Coal-Water Mixture Flame
THE COMBUSTION MECHANISMS
OF COAL SLURRY FUELS

A thesis presented for the degree
of Doctor of Philosophy of the
University of Surrey

by

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July 1986
The formation and subsequent burnout behaviour of coal slurry fuel chars has been studied using a suspended single droplet technique and solid sampling techniques in large turbulent diffusion flames. Both these techniques yielded comparable results on the structure of carbonaceous residues from a range of coal slurry fuels containing coals of different rank, size and concentration.

The structure and burnout behaviour of all the fuels tested was dependent on coal rank, particle size, and concentration, although these variables did not always produce the same differences in behaviour in coal-oil and coal-water chars. Mid-rank coals produced swollen well-fused chars which were substantially hollow and incorporated large surface blowholes. Such residues showed little tendency to fragment during combustion. Low and high rank coals produced less swollen chars which were comprised of loosely agglomerated coal particles causing more extensive internal structure and smaller surface blowholes. The furnace results of this and other studies indicate that the latter type of char structure is more conducive to rapid burnout.

Small concentrations of emulsified water in coal-oil slurries were observed to increase the intensity of ebullition during devolatilisation although no evidence was obtained from any of the experimental techniques to suggest that this caused droplet shattering. However, water addition did increase the rate of combustion of coal-oil fuels.

A theoretical model of the behaviour of coal slurry fuel chars during combustion has been presented which explains the experimental results in terms of the internal surface area of the char and the availability of this area to the gaseous reactants. It has been concluded that the rate of combustion of coal slurry chars of the size encountered in flames is largely controlled by the rate of internal diffusion of gaseous reactants and reaction within the porous char structure. The different reactivities of coal slurry fuels of different coal ranks has therefore been explained in terms of the various char structures which were observed.

The beneficial effects of water on the combustion of coal-oil fuels has also been explained within this theory since the addition of water could increase the porosity of the chars. However this has not been confirmed experimentally.
DEDICATION

To John, Peggy and Caroline
This work could neither have been started nor completed without the help of many organisations and individuals. I therefore offer my thanks to the members, past present and honorary, of the Fuels and Energy Research Group of the University of Surrey, particularly Dr. B.G. Jenkins, for the original inspiration; Dr. G. Hart, for his many efforts during the project; Mr. K.I. Walters, for his assistance in the experimental work; Mr. J. Webb, for building the equipment and Mrs. C. Milton for typing.

I am also indebted to the Central Electricity Generating Board, for their financial assistance, the staff of CEGB Marchwood Engineering Laboratories for their technical help and Airoil-Flaregas Ltd., for allowing me to participate in their coal-water fuel trials.

My thanks are especially due to Dr. P.J. Street of the CEGB, who was the industrial supervisor of this work, and who gave his time and expertise freely.

Above all I would like to thank my friend and supervisor, Frank D. Moles, for allowing me to join FERGUS, for much useful discussion, and for guidance and assistance beyond the call of duty. Thank you 'Guvnor'.
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1.1 The Changing Pattern of Energy Usage

The first major change in the history of energy usage was the switch from wood to coal. This was the key to the Industrial Revolution, and set a precedent for an ever changing, and ever more complex, pattern of energy usage. For the past two hundred years, primary fossil fuels have dominated the energy supply, and, for much of that time, the demand has mainly been met by coal. Even as recently as 1950 coal was responsible for 55.7% of the total global consumption of energy, whilst oil held 28.7% of the market. The consumption figures vary between Europe and the United States of America, where the indigenous and easily recoverable oil reserves meant that coal and oil jointly occupied a 38% market share, whereas Europe, at this time, still relied on coal for 77% of its total energy, with only 17% coming from oil (Darmstadter, 1974). The use of coal increased in absolute terms until very recently, but its share of the market diminished as oil and natural gas became increasingly more popular.

In 1974 oil was responsible for 44.1% of the World's energy consumption, and coal 32.8%. The reasons for this change are social as well as economic; the trend towards fuels for transport as opposed to space heating, fears about the effects of pollution on the environment and health, and the constant demand for an increasing standard of living. However, it was undoubtedly the low price and increasing availability of crude oil products that caused a dramatic move away from the combustion of coal. This was especially so in the late 1950's and early 1960's when the massive Middle Eastern fields became fully developed.

The social, economic and technical implications of this period of cheap and abundant energy were as far reaching as any of the major historical developments since the Industrial Revolution. The industrialised Western Hemisphere and Japan achieved higher economic growth rates than had ever previously been experienced, which consequently fueled an even greater demand for oil. The political complexion of the world also altered dramatically, with hitherto unknown countries rising to
positions of wealth and power. At the same time coal-fired capacity was being reduced by closure or conversion to oil. Much the same situation existed in the rest of Europe and the United States, and Japan and Holland had even closed down their coal mines, the only indigenous source of fuel, thereby relying totally on imported oil for energy. With hindsight, the disastrous consequences of the 1973 oil embargo were inevitable, but the fact remains that they were largely unforeseen, and without precedent. In the U.K. several large oil-fired power stations (namely Grain, Littlebrook D, and Ince B) were under construction (CEGB Statistical Yearbook 1974 - 75) which would never operate at full load factor (except during the 1984 - 85 miners strike).

It is against this background, of a continually changing energy mix and economic necessity, that coal slurry fuels have evolved during the last century. Unlike many technological proposals which have their origins in the 19th century, the development of coal slurry fuels has relied only to a minor extent upon the development of new technology. It has always been the aim to manufacture and handle such fuels using existing methods, and to burn them in existing combustion equipment. They are, and have always been, viewed as substitutes for other liquid fuels and their potential use is entirely dependent on the question, "How much will it cost?". This reliance on economic factors, as opposed to technical innovation, has led to interest in coal slurry fuels waxing and waning several times in the past century, not only as potential industrial fuels, but also as subjects of combustion research.

1.2 Coal Slurry Fuels

The extensive and voluminous recent literature on this subject has given rise to its own vocabulary, principally in the naming of the many variations of coal slurry fuels. Throughout this dissertation the names of the fuels and the abbreviations used are, as far as possible, the same as those used in the bulk of the modern literature. However, many of the terms have been used loosely by some authors, and the term "coal slurry fuels" has therefore been adopted to describe all of the fuels discussed herein. Such fuels can be described as any liquid, or combination of liquids, which contains ground particles of carbonaceous
solids. The solid particles are normally coal, but reference is made in Section 2 to fuels in which the solids are petroleum coke, wood charcoal, graphite, straw and carbon black.

Coal-oil mixtures (COM) contain coal, ground to normal pulverised fuel distribution (p.f.d.), mixed with oil. Several grades of fuel oil have been used, ranging from 35 Redwood second oil to 3500 Redwood second oil, but this does not affect the naming of the fuel. The average particle size in COMs is approximately 70 μm, and the addition of chemical additives in small quantities (< 2 wt%) to prevent particle settling is common. An alternative method of stabilising the fuel is to grind the coal particles to a smaller size distribution. The process patented by the British Petroleum company, for instance, involves wet grinding of coal in oil until most of the particles are less than 10 μm in diameter. These fuels are called coal-oil dispersions (COD).

Slurry fuels made with oil and petroleum coke instead of coal are often grouped indiscriminately with the COM and COD fuels. However if distinction needs to be made they are termed petroleum coke-oil mixtures/dispersions which is often abbreviated (PETCOM and PETCOD).

Coal-oil fuels to which water has been added are called coal-oil-water mixtures (COW). These fuels are normally emulsions of small water droplets, approximately 2 - 5 μm in diameter, dispersed in the oil phase together with the coal particles. Slurries of coal particles in water only, or water plus stabilising additives, are known as coal-water mixtures (CWM). They often contain coal which has been treated to remove some of its inherent mineral matter, and are thus referred to as beneficiated, deep-cleaned or de-ashed coal-water mixtures. The other variations of coal slurry fuels, coal-methanol mixtures for instance, will not be abbreviated in the text.

1.3 The Role of Coal Slurry Fuels

In 1981 Moles et al. posed the question, "Why mix coal with oil?". His answer was that an economy not based upon non-renewable energy resources would not be possible for at least fifty years. In the
meantime, many present day oil and gas resources would be exhausted, leaving only coal to make up for a world-wide scarcity of energy. Coal slurry fuels represent a step in this direction, the return to coal.

Political and economic developments since 1981 have probably altered the timescale of this major, and enforced, change in the pattern of energy usage. It is almost certain that oil and gas reserves will not be exhausted as quickly as was predicted at that time. Demand has dropped and enhanced oil recovery techniques are being developed to ensure that existing fields yield more oil, and perhaps to make possible the exploitation of large oil shale reserves. However the current anxiety over nuclear safety and waste has hindered the progress of fission technology and realistic alternatives to the combustion of primary fossil fuels have not emerged. The case for coal is still strong, compared with oil it exists in abundance. There is approximately seven times as much coal in proven reserves and possibly forty times as much in resources (Kirk and Othmer, 1981). Moreover, the oil reserves are being used at a far greater rate. In 1976, the reserve to production ratio for coal was 245 whereas that for oil was 30.

The theoretical case for a switch from oil to coal is clear, but in practice it has not yet happened to the extent which seemed inevitable after the upheaval of the 1970's. Oil prices doubled in real terms between 1973 and 1982 but oil's share of the U.K. market only fell from 48% to 42% (Anon, 1982). The demand for oil reached an all time high in 1979, whilst the spot price peaked at $37.00 per barrel in 1981. The economic incentives for a rapid conversion to coal firing were well reported at the time (Hawthorne, 1981) and the prospects for COM, COD and COW fuels, as an intermediate solution, had never been better. However, despite a major global research and development effort from 1974 onwards, the era of coal-oil fuels failed to dawn, yet again! Research on coal-oil fuels dwindled, and instead, coal-water fuels, which had the advantage that they were cheaper and could be partly demineralised during their manufacture, were hailed as the potential replacement for oil. In the meantime oil remains as the dominant fossil fuel. The failure of coal-oil fuels was mainly due to the cost of converting modern, highly-rated, oil-fired equipment. The technical problems, associated with ash deposition, and insufficient fan capacity to supply the extra combustion air needed to prevent unburnt carbon in
flue gases, were expensive to overcome. The alternative was derating
the equipment. A comparison of the conversion costs and running
expenses of several coal slurry projects is shown in Figures 1.1, 1.2
and 1.3. The data for these graphs was obtained from the estimates and
actual costs published by several authors. They show that the economic
case for coal-water fuels is better than that for coal-oil fuels, but
more significantly, the case for coal is as favourable as either, if
not more so.

There are dangers in any form of forecasting of the global energy
situation. It is affected by many factors and is constantly changing.
History has shown that forecasts based on current economics and
politics are often proved inaccurate, and that attempts to make
detailed predictions in the long term are best left to clairvoyants,
who, for instance, could have predicted in 1981 that the price of oil
would drop to $10.00 per barrel by 1986. However it is fair to say
that coal is probably the fuel for the future, until a satisfactory
alternative is found. Coal-water mixtures could have a role to play as
an intermediate step in the switch to coal, but equally they could
follow coal-oil fuels as an expensive diversion, which does no more
than occupy research workers for a few years. The future role of coal
slurry fuels is by no means assured.

1.4 The Scope of this Research

The economics of coal slurry fuels has little to do with the work
described in this dissertation. This study originated as a
continuation of an earlier investigation at the University of Surrey
into the combustion and handling of coal-oil dispersions. As a result
of that work, Jenkins B.G. (1981) developed a model of the combustion
of COD droplets which incorporated a simple, rank dependent physical
mechanism to describe the behaviour of such droplets in flames. The
objectives of this work were to investigate this mechanism more fully
using a larger range of coals and coal particle sizes. In addition the
effect of emulsified water and ash behaviour were to be considered, and
finally, because the work was partly funded by the CEGB, the use of
twin-fluid atomisers, of the type found in power stations, was to be
investigated.
(After Moles and Lapwood, 1984 - Reference numbers refer to the original reference.)
Single droplet techniques and furnace trials were used in the pursuit of these objectives, and work began in 1981. The changing emphasis in coal slurry research led, later, to an investigation of coal-water fuels being included in the program. The same techniques were used to study these fuels as were used with previously coal-oil fuels.
2.1 The Development of Coal Slurry Fuels

2.1.1 Coal-Oil Fuels

The first proposal to use coal-oil mixtures as a fuel was made in 1879 (Smith and Munsell). At this time the oil exploration and refining industry was still in its infancy, and was concentrated in the United States of America after Drake's discovery of oil in Titusville, Pa in 1859 (B.P., 1947). Coal was considerably cheaper and more widely available than oil. However, the advantages of easily transportable, liquid fuels were rapidly becoming apparent. The internal combustion engine, designed by Otto in 1876, was already being used to power motor vehicles, which inspired many people to develop this new technology, including Rudolph Diesel who patented his engine in 1892 (Diesel, 1894).

However Moles et al. (1981) pointed to marine applications as the most likely market for liquid fuels, especially coal-oil mixtures. Indeed, the review of coal-oil mixture studies during the period 1879 - 1936 by Manning and Taylor (1936) showed that there was a maritime thread running through the entire early history. This was especially so during the First World War.

Notable events in the early days were the COM combustion trials on the USS Scout Gem in 1917 (Bates, 1918, 1920) and the voyage of the SS Scythia between Liverpool and New York in 1932, during which one of the boilers was fired on COM (Cunard Steamship Company, 1932). Other trials with the fuel included tests on locomotives (Robinson, 1922), on land-based boilers (Schultes, 1932 and Wyndham, 1935), and as a feedstock for carbonisation processes (Brownlie, 1936). It is true to say, however, that the majority of studies at this time were concerned with preparation and handling coal-oil mixtures, as opposed to combustion trials. Most of the 78 patent proposals reported by Manning and Taylor refer to methods of stabilisation.
Later workers attempted to make more detailed investigations into the combustion characteristics of coal-oil fuels. Barkley et al (1944) reported a decrease in boiler efficiency when coal-oil mixtures were substituted for heavy fuel oil in a water-tube boiler. The level of unburnt carbon in the flue gases increased, as did ash deposition on the heat transfer surfaces and furnace walls. This study also stated that "about two-thirds more atomising steam was required for the coal-in-oil fuels than for the oil".

Schroeder (1942) had previously reported similar results to those obtained by Barkley et al., but did not provide as much experimental detail. Both studies were optimistic about the future of coal-oil mixtures as boiler fuels, however they marked the end of the early history of these fuels, and the onset of a thirty year lull in research activity. The reasons for this decline in interest were mainly economic, as has been outlined in Section 1. Clean, cheap liquid fuels had become more easily available, and the problems of ash deposition and insufficient combustion space in the newer types of oil-fired equipment meant that derating would be inevitable if COM fuels were substituted. As early as 1932, the British Navy had been deterred from any further COM research for these same reasons (Brand, 1932).

There was, however, another source of competition, quite apart from liquid petroleum fuels, that of pulverised coal. The history of pulverised coal technology runs almost parallel to that of coal-oil fuels. The initial objective in both cases was to make coal more easily transportable. In his classic review of the history of coal firing, Essenhigh (1961) showed that the development of new technology in the early part of the century had caused a rapid increase in the use of p.f., especially in steam-raising boilers. The boiler patent reported by Bettington (1914) is a good example. Before the First World War, the use of pulverised coal had been limited to cement and metallurgical kilns. Its use increased by a factor of 6 between 1917 and 1922, and continued to increase steadily until the late 1930's, when it displaced stoker-firing as the most widely used method of generating electricity.
The period of quiescence for coal-oil fuel research lasted until the 1970’s. Very little work was done during this period, although there was some slight activity in the iron and steel industry, when Whittingham and Winsor (1964) reported the British Petroleum Co. work on injection of coal-oil fuels into blast furnaces.

The modern history of coal-oil fuels begins in 1974, just one year after the OPEC oil embargo. The General Motor Co. resurrected COM combustion research with a project which was funded by 26 American organisations (Dingo, 1977). The United States Department of Energy (DOE) joined in the support of this project in 1975 and thus began their association with coal slurry research and development in which they now play a leading role by organising annual International Symposia (1978, 1981, 1982, 1983, 1984, 1985). A review of the modern development of coal-oil fuels, from 1974 - 1983, was given by Bienstock (1983) at the first European symposium on that subject. A summary of this review is given in Table (2.1).

There can be no doubt that, up until 1981, the prospects for conversion of several oil-fired installations to coal-oil fuels were good. Bienstock (1983) indicated that this was still the case in the United States, despite the fact that the economics of coal-water mixtures were potentially rather more favourable. Table 2.1 shows that several trials were conducted at power stations between 1977 and 1983, and one permanent conversion was undertaken. In 1979 the Florida Power and Light Company converted an oil-fired boiler at the Paul L. Bartow Station, Tampa, to COM fuel containing 46 wt% coal with an average particle size of 30 μm. Higgins (1983) reported that this conversion had required modifications to the fuel handling and atomising equipment, installation of electro-static precipitators, wall-blowers, and a bottom ash removal system. No derating was said to be necessary, and the unit could apparently operate above its rated design capacity.

The first European power station demonstration project was a joint undertaking between the CEGB and BP at Padiham power station, Lancashire. Three COD trials were reported by Conolly et al.(1982) and Matthews and Conolly (1983), however this was to be the first and last time that coal-oil fuels were burned in British power stations. The reason for the failure of Great Britain to follow the American lead, as Japan had done, was explained by Matthews and Conolly (1983) in the form of a diagram which
### COM UTILITY BOILER DEMONSTRATIONS

<table>
<thead>
<tr>
<th>Country</th>
<th>Power Station</th>
<th>MWe</th>
<th>Design Fuel</th>
<th>Test Period</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada</td>
<td>Chatham Station</td>
<td>10</td>
<td>coal</td>
<td>1977 - 1980</td>
<td>20, 21, 22</td>
</tr>
<tr>
<td>China</td>
<td>Yang Shugu Station</td>
<td>20</td>
<td>oil/coal</td>
<td>1981 - 1983</td>
<td>23</td>
</tr>
<tr>
<td>Japan</td>
<td>Takashara Unit 1</td>
<td>250</td>
<td>coal</td>
<td>1981 - 1982</td>
<td>14, 24</td>
</tr>
<tr>
<td>Japan</td>
<td>Takashara Unit 2</td>
<td>350</td>
<td>oil</td>
<td>planned</td>
<td>24</td>
</tr>
<tr>
<td>Japan</td>
<td>Yokosuka (2 units)</td>
<td>265</td>
<td>N.A.</td>
<td>planned</td>
<td>14</td>
</tr>
<tr>
<td>Spain</td>
<td>Almartia Plant</td>
<td>30</td>
<td>coal</td>
<td>1981 - 1982</td>
<td>25</td>
</tr>
<tr>
<td>Sweden</td>
<td>Upplands, Kraftvarma,</td>
<td>200</td>
<td>oil</td>
<td>1980</td>
<td>26</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>Padlin Power Station</td>
<td>120</td>
<td>coal</td>
<td>1981</td>
<td>19</td>
</tr>
<tr>
<td>United States</td>
<td>Crystal River Station</td>
<td>181</td>
<td>coal</td>
<td>1977 - 1978</td>
<td>17</td>
</tr>
<tr>
<td>United States</td>
<td>Salem Harbor Station</td>
<td>80</td>
<td>coal</td>
<td>1979 - 1981</td>
<td>16</td>
</tr>
<tr>
<td>United States</td>
<td>Sanford Station</td>
<td>400</td>
<td>oil</td>
<td>1980 - 1981</td>
<td>16</td>
</tr>
<tr>
<td>United States</td>
<td>P.L. Bartow Unit 1</td>
<td>120</td>
<td>oil/coal</td>
<td>1982 - current</td>
<td>15</td>
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### COM INDUSTRIAL BOILER EXPERIENCE

<table>
<thead>
<tr>
<th>Country</th>
<th>Project</th>
<th>Capacity</th>
<th>Design Fuel</th>
<th>Test Period</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada</td>
<td>Ontario Research Foundation</td>
<td>1.2 MWth</td>
<td>oil</td>
<td>1980 - 1981</td>
<td>31</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>British Petroleum Inc.</td>
<td>Various boilers</td>
<td>Mostly oil</td>
<td>1979 - 1981</td>
<td>32</td>
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<td></td>
<td>Shell Research Ltd.</td>
<td>60,000 pph</td>
<td>coal</td>
<td>1976 - 1977</td>
<td>26</td>
</tr>
<tr>
<td>United States</td>
<td>FERC/DER</td>
<td>100 Hp</td>
<td>oil</td>
<td>1976 - 1981</td>
<td>1, 34</td>
</tr>
<tr>
<td>United States</td>
<td>Coalguides, Inc.</td>
<td>65,000 pph</td>
<td>coal</td>
<td>1980</td>
<td>37</td>
</tr>
<tr>
<td>United States</td>
<td>General Motors</td>
<td>120,000 pph</td>
<td>oil</td>
<td>1977</td>
<td>10</td>
</tr>
<tr>
<td>United States</td>
<td>Occidental Petroleum</td>
<td>135,000 pph</td>
<td>oil</td>
<td>1981</td>
<td>36</td>
</tr>
<tr>
<td>United States</td>
<td>Ohio Univ. at Athens</td>
<td>150 Hp</td>
<td>oil</td>
<td>Ongoing since 1981</td>
<td>39</td>
</tr>
<tr>
<td>United States</td>
<td>Adelphi Energy Center</td>
<td>350 Hp</td>
<td>oil</td>
<td>1978 - 1981</td>
<td>40</td>
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</table>

### COM BLAST FURNACE APPLICATIONS

<table>
<thead>
<tr>
<th>Country</th>
<th>Blast Furnace</th>
<th>COM Injection</th>
<th>Test Period</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Japan</td>
<td>Kashima Works</td>
<td>COM Injection through all tuyeres</td>
<td>1981 - 1982</td>
<td>27</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>British Steel Corp.</td>
<td>One out of 20 tuyeres</td>
<td>1979</td>
<td>28</td>
</tr>
<tr>
<td>United States</td>
<td>Interlake Inc.</td>
<td>3 out of 9 tuyeres at 13 GPM (85 lb/NTHM)</td>
<td>1980 - 1982</td>
<td>29</td>
</tr>
<tr>
<td>United States</td>
<td>Republic Steel</td>
<td>6 out of 9 tuyeres at 13 GPM (85 lb/NTHM)</td>
<td>1980 - 1982</td>
<td>30</td>
</tr>
</tbody>
</table>

THM/D = Tons of Hot Metal Per Day

**TABLE 2.1** Coal-Oil Fuel Projects 1977 - 1982

(After Bienstock (1983). Reference numbers refer to original reference.)
compares coal-oil mixture demonstration test conditions with conditions found in CEGB plant (Figure 2.1). The diagram shows that modern CEGB oil-fired equipment is too highly rated to be considered for conversion to coal-oil fuel. Severe derating would be necessary on such equipment. In fact, the Board's modern coal-fired equipment is of a higher rating than that on which the successful coal-oil demonstrations and conversions have taken place.

**Figure 2.1** COM Demonstration Test Conditions Compared with Performance Study Design Conditions and CEGB Plant Conditions (After Matthews and Conolly 1983).
The only units which could be considered for conversion are the few coal-designed power stations which were converted to oil during the 1960's, or the few units which were designed to run on both coal and oil. The other potential use for coal-oil fuels would be as a light-up fuel in coal-fired power stations.

Shortly after the last Padiham trial, BP, who supplied the fuel, announced their intention to withdraw from coal slurry fuel research, and to close their COD manufacturing plant at West Thurrock, Essex. This decision ended a six year program, during which COD had been tested in many types of industrial equipment, and had produced a great deal of fundamental and practical combustion data. Wall (1981) reported combustion and handling trials on a marine water-tube boiler, a utility boiler, a cement kiln, a shell boiler, a hot-walled furnace, a fluidised-bed combustor, and a diesel engine. Moles et al. (1981) reported a coal rank dependent combustion mechanism for COD droplets, which had been proposed, and further developed by Jenkins B.G. (1981) at the University of Surrey.

The maritime interest has continued in the modern era of coal-oil fuels. Chevron converted some vessels in their tanker fleet to burn PETCOM (Nunn, 1982), and other workers have stated the advantages of such fuels for maritime boilers (Beshore, 1983). However, the total number of steam ships has reduced dramatically in modern times, in favour of diesel engines. The use of coal-oil fuels in such engines was proposed by Sheppard in 1921, however research is still in early stages of development (Kowalczewski, 1983).

In the absence of a large, potential, supplier of coal-oil fuels to the British market, and given the current marginal economic advantages of such fuels over fuel oil firing (Bogle, 1983), it appears that coal-oil fuels are now destined for another period of quiescence in the UK, with their use restricted to a fairly small range of applications elsewhere. It is apparent that the development of coal-oil fuels has now been abandoned in favour of coal-water fuels and advanced p.f. firing techniques.
2.1.2 Coal-Oil-Water Fuels

Since the revival of interest in coal-oil fuels, in 1974, by the General Motor Company consortium, several workers have proposed addition of water to coal-oil fuels as a means of reducing particulate emissions and increasing fuel stability (Cottel 1976, Hopton and Vergeer 1980, Clayfield et al 1981, Larsson 1981, Matthews and Conolly 1983). Indeed, the second of the combustion trials conducted by GMC, between 1974 and 1977, used a fuel containing 6.5 wt% water (Timnat et al, 1980).

This idea is by no means novel. Jordan and Williams (1981) state that addition of water to combustion systems was proposed in 1791, and that early combustion trials on emulsified fuels were carried out at the beginning of this century. Most of the early work refers to the well-established idea of emulsifying water with fuel oil or diesel fuel. However, Manning and Taylor (1936) noted the beneficial effect of small amounts of water in coal-oil fuels, and Cottell (1976) was granted a patent for the preparation of COW fuels. This proposal relates to the manufacture of a fuel containing 45 wt% pulverised coal, 33 wt% oil, and 22 wt% water. High frequency sonic energy has used to mix the oil and water, with the optional addition of lime to the water, in order to reduce sulphurous emissions. The flame from this fuel was compared favourably with that of an oil flame, but no combustion measurements were presented.

The concentration of water, recommended by Cottell (22 wt%) was very much higher than that suggested, as a maximum by other workers. Cunningham et al (1983) state that there is little point in increasing the water concentration in a fuel oil emulsion above 10 wt%, due to the latent heat losses in the flue gases.

Clayfield et al (1981) described the manufacturing process for "Colloil", in which 10 - 20 wt% water was used as a stabiliser for coal-oil mixtures. In this process, water was added to crushed coal prior to wet grinding in a ball mill with fuel oil. The water, it was claimed, promoted the formation of a flocculated structure which was a more effective method of stabilisation than addition of dry coal to a fuel oil-water emulsion. It is also probable that this method increases the stability of the COW fuel by increasing the liquid phase.
viscosity. "Colloil" was used in combustion trials at the British Steel Corporation's Cleveland works in 1979. Approximately 14 tonnes of the fuel, containing 40 wt% coal, 50 wt% oil and 10 wt% water were injected into one tuyere of a blast furnace. No handling or operational difficulties were reported.

Hopton and Vergeer (1980) compared the gaseous and particulate emissions of coal-oil mixtures and coal-oil-water mixtures with those of No. 6 fuel oil when burned in high intensity and low intensity burners. COW fuels, containing 30 wt% coal and 8 wt% water, were prepared by mixing coal with water-oil emulsions. The results showed no significant decrease in total particulate emissions between COM and COW fuels, while both were an order of magnitude greater than those of fuel oil alone. Some evidence was presented to suggest that COW particulates were smaller in diameter than those of either COM or fuel oil. However, this could be a result of poor solids sampling.

In the third of the joint BP/CEGB trials at Padiham power station, provision was made to add up to 11% water into the COD supply line using a 500 psig injection system. The results showed that the poor particle burnout, which was evident during the previous two trials, could be improved by addition of 5% water to the fuel, without increasing the excess air to an unacceptably high level (Matthews, 1985).

2.1.3 Coal-Water Fuels

Slurries of coal particles in water have been used as a means of transporting coal by pipeline for many years. The earliest patents on this subject were granted to Wallace C. Andrews, of the New York Steam Company, in the 1890's (Wasp, 1983). However, the first operational coal slurry pipeline was commissioned during 1914 in London. It was designed by G.C. Bell and was used to transport 50 tons of coal per hour from barges on the Thames to a nearby power station. Transporting coal, in slurry form, through pipelines is now a well established technology, although political and economic problems have prevented its widespread development. Of the thousands of miles of coal slurry pipelines installed worldwide, the longest is the Black Mesa line in
the USA. This is 273 miles long and is used to move 5.5 million tons of coal per year, as a 50% slurry, from the Black Mesa mines in Arizona to the Mohave power station in Nevada.

Coal slurries have been available for about 100 years from mine washery tailing ponds (Atkins, 1983) and several attempts have been made to use this cheap source of coal. In the early 1930's these slurries were used as a boiler fuel at the Mine Orange Nassau, Heerlen plant, in the South of Holland. In the early 1950's a 60 MWq power station was constructed at Barony, Scotland, which operated for 27 years on local mine pond slurries. A similar plant was installed in 1965 at Methil power station, Fife, which is, to this present time, operating on coal water slurry.

These early projects however did not supply the fuel to the combustion chamber as a liquid. The slurries were dewatered and dried prior to combustion and the resultant pulverised coal then burned. Indeed this is still the practice with the modern pipeline projects such as Black Mesa. The reason for this is the high water content (typically 40 -50%) and the inherent instability of the slurries, which must be kept moving to prevent settling.

Kelcec (1961) reported the results of a continuous eleven day test in which a 67 - 68 wt% coal-water slurry was fired directly at the Werner power station of the Jersey Central Power and Light Company. In Germany, tests were conducted on a coal-designed boiler, using a 50 wt% coal-water slurry with no additive (Schwarz 1966 & 1967). Russian investigators carried out similar work in 1965 (Delyagin 1965a, 1965b and Davydora 1965). These early combustion trials were discontinued due to lack of economic incentives to replace oil with coal.

When interest in coal-oil fuels declined again in the early 1980's, (see Section 1), research attention once again turned to coal-water slurries. The emphasis now was on producing a highly-loaded, stable coal-water mixture which could be burned in oil-designed boilers. One of the first of the modern studies was done in 1979 by the Atlantic Research Corporation in America (Diamond, 1984), and, in 1982, the U.S. D.O.E. annual symposium was renamed the "Coal Slurry Combustion Symposium" to accommodate the rising interest in CWM. The recent CWM combustion trials are summarised in Table (2.2) (After Bienstock 1983).
### CWM INDUSTRIAL APPLICATIONS

<table>
<thead>
<tr>
<th>Country</th>
<th>Project/Name</th>
<th>Application</th>
<th>Test Period</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada</td>
<td>EMA/DIW</td>
<td>Fluidized Bed Combustor</td>
<td>1983</td>
<td>91</td>
</tr>
<tr>
<td>Italy</td>
<td>Centro Sperimentale Metalurgico</td>
<td>Blast Furnace Fuel Injection</td>
<td>Planned</td>
<td>93</td>
</tr>
<tr>
<td>Sweden</td>
<td>Carboqel AB</td>
<td>Gasifier</td>
<td>N.A.</td>
<td>26</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>National Coal Board, Coal Utilization</td>
<td>Pressurized Fluidized Bed</td>
<td>1982</td>
<td>94</td>
</tr>
<tr>
<td>United States</td>
<td>Standard Havens Research Corporation</td>
<td>Rotary Rock Dryer</td>
<td>1983</td>
<td>95</td>
</tr>
</tbody>
</table>

### CWM UTILITY BOILER DEMONSTRATIONS

<table>
<thead>
<tr>
<th>Country</th>
<th>Power Station</th>
<th>MWe</th>
<th>Design Fuel</th>
<th>Test Period</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada</td>
<td>Chatham Station</td>
<td>12</td>
<td>Coal</td>
<td>1983</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22</td>
<td>Coal</td>
<td>1983</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 - 150</td>
<td>Oil</td>
<td>1984</td>
<td>86</td>
</tr>
<tr>
<td>Italy</td>
<td>S. Barbara Station</td>
<td>125</td>
<td>Lignite/oil</td>
<td>1982</td>
<td>85</td>
</tr>
<tr>
<td>United States</td>
<td></td>
<td></td>
<td></td>
<td>To Be Determined</td>
<td>1984 - 1985</td>
</tr>
</tbody>
</table>

### CWM INDUSTRIAL BOILER DEMONSTRATIONS

<table>
<thead>
<tr>
<th>Country</th>
<th>Organization/Name</th>
<th>Size</th>
<th>Design Fuel</th>
<th>Test Period</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweden</td>
<td>NYCOL AB Seahns Fluidcarbon Thermal Engineering Research Foundation</td>
<td>5 MW Oil</td>
<td>Oil</td>
<td>1981</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50,000 pph Oil</td>
<td>Oil</td>
<td>1983</td>
<td>91</td>
</tr>
<tr>
<td>United States</td>
<td>PETC</td>
<td>100 Hp Oil</td>
<td>Oil</td>
<td>From 1981</td>
<td>35,36</td>
</tr>
<tr>
<td></td>
<td>Dupont Co. Occidental Research Corp.</td>
<td>700 Hp Oil</td>
<td>Oil</td>
<td>From 1981</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65,000 pph Oil</td>
<td>Oil</td>
<td>1983</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>130,000 pph Oil</td>
<td>Oil</td>
<td>1984</td>
<td>92</td>
</tr>
</tbody>
</table>

### RECENT CWM COMBUSTION TRIALS

<table>
<thead>
<tr>
<th>Country</th>
<th>Organization/Name</th>
<th>Test Furnace</th>
<th>Test Period</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Japan</td>
<td>Babcock Hitachi K.K. Electric Power Development Co. Ltd.</td>
<td>80 x 10^6 Btu/hr test furnace</td>
<td>1982</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.3-Mw Btu/hr cylindrical test furnace</td>
<td>1982</td>
<td>76</td>
</tr>
<tr>
<td>Spain</td>
<td>UNESA</td>
<td>4-MW test furnace</td>
<td>1983 - 1985</td>
<td>78</td>
</tr>
<tr>
<td>Sweden</td>
<td>AB Carboqel</td>
<td>Various prototype burners with capacities up to 3.5-MW have been tested</td>
<td>From 1979</td>
<td>26</td>
</tr>
<tr>
<td>United States</td>
<td>Atlantic Research</td>
<td>1.3 x 10^6 Btu/hr furnace at ARC, and 4.0 x 10^6 Btu/hr test furnace at Babcock &amp; Wilcox Alliance Research Center</td>
<td>From 1979</td>
<td>80,81</td>
</tr>
<tr>
<td></td>
<td>Slurrytech, Inc.</td>
<td>4.0 x 10^6 Btu/hr test furnace at RM Alliance Research Center</td>
<td>1980</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>Gulf &amp; Western Industries Inc.</td>
<td>80 x 10^6 Btu/hr test furnace at Combustion Engineering Inc.</td>
<td>1982</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70 x 10^6 Btu/hr test furnace at Forney Eng. Co.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>United Kingdom</td>
<td>HEI International Combustion, Ltd.</td>
<td>5 x 10^6 Btu/hr test furnace</td>
<td>1982 - 1983</td>
<td>79</td>
</tr>
</tbody>
</table>

**Table (2.2) Coal-Water Fuel Projects 1980 - 1983**

(After Bienstock (1983) - Reference numbers refer to original reference.)
As in the early days of coal-oil fuel development much of the early work on CWM has been concentrated on preparation and handling.

Stability is attained either by use of additives or, by controlling the particle size distribution. In practice both techniques are often used, as, for example, in the case of "Co-Al" (Dinger et al., 1982). For this fuel, the theoretical optimum packing of particles is achieved by controlling the size distribution, according to the formula:

\[
CPFT = \frac{D^n - D_s^n}{100} \left( \frac{D_L^n - D_s^n}{D_L^n - D_s^n} \right)
\]

where \( CPFT \) = cumulative percent less than \( D \)

\( D_L \) = largest particle diameter

\( D \) = any particle diameter

\( D_s \) = smallest particle diameter

\( n = 0.37 \)

Additives are used to ensure separation of the particles, and the fraction of particles less than 1μm in diameter is adjusted to give a specific surface area greater than 1.25 m²/cc. This inevitably leads to a bimodal particle size distribution. The literature on coal water slurry preparation is extensive, however it may be briefly summarised by two points:

(i) Highly loaded slurries can be obtained by careful selection of particle size distribution, and use of flocculating additives.

(ii) Low viscosity can be obtained by use of dispersing additives.

Several coal-water fuels are now commercially available, with coal concentrations in the range 60 – 70 wt%. However, comparatively little information is available on the combustion of such fuels. The problems all appear to be concentrated on burner design. It is essential that such fuels be efficiently atomised, in such a manner so as to give good flame ignition and stability characteristics, without air preheat and
excessive burner wear. Several studies have been presented on CWM burner design (Hickman and Buckingham, 1983, Batra and Walsh, 1983 and Allen et al., 1983) but the problem is, as yet, unsolved.

2.1.4 Other Types of Slurry Fuels

Interest in slurry fuels has always been centred on the various combinations of coal, oil and water which have previously been mentioned. However, there are also several references to fuels which contain other types of carbonaceous solids, and different liquids.

In recent years, the increased demand for premium fuels, such as petrol and aviation spirit, had led to changes in the crude oil refining process. The 'heavy end of the barrel' has become increasingly more viscous as refineries employ more sophisticated cracking techniques and coking processes. In 1981, Browning estimated that 40 mtoe additional upgrading equipment was being installed in Western Europe to satisfy the demand for light and middle distillates. This has resulted in an increase in the amount of vacuum residue and petroleum coke available. Vacuum residues, which can contain 3 - 8 wt% solids particles (Passo, 1983), are mostly used as refinery fuels. Petroleum coke has been proposed for use in slurry fuels by several authors, either mixed with oil (Beshore, 1983) or with water (Fu, 1983). The author's own work on petroleum coke oil dispersions show that the combustion mechanism of such fuels is favourable to good burnout characteristics (Lapwood et al., 1983). Petroleum cokes contain less ash than most coals, they contain more volatiles than anthracite, and are non-agglomerating. However, they also normally contain high quantities of sulphur, which is possibly why they have, so far, only been adopted as maritime fuels (Nunn, 1982).

Jenkins D.P. (1983) investigated the possibility of using coke breeze-oil mixtures in blast furnaces, and compared these with anthracite-oil mixtures.

Hubbard (1959) added 0.5 μm diameter carbon black particles to gasoil and fuel oil, in order to investigate the effect of solid carbon particles on flame radiation characteristics. Settling was a problem
at solids concentrations above 6 wt%, and therefore the maximum concentrations used were 9 wt% in gasoil and 4 wt% in fuel oil. The effect of adding carbon to the fuel was to increase the C/H ratio which caused an increase in flame emissivity and thus radiation from the flame. Added carbon caused a greater increase in emissivity at the tail end of the flame than natural soot formed within the flame. This was probably due to the size difference between the two types of particles. Hubbard's results are shown in Figure (2.2).

![Figure 2.2 Comparison Between Natural and Added Carbon](image)

**Figure 2.2 Comparison Between Natural and Added Carbon (After Hubbard, 1959)**

(a) Gas Temperature on Flame Axis, (b) Carbon on Flame Axis, (c) Max. Narrow Angle Flame Radiation to Cold Receiver, (d) Flame Emissivity.

This method of increasing radiative heat transfer was used by Tesky (1958) and Swett (1958) to improve the performance of open-hearth furnaces.

Szekely and Faeth (1981) examined the use of carbon black and graphite particles in 'JP-10' liquid fuel as a means of increasing the energy density of such fuels for gas turbines and jet propulsion systems. The
carbon particles were approximately 0.3 μm in diameter and the slurries contained 49.2 - 50.4 wt% of solids. The combustion mechanism of individual droplets of these fuels and the mathematical analysis will be referred to in a later section.

Ruskan (1982) reported the advantages of slurries containing 60% coal and 40% methanol over coal-water mixtures. Coal-methanol mixtures are easily pumped, and have a much higher energy content than coal-water slurries, however, methanol is an expensive fuel and Ruskan stated that coal-methanol-water mixtures were a more practical proposition. The addition of a small amount of methanol to coal-water mixtures produced higher flame temperatures, reduced the stoichiometric air requirement, reduced ignition delay, and apparently caused swelling of the coal particles so that they burned more efficiently. However, no experimental evidence was provided to back these claims.

Pan (1982, 1983) described coal-methanol-water slurry combustion trials in a 100 hp fire-tube boiler. Results were reported for three coals of different ranks, water concentrations between 0 and 48%, and alcohol concentrations between 0 and 53%. This study showed that methanol, in small concentrations, substantially reduced the need for combustion air preheat [Table 2.3] and increased carbon conversion efficiency and boiler efficiency [Table 2.4].

Haag (1983) described the Swedish straw-oil mixture project. Approximately 3m tonnes/year of straw are available as waste in Sweden, and combustion tests have been conducted using 28 wt% pulverised straw in heavy fuel oil. The fuel was successfully burned in a 25 MW water-tube boiler. Although difficult to shred and grind, straw has the advantage that it is cheaper than coal and has a low ash content (approx. 4 wt%). However, Haag pointed out that the low energy content of straw makes boiler derating inevitable.

In Brazil, the availability of large quantities of wood and the soaring price of oil led to examination of Gmelina and Carribean wood charcoal as substitutes for oil. The wood charcoal-oil mixtures were shown to burn easily but caused increased NOx formation due to the inherent nitrogen in the wood (Lopez, 1981).
### Table 2.3: The Effect of Methanol on Combustion Air Preheat

*(After Pan et al., 1982, 1983)*

<table>
<thead>
<tr>
<th>Coal Type</th>
<th>Concentration (wt%)</th>
<th>Air Preheat °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coal</td>
<td>Methanol</td>
</tr>
<tr>
<td>Bituminous</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>(Pittsburgh</td>
<td>56</td>
<td>9</td>
</tr>
<tr>
<td>seam)</td>
<td>55</td>
<td>18</td>
</tr>
<tr>
<td>Sub-bituminous</td>
<td>53</td>
<td>-</td>
</tr>
<tr>
<td>(Montana)</td>
<td>47</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>13.5</td>
</tr>
<tr>
<td>Lignite</td>
<td>54</td>
<td>-</td>
</tr>
<tr>
<td>(Texas)</td>
<td>48</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>49</td>
<td>22</td>
</tr>
</tbody>
</table>

### Table 2.4: The Effect of Methanol on Carbon Conversion Efficiency

*(After Pan et al., 1982, 1983)*

<table>
<thead>
<tr>
<th>Coal Type</th>
<th>Concentration (wt%)</th>
<th>Carbon Conversion Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coal</td>
<td>Methanol</td>
</tr>
<tr>
<td>Bituminous</td>
<td>61</td>
<td>39</td>
</tr>
<tr>
<td>(Pittsburgh)</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>Sub-bituminous</td>
<td>45.9</td>
<td>53.3</td>
</tr>
<tr>
<td>(Montana)</td>
<td>53.2</td>
<td>-</td>
</tr>
<tr>
<td>Lignite</td>
<td>48.2</td>
<td>47.6</td>
</tr>
<tr>
<td>(Texas)</td>
<td>53.6</td>
<td>-</td>
</tr>
</tbody>
</table>
2.2 Combustion Mechanisms

2.2.1 Chemical and Physical Considerations

Rosin (1958) defined a combustion mechanism as "an arrangement of a number of different partial processes which are made to act together in a predetermined way so as to achieve a desired result." Many authors have examined these partial processes; separately, and in connection with specific fuels. Before considering the previous work on the combustion mechanisms of coal slurry fuels, some of the partial processes will first be discussed together with some of the previous mechanism studies on coal and oil.

Griswold (1946) said of combustion chemistry: "Combustion is high temperature oxidation. With the exception of combustion of elementary carbon, oxidation reactions occur in the gas phase." Several authors have discussed the numerous and complex homogeneous gas-phase reactions which can occur in flames (e.g. Minkoff and Tipper, 1962), but the full range of chain and branching chain reactions which can occur are generally far too numerous to be analysed.

Lewis and von Elbe (1938) identified the reactions involved in the combustion of carbon monoxide and methane. However, Edelman and Harsha (1984) described the kinetic analysis of more complex hydrocarbon fuels as: "all but impossible, even if all intermediate reactions and their rates were fully characterised, if for no other reason than the sheer number of the species and reactions involved". Their solution was to adopt an approximation technique, which they called 'the toluene-isooctane quasiglobal method', to model the chemical kinetics of higher hydrocarbons. The method assumed that, from a kinetic standpoint, hydrocarbon fuels can be considered as mixtures of aromatic and aliphatic components which can be approximated to by different proportions of toluene and isooctane.

In a discussion of the kinetics of the heterogeneous reactions which may occur in combustion systems Thring and Essenhigh (1962) listed the seven reactions which were most likely to occur (Table 2.5). Of these it has been stated (Calleja et al., 1981, and Moles 1984) that reactions 1, 2 and 3 are the most significant.
C (solid) reacting with $O_2$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $C + O_2 \rightarrow CO_2$</td>
<td>-94.0</td>
</tr>
<tr>
<td>(2) $C + \frac{1}{2}O_2 \rightarrow CO$</td>
<td>-26.6</td>
</tr>
<tr>
<td>(3) $CO + \frac{1}{2}O_2 \rightarrow CO_2$</td>
<td>-67.4</td>
</tr>
</tbody>
</table>

C (solid) reacting with $CO_2$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4) $C + CO_2 \rightarrow 2CO$</td>
<td>+40.8</td>
</tr>
</tbody>
</table>

C (solid) reacting with $H_2O$ (gas)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5) $C + H_2O \rightarrow CO + H_2$</td>
<td>+31.1</td>
</tr>
<tr>
<td>(6) $CO + H_2O \rightarrow CO_2 + H_2$</td>
<td>-9.7</td>
</tr>
<tr>
<td>(7) $C + H_2 \rightarrow CH_4$</td>
<td>-17.9</td>
</tr>
</tbody>
</table>

**TABLE (2.5) Heterogenous Reactions of Carbon and Associated Reactions**

(After Thring and Essenhigh, 1962)

Particular attention has been given to the proportions of CO and $CO_2$ formed in the first stage of the reaction between solid carbon and oxygen. The early work of Rhead and Wheeler (1912) suggested that both gases were formed together in a temperature dependent ratio, with CO being the dominant product at higher temperatures (> 1000°C). However, opponents of this view (for example Langmuir, 1915) dominated the argument for forty years. The difficulty in establishing the truth was, and to a certain extent still is, the alteration of the equilibrium by the conversion of CO to $CO_2$. Arthur (1946) used $POCl_3$ to inhibit this reaction and correlated his results with the following relationship:

$$\frac{CO}{CO_2} = F \exp \left[ -\frac{\Delta E}{RT} \right]$$

(2.2)
where $F = \text{frequency factor (10}^{3.4})$

$\Delta E = \text{difference in activation energies (12.4 kcal)}$

$R = \text{Universal gas constant}$

$T = \text{temperature}$

This equation produced good agreement with the data of Rhead and Wheeler and predicts CO to be the primary product. However Arthur's work has been criticised because the chlorinated chain breaking compounds used to inhibit CO oxidation could also have modified the carbon surface in such a way as to favour the production of CO. The matter is still contentious.

Few combustion processes can be explained purely in terms of chemical kinetics, even if the reactants are all gaseous. Physical effects, such as the rate of mixing between fuel and oxidant, are also important. Thring and Newby (1953) modelled the combustion of fuels in turbulent diffusion flames by considering only the space required for mixing the two streams. A similar approach was adopted by Craya and Curtet (1955) and Pieri (1973).

Dependence on both physical and chemical factors is well-illustrated in the past work on solid particle combustion. Most models of heterogeneous combustion consider the particle to be surrounded by stagnant gas, through which reactants must diffuse before they can react. This principle was first proposed by Nusselt (1924) and subsequently developed by several workers. Nusselt calculated the burning times of the solid particles by assuming that the burning rate of a single particle, in an infinite atmosphere was controlled solely by the rate of diffusion through a boundary layer around the particle. The burning time was then shown to be proportional to the square of the particle diameter ($d_o$):

$$ t_b = K_d \, d_o^2 \quad (2.3) $$

$K_d$, the burning constant, is a function of ambient conditions. For particles in a flame Nusselt showed that burning times were modified, due to vitiation of oxygen, by a factor $F_p$:

$$ t_b = F_p \, K_d \, d_o^2 \quad (2.4) $$
Implicit in Nusselt's analysis is the assumption that chemical reaction takes place instantaneously at the particle surface, and therefore the model may be described as a single film diffusional model. Calleja et al. (1981) described two limiting cases for this mechanism which correspond to the exclusive production of CO [Figure 2.3a] and the exclusive production of CO\(_2\) [Figure 2.3b].

Burke and Schumann (1931) proposed a mechanism in which the incoming oxygen reacts with outgoing carbon monoxide at some fixed point within the stagnant film to form carbon dioxide. Some carbon dioxide then diffuses outwards, and some inwards, to react on the surface to form more carbon monoxide. This is known as the double-film mechanism [Figure 2.3c].

The inclusion of a finite chemical reaction rate into the burning time equations was proposed by Tu, Davies and Hottel (1934). Their specific combustion rate equation has formed the basis of many subsequent analyses.

\[
K = \frac{RA \phi P_{OG}}{\pi T_a - \log \left( \frac{B}{d} \left( \frac{u g}{dT_a^2} + \frac{2}{d} \right) \right) + C \sqrt{T_S} \cdot \frac{eE}{RT_S}} 
\]

(2.5)

where \(a, B, C, n\) = constants

- \(A\) = proportionality factor
- \(P_{OG}\) = pressure of O\(_2\) in gas stream, atm.
- \(P_i\) = log mean pressure of inert film, atm.
- \(d\) = particle diameter, cm.
- \(u\) = gas velocity, cm/s.
- \(g\) = gas density, g/cm\(^3\)
- \(T\) = arithmetic mean film temp, K
- \(T_S\) = particle surface temp, K
- \(E\) = activation energy, cm\(^5\)atm/mol. O\(_2\)
- \(R\) = gas constant, cm\(^5\)atm/K.
- \(\phi\) = mechanism factor, 1 for CO\(_2\), 2 for CO
- \(K\) = specific combustion rate, g\(^2\)/cm\(^2\)s.
FIGURE 2-3 SOLID PARTICLE REACTION MECHANISMS

(a) Single Film Model of Complete Combustion
(b) Single Film Model of Incomplete Combustion
(c) Double Film Model of Complete Combustion

R = radius
s = solid surface
b = bulk gas
d = diffusion layer

(d) Gas Film Diffusion Control
(e) Ash Diffusion Control
(f) Surface Chemical Reaction Control

(g) Progressive Conversion Model

Low conversion
Time
High conversion

Original concentration
Solid Conc.
The denominator is the sum of two terms; a chemical and a diffusional resistance to combustion. Tu et al showed, experimentally, that chemical reaction rate was the controlling factor at temperatures below 1000°C whilst diffusion controlled the combustion rate at higher temperatures. However their experiments were conducted on large carbon particles (approx. 3 cm in diameter), and the results may not be applicable to smaller particles.

A general film model was considered by Caram and Amundsen (1977) in which CO combustion could occur anywhere within the boundary layer at a finite reaction rate, and in which both O₂ and CO₂ could react at the carbon surface. The computational difficulties were too great to be solved.

The application of such models relies, to some extent, on knowledge of particle behaviour during combustion. Yagi and Kunii (1955) described an 'unreacted shrinking core model' of particle behaviour in which three possible rate controlling steps could occur. In this model the particle either becomes progressively smaller as the core reacts or remains constant in size as an ash layer forms around the shrinking unreacted core. The formation of an ash layer adds another diffusional resistance to the combustion rate equation. Therefore gas film diffusion rate, ash layer diffusion rate or chemical reaction rate could be the rate controlling factors. These three modes are represented diagramatically in Figures 2.3d, 2.3e, 2.3f.

An alternative to the shrinking core model is the progressive conversion model (Levenspiel, 1962). Here the reactant gas is assumed to enter the solid particle and react throughout its volume at all times. [Figure 2.3g].

The nature of particles in flames depends on the fuel from which, and the conditions under which they were formed. Soot particles consist of finely divided carbon particles, approximately 0.005 - 0.25 μm in diameter. The formation of soot particles from gaseous fuels, or the gaseous volatiles of liquid and solid fuels, was discussed by Gaydon and Wolfhard (1970). They stressed the importance of flame type on the structure and size of the particles and presented experimental evidence to show that fuel composition, oxygen concentration, temperature and
pressure all affect the quality and quantity of soot formed. Lee et al. (1962) proposed the following expression for the combustion rate of these particles in a laminar flame:

\[ q = 1.085 \times 10^4 \frac{P_{O_2}}{T^{1/2}} \exp \left( -\frac{39300}{RT} \right) \]  

(2.6)

where \( q \) = burning mass velocity, kg/m².s.,
\( P_{O_2} \) = partial pressure of O₂
\( T \) = temperature, K
\( R \) = Universal gas constant, atm. m³/mol.K

The predictions of this equation result in differences of ten times lower in order of magnitude than those of a diffusion controlled rate equation, thus indicating a marked degree of chemical control at all temperatures.

The other types of particles which may occur in flames are the carbonaceous residues from solid or liquid fuels. These are known as chars or cenospheres. The term 'cenosphere' was first proposed by H.B. Dixon and was used by Sinatt (1927) and Newall et al. (1924, 1926) to describe particles formed in nitrogen atmosphere from the vitrain and clarain components of coking coals. These were "reticulated, being built up of two main structures, namely ribs or frames of the brownish-black substance, and 'windows'". The term has since come to be applied to any type of carbonaceous residue from oil droplets and coal particles, and these will be discussed more fully in sections 2.2.2 and 2.2.3.

2.2.2 Pulverised Coal

2.2.2a Stages in Combustion

The important stages in the combustion of pulverised coal are (Rosin, 1958):

(1) The period prior to ignition which includes the heating of the air-dust stream and the partial expulsion of volatiles.
(i) The ignition period of the solid residue which normally coincides with combustion of the volatiles by which it is supported.

(iii) The combustion period of the carbonised residue.

In a review of the literature, Gill (1975) noted that: "The common aim of many workers in this field has been to develop a mathematical model by means of which burnout and heat transfer rates can be predicted for a given set of input data defining furnace geometry and firing arrangements". Several other authors (for instance Field et al., 1967, and Smoot and Smith, 1985) have presented comprehensive reviews of the relevant literature on combustion aerodynamics, heat transfer, pyrolysis and char combustion, in order to produce such a model. However, the assumptions which have been made in theoretical analyses of coal particle combustion for the sake of computational simplicity are often contrary to experimental observations. Even the contention that the process takes place in three independent stages has been shown to be an oversimplification (Fells and Richardson, 1969) and it has been claimed that combustion occurs on the particle surface even before devolatisation begins (Howard and Essenhigh, 1966). It is apparent that a large gap exists between experimental data on combustion mechanisms and the current pulverised coal combustion models.

2.2.2b Particle devolatilisation

The early work on particle devolatilisation was reviewed by Badzioch in the monograph by Field et al. (1967). It was claimed that the earliest work was in which coal particles, in the size range 147 - 227 μm and 150 - 200 μm, were dropped through an inert atmosphere in a vertical tube furnace which was maintained at constant temperature. Particles could be withdrawn from the furnace at any time after the minimum residence time of 0.45 seconds. This study revealed that the composition of the volatiles differed from that of those obtained by slow decomposition, and that the rate of devolatisation was high in the first 0.5 seconds and low thereafter. The criticisms of this work were that the particle size distribution used were not representative, the maximum furnace temperature (550°C) was too low, and the minimum residence time was too high. These points were noted in later experiments by other workers (Badzioch et al., 1970, Kimber and Gray 1967) but the results were similar.
Loison and Chauvin (1964) reported the important result that faster heating rates and higher final temperatures produced greater yields of volatiles. They also analysed the volatile components of several coals, which were subjected to rapid heating and high final temperatures, and concluded that tar/gas yield ratios were much higher than those observed in slow decomposition. However, in their experimental method the coal particles were supported and heated on a metal grid in such a way that heating rate and final temperature could not be independently varied. It is therefore impossible to ascertain which was the dominant factor.

Anthony et al. (1975) concluded that volatile yield was dependent only on final temperature and that increasing the final temperature caused an increase in volatile yield. However, the results of Loisin and Chauvin suggest that, whilst this may be true of swelling coals, the residual mass of low rank coals is independent of temperature. Smoot and Pratt (1979) presented evidence to show that volatile composition changes markedly as pyrolysis proceeds. The first volatiles released are much richer in carbon than the subsequently liberated components.

In considering the mechanisms of thermal decomposition, Field et al. (1967) stated that any such mechanism must explain the differences in behaviour between slow and rapid heating and the observed changes in volatile composition as pyrolysis proceeds. Such a mechanism should also explain why, despite having sustained a weight loss in excess of that indicated by proximate analysis, a residual volatile yield amounting to 10 - 15% of the initial value persists in devolatilised chars.

Dryden (1957) and Loison and Chauvin (1964) postulated the existence of large, loosely bound molecules, or groups of molecules, within the coal which were too large to evaporate during slow heating but could be forcibly ejected or escape in some other way during rapid heating. Van Krevelen et al. (1956) showed that, during slow decomposition, a small portion of the fluid phase of the coal (the metaplast) was carried away as a tar mist by escaping volatiles. This effect could be greatly increased during rapid heating due to the greater rate of volatile evolution. More recently, Spiro (1981) explained the decomposition mechanism with the aid of 'space-filling models' of bituminous coals.
These models demonstrated that rapid heating could cause the aliphatic “lubricating fragments” between the aromatic planes, which constitute the bulk of the coal structure, to be lost before the planes could unlock and slide over one another thus preventing the exposure of more aliphatic molecules and trapping them within the coal structure. Spiro and Kosky (1981) extended this modelling approach to the structure of high and low rank coals and used the results to explain the observed swelling and plasticity differences between coals of different rank, and the differences between degree of swelling of coals of the same rank at different heating rates.

2.2.2c Particle structure during burnout

The importance of the devolatilisation period in coal combustion is not so much the effect on the subsequent combustion of the evolved volatiles. This, being a homogenous, gas-phase reaction is unlikely to influence the overall combustion rate of the coal particles. More pertinent to the overall process is the effect of devolatilisation on the structure of the residual char. Street (1969) reports the growth of protrusions, resembling worm-casts, from the surface of the devolatilising coal particles. These outgrowths were probably due to gases expanding beneath the plastic surface of the coal, and constitute just one example of a whole range of char structures which have their origins in the devolatilisation phase of combustion.

The work of Sinatt and his co-workers on the structure of coal chars formed during rapid heating in a variety of gases (nitrogen, steam, carbon dioxide, hydrogen, and air) has been mentioned in Section 2.2.1. These studies, although not directly concerned with pulverised coal combustion, are important in that they showed that hollow spheres could be formed above about 600°C and that various lithotypes were important in controlling char structure. The formation of hollow carbonaceous residues with holes in the surface during the combustion of pulverised coal was confirmed by Orning (1947) in laboratory scale tests and it had even been suggested by Bangham and Franklin (1946) and Crone and Bowering (1950) that combustion could possibly occur on the internal surface of such particles.
Alpern et al. (1960) sampled partly burned coal particles from a large p.f. flame and examined them using optical and electron microscopy. They identified four main types of structure: raw coal, plasticised coal, semi-coke cenospheres and coke cenospheres. Littlejohn (1967) reported that all coals behave as a mixture of particles of different swelling properties, which could be grouped into five broad classes:

(a) particles that appear unchanged after heating,

(b) particles that fuse and become spherical but do not swell,

(c) particles that swell into opaque spheres thus indicating a thick wall or a very porous solid,

(d) particles that swell into transparent spheres thus indicating a thin wall, and

(e) particles that show mixed behaviour.

The subjects of coal particle swelling, char structure and surface area received much attention in the late 1960's. Gray et al. (1967) confirmed that combustion could take place inside hollow particles and that the porosity of the particle during formation of the hollow spheres increased from 10% to 50%. These results were confirmed by sampling solids from large flames (Ramsden and Smith, 1968).

Shibaoka (1969) used a single droplet technique to investigate the effect of coal rank and petrographic composition on the burnout mechanism of four Australian coals. He concluded that vitrite was responsible for the swelling behaviour of coals whereas fusite does not swell or plasticise even in coking coals. The degree of particle swelling was found to affect combustion rate and for this reason vitrite burned faster than fusite.

A notable contribution to the literature was made as a result of work at the Marchwood Engineering Laboratories of the CEGB. The experimental program on p.f. combustion, described by Street (1969), employed single particle techniques, a vertical drop-tube furnace, shock tube techniques and sampling from large, power-station flames. Results were published on char structure (Lightman and Street, 1968),
density and swelling (Street, Weight and Lightman, 1969), surface area (Anson, Moles and Street, 1972) and particle temperature (Bach, Street and Twamley, 1968). Four main types of char structure were identified in these investigations: thin-walled, hollow chars, thick-walled hollow chars, 'lacy' chars and solid particles. To a certain extent these structures were attributable to the maceral groups from which they were formed: fusain always formed solid particles, vitrains and clarains composed mainly of vitrinite tended to form thin-walled chars when compared with those formed from durains composed mainly of exinite and inertinite. However, the relationship was tenuous and difficult to classify exactly.

The atmosphere, in which the particle was heated was also shown to be important, with particles heated in nitrogen showing marked structural differences to those heated in air. This observation was also made by Fells and Richardson (1969) who wrote, "hollow particles were more likely to come from oxygen starved regions". This could, however, be due to the fact that thin-walled, hollow particles do not survive as long as solid particles in regions of high oxygen concentration and are thus more likely to be sampled in vitiated atmospheres.

The picture of structural change which was postulated from the microscopic studies of Street and co-workers was confirmed by surface area and density measurement at different stages in the particle's lifetime. Xenon sorption at 0°C indicated that specific surface area progressively decreased as char combustion proceeded and that lower rank coals had higher specific surface areas at all stages than mid-rank coals. Despite a decrease in specific area during combustion, probably due to destruction of the micropore system, the authors stated that; "the results obtained are not unambiguous when used to determine surface areas relevant to heterogeneous combustion". However, the apparent density measurements did confirm the swelling observations, in that apparent density reached a minimum at the point of greatest swelling and then proceeded to increase as more surface holes were formed (this allowing the silicone oil used in this technique to penetrate).
2.2.2d Modelling p.f. combustion

Since it is now generally accepted that the analysis presented by Nusselt (1924) of an entirely diffusion controlled mechanism for solids particles is an oversimplification, it is appropriate to consider the chemical kinetics of char combustion and particularly the effects of pore diffusion and char reactivity. The work of Tu, Davies and Hottel, in which a chemical reaction rate term was included in the equation for specific reaction rate of carbon spheres has already been considered (Section 2.2.1). Essenhigh (1961) developed Nusselt's analysis by using Langmuir's absorption isotherm to deduce the solid surface reaction rate ($R_s$) in terms of surface oxygen concentration ($P_s$).

Thus:

$$R_s = \frac{K_1 K_2}{K_1 P_s + K_2} \quad (2.7)$$

where $K_1$ and $K_2$ are the velocity constants for respectively: absorption of oxygen to form a chemisorbed layer; and decomposition of the oxide layer. This was combined with the mass transfer equation for $R_s$:

$$R_s = \frac{K_o (P_o - P_s)}{K_0 P_o} \quad (2.8)$$

where $K_o$ = mass transfer velocity constant and $P_o$ is the mainstream oxygen concentration, thus giving the combined resistance equations:

$$\frac{1}{R_s} = \frac{1}{K_0 P_o} + \frac{1}{K_1 P_o} \quad : \ 1000^\circ C \leq T \leq 2000^\circ C \quad (2.9)$$

or

$$\frac{1}{R_s} = \frac{1}{K_2} \quad : T < 1000^\circ C \quad (2.10)$$

By equating $R_s$ to the rate of mass lost, substituting for $K_o$, $K_1$ and $K_2$, integrating, and allowing for variation of $P_o$ due to progressive consumption of oxygen, Essenhigh derived the following equation for particle burning time in a flame:

$$t_B = P_c K_o d_o + P_D K_D d_o^2 \quad (2.11)$$
where \( F_c, F_D = \) vitiation constants
\[ K_c = \text{chemical burning rate constant} \]
\[ K_D = \text{diffusional burning rate constant} \]
\[ d_0 = \text{initial particle diameter}. \]

This analysis assumes a constant particle density, and thus progressive size reduction during combustion, and that the reaction occurs on a smooth external surface. The work on char structure shows that neither of these assumptions are correct. Wheeler (1951) proposed a modified specific reaction rate constant to account for internal reaction:

\[ R_v = (K_S \cdot S \cdot D)^{1/2} \cdot \rho_s^{(m + 1)/2} \quad (2.12) \]

where \( S \) is the internal surface area, \( D \) is the diffusion coefficient of oxygen in nitrogen, \( K_S \) is the reaction velocity constant which may take the value \( K_1 \) or \( K_2 \) and \( m \) is the reaction order.

Field et al. (1967) correlated the data of several workers with that done at ECURA on the chemical rate constant of several types of coal to produce the following empirical equation:

\[ K_S = 8710 \exp \left( -\frac{35700}{RT_g} \right) \quad (2.13) \]

where \( K_S = \) surface reaction rate coefficient (g./cm\(^2\).s.atm)
\[ R = \text{gas constant (cal/mol. K)} \]
\[ T_g = \text{particle surface temperature (K)} \]

In the authors' own words: "This must be an oversimplification. The universal use of such an expression implies that there is no effect of coal type, give a reaction rate proportional to oxygen at the surface, and implies that the differences in surface structure are of no importance since the rate is expressed in terms of external geometric surface area". They could also have added that such an expression takes no account of particle size.

Smith I.W. (1971a and 1971b) and Hamor et al. (1973) calculated the chemical rate constants of size graded fractions of several types of coal by measuring the progressive burnout of the particles in
electrically heated, tubular reactor. The overall reaction rate, $R_m$, was determined from successive $\mathrm{CO}_2$ measurements in the reactor. The diffusional component of this rate was calculated from:

$$R_{m, D} = \frac{3.37 \times 10^{-5} \left[ \left( \frac{T_p + T_g}{2} \right) \right]^{0.75}}{d^2 \sigma_A}$$

(2.14)

where $R_{m, D}$ = diffusional rate constant based on mass (g/g. s. atm O$_2$)

$T_p$ = particle temperature, K

$T_g$ = gas temperature, K

$d$ = particle diameter, $\mu$m

$\sigma_A$ = particle density, g/cm$^3$

The chemical rate constant was then calculated from

$$R_{m, C} = \left[ \frac{R_{MD} \cdot R_m}{R_{MD} - R_m} \right]^n \left( \frac{g_m}{g_m} \right)^{1-n}$$

(2.15)

where $g_m$ = reaction rate, g/g. s.

$n$ = reaction order (assumed to be unity)

The conclusions of this work were that the chemical reaction rate could be expressed by an Arrhenius type equation:

$$R_{A, C} = A \exp \left[ - \frac{E_A}{RT_p} \right]$$

(2.16)

The measured values for the pre-exponential factor, $A$, and the apparent activation energy $E_A$, are given in Table (2.6).
These workers suggested that, in the absence of restrictions by external diffusion, three rate controlling regimes can be distinguished.

(i) Reaction proceeds uniformly throughout the pore structure and rates are entirely chemically controlled. Particles would then be observed to react with decreasing density and substantially constant diameter.

(ii) As reaction rates increase the rate becomes controlled by the combined effects of chemical reaction and pore diffusion, and owing to the depletion of reactant gas the reaction occurs more slowly near the centre of the char than at the outside. Particles react with a decrease in size and in density although the latter is less than in the first regime.

(iii) At increased reaction rates the consumption of reactant gas occurs without any appreciable penetration into the pore structure. Particles are burnt at constant density.

Based on measurement of density and diameter against burnout Smith and co-workers concluded that the second regime was applicable to most of their results. The few exceptions were brown coals at temperatures less than 650°C which burn according to regime (a) and all coals at particle sizes above 77μm. External resistance to diffusion was important with larger particles, whereas particles of less than 4μm burned according to regime (c).
Evaluation of chemical reaction rate based on external surface area requires a knowledge of the relationship between particle diameter, particle density and burnout. The same is true in the evaluation of particle surface temperature by energy balance. Regime (a) can be represented by the relationship:

\[ \sigma_A = \sigma_{A,0} (1 - U) ; d = d_0 = \text{const} \]  \hspace{1cm} (2.17)

where \( \sigma_A, \sigma_{A,0} \) = particle density
\( U \) = burnout
\( d, d_0 \) = particle diameter

Regime (c) can be represented by

\[ d = d_0 (1 - U)^{1/3} ; \sigma_A = \sigma_{A,0} = \text{const} \]  \hspace{1cm} (2.18)

Regime (b) is an intermediate between these two extremes. Smith and co-workers assumed the relationship of equation 2.17 to analyse the majority of their results, even though experimental measurements indicated that this was not correct. For semi-anthracite, it was found that the relationship

\[ d = d_0 (1 - U)^{1/4} \]  \hspace{1cm} (2.19)

gave a closer fit to the data. The assumption of a mechanism prior to calculation of results could have introduced errors into the calculations of diffusion rate coefficient, chemical rate coefficient and particle temperature.

Beer et al (1964) determined the combustion rates of polydisperse suspensions of anthracite (98% < 124\mu m, 50% < 49\mu m) over the range of gas temperatures, \( T_g \), 1493 - 1766 K. The results were fitted to the equation:

\[ R_{A,C} = \frac{199}{N T_g} \exp \left[ - \frac{18900}{R T_g} \right] \]  \hspace{1cm} (2.20)
This equation gives values for $F_{A,C}$ which are an order of magnitude lower than those of the previously mentioned workers.

In conclusion, it may be said that all mathematical models of pulverised coal combustion vary in specific details, some of which have been mentioned, but all are similar in so much as they include assumptions about the physical and chemical processes that occur which are not supported by experimental results. Field et al. (1967) referred to this as "restricted modelling of particle combustion". Such simplifications include: consideration of only a few of the possible gas and solid chemical reactions; consideration of the char combustion stage only; assumptions about particle structure; assuming the combustion chamber to be a stirred tank (Beer and Lee, 1964); assumptions of isothermal heat transfer (Hottel and Stewart, 1940); and assumptions of adiabatic heat transfer (Hedley and Jackson, 1966). Such models have been published frequently and are too numerous to be reviewed profitably in this text.

2.2.3 Liquid Fuels

The combustion behaviour of liquid fuels is as pertinent to a discussion of coal slurry fuels as the behaviour of solid particles. Coal slurry fuels, whether they be burned in conventional flames, or in fluidised bed combustors, must first be atomised into a spray of droplets and behave as liquid fuels for at least the first part of their combustion history.

Several reviews of the extensive literature, which dates from the beginning of the century, have been published on atomisation (e.g. Chigier, 1976) and combustion of liquid fuels (Hedley et al., 1971, Williams, 1973, and 1976). Atomisation characteristics are considered to be outside the scope of this study, as indeed is the majority of the previous work on liquid fuel combustion. Previous theoretical analyses and combustion mechanism studies have largely concentrated on single component, low molecular weight fuels.

Williams (1973) described several theoretical analyses which were all based on the spherico-symmetrical, diffusion controlled model of combustion of a droplet in an oxidising atmosphere. Each droplet is
considered as being a discrete, burning component of the flame, even though this may not be the case in dense sprays where evaporation of volatiles to the spray boundary followed by combustion may be the dominant mechanism. However for isolated droplets the mass burning rate can be related to the rate of decrease in droplet size by the "d2-law"

\[
\frac{d (d_L)^2}{dt} = - \frac{2 \dot{m}_F}{\pi \rho_L r_L} = K
\]  

(2.21)

where \(d_L\) and \(r_L\) are the droplet diameter and radius, \(\rho_L\) is the liquid density, \(\dot{m}_F\) is the mass burning rate and \(K\) is the burning constant for droplets surrounded by a flame or the evaporation constant when an envelope flame is absent. By solving the continuity equations for global mass conservation, species mass conservation, energy conservation and the equation of motion with the assumption of quasi-steady state (thus the time dependent terms become zero) and infinitely fast reaction rate, Spalding (1955) derived the following expression for burning rate coefficient.

\[
K = \frac{8\lambda}{C_p \rho_L} \ln (1 + B)
\]  

(2.22)

\(\lambda\) = vapour thermal conductivity
\(C_p\) = specific heat of vapour at constant pressure
\(B = \frac{H M_{O_2} + C (T_g - T_s)}{Q r + Q} = \) the transfer number

(2.23)

\(H\) = calorific value of fuel
\(M_{O_2}\) = weight concentration of oxygen in the gas
\(Q\) = heat reaching droplet surface/unit mass of fuel evaporated
\(T_g, T_s\) = temperature of gas and droplet surface
\(r\) = stoichiometric mixture ratio

Equation (2.22) is based on temperature independent transport properties and a value of unity for the Lewis number.
Williams (1973) also described the work of several other authors in this field in which temperature dependent transport properties were used (Kassoy and Williams, 1968), finite chemical kinetics were considered (Agafanova et al., 1958), non-steady state heat and mass transfer equations were solved (Kotake and Okazaki, 1969) and the influence of a weak velocity field were included. In general, the increased complexity of the analyses does not alter the mass burning rate relationship given by the quasi-steady state, infinite kinetics model except under extreme conditions of droplet size and pressure, although convective transport was found to augment the purely diffusion controlled rate of combustion.

Most theoretical models are generally only applicable to the zero convection case and in most cases it is necessary to apply a correction factor to the theoretical burning rate coefficients to account for the influence of gas flow, i.e.

\[ K = K_0 [1 + f(Gr, Sc, Le)] \] (2.24)

for natural convection and

\[ K = K_0 [1 + f(Re, Pr, Sc)] \] (2.25)

for forced convection. Here Gr, Sc, Le, Re and Pr are the Grashof, Schmidt, Lewis, Reynolds and Prandtl numbers, respectively. Several empirical relationships have been proposed in this form.

\[ \dot{m}_f^{\text{(forced)}} = \dot{m}_o [1 + 0.276 Re^{1/2} Sc] \] (2.26)

(Prossling, 1938)

\[ \dot{m}_f^{\text{(forced)}} = \dot{m}_o [1 + 0.3 Re^{1/2} Pr] \] (2.27)

(Ranz and Marshall, 1952)

\[ \dot{m}_f^{\text{(forced)}} = \dot{m} [1 + 0.24 Re^{1/2}] \] (2.28)

(Agoston et al., 1957)

Aerodynamic data, such as droplet drag coefficients, was also identified as being essential in the calculation of spray penetration and droplet movement in combustion chambers.
Masdin (1961) showed that the burning rate coefficient for droplets burning in air was higher than the constant for droplets evaporating in hot nitrogen. It was therefore concluded that progressive vitiation of combustion air in flames caused progressive reduction of burning constant. Masdin and Thring (1962) also addressed the problem of measuring burning rate coefficient for the residual fuel oils using a single droplet technique. Here the "d^2-law" no longer applied to the entire droplet lifetime. After the initial heating, distillation and ignition period the usual envelope flame was established. However, during the subsequent combustion, swelling and contraction of the droplet occurred the surface became more viscous until finally a non-volatile solid residue was formed by cracking of the liquid hydrocarbons. The solid residue burned away more slowly by heterogeneous surface reaction. The burning time for the entire droplet was correlated with initial diameter by considering the two stages separately

\[ D_0^2 = K_v t_v + K_c t_c \]  

where \( K_v \) = volatile burning constant (0.0113 cm^2 sec^-1 at \( T_c = 600 - 800°C \)), \( K_c \) = cenosphere burning constant (0.0025 cm^2 sec^-1 at 890°C), and \( t_v \) and \( t_c \) are the volatile and cenosphere combustion times.

However these relationships appear to be based on very few results and take no account of the type of heavy fuel oil. It has been observed that droplet "splashing" occurs during the ebullition period of some fuel oils, which would also cause a decrease in droplet size.

Lightman and Street (1961) examined the effects of asphaltenes content in the heavy fuel oil on coke formation and structure. Fuels of high asphaltenes content were more liable to form large thin-walled cokes whereas low asphaltene fuels produced relatively thick-walled cokes of much smaller diameter than the original droplet, and a lower carbon content than the high asphaltene fuels. However the higher the asphaltene content the lower the mechanical mass loss during droplet ebullition (Street, 1981). Substantial mass loss occurred during the boiling of some maltene fractions.
2.2.4 Coal Slurry Fuels

The combustion mechanisms of coal slurry fuels has been the subject of several qualitative and quantitative studies during recent years. The experimental techniques which have been used for such studies are not novel, and the subsequent theoretical analyses have drawn heavily on experience gained from coal particle and oil droplet combustion investigations. Most authors are agreed that coal slurry droplet combustion is similar to that of coal particles and heavy fuel oil droplets in that it takes place in two distinct, or slight overlapping stages; firstly, devolatilisation and combustion of the gaseous volatiles, followed by combustion of the solid carbonaceous residue or char. Qualitative studies have established that the solid particles within each droplet agglomerate to some extent during devolatilisation, and it is the behaviour of this agglomerate which has solicited most attention.

Miyasaka and Law (1980) used a free-falling droplet technique to examine the behaviour of COMs, containing 10 - 30 wt% coal, during combustion. They concluded that, "it is very likely that agglomerates form during the burning of COM", and that oil type has a significant effect on the structure and burnout of these agglomerates. Their experiments show that char formation and ignition occur faster with No. 6 fuel oil that with No. 2 fuel oil (diesel fuel). The explanation for this was that the heavier liquid fuel reached a much higher temperature during the devolatilisation stage than the lighter oil. This caused COMs made with lighter oils to form initial chars containing lightly-fused and virtually unreacted coal particles, whereas chars formed from heavy oil COMs consist of well-fused coal particles covered by a layer of oil coke. This dependence of char structure on devolatilisation temperature history could be of considerable importance when coal-water or coal-oil-water fuels are considered. However, Miyasaka and Law only considered one type of coal (Pittsburgh seam coal), and their experimental technique employed particularly large droplets (600 - 1000 μm), which could give a false impression of the temperature history of smaller droplets.

Braide et al. (1979) used a single suspended droplet technique to investigate the combustion of coal-oil fuels containing 20 wt% coal in medium fuel oil. Three coals were used, corresponding to NCB ranks
101, 501 and 802. Agglomeration of the coal particles occurred in each case, although no details were given on the structure of the agglomerates. However, the initial size of the chars was dependent on coal rank. Mid-rank coal produced chars which were approximately 25% larger in diameter than the non-swelling anthracite fuels, despite having a much higher volatile content (34.4 wt% for 501, 5.7 wt% for 101). There was obviously a large density, and thus structural, difference between the two chars.

Alabaf et al. (1981) sampled solid particles from the flue gases of 101, 301 and 502 COD flames. Electron micrographs of these samples showed distinct structural differences, which were a function of coal rank. The anthracite chars were not well-fused, had a complicated internal structure, and had not undergone swelling. The 301 and 501 rank dispersions formed chars which were well-fused, hollow, and swollen. This effect was more noticeable with the medium volatile 301 coal than with the high volatile 502 coals. It was also noted, in this study, that the mean particulate diameter (72 - 95 μm) was, in all cases, much larger than the mean coal particle diameter (< 10 μm).

Pourkashanian and Williams (1983) reported the result of single droplet experiments on CWM fuels. They concluded that the mechanism was similar to that of very heavy fuel oil, and that coal particle agglomeration caused significant differences between CWM and p.f. combustion. A similar technique was used by Matthews and Street (1984) to investigate CWM droplet combustion mechanisms. The results of this work were compared with samples taken from two points in CWM flames, and good agreement of results was obtained. They observed similar mechanisms to those described by other workers for coal-oil fuels: "The devolatilisation behaviour followed a clearly defined pattern which depended on the rank of the coal. In all cases the individual coal particles were found to adhere together, but in the case of low rank coals (high volatile, low swelling index) fusion was less pronounced than in the case of mid-rank coals. Subsequent burning was influenced both by the extent of particle aggregation, and the particle reactivity; the latter is known to be a function of coal rank."

Photomicrographs of cross-sections of solids taken from the flame at two sampling points illustrated three types of char structure which, as with coal particles, were labelled, 'C-shaped', 'balloon-shaped' and 'lacy' spheres. The 'C-shaped' particles were more commonly observed
than the other two, and were generally somewhat larger.

Unchangedcoal particles were observed even at the tail end of the
flame. Only mid-rank coals (301b, 401, 501) were used in this section
of the work, and it is therefore difficult to assess whether these
structures were dependent on coal rank, or some other variable such as
initial droplet size, coal maceral type, or temperature and mixing
histories.

There does, however, appear to be an anomaly between the single droplet
results, published by Matthews and Street, and the author's results
from a similar study on coal-oil fuels (Lapwood, Street and Moles,
1981) which forms a part of this thesis.

The CWM chars have been observed, in both cases, to be oxidised in one
of two ways; either by slow, constant erosion in the vicinity of
surface blowholes, or by the unfolding of large lumps of char residue
from the surface. In the former case char combustion continued at
almost constant diameter, with slight fragmentation, until the ash
residue finally collapsed. In the latter, the structural disruption of
the residue caused its diameter to vary significantly as the surface
unfolded, and as large fragments of loose material broke away. The
anomaly arises from the types of coal which are associated with these
two mechanisms. Matthews and Street showed that mid-rank CWM chars
tended to unfold, whereas low-rank chars burned at constant diameter.
The results of Lapwood et al., and further results in this thesis, show
that the reverse is true for coal-oil fuels. That is to say that the
unfolding and platelet fragmentation behaviour is typical of high and
low rank COM's, whereas mid-rank COM's erode slowly at the surface
blowholes for most of the droplet's lifetime.

Yao and Lin (1983) conducted single droplet experiments on CWM fuels
containing mid-rank coal and lignite in order to investigate
evaporation and heating effects. They observed swelling in both cases
but no droplet disintegration and concluded that the non-caking lignite
was likely to burn faster because it agglomerated less. However,
disruption of the droplet surface did occur during heating and was
explained using a simple drying theory which assumed that the outer
droplet surface could fuse before the inner core had dried completely.
This mechanism could explain the surface disruption effects noticed by Matthews and Street (1984) and Lapwood and Moles (1983) which were described as “wormcasts”.

Figure (2.4) Combustion Model of CWM (After Sakai et al., 1981)

Sakai et al. (1983) presented a theoretical model for CWM droplet combustion [Figure 2.4] in which droplet heating rate and droplet size were important variables. However very large droplets (3000 μm) were used in this investigation and the heating rates cannot be considered to be representative of those in a real furnace.

Jenkins D.P. (1983) and Kikkawa et al. (1984) emphasised the importance of coal particle size in COM and CWM droplet combustion mechanisms. Kikkawa et al. compared two CWM fuels with different particle size distributions. They described these two distributions using Gaudin-Schuman plots with distribution moduli of 0.4 and 0.8. These correspond approximately to 70 wt% < 48 μm and 70 wt% < 80 μm respectively. The combustion efficiency was nearly 4% higher for the 0.4 distribution than for the 0.8 distribution when a mid-rank CWM was burned. This implies that smaller coal particles lead to higher combustion efficiency in spite of the fact that the particles agglomerate.
Jenkins D.P. (1983) proved that the closeness of coal particle size
distribution and droplet size distribution could cause significant
numbers of free coal particles to be formed in the fuel spray. His
reasoning was purely statistical and took no account of inter-particle
forces or surface tension effects. However, this work does raise a
question mark over previous mechanism investigations. It is a
possibility that coal particles can separate and burn individually, a
fact which is not apparent in single droplet investigations since the
initial droplet size is normally much larger than the average coal
particle size.

The combination of both liquid and solid fuels, structural complexity
and varying degrees of particle agglomeration have combined to make
attempts at quantifying or mathematically modelling coal slurry fuel
burnout behaviour a difficult undertaking. Cossee and Hedley (1983,
1984) based their analysis of COM char combustion on the work of Field
et al. (1967) which was discussed in Section (2.2.2). Char particles
were assumed to be spherical and reaction rate controlled by a
combination of diffusion of oxygen to the particle surface and first
order chemical reaction with respect to oxygen. The reaction rate was
based on external surface area alone, and coal reactivity was accounted
for by using the empirical parameters recommended by Field (1970).
Particle temperature was calculated by using iterative techniques to
solve the heat balance.

\[ R_A = \frac{Q}{\Delta A} = \frac{Nu \cdot \lambda (T_S - T_g) + \varepsilon (T_S^4 - T_w^4)}{T_g} \]  \hspace{1cm} (2.30)

\( R_A \) = reaction rate

\( Q \) = heat of reaction at particle surface

\( Nu \) = Nusselt number; assumed to be 2

\( \lambda \) = thermal conductivity

\( T_S \) = particle surface temperature

\( T_g \) = gas temperature

\( T_w \) = furnace wall temperature

\( \varepsilon \) = particle emissivity; assumed to be unity

\( \sigma \) = the Stefan-Boltzmann constant.
Using the 'restricted model', Cossee and Hedley showed that the following parameters were important in determining combustion efficiency:

(a) Coal reactivity
(b) Char density
(c) Yield and size distribution of chars

The physical combustion mechanism was accommodated by using either constant density or constant size expression (Eqs. 2.17 and 2.18), or an intermediate mode in which change in density was assumed to be proportional to the fraction of the overall combustion resistance that was contributed by chemical factors alone:

\[ d_n = d_i \left[ \frac{(1 - R_m \cdot \Delta t)}{(1 - R_m \cdot \Delta t \cdot \frac{K_n}{K_s})} \right]^{1/3} \]  \hspace{1cm} (2.31)

\[ \rho_n = \rho_i \left[ 1 - R_m \cdot \Delta t \cdot \frac{K_n}{K_s} \right] \]  \hspace{1cm} (2.32)

where \( d_i, d_n \) = particle diameter at time \( t \) and \( t + \Delta t \) respectively, \( m \)
\( \rho_i, \rho_n \) = particle diameter at time \( t \) and \( t + \Delta t \) respectively, \( \text{kg/m}^3 \)
\( \Delta t = \text{time interval, s} \)
\( \frac{K_n}{K_s} = \text{fractional resistance to chemical control} \)

Jenkins B.C. (1981, 1983) employed the same char combustion equations as Cossee and Hedley, but he also included combustion rate terms for soot (Eq. 2.6) and for gaseous volatiles:

\[ q_{\text{vol}} = \frac{4 P_{O_2} \cdot \rho_g D}{\rho_g \cdot d_v} \]  \hspace{1cm} (2.33)

\( q_{\text{vol}} \) = mass burning velocity of volatiles
\( P_{O_2} \) = partial pressure of oxygen
\( \rho_g \) = gas density
\( D \) = diffusivity of oxygen in nitrogen
In this work the temporal equations for combustion rate were combined with the spatial equations for jet aerodynamics and combustion heat transfer in order to produce a mathematical model of a COD and COM flames. This involved calculating droplet and particle velocity throughout the flame by balancing the momentum forces of the particle against the drag forces acting on it. The model was particularly sensitive to droplet size distributions, an effect which was used to account for physical differences in char combustion mechanism. The coal particles were assumed to either completely agglomerate and form a residue which was approximately the same size as the initial droplet, or they did not fuse at all and disintegrated to form chars the same size as the original coal particles [Figure 2.5]. The decision as to which of these two extremes of behaviour was used was dependent on coal rank. The results of the model showed "encouraging agreement for COD and COM fuels".

Figure (2.5) Combustion Model of COD (After Moles et al., 1981)
Braide (1980) considered how the liquid phase affected COM droplet combustion. The results of several single droplet and mass-loss history experiments showed that there were significant differences between the rate of COM devolatilisation and that of the base fuel oil alone. The combustion characteristics of COM droplets were shown to depend on their coal content, type of coal, the degree of internal recirculation and the augmentation of heat transfer to the droplet by the added coal. For the same mass concentration of coal in COM droplets there was no appreciable difference in mass-loss characteristics between different types of coal. Therefore an equation was developed which expressed the initial char mass in terms of furnace temperature and coal particle concentration.

\[ M_{\text{res}} = 396.14 \cdot b^{0.659} \cdot \exp (-0.00653 \cdot T) \]  \hspace{1cm} (2.34)

For \( 673 < T < 823 \) K

where

\[ M_{\text{res}} = \frac{\text{mass of residue x 100}}{\text{mass of original COM}} \]

\[ b = \frac{\text{mass of coal particles in COM x 100}}{\text{mass of original COM}} \]

\[ T = \text{furnace temperature}, \text{ K} \]

This implies that increased furnace temperature causes increased cracking of the liquid fuel, but does not cause the coal particles to devolatilise. However, this is unlikely to be the case at the temperatures and heating rates found in turbulent diffusion flames since substantial devolatilisation and plasticisation of swelling coals occurs in the range 673 - 823 K (Van Krevelen, 1957). Based on this experimental evidence, a temperature dependent kinetic scheme for RFO and COM combustion was proposed which was based on a thermal cracking sequence. This was essentially a set of successive 1st order equations which applied to successive decomposition reactions in the cracking sequence. Braide also considered the fluid mechanical variables which influence the disruption of droplets during devolatilisation, and developed a hydrodynamic model to predict the onset of microexplosions within the bulk liquid. The approach was also adopted by Law, in his analytical treatments of the combustion of liquid fuels (1976a, 1976b,
1977), coal-oil fuels and coal-oil-water fuels (1979b). He identified
two limits of behaviour for the combustion of fuel droplets which were
a function of the intensity of internal convection.

In the so-called rapid-mixing limit, internal recirculation is of
sufficient intensity to maintain uniform temperature and concentration
profiles within the droplet. Vapourisation in this case is analogous
to batch distillation with the more volatile components constantly
being preferentially vapourised at the surface, and the droplet
becoming more concentrated in the less volatile components. In a COM
droplet, since coal is essentially non-volatile compared with oil, a
large agglomerate will eventually form consisting of unreacted coal
particles. However, if the intensity of internal recirculation is
weak, diffusion, rather than convection, will be the dominant transport
mechanism. Since the rate of thermal diffusion is one to two orders of
magnitude greater than the rate of mass diffusion, pockets of volatile
gases could form inside the droplet which in could cause partial or
complete fragmentation of the droplet. This is especially true when
solid particles are present to act as heterogeneous nucleation sites for
initiation of internal boiling. This mechanism is more likely to occur
with small droplets in which interfacial shear is low, and with viscous
liquids. These both tend to decrease internal recirculation. It is
also necessary that there be high and low boiling point components in
the liquid phase.

In COW fuels the water content both increases liquid phase viscosity
and provides an immiscible, low boiling point component within a high
boiling point mixture. Law reports catastrophic explosions in COW
droplets containing 5 vol% water.

Szekely and Faeth (1981) developed a model to predict the temperature
and diameter of droplets of carbon slurry during combustion. Their
analysis consisted of both liquid gasification phase and agglomerate
reaction phase. During the latter reactions of carbon with oxygen,
carbon dioxide and water vapour were considered. They found that
convective heat and mass transport measurements were much higher than
those predicted for smooth spheres. This was attributed to the fact
that droplets have an open porous structure near the surface, providing
roughness effects and allowing surface flow penetration. This
enhancement of convective transport rates was accommodated in the model by multiplying the Nusselt and Sherwood number by an enhancement factor:

\[ Nu \text{ or } Sh = \delta (Nu' \text{ or } Sh') \]

where \( Nu' \), \( Sh' \) = Nusselt and Sherwood number
\( Nu, Sh \) = Modified Nusselt and Sherwood numbers
\( \delta \) = enhancement factor = 6.7

Furthermore, they included an empirical area/reactivity factor in their surface reaction equations to account for the effects of surface porosity, reactivity and catalytic action. The expression for mass burning rate was given by:

\[
K = \frac{r_p a R}{\rho D}
\]

\( K \) = mass burning rate
\( r_p \) = particle radius
\( \rho \) = density
\( D \) = effective binary diffusivity
\( R \) = reaction rate constant
\( a \) = area/reactivity factor

\( a \) was always greater than unity due to the surface structure. The model results compared well with experimental results obtained from a single droplet apparatus.

Cen Kefa et al. (1983) presented an analytical model of CWM droplet combustion which incorporated three stages; water evaporation, devolatilisation and char combustion. The model can be summarised using the following equations, together with a particle heat balance (Eq. 2.30).

\[
\frac{d G_w}{d \tau} = - 4\pi r_p^2 R_w
\]

\[
\frac{d G_v}{d \tau} = - R_v G_o
\]
The model gave a good fit to experimental data, and showed that the porosity of the carbon residue decreased the activation energy of the coke below that of the raw coal, thus accelerating combustion. Devolatisation was also facilitated by the porous structure left after evaporation of the water.

These equations were found to give a good fit to experimental data obtained from 60 wt% CWS droplets, 2000 μm in diameter. It was assumed that the equations also applied to smaller droplets and, based on this assumption, evaporation time was found to account for 1.2 - 1.4% of the droplets' lifetime at 1600°C.
Volatile release rate was calculated using an Arrhenius type equation:

\[
\frac{dV}{dt} = R_v = K_v \exp \left( \frac{-E_v}{RT} \right) (v^F - v)
\]  

(2.42)

2.2.5 The Effects of Water on Combustion

It has long been known that the addition of water, in various forms, to combustion systems has a marked beneficial effect, particularly in the reduction of unburnt carbon emissions. Water can participate in the combustion of both gaseous and solid fuels, but its effect on droplets of liquid fuel in fuel sprays has attracted most experimental effort and commercial interest. Reductions in carbon emissions of up to 62% were reported in trials of steam raising boilers by Holling (1977), and fuel savings of up to 8% were obtained in diesel engines (Katsoulakos, 1983) with the addition of up to 10% of water. The fuels used in most of the previous trials have been emulsions of water droplets in oil although this is not the only way in which water can be added.

Twin-fluid atomisers, which are commonly used in oil-fired furnaces to produce a spray of fuel droplets, generally use either steam or air as the atomising medium. It has been reported (Jordan and Williams, 1979) that the use of steam as opposed to air in such atomisers reduces smoke and particulate emissions. However previous work by Hubbard (1959) indicated that the reverse was true. This indicates one of the most severe difficulties in assessing the effects of water on combustion mechanisms. It is often impossible to ascertain whether reductions in carbon emissions have been caused by physical effects, such as more efficient atomisation causing smaller droplets, or by chemical effects, such as the water gas shift reaction (Table 2.5, Eq. 6) in the case of steam atomising and increased availability of oxygen in the case of air atomising. In order to overcome this difficulty most mechanism studies of fuel oil/water emulsions have involved the use of single droplet techniques.

Several mechanisms have been proposed for the reduction in carbon emissions by fuel oil/water emulsion firing:

(a) Microexplosions resulting in secondary atomisation
(b) Increased droplet swelling resulting in a more porous and easily combustible oil coke

(c) Enhanced radiative heat transfer to the droplet

(d) Chemical reaction between water and the carbonaceous residue  
(Table 2.5, Eq. 5)

(e) Water gas shift reaction

(f) Catalysis of the $\text{CO} \rightarrow \text{CO}_2$ reaction.

Of these, secondary atomisation caused by 'micro-explosions', a term first used by Ivanov and Nefadov (1965) appears to be the most fashionable. The mechanism was described in detail by Law (1976a): "An interesting phenomenon has been postulated to occur during combustion of high boiling point fuel emulsified with water. It is suggested that since the droplet can sustain very high temperatures during combustion the embedded water micro-droplets may easily be heated beyond boiling point and may reach superheat. At this temperature for a given pressure homogeneous nucleation occurs and the water subsequently boils disruptively. The disintegration of the parent droplet essentially constitutes a secondary atomisation producing droplets of very fine sizes which can be readily vapourised. Furthermore, the severity of the liquid phase coking process is reduced because of a much shortened droplet lifetime available for pyrolytic reactions to proceed and also because of the upper boundary placed on the droplet temperature by the limit of superheat. Violent disintegration promotes better mixing by dispersing the droplets into a larger volume".

A wealth of experimental evidence documenting the existence of these microexplosions may be found in the literature (Dryer, 1975, Gollahalli, 1979, and Jordan and Williams, 1981), but this is almost entirely restricted to single droplet studies in which the droplet sizes were large, in comparison with those found in flames, and in which the support filaments can provide sites for heterogenous nucleation. Cunningham et al. (1983) drew attention to some apparent anomalies which arise from the theoretical studies which have been done on this subject: "If conditions are conducive to microexplosions, then explosions can be expected to occur on a very fast timescale
(micro-rather than milliseconds). For power station-sized atomisers this would imply disruption of the initial oil sheet, rather than subsequent microexplosions of oil droplets. However explosion delays could occur due to the finite time required for nucleation and bubble growth.

Jaques (1975, 1977) argued that microexplosions alone could not account for reductions in soot concentration and examined the effects of water on liquid-phase thermal cracking. He concluded that the cooling effect of water evaporation leads to lower temperatures within the droplet, so that the extent of the cracking reactions and subsequent solids formation is reduced. However, the modelling approach used by Jaques has been criticised (Law, 1976) as being too simple to be realistic since all the water was assumed to stay within the droplet until it had been fully vapourised at which point it left instantaneously allowing the rapid rise in droplet temperature. In his own work, Law (1976) maintained that the degree of internal recirculation within the droplet was an important factor and described a model based on the two limits which have previously been described [i.e. the rapid mixing limit (Lewis No = 1) and the quiescent limit (Le >> 1)]. In the first instance the thermal diffusivity is equal to the mass diffusivity and microexplosions do not occur, in the second thermal diffusivity is greater than mass diffusivity thus allowing disruptive boiling.

Jordan and Williams (1981) stated that the addition of 5% water to 950 Redwood No. 1 fuel oil causes the amount of radiative heat absorbed by a typical fuel spray sized droplet to be doubled. This would cause a more rapid rise in emulsion droplet temperature, and perhaps promote more efficient devolatilisation, although this does not appear to be consistent with the mechanism proposed by Jaques (1977).

In recent years, the chemical effects of water on combustion have largely been overshadowed by work on physical phenomena. It is well known that the hydroxyl radical, OH, is important in carbon (especially soot) combustion. A comprehensive review of the chemical mechanism of this reaction was presented by Walker et al. (1959). However, it has been argued by most workers that since the water present in a fuel oil/water emulsion produces negligible increase in the concentration of water vapour in the combustion products (< 1% for stoichiometric combustion of a 10 wt% emulsion) the chemical reaction mechanism is
unlikely to account for the observed reductions in emissions. Cunningham et al. (1983) sprayed steam directly into a fuel oil flame and observed no significant decrease in unburnt carbon. It is also true that the rate of chemical reaction of carbon with water is very much lower than that of carbon with oxygen (Table 2.7).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Relative Rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C - O_2$</td>
<td>$1 \times 10^5$</td>
</tr>
<tr>
<td>$C - H_2O$</td>
<td>3</td>
</tr>
<tr>
<td>$C - CO_2$</td>
<td>1</td>
</tr>
<tr>
<td>$C - H_2$</td>
<td>$1 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Table 2.7 Approximate Relative Rates of Gas-Carbon Reactions at 800°C and 0.1 Atm. Pressure (After Walker et al., 1959).

However it has been argued that, although there is little water present, that which is available occurs in the 'right place at the right time' (Dryer, 1977).

Arthur (1949) presented evidence which suggested that very small amounts of water could catalyse the conversion of carbon monoxide to carbon dioxide. Wicke (1954) reported the effects of passing moist and dry air through beds of carbonaceous material. No appreciable difference was observed between the wet and dry air at low temperatures (647°C) but at 830°C the $CO/CO_2$ ratio was approximately six times larger for dry air than for wet (dry air, $CO/CO_2 = 3.58$; wet air, $CO/CO_2 = 0.59$). This suggests that the oxidation of carbon monoxide to carbon dioxide was catalysed by the water vapour, or the carbon monoxide reacted with water to produce carbon dioxide (water gas shift reaction).
SECTION 3

THEORETICAL ANALYSIS OF THE COMBUSTION OF A SINGLE DROPLET OF COAL SLURRY FUEL.

3.1 The Mathematical Model

The results of other workers, and the experimental results presented in this thesis demonstrate that the relationship between the structure of the carbonaceous residue which is left after devolatilisation, and its subsequent burnout mechanism is very significant. The burnout vs. time results for all of the fuels tested suggest that the reaction rate is neither controlled by external diffusion of gaseous reactant to the particle surface, nor by the rate of chemical reaction at that surface. The evidence points to the occurrence of internal reaction, which in turn implies that internal diffusion is a relevant factor. It is thought unlikely that the gaseous reactant must first diffuse through an inert ash layer to react at the outer surface of a shrinking carbon core since there was very little ash present in any of the fuels tested. It is therefore suggested that the resistance to reaction is a combination of diffusion through the porous solid reactant, and chemical reaction on the internal pore surfaces. If this is so, the dependence of reaction rate on char structure is likely to be equally important in other fuels which form solid residues during combustion, such as pulverised coal and heavy fuel oil.

In order to test this hypothesis an attempt has been made to mathematically model the structural behaviour of carbonaceous chars during combustion. The model is an adaptation of the porous solid reaction model proposed by Petersen (1957), which has the advantage of simulating changes in internal surface area as the porosity increases due to reaction.

The unsteady state equation describing the simultaneous reaction and mass transport in a porous solid is:
\[
\frac{\partial C}{\partial t} = - \text{div}(-D \text{ grad } C) - \text{div}(uC) - S_v R' \quad (3.1)
\]

**diffusive transport**  **convective transport**  **chemical reaction**

Petersen assumed that the solid contained an idealised network of cylindrical pores with random intersections (Figure 3.1).

![Figure 3.1 Idealised Structure of Porous Solid](image)

The rate of reaction per unit volume for such a system is given by

\[
\frac{\rho_s}{b} \frac{dS_v}{dt} = \frac{\rho_s}{b} \frac{d\varepsilon}{dt} \quad (3.2)
\]

thus

\[
S_v = \frac{d\varepsilon}{dr} \quad (3.3)
\]

The radius of the pores depends on the rate of internal reaction.
Therefore equations (3.1) and (3.4) must be solved simultaneously, which requires that a relationship between $S_v$ and $r$ be derived.

From Figure (3.1), the length of the pore system per unit volume of solid is defined as the sum of the centre line distances.

$$L = ac + bc + cd + gh + \ldots$$

There are $N$ pore intersections per unit volume. If the pores enlarge uniformly then the surface area of the smooth pores of radius, $r$, is given by:

$$S_v = 2\pi r \left[ L - r \sum_{i=1}^{N} \frac{1}{\sin \phi_i} \right] - r^2 \sum_{i=1}^{N} \beta(\phi_i) \quad (3.5)$$

The second term of the right accounts for the area of the openings in the pore walls and $\beta(\phi_i)$ is the shape factor of the $i^{th}$ intersection, which is based on the angle $\phi_i$.

The term

$$\sum_{i=1}^{N} \frac{1}{\sin \phi_i}$$

accounts for the shortening of the actual length of the pore as the intersection enlarges. If no new intersections are produced, the terms

$$\sum_{i=1}^{N} \frac{1}{\sin \phi_i} \quad \text{and} \quad \sum_{i=1}^{N} \beta(\phi_i)$$

are constants for a given solid. Equation (3.5) becomes

$$S_v = 2\pi r (L - Ar) - Br^2 \quad (3.6)$$

Combining equations (3.3) and (3.6):-

$$\frac{dr}{dt} = \frac{bMkC^n}{\rho_0} \quad (3.4)$$
Integrating:
\[ \varepsilon = \pi r^2 l - \left[ \frac{2\pi A + B}{3} \right] r^3 \]

Therefore:
\[ \frac{\varepsilon}{\varepsilon_0} = \frac{\pi r^2 l - \left[ \frac{2\pi A + B}{3} \right] r^3}{\pi r_0^2 l - \left[ \frac{2\pi A + B}{3} \right] r_0^3} \]

or \[ \frac{\varepsilon}{\varepsilon_0} = \zeta^2 \frac{(G - \zeta)}{(G - 1)} \]  

where \( G = \frac{3\pi L}{r_0 (2\pi A + B)} \) and \( \zeta = \frac{r}{r_0} \)

\( G \) can be evaluated if equation (3.7) is valid for \( \varepsilon = 0 \) to 1. As \( \varepsilon \to 1 \), \( S_V \to 0 \). Therefore:
\[ S_V = \frac{d\varepsilon}{dr} = \frac{d\varepsilon}{r_0 \zeta} \left[ \frac{\varepsilon_0}{r_0} \right] \frac{(2G - 3\zeta)\zeta}{(G - 1)} \]  

\[ \zeta \bigg|_{\varepsilon = 1} = \frac{2}{3} G \]  

Substituting equation (3.9) into equation (3.7) gives
\[ \frac{4}{27} \varepsilon_0 G^3 - G + 1 = 0 \]  

Thus \( G \) is a function of \( \varepsilon_0 \) and may be obtained by evaluating the positive root of equation (3.10).

The following restrictions are applied to the system:

(a) The convective term in equation (3.1) is negligible because the reaction yields no net change in the number of moles, or because the pore radii are so small that convective transport is small compared with diffusive transport.

(b) The reaction is first order.
(c) The pore walls are smooth.

(d) The diffusivity is constant. Thus the equation does not apply in the Knudsen region for large change in \( r \).

(e) The system is isothermal.

(f) The system is axi-symmetrical.

Equation (3.1) can therefore be written in dimensionless spherical coordinates:

\[
\frac{\partial \psi}{\partial r} - \frac{1}{\eta^2} \frac{\partial}{\partial \eta} \left( \eta^2 \frac{\partial \psi}{\partial \eta} \right) - \alpha^2 \left( \frac{2G - 3\xi}{G - 1} \right) \xi \psi = 0
\]  

(3.11)

where \( \psi = \frac{C}{C_o} \), \( \eta = \frac{R}{R_o} \), \( \tau = \frac{D_{\text{eff}} t}{R_o^2} \), \( \xi = \frac{r}{r_o} \)

and \( \alpha^2 = \frac{R_o^2 K e_o}{D_{\text{eff}} r_o} \)

Equation (3.4) becomes:

\[
\frac{d \xi}{d \tau} = \frac{b \rho e_o}{C_o} \left( \frac{\alpha^2}{\rho} \right) \psi
\]

(3.12)

The rate of reaction at time, \( t \), is:

\[
R(t) = 4\pi R_o^2 e_0 D_{\text{eff}} \left[ \frac{\partial \psi}{\partial \eta} \right]_{R_o}
\]

(3.13)

Equations (3.11), (3.12) and (3.13) are subject to the boundary conditions

\[
\frac{\partial \psi}{\partial \eta} \bigg|_{\eta = 0} = 0
\]

(3.14)

\[
\psi(1) = 1
\]

(3.15)
3.2 Solution

Petersen demonstrated that, although unsteady state solutions are required the concentration within the porous solid approaches steady state before any appreciable change has occurred in the pore radius. It is therefore possible to adopt a quasi-steady state approach to the solution. Equation (3.11) becomes:

\[
\frac{1}{\eta^2} \frac{d}{d\eta} \left[ \eta \frac{d\psi}{d\eta} \right] - \alpha^2 \frac{(2G - 3\xi\iota)}{(G - 1)} \psi = 0
\]

or

\[
\frac{d^2\psi}{d\eta^2} + \frac{2}{\eta} \frac{d\psi}{d\eta} - \alpha^2 \frac{(2G - 3\xi\iota)}{(G - 1)} \psi = 0
\]

Equation (3.17) was solved numerically, subject to the boundary conditions in equation (3.14) and (3.15), using a 4th order Runge-Kutta routine. This gave a concentration profile throughout the droplet which was then used in equation (3.12) to calculate a new pore radius profile which was subsequently used in equation (3.17) to calculate the next concentration profile.

The computer program and flowsheet are shown in Appendix IV. The diffusivity of the reactant gas in its surrounding medium was calculated using the empirical relationship of Chen (1962)

\[
D_{12} = \frac{0.43(T/100)^{1.81} \left[ \left( \frac{1}{M_1} \right) + \left( \frac{1}{M_2} \right) \right]^{0.5}}{P(T \cdot T_c / 10000)^{0.1405} \left[ \left( \frac{V_1}{100} \right)^{0.4} + \left( \frac{V_2}{100} \right)^{0.4} \right]^{2}}
\]

Effective diffusivity was then calculated using the equation given by Weisz (1959) for carbon particles:

\[
D_{eff} = \frac{\varepsilon \cdot D_{12}}{\gamma^2}
\]

where \( \gamma^2 \) is the value given to the tortuosity of the diffusion path within the particle.
An inherent assumption in the application of such a model to the combustion of coal-based chars is that the differences in reactivity due to coal rank are due to the internal structure of the carbonaceous residue, not to any difference in the true chemical reaction rate. It was therefore necessary to find a relationship between the true chemical kinetics at the char surface and particle temperature.

Frank-Kamenetski (1955) presented an empirical correlation based on the work of Vulis and several other workers with graphite, electrode carbon, and coke:

\[ K = K_0 \exp \left[ \frac{E}{T^* - 1/T} \right] \]  

(3.20)

where \( K_0 = 31.6 \) cm/s, \( T^* = 1240^\circ K \) for the reaction of carbon with oxygen, and \( T^* = 1840^\circ K \) for the reaction of carbon with carbon dioxide. The ratio of the activation energies for the two reactions is a constant irrespective of the type of carbon:

\[ \frac{E_{C + CO_2}}{E_{C + O_2}} = 2.2; \quad E_{C + CO_2} = 32 \text{kcal/mol.} \]  

(3.21)

Finally, in order to test this model with the fuels used in this study it was necessary to be able to predict the initial porosity, \( \varepsilon_0 \). This is a function of the volatile content of the droplet of fuel, and the initial char diameter, both of which were measured experimentally.

\[ \varepsilon_0 = 1 - \left[ \frac{\rho_d (1 - V_m)}{\rho_{ch} \chi^3} \right] \]  

(3.22)

The true density of the solid material in the char was not measured, but it was assumed that the char consisted of amorphous carbon with a density of 2.1 g./cm\(^3\).
3.3 Results of Theoretical Model

The model was run for a large range of input conditions in order to assess its sensitivity to changes in each of the system variables. In each case a sufficiently small time increment was selected to ensure that the mass of the particle approached zero as the internal surface area approached zero. This required an approximate run time of 15 minutes on a system of linked Prime computers.

The results of these tests are shown in Figures (3.2) - (3.7). It can be seen that the concentration profile predictions within the particle are as one would expect. That is, the concentration gradients are larger in larger particles, or in particles with very small pores. These concentration gradients gradually decreased with time due to the increased porosity of the particle. The model is very sensitive to temperature effects, and there are large variations in burnout time between the two chemical reactions tested. Again, these points are perhaps to be expected, but what is surprising is the very large variations which can be generated in surface areas and rates of reaction by small changes in structure such as initial pore size and porosity. The model predicts an order of magnitude difference in reaction rate when the pore size increases from 1% of droplet diameter to 10% of droplet diameter. The model also shows that the reaction rates vary by a very large amount as burnout proceeds.

An attempt was also made to compare the results of the model with the results of the furnace trials described in this thesis. Of necessity, this is a very imprecise comparison for reasons which will be considered in Section (6). However, the rate of reaction and mass burnout vs. time behaviour of five coal slurry fuels was predicted by the model using the input data given in Table (3.1). These data were mainly derived from the experimental results described in this thesis, but it was necessary to assume that the chemical reaction occurring was

\[ C + O_2 \rightarrow CO_2 \]

and that devolatilisation was an instantaneous process which occurred at the beginning of the droplet's lifetime.
Figure 3.2 Internal Concentration Profiles

\( T = 1573K, \ v_o = 0.7, \ C + O_2 = CO_2, \ P_o = 0.1 \text{atm.} \)
Fig. (3.3) Radius Profile (Drop dia. 250µm, pore dia. 1µm.)

Fig. (3.4) Variation of Surface Pore Radius With Time

\[ T = 1573K, \varepsilon = 0.7, \text{C} + \text{O}_2 = \text{CO}_2, P_{\text{O}_2} = 0.1\text{atm.} \]
(a) Effect of Initial Porosity on Surface Area

\( D = 100 \mu m, d = 1 \mu m \)

(b) Effect of Drop Diameter on Surface Area

(c) Effect of Initial Pore Size on Surface Area

Figure 3.5 Variation of Surface Area with Time

\( T = 1573K, \, \epsilon_o = 0.7, \, C + O_2 = CO_2, \, P_{O_2} = 0.1 \, atm \)
Figure 3.5 Variation of Char Reaction Rates with Time

(T = 1573K, $\varepsilon_0 = 0.7$, $C + O_2 = CO_2$, $P_{O_2} = 0.1$ atm)
Figure 3.7 Predicted Combustion Times

(T = 1573K, $e_0 = 0.7$, $C + O_2 = CO_2$, $P_{O_2} = 0.1$ atm - unless otherwise stated)
The model predictions for these five fuels are shown in Figures (3.8) and (3.9).

3.4 Notation

\( b \) - stoichiometric coefficient
\( C \) - gaseous reactant concentration \((\text{kg-mol/m}^3)\)
\( D \) - diffusivity \((\text{m}^2/\text{s})\)
\( E \) - activation energy \((\text{kcal/g mol})\)
\( G \) - see Eq. (3.10)
\( K \) - reaction rate constant \((\text{m/s})\)
\( L \) - length of pore system \((\text{m})\)
\( M \) - molecular weight
\( n \) - order of reaction (assumed = 1)
\( P \) - pressure \((\text{atm})\)
\( P' \) - integral rate of reaction \((\text{kg/s})\)
\( R' \) - rate of reaction per unit internal surface area \((\text{kg/s m}^2)\)
\( R \) - droplet or particle radius \((\text{m})\)
\( R \) - Universal gas constant (Eq. 3.20)
\( r \) - pore radius \((\text{m})\)
\( S_v \) - surface area per unit total volume of particle \((\text{m}^2/\text{m}^3)\)
\( T \) - temperature \((\text{K})\)
\( t \) - time \((\text{s})\)
\( u \) - average bulk gas velocity in pores \((\text{m/s})\)
\( V \) - volume \((\text{m}^3)\)
\( V_m \) - volatile content

Greek

\( \beta(\phi_i) \) - shape factor
\( s \) - porosity
\( \eta \) - dimensionless particle radius
\( \phi_i \) - angle of intersection of \( i \)th pore
\( \gamma \) - linear swelling coefficient
\( \psi \) - dimensionless concentration
\( \rho \) - density
\( \zeta \) - dimensionless pore radius
\( \tau \) - dimensionless time
\[ \alpha = \text{dimensionless constant} = \frac{K \varepsilon_0}{D_{\text{eff}} R_0} \]

\text{div} = \text{divergence operator}

\text{grad} = \text{gradient operator}

\text{Subscripts}

1 = \text{component 1}
2 = \text{component 2}
o = \text{initial}
d = \text{droplet}
ch = \text{char}
s = \text{molar}
c = \text{critical}
\text{eff} = \text{effective}
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<th>502 Rank COM (35.5/64.5)</th>
<th>902 Rank COW (29.4/6/64.6)</th>
<th>502 Rank COW (30.6/6.8/62.6)</th>
<th>401 Rank CWM (70/30)</th>
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<td>0.1</td>
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<td>Gaseous Reaction Molecular Mass</td>
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<td>32</td>
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<tr>
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<tr>
<td>Combustion Time (calculated) (sec)</td>
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Table (3.1) Input Variables for Coal Slurry Fuels
Fig. (3.9) Reaction Rates of Coal Slurry Fuels
4.1 Description of the Single Droplet Experiment

The shortcomings of the single droplet technique have been thoroughly dealt with elsewhere (e.g. Street, 1969, Braide, 1980, Masdin, 1961), and it is not proposed to consider the problems at length here. The effects of the support filament, the relatively large size of the droplets, the lack of particle interactions and the heat transfer mechanism are all areas in which criticisms can and have been made. However the technique does allow the combustion of single particles and droplets of fuels to be visually examined in detail and is therefore an invaluable tool in the study of combustion mechanisms.

The single droplet experiments were conducted at the Marchwood Engineering Laboratories of the Central Electricity Generating Board. The equipment has previously been described in the literature (Bach, Street & Twamley, 1970) and has been used by previous workers for coal and oil combustion experiments.

4.1.1 The Heating Enclosure

The apparatus is shown in Figures 4.1 and 4.2. It consists of a refractory heating enclosure at the centre of which was suspended a single droplet of fuel. Radiation from two 1000W tungsten filament lamps was focussed onto the droplet from two adjacent sides of the chamber through two collimating lenses. Concave mirrors, mounted directly opposite each lens, reflected back radiation which bypassed the droplet, thus ensuring that the droplet was evenly heated from all four sides. Thin brass shields were placed between the lenses and the openings to the enclosure to prevent premature exposure of the droplet to radiation, and the removal of these shields marked the beginning of the heating period. This arrangement enabled the droplet to be exposed to heating rates typical of those found in large boilers, approximately $10^4$ to $10^5 \text{ } ^\circ\text{C} \text{ s.}^{-1}$, within 6 milliseconds.
Figure (4.2) The Single Droplet Apparatus
A small gas pilot flame, about 2 mm long, was positioned 5 mm above the suspended droplet to ignite the volatile gases which were evolved during heating.

4.1.2 Droplet Mounting

The droplets of coal slurry fuel, which were typically 400 - 800 μm in diameter, were mounted on quartz filaments, 40 - 60 μm in diameter. The filaments were cemented, at one end, to a metal fork with a quick-setting refractory cement, and the fork was then positioned in the chamber. Prior to heating, the droplets and filaments were measured under an optical microscope using a graticule. The filament caused distortion of the droplet shape from spherical to elliptical, and thus the minor and major diameters of the droplet were measured, so that equivalent spherical diameters could be calculated.

4.1.3 Fuel Preparation

Several fuels were tested using this equipment, some of which came ready prepared by manufacturers, others which had to be prepared in the laboratory. A number of coal-oil dispersions, containing a range of coals from high to low rank, were supplied by the British Petroleum Company. The coal in these fuels was ground to a sufficiently small size to ensure the long term stability of the fuel. These samples included medium and low rank coals in 3500 seconds fuel oil, petroleum coke dispersions, and dispersions doped with kaolin to simulate high ash content. Dispersions of anthracite and 301a rank coals in 950 seconds fuel oil were prepared in the laboratory by wet grinding.

Coal-oil mixtures were prepared by mixing samples of coal, ground to normal p.f. distribution, with 950 seconds fuel oil. These lacked the inherent stability of the coal-oil dispersions and were used soon after preparation. The effect of coal particle size was further investigated by mixing specific size cuts of coal, in the ranges 45 - 53 μm, 53 - 63 μm, 63 - 75 μm and 75 - 125 μm, with fuel oil. The concentration of coal in all of the coal-oil fuels investigated was, typically, 35% by weight.
Different amounts of water, up to 20\% by weight, were added to some of the coal-oil mixtures using a laboratory homogeniser. This produced an emulsion of approximately 2 \mu m diameter water droplets in the oil phase.

The fuels used in these experiments are listed in Appendix I.

4.1.4 Cinematography

The combustion histories of the single droplets of coal slurry fuels were recorded using a 16 mm WF14(T) Fastax camera. The camera was nominally operated at 1000 frames per second, however the actual framing speed was determined by superimposing the image of a 100 Hz spark onto the film. A calibration curve was then constructed by counting the image frequency on the developed film thus allowing the initial acceleration of the camera to be accounted for (Appendix II).

4.1.5 Analysis of the Cine Films

The filmed combustion histories were studied using a Specto motion analysis projector.

4.2 Description of the University of Surrey Furnace and Associated Equipment

A series of coal-oil mixture and coal-oil-water mixture trials were conducted using the University of Surrey combustion facility. This plant had previously been used by other workers for coal-oil dispersion combustion investigations (Alabaf et al 1981).

4.2.1 The Combustion Chamber

The 0.7 MW combustion chamber at the University of Surrey consists of a horizontal cylindrical steel shell lined with HTI refractory bricks and an intermediate layer of insulation (Figures 4.3, 4.4). The chamber is connected to a refractory-lined, natural draught flue duct which incorporates a draught regulating damper, and exhausts to the atmosphere approximately 20 metres above the furnace.
Figure (4.3) The University of Surrey Furnace
FIGURE (4·4) UNIVERSITY OF SURREY FURNACE
The combustion chamber has 15 gas sampling points, equally spaced, along its entire length, and six larger access points along one side which can be closed, when not in use, by water-cooled doors.

Air was ducted to the furnace from a fan and entered via the burner windbox which was bolted to the refractory quarl at the front of the chamber (Figure 4.5).

The light-up procedure involved establishing a gas pilot flame in the chamber, and then warming the refractory walls to approximately 700°C with a gasoil flame. The wall temperatures along the length of the chamber could be monitored using six platinum/rhodium thermocouples, which were set into the refractory.

4.2.2 Burners

Two burners were used in the combustion trials at the University. For the initial equipment proving tests, in 1983, a Babcock & Wilcox Ltd. steam-atomised, Y-jet burner (mark Y, size No. 1) was supplied to the project by the CEGB. This burner, together with its associated windbox and parallel throat quarl (Figure 4.6), was similar to those which are used in large, oil-fired, power stations. However, it had already been tried with coal-oil fuels, with little success, by the CEGB (Matthews, 1985).

Dry atomising steam was supplied to the burner from the laboratory services through a pressure regulator and a calibrated variable area flowmeter. The burner proved to be extremely difficult to operate due to coking at the tip, and was therefore replaced by the Stordy-Hauck low pressure air burner (Type 783) which had already, successfully, been used with coal-oil dispersions.

The low pressure air burner (Figures 4.5 and 4.7) uses the combustion air as the atomising medium. Air is supplied to the burner through a single inlet connection. It is then split into two streams; primary and secondary atomising air. The primary air enters the atomising chamber (B) through tangential inlets (C) thus imparting a swirling motion. This stream impinges on the liquid fuel, which enters the chamber through large bore orifices (D) at right angles to the direction of the air flow. A liquid film is formed around the outside
Figure (4.5) LPA Burner and Quarl
Figure (4.6) Y-Jet Twin Fluid Burner
FIGURE (4.7) STORDY-HAUCK LOW PRESSURE AIR BURNER
of the chamber outlet nozzle. The secondary atomising air is directed around the outside of the atomising chamber and out through the outer nozzle (F), where it forms a convergent jet which impinges on the primary jet. The primary jet, consisting of a thin divergent cone of liquid fuel plus primary air, is thus disrupted by the convergent secondary air jet and droplets are formed.

Air discharge and oil valve orifice areas can be increased or decreased by adjustment of the burner control lever (A), which causes the inner air nozzle to move in relation to the stationary outer air nozzle (E). The total air supply to the burner is adjusted using the butterfly shut-off valve in the air supply duct.

This burner has several advantages in coal slurry fuel firing. The oil passages are large and thus blockages can be minimised. The oil control valve is an integral part of the burner and may be easily unblocked by swift movement of the control lever to the fully open position and then back to the running position. The burner nozzle is constantly cooled by a large air flow thus preventing coking at the tip, and fuel velocities are low within the burner thus reducing abrasive wear.

4.2.3 Fuel Storage and Mixing

The fuels used in the University combustion trials were generally mixed on the same day as they were required. This prevented difficulties which may have been caused by the lack of stability, and eliminated the need for stabilising additives.

Heavy fuel oil was pumped to a mixing vessel from an electrically heated barrel at a temperature of 40°C. A Sandpiper pneumatic reciprocating pump was used for this purpose. The mixing vessel was well insulated and the oil temperature was maintained or increased by passing steam through the vessel's external heating coils (Figure 4.9).

Pulverised coal was supplied by the manufacturers in 25 kg paper sacks and was added to the mixer manually. The coal and oil were mixed by a 1½ hp motor operating a flat, single-blade, mixer paddle. The mixer
Figure (4.8) Coal-Oil-Water Fuel Mixing Tank

Figure (4.9) Mixing Tank and Weighing System

Figure (4.10) Ultrasonic Emulsifier
speed was controlled at between 30-40 rpm, by a gear mechanism between the motor and the paddle. The mixing vessel also contained internal baffles to promote turbulence.

The whole mixer assembly was mounted on a weighing platform (Figure 4.9), which incorporated a load cell. The output signal of the load cell was shown on a digital display thus enabling accurate monitoring of the quantities of oil and coal added to the mixer. The load cell signal was also fed to a timing and subtracting circuit so that fuel flowrates to the burner could be measured by weight difference. The weighing platform was calibrated regularly by addition of known volumes of water to the mixing tank.

The addition of water to the coal-oil fuels was accomplished downstream of the mixing vessel. An in-line mixing system was devised which involved a vortex-type mixing chamber followed by an ultrasonic sound generator (Figure 4.10). The coal-oil fuel was introduced tangentially into a cylindrical chamber. Water was supplied via a flowmeter to the mixer, entering through four tangential jets. The vortex flow pattern, set up by the passage of the liquids through the chamber, caused a partial mixing of the coal-oil fuel and the water. The partially mixed liquid left the chamber by an axial outlet, to be immediately passed across the end of an ultrasonic probe, which was positioned on one side of a 4 mm wide chamber. This equipment produced emulsions of approximately 5-10 μm water droplets in coal-oil mixture. This is slightly larger than is normally quoted for stable oil-water emulsions but was regarded as acceptable in this instance.

The properties of the fuels which were used during these trials are given in Appendix I.

4.2.4 Fuel Supply System

A flow diagram of the mixing rig, furnace, and fuel supply train is shown in Figure (4.11).

Coal-oil mixtures were pumped from the mixing and weighing platform to the emulsifier and then on to a fuel preheater and the burner, by a progressive cavity pump. This type of pump has been widely used for coal slurry fuels due to its ability to withstand abrasion and its low...
shear-rate. A helical tool steel rotor, turning within a rubber starter, creates a progressive cavity action which propels the fluid. On the manufacturer's advice, a slightly undersized rotor was used in order to increase the wear resistance of the pump. The rotor shaft was coupled to a 1 hp motor via a variable speed drive thus enabling fuel flow rate and rate of pressure increase to be varied. The fuel was supplied to the preheater through a 1" diameter pipe which was well-lagged and electrically trace-heated. Pumping temperatures were controlled at approximately 70°C. An automatic flow control valve on the steam inlet to the preheater was used to regulate the temperature at which the fuel was delivered to the burner. Temperatures between 100°C and 110°C were sufficient for good atomisation. All of the valves used in the fuel supply line were full-bore, ball valves, and the pipework was kept as straight and short as was practical. Unnecessary obstructions to flow, such as non-return valves and strainers, were removed from the line after the preliminary runs, in order to reduce blockage problems.

The Stordy-Hauck burner was found to operate best when a drip return line to the storage tank was installed. This allowed non-atomised fuel to by-pass the burner and resulted in better pressure and flow control of the fuel to the burner.

4.3 The Airoil-Flaregas Trial

Coal-water slurry combustion trials were performed by Airoil-Flaregas Ltd. on their 10 MW test facility (Fig 4.12), in August 1984, in order to evaluate the suitability of experimental burners for these fuels. The Fuels & Energy Research Group of the University of Surrey were invited to participate in these trials to monitor the combustion processes and to advise on the handling characteristics.

4.3.1 The Combustion Chamber

A diagram of the combustion chamber is shown in Figure (4.13). The plant was constructed to test large process heater burners and may be up-fired, down-fired or side-fired. The main chamber is a vertical, refractory-lined cylinder which is enclosed in a water jacket. When the furnace is up-fired the combustion gases leave the combustion chamber through a 10 m high flue stack directly above the chamber.
Figure (4.12) The Airoil-Flaregas Furnace
FIGURE (4.13) - №1 TEST FURNACE - VERTICAL FIRING MODE
Natural draught and forced draught burners may be tested on this equipment by altering the burner windbox configuration. Access to the flame was via the five inspection ports around the circumference of the combustion chamber. Solids burden measurements were made in the flue stack, and flue gas temperature was continually monitored at this position.

4.3.2 The Burners

The disadvantages of the Y-jet type twin fluid atomiser have already been discussed in Section 4.2.2. The mechanical simplicity of the Y-jet is its greatest virtue but also the major cause of its shortcomings. The asymmetric injection of oil into the injection or mixing port leads, inevitably, to the formation of a thick film of oil on one side of the exit port. This film persists to the end of the exit port, where it forms a thick ligment and breaks down into relatively large droplets.

In an attempt to overcome this problem Anson and Denham (1977) devised a means of manufacturing a multi-ported atomiser which incorporated axisymmetrical injection of oil into each mixing chamber. From their original design, the symmetrical twin-fluid atomiser (STFA) and the two-piece twin fluid atomiser (F-jet) were developed by the CEGB at their Marchwood Engineering Laboratories, Southampton. Both the STFA and a modified version of the F-jet (Fig. 4.14) are manufactured by Airoil-Flaregas Ltd. under licence, and both were used during the coal slurry combustion trials. The modified F-jet atomiser with a spray angle of 30° was found to give a very satisfactory performance, although it was believed that a spray angle of 45° would have given a better flame shape. The atomisation performance of the STFA was almost as good as that of the F-jet, although the 90° spray angle which was tested caused the fuel spray to impinge on the quarl and resulted in rapid build up of massive carbon deposits around the nozzle. On balance, the modified F-jet atomiser was considered to be better than the STFA due to its larger internal passageways which reduced erosion and fouling problems. The design of the F-jet is also more readily modified to include hardened sections in those zones which are prone to wear.
The atomising fluid for both types of burner was air which was supplied at approximately 60 psi. The flame was initially supported by five gas pokers which extended into the combustion zone.

### C.W.M. AIR ATOMIZER ASSEMBLY

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![Diagram of F-jet Atomiser](F-jet Atomiser.png)

Figure (4.14) The F-jet Atomiser

#### 4.3.3 Fuel Supply to the Burner

The fuels for this trial were prepared by English China Clay and Ankersmit Holdings and supplied to the test site in drums. Details of these fuels are given in Appendix I. The fuel was pumped from a storage tank, around a loop, and back to the tank. The burner was connected to a spur in the pumping loop. Again all valves used were full-bore ball valves and pipework and fittings were kept to a minimum. A filter, in the line to remove oversized coal particles, needed to be cleaned every two hours during the combustion trials. The pipework and burner fuel-ways were flushed with water after the trial, to prevent deposits of dried coal-water slurry from forming. A progressive cavity pump was used in the pumping loop similar in design to that described in Section 4.2.4 and the same flow monitoring by weight difference equipment as described in Section 4.2.3 was employed.
Figure (4.15) Gas Analysis Instruments
4.4 Measurement, Monitoring and Analytical Techniques

For the most part, the measurement and analysis equipment, and techniques, were the same for both furnace trials. Gas analysis and solid sampling equipment was transported from the University of Surrey to the Airoil-Flaregas site in order to maintain consistency in measurement methods. However, some modifications were necessary due to practical considerations, particularly in the solids sampling methods.

4.4.1 Gas Analysis

A mobile gas analysis trolley comprising of several instruments, gas sampling, and conditioning systems was constructed at the University of Surrey in order to service the coal slurry research program and other combustion projects undertaken by the Fuels and Energy Research Group (Figures 4.15).

Gas samples were withdrawn from the furnaces through water-cooled probes and cooled to room temperature by passage through a water-cooled heat exchanger. The samples were then passed through glass wool filters to remove dust, and through silica gel dessication columns. The gases, thus conditioned, were distributed, at the correct flowrate, from a manifold to the analysis instruments. No further conditioning was necessary, except for the sample to the Utox 90 electrochemical oxygen meter, which required a desulphurised gas feed. A separate conditioning system was used for this instrument which included a sodium hydroxide scrubber to remove oxides of sulphur. The hydrocarbons meter was able to accept a sample containing water vapour and thus the dessication columns were by-passed for this particular instrument.

ADC infra-red gas analysers were used to measure carbon monoxide and carbon dioxide concentrations. A flame ionisation detector (FID) instrument, manufactured by Analysis Automation Ltd., was used for hydrocarbon analysis. Oxygen concentrations were measured using a Neotronics Utox 90 electrochemical cell meter and a Servomex paramagnetic device. In addition to these two instruments, a Westinghouse zirconia probe was used to continually monitor the flue gas oxygen concentration. A comparison between the reading given by
the Westinghouse instrument, and oxygen concentrations measured in the flue by one of the other two methods gave the moisture concentration in the flue gases.

The instruments were all zeroed with oxygen-free nitrogen and calibrated with the appropriate gaseous mixtures of known concentration prior to each run.

4.4.2 Solids Sampling

Three methods of sampling solid particles from the flame and flue gases were used during this investigation. Water-cooled and hot probes were employed, but in each case samples were taken isokinetically. This is to say that, the sample flowrate or probe nozzle diameter was adjusted to ensure that the velocity of the gases passing through the nozzle was equal to that of the gases passing around the nozzle. This is an essential requirement if the solids sample is to have a representative size distribution and if accurate solids burden measurements are to be obtained. Gas velocities at the point of sampling were measured prior to the insertion of the solids probe with a water-cooled pitot-static probe. Cold aerodynamic checks were carried out on the two furnaces to ensure an even air distribution and to correct any deviations of the fuel jets from the central axis of the combustion chamber by adjustment of the burner position. Such flow checks proved difficult when a flame was present due to the turbulent fluctuations induced by combustion. Cold aerodynamic measurements indicated that no recirculation zones were present in the jet region. This again was an important requirement for the solids sampling results to be meaningful. However, this factor was considered in the original design of the furnace, and flame stabilisation is not dependent on there being recirculation zones in the nozzle region, but instead relies on radiation from the hot walls adjacent to the nozzle. The same, however, cannot be said for the Airoil-Flaregas furnace in which the fuel spray was a free jet which was entirely stabilised by the recirculation of hot combustion products into the region of spray formation. It was impossible, in this case, to calculate accurate droplet lifetimes for the solid samples collected at various positions in the flame.
It was decided that a water-cooled probe, with external sample separation, was the most suitable technique for sampling from the flame. A water-cooled probe containing a 10 μm sinter-bronze filter [Fig 4.16, 4.18] immediately after the inlet nozzle was found to clog quickly when the probe was placed close to the burner. This made sample retrieval very difficult and therefore this technique was only used for flue gas solids sampling. However, this method is useful when accurate flue-gas solids burden measurements are required. Hot probes are not suitable for sampling from the flame because the combustion reactions are not quenched at the sampling point. This necessitates a correction being made to the droplet residence time values calculated from the furnace velocity measurements. This type of probe is also prone to rapid corrosion in the hot, oxidising environment of the flame. In spite of this, the hot probe and silica wool filter method, recommended by Rendle (1978), was used for sampling from the Airoil-Flaregas flue stack, principally because the necessary equipment was already permanently installed on the furnace (Figure 4.17). The method does have the following advantages, most of which are particularly relevant for oil-fired installations in which the mass of sample is much lower:

(i) Condensation of acid does not occur in the probe or filter.

(ii) A high, constant gas velocity is maintained in the probe thus preventing settling of the larger particles before the filter.

(iii) Silica wool does not react with the sulphurous oxides in the flue gases.

Samples taken from the flame with the water cooled probes were kept above the acid dewpoint by adjustment of cooling water flowrate. For the external separation technique, samples were sucked through a cyclone and PTFE filter (Figure 4.19) which were positioned in an oven maintained at 180°C. The cleaned gas left the oven and was cooled and dried before passing through a rotameter and dry gas meter.
1. flue gases
2. sampling nozzle
3. sintered bronze filter
4. water-cooled stainless steel modified Land solids sampling probe
5. drying tower (silica gel)
6. clip
7. vacuum pump
8. gas meter
9. pressure gauge
10. thermometer
11. rotameter

Figure (4.16) Schematic Flow Diagram of the Land Solids Sampling Equipment

FLUE GAS DUCT

A - Sampling nozzle
B - Electrically heated sampling probe
C - Filter
D - Heated enclosure
E - Gas cooler
F - Drying tower
G - Rotameter

P1 - Vacuum pump
V1 - Control valve
V2 - Bypass valve

Cooling water to drain

Figure (4.17) Schematic Flow Diagram of the Rendle Solid Sampling Equipment
4.4.3 Temperature Measurements

A Land suction pyrometer was used to measure the temperature of the flue gases in the University of Surrey furnace. Such measurements were taken at regular intervals during the trials. The flue gas temperatures of the Airoil-Flaregas furnace were measured with a shielded thermocouple, which had been calibrated against a suction pyrometer, and were recorded on a chart recorder. The University furnace had platinum/rhodium thermocouples set into the refractory wall at regular intervals. These were connected to an Orion datalogger, as were all the thermocouples on the plant, so that temperatures could be automatically scanned and recorded at preset intervals.

Flame temperatures were measured with an infra-red pyrometer which had been calibrated in the black-body furnace. The drawback of this technique is that the emissivity of the flames was not known. However, estimates were made based on emissivity measurements taken by other workers on coal slurry fuels in the same furnace (Alabaf et al., 1981).

4.4.4 Microscopic Techniques

Qualitative and quantitative techniques involving the use of several types of microscope were employed in the analysis of the solid samples obtained from the flames and flue gases. A Reichart-Jung Polyvar-Met optical microscope was used for particle sizing. The microscope was focussed on a sample of the solid particles which were spread thinly on a glass slide and illuminated with transmitted light. Several photographs were taken of the particles with the slide being moved randomly after each exposure. A graticule was also photographed at the same magnification settings so that the particle diameters could be calculated from the photographs. This method of determining size distributions was very time consuming and tedious but was preferred to automatic image analysis equipment, because it allowed some judgement to be exercised in deciding whether particles had agglomerated or were simple touching on the slide. This technique was also preferred to the Coulter particle sizing equipment which was available, since most of the particles were hollow and thus caused erroneous results on such equipment.
Figure (4.18) Water-Cooled Solids Sampling Probe

Figure (4.19) Particle Filtration System
In order to examine the internal structure of the particles, a mounting and sectioning technique was used. Plastic mounting blocks were made in moulds, using a mixture of thermoplastic resin and hardener. These were degassed in a vacuum oven and allowed to set. A dry sample of particles was placed into a hole, which was drilled in each mounting block, and then filled with more resin. Once this central core had been degassed and allowed to set the whole block was sawn in half along the axis of the particle laden core. The sawn face was filed, sanded, and finally polished with diamond pastes to give a 0.25 μm finished surface. The polished face of the mount incorporated sectioned particles which could be viewed under an optical microscope using incident light. Two microscopes were used for this work. A Zeiss metallurgical microscope was used to give high magnification images with good resolution. In addition, the Reichart-Jung microscope was used because it incorporated an interference contrast device which enhanced the internal details of the particles, such as different petrographic groups and trapped volatile bubbles.

A Jeol JAM-35C scanning electron microscope was used to study the surface detail of the solid samples. The samples were mounted on metal plinths and vacuum splutter coated with a layer of gold to reduce particle charging. The plinths were then placed into the high vacuum chamber of the microscope where they were bombarded by a high energy electron beam. Very highly magnified surface details were visible using this equipment.
5 EXPERIMENTAL RESULTS

5.1 Single Droplet Experiment

In total 57 experimental runs were undertaken on the single droplet equipment, with at least three films being obtained for most of the fuel samples. The experimental details of each of these runs are recorded in Appendix III, which also serves as an index to the code numbers by which individual experiments were identified and are referred to in this section.

It should be noted that results obtained were more of a qualitative nature than quantitative, for several reasons. The technique is prone to large experimental errors particularly in the temporal measurements, due to the problems involved in identifying where one period ended and another began. For example, it proved very difficult to determine the point of total burnout in most instances due to the structural and visual similarity between partially burned chars and final ash residues. Comparison of combustion times was generally not possible since the initial droplet sizes were very different and not easily controlled. The majority of the results derived from these experiments were therefore based on the variations in droplet diameter throughout the combustion period.

5.1.1 The Effects of Fuel Type

In all, six types of fuel were tested: coal/oil dispersions; coal/oil mixtures; coal/oil/water mixtures; coal/water mixtures, petroleum coke/oil dispersions and heavy fuel oils. Typical examples of the equivalent spherical droplet diameter vs. time graphs for each of these fuels are shown in Figure 5.1. Such graphs demonstrate that there are significant differences in the droplet diameter histories, and perhaps structural histories, of single droplets of the fuels tested throughout the combustion period. In order to assess the extent of these changes and to make quantitative comparisons, normalised diameters which were based on initial droplet diameters, were also plotted against time for each of the films analysed. However, this technique proved inadequate to describe all events and changes that occurred in each two minute
Figure (5.1a) - Grimethorpe Coal (COO/3)

Figure (5.1b) - Petroleum Coke Dispersion (COO/2)

Figure (5.1c) - 30% CO (COV/3)

Figure (5.1d) - Coal-oil-water mixture (30% water, 30% 30th coal)

Figure (5.1e) - Coal Water Mixture (COV/5)

Figure (5.1f) - 95% Second Fuel Oil (RFQ/2)

Figure 5.1b) Diameter vs. Time Histories
film sequence, and thus qualitative analysis of the films was found to be essential. Figures 5.2 - 5.7 illustrate important events during the lifetimes of the six fuel types which were used.

The combustion of each droplet consisted of three main stages: initial heating; ebullition; and combustion of the residual carbonaceous char. The first evolution of volatile matter occurred during the initial heating period. The volatile components of the fuel diffused out of the droplet and formed a gaseous shell around the surface. This continued in all fuel types until the boiling point of the droplet was exceeded. This point was marked by the commencement of vigorous boiling. Dense clouds of volatiles were produced by explosive bursts at the surface and the diameter of the droplet fluctuated rapidly. This was more pronounced in the fuel oils alone, less so with coal/oil fuels and hardly evident in coal/water fuels. Ebullition was intensified in coal/oil fuels by the addition of emulsified water. Ignition of the volatile matter could occasionally be observed during this period, causing a thin flame front to surround the droplet. As the oil and coal/oil droplets continued to bubble they became increasingly more viscous causing surface craters and blowholes to appear at the points where explosions had taken place. Eventually surface bubbling ceased and the volatile cloud disappeared, leaving a solid residue on the filament. The behaviour of the coal/water mixtures was slightly different from that of the oil-based fuels. As the surface bubbling and devolatilisation subsided, large outgrowths appeared on small areas of the surface. The protrusions resembled wormcasts and often grew to almost the size of the original droplet (Figure 5.7), thus the initial char was greatly distorted in shape.

Since the lifetime of the char residue accounted for the majority of the droplet combustion period in almost all of the tests it will be dealt with in detail in subsequent sections. In coal-oil fuels the initial char was observed to have a very shiny surface (Figure 5.2d) which rapidly faded, accompanied by a slight reduction in diameter, to reveal a duller surface. The surface of such residues appeared to vary with coal type. Petroleum coke/oil, low and high rank coal/oil fuels all produced chars that had a grainy, sponge-like surface. Such surfaces rarely incorporated large blowholes. Mid-rank coals however formed smoother, more homogeneous char surfaces which often incorporated several large blowholes. The combustion of the former
Figure 5.2 – 35% Coal-Oil Mixture [301a NCB Rank(75-90\(\mu\)) and 950 Second Oil]
Figure 5.3 - 950 Redwood Second Fuel Oil

- a-Droplet (35 msec)  
- b-Ebullition (420 msec)  
- c-Initial char (600 msec)  
- d-450μ

Figure 5.4 - 34.2% Coal-Oil Dispersion [602 NCB Rank and F80 Oil]

- a-Initial char (620 msec)  
- b-Burning char (1530 msec)  
- c-Ash residue (1970 msec)  
- d-770μ
Figure 5.5—35% Coal-Oil Mixture [101 NCB Rank and 950 Second Oil]

Figure 5.6—Coal-Oil-Water Mixture [29% 101 NCB Rank, 51% 950 Second Oil, 20% Water]
(a) 0 msec.
Initial droplet

(b) 86 msec.
First volatiles and swelling

(c) 657 msec.
Violent devolatilisation

(d) 1385 msec.
"Wormcast" growth

(e) 2100 msec.
Carbon residue combustion

(f) 2874 msec.
Ash residue

Figure (5.7) - COS/1: Slurrytech Coal Water Mixture
chars proceeded by disintegration into small clusters of loosely agglomerated particles, whereas the latter retained their shape and lost mass by gradual erosion around the circumference of the surface blowholes.

The behaviour of the coal/water fuel residues can best be described as a combination of both mechanisms, with the outgrowths gradually flaking away and simultaneous erosion around the surface blowholes.

All chars continued to erode until only an ash residue remained. The structure of the ash residues appeared to depend on the structure of the carbonaceous chars. Lightly fused chars, as formed by low or high rank coals and petroleum cokes, disintegrated into individual ash particles, or clusters of several particles (Fig. 5.5d). Well-fused chars formed large ash residues which did not fragment to an appreciable extent. These chars often collapsed to form fused spheres which were far larger than the original coal particles (Figure 5.4c).

5.1.2 The Effect of Coal Rank

It has previously been stated that the type of coal used in these experiments affected the size and structure of the initial carbonaceous residues. The diameter of the initial char which was left on the quartz filament after the volatiles had cleared and bubbling on the surface had ceased was used to determine the maximum degree of swelling. This diameter, in relation to the initial droplet diameter, was plotted against the original coal carbon content which is dependent on coal rank (Figure 5.8). It is apparent from this graph that mid-rank coals produce maximum swelling, whilst high and low rank coals produce chars which are approximately the same diameter as, or slightly smaller than, the initial droplet diameter.

The changes in structure which accompanied these variations in char size were mentioned in Section 5.1.1. The effects of coal rank on coal/water fuels was not investigated fully due to lack of sufficient types of fuel. All CWM fuels investigated contained mid-rank coals which produced similar char behaviour.
Fig. (5.8) Carbon Content of Coal vs Initial Coke Diameter

Fig. (5.9) Effect of Coal Concentration on Initial Coke Diameter
5.1.3 The Effect of Coal Concentration

The concentration of coal particles in coal-oil fuels was varied between 10% and 40% by wt. The most obvious effect of this was the variation in size of the initial carbonaceous residues. Higher coal concentrations resulted in larger chars (Figure 5.9), although coal rank also affected char size. It is probable that increased coal concentration resulted in longer combustion times but no evidence was obtained to prove this.

5.1.4 The Effect of Coal Particle Size

A series of experiments were performed using one particular coal slurry fuel to investigate the effect of coal particle size. Several coal-oil mixtures were prepared containing 301a coal particles of specific size in 65 wt% 950 second fuel oil. The effect on total droplet combustion time and initial char diameter are shown in Figure 5.10 and 5.11, respectively.

It is apparent that fuels made with 50 - 60 μm diameter coal particles produce less swollen residues and burn out faster than those made with smaller or larger coal particles. Care was taken during these experiments to ensure that approximately equal sized droplets were used so that the comparison between combustion times was accurate. The 301a coal was chosen because it exhibited particularly noticeable ash formation behaviour so that the burnout point could be accurately determined.

5.1.5 The Effect of Emulsified Water

Apart from increasing the intensity of ebullition and the occurrence of 'splashing', the effect of adding water to coal-oil fuel was to increase the devolatilisation period. This was evident from the films since volatiles were observed to evolve long after the surface bubbling had finished. Figure 5.12 shows devolatilisation time as a proportion of the droplet lifetime against the amount of water added.

Figure 5.13 shows that once devolatilisation has ceased the initial char size is smaller than that which would be produced with no water present, however this could be the result of less coal being present.
Initial drop size = 505µm ± 7%

Initial drop size = 689µm ± 5%

Fig (5.10) Effect of Coal Particle Size on Combustion Time

Fig (5.11) Effect of Coal Particle Size on Char Swelling
Fig. (5.12) Effect of Emulsified Water on Devolatilisation Time

Fig. (5.13) Effect of Emulsified Water on Char Size
5.2 Furnace Combustion Trials

The data accumulated during the furnace trials at the University of Surrey and at Airoil-Flaregas Ltd. was presented in tabular form in an earlier report (Lapwood & Moles, 1986). This has been included as an Appendix to this thesis (Appendix IV). The results which are presented in this section were either derived from the raw data by calculation or represent an average of several experimental values.

5.2.1 Solids Sampling Experiments

In order to obtain a qualitative picture of the structure of char residues as combustion proceeded, the solids sampled from different points in the flame were examined using two microscopic techniques. Scanning electron microscopy and particle cross-sectioning were used to detect changes in char structure with time. However, several types of structures were observed in each sample of solids, thus indicating the presence of particles with different residence time and reaction histories at each point. It was usually possible to identify a predominant type of particle and therefore to form a general picture of the complete combustion mechanisms for comparison with those obtained from the single droplet experiments.

Figures 5.14 and 5.15 show several photomicrographs of particles from 502 rank COM flames. It was noted that the addition of small amounts of water to COM fuels produced no qualitative difference in structure and therefore no photomicrographs of COW particles have been included. Individual coal particles in 502 COM droplets do agglomerate and fuse in the early part of the flame (Figure 5.14b), eventually forming hollow cenospheres with thick, blowholed walls (Figure 5.14d). The ash residues remaining after combustion were either solids spheres (5.14c) or were similar in shape to the original cenospheres (5.14f). At all stages during combustion there occurred separate and virtually unchanged coal particles. These photographic sequences were in good agreement with the cine film sequences of the combustion of single droplets of mid-rank coal/oil fuels.
Figure (5.14) Electron Micrographs of 501 Rank Coal-Oil Mixture Particles
(a) 23 msec.  
Agglomerated particle

(b) 55 msec.  
Agglomerated particle

(c) 98 msec.  
Single coal particle

(d) 118 msec.  
Carbon cenosphere

(e) 118 msec.  
Spherical ash particles

(f) 131 msec.  
Ash particle
Figure (5.15) Section Photomicrographs of 501 Rank Coal-Oil Mixture Particles
Figure (5.16) Electron Micrographs of 902 Rank Coal-Oil Mixture Particles
(a) 23 msec.
Initial agglomerate

(b) 23 msec.
Devolatilising carbon residue

(c) 33-79 msec.
Carbon residue

(d) 33-79 msec.
Partially burnt char

(e) 97 msec.
Partially burnt char

(f) 97 msec.
Ash fragments
Figure (5.17) Section Photomicrographs of 902 Rank Coal-Oil Mixture Particles
Figure (5.18) Electron Micrographs of 401 Rank Coal-Water Mixture Particles (ECC CWM)
(a) 19.51msec.  
Devolatilising particle

(b) 33.79msec.  
Carbon residue

c) 33.79msec.  
Carbon residue

d) 187.97msec.  
Ash particles
Figure (5.19) Section Photomicrographs of 401 Rank Coal-Water Mixture Particles (ECC CWM)
(a) 19.51 msec. (x 625)

(b) 33.79 msec. (x 625)

(c) 187.97 msec. (x 430)

(d) 187.97 msec. (x 1200)
Figure (5.20) Section Photomicrographs of 401 Rank Coal-Water Mixture Particles (Ankersmit CW4)
The 902 rank COMs produced very similar solid structures at all stages
to the mid-rank fuels. The differences which did exist were small, and
perhaps debatable, but again the results did seem to corroborate the
single droplet evidence. The particles samples from the early part of
the flame consisted of loose agglomerates of individual coal particles
(Figures 5.16a & 5.16b). The chars were mostly hollow but with a more
complex internal structure than those of mid-rank COMs, and with
thinner, less blowholed walls. It was apparent that these loosely
agglomerated chars could fragment easily during combustion, thus
forming plate-like ash fragments (Figure 5.16d). Individual coal
particles were again visible at each stage, and again there was no
obvious effect of adding water.

The CWM fuels used in these trials were both similar in rank, and thus
produced similar solids structures (Figures 5.18, 5.19 & 5.20). The
cenospheres were well-fused and hollow, with surface blowholes in very
thin walls. There was some evidence of the "wormcast" growth which was
observed in the single droplet experiments (Figure 5.19b). Again
individual and unfused coal particles were evident at all points.

Chemical analysis of the solids samples enabled carbon burnout to be
calculated and plotted against residence time. Figures 5.21 and 5.22
show the progressive depletion of carbon with time. Similar results
were obtained for hydrogen but here depletion was so rapid that it was
not possible to distinguish between the rates for each fuel. The
carbon burnout results were used to calculate rates of reaction
throughout the flame (Figure 5.23).

The changes in mean particle size in the flame and the variation in
particle size distribution were also used to quantify changes in
combustion mechanisms. (Figures 5.24, 5.25 & 5.26). These results
show some similarity to the more extensive measurements of particle
size which were obtained from the single droplet experiments. However
the exceptionally large variations in diameter throughout the flame are
thought to be unrealistic and perhaps indicate errors in solids
sampling.
Fig. (5.21) CARBON BURNOUT VS RESIDENCE TIME (COMs & COWs)

Fig. (5.22) CARBON BURNOUT VS RESIDENCE TIME (CWM FUELS)
Figure (5.23) Rates of Reaction
Figure (5.24) Mean diameter of flame solids vs residence time (COMs, COWs)

Figure (5.25) Mean diameter of flame solids vs residence time (CWM's)
Figure (5.26) Particle Size Distributions Throughout Coal Slurry Flames
Figure (5.27) Furnace Wall Temperatures

Figure (5.28) Furnace Gas Temperatures (COM's & COW's)
5.2.2 Temperature

The furnace wall temperature profiles and flame temperatures are shown in Figures 5.27, 5.28 and 5.29. It is difficult to assess the relative significance of these results and to make comparisons between the various fuels tested due to the differences which existed between fuel and air flowrates, and fuel composition. It is, however, interesting to note that CWM fuels produced much lower flame temperatures, and that the addition of a small amount of water to COM fuel resulted in higher flame temperatures.

![Diagram showing temperature profiles](image)

**Figure (5.29) Furnace Gas Temperatures (CWM's)**

5.2.3 Furnace Gas Analysis

These results further highlight the problems associated with the use of large, turbulent diffusion flames in mechanism studies of this type. The concentration profiles shown in Figure 5.30, 5.31 and 5.33 illustrate that the concentrations of various gas species fluctuated markedly with time at specific points in the flame. Even the practice of averaging several readings over a long period of time yielded widely varying results.
The problem of spatial and temporal variation in gas concentration was greater during the CWM trials than during the COM or COW trials due to the complex aerodynamic behaviour of the gases in the near-burner zone. This is illustrated in Figure 5.33. The experimental errors are discussed more fully in Section (6).
Figure 5.30 Furnace Gas Composition (COM's & COW's)
Figure (5.31) Furnace Gas Composition (ECC CWM)
Figure (5.32) Furnace Gas Composition (Ankerschmitt CWM)
Figure (5.33) Gas Concentration Profiles in ECC CWM Flame (Trial 6)
6.1 Appraisal of Experimental Techniques

The original approach to the problem of investigating combustion mechanisms in coal slurry fuels was to make a thorough investigation using an established single droplet technique, and then to compare the results of this work with samples and measurements taken from large flames. These two techniques eventually led to the theoretical analysis, presented in Section (3) of this thesis, which approximately models the structural changes in carbonaceous chars during combustion. However, it is not possible to claim that the experimental evidence derived from these three sources is totally conclusive. Individually the techniques suffer several inherent disadvantages and rely on many unproven assumptions. Direct comparisons between the results of each technique is difficult to justify, but there is sufficient agreement to enable some conclusions to be drawn and to indicate in which areas future studies should be made.

The single droplet experiments provided an excellent visual method of evaluating combustion mechanisms. The results however were largely qualitative as opposed to quantitative. The most important reasons for this were: the size of the droplets, which were large compared with those in a conventional fuel spray, the interference of the support filament, and the droplet heating mechanism. Droplets or particles of fuels in a flame are mainly heated by convection due to the relative velocity and temperature of the ambient atmosphere. The single droplet equipment used in this study produced a similar rate of heating to that found in flames, but the system of heating was by focussed quartz lamp radiation. This almost certainly resulted in less convective heat transfer than radiative heat transfer. The implication of this is that the lower ambient air velocity could result in less surface friction and thus a lower degree of internal recirculation. Other workers have reported internal recirculation to be an important factor in the combustion mechanism. Its absence could lead to a false impression of the behaviour of coal slurry droplets during the important devolatilisation phase. It is, perhaps, significant to note that many
of those workers who have suggested that internal recirculation is important have had highly convective heat transfer in their single droplet experiments (e.g. Law, 1976a, 1976b).

Whilst some events in the combustion histories were very clearly demonstrated in the single droplet results, there was some difficulty in distinguishing others. For example the moment of ignition of the volatile cloud was usually invisible due to the intense background illumination. This point could occasionally be inferred by the sudden disappearance of the volatile cloud but the thin, enveloping flame, reported by others, was never visible. The point of complete carbon burnout was also difficult to measure, due to the similarity in appearance of partly burned chars and ash residues. In spite of these problems, much useful information was obtained from these experiments which was the basis of the latter hypotheses. (See Section 3)

It was thought, perhaps naively, that the results of the single droplet work could be confirmed if a similar sequence of events could be constructed from pictures of solids sampled at different points in a flame. There were grounds for optimism in this respect since the results of the single droplet tests compared very favourably with the photomicrographs of solids sampled from the flue gases of anthracite COD flames and mid-rank COD flames at the University of Surrey by Alabaf et al. (1981). In reality however, the extension of the furnace trials to include full length flame sampling of mid-rank COMs, low-rank COMs and coal water slurries did not provide such conclusive agreement with the single droplet work. The reason for this is quite simply the difficulty in taking accurate measurements in large, turbulent combustion systems. If feasible comparisons were to be made between the furnace results and the single droplet results it was important that the solids sampling and residence time results were reliable. Efforts were made to ensure that the solids were sampled isokinetically and were immediately quenched in the sampling probe to a temperature just above the acid dew-point. Velocity and temperature at the sampling points were regularly measured, and the sampling flowrate adjusted to account for variations. However, it was not possible to maintain steady state conditions in the flame and this almost certainly introduced errors in the particle size analysis results and perhaps in
the solids ultimate analysis results. This inability to maintain steady conditions is adequately demonstrated in the flame gas concentration profiles in Section (5).

Particle residence times were calculated from axial velocity profiles in the flame. Here again errors were inevitable due to:

(i) Variations in temperature and flowrate.

(ii) Recirculation of particles within the flame.

(iii) The particles travelling faster than the surrounding gases due to their higher momentum and reduced drag caused by wake flames.

Of course these problems were foreseen and an attempt was made to compensate by taking samples of solids for a long period of time and time averaging instantaneous readings such as velocity, temperature and gas composition.

Even assuming that representative solids samples were obtained, the analysis of particle structure and combustion mechanism using qualitative optical techniques, such as sectioning and electron microscopy, was also prone to errors. Every effort was made to be impartial in the selection of solids to be analysed, and to present a representative sample of structures in this thesis. However it is difficult to be totally unbiased, in a statistical sense, by larger structures, or unusual structures. The problem is analogous to trying to describe a large city with the aid of a few snapshots. It depends on who does the describing and who takes the snapshots.

A mathematical model of particle behaviour during combustion has been used to explain some of the experimental observations. It is perhaps, more difficult to have confidence in the predictions of such a model than it is in experimental results. Again, direct comparisons between the model results and the furnace results are not possible. The model takes no account of aerodynamic effects, depletion of reactant, variations in ambient temperature or particle size distribution. The model also depends on input variables such as diffusivity, tortuosity, reaction rate, reactant species and assumes that these are constant throughout the combustion history of the particle. The measurements of initial pore diameters were very approximate, being taken from electron
micrographs and section photographs. The initial porosity was calculated on the assumptions that particle swelling could be accurately predicted from the single droplet results, that the density of the carbonaceous solid was constant for each fuel and that the amount of volatile matter could be measured by proximate analysis. The work of Loisson and Chauvin (1964) on devolatilisation of coal showed that the last assumption is incorrect.

Despite these reservations, the three techniques combined have produced several areas of agreement. They are also techniques which have been used extensively in the past for combustion mechanism studies, and although they can be improved upon and augmented by others it is difficult to see how they could be replaced. Suggestions for improvements and further experimental studies will be considered later.

6.2 Implications of the Experimental Results

In order to test the combustion performance of a wide range of coal slurry fuels in industrial sized furnaces, it was necessary to develop some new equipment and to test existing equipment in novel applications. Three types of atomiser were employed in these trials with varying degrees of success. The Stordy-Hauck LPA burner performed well with coal-oil and coal-oil-water fuels and it is likely due to its design that it would also perform well with coal-water fuels. However, this device required large volumes of atomising air, and would be unsuitable for large combustion chambers. The Y-jet, steam-atomised burner proved totally inadequate in service, but the P-jet atomiser was found to produce a consistent spray of fine droplets at a high level of atomising fluid efficiency. However, it was not possible to maintain a stable CWM flame with this device without natural gas support flames amounting to at least 10% of the total heat released in the furnace. There was evidence that this performance could be improved by optimising burner design variables such as spray angle and port sizes.

The coal-oil fuel preparation plant demonstrated that such fuels can be made without the use of stabilising additives if they are burned soon after manufacture. The in-line ultrasonic emulsifier operated efficiently and produced fuels with better burnout characteristics. Accurate flow measurement of coal slurry fuels was obtained using a
constant storage tank weighing system, which overcame the problems caused by wear and coal slurry rheology in conventional flow measurement equipment.

In general the experimental results show that the combustion mechanism of coal slurry fuels is dependent on the structure of the residue which remains after devolatilisation, and that this structure changes as combustion proceeds. Individual coal particles agglomerate, fuse and swell according to coal rank, coal concentration, and type of slurry fuel. It is obvious that many complex processes occur during the short devolatilisation phase which affect the majority of the fuels lifetime. The single droplet results indicate that the size and shape of the initial char are a function of coal rank and concentration. High coal concentrations and high swelling mid-rank coals form larger chars. The degree of swelling however, even in highly loaded coal-water fuels, is substantially less than that given by the empirical swelling tests which are used in coal classification systems. This is a common observation in pulverised coal mechanism studies and is attributable to the much higher rates of heating found in flames. The single droplet experiments also indicated that coal particle size can affect the size of the initial char. It was found that coal-oil fuels made with coal particles in the range 40 - 70 \( \mu \text{m} \) produced smaller chars than those made with smaller or larger coal particles. This minimum swelling range coincided with the minimum char burnout time which leads to the conclusion that low swelling chars burn faster. However, this is an oversimplification and can be shown to be incorrect if one compares mid-rank COM's with high rank COM's. Other structural differences, apart from the initial char size are also important in determining the combustion mechanism. It is thought that these differences, together with the swelling behaviour, are a function of the degree of plasticisation of the coal particles within coal slurry droplets during the heating period. Both the single droplet experiments and the furnace trials showed that mid-rank coals formed well-fused hollow chars with large surface blowholes and thin walls. The anthracite and petroleum coke based fuels formed loosely agglomerated chars with small surface pores and a sponge-like internal structure. The behaviour of low rank coals was intermediate between these two extremes. Solids sampled from the flames of low rank coal slurries formed chars which, although agglomerated had a much more extensive internal structure than mid-rank slurry chars. These results led to the conclusion that char structure
was the most important variable in determining the combustion mechanism of coal slurry fuels. The importance of the structure appears to be in its effect on internal surface area and the availability of that area of chemical reaction.

The situation is complicated by the fact that the char structure changes as burnout proceeds. This can be seen very clearly in the single droplet results where pore sizes increased by a gradual erosion of material from around the circumference, overall particle diameter was often observed to slowly decrease, and large sections of the surface were seen to unfold. There are also differences between the behaviour of COM's and CWM's made from similar coals. The mid-rank CWM fuels all produced large swellings at specific points on their surfaces during devolatilisation, resulting in very thin walled structures which were preferentially burned away. This behaviour was not observed with mid-rank COM's. This difference in behaviour was probably due to different rates of surface heating in coal-water fuels. If one part of the surface became hotter than the rest and thus more plastic it would provide an easy route by which trapped volatiles within the particle could escape. The longer liquid phase of coal-oil fuels could prevent such differential heating taking place during devolatilisation. Whatever the reason, the result is a difference in structure and thus a difference in burnout mechanism. The outgrowths from the surface of the CWM particles tend to unfold from the surface and break away. This is similar to the behaviour of low and high rank COM's and COD's. The latter do not form "wormcast" outgrowths but it is thought that preferential reactant diffusion pathways within the char could cause increased localised reaction and thus result in lumps of the surface breaking away.

The structural variables which have previously been mentioned (char size, degree of agglomeration, degree of internal structure, pore diameter, wall thickness etc.) were represented in the mathematical model of the system by two parameters: porosity and pore diameter. The model was used to test the concepts which had arisen from the experimental results, and it was therefore important that it could simulate changes in structure with burnout. It would be optimistic in the extreme to say that this can be done accurately especially when one considers the complexity of the structural changes previously described. However, the model does show that small structural changes
can have a very large effect on the burnout behaviour of the char, thus
demonstrating the importance of structure. What is even more
surprising is that, despite the assumptions made and the inherent
inaccuracy of some of the input data for the model, there is a
good agreement between the predicted results and the actual results
(Figures 3.8a, 3.8b, 3.9, 5.21, 5.22 and 5.23) for mass burnout and
rates of reaction.

The model predicts higher rates of reaction for coal-oil-water fuels than for
similar coal-oil fuels which appears to be due to the increased porosity of
the COW chars. This is difficult to substantiate by the experimental
results since little difference was observed in the structure of chars
when water was added to coal-oil fuels. The single droplet experiments
showed an increase in the intensity of droplet boiling during the
devolatilisation phase, but no appreciable increase in mass lost by
droplet shattering except for very high water concentrations. The
behaviour of the char after devolatilisation was in all cases the same
as when no water was present, except for a decrease in size. The
arguments against the occurrence of an appreciable reaction between
water and carbon have been presented by other workers. Principally,
there is a very low concentration of water in the atmosphere compared
with the other possible reactants. It is also true to say that the
rates of diffusion and reaction of water in porous carbon solids is
similar in magnitude to that of carbon dioxide. The model predictions
shown in Section (3) indicate that this would produce a much slower
reaction rate than that which was measured. It must therefore be
concluded that the increases in reaction rate are due to an increase in
char porosity, but more work is necessary to establish whether this is
associated with variations in the initial pore size. From a more
practical point of view the effect of water was to increase the
temperature of the coal-oil flames, but to produce quite low
temperatures in the coal-water flames. This could be a concentration
effect, demonstrating that the small amounts of water present in the
COW fuels caused higher rates of reaction and thus higher temperatures
whereas the 30% water present in CWM flames caused a decrease in
reaction rates due to flame saturation.
Interesting ash behaviour was observed during the single droplet experiments. As a broad generalisation, well-fused chars tended to form large well-fused ash particles, whereas loosely agglomerated chars formed small fragments of fine, fluffy ash. The structure of the final ash residue was apparently more influenced by the burnout behaviour of the char than by the chemical nature of the original mineral matter. This has important implications since the larger ash particles are more likely to form slagged and soot-blower resistant deposits. However, they are also less likely to present problems in gas cleaning, the efficiency of which is universally related to the size of the solids carried forward.

6.3 Comparison of Results with those of Other Workers

In general, the results presented in this thesis on the structure of coal slurry chars during combustion agree well with those from previous studies on both coal slurry fuels and pulverised coal. Few workers have disputed that the structure of the char is determined during devolatilisation and subsequently has an important effect on the burnout behaviour, at least in so much as it affects the size of the char. Gray et al (1967) showed that the porosity of mid-rank coal particles could increase from 10% to 60% during devolatilisation. Braide (1980) demonstrated that the diameter of droplets of coal-oil fuels could increase by as much as 25% to form large hollow particles, which is a similar degree of swelling to that described in Section 5.1. Street (1969) described range of p.f. char structures which had been sampled from large flames, and again these were very similar to those of coal slurry flames shown in Section (5.2). The predicted variations in surface area with particle burnout shown in Section (3) show the same trends as the experimental results of Jolley and Stantan (1958), as do the predicted reaction rates.

There is also evidence in the literature that the structures of p.f. chars and coal slurry chars vary with coal type. This observation was particularly true in the case of coal-oil fuels (Alabaf et al, 1981) and coal-water fuels (Matthews and Street, 1984). There is nothing however in the experimental results of this study to confirm the assertion of Miyasaka and Law (1980), that the degree of coal particle
agglomeration was dependent on the type of oil used in coal-oil fuels. Coal particle fusion was found to be a function of coal rank for all the fuels tested.

The potential significance of carbonaceous char structure has not been so widely reported. The possibility of combustion occurring on internal surfaces was reported in 1943 by Bangham, and Shiboaka (1969) demonstrated that increased char swelling caused more rapid combustion. Ruskan (1982) postulated that the more efficient combustion observed in coal-methanol mixtures was due to increased char porosity, and Szekely & Faeth (1981) suggested that gaseous reactant could more easily penetrate agglomerates of carbon particles. Jenkins et al (1981) showed that the structure of coal-oil chars could be a rate determining factor, and modelled the behaviour of such chars with an agglomerating/non-agglomerating model (Figure 2.5). Detailed studies on the structure of coal chars at BCURA highlighted the complex nature of the problem and showed that there was a relationship between porosity and pore diameter for synthetic graphites (Spencer 1968), however this work was not applied to combustion mechanism studies.

The overwhelming body of opinion for over fifty years has been that combustion is controlled by the rate of reactant diffusion to the particle surface, or, at lower temperatures, by a combination of diffusion and chemical reaction rate. The basis of these assertions was the early work of Nusselt (1924) and Tu et al (1934). The experimental evidence in favour of these two mechanisms is substantial but it should be stressed that the early experiments were conducted on very large particles which were two orders of magnitude larger than p.f. particles or coal slurry droplets. Later workers (Field et al, 1967, Street 1969, Smith 1971, and Hamor et al, 1973) conducted careful measurements of pulverised coal reaction rates, and concluded that the combined effects of pore diffusion and internal chemical reaction were significant. However, they fitted their results to empirical surface rate equations. Field et al used one equation to describe the chemical reaction rate of all coals (Eq. 2.13) whereas Smith and his co-workers used different Arrhenius type rate equations for different coal ranks (Table 2.6). The effects of external diffusion were neglected in the model presented in this study to describe coal slurry char behaviour because the model was principally used to investigate changes in reaction rate with changes in structure. In order to test the validity
Figure 6.1 Comparison of Char Combustion Models
of this assumption the predictions of the porous solid reaction model were compared with an external diffusion only model and an external diffusion with surface chemical reaction model. The input data for all cases was the same as in Table (3.1). These comparisons are shown in Figure (6.1a) for a 902 rank COM char and Figure (6.1b) for a 401 CWM char. Two cases were considered for the external diffusion mechanism: firstly it was assumed that the COM immediately devolatised to leave a solid spherical residue of carbon which subsequently burned with constant density; secondly, the mass left after devolatilisation was assumed to be concentrated in a hollow shell with a diameter equal to the initial droplet diameter multiplied by the linear swelling coefficient. In the latter case, constant diameter was maintained throughout the particle's lifetime.

It can be seen that there is a good agreement for most of the particle's lifetime between the porous solid model and the other two models with the assumption of constant density. The external diffusion plus chemical reaction model predicts almost exactly the same combustion time, but it can be seen that the effect of reaction on the particle surface is small. However, the assumption of a solid, constant density char leads to a much smaller diameter char than that which is known to occur. The assumption of a constant diameter equal to the droplet diameter multiplied by the swelling factor leads to much higher rates of reaction due to external diffusion.

Smith and his co-workers showed that the resistance to external diffusion was much less than resistance to chemical reaction for particles of 87μm or less. Figure (6.2) compares the surface combustion coefficients predicted by Smith's empirical correlations with the porous solid rates, and the external diffusion rates. This graph suggests that, initially at least, the combustion resistance due to external diffusion is not negligible especially for larger particles and at high temperatures. The magnitude of this diffusional resistance is similar to that of the pore diffusion plus reaction resistance, and these two mechanisms should be considered jointly. There is obviously a strong case for including a resistance to external diffusion term in the overall rate equation.
Figure 6.2: Comparison of Predicted Surface Reaction Rates and External Diffusion Rates.
The main conclusion of this work is that the existing theories on the combustion of coal slurry char residues are based on unrealistic assumptions about the structure of chars during burnout. It has been demonstrated that significant variations exist in initial char structures and that changes in structure occur during burnout, often in a very complicated fashion. Such differences in structure and burnout behaviour result in markedly different combustion rates which are more than sufficient to account for the observed differences in char reactivity for coals of different rank. Changes in char structure can also account for the observed increases in combustion efficiency when water is added to coal-oil fuels. Although the effects of external reactant diffusion cannot be ignored, it has been shown that pore diffusion plus internal chemical reaction are important, rate determining variables.

The structure and burnout behaviour of coal slurry fuel chars were mainly dependent on coal concentration and rank. Coal particle size and concentration of emulsified water had a lesser effect. The structural variables identified in the course of this study were: char diameter, pore diameter, wall thickness, porosity and degree of particle agglomeration. However, these are all inter-related and only char swelling, pore diameter and porosity were used to model char behaviour. These structural variables are important because they affect the amount of internal surface area of the char and the accessibility of this surface area.

Fuels made with mid-rank coals (300 - 700 CRC) formed well-fused, swollen chars which tended to be completely hollow and had large blowholes in an otherwise homogenous surface. High rank coals (100 - 200 CRC), low rank coals (800 - 900 CRC) and petroleum coals formed loosely agglomerated, less swollen chars which had a higher degree of internal structure and smaller surface blowholes. The evidence of this study and of other workers indicates that these chars burned more
efficiently and quickly. Higher concentrations of coal produced larger chars, although coal particle size could increase or decrease char size.

Differences were observed between the combustion mechanisms of coal-oil fuels and coal-water fuels. These were possibly due to differences in the local surface heating rates of the two types of fuel. However, the behaviour of mid-rank coal water fuels was sufficiently similar to that of coal-oil fuels to be explained by the same theoretical model. More work needs to be done on coal-water fuels made with different coal ranks.

In common with many other workers, it has been shown that emulsified water can increase the combustion efficiency of oil-based fuels. No conclusive explanation has been found for this, but there was no evidence to suggest that water caused droplets of coal-oil or coal-water fuels to shatter during devolatilisation. Neither the single droplet studies nor the flame particle size analyses showed this to be true. It has also been shown to be theoretically unlikely that the small quantities of water present could react to a significant effect with the carbonaceous chars. However, it has been shown to be theoretically possible that the observed increases in combustion efficiency are due to differences in porosity, or some other char structure variable, which occur due to the presence of water.

The results suggest that final ash structure could be dependent on the preceding burnout behaviour, as well as on the initial mineral matter chemistry. It would appear that lightly-fused coal chars form lightly-fused particles of fly-ash regardless of whether the ash has a high fusion temperature or a low fusion temperature. This could be a suitable topic for future research involving both coal slurry fuels and pulverised coal.

This work has proved that the single droplet technique is a very useful tool for combustion mechanism studies, and that the qualitative results of such techniques can be verified in full scale combustion trials. The experiments have also shown that one of the greatest problems in using coal slurry fuels in conventional combustion equipment is the design of the burner. A suitable burner was found in the form of the LPA device but more work is necessary on twin-fluid atomisers, such as
the F-jet, before they can be reliably used with coal-water fuels. It is possible that such fuels will always require gas support flames, or preheated combustion air when fired in cold-walled furnaces.

The results of this study imply that mid-rank coals are the least suitable types of coal for coal slurry fuels.\(^2\) Petroleum coke, anthracite and low rank coals form char structures which are more conducive to rapid burnout. There is perhaps some scope for altering char structures by the addition of more volatile components to coal-based fuels, such as water or methanol, and obviously an optimum level of volatiles would exist for each fuel. It is also felt that more work could be usefully directed in the following areas:

(a) A further and more detailed examination of the structure of coal slurry chars formed under different controlled conditions. The study could include: porosimetry by metal injection, density measurement, heat of immersion measurements to evaluate ultrafine pore structures, elevated temperature sorption uptake and thermal cycling studies, as well as ultimate chemical analyses.

(b) An extension of the above work to pulverised coal chars.

(c) An extension of the theoretical analysis presented in this thesis to incorporate external diffusion and furnace aerodynamic variables, non-isothermal behaviour, decreasing particle diameter, and ash inclusion.

Authors Footnotes

\(^1\) This conclusion is based on the results in Figures 3.8a,3.8b,3.9,5.21,5.22 and 5.23, as well as on the other observations reported throughout this thesis. It is accepted that these results are by no means definitive and are indeed open to different interpretations. Therefore it must be said that this conclusion is based on the general trends in char combustion behaviour which were apparent to the author.

\(^2\) Whilst the results presented do indicate that this conclusion is valid it must be stated they relate only to the range of coal types and slurry fuels tested, which was not exhaustive. This is particularly true of the coal-water slurries which were only prepared with mid-rank coals, and it is felt that more work needs to be done in the future on such fuels prepared with different types of coal.
REFERENCES


APPENDIX I

SUMMARY OF COAL SLURRY FUELS TESTED
Table (Ia) Single Droplet Experiments

<table>
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<tr>
<th>Fuel Type</th>
<th>Coal Rank</th>
<th>Oil Type</th>
<th>Coal Conc. (% wt)</th>
<th>Water Conc. (% wt)</th>
<th>Coal Particle Size</th>
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Note (1) Coal ground to a size at which stability is ensured.

n/a = not available
### Table (Ib) Furnace Trials

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<th>Date of Trial</th>
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<th>Water Conc. (%) wt</th>
<th>Coal Particle Size</th>
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### Table (1c) Analysis of Coals Used in Coal Slurry Fuels

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<th>Ultimate analysis (% wt)</th>
<th>Ash Content (% wt)</th>
<th>Ash Fusion Temp (°C)</th>
<th>Moisture (% wt)</th>
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<td></td>
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<td>H</td>
<td>N</td>
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* dmmf
Table (Id). Analysis of Fuel Oils Used in Coal Oil Fuels

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<th>Oil</th>
<th>Specific Gravity (d15.5°C/15.5°C)</th>
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<th>Ash (% wt)</th>
<th>Moisture (% wt)</th>
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APPENDIX II

HIGH SPEED CAMERA CALIBRATION CURVE
Fastax High Speed Camera Calibration Curve
APPENDIX III

SINGLE DROPLET EXPERIMENTAL DATA
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<th>Expt Code</th>
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<th>Filament diam. (μm)</th>
<th>Initial char diam (μm)</th>
<th>Estimated combustion time (ms)</th>
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<td>Initial char diam (μm)</td>
<td>Estimated combustion time (msec)</td>
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*Obscured on film*
APPENDIX IV

FURNACE TRIAL RESULTS
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<th>Trial</th>
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<th>Average Fuel Flowrate (kg/hr)</th>
<th>Average Flue Gas O₂ (%)</th>
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Table (IVb) Gas Analyses - Trial 2

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Time (minutes) from start of trial in brackets.
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(a) >20000 ppm

Time (minutes) from start of trial in brackets.
### Table (IVg) Gas Analyses - Trial 7

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Time (minutes) from start of trial in brackets:
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4 = Part 4 (3.36m from burner)
Table (IVi) Solids Sampling Trial (2)

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Table (IVj) Solids Sampling Trial (4)

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Table (IVk) Solids Sampling Trial (5)

<table>
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<tr>
<th>Distance from burner (m)</th>
<th>Gas Temp (°C)</th>
<th>Gas Velocity (m/s)</th>
<th>Ultimate analysis (%)</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>0</td>
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<td>-</td>
<td>77.4</td>
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<td>0.76</td>
<td>1850</td>
<td>27.45</td>
<td>90.33</td>
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<td>1.21</td>
<td>1650</td>
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<td>85.73</td>
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<td>3.11</td>
<td>1067</td>
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<td>25.11</td>
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### Table (IV1) Solids Sampling Trial (6)

<table>
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<th>Gas Temp (°C)</th>
<th>Gas Velocity (m/s)</th>
<th>Ultimate analysis (%)</th>
</tr>
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<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
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<td>-</td>
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### Table (IVm) Solids Sampling Trial (7)

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### Table (IVn) Solids Sampling Trial (8)

<table>
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<td>Trial</td>
<td>Fuel Pressure (psig)</td>
<td>Fuel Temp. (°C)</td>
<td>Atomising air pressure (psig)</td>
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<tr>
<td>8</td>
<td>94.0</td>
<td>15</td>
<td>97.0</td>
</tr>
</tbody>
</table>
10 DEFINE FILE #1="INBURNM"
15 DEFINE FILE #4="DIFFDATA"
20 DEFINE FILE #2="OUTBURN1"
30 DEFINE FILE #3="OUTBURN2"
40 G=20
50 H=0.001
60 M=1
70 P=21000
80 READ #1,E0,D0,H,F1,G1,V0,P1,M2,T1,X,Z1
90 M6=R0*R0*R0*3.142*P1/6
95 R0=R0*G1
100 E0=-(F1*(1-V0))/(P*G1*G1)
110 GOSUB 4000
115 PRINT "INITIAL POROSITY ";E0
120 M0=M6*E0
121 M5=M0
123 WRITE#3,T1,M6/M6
125 PRINT "INITIAL CHAR MASS (GM.) ":M0*1000
130 CO=P2*M2*273/(22.414*71)
135 PRINT "INITIAL GAS CONC. (GM./CC.) ":CO/1000
140 READ £4,M3,M4,T3,T4,C3,C4
150 D=(0.438*(((T3/100)**1.81)*(((1/M3)+(1/M4))**0.5)))/(1*((T3*T4/10000)**0.1405)*(((C3/100)**0.4)+((C4/100)**0.4))**2))
155 PRINT "DIFF = ";D
160 E0=£0+1*E-4*£2**0.5
165 PRINT "EFFECTIVE DIFF = ";E0
170 READ £4,K2,E2,U,T5,F
175 E2=E2/F
180 K=K*EXP((E2/U)*((1/T5)-(1/T1)))
190 K=K/1000
195 PRINT "REACTION RATE (M/SFO) ":K
210 DIM C(11)
220 DIM R(11)
230 DIM V(11)
240 DIM D(11)
250 A=(R0/2)+(R0/2)*E0*K/(D*NO/2)
255 PRINT "ALPHA SQ. ":A1
280 GOSUB 2000
300 GOSUB 1000
305 Z=Z+1
306 IF Z=Z1 THEN GOSUB 5000
310 GOSUB 2000
320 GOTO 300
330 PRINT "TIME ":T
331 PRINT "REAL TIME (SEC.) ":T*(R0*0.5)*(R0*0.5)/D
340 STOP
1000 H=-0.1
1001 S=0
1010 H1=1
1015 V(1)=0
1020 R(1)=1.001
1025 C(1)=1
1040 FOR N = 4 TO 10
1045 A = A1*+(2*8)-(8*D(N)))*D(N)/(G-1)
1050 V=V(N)
1060 R=R(N)
1070 C=C(N)
1080 K1=H*V
1090 L1=H*(A*C)-(2*V/R))
1100 V(V(N)+L1/2
1110 R=R(N)+H/2
1120 C=C(N)+K1/2
1130 K2=H*V
1140 L2=H*(A*C)-(2*V/R))
1150 V=V(N)+L2/2
1160 C=C(N)+K2/2
1170 K3=H*V
1180 L3=H*(A*C)-(2*V/R))
1190 U=V(N)+H
1200 R=R(N)+H
1210 C=C(N)+K3
1220 K4=H*V
1230 L4=H*(A*C)-(2*V/R))
1240 V(N+1)=V(N)+(L1+L2+L3+L4)/6
1250 C(N+1)=C(N)+H*V(V(N)+(L1+L2+L3)*H/6
1260 R(N+1)=R
1270 NEXT N
1280 IF V(1)>0 THEN S=S+1
1290 IF V(1)<0 THEN S=S-1
1300 IF ABS(V(1))<0.0000001 THEN GOTO 1403
1310 IF ABS(S)<2 THEN GOTO 1380
1320 IF ABS(S)=1 THEN GOTO 1360
1340 V(1)=V(1)-H1
1350 H1=H1/10
1355   GOTO 1020
1360   V(1)=V(1)+H1
1370   GOTO1020
1380   S=0
1390   GOTO 1020
1400   IF C(11)<0 GOTO 330
1404   PRINT
1410   RETURN
2000   REM POSE RADIUS PROFILES
2005   I=DX/((RO/2)*(RO/2))
2010   K1=R*CO/(RO*P)
2015   PRINT "PORE RADIUS", "AREA"
2020   FOR N=1 TO 11
2030   D(N)=(K1*R1*C(N)*T)+1
2035   S1=(E0*2/D0)*((2*G)-(3*E(N)))*D(N)/(G-1)
2040   IF S1=0 GOTO 330
2050   NEXT N
2052   WRITE,3,T*(RO/2)*(RO/2)/D,M0*0.001
2060   IF D(N)>RO/D0 GOTO 330
2070   E1=E0*D(1)*D(N)/(G-1)
2080   R=12.568*E1*CO*D*(RO/2)*V(1)*M
2090   M2=M*E1
2092   WRITE,2,T*(RO/2)*(RO/2)/D,R/M0
2100   M0=M0-M2
2104   PRINT
2105   PRINT "CHAR MASS " M0
2106   PRINT
2110   IF MO<=0 GOTO 330
2112   IF S1<=0 GOTO 330
2120   PRINT R,M2,T*(RO/2)*(RO/2)/D
2121   IF M2=0 GOTO 2130
2125   PRINT "RATE (GM/GM-SEC) ":R/M0
2130   T=T+1
2135   RETURN
4010   REM FIND ROOT
4016   Y1=(4*E0/27)*G*G*G-G+1
4020   G=G-1
4030   Y2=(4*E0/27)*G*G*G-G+1
4040   IF Y1=0 GOTO 4170
4050   IF Y2=0 GOTO 4160
4060   IF Y1>0 GOTO 4080
4070   IF Y1<0 GOTO 4100
4080   GOTO 4110
4090   GOTO 4110
4100   IF Y2<0 GOTO 4010
4110   N=N+1
4120   IF N=19 GOTO 4170
4130   G=G+H
4140   H=H/2
4150   GOTO 4010
4160   Y1=Y2
4170   PRINT "ROOT= ":G
4180   RETURN
5000   REM OUTPUT ROUTINE
5005   FOR N=1 TO 11
5030   NEXT N
5040   Z=0
5050   RETURN
5300   END
Computer Program Flowsheet

Read
\[ M_{ch}, \rho_{ch}, R_d, r, b, \rho_d, V, V_m, P_s, M_g, T \]

Calculate
Droplet mass, Char diameter, Gas concentration, Porosity (Eq. 3.22), Initial char mass

Calculate
Highest positive root of Eq(340)

Read
\[ M_1, M_2, T_{c1}, T_{c2}, V_{c1}, V_{c2} \]

Calculate \( D_{eff} \) (Eq. 3.18)

Read \( K_0, E, T^*, R \)

Calculate \( K \) (Eq. 3.20)

Calculate \( \alpha^2 \)

Calculate pore radius profile for 10 increments of droplet radius (Eq. 3.12)

Solve concentration profile equation by 4th. order Runge-Kutta numerical method for 10 radial increments

Increment time

Calculate mass reacted

Is char mass > 0

Yes

No

Print results

Stop

See Page(71) for notation