POLLUTANT FORMATION AND INTERACTION
IN THE COMBUSTION OF HEAVY LIQUID FUELS

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ABSTRACT

Decreasing quality and stricter environmental regulations impose potential limitations to the use of heavy fuel oils in combustion. Because of their low cost they are economical alternatives for power generation. However, they contain large amounts of nitrogen and sulphur, which form NO\textsubscript{X} and SO\textsubscript{X} during combustion and cause undesirable pollution. Additionally they often produce carbonaceous particulates.

A knowledge of the formation and interaction of nitrogen and sulphur compounds in combustion is necessary to establish pollution abatement strategies. In this thesis a study of those processes was performed using a number of heavy petroleum-based fuels.

An extensive literature review on relevant aspects of heavy fuel combustion was carried out, with particular emphasis on the formation of NO\textsubscript{X}, SO\textsubscript{X}, particulates and ash.

In the first stage of the experimental work, the ignition characteristics of the fuels were determined by means of the single suspended droplet technique. They were found to comply with most of the correlations for heavy fuel combustion established by Taylor and Burgess, relating the combustion characteristics of a fuel droplet to its dimensions.

The formation of NO\textsubscript{X} and SO\textsubscript{2} was studied in a drop-tube furnace as a function of the stoichiometry, flame temperature and residence time. Additional information about other species formed was also obtained, as well as about the formation of thermal-NO\textsubscript{X}.

In a further stage, a numerical model was used to simulate mathematically the experimental results and study the mechanisms of interaction between N and S species. These calculations were aided by measurements of the flame temperature in the drop-tube furnace.

In the last stage of the experimental work, the interaction of sulphur species with NO\textsubscript{X} (ie NO and NO\textsubscript{2}) was studied experimentally by adding SO\textsubscript{2\textsubscript{gas}} to the combustion system in the drop-tube furnace. Sulphur was found to influence the formation and emission of NO and NO\textsubscript{2} in different ways according to the equivalence ratio. Nitrogen-sulphur interactions were also studied as a function of the residence time.
ACKNOWLEDGEMENTS

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Table 1: Physical and chemical properties of several typical heavy oils

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OBJECTIVE OF THE PRESENT WORK

The quality of heavy fuel oils continues to decrease world-wide. Although the total amount available is large, not only from refining operations but also as natural occurrences, difficulties for their use arise not only from the pitfalls of their manipulation but also as a result of their noxious combustion emissions, predominantly NOx, SOx and particulates. These fuels become major contributors to the processes of acidification and eutrophication associated to transboundary pollution by virtue of the large amounts of nitrogen and sulphur compounds that they contain. As a result, strict legislation is being implemented that specifically limits the amount of sulphur contained in some heavy liquid fuel oils.

In this thesis, a number of heavy distillate fuels intended for gas turbine use are studied with respect to their NOx and SOx formation capacity. The fuels investigated are by-products of refining operations, and can be differentiated in two groups, namely heavy vacuum gas oils and heavy coker gas oils. The former are distillate fuels produced during the vacuum distillation of crude oil. Distillation at 30-40 mm Hg allows heavier hydrocarbons to vaporise at much lower temperatures than their boiling points at atmospheric pressure, thus avoiding thermal cracking. On the contrary, heavy coker gas oils are produced as a distillate stream during the delayed coking stage. This is a process of thermal cracking, in which heavy hydrocarbons are heated up to 520 °C and passed through a coke drum at 4 - 5 atm, where they break to produce lighter hydrocarbons at a low rate.

In addition, Orimulsion was another fuel studied in this thesis. This oil:water emulsion is a natural occurrence in the Venezuelan Orinoco basin. In spite of its controversial reputation, this 30 %-water emulsion has several advantages over other conventional fuels, such as ease of handling, transportation and processing, and environmental emissions comparable to those of other heavy fuels.

All of the fuels studied contain large amounts of sulphur and nitrogen (details on their composition can be seen in "Appendix II", page 265). Nitrogen and sulphur in the fuel form NOx and SOx, which can interact during combustion, sometimes in unpredictable ways. Limited research has been reported in the past about the interactions between NOx
Furthermore, a large part of the work has been focused on the interaction of thermal-NO\textsubscript{X} and oxides of sulphur. However, few and contradictory results have been reported on the effect of sulphur oxides on fuel-NO\textsubscript{X}, ie nitrogen oxides originating from nitrogen compounds in the fuel.

As well as providing information about the fundamental NO\textsubscript{X} formation processes, a knowledge of their interaction with sulphur compounds in combustion can assist devising pollution abatement strategies, similar to the way in which the design of low-NO\textsubscript{X} burners was aided by the detailed knowledge of the NO\textsubscript{X} formation processes.

It is the object of this thesis to provide experimental information and analysis of the processes whereby fuel-NO\textsubscript{X} (NO and NO\textsubscript{2}) and -SO\textsubscript{X} interact in the combustion of heavy hydrocarbon liquid fuels.

Most of the experimental work was carried out in a semi-industrial scale drop-tube furnace. Although the conditions of combustion in the drop-tube furnace differ from those in a gas turbine (higher combustion intensities, higher pressures and shorter residence times would be encountered in the latter), considerable gains can be obtained from the understanding of the fundamental NO\textsubscript{X}-SO\textsubscript{X} interaction processes at atmospheric pressure.

In addition, numerical modelling is a tool that provided further information about the interactions sought. The Sandia CHEMKIN suite of codes can simulate different flow regimes, and be customised to suit the experimental combustion conditions, fuel input and reaction system. The effect of varying amounts of fuel-S and -N can be simulated by modifying the input to the code.

Five variables were important when determining the interaction effects between NO\textsubscript{X} and SO\textsubscript{X}:

- The stoichiometry of the combustion environment, which was varied by modifying the amounts of combustion air present in the furnace.
• The flame temperature, which was varied by setting different furnace wall temperatures and equivalence ratios
• The residence time in the combustor, by sampling at various locations along the furnace tube
• The amount of total sulphur present in the combustion system: fuels with different S contents were studied, and increased amounts of fuel-sulphur were simulated with the addition of $\text{SO}_2$-gas.
• The amount of nitrogen present in the fuel, by studying fuels with different N contents

A series of complementary experimental techniques were used to obtain further information about the fuels studied. For instance, experiments with the single suspended droplet technique enabled the determination of their basic ignition characteristics. In addition, the size variation of a fuel droplet prior to ignition, the formation of soot or coke particulates from isolated single suspended droplet experiments were observed by means of video recordings.

Other information, such as the potential for NO$_x$ and SO$_x$ formation of the range of fuels studied, the axial flame temperature profile, the formation and emission of other combustion species and of thermal-NO$_x$ also assisted to establish and validate the numerical model and provide further information about the interactions studied.
1. **Heavy oils**

1.1. **General characteristics of heavy oils and oil:water emulsions**

The composition of a particular crude oil is unique and it is not possible to define it with precision. As a rough approach, there are alicyclic, cyclic and aromatic hydrocarbons; compounds of S, N, O and traces of others containing Ni, Fe, V, Mo, Cl, F...

Heavy oils are products derived from crude oils. Thus, their composition varies with that of the source crude. They are composed entirely, or substantially, of the residuals or bottoms from petroleum refining operations, i.e., materials which remain in a condensed form in the processing. The atmospheric distillation temperature for these components exceeds 540 °C, and they appear after all other lighter products have been removed from the refinery stream.

Some physical and chemical properties of heavy oils are given in the following Table as a function of the sulphur content:

<table>
<thead>
<tr>
<th>Property</th>
<th>High sulphur</th>
<th>Intermediate sulphur</th>
<th>Low sulphur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur, % by weight</td>
<td>2.2</td>
<td>0.96</td>
<td>0.50</td>
</tr>
<tr>
<td>Carbon, % by weight</td>
<td>86.25</td>
<td>87.11</td>
<td>87.94</td>
</tr>
<tr>
<td>Hydrogen, % by weight</td>
<td>11.03</td>
<td>10.23</td>
<td>11.85</td>
</tr>
<tr>
<td>Nitrogen, % by weight</td>
<td>0.41</td>
<td>0.26</td>
<td>0.16</td>
</tr>
<tr>
<td>API gravity</td>
<td>17.3</td>
<td>21.5</td>
<td>24.7</td>
</tr>
<tr>
<td>Viscosity, cSt @ 38 °C</td>
<td>690</td>
<td>129</td>
<td>49</td>
</tr>
<tr>
<td>Conradson Carbon, % by weight</td>
<td>12.51</td>
<td>5.64</td>
<td>2.43</td>
</tr>
<tr>
<td>Hexane insoluble, %</td>
<td>10.33</td>
<td>4.72</td>
<td>2.25</td>
</tr>
<tr>
<td>Ash, %</td>
<td>0.08</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Metals, ppm:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vanadium</td>
<td>350</td>
<td>155</td>
<td>70</td>
</tr>
<tr>
<td>Nickel</td>
<td>41</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Sodium</td>
<td>25</td>
<td>10</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Iron</td>
<td>13</td>
<td>9</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

**Table 1: Physical and chemical properties of several typical heavy oils**

An important physical property is viscosity, which ranges from 245 to 1,000 cSt at 38 °C, although such values are not rigidly established. The nitrogen and sulphur contents are two of the most important chemical parameters. The following graph shows the dis-
tribution of nitrogen and sulphur contents in various types of vacuum residues according to their geographical origin:

![Graph showing sulphur and nitrogen contents in vacuum residues](image)

**Figure 1: Sulphur and nitrogen contents in vacuum residues according to their geographical origin**

Since heavy oils are some of the last products from crude refining, and their production is subject to that of other more profitable streams, the quality and characteristics of those materials fluctuate from one refinery to another. Until the mid seventies oil crisis, variations in heavy oil composition were small due to the continuity of suppliers and their uniform refining techniques. This was helped also by the less strict environmental regulations in force by then. As the crisis deepened in the late seventies and environmental regulations became more rigid, a shift in oil sources lead to an increase of sulphur content and increases of other contaminants of reduced volatility.

![Graph showing evolution of proven worldwide reserves of crude oil and natural gas](image)

**Figure 2: Evolution of proven worldwide reserves of crude oil and natural gas**

![Graph showing percentage of heavy fuel oils in total worldwide production of petroleum products](image)

**Figure 3: Percentage of heavy fuel oils in total worldwide production of petroleum products**
Whilst the World reserves of crude oil and natural gas increased during the last twenty five years (see Figure 2), the production and consumption of heavy oils decreased (Figure 3), giving way to lighter, more valuable compounds and residual products with lower H content and heating value.  

Refineries have been adapted to intensify the production of light compounds in processes like that shown in Figure 4. For instance, visbreaking units (intermediate temperature, high pressure cracking) are being added to existing processes. Visbreaking produces additional volatile materials and a "cracked" residual material. The volatiles so produced may be used either to increase the yield of light products or to replace gas oil as a "cutter" stock for adjusting the viscosity characteristics of heavy oil by blending with the residual fractions.

The "cracked" material produced by visbreaking has higher asphaltene content with different characteristics than that in the original distillation residua. Since N, S and ash components tend to concentrate in the residua, their amounts are directly related to the residual fraction in the final blend.

Delayed coking is another process which increases the proportion of light products, with total transformation of residues into gases, condensates, gasolines, distillates and coke. Delayed coking is performed at 500 °C and 5 bars at a very low rate. The products are subsequently separated by distillation, although the large formation of coke in the chambers makes it necessary to run the process in cycles so that these deposits can be removed.

An additional practice in heavy fuel oil commercialisation is the marketing by "jobbers", agents who blend heavy oils to meet specifications, thus making it difficult to track the
original source and quality of the oil. Heavy oils can be supplied as blends of residual and distillate materials, ie, “reduced” crude (crude which has had only the most volatile fractions removed) or “straight run” residues (fluid residue after atmospheric and/or vacuum distillation). Blending may give rise to incompatibility problems with precipitation of non-compatible components which may cause clogging and other handling difficulties.

Figure 5: World reserves of extra-heavy hydrocarbons and bitumen

Heavy oils are also a natural occurrence in some parts of the World. They represent a substantial part of the petroleum reserves, almost as large as those of crude oil. A comparative chart of heavy hydrocarbon reserves is presented in Figure 5. In particular, the Orinoco belt contains the World’s largest reserves of heavy crude oil and bitumen.

Emulsification is the most viable way for heavy crude oil exploitation. An emulsion can be defined as a heterogeneous system of liquid phases, consisting of at least one immiscible liquid dispersed in another as droplets. The liquid that is broken into droplets is the internal or dispersed phase, whereas the liquid surrounding the droplets is called the continuous or external phase.

The commercial name of oil:water emulsions from the Orinoco area is Orimulsion. The industrial process of Orimulsion production starts with the extraction of the crude oil. This is carried out by pumping water underground, forming a primary emulsion that contains some amounts of gas. The gas is subsequently stripped in heat exchangers. The primary emulsion is then broken, and the pure oil goes to a reformation process. The fi-
nal oil:water emulsion is formed by mixing with 30% desalinated water containing surfactants of the type onylphenol ethoxylate. In some cases residual oils contain sufficient amounts of natural surfactants that stabilise the emulsion for long periods of time.

The large amounts of vanadium and sulphur contained in Orimulsion present difficulties for refining, basically due to interaction with catalysts. However, its low viscosity facilitates handling, pumping and transportation. Orimulsion can also be burnt in boilers and heaters, and this is one of its most successful applications.

1.2. Chemical composition of heavy oils

As described earlier the composition of heavy oils is dependent on the source crude oil composition. Since this is unique and varies from source to source and geographical origin, the chemical composition of heavy oils cannot be defined with absolute precision.

If deasphalted oil and petroleum distillates are separated during refining, a more complex, higher molecular weight, residual fraction known as asphaltic bitumen remains. This fraction, along with a variety of other petroleum oils and residues will become fuel oils.

Classification of samples into various fractions by using precipitation by solvent treatment is a widely-used method for assessment of petroleum stock characteristics. None of the fractions defined contain a single molecular structure but a class of structures with a range of molecular weights and polarity characteristics that cause the fraction to be insoluble in other compounds.

The asphaltic bitumen components of petroleum are traditionally separated by a paraffinic solvent, n-heptane, into:

a. A soluble maltene portion, containing high molecular weight waxes (C_{30} - C_{90}), washed out of precipitated asphaltene with hot n-heptane. Further solvent addition separates this fraction into saturates (with n-heptane), aromatics (with benzene) and resins (with methanol/benzene/trichloroethylene).
b. A precipitated asphaltene (sometimes called “hard asphalt”), wax-free material insoluble in large quantities of n-heptane, but soluble in hot benzene. This fraction normally represents 19% of the initial oil mass.

The structure and proportion of asphaltenes vary with the source of crude oil. The asphaltene fraction separated by heptane is characterised by a large molecular weight (1 - 2×10^3 or 2 - 16×10^3 according to different authors and depending on temperature and the polar strength of solvent), whereas maltenes (saturates, aromatics and resins) have smaller molecular weights (200 - 400 or 500 - 1,200, according to different authors).

The colloidal nature of petroleum bitumens has been clearly established. Phenomena occurring in this colloidal system involve the aromatic high molecular weight asphaltenes being peptised by the maltenes and the resins contained in the latter. Interactions between asphaltene-maltene-resin are deemed to occur by means of strong hydrogen bonding between many of the components. The presence of phenols, carboxylic acids, esters, ketones and basic nitrogen components reinforce hydrogen bonding.

Resins (the petroleum fraction which is soluble in pentane and easily absorbed on surface-active materials such as Fuller’s earth) also act as co-solvents for asphaltenes and other hydrocarbon fractions.

A dynamic equilibrium between different heavy oil components has been suggested:

```
Petroleum, bitumen or pitch

Maltenes
Oil<br>Resins<br>Asphaltenes<br>Carbenes<br>Carboids<br>Coke
```

Asphaltenes can be reduced by hydrogenation to lower molecular weight oils (maltenes, resins...). The opposite procedure, ie oxidation, will shift the dynamic equilibrium towards asphaltene formation. Thus asphaltenes can be formed by air blowing from resins, aromatics and maltenes. Also heating with sulphur causes the same effect as it produces dehydrogenation. The addition of strong acids into oil could cause precipitation of asphaltenes.
1.3. Molecular structure of asphaltenes

One of the best representations of the asphaltene micelle is that reported by Yen: He suggests molecular weights of $1 - 5 \times 10^3$, a molecular formula of approximately $(C_{79}H_{92}N_2S_2O)_3$ and molecular shape as in Figure 6.

This structure would be formed by several flat, stacked condensed rings. Five of these rings, each containing from 8 to 16 condensed rings could be placed at distances of 3.5 Å - 3.7 Å, and connected by systems of sulphide, ether, aliphatic chain and/or naphthene ring linkages. The condensed sheets may contain O, S and/or N atoms which may act as free radicals for anchor points of bound metals like Ni, V, Mo or Fe.

The whole asphaltene complex would be 8 - 16 Å in diameter and 16 - 20 Å in height.

1.4. Characterisation of heavy oil properties

Both physical or chemical properties of heavy oils must be defined as they influence the oil’s performance. The properties listed below provide a qualitative indication of the oil’s performance, and most of them are of common interest in any other liquid fuels.

Figure 6: Asphaltene molecular shape, as proposed by Yen
start-up and shut-down procedures as both processes are accomplished by successive shift from light distillate to heavy oil or vice versa.

5. Emulsion stability: The stability of an emulsion is an important parameter. Long-term stability is required in some cases, whereas in other cases, for instance to recover the initial crude oil, limited stability is wanted. This parameter is controlled by variables such as the type and amount of surfactant and non-surface active components, temperature, mechanical agitation, physical properties of the oil, age of the emulsion...

There are five ways in which the structure of an emulsion can change. The first four may appear concurrently:

a. Accumulation of droplets on one end of the system, with no change in droplet size or size distribution. This is the effect of external forces: gravitational, centrifugal, electrostatic... “Creaming” is the formation of a layer at the top of a emulsion.

b. Flocculation: Aggregation of droplets within the emulsion, with no change in droplet size. This is the result of attractive forces between droplets.

c. Droplets resulting from the former two processes aggregate into larger droplets.

d. Increase of the average droplet size as a result of the emulsion liquids not being totally immiscible (Ostwald ripening)

e. Inversion of the emulsion, ie a water:oil emulsion becomes oil:water.

1.4.2. Chemical properties

Chemical properties determine pollutant emissions, corrosion, solid deposits due to carbonaceous and ash substances and, as a result, other harmful effects on metal surfaces, such as hot corrosion.

1. Ash and metallic elements (see also section “4.4.4. Ash”) : Ash is formed by mineral inorganic compounds present in the crude oil that concentrate in residual oils during the refining process. Ash residua left after combustion generally increases with the asphaltene content. Residual fuels may contain up to 0.1 % ash.
Ash compounds may contain elemental metals and alkaline earth elements (Al, Fe, Ni, V, Ca...) in the form of oxides and sulphates, non metals (Si) as oxides and alkaline elements (Na) as sulphur and vanadium compounds. They all form corrosive combinations.

The effect of ash deposition on components located in the hot gas path is to reduce the cross-sectional areas for flow, to increase surface roughness and to alter surface profiles leading to reduced performance and corrosion of metallic materials. Other effects include the erosive and abrasive action of ash particles.

2. Sulphur content (see also section “4.2. SOx”): It has an obvious influence on the formation of harmful sulphur compounds. Although sulphur causes corrosion and deposits, the removal of sulphur by desulphurisation is an expensive process. No limit is generally imposed in specifications, although a proposal to reduce the S content in fuels is being reviewed by the EU at the time of editing this thesis. The effects of sulphur can be minimised by restricting the metallic elements in oil which may form harmful combinations. The sulphur content in heavy fuel oils can sometimes exceed 3%, mainly in organic form.

Sulphur is oxidised in flames to form SO₂, and subsequently SO₃ in small amounts. SO₃ represents a serious problem if a heat recovery unit is placed downstream from exhaust, as it may work at a metal temperature below 120 °C, where acid corrosion may take place if SO₃ reacts with water vapour to form H₂SO₄.

3. Nitrogen content (see also section “4.1. NOₓ”): Nitrogen in fuel normally concentrates in the fractions of higher boiling point during distillation. As a result, the nitrogen content in fuel varies considerably. The following contents can be found, according to the type of fuel:

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>Average N (% by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil</td>
<td>0.65</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>2.30</td>
</tr>
<tr>
<td>Heavy distillates (nos. 4, 5, 6)</td>
<td>1.40</td>
</tr>
<tr>
<td>Light distillates (nos. 1, 2, 3)</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table 2: Typical nitrogen content of standard fuels
The nitrogen content increases with the asphaltene content in heavy oils. Fuel-NO\textsubscript{X}, originated by the oxidation of fuel-N, can then become important. NO\textsubscript{X} emissions from Orimulsion are comparable to those of heavy oils.

Nitrogen oxides are regarded as environmental pollutants, and all sources of NO\textsubscript{X} are subject to environmental regulations.

4. Water and sediment: They tend to cause fouling of the fuel-handling facilities. These impurities may be incorporated during sea transportation in unclean tanks and because of careless storage practices. They must be kept as low as possible, although they are not likely to exceed 0.5 % or 0.005 % respectively. Filtration is required if these limits are exceeded.

5. Carbon residue: A measure of the quantity of solid deposits formed when medium or heavy oils are heated so that evaporation and pyrolysis take place. Carbon residue tests are intended to provide an indication of the extent of carbon formation which may be expected in real operation. Carbon residue formation can be estimated by two tests:

a) Ramsbottom Carbon Residue of Petroleum Products \(^7\): A weighed sample in a glass bulb with a capillary opening is placed inside a metal furnace at approximately 550 ºC. The sample is quickly evaporated from the bulb, leaving the heavier residue behind to undergo cracking and coking reactions in the presence of air. The Ramsbottom Carbon Residue is reported as the weight percentage of original sample remaining and therefore it includes ash in the value.

b) Conradson Carbon Residue of Petroleum Products \(^2\): Porcelain or silica crucibles are the sample container. The heat treatment temperature is less well controlled than in the Ramsbottom test, although heating times are specified.
2. Combustion

2.1. Combustion of heavy fuels and emulsions

Heavy fuels consist of mixtures of hydrocarbons with widely different boiling points. When a heavy fuel is subjected to low temperatures in a combustion atmosphere, selective distillation occurs. Lighter fractions evaporate forming bubbles which cause the swelling and probable destruction of the droplet, as well as change the chemical composition of the fuel. This is called disruptive evaporation.

A further increase of the fuel temperature to values close to the boiling point may result in thermal decomposition, ie pyrolysis, leading to the formation of coke-like residues, named cenospheres (see section “4.4.3. Coke”). Because of these carbonaceous bodies formed during combustion, radiation plays a more important role than in light fuels, where such effects can be neglected.

As a result, the droplet size during the combustion process is not governed by a $D^2$ law as in volatile fuels (see section “2.3.2. Free droplet technique”):

$$D^2 = D_0^2 - Ct$$

where the droplet diameter at time of combustion $t$ can be calculated from the initial droplet diameter $D_0$ and a proportionality constant $C$.

Four major inconveniences arise when firing heavy fuels:

1. Need for heated storage, transportation and additional heating before atomisation, due to high viscosity
2. Tendency to form coke particles
3. Emission of SO$\text{X}$ and NO$\text{X}$
4. Formation of corrosive deposits.
1 and 2 are caused by the high molecular weight and the asphaltene nature of some constituents. 2, 3 and 4 stem from the presence of sulphur, nitrogen, vanadium and other metals in the fuel.

In the case of emulsions the physical effects of water addition lead to better combustion properties by improved atomisation\textsuperscript{72,90}. \textit{Micro-explosions} are produced as the result of the formation, growth and bursting of vapour bubbles within the superheated droplet. Since the oil can sustain very high temperatures during combustion, the water droplets can be superheated. The emulsion droplet is eventually shattered by the internal formation of water bubbles and their rapid vaporisation. This process is called secondary atomisation, which increases the evaporation surface area and the mixing of the burning species in air. The amounts of particulates and smoke formed are minimised.

2.2. \textit{Stages in heavy fuel combustion}

From both theoretical and practical studies the following stages of heavy fuel combustion in hot air have been differentiated:

a. \textit{Volatile release}: After injection, fractional distillation occurs as the fuel droplets are heated in hot air or oxidising atmosphere. Gases cause the ejection of tiny droplets away from the droplet surface, although sometimes boiling may become violent enough to cause the total disruption of the original droplet. Evaporation of the low boiling point components carries on with swelling until the onset of ignition.

b. \textit{Ignition}: Vapour from the droplets and the hot air mix, causing an increase in the mixture temperature. Ignition occurs when the mixture reaches its flammability limits. The time taken for ignition is named Pre-ignition Delay ($t_i$), which has been frequently related to an Arrhenius-type expression like the following\textsuperscript{86}:

\[
\frac{1}{t_i} = A_i \exp \left( -\frac{E_{\text{act}}}{R T_f} \right)
\]
where $E_{act}$ represents an overall activation energy and $T_f$ is the temperature of the combustion environment. Ignition time depends upon the chemical structure of the hydrocarbons, as it has to facilitate gaseous reactions.

The onset of combustion causes slight thermal decomposition. The heat released produces further fuel evaporation from the fuel droplet. Then the viscosity of the residue increases as large paraffins are broken down, side chains are stripped from asphaltenes and similar molecules, undergoing condensation to form carbon-like structures.

c. **Coke formation**: The evolution of the volatile matter ends abruptly and the droplet collapses forming a rigid carbonaceous residue, known as cenosphere. Oils with higher asphaltene content show the least contraction and form large thin-walled coke shells approximately the size of the original droplet. Experimental observations indicate that these materials become rigid while still evolving decomposition vapour, because their aromatic structures are very suitable for rapid carbon formation (see section “4.4.3. Coke”).

The final amount of oil mass remaining in the solid residue represents between 0.5 and 10 % of the original drop mass.

d. **Coke structure and burn-out**: Coke particles thus formed are spherical and hollow. The carbonaceous residue then undergoes slow heterogeneous combustion at a rate of one-tenth of that of the initial droplet, representing as much as 50 % of the total burning time of the droplet. In large particles at high temperature, diffusion of oxidant species control the reaction rate, whereas in small particles at low temperature the surface reactions control the reaction rate $^{150}$.

2.3. *Study techniques of the combustion of heavy oil droplets*

Several techniques have been evolved to reproduce the very demanding conditions occurring in combustion chambers $^{83,99}$:
2.3.1. Single suspended droplet technique

The single suspended droplet technique consists of placing a droplet of chosen, but variable, size on a fibre or metal wire and subjecting it to the effects of energy emission in the form of gas-flame ignition, immersion in a furnace or radiation from a lamp.

Criticism of the Suspended Droplet technique stems from various facts:

- Droplet sizes used are generally several times larger than those in real furnace operation, thus not truly representative of spray combustion.
- Heating rates may be comparable to those in large furnaces, but convective streams affect the natural shape of the flame.
- If a radiative source of heat is employed, the heating rate is influenced by the different infrared absorbances of the sample components.
- The supporting fibre causes distortion of the droplet shape and increased heat transfer to the droplet, which results in inaccurate droplet temperatures. Metallic wires can catalyse the combustion of the carbon residue.
- The amount of coke eventually formed is also modified by the alteration in droplet temperature, which affects the rate of pyrolysis.

However, this method provides a quick initial understanding of the comparative behaviour of a range of fuels. In addition, some of these drawbacks can be avoided with the use of very fine wires or fibres and by suitably coating the wires.

A variety of fuels have been studied in the past, ranging from coal slurries to heavy or distillate oils, lubricating oils, etc.

One of the earliest studies with the single suspended droplet technique was published by Masdin and Essenhigh. Droplets suspended from a silica fibre were subjected to both convective and radiative fields of variable intensity provided by two coils. By using pitch creosote as a sample fuel they observed that a fixed gas temperature was necessary for the droplets to ignite. Below such temperatures droplets would only evaporate.
In their experiments they observed the combustion of pitch creosote to undergo two stages:

a. Volatile combustion followed by carbon "cenosphere" formation
b. Combustion of the carbon cenosphere.

