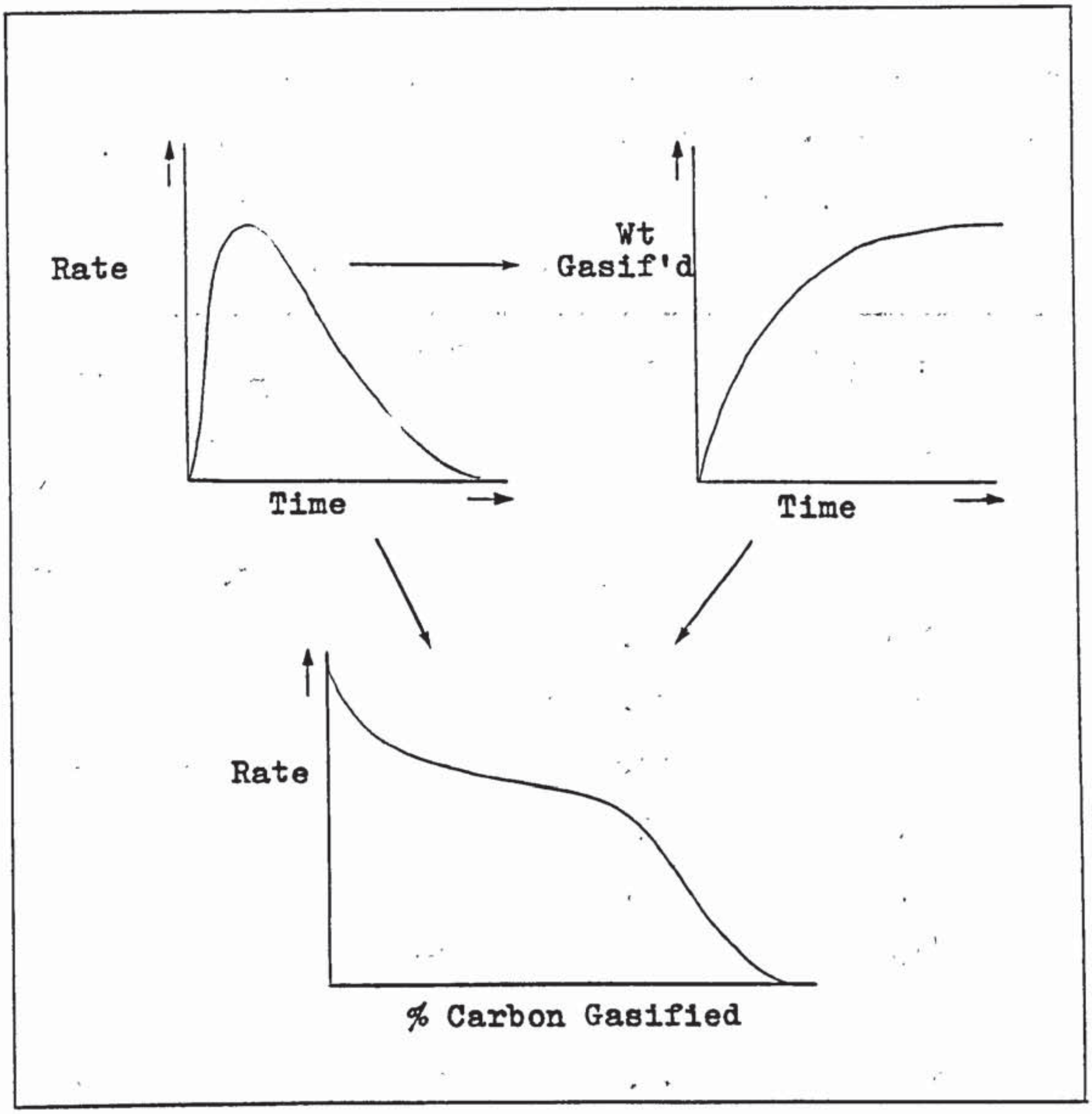


Fig.12.1 Illustration of Method 2) Treatment

12.3 Gasification with Air

12.3.1 Rate Data

Table 12.1 gives the average rates obtained under various physical conditions for char gasification corrected via analytical data to defined pyrolysis char. (The first method from the previous section was used.) From this table, Figure 12.2, the average rate of char gasification against temperature and Figure 12.3, the average rate of char gasification against air flow rate were plotted. Up to 600 rpm the rate increased with stirrer speed but higher speeds had little effect, so the data used in these plots and in all subsequent presentations has been recorded at this speed.

Temp. °C	Air, l/min	Agitator rpm	Av. Rate Char Gas^n, g/min	Av. Rate Gas^n ex-reactor g/min
600	1.5	600	0.02	0.03
675	1.5	250	0.17	0.21
		600	0.21	0.26
		900	0.22	0.28
750	1.5	600	0.15	0.19
	3.5		0.47	0.59
	7.0		0.63	0.79
825	1.5	250	0.38	0.48
		600	0.34	0.43
		900	0.40	0.50
	3.5	250	0.54	0.68
		600	0.55	0.69
		900	0.57	0.64
	7.0	600	0.86	1.08
900	1.5	600	0.35	0.44
	3.5		0.60	0.75
	7.0		1.05	1.31

Table 12.1 Batch-averaged Air Gasification Rates

Table 12.2, showing the rates of char gasification and the cumulative char gasified with respect to time, was constructed using the second of the methods described in the previous section.

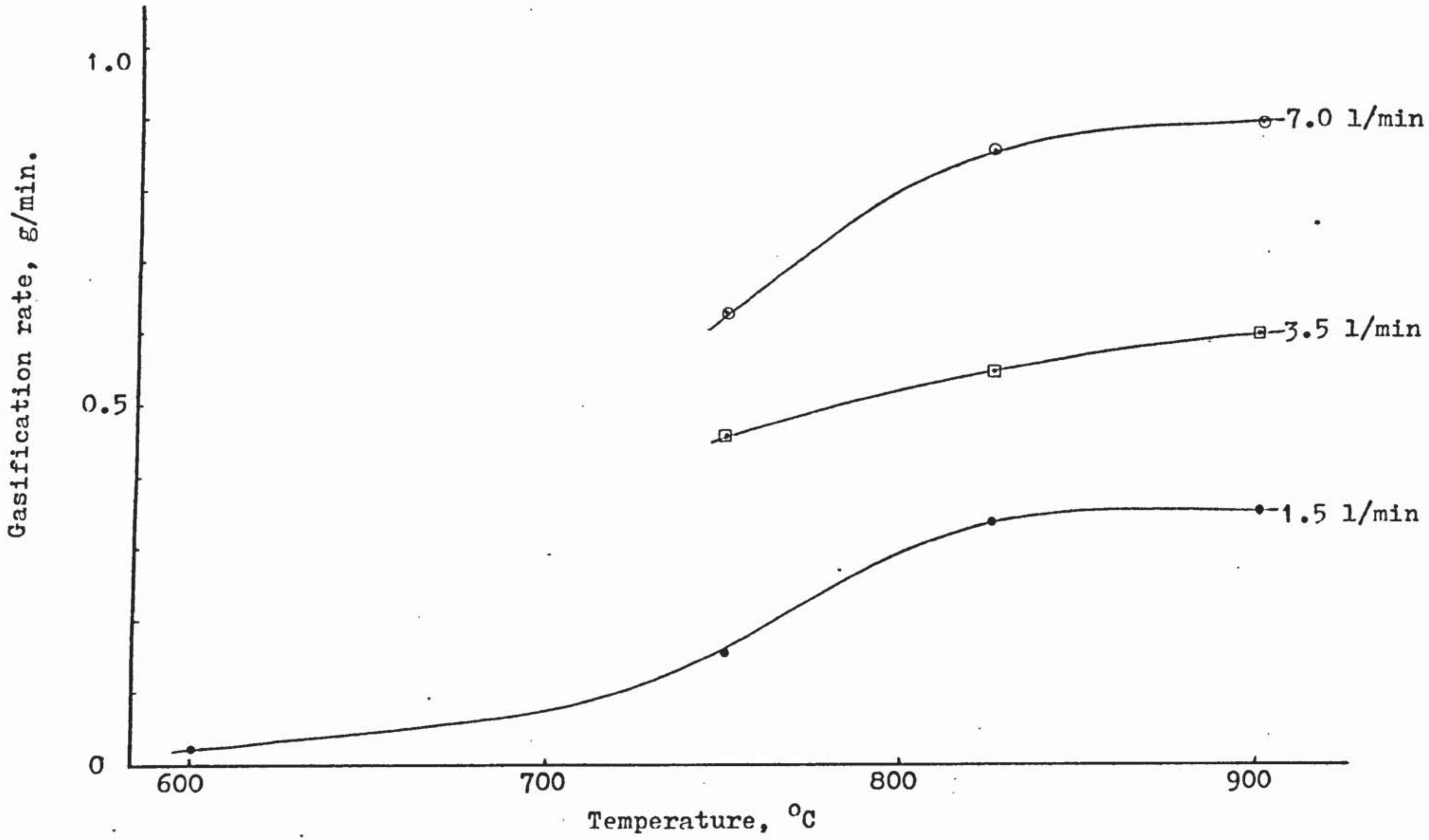


Fig.12.2 Temperature Dependence of Gasification Rate

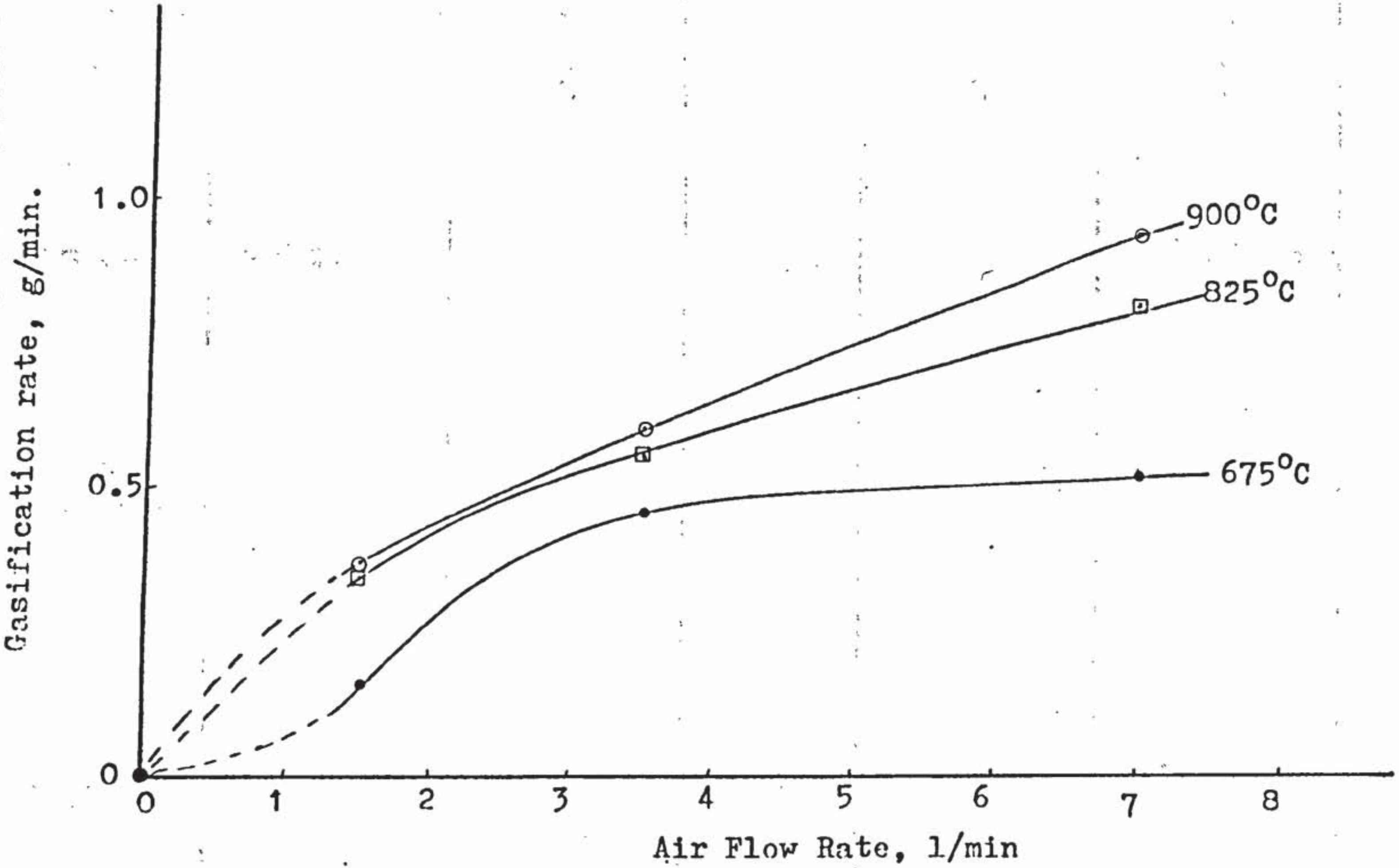


Fig.12.3 Air Flow Dependence of Gasification Rate

Temp. °C.	Air, ^{1}/min	Time, mins.	Rate of Gasification g/min	Carbon Gasified g.
675	7.5	5	0.211	1.0
		15	0.132	2.0
		30	0.070	3.0
		45	0.054	3.7
		60	0.016	4.2
		75	0.000	4.3
750	1.5	0	0.325	0
		5	0.280	1.2
		10	0.234	2.2
		15	0.175	3.1
		20	0.109	4.1
		30	0.007	4.6
	3.5	0	0.675	0
		5	0.489	2.4
		10	0.401	4.8
		20	0.041	6.9
		25	0.006	7.4
		30	0.000	7.4
		0	0.546	0
		5	0.435	2.1
		10	0.049	3.4
		15	0.000	3.8
825	1.5	0	0.341	0
		5	0.334	1.5
		10	0.255	3.0
		15	0.131	4.2
		25	0.008	4.6
		30	0.000	4.9
	3.5	0	0.700	0
		5	0.563	2.8
		10	0.409	5.0
		15	0.285	6.7
		25	0.090	7.1
		30	0.000	7.3
	7.0	0	1.025	0
		2	0.829	1.9
		5	0.521	4.2
		10	0.002	5.2
		15	0.000	5.6

continued . . .

900	1.5	0	0.348	0
		5	0.310	1.8
		10	0.310	3.6
		15	0.178	5.1
		20	0.008	5.6
		25	0.000	5.7
	3.5	0	0.515	0
		5	0.466	2.9
		10	0.515	5.2
		15	0.008	6.3
		20	0.003	6.7
		25	0.000	6.9
	7.0	0	0.736	0
		2	0.735	1.9
		5	0.883	4.5
		10	0.002	5.6
		15	0.000	5.8

From the data in Table 12.2 it is possible to plot several mass related variables against time or rate. Here the percentage of carbon gasified is, in Figure 12.4, plotted against time, and in Figure 12.5 against rate.

As the data stands it is difficult to make direct comparisons between rates of gasification under differing sets of conditions. However, the data does enable the rates at identical carbon concentrations to be made. The carbon concentration in the melt ex-pyrolysis is in the region 10-15 g/l but, as will be seen later, the likely operational concentration will be at the lower end of this region. It was thus proposed to compare, where possible, the rates at 10g/l of melt. This is done in Table 12.3. From this table the plot of

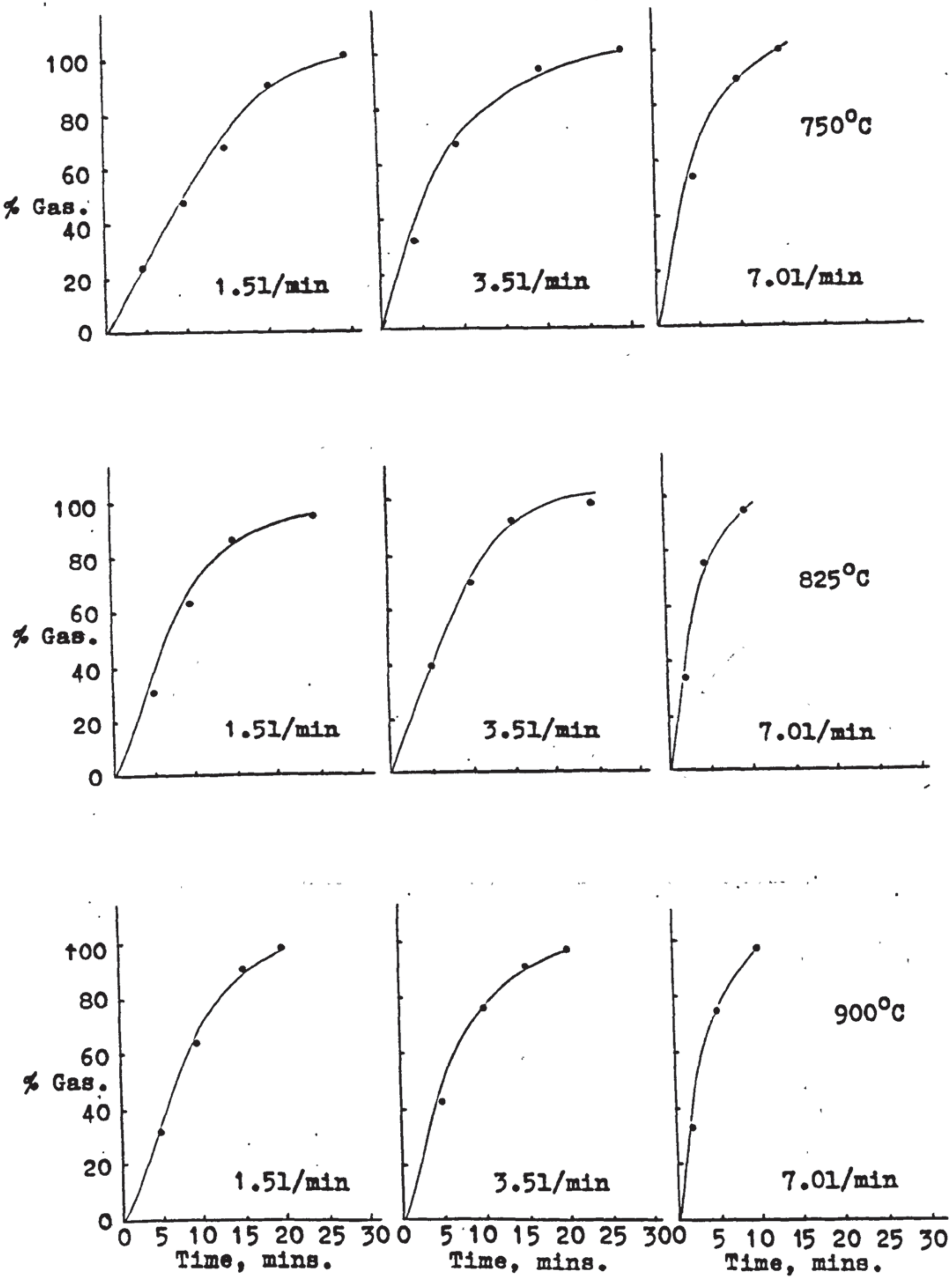


Fig.12.4 Percentage Carbon Gasified with Time

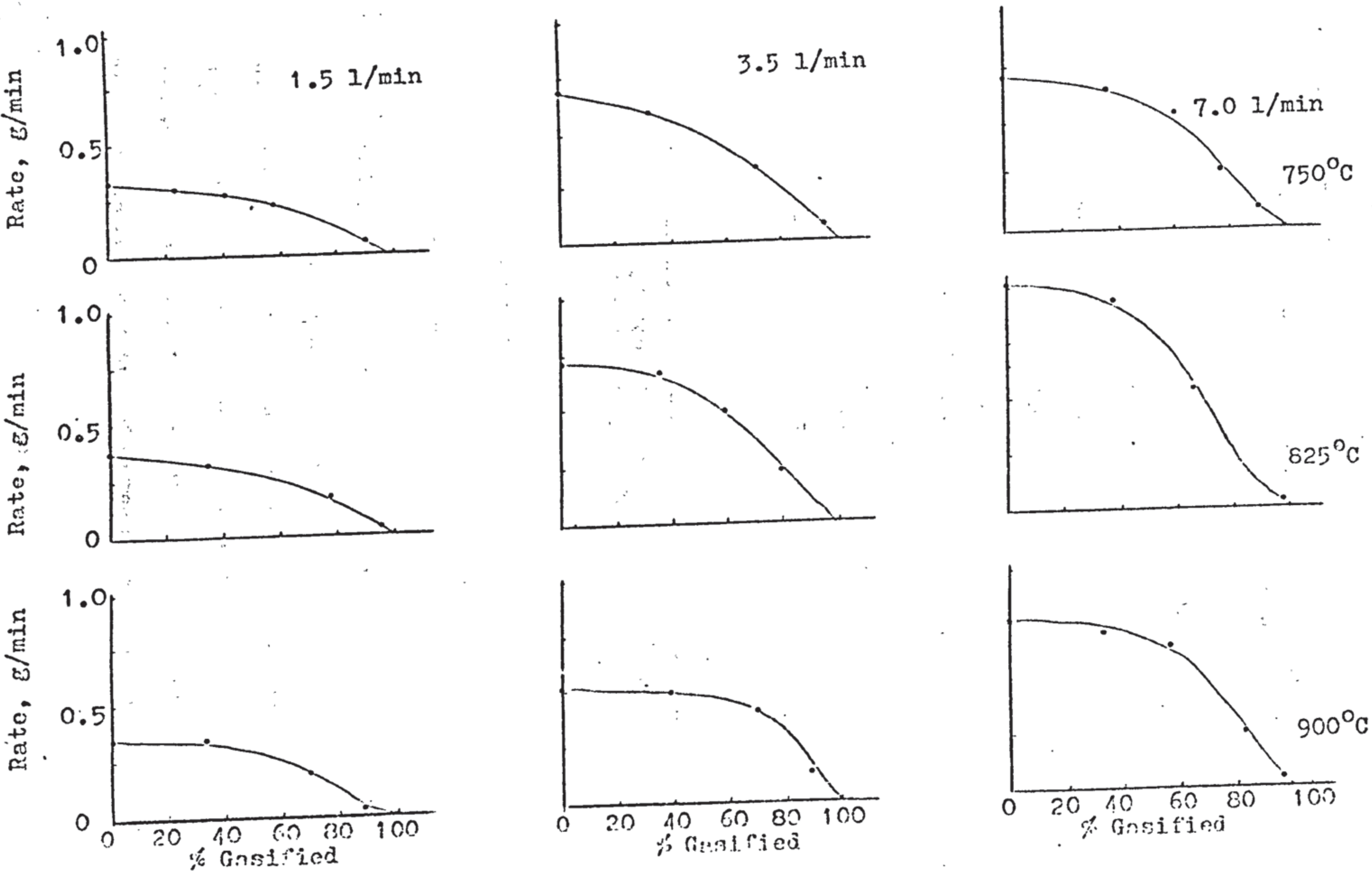


Fig.12.5 Percentage Carbon Gasified vs. Rate

straightforward gasification rate against temperature was made and is shown in Figure 12.6; rate against O_2 flow being shown in Figure 12.7

Temp. °C	Air, l/min	Carbon Gas^n Rate, g/min
675	1.5	0.385
750	1.5	0.419 *
	3.5	0.600
	7.0	0.685 *
825	1.5	0.419
	3.5	0.593
	7.0	0.920
900	1.5	0.431
	3.5	0.713
	7.0	1.163

* Estimate

Table 12.3 Gasification Rates at Char Concentration 10g/l.

12.3.2 Product Characterization

12.3.2.1 Chemical Analyses

The air gasification product analyses were performed entirely by mass spectroscopy as described in Section 11.4.2.1. Since the gasifications were performed on a batch basis, the concentration of carbon changes with time whereas that of the input oxygen remains constant. The result of this is that the composition of the product gases, the amounts and ratios of carbon monoxide and dioxide, changes

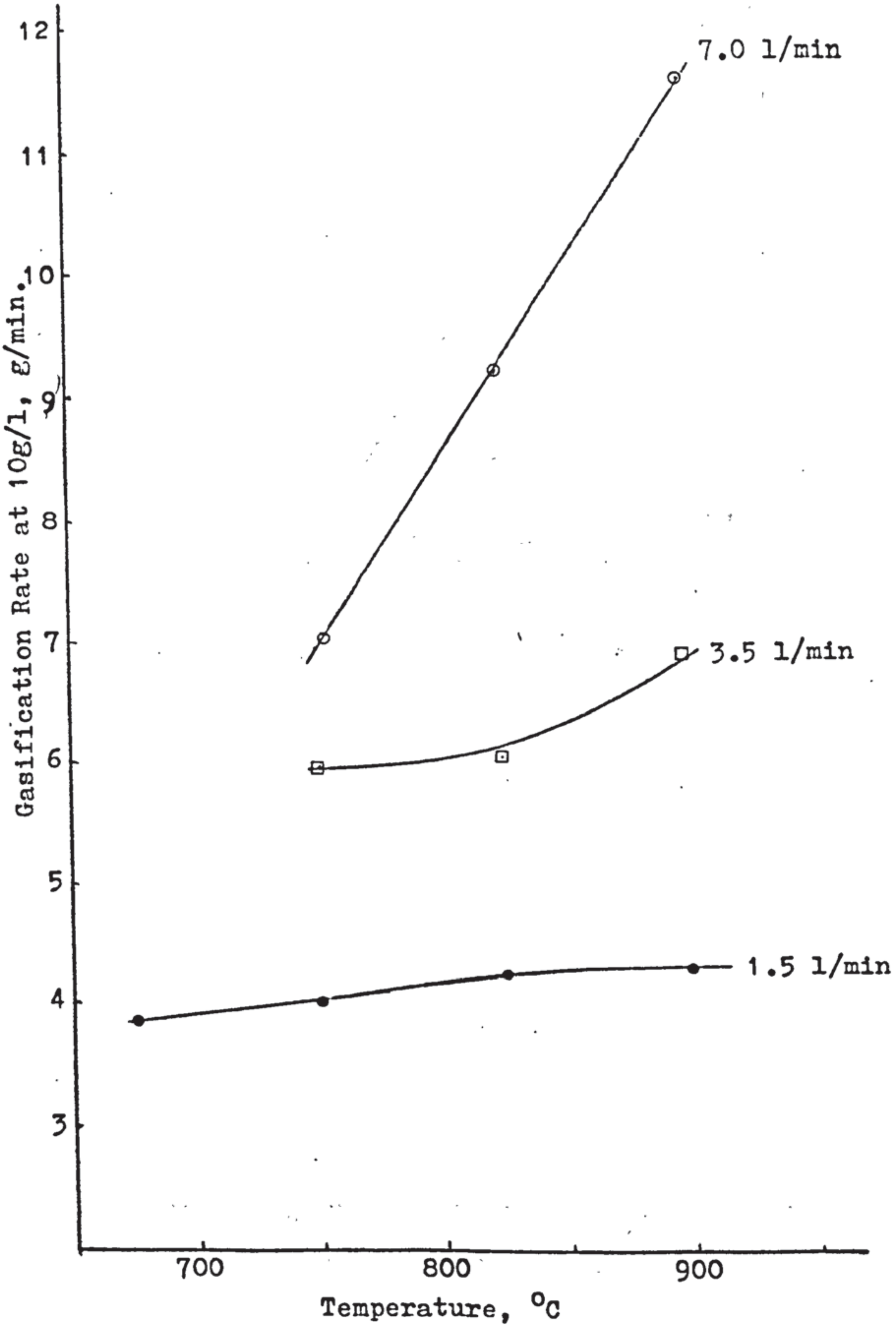


Fig.12.6 Gasification rates vs. Temperature

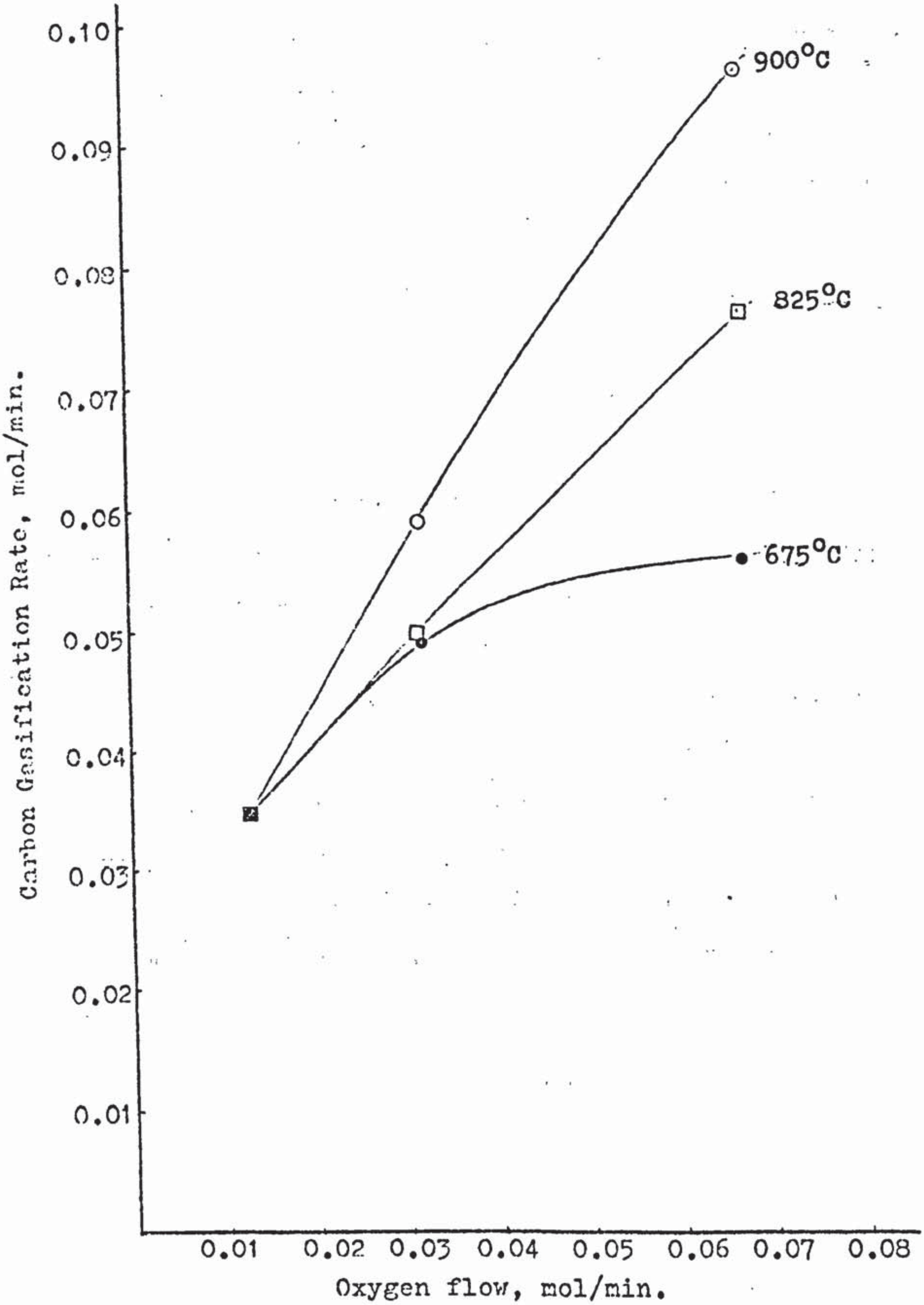


Fig.12.7 Gasification rate vs. Oxygen flow

as the carbon concentration falls through the gasification experiments. Table 12.4 shows the composition of the product stream with respect to time through all the air gasification experiments. The table also gives the production ratios of carbon monoxide and dioxide, in calculating which it should be noted that the input air contained about 0.03 vol. % carbon dioxide itself.

Data taken from Table 12.4 is used to demonstrate the effect of temperature on product composition. Figure 12.8 shows product composition against time and carbon consumed at a fixed air flow rate of 3.5 l/min.. An example of the effect of air flow variation on product composition at a fixed temperature (825°C) is given in Figure 12.9.

Using the same reasoning as in the rate data presentation, the product compositions should also be given at comparable stages of each experiment. In Table 12.5 the compositions are given for the point when the carbon concentration was 10 g/l melt. For comparison with the gas compositions, the equilibrium concentrations expected from the equilibrium constants, are calculated and given in Table 12.6.

Temp. °C	Air l/min	Time mins	CO	CO_2	N_2	O_2	Ar	$^{CO}/CO_2$
600	1.5	0	2.0	3.0	77.5	16.7	0.8	0.67
		4	2.0	2.9	77.5	16.8	"	0.69
		8	2.8	2.7	77.5	17.0	"	1.04
		14	1.8	2.5	77.6	17.2	"	0.72
		20	1.6	2.3	77.6	17.5	"	0.70
		50	1.0	2.0	77.9	18.3	"	0.50
		78	2.5	1.4	77.9	18.6	"	1.79
		100	1.4	1.4	77.8	18.6	"	1.00
		140	1.5	1.0	77.8	18.9	"	1.50
		185	1.0	0.9	78.0	19.4	"	1.11
		220	0.5	0.5	78.9	20.3	"	1.00
		250	0.9	0.5	77.7	20.6	"	0.80
		285	0.4	0.5	77.5	20.8	"	0.80
675	1.5	2	22.5	0.0	69.7	7.0	0.8	
		10	12.3	0.0	73.4	13.5	"	
		15	8.0	0.2	75.0	16.0	"	40.00
		20	7.4	0.2	74.9	17.7	"	37.00
		31	6.5	0.0	75.7	17.0	"	
		56	4.0	0.2	76.5	18.5	"	20.00
		70	1.0	0.4	77.8	20.0	"	2.50
		75	0.0	0.5	78.0	20.7	"	0.00
750	1.5	0	32.8	0.0	65.3	1.1	0.8	
		3	27.5	0.0	68.2	3.5	"	
		9	21.8	0.3	70.6	6.5	"	72.67
		15	17.9	0.6	72.1	8.6	"	29.83
		20	12.5	0.7	73.7	12.3	"	17.86
		25	4.3	0.5	76.2	18.2	"	8.60
		30	0.9	0.5	77.8	20.0	"	1.80
		37	0.0	0.4	78.2	20.6	"	0.00
	3.5	0	33.6	0.2	64.8	0.6	0.8	168.00
		2	25.0	0.3	69.2	4.7	"	83.33
		4	24.0	0.3	67.7	5.2	"	80.00
		8	21.6	0.7	70.7	6.2	"	30.86
		13	19.0	1.0	71.6	7.6	"	19.00
		17	12.0	0.9	73.9	12.4	"	13.33
		22	2.1	0.6	76.8	19.7	"	3.50
		30	0.0	0.4	78.2	20.6	"	0.00
	7.0	0	5.2	9.8	75.3	8.9	0.8	0.53
		3	2.7	8.0	76.5	11.0	"	0.46
		5	6.6	5.5	75.1	12.0	"	1.20
		8	2.0	1.4	76.8	19.0	"	1.43
		12	0.4	0.5	77.7	20.6	"	0.80
		15	0.0	0.5	78.1	20.6	"	0.00

continued . . .

825	1.5	2	34.0	0.0	65.2	0.0	0.8	
		8	33.5	0.2	65.5	0.0	"	167.50
		12	25.6	0.5	69.0	4.1	"	51.20
		16	14.6	0.8	73.8	10.0	"	18.25
		21	1.0	0.5	77.7	20.0	"	2.00
		25	0.0	0.4	78.2	20.6	"	0.00
		30	0.0	0.5	78.2	20.5	"	0.00
	3.5	0	34.0	0.2	64.5	0.5	0.8	170.00
		4	24.3	0.3	69.6	5.0	"	81.00
		9	21.2	0.7	70.8	6.5	"	30.29
		13	19.2	1.0	71.5	7.5	"	19.20
		17	12.0	0.6	74.0	12.6	"	20.00
		20	6.4	0.4	75.8	16.6	"	16.00
		25	0.0	0.5	78.1	20.6	"	0.00
		30	0.0	0.5	78.1	20.6	"	0.00
	7.0	0	24.5	2.2	69.5	3.0	0.8	11.14
		1	19.8	3.0	71.3	5.1	"	6.60
		3	18.3	2.5	71.8	6.6	"	7.32
		5	12.6	1.6	73.7	11.3	"	7.88
		7	3.1	1.0	76.7	18.4	"	3.10
		9	0.0	0.5	78.1	20.6	"	0.00
		12	0.0	0.4	78.7	20.7	"	0.00
900	1.5	0	35.2	0.0	64.0	0.0	0.8	
		3	34.0	0.0	65.2	0.0	"	
		10	34.0	0.0	65.2	0.0	"	
		16	20.1	0.0	65.2	8.0	"	
		20	0.2	0.0	78.0	20.6	"	0.50
		25	0.0	0.5	78.0	20.7	"	0.00
	3.5	0	20.5	6.0	71.0	1.7	0.8	4.08
		3	19.0	6.2	71.7	2.3	"	3.06
		6	19.5	3.7	73.4	2.6	"	5.27
		9	24.0	2.5	69.8	2.9	"	9.60
		12	16.2	1.7	72.6	8.7	"	9.53
		16	1.4	1.0	76.9	19.9	"	1.40
		18	1.4	0.8	76.9	20.1	"	1.75
		22	0.2	0.5	78.0	20.5	"	0.40
		25	0.0	0.5	78.1	20.6	"	0.00
	7.0	0	1.0	19.1	77.1	2.0	0.8	0.05
		2	18.2	5.2	71.8	4.0	"	3.50
		6	6.6	2.0	75.6	15.0	"	3.30
		8	1.0	1.0	78.1	19.0	"	1.00
		10	0.0	0.5	78.3	20.4	"	0.00
		12	0.0	0.5	78.1	20.6	"	0.00

Table 12.4 Air Gasification Products

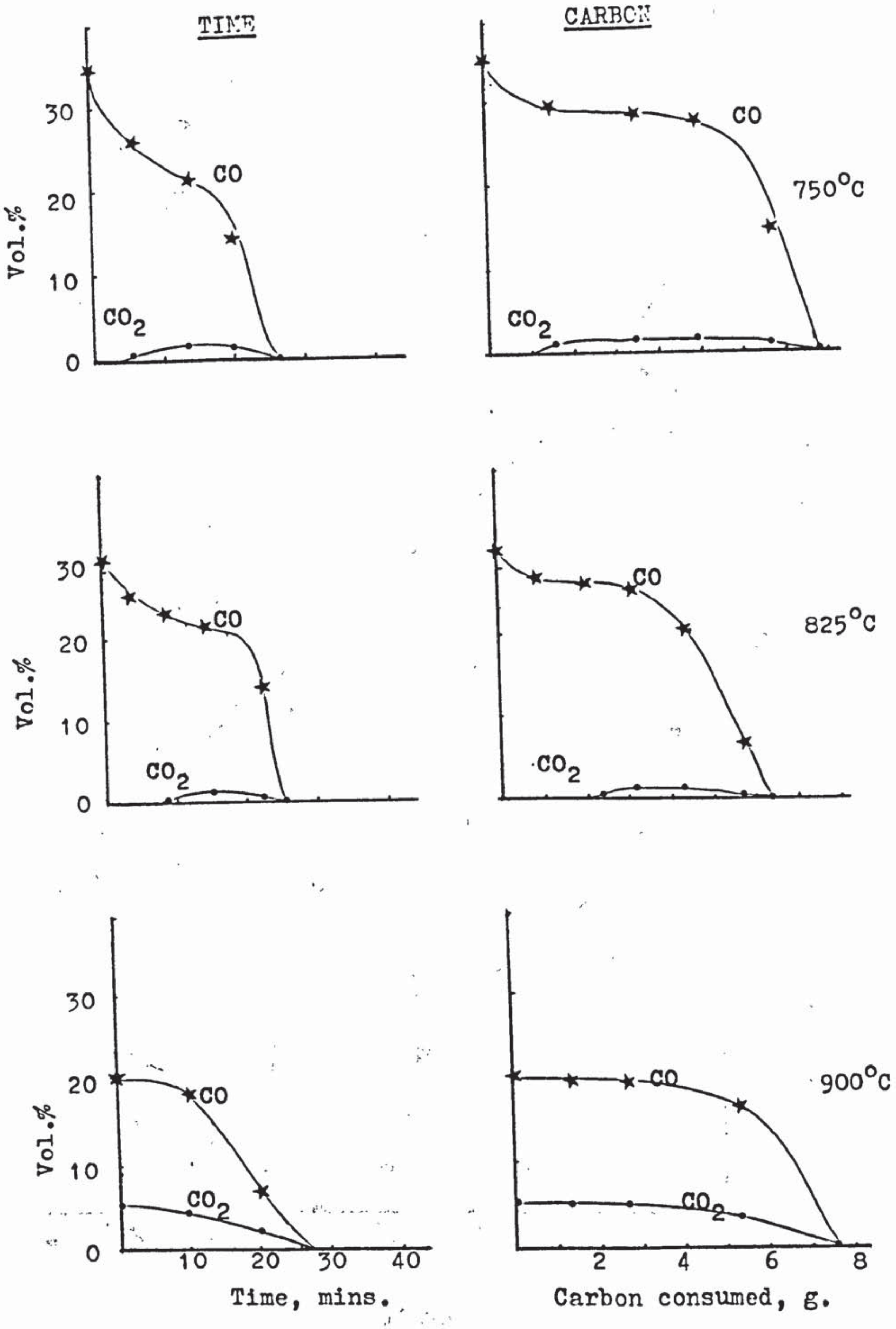


Fig.12.8 Product Compositions , (3.5 l/min.)

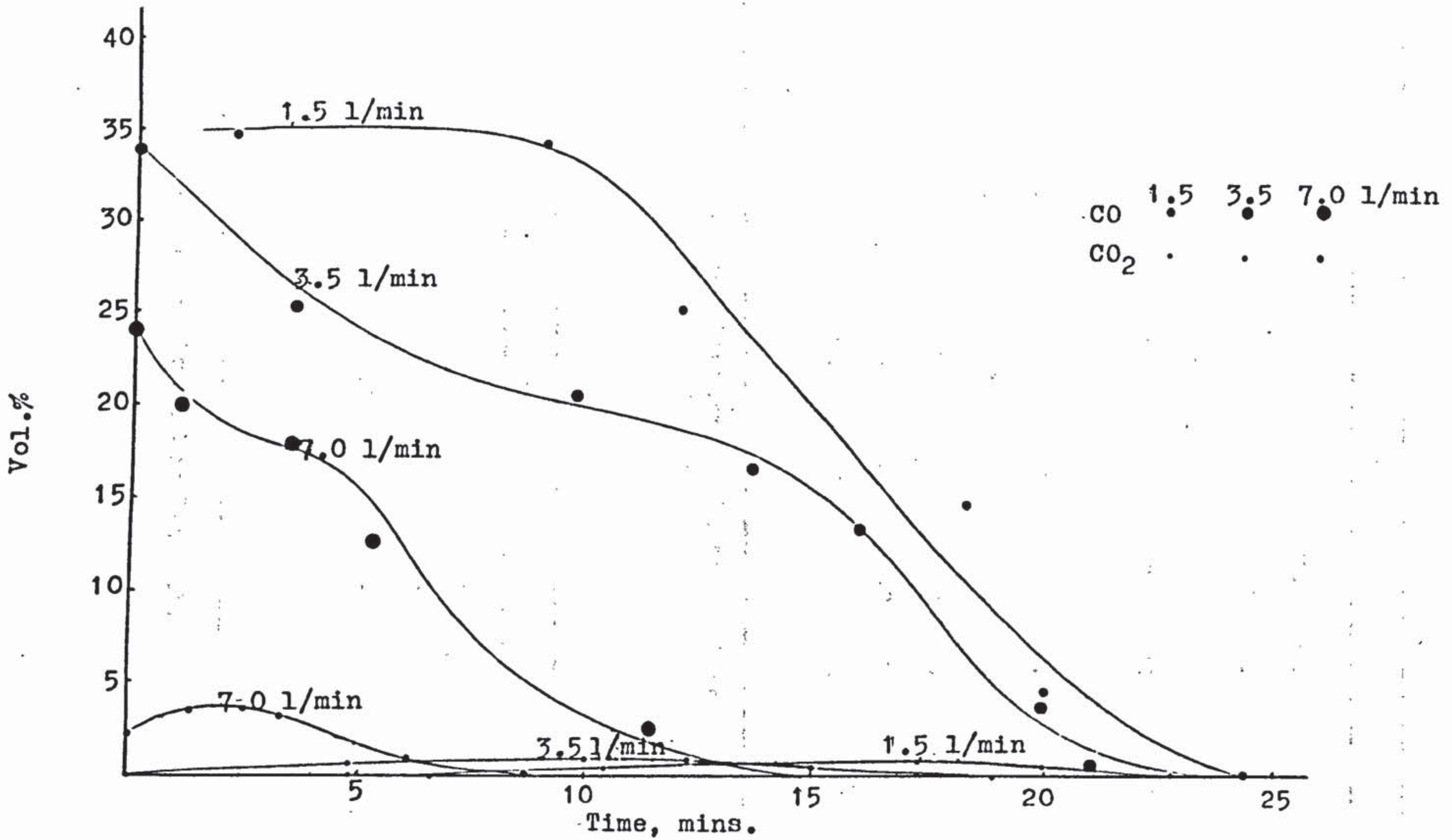


Fig.12.9 Product Composition with Time, (825°C)

Temp.°C	Air, l/min	CO	CO_2	N_2	O_2	Ar
600	1.5	2.0	3.0	77.5	16.8	0.8
675	1.5	22.5	0.0	69.7	7.0	"
750	1.5	-	-	-	-	-
	3.5	24.0	0.3	67.7	5.2	0.8
	7.0	-	-	-	-	-
825	1.5	34.0	0.0	65.2	0.0	0.8
	3.5	24.3	0.3	69.6	5.0	"
	7.0	19.8	3.0	71.3	5.1	"
900	1.5	25.2	0.0	64.0	0.0	"
	3.5	19.0	6.2	71.7	2.3	"
	7.0	1.0	19.1	77.1	2.0	"

Table 12.5 Air Gasification Products at Char Concentration 10g/l

Temp.°C	CO	CO_2	N_2	O_2	Ar
600	15.2	27.0	57.0	-	0.8
750	35.2	5.6	58.4	-	0.8
900	36.5	1.1	61.6	-	0.8

Table 12.6 Air-Carbon Equilibria

12.3.2.2 Physical Properties

Since the gasification products may be used as gaseous fuel, their calorific value was of primary interest. This is calculated from the gas compositions, using those in Table 12.5. The values thus obtained are given in Table 12.7

Temp. °C	Air, l/min	Calorific Value MJ/m^3
600	1.5	0.2
675	1.5	2.5
750	1.5	-
	3.5	2.8
	7.0	-
825	1.5	4.0
	3.5	2.9
	7.0	2.3
900	1.5	4.2
	3.5	2.2
	7.0	0.1

Table 12.7 Calorific Values

12.4 Gasification with Steam

12.4.1 Rate Data

Rate data for steam gasification of the char was gathered in much the same way as air gasification rate data. However the completion point of the reaction was hard to measure introducing errors to the time averaged batch data. The rates averaged over complete batches are given for the three temperatures involved in Table 12.8 (the steam flow in this series was constant at 2.15 g/min).

Temp. °C	Steam, g/min	Rate of Gasification g/min
675	2.15	1.23×10^{-4}
825		4.03×10^{-4}
900		10.72×10^{-4}

Table 12.8 Rates of Steam Gasification of Char

Unlike the air gasification, where nitrogen was used as an inherent calibrant to obtain quantitative data with respect to time, the steam gasification experiments had no inherent constant flow. Hence an artificial fixed stream of nitrogen was passed through the reactor to obtain quantitiative data. The rate data for steam gasification with respect to time is given in Table 12.9, but as it is a relatively involved measurement it was only performed on a limited number of occasions. Selected rate data at a constant carbon concentration of 0.25 g/l (this is an arbitrary concentration imposed by the rates of gasification) are shown in Table 12.10.

The three plots of gasification rate against time are shown in Figure 12.10. The data from Table 12.10 is used to plot rate against temperature in Figure 12.11 and log rate against $^1/$Temperature shown in Figure 12.12. (Figure 12.10 can, if necessary, be used to plot rate against carbon remaining, a function that was actually used in obtaining data for Table 12.10.)

Temp. °C	Time mins	Rate, g/min	Carbon Gas$^{\underline{d}}$, g.	Char Gas$^{\underline{d}}$, g.
675	0	0	0	0
	30	-	0.002	0.003
	100	1.3×10^{-4}	0.012	0.015
	400	-	0.048	0.060
	1000	-	0.120	0.150
	1200	1.4×10^{-4}	0.144	0.180
	1750	-	0.222	0.278
	1950	0.2×10^{-4}	0.240	0.300
825	0	0	0	0
	45	2.1×10^{-4}	0.001	0.001
	145	-	0.048	0.060
	220	4.0×10^{-4}	0.132	0.165
	485	-	0.204	0.255
	680	5.5×10^{-4}	0.300	0.375
	725	-	0.307	0.384
	790	0.1×10^{-4}	0.318	0.398
900	0	0	0	0
	5	-	0.012	0.015
	30	-	0.018	0.023
	75	2.6×10^{-4}	0.030	0.038
	200	-	0.120	0.150
	350	-	0.318	0.398
	510	11.3×10^{-4}	0.540	0.675
	640	-	0.720	0.900
	720	1.9×10^{-4}	0.786	0.983
	750	-	0.804	1.005

Table 12.9 Steam Gasification Rate Data

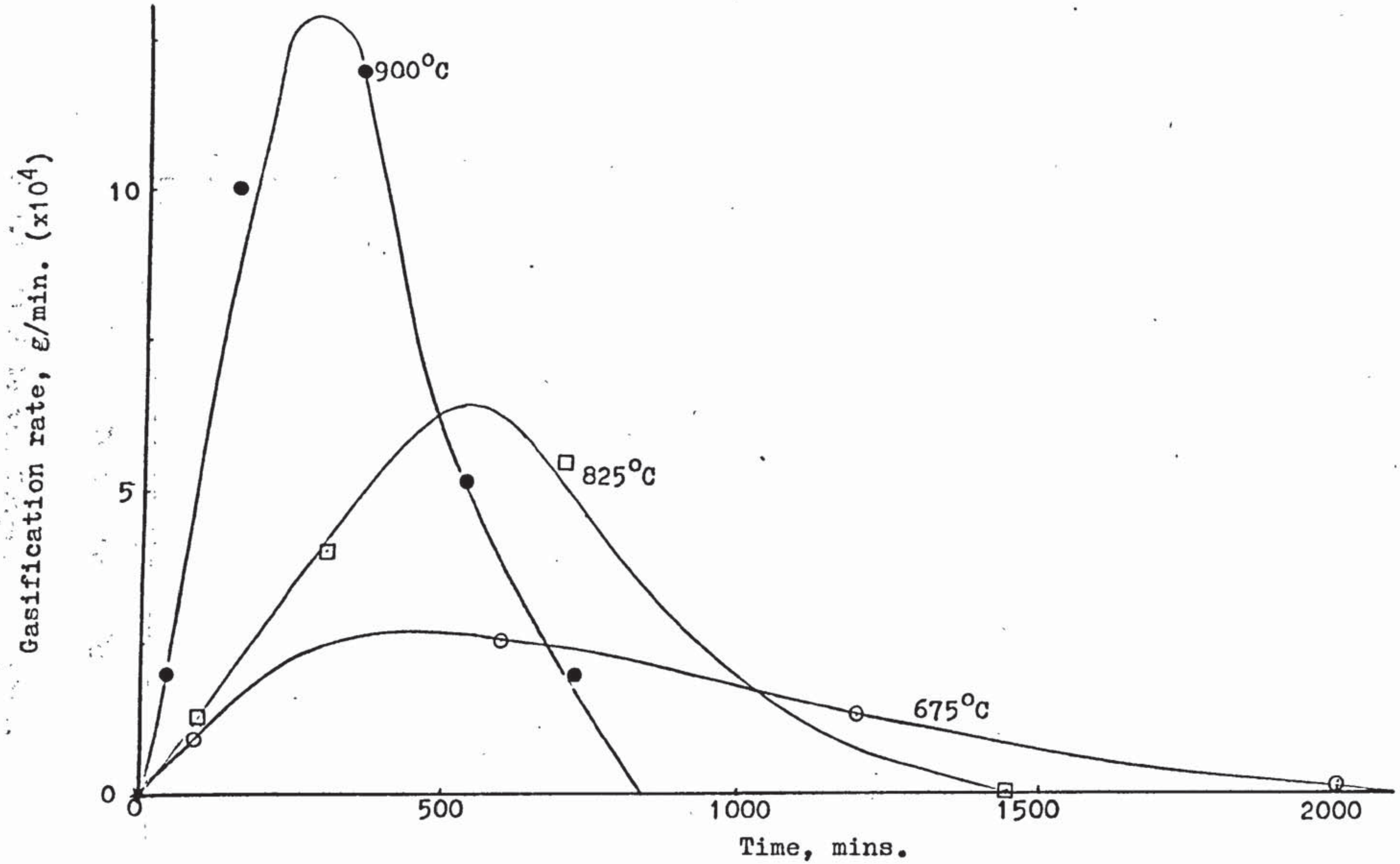


Fig.12.10 Rates of Steam Gasification vs. Time

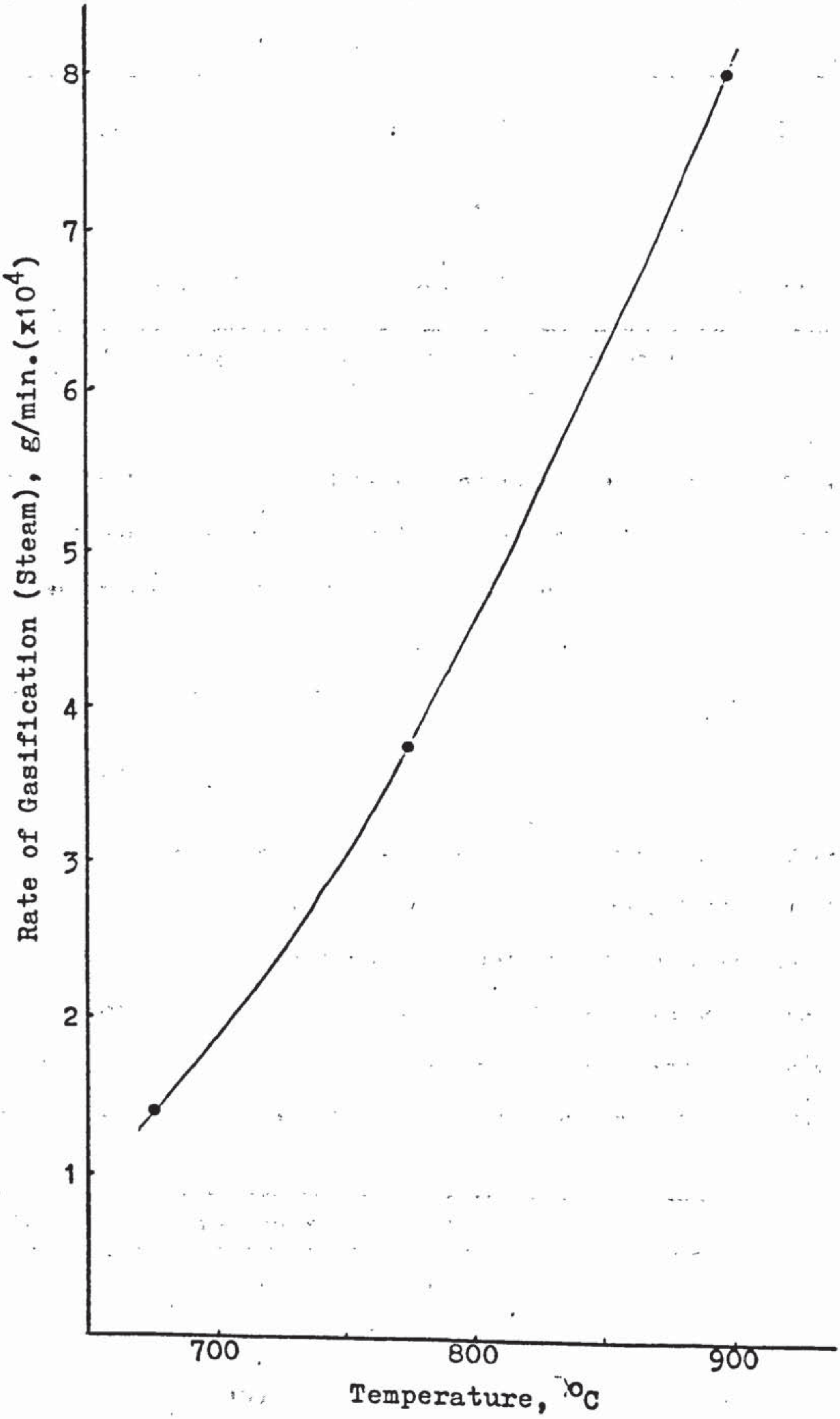


Fig.12.11 Rate vs. Temperature (Steam)

Temp.°C	$^1/T$, °K	Rate of Carbon Gasification, g/min(R)	Log R
675	1.05×10^{-3}	1.4×10^{-4}	-3.85
825	0.91×10^{-3}	3.8×10^{-4}	-3.42
900	0.85×10^{-3}	8.0×10^{-4}	-3.10

Table 12.10 Steam Gasification Rate Data at Char Concentration 0.25g/l

The calculation of this data and the subsequent plotting of log rate vs $^1/$Temperature is considered valid since it was evident that the concentration of neither reactant was rate controlling.

12.4.2 Product Characterization

12.4.2.1 Chemical Analyses

The on-line mass spectroscopy allowed easy determination of product gas compositions with time. These are given in Table 12.11 while those extracted from this table and given in Table 12.12 are those that occur when the carbon concentration is 0.25 g/l. These cases occasionally contained a trace of hydrogen sulphide detectable by smell. The major components for the three experiments are plotted in Figure 12.13.

Temp.°C	Time, mins	CO	CO_2	H_2
675	0	40	7	53
	30	42	6	52
	100	44	6	50
	400	23	13	64

cont'd . . .

675	1000	40	10	50
	1200	38	10	52
	1770	35	15	50
	1950	60	10	30
825	0	21	12	67
	45	18	15	67
	145	30	15	55
	320	25	20	55
	485	32	17	50
	680	33	17	50
	725	34	10	52
	790	44	18	38
900	0	15	18	67
	5	16	17	67
	30	18	15	67
	75	19	21	60
	200	27	15	58
	350	22	21	57
	510	28	18	54
	640	32	18	50
	720	56	13	31

Table 12.11 Steam Gasification Products,Vol.%

Temp.°C	CO	CO_2	H_2
675	38	10	52
825	25	20	55
900	22	21	57

Table 12.12 Product Compositions at Char Concentration 0.25g/l

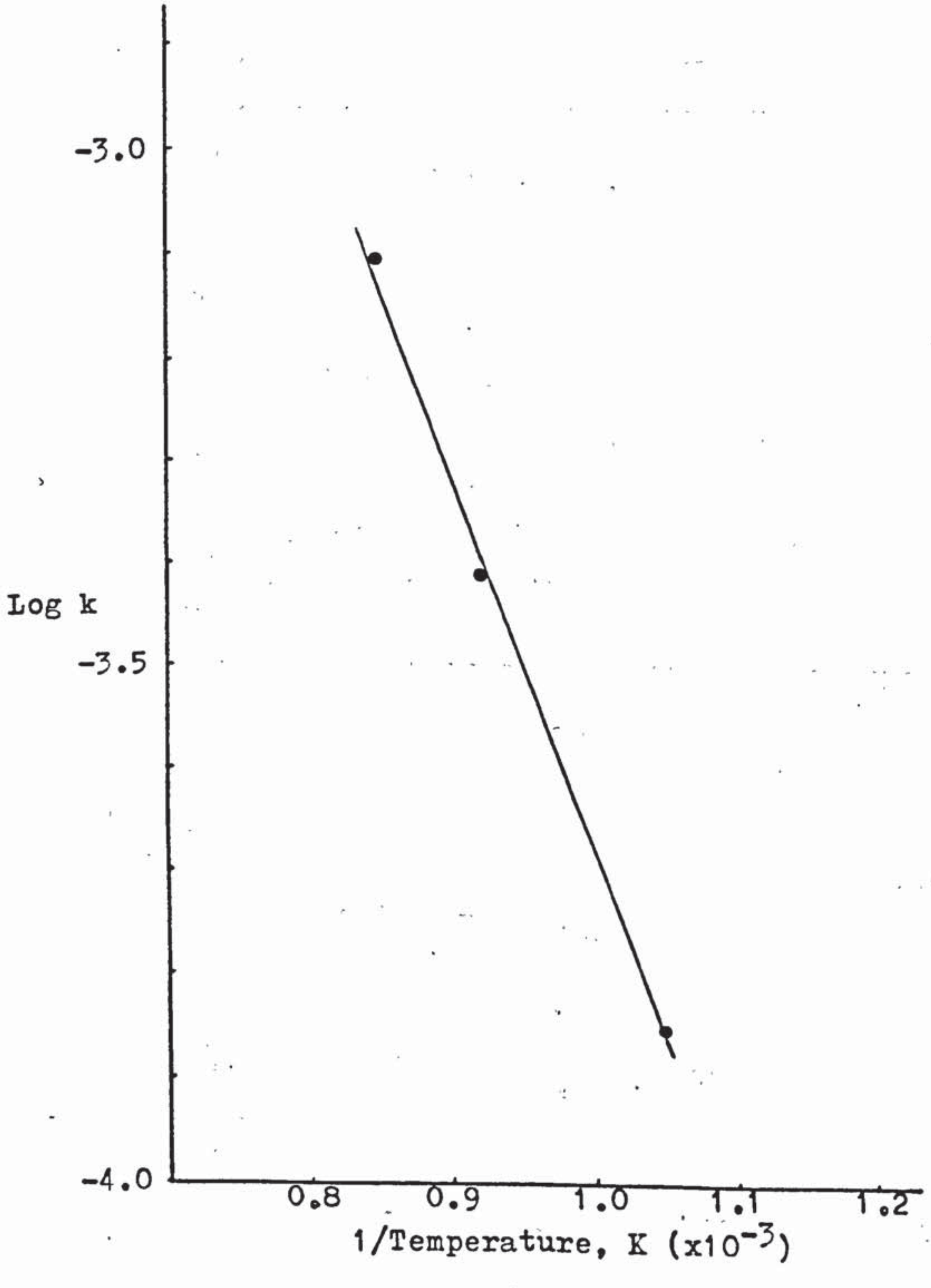


Fig.12.12 Log k vs. 1/Temperature

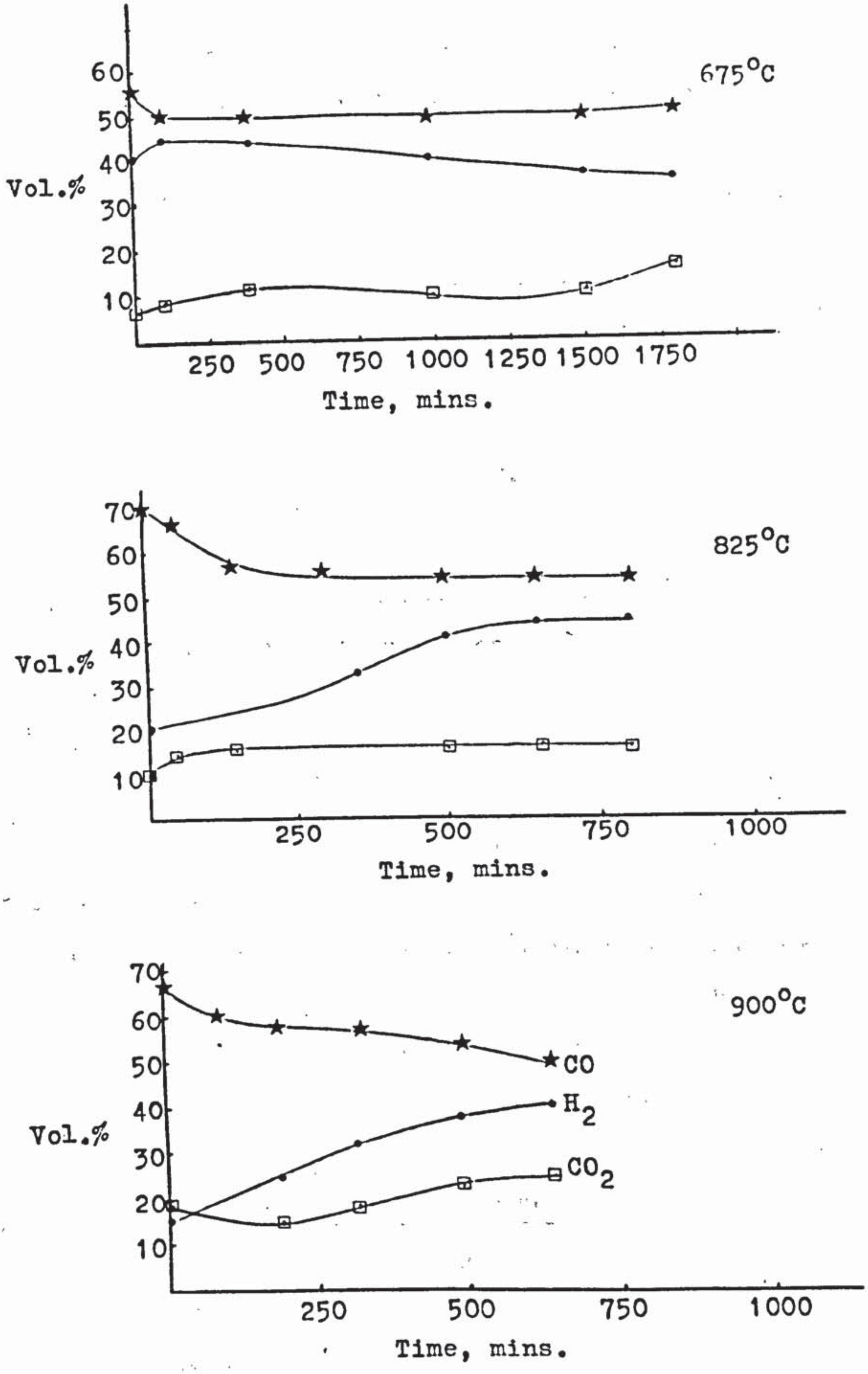


Fig.12.13 Steam Gasification Products

Melt analyses were not regularly performed during these experiments due to the technical difficulties in sampling from the reactor. However, a few samples of melt were taken during the experiment at 675°C ; the results of which are given in Table 12.13.

Temp°C	Time, mins	OH^- mol. %
675	0	0
	100	2.3
	500	5.4
	1000	3.6
	1950	3.9

Table 12.13 Melt Compositions

12.4.2.2 Physical Properties

The calorific values obviously vary with composition of product gases through each experiment. Given in Table 12.14 are the values that correspond to the compositions in Table 12.12 when the carbon-in-melt concentration is 0.25 g/l. Since hydrogen and carbon monoxide are very similar in calorific value it can be said that the values are proportional to the sum of these two gases.

Temp. °C	Calorific Value, MJ/m^3
675	10.7
825	9.5
900	9.4

Table 12.14 Calorific Values

12.5 Simultaneous Gasification with Air and Steam

12.5.1 Rate Data

Due to the use of air, higher gasification rates were again obtainable and so experiments reverted to the 7.5g sample weight. Table 12.15 shows the batch averaged rates and the rate at a carbon-in-melt concentration of 10 g/l for various combinations of air and steam. Although the detail is not shown here, clearly the latter rate expression involves all the calculation elaborated for air and steam gasifications covered in earlier sections.

Taking the data from experiments at 825°C, Figure 12.14 shows the air flow rates plotted against rate of gasification. The figure also shows the plot of air flow rate against gasification rate from Figure 12.6 where only air was used. The purpose of this is to show the effect of adding steam to the air flow.

To evaluate the effect of temperature, the rates of gasification for the 3.5 l/min air/3.0 g/min steam input were plotted against temperature. This is illustrated in Figure 12.15.

Temp. $^\circ$C	Air, l/min (mol / min)	Steam, g/min (mol / min)	Batch Rate, g/min	Rate 10 g/l g/min
675	1.0 (0.04)	3.0 (0.16)	0.13	0.16
	2.0 (0.08)	3.0 (0.16)	0.35	0.37
	3.5 (0.13)	3.0 (0.16)	0.42	0.45
	7.0 (0.26)	0.7 (0.04)	0.35	0.50
825	1.0 (0.04)	3.0 (0.16)	0.33	0.32
	2.0 (0.08)	3.0 (0.16)	0.44	0.46
	3.5 (0.13)	3.0 (0.16)	0.47	0.49
900	3.5 (0.13)	3.0 (0.16)	0.47	0.52

Table 12.15 Simultaneous Air/Steam Gasification Rates

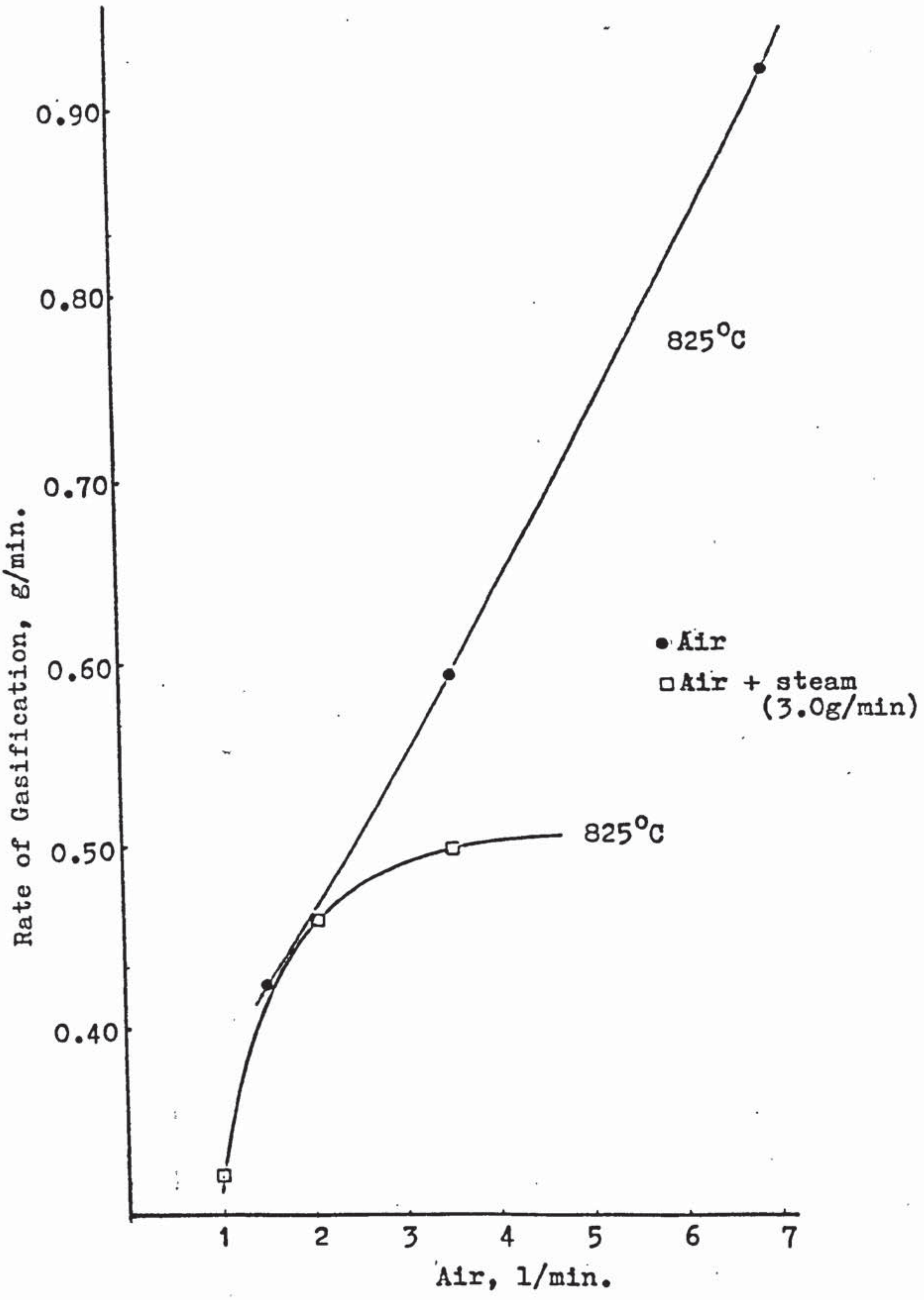


Fig.12.14 Rate of Gasification vs. Air Flow

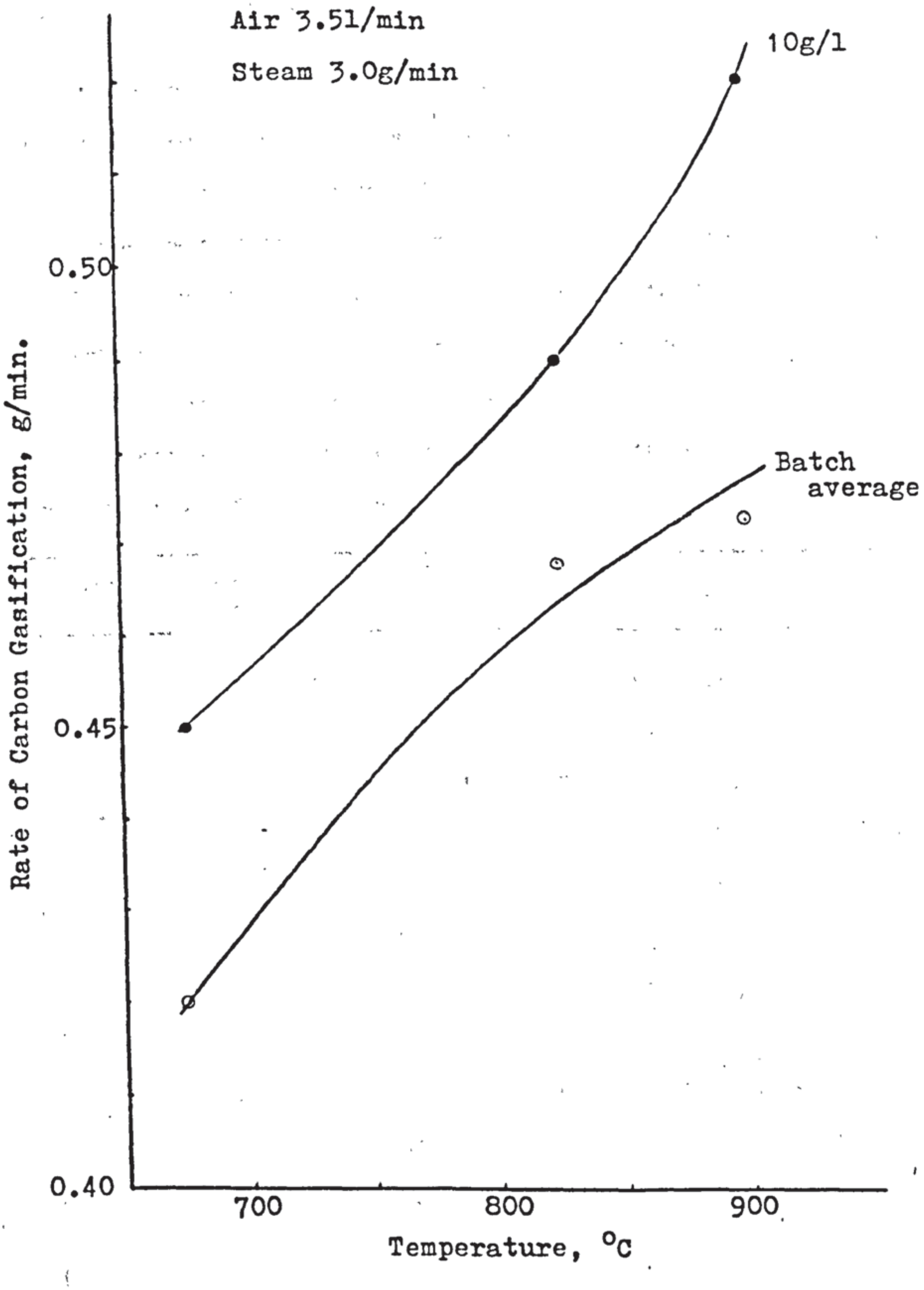


Fig.12.15 Rates of Gasification (Air/Steam) vs. Temperature

12.5.2 Characterization of Products

12.5.2.1 Chemical Analyses

The result of product gas analyses are given in Table 12.16. The mass spectrometer, which gives a running composition read out, was unable to separate the masses of nitrogen and carbon monoxide. In these experiments there was no simple satisfactory method of calculating the overlapping gases and so GLC was used. The GLC samples were taken over the whole run and so only represent an average. The gases occasionally contained a trace of hydrogen sulphide detectable by smell. The compositions at the carbon-in-melt concentration of 10 g/l are given in Table 12.17.

Temp. °C	Air, l/min	Steam g/min	Time, mins	O_2	CO_2	CO + N_2	H_2	Ar	(N_2	CO)
675	1.0	3.0	0	5	27	52	15	0.6	(55	5)
			3	5	19	65	9	0.7		
			10	5	14	77	3	"		
			30	"	"	75	2	"		
			47	13	8	77	1	"	-	
			75	20	1	77	0	"		
	2.0	3.0	0	15	5	74	5	"	(50	30)
			5	12	8	76	3	"		
			10	9	4	84	1	"		
			20	17	2	80	0	"		
			25	20	1	78	0	"		
			0	10	5	79	0	"		
			3	12	8	77	0	"		

Table 12.16 Air/Steam [illegible]

cont'd . . .

	3.5	3.0	7	13	4	76	0	0.7	(50	33)
			19	17	2	79	0	"		
			27	20	1	77	0	"		
	7.0	0.7	0	0	0	99	0	"	(60	20)
			5	2	2	95	0	"		
			15	11	2	88	0	"		
			25	19	2	80	0	"		
			30	21	1	77	0	"		
825	1.0	3.0	0	0	0	0	0	0	(40	10)
			2	1	22	43	33	0.5		
			10	2	5	87	1	0.7		
			15	8	3	88	0	"		
			25	20	1	78	0	"		
	2.0	3.0	0	0	25	64	10	"	(55	20)
			4	2	20	77	1	"		
			7	4	13	82	0	"		
			15	15	6	78	0	"		
			21	20	5	74	0	"		
			27	21	1	77	0	"		
	3.5	3.0	0	10	39	49	1	"	(50	5)
			2	11	14	74	1	"		
			6	12	12	75	1	"		
			12	16	9	74	1	"		
			20	20	4	75	0	"		
			25	21	1	77	0	"		
900	3.5	3.0	0	0	28	71	0	"	(50	35)
			4	1	12	86	0	"		
			10	5	6	88	0	"		
			15	16	4	79	0	"		
			20	18	2	79	0	"		
			25	20	1	77	0	"		

Table 12.16 Air/Steam Gasification Products, Vol.%

Temp.°C	Air, l/min	Steam, g/min	O_2	CO_2	CO + N_2	H_2	Ar	(N_2	CO)
675	1.0	3.0	5	19	65	9	1	(55	5)
	2.0	3.0	12	8	76	3	1	(50	30)
	3.5	3.0	13	4	76	0	1	(50	33)
	7.0	0.7	11	2	88	0	1	(60	20)
825	1.0	3.0	1	22	43	33	1	(40	10)
	2.0	3.0	0	25	64	10	1	(55	20)
	3.5	3.0	11	14	74	0	1	(50	5)
900	3.5	3.0	16	4	79	0	1	(50	35)

Table 12.17 Air/Steam Gasification Products at Char Concentration 10g/l

12.5.2.2 Physical Properties

The calorific values of the gases given in Table 12.17 are shown in Table 12.18.

Temp.°C	Air, l/min	Steam, g/min	Calorific Value, MJ/m^3
675	1.0	3.0	3.1
	2.0	3.0	3.8
	3.5	3.0	3.7
	7.0	0.7	2.3
825	1.0	3.0	3.8
	2.0	3.0	2.6
	3.5	3.0	2.6
900	3.5	3.0	4.1

Table 12.18 Air/Steam Gasification - Calorific Values

CHAPTER

THIRTEEN

CHAR GASIFICATION DISCUSSION

13 CHAR GASIFICATION DISCUSSION

13.1 General Comments

The main purposes of char gasification are to remove the unwanted char from the melt and in so doing to provide enough heat to counter heat losses and run the process. The first purpose is conceptually straight forward but the second, which still relates to the first is a little more complex. Basically the process can be operated in such a way as to generate heat in-situ, provide fuel that can then be burnt for heat or operate at intermediate stages. Being gases of relatively low calorific value it is not worthwhile taking steps to store the products of char gasification. In operating this process it will be necessary to first calculate the heat required within the reactor, the heat required by ancilliary equipment and the heat that can be used in the immediate vicinity of the plant for unrelated purposes (e.g. space heating). The process would then be operated in such a way as to fulfill all these needs. Any heat or fuel that cannot be utilized in this system will unfortunately have to be dissipated or flared.

It has been shown in the experimental and results sections that char gasification can be achieved by air, steam or mixtures of these agents. Gasification using air is an exothermic process providing in-situ heat but, by restricting the flow of air as has been done in most of these experiments, it is possible to achieve a situation where an intermediate amount of heat is produced in-situ and a notable amount of fuel is also produced. This restricted air technique has a number of process advantages over the excess air situation but from a scientific viewpoint it makes the study of reaction mechanisms extremely difficult. If the restricted air situation is still producing excess heat the next option is to start introducing steam. Char gasification using steam alone is an endothermic process producing fuels. These fuels are superior in calorific value to those of other options and can be burnt to provide the heat required in the process and other areas mentioned. It is theoretically possible to mix the degrees of air and steam gasification to reach a situation where the heat requirement is precisely catered for and the remainder produced as fuels.

The sum of gasification thermicity and product calorific values for all these cases will be equal, the value corresponding to the calorific value of the original carbon char. The differences in method of heat release are purely features of the method of char processing. It was the object of these experiments to determine the most advantageous way of utilizing the char produced in pyrolysis.

13.2 The Chemistry of Char Gasification

13.2.1 Char - Air Reactions

Although the basic chemistry of carbon combustion, as represented by equations 13.1 and 13.2 has been known for some time, the mechanisms by which these reactions occur have even recently been a matter for controversial discussion. In addition to the primary combustive reactions

$$C + \tfrac{1}{2}O_2 \longrightarrow CO \qquad \text{Eq. 13.1}$$

$$C + O_2 \longrightarrow CO_2 \qquad \text{Eq. 13.2}$$

it is generally accepted(289) that two secondary reactions can occur. These are shown in equations 13.3 and 13.4 :

$$CO + \tfrac{1}{2}O_2 \longrightarrow CO_2 \qquad \text{Eq. 13.3}$$

$$CO_2 + C \longrightarrow 2\,CO \qquad \text{Eq. 13.4}$$

The former is accompanied by energy emission in the visible waveband which is familiar as flame.

Since the advent of modern techniques there has been considerable debate over whether both carbon oxides are formed as primary products or occur only by the secondary reactions(289). It is now generally accepted that both products are primarily formed. Arthur(293) found, for two different carbons, that the primary product ratio was given by

$$CO/CO_2 \doteq 10^{3.4}\, e^{-12,400/RT}$$

which was confirmed by Rossberg(294). However although it is not possible to say for certain what is the sequence of events leading up to the release of these products, it is possible to visualize the collision of an oxygen molecule with the carbon surface where, at a suitable site, it becomes chemisorbed. It has been suggested(298) that it remains mobile and on reaching a carbon site with suitable characteristics dissociates to two independent oxygen atoms. Walker(289) has proved this subsequent independence using radioactive tracing techniques. Once the chemisorbed atom stage has been reached it may remain unchanged, become mobile or form a surface complex. It appears that eventually the last of these is formed and that then interactions between complexes occur before the product gas is released.

At this point one of the secondary reactions can be brought into the mechanism. The surface complexes can react with gases present including carbon dioxide as indicated by equation 13.4. The entire general scheme is illustrated in Figure 13.1. It has also been postulated(299) that mobile complexes may exist in which case the final steps in the scheme can be duplicated.

In section 13.3 these proposals are related with physical conditions to evaluate the controlling processes of these reactions. The discussion so far is only intended to give a feeling for the chemistry involved in the process.

13.2.2 Char-Steam Reactions

The standard chemical reaction for the gasification of carbon by steam is written as,

$$C + H_2O \longrightarrow CO + H_2 \qquad \text{Eq. 13.5}$$

However this system is also subject to a secondary reaction often known as the shift reaction,

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \text{Eq. 13.6}$$

Unlike the work of Walker(289) on the carbon-oxygen system there is no decisive evidence to show a dissociative step in the carbon-steam mechanism. However, Long and Sykes(304) propose a mechanism based on this pretext; on reaching the carbon surface at an active

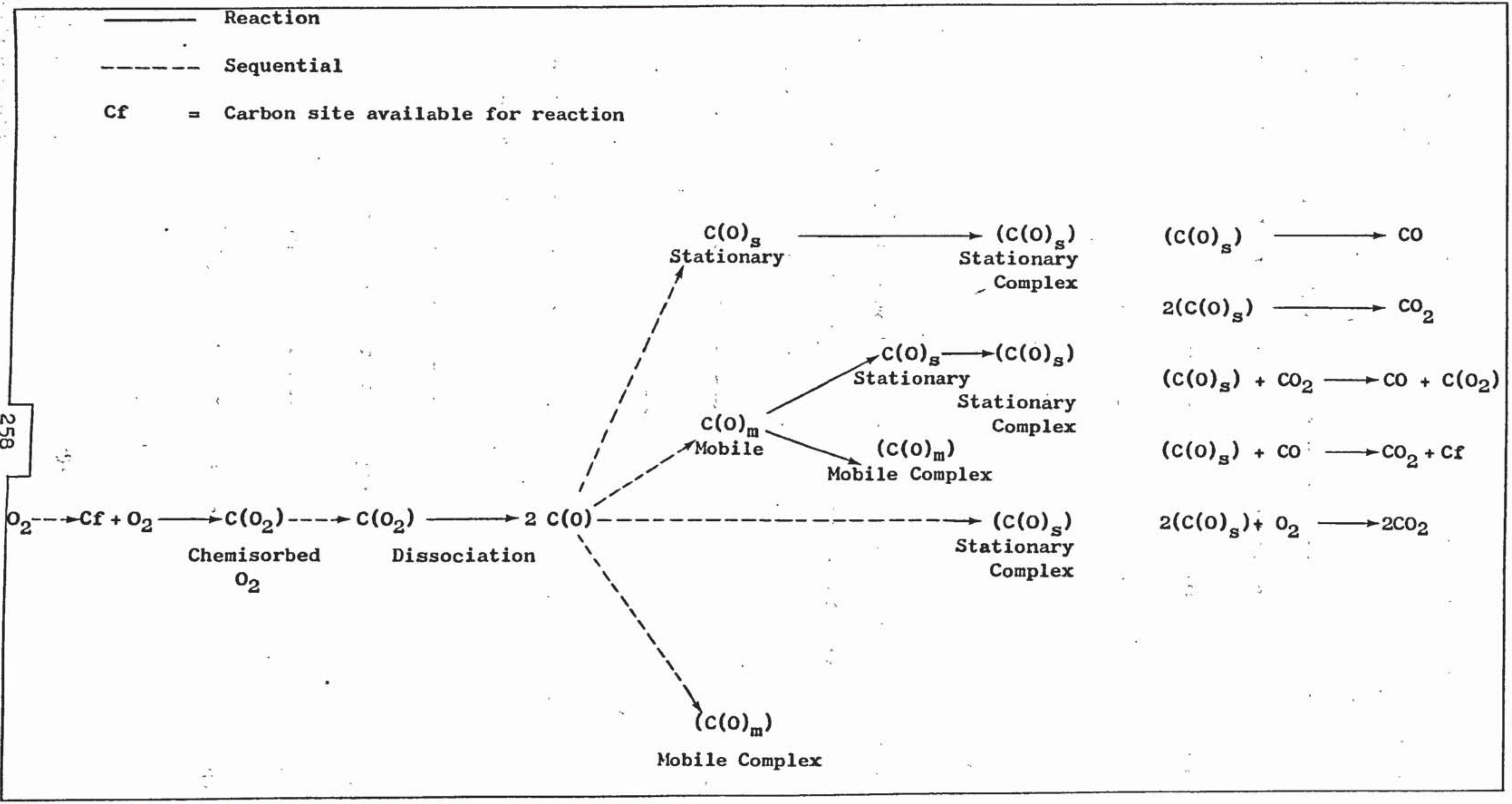


Fig.13.1 Mechanism Sequences

site the steam dissociates and the products are chemisorbed on adjacent sites. The hydroxyl hydrogen is then said to jump to join the lone hydrogen atom and at a suitable point the pair leave as hydrogen gas. Likewise the remaining oxygen extracts a carbon atom at its site and leaves as carbon monoxide.

$$2\,Cf + H_2O \longrightarrow C(H) + C(OH) \qquad \text{Eq. 13.7}$$

$$C(H) + C(OH) \longrightarrow C(H_2) + C(O) \qquad \text{Eq. 13.8}$$

$$C(H_2) \rightleftharpoons Cf + H_2 \qquad \text{Eq. 13.9}$$

$$C(O) \longrightarrow CO \qquad \text{Eq. 13.10}$$

The alternative mechanism suggested by Gadsby et al.(302) and Johnstone et al.(303) involves chemisorption of intact steam followed by release of both product gases simultaneously,

$$Cf + H_2O \longrightarrow C(H_2O) \qquad \text{Eq. 13.11}$$

$$C(H_2O) \longrightarrow CO + H_2 \qquad \text{Eq. 13.12}$$

However it does not seem unreasonable to suggest that this could more accurately be,

$$Cf + H_2O \longrightarrow C(O) + H_2 \qquad \text{Eq. 13.13}$$

$$Cf + H_2 \rightleftharpoons C(H_2) \qquad \text{Eq. 13.14}$$

$$C(O) \longrightarrow CO \qquad \text{Eq. 13.10}$$

$$C(H_2) \rightleftharpoons H_2 + Cf \qquad \text{Eq. 13.9}$$

At this stage it is not possible to say which is the correct mechanism for the primary reaction. Since the C(O) species exists in both mechanisms a surface shift reaction of the following mechanistic form may occur:

$$C(O) + H_2O \longrightarrow C(O_2) + H_2 \qquad \text{Eq. 13.15}$$

$$C(O_2) \longrightarrow CO_2 \qquad \text{Eq. 13.16}$$

although in the dissociative case this is not so simple. Both systems would more correctly follow the detail shown in the carbon-oxygen mechanisms.

13.2.3 Simultaneous Use of Air and Steam

Where air and steam mixtures are used as gasification agents the chemistry and mechanisms are basically the same as in the separate systems. However there are one or two additional considerations that should be noted.

The first of these is the reaction between hydrogen, a product of the steam reaction, and oxygen.

$$H_2 + O_2 \longrightarrow H_2O \qquad \text{Eq. 13.17}$$

Carbon monoxide formed by steam reaction may also be oxidized to the dioxide as can the air product. Likewise carbon monoxide from the air reaction is equally susceptible to the steam shift reaction as is steam produced carbon monoxide. A further point of note is the possibility that the mixed system may result in a lower rate than that expected for air alone. The mechanism suggests that this could be due to blocking of active sites on the carbon surface by water molecules.

13.2.4 Catalytic Activity

Much has been made of the significance of catalysis of the carbon-oxygen reactions in molten salt systems. Lewis et al.(295) report activity at 650°C while Blayden et al.(330), working on ignition conditions, report it as low as 300°C. During this work there has been little opportunity to pursue this line of investigation; the ignition temperatures of most cokes and chars being well below the experimental temperatures in use.

The literature presents nothing in the way of mechanistic proposals, neither is there any suggestion as to which step is catalysed. However hints have been made that the melt equilibrium,

$$CO_3^{2-} \rightleftharpoons O^{2-} + CO_2 \qquad \text{Eq. 13.18}$$

may be involved. It is possible that carbon dioxide so produced may have an additional oxidizing effect.

13.3 Physical Models

13.3.1 Reactor Bed Model

The purpose of the reactor bed model is to describe how the physical conditions in the reactor may effect the composition of the products and thermicity of the reactions.

It is now generally accepted that both carbon monoxide and carbon dioxide are primary oxygen-carbon products. According to Arthur(293) the monoxide will be dominant at these temperatures. If a stable bed is taken where the oxygen is introduced at the bottom the product gases will be formed in this lower region before this mixture of oxides starts to rise through the bed. Subsequent reactions are dependent on the concentrations of unreacted carbon and oxygen and the rate of gas flow. The possible models are:

1. That unreacted oxygen meets further carbon and more primary products are formed,

2. That unreacted oxygen reacts with carbon monoxide and flames to form carbon dioxide,

3. That unreacted oxygen passes completely through the reactor unaltered. (Not meeting any reactive materials.)

Next there is a model applying to the situations where all oxygen is used up in the primary reaction:

4. That the primary carbon dioxide reacts with carbon to form carbon monoxide.

The final models are those applying to complete use of carbon in the primary reaction:

5. That unreacted oxygen passes straight through the

reactor (similar to 3).

6. That unreacted oxygen reacts with carbon monoxide to form dioxide (similar to 2).

Those options are illustrated in Figure 13.2 where it becomes clear that certain combinations of these are also possible. It may be argued that this is an over-simplistic view of likely occurrences in an agitated molten bed. However, the model is applicable to each char particle on a micro-scale; the layers described merely being layers around the particle.

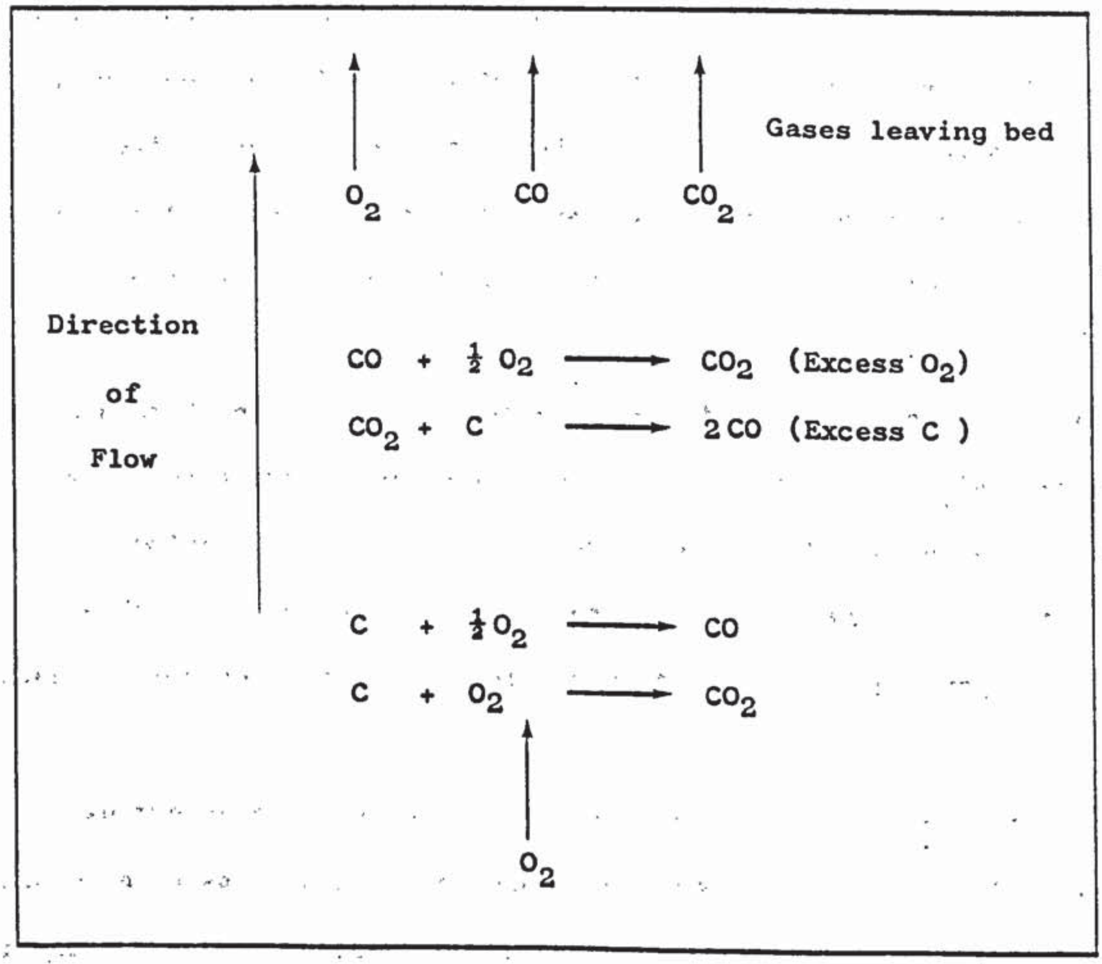


Fig.13.2 Bed Model

It has been observed that the product of air gasification of char is predominantly, typically over 95 vol. %, carbon monoxide. In these cases oxygen is restricted in supply limiting the secondary options. The explanation for the product composition is therefore that any dioxide formed reacts with carbon to give monoxide although some dioxide may avoid contact with carbon in the upper zones of the bed and thus be seen in the product. As the air flow is increased the likelihood of oxygen surviving to the secondary zone is increased or viewed another way the height of the primary zone is increased. However viewed the result will be a greater concentration of dioxide in the final gases. It may also be that more oxygen passes totally unreacted. Both these are found in experimental results. Theoretically it should be possible either by greatly increasing the air flow or by narrowing the bed depth to produce entirely carbon dioxide and excess oxygen in the final stream. However in a simple geometry reactor this would probably be impossible on grounds of flow evidence.

In studying this model the sizes of the various zones are unknown and so effects are to be considered only qualitatively. Further bulk mass transfer (bubble flow) may play a considerable role in this model. However the conclusion is that operated under reasonable conditions carbon monoxide is highly likely to be the dominant product.

In the case of carbon-steam gasification there is evidence that steam was always in considerable excess and so the bed can be considered as uniform, although on a micro-scale the primary reaction must occur before the shift reaction. The experimental results show carbon dioxide concentrations around 20 vol. % which indicates a considerable shift:

$$C + H_2O \longrightarrow CO + H_2 \quad \text{Primary reaction} \qquad \text{Eq. 13.5}$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad \text{Shift reaction} \qquad \text{Eq. 13.6}$$

The primary reaction produces equal amounts of carbon monoxide and hydrogen, carbon dioxide resulting from a shift. At 800°C the equilibrium constant for the shift reaction is almost one(314) which indicates a product mix of 60 vol. % hydrogen and 20 vol. % each of carbon oxides. This shows that the shift reaction is near equilibrium, agreeing with Lewis et al.(295).

In the system where both air and steam are used as gasification agents the bed model will follow that of the air system. However steam will certainly be present in all layers of the system. Since all carbon monoxide is susceptible to the shift reaction, carbon dioxide levels will be higher than those obtained by air alone, explaining experimental observations.

13.3.2 Rate Control Model

In order to achieve gasification three features must, in varying degrees, be satisfied. Firstly the reactants, in this case carbon and the gasification agents air and/or steam must be brought together. This is achieved by bulk mass transfer or by diffusion of the gases through the surrounding medium. Secondly heat must be supplied to the reactants if they are to reach activation energies. This involves the normal heat transfer phenomena. Finally, the products of gasification must be allowed to escape from the reaction zone so as not to have a hindering effect on the chemical equilibria.

The main aim here is to discover how the gasification is affected by physical parameters and which parameters are responsible for control of the rate under the various conditions studied. Experimental results have suggested that most of the air gasification rates are controlled by an external factor; air supply. Even assuming total conversion to carbon monoxide only, the maximum possible rates of gasification at the air flow rates of 1.5, 3.5 and 7.0 l/min are 0.32, 0.76 and 1.52 g/min. At an air flow of 1.5 l/min this maximum rate is always reached indicating oxygen deficiency control. At 3.5 l/min it is closely approached from 825°C upwards but at 7.0 l/min the maximum is not reached regardless of temperature. Generally air supply is the controlling factor at lower air flow rates and higher temperatures.

In the cases where external air supply is not responsible for rate control there are three main factors to consider: heat transfer, chemical kinetics and mass transfer. The latter can be subdivided into bulk and diffusional mechanisms.

Heat transfer would appear highly unlikely to be a controlling factor since the whole system being in a molten bath is already at temperature. In addition most of the reactions are exothermic, so if the reactants are above ignition temperature once the reaction has been initiated the particulate surface temperature will rise rapidly to a stable combustion temperature around 700°C (289). It is however possible to show scientifically that heat transfer is definitely not the controlling factor; this can be done by studying the mechanisms of conduction, convection and radiation. Conductive heat transfer between media is related to surface area which even disregarding pores is considerable in the irregular carbon particles and small gas bubbles. Convective heat transfer is assisted by two features: artificial stirring and turbulence caused by rising gases, so is not likely to be restrictive. Both conduction and convection are normally proportional to temperature gradients. Radiation is of questionable effect in this situation, although the black colouration of the char could be considered important. The efficiency of heat transfer by radiation is proportional to the medium temperature to the power of four. The combined effects would tend to give a near to exponential increase in rate with temperature but as Figure 12.2 shows this is clearly not the observed case and so heat transfer can be eliminated.

A general guide to the remaining controlling parameters is given by Marsh(331) whose findings are illustrated in Figure 13.3. The positions of T_1 and T_2 will vary with char characteristics (particle size, film effects, particle porosity, etc.) and reaction conditions (air flow rates, etc.). The diffusion may be considered as two types: diffusion of oxygen through the melt and through the char particle pores. The latter makes very large surface areas available.

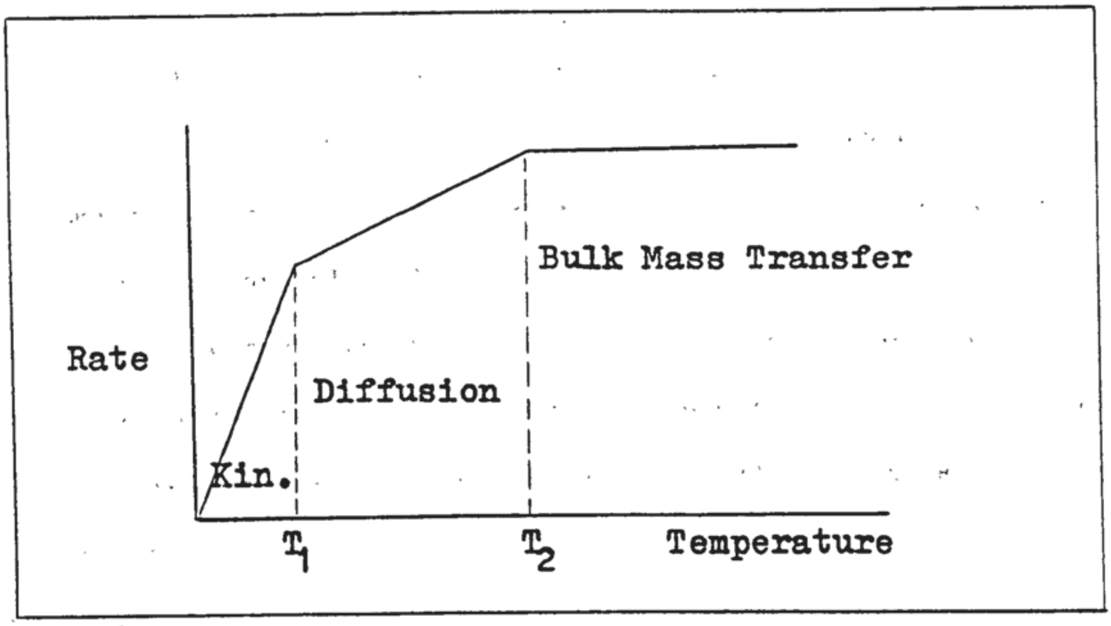


Fig.13.3 Effect of Temperature on Rate Control

Kinetic control is only likely at low temperatures where rate constants are very low. Here the experiment at 675°C is the only possible candidate for kinetic control. For most experiments the Arrhenius plot of log k vs $^1/$Temp is not valid due to external restriction. However the experiments performed using an air flow rate 7.0 l/min it could be argued this test of kinetic control is valid; nevertheless this does not show linearity and so kinetic control is extremely unlikely.

This leaves only mass transfer phenomena to evaluate. Since the reactor is very well mixed it is unlikely that bulk mass transfer is rate restricting within the reactor. It has already been shown that ex-reactor air supply is often rate restricting. The diffusional mass transfer can be considered in two ways: diffusion of oxygen through the melt to the superficial carbon surface or pore diffusion through the carbon to gain access to a greater surface area. As the oxygen solubility in the melt at these temperatures is low the former can be neglected. The mechanism of mass transfer can thus be summarized as the initial air bubble coming into bulk contact with the char particle followed by diffusive transfer of the gas through the porous structure of the char. This type of pore diffusion model has been described by Hashimoto in other solid-gas reacting systems where it is the rate controlling feature. It may be the controlling feature in these reactions where the stoichiometric rate is not reached. Diffusion is normally proportional to temperature to the power of $^3/_2$; this is tested in Figure 13.4 where rate is plotted against temperature to this power. The figure shows diffusional dependence for air flows of 7.0 l/min and for the lower air flows at lower temperatures. The three plots show clearly a transition from external supply control to diffusional control.

The conclusions regarding air gasification under these experimental conditions are that kinetic control is only found under suitable concentrations of higher air flow and lower temperature, air supply restricts most cases and diffusion controls rate where excess air is present.

Where steam is used as a gasification agent the situation is entirely different. As nearly all steam passes through the reactor unreacted it is clear that it is present in considerable excess which might also be expected from the rate data. Here kinetic control is a likely possibility and using the standard Arrhenius plot it is seen that this is at least close to being true; Figure 13.5 shows near linearity. However the diffusional effects must still apply which may

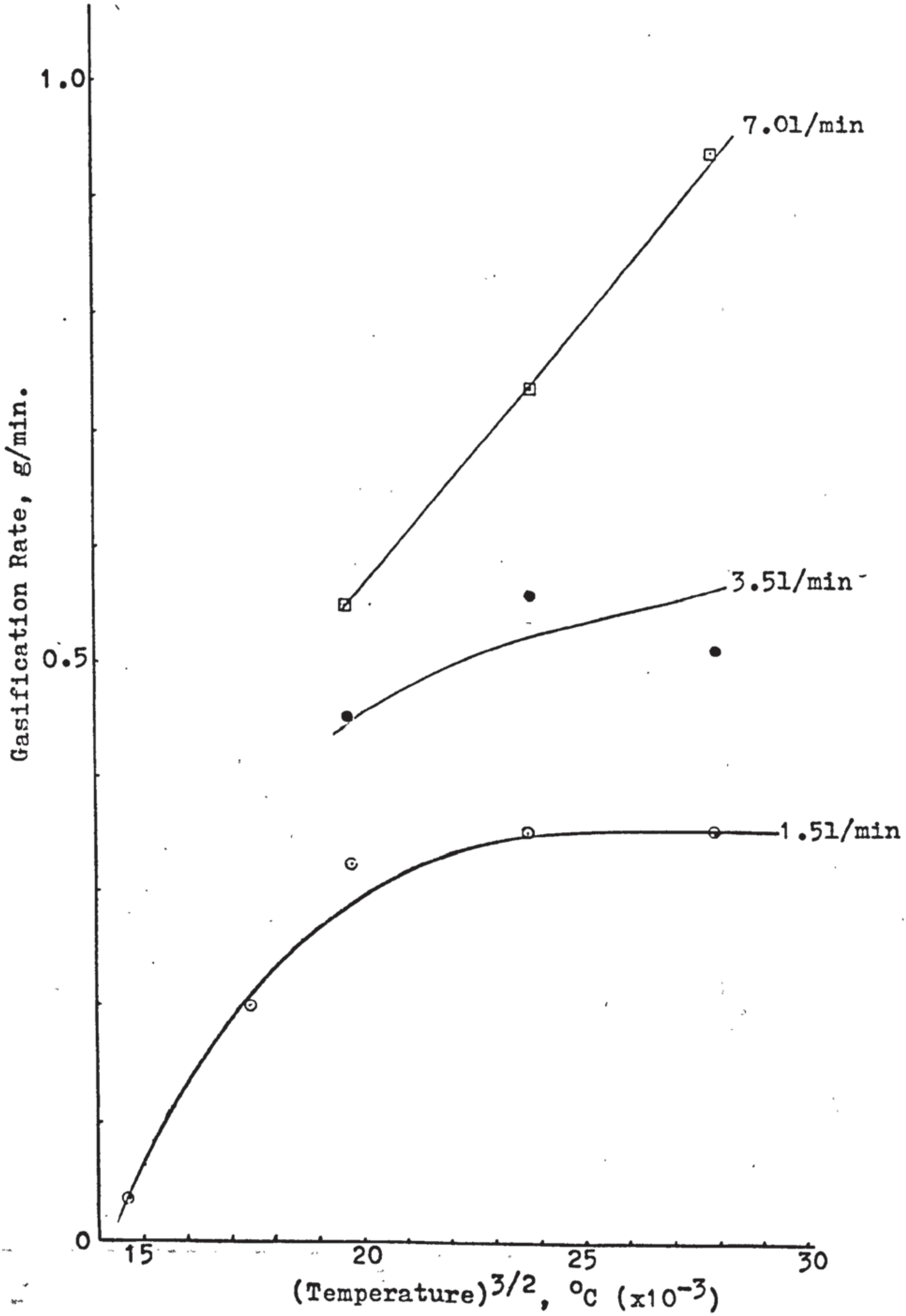


Fig.13.4 Rates vs. (Temperature)$^{3/2}$

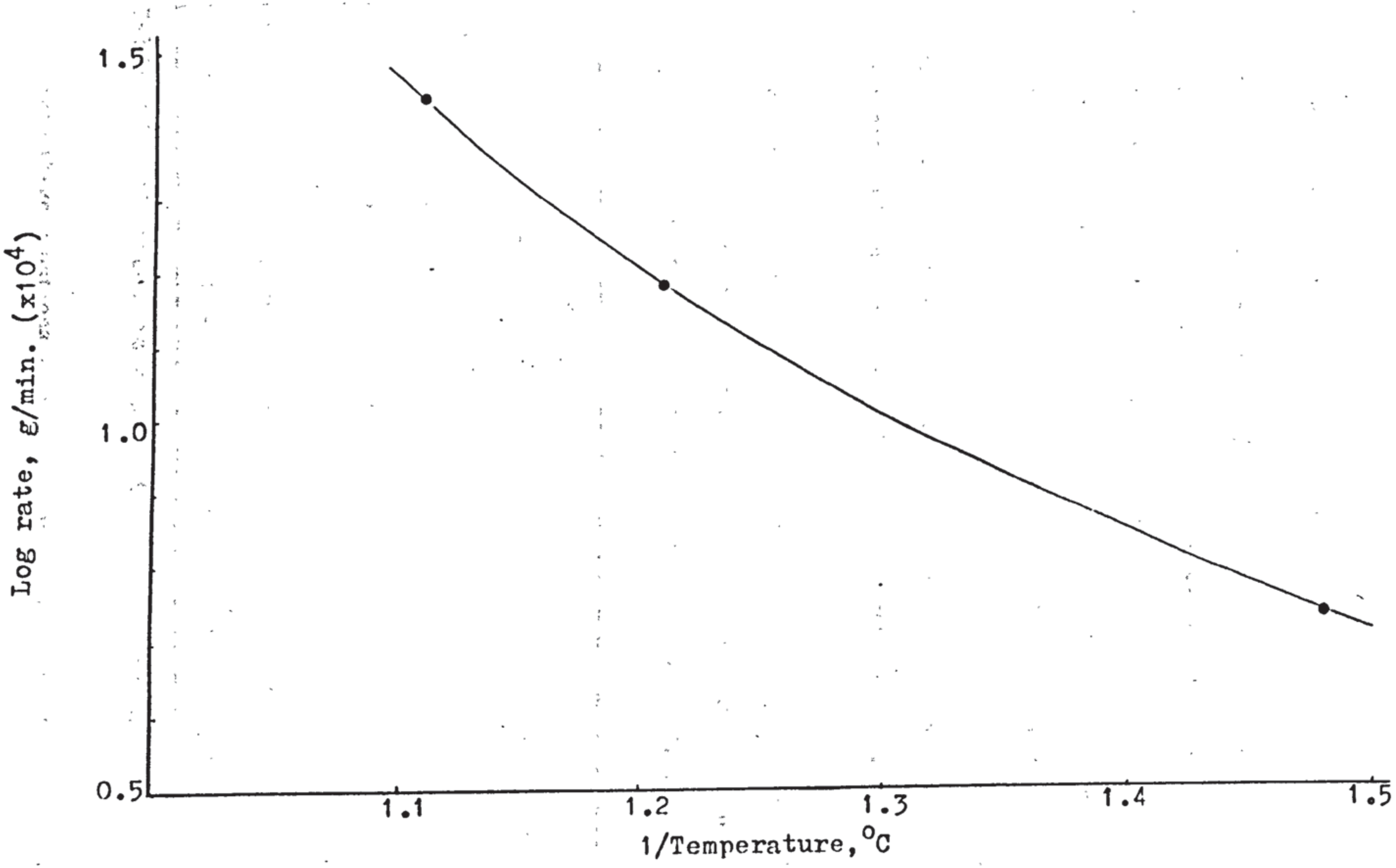


Fig.13.5 Arrhenius Plot of Steam Gasification Rate

explain the slight curvature over the whole temperature range.

13.4 The Thermochemistry of Gasification

It is well known that the reactions between carbon and oxygen are exothermic while that between carbon and steam is endothermic. At an early stage in this thesis (Chapter 6) it was suggested that it might be possible to use both air and steam to gasify the char in such proportions so as to provide just enough heat from the reactions to operate the process. This would involve calculation of all the heats necessary for pyrolysis, to counter heat losses and to run any ancilliary plant equipment or feed heat to nearby installations.

The heats of reaction for the various reactions occurring are given below; using free energies the standard temperature figures have been adjusted to 825°C. These are shown in Table 13.1.

Kp	Reaction	ΔH, kJ
8.8×10^{9}	$C + \frac{1}{2} O_2 \longrightarrow CO$	ΔH = -112.5 kJ(- 9.4 MJ/kg carbon)
6.3×10^{18}	$C + O_2 \longrightarrow CO_2$	= -394.4 (-32.9 ")
10^{10}	$CO + \frac{1}{2} O_2 \longrightarrow CO_2$	= -281.9 (-23.5 ")
1.2×10^{1}	$CO_2 + C \longrightarrow 2\,CO$	= +169.4 (+14.1 ")
1.2×10^{1}	$C + H_2O(g) \longrightarrow CO + H_2$	= +135.6 (+11.3 ")
1.0	$CO + H_2O(g) \longrightarrow CO_2 + H_2$	= - 33.8 (- 2.8 ")

Table 13.1 Thermodynamic Data for Gasification Reactions

From these equations it is calculated that complete combustion (not that this is necessarily achievable here) to carbon dioxide would yield 32.9 MJ per kg of carbon. Complete gasification with steam assuming the proven equilibrium shift will require a heat input of 9.9 MJ/kg. Thus no net heat is produced when carbon reacts with oxygen and steam in the molar ratio 1 : 3.3. Figure 13.6 shows the heat generated for complete reactions of all possible ratios. However there are two complications to this description. The first is that complete reaction between carbon and air to carbon dioxide does not in this case take place and the second is one of very different rates for the two gasifications.

Air gasification thermochemistry has so far only been considered as total combustion. Experiments have shown that under the temperature conditions of 675 - 900°C and air flows of 1.5 - 7.0 l/min, the gas produced is 80 - 97 vol. % carbon monoxide; the higher figure being favoured by lower temperatures and flow rates. Now, although this makes no difference to the total energy available it indicates that the heat of reaction (i.e. the heat liberated in the reactor) is only 12.5 MJ/kg carbon. Assuming this and applying the shift reaction to all carbon monoxide the realistic heat figures are those illustrated in Figure 13.7 and tabulated in Table 13.2. The theoretical autothermal point now occurs when 68% of the carbon reacts with steam and 32% with oxygen. (The curvature of Fig. 13.7 is due to the shift reaction's action on air produced carbon monoxide.)

Achieving these ratios of reacting gases is complicated not only by the oxygen content of air but even more so by the fact that carbon gasification with air has been shown experimentally to be at

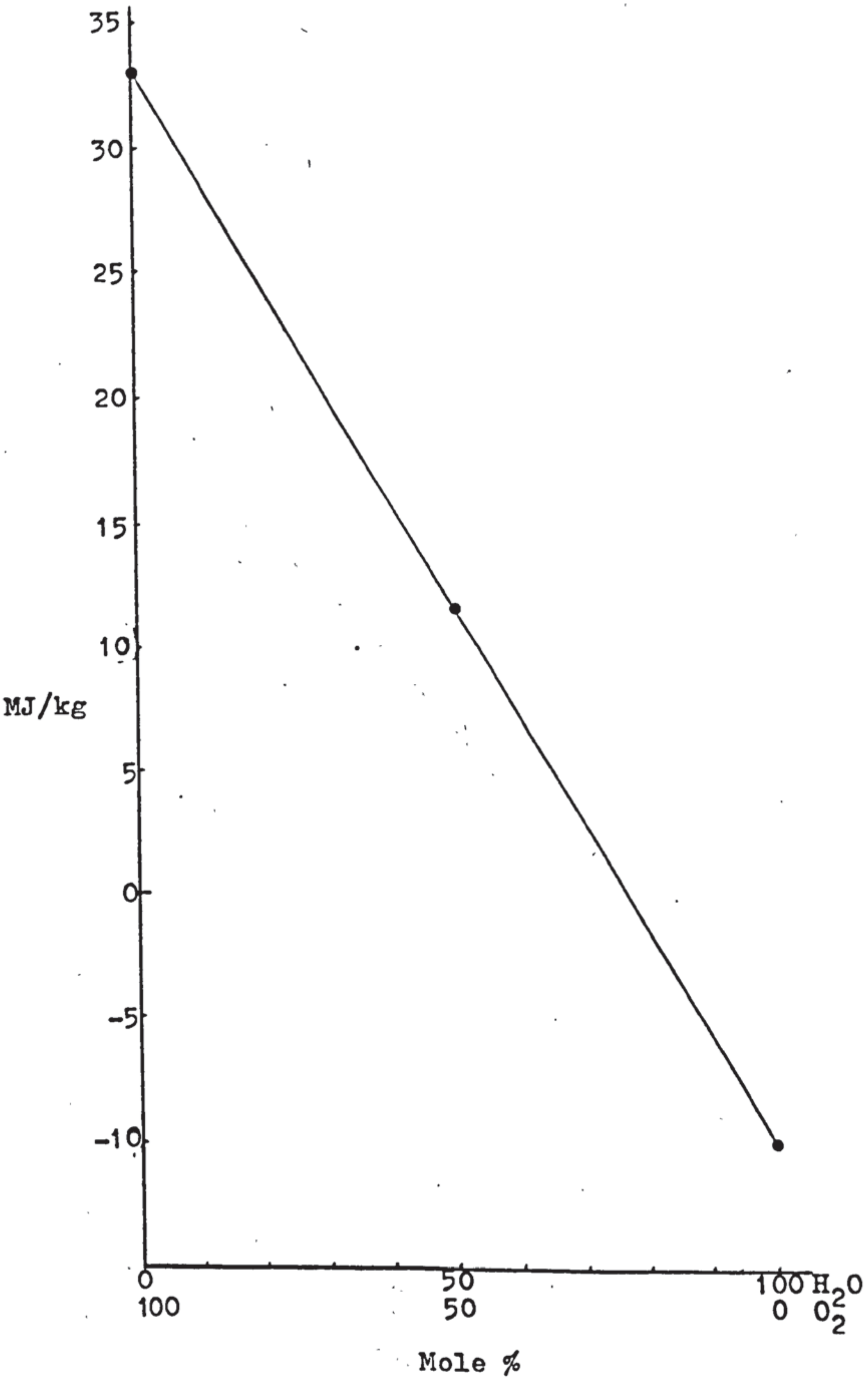


Fig.13.6 Maximum Theoretical Heats of Gasification

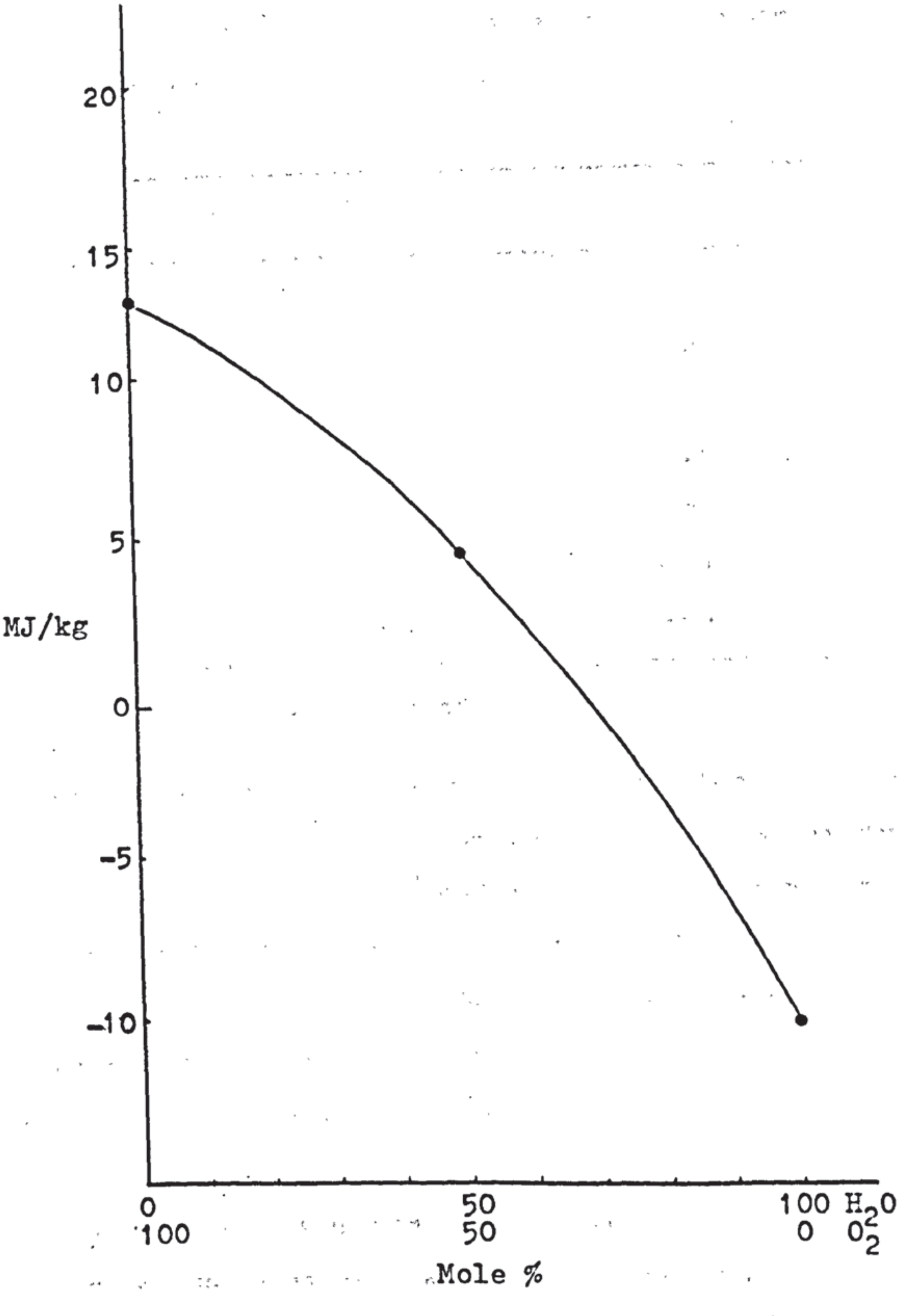


Fig.13.7 Practical Heats of Gasification

least some 1500 times faster than with steam. So to achieve a balance it will be necessary to increase the steam reaction or reduce the air reaction. The first can only be done by increasing the char-steam contact, that is to say increasing the volume of the reactor so it contains more char.

Oxygen, mol. %	Steam, mol. %	Heat of Gasification MJ/kg
100	0	12.5
80	20	10.0
60	20	6.6
40	60	2.1
32	68	0
20	80	-2.9
0	100	-9.9

Table 13.2 Heats of Gasification

Increasing the reactor size is mainly a cost consideration although its effect on other parts of the process will have to be considered as matters for further experimental evaluation. The present implication is a theoretical steam reaction volume allocation much larger than that of the air reaction. The alternative of reducing the air reaction to meet the steam rate is not practical since it will result in a drastic overall fall in rate.

At this point it appears that achieving an autothermal balance between air and steam gasification reactions is impractical. However there are external heat demands and losses to consider which are discussed in Chapter 15.

13.5 Rates of Gasification

13.5.1 Comparative Discussion

It has already been shown that the rates of char gasification with air are, at 1.5 and 3.5 l/min, controlled by the available air supply. This is not true at the higher air flow rate where the rate of gasification is controlled by diffusive mass transfer of gases in the char particle. Given the reactant air/gasification products counter-flow situation this is perhaps not surprising. In the case of steam gasification there is evidence of kinetic control but it seems likely that diffusion still plays a major role in rate determination. However at the lowest temperatures studied kinetic control is universal. These factors often make comparisons with the literature difficult as most other workers, specifically studying kinetics and mechanism, use excess oxidants.

The rates of air gasification found in this work are given in Table 12,3 and plotted with respect to various parameters in Figure 12.2 and 12.3. These confirm the superficial rate restrictions of low air flow and low temperature. Since the probable operating concentration of char is about 10 g per litre of melt this value was used for comparative purposes. In the case of the carbon-steam reaction the comparative concentration was only 0.25 g per litre and so it was not possible to make comparisons between air and steam. Total kinetic control would allow linear adjustment but diffusive control makes this unjustifiable. Table 13.3 shows all the rate data for air and steam char gasification corrected to 10 g/l.

Temp. °C	Air, l/min	Steam, g/min	Rate, g/min	Stoichiometric Max. Rate, g/min
675	1.5	-	0.385	0.32
	1.5	-	0.419	0.32
750	3.5	-	0.600	0.76
	7.0	-	0.685	1.51
	1.5	-	0.419	0.32
825	3.5	-	0.593	0.76
	7.0	-	0.920	1.51
	1.5	-	0.431	0.32
900	3.5	-	0.713	0.76
	7.0	-	1.163	1.51
675	-	2.15	5.6×10^{-4}	1.53
825	-		15.2×10^{-4}	
900	-		32.0×10^{-4}	

Table 13.3 Comparative Rate Data

In addition to the complications already mentioned it should be noted that comparisons with the literature are also subject to a variation in types of carbon used. The units of rate expression also vary between publications, therefore it is necessary to make some temporary assumptions about the experiments performed in this work. If the reactions are treated as following first order kinetics which may be partially true, rate constants for carbon-air reactions are

1.50 - 4.40 s^{-1} and those for carbon-steam reactions are 0.0008 - 0.0035 s^{-1}. This further shows air gasification to be faster by a factor of 1500.

The rate constants for graphite under oxygen attack quoted in the literature(289) are as high as 500 s^{-1}. This rate was obtained with the use of pure oxygen and an excess flow rate. Goring(311) gives a carbon-steam rate constant of 5.5×10^{-5} s^{-1} which can be directly compared with this work. Goring's rate is slower than that obtained here, suggesting that the pyrolysis char is particularly reactive towards steam.

Another possible comparison is in the air-to-steam gasification rate ratio, here 1500. The same ratio calculation Walker et al.(289) quote 3×10^4, Goring and Fuchs quote(297,313) 5×10^5 and Lisyutkina quotes(308) 10^4. All greater than in this work, but the degree is not quantifiable due to the use of restricted air supply. However all workers agree that the steam reaction is far slower. In fact it is almost certain that it is too slow for effective use in gasification of char produced as part of a tyre pyrolysis process. The best option will be to stick to the restricted air flow condition for gasification, while noting the great scope for higher rates at increase air supply.

13.5.2 Evaluation

It was stated at the opening of this chapter that one of the main purposes of char gasification was to remove the essentially unwanted char from the melt. Clearly, in a continuously operating process, to achieve this the rate of char gasification must keep pace with the rate of char production simultaneously occurring during pyrolysis. The rates of char production can easily be calculated from the pyrolysis results. Expressed in terms of the pyrolysis rate at a tyre concentration of 40g per litre of pyrolysis melt, the rates of char production are given in Table 13.4. It was shown in Chapter 10 that the optimum pyrolysis temperature was no higher than 500°C which, from Table 13.4, indicates that a gasification rate of at least 5.6g of char per minute per litre of pyrolysis melt would be required. If the volume of melt in the gasifier is increased clearly the rate of gasification required in terms of gasification melt will be lower.

Temp. °C	Pyrolysis Rate, g/min.l	Char Production, g/min.l
475	15.0	5.6
525	32.0	11.7
650	40.0	14.8

Table 13.4 Char Production Rates

For reasons concerned with product value, corrosion and heat exchange it is desirable to restrict the temperature. However it may be necessary to operate at higher temperatures to achieve the rate desired. The rates of char gasification at a char concentration of 10g/l (about that occurring in the pyrolysis reactor) are given in terms of melt volume in Table 13.5.

Temp. °C	Air, l/min. l melt	Steam, g/min. l melt	Gasification Rate, g/min. l melt
675	3.0	-	0.770
750	3.0	-	0.838
	7.0	-	1.200
	14.0	-	1.370
825	3.0	-	0.838
	7.0	-	1.186
	14.0	-	1.840
900	3.0	-	0.862
	7.0	-	1.426
	14.0	-	2.326
675	-	4.6	11.2×10^{-3}
825	-	4.6	30.4×10^{-3}
900	-	4.6	64.0×10^{-3}
675	2.0	6.0	0.320
	4.0	6.0	0.740
	7.0	6.0	0.900
	14.0	1.4	1.000
825	2.0	6.0	0.640
	4.0	6.0	0.920
	7.0	6.0	0.980
900	7.0	6.0	1.040

Table 13.5 Volume-corrected Rate Data

It is interesting to note that addition of steam to a fixed air flow rate actually causes a drop in rate, not the additive increase that might be expected. A possible explanation of this is that water occupies many active sites on the carbon surface making them unavailable to oxygen. If the water complexes are more stable or preferentially formed the rate of the mixture will be lower than that of air alone.

Comparing the rates of char production in Table 13.4 with those of char gasification in Table 13.5 it is clear that char cannot be produced and gasified in reactors of equal volumes under these conditions. It will be necessary, in some way, to increase the capacity of the gasification reactor. This can be achieved in the following ways: increasing the temperature, increasing the air flow rate, increasing the air flow rate and char concentration or by increasing the reactor volume.

Increasing the temperature has the disadvantages of increasing the carbon dioxide production which reduces the value of the product and releases more heat in the reactor. It will also increase corrosion and so temperature should be restricted, if possible, to 800°C. Increasing the air flow has a considerable effect on product carbon dioxide content and likewise increasing heat release in the reactor to what may well be an excessive amount. Increasing the char concentration simultaneously with air flow so as not to alter the thermal and product characteristics may prove to be the best method of increasing capacity. However this may raise the solids content of the melt above the limits; little work has been done on the physical effect of relatively large pieces of char. Varying char concentration for this purpose should be evaluated at the next stage of scale-up. Increasing reactor size together with air supply has the disadvantages of scale and cost but on balance, given only the presently available information, this is the best clear option.

Experimental results have shown that at 825°C an air flow rate of 14.0 litres per minute per litre of melt gives a gasification rate of 1.84 g/min. per litre of melt. Under such circumstances the volume of the gasification reactor would have to be $^{5.4}/1.84$, 2.9 times that of the pyrolysis reactor. This assumes that the air flow remains unaltered but by increasing the air flow to the region of 15 - 20 l/min per litre of melt it should be possible to increase the rate of gasification to around 2.2 g/min/litre of melt and hence reduce the volume ratio to around 2.5. This would only slightly affect reaction thermicity and products.

This difficulty in obtaining sufficient gasification rates even using air alone points to the growing argument of steam impracticality. It also indicates the need for further investigations.

Applying linear scale-up techniques it is possible to estimate the volumes of gasification reactors for various scales of operation. Table 10.20 indicates that the volumes of melt required for pyrolysis on 4,000, 10,000 and 50,000 t/yr operations at 475°C would be 1.5, 3.7 and 18.5 m^3. These reactors would produce 1,490, 3,3730 and 18,650 tonnes of char per year. If char gasification is carried out at 825°C with air flows of 15 - 20 l/min.litre of melt, the volume ratio of 2.5 indicates that the corresponding reactor must be of melt volumes 3.8, 9.3 and 46.3 m^3.

At this stage it is interesting to compare the operating implications detailed above with other published process literature. A great deal has been published concerning the M. W. Kellogg Coal Gasification Process which gasifies coal using steam pressurized at 45 p.s.i. At a temperature of 970°C it has been reported that a rate of 25 lbs/hr. ft^3 melt was obtained(316). This corresponds to about 20 g/min. l melt which is an order of magnitude greater than has ever been achieved here. Given this data the only explanation is that the temperature, the design of the reactor, or pressure are responsible.

A later development of the Kellogg system by the Rockwell Corp.(320) replaces steam as the gasification agent by air. This plant, utilizing some 2 m^3 of molten sodium carbonate, gasifies coal at a rate equivalent to 4.2 g/min. l melt. The temperature was 970°C and the process operates at a pressure of 20 atmospheres. Taking into account these physical conditions, this rate is similar to that obtained using tyre char; it may even be slightly slower. It would also appear to contradict the earlier Kellogg work(316).

Another process, the Otto-Saarberg process(332) gasifies coal in a slag both at 1700°C and 360 p.s.i. The process makes use of oxygen and steam in the ratio of 1 to 0.4. In this work this would have a negligible affect over the use of air alone but given the physical conditions of the Otto-Saarberg process it is evidently worthwhile.

13.6 Products

13.6.1 Comparative Discussion

Where air is used as the gasification agent at less than stoichiometric rates, which is so in most experiments, the dominant product is carbon monoxide. The carbon dioxide product can be increased slightly by elevating the temperature or quite considerably by increasing the rate of air supply.

In this work the proportions of the primary products were not determined but if the equation proposed by Arthur(293) is accepted it can be expected that carbon monoxide will dominate the primary products by a factor of some 600 - 700 times over carbon dioxide. This indicates that anything above the smallest proportion of carbon dioxide is due to the secondary reaction of carbon monoxide with oxygen. This would appear to be reasonable since some outgoing carbon monoxide may possibly come into contact with air before the primary carbon-oxygen reaction can take place. In fact given this it is perhaps surprising that more carbon dioxide is not formed. The explanation is probably one of chemical kinetics. In some experiments the small amount of natural carbon dioxide in the air, just detectable by mass spectroscopy, is seen to disappear. This indicates that under certain conditions carbon dioxide reacts with carbon to form the monoxide which is a further explanation for the low levels of dioxide in the final product.

The Rockwell development which uses air as the gasification agent produces a gas whose calorific value is 5.8 MJ/m^3. This indicates all the oxygen must be converted to carbon monoxide and that there must in addition be some hydrocarbon gases in the product.

The reaction of carbon with steam produces carbon monoxide and hydrogen as primary products. By the shift reaction carbon dioxide and more hydrogen are produced as secondary products. From the experimental results it is clear that the shift plays a significant role here. It was shown by Lefrancois et al.(316) that this shift often occurs before the steam is able to reach the carbon present.

13.6.2 Product Evaluation

The experimental results have shown that the char gasification process is faced with three main options for operation:

1) To react the char with unrestricted air supply to produce large amounts of heat and a product dominant in carbon dioxide. (If physically possible in this reactor.)

2) To react the char with restricted amounts of air to give an intermediate quantity of heat and a product dominant in carbon monoxide suitable as a low value gaseous fuel.

3) To react the char with steam giving a slow rate of gasification, a reasonable product fuel and requiring a heat input to maintain the reaction.

Of these options, 3) produces the best product; a mixture of carbon oxides and hydrogen whose calorific value is likely to be 8 - 9 MJ/m^3. However as the rate is intolerably slow this option is becoming less attractive. The choice between 1) and 2) will depend on the nature and location of heat demand. Both eventually produce 33 MJ/kg of original carbon but in 1) all is produced in the melt whereas in 2) only about $\frac{1}{3}$ is produced in the melt. It seems likely that 2), giving about 11 MJ/kg of carbon to the melt and a gas whose calorific value is 3 - 4 MJ/m^3 will be the best option.

13.7 Summaries and Conclusions

Rates of gasification sufficient to keep pace with rates of pyrolysis and hence rates of char production can only be achieved by the use of air as the sole oxident of carbon. By restricting the air flow it is possible to control the amount of heat delivered immediately into the melt. This strategy also yields a product that is dominant in carbon monoxide which can be used as a distributable low value fuel. Thus the amount of air passed can easily be used to vary the external and in-situ heat requirements.

Under conditions of restricted air supply it will be necessary to allocate 2.5 volumes of melt to char gasification at 825°C to every volume of melt allocated to pyrolysis at 475°C. The system is only flexible through changing the melt volume or the air flow used in gasification. The problems associated with the large heat exchange necessary to achieve this should be evaluated at the next stage of development.

It has been shown that rates of reaction between air and carbon have been restricted by air flow rate. In cases where excess air is supplied it would appear that rates are controlled by diffusional mass transfer.

CHAPTER

FOURTEEN

RELATED EXPERIMENTATION

14 RELATED EXPERIMENTATION

14.1 Introduction

At the outset of the project it became evident that several areas other than those of the main process concepts would require at least brief investigation. These tend to occur in what might be called side effects of the process and include the chemistry of inorganic pyrolysis products, melt hydrolysis and corrosion. These subjects are major projects in themselves and might normally be researched as separate entities. However, they do have a crucial bearing on the process and so it was decided to carry out preliminary studies in each area, providing at least some data. These studies were, out of time restriction, brief and to a large extent only semi-quantitative but provide an insight sufficient for this stage of the process development.

14.2 Sulphur

14.2.1 Experimental and Qualitative Results

Sulphur has traditionally been, and still is, used as the major vulcanizing agent in tyre manufacture. It is present at about 1 wt.% in most tyre formulations. It is generally accepted(78) that sulphur achieves vulcanization by the formation of mono-, di- and polysulphide bridges between the rubber polymer chains. This has been one of the main reasons for using sulphides to simulate the occurrence of sulphur compounds in the melt.

However to confirm the presence of sulphides in the system some spot tests were carried out. The standard nitro-prusside test was applied to samples of melt taken from the pyrolysis reactor after it had been in use. This was inconclusive but exposure of these melt samples to hydrochloric acid liberated hydrogen sulphide which indicates that sulphides are indeed present in the pyrolysis melt. Samples taken from the char gasification reactor after air passage gave a negative nitro-prusside test and although hydrogen sulphide was liberated on exposure to hydrochloric acid it was not immediately obvious. It may be suggested that sulphides are converted to sulphates in the gasification but tests for this were inconclusive in such an excess of carbonates.

Having established the presence of sulphides in the melt some experiments were carried out to establish the effects of these compounds on the melt. The main consideration was of physical effects. It was found that additions of relatively large amounts of sulphides (and sulphates) to the melt ($\sim$ 40 wt.%) made virtually no difference to the mobility of the melt but no melting points were measured.

14.2.2 Discussion

Analyses of the pyrolysis product, given in Chapter 9, show very low sulphur levels; $<$ 0.2 wt.% in the oil, no detectable hydrogen sulphide in the gas and 1.4 wt.% in the char. If these values are multiplied up by their respective yields the total sulphur presence is only 0.52 wt.% of the tyre input. Although no quantitative analyses of the melt have been carried out it is clear from a mass balance by difference that at least half the sulphur in tyre remains in the melt after pyrolysis.

The pyrolysis products ensure that predominantly reducing conditions prevail in the pyrolysis reaction, making it quite plausible that sulphur released in these circumstances will be immediately converted to hydrogen sulphide. In a dry pyrolysis process this would be found in the pyrolysis gas making it unacceptable as a fuel without further treatment. However in the presence of molten carbonates or carbonate solutions hydrogen sulphide reacts to form the corresponding metal sulphide.

$$H_2S + M_2CO_3 \rightleftharpoons M_2S + H_2O + CO_2 \qquad \text{Eq. 14.1}$$

Clearly at pyrolysis temperature the water and carbon dioxide distil off and so the reaction is not reversed. This is the basis of Glueck's stack gas scrubbing and coal desulphurization proposals(285). It is also an important feature of the Kellogg coal gasification process(316). The reaction is discussed further in its consequences for char gasification and melt regeneration.

In the char gasification reactor excess oxygen is often present and there are no reducing gases. Analytical results suggest that the sulphides present in the pyrolysis melt are in these conditions converted to sulphates. Sulphites, if formed, will immediately disproportionate at these temperatures to give sulphate and sulphide. However, it is thought that sulphide concentrations here are very low. In addition when air and steam are used simultaneously to gasify the char conditions to reverse Eq. 14.1 would exist; since no hydrogen sulphide is formed it appears no sulphides can be present. It is reasonable to suggest that sulphide is converted before this can occur or that the concentration of carbon dioxide is too low. In either case the important result is that hydrogen sulphide is not liberated into the product gases.

The results and discussion above show that the effect of sulphur vulcanate in the tyre input is to convert the carbonate melt into sulphide/sulphate melt. Given that quite large amounts of sulphide/sulphate have little effect on the physical properties and so superficially appear not to be detrimental. However, firstly, the toxicity of sulphides must be considered; this would cause great difficulties in disposal of washings or other effluent contaminated with melt. Obviously under these conditions melt-acid contact would be extremely dangerous. Secondly, if the melt were to undergo 100% conversion then it would cease to absorb sulphur and product gases would become contaminated. In the absence of an effective melt regeneration system this factor would limit the salt life.

As might be seen from Eq. 14.1 sulphides can be reconverted to carbonate by passage of suitable quantities of steam and carbon dioxide,

$$M_2S + H_2O + CO_2 \longrightarrow M_2CO_3 + H_2S \qquad \text{Eq. 14.2}$$

The disadvantage of course is the formation of the hydrogen sulphide. However, the conditions required would allow this to be done in controlled circumstances, probably in a side-reactor fed by a bleed stream from the pyrolysis reactor. The pure hydrogen sulphide so produced could be recovered as elemental sulphur (Clauss process) if desired. The carbonate product can be returned to the main melt volume.

14.3 Zinc Salts

14.3.1 Experimental

Modern vulcanizing mixtures contain zinc oxide, stearic acid and benzthiazoles acting as accelerators. The organics are broken down during pyrolysis but any zinc salts remain in the melt. Zinc oxide is used in tyres at about 2.0 wt.% but its form in the finished product and hence in the pyrolysis melt is uncertain and so is probably best considered as Zn^{2+} ions. Zinc salts are thus likely to build up in the melt, making an evaluation of their effect an important task.

Experiments were carried out with two basic aims: to obtain a rough measure of the solubility of zinc compounds in various melts and to note the affect of undissolved solids on the melt. The first series of quick experiments involved study of the solubility of zinc oxide in the pure carbonate eutectic and in melts containing 10 and 20 mol. % hydroxide. Usually 100g of melt was taken to which was added an excess quantity (25g) of zinc oxide. The melt was maintained at 600°C for 1 hour after which solids were allowed to settle before a sample of supernatent melt was taken. The method used was to suck up the liquid through a glass-wool plug, to help filter out solids, in a glass tube where it solidified. The analysis for zinc was performed using atomic adsorption spectroscopy using the methods described in Chapter 8. The study of the effects of large amounts of solids in the melt were carried out simultaneously to the above experiments. The effects of solid zinc oxide were visually observed before any dissolution could take place. (Attempts to use a specially designed Redwood type viscometer were largely unsuccessful.)

14.3.2 Results

On addition to the melt all samples of zinc oxide immediately turned yellow as would be expected at this temperature. The colouration served well to determine the distribution of the zinc oxide. In the case of the pure melt it was accumulated at the bottom of the reactor, whereas where more effective dispersion occurred it was more uniformly spread. To take full advantage of this and other visual effects it was occasionally necessary to use glass flasks in place of the standard steel beaker.

The results for solubilities of zinc oxide in the melts mentioned are given in Table 14.1. These results are in fact the average of several samples taken at the end of each experiment.

Initial Carbonate, mol. %	Initial Hydroxide, mol. %	Zinc, mol. %
100	0	0.5
90	10	4.0
80	20	7.9

Table 14.1 Solubility of Zinc Oxide

It was noticeable that additions of zinc oxide to the pure carbonate eutectic tended to increase the viscosity, especially from about 10 wt.% upwards. Where hydroxide was present and the zinc oxide rapidly dissolved there was still a marked increase in viscosity but not as great as in the pure eutectic case.

14.3.3 Discussion

The results show that zinc oxide is soluble to a small degree in the pure eutectic, although analytical errors may result from a small amount of solids being accidentally collected during melt sampling. The low zinc concentration may also be due to a slow kinetic rate rather than a solubility equilibrium. Experiments of greater duration may be of benefit here. The likely dissolution reaction for the pure eutectic is,

$$M_2CO_3 + ZnO \longrightarrow M_2ZnO_2 + CO_2 \qquad \text{Eq. 14.3}$$

but no carbon dioxide was detected due to the small amounts that might have been present. The overall indication must be that in this case zinc salts, most likely solids, will build up in the melt. Pyrolysis experiments have only involved small amounts so no build-up has been seen here. It is possible that in the presence of carbon dioxide, as formed in char gasification, soluble zinc salts such as zincates may precipitate solid zinc oxide which would settle in the reactor,

$$ZnO_2^{2-} + CO_2 \rightleftharpoons ZnO + CO_3^{2-} \qquad \text{Eq. 14.4}$$

The reaction would also regenerate the melt.

Where hydroxide is present in the melt, making it more basic, the dissolution of zinc oxide reaches a far higher level in the one hour used for these experiments. The likely reaction here is,

$$2MOH + ZnO \rightleftharpoons M_2ZnO_2 + H_2O \qquad \text{Eq. 14.5}$$

Furthermore the amounts of zinc found in the melt approach the maxima that might be expected from the original hydroxide presence and the stoichiometry of this reaction. This supports the suggestion that the equilibrium lies far to the right. Considerable quantities of water vapour were found (by mass spectroscopy) in the air immediately above the surface of these melts. However where glass vessels were used a contribution will be made by attack of the glass,

$$2OH^- + SiO_2 \rightleftharpoons SiO_3^{2-} + H_2O \qquad \text{Eq. 14.6}$$

The dispersion of solid zinc oxide particles in the melts has the expected effect of increasing viscosity. This system will probably have non-Newtonian characteristics. The increase in viscosity of a melt containing dissolved zinc is rather more complex to explain but may be due to the normal power relationship for the viscosity of one medium dissolved in another or there may be some special effect such as the formation of polyzinate chains.

The observed solids/melt acceptability of around 10 wt.%, for particles of this particular size, agrees well with the values of acceptability found in the literature(320) of 8-15 wt.%.

If further study should confirm these preliminary findings and it is found that zinc compounds are detrimental above certain levels, it will be necessary to devise a means of removing them from the melt. The present indication is that a tonne of melt can only be used to pyrolyse some 650 tyres or 5 times its own weight before this treatment becomes necessary. Some alternative melt treatments are discussed fully in the next chapter but these briefly comprise of a molten zinc oxide precipitation/recarbonation process or an aqueous melt regeneration process.

14.4 Melt Hydrolysis

14.4.1 Experimental

Melt hydrolysis will have the effect of converting the carbonate to hydroxide. This will occur when steam or water are passed through or come into contact with the melt,

$$M_2CO_3 + H_2O \rightleftharpoons 2\,MOH + CO_2 \qquad \text{Eq. 14.7}$$

The presence of hydroxide is of interest for two reasons; firstly the effect on zinc behaviour already discussed and secondly, it is extremely corrosive and may have a bearing on containment materials. The aim of these experiments therefore was to evaluate the rates and extent of hydrolysis and to study means to combat it.

The first experiments merely studied the effect of steam passage on the pure carbonate eutectic. The melt, (100g) contained in a stainless steel beaker and heated by an electric furnace, was subjected to a steam flow of 2.4g/min from the steam generation arrangement already described in Chapter 11. These experiments were performed at 750°C as were the second series and designed to study the effect of carbon dioxide on a hydrolysed melt. This was carried out simply by passing the gas at 3.0 l/min through a melt containing 10 mol. % hydroxide.

The melt samples taken from the melt at various times during each experiment were analysed for carbonate and hydroxide by an adaption of the Belcher and Nutten method(323) described in Chapter 11. The gas over the melt during each experiment was also monitored by scanning mass spectroscopy.

14.4.2 Results

The averaged results of each of the series mentioned in the previous section are given here. Table 14.2 shows typical results for a pure eutectic hydrolysis experiment and Table 14.3 the results of a recarbonation experiment.

Time, mins	Carbonate, mol. %	Hydroxide, mol. %
0	100.0	0
10	99.1	0.9
30	96.8	3.2
75	97.2	2.8
210	94.2	5.8
360	92.8	7.2
600	91.1	8.9
840	89.8	10.2
900	89.0	11.0
960	88.4	11.6

Table 14.2 Hydrolysis of Pure Eutectic

Time, mins	Carbonate, mol. %	Hydroxide, mol. %
0	90.0	10.0
10	90.2	9.8
20	91.0	9.0
40	91.8	8.2
60	93.0	7.0
210	95.9	4.1
360	99.1	0.9
480	99.5	0.5
570	100.0	0
600	100.0	0

Table 14.3 Recarbonation of Hydrolysed Melt

The flow rates of 2.4 g/min for steam and 3.0 l/min for carbon dioxide approximately equal in molar terms. The data from both Table 14.2 and 14.3 are thus plotted together in Figure 14.1.

14.4.3 Discussion

The results given in Table 14.2 show that under the conditions of steam gasification of char the melt may well undergo hydrolysis, giving the inherent characteristics already mentioned. The rate of hydrolysis is far lower than the stoichiometric potential which could be attributed to dynamic or kinetic causes. When the size of steam bubbles is considered it seems likely that the rate is controlled purely by mass transfer. The plot of Table 14.2 in Figure 14.1 shows, perhaps debatably, that the rate of hydrolysis tails off with time; an equilibrium value of 15-20 mol. % hydroxide is shown to be established.

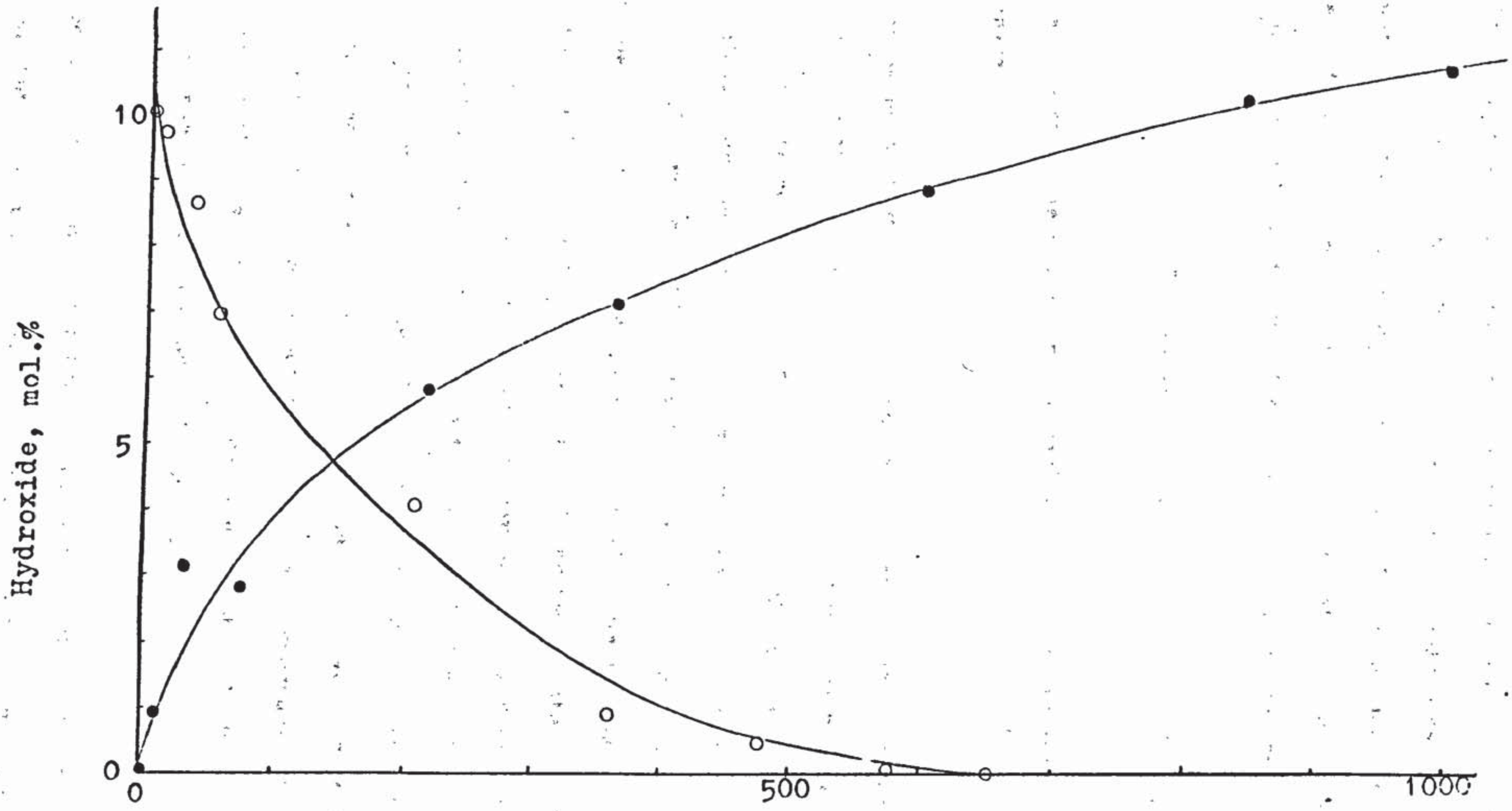


Fig.14.1 Hydrolysis and Recarbonation

At first there seems no explanation as to how this could occur but it should be noted that carbon dioxide is unavoidably present in the water used to generate steam and so establishes a carbon dioxide concentration in the melt. In addition a possible source of carbon dioxide in the melt is through the dissociation of carbonates,

$$CO_3^{2-} \rightleftharpoons O^{2-} + CO_2 \qquad \text{Eq. 14.8}$$

However the oxide here would react rapidly with water to form hydroxide anyway.

Assuming that steam is in considerable excess, the rate of hydrolysis in the 100g aliquot is about 0.025 g/min which gives a first order rate constant of $2.5 \times 10^{-4} s^{-1}$. Although this may appear to be slow, over long periods of time, such as those envisaged in a tyre pyrolysis process, this would build up significant amounts of hydroxides. It is clear that unless an equilibrium is reached all the melt could be hydrolysed. However an equilibrium is attained which would, in the reactor, be encouraged by carbon dioxide formed in the shift reaction. The equilibrium in the region 15-20 mol. % may still, from a corrosion point of view, be too high for use with any standard containment materials. It would therefore appear that in general steam should not be allowed to contact the melt. This encourages the use of air alone as the char gasification agent, a feature already found to be desirable from the gasification work itself.

Some water is bound to enter the reactor through wet tyre introductions but this will be low. Table 14.3 shows that small amounts of hydroxide in the melt are not likely to remain stable for long. Zinc salts tend to react with the hydroxide to form zincates which appear, from Section 14.3, to be soluble in the melt. The second means of removal of hydroxide from the melt is by recarbonation which, as is illustrated in Figure 14.1, is as rapid as hydrolysis given the same reactant concentrations. If air is used to gasify the char a certain amount of carbon dioxide will be formed. Although this will not be enough to produce this rapid recarbonation it is likely to be sufficient to keep "wet tyre" hydrolysis in check.

In summary, a carbonate-hydroxide equilibrium is established but the level of hydroxide may still be unacceptable. However if steam is not used for gasification of the char a lower level will exist. This is such that the carbon dioxide formed by air gasification will be sufficient to achieve recarbonation.

14.5 Corrosion

14.5.1 Experimental

Corrosion in molten salt reactors is known to present considerable problems(267). So as plant life may be a crucial feature in the economic viability of molten salt tyre pyrolysis it was thought necessary to carry out some basic corrosion studies. Although some information is available in the literature(268,269) it tends to be highly involved and academic rather than of the empirical nature required here.

As noble metals cannot be considered on economic grounds, this study has concentrated on mild EN2 steel, stainless EN58 steels and titanium. These materials are listed in Table 14.4. All samples were presented as 20 x 20 x 1 mm plates; supplied by Goodfellow Metals Ltd.. These plates gave 8 cm^2 face surface and 0.8 cm^2 cut surface. Their weights varied according to density.

Metal	Classification		Stabilizing Elements/ wt. %
Mild steel	EN 2		
Stainless steels	EN58 E	304	Cr/18, Ni/10, Mn/2
	EN58J	316	Cr/18, Ni/8, Mo/3
	EN58 F/G	347	Cr/18, Ni/10, Nb/10 x C
Titanium	-		-

Table 14.4 Corrosion Test Materials

The corrosivity of the melt will vary with even slight changes in its composition. In these tests the melt used was the Standard Fouled Melt whose composition is given in Table 14.5. The materials included deliberately pose the worst possible situation. Likely to be of particularly aggressive action are hydroxide and zinc.

Component	wt.%
Carbonate Eutectic	64.0
Hydroxides (∝ eutectic)	7.5
Zinc oxide	10.5
Sulphides (∝ eutectic)	18.0
	100.0

Table 14.5 Standard Fouled Melt

The test metal was usually placed in 50g of this melt contained in a Vitrosil crucible. The crucible was suspended in a steel frame inside a small electric furnace which was maintained at 500°C for the test. The duration was normally 100 hours although samples were removed for short periods at intermediate times so that quick assessments could be made. The atmosphere over the surface of the melt at all times was air.

It was planned to evaluate the corrosion of the test samples by four techniques:

1. Visual/Microvisual observation.
2. Weight changes.
3. Melt dissolution into the melt.
4. Elemental electroscan of corroded samples.

However in the event it was not possible to perform the last of these tests. The exposed metals were prepared firstly by boiling in distilled water for 20 minutes to remove any adhering traces of melt; no abrasives were applied or necessary. The samples were then dried at room temperature under a stream of nitrogen.

14.5.2 Results

14.5.2.1 Visual

The results of visual studies of the corroded samples of containment metals are given as comments in Table 14.7. Microscope photographs of the surfaces of mild steel EN2 and of stainless steel EN58 F/G 347 show the former to be prone to severe pitting whereas the corrosion of stainless steels is more uniform and far less severe. (All these steels appear to have an untarnished fine grain surface prior to corrosion exposure.)

Test Metal	Naked Eye	Microscopy
EN2	Dark oxide surface layer. Blistering & pitting evident.	Pit/Saucers 0.7 - 1.0 mm D. > 10 μm depth
304	Black surface tarnish. No pitting.	-
316	Loose grey surface tarnish. No pitting.	-
347	Partial grey tarnish. No pitting.	Tarnished areas very fine grain.
Titanium	Partial tarnish, mostly clean metal.	-

Table 14.6 Visual Analysis of Corrosion Test Samples

14.5.2.2 Weight Changes

The results in Table 14.7 show the initial weight, 50 hour exposure weight and final 100 hour exposure weight. Also given is a final percentage weight change which, as surface areas are constant, gives a direct comparison of corrosion penetration.

The measurements were made on a Sartorius four-figure chemical balance. Although great care was taken throughout these experimental measurements, it should be noted that the weight changes recorded are close to the accuracy of the instrument.

The changes observed are nearly all positive which corresponds to an oxide build-up; although it may be questionable whether or not the degree of build-up relates to severity of corrosion. It is also debatable that oxides would not form in the predominantly reducing conditions of the pyrolysis reactor.

Test Metal	Initial wt.g	50 hr. wt.g	100 hr. wt.g	% wt. change
EN2	4.6915	4.6011	4.7110	+ 0.42
304	4.5522	4.5478	4.5682	+ 0.35
316	4.5915	4.5938	4.5977	+ 0.14
347	4.4519	4.4521	4.4521	+ 0.04
Ti	2.7757	2.7792	2.7802	+ 0.02

Table 14.7 Corrosion Weight Changes

14.5.2.3 Metal Dissolution

Results of metals dissolved in the melt were obtained by sampling small quantities of melt during the test. These samples were analysed for iron and nickel by atomic adsorption spectroscopy; the method is described earlier in section 8.3.1.1. The results are given in Table 14.8 and are then plotted in Figure 14.2.

Test Metal	Composition	Time, hrs.	Fe ppm	Ni ppm	Total mg/cm^2/yr
EN2	-	10	50	-	
		24	540	-	
		48	1025	-	
		72	1600	-	
		100	1975	-	2160
304	Fe 70	0	-	-	
	Cr 18	10	350	125	
	Ni 10	24	510	145	
	Mn 2	48	555	155	
	C 0.08	72	510	210	
		100	595	215	885
316	Fe 71	0	-	-	
	Cr 18	24	400	-	
	Ni 8	48	705	180	
	Mo 3	72	945	275	
	C 0.08	100	1070	295	1490
347	Fe 71	10	330	50	
	Cr 18	24	620	80	
	Ni 10	48	675	95	
	Nb 1	72	690	100	
	C 0.08	100	700	95	870

Table 14.8 Corrosion Melt Compositions

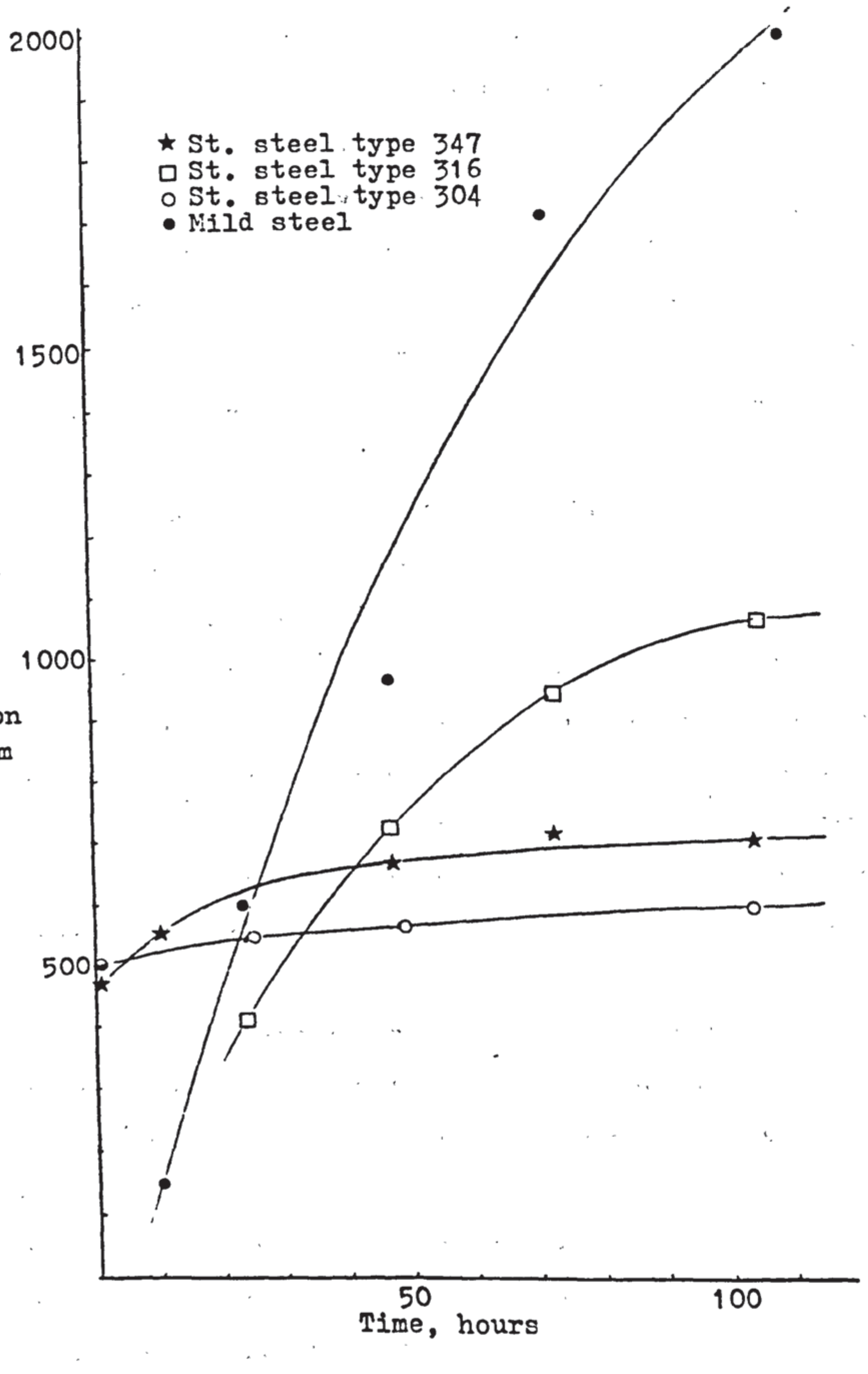


Fig.14.2 Leaching of Iron from Steels

14.5.3 Discussion

Even from visual results it is quite clear that mild steel, EN2 will be inadequate for the containment surface of this melt. The linear rate of corrosion on what is a good surface approaches 1 mm a year. If the metal were to contain fissures or cracks, as is quite likely in the forming of the reactor, the rate would be increased several fold. The plots in Figure 14.2 show clearly that EN2 is in no way stabilized and that corrosion is faster and more severe.

Type 316 stainless steel shows loose surface layer that are probably oxides which although protective cannot be guaranteed to form in the pyrolysis réactor. In addition these layers are easily removed under even the slightest abrasive conditions. Pitt(77) noted that this material experienced excessive wear under the combination of molten salt contact and abrading surfaces. However the weight gain of this material is only one third of that experienced for mild steel. The degree of metal dissolution into the melt is also correspondingly lower but is the least impressive of the stainless steels.

The surface layer found on type 304 stainless steel is considerably darker than found on all the other materials. It may be that the presence of manganese as a stabilizing agent is responsible for this colouration. Although removable the surface layer is smooth and compact requiring some effort to remove it. This metal has a surprisingly high weight gain which may go some way to explain the low iron dissolution found in melt samples.

Type 347 shows a very fine, hard surface layer. It has little weight change and does not dissolve into the melt to any great degree. It would appear the best steel here to resist melt attack.

The results obtained for titanium are not complete so it is hard to assess its performance but it is well known as a resistive material. Although the weights hardly change during the test, titanium would certainly be a very costly constructional metal.

The nature of surface layers formed under these circumstances is a matter of debate. Janz and Conte(268) working with types 304 and 347 stainless steels claim that $LiFeO_2$ was formed. If this is so iron carbonyls and/or carbon monoxide and lithium oxide must be formed. The aim of the electroscan studies would have been to measure the elemental concentrations in these layers and thus suggestions as to their compound composition could be put forward.

Perhaps the most interesting results obtained here are those relating to melt composition. In all cases iron and the stabilizing agents are leached out of the metal, as is shown in Table 14.8. Figure 14.2 shows that the concentration of these elements rises in the melt to a certain level and then levels-off. This indicates no further leaching is occurring; the corrosive action has ceased. This indicates in turn the formation of a passivating layer protecting the metal; the $LiFeO_2$ suggested by Janz and Conte(268) found the stabilization of 304 and 347 to be complete at 600°C in about 24 hours. Here at 500°C melt compositions indicate it occurs in 30 hours. Although sample and melt bath sizes are different and hence the equilibria effect may be different, the results by radically different experimental methods come to very similar conclusions.

Zinc is known to cause embrittlement of stainless steels. The penetration of this metal from the melt into the test samples was also to have been measured by the electroscan technique, so little quantitative data is available. However it was noted that stirrer shafts and thermocouple wells used in this work had a marked tendency to snap under strain. Likewise it has been hard to evaluate the effect of hydroxide but this has been studied in detail by Simons and Stang(272) with the nuclear application in mind.

These results show that the resistance of the test metals to the melt in question are probably in the order:

$$\text{Ti} > 347 \gg 304 \gg 316 \ggg \text{EN2}$$

According to Janz and Conte(269) stainless steels range above nickel and silver in resistance but below other noble metals. In terms of weight change 347 is quoted as being three times as resistive as nickel. (The passivation by surface layers can be supplemented by galvanic coupling with noble metals (273) but is obviously costly.)

The vapour pressure of the melt and the pyrolysis products are unlikely to cause severe corrosion but the gasification products will effect the melt equilibrium,

$$CO_3^{2-} \rightleftharpoons CO_2 + O^{2-} \qquad \text{Eq. 14.8}$$

and hence alter melt composition and corrosion potentials. If oxygen or carbon dioxide are present Janz claims the nobility and resistance of the metal will increase. This must be balanced with carbon monoxide and nitrogen that have the opposite effect.

This work and the literature suggest that stainless steels 304 and 347 are suitable metals for reactor construction. Costing indications show stainless steels used in this mode increase the cost ten-fold over mild steel. High grade types such as 304 and 347 are again slightly more. If economic consideration bears weight, it would seem likely that mild steel vessels be constructed to bear the stresses while they are refractory lined to resist corrosion; Monofrax A has often been used for this purpose in similar applications.

CHAPTER

FIFTEEN

SYSTEM DEVELOPMENT

15 SYSTEM DEVELOPMENT

15.1 Introduction

15.1.1 Methods

Using the data obtained from the literature and experimental investigation, it is the object of this chapter to bring together the information necessary for further planning of the process. Data such as rates and product characteristics are essential in carrying out such a study. The literature data is equally important when the scale of the operation is considered. This evaluation concentrates on the full commercial operation of the process deliberately omitting pilot and developmental stages as these involve detailed design information that is not at this stage available.

The process is first studied in "black-box" terms giving no detail of how each process is or might be carried out. A unitary method, based on one unit of tyre is used to carry through mass and energy balances. After this the methods by which each "black-box" process might operate are discussed together with the type of unit in which such processes would be carried out. Finally these two evaluations are put together to quantify each unit in terms of the proposed process scales.

15.1.2 Summary of Experimental Conclusions

Pyrolysis experiments have shown that this part of the process would best be carried out at 475°C. At this temperature the breakdown of tyre yields 29 wt.% oil, 11 wt.% gas, 38 wt.% char, 17 wt.%

steel and 5 wt.% inorganics. The rate of pyrolysis and hence char production was, at this temperature, in a range compatible with char gasification rates.

The results of gasification experiments and some of the results from Chapter 14 showed that gasification of char would best be performed using air. The use of restricted air flows can be used to control the heat generated and improve the quality of the product. The optimum temperature for gasification will be in the region of 800°C. At this temperature the rate is high enough to gasify the char at its production rate thus establishing a steady state system. The air flow rate to be used is 15 - 20 l/min. l melt. The use of steam was eliminated on the grounds of insufficient rate and detrimental effects on the melt.

Less data is available for use in the planning of melt regeneration. However it has been found that sulphur removal is an established technique whereas zinc salts may pose more severe problems requiring further work. The amount of dissolved impurities, such as sulphides, have little effect on the physical properties of the melt. Solids however are likely to be limited to below 15 wt.%; these may well be zinc salts. The combined effects of all in-melt materials, including char, need to be further evaluated preferably on a continuous operation.

Rate conditions have indicated that for every volume of melt used in pyrolysis some 2.5 volumes will be needed for gasification. The allocation to melt regeneration has not been calculated but is likely to be considerably less than one volume.

15.2 Process Flow

15.2.1 Basic Processes

From Chapter 6 it was clear that the process would be based on a dual operative pyrolysis-char gasification system. In addition it has been found through experimentation that the melt will have to undergo a regenerative stage if it is not to be replaced after processing only some 5 - 10 times its own weight in tyres. The experimental results have also brought to light other operations that are necessary to run the process; these are discussed in full in section 15.3.

Having obtained the experimental results and drawn conclusions therefrom there is still perhaps the most basic conceptual decision to be made; the mode of operation, repetitive batch or continuous. The repetitive batch option would utilize one reactor for all the basic operations in sequence while the continuous option would have separate reactors for each basic operation. A continuous system would require a more complex and costly plant but, from the experimental results, a batch operation will either require a single reactor equal in size to the sum of all the continuous unit reactors or operate at a lower capacity.

On closer analysis it is seen that the batch operation is in fact not as simple as might have first been imagined. It would involve a considerable amount of purging and switching not required on a continuous operation. The use of qualitative judgement has generally favoured a continuous operation and it is this mode which is from now on considered. The basic form of the process flow is illustrated below in Figure 15.1

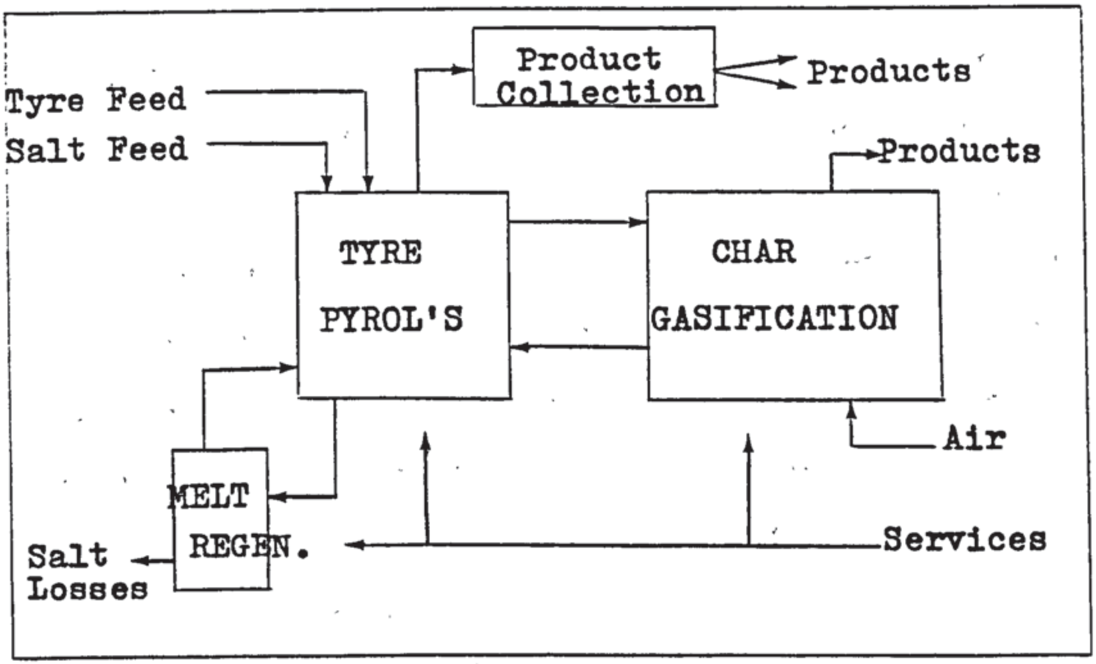


Fig.15.1 General Form of Process Flow

15.2.2 Mass Balance

Applying the unitary method, the mass balance is, at this stage, based on an input of 1 tonne (1000 kg) of tyre.

The tonne of tyre will in the primary action, pyrolysis, be broken down into 290 kg of oil, 110 kg of gas, 380 kg of char, 170 kg of steel and 50 kg of inorganic materials. The char is then transferred to the gasification unit, where it is combined with 520 kg of oxygen to yield 825 kg of carbon monoxide and 75 kg of carbon dioxide.

At a char concentration of 10 g/ l it will be necessary to circulate the melt between pyrolysis and gasification units at 37m^3 per tonne of tyre processed. However if higher levels are tolerable this rate will be lower. This is an area for further developmental work.

The melt losses involved in regeneration of the melt will depend on the methods utilized. If a totally molten system is used the losses will be virtually zero whatever the rate of melt cycling through the regeneration loop. If an aqueous process is used literature values indicate that the losses will be about 3.5% per pass. The concentrations of inorganic impurities in the melt show that assuming efficient reaction the melt cycling rate through the regeneration loop must be 0.5 - 0.75 m^3 per tonne of tyre processed. Given this and the loss percentage it is calculated that if an aqueous regeneration is used it will be necessary to add make-up to the melt at the rate of 35 - 53 kg per tonne of tyre processed. Molten regeneration may well be preferable.

The main reactor services that will be required by this process are compressed air, cooling water, process water, steam and carbon dioxide. Air is required primarily as a gasification agent, the rate of supply being about 2480 kg for every tonne of tyre. (This is the amount containing 520 kg of oxygen.) A further small amount (50 m^3) may be used if an acid egg pumping system is needed for melt cycling. Cooling water is merely required to supply the condensers where 420 kg of vapours must be cooled from 475°C to 25°C and partially condensed. Taking into account the sensible heats of these pyrolysis products and the efficiency of heat transfer the requirement per tonne of tyre is about 2500 l. Process water will only be required if an aqueous melt regeneration system is used. Since little practical experimentation has been carried out it is not possible to give an accurate figure for process water. However based on solubilities of melt carbonates it is likely to be in excess of 50 m^3 per tonne of tyre processed. Steam is used in two areas of the process; melt regeneration and steam stripping of the product oil. The stoichiometric requirement for regeneration will be about 35 kg at 475°C but kinetic and mass transfer factors will affect the reaction to an unknown degree. The stripping requirement will be 170 kg at 200°C. Carbon dioxide used in melt regeneration will depend on the degree of hydrolysis and sulphur input to the system. The best estimate is around 30 kg per tonne of tyre processed.

This mass balance is not formally tabulated but shown in a diagrammatic form in Figure 15.2. It is perhaps worth saying at this point that the flows suggested pose quite reasonable quantities. The volumes and relative flows of the Rockwell coal gasification unit (320) are of the same orders as those calculated here.

15.2.3 Energy Balance

The unitary method is again used for the process energy. The figures quoted are based on 1 tonne of tyre processed which enables the mass balance calculations to be used in arriving at many of the energy flows.

Calculations in section 10.3.2 have shown that the pyrolysis of tyre is slightly exothermic, 0.58 MJ/kg. This multiplies up to 580 MJ for each tonne of tyre processed. The air gasification of char is of course highly exothermic; under the restricted air situation the heat liberated on gasification of 370 kg of char would be 3392 MJ.

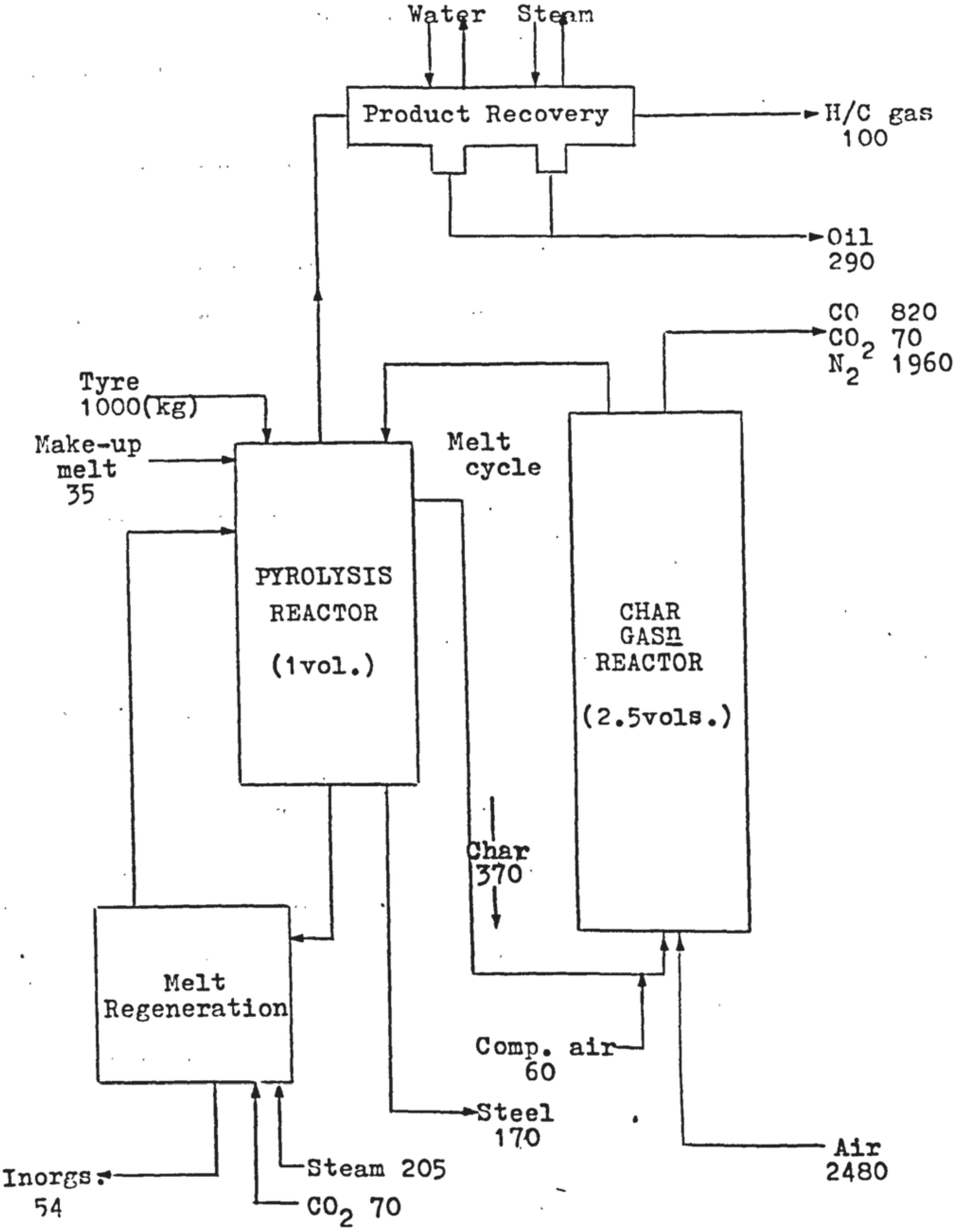


Fig.15.2 Process Mass Flow (per 1000 units tyre)

The energy required for the melt regeneration loop depends on the method of regeneration. The reactions involved are mostly slightly endothermic but as the amounts are small it is unlikely that the total heat requirement will exceed 150 MJ for a tonne of tyre. In a molten system this is the only energy, other than heat losses, that need be considered. The data available does not allow accurate estimations of the requirement in the aqueous case but energy needs of the order of 1500 MJ are possible.

The tyre feed, although not directly requiring preheating, will take energy out of the system if introduced cold. The sensible heat of the tyre, calculated from its specification, shows that introduction and processing of tyre requires an input of 700 MJ per tonne of tyre. If make-up melt is required a similar calculation shows an additional 10 MJ is needed.

The major source of energy in the process are the hydrocarbon products. Valued at 41 MJ/kg the total heating value of the oil produced from one tonne of tyre is 11890 MJ. The gas at 50.3 MJ/kg gives 5640 MJ on the same basis. In addition the cooling of products in the condenser train will also impart energy to the cooling water. This is estimated at 350 MJ.

The products from the proposed conditions of char gasification will have a calorific value of 8.3 MJ/kg. This will give a total heating value for a tonne of tyre of 7350 MJ. The product gas will also, on cooling, dissipate energy. However this energy will be required to preheat in air input used in gasification making the net change zero.

The next consideration is heat losses from the reactor. Since no reactor design has been proposed it is impossible to be specific over heat losses, furthermore these will be highly dependent on the size and degree of insulation of the plant. However some very rough estimates have been made. These are, for plants of capacity 4000, 10,000 and 50,000 tonnes a year, 1750, 3250 and 13,500 GJ/yr respectively.

Finally the energy required to supply the quantities of the services itemized in the previous section must be accounted. To supply some 2480 kg of air ($\sim 1910\ m^3$) the energy input to a centrifugal compressor would be comparatively very small. This assumes a pressure of less than 100 psig which is in this case reasonable. The energy input for steam supply is based simply on specific and latent heats. The temperature of supply varies from 200°C at the stripper to 475°C at the melt regeneration loop. The total energy input per tonne of tyre is put at 640 MJ. The carbon dioxide which is likely to come from combustion of the monoxide in the gasification product will have to undergo slight pressurization but, as has been mentioned, compressor demands are, in this context, very small.

The energy balance is presented here, as the mass balance, in chart form; Figure 15.3. In section 15.4 this data is applied to each of the mentioned scales of commercial operation.

In addition to these specific itemized uses of energy, advance consultation of Figure 15.4 will show other uses. These are mostly

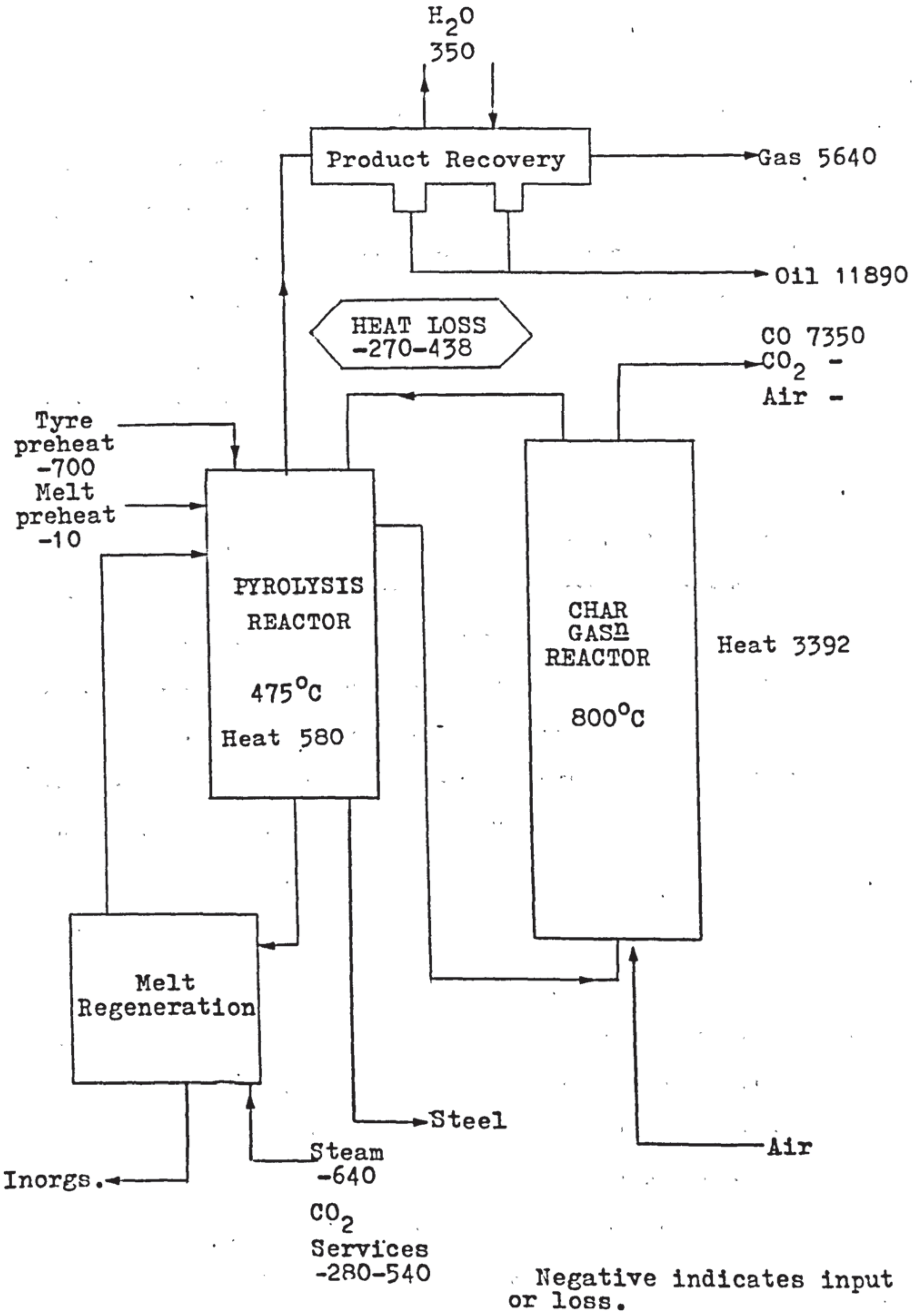


Fig.15.3 Process Energy Flow (per 1000 mass units tyre)
Units, MJ

small pumps and stirring motors; lighting may also be considered part of the process. This is also a scale related factor rather than a throughput related factor. The estimated requirements for the 4,000, 10,000 and 50,000 tonne/yr plants are average levels of 25, 95 and 300 kw. By considering the rates of processing these are equivalent to 540, 430 and 280 MJ per tonne of tyre processed.

15.3 Functional Unit Options

15.3.1 General Form

In this section each unit shown in the process flow diagram, Figure 15.4, is discussed in terms of its function with respect to the rest of the system. One or more descriptions of the possible options are put forward in each case. The detailed designing of each reactor requires data that can only be obtained from full simulated operation - a pilot study. As will be recommended later this is one of the major areas for further work.

15.3.2 Pyrolysis Reactor

The function of the pyrolysis reactor is simply to convert the used tyre into the oil, gas, char, steel and inorganics found through experimentation. This is achieved by heat application through molten carbonates. The oil and gas distil off, leaving the char, steel and inorganics in the reactor. It is thought that when whole tyres are fed into the reactor the steel formation will remain intact and can be removed on the empty tyre stacking frame. This may also result in some of the char being removed from the reactor but most will remain behind and could be dispersed in the melt with the inorganic products

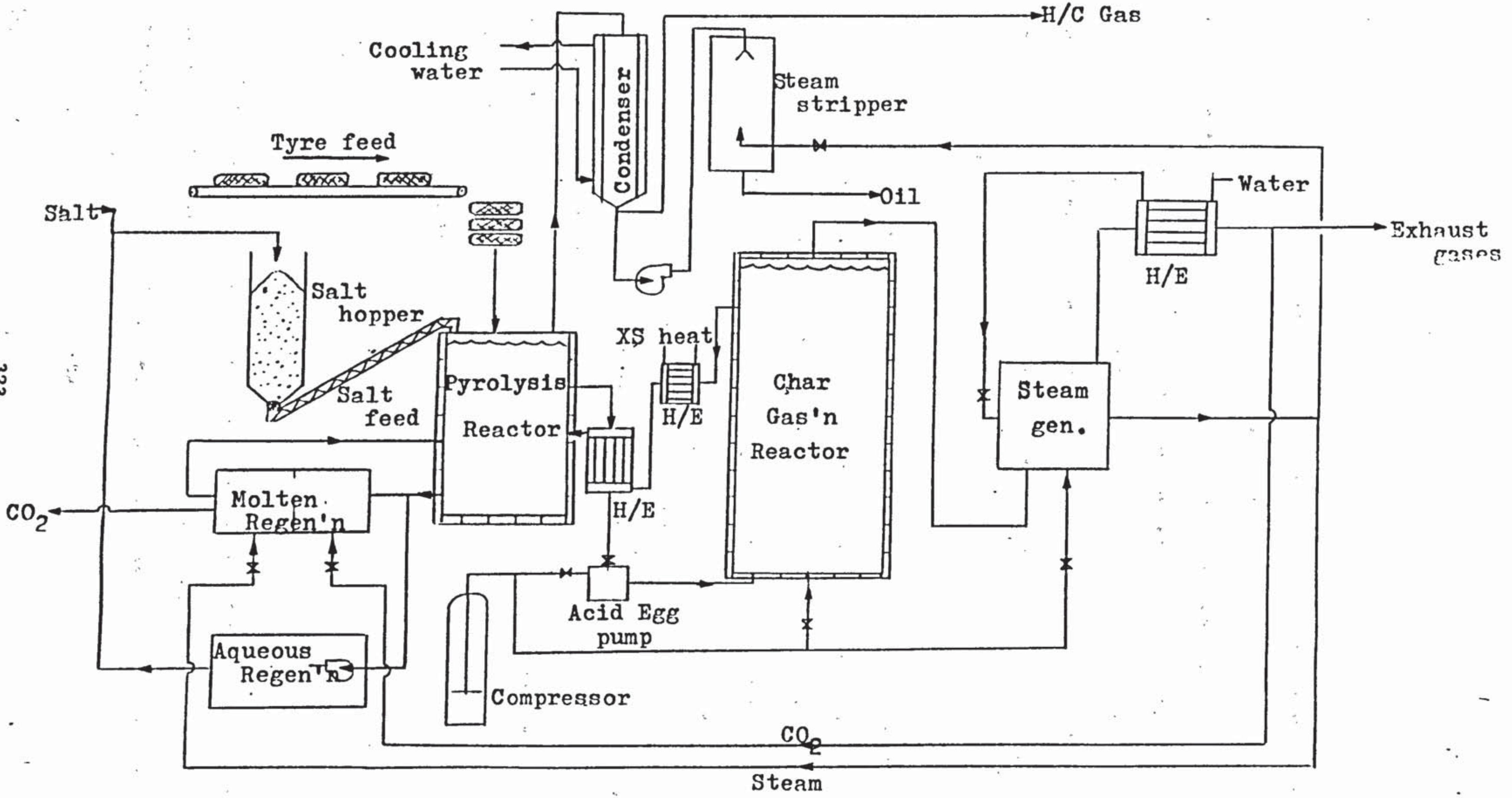


Fig.15.4 Molten Salt Pyrolysis Process Flow

to be removed in other units.

The reactor must clearly have a purged air-lock feeding arrangement for tyres in which they can be stacked on a suitable frame. To obtain psuedo-continuity this must be at least duplicated. This arrangement could be simultaneously used to feed make-up salt. The upper region of the reactor must also incorporate an outlet for the volatile products. In the lower regions the reactor must have the requisite number of entry and exit points to other units and to an emergency dumping pit.

Corrosion tests have shown that only specialized stainless steels are suitably resistant. This would probably lead to a very costly reactor which will be shown later (Section 16.9) to be highly undesirable. It therefore seems likely that the stress bearing vessel should be constructed of mild steel and lined with either stainless steel or, probably more cheaply, ceramic bricks. Being heated by an internal source a total or partial (between the bricks) frozen wall effect might be employed as the operating temperature of around 500°C is only 100°C or so above the melting point. This will depend on temperature gradients in the final plants, but lining of some kind would appear to be imperative. Internal heating does however present problems in the design of a start-up procedure.

15.3.3 Gasification Reactor

The options for the method of char gasification have been suggested but due to hydrolysis of the melt and slow rate features of steam gasification, the air method has been considered most satisfactory. Melt arriving from the pyrolysis reactor will, among other materials, contain entrained in it (by violent agitation) the char product. By injection of air at the lower end of the reactor this will be burnt in-situ producing heat and carbon oxide gases. The heat produced will maintain the higher temperature in the gasification unit and the excess used to heat other parts of the system. The residual heat surplus will have to be used outside the reactor.

The reactor must be designed with an upper port for the gasification products as well as lower ports for melt passage and air injection. The basic construction techniques are identical to the pyrolysis reactor but due to the higher temperatures the frozen wall effect may prove less practical, in which case a cast lining might be considered. For reasons that will become apparent in later sections the design may be more intricate than the simple cylindrical vessel likely to be used as the pyrolysis reactor.

15.3.4 Melt Regeneration

15.3.4.1 Introduction

The inorganic products of pyrolysis, mostly sulphides and zinc salts, will unless removed, build-up in the melt. Although some uncertainty exists zinc salts tend to cause an increase in melt viscosity whether they are dissolved or exist as suspended solid particles. Sulphides are essentially soluble in the melt but are undesirable on grounds of toxicity.

15.3.4.2 Sulphur

Sulphides can be converted to hydrogen sulphide and carbonates by the passing of carbon dioxide and steam, only limited quantities of which are needed. The hydrogen sulphide, about 10 kg per tonne of tyre processed, is thus produced in a controlled manner and utilized or disposed of conventionally.

The volume of this reactor is likely to be only a tenth of the pyrolysis and gasification reactors and therefore the lining with ceramic materials is likely to be impractical which indicates construction from stainless steels. The design is likely to be a simple baffled tube with the appropriate ports for melt circulation and gas passage.

Molten carbonate sulphur recovery systems are well documented in the literature. Eventually disposal may have to be contemplated.

15.3.4.3 Zinc Salts

If zinc salts exist in a continuously operating reactor as suspended solids, the options for removal are hot filtration or settling. Both are complex options and are likely to be costly. If zinc salts are dissolved in the melt there are a further two alternatives. The first is precipitation of zincates as zinc oxide by carbon dioxide followed by settling. The second is an aqueous process involving the dissolution of melt by quenching in water, the settling of insoluble solids, carbonation of the liquor by carbon dioxide in a standard carbonation tower to precipitate bicarbonates, filtration to recover the biocarbonate and finally reintroduction to the pyrolysis reactor where conversion to carbonate will automatically take place. This is a highly involved process which would also remove the sulphur compound in the filtrate.

At present there is insufficient data to discuss these options further or make a choice. However whatever system may be adopted stainless steel will almost certainly be used in construction which will relate to costs. Again design of the molten system will be important to assist melt circulation.

15.3.5 Melt Circulation

Melt must be circulated between the pyrolysis and gasification reactors at a rate approximately equivalent to the volume of the pyrolysis reactor every 20 minutes. The circulation through the melt regeneration stages is somewhat lower; calculated from the concentrations of inorganics the rate corresponds to the pyrolysis volume every 2 hours.

It is desirable to pump the melt without bringing it into contact with moving parts, although centrifugal pumps have been used for the purpose.(333) The two most obvious methods are gas-lift and acid egg pumps. The acid egg arrangement, although easily capable of these rates, does have a moving value and is only a semi-continuous method of pumping which may be a disadvantage in the final design. The gas-lift principle relies on gas bubbles giving a positive displacement in a liquid, a situation that will exist in the gasification reactor and the molten salt regeneration system. The efficiency of gas-lift pumps is related to vessel and bubble dimensions, flow characteristics and liquid viscosity. This system is most attractive in principle but cannot at this stage be taken further as the final reactor design is not known (conversely reactor design should if possible accommodate gas-lift circulation).

The circulation of melt between main reactors will also undergo a change in temperature of some 300°C. This is by no means demanding until the melt flow rates are considered when it transpires that a 10,000 t/yr plant will require a heat exchanger in this region whose surface area (assumed steel) is over 550 m^2. There may also be required additional heat exchange facilities for raising of steam and so on. The materials of construction must, for corrosion reasons, be stainless steel although this is not ideal for heat transfer.

15.3.6 Material Feed

Material feed is concerned entirely with tyres and make-up salts; gases are considered elsewhere. It is highly desirable that tyres are fed whole and without pretreatment straight from the storage area to the reactor. The obvious methods, saving labour, are conveyors and hook-lines, the latter is easily applicable to whole tyres and is found throughout the industry. The need to stack tyres and forcibly immerse them in the reactor requires some further inlet design consideration.

The make-up salt feed can be achieved in two ways. Firstly by direct screw feed into the reactor or secondly as a batch addition with tyre inputs. The former may be preferable on very large plants as at a feeding rate of 50 kg per tonne of tyre this becomes significant. However on smaller plants it would be quite feasible to periodically add even an unopened bag of salt with tyre input. This would do away with storage silos that would otherwise have to be similar in capacity to the pyrolysis reactor. There is also a connection here with the method of zinc salt removal which may produce dry salt to be readded.

15.3.7 Product Recovery

Oil and gas distil from the pyrolysis reactor and can be collected in a number of ways. Oil is recovered on the laboratory rig by water cooled and glycol cooled condensers which were used in conjunction with a bubbling arrangement. Co-current water-cooled condensers allowed mists to pass uncoallesced, addition of bubble columns and colder counter-current condensers cured this although electrostatic precipitaters and spray demisting equipment were also considered. It is not possible to predict the larger scale behaviour but this is a standard problem and the required equipment will be available at reasonable cost. If possible simple plant should be used but a steam stripping operation will almost certainly be necessary. The permanent gases pass through these units but, unlike the oil, they are better not stored and so must be used on site.

The condensers may possibly be constructed of a mild steel but the spray demister, being exposed to oil, vapours and steam should be formed of stainless steel. The cooled area required assuming water is used as the coolant would be around 400 m^2 for the 10,000 t/yr plant. The design is open to further debate but an angular internal design would facilitate drop formation thus clearing the cooled surface and would encourage turbulence in the surface gas layers.

The recovery of steel, inorganics and char has been covered elsewhere.

15.3.8 Services

The services required by the process flow design given in Figure 15.4 are: air, water, heat, steam and electric power.

Air is required for char gasification and possibly for acid egg pumping, the former representing the vast majority of the demand. Air would be compressed and fed by pipe under pressure to the required areas of the plant. Taking the 4,000 t/yr, 10,000 t/yr and 50,000 t/yr plants the approximate rates of air supply must be 3,000, 7,500, and 75,000 m^3/hr respectively. The respective compressor types most suited to these deliveries are all of the centrifugal type which are capable of delivery pressures up to 25 kg/cm^2(350 psig). The compressor is clearly fed from the atmosphere.

Water is required as a coolant for the condensers used in oil collection and a possible reactant in any aqueous melt regeneration. Water in the form of steam is likely to be used in the melt recycling and in the stripping of volatiles from the oil. The total requirement at 250/450 psig is at present unknown as no experimentation has been carried out in this area. It is the plan to use the char gasification products and/or the gaseous pyrolysis products to fuel the boiler. The costing has assumed this, 200°C of super heating capacity and an average industrial boiler of 20,000 - 30,000 kg/hr in the case of the largest plant, much of which may well in the event be used for space heating. (It is assumed that the origin of all heat requirements is the char combustion.)

The carbon dioxide required for melt regeneration can be obtained by combustion of the gasification product which is almost entirely carbon monoxide. This can be supplied to the reactor by a low capacity compressor possibly of the sliding rotary vane type.

15.4 Scales of Operation

15.4.1 Process Scales

It was shown in the literature survey that the probable current rate of tyre tipping is 13.4 million tyres (102,000 tonnes) a year. This volume is the prime target feed for any pyrolysis process. However if it is accepted that tyre pyrolysis has advantages over more conventional reuse this figure of availability could well be greater. The obvious area from which tyres mightt be poached is incineration. This considered the total availability may well be considered as high as 16.6 million tyres (125,000 tonnes). Although due to geographical distribution it is impractical to collect all these tyres, the existing network of casing selectors and their patterns of operation make it reasonable to assume that 85% or more are accessible. This puts an availability of some 11 - 14 million tyres (83,000 - 105,000 tonnes) before any prospective operator. This process of supply evaluation is emphasised in the next chapter.

Given this supply availability there are four basic strategies that may be adopted. These are summarized as:

1) 50,000 + t/yr. A single plant nationwide operation.

2) 10,000 t/yr. A regional operation, possibly in more than one region.

3) 10,000 t/yr. A regional operation based on a mobile plant.

4) 4,000 t/yr. A casing selector site operation.

Needless to say, the peculiar circumstances of any part or all of the country may lend themselves to various combinations of these strategy options.

The 50,000 t/yr scale strategy is to place a large single plant in a location giving the least mean distance to the supply sources for this scale. The major differences in this type of development are the probable green field starting site, the wide tyre collection radius (up to 100 miles) and the necessity to redistribute the products. These will become clearer as other options are considered. This strategy appears to be that adopted by Batchellor Robinson Metals and Chemicals(89) whose mooted site for a plant of this size is said(96) to be South Wales. This siting has been clearly influenced by known current stocks in this region(3). In the long term a geographically more central site within collection range of current steady arisings might be more suitable. In the USA Goodyear-Tosco have also opted for a large plant but here the total market is also larger. These large units will obviously, considering the economies of scale, show the greatest return (see Chapter 16), and probably, in engineering terms, be the most efficient. However due to the wider area of tyre collection, the transport will not be used so efficiently as for smaller plants. Sited even in the Midlands, Glasgow, which is a relatively large source, would have to be neglected. In addition there may well be unknown technical difficulties associated with this scale. Such unknowns often make raising large sums of capital more difficult.

The 10,000 t/yr strategy would probably involve development on a partially existent site and if such a site were on or adjacent to a casing selector site part of the feed supply would be immediately to hand. Although less efficient in engineering terms, this scale of operation is bound to be more efficient when it comes to tyre collection. Five or six of these units placed strategically over the country would be able to "cover the ground" far more effectively, probably increasing the total collectable volume of tyres as a result. The collection radius for such a plant is probably at most 25 miles.

The mobile plant of the same scale may, if transport costs become a lot higher, offer a very different strategy; that of moving the plant to the feed supply rather than the more conventional reverse. Such a system has been proposed for wood pyrolysis(334) on the premise that wood pyrolyses faster than it grows. The compact nature of a molten salt plant may lend itself to such a strategy but there may also be technical and legal problems with which to contend. The unit would not be restricted by collection radius and would be particularly useful in clearing even relatively small existing tyre tip sites.

The 4,000 t/yr scale is intended for use on or adjacent to a large casing selector site or alternatively in the immediate vicinity of several smaller casing selectors. This has the advantage of very low or no transport costs. The scale is smaller than anything suggested in the literature. It is probable that, being small and despite low operating cost, the return on this scale is inadequate.

15.4.2 Unit Scales

In this section the mass and energy data from section 15.3 is combined with the strategies discussed in section 15.4.1 to give quantitative process flows for each scale.

The first quantity to be derived for each scale is the volume of melt required in each unit. Melt volumes are given in Table 15.1.

Scale, t/yr	4,000	10,000	50,000
Pyrolysis Reactor, m^3	1.5	3.7	18.5
Gasifier, m^3	3.8	9.3	46.3
Regeneration Loop, m^3	0.4	1	5

Table 15.1 Melt Volumes

The rates of melt cycling between reactors will depend on the maximum acceptable char concentration, being lower at higher concentrations. This is an area for detailed study on a continuous system.

The mass balance for the three scales of operation are given in

Table 15.2. All values quoted are in tonnes per year. A molten system for melt regeneration is assumed.

	IN			OUT		
Tyre	4,000	10,000	50,000	4,000	10,000	50,000
Melt	(140)	(350)	(1,750)			
Oil				1,170	2,930	14,630
Gas				450	1,130	5,630
(Char)				(1,480)	(3,700)	(18,500)
Steel				680	1,700	8,500
(Inorgs.)				(220)	(550)	(2,750)
Melt Waste				(140)	(350)	(1,750)
Air	9,920	24,800	124,000	7,840	19,600	98,000 N_2
CO				3,280	8,200	41,000
CO_2				280	700	3,500
Prod.Inorgs.				360	900	4,500
Steam	820	2,050	10,250	680	1,700	8,500
Water	(10,000)	(25,000)	(125,000)	(10,000)	(25,000)	(125,000)
TOTALS	14,740	36,850	184,250	14,740	36,860	184,250

Table 15.2 Scaled Process Mass Flows, t.

The energy data can be treated in exactly the same way to give energy inputs and exports for each scale. These data are then used to calculate the overall energy surplus generated by each plant (see Figure 15.3).

	Energy input			Energy export		
	4,000	10,000	50,000	4,000	10,000	50,000
Tyre preheat	2,800	7,000	35,000			
Melt "	50	130	630			
Regener$^{\underline{n}}$	6,000	15,000	75,000 max			
Air preheat net	0	0	0			
Pyrolysis				2,320	5,800	29,000
Gasification				13,570	33,920	169,600
Oil				(47,560	118,900	594,500)
Gas				(22,560	56,400	282,000)
CO				(29,400	73,500	367,500)
Condensers				1,400	3,500	17,500
Services	2,160	4,300	14,000			
Heat loss	1,750	3,250	13,500			
Total input	12,760	29,680	138,130			
Total export				17,290	43,220	216,100
			NET SURPLUS	4,530	13,540	77,970

Table 15.3 Scaled Process Energy Flows, GJ.

These figures show that the process yields a considerable overall surplus of energy. Most of this surplus is fortunately accounted for in the liquid and gaseous fuels produced by the process. These can to a certain extent be stored for later use but can also be transported for combustion (hence energy release) elswhere. This is perhaps the major advantage of this type of system over straight forward tyre incineration. When the energy surplus due to exported fuels is accounted for the in-situ energy surpluses for 4,000, 10,000 and 50,000 t/yr plants becomes 4,530, 13,540 and 77,970 GJ respectively. If a steadily increasing reactor temperature is to be avoided it is these quantities of energy that will have to be removed from the melt. This would be done by an additional heat exchange facility; the energy so extracted being dissipated to the air or immediately used to raise steam for ex-reactor uses.

CHAPTER

SIXTEEN

ECONOMIC EVALUATION

16 ECONOMIC EVALUATION

16.1 Introduction

The previous chapters have been concerned with the general desirability and the technical feasibility of the molten salt tyre pyrolysis process. While these features are important it is equally essential to any corporate body that the process is economically viable. It is the object of this chapter to describe the economic evaluation that has been carried out and to assess the results. This was done using a number of costing and accounting techniques described in the next section and elsewhere in the text. The data required was obtained from the experimental work carried out and from other more general sources. It should be emphasised that at this stage of development these evaluations can only be considered as useful guidelines. However where there is doubt over any criterion or viability factor the least favorable situation is used in any calculation. This avoids any trend to be over optimistic.

16.2 Method of Evaluation

There are a number of varied methods of investment appraisal currently in use through British industry; qualitative judgement, pay-back period, return on investment, net present value rate of return and discounted cash flow rate of return(74). The method used varies with the nature and expected duration of the project. In the case of the novel molten salt tyre pyrolysis clearly qualitative judgement cannot be applied. The pay-back period and the simple return on investment are current value only methods while the net present value and discounted cash flow rate of return are time-value methods. Of the last two the DCF rate of return allows variable project earnings and taxation to be taken into account and so is used here.

The DCF method employs two basic steps; firstly a year-by-year net cash flow calculation (tax accounted) over the expected project life, then secondly the cash flows are discounted to obtain net present values for estimated rates of return. The DCF rate of return is defined as that which gives a net present value of zero. Although the method uses trial and error, the plotting of successive rate of return estimates against net present value will give a reasonably accurate DCF rate of return from the axial intercept. The method is often used to compare projects but careful calculation of the input data enables realistic quantitative results to be obtained.

The DCF method does not in itself make any allowance for inflation. The prevalent school of thought(335) is that this is of no consequence as inflation affects all parts of the cash flow equation equally. Hence current value can be used for future years. However since this process produces fuels the increase in product value and hence income may well exceed the rate of inflation. It is also arguable whether processing costs are increasing in line with inflation, the claims varying with the source concerned. Since these factors are uncertain, favorable or debatable it was thought best to ignore inflation for these purposes.

The DCF method requires a considerable amount of data. The methods used in calculating each of these is described in the section concerned.

16.3 Scales of Operation

It was estimated in Section 4.3 that by 1980 some 13.4 million (increasing) car/van tyres will be tipped each year. In addition, 3.5 million will be incinerated, 2.0 million used in secondary industries, 6.0 million reclaimed and 3.5 million retreaded. The number available to a pyrolysis process will largely depend on its ability to compete with present reuse and disposal methods. Theoretically all those tyres currently being tipped are a competition free feedstock. However not all are tipped in an orderly manner and with increasing transport and labour costs random dumpings may not be economic to collect. Those tyres being tipped by casing selectors in a controlled manner are likely to account for 9 - 11 million a year, Tyre Disposal Services alone tip some 3.5 million a year.

In addition to tipped tyres it would appear, commercial factors permitting, that some may be "poached" from other disposal industries. It was seen in the strategic policy study (Chapter 5) that it is hard to estimate the effects on the market of tyre pyrolysis but some conservative estimates of the potential poach are shown in Table 16.1

	Present Reuse	Potential Poach	Projected Reuse
Retread	3.5 million	0.0	3.5
Reclaim	6.0	0.5	5.5
Secondary	2.0	0.0	2.0
Incineration	3.5	1.5	2.0
Tip	13.4	9.0-11.0	2.4-4.4
Pyrolysis	-	-	11.0-13.0
Total	28.4	-	28.4

Table 16.1 Tyre Availability

The table shows that some 11.0 - 13.0 million tyres are likely to be available for pyrolysis. Taking the lower figure of 11.0 million per year it should be noted that this is equivalent to about 83,000 tonnes as tonnages are used elsewhere. On the basis of a 6000 hour operating year a total plant capacity of 1800 tyres per hour (13.8 t/hr) would be required. Practical considerations and experimental evidence indicate that given sufficient melt (0.2 m^3) an average sized tyre will pyrolyse in 10 minutes. This in turn indicates a total batch capacity at any one time of 300 tyres and a melt volume of over 60 m^3 or around 30 m^3 on a continuous operation.

This would clearly be a very large plant and when the distribution of casing selector sites is considered it might well be more realistic to consider 8 - 10 smaller, strategically placed plants. Such units would be based on a salt bath of no more than 7.5 m^3 and have a maximum capacity of 10,400 t/yr. However to cover all eventualities units of 50,000, 10,000 and 4,000 tonnes per annum will be considered.

16.4 Capital Cost

16.4.1 Methods

The first method of capital costing was a scaling-up of the basic reactor unit and supporting structures using an index power method(336). The base cost used was a 1978 pilot plant costing which was thought to be reasonably accurate. Having obtained the basic reactor cost at the desired scale the Lang factor technique was used to cost installation, land, services, instrumentation and so on, thus obtaining a total cost.

The second method employed was one of direct cost comparison with similar units of similar size in other industries. This was done using standard costing data (337,338) available in the literature. In many cases special allowances were made with the specific application in mind; usually this increased the cost. This method involved costing each item described in Chapter 15. Having costed the plant allowances for land, labour, installation and so on were made in the usual way. Due to lack of data most of this costing was carried out at 1967 costs and adjusted using a cost index(339).

Both methods have disadvantages either of massive scale-up or of dated information but acting together they form a cross check which if close enables an average to be taken.

16.4.2 Plant Costing

16.4.2.1 Scale-up and Lang Factor Analysis

This method is based on the accurate costing of a planned 1978 pilot plant of capacity 3.5 kg/hr. A very brief summary of this costing is given in Table 16.2. It is clear that this scale of plant requires disproportionate investment in safety gear and instrumentation; a feature of research plant. Therefore the basic reactor and support figure of £2080 is used for scaling-up.

Item	Cost £
Reactor & Supports	2080
Instrumentation	3090
Services	595
Safety gear	1140
Total	6905

Table 16.2 Pilot Plant Costing, 1978

The capital costs of two scales of plant are normally not related by direct proportion but by the form in Eq. 16.1

$$C_1/C_2 = (Q_1/Q_2)^x \qquad \text{Eq. 16.1}$$

where,

C_1 = capital cost plant 1

C_2 = capital cost plant 2

Q_1 = size plant 1

Q_2 = size plant 2

x = scale/cost index

This can be rewritten as Eq. 16.2 so as to give the unknown cost.

$$C_2 = (Q_1/Q_2)^x . C_1 \qquad \text{Eq. 16.2}$$

The value of x varies with the type of plant involved. For high temperature pyrolytic plant it is taken as 0.78(336) and so gives the plant costs in Table 16.3. Then using the cost index published in August 1980(339) the values were brought up to date. All figures are corrected to the closest £1000.

Scale of Operation t/yr	Reactor Capital Cost 1978	Reactor Capital Cost 1980
50,000	£895,000	£1,069,000
10,000	255,000	305,000
4,000	124,000	150,000

Table 16.3 Capital Costs - Reactor, £

Element	Lang Factor Range	Lang Factor	Comments
Basic Unit	1.00	1.00	
Installation	0.18 - 1.00	0.35	Solid-fluid plant
Instrumentation	0.06 - 0.20	0.06	Simple design
Piping	0.07 - 0.60	0.11	Water and gas
Electrical	0.06 - 0.35	0.06	Limited
Land	0.02 - 0.10	0.07	Industrial
Site improvement	0.04 - 0.25	0.06	Clearance only
Buildings	0.15 - 1.20	0.20	Basic partial cover
Services	0.10 - 1.00	0.30	Lighting and water
Labour and Supervision	0.15 - 0.60	0.30	Solid-fluid plant
Construction	0.15 - 0.60	0.20	Small design
Contractor Fee	5 - 15%	5%	-
Contingency	5 - 15%	10%	-
TOTAL	-		-

Table 16.4 Lang Factors

Element	Lang Factor	50,000 t/yr	10,000 t/yr	Mobile 10,000 t/yr	4,000 t/yr
Basic Unit	1.00	1,069,000	305,000	305,000	150,000
Installation	0.35	374,000	106,000	106,000	53,000
Instrumentation	0.06	64,000	18,000	18,000	9,000
Piping	0.11	118,000	34,000	34,000	17,000
Electrical	0.06	64,000	18,000	18,000	9,000
Land	0.07	74,000	21,000	-	10,000
Site Impr.	0.06	64,000	18,000	-	9,000
Buildings	0.20	214,000	61,000	-	30,000
Services	0.30	320,000	92,000	46,000	45,000
Labour etc.	0.30	320,000	92,000	92,000	45,000
Construction	0.20	214,000	61,000	61,000	30,000
Contractor	5%	107,000	41,000	34,000	20,000
Contingency	10%	214,000	82,000	68,000	40,000
TOTAL		3,216,000	949,000	782,000	467,000

Table 16.5 Total Capital Costs, £

The values in Table 16.3 represent the capital cost of the basic reactor unit, to which costs of installation and ancillary equipment must be added. The Lang factor technique assigns a value of 1.00 to the basic unit and expresses these extra parts (e.g. instrumentation) as a fixed relation to this cost. Most texts give a variation of Lang factors for each element but by sub-categorizing to a high temperature fluid-solid process and using general experience a finite value was obtained. Table 16.4 shows the elements concerned, the Lang factor variation and a finite value with a comment relevant to its derivation. Table 16.5 uses the finite Lang factors to obtain the element costs and total costs in monetary terms.

In addition to these capital costs are those of transport equipment. Estimates of these requirements are given in Table 16.5; they are used later, based on a deliberately harsh 3 year truck life, for inclusion in the DCF rate of return method. Detailed transport costing can be seen in section 16.5.3.

Scale of Operation t/yr	Total Transport/Mobility Costs £, 1980
50,000	600,000
10,000	60,000
Mobile 10,000	40,000
4,000	0

Table 16.6 Transport/Mobility Costs, £

16.4.2.2 Current Operational Units

The capital costing by this method is considerably more complex than by the scale-up method as it is necessary to be specific in costing each component. At this stage of the process development it is not possible to be wholly authoritative on the type of component used in each unit. Therefore where there is doubt over the type of component a number of possibilities, mentioned in Chapter 15, are considered. If one type of component appears likely to be used on a commercial plant then it will be selected for cost summation, if it is not clear the most expensive component is used. (This chapter will pay constant reference to the process development chapter.)

I. Pyrolysis Reactor

The options for the pyrolysis reactor are discussed in section 15.3.2; of these it is possible that the reactor body may have to be constructed of 22 mm stainless steel and lined with ceramic (Monofrax A) possibly also utilizing a frozen wall effect. The cost of this unit is given in Table 16.7.

Feature	50,000 t/yr	10,000 t/yr	4,000 t/yr
Steel vessel (St.St.)	20,500	11,200	8,200
Lining	1,000	700	500
Ports	1,000	800	500
SUB-TOTAL	£22,500	£12,700	£9,200

Table 16.7 Costs of Pyrolysis Reactor, 1980, £

II. Gasification Reactor

From the Chapter 15 it is clear that the gasification reactor will be of similar construction to the pyrolysis reactor. However the slightly higher temperature may necessitate the use of a better quality ceramic. The costing details are given in Table 16.8

Feature	50,000 t/yr	10,000 t/yr	4,000 t/yr
Steel vessel (St.St.)	30,900	16,900	12,400
Lining	2,000	1,100	800
Ports	-	-	-
SUB-TOTAL	£32,900	£18,000	£13,200

Table 16.8 Costs of Gasification Reactor, 1980, £

III. Desulphurization Unit

It has been seen that two options for the desulphurization unit are available; stainless steel unlined or with ceramic lined. Both are costed here assuming a 6 mm metal thickness.

Feature	50,000 t/yr		10,000 t/yr		4,000 t/yr	
	Lined	Unlined	Lined	Unlined	Lined	Unlined
Steel vessel	7,700	7,700	4,200	4,200	3,100	3,100
Piping	800	800	500	500	300	300
Lining	200	-	150	-	100	-
SUB-TOTAL	£8,700	£8,500	£4,850	£4,700	£3,500	£3,400

Table 16.9 Costs of Desulphurisation Unit, 1980, £

IV. Ash Removal

Of the ash removal options two are worth costing: the aqueous reprocessing system and the molten precipitation system. The former is technologically feasible while the latter is questionable technically but would be simpler. Table 16.10 shows the aqueous route costs and Table 16.11 the molten route costs. Most features are constructed of 6 mm stainless steel.

Feature	50,000 t/yr	10,000 t/yr	4,000 t/yr
Quench tank	17,000	9,300	7,700
Settling tank	7,400	4,100	3,000
Carbonator	20,000	10,000	7,000
Piping	Services	Services	Services
Calciner	19,500	9,800	7,000
Filter	6,500	3,500	2,500
SUB-TOTAL	£70,400	£36,700	£27,200

Table 16.10 Ash Removal - Aqueous Process, £

Feature	50,000 t/yr	10,000 t/yr	4,000 t/yr
Hot settling tank	14,400	7,800	5,700
Precipit$\frac{n}{}$ Reactor	15,000	8,000	6,000
Piping	3,000	2,000	1,500
Sand filter	10,000	5,500	3,800
SUB-TOTAL	£42,400	£23,300	£17,000

Table 16.11 Ash Removal - Molten Process, £

It would appear that in terms of capital cost there is likely to be relatively little to choose between these two systems. It is probable that the aqueous system will be more costly to run in terms of energy. However the process is likely to produce excess energy that would otherwise go to waste, and so there remains no obvious preference. The aqueous system has the advantage of standard technology and is in use in similar systems gasifying coal(320).

V. Product Collection

The design of collection gear is likely to be fairly straightforward. An air cooled condenser, followed by a water cooled condenser and a steam stripper. The gaseous products will be piped to burners or flared while the steel is recovered on the empty tyre feeding frames. The oil product will of course have to be stored in conventional tanks. The collection train has to be constructed of 2 and 4 mm stainless steel, with the exception of the storage tank that may be of thin gauge mild steel.

Feature	50,000 t/yr	10,000 t/yr	4,000 t/yr
Air condenser	12,800	5,000	2,600
Water condenser	6,000	2,800	1,200
Steam stripper	14,500	8,000	5,000
Piping	5,500	1,100	500
Values	500	250	150
Storage tanks	3,500	2,000	700
SUB-TOTAL	£42,800	£19,150	£10,150

Table 16.12 Costs of Product Collection Unit, £

VI. Feed

Excluding gases the reactor feeds are tyres and salt. For the larger scales tyre feed would have to be conveyor assisted and the salt would require a silo and screw feeder. The small scale relies on manual feeding. The cost increase with size is at a low proportion here, the greater part of these costs being associated with the power of the driving motors discussed later.

Feature	50,000 t/yr	10,000 t/yr	4,000 t/yr
Tyre conveyor	10,500	6,500	-
Salt silo	5,000	2,000	-
Screw feed	2,500	1,000	-
SUB-TOTAL	£18,000	£9,500	-

Table 16.13 Reactor Feeding Costs, 1980, £

VII. Melt Circulation

Three options are open for salt cycling (Section 15.3.5) however if major moving parts are to be avoided a gas lift or acid egg system must be used. Here only the acid egg in stainless steel is costed as gas lift operation would involve reactor design changes that are hard to evaluate but would probably be equal in cost. The major heat exchange facility is also costed here; a clad shell type in which both shell and tubes are to be constructed of high grade stainless steel.

Feature	50,000 t/yr	10,000 t/yr	4,000 t/yr
Acid egg/Reactor Mod.	6,200	3,600	2,500
Piping, 4"	2,800	1,500	1,100
Heat Exchange	62,000	40,000	27,000
SUB-TOTAL	£71,000	£45,100	£30,600

Table 16.14 Costs of Melt Circulation Unit, 1980, £

VIII. Services

In this part services are considered together with their delivery and associated systems.

Feature	50,000 t/yr	10,000 t/yr	4,000 t/yr
Air compressors	65,000	20,000	10,000
Valves	1,000	600	500
Piping	1,000	600	600
Steam facility	86,000	36,500	18,000
Values	1,000	600	500
Piping	1,800	1,000	800
Water tank	14,000	5,000	1,200
Piping	1,600	1,000	700
Valves	900	600	500
CO_2 compressor	18,500	5,500	2,000
Valves	800	400	400
Piping	1,000	500	400
Pumps incl. motors:			
Oil spray	1,800	1,000	700
Cool water	2,400	1,500	1,100
Quench tanks	2,400	1,500	1,100
Calciner	1,800	1,000	800
Carbonator	1,800	1,000	700

Cont'd . .

Motors:			
Conveyor (tyre)	2,000	1,200	900
Screw feed (salt)	1,000	400	-
Filter	1,000	400	-
SUB-TOTAL	£206,800	£80,300	£40,900

Table 16.15 Service Costs, 1980, £

IX. Insulation

Clearly to channel the available energy surplus to desired areas insulation will be required as discussed in Section 15.3. This is costed in Table 16.16.

Feature	50,000 t/yr	10,000 t/yr	4,000 t/yr
Pyrolysis Reactor	2,000	1,200	900
Gasification Reactor	2,400	1,500	1,000
Melt Pipes	600	300	300
Quench Tank/Pptn. Reactor	1,300	700	400
Desulphurization Reactor	1,300	700	400
Steam Pipes	900	500	300
SUB-TOTAL	£8,500	£4,900	£3,300

Table 16.16 Insulation Cost, 1980, £

X. Instrumentation and Control

Instrumentation is the area that is least susceptible to size of plant; costs are almost constant.

Feature	50,000 t/yr	10,000 t/yr	4,000 t/yr
Flow Indicators:			
Gas x 4	400	200	200
Liquid x 5	400	200	200
Molten Salt x 2	400	400	400
Temp. Indicators x 5	400	400	400
Press. Indicators x 2	100	100	100
SUB-TOTAL	£1,700	£1,300	£1,300

Table 16.17 Instrumentation Costs, 1980, £

Feature	50,000 t/yr	10,000 t/yr	4,000 t/yr
General hydraulic & automatic gear not mentioned	45,000	15,000	-

Table 16.18 Costs of Additional Control Gear, 1980, £

XI. Land, Site and Buildings

The land required for this plant would, with the exception of the 50,000 t/yr unit, need to be a prime urban and industrial site.

This arises due to two factors; firstly there must be a ready demand for the products which given the non-storable nature of the gas will have to be on site. Secondly, it must be near the raw materials and services which would mean near or adjacent to existing casing selector sites or other industrial units. As well as land for the construction of the plant, a certain amount of space is needed for tyre storage. A total area of 100 m square (2 acres) might well in 10,000 t/yr case be needed if approach roads and so on are included. The 50,000 t/yr site may be green field.

Before buildings can be erected the site must be made suitable. If it is assumed that the site is a derelict industrial unit, it will be necessary to clear the site and then prepare the ground. Preparation in this case is likely to include a large area of laid concrete. Suitable approach roads and so on must also be laid.

Buildings fall into two categories: process/maintenance and administrative/recreational. The former could easily be a low cost single storey structure of 1250 m^2 for the 10,000 t/yr (or part of a larger building). The floor could thus be the concrete, spread footing type and the roof the flat type with monitor for any plant item over 6 m in height. The area required for the later building would probably be rather less and only require a 3 m height. (A further option is a temporary type structure.) At present the cost of the land required here is likely to approach £30,000 in the 10,000 t/yr plant.

The cost of site improvement, including drainage, fire protection, surveys, roads etc. clearance and grading is given in Table 16.19.

Building costs are given in Table 16.20.

Feature	50,000 t/yr	10,000 t/yr	4,000 t/yr
Clearance & Grading	28,500	11,400	7,800
Paved surfacing Roads	65,000	32,000	21,900
Drainage	19,500	2,000	1,500
SUB-TOTAL	£113,000	£45,400	£31,200

Table 16.19 Site Improvement Costs, 1980, £

Feature	50,000 t/yr	10,000 t/yr	4,000 t/yr
Process building:			
Low cost shell	40,000	23,000	7,000
Foundations	7,000	3,500	1,200
Roofing	15,000	8,500	2,600
Admin. building:			
Low cost shell	35,000	12,000	-
Foundations	4,500	1,500	-
Roofing	9,000	3,000	-
SUB-TOTAL	£110,500	£51,500	£10,800

Table 16.20 Building Costs, 1980, £

Services that must obviously be supplied to these buildings are costed later. It is also recognised that circumstances may eliminate the needs for all these buildings and features but that as they may occur they should be included.

XII. Services

Services calculated here exclude those directly associated with the plant operation which are given in Table 16.15.

Service	50,000 t/yr	10,000 t/yr	4,000 t/yr
Electric - lighting	25,000	10,000	3,000
Gas	25,000	5,000	1,000
Water	25,000	7,500	1,000
SUB-TOTAL	£75,000	£22,500	£5,000

Table 16.21 Site Services Costs, 1980, £

XIII. Installation

Plant installation costs are usually put at about 50% of the plant costs provided it does not exceed 6 m in height. This would give an installation cost of around £260,000 for the 50,000 t/yr plant, £140,000 for the 10,000 t/yr plant and £103,000 for the 4,000 t/yr plant. It may be advisable here to make an addition of 10% bringing the figure to £286,000, £154,000 and £112,000. This is due to the novel nature of the plant.

XIV. Labour and Supervision

Calculation of labour costs by a direct method is probably the most complex costing to be carried out in this survey. Using a standard method it is possible to estimate the total man hour requirement. The system involves calculation of components for a base cost, bulk material costs (the sum being the total material component) and then labour/material relationships for process vessels, pumps, exchangers, compressors, steel work, piping, concrete, instruments, electrical and insulations. Table 16.22 shows the requirements in each case.

Component	50,000 t/yr,£	10,000 t/yr, £	4,000 t/yr, £
Base cost equipment	423,400	202,400	116,100
Bulk material cost	76,900	31,900	12,600
	Hrs	Hrs	Hrs
Material component	45,000	21,000	11,600
Process vessels Exchangers Pumps Compressors Boilers	6,800	3,500	2,100
Piping	2,900	1,500	900
Concrete	-	-	-
Steel	-	-	-
Instruments	1,000	500	300
Electrical	-	-	-
Insulation	2,300	1,200	700
Site & Bldg.Materials (£)	223,500	96,900	42,000
Site & Bldg Component (hrs)	19,700	8,500	5,100
TOTAL MAN HOURS	77,700	36,200	20,700

Table 16.22 Manhour Generation

From this data it is also possible to estimate the optimum number of men required and the constructional duration with this labour force. These details are given in Table 16.23

Plant	Manpower Density (Men)	Field Duration (Months)
50,000 t/yr	70	7.5
10,000 t/yr	60	4.0
4,000 t/yr	45	3.0

Table 16.23 Manpower Density and Field Duration

At this stage the total man hours are distributed amongst the trades required to build a chemical plant. Each trade has a cost rating and hence a composite unit rate and total labour cost are obtained.

Trade	Trade distribution(337)		Unit cost, £/hr		
Foremen	3.5	x	5.1	÷ 100 =	0.19
Boilermen	7.3		4.0		0.29
Bricklayers	3.9		3.4		0.13
Carpenters	6.6		4.8		0.32
Masons	5.9		3.3		0.19
Electricians	5.3		3.6		0.19
Insulators	1.3		3.5		0.05
Ironworkers	10.4		3.9		0.41
Engineers	4.3		3.2		0.14
Pipefitters	18.1		4.4		0.80
Painters	1.7		3.3		0.06
Sheet Metal	7.8		3.9		0.30
Millwrights	2.0		3.6		0.07
Labourers	21.9		3.1		0.68
	100.0	Total composite unit rate = 3.82 £/hr			

Table 16.24 Unit Rate Generation

Plant Scale	Total Labour Costs, £
50,000 t/yr	297,000
10,000	138,000
4,000	79,000

Table 16.25 Labour and Supervision Costs, 1980, £

XV. Contractor Fees and Contingency

The contractor's fee on this type of project is likely to be around 5% of material and labour costs. For the 50,000 t/yr, 10,000 t/yr and 4,000 t/yr plants this will therefore be £87,000, £29,500 and £16,000 respectively.

Due to the highly itemized method used here a contingency of 15% is thought appropriate. This gives values of £260,000, £118,400 and £48,000.

XVI. Total Capital Investment

The total capital investment for each plant calculated by this method are given in Table 16.26.

Element	50,000 t/yr	10,000 t/yr	Mobile 10,000 t/yr	4,000 t/yr
Pyrol. Reactor	22,500	12,700	12,700	9,200
Gas$^{\underline{n}}$ Reactor	32,900	18,000	18,000	13,200
Desulph. Unit	8,700	5,000	5,000	3,500
Ash Removal	70,400	36,700	36,700	27,200
Product Coll$^{\underline{n}}$	42,800	19,200	19,200	10,200
Feeders	18,000	9,500	-	-
Melt Circul$^{\underline{n}}$	71,000	45,100	45,100	30,600
Services	281,800	102,800	80,300	45,900
Insulation	8,500	4,900	4,900	3,300
Instrument	46,700	16,300	8,000	1,300
Land	75,000	30,000	-	5,000
Site Impr.	113,000	45,400	-	31,200
Buildings	110,500	51,500	-	-
Installation	286,000	154,000	154,000	112,000
Labour	297,000	138,000	106,000	79,000
Construction	250,000	100,000	100,000	50,000
Contract Fee	87,000	39,500	29,500	16,000
Contingency	260,000	118,400	88,500	48,000
TOTAL	2,082,000	947,000	708,000	485,000
Transport	600,000	60,000	40,000	-

Table 16.26 Capital Costs by Unit Method, 1980, £

16.4.3 Summary and Comment

The two methods show some differences in various areas of the cost make-up. This is partially attributable to the characteristics of the methods themselves, however with the possible exception of the largest plant the total capital costs are reasonably close. Since it is possible to criticize both methods an average of the two is taken. It is felt that the unitary method is slightly more meritorious and hence the average cost is likely to be a high estimate.

Plant	Cost by Scale-up, £	Cost by Units, £	Average, £
50,000 t/yr	3,316,000	2,082,000	2,699,000
10,000	949,000	947,000	948,000
Mobile 10,000	782,000	708,000	745,000
4,000	467,000	485,000	476,000

Table 16.27 Capital Cost Summary, 1980, £

Figure 16.1 shows the relationship between capital costs and scale as calculated here. This also enables direct comparisons with literature quotes to be made. In the U.K. Batchellor Robinson have published cost details; their 50,000 t/yr plant was costed between £2.25m (95) and £2.5m (96) in 1979 which in the third quarter of 1980 would be £2.4 - 2.8m. This is very similar to the £2.7m for the 50,000 t/yr molten salt plant. In the U.S.A. most of the commercial claims are centred on the Thermex Inc. process where a 10,000 t/yr plant is costed at the 1980 U.K. equivalent of £0.2m for the plant alone (143). This appears cheap at any level, but is revised, on a fully contained

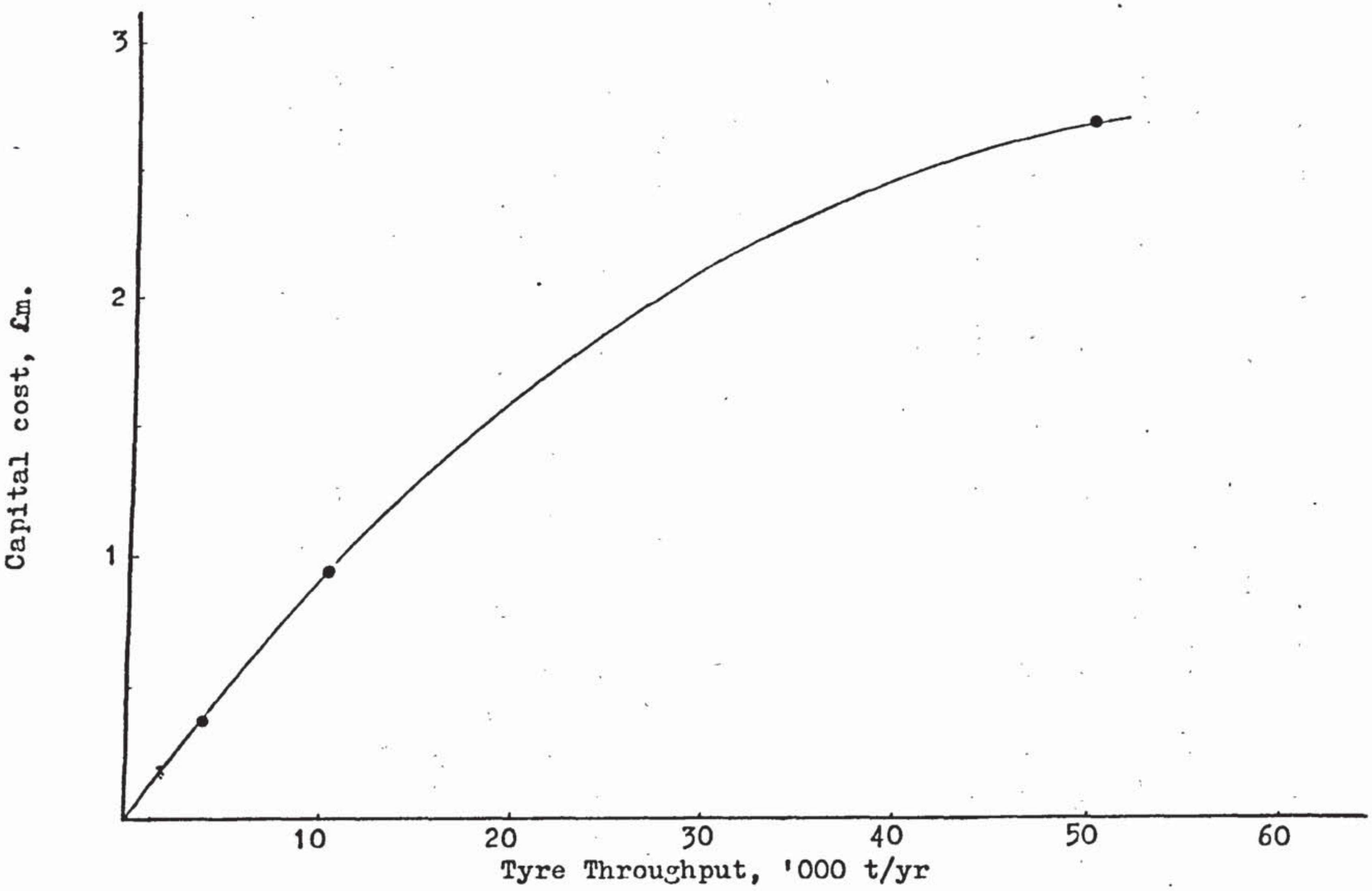


Fig.16.1 Scale vs. Capital Cost

unit to £0.5m for a slightly smaller unit. Also costed are a 17,000 t/yr unit and a 30,000 t/yr unit at U.K. 1980 equivalents of £1.0m and £1.6m respectively(340). There would appear to be some confusion here as the Thermex 30,000 t/yr unit is elsewhere quoted at £0.8m. However there is little doubt that these designs are either considerably cheaper or drastically miscosted. The Carbon Development Corp. have published a costing for a 15,000 t/yr carbon black producing plant. The capital investment plus some working capital is put at a 1980 U.K. equivalent of around £2.0m. This is costly by any judgement but appears justified in the high value of carbon black products.

16.5 Operating Costs

16.5.1 Elements of Cost

Operating costs are usually defined as the recurrent costs that are found in operating a process. In a full scale operational plant there are a wide number of costs making up the total operating cost. These are described by the "cost tree" illustrated in Figure 16.2. Obviously this is a highly detailed costing scheme that would be too involved for full application here. However the costing performed was designed to take some account of each item while giving a fuller application to the important items.

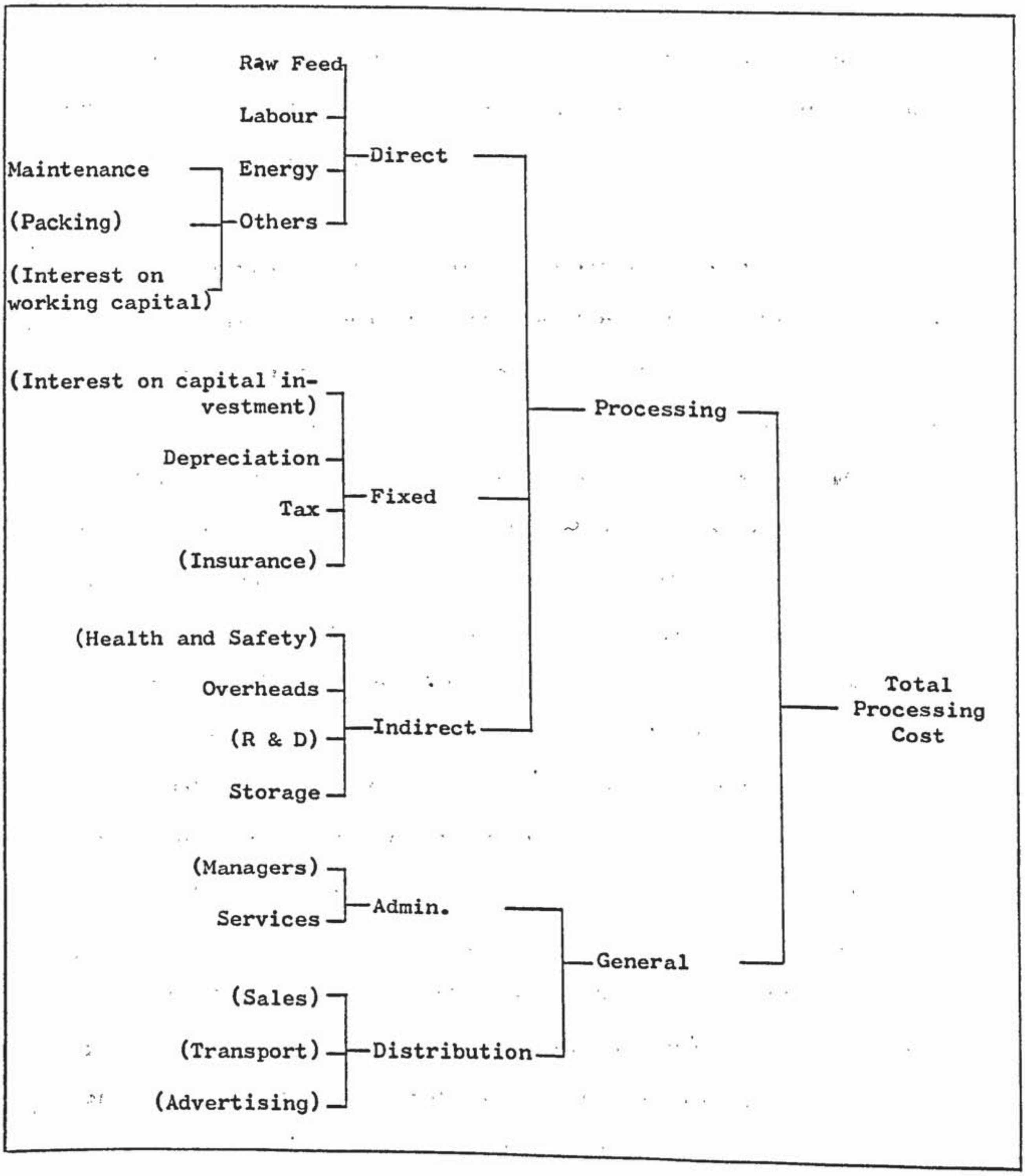


Fig.16.2 Operating Cost Tree

16.5.2 Processing Costs - Direct

16.5.2.1 Raw Materials

The process requires two main raw materials; tyres and salt. The cost of the former is tied-up with the cost of transportation and subject to negotiation.

In the case of the 50,000 t/yr plant it is assumed that all the tyres must be transported to the plant site, in the 10,000 t/yr case some 60% must be collected and in the 4,000 t/yr case it is assumed all are on-site. The collection radii for the 50,000 t/yr and 10,000 t/yr plants are assumed to average 100 miles and 25 miles respectively. Transport costs may now be as high as 10p per tonne/mile if contracted externally, putting the total transport costs for the two plants at £1,000,000 and £25,000 - clearly a great deal. The method more likely to be adopted is the use of self-operated haulage. The costs of this for the 50,000 t/yr and 10,000 t/yr operations, including fuel, maintenance and tax but excluding capital cost, depreciation (accounted in the DCF method) and labour, are £110,000 and £5,500 respectively.

The cost of tyres is very hard to assess since the effect of profitable tyre disposal on the market is unpredictable; however one or two factors are worth noting. On average the cost of tipping is currently around £8.50 a tonne and, since sites are now scarce a transport cost of £10.00 a tonne may also be experienced. This might, market forces ignored, seem to imply that disposal is worth paying £18.50 a tonne. The second indicator is the price paid by reclaimers for supplies, in the case of United Reclaim, £4.50 a tonne delivered. Assuming a £10.00 a tonne transport cost this will be costing a casing selector £5.50 a tonne in disposal. These considerations indicate that collected at source (Casing Selector) an operator might expect a fee for removal of £5.50 to £18.50, but in reality an operator would be fortunate to even get into this range. If tyres are to be bought delivered to the operator it would appear that a cost of £4.50 a tonne is the going rate, but supply factors considered an operator would not offer this rate. A conservative suggestion is delivery at scratch or collection at slightly below transport cost; £0.00 - £8.00.

In Chapter 10 it was calculated that melt consumption for the 50,000 t/yr, 10,000 t/yr and 4,000 t/yr would be 100, 20 and 8 tonnes a year. Assuming a reduction in lithium content the cost of melt is unlikely to exceed £250 a tonne. A similar figure to this total cost is assumed for other process chemicals. (These figures are taken as best estimates for evaluation.)

Material	50,000 t/yr, £	10,000 t/yr, £	4,000 t/yr, £
Transport *	110,000	5,500	-
Tyres *	-400,000	-132,500	-74,000
Melt etc.	50,000	10,000	4,000
TOTAL	-250,000	-117,000	-70,000
* If delivered sum = £0.00			

Table 16.28 Raw Material and Transport Costs, £

16.5.2.2 Operative Labour

The operating labour requirements for each type of plant are set out in Table 16.28 and costed in Table 16.29.

Labour	Rate, £/yr	50,000 t/yr	10,000 t/yr	Mobile 10,000 t/yr	4,000 t/yr
Engineer	10,000	1	0.5	0.5	0.2
Plant	5,000	9	6	4	8
Loader	4,500	6	3	4	-
Driver	5,500	18	2	1	-

Table 16.29 Labour Requirements

Labour	50,000 t/yr	10,000 t/yr	Mobile 10,000 t/yr	4,000 t/yr
Engineer	10,000	5,000	5,000	2,000
P/Op.	45,000	30,000	20,000	40,000
Loader	27,000	13,500	18,000	-
Driver	99,000	11,000	5,500	-
TOTAL	£181,000	£59,500	£48,500	£42,000

Table 16.30 Annual Labour Costs, £

The system is designed to work a three shift system although there will of course have to be some arrangement for stand-by labour.

16.5.2.3 Energy

The plant is designed to have only a few major moving parts so much of the energy supplied will be in the form of services. There will however be short periods of high energy consumption such as start-up but as the duration is short these are ignored. Table 16.31 shows energy requirements and Table 16.32 calculated costs.

Energy Use	50,000 t/yr	10,000 t/yr	Mobile 10,000 t/yr	4,000 t/yr
Lighting	50 kw	30 kw	15 kw	5 kw
Pumps	100	25	25	8
Other motors	100	20	20	4
Compressors	50	20	20	8
TOTAL	300	95	80	25

Table 16.31 Energy Requirements

	50,000 t/yr	10,000 t/yr	Mobile 10,000 t/yr	4,000 t/yr
Total cost, given 6000 hr operation (~3.5p per kwh)	60,000	18,000	17,000	5,000

Table 16.32 Energy Costs, 1980, £

16.5.2.4 Maintenance

Maintenance costs are related to the degree and type of use of plant as well as to its desired life. The figure is normally(336) calculated in terms of the capital investment (I). In chemical plants this varies from 0.02 I for low utilization to 0.12 I for corrosive, high utilization. In this case a value of 0.10 I would be appropriate, giving costs of £269,000, £95,000, £75,000 and £43,000 for the 50,000 t/yr, 10,000 t/yr, Mobile 10,000 t/yr and 4,000 t/yr respectively.

16.5.2.5 Effluent Treatment

The process is likely to produce waste water from various parts. High toxicity materials, such as sulphides, must be removed but the remainder can, with the consent of the water authority, be discharged into the public sewer. This is treated by the authority and the operator charged by volume at a rate depending on chemical/biological oxygen demand, suspended solids and so on. The charge can be approximated to 5% of the plant throughput at £10 a tonne. For the three plant sizes this would thus cost £25,000, £5,000 and £2,000.

16.5.3 Processing Costs - Fixed

Interest on capital investment, depreciation and tax are integral parts of the DCF method and so are not costed here. Insurance is usually related to capital investment at 0.004 I to 0.02 I depending on the risks of the process. Here a figure of 0.01 I is used for the housed plants giving £27,000, £9,000 and £4,000 approximately. The mobile plant is charged at 0.007 I on the grounds of being "open-air", giving £6,500.

16.5.4 Processing Costs - Indirect

The main components here are overheads and storage, the others being considered either small or part of the capital costing. Storage is covered by the depreciation inherent in the DCF method as it merely involves land space.

Overheads are usually costed in relation to the labour cost (L) on the scale 0.04 - 0.08 L. Here a value of 0.05 L is used since the plant design is simple. For the 50,000 t/yr, 10,000 t/yr, Mobile and 4,000 t/yr this gives £9,000, £3,000, £2,500 and £2,000. These values seem very low but in order to maintain uniformity of method they are accepted.

16.5.5 General Costs

Among the general costs, transport refers to product distribution and so does not exist here while sales and advertising do not apply. Services have already been costed as energy. A possible involvement in distribution on the largest plant would possibly incur a small cost of around £100,000.

It is reasonable to cost administrative costs as 0.01 - 0.04 I. Here these would be a minimum hence giving costs of £27,000, £9,500, £4,000 for the three sizes. Since the engineer would carry out many of these duties figures of £13,500, £5,000 and £2,000 would be more appropriate.

16.5.6 Total Operating Costs

The total operating costs for each plant are given in Table 16.33

Op. Cost	50,000 t/yr	10,000 t/yr	Mobile	4,000 t/yr
Raw Materials*	160,000	15,500	10,000	4,000
Labour	181,000	59,500	48,500	42,000
Energy	60,000	18,000	17,000	5,000
Maintenance	269,000	95,000	75,000	43,000
Effluent	25,000	5,000	5,000	2,000
Insurance	27,000	9,000	6,500	4,000
Overheads	9,000	3,000	2,500	2,000
Admin.	13,500	5,000	5,000	2,000
Distrib$^{\underline{n}}$	100,000	-	-	-
TOTAL	844,500	210,000	169,500	104,000
*TYRES	-400,000	-132,500	- 80,000	- 74,000

Table 16.33 Total Annual Operating Costs, £

The total process cost of this process estimated by Markham et al.(340) was only £540,000 for the 50,000 t/yr plant but £277,000 for the 10,000 t/yr plant. The scale effect is less pronounced here due to a heavy penalty for wider radius collection required in a larger plant. Markham also compares the process costs of "dry" pyrolysis units of the same size at £740,000 and £227,000, the latter being close to this estimation. Interestingly Markham quotes incinerators of 10,000 t/yr as costing £20,000 a year to run.

A patent on the Thermex process rates operating costs for various plant sizes as: 7,500 t/yr at £228,000, 15,000 t/yr at £330,000 and 30,000 t/yr at £600,000. These figures would appear to be high but the capital investment required for a Thermex unit is very low; features giving a very different cash flow pattern.

16.6 Operating Income

16.6.1 Introduction

In the long run income may be derived from a number of spin off sources such as licencing or selling plant. However in this evaluation only the income derived from operation is to be considered.

The primary source of income from the process must be from the products. Now in most cases these will not be sold on the open market for cash but be used internally and accounted against savings in expenditure. That is to say the oil will be valued as fuel oil, the gas as heating fuel and so on. The steel is the only product likely to be sold. The values of these products have already been discussed and are given in Table 16.34.

Product	Value
Hydrocarbon oil	£110.00 tonne
Hydrocarbon gas	28p Therm
H_2/CO gas	28p Therm
Steel (scrap)	£ 90.00 tonne

Table 16.34 Product Values, 1980

An additional consideration as a source of income is tyre disposal. This has already been discussed but to summarize: tyres collected are valued at - £8.00 tonne, those internally arising at - £18.50 tonne and those delivered at £0.00. It is realized that this is a highly questionable area and so it is given the widest consideration in the sensitivity analysis (Section 16.9).

16.6.2 Income Calculations

These calculations are based on the "best estimate" figures so far discussed. These assumptions have been used to calculate the total income for each of the four plants. This is shown in Tables 16.35-38.

Income Source	Volume	Value, £/yr
Hydrocarbon Oil	14,500 t	1,595,000
Hydrocarbon Gas	6,250 t	758,000
Char Gas	2,500 t	45,000
Steel	8,000 t	720,000
	PRODUCT VALUE =	£3,118,000
Tyre disposal	50,000 t	400,000
	TOTAL =	£3,518,000

Table 16.35 Income, 50,000t/yr

Income Source	Volume	Value, £/yr
Hydrocarbon Oil	2,900 t	319,000
Hydrocarbon Gas	1,200 t	145,000
Char Gas	500 t	10,000
Steel	1,600 t	144,000
	PRODUCT VALUE =	£618,000
Tyre disposal	10,000 t	133,000
	TOTAL =	£751,000

Table 16.36 Income, 10,000t/yr

Income Source	Volume	Value, £/yr
Hydrocarbon Oil	2,900 t	319,000
Hydrocarbon Gas	1,200 t	10,000
Char Gas	500 t	
Steel	1,600 t	144,000
	PRODUCT VALUE =	£473,000
Tyre disposal	10,000	80,000
	TOTAL =	£553,000

Table 16.37 Income, Mobile

Income Source	Volume	Value, £/yr
Hydrocarbon Oil	1,200 t	132,000
Hydrocarbon Gas	500 t	60,000
Char Gas	200 t	4,000
Steel	600 t	54,000
	PRODUCT VALUE	=£250,000
Tyre disposal	4,000 t	74,000
		TOTAL = £324,000

Table 16.38 Income, 4,000t/yr

In these tables certain assumptions are made about product usability; gases produced by the mobile plant would for instance largely have to be flared. The differences in tyre disposal income rates are due to difference in likely tyre sources.

16.6.3 Grants and Cost Benefit

In this evaluation the accounting is carried out on a 100% commercial basis. In reality this type of plant may under certain conditions be subjected to different conditions. It is quite likely due to the novel technology involved that such a process might be considered for a Department of Industry development grant. There may be other bodies similarly willing to supply funding.

As the plant is one which is likely to improve the environment and the quality of life for those in its vicinity a public operator would evaluate the project by a Cost-Benefit method. This is a very involved procedure which would include considerable discussion. In brief the method puts a value on the environmental and quality of life factors and would thus make the process highly attractive.

16.7 Cash Flow and DCF Assumptions

The net annual cash flow is normally defined simply as the operating income minus the operating expenses. In this evaluation the life of the project is taken as being seven years; historical reality indicates this time is likely to be far more(74). The DCF method used assumes the first year as required for construction, that the second year (the first operating year) the plant runs at 75% capacity and that in the final year it has a 5% scrap value. It is understood that the capital is raised internally and no interest is due on a loan. The transport capital is costed into years 0 and 3 indicating a 3.5 year vehicle life which is clearly not generous.

The tax account makes standard allowances for running costs and is charged a year in arrears in the normal way. The corporation tax charged here is 52% on taxable profits. Although this is the current rate it is likely to fall over the next few years; this is not accounted for.

16.8 Rate of Return by DCF Method

16.8.1 Results

The method is briefly described in section 16.2 and no further detail is given here as it is available in standard texts(336). The method was firstly worked manually for each of the four systems using the best estimated figures proposed in earlier sections. In section 16.9 these figures are subjected to sensitivity analysis by a computer aided method to evaluate the effects of changes or errors in the best estimates.

The results for the best estimate calculations are given in Table 16.39

Plant	DCFRR
50,000 t/yr	59.5%
10,000 t/yr	31.5%
10,000 t/yr Mobile	29.0%
4,000 t/yr	32.0%

Table 16.39 Best Estimate DCFRR

16.8.2 Discussion

The results show very clearly that despite having to collect tyres from greater distances and at less favourable rates the largest plant shows by far the best return on investment. The theory of the economy of scale is vindicated.

The pattern of returns among the smaller plants can be almost entirely attributed to the negative price of tyres. The 10,000 t/yr plant relies on a 50 : 50 mix of tyres internally generated and collected.

Assuming operation of this unit by a casing selector 50% may occur internally and would otherwise be tipped at a cost of £18.50 a tonne, thus this value is assigned. The remaining 50% is collected at a compromise value of £8.00 a tonne. The Mobile plant collects all its tyre at the £8.00 value. The 4,000 t/yr plant relies entirely on internal tyres, the negative disposal value of which is £18.50 a tonne. Table 16.40 shows the average fee charged for disposal by each situation. In section 16.9.2.4 average fee variation is discussed.

Plant	Tyre Fee £/tonne	Comment
50,000 t/yr	£ 8.00	Collected
10,000 t/yr	£13.25	50 : 50
Mobile	£ 8.00	Collected
4,000 t/yr	£18.50	Internal

Table 16.40 Average Disposal Fees

In finite terms the 50,000 t/yr plant shows a very attractive return on investment but the other plants are open to debate. Firstly it should be noted that cash sums of the magnitude involved here would earn an investor over 20% on the international money market. Secondly there is the question of risk. This type of project could well be classed as new technology. It is also essentially alien to the experience of the rubber industry, including Dunlop, although it could be argued that Tyre Disposal Services are in the scrap market. Combining these factors it would seem that a risk value in excess of 10% is justified. This would, as the figures stand, make the smaller plants a poor investment but does not prejudice the merits of the largest unit.

The rates of return on other pyrolysis projects have been variously quoted and it is not always clear how they have been calculated. Markham et al.(340) evaluating this process are rather more generous to the 50,000 t/yr plant at 113% but less generous to the 10,000 t/yr plant at 23%. This arises because: 1) they assume a tyre cost of scratch and 2) take less costly transport arrangements (both are covered here later). However the clear dominance of the large unit is in good agreement. Their calculated return on dry plants at 71% and 25% is in even closer agreement.

Thermex claim their units of 30,000 t/yr, 15,000 t/yr and 8,000 t/yr would return 58%, 43% and 35% which considered that they are calculated on an eight year life are similar(143). Carbon Development Corp.'s(144) 20,000 t/yr carbon black unit appears to return as little as 15% but the basis is very unclear. It is interesting that Stribling(43) claims a return on incineration of scratch cost tyres at 76% for a 10,000 t/yr operation.

16.9 Sensitivity Analysis

16.9.1 Introduction

In calculating the DCF rate of return so far only a single set of cash flow data figures have been applied. Clearly it is naive to assume that these figures are unequivocal. The purpose of sensitivity analysis is to examine the effects of changes or errors in these figures on the overall rate of return. This is done by taking each particular component of the cash flow in turn, amending it and reworking the DCF calculation to see the effect. Obviously this is an extremely long and laborious process but fortunately it can be shortened by using a computer. In this case two or three values for each cash flow element and plant size were calculated manually before a larger number of computer predicted values were added. (The author is indebted to L. M. Chiviya for carrying out the computer work.) As will be seen later this enables each cash flow element to be plotted against DCF rate of return and hence the importance of each element can be determined.

In this evaluation it was thought essential to study variations in the following cash flow elements.

1. Capital Investment
2. Operating Costs (incl. transport)
3. Transport Costs
4. Tyre Costs
5. Product Values

16.9.2 Sensitivity Results

16.9.2.1 Capital Costs

The plant capital costs from Table 16.26 are reproduced here in Table 16.41 together with the range of variations considered. Figure 16.3 shows a percentage of best estimate capital cost against DCF rate of return for all four plant options. The points marked are manually calculated while the line plotted is taken from computer results.

Plant Size	Capital Investment, £	Percentage	DCF RoI
50,000	2,699,000	50	150.0%
		100	59.5%
		200	17.0%
10,000	948,000	50	76.0%
		100	31.5%
		200	1.5%
Mobile	745,000	50	75.0%
		100	29.0%
		200	1.0%
4,000	426,000	50	78.5%
		100	32.0%
		200	1.5%

Table 16.41 Capital Cost Sensitivity

16.9.2.2 Operating Costs

The operating costs, including transport which is also treated alone, were subjected to the same degree of variation for each plant option. The results are displayed directly in Figure 16.4. As before the variation is shown as a percentage of the best estimate and only a few of the points were calculated manually.

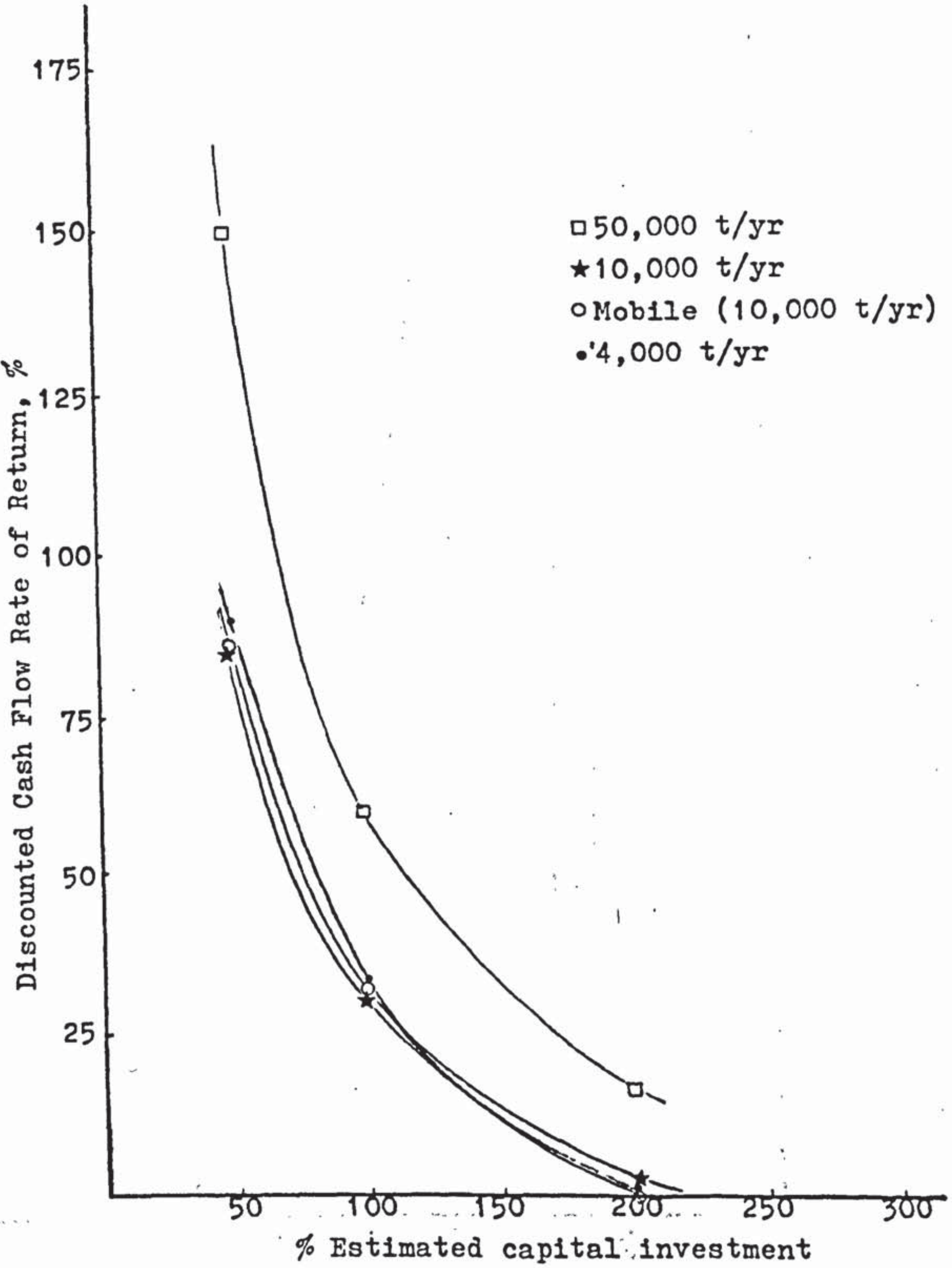


Fig.16.3 Capital Investment Sensitivity

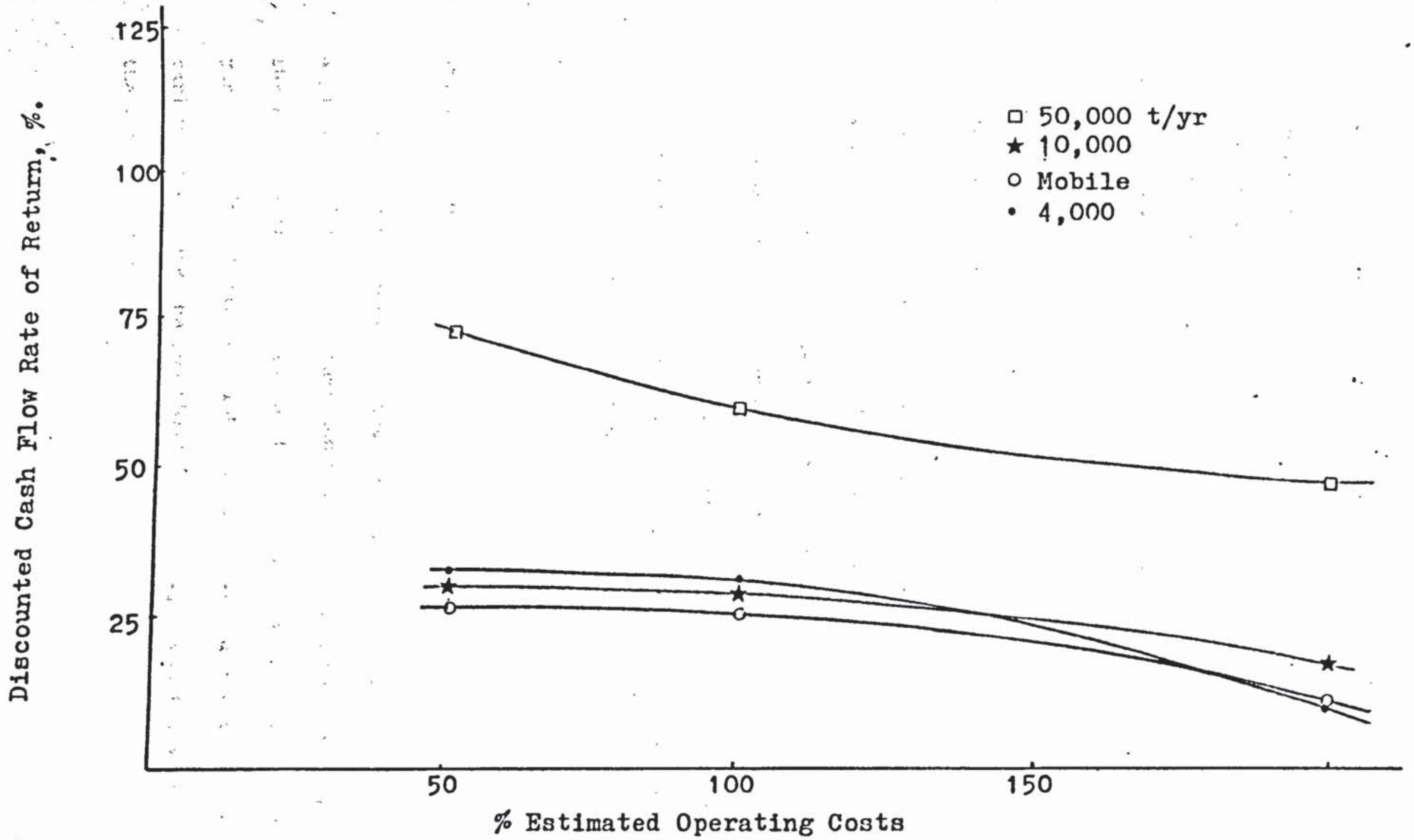


Fig.16.4 Operating Cost Sensitivity

16.9.2.3 Transport Costs

Transport costs are strongly related to fuel costs and labour costs both of which can be notoriously out of line with inflation or economic conditions. For this reason the span above the best estimate covers up to 400% linear. The results are given in Figure 16.5.

16.9.2.4 Tyre Costs

This is probably the area in which least faith can be placed in the best estimate costs due to the market being unpredictable. The various plant options draw tyres from a number of sources in differing amounts. However each plant does have an average price paid. Since these average prices are not the same in each case the DCF return on investment is actually plotted against the finite average cost of tyres in £/tonne. The results are shown in Figure 16.6.

16.9.2.5 Product Values

Here the percentage of best estimate expression is used again, applying a wide span to take account of irregular variations. All the products are considered as behaving in a similar way which is perhaps a simplification. Table 16.42 shows the finite values of various percentage changes while Figure 16.7 shows the effect on the rate of return.

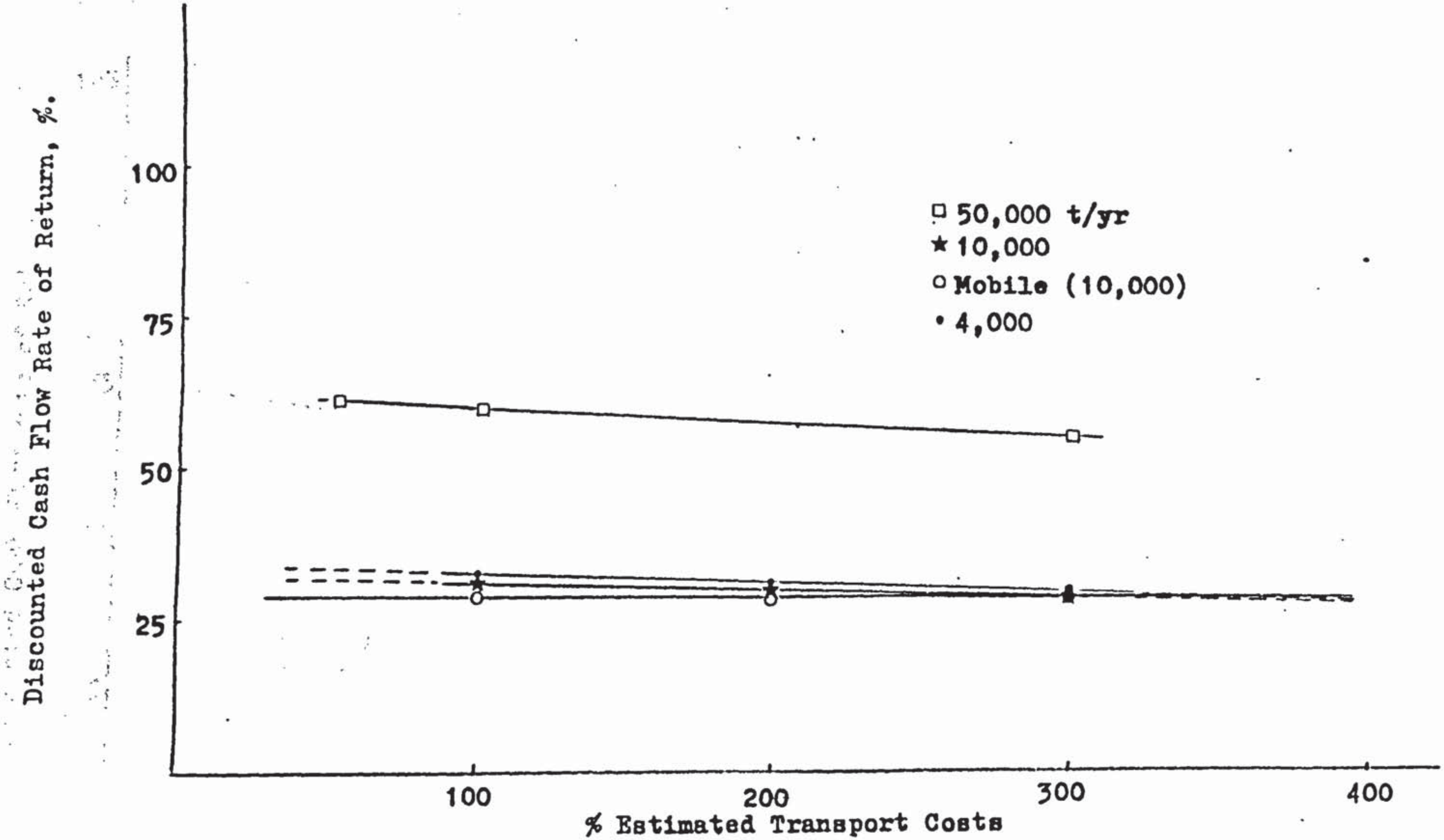


Fig.16.5 Transport Cost Sensitivity

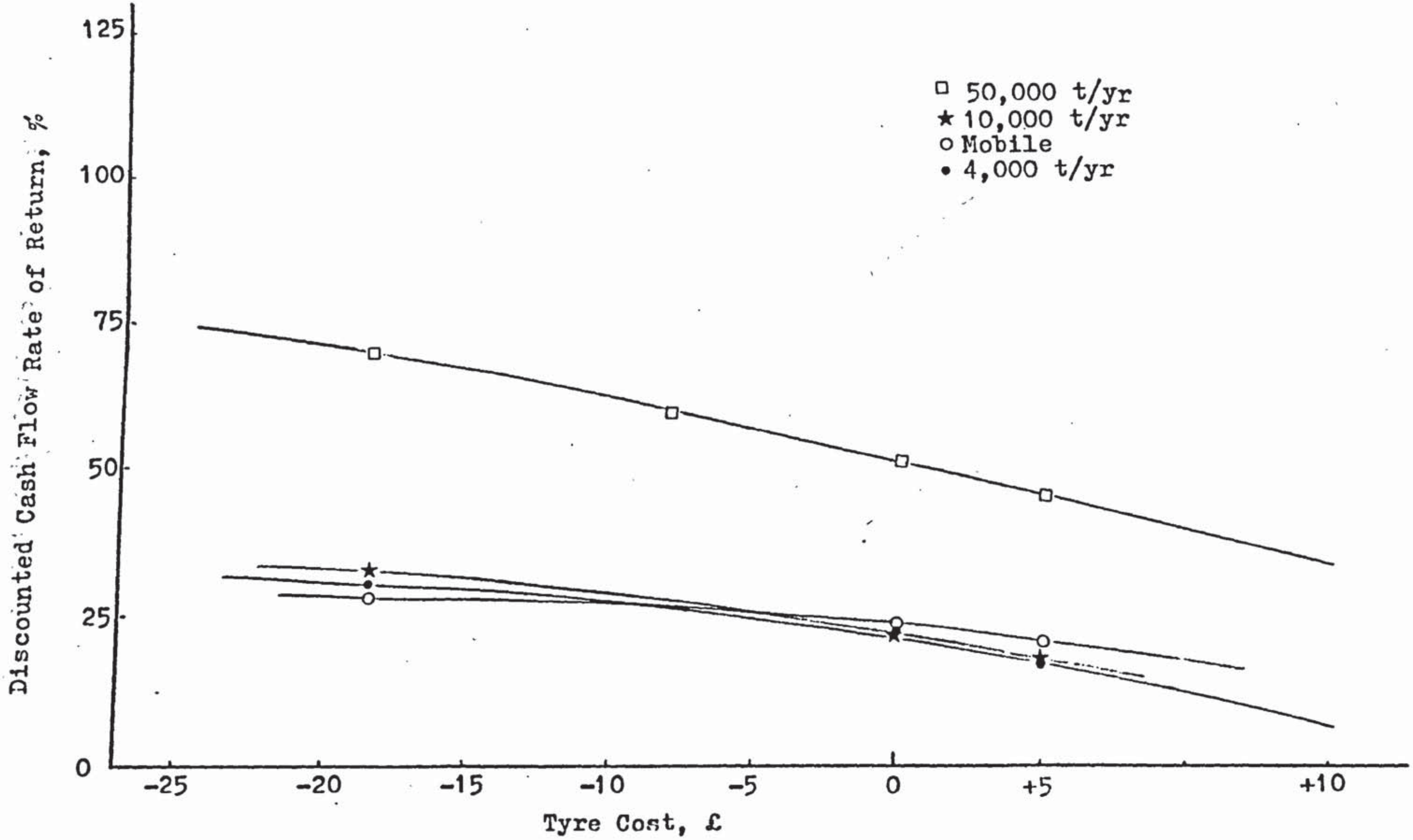


Fig.16.6 Tyre Cost Sensitivity

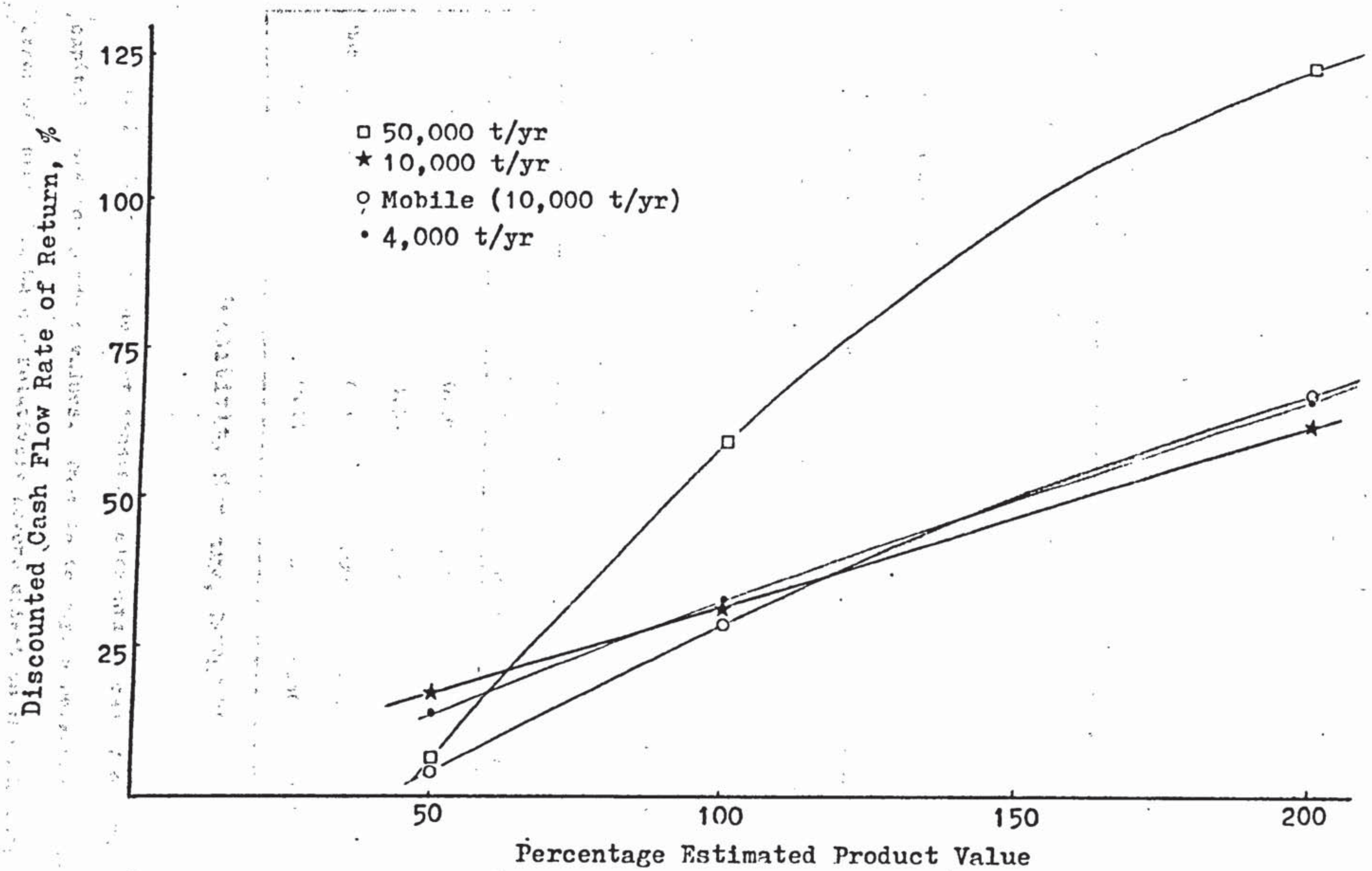


Fig.16.7 Product Value Sensitivity

Percent Best Estimate	Oil, £/t	Gas, p/Therm	Steel, £/t
25	28	7	23
50	55	14	45
100	110	28	90
200	220	56	180
300	330	84	270

Table 15.42 Finite Product Values

16.9.3 Discussion

The degree of sensitivity of each plant to each cash flow element can, to a certain extent, be quantified by the average gradient of the appropriate graphs. Here the average gradients are taken between 50 and 200%, expressing the results as DCFRR/%; the data being given in Table 16.43. Using this notation the cases of greatest sensitivity are those with the highest index.

Plant Scale	Capital Inv	Op. Costs	Transport	Tyre Cost	Prod. Value
50,000	0.88	0.16	0.02	0.09	0.80
10,000	0.57	0.09	0.01	0.07	0.29
Mobile, 10,000	0.56	0.11	0.00	0.03	0.41
4,000	0.57	0.11	0.00	0.10	0.33

Table 16.43 Sensitivity Summary, DCFRR/%

It is clear that the most sensitive elements of cash flow are capital costs and product values. That is to say, a relatively small error of these will have a relatively severe effect on the DCF rate of return. The area in which costing is not so crucial is transport while tyre costs and operating cost estimates are of intermediate sensitivity.

Firstly if capital costs are examined it is seen that an underestimate by a factor of two would reduce the rate of return for all plants by about 30%. Only the 50,000 t/yr plant could even hope to survive an error of anything approaching this magnitude. However overestimation of the costs of a plant by a similar factor would generally increase the return by between 45% and 90% depending on size.

Taking operating costs it can be seen that a lowering of cost below the expected value has little benefit in small plants but is of noticeable effect in the 50,000 t/yr plant, but on the whole the gradients are very similar. Conversely increasing costs are more crucial to small operations.

The effect of changes in transport costs are, in all cases, minimal. The mobile and 4,000 t/yr plants essentially have no transport costs so are totally unaffected. The 10,000 t/yr plant experiences a small effect since part of its feed has to be collected over a small area. Escalating transport costs are most serious in the 50,000 t/yr plant because all the feed is purpose collected and over a wide radius. However it should be emphasized that this is not an area for concern.

Tyre costs have about the same degree of sensitivity as operating costs. As about 10 - 30% of income in the best estimates was derived from tyre disposal (negative costs) it is not surprising to find a similar relationship in the sensitivity gradients.

Most crucial estimation after capital investment is cash realization from the products. Here it is expressed as a product value change and shows the most drastic effect in the largest plant. All the plots in Figure 16.7 show a levelling-off of return with increasing value which can be attributed to the fact that this is not seen as the only source of income.

If a flat 25% is taken as the very minimum return, 20% investment and 5% risk, then a quantitative error in estimate can be placed on each element. Assuming that all other estimates are correct the maximum tolerable error on each element is as shown in Table 16.44 (Changes over best estimates).

Element	50,000 t/yr	10,000 t/yr	Mobile 10,000 t/yr	4,000 t/yr
Capital Investment	+ 70%	+ 14%	+ 8%	+ 20%
Op. Costs	+ 400 - 500%	+ 60%	+ 35%	+ 45%
Transport	+ 1000%	+ 1000%	+ ∞	+ ∞
Tyre Costs	£20	- £5	- £5	- £6
Prod. Values	- 35%	- 20%	- 10%	- 20%

Table 16.44 Element Tolerances

Table 16.44 shows that the cost estimates on capital and product values have least margin for error. However the table also shows that all except the 50,000 t/yr plant rely on receiving an average fee for tyre removal of £5 - 6 / t. (The 50,000 t/yr plant could theoretically afford to pay £20 a tonne for its tyres.) There is an intuitive feeling (qualitative judgement) that charging a disposal fee may only be acceptable in the market for a short time in specific circumstances.

16.10 Conclusions

The first broad conclusion is that only the largest plant option offers a rate of return (59.5%) that is likely to be safe from the affects of errors in the costing and cash flow estimates. The remaining plants are of a borderline nature; if 20% is taken as the investment interest rate the smaller units only have some 10% allowance for risk which for a novel technology process is perhaps a little mean. In order to push these units into a preferable region it would be necessary to see: a drop in capital investment, operating cost or transport cost, or alternatively an increase in tyre disposal fees or product values. Transport costs, operating costs and tyre disposal fees have limited sensitivity therefore capital investment or product values are the areas in which the return can be improved. Fuel prices, despite global uncertainty are probably accurately costed and so the most promising area for cost rate appears to be capital investment. However literature capital estimates are in line with those here, so it must be concluded that the smaller plants are unlikely ever to show a more favourable return.

The effects of errors are, of course, additive but the 50,000 t/yr plant has a return of over 25% above the minimum acceptable. This would be sufficient to allow a considerable error in the estimates for tyre cost and operating cost which might be thought prime suspect areas. (Based on literature support of capital cost, accurate costing of products and relative unimportance of transport costs.) However there is a greater unwillingness to commit larger capital sums based on the incorrect feeling that the risk is somehow greater. If this can be overcome the return on larger units should be attractive to an organization with ability in, experience and knowledge of, this type of operation.

CHAPTER

SEVENTEEN

CONCLUSIONS & RECOMMENDATIONS

17 CONCLUSIONS AND RECOMMENDATIONS

17.1 The Used Tyre Problem

Investigation of the used tyre problem has been carried out entirely by compilation of the literature and by private communication within the tyre industry. Although it has been said that most of the major reports on the reuse of tyres in the U.K. are out of date, there are few discrepancies between published information and the opinions currently expressed in the industry. It can therefore be concluded that with one or two exceptions flows within the used tyre industry have been largely stable for some time. The advent of incineration and pyrolysis will certainly cause this to change.

Current used tyre arisings are almost universally estimated at around 23.5 million (176,500 tonnes) of which some 13.4 million (100,500 tonnes) are eventually tipped. It is clear that this rate of tipping cannot continue for economic and ecological reasons; the cost is currently about £18.50 a tonne and the number of acceptable sites is falling.

There is little scope for reducing the tip volume by increasing other reuse volumes. Retreading is beginning to decline due to safety concerns, reclaim is suffering from inadequate supplies of suitable tyres and secondary industries are of a very limited volume. If the idealistic mammoth schemes are discounted it is clear that the only viable volume solutions lie in the new technologies of incinceration and pyrolysis. The former is already making inroads into the problem, although it has been argued that pyrolysis presents a better solution.

17.2 Technical Study

17.2.1 Experimental Conclusions

It has been conclusively shown that tyres can be efficiently pyrolysed in molten carbonates at 450 - 650°C. The rates of pyrolysis, ~2700 t/m^3yr enabling a small unit (~6 m^3 total melt) to have the high throughput of ~ 4,000 tonnes/yr. The basic range of products have been; a hydrocarbon oil, a hydrocarbon gas, a carbonaceous char, steel wires and some inorganics. The former three products vary in proprotion depending mainly on melt temperature. The oil (max. 33 wt.%) and gas distil from the reactor and can be separated and collected using standard techniques. The other products remain in the reactor although if whole car/van tyres were used most of the steel would be removed mechanically without a great deal of difficulty.

Much of the experimental work has been concerned with study and removal of the two products remaining in the reactor. The char, being less dense, floats on the surface of the melt and a number of removal proposals have been considered. However in order to avoid mechanical devices it was decided to gasify the char by chemical means in a second reactor. The problem of transfer to this second reactor has not as yet been studied experimentally. The gasification reactions studied were using air, steam and a mixture of the two which produces carbon oxides and hydrogen leaving the reactor. The studies have shown that the rate of char-steam reaction was ~1500 times slower than the char-air reaction. Furthermore steam gasification did not improve the gas to any significant degree. The use of large quantities of steam is costly and may also have a detrimental effect on the melt.

Therefore it was concluded that the char is best gasified using a less than stoichiometric quantity of air which will supply the heat required and produce a reasonable gas for combustion elsewhere.

The inorganic quantities left in the melt after pyrolysis are likely to be mostly sulphides and zinc^{2+} compounds. Little work has been done in this area since it is uncertain what effect on melt condition these compounds will have in a continuously operating unit. However it has been shown that zinc compounds dissolve only slowly in the carbonate melt but dissolve stoichiometrically in hydroxide mixtures. It appears that zinc solids increase the viscosity of the melt and so can only be tolerated up to a certain concentration, about 10 wt.%. No experimental work has been done on the removal of zinc salts but aqueous and molten processes have been proposed for precipitation of zinc oxide. The sulphur present as vulcanate in tyres is absorbed in the carbonate melt (avoiding product contamination) as sulphides but there is some evidence that conversion to sulphates occurs during gasification. These compounds are soluble in the melt causing no adverse effects beyond the toxicity hazards. The reprocessing of sulphides in the molten state to regenerate the original carbonate is well documented and is proposed for adoption here.

The products of tyre pyrolysis have been analysed and evaluated. The oil is highly aromatic and has a calorific value comparable with fuel oils. It contains only 0.2wt.% sulphur but has a flash point of only 37°C due to volatiles that will have to be removed by steam stripping. On this basis it has been valued at around £110 per tonne. The gas is a mixture of hydrocarbons, a little hydrogen and has a calorific value similar to bottled hydrocarbon gases. It has no significant impurities and has been valued at 28p per Therm. The char considered in the reactor must be almost entirely carbon which indirectly provided data to be used in estimating the heat release on gasification as this could not be measured experimentally. Only a visual inspection of the steel has been carried out and it was seen that the bronze coating had been removed giving the material a fair scrap value.

17.2.2 Reactor and Process Design

Although the next stage of development for this process is likely to be a small pilot unit no detailed design is proposed here although data collected in this project does provide information essential to this end.

A conceptual process design was studied by the use of mass and energy balances seen in the overall context of a planned process flow design. The mass balance analysis showed that indeed a large volume of tyres could be pyrolysed in a relatively small volume of melt but that approximately 3 times this volume of melt would have to be simultaneously employed in char gasification and other process units. This analysis also gave data on the melt cycling rates which will have to be investigated practically on continuous equipment. Clearly flow rates led to data on residence times and concentrations but this posed no additional problems. Together with energy balances it became even clearer that the use of steam as a major process reactant was inadvisable. The low rates of carbon-steam reaction indicates that a very large melt volume would be required to achieve the desired gasification rate (0.37 x pyrolysis rate). Even given efficient recovery of energy from unreacted steam the net input would also be unacceptably high. The energy evaluation also showed that the calculated energy surplus from air gasification of char could be used in other areas of the process. The process flow design enabled the true complexity of the process to be appreciated; a factor not seen in the experimental or earlier stages. This was essential in the capital costing of process plant.

The corrosion studies of containment materials have been confined to steels and show that only highly resistant stainless steels, such as types 304 and 347, show satisfactory characteristics. Mild steel experiences pitting while lower resistance stainless steels are considerably leached and show considerable weight gain due to oxide surface layer formation. Type 304 and 347 will probably prove too costly for general use, so it is recommended that containment strength be obtained by mild steel and corrosion resistance by a ceramic lining.

17.2.3 Recommendations for Technical Development

The major inadequacy of the reactor apparatus used in this project to date has been the inability to study long-term continuous operation. The rate data has so far only been projected from batch and concentration information. It has been difficult to assess with any great certainty the behaviour of compounds in the melt. The relationships between pyrolysis rate, melt cycling, gasification rate, melt reprocessing and in fact all the factors involved in the smooth running of a continuous process have been obtained from experimental batch data.

It has also been difficult to accurately determine scaled-up behaviour for the same reasons.

However the data so far collected indicates that tyre pyrolysis in molten carbonates is certainly a technical feasibility. On the technical information therefore the general recommendation must be to study the process further on a small continuous basis. This would enable the many inter-relationships mentioned above to be fully evaluated.

The first basic relationship to be studied further is that of pyrolysis and gasification rates. It must be known if the batch implications of rate compatibility can be worked in continuous situations and what volumes are required for each process. The system would also serve to evaluate the methods by which melt might be pumped between the units and at what rate. As this system is brought under control, a third unit for melt regeneration might be brought into the system and made compatible in volume and rate terms The pilot unit would help to gain a further insight into the behaviour of the solid products, namely char and steel, circulating through these units. It will be important to establish the degree of breakdown of char pieces and their eventual size. The amount of steel entrained in char or removed mechanically could also be studied here, as could the settling of inorganic sludge.

Although of less direct importance, a small pilot unit would be a useful means by which to establish the best modes of operation for ancilliary equipment. Obvious examples include the methods by which services are applied and products collected.

Before such a pilot plant is planned further study of the chemistry of pyrolysis products in the melt is necessary. The method of sulphur removal has so far been taken only from literature. Although there is no doubt over these systems in other environments, it would be wise to check out that the chemistry can be applied and be practically operated in this case before incorporation in a pilot plant. This is probably even more important in the case of zinc compound removal.

A practical study of the process thermodynamics is necessary to supplement the theoretical study in the energy balance work. In the laboratory to date the nature and scale of plant has made this impractical. It would be useful to show that the process can be practically operated under its own energy after starting up. This would also confirm heat loss estimates and evaluate the heats available and used elsewhere in the process. Such work would include the practical trial of heat transfer under operative circumstances.

The continuous unit would provide a superior means for carrying out a full operability study. This in turn would enable more accurate costings of the commercial scales to be made.

17.3 Economic Study

17.3.1 Return on Investment

The capital costs (1980) of full scale pyrolysis operations vary from less than £0.5m for 4,000 t/yr to £2.5m for 50,000 t/yr. These costs are in line with expectations and together with other calculated cost have been used to obtain projected DCF rates of return for various scales of operation. The rates are 59.5% for the 50,000 t/yr operation and around 30% for the 10,000 and 4,000 t/yr operations.

Sensitivity analysis has shown capital cost and product value estimation to be crucial while operating, transport and tyre costs are less important. However allowing for current investment rates and high technology risk only the 50,000 t/yr operation can be considered a safe viability.

17.3.2 Improvements in Economic Performance

The economic evaluation was a broad study reliant on a number of generalizations and estimates. It therefore would be logical to suggest that the results are not final or definitative.

It was shown in the sensitivity analysis that capital investment was the parameter bearing the heaviest combination of uncertainty and effect on return. The high cost of plant can largely be attributed to its high technology which may in turn be due to the use of molten salts as the heat transfer medium. This indicates that plant designers would be well advised to consider simplifications in design concepts, perhaps avoiding the use of molten salts altogether.

17.3.3 Investment Recommendations

The 50,000 t/yr operation appears to offer a safe and attractive but by no means irresistable return of capital investment. The smaller units do not merit the risks involved.

However there are several further considerations to be taken into account. The first is cash supply; the return (30 - 60%) is not as high as may be obtained from other projects, so if cash is tight available resources should be invested on a more certain return. If extra cash were to be borrowed for this specific purpose approximately a further 4% must be added to the minimum acceptable rate of return. (20% + risk)

The second factor is the size of the market; currently estimated at 127,000 tonnes times a collection factor. This indicates that the supply will not support two such units and it is well known that plans for one such unit have been under consideration for some time.

The final factor is a matter of to whom these rates of return apply. The risk factor, in particular, can be said to vary with technical abilities and experience in the areas of operation. In this particular case abilities in high temperature engineering technology and experience in the scrap business are important. A large engineering and rubber goods group, such as Dunlop Ltd., would certainly have part of the required technological background but none of the experience in the scrap business and it is doubtful whether such a company should be taking steps to acquire this experience at the present time. These factors indicate that investment in this area would not be justifiable for such a commercial concern.

APPENDICES

APPENDIX I

A summary of commercial and academic concerns known to currently be or have recently been carrying out major work on the pyrolysis of polymeric materials. The summary is primarily concerned with tyre pyrolysis but also included is work on plastics as many processes are applicable to either material. The list is by no means comprehensive but covers all important contributions.

Operator	Associates	Dates	System Type	Scale	Main Products	Ref.
ACI Pl. Inc.		1970-	Vert.retort	0.5 t/hr	Oil, Gas	(341)
Asahi Carbon Co./ Bridgestone Tyre Co.		1973-	Kiln	-	Activated carbon	(154)
U. of Aston	Dunlop Ltd.	1977-1980	Molten salt	Laboratory	Oil, Gas, Char, Steel	-
Babcock-Rohrbach		1978-	Fluidized bed			(176)
Batchelor Robinson (Met. & Chem.) Ltd.	Warren Spring Laboratory	1976-	Cross-flow kiln	Pilot 6 t/d. Planned 50,000 t/yr	Oil, Gas, Char, (carbon black) Steel	(89-96)
Berlin Tech. Univ.		1974-	-	Laboratory	Gas	(342)
Carbon Dev. Corp.		-	Rotary kiln	Pilot	Carbon black, Oil, Gas	(144)
Cirta-Extramet		1979-	Molten salt	Feasibility study	-	(189)
Duke Eng. Co. (DECO)	Intenco, Ugland (UK)	1974-	1. Kiln 2. Molten salt	50 t/d	Oil, carbon black	(136-138)
Firestone Tyre & Rubber Co.	U.S. Bur. of Mines	1970-1978	Retort	100 lb batch	Oil, Gas, Char	(119-124)
Foster Wheeler Power Prods. Ltd.	Warren Spring	1975-	Cross-flow kiln	Commercial	Oil, Gas, Char, Steel	(97-99)
Goodyear Rubber Co.	1. Cities Serv. Co.	-1970	-	Pilot	-	(135)
	2. Tosco	1971- 1976-	Ceramic balls Microwave	Pilot/Comm. Pilot	Oil, Carbon black, Steel DSR	(127-130) (343-345)

Univ. of Hamburg	Fa.C.Peters AG C.R.Eckelmann	1971-1974 1972-	1. Molten salt 2. Fluidized bed	Laboratory Pilot	- Oil, Gas, Steel, Char	(166) (169-175)
Herko	O. Herbold		Rotary kiln	Pilot/ Commercial	Oil, Gas, Carbon black	(102-105)
Hokkaido Gov. Res. Labs.	Jap. Gas Co.	1974-	1. Fluidized bed 2. Kiln	Laboratory	Oil, Gas, Carbon black/activate	(178,179)
Hydrocarbon Res. Inc.		1973-	Hydrogen autoclave	Laboratory/ Pilot	Oil, Gas, Carbon black	(346)
Intenco	DECO	1974-	Kiln	50 t/d	Carbon black, Oil, Gas	(347)
Japan Gas Co./ Nippon Zeon Co.	Hokkaido Gov. Labs.	1974-	Fluidized bed	17 t/d Commercial	Oil, Gas, Active carbon	(177)
Kawasaki H.I. Ltd.		1975-	Retort	5 t/d	-	(192)
Kobe Steel Co.		1973-	Rotary kiln	30 t/d	Oil, Gas, Char, Steel	(67, 146-9)
Marathon Oil Co.	U.S.B.M.	-	Retort	Laboratory	Char filler	(126)
Mining & Fuel Inst.		1972-	2-stage kiln	12 t/d	Carbon black	(220)
Mitsubishi H.I. Ltd.		1973-	Kiln	2½ t/d	-	(348)
Mitsui Co.		1971-	2-stage kiln	Commercial	Organic liquids	(201)
Pechuro et al.		1972-1974	Molten lead	Laboratory	Gases	(188)
Pyrotech Ind. Co.		-	Counter-current vertical shaft	Commercial	Gas	(349)
Rockwell Int. Corp.		1975-	1. Molten salt 2. Kilns	Laboratory	Oil, Gas	(186, 187)
Sanyo Co.		1976-	Microwave kiln	0.5 t/d	Gas	(156, 157)
W. Shaefer		-	Vertical retort	Laboratory	Oil, Gas, Char	(106)

Sumitomo H.I. Ltd.		-	Fluidized bed	3 t/d	-	(192)
Univ. of Tennessee		1976-	Molten salt	Laboratory	Oil, Char, Gas	(181-184)
Thermex Inc.		1974-	Conveyor	9 t/d	Oil, Carbon black	(142, 143)
Ugland (UK)	DECO	1978-	Kiln	Commercial	Oil, Gas, Char, Steel	(138)
Warren Spring Laboratory	Batchelor Rob. Foster Wheeler	1974-1977	Cross-flow kiln	Pilot	Oil, Gas, Char	(350)
Univ. of Wyoming		-	Fixed bed	-	-	(351)
F. Zeplichal		1971-1974	Conveyor	-	Carbon black	(107-110)

APPENDIX II

A summary of important general and municipal waste processes.

Operator	System Type	Scale	Products	Comments	Ref.
Andco-Torrax	Slagging kiln	200 t/d	Gas	Luxembourg plant	(226-228)
Anti-pollution Inc.	Molten salt	Pilot	-	-	(352)
AWT Systems Inc.	Fluidized bed	-	-	Assoc. Hercules Inc.	(346)
Barber-Coleman Co.	Molten lead	-	-	Terminated 1975	(353)
Battelle N.W. Laboratories	Molten salt	10 t/d	Gas, Char	-	(354)
BSP Environmental Technology Ltd.	Moving hearth	Commercial	Gas	-	(355)
Chevron Res. Inc.	Kiln	-	-	-	(349)
Cities Services Co.	-	Pilot	-	Terminated 1970. Assoc. Goodyear Co.	(356)
Combustion Power Co.	Fluidized bed	400 t/d	Gas	"PUROX"	(215)
A. Coors Co.	Fluidized bed	1 t/hr	-	Terminated	(357)
Univ. California	Moving hearth	35 kg/hr	Gas	-	(358)
Devco Man. Inc.	Rotary kiln	150 t/d	Gas	-	(359)
Ecology-Recycling Un Ltd.	Rotating retort	Pilot	-	-	(352)
Enterprise Co.	Conveyor	Commercial	-	-	(352)
EPA	Fluidized bed	Pilot	-	-	(360)
ERCO	Fluidized bed	-	-	Assoc. Maecon Inc.	(360)
F.Fink Co.	Arc furnace	Laboratory	-	-	(361)
Foster Wheeler Power Products Ltd.	Cross-flow kiln	1 t/d	Oil, Gas, Char	Assoc. Warren Spring Lab.	(97)
H.F.Funk Co.	Vertical shaft	-	-	-	(362)
Garrett Res.Co./ Occidental Pet.Co.	Shaft	200 t/d	Oil, Gas Char	San Diego plant	(218-225)
Georgia Inst. of Technology	Counter-current shaft	50 t/d	Gas	-	(363)
Hercules Inc.	Fluidized bed	-	-	Terminated	(346)

Hitachi Co.	Fluidized bed	Laboratory	Oil, Gas, Char	-	(364)
Kawasaki H.I. Ltd	Rotary kiln	9 t/hr	Gas	"LANDGARD" Assoc. Monsanto	(229)
Keiner Pyrol,Co.	Steel retort	300 kg/hr	Gas, Liquids	-	(361)
Kellog Co.	-	1 t/d	Gas	-	(365)
Kemp Reduction Co.	Conveyor	-	-	Volume reduction	(357)
Krauss-Maffei Co.	Rotary kiln	2 t/d	Oil, Gas, Char	-	(192)
AD Little Inc.	Fluidized bed	-	-	-	(352)
Mansfield Co.	Grate	Laboratory	-	-	(352)
Mannesmann GmBH	Rotary kiln	Laboratory	-	-	(191)
Mars Energy Co.	Catalytic	10 t/d	H_2	-	(366)
Maecon Inc.	Oil bath	Bench	Liquids	Assoc. ERDA	(367)
Michigan Tech.	Molten lead	-	-	-	(352)
Monsanto Ltd.	Rotary kiln	1000 t/d	Gas	"LANDGARD"	(216)
Motala AB	Vertical shaft	-	Gas	-	(368)
Pan Am. Res. Co.	Rotary retort	Laboratory	-	-	(352)
Pyro-Energy Inc.	Kiln	-	-	-	(352)
Pyrolysis Systems Inc.	-	10 t/hr	Gas	-	(369)
Pyrotech Inc.	Vibratory shute	30 kg/hr	Gas	-	(370)
Pollution Control Ltd.	Vertical shaft	5 t/d	Gas (H_2), Char	"DESTRUGAS" Kalundborg plant	(213) (214)
Rens'v Tech.	Fluidized bed	Pilot	-	-	(371)
R.Jenkins Ltd.	-	-	Gas	-	(372)
Rust Eng.Co.	Rotating retort	Bench	-	-	(373)
Sodeteg Co.	Shute/kiln	12 t/d	Gas	-	(361)
Stanford Univ.	Retort	Bench	Oil, Gas	-	(352)
Tsukishima Mach. Co.	Double fluidized bed	Pilot	Gas	-	(374)
Union Carbide Ltd.	Kiln	Pilot	Wax, Oil, Gas	"PUROX"	(375)
Urban Refuse Dev. Co.	Shaft furnace	125 t/d	Gas	-	(359)

U.S.Bureau of Mines	Retort	Laboratory	Oil, Gas, Char	Assoc. Firestone Rubber Co.	(76)
Warren Spring Laboratory	Cross-flow kiln	Pilot	Oil, Gas, Char	Assoc. Foster Wheeler Ltd.	(97)
Watson Energy Co.	Rotary kiln	-	-	-	(352)
Whitfield Ltd.	Vertical shaft	13 t/d	Gas	-	(357)
Wotsche-Ebarra Co.	Reverbutory furnace	25 t/d	Gas	-	(192)
Wright Corp.	Rotary kiln	Bench	Gas	-	(352)
Univ. West Virginia	Fluidized bed	1 t/d	Gas	-	(350)

ABBREVIATIONS

AAS	Atomic Adsorption Spectroscopy	
ACS	American Chemical Society	
AF	Across face	
AGA	American Gas Association	
BRMA	British Rubber Manufacturers Association	
BSMMT	British Society of Motor Manufacturers and Traders	
Comm.	Commercial, (scale)	
DCF (RR)	Discounted Cash Flow (Rate of Return)	
DSC	Differential Scanning Calorimetry	
DSR	Depolymerized Scrap Rubber	
EEC	European Economic Commission	
FDV	Flame Devulcanization	
GLC	Gas-liquid Chromatography	
IP	The Institute of Petroleum	
L, Lab	Laboratory, (scale)	
LGORU	Local Government Operational Research Unit	
mmT	Millimetres of tread	
MS	Mass Spectroscopy	
NASA	National Aeronautic and Space Administration	U.S.A.
NBS	National Bureau of Standards	
NTIS	National Technical Information Service	
P, Pil.	Pilot, (scale)	
PTFE	Polytetrafluoroethylene	
PVC	Poly(vinyl chloride)	
RAPRA	Rubber and Plastics Research Association	

SFM	Standard Fouled Melt
SBR	Styrene-butadiene Rubber
USBM	United States Bureau of Mines
USEPA	United States Environmental Protection Agency

GLOSSARY OF TECHNICAL TERMS

AUTOTHERMAL	State of a system providing all its own heat requirements, producing no excess and needing no heat input.
BEAD	That part of the tyre designed to fit the wheel rim and hold the tyre in position on the wheel.
BREAKER	Reinforced rubber layer embodied circumferentially in the tyre immediately over the casing and about the same width as the tread.
CASING	Laminated ply structure of tyre.
CASING SELECTOR	That operator who collects used tyres from outlet dealers and redistributes them to the reuse industries.
CHAR	Solid carbonaceous material produced by most pyrolysis processes.
CRUMB	Finely granulated vulcanized rubber obtained by grinding or buffing rubber goods.
FINITE RESOURCE	A non-renewable resource whose forseeable supply is limited. These are usually those formed on a geological timescale.
GASIFICATION	Here the term is used to describe the process of converting a solid, typically char, into gases.
INCINERATION	Burning of refuse and waste; usually used in reference to purpose built incinerators.
LANG FACTORS	Numerical multipliers which when applied to capital cost enable other costs to be calculated.
OIL	The liquid fraction produced by pyrolysis.
PYROLYSIS	The thermal degradation of material under non-oxidative conditions (U.S.A. - conditions not defined).
PHASE DISTRIBUTION	A term used to express the quantities of oil, gas, char, steel and inorganics formed by pyrolysis. (An extension of the solid, liquid, gas definition.)

RECLAIM	Sheeted, depolymerized rubber. The production process is often referred to as RECLAIMING.
REGENERATION	Here the term is used to describe the reconditioning of molten salt required to maintain it in condition suitable for the pyrolysis process.
RETREADING	A term describing the renewing of the tread and shoulders of a worn tyre.
SCALE/COST INDEX	That power to which the relative scales of plants must be raised to obtain their relative costs.
SCRAP TYRE	A used tyre which is unsuitable for retreading.
SECONDARY INDUSTRIES	Here these are taken as those small industries that split used tyres and manufacture small stampings, e.g. link matting, shoe soles, etc.
SERVICES	Usually defined as electric, gas and water supplies.
RATE OF RETURN	A method of calculating profitability based on cash realization expressed as a percentage of investment. (There are several detailed technicalities.)
RENEWABLE RESOURCE	A resource that is constantly being produced. Normally qualified as resource formed on a biological timescale.
SENSITIVITY	A measure of the effect of cost errors on rate of return.
STANDARD FOULED MELT	A melt whose composition is thought to be typical of the continuously operating pyrolysis process.
TYRE - CAR/VAN	Tyres to fit wheel rims up to 16 inch diameter.
TIRE	U.S. spelling of "tyre".
USED TYRE	A tyre taken from a vehicle after at least some use.
WASTE TYRE	A tyre which is not reused in any of the currently available ways.
YIELD	Here yields are always expressed in terms of mass input to any system.

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