The variation of burning times with drop diameter followed the form:

\[ t_c = Kd_0^2 \]

where K represents a burning constant, calculated from the experimental values of \( d_0 \) and \( t_c \) obtained from ciné records.

If the heat was intense enough the droplets would ignite. Cenospheres formed from droplets which underwent ignition, for which a convective field was needed, were half the size of those formed after simple evaporation in radiation field.

Similar equipment was used later by the same investigators. They observed the changing character of the droplet size throughout the combustion of heavy residual oil. Swelling and contraction alternated, eventually to produce a solid residue (cenosphere) which combusted heterogeneously after the volatiles burned in a flame. They established that, although the process of burning is not uniform, a certain relationship exists between \( d_0 \) (initial drop diameter) and \( t_v \) (burning time of volatiles). The values of the proportionality constant K for heavy residual oils reported by the researchers were close to those obtained for kerosene, meaning that under equal conditions it takes similar time to burn the volatiles produced by any type of fuel.

Natarajan burned residual fuel droplets of around 3,000 \( \mu \text{m} \) initial diameter by using a \( \text{H}_2-\text{O}_2 \) micro torch at 2,200 °C. His observations included disruptive behaviour with large coke particles being expelled from the burning mass, after the burning of volatiles. These particles would leave an smoky trail behind.
It was also observed that combustion was not self-sustained, as when the heat source was removed the flame would be quenched. Only in the final stages the residue remaining after distillation and burning of the volatiles burned rather slowly.

Lightman and Street and Marrone et al. conducted studies of heavy oil droplet ignition that were published almost concurrently. Lightman and Street employed a heating lamp to irradiate droplets attached to silica fibres, and a gas flame to ignite the vapour ejected at heating rates similar to those experienced in real plant operation (approximately $10^4 \, ^\circ C/s$). The samples studied included a range of residual oils of different geographical origin and varying carbon-forming propensity, their asphaltene and maltene fractions and, in a further division, the acetone-soluble and insoluble fractions of the maltenes.

Marrone et al. suspended droplets of 1.0 to 1.5 mm on a quartz filament above a premixed $C_3H_8$-air flat-flame burner at an equivalence ratio of 0.8 and a temperature of 1,500 °C. An atmospheric residual oil, a high-sulphur no. 6 oil and a blend of residual oil and no. 2 oil were studied.

Lightman and Street divided the combustion processes into three separate stages: The pre-coking stage commenced with slight swelling and volatiles evolution under the form of granules around the droplet at 250 - 350 °C. It was followed by sharp ebullition at 300 - 400 °C and bubbling up to 800 °C along with a series of expansion and collapse alternating very rapidly with increasing diameter over twice the original size. Violent ejection of vapour also occurred, which was attributed by Marrone et al. partly to volatiles produced by cracking.

It is in this stage that ignition begins, marked by radiation of high intensity.

The second stage (the coke formation) was marked by the end of volatiles evolution and the formation of a porous, rigid coke residue after final contraction, but before the end of the combustion of volatiles. The coke residues (studied under the Scanning Electron Microscope) were hollow and roughly spherical. The mass was concentrated in a shell of
thickness only 5% of the total diameter. The shell contained large holes and cavities. At the end of the coke formation the temperature had risen to 1,300 °C.

The third and final stage involves the burn-out of the coke residue; its diameter decreasing, pores widening and fragments being ejected. The complete disappearance of the particle marked the end of the burn-out stage. Peak temperatures of 1,400 - 1,500 °C were attained.

Taylor and Burgess and later Malik and Burgess used silica-coated Pt/Pt 13%-Rh thermocouples of 25 µm diameter in a furnace and ciné camera recordings to obtain the behaviour history of droplets of as small sizes as 450 µm diameter. Various samples were analysed: Medium fuel oil, heavy fuel oil, atmospheric residue and gas oil.

Three clearly differentiated combustion stages were observed (see Figures 7 through to 10 in page 46):

a) The pre-ignition delay period: This is the time elapsing between the insertion of the droplet in the furnace and the time when an envelope flame establishes around the droplet. The most important process taking place involves the evaporation of volatiles from the droplet.

b) The flame period: Ignition is marked by a sharp increase in the temperature and light emitted by the burning specimen. The temperature rises as smaller amounts of volatiles are evaporated. Cracking turns out to be the source of more volatiles. A solid residue is left, which collapses onto the thermocouple when the flame disappears.

c) The coke-ignition period: Hot gases reach the particle surface and heterogeneous reactions take place between oxygen and carbon, in a highly exothermic process that increases the particle temperature while a red glow is emitted. Quenching occurs when heat losses exceed heat generation.
Figure 7: The pre-ignition delay period

Figure 8: The flame period

Figure 9: The coke-ignition period

Figure 10: Soot residue left after combustion
Malik and Burgess observed a linear relationship between the Pre-ignition Delay and the initial diameter of the droplet:

\[ t_i = K'd_o + A \]

where:
- \( t_i \): Pre-ignition Delay
- \( K' \): slope
- \( d_o \): initial diameter
- \( A \): intercept.

Taylor and Burgess studied a wide range of residual oils and atmospheric residues of varying geographic origin, and attempted to relate fuel composition to combustion parameters.

An inverse linear relationship was proposed between the Ignition Temperature and the initial diameter:

\[ T_i = \frac{A}{d_o} + T_\infty \]

where \( T_\infty \) is a constant, possibly the ignition temperature of a large pool of oil (when \( d_o \) is very large). The inverse relationship of \( T_i \) with \( d_o \) proves that it is larger for small droplets than for large ones. The latter was explained as a consequence of the ease for larger droplets to produce enough vapour to reach the flammability limits of the fuel in the surroundings of the droplet, in comparison to small ones.

Other relationships of the combustion parameters with the initial droplet diameter for other combustion stages reported by Taylor and Burgess are:

\[ t_i = K_i d_o \quad t_f = K_f d_o^2 \quad t_c = K_c d_o^2 \]

where:
t,: Pre-ignition Delay
\(t_f\): Flame Time.
\(t_c\): Coke Combustion Time

\(K_i, K_f, K_c\): constants dependent upon the fuel type and the combustion conditions.

From their studies they concluded that \(K_i\) seemed to increase with high aromatic and low saturates content.

Like Masdin and Thring, Taylor and Burgess observed little variation of \(K_f\) in different fuels. They concluded that at high temperature, fuel composition is not relevant as long as the flame is established and it provides heat for evaporation and cracking.

Although \(K_c\) varied considerably throughout the group of fuels studied it showed a good, although not complete, relationship with the Conradson Carbon Residue:

\[
K_c = 0.295 \text{ (CCR)}^{0.72} - 0.071
\]

which evidences a relationship between the coke combustion time and the amount of coke produced by the droplet.

2.3.2. Free droplet technique

The free droplet technique, also known as the single droplet technique, consists of firing isolated, unsupported droplets into a hot furnace. The droplets burn as they travel across the hot oxidising atmosphere created by electric coils or the combustion of an ancillary flame \(^{53}\). If the droplets fall vertically through a furnace the residence time, and therefore the extent of the combustion process, are limited by the length of the combustion duct. An alternative option is to fire the droplets upwards against gravity \(^{21}\). The combustion history of droplets burning in the single droplet technique is followed by optical and photographic instruments \(^{21,91,105}\).

This technique provides a better approach to real combustion conditions if compared to the single suspended droplet technique as the interference created by the supporting fila-
ment (heat transfer, nucleation, catalysis) is eliminated. However, even then the conditions created cannot match those of real combustion devices, as the effect caused by the simultaneous burning of adjacent droplets is not reproduced.

The changes in droplet size, flame evolution and other processes are observed, and they can be related to the combustion time. Bolt and Saad found that the diameter of droplets of light hydrocarbons followed the equation:

\[ D^2 = D_o^2 - Ct \]

where:

- \( D \): droplet diameter at time \( t \)
- \( D_o \): initial droplet diameter
- \( C \): coefficient of combustion

Experiments with n-heptane, iso-octane and kerosene revealed an increase of the mean velocity of the falling drops during the period of existence of the flame with respect to that of falling liquid spheres. Such an increase is due to a reduction of the drag force caused by mass transfer from the droplet to the surrounding atmosphere as a result of the flame.

Malik and Burgess carried out experiments by forming droplets from an oil jet using a slotted disc. Droplets of sizes ranging from 175 \( \mu \)m to 800 \( \mu \)m travelled upwards in a laminar, oxidising environment produced by a flat flame. The results obtained showed shorter Pre-ignition Delays compared to those in the suspended droplet technique for a given droplet size, although also in linear relationship with the initial diameter. In addition to the increased mass transfer from the droplet because of its motion, the presence of active radicals originated in the
auxiliary flat flame accelerated the ignition of the droplet, whilst in the suspended droplet the radicals are formed solely from the burning droplet. The Pre-ignition Delay also varied with the oxygen concentration in the post-combustion gases, showing that larger droplets need higher oxygen concentration to ignite.

Marrone et al. generated droplets of heavy oils and some mixtures by a similar method to that of Malik and Burgess. It was observed in the photographic observations made that, although there was a considerable loss of mass, the droplet diameter remained constant, if not increase, throughout the droplet lifetime.

The study of the residues left after the combustion has also been undertaken by some researchers. Sampling of particles at different combustion stages by Marrone et al. showed that a cenospheric structure is already formed before the flame is quenched after the burnout of the remaining volatiles. No. 2 fuel oil burned in a similar fashion to that of residual oils, although no coke particles were formed and little swelling was detected.

Urban and Dryer found that a parameter which they called the Coke Formation Index (CFI), relating the particle mass to the initial droplet mass, is constant for a given oil (see also section “4.4.3.a. Coke emissions”). They also established that this parameter related the physical characteristics of both the original droplet and the coke particle:

\[
CFI = \frac{\text{particle mass}}{\text{droplet mass}} = 6\frac{D_c^2 \rho_{cs} \tau}{D_o^3 \rho_o}
\]

where:

- \(D_c\): coke particle diameter
- \(D_o\): droplet diameter
- \(\rho_{cs}\): coke shell density
- \(\rho_o\): oil density
- \(\tau\): coke shell thickness
2.3.3. Supporting sphere technique

This technique has been used less frequently. A porous sphere of solid material is fed with fuel through a capillary. The fuel flows outwards through the pores and the flow rate can be adjusted so that it allows the study of combustion and evaporation rates.

3. The generation of electricity from heavy liquid fuels burned in gas turbines

3.1. General considerations

Although declining, petroleum products still account for a large percentage of electricity generation. In Europe, almost 18% of the electricity produced by thermal means in 1993 (54% of the total) was from petroleum products. The interest in using heavy oils as fuels for generation of electricity stems from their economic advantage. The ratio of distillate oil price to that of residual oil can be 1.6:1, and in some parts of the World 2:1.

One preferred means for the generation of electricity is gas turbines. The fundamental aspects of gas turbines are reviewed in the next sections.

3.2. Gas turbines

3.2.1. Basic principles

The basic principles of gas turbines can be summarised in three stages:

a. Compression: A rotating compressor acts as a fan to drive the working fluid into the heating system. The fluid is pressurised adiabatically, thus its temperature in-
creases. Compressors are of the dynamic type, in which each stage increases the fluid velocity, then lets it diffuse to gain pressure.

b. **Combustion**: The fluid is heated by internal combustion, in a continuous process taking place at constant pressure. A steady supply of fuel mixes with air at high velocity from the compressor and burns as it flows through a flame zone. Combustion occurs in a very small volume, partly because it takes place at high pressure. The flame does not touch the container, which is cooled by the inlet airflow pattern.

c. **Expansion**: The working fluid at high pressure is then released to the turbine, which converts the fluid's energy into useful work as the temperature of the working fluid decreases. Part of this work is returned to the compressor. The remainder is used for the application intended: Generation of electricity, pumping, turbojet propulsion... Axial flow turbines are able to lower the stagnation pressure by about 30 - 50 %. Temperature falls between 8 and 16 %. Several stages are combined for increased work output.

![Diagram](image)

**Figure 13: Gas turbine cycles**

If the fluid employed is recycled the turbine works on closed cycle, whereas if the fluid is not re-used it is open cycle.

### 3.2.2. Efficiency in gas turbines

The use of a compressible gas such as air as working fluid permits the absorption and release of considerable amounts of energy. Such energy is basically the kinetic energy of
its molecules, which is proportional to its temperature. Ideal gas turbine cycles are based on the Joule or Brayton cycles, i.e., compression and expansion at constant entropy, and heat addition and release at constant pressure. In an ideal cycle, efficiency varies with the temperature ratio of the working fluid in the compression process, which is related to its pressure ratio. The inlet temperature in the turbine section is generally limited by turbine technology, materials strength, corrosion and other considerations. The increment of temperature also depends on the initial temperature of the working fluid.

Various process modifications can be applied to improve the thermal efficiency of gas turbines. For example, regeneration improves efficiency by transferring waste heat to the inlet air, thus reducing fuel consumption. Co-generation is a process where the exhaust gases are used to raise steam in a boiler. The steam can be used in a different application, be it an industrial process, district heating, etc. The quality of the fuel used must be higher as contaminants likely to produce corrosion must be avoided. In combined cycles, the waste heat generated in a gas turbine is re-directed to a boiler in order to drive a steam turbine. Both the gas turbine and the steam turbine generate electricity.

Some effects must be considered which diminish efficiency in real operating cycles, such as inefficiency in compression and expansion, loss of pressure during heat addition and rejection, variation of working fluid specific heat with temperature, incomplete combustion, etc.

3.2.3. The combustion stage in gas turbines: Combustors

Since the turbine power output is directly related to the thrust produced, the use of a large mass flow rate of air through the combustor is needed. The combustion chamber must be able to burn fuels efficiently with different operating conditions (depending on the application characteristics), must be stable against blow-out and with easy ignition. Moreover, gas turbine engines normally combust fuel-rich mixtures to prevent the exhaust temperature from exceeding that of the turbine materials limitations. The temperature of combustion gases of a stoichiometric mixture is 2,200 °C in a standard engine.
A typical gas turbine design \(^{137}\) may be as in Figure 14:

a. **Primary zone**: The primary zone extends from the fuel nozzle face to the first row of air addition holes. Air flow enters at high velocity but it is decreased by means of diffusers. Ignition is caused by an applied source of energy, be it a high voltage spark, a torch supplied by an auxiliary burner... The flame size depends on the fuel burned and the flow pattern, and as a result it determines the combustor size. The flame intensity may be reduced by products of high emissivity that may radiate heat away.

Since even the reduced gas velocity is much higher than the actual velocity of the fuel spray, the flame must be stabilised by a high degree of recirculation, allowing ample time for reactions to take place.

In the primary zone equivalence ratios approach unity \((\phi \sim 1)\), providing favourable conditions for fuel ignition and stability. Normally the air flow through the dome is swirled, creating a low pressure recirculation zone for flame holding. Between the higher velocity dome air flow and the lower velocity central recirculation zone flow, a region of high turbulence (the shear layer) is created due to the large velocity gradient.

The cone of fuel injected penetrates directly into the shear layer region where fuel vaporises, mixes with the oxidiser and burns. Typically 20 - 30 % of the air is injected in the primary zone, whereas the remainder is injected in the secondary zone.
b. **Secondary zone**: The secondary zone begins where the injection of air through the liner holes is produced. The equivalence ratio decreases ($\phi \approx 0.5$), providing an excess of air for all remaining fuel molecules, CO, H radicals to be fully oxidised. Air and fuel flow may recirculate back into the primary zone, but largely penetrate to the combustor centreline. In addition, the temperature is lower here than at stoichiometric mixture but still too high for the turbine blades.

c. **Tertiary or dilution zone**: The aim of this zone is to inject extra dilution air in order to reduce the combustion exit temperature to that acceptable for the turbine inlet.

### 3.2.4. Heavy oils as gas turbine fuels

The efficient use of heavy oils in gas turbines is aided by standardising its properties. Work was carried out jointly by ASME (American Society of Mechanical Engineers) and ASTM (American Society for Testing and Materials) to supply users, transporters and refiners with both fundamental and practical aspects on how to provide clean fuels for gas turbines, nature of impurities, their measurement, their effect on performance and means of control and removal.

<table>
<thead>
<tr>
<th>Property</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no. 3-GT (low-volatility low-ash fuel that may contain residual components)</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>54 or legal limit</td>
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<td>Ash, % by weight</td>
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<tr>
<td>@ 50 °C, cSt</td>
<td>638 (max)</td>
</tr>
<tr>
<td>Sulphur, % by weight</td>
<td>legal limits</td>
</tr>
<tr>
<td>Metals, ppm by weight (maximum)</td>
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</tr>
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<td>Vanadium</td>
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<tr>
<td>Sodium plus Potassium</td>
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</tr>
<tr>
<td>Calcium</td>
<td>0.5</td>
</tr>
<tr>
<td>Lead</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*Table 3: Properties of heavy fuel oils as gas turbine fuels according to ASTM standard D 2880-90a*

Their work evolved to produce the ASTM specification D2880. Specifications for heavy and distillate oils used as fuels in gas turbines are partially reproduced in Table 3. Whilst complying with physical properties and sulphur content is the responsibility of the
fuel supplier, trace metal values are the responsibility of the turbine operator. These lev­e­ls are being progressively lowered in order to adapt to modern combustion practice. As a result of splitting liabilities, gas turbine operators become responsible for prevention of contamination.

The main requirements of any fuel for the use in gas turbines are:

- heating value
- consistency of heat input to the turbine
- cleanliness
- low corrosivity, either to accessories or to hot turbine blades
- low deposition and fouling tendencies, especially on hot turbine blades.

3.3. Patent search

An extensive search for patents on combustion of heavy and distillate oils in gas turbines was carried out at the Patent Office of the British Library, London. Although a large number of patents were related to combustion hardware, the following two referred to the topic searched. A summary of each patent is included.

3.3.1. UK Patent Application GB 2,187,273

Title: A gas turbine binary cycle
Applicant: George Bernard Ediss
Application published: 3 September 1987

The efficiency of a gas turbine cycle that uses ambient air as a working fluid can be improved by either increasing the turbine inlet temperature, or by introducing means to recover some of the energy from the turbine exhaust gases.

The turbine inlet temperature is governed by the temperature limits of the highly stressed turbine blades. Stoichiometric combustion temperatures for typical fuels are in the range of 1,870 to 2,200 °C, whilst turbine materials are limited to 760 to 980 °C.
The work output from a gas turbine depends upon the value of the exhaust temperature at the completion of expansion, which in turn depends upon the value of the specific heat ratio \( \gamma \). Greater temperature drop is obtained from fluids with low values of \( \gamma \). Performance can be greatly improved by expanding a mixture of air and steam. When the steam is generated by heat from the turbine exhaust gases, the cycle becomes thermally more efficient.

Inferior grade and relatively inexpensive petroleum fuels include petroleum fractions which boil at about 425 °C, compounds of sodium, calcium, nickel, iron and from 2 to 400 ppm of vanadium. They also have sulphur concentrations in the range from about 0.5 to 5 % by weight. The combustion products of these fuels are excessively corrosive and have a high capacity for ash formation. If a fuel of this type is burnt with near stoichiometric quantities of air, ie, 0 to 3 % excess air, the corrosion and fouling effects are substantially decreased. However, if larger quantities are used, ie, 5 to 500 % above stoichiometric, then ash is produced together with the combustion products and they form corrosive deposits. In conventional gas turbine operation the following pollutants are produced: NOx, SOx, CO and ash (compounds of Na, V, Ca, Mg, Fe, Ni, Si).

It is known that injection of water reduces the maximum temperature reached in the turbine cycle. However, solid particles in the water may have an adverse effect on the turbine parts.

This patent application presents a gas turbine cycle (Figure 15) in which the turbine exhaust gases are directed into a waste-heat boiler in order to raise saturated or supersaturated steam. High pressure steam injected adds to the mass of working fluid, leading to increased power and thermal efficiency.

Combustion must be carried out with air quantities from at least 3 % greater than
stoichiometric. Steam is able to reduce temperatures to levels where the ash-forming compounds will not oxidise further when more air is added to complete the tempering process.

However, in view of the presence of sulphur compounds within the fuel oil, the temperature reduction of the exhaust gas must be limited to avoid condensation. The gas within the pre-heater section should be kept above its acid dewpoint (see section “4.2.1.c. Sulphur trioxide (SO$_3$)”). A limiting value of about 150 °C has been used.

The final exhaust gases, containing a mixture of combustion products, air and steam are expelled into the atmosphere at atmospheric pressure and about 150 °C. The exhaust emissions have very low environmental pollution levels.

In the process within the combustor the formation of harmful compounds is restricted by limiting the amount of primary air (at a pressure of approximately 10 atmospheres) in zone A (see Figure 16) to be no significantly less than 3 % above stoichiometric and by completely surrounding this near adiabatic flame by a continuous curtain of steam. The atmosphere outside the flame but contained within zone A is completely free from air. The steam used is at a much lower temperature than that of the combustion products. Its amount is regulated to ensure that the temperature of the mixture of steam and combustion products is much less than the minimum temperature required to produce the sodium-vanadium products. Additional steam is introduced into zone B so that intimate contact takes place at the adiabatic flame boundaries. The internal cylindrical walls are protected from the effects of the high temperature. The amount of steam introduced into zone B may vary and the amount selected is that which achieves the balance between the approach temperature and the exit temperature from the waste heat boiler.
The remainder of the air is passed over the inner cylinder which contains zones A and C, becoming heated by the cooling effect it has on the inner cylinder wall, and then introduced into zone D for cooling of the steam and the mixture of combustion products. The amount of this secondary air is regulated to ensure that the temperature of the mixture leaving the combustion chamber is correct for use in the turbine section.

It should be noted that the exhaust gases contain large proportions of unburned oxygen and no attempt is made to combust it by auxiliary firing. Thus the basic concept of the present invention is to burn typical distillate fuels.

Although at the extremely low steam pressures encountered in this cycle (10.5 kg/cm²) the required quality of feed water treatment is low, some degree of treatment will be necessary to operate the waste heat boiler to prevent the possibility of the carry-over of impurities into the turbine section.

The turbine can be started in a dry mode and if required can be operated continuously in the dry mode, because it will require 15-30 minutes from lighting the burner before steam can be raised and thus injected into the combustion chamber.

3.3.2. UK Patent Application GB 1,140,757

Title: Improvements in gas turbine engines
Applicants: Esso Research Company
Complete specification published: 22 January 1969

In the present arrangement an approximately stoichiometric mixture of fuel and air is introduced into the primary zone I (see Figure 17) chamber at about 6 atm. Combustion is almost complete in this section.

Simultaneously, steam is introduced into the annular area around the primary zone. Steam cools the casing walls of this and the secondary zone II. The steam is eventually introduced into the secondary zone II, where it mixes with the hot combustion gases. The amount of steam introduced into the secondary zone II is about 6 to 10 kilograms of steam per kilogram of fuel at a pressure of 5 to 13.3 atm.
In the tertiary zone III, where the combustion is essentially complete, the hot gases mixed with steam are quenched by additional compressed air which had by-passed the first two zones of the combustion chamber. The amount of additional air introduced in this zone is between 25-35 kg per kilogram of fuel.

Finally, the exhaust gases are discharged to the turbine section. The temperature of the gases is between 1,350 and 1,700 °C, and its pressure is in the range of 3 to 13.3 atm.

The spent turbine gases are passed into a waste heat boiler, where they are utilised to raise steam at a pressure higher than that of the turbine cycle. Additional steam may be generated by an oil-fired boiler, which may be separated from the waste heat boiler.

The turbine is operated with essentially the stoichiometric amount of air (0 to 3 % excess), whereas in conventional turbines up to 500 % excess air is used. This is accomplished by the addition of steam. This low excess of stoichiometric air maintains the combustion products of the metals and sulphur in a low valence state so that the harmful deposits characteristic of the higher valence states are avoided. If quenching had been performed by air, the ash and sulphur would be oxidised, thus losing the benefits of the stoichiometric combustion.

### 4. Problems derived from the combustion of heavy liquid fuels

The use of heavy oils has several handicaps under practical conditions. Most of them stem from the chemical composition of the fuel. For instance, emissions of NO\textsubscript{X} and SO\textsubscript{X}, which lead to air pollution, smog, acid rain, etc., can arise from the nitrogen and sulphur contained in the fuel. Particulates, which originate from the heavier fractions of the fuels, cause severe environmental pollution and intense public health concern. Moreover, they also inflict severe economic losses on operators as unburned fuel and
deposits in combustion facilities. In addition, expensive fines are imposed if the legislated emission limits are exceeded.

A clear understanding of the processes whereby these species are formed and emitted can facilitate the formulation of practical strategies aimed at their reduction.

4.1. NO\textsubscript{x}

Nitrogen present in the combustion system, provided either in the combustion air or the fuel, reacts during combustion to form NO and NO\textsubscript{2}, and also N\textsubscript{2}O in fairly minor amounts. It is generally understood that the oxides of nitrogen (NO\textsubscript{x}) consist of nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}). Normally NO is formed in much larger amounts than NO\textsubscript{2}, and the latter is thought to be formed by further reaction of NO. Hence, NO formation determines the total amount of NO\textsubscript{x} emitted.

Nitrogen oxides are atmospheric pollutants. They contribute to the ozone-depletion cycles in the stratosphere and to photochemical smog, and they constitute the most important emission from combustion devices. Motor vehicles, electric power plants and industrial boilers account for most of the emissions of NO\textsubscript{x}.

However, the most noxious effects are caused by NO\textsubscript{2}, by reacting with hydrocarbons, ozone and light to produce smog. In addition, NO\textsubscript{2} reacts with water to produce acid which causes corrosion problems and acid rain.

The maximum NO\textsubscript{x} emissions from liquid fuels permitted in Europe by EU Directive 88/609 are 450 mg/nm\textsuperscript{3}\textsuperscript{29}.

4.1.1. Formation and emission of NO

Many studies have emphasised the strong dependence of the NO formation rate on gas temperature and the amount of nitrogen in the fuel. Both characterise the most important routes for the formation of NO.
The amounts of NO emitted from larger systems depend on the combustion hardware used. Considering NO emissions by Emission Index (EI, milligrams of NO per gram of fuel), spark-ignition engines yield EI = 16.3 whereas regenerative gas turbines reach EI = 13.5 and aircraft turbojets have EI = 5.5.

Other practical factors have also been studied: When burning residual fuel oils in boilers air preheat has considerable influence on NO formation, whereas oil preheat showed little influence on NO. Conditions that favour high combustion intensities yield relatively higher NO emissions, such as small droplet size, narrow spray angle, etc.

The NOx concentration in the exhaust of an oil-fired boiler indicates that the NOx concentration decreases with excess air. Also the boiler size plays an important role on the concentration of NOx in the flue gases. Factors like the method of firing have little influence.

Maximum formation of NO occurs in gas turbines when the temperature is at its peak and at an equivalence ratio between 0.8 and 1.0. The most important factor affecting NO formation in gas turbines is flame temperature (NOx ∝ exp(0.009 T)); other important factors are residence time and oxygen concentration, and they are significant insofar as they affect flame temperature.

Modelling of NO formation by Bartok et al. shows the effect of several variables:

- higher residence times at higher temperatures yield higher NO.
- maximum formation of NO occurs at 5% excess air, and NO levels drop off at 10% excess air.
- increase of preheat temperature has dramatic effect by increasing NO.

Three mechanisms have been proposed to explain the formation of NO in combustion, which, although different, may operate concurrently:
4.1.1.a. High-temperature oxidation of atmospheric nitrogen: Thermal-NO

The role of nitrogen contained in the air in NO formation was initially postulated by Zeldovich \(^{154}\). In near-stoichiometric or lean systems the mechanism is the following:

\[
\begin{align*}
O_2 & \rightleftharpoons O + O & 1 \\
O + N_2 & \rightleftharpoons NO + N & 2 \\
N + O_2 & \rightleftharpoons NO + O & 3
\end{align*}
\]

In near-stoichiometric and fuel-rich mixtures, where the concentration of OH radicals can be high, the following reaction also takes place:

\[
N + OH \rightleftharpoons NO + H & 4
\]

which, together with reactions 1, 2 and 3, is known as the extended Zeldovich mechanism.

The formation of NO via the Zeldovich mechanism is controlled by reaction 2 due to its very high activation energy \((E = 314 \text{ kJ/mol})\). For this reason thermal-NO\(_x\) shows a strong exponential dependence on temperature. The contribution of thermal-NO to the total NO formation is small below \(1,370 \degree C\) \(^{56}\), but becomes very important above \(1,400 \degree C\). Thus the peak flame or combustion temperatures are used as an indication of the importance of thermal-NO.

Other factors which also affect NO\(_x\) formation are fuel/air mixing processes (related to local levels of excess air), combustion intensity and pre-heating of the combustion air. Thermal-NO has also been shown to increase linearly with residence time.

Several mathematical expressions have been derived to estimate the rate of thermal-NO formation in combustion systems.

If the processes leading to the formation of thermal-NO\(_x\) occurred long after those of combustion, the amounts of NO could be calculated from the equilibrium conditions \(^{18}\).
Thus assuming a steady-state approximation for the N atom concentration, the formation rate of NO would involve the knowledge of the local temperature and the concentrations of O₂, N₂ and OH only, these being obtained from the post-combustion conditions. The following expression shows the large dependence of NO formation on temperature and oxygen concentration:

\[
\frac{d}{dt} [\text{NO}] = 6 \times 10^{16} \exp\left(-\frac{69,090}{T_{\text{eq}}}\right) \sqrt{\frac{[O_2]_{\text{eq}}}{[N_2]_{\text{eq}}}}
\]

Toof found the residence time for NO formation in gas turbines to be proportional to the velocity of the air jet entering the combustor (V), the diameter of the combustor (D), and also to a function of the amount of excess air (\(\lambda\)):

\[
t = \frac{0.161D}{V (0.5 + 0.22(\lambda - 1))}
\]

Another attempt to estimate the formation of NO in gas turbines was given by Sawyer and Starkman. Based only on the reaction:

\[
O + N_2 \longrightarrow NO + N
\]

where the O atom concentration is fixed by the equilibrium

\[
O_2 \rightleftharpoons O + O
\]

and assuming that the level of NO is fixed by the kinetics of formation rather than from equilibrium formation in the primary zone, they proposed the following expression:

\[
\frac{[dX_{NO}]}{[dt]} \propto \sqrt{P} \cdot \exp\left(-\frac{133,800}{RT}\right)
\]

It shows a very strong dependence on temperature and inverse dependence on pressure, which are consistent with experimental results.
The reverse reactions which would result in conversion of NO back into \( \text{N}_2 \) and \( \text{O}_2 \) are relatively slow in gas turbines \(^{126}\). Thus, NO, once formed, does not decrease in concentration at an appreciable rate by cooling.

4.1.1.b. Reaction of \( \text{N}_2 \) with hydrocarbon fractions: Prompt-NO

It was observed by many authors (initially by Fenimore \(^{46}\)) that in the vicinity of the flame zone, NO formation rates are considerably larger than in the post-flame zone. Numerical modelling showed that if the reactions leading to NO formation are decoupled from those of combustion processes (thermal-NO), calculations of NO formation rate yield lower values than those experimentally observed \(^{18}\). Also the amount of NO formed near the flame is higher as the fuel-air ratio increases \(^{50}\), being a maximum in the fuel-rich region and dropping off sharply at an equivalence ratio of 1.4. Such discrepancies become still larger in combustion of fuel-rich hydrocarbon mixtures.

This anomalous concentration of NO is said to be due to a different route from that to thermal-NO. Such rapidly-formed NO (produced before thermal-NO, and thus always within a given residence time) is named "prompt-NO".

Various arguments have been proposed to explain the rapid formation of these anomalous quantities of NO. Some authors postulate that in lean and near-stoichiometric flames they are caused by an overshoot of radical concentrations (O, OH) above the equilibrium values, which in turn has the effect of enhancing thermal-NO. A simple approach to the radical species involved is given by the pool of radicals formed in the following set of reactions \(^{23}\), which are locally equilibrated:

\[
\begin{align*}
\text{O} + \text{H}_2 & \rightleftharpoons \text{OH} + \text{H} & 5 \\
\text{H} + \text{O}_2 & \rightleftharpoons \text{OH} + \text{O} & 6 \\
\text{H}_2 + \text{OH} & \rightleftharpoons \text{H} + \text{H}_2\text{O} & 7
\end{align*}
\]

O and OH radicals would thereafter enter the mechanism of thermal-NO formation. Accurate values of the temperature and radical concentrations used in calculations of the thermal-NO mechanism yielded results that were closer to experimental values.
$N_2O$ has been suggested to play an important role in the low temperature ($<1,225 \, ^\circ C$) combustion of lean CO-air mixtures, as radical concentration overshoots cannot explain the increase of NO formation $^{18}$. The following mechanism was proposed:

\[
\begin{align*}
N_2 + O + M & \rightleftharpoons N_2O + M & 8 \\
N_2O + O & \rightleftharpoons \{NO + NO\} \quad \{N_2 + O_2\} & 9 \\
N_2O + H & \rightleftharpoons N_2 + OH & 10
\end{align*}
\]

However, kinetic modelling demonstrates that $N_2O$ does not play a significant role at high temperatures, and such are the conditions in internal combustion engines and other combustion hardware.

Finally, although $[O]$ and $[OH]$ were found to be high in fuel-rich mixtures, they do not account for the large formation of NO. A more plausible explanation is provided by reactions involving hydrocarbon fractions and atmospheric nitrogen as the source of nitrogen-containing radicals, which are eventually oxidised to form NO. The following reactions have been proposed by several authors $^{18,50,133,150}$:

\[
\begin{align*}
\text{Fuel, RH} & \rightarrow CH, C_2 & 11 \\
C + N_2 & \rightarrow CN + N & 12 \\
C_2 + N_2 & \rightarrow 2 CN & 13 \\
CH + N_2 & \rightarrow CN + HN & 14 \\
CH + N_2 & \rightarrow CNH + N & 15 \\
CH_2 + N_2 & \rightarrow HCN + N & 16 \\
C_2H + N_2 & \rightleftharpoons HCN + CN & 17 \\
HCN + \text{oxidant} & \rightarrow NH_i & 18
\end{align*}
\]

In a further stage, $NH_i$ species yield NO by:

\[
\begin{align*}
NH + H & \rightarrow N + H_2 & 19 \\
N + O_2 & \rightarrow NO + O & 3
\end{align*}
\]
in a similar system of reactions to that of fuel-NO (see next section).

The formation of HCN has been observed experimentally in all hydrocarbon-rich flames. When the equivalence ratio is below 1.4 there are enough oxygen radicals to react with HCN in order to form amine compounds and eventually NO.

Fenimore estimated that at stoichiometric equivalence ratio in the turbulent flame of combustors, prompt-NO was responsible for 30% of the total NOx emissions from gas turbines, according to:

$$[\text{NO}]_{\text{prompt}} = f(\varphi)\sqrt{P\, [\text{NO}]_{\text{eq}}}$$

where:

- $f(\varphi)$: an empirical function of the equivalence ratio, whose value is 0.016 for stoichiometric mixtures ($\varphi = 1$).
- $P$: pressure, atm
- $[\text{NO}]_{\text{eq}}$: equilibrium concentration of NO

The previous formula reveals that prompt-NO is highly dependent on pressure. Experimental results on premixed ethylene/air flames at pressures up to 18 atm have confirmed this finding. However, unlike thermal-NO, its dependence on temperature is very weak. At temperatures above 1,325 °C prompt-NO constitutes only a small fraction of total-NO, if compared to thermal-NO.

4.1.1.c. Oxidation of fuel-bound nitrogen compounds: Fuel-NO

When fuels containing nitrogen are burned, the concentration of NO in the flame increases. Fuel fractions containing nitrogen, mostly in the form of heterocycles, undergo rapid vaporisation and thermal decomposition prior to entering the combustion
zone. The rate at which fuel-N is released is highly dependent on the combustion temperature. Hydrogen cyanide is eventually formed, which leads to the formation of amine species (NH$_3$, NH$_2$ and NH) through different routes according to the combustion environment. In fuel-lean atmospheres HCN reacts to form NH:

\[
\begin{align*}
\text{HCN} + \text{O} &\rightarrow \text{NCO} + \text{H} \\
\text{NCO} + \text{H} &\rightarrow \text{NH} + \text{CO}
\end{align*}
\]

whereas in fuel-rich systems the mechanism is through NH$_2$:

\[
\begin{align*}
\text{HCN} + \text{OH} &\rightarrow \text{HNCO} + \text{H} \\
\text{HNCO} + \text{H} &\rightarrow \text{NH}_2 + \text{CO} \\
\text{NH}_2 + \text{H} &\rightarrow \text{NH} + \text{H}_2
\end{align*}
\]

The subsequent oxidation of the amine species is a rapid process which occurs via two routes, depending on the availability of oxidant in the combustion environment:

\[
\begin{align*}
\text{NH} + \text{H} &\rightarrow \text{H}_2 + \text{N} \\
\begin{cases}
\text{oxidant (OH, O)} &\rightarrow \text{NO} \text{ (in fuel-lean conditions)} \\
\text{NO, NH}_2 &\rightarrow \text{N}_2 \text{ (in fuel-rich conditions)}
\end{cases}
\end{align*}
\]

Once NO is formed it plays a synergistic role against amine oxidation by reduction to molecular nitrogen. As a result, the fraction of fuel-nitrogen converted into NO depends on the relative rates of the parallel paths:

\[
\begin{align*}
\text{N} + \text{oxidant} &\rightarrow \text{NO} + ... \\
\text{N} + \text{NO} &\rightarrow \text{N}_2 + ...
\end{align*}
\]

Once NO has been formed its disappearance can occur by conversion into HCN with CH and CH$_2$ radicals. HCN can then re-enter the NO formation process.
The overall formation of fuel-NO has a weaker dependence on flame temperature than thermal-NO. However, its dependence on oxygen concentration is very strong: Relatively high yields of fuel-NO are attained in lean and stoichiometric mixtures, whereas low yields are found from fuel-rich mixtures as in reducing atmospheres the formation of N₂ is favoured with respect to that of NO. Also, the extent of the conversion is an inverse function of the fuel-N content: For low levels of fuel-bound nitrogen (0.1%), conversion may reach 100%, whereas for higher yields (0.5%) it is reduced to about 50%.

The conversion of different forms of fuel-N into NO is the subject of controversy among researchers. Additives with low boiling point are reported to produce lower yield than those with high-boiling point. However, some other authors state that the conversion is nearly independent of the parent molecule. The speed at which intermediate species are formed seems to vary for different fuel-nitrogen compounds, being faster for nitrogen compounds of low boiling point.

Attempts have been made to estimate the amounts of fuel-NO formed in combustion systems. Fenimore derived an expression for the calculation of the conversion fraction of fuel-N into NO. By assuming that amine species always take part in the mechanism, the following formula was proposed for the addition of various nitrogen compounds to premixed ethylene-air flames, in which fuel-NO is formed prior to thermal-NO:

\[
Y = \frac{X}{[N_f]_o} \left\{ 1 - \exp \left[ - \frac{[N_f]_o}{X} (1 + Y) \right] \right\}
\]

where:

- **Y**: NO conversion fraction = \( \frac{[NO]}{[N_f]_o} \)
- **\([N_f]_o\)**: Total N in the added nitrogen compound, ie the amount of NO which would be formed if all the fuel nitrogen was converted to NO
- **X**: \( \frac{k_a}{k_b} \) [oxidant]
As opposed to other authors, Fenimore proposed that the oxidant involved in NHi transformation to NO was the OH radical.

Another correlation was provided by Soete \(^{18}\):

\[
Y = \frac{2}{\frac{1}{k_b[N_t]} - 1} \frac{Y}{k_a[O_2]}
\]

in which it was assumed that the N atom was the only nitrogen intermediate that reacts with oxidant or NO, and that the formation of both NO and N\(_2\) would be governed by the standard reactions of the Zeldovich mechanism:

\[
\begin{align*}
N + O_2 & \rightarrow NO + O & 3 = a \\
N + NO & \rightarrow N_2 + O & -2 = b
\end{align*}
\]

In lean flames with small amounts of fuel-N, ie \(k_a[O_2]>>k_b[N_t]\), the conversion fraction of NO would rise to unity, ie all fuel-nitrogen would be converted to NO.

4.1.2. Formation and emission of NO\(_2\)

Nitric oxide formed by any of the routes previously described can react with O-containing species to form NO\(_2\). Theoretical and kinetic studies conclude that at typical flame temperatures the formation of NO\(_2\) from NO should be negligibly small \(^{36}\). However, it has been observed experimentally that NO\(_2\) emissions from gas turbine exhausts can reach between 15 and 50 % of the total NO\(_X\) \(^{150}\). Experiments on large power station plants at different levels of oxygen and boiler loads produce NO and NO\(_2\) in ratios in the range 19:1 to 9:1.

At low temperature (below 1,100 °C) the reaction

\[
NO + NO + O_2 \rightarrow 2 NO_2
\]

25
is slow. However, other reactions are important at low temperatures below 900 °C, such as:

\[
\begin{align*}
\text{HNO}_2 + \text{O} & \rightleftharpoons \text{NO}_2 + \text{OH} \quad 26 \\
\text{NO} + \text{O}_3 & \rightleftharpoons \text{NO}_2 + \text{O}_2 \quad 27 \\
\text{HNO}_2 + \text{OH} & \rightleftharpoons \text{NO}_2 + \text{H}_2\text{O} \quad 28 \\
\end{align*}
\]

An important mechanisms proposed for \text{NO}_2 formation and disappearance is the following:

\[
\begin{align*}
\text{NO} + \text{HO}_2 & \rightarrow \text{NO}_2 + \text{OH} \quad 29 \\
\text{NO}_2 + \text{O} & \rightarrow \text{NO} + \text{O}_2 \quad 30 \\
\end{align*}
\]

\text{NO} oxidises to \text{NO}_2 very rapidly through reaction 29 in the early parts of the flame, where the concentration of \text{HO}_2 is high. Subsequently \text{NO}_2 may disappear in reaction 30 as a surge of \text{O} radicals is formed concurrently. Both reactions 29 and 30 are fast at low temperatures.

\text{HO}_2 radicals abound in initial low-temperature, oxygen-rich flame zones, where they are formed via the reaction:

\[
\begin{align*}
\text{H} + \text{O}_2 + \text{N}_2 & \rightleftharpoons \text{HO}_2 + \text{N}_2 \quad 31 \\
\end{align*}
\]

The balance between its formation and destruction is mainly determined by temperature. Thus, for a 0.1 \text{O}_2 mole fraction, 20 ppm \text{HO}_2 are found at 1,125 °C, 50 ppm at 725 °C and 400 ppm at 230 °C. It can be seen that formation of \text{NO}_2 via \text{HO}_2 is inversely dependent on the temperature.

Under normal circumstances \text{NO}_2 only exists as a transient species in combustion systems. \text{NO}_2 would only be emitted if some kind of quenching was applied on the re-conversion reactions of \text{NO}_2 into \text{NO}. Rapid mixing of hot and cold regions can act so that reaction 30 is halted. High \text{NO}_2/\text{NO}_x ratios have been found in cooler regions near the combustion zone. High equivalence ratios increase the \text{NO}_2/\text{NO}_x ratio to
values close to unity partly due to an excess of \( \text{HO}_2 \) radicals. In addition, OH radicals in fuel-rich flames can react with unburned hydrocarbon species in order to form alkyl peroxy radicals, which are very efficient at oxidising NO to \( \text{NO}_2 \). They may also increase the amount of \( \text{HO}_2 \) radicals available.

Cernansky and Sawyer found evidence for the formation of \( \text{NO}_2 \) in the early, fuel-rich regions of flames. Although the stoichiometry of the mixture is fuel-rich, oxygen penetration can provide \( \text{O} \) concentrations required for the \( \text{HO}_2 \) mechanism. The formation of nitrogen dioxide was again explained as a result of rapid cooling and turbulent mixing of the combustion gases, in situations where oxygen, low temperature and superequilibrium radical concentrations exist. Large superequilibrium concentrations of \( \text{HO}_2 \) radicals are formed then, and they can outlive \( \text{H}, \text{O} \) and \( \text{OH} \) radicals.

Such explanations are not totally conclusive and other hypotheses are sustained. Some authors argue that the levels of \( \text{NO}_2 \) reported in the flame zone are the consequence of reactions occurring due to rapid quenching of the combustion gases on the probe wall through reaction:

\[
\text{NO} + \text{O} \rightarrow \text{NO}_2
\]

or by means of high concentrations of \( \text{HO}_2 \) formed at low temperature in the sampling system. The same low-temperature, oxygen concentration and superequilibrium radical concentrations that favour \( \text{NO}_2 \) formation in the flame can be found in sampling probes. Hargreaves et al. also showed that sampling pressure can alter the \( \text{NO}_2/\text{NO} \) ratio substantially.

The removal of \( \text{NO}_2 \) is promoted by large concentrations of radicals present at high temperatures in reactions such as:

\[
\text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH}
\]

\[
\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2
\]
4.1.3. Reduction and control of NO\textsubscript{x} emissions

The most important variable that can be manipulated in order to reduce NO\textsubscript{x} emissions is combustion temperature, and thus other variables which may affect it.

Fundamental studies of individual droplet combustion in diffusion flames\textsuperscript{116} indicate that low combustion temperatures associated with small (flame)/(droplet diameter) ratios are responsible for the low NO\textsubscript{x} production detected in some instances. Spray combustion results in droplet interactions which decrease the local oxygen concentration around burning droplets, thus both flame temperature and NO\textsubscript{x} are reduced.

Experiments have demonstrated the destruction of NO in hydrocarbon flames. Excess NO added to hydrocarbon flames is partially converted into HCN in the pre-flame (rich) zone, and the latter is transformed back into NO in amounts which depend on the flame stoichiometry.

A practical way to form less NO\textsubscript{x} is the addition of water or steam\textsuperscript{49,14} to the combustion environment, although at the expense of high running costs and loss of thermal efficiency. The decrease in the formation of NO is caused by extra OH radicals produced by means of the reaction:\textsuperscript{39}

\[
\text{H}_2\text{O} + \text{O} \rightarrow \text{OH} + \text{OH} \quad 34
\]

which withdraws O radicals, thus slowing the Zeldovich mechanism.

Experiments in gas turbines\textsuperscript{120} with injection of water showed a large decrease of thermal-NO\textsubscript{x} emissions by up to 85\% if the ratio (water/fuel) mass flow is between 0.01 and 0.4-0.5\textsuperscript{119}. In addition, other positive side-effects have been noted, like smoke reduction and power increase\textsuperscript{120}. A similar effect is achieved by injection of steam, with NO\textsubscript{x} reductions that can be ten-fold. However, steam does not affect the formation of smoke but increases emissions of CO and unburned hydrocarbons\textsuperscript{120,121}. 

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The influence of water injection on fuel-N conversion to NO\textsubscript{X} in gas turbines was also studied\textsuperscript{120}. The conversion of fuel-bound nitrogen increases with higher (water/fuel) ratios, although the increase of conversion is more dramatic for water injected as a spray. It also has some influence on the conversion of NO to NO\textsubscript{2} as the ratio NO\textsubscript{2}/NO is increased when the weight percentage of water in fuel is increased\textsuperscript{119}.

Fuel modifications have also been attempted in gas turbines as a method for reducing NO\textsubscript{X}. An exhaustive study upon the effect of additives\textsuperscript{119} demonstrates that soluble additives can act as heterogeneous catalysts efficient on NO\textsubscript{X} reduction. Suitable additives are compounds of Mn, Fe, Co and Cu, whose effect is either to catalyse NO decomposition or to collect O ions. However, efficiency decreases as their concentration is increased. Other effective compounds are Na\textsubscript{2}CO\textsubscript{3} (reducing NO\textsubscript{X} by 20\%) and LiCO\textsubscript{3} (10\% reduction). Carbonates remove O ions by forming metal peroxides. NO\textsubscript{X} depletion was also obtained with NaOH (17\% reduction) or hydrazine acetate (16\%).

Alternatively, fuel-water emulsions can be used to reduce NO\textsubscript{X}\textsuperscript{120}. In fact emulsions are more effective than water injection as experiments prove larger NO\textsubscript{X} reductions with emulsions at similar (water/fuel) ratios. The reason seems to be the disruption caused by evaporation of the water, which decreases the size of the droplets formed.

One further method is to reduce the stoichiometric ratio of the combustion chamber. This can be achieved by recirculating the combustion products into the combustion air of boilers\textsuperscript{49}, which causes reduction of the flame temperature. Thermal-NO is depleted, but not fuel-NO as its dependence on temperature is weak\textsuperscript{36}. Experiments with vitiated air and fuel no. 2 oil or natural gas\textsuperscript{121} in gas turbines at an equivalent recirculation rate of about 26\% obtained a reduction of NO\textsubscript{X} of 38\% and 30\% respectively. Recirculation of combustion gases also reduced the formation of CO and the emission of unburned hydrocarbons, although it has the drawback of increasing the amount of particles.

Conversely, leaning the primary zone of a combustor can be achieved by injecting increased amounts of air\textsuperscript{145}. Maximum reductions between 10 and 20\% can thus be obtained.
Minimisation of thermal and fuel-NO\(_X\) in gas turbines can be achieved by staging combustion in separate zones with different equivalence ratios. Two combustor arrangements have been proposed:

a) Rich-lean configuration: A rich primary zone burns approx. 70% of the fuel input, consuming most of the available oxygen. More secondary air is injected then, with reactions occurring at the limiting NO\(_X\) generation temperature. By this method fuel-NO\(_X\) is reduced. The emission of particles suffers an increase as they are formed in the primary zone and they are more difficult to burn-out at a later stage.

b) Lean-lean configuration: Air and fuel are mixed and vaporised as much as possible before entering the lean primary zone. Low thermal-NO\(_X\) is achieved, but the yield of fuel-NO\(_X\) is higher.

Out of the combustion environment, several techniques can be employed to reduce NO\(_X\). Addition of small amounts of fuel and oxygen to the hydrocarbon-NO exhaust mixture (the re-burning process) promotes the formation of the reducing species CH and CH\(_2\) (radicals), which may act in the following reactions:

\[
\begin{align*}
\text{CH} + \text{NO} & \rightarrow \text{HCO} + \text{N} \quad \text{(35)} \\
\text{CH} + \text{NO} & \rightarrow \text{HCN} + \text{O} \quad \text{(36)} \\
\text{CH} + \text{NO} & \rightarrow \text{H} + \text{CO} + \text{N} \quad \text{(37)}
\end{align*}
\]

All are exothermic reactions. Shortcomings of this method are the likely emission of unburned fuel and efficiency loss.

Based on the reaction of nitric oxide with amine species, addition of ammonia to the combustion products (the SNCR process) at 1,000 °C can reduce NO\(_X\). NH\(_3\) will form NH\(_2\) radicals, which may undergo reaction with NO through the following channels:

\[
\begin{align*}
\text{NH}_2 + \text{NO} & \rightarrow \text{HN}_2 + \text{OH} \quad \text{(38)} \\
\text{NH}_2 + \text{NO} & \rightarrow \text{N}_2 + \text{H}_2\text{O} \quad \text{(39)}
\end{align*}
\]
Finally, a reduction of the residence time of the combustion gases can be used as an alternative method. Thus $N_2$ and $O_2$ are allowed less time for reaction. Reductions of up to 25% have been achieved in gas turbines by moving air diluent holes upstream, thus shortening the flame length and the residence time.

4.2. $SO_x$

Sulphur is to be found in hydrocarbon fuels, normally up to a maximum of 3% by weight, and mostly in organic form, although also in inorganic compounds. Heavy fuel oils usually contain higher amounts of S than other petroleum products as it tends to concentrate in the residua along with asphaltenes during the refining processes.

At the high temperatures and oxygen concentrations typical of combustion, sulphur combines with carbon, hydrogen and oxygen to form $SO_2$, $SO_3$, SO, CS, CH, COS, $H_2S$, S and $S_2$. Under such circumstances almost all of the sulphur is in the +4 oxidation state, hence sulphur dioxide ($SO_2$) is the predominant sulphur compound formed in combustion. Even with 20% air deficiency, 90% of the sulphur is in the form of $SO_2$ and as little as 0.1% is as $SO_3$; SO accounts for the remainder of the sulphur.

At lower oxygen concentration (40% deficiency) $H_2S$, $S_2$ and SH are also present in significant proportions, while $SO_3$ becomes negligible. During combustion these species are in superequilibrium concentrations. As the gases cool their rates of consumption decrease and equilibrium may be “frozen” before the products reach room temperature.

In oxygen-rich flames, i.e. normal operation in combustion facilities, SO and $SO_3$ are present, as well as $H_2SO_4$ as a result of the combination of $SO_3$ and $H_2O$. Sulphuric acid is responsible for corrosion in combustion equipment. This is a major reason for controlling sulphur combustion.

The European Union has set the limits of $SO_2$ emissions to be dependent on the power output of the plant. Thus, for less than 300 MW, the emissions of sulphur dioxide allowed are 1,700 mg $SO_2/m^3$. For power output greater than 500 MW, only 400 mg $SO_2/m^3$ are allowed.
4.2.1. Formation of sulphur compounds in combustion environments

4.2.1.a. Sulphur monoxide (SO)

Sulphur monoxide has been observed to form in a variety of reactions between oxygen atoms and sulphur

\[ O + S_2 \rightarrow SO + S \]  \hspace{1cm} (40)

hydrogen sulphide

\[ O + H_2S \rightarrow OH + SH \]  \hspace{1cm} (41)
\[ O + SH \rightarrow SO + H \]  \hspace{1cm} (42)

carbonyl sulphide

\[ O + COS \rightarrow SO + CO \]  \hspace{1cm} (43)

carbon disulphide

\[ O + CS_2 \rightarrow CS + SO \]  \hspace{1cm} (44)

SO thus formed is highly reactive and has a lifetime of about a few milliseconds.

4.2.1.b. Sulphur dioxide (SO$_2$)

Subsequently SO is readily oxidised by oxygen atoms to SO$_2$ in a termolecular process$^{35}$ with emission of pale blue light$^{50}$:

\[ O + SO + M \rightarrow SO_2 + M + hv \]  \hspace{1cm} (45)

Some authors postulate that the formation of SO$_2$ is actually a process in two steps$^{35}$:
SO₂ is formed in the flame at rates comparable to H₂O, and faster than CO₂, its concentration rapidly rising to between 200 and 2,000 ppm.

SO₂ may undergo reaction with water in order to form sulphurous acid H₂SO₃:

\[
\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3
\]

However, the amount of H₂SO₃ formed does not represent a problem as its solubility in water is very small at low temperatures and it decreases at higher temperatures (10% at 20 °C and only 0.58% by weight at 90 °C). Its solutions are mainly composed of hydrogen sulphite ions (HSO₃⁻) and a small percentage of sulphite ions (SO₃²⁻).

4.2.1.c. Sulphur trioxide (SO₃)

Further oxidation of SO₂ leads to the formation of SO₃, sulphur trioxide. The conversion of SO₂ to SO₃ in practical combustion systems varies according to the type of installation: In boiler plants values lie normally between 0.5% and 2.5%, with concentrations of SO₃ normally under 50 ppm. Larger boilers yield conversions near 1%.

In gas turbines the concentration of sulphur trioxide in the exhaust gases is normally between 7 and 11 ppm due to high dilution. However, cases have been reported of conversion up to 20%.

Thermodynamic calculations show that the theoretical conversion of SO₂ into SO₃ at flame temperatures is less than 0.1%. The direct formation of SO₃ by oxygen attack

\[
\text{SO}_2 + \text{O} \rightleftharpoons \text{SO}_3
\]

\[
\text{SO}_2 + \text{O}_2 \rightleftharpoons \text{SO}_3 + \text{O}
\]
is almost completely displaced to the left at typical combustion temperatures (over 1,000 °C), thus conversion of SO₂ into SO₃ is very small. In addition, the reaction is extremely slow at such high temperatures, although it can be catalysed by oxides of W, V, Mo, Cr, Ni and Fe.

However, in practical systems the amount of SO₃ produced in the flame is greater than predicted by the equilibrium between SO₂ and oxygen at flame temperatures. The reaction is thus assisted by labile species in the flame.

The non-linear dependence of the reaction rate on SO₂ concentration suggests that a collisional reaction would be involved with the formation of an activated sulphur trioxide intermediate, which eventually yields SO₃:

\[
\begin{align*}
\text{O} + \text{SO}_2 & \rightarrow \text{SO}_3^* \quad \text{(52)} \\
\text{SO}_3^* + \text{M} & \rightarrow \text{SO}_3 \quad \text{(53)}
\end{align*}
\]

The three-body character of this reaction is demonstrated by its dependence on pressure.

SO₃ is also involved in concurrent formation and disappearance reactions. Apart from thermal decomposition, SO₃ is reduced by:

\[
\begin{align*}
\text{O} + \text{SO}_3 & \rightarrow \text{O}_2 + \text{SO}_2 \quad \text{(54)} \\
\text{H} + \text{SO}_3 & \rightarrow \text{OH} + \text{SO}_2 \quad \text{(55)} \\
\text{SO}_3 + \text{H}_2 & \rightarrow \text{SO}_2 + \text{H}_2\text{O} \quad \text{(56)}
\end{align*}
\]

thus reducing radical concentrations.

Simultaneous combustion of CO in the presence of the oxidation of SO₂ to SO₃ enhances such a process. Every time one CO molecule is burned one oxygen atom disappears but two of them are formed, thus a surplus of oxygen atoms is created.

The conversion of SO₂ into SO₃ is affected by several factors:
- Excess oxygen: At equivalence ratios above stoichiometric no SO$_3$ is formed, whereas increase of oxygen from 0 to 1% excess causes a sharp increase and no significant rise after that.

- Sulphur content in the fuel: The lower the S content, and thus the lower the SO$_2$ content, the higher the conversion to SO$_3$. The SO$_3$ conversion is not a function of the initial SO$_2$ concentration.

- Catalytic substances: It has been suggested that in combustion of residual oils heterogeneous catalysis by steel surfaces and vanadium pentoxide plays an important role in SO$_2$ oxidation to SO$_3$. Experimental evidence has been collected of increased SO$_3$ formation by ash deposits and other solid particulates. Cunningham reports that SO$_3$ formation in large boilers is catalysed by ash and coke deposits on the heating tube banks (900 - 1,200 °C). The fact that conversion drops when such deposits are removed provides evidence of the former.

- Combustion and mixing processes
- Dwell time of the flue gases in the system
- Combustor design.

Hunter studied the formation of SO$_3$ in gas turbines and provided an expression for the calculation of the amount of SO$_3$ formed with time in the combustion chamber. By assuming that formation of SO$_3$ occurs mainly by means of reaction 50 and its destruction by reaction 54 he reached the following expression:

$$\frac{(X_{SO_3})}{(X_{SO_3})_{eq}} = 1 - \left[ 1 - \frac{(X_{SO_3})_o}{(X_{SO_3})_{eq}} \right] \cdot \exp \left( - \frac{t}{\tau} \right)$$

where:

$$(X_{SO_3})_o$$: mole fraction of SO$_3$ initially present, at $t = 0$$$

$$(X_{SO_3})_{eq}$$: mole fraction of SO$_3$
\( \left( X_{SO_3} \right)_{eq} \): equilibrium \( SO_3 \) mole fraction, which is a function of equivalence ratio, pressure and temperature, so that at high temperature its values are low.

\[ \tau: \text{relaxation time} = \frac{RT}{P \left( k_{-50} + k_{54} X_0 \right) \cdot 1,000} \]

\( k_{-50} \): reverse reaction constant for reaction 50 = \( 7.41 \times 10^{30} \ T^{-1} \exp(-82,689/RT) \), \( \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \)

\( k_{54} \): reaction constant for reaction 54 = \( 1.2 \times 10^{12} \exp(-9,500/RT) \), \( \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \)

\( X_0 \): \( O \)-atom concentration

Typical residence times in the dilution zone of a gas turbine combustor are in a range from 1 to 100 ms, and measured values of \( SO_3 \) range from 2 to 8 \% of \( SO_X \). These values are similar to those calculated by Hunter's model: For relaxation times between 0.3 and 30 ms equilibrium levels of \( SO_3 \) range from 2 to 8 \% of \( SO_X \).

Hedley performed experiments in a monodimensional boiler and found \( SO_3 \) concentrations in the flame stage to be much higher than theoretical equilibrium values, decaying afterwards to remain lower than those of theoretical equilibrium.

By assuming that an activated \( SO_3 \) molecule was formed and decomposed by means of

\[ \text{SO}_3 + O \xrightarrow{k_a} \text{SO}_3^* \xrightarrow{k_b} \text{SO}_2 + \frac{1}{2} \text{O}_2 \]

a maximum concentration of sulphur trioxide was calculated

\[ [\text{SO}_3]_{\max} = a \cdot \left( \frac{k_b}{k_a} \right) \frac{k_b}{(k_a - k_b)} \]

which is reached at a time

\[ t_{\max} = \frac{\ln \left( \frac{k_a}{k_b} \right)}{k_a - k_b} \approx 0.03 \text{ s} \]
However this model is only applicable to isothermal conditions as the rate coefficients are temperature dependent.

Formation of SO₃ in combustion systems is undesirable because it forms H₂SO₄ with H₂O:

\[
\begin{align*}
\text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4 \quad 58 \\
\text{H}_2\text{SO}_4 + 2 \text{H}_2\text{O} & \rightarrow 2 \text{H}_3\text{O}^+ + \text{SO}_4^2- \quad 59
\end{align*}
\]

As the combustion gases exit from the combustor their temperature decreases, and H₂SO₄ is formed which eventually condenses at a suitable temperature, the acid dew point. Sulphuric acid causes corrosion on Ni-based alloys used in boilers and in other equipment located downstream from the combustor, such as that in combined systems.

The acid dew point is defined as the highest temperature at which H₂SO₄ vapour (SO₃ + H₂O) is in equilibrium with H₂SO₄ liquid at a given pressure. Typical values are around 130 °C, and they increase (ie condensation is more easily attained) as the amounts of SO₃ and moisture in the exhaust increase. Also dust and solid particulates in the gas exhaust can increase the acid dewpoint.

An expression for calculation of acid dew points was given by Verhoff and Banchero:

\[
\frac{1}{T_{\text{DP}}} = 2.276 \times 10^{-1} - 2.943 \times 10^{-5} (\ln P_{\text{H}_2\text{O}}) - 8.58 \times 10^{-5} (\ln P_{\text{H}_2\text{SO}_4}) - 8.58 \times 10^{-5} (\ln P_{\text{H}_2\text{SO}_4}) + 6.20 \times 10^{-6} (\ln P_{\text{H}_2\text{SO}_4}) (\ln P_{\text{H}_2\text{O}})
\]

where:

T_{DP}: dew point
P: partial pressure
SO$_3$ is a well-known promoter of carbon formation when added in small amounts (approximately 0.1 %) \(^{35}\). However, if added in larger proportions (several percent) along with hydrogen sulphide it helps to decrease carbon formation.

If carbonaceous deposits are present, sulphuric acid may condense in corrosive particles forming acid smuts, especially below 1 % excess oxygen \(^{36}\) where particulate emissions are high. A threshold of 3 ppm SO$_3$ has been found for the formation of acid smuts. Additives like ammonia, dolomite (CO$_3$CaMg) and oxides (MgO), hydroxides and carbonates of magnesium have been used to neutralise H$_2$SO$_4$, as emissions of Mg or MgSO$_4$ have little environmental effects.

Experimental trials with sorbents like dolomite, hydrated lime and pressure hydrated dolomite lime for sulphur control were made by Cowell et al. \(^{33}\). The amount of reduction achieved at a Ca/S ratio of 3 ranged from 55 % for dolomite, 82 % with pressure hydrated dolomite and 90 % with hydrated dolomite. Dolomite is economically most favoured among the three.

4.3. Interactions between S and N species: Their effect on NO$_x$ formation and emission

The interaction between sulphur and nitrogen species during combustion has been the subject of limited study for some thirty years. In this period of time only a small number of investigations have been carried out aimed at determining the effect of fuel-sulphur on combustion reactions that involve nitrogenous species, originating both from the fuel or the combustion air.

An understanding of the role of nitrogen and sulphur species in the formation of pollutants may lead to the development of more accurate ways to predict emissions. Design strategies for the reduction of emissions may ensue from such conclusions.

Another relevant implication of such work lies in the fact that a possible reduction of NO$_x$ due to the effect of fuel-sulphur may make desulphurisation inadvisable as the compliance with NO$_x$ emission environmental regulations may be facilitated by the sulphur in the fuel. At the time of editing this thesis, the European Union is debating the
implementation of a reduction in the sulphur content of certain liquid fuels, in order to prevent acidification and trans-boundary air pollution.

Given the distinct nature of the main processes of formation of NO\textsubscript{x} in combustion, sulphur species will produce different effects according to the origin of the nitrogenous compounds.

4.3.1. \textit{Thermal-NO\textsubscript{x}}

It has been reported in previous sections of this thesis that thermal-NO\textsubscript{x} stems from the oxidation of atmospheric nitrogen. It is commonly accepted that thermal-NO is formed via the so-called Zeldovich mechanism, which is shown here in its extended form:

\[
\begin{align*}
O + N_2 & \rightleftharpoons NO + N \quad 2 \\
N + O_2 & \rightleftharpoons NO + O \quad 3 \\
N + OH & \rightleftharpoons NO + H \quad 4
\end{align*}
\]

Nitrogen-free fuels thus provide the best means to study the effect of sulphur on the formation of thermal-NO\textsubscript{x} as this would be formed from fixation of atmospheric nitrogen only. One such example is the experimental work of Wendt and Ekmann\textsuperscript{141}. They observed notable decreases of thermal-NO emissions from methane/air flames at all equivalence ratios, which included fuel-rich and fuel-lean, when SO\textsubscript{2} and H\textsubscript{2}S were added in relatively large amounts (4.9 % SO\textsubscript{2} by volume in the fuel). Maximum reductions of 36 % of NO were obtained at slightly sub-stoichiometric conditions. The authors postulated that SO\textsubscript{2} was responsible for the inhibition of NO formation, and that H\textsubscript{2}S acted by being converted to SO\textsubscript{2} before interacting with the NO formation process. In that respect, pre-heating of the combustion air enhances NO inhibition by hydrogen sulphide as it accelerates its conversion to SO\textsubscript{2}, especially in fuel-lean conditions.

More complex fuels were used in the recent work by Hampartsoumian and Nimmo\textsuperscript{60} who reported reductions of thermal-NO. Several gas oils and fuel oils were doped with tetrahydrothiophene or SO\textsubscript{2} (gas) and burned in a staged flame. Although reductions of up to 20 ppmv were caused by sulphur dioxide, such an effect decreased or disappeared...
when conditions in the initial stages of the flame were relatively fuel-rich ($\phi > 1.21$). In this study air staging turned out to be the most important single parameter influencing the effect of S on NO\textsubscript{X} emissions, which may show to have practical implications for NO\textsubscript{X} reduction strategies in staged burners.

Although the formation of thermal-NO is understood to depend mainly on flame temperature, the reduction observed was explained in terms of the catalytic recombination of radicals by means of third-body reactions such as \textsuperscript{136,152}:

$$
X + \text{SO}_2 + \text{M} \leftrightarrow X\text{SO}_2 + \text{M} \quad 60
$$

$$
Y + X\text{SO}_2 \leftrightarrow \text{SO}_2 + Y\text{X} \quad 61
$$

where $X, Y = \text{O}, \text{OH}, \text{H}$

Catalytic recombination would in turn reduce the rate of the Zeldovich mechanism.

The radical recombination of OH and H radicals by SO\textsubscript{2} in fuel-rich combustion conditions had been investigated previously by Durie \textit{et al.} \textsuperscript{41} and Kallend \textsuperscript{73}. The mechanism was thought to occur through the reactions:

$$
\text{H} + \text{SO}_2 + \text{M} \leftrightarrow \text{HSO}_2 + \text{M} \quad 62
$$

$$
\text{H} + \text{HSO}_2 \leftrightarrow \text{SO}_2 + \text{H}_2 \quad 63
$$

$$
\text{OH} + \text{HSO}_2 \leftrightarrow \text{SO}_2 + \text{H}_2\text{O} \quad 64
$$

The mechanism is completed with the following slower, uncatalysed recombination reactions:

$$
\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M} \quad 65
$$

$$
\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M} \quad 66
$$

$$
\text{H} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{OH} \quad -7
$$

where reactions \textsuperscript{62} and \textsuperscript{63} involve H radicals and can modify the pool of radicals established by reactions \textsuperscript{23}. 

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Kallend \(^{73}\) found experimental evidence that SO\(_2\) accelerates the recombination of H radicals, decreasing its concentrations shortly after the flame reaction zone. The existence of H radicals can modify the concentrations of reduced sulphur species, such as HS, H\(_2\)S, S, S\(_2\) and SO \(^{41}\), with effects on other reactions.

According to the radical recombination scheme (reactions 62, 63 and 64), the HSO\(_2\) radical plays a key factor in the process. Numerical simulation was performed by Zachariah and Smith \(^{152}\) in order to investigate the matter. Although not detected experimentally, their calculations confirmed that the HSO\(_2\) radical is essential as an intermediate step in the formation of other radical species. Further work by Halstead and Jenkins \(^{58}\) emphasised the relevance of HSO\(_2\) radicals in the catalytic recombination of H radicals by SO\(_2\) in H\(_2\)/O\(_2\)/N\(_2\) flames. They concluded that the recombination of H radicals is a second order process which is rate-controlled by reactions 63 and 64:

\[
\begin{align*}
\text{H} + \text{HSO}_2 & \rightleftharpoons \text{SO}_2 + \text{H}_2 & 63 \\
\text{OH} + \text{HSO}_2 & \rightleftharpoons \text{SO}_2 + \text{H}_2\text{O} & 64
\end{align*}
\]

However, Kallend \(^{73}\) remarked that another effect of addition of SO\(_2\) is the change of adiabatic flame temperature. Experimental results in rich H\(_2\)/O\(_2\)/N\(_2\) flames revealed that SO\(_2\) was able to rise the flame temperature in fuel-rich flames, with temperature increases of up to 200 \(^\circ\)C in the most extreme cases. This change of temperature determined that the distribution of radicals and S species varied according to stoichiometry and amount of sulphur added.

One of the most comprehensive studies on N-S interactions published to date is that of Pfefferle and Churchill \(^{111}\), which included both experimental results and numerical modelling of the effect of fuel-S on nitrogenous species. The experimental work was performed in a thermally stabilised burner (TSB), where combustion of ethane, air, am-


\[
\begin{align*}
\text{O} + \text{H}_2 & \rightleftharpoons \text{OH} + \text{H} & 5 \\
\text{H} + \text{O}_2 & \rightleftharpoons \text{OH} + \text{O} & 6 \\
\text{H}_2 + \text{OH} & \rightleftharpoons \text{H} + \text{H}_2\text{O} & 7 \\
\text{H}_2\text{O} + \text{O} & \rightarrow \text{OH} + \text{OH} & 34
\end{align*}
\]
monia (fuel-N) and hydrogen sulphide (fuel-S) was forced past a hot surface. The nu-
merical model comprised a variety of sulphur reactions (oxidation, reactions of \( \text{SO}_2 \) and \( \text{SO}_3 \) with atomic oxygen, sulphur-nitrogen and sulphur-carbon) in a simulated TSB
burner (the so-called “sparse” model). In their experimental results thermal-NO\(_X\) was
reduced on addition of sulphur. Almost no difference in the small decrease of thermal-
NO\(_X\) (between 5 and 10 %) was observed with different levels of S doping. The decrease
of thermal-NO\(_X\) was thought to be, again, due to the decrease of the concentrations of H
and OH radicals, which in turn reduced the rates of reactions 2, 3 and 4 of the Zeldovich
mechanism.

Nitrogen-sulphur interactions discussed so far are based on indirect routes through in-
termediate species that would inhibit the formation of NO. In addition, nitric oxide can
also be recombined after its formation. Direct nitrogen-sulphur post-formation reactions
were postulated by Chagger et al.\(^{26}\) to explain small decreases of nitric oxide in the
slightly fuel-rich conditions of methane flames with re-burning (the re-burn fuel was also
methane):

\[
\begin{align*}
\text{SH} + \text{NO} & \rightarrow \text{NS} + \text{OH} \quad 67 \\
\text{SH} + \text{NO} & \rightarrow \text{SO} + \text{NH} \quad 68 \\
\text{SH} + \text{NO} & \rightarrow \text{S} + \text{HNO} \quad 69
\end{align*}
\]

where SH would be formed by the reduction of \( \text{SO}_2 \) via \( \text{H}_2\text{S} \) in fuel-rich conditions. The
latter reaction 69 is unlikely to constitute a major NO reduction path as the formation of
HNO would lead to NO regeneration.

Chagger et al.\(^{26}\) deemed that the most likely path for nitrogen recombination was reac-
tion 67, followed by other reactions as in the following scheme:

\[
\begin{align*}
\text{SH} + \text{NO} & \rightarrow \text{NS} + \text{OH} \\
\text{NS} + \text{NO} & \rightarrow \text{N}_2 + \text{SO} \quad 70 \\
2 \text{NS} & \rightarrow \text{N}_2 + \text{S}_2 \quad 71
\end{align*}
\]
However, the overall process turned out to be inefficient for NO\textsubscript{x} reduction as 0.1 \% SO\textsubscript{2} caused only a small further 1-2 \% NO\textsubscript{x} reduction, whereas the sole addition of methane re-burning achieved reductions up to 65 \% over the initial NO\textsubscript{x} emissions.

Other sulphur species can also interact with NO\textsubscript{x} after its formation. Lyon \textit{et al.} \textsuperscript{85} reported decreases in the conversion of NO into NO\textsubscript{2} by methanol when SO\textsubscript{3} was present in the low-temperature (700 - 800 °C) post-combustion gases of coal or natural gas burning. SO\textsubscript{3} was concurrently reduced to SO\textsubscript{2} as both NO and SO\textsubscript{3} competed for the HO\textsubscript{2} radicals supplied by the combustion of methanol:

\begin{align*}
\text{NO} + \text{HO}_2 & \leftrightharpoons \text{NO}_2 + \text{OH} & 29 \\
\text{SO}_3 + \text{HO}_2 & \leftrightharpoons \text{HSO}_3 + \text{OH} & 72 \\
\text{HSO}_3 + \text{M} & \rightarrow \text{SO}_2 + \text{OH} + \text{M} & 73
\end{align*}

A further similar study was carried out by Zamansky \textit{et al.} \textsuperscript{153}, in which hydrogen peroxide was the source of HO\textsubscript{2} radicals. Removal efficiencies of up to 98 and 85 \% were achieved for NO and SO\textsubscript{3}, respectively.

The efficient displacement of nitrogen species towards NO\textsubscript{2} could have practical implications for NO\textsubscript{x} removal, as SO\textsubscript{2} scrubbers are also capable of eliminating NO\textsubscript{2}, but not nitric oxide.

4.3.2. Fuel-NO\textsubscript{x}

The course of fuel-NO formation is detailed in section “4.1. NO\textsubscript{x}” . It is based on the formation of HCN from which amine species are subsequently formed. Finally these amine species would react according to the combustion conditions to form either NO or nitrogen molecules:

\begin{align*}
\text{NH} + \text{H} & \leftrightharpoons \text{H}_2 + \text{N} \\
\text{oxidant (OH, O)} & \rightarrow \text{NO (in fuel-lean conditions)} \\
\text{NO, NH}_3 & \rightarrow \text{N}_2 \text{ (in fuel-rich conditions)}
\end{align*}
An understanding of the fuel-NO formation process shows that changes in HCN concentrations engendered by sulphur would be of crucial importance. Investigations in moderately fuel-rich CH4/He/O2 flames doped with C2N2 were carried out by Corley and Wendt. The fate of various nitrogenous species such as HCN, NO and N2 was monitored. Their results showed that concentrations of both NO and HCN were increased by the presence of SO2. This data suggested that SO2 could interact with the cyanide-amine subsystem that leads to the formation of fuel-NO.

On the contrary, concentrations of N2 decreased when SO2 was present. A discrepancy in the mass balance of nitrogen led to the conclusion that some N2O was formed from the initial nitrogenous species, which was also postulated by Tseregounis and Smith (see next paragraphs).

Pfefferle and Churchill also investigated the effect of fuel-S on nitrogenous species. Combustion of ethane, air, NH3 (fuel-N) and H2S (fuel-S) in a Thermally Stabilised Burner (TSB) was forced by a hot surface, as detailed in previous paragraphs on thermal-NOx. Again the “sparse” numerical model, comprising a variety of sulphur reactions (oxidation, reactions of SO2 and SO3 with atomic oxygen, sulphur-nitrogen and sulphur-carbon) in a simulated TSB burner, was employed in the calculations. Fuel-NOx emissions were decreased by H2S between 10 and 20 %, which was greater than the reduction of thermal-NOx. Results from the numerical model ruled out competition for the available oxidant as the only source of NOx decrease, whilst indirect radical rearrangements were also thought to play an important role.

As opposed to work by other authors, the numerical model performed by Pfefferle and Churchill demonstrated the importance of the reactions in which the NS was involved. Inclusion of these reactions (numbers 259 through to 261 in “Appendix III” of this thesis) yielded a better agreement between experimental and numerical results due to their action to reduce NO to N2, especially at fuel-rich equivalence ratios, where formation of NS is favoured. However, the reductions of NOx predicted by the model were lower than those registered experimentally. The researchers concluded that key reactions in the N-S interaction processes were still missing from the model, although it was successful at predicting diminished concentrations of O and OH radicals.
Experimental evidence of the existence of substantial quantities of NS radicals have been found in the flame front of fuel-rich methane and natural gas flames doped with NH₃ and H₂S or SF₆. Jeffries and Crosley ⁷⁰ found the concentration of NS radicals to be relatively high at approximately 0.1% of that of H₂S added to the flame in most cases, depending on the oxidiser. NS concentration was in steady state as a result of rapid production and recombination processes in the flame front. Formation reactions were thought to be those of NO and NH₄ radicals with reduced S species such as CS₂, S₂, H₂S and SH. NH₄ radicals were also important in recombination reactions with NS, as well as oxidation reactions with NO, O₂, O, OH, N₂O and NO₂.

Other possible direct reactions between sulphur and nitrogenous species have also been investigated. Wendt and Sterluing ¹⁴³ performed computer calculations of the oxidation of SO₂ to SO₃ via NO catalysis through the following mechanism ¹³,³⁴:

\[
\begin{align*}
\text{NO} + \text{O}_2 & \rightleftharpoons \text{NO}_3 \\
\text{NO}_3 + \text{SO}_2 & \rightleftharpoons \text{SO}_3 + \text{NO}_2
\end{align*}
\]

However, they found that at NO concentrations typical of post-flame stack gases SO₃ was formed in negligible amounts via this mechanism.

The existence of NS radicals has been contemplated in previous paragraphs. Other sulphurous species are also present in combustion systems. Sulphur normally exists in the fuel in its reduced state as H₂S, but Zachariah and Smith ¹⁵² found a variety of sulphur species formed in fuel-rich H₂/O₂/SO₂ flames. SO₂ was the predominant compound, but SO was also formed in the reaction zone of the flame. Subsequent decay of its concentration leads to renewed formation of reduced species: H₂S, SH and S₂, the latter being the most important species after SO₂. At long residence times H₂S becomes the most important species, with concentrations higher than those of SO₂.

One possible path for NO reduction in a post-flame situation is the recycling process with CH and CH₂ to give place to HCN (see section "4.1.1.c. Oxidation of fuel-bound nitrogen compounds: Fuel-NO"). Can this path be affected by sulphur compounds? Work by Tseregounis and Smith ¹³⁵ revealed large increases in fuel-NO formation when
SO₂ (gas) was added to premixed, laminar, fuel-rich H₂/C₂H₂ flames doped with C₂N₂ to simulate fuel-N. The results from H₂ flames (thus absence of hydrocarbons) ruled out the postulate that the increase of NO concentrations was due to inhibition of the recycling process between NO and hydrocarbons by the addition of a sulphur compound. In addition, their calculations showed that direct interactions between fuel-N and fuel-S of the kind

$$N + SO \rightleftharpoons NO + S$$  \hspace{1cm} 76

were not plausible as this would have led to a decrease in NO concentrations in fuel-rich conditions. The relatively low importance of this kind of direct interactions was also assessed by Chen et al. 27, as reported in following paragraphs.

However, opposite conclusions were obtained experimentally and numerically by Wendt et al. 144 in studies of rich, moist, CO/Ar/O₂ flames doped with C₂N₂. The absence of H radicals ruled out the potential role of radical recombination as a NOₓ reduction means in this case. Although the results could not be extrapolated to hydrocarbon flames, the authors attributed reductions of NO in the post-flame zone to the action of the reverse Zeldovich mechanism only:

$$N + NO \rightarrow N₂ + O$$  \hspace{1cm} -2

the N radicals being formed in:

$$O + NO \rightarrow N + O₂$$  \hspace{1cm} -3

Direct interactions of sulphur species with nitrogenous species were ascribed for accelerated reductions of NO and N₂ formation by means of:

$$N + SO \rightleftharpoons NO + S$$  \hspace{1cm} 76
$$NO + S \rightleftharpoons NS + O$$  \hspace{1cm} 77
$$NS + O \rightleftharpoons SO + N$$  \hspace{1cm} 78
Their work was continued by Corley and Wendt with rich CH₄/He/O₂ flames doped with C₂N₂ and SO₂. Contrary to results with the simpler CO flames, greatly increased concentrations of NO were found at $\varphi = 1.71$. HCN also increased, whereas N₂ decreased on addition of SO₂. Increased NO concentrations were considered to be caused by the direct interaction of N and SO radicals in reaction 76. This reaction was complemented by other interactions of SO₂ and its reduced species in the cyanide and amine subsystems, such as:

\[
\begin{align*}
\text{CN} + \text{SO} & \longrightarrow \text{NCO} + \text{S} \\
\text{NH} + \text{SO} & \longrightarrow \text{HNO} + \text{S}
\end{align*}
\]

Corley and Wendt also found that the addition of SO₂ decreased the amounts of soot formed at fuel-rich conditions, and that this soot contained some nitrogenous compounds. Interaction between the soot formation mechanism, SO₂ and nitrogenous compounds was thus postulated.

Interactions of SO₂ with the mechanism of soot formation were also observed by Lawton. Significant decreases of the concentration of polycyclic aromatic hydrocarbons (PAH's) were caused by the action of SO₂ in rich-premixed ethylene flames. By interaction with the soot formation processes, sulphur dioxide can disappear and remove carbon to give place to other species such as CO, CO₂, COS and CS₂. These species may enter other reaction channels.

Detailed work performed by Tseregounis and Smith showed that SO₂ decreased the concentrations of most radicals (O, OH and H) by almost 50% in fuel-rich H₂/O₂/Ar flames. The dopants were C₂N₂ and SO₂. The highest reductions took place in near-stoichiometric conditions. Conversely, the profiles of HCN were not greatly changed with addition of SO₂. The overall effect of SO₂ addition on fuel-NO emissions was an increase of its formation rate in the initial stages, followed by a decrease in its consumption in the downstream regions of the flame. Thus, increases of fuel-NO were observed again. Tseregounis and Smith suggested a mechanism of NO reduction in the post-flame zone which, because of its dependence on H radical concentrations, leads to the increase of NO emissions by SO₂:
Tseregounis and Smith observed increases in the concentration of HCN only at slightly fuel-rich conditions, and no changes at other equivalence ratios. Increased HCN concentrations would decrease NO concentrations, which was not the effect observed.

The fact that radical concentrations are lowered by the presence of sulphur was also observed in fuel-rich hydrogen flames by Chen et al. \(^{27}\). In a variety of equivalence ratios (mostly fuel-rich) the concentrations of H radicals were seen to decrease on addition of SO\(_2\), thus lowering the formation of NH and N from NO via HNO. The reduction mechanism was similar to that reported by Tseregounis and Smith \(^{136}\), and was extended to incorporate reactions of amine species:

\[
\text{NO} + \text{H} + \text{M} \rightleftharpoons \text{HNO} + \text{M} \quad 81 \\
\text{HNO} + \text{H} \rightleftharpoons \text{NH} + \text{OH} \quad 82 \\
\text{HNO} + \text{OH} \rightleftharpoons \text{NO} + \text{H}_2\text{O} \quad 83 \\
\text{NH} + \text{NO} \rightleftharpoons \text{N}_2 + \text{OH} \quad 84
\]

Thus lower H concentrations caused a decrease in the extent of NO reduction, which would give rise to higher NO emissions.
When experiments were carried out by Chen et al. in propane flames in a jet stirred reactor, increases of NH\textsubscript{3} and HCN with the addition of SO\textsubscript{2} were reported which led to increased NO emissions. In relatively complex flames such as this it is likely that the processes for NO reduction will be different according to the flame zone considered, which is a concept that was also incorporated by Graville. Chen et al. acknowledged four major routes for the reaction of NO in hydrocarbon flames:

1. Reaction of NO with free hydrocarbon radicals (NO + CH\textsubscript{x} \rightarrow HCN + ...)
   which is predominant in the injection zone, where hydrocarbon concentrations are high (prompt-NO)
2. Reaction of cyano species to form NH and NH\textsubscript{2}, which is important in the zones of high recirculation
3. Oxidation of NH\textsubscript{i} (where i = 0, 1, 2) to NO in reaction:
   \[ N + \text{OH} \rightarrow NO + H \]
4. Reduction of NO to N\textsubscript{2} by reaction with NH\textsubscript{i} in recirculation zones

Direct interactions between N intermediates and SO such as in reactions 79 and 80 were deemed to be of secondary importance: Model calculations did not show major variations when they were included. Also a decrease of N atoms was noticed, which caused lower reduction of NO. Both nitric oxide and SO\textsubscript{2} were found to compete for hydrocarbon fragments, which inhibited the formation of HCN and its path of NO reduction.

Wendt et al. acknowledged that sulphur can change the formation of NO substantially in fuel-rich environments. They studied the dependence of such a change on local stoichiometry, as local fuel-rich conditions present in many realistic combustion systems are likely to promote N-S interaction. Combustion air was pre-heated and the fuel was methane.

Increases of NO concentrations were obtained near the burner front, whereas a gradual decrease was caused by S as the residence time became longer. Wendt et al. attrib-
uted the change in NO profiles to two different effects: Its initial enhancement may be due to reaction 76:

\[
N + SO \leftrightarrow NO + S \quad 76
\]

A subsequent reduction is caused by NH\textsubscript{x} species in reactions such as -2, 39 and 87. Although amine species are expected to disappear shortly after the flame front, the presence of sulphur may extend their lifetime. This was also observed by Tseregounis and Smith.\textsuperscript{135}

Wendt \textit{et al.}\textsuperscript{142} also investigated the effect of local stoichiometry in turbulent diffusion flames of distillate oil. Various forms of sulphur dopant caused a 40 \% increase of NO as long as mixing was poor. In high swirl flames (good air-fuel mixing, therefore no fuel-rich conditions present) sulphur had no effect on emissions of nitrogen oxides.

The stoichiometry of the combustion mixture was also an important parameter in the work performed by Tang \textit{et al.}\textsuperscript{130} in a refractory burner. Hexane was doped with varying amounts of tertiary butyl mercaptan and pyridine in order to simulate fuel-S and fuel-N, respectively. Experiments were performed at fuel-lean, stoichiometric and fuel-rich equivalence ratios. NO\textsubscript{X} formed from pyridine was reduced by sulphur at all equivalence ratios, but the extent of the reduction was largely independent of the amounts of sulphur added.

On the contrary, recent work by Hampartsoumian and Nimmo\textsuperscript{60} showed that fuel-NO could be increased with the concentration of sulphur in the flame at all combustion stoichiometries. A nearly linear increase of fuel-NO was found when increasing amounts of S were added to flames from a variety of complex fuels. Conversely, it was also found that the increase of fuel-NO emissions caused by sulphur was directly proportional to the amount of N in fuel. In addition, and similar to the results reported by Wendt \textit{et al.}\textsuperscript{142}, staging of the combustion air had a strong effect on fuel-NO as a more pronounced NO enhancement was observed when the conditions in the primary zone became fuel-rich. Reactions of sulphur with N species have been proposed to explain the increase of fuel-NO caused by fuel-sulphur:
the latter three being able to remove amine species from NH₄-NO reduction reactions like:

\[
\begin{align*}
\text{NH}_2 + \text{NO} & \rightleftharpoons \text{N}_2 + \text{H}_2\text{O} & 39 \\
\text{NH} + \text{NO} & \rightleftharpoons \text{N}_2 + \text{OH} & 87 \\
\text{N} + \text{NO} & \rightleftharpoons \text{N}_2 + \text{O} & -2
\end{align*}
\]

which in turn may lead to higher NO concentrations.

Graville published the only report on N-S interactions in heavy fuel oils to date. These fuels contain large amounts of sulphur and nitrogen, the latter usually in the form of asphaltenes of high boiling point. The release of nitrogen and sulphur from these compounds is thus gradual, and they can enter the NOₓ formation or reduction processes at different stages, normally later than volatile nitrogen compounds. This feature has a strong potential for achieving large NOₓ reductions, and also shows the importance of the residence time in these processes. In his experimental work, Graville reported reductions of NOₓ emissions between 20 and 30 % on addition of 1 % S as thianthrene (fuel-S) to a residual fuel oil. The efficacy of sulphur as a NOₓ suppresser was diminished as the fuel-N content increased. Conversely, addition of light N and S additives to a hydrogenated gas oil did not cause change of NOₓ concentrations. The early release of N and S from this light fuel could not contribute to the NOₓ reduction processes in the post-flame zone. His results, which were partly predicted by means of numerical modelling, provided supporting evidence for the competition of oxygen-containing radicals at long residence times, resulting in a decrease of NOₓ emissions. Turbulence effects were also considered of importance as they can influence the distribution of radicals.
4.3.3. Conclusions

The literature survey reported in the previous pages has shown that sulphur compounds can exert an effect on nitrogen compounds at three different stages and by three mechanisms of NOX formation and emission:

1. By intervening in the thermal-NOX formation process
2. By intervening in the fuel-NOX formation process
3. By intervening in the recombination of NOX, irrespective of their nature.

A general agreement exists that thermal-NOX is reduced by sulphur via the catalytic recombination of radicals H, O and OH, which, in turn, are related by the reactions of the so-called "radical pool" (reactions 5, 6 and 7). Direct N-S reactions have been accounted for, but are thought to be of secondary relevance and lesser effectiveness.

The situation is rather more confusing with respect to fuel-NOX. Increases and reductions of fuel-NOX have been found mainly in fuel-rich conditions, although other equivalence ratios have also been studied. A variety of mechanisms have been proposed, such as direct N-S interactions, radical rearrangements, interference with NOX-hydrocarbon reactions or the amine subsystem... In addition, the recombination of radicals by the presence of sulphur species can affect the reduction of nitric oxide after its formation.

The need for further work to clarify the array of possible routes for the interaction of NOX and SOX compounds originated from the fuel is thus clear. The experimental work carried out on the topic in this thesis is reported in chapter VII.

4.4. Particulate emissions

Particulate emissions from the combustion of heavy oils may contain two major fractions:

1. Material arising from the organic content of the fuel and its failure to complete the burn-out process:
1.a. Unburned hydrocarbons (smoke)
1.b. Particulates formed via gas phase combustion or pyrolysis (soot)
1.c. Cenospheres produced from cracked fuel or carbon along with ash (coke).

2. Material from the inorganic content of the fuel:
2.a. Ash.

Solid particulates cause corrosion, erosion and abrasion, which diminish the lifetime of hardware. Carbon particulates also may increase the radiative power of the flame causing damage to the materials of the combustion chamber. In addition, economic penalties are incurred both by non-compliance with stringent environmental regulations, which may result in fines and by loss of unburned material to the atmosphere, which decreases fuel efficiency.

European legislation imposes the maximum limit for particulate emissions at 50 mg/m^3 from sources burning liquid fuels.

4.4.1. Smoke

4.4.1.a. Smoke emissions

Unburned fractions of hydrocarbon fuel may be exhausted in the form of a fine spray. Such hydrocarbon fractions are the remainders of reactions frozen by thermal quenching. Emissions of unburned hydrocarbons are maximum at high equivalence ratios (fuel-rich conditions). Their main effect is to react in the atmosphere with NOx and sunlight to form photochemical smog.

Smoke emissions in gas turbines occur when the combustion gases reach the relatively cool secondary zone. Considering the primary zone of the combustor as a stirred reactor, the composition of the gases leaving determines the smoke emissions from the secondary zone, where reactions are "frozen" and do not proceed further. Emissions of unburned hydrocarbons from gas turbines are maximum at idle conditions and low at any other conditions.
4.4.2. Soot
4.4.2.a. Soot emissions

Soot is formed in gas-phase reactions of vaporised organic matter in a complex process involving fuel pyrolysis, polymerisation reactions, nucleation, particle growth and burn-out. Fuel droplets burning in envelope flames are subjected to very high temperatures, leading to fuel evaporation and thermal cracking of the large molecular structures, thus resulting in species of higher C/H ratio than the fuel source. Eventually nucleation and growth take place, forming particles with C contents ranging from 90 to 98% \(^{40,102}\), which appear after 1 ms of combustion and may grow up to 1,000 \(\mu\)m in 10 ms and agglomerate into filament-like structures \(^{50}\).

Soot is most likely to be formed in fuel-rich conditions, and is normally fully burned as it mixes with air at very high temperature in highly oxidising zones, eg, as secondary air is injected in the combustion chamber of a gas turbine.

Experiments involving soot formation in premixed conditions with different fuels showed similar sooting tendency \(^{51}\). It was suggested that all fuels break down into the same species, which leads to soot. Such a species has been postulated to be acetylene, which builds up into ring structures to give a soot particle by polymerisation and cyclisation processes \(^{51,132}\) aided by H and vinyl radicals \(^{51}\). Assuming that a minimum soot particle is formed by 25 acetylene molecules, the time necessary for the formation of such a soot precursor has been calculated to be \(10^{-5}\) seconds \(^{132}\).

The activity of the ring structure decreases as the size of the structure grows by the successive addition of radicals (\(C_4, C_6\) ...). Eventually a constant value is reached which indicates the formation of a physical surface, ie, the smallest soot particle \(^{132}\). In fact, the final particle size is determined by a decrease in the reactivity of the soot particles as they grow \(^{51}\).
4.4.2.b. Factors that influence soot formation

1. **The flame temperature**, due to the high activation energy of the pyrolysis processes. Several researchers have reported the existence of a threshold temperature (between 1,000 and 1,300 °C) above which soot formation occurs in flames. Soot is eventually emitted when burnout ceases at temperatures below 1,000 °C.

2. **Local oxygen concentration**: Single droplet experiments with furfuryl alcohol showed that incipient soot formation commences as the space between consecutive droplets is diminished below a distance equivalent to 10 diameters. Network flames formed in such conditions are thought to cause a depletion in local oxygen concentration. Soot particles can also be eliminated by reducing the overall oxygen concentration, although this may be an indirect effect by the lower flame temperatures associated with low oxygen concentrations.

3. **Pressure**, provided it affects temperature, and then only to a small extent. Pressure increases cracking to a greater extent than evaporation, thus promoting soot formation. Najjar observed a two-fold increase of soot formation when pressure was increased from 0.3 to 1 MPa in gas turbines. Improved atomisation caused by higher pressure led to lower penetration of the droplets into the combustion chamber. Thus, the high concentration of fuel in the high temperature, low oxygen region establishes the conditions for soot formation.

4. **Chemical additives** may enhance pyrolysis reactions. Halogens cause increase of hydrocarbon radicals by scavenging H radicals. On the other hand, emulsification with water may deplete soot formation. Metals such as nickel or manganese, charge the soot particles electrostatically and reduce agglomeration. The smaller particles thus formed burn more easily.

5. The following **characteristics of the fuel** also affect soot occurrence:
a. Viscosity, as it determines atomisation characteristics.
b. Volatility, particularly the final boiling point, as it determines evaporation.
c. Thermal stability, as it determines the tendency for the fuel to crack.
d. Higher aromatic content and higher C/H ratio give more soot. Under premixed conditions hydrocarbons show the following smoking tendency:

\[
\text{aromatics} > \text{alkanes} > \text{alkenes} > \text{alkynes}
\]

However soot formation correlates to H content rather than to global aromatics as different aromatics may have different H content \(^{103}\).

4.4.3. Coke

4.4.3.a. Coke emissions

Coke particulates \(^{40}\) are formed in liquid-phase processes, and contain all the non-soot carbon and also part of the ash material. Such particles are nearly spherical, hollow and porous, and they range in size from 1 to 100 \(\mu\text{m}\). They are called cenospheres.

Two consecutive processes can be distinguished in the emission of coke particulates \(^{138,139,140}\), namely particle formation followed by its oxidation or burnout. The process of particle formation is strongly dependent upon the fuel properties, although mostly independent of the combustion environment \(^{139}\). On the contrary, the particle oxidation process is affected by the combustion environment, but also by the fuel composition as it provides the material for the coke particle.

The stages of the combustion of heavy fuel oil droplets are described in section "2.3.1. Single suspended droplet technique". Droplets undergo considerable swelling before and during ignition, although a large part of the mass is expelled by fractional distillation and pyrolysis. Coking starts when a threshold temperature is reached, lower than that of soot formation but higher than that of distillation. It lasts only for a few milliseconds, in the last 10 to 15 % of the droplet vaporisation time \(^{91}\). An immature tarry coke particle appears 15 ms prior to the flame quenching. This immature particle eventually becomes a coke particle of much larger size than the original droplet but of reduced mass.
The structural characteristics of coke particles reveal that the non-volatile components that remain after combustion of the volatile fractions provide the material for the cenospheres. Their mass is related to the asphaltene content of the fuel, but also to the amount of maltene and resin components. Fuels containing aromatics form coke more readily than others. However, the mass of the coke particle is independent of the diameter of the initial droplet.

Scanning Electron Microscopy is a useful tool for the characterisation of cenospheres. Clayton and Back showed cenospheres to be hollow and spherical, and with at least one large "blowhole" through the shell. Their structure shows porous layers (the volume of the solid material represents only 18% of the total envelope volume), which provide effective porosity for oxidation reactions. Urban and Dryer reported differences in pore abundance between the inner side and outer surface. Also, pores seem to concentrate on certain regions of the surface, indicating that it may condense onto the surface as the particle is quenched.

Detailed examination by the EDS technique provides an insight of the chemical composition of cenospheres, which varies with size: In particles larger than 10 μm diameter the C content exceeds 80%, whereas for smaller particles it is reduced to 70%. Cenospheres analysed by Clayton and Back were composed mainly of C, N, H and P. High concentrations of S, Na, Mg, Fe, V and Ca were also found. According to Urban and Dryer, catalytic elements such as V and Si are evenly distributed on the particle surface, therefore they are not responsible for large blowholes. However, Si is present only on the outer surface, indicating that it may condense onto the surface as the particle is quenched.

The role of sulphur in coke burn-out has not been clarified yet as contradictory effects have been described. Sulphur in heavy fuels is normally associated with the heavy fractions of the fuel. It may either diminish the catalytic activity of metals or increase the oxidation rate of the carbonaceous particle. X-ray and diffraction microscopy show that fuel-S is uniformly distributed in the particulates, and is released only in the latter stages of combustion. Goldstein and Seigmund studied the effect of blending a high-S fuel and a S-free fuel to simulate a low-S fuel. The effect of dilution was to diminish par-
particulate emissions: When S was reduced from 2.2 % to 0.5 % the total particulate emission decreased by 75 %.

The burn-out of cenospheres\(^{74}\) is much slower than the liquid phase vaporisation processes in droplets. Oxidation is controlled by diffusion in pores, and its rate depends upon the chemical reactivity of the coke, temperature, oxygen concentration, size and porosity of the particles. However, some authors argue that given the normal pore size, diffusion is not a limiting factor for oxidation, and therefore it also takes place on the internal surface\(^{138}\). Also the catalytic action of metals contained (V and Ca)\(^{131}\) may accelerate burn-out, although paradoxically, their contribution seems to be rather unnecessary at such high temperatures (around 1,800 °C).

4.4.3.b. Predictability of coke particulate formation

Although no single property seems to correlate well with particulate emissions, several expressions have been evolved for its prediction\(^{40}\).

Exhaustive work on particulates from power station boilers carried out by Cunningham and Datschefski\(^{37}\) led to the conclusion that the asphaltene and vanadium contents are the most important variables related to particulate emissions, which was also confirmed experimentally by Taylor and Burgess\(^{131}\). However, they obtained scattered results when attempting a relationship between particulate emissions at 4 % oxygen and the Conradson Carbon Residue, as an indicator of the carbon forming tendency of a fuel.

Whitehead \textit{et al.}\(^ {147}\) and later Kelly \textit{et al.}\(^ {74}\) found best correlation of the particulate formation in atmospheric residues with the following equation which shows the complex nature of the coke formation and burnout process:

\[
P_c = \text{Plant factor} \cdot \frac{\left[\frac{1}{2} (\text{Asphaltenes} + \text{TLC resins})\right]^{2.7} S}{Na^{0.3} V}
\]

in which:
Pc: particulate carbon emissions (no ash) at 4 % excess O2, % by weight in fuel
Plant factor: a proportionality constant particular for each set of operating conditions
Asphaltenes: asphaltene content of the fuel
TLC resins: residue measured by Thin Layer Chromatography
S: sulphur content in the fuel, % by weight
V, Na: vanadium and sodium contents, ppm.

King 76 reports the following formula which, although specific for his study, takes both
particle formation and burnout processes into account:

\[ P - A = \frac{k_1 PN^{1.66}}{M_1^{0.55} M_2^{0.34} M_3^{0.23} - 0.05} \]

where:

P: particulates, % mass/mass fuel
A: fuel ash content, % mass/mass fuel
k1: constant
PN: fuel pentane insolubles
M1: (V + Ni + Fe + Mn) in fuel, mg/kg
M2: Ca in fuel, mg/kg
M3: Na in fuel, mg/kg

Later Urban and Dryer 140 proposed a parameter called the Coke Formation Index (CFI)
as the ratio of the coke particle mass to the initial droplet mass before the onset of burn-
out in free, isolated droplet combustion experiments. The Coke Formation Index 138 was
based on the geometric and physical characteristics of both fuel and coke particle only:

\[ CFI = \frac{\text{particle mass}}{\text{droplet mass}} = \frac{\frac{D_c^2}{D_o^2} \rho_{cs} \tau}{\rho_o} \]

where:
De: coke particle diameter
D₀: droplet diameter
τ: coke particle shell thickness ratio
ρ₀: density of fuel droplet
ρₚ: density of the coke particle shell

The Coke Formation Index is mostly invariant over a wide range of droplet sizes, temperature profiles and oxygen concentrations\(^{138}\), but strongly influenced by the fuel type. Its values are maximum at the point where the vapour-phase flame extinguishes. Subsequently it decreases as both oxidation and burnout progress.

A relationship between CFI and the fuel composition was also pursued by Urban and Dryer\(^{140}\). The CFI seems to correlate with the heptane asphaltene content (ASP), according to:

\[
\text{CFI} = 0.0021 + 0.0075 \times \text{ASP}
\]

4.4.3.c. Reduction of coke particulate emissions

Since no technique has been found so far to prevent the formation of cenospheres, it seems reasonable to accelerate their disappearance. Some possible means are\(^{149}\):

1. **Excess air**: Conditions in the primary zone require small amounts of excess air in order to achieve high temperature and high combustion intensity. Also increasing the amount of excess air will enhance carbon burn-out up to a certain optimum value\(^{52}\), with reductions of 60-70 \%. However, if very high amounts of excess air are used, reactions may be quenched leading to increased particulate emissions and loss of thermal efficiency.

2. **Sufficient residence time**, by promoting recirculation and high turbulence, to allow completion of the combustion of hydrocarbon fractions and an increase in droplet vaporisation. In order to achieve a two-fold decrease in particulate emissions the residence time must be increased by a factor of 3.3 - 4.7\(^{52}\)
3. **Blending** of the heavy oil with another lighter component.

4. **Addition of water** to the fuel assists a reduction in coke formation in two different ways. Firstly, because it intensifies droplet disruption by forming smaller particles which burn out more rapidly. Secondly, as a source of OH radicals that may speed up heterogeneous burnout reactions. Experiments on large scale boilers show that 13% of water in a fuel can drastically reduce particulates by 70%.

5. **Improved atomisation** also increases coke burnout rates.

6. Incorporation of **metal additives** to the fuel: Fuels containing a high concentration of V form lower levels of carbonaceous particulates. It was suggested that vanadium oxides formed during combustion catalyse the formation of sulphates from organically-bound S. Experiments by Taylor and Burgess confirmed the importance of this element in assisting coke burnout: Addition of vanadium to a low-V fuel accelerated particulate burnout. A similar effect, but with a so-called "metal containing combustion additive" was reported by Whitehead. It is likely that the metals catalyse pyrolysis at an early stage (at low temperature) of cenosphere formation, leading to the formation of blowholes which stimulate burnout.

Other metals tested by Feldman can be ordered according to their ability to reduce particulate formation:

$$Zr > Fe > Mg = Mn > Ba$$

where Mn and Mg do not cause reduction and Ba caused increase of particulates due to the formation of stable vanadates, thus reducing V availability.

Fe is reported to form high melting point, non-toxic, non-fouling and non-corrosive deposits. Cunningham reports that addition of 130 ppm of organically-bound Fe reduced particulates by 60%.
4.4.4. Ash

4.4.4.a. Ash formation from heavy oils

Ash fouling and corrosion are major problems when burning heavy oils. Ash deposits jeopardise heat transfer to metallic surfaces and cause corrosion of the combustion hardware, thus decreasing its lifetime. In gas turbines ash reduces the aerodynamic path for gas flow, and therefore the turbine performance. Values given in the literature show that a mere 0.32 cm thick deposit can cause a 10% decrease in turbine power.

Ash stems from the inorganic content of the fuel. The origin of these constituents is varied:

a. The animal and vegetable sources from which the oil was formed
b. Contact of the oil with the underground rock structure
c. Production, storage, handling and transportation facilities.

In general, inorganic components concentrate in the asphaltic constituents of residual oils to a typical maximum concentration of 0.2%. Ash deposits have a much higher concentration of these constituents and are therefore very damaging to the metallic parts.

Two aspects are particularly important when corrosion caused by ash is studied:

1. The deposition of substances, resulting from the combination of three processes:

   1.a. Particle delivery to the surface, which depends on the particle size

   1.b. Adherence and removal of particles: Dry particles will adhere by metal attraction or roughness. Molten or semi-molten particles will obviously adhere readily. Because of their low thermal conductivity deposits will be at a higher temperature than the metal and in molten or semi-molten state, which enhances the adherence of more deposits. Ca and V compounds enhance the sticking tendency of deposits.
1.c. Gross detachment of previously built-up deposits, sometimes caused by spal­
lation (see section “4.4.4.c. Preventing or reducing ash deposition and cor-
rosion”).

2. The corrosion caused by the substances, which is increased exponentially by the
metal temperature \(^{82}\). In addition, higher temperatures make ash residues more
difficult to remove as they are produced at a higher rate and are also harder.

4.4.4.b. Ash forming contaminants in fuel: Vanadium, sodium and lead

Vanadium and sodium are the most harmful elements, respectively forming vanadium
pentoxide \((V_2O_5)\) and sodium sulphate \((Na_2SO_4)\).

Vanadium appears in fuel in the form of oil-soluble porphyrins. These organic vanadium
compounds decompose in the gas stream to give mainly \(V_2O_5\). Vanadium pentoxide is
most damaging since due to its low melting point \((690 \, ^{\circ}C)\) it is in its liquid state at nor-
mal combustion temperatures.

The mechanism of formation of vanadium compounds can be explained as follows \(^{128}\) :
In high-temperature (approximately \(1,730 \, ^{\circ}C)\), low-oxygen zones, the solid, non-volatile
vanadium tetroxide \((V_2O_4)\) is formed. Vanadium pentoxide is formed from the tetroxide
in low-temperature (approximately \(800 \, ^{\circ}C)\), high-oxygen zones. In fact, deposits are ob­
served to comprise both oxides, although the tetroxide oxidises to the pentoxide in ex­
cess air \(^{15,38}\).

The extent of the vanadium attack on metal is determined by two factors \(^{15,38}\) : The
amount of corrosive vanadium compounds at the metal/oxide interface and the diffusion
rate of oxygen to the metal oxide interface. In that respect, the nature of the oxide layer
on the metal surface is very important as it may hinder oxygen diffusion towards the
metal surface. For instance, Ni\(_3\)(VO\(_4\))\(_2\) is formed on nickel-based alloys which forms a
stagnant phase on its surface which stops oxidation \(^{15}\).
Sodium is normally present in the fuel as NaCl collected by the fuel either from underground water or transportation facilities. It can be removed by combined water-washing and subsequent centrifugation.

Sulphidation attack (also known as "hot corrosion") is corrosion caused by sulphates, mainly Na₂SO₄, on nickel and aluminium alloys, by dissolving the carbide network of the metal. These alloys (eg, Udiment 500) are commonly used in high metal temperature applications, in place of stainless steel and cobalt-based alloys. Experimental work by Stevens and Tidy using Na-doped fuels shows that, regardless the initial form of sodium, its main post-combustion compound is Na₂SO₄, where sulphur arises from the fuel-S content. Whether Na₂SO₄ is formed in the flame or on the metal surface remains unclear. Gaseous sodium sulphate is almost harmless, unlike its solid or liquid forms, which are particularly harmful when they exceed the theoretical Na "dew point", over 60 ppm. This threshold is lowered by the presence of Mg, which could be introduced as an anti-vanadium reagent, and also by other alkaline metals such as Ca and K, which form eutectic mixtures with sodium (eg, Na₂Mg(SO₄)₂·4H₂O).

As a result, sodium can work to decrease the efficiency of Mg additives on vanadium corrosion, by forming eutectic mixtures of low melting point (below 590 °C) with liquid vanadium pentoxide. Sodium vanadyl vanadate (Na₂O·V₂O₄·V₂O₅), very corrosive above 647 °C, is of particular importance. However, there seems to exist a threshold of Na₂SO₄ concentration beyond which the addition of more sodium sulphate decreases the corrosion activity of vanadium pentoxide.

Solid carbon deposits increase hot corrosion by reducing Na₂SO₄ to the very corrosive Na₂S.

The harmful effects of Na are enhanced when Pb is present in the fuel. However, lead corrosion can also be tackled by Mg by means of the formation of compounds such as PbO and PbSO₄ of high melting point. However, in the more realistic case of Pb, V and Na mixtures acting at high temperatures, Mg alone does not suffice against corrosion, and combinations of magnesium and silica are efficiently used if the concentration...
of sodium is reduced below 0.5 ppm by water-washing \( \text{82,124} \). Silica does not inhibit corrosion on its own \( \text{82} \), but enhances the efficiency of Mg additives \( \text{80} \) and increases the friability (capacity of deposits to break into small pieces) of the ash deposits \( \text{82,95} \). Finally, greater amounts of Mg are to be used if the metal surface is exposed to higher temperatures \( \text{95} \).

4.4.4.c. Preventing or reducing ash deposition and corrosion

Several different methods have been devised in order to either diminish, avoid or remove corrosive deposits:

1. **Coatings** \( \text{108} \): Oxide scales build up a protective layer on the metal surface, separating the substrate from the corrosion environment. Coatings provide active elements for building-up this protective oxide scale \( \text{38,81} \).

2. **Cooling of metal surfaces** \( \text{81} \), intended to solidify deposits before their attack is initiated. Corrosion is increased exponentially by the metal surface temperature.

3. **Additives** \( \text{16,80,82,129} \): Additives combine with fuel constituents and combustion products to form solid, innocuous products that pass harmlessly through the combustion equipment \( \text{81} \). Additives may contain metals such as Mg, Al, Si, Mn or Ba \( \text{82} \), or combinations like Mg-Si, Mg-Al-Si, Al-Si \( \text{94,95,96} \). Data obtained by May et al. \( \text{95} \) indicate that at certain temperatures and with sufficient additive the corrosion rates can be reduced to zero. Additives also help to decrease corrosion by preventing the catalytic formation of \( \text{SO}_3 \) \( \text{15} \). However, large concentrations of additives may increase particulate output.

4. **Surface cleaning procedures** \( \text{16} \) in gas turbines: These can be split in three categories:
4.1. On-line techniques: Injection of an abrasive material such as crushed nutshells or coke. These techniques are effective on low temperature (under 970 °C) deposits.

4.2. Off-line techniques: Usually a sequence of successive water-wash, soak and re-start is used to soften the MgSO₄ deposits, then followed by the breakage of other deposits. Off-line techniques are efficient on deposits formed at any temperature, although at the cost of efficiency loss as the engine must be switched off.

4.3. Thermal excursions: Deposits suffer spallation if a sudden momentary increase of the turbine inlet gas temperature is caused.
INTRODUCTION TO EXPERIMENTAL CHAPTERS

In the previous chapter, a review of various aspects of combustion science relevant to this thesis has been carried out.

Firstly, the physical and chemical characteristics of heavy liquid fuels have been reviewed, with focus on the refining processes (vacuum distillation, delayed coking, visbreaking, etc.) that increase the yield of lighter products and the changes in the characteristics of the heavy fuels that these processes can cause. The physical and chemical properties of liquid fuels were also reviewed.

The previous research on the combustion of heavy fuel droplets was examined in the next part of the literature survey. Two main techniques were reviewed, namely the single suspended droplet technique and the single droplet technique. The former technique consists of suspending a small droplet of fuel on a wire, which is then subjected to a source of heat or radiation. This technique will be used in the experimental part of the present thesis (see chapter II) to determine the basic ignition and burnout characteristics of the fuels under study. Also, the variation of the fuel droplet size during the pre-ignition period will be examined by means of video recordings.

The use of heavy liquid fuels for the generation of electricity by means of gas turbines was the object of the next section of the literature review. Atmospheric pollutants are formed in the generation of electricity by thermal means. These are, mainly, oxides of nitrogen (NO and NO₂), oxides of sulphur (predominantly SO₂) and particulate matter. The processes leading to the formation of these species were reviewed, as well as methods to reduce their formation and emission. In chapter III of this thesis the formation of these and other pollutants from the fuels under study will be examined experimentally in a drop-tube furnace. In this furnace, a spray of fuel and air was burnt at varying furnace wall temperatures and stoichiometric ratios, and the combustion gases were sampled at various distances from the atomiser. The data so obtained enabled the study of the formation of pollutants as a function of the flame wall temperature and stoichiometry of the combustion system.
This thesis is concerned with various aspects of the formation and emission of fuel-NO\textsubscript{X}. Since thermal-NO\textsubscript{X} is also a common occurrence at high flame temperatures in combustion processes, it was necessary to determine the amounts of thermal-NO\textsubscript{X} formed in the drop-tube furnace. This was achieved by burning a fuel with a low nitrogen content, as the formation of thermal-NO\textsubscript{X} is independent from the nitrogen content of the fuel, and is described in chapter IV.

The results from a numerical model are reviewed in chapter VI. The model was used to investigate further the reactions that take part in the formation of oxides of nitrogen. Some of these reactions are detailed in the literature survey reported in chapter I. In addition, the reactions that lead to interactions between sulphur and nitrogen compounds are studied in chapter VI. The model is aided by measurements of the flame temperature in the drop tube furnace, which are shown in chapter V.

Also in the literature survey, the interaction of oxides of sulphur in the formation and emission of oxides of nitrogen has been examined, with particular emphasis on the previous research on the effect of fuel-S on fuel-NO\textsubscript{X}, ie oxides of nitrogen formed from the nitrogen contained in fuel. The fuels under study in this thesis were used to experimentally assess the effect of increased concentrations of fuel-S on the formation and emission of oxides of nitrogen. This was done at one furnace wall temperature and as a function of the stoichiometric ratio, so that fuel-lean, stoichiometric and fuel-rich conditions were investigated. Also, sampling at different distances from the atomisation nozzle was performed to investigate the stages of the combustion processes where N-S interactions occur. The experimental procedure and the results are detailed in chapter VII.
CHAPTER II. EXPERIMENTS WITH THE SINGLE SUSPENDED DROPLET TECHNIQUE

1. Objective

The Single Suspended Droplet technique was described in section “2.3.1. Single suspended droplet technique” of chapter I. In addition, experimental work previously reported was reviewed.

In the present work the technique was used to obtain preliminary, comparative, qualitative and quantitative information of the combustion performance of the fuels studied.

Quantitative information collected comprised the duration of the various stages of the droplet combustion. The ignition temperature of the fuels was another parameter studied, as well as the maximum temperature of combustion of coke residues, in the case where the existence of a residue was detected.

Qualitative information collected by visual observation included the ejection of soot and disruptive behaviour. In particular, the variation of the droplet size, swelling and contraction, were studied by means of video recordings.

2. Experimental

2.1. Equipment description

In the experimental set-up used at UCL oil droplets were suspended from 25 μm diameter R-type thermocouple wires of the following composition: Positive wire: platinum 99.9 %, negative wire: platinum/rhodium 87/13. Initial runs were performed on 50 μm wires as an approach to study the most suitable wire diameter for the oils under research. However, wires of 25 μm diameter were eventually used as their resilience was sufficient and they represent a closer approach to real operation conditions than larger diameters.

The wires were coated by projecting vaporised silica (Silicone Fluid, by Dow Corning Corporation) from a Bunsen burner. Coating reduces catalytic action of the metal upon
carbon residues, should they exist. Also, the thermocouple arm was earthed in order to eliminate electronic disturbances on the oscilloscope caused by the BBC computer that logs the combustion sequences. The combustion thermocouple, mounted on a silica support, was thus introduced in an electrically heated furnace.

The furnace is formed by three silica tubes, one main tube and two side arms sealed to the main tube in right angles. Dimensions are shown in Figure 18.

Heating was generated by a Kanthal coil placed around the main tube (see Figure 19), operated by means of a Sirect controller and a 10 amp. full-scale-deflection ammeter. The temperature in the furnace was controlled by a probe thermocouple inserted in the main tube at a long distance from the combustion thermocouple so that temperature variations due to convective streams were avoided. The furnace insulation was provided by Kaowool placed between the tubing and the case.

The light emitted by the burning samples was detected by a planar photodiode placed opposite the combustion thermocouple.
The droplet samples suspended on the combustion thermocouple were swiftly introduced into the furnace by a manually controlled stepping-motor. The temperature history registered by the combustion thermocouple and the light recorded by the planar photodiode were conveyed to and processed in a Gould Digital Storage Oscilloscope 4035, where combustion sequences lasting from 1 to 500 seconds can be stored. The signal was filtered to eliminate noise disturbances. Subsequently, the sequences were stored on a BBC Computer via an IEEE interface. Hard records of the combustion sequence were obtained by plotting the oscilloscope display by a Hewlett Packard 7475 A plotter.

2.2. Samples studied

The samples studied in the present work were supplied by Repsol Petróleo S. A. They can be classified in two main groups, namely three heavy vacuum gas oils (designated G3, G4 and G5) and two heavy coker gas oils (designated M2 and M3). Their average overall chemical analyses can be found in "Appendix II", page 265. In general, their specifications complied with those of ASTM no. 3-GT fuel for gas turbine use and ASTM no. 5 (light) fuel oil or grade no. 4 fuel oil.

2.3. Size parameters

The image of every droplet was projected on a screen before insertion in the furnace. From their profiles the size characteristics (volume, surface area, length on the X axis and length on the Y axis) were evaluated with a Hewlett Packard digitiser. Assuming perfect sphericity an equivalent volume diameter ($d_v$) was calculated from the droplet volume:

$$d_v = \sqrt[3]{\frac{6}{\pi}} \text{ droplet volume from digitiser}$$

This diameter was used to establish correlations with the combustion parameters.
Figure 20: General view of the single suspended droplet apparatus

Figure 21: (from left to right) BBC computer, Gould processor, Gould oscilloscope and motor drive
Figure 22: (from left to right) Light projector and single suspended droplet furnace

Figure 23: Photo-diode, furnace and control probe thermocouple
Fifteen valid runs were performed with every fuel at each furnace temperature attempted. The diameters of the droplets ranged from 0.4 mm to 1.2 mm. For droplets of 1 mm diameter the ratio of the volume occupied by the thermocouple wires to the total droplet volume is approximately 0.8%, whereas for droplets of 0.5 mm diameter it approaches 3%, and so it begins to be significant.

The low viscosity of the sample M2 did not allow the suspension of droplets at room temperature. In fact, this oil had to be cooled in ice prior to the experiments.

2.4. Combustion parameters

The experiments were run with every sample at five furnace temperatures: 600, 650, 700, 750 and 800 °C. Below 600 °C ignition becomes somewhat difficult, whereas above 750 °C heat is so intense that it the fuel may ignite before its arrival at the centre of the furnace.

The furnace was flushed with air during 10 minutes prior to each experiment.

During the insertion process the sample is protected by a tubular silica shield, covered with aluminium foil, in order to prevent heat (mainly radiation) from the arm tube from reaching the droplet. The shield retracts in the later stages of the insertion process, allowing the sample to be exposed to the highest temperatures in the central part of the furnace.

The combustion parameters defined in the next pages were correlated to the initial droplet diameter by means of the Least Linear Squares Method, according to the relationships proposed by Taylor and Burgess [131]. The vast majority of the regression coefficients proved good correlation between the initial droplet diameter and the combustion parameters ($r^2 > 0.85$ at 600 °C furnace temperature and greater than 0.90 at higher temperatures).

In order to compare the performance of the fuels under study, calculations were made of the burning times for a standard droplet of 1 mm of initial diameter as obtained from the
linear regressions. This diameter was chosen as data was available at this diameter from all fuels at all furnace temperatures. Although a smaller diameter would have been more representative of actual operating conditions, data availability was hampered by lack of ignition at low furnace temperatures (see section "4.6. Critical Diameter for Ignition (d_0^c)" in this chapter).

Since none of the fuels studied exhibited a measurable formation of coke residue, no attempts were made to correlate the coke burn-out time with the initial droplet diameter.

3. Definitions

3.1. Pre-ignition Delay (t_i)

This is the period of time elapsing from the arrival of the droplet suspended on the thermocouple at the centre of the furnace until the homogeneous ignition of the vapour surrounding the sample. The processes taking place during this stage involve mainly heating-up of the fuel, evaporation of volatile components, cracking of fuel components and gas phase reactions that eventually lead to the ignition of the fuel.

The Pre-ignition Delay relates to the initial droplet diameter in the following way:

\[ t_i = K_i d_o \]

3.2. Flame Time (t_f)

The Flame Time comprises the period between the onset of homogeneous ignition around the droplet and its extinction. During the flame stage cracking and further volatilisation of material from the droplet occur.

The flame resulting from ignition is detected by means of a planar photodiode. The duration of the Flame Time is obtained from the photodiode trace on the oscilloscope screen.

The Flame Time is related to the squared power of the initial droplet diameter:
3.3. Total Combustion Time (t)

This parameter includes the time taken by all measurable combustion processes taking place in the sample droplet. In the case of the samples studied it includes the Pre-ignition Delay and the Flame Time, and it is calculated by their addition in every single experiment \( t = t_i + t_f \). The coke burn-out time \( (t_c) \), ie, the time taken by any solid carbon residue (if present) to disappear, was not included in the evaluation of the Total Combustion Time in these experiments (see section "3.6. Peak Temperature \((T_p)\)").

The Total Combustion Time is related to the squared power of the initial droplet diameter:

\[
t = K d_i^2
\]

3.4. Ignition Temperature \((T_i)\)

The Ignition Temperature is the temperature recorded by the combustion thermocouple at the onset of homogeneous ignition. The temperature measured is that of the centre in the droplet.

The Ignition Temperature was obtained from hard records of the combustion sequences.

According to Taylor and Burgess \(^{131}\) the Ignition Temperature is related to the inverse of the initial droplet diameter by:

\[
T_i = T_\infty + \frac{A}{d_o}
\]

where \( T_\infty \) represents the theoretical ignition temperature of a large pool of oil, ie when the initial diameter is \( d_o = \infty \).
3.5. Critical Diameter for Ignition ($d_{ig}^c$)

It is the minimum droplet diameter of a given fuel which exhibits homogeneous ignition at certain experimental conditions of furnace temperature. Ignition is understood as the presence of a flame emerging from the droplet surroundings.

Ignition takes place when the mixture of gases around the droplet is within the ignition limits at the furnace temperature. Small droplets have to produce vapour at a sufficiently fast rate so that the right mixture is formed. At low furnace temperatures the fuel diffuses away before the mixture is formed, and thus ignition is not reached. At higher temperatures the ignitable mixture is attained more rapidly due to increased volatilisation.

Since only a limited number of runs was performed with each fuel, the determination of the Critical Diameter for Ignition was imprecise. Experimentally the Critical Diameter for Ignition is assumed to lie between the largest initial droplet diameter showing lack of ignition and the lowest diameter showing homogeneous ignition.

3.6. Peak Temperature ($T_p$)

The Peak Temperature is the highest temperature reached in the centre of the burning sample. The existence of a peak reveals the presence of further combustion reactions taking place after the flame is quenched. Such reactions are usually heterogeneous processes caused by the diffusion of oxygen towards a coke particulate formed from the heavy components of the fuel. The measurement of the Peak Temperature is made from hard records of the combustion sequences.

4. Experimental results

4.1. Visual observations

The droplet temperature histories recorded show a similar behaviour for all of the samples studied. A typical combustion sequence can be seen in Figure 24.
Figure 24: Combustion sequence of a droplet of fuel M2 of $d_o = 0.88$ mm burned at 750 °C furnace temperature (horizontal axis: time, s; vertical axis: output voltage (temperature, light), µV)

The temperature of the droplet rises uniformly after insertion until the onset of homogeneous ignition. Simultaneous to ignition, which is observed as a stretched vertical yellow envelope flame, soot is ejected. The amount of soot emitted varies from fuel to fuel, being maximum for the heavy coker gas oils and minimum for the heavy vacuum gas oils.

The droplet temperature continues rising as the flame progresses. The rate of heating at the centre of the droplet decreases, due to cracking and evaporation withdrawing energy from the remaining liquid fuel. A further rapid increase is recorded when the flame disappears. Such an increment is large for the heavy coker gas oils (particularly for M2) and almost imperceptible for the heavy vacuum gas oils. In the case of the heavy coker gas oils the temperature may reach up to 1,450 °C.

Visual observations of the combustion of the heavy coker gas oil M2 reveal the existence of a small carbonaceous residue burning heterogeneously for a very short period of time, which is coincidental with the increase of the droplet temperature. This was confirmed by video recordings performed (see section “5.3. Experimental results”). The existence of a solid residue agrees with the presence of 0.1 % by weight asphaltenes among its con-
stituents. Unfortunately the light emitted by the burning sample is too low for the experimental facility to detect it.

Subsequently the soot trail settles onto the thermocouple wires as it burns out. The temperature registered by the combustion thermocouple returns to that of the furnace. Eventually the soot residue disappears after a period of time which may last several minutes at low furnace temperature and a few seconds at the highest furnace temperatures attempted.

4.2. Pre-ignition Delay ($t_i$)

Correlations between $t_i$ and $d_i$ show low correlation coefficients, although they increase at higher furnace temperatures as the regressions become more reliable.

The trend observed from the experimental results is that of an overall decrease of $t_i$ throughout the range of temperatures studied (see Figure 25). At high combustion temperatures the results converge towards a narrow range of values. Results previously obtained by Malik and Burgess also showed the Pre-ignition Delays of different fuels to become coincidental as the ambient temperature rose.

The Pre-ignition Delay can be considered the result of three distinct successive processes. For each of these processes a time delay can be defined:

1. Heating-up delay ($t_h$): The time taken by the droplet to reach the evaporation temperature.
2. Evaporation delay ($t_e$): The time necessary for the evaporation of the fuel to take place.

3. Chemical delay ($t_{chem}$): The time between the introduction of the homogeneous combustible mixture into a hot atmosphere and its eventual ignition.

At high ambient temperatures the limiting step for fuel ignition is the heating-up of the droplet, whereas evaporation and chemical processes are no longer limiting steps. It is logical that fuels of similar physical and chemical characteristics, such as those studied in this thesis, would present similar delays. Thus, the overall Pre-ignition Delay would have similar values for all of them.

The values of the Pre-ignition Delay measured are lower than those obtained with other heavy fuels, such as residual oils and coal-water slurries in the same experimental facility. This can be attributed to the presence of lighter fractions of low volatility that form an ignitable cloud around the droplet more quickly.

Although no major differences were observed in the Pre-ignition Delay of the fuels studied, the experimental results reveal three distinct behaviour patterns:

1. Group 1: Includes the heavy coker gas oils: M2 and M3.
2. Group 2: Includes two heavy vacuum gas oils: G4 and G5.

Group 2 exhibits the longest Pre-ignition Delay among all samples studied. Group 1 shows intermediate values whilst Group 3 (fuel G3) becomes the most easily ignitable oil sample at 800 °C, with the shortest Pre-ignition Delay.

The fact that the pre-ignition delays are longer for some heavy vacuum gas oils than for the heavy coker gas oils does not agree with the characteristics of their distillation ranges. These show that the evaporation of components from the heavy coker gas oils commences at higher temperatures than those in the heavy vacuum gas oils (see Figure 26). The significance of this fact should be the faster production of volatiles from heavy vacuum gas oils.
However, differences in the chemical composition of both types of fuel can establish the conditions for different Pre-ignition Delays. With similar contributions from the heating-up delay \( t_h \) and the evaporation delay \( t_e \) at the same experimental conditions, differences in the chemical delay \( t_{chem} \) can determine the varying values of \( t_i \). These differences can be caused by the chemical composition of both types of fuels. One example is the aromatics content, 33 % in heavy coker gas oils vs 23 % in heavy vacuum gas oils, as detailed in “Appendix II”. The flammability of (fuel:air) mixtures is greatly dependent on the chemical composition of the fuel and its vaporised components. Shorter Pre-ignition Delays and lower Ignition Temperatures are obtained from the for heavy coker gas oils, which is also explained in section “4.5. Ignition Temperature \( (T_I) \)” as flammability is reached in a shorter period of time.

The influence of the furnace temperature on the Pre-ignition Delay can be expressed by the following Arrhenius-type equation:

\[
\frac{1}{t_i} = A_i \exp \left( -\frac{E_{act}}{R T_f} \right)
\]

where:

- \( t_i \): Pre-ignition delay, s
- \( T_f \): furnace temperature, K
- \( A_i \): pre-exponential factor
- \( E_{act} \): activation energy of the overall ignition process
- \( R \): gas constant

\[\begin{align*}
\text{Figure 26: Generic distillation range for heavy vacuum gas oils and heavy coker gas oils}
\end{align*}\]

\[\begin{align*}
\text{Figure 27: Graph showing In } 1/t_i \text{ vs } 1/T_f \text{ for droplets of } d_o = 1 \text{ mm of all fuels under study}
\end{align*}\]
Figure 27 shows a plot of ln 1/ti vs 1/Tf. The values of the activation energy and the pre-exponential factor obtained are shown in the following Table:

<table>
<thead>
<tr>
<th>Fuel</th>
<th>E_{act} kJ/mol</th>
<th>A, 1/s</th>
<th>r^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>M2</td>
<td>30.3</td>
<td>22.5</td>
<td>0.997</td>
</tr>
<tr>
<td>M3</td>
<td>36.1</td>
<td>45.2</td>
<td>0.986</td>
</tr>
<tr>
<td>G3</td>
<td>34.0</td>
<td>35.5</td>
<td>0.989</td>
</tr>
<tr>
<td>G4</td>
<td>28.1</td>
<td>16.0</td>
<td>0.946</td>
</tr>
<tr>
<td>G5</td>
<td>30.6</td>
<td>21.3</td>
<td>0.992</td>
</tr>
</tbody>
</table>

Table 4: Overall ignition activation energy and pre-exponential factor for the fuels studied

As explained earlier, the overall activation energy is the sum of the activation energies of the processes that precede ignition, that is, heating-up, chemical and evaporation processes. According to the results shown in Table 4, fuel G4 would be, in principle, the most ignitable fuel studied. However, similar slopes show that no large differences exist among the calculated activation energies, and they would possess similar ignition characteristics.

High activation energies are normally associated with high aromatic contents. Unfortunately, no detailed information on the aromatic content of the fuels was available.

4.3. Flame time (t_f)

As in the Pre-ignition Delay three groups of behaviour can be differentiated. Groups 1 and 2 show an increase of the Flame Time with the furnace temperature, their values rising to become nearly coincidental (Figure 28), although the increase is greater for Group 1 (fuels M2 and M3) than for Group 2 (fuels G4 and G5).
However, the trend shown by Group 3 is that of a net increase in the values of \( t_r \), although at a lower rate than other groups. Finally the duration of its Flame Time decreases between 750 and 800 °C furnace temperature.

In general, the Flame Time increases with the furnace temperature. This can be explained in terms of the evaporation of fuel that takes place in order to form an ignitable mixture during the Pre-ignition Delay. At low furnace temperatures much fuel evaporates and diffuses into the surrounding air before an ignitable mixture is accomplished. Little mass of fuel is left in the droplet when ignition starts, and thus vaporisation and combustion of this remaining fuel take a shorter time to complete. As the furnace temperature rises the ignitable mixture is attained more rapidly, and the mass of fuel left in the droplet after ignition onset is large. Longer periods of time are required to vaporise and burn this fuel.

4.4. Total Combustion Time (\( t \))

The trend observed is that of shorter Total Combustion Time for all fuels studied as the furnace temperature was increased. However, as a result of the behaviour of the flame stage both Groups 1 and 2 exhibit a net increase of the Total Combustion Time at 800 °C furnace temperature, which reverses the trend registered at lower furnace temperatures. Values of \( t \) are totally coincidental for oils of Group 2 (G4 and G5), similar to those of fuel M2, but values corresponding to M3 are lower within Group 1.

Group 3 (fuel G3) exhibits a distinct pattern of steady decrease of \( t \) values, thus becoming the sample with the shortest value of the Total Combustion Time at 800 °C.
4.5. Ignition Temperature ($T_i$)

Due to technical difficulties the Ignition Temperature could not be recorded adequately at furnace temperatures below 800 °C. Improvements in the equipment allowed its measurement at 800 °C with high accuracy. Most correlations performed yielded correlation coefficients ($r^2$) greater than 0.85. One example is given in Figure 30.

The values of $T_i$ are correlated to the inverse of the initial droplet diameter $d_0$ according to:

$$T_i = T_\infty + \frac{A}{d_0}$$

Calculation of the Ignition Temperature for a standard 1 mm diameter droplet at 800 °C provided the values listed in Table 5:

<table>
<thead>
<tr>
<th>Fuel</th>
<th>$T_i$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>M2</td>
<td>314</td>
</tr>
<tr>
<td>M3</td>
<td>321</td>
</tr>
<tr>
<td>G3</td>
<td>359</td>
</tr>
<tr>
<td>G4</td>
<td>364</td>
</tr>
<tr>
<td>G5</td>
<td>367</td>
</tr>
</tbody>
</table>

Table 5: Ignition Temperatures of the samples studied at 800 °C furnace temperature

Clearly two types of behaviour can be distinguished: That of heavy coker gas oils (previously quoted as Group 1), their calculated Ignition Temperatures lying at about 318 ± 4 °C, and that of heavy vacuum gas oils (referred to as Groups 2 and 3), whose values of the calculated Ignition Temperature lie at about 363 ± 4 °C.

4.6. Critical Diameter for Ignition ($d_c^i$)

The experimental Critical Diameter for Ignition exhibits a decrease as the furnace temperature is increased in almost all cases (see Table 6). This is expected to occur as ignition of small droplets is achieved more easily at high furnace temperatures. Although no
clear trend of behaviour could be ascertained from the results obtained, at 800 °C the fuels of each given group show similar values of $d_i^o$.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>600 °C</th>
<th>650 °C</th>
<th>700 °C</th>
<th>750 °C</th>
<th>800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>M2</td>
<td>0.90</td>
<td>0.73</td>
<td>0.63</td>
<td>0.47</td>
<td>0.48</td>
</tr>
<tr>
<td>M3</td>
<td>1.15</td>
<td>0.93</td>
<td>0.70</td>
<td>0.66</td>
<td>0.49</td>
</tr>
<tr>
<td>G3</td>
<td>0.91</td>
<td>0.76</td>
<td>0.61</td>
<td>0.51</td>
<td>0.53</td>
</tr>
<tr>
<td>G4</td>
<td>0.97</td>
<td>0.91</td>
<td>0.78</td>
<td>0.55</td>
<td>0.45</td>
</tr>
<tr>
<td>G5</td>
<td>1.06</td>
<td>0.93</td>
<td>0.68</td>
<td>0.51</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table 6: Experimental values of the Critical Diameter for Ignition

4.7. Peak temperature ($T_c$)

Only one of the samples studied (M2) exhibits an appreciable increase of the droplet temperature after the extinction of the flame, especially at high furnace temperatures. The temperature of the droplets may reach up to 1,450 °C. Such a fact proves the existence of a solid residue on which heterogeneous reactions increase the temperature measured. Fuel M2 contains 0.10 % asphaltenes which is likely to form a small solid particulate.

In general, the tendency is that of increasing Peak Temperature for larger initial diameter and higher furnace temperature, although such pattern was not thoroughly obeyed in all experiments. Larger amounts of fuel give rise to higher heat release which is added to that stemming from the hot surrounding atmosphere.

A relationship between the Peak Temperature ($T_c$) and the initial droplet diameter can be ascertained from the experiments with fuel M2 at 700 °C. The relationship takes a quadratic form at 750 °C ($T_c = 794 + 266d_i^2$, $r^2 = 0.9249$). It can be seen in Figure 31.

Other samples did not cause an increase of the Peak Temperature.
addition, visual observations did not reveal the appearance of solid residues except for fuel M2.

However, the combustion of all samples investigated is accompanied by the ejection of considerable amounts of soot. Soot emerges from the internal side of the flame, which agrees with observations previously made by other researchers. Its formation occurs as convective streams are established in the droplet centre at the onset of ignition, forming a fuel-rich zone that promotes soot formation. This effect is enhanced by the aromatic compounds contained in the fuels, which average 23.4% for heavy vacuum gas oils (fuels G2, G3 and G4) and 32.9% in heavy coker gas oils (fuels M2 and M3). The layer of soot particles is eventually expelled in the outward flow of the combustion gases. It settles on the thermocouple wires and burns out.

4.8. Conclusions

The basic combustion characteristics of five heavy gas oils have been investigated by the Single Suspended Droplet technique. The experimental results obtained confirmed that these fuels comply with most of the relationships established by Taylor and Burgess for heavy oil droplet combustion.

Three groups of fuels with distinct combustion behaviours have been distinguished among the samples studied:

- Group 1: Includes fuels M2 and M3
- Group 2: Comprises fuels G4 and G5
- Group 3: Includes fuel G3.

The following conclusions can be drawn:

1. As the furnace temperature rises up to 800 °C Group 3 (fuel G3) becomes the most easily ignitable sample, followed by Group 1 (M2 and M3) and Group 2 (fuels G4 and G5), the latter displaying the longest t, among the results obtained. The generic distillation ranges of the two groups of fuels suggest opposite behaviour, since heavy vac-
uum gas oils contain larger amounts of volatile matter which should assist rapid igni-

2. The Flame Time of Group 3 is also the shortest, as it shows a net decrease at 800 °C. However, Groups 1 and 2 experience an increase of $t_f$ up to similar values in experiments at 800 °C.

3. As a result, Group 3 yields the shortest Total Combustion Time (t) at 800 °C, whereas both values of Group 2 are coincidental and intermediate between those of Group 1.

4. The Ignition Temperature of Groups 2 and 3 (ie, all heavy vacuum gas oils) measured at 800 °C lie within the same range, approximately $363 \pm 4$ °C, which is higher than that of Group 1 (heavy coker gas oils) whose $T_i$ lie at around $318 \pm 4$ °C.

5. As expected the Critical Diameter for Ignition decreased as the furnace temperature was increased for all samples. However, this variable could not be correlated mathematically to any other parameter, possibly due to the inherent uncertainty of its measurement. At 800 °C furnace temperature the Critical Diameter for Ignition of all fuels converge to a narrow range of values at about 0.49 mm.

6. Coke burn-out was present in experiments with fuel M2 only.

5. Video recordings of experiments with the single suspended droplet technique

5.1. Objectives

In order to obtain more detailed information about the behaviour of the fuels under research video recordings of experiments run with the Single Suspended Droplet technique were made. Video recordings were expected to provide a visual knowledge of events happening before and after homogeneous ignition. Unfortunately, the large amount of light produced by the flame saturated the camera lens, thus making video recording unfeasible during the flame stage.
The experimental rig described in paragraph “2.1. Equipment description” is fitted with a silica window which allows direct observation and video recording from outside (see Figure 22).

5.2. Experimental

The samples investigated in the present set of experiments were those used in the previous sections of this chapter, namely three heavy vacuum gas oils (designated G3, G4 and G5) and two heavy coker gas oils (designated M2 and M3). Again, their specifications can be found in “Appendix II: Analyses of the fuels used in this thesis”

The diameter of the sample R-type thermocouple wire chosen was 25 μm. The wires were coated with silica as in previous experiments. The furnace temperature was set at 700 °C, as it was intended to run the experiments at the highest possible temperature. However, intense heat emitted from the furnace did not allow the furnace temperature to rise above such a value without causing damage to the video camera. Indeed the camera was cooled by a fan.

Five experiments with droplets of varying initial diameter were performed with every oil sample. Initial droplet diameters ranged from 0.80 to 1.13 mm. A Hitachi CCTV camera fitted with a Computar Zoom Lens 18-108/2.5 Japan Lens was used, with which enlargements of 20.5/1 could be achieved at the desired focal length. The camera was connected to a Hitachi B/W monitor and a JVC BR-S611E video cassette recorder.

Subsequently, the variation of the droplet diameter during the Pre-ignition Delay was evaluated on a frame-by-frame basis by using an image analysis computer package named “OPTIMAS”. Calibration was achieved by filming graph paper of known gridsize.

Video recordings were obtained at a speed of 25 frames per second. Therefore, there is a 0.04 seconds interval between two successive images.

The variables under consideration were time and droplet diameter. Since Pre-ignition Delay varies according to the initial diameter both variables were normalised:
a. Time was normalised with respect to the Pre-ignition Delay \( t_i \) of each individual run:

\[
\text{Normalised Pre-ignition Delay} = 100 \cdot \frac{\text{current time}}{t_i}
\]

b. Diameter was normalised with respect to the initial droplet diameter \( d_o \):

\[
\text{Normalised Droplet Diameter} = 100 \cdot \frac{\text{current diameter}}{d_o}
\]

Plots of Normalised Pre-ignition Delay vs Normalised Droplet Diameter were thus obtained for the fuel samples under study.

5.3. Experimental results

The experimental results are shown on page 134 (Figure 32). The most important common features exhibit swelling of the droplets in the initial 45-50 % of the Pre-ignition Delay, up to an average 103-105 % of the initial diameter. Droplets of fuel G3 show the smallest relative size increase (up to 102 %) amongst the fuels under study, whereas all other fuels suffer larger size increases. The droplet diameter reaches a maximum at approximately 50 % of the Pre-ignition Delay.

All samples except G3 showed the extent of swelling to be inversely proportional to the initial droplet diameter. Thus small droplets presented larger proportional swelling than larger ones. Fuel G3 does not follow such behaviour pattern, but swelled to a similar extent regardless the initial droplet diameter.

Contraction starts in the second half of the Pre-ignition Delay. It is faster for fuel G3 than for other samples. Droplets of fuel G3 recover 100 % of their original size at approximately 75 % of the Pre-ignition Delay (as an average), whilst others reach the same percentage at approximately 85-90 % of \( t_i \). Results from G5 show contraction to proceed back to the initial droplet size while approaching the end of the Pre-ignition Delay.
Figure 32: Graphs showing the evolution of the Normalised Droplet Diameter with respect to the Normalised Pre-ignition Delay

The reduction of the droplet diameter continues until the onset of the homogeneous ignition. Ignition occurs when the droplet diameter is reduced to 95% of its original value, except for fuel G3, whose size is reduced to nearly 90% of $d_o$ as contraction starts at an earlier stage. The decrease of droplet volume at the point of ignition is, in most cases, lower than 0.1 mm³.
No disruptive behaviour was observed during the Pre-ignition Delay. The droplet size was seen to vary uniformly as the Pre-ignition Delay progressed. In addition, the violent, sudden changes in droplet size that characterise fuels which contain heavy fractions were not observed.  

Unlike other heavy fuels, ignition does not start at a specific location on or around the fuel droplet, but uniformly in the fuel-air cloud that surrounds it. Once ignition has started an envelope flame is established.

Finally, video recordings confirm the presence of coke residues in only one of the samples studied, M2. The existence of coke residue is denoted by a red glow which begins after the extinction of the flame.
CHAPTER III. EXPERIMENTS ON SPRAY COMBUSTION IN THE DROP-TUBE FURNACE

1. Objective

As explained in the general objective of this thesis on page 25, one of the main aims was the study of pollutant emissions from the combustion of a range of heavy liquid fuels.

In this stage of the experimental work, two fuels of different nature and nitrogen and sulphur contents were selected to investigate the formation and emission of gaseous species. Three variables were significant in this work:

- The equivalence ratio ($\varphi$), as it reproduced various operating conditions. The predominant processes of pollutant formation vary with the equivalence ratio, which modifies the extent of the formation and disappearance of different compounds.
- The sampling distance, as it provided information on the rate, extent of formation and emissions of species.
- The furnace wall temperature, as it influenced the flame temperature which, in turn, affects the extent of formation of species.

2. Description of the drop-tube furnace

This experimental work was carried out in a drop-tube furnace, suitable for burning a spray of liquid fuel. Emissions are measured by a series of gas analysers, and the output data is collected by a complex data-logging system.

A photograph of the drop-tube furnace and its flow diagram can be seen in Figures 34 and 35 on page 139.

The combustion chamber is an electrically-heated, vertical ceramic cylinder, 8 cm in diameter and 1.3 m in height. The hot zone is about 1 m in length. It is heated by 44 Crucilite low voltage heating elements distributed in ten separate zones, which ensures isothermal operation in the furnace. The maximum furnace wall temperature is 1,200 °C, which is controlled by a Eurotherm 810 master programmable controller and nine Eu-
rotherm 815 controllers. R-type thermocouples provide control, trip and data-logging functions.

The fuel is placed in a can, heated if necessary, which rests on a Sartorius 18100 P balance. The balance measures the weight of the fuel can and transmits it to an HP85 microcomputer every ten seconds. The computer calculates an 8-minute average of the fuel mass flow rate and relays the data to the Orion data-logger.

Various devices were used to pump the fuels. Initially a Gilson Minipump 3 was employed, this being subsequently replaced by a piston pump (see chapter VII for experiments with Orimulsion) and a Fluid Metering Inc. “Q” reciprocating pump (for non-emulsified-oils). Both were driven by a step motor. High flow rate stability was achieved by the latter two devices, which led to accurate readings with low standard deviation and simplifications in the data-handling software package.

The fuel lines of the injection system are fitted with heating devices and thermal insulation to enable the handling of fuels of high viscosity.

The fuel is sprayed downwards into the furnace through a coaxial external-mix twin-fluid atomiser formed by a fuel cap, air cap and retaining ring (see Figure 33). This atomiser assembly (manufactured by Spraying Systems Co.) produces a fine round spray with an angle of 21° and a length of 0.41 m at a pressure of 1.5 bar-g.

![Diagram of twin-fluid atomiser](image)

**Figure 33: Twin-fluid atomiser used in experiments in the drop-tube furnace**
Figure 34: The drop-tube furnace. Below, description of numbered parts

1. Furnace
2. Sampling probe
3. Sampling probe step motor
4. Solids collection box
5. Flue gas exit by-pass
6. Cyclones
7. Heated filter and permapure assembly
8. NOX analyser
9. CO2 analyser
10. Coalescers
11. O2 analyser
12. SO2 analyser
13. CO analyser
14. N2O analyser
15. Furnace current and temperature indicators
16. Step-motor control
17. Alarm panel
18. Pressure/temperature controllers
19. Over temperature trips
20. Heating switches
21. Pressure/temperature indicators
22. Atomising air controller
23. Secondary air controller
24. Peristaltic pump controller
25. By-pass/solids-box switch
26. Schlumberger data-logger
27. Cooling water flowmeters
28. Heated fuel can
29. Pumps: peristaltic/piston/reciprocating
30. Injection probe

Figure 35: Flow diagram of the drop-tube furnace
The fuel flows through the central orifice and is atomised by the flow of air which circulates between the fluid and air caps. Secondary air is directed around the air cap to establish the overall stoichiometry of the combustion environment. Atomising and secondary air mass flow rates are measured by Bronkhurst HI-TECH mass flow controllers.

The fuel and atomising air lines can be heated by a low voltage-high current supply. Fire-rod 50 W cartridge heaters facilitate steady temperature at the injection nozzle. Water circulates through the atomiser block to protect the nozzle from overheating from the flame and radiation from the furnace wall.

Sampling of combustion products is achieved by a water-cooled probe controlled by a step motor below the furnace duct. Its axial positioning in the furnace is achieved to a tolerance of ±0.5 mm.

If solid particulates are to be sampled, gases and solids are directed through two cyclones connected in series in the solids collection box, where most of the solid matter is removed for analysis.

If solid particulates are not required, the exhaust gases are directed through a by-pass line and eventually into the facility reproduced in Figure 36 and described here:

![Figure 36: Sample treatment facility and gas analysers in drop-tube furnace](image-url)
1. Sample treatment: The water formed during combustion is removed in a water-cooled condenser and a Ballots coalescer. Thereafter the sample is heated at 160 °C to ensure that the remaining moisture is kept in the gas phase. The sample gas is then filtered for solids in a Ballots DH solids filter.

The gas sample is split and it feeds both an NO\(_x\) analyser and a Permapure drier, which uses compressed air to remove all remaining moisture. This latter sample line feeds all other gas analysers.

2. NO\(_x\) analyser: A Model 10 analyser, manufactured by Thermo Electron allows alternate monitoring of NO and NO\(_x\) (NO+NO\(_2\)). Both are measured by chemiluminescence, NO\(_2\) being previously reduced to NO in a stainless-steel thermal converter operating at 650 °C. The analyser is fitted with an ozone trap to remove ozone from the exhaust, and small ballast vessels to stabilise the flow of gases.


4. Carbon dioxide analyser: A type SB-305 infrared analyser, manufactured by ADC. In order to avoid interference with carbon dioxide in the air, CO\(_2\) is continuously removed from the reference gas housing with soda lime.

5. Sulphur dioxide analyser: A type RF/2E-002 infrared analyser, manufactured by ADC. The gas sample is scrubbed of carbon dioxide and water vapour by passing through a column of magnesium perchlorate.

6. Carbon monoxide analyser: A type RF/2E-002 infrared analyser, by ADC.

7. Nitrous oxide analyser: A type RF/2E-002 infrared analyser, manufactured by ADC. Since some interference is caused by carbon monoxide, a signal from the CO analyser indicating its concentration in the sample gas is used for compensation.
Zeroing of the gas analysers was achieved with nitrogen, except for the NO\textsubscript{x} analyser, in which air was used. Span gases with the following mixtures were used for calibration of the gas analysers:

- \text{NO} \quad [\text{NO}] = 950 \text{ ppm} / \text{balance N}_2
- \text{SO}_2/\text{CO}_2 \quad [\text{SO}_2] = 2,000 \text{ ppm} / [\text{CO}_2] = 14 \% / \text{balance N}_2
- \text{CO}/\text{N}_2\text{O} \quad [\text{CO}] = 800 \text{ ppm} / [\text{N}_2\text{O}] = 80 \text{ ppm} / \text{balance N}_2
- \text{NO}_2 \quad [\text{NO}_2] = 40 \text{ ppm} / \text{balance N}_2

The validity of the sampling procedure was checked with traverse experiments, in which the sampling probe was continuously displaced as the gas analysis proceeded. Agreement between these measurements and those at stationary positions was high.

The rig was initially built at BP-Sunbury, and when transferred to UCL the gas exhaust system was modified. A main exhaust duct was fitted to direct the combustion gases to the main College extraction system. Also, a water-cooled drain pot was fitted in order to collect most condensables such as H\textsubscript{2}SO\textsubscript{4}, H\textsubscript{2}O. To provide better control of the condensing liquids and ensure their removal, thermocouples were fitted upstream and downstream from the drain pot. A low temperature on the downstream thermocouple implies correct water flow through the drain pot and elimination of condensables. Signals from both thermocouples are collected by the data-logger.

Data-logging is performed as follows. Sixty five channels send information from the rig onto a Schlumberger Orion 3531 D data-acquisition system. Such a system allows storage and replay of logged data. Data collection can be set at different time intervals, ranging from 15 seconds to 30 minutes. The data-logger is configured by a programme, "LOGGER\_1.CFG", which was modified to include new channels for monitoring of various temperatures, fuel line pressure, mass flow of dopant gases into the furnace and a counter of logs on the computer, among other changes.

The data collected by the Orion data logger are sent via a General Purpose Interface Bus (GPIB) to a Zenith 486 PC computer. The computer handles the data by means of a specific Schlumberger software package named "AXIS". Data are finally presented on the
screen in Microsoft EXCEL 4.0 spreadsheet format. Two spreadsheets were developed which present data updated every five seconds, namely “DTFSYS.XLS” (reproduced in Figure 37) and “DTFSIGS.XLS”. Spreadsheet “DTFSYS.XLS” shows graphs for real-time monitoring of the weight measurements provided by the fuel balance and the temperature of various locations along the fuel injection lines. They provide better diagnosis of problems related to fuel flow, stability of measurements, validity of experiments, reliability of results, etc.

Data-handling was performed on a proprietary Excel 4.0 Macro, “ACTIGRA.XLM”. This and its ancillary macros plotted the data out, performed statistical calculations and allowed other useful data-handling operations.

Finally, a “Manual of Operation” was completed following instructions provided by the furnace manufacturer, Severn Furnaces plc, and its previous operator, British Petroleum plc. It complies with the characteristics of the equipment and its location at University College London.
3. Calculation of the volume of combustion air and of combustion gases

The next paragraphs present formulae for the calculation of the volume of air necessary for combustion and the volume of the combustion gases produced as a function of the net calorific value of the fuel and the equivalence ratio (\( \phi \)). The mathematical expressions are based on data for liquid fuel combustion published in “Technical Data on Fuel”, by H.M. Spiers.

The equivalence ratio is defined as:

\[
\phi = \frac{\text{fuel \ air}}{\text{fuel \ air \ theoretical}}
\]

Values below unity mean fuel-lean (oxidising) combustion conditions, whereas equivalence ratios above unity indicate fuel-rich (reducing) conditions. \( \phi = 1.000 \) indicates stoichiometric conditions.

The theoretical (ie at \( \phi = 1.000 \)) air requirements (\( A_0 \), \( \text{nm}^3/\text{kg fuel} \)) and the theoretical volume of wet combustion gas (\( V_0 \), \( \text{nm}^3/\text{kg fuel} \)), produced in the combustion of a fuel are related to the net calorific value of the fuel by the formulae:

\[
A_0 = 2.080 + \frac{0.201}{1,000} C_N \quad V_0 = -0.147 + \frac{0.269}{1,000} C_N
\]

where \( \text{nm}^3 \) represents volume at normalised conditions, ie at 0 °C and 1 atm, and \( C_N \) is the net calorific value of the fuel, kJ/kg fuel.

The actual volume of air used for combustion (\( A \), \( \text{nm}^3/\text{kg fuel} \)) and the volume of the wet combustion gases (\( V \), \( \text{nm}^3/\text{kg fuel} \)) for various equivalence ratios are represented in Figure 38.
Figure 38: Graph showing the volume of air used for combustion and the volume of wet combustion gases formed, according to the net calorific value of the fuel and the equivalence ratio

Assuming a linear relationship of $A$ and $V$ with the equivalence ratio, the following formulae can be obtained for any value of $\phi$ and net calorific value with an estimated error lower than 1%:

$$A = (-0.116 + \frac{2.148}{\phi}) + (3.533 \times 10^{-6} + \frac{1.990 \times 10^{-4}}{\phi}) C_N$$

$$V = (-1.645 + \frac{1.476}{\phi}) + (5.576 \times 10^{-5} + \frac{2.142 \times 10^{-4}}{\phi}) C_N$$

4. Experiments in the drop-tube furnace

4.1 Experimental conditions

The samples under study were provided by Repsol Petróleo S.A. They consisted of one heavy vacuum gas oil (designation G1) and one heavy coker gas oil (designation M1). Analyses provided for both fuels are shown in “Appendix II”, page 265.

The temperature of the furnace wall was set at 900, 1,100 and 1,200 °C. Fuel injection was achieved through a coaxial external-mix twin-fluid atomiser (see Figure 33). The
fuel cap used was 1650ss, with an internal diameter of 0.75 mm, and external diameter of 1.3 mm. The air cap used had designation 64ss. The diameter of its orifice was 1.59 mm.

Following previous work on the same rig by Graville, a constant flow rate of atomisation air was set at 23.2 g/min at 1.6 bar-g. When used with an air cap of 1.59 mm diameter it produces an air velocity greater than 325 m/s when leaving the nozzle annulus, thus creating the fuel spray.

The atomisation air stream creates a fuel-rich, conical jet of equivalence ratio 2.25 immediately after injection, prior to mixing with the stream of secondary air.

Runs were performed at overall equivalence ratios of 0.714, 0.833, 1.000 and 1.200. The flow rate of secondary air was altered to meet the requirements of equivalence ratio in the combustion chamber.

Experiments in fuel-rich conditions (\(\varphi = 1.200\)) were not performed at 1,200 °C furnace wall temperature. The flame temperature was low in some sections of the furnace and the furnace heating elements were not able to supply enough current to keep the set point.

From the values of the net calorific value provided in the analyses of the fuels the following secondary air mass flow rates were calculated for various equivalence ratios (\(\varphi\)):

<table>
<thead>
<tr>
<th>Equivalence ratio ((\varphi))</th>
<th>Secondary air mass flow rate, g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.714</td>
<td>41.2</td>
</tr>
<tr>
<td>0.833</td>
<td>32.2</td>
</tr>
<tr>
<td>1.000</td>
<td>23.3</td>
</tr>
<tr>
<td>1.200</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Table 7: Secondary air mass flow rates calculated for various equivalence ratios

4.2. Fuel addition and handling issues

A constant fuel mass flow rate of 3.5 ± 0.2 g/min was maintained in all experiments.

Each fuel investigated presented different handling characteristics. Fuel M1 is in its liquid state at room temperature, and therefore no further heating was needed in order for it to
flow. However, fuel G1 is a highly thixotropic fluid which does not flow at room temperature. Heating above 55 °C and agitation decrease its viscosity and allows it to flow. Supplementary heating was provided around the pumps.

It was observed that a yellow layer appears on the surface when fuel G1 is stirred within the fuel can. It was presumed that this layer could be formed by sulphur released by the fuel. Agitation was then increased to incorporate such a layer back into the fuel.

Based on the work published by Graville the viscosity of the fuels was set at 46 cSt at the atomiser nozzle. This was achieved by setting the atomiser block temperature at certain values according to the viscosity data provided in “Appendix II”. These temperatures were: M1: 33.5 °C, G1: 48 °C.

Fuel M1 required extra cooling of the atomiser block in order to achieve the optimum 33.5 °C, as radiation from the flame and the furnace walls tended to increase the temperature above this value. This was attained by increasing the flow rate of cooling water in the atomiser block.

4.3. Sampling of combustion products and data processing

Sampling of gaseous and solid products entrained in the gaseous stream was attempted, whenever possible, at eleven distances from the atomiser, namely 100, 150, 200, 250, 300, 350, 400, 450, 500, 600 and 700 mm. The sampling time was 8 minutes for all gases, except for NO and NOx, which were sampled for 4 minutes each as they cannot be measured concurrently. Since the data-logging system collects data every 15 seconds, the calculated values are the result of approximately 32 consecutive readings.

The results from experiments at three furnace wall temperatures and four equivalence ratios are plotted versus distance from the atomiser nozzle in the following pages. The data points are represented by vertical error bars, whose size denotes the standard deviation of the measurements. In the case of the NO2 graphs the standard deviation is not provided as its concentrations are calculated by subtracting the concentration of NO from that of NOx.
4.4. Experimental results

4.4.1. NO

4.4.1.a. 900 °C

The formation and emissions of NO, represented in Figures 39 and 40, vary greatly with the equivalence ratio for both fuels investigated.

Minimum emissions of nitric oxide are attained in fuel-rich mixtures (φ = 1.200). Measurements in stoichiometric and fuel-rich conditions at short distance suggest that NO is formed at distances lower than 150 mm in appreciable amounts (approximately 77 ppm-wet from fuel M1 and 42 ppm-wet from fuel G1), undergoing subsequent decay to exhaust levels.

Higher values of NO emissions are obtained in fuel-lean combustion environments. Values obtained from fuel G1 at φ = 0.833 are similar to those at φ = 0.714, approximately 140 ppm-wet. However, when fuel M1 is burned at φ = 0.833 it produces less NO than at φ = 0.714.

![Figure 39: NO concentrations from fuel M1 at 900 °C](image)

![Figure 40: NO concentrations from fuel G1 at 900 °C](image)

The emissions of NO depend on the nitrogen content of the fuels. Analyses provided by Repsol Petróleo S.A. (see “Appendix II”) show that the amount of nitrogen contained in fuel M1 (3,231 ppm N) is much greater than that in fuel G1 (1,619 ppm N). Consequently, greater NO emissions are caused by fuel M1 than from fuel G1.
On the contrary, the conversion of fuel-N into NO increases as the fuel-N content decreases. A graph showing fuel-N conversion to NO is shown in Figure 45, page 150. For fuel M1 (3,231 ppm N) the exhaust concentration of NO at $\phi = 0.714$ (where formation of NO$_2$ is negligible) reaches 253 ppm-wet. Such a value represents 45 % conversion from fuel-N. Fuel G1 (1,619 ppm N) produced 127 ppm-wet NO at exhaust, which accounts for 50 % conversion. It is assumed that at 900 °C furnace temperature all NO detected originated from nitrogen in the fuel (see chapter IV for determination of thermal-NO$_X$).

4.4.1.b. 1,100 °C

At 1,100 °C furnace wall temperature the concentrations of NO measured are again higher for the fuel with a greater nitrogen content, ie M1. At $\phi = 0.714$ the exhaust NO concentration reaches 325 ppm-wet for fuel M1 (94.4 % fuel-N to NO conversion) whereas only 167 ppm-wet (95.7 % conversion) are obtained from fuel G1 (see Figures 41 and 42).

![Figure 41: NO concentrations from fuel M1 at 1,100 °C](image1)

![Figure 42: NO concentrations from fuel G1 at 1,100 °C](image2)

NO from fuel M1 is formed at a much faster rate than from fuel G1. Approximately 210 ppm-wet are formed between 150 and 250 mm from the atomiser nozzle from fuel M1, whereas only 100 ppm-wet are formed in the same distance from fuel G1.

Comparison of Figures 40 and 42 shows that at 900 °C furnace wall temperature the formation of NO occurs at shorter distances at $\phi = 0.833$ than at $\phi = 0.714$. However, at
1,100 °C the trend is reversed and greater amounts of NO are formed at shorter distances at $\phi = 0.714$ than in less fuel-lean conditions ($\phi = 0.833$).

4.4.1.c. 1,200 °C

The experimental results are shown in Figures 43 and 44. At this furnace wall temperature the experimental readings of NO at fuel-lean conditions ($\phi = 0.714$) did not differ greatly from those at 1,100 °C. The flame temperature is high enough to transform most fuel-N into NO, but low enough so that no thermal-NO is formed.

The conversion of fuel-N into NO shows a dependence on both the fuel-N content and the furnace wall temperature. A graph showing fuel-N conversion to NO from both fuels is given in Figure 45.

At fuel-rich conditions ($\phi = 1.200$) the conversion of fuel-N into NO reaches minimum values below 5 %. The conversion is higher at stoichiometric conditions.
The conversion of fuel-N into NO increases drastically in fuel-lean conditions \((\varphi = 0.833\) and 0.714). In these environments the formation of NO is favoured by the high concentration of oxygen-containing species. The highest conversions were attained at low equivalence ratios (fuel-lean conditions) and high furnace wall temperatures. At \(\varphi = 0.714\) and 1,200 °C furnace wall temperature, the conversion of fuel G1 reaches values close to 100%.

In the case of fuel M1 at \(\varphi = 0.714\) and 0.833, the transition from 1,100 °C to 1,200 °C causes a small reduction of fuel-N conversion.

Figure 45 also shows that in general M1, the fuel with higher N content (open symbols), achieves lower conversion.

4.4.2. \(NO_2\)

4.4.2.a. 900 °C

Emissions of \(NO_2\) were calculated by subtracting the values of NO concentration from those of total-NO\(_x\).

At 900 °C furnace wall temperature the emission of \(NO_2\) is significant only at stoichiometric and fuel-rich conditions, especially the latter (see Figures 46 and 47). Very small amounts of \(NO_2\) are formed in fuel-lean conditions \((\varphi = 0.714\) and 0.833) at short distances from the atomiser nozzle. All \(NO_2\) thus formed disappeared shortly afterwards. Negative values obtained at longer distances are attributed to instrumental errors.

Relatively large amounts of \(NO_2\) are also formed at short distances at stoichiometric conditions \((125\ ppm\text{-wet from fuel M1 and 108 ppm\text{-wet from fuel G1 are formed at 250 mm})}. However, they tend to disappear as combustion progresses at longer distances, although 50 ppm-wet \(NO_2\) are emitted by fuel G1.

Emission of \(NO_2\) is important under fuel-rich conditions only \((\varphi = 1.200)\). 277 ppm-wet of \(NO_2\) were emitted from fuel M1, whereas 144 ppm-wet were emitted from fuel G1.
In both cases the formation of NO\textsubscript{2} is very fast in the first 100 mm after the atomiser nozzle, increasing almost linearly afterwards until a maximum value is reached at about 500 mm from the atomiser nozzle. The concentrations of NO\textsubscript{2} stabilise subsequently at the values of emissions quoted above.

4.4.2.b. 1,100 °C

The emissions of NO\textsubscript{2} obtained at 900 and 1,100 °C show a low dependence on the furnace wall temperature.

Significant amounts of NO\textsubscript{2} are formed from both fuels at 1,100 °C near the atomiser at low equivalence ratios. The values measured from fuel M1 at 100 mm from the atomiser
nozzle reach 44 ppm-wet in fuel-lean conditions ($\varphi = 0.714$), whereas 15 ppm-wet are measured from fuel G1 at similar conditions.

As the combusting mixture becomes less fuel-lean ($\varphi = 0.833$ and 1.000) larger amounts of NO$_2$ are measured from both fuels at short distances. Also, the time taken by NO$_2$ to disappear increases (see green diamonds in Figures 48 and 49).

Finally, formation and emission of NO$_2$ in fuel-rich mixtures are high. NO$_2$ is formed at 1,100 °C at a faster rate than at 900 °C furnace wall temperature. The maximum values of emissions are reached at approximately 350 mm from the atomiser nozzle, a much earlier stage than at 900 °C.

However, the effect of the furnace wall temperature (and, in turn, the flame temperature) on NO$_2$ emissions at $\varphi = 1.200$ cannot be clearly established. Whilst emissions of NO$_2$ from fuel M1 suffer an increase of 50 ppm-wet from 900 to 1,100 °C, emissions from fuel G1 decreased by 12 ppm-wet. This can be observed in Figure 52, which shows a graph of fuel-N conversion to NO$_2$ at exhaust.

4.4.2.c. 1,200 °C

Readings of NO$_2$ could not be performed at $\varphi = 1.200$ and 1,200 °C, as explained earlier.

Measurements of NO$_2$ obtained in other conditions are shown in Figures 50 and 51.
Emission of NO\textsubscript{2} in fuel-lean conditions was negligible, as at lower furnace wall temperatures. Although measurements could not be made at very short distances from the atomiser nozzle, readings of NO\textsubscript{2} at \( \phi = 1.000 \) were higher than at lower furnace wall temperatures. Figure 51 seems to indicate the existence of a peak of NO\textsubscript{2} concentration at 200 mm from the atomiser nozzle or less. Approximately 58 ppm-wet were emitted finally by fuel M1, whereas fuel G1 emitted 20 ppm-wet. They represented conversions of 58 \% and 47 \% for fuels M1 and G1, respectively.

Figure 52 shows a graph of fuel-N conversion to NO\textsubscript{2} at exhaust. Maximum conversions are reached at fuel-rich conditions, ranging from 50 to 60 \%. Lower equivalence ratios yielded lower conversions, whilst in fuel-lean conditions it was negligible at all furnace wall temperatures. Factors such as the furnace wall temperature or the nitrogen content of the fuel did not seem to influence the conversion of fuel-N into NO\textsubscript{2}.

4.4.3. NO\textsubscript{X}
4.4.3.a. 900 °C

As can be seen in Figures 53 and 54, the highest values of NO\textsubscript{X} emissions were obtained at \( \phi = 1.200 \) from both fuels investigated. Emissions at fuel-lean conditions (\( \phi = 0.714 \) and 0.833) were intermediate, whereas they were minimum at stoichiometric conditions, where formation and emission of both NO and NO\textsubscript{2} was very low.

Emissions at \( \phi = 1.200 \) are largely dominated by those of nitrogen dioxide as emissions of NO are minimum. Conversely, in fuel-lean conditions NO represent the most important fraction of NO\textsubscript{X} emissions and those of NO\textsubscript{2} are negligible.
The concentration profile of NO\textsubscript{x} in stoichiometric conditions deserves particular attention. After an initial increase up to a distance of 250 mm a sharp drop ensues. Within the next 100 mm the concentration of NO\textsubscript{x} decreases to a fraction of its maximum value. Eventually, the emissions of NO\textsubscript{x} at \( \phi = 1.000 \) are much lower than at any other equivalence ratio.

Calculations of the conversion of fuel-N into NO\textsubscript{x} offered a view of the experimental results from a different angle. The highest values were obtained at \( \phi = 0.714 \), but decreased as the equivalence ratio rose to stoichiometric conditions due to the lower formation of NO. In fuel-rich environments the conversion increased again to intermediate values, caused by low concentrations of NO but larger formation and emission of NO\textsubscript{2}.
Comparison of Figures 55 and 56 evidences that NO\textsubscript{X} conversion is inversely related to the fuel-N content. Higher values were obtained from fuel G1 (nitrogen content: 1,619 ppm) than from fuel M1 (nitrogen content: 3,231 ppm) at all equivalence ratios.

It is worth noting that at short distances from the atomiser nozzle (less than 200 mm) fuel-N is converted into NO\textsubscript{X} to a similar extent at all equivalence ratios. The conversion in this early stages of the combustion process ranges between 35 and 45 \% for fuel M1 and is higher (40 to 55 \%) for fuel G1. Once again, it followed an inverse dependence with the fuel-N content.

4.4.3.b. 1,100 °C

The experimental readings of NO\textsubscript{X} at 1,100 °C are shown in Figures 57 and 58. Again, formation and emission of NO\textsubscript{X} are higher for fuel M1 due to its high fuel-N content.

![Figure 57: NO\textsubscript{X} concentrations from fuel M1 at 1,100 °C](image1)

![Figure 58: NO\textsubscript{X} concentrations from fuel G1 at 1,100 °C](image2)

NO\textsubscript{X} values are similar at all equivalence ratios except stoichiometric, which are much lower as NO is low in these conditions.

Increasing the furnace wall temperature from 900 to 1,100 °C causes an increase of NO\textsubscript{X} emissions, particularly at fuel-lean equivalence ratios. It also accelerates the formation of NO\textsubscript{X} at short distances; also in stoichiometric conditions the drop in NO\textsubscript{X} concentrations occurs at a higher rate.
The following graphs show the conversion of fuel-N into NO$_x$ vs distance from the atomiser at 1,100 °C furnace wall temperature.

![Figure 59: Conversion of fuel-N to NO$_x$ from fuel M1 at 1,100 °C](image1)

![Figure 60: Conversion of fuel-N to NO$_x$ from fuel G1 at 1,100 °C](image2)

The increase of the furnace wall temperature caused the conversion of fuel-N into NO$_x$ to rise at all equivalence ratios (a graph of conversion at exhaust is provided in Figure 63).

With the exception of fuel M1 at $\phi = 1.200$, both fuels show conversion of fuel-N into NO$_x$ at short distances to be similar at all equivalence ratios. This feature was also observed at 900 °C furnace wall temperature. At 1,100 °C furnace wall temperature conversions at different equivalence ratios start diverging at shorter distances than at 900 °C.

Also, calculations of the conversion of fuel G1 yielded slightly higher values than from fuel M1 at the same equivalence ratios.

4.4.3.c. 1,200 °C

Another increase of NO$_x$ concentrations was registered at all equivalence ratios when the furnace wall temperature was increased from 1,100 to 1,200 °C. However, the increases were smaller than from 900 to 1,100 °C.
At $1,200 \, ^\circ C$ the formation and decay of NO$_x$ concentrations in stoichiometric mixtures is greatly accelerated with respect to other experimental conditions. Maximum concentrations are formed at or before 200 mm from the atomiser nozzle.

Comparisons were made between experimental readings and the maximum calculated NO$_x$ emissions from the fuels investigated. Calculations of the latter yielded the results in the following Table:

<table>
<thead>
<tr>
<th>Equivalence ratio</th>
<th>M1</th>
<th>G1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.714</td>
<td>347</td>
<td>174</td>
</tr>
<tr>
<td>0.833</td>
<td>400</td>
<td>200</td>
</tr>
<tr>
<td>1.000</td>
<td>473</td>
<td>237</td>
</tr>
<tr>
<td>1.200</td>
<td>559</td>
<td>280</td>
</tr>
</tbody>
</table>

Table 8: Maximum NO$_x$ emissions from the fuels studied

The dependence of fuel-N conversion to NO$_x$ with equivalence ratio, furnace wall temperature and fuel-N content can be seen in Figure 63.

The highest conversions were obtained at the leanest conditions ($\phi = 0.714$). Increases of the equivalence ratio led to decreasing conversion, with minimum values at $\phi$
In fuel-rich conditions the conversion increased due to the greater formation of \( \text{NO}_2 \).

An increase of the furnace wall temperature between 900 and 1,100 °C (and, in turn, the flame temperature) caused a sharp increase of the fuel-N conversion at fuel-lean equivalence ratios. The extent of the increase was smaller between 1,100 and 1,200 °C.

In stoichiometric and fuel-rich mixtures the conversion of fuel-N into \( \text{NO}_x \) showed no dependence with the temperature of the furnace walls.

Higher values of the conversion were normally obtained from the fuel with lower fuel-N content, ie fuel G1, although this tendency was not seen at \( \phi = 1.200 \).

4.4.4. \( \text{SO}_2 \)

4.4.4.a. 900 °C

In general, the readings of \( \text{SO}_2 \) at 900 °C reported increasing values as the equivalence ratio rose. This effect can be partly attributed to dilution by the higher amounts of air added at low equivalence ratios (see Figures 64 and 65).

![Figure 64: \( \text{SO}_2 \) concentrations from fuel M1 at 900 °C](image1)

![Figure 65: \( \text{SO}_2 \) concentrations from fuel G1 at 900 °C](image2)

The exhaust concentrations of \( \text{SO}_2 \) are also dependent on the initial sulphur content of the fuel. For example, at \( \phi = 0.714 \) the emissions of \( \text{SO}_2 \) from fuel G1 (which contains...
1.74 % sulphur) reach of 930 ppm. However, fuel M1 (3.59 % S) reaches 2,080 ppm 
SO$_2$ at exhaust at the same equivalence ratio.

The trends presented in Figures 64 and 65 show that the concentration of SO$_2$ increases 
steadily after injection. Formation of sulphur dioxide is rapid at fuel-lean equivalence ra­
tios, especially at $\varphi = 0.714$, where the exhaust values are reached before 200 mm. This 
represents a much shorter residence time than at any other set of conditions due to the 
large mass flow rate involved. At other equivalence ratios the final values of the concen­
tration of SO$_2$ were reached between 250 and 350 mm from the atomiser nozzle.

Readings in stoichiometric and fuel-rich conditions show a propensity to reach maximum 
values, followed by a decrease of SO$_2$ concentrations. This tendency was observed to be 
stronger at higher furnace wall temperatures, and will be discussed later.

Comparison of results from both fuels at the same equivalence ratios show that SO$_2$ from 
fuel M1 forms more slowly than that from fuel G1. When both fuels are burned at $\varphi = 
1.000$ and sampled at 150 mm from the atomiser, the readings of SO$_2$ from fuel M1 only 
account for 68 % of the final emission, whereas 92 % of the total SO$_2$ from fuel G1 is 
formed at that stage.

4.4.4.b. 1,100 °C

The graphs of SO$_2$ concentration obtained from both fuels at 1,100 °C furnace wall tem­
perature show different characteristics from those at 900 °C (see Figures 66 and 67).

Experimental values registered from both fuels at 1,100 °C and fuel-lean conditions are 
almost identical to those obtained at 900 °C, showing that in excess of oxygen all sulphur 
is readily transformed into SO$_2$.

A different behaviour was found at $\varphi = 1.000$ and 1.200. In these conditions the meas­
ured concentrations of SO$_2$ also increased immediately after injection, reached maximum 
values between 200 and 300 mm, and decreased subsequently until the combustion gases 
exit the furnace. This effect, which implies reaction of SO$_2$ along the furnace, was most
accentuated in fuel-rich conditions, where the drop of SO$_2$ concentration reached 30% of the maximum values (1,171 ppm from fuel M1 and 457 ppm from fuel G1)

4.4.4.c. 1,200 °C

Readings of SO$_2$ concentrations at 1,200 °C in fuel-lean conditions remained mostly unchanged with respect to those at 900 and 1,100 °C.

In stoichiometric conditions a maximum value was again found between 200 and 250 mm. The maximum value is followed by a sharp drop, which in the case of fuel G1 represents 50% of the maximum SO$_2$ concentration, from 1,586 to 710 ppm.
4.4.5. \(O_2\)

4.4.5.a. 900 °C

The results obtained on residual oxygen concentrations show the expected dependence on the amount of combustion air added. Increasing the equivalence ratio causes lower amounts of oxygen to be exhausted after combustion has been completed. At stoichiometric and fuel-rich equivalence ratios all oxygen is consumed.

The concentration of oxygen decreases very rapidly in the first 100 mm of the furnace. The first measurement of oxygen at such a distance yielded concentrations of oxygen at about 7 %. This implies the consumption of larger amounts of oxygen at low equivalence ratios than at high equivalence ratios.

Subsequently, concentrations of oxygen decrease further as combustion progresses along the furnace. The final amounts are reached at 400 mm from the atomiser nozzle.

The amounts of excess oxygen measured in fuel-lean conditions range from 3.0 to 3.5 % at \(\phi = 0.714\) and from 1.2 to 2.0 % at \(\phi = 0.833\). All oxygen was consumed at \(\phi = 1.000\) and 1.200.
4.4.5.b. 1,100 °C

A higher furnace wall temperature seems to accelerate the consumption of oxygen (see Figures 72 and 73), as lower concentrations of oxygen were found at shorter distances. Also at this furnace wall temperature there was an increase of the amount of excess oxygen at $\phi = 0.714$. This increase also was observed at 1,200 °C furnace wall temperature.

![Figure 72: O$_2$ concentrations from fuel M1 at 1,100 °C](image1)

![Figure 73: O$_2$ concentrations from fuel G1 at 1,100 °C](image2)

4.4.5.c. 1,200 °C

Increasing the furnace wall temperature up to 1,200 °C causes an increase of excess oxygen exhausted at fuel-lean conditions, especially at $\phi = 0.714$. The concentration of O$_2$ in the exhaust gases of fuel G1 increased from 3.0 % at 900 °C to 4.2 % at 1,200 °C and $\phi = 0.714$.

![Figure 74: O$_2$ concentrations from fuel M1 at 1,200 °C](image3)

![Figure 75: O$_2$ concentrations from fuel G1 at 1,200 °C](image4)
Also, the consumption of oxygen occurs at a faster rate than at lower furnace wall temperatures at all equivalence ratios investigated. Figures 74 and 75 show the oxygen concentration profiles at 1,200 °C furnace wall temperature.

4.4.6. CO$_2$

4.4.6.a. 900 °C

The most outstanding feature observed from the CO$_2$ signals recorded is that the highest concentrations of carbon dioxide are recorded at $\varphi = 0.833$. The readings yield values approaching 16 % CO$_2$ for both fuels investigated.

![Figure 76: CO$_2$ concentrations from fuel M1 at 900 °C](image1)

![Figure 77: CO$_2$ concentrations from fuel G1 at 900 °C](image2)

Both fuels produce similar amounts of CO$_2$ at exhaust when burned at $\varphi = 0.714$ and 1.000, ie approximately 13.8 %.

Lastly, minimum formation and emission of CO$_2$ was detected at fuel-rich conditions ($\varphi = 1.200$), with concentrations of CO$_2$ at about 11 % (see Figures 76 and 77).

Carbon dioxide is formed rapidly in the first 100 mm of the furnace. Subsequently, its concentration increases to reach values close to those of emission at approximately 250 mm.
4.4.6.b. 1,100 °C

The exhaust concentrations of carbon dioxide obtained at 1,100 °C were essentially similar to those at 900 °C for both fuels investigated. However, at $\phi = 1.000$ fuel M1 produced a slightly higher amount of CO$_2$ than fuel G1 (15.0 vs 14.3 %).

A major difference is, however, given by the fact that such concentrations are reached at shorter distances, i.e. earlier residence times. At 1,100 °C, formation of CO$_2$ reaches completion at about 200 mm from the atomiser, whereas it is achieved at 250 or 300 mm at 900 °C.

4.4.6.c. 1,200 °C
No substantial changes in the emissions of CO\textsubscript{2} were observed as the furnace wall temperature was increased to 1,200 °C.

Again, the emissions of CO\textsubscript{2} at stoichiometric conditions were higher for fuel M1 than fuel G1 (15.3 vs 13.0 %).

4.4.7. CO

Only results obtained in fuel-lean conditions (\(\varphi = 0.714\) and 0.833) will be considered in this section. In stoichiometric and fuel-rich conditions the measured concentrations of carbon monoxide exceeded the instrumental range (1 %).

Values of CO concentration obtained in fuel-lean conditions and short distances are affected by large standard deviation due to turbulent conditions in the neighbourhood of the atomiser nozzle.

4.4.7.a. 900 °C

Graphs of CO concentration are shown in Figures 82 and 83. The most important feature of the CO readings obtained at 900 °C is the low concentrations observed at short distances when fuel M1 is burned at \(\varphi = 0.833\). This effect is thought to be due to CO being formed and destroyed as the flame progresses downward in the furnace. The peak value obtained at 150 mm from the atomiser nozzle reached 4,340 ppm.

![Figure 82: CO concentrations from fuel M1 at 900 °C](image)

![Figure 83: CO concentrations from fuel G1 at 900 °C](image)
Peak values of CO were also observed in traverse experiments, in which continuous measurements were performed along the furnace tube. The following graphs show a comparison of traverse and measurements at stationary positions at 900 °C and $\phi = 0.833$ from both fuels investigated.

![Graph](image)

Figure 84: Traverse and position measurements of CO from fuel M1 at 900 °C and $\phi = 0.833$

The peak of maximum CO concentration was almost coincidental with the maximum flame temperature. Subsequent to the peak, the concentrations of carbon monoxide decreased until complete disappearance, as expected in an oxygen-rich atmosphere.

4.4.7.b. 1,100 °C

The results from carbon monoxide measurements at 1,100 °C from both fuels show a more rapid consumption of CO than at 900 °C. A peak in carbon monoxide concentrations (4,870 ppm) is also observed from fuel M1 at 150 mm from the atomiser nozzle. Subsequently, the values recorded decreased very rapidly to yield only 66 ppm at 200 mm from the atomiser nozzle (see Figures 86 and 87).

A similar rapid decrease in CO concentrations is also observed from fuel G1, although a peak of CO concentration could not be recorded.
4.4.7. 1,200 °C

The formation and disappearance of CO is accelerated by a further increase of the furnace wall temperature, which, in turn, caused an increase of the flame temperature. This effect is particularly strong at \( \varphi = 0.714 \), where formation and disappearance of CO is complete within the first 150 mm from the atomiser nozzle (see Figures 88 and 89). The large differences observed in these graphs are due to the lack of data for fuel M1 at short distances.

4.4.8. \( N_2O \)

Results of \( N_2O \) measurements can only be considered accurate at \( \varphi = 0.714 \) and 0.833. In stoichiometric and fuel-rich conditions, the high concentrations of CO caused interfer-
ence with measurements of nitrous oxide. Experimental readings were negative, and it could not be established whether changes originated from varying concentrations of \( N_2O \) or CO.

4.4.8.a. 900 °C

The measurements of \( N_2O \) performed reveal a contradictory behaviour of this species. A clear trend of larger \( N_2O \) concentrations at short distances and subsequent destruction was obtained in experiments with fuel M1 at \( \phi = 0.714 \) and other preliminary tests. However, such a trend was not found in experiments with fuel G1, as can be seen in Figures 90 and 91, although measurements could not be performed at distances lower than 200 mm.

Trends of \( N_2O \) concentrations at \( \phi = 0.833 \) were similar for both fuels investigated. A similar flat pattern can be observed from results with fuel G1. The final emissions of \( N_2O \) were similar from both fuels, being between 3.5 and 4.5 ppm.

![Figure 90: \( N_2O \) concentrations from fuel M1 at 900 °C](image1)

![Figure 91: \( N_2O \) concentrations from fuel G1 at 900 °C](image2)

4.4.8.b. 1,100 °C

Similar contradictory results are obtained from \( N_2O \) measurements at 1,100 °C, as can be observed in Figures 92 and 93. The instability of \( N_2O \) measurements at short residence times, caused by the presence of rapidly changing amounts of carbon monoxide near the atomiser tip, is evidenced by the large standard deviation of such measurements.
Figures 90 and 92 show that the disappearance of N\(_2\)O formed at short distances is accelerated by an increase of the furnace wall temperature.

![Figure 92: N\(_2\)O concentrations from fuel M1 at 1,100 °C](image)

![Figure 93: N\(_2\)O concentrations from fuel G1 at 1,100 °C](image)

Emissions of N\(_2\)O were again between 3 and 5 ppm.

4.4.8.c. 1,200 °C

Experimental readings of N\(_2\)O at 1,200 °C furnace wall temperature confirmed that this variable and, in turn, the flame wall temperature, exerts little influence on the emission of nitrous oxide. No significant change in the emissions of N\(_2\)O was observed. These ranged between 2.8 and 3.5 ppm for fuel M1 and 4.0 and 4.7 for fuel G1.

![Figure 94: N\(_2\)O concentrations from fuel M1 at 1,200 °C](image)

![Figure 95: N\(_2\)O concentrations from fuel G1 at 1,200 °C](image)
4.4.9. Particulates

Sampling of solid particulates was attempted in experiments at 900 °C at fuel-rich conditions for periods of 20 minutes at selected probe positions. However, the mass of particulates collected in the cyclones from both fuels was very low, although not negligible, usually lower than 0.1 g. Such small amounts did not allow examination under the Scanning Electron Microscope. As a means of comparison, a standard residual fuel oil produces approximately 1 gram of solid particulates in the same conditions and time.

Since the lowest cyclone cut-off is 1.4 μm, smaller particles are expected to by-pass the cyclones in the form of a fine aerosol. This is shown by silica wool placed after the cyclones, which collects some of these smaller particulates.

5. Discussion

5.1. NOx

5.1.1. Formation of NO at short distances

A common feature observed from both fuels at all equivalence ratios was the rapid formation of NO at distances shorter than 100 mm from the atomiser nozzle. This is observed especially under fuel-lean conditions (φ = 0.714 and 0.833), but also at stoichiometric and fuel-rich equivalence ratios. In these cases it is accompanied by significant amounts of NO₂.

In the first 150 mm of the furnace, the flame temperature profile exhibits a similar pattern at all equivalence ratios at a given furnace wall temperature, as it is largely determined by radiation from the furnace walls. The fuel is injected in a cone of (fuel-atomising air) mixture, surrounded by the secondary air stream. In this cone the conditions are more fuel-rich than in the overall combustion system (φ = 2.03 in the spray cone alone). Injection and the onset of ignition create a region of high turbulence, where mixing of the atomisation and secondary air streams is accomplished. At the end of this zone the oxygen supplied in both air streams has not been consumed totally, although its concentration decreases from 20.9 % to approximately 7.0 % at all equivalence ratios (see Figures 70 and 71). This implies the consumption of larger amounts of oxygen at the lower (fuel-
lean) equivalence ratios. Significant amounts of CO are also present (see Figures 82 and 83).

Nitric oxide found in this stage is formed by the fuel-NO mechanism. The extent of the fuel-N conversion by this mechanism is dependent on various factors, such as flame temperature, equivalence ratio or residence time. The influence of the equivalence ratio will be examined in paragraphs 5.1.3. to 5.1.5.

It was found that at 900 °C furnace wall temperature no large differences exist in the conversion of fuel-N to NOx before 200 - 250 mm at all equivalence ratios from both fuels studied (between 30 and 40 % for fuel M1 and slightly higher for fuel G1, as shown in Figures 55 and 56). Increasing the furnace wall temperature (thus, the flame temperature) alters the fuel-N to NO conversion at short distances. At 1,100 °C furnace wall temperature the conversion is higher at fuel-lean equivalence ratios than in stoichiometric or fuel-rich mixtures at a given distance from the atomiser nozzle. Larger differences were encountered at 1,200 °C furnace wall temperature, as the rates of reaction are increased by higher flame temperatures and higher oxygen availability under fuel-lean conditions.

Although the participation of the prompt-NO mechanism cannot be totally dismissed, especially since amounts of N₂O are formed (Figures 90 and 92) the fuel-NO mechanism is deemed to be predominant at this stage (see section “4.1.1.b. Reaction of N₂ with hydrocarbon fractions: Prompt-NO” in chapter I for the role of N₂O in the prompt-NO mechanism). If the prompt-NO mechanism prevailed, similar concentrations of NO would be encountered from both fuels as this process depends on the reaction of hydrocarbon radicals with atmospheric nitrogen. In addition, experimental work performed with a low-nitrogen diesel fuel, reported in chapter IV, showed a similarly low amount of NO formed, thus ruling out a large contribution of the prompt-NO mechanism.

A possible participation of the thermal-NO mechanism is discussed in paragraph 5.1.6.
5.1.2. Formation of NO\textsubscript{2} at short distances

Significant concentrations of NO\textsubscript{2} were found in the drop-tube furnace at stoichiometric and fuel-rich equivalence ratios and at short distances from the atomiser. Nitric oxide formed before 150 mm can give place to NO\textsubscript{2} by the well known mechanism of reaction of NO with HO\textsubscript{2}, or by reactions with hydroperoxyl radicals (RO\textsubscript{2}). The HO\textsubscript{2} mechanism would be favoured by the low flame temperature, as the formation of this radical is inversely dependent on temperature. High concentrations of HO\textsubscript{2} radicals are likely to be found in low temperature regions where oxygen is present (see section "4.1.2. Formation and emission of NO\textsubscript{2}" in chapter I). Although the stoichiometry in the initial stages of the combustion system is fuel-rich, diminishing concentrations of oxygen can provide the conditions for HO\textsubscript{2} formation \textsuperscript{25}. 

Other reactions of NO\textsubscript{2} formation are also important at low temperatures below 900 °C, such as \textsuperscript{25}:

\[
\begin{align*}
\text{HNO}_2 + O & \leftrightarrow \text{NO}_2 + \text{OH} & \text{26} \\
\text{NO} + \text{O}_3 & \leftrightarrow \text{NO}_2 + \text{O}_2 & \text{27} \\
\text{HNO}_2 + \text{OH} & \leftrightarrow \text{NO}_2 + \text{H}_2\text{O} & \text{28}
\end{align*}
\]

and are likely to occur as amounts of NO are found in early stages of the flame.

5.1.3. Formation of NO\textsubscript{x} beyond 100 mm

5.1.3.a. Fuel-lean conditions (\(\varphi = 0.714\) and 0.833)

The formation of nitric oxide beyond 100 mm from the atomiser is extensive in fuel-lean conditions. The concentrations measured are greater for the fuel with higher fuel-N content, namely M1, than for fuel G1. However, calculations of the conversion of fuel-N into NO yield opposite results, with higher conversion for fuel G1. This can be observed in Figure 45, page 150. Previously, other researchers have reported an inverse relationship between conversion to NO and fuel-N content \textsuperscript{47,150}. Increasing the furnace wall temperature causes an increase in the conversion of fuel-N into NO, larger between 900
and 1,100 °C than between 1,100 and 1,200 °C. In fact, small decreases of the conversion were observed from 1,100 to 1,200 °C for fuel M1.

Although the measured concentrations of NO at $\varphi = 0.714$ do not differ greatly from those at $\varphi = 0.833$ the values of the conversion are greater at $\varphi = 0.714$, possibly due to the higher availability of oxidising species in larger amounts of oxygen. The presence of oxidising species is ensured at both fuel-lean equivalence ratios, as can be seen in Figures 70 through to 75, where residual oxygen can reach 4% at $\varphi = 0.714$. It seems logical that with higher concentrations of oxidising species (ie lower equivalence ratio in fuel-lean conditions) N radicals are more likely to find an oxidising species to undergo NO formation. Also, although no information is available about flame temperature in the drop tube furnace at $\varphi = 0.714$, it is predictable that it will be higher than at $\varphi = 0.833$, which may add to the larger conversion.

Another effect caused by the furnace wall temperature is an increase of the rate of formation between 900 and 1,100 °C furnace wall temperature, which can be observed by comparing Figures 39 through to 42. Higher flame temperatures increase the rate of formation of fuel-NO by increasing the rates of fuel evaporation and nitrogen release, as well as by accelerating the reactions of the fuel-NO mechanism.

Eventually NO readings at fuel-lean conditions stabilise at approximately 300-350 mm. At $\varphi = 0.833$ and 350 mm from the atomiser the flame temperature has decreased from its maximum value (1,691 °C measured at 201 mm) to approximately 1,300 °C. The concentration of oxygen has already reached the values that will be exhausted, as can be seen in Figures 70 and 71. At this stage the fuel-NO process is extinguished due to the long time elapsed since injection, although fuel-N may have not been transformed totally into NO.

The formation of NO$_2$ is low in fuel-lean conditions. Although small amounts of NO$_2$ are detected at very short distances from the atomiser, they disappear subsequently and no nitrogen dioxide is eventually emitted. NO$_2$ is likely to be formed at short distances (low temperature and existing O$_2$) via the HO$_2$ and the RO$_2$ mechanisms.
Experimental results reported by Merryman and Levy from CH$_4$ flames doped with pyridine as N-containing agent showed early formation of NO$_2$, whose disappearance gives place to NO. This phenomenon was explained in terms of the reaction of NO$_2$ with O radicals:

\[
\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2
\]

which is a fast reaction. Concentrations of O radicals increase as those of O$_2$ decrease and the temperature increases early in the flame. Simultaneously, O radicals contribute to the formation of NO via amine oxidation reactions, i.e:

\[
\text{N} + \text{oxidant (O)} \rightarrow \text{NO}
\]

which explains the high levels of NO and negligible concentrations of NO$_2$ obtained in fuel-lean conditions.

5.1.3.b. Stoichiometric conditions ($\phi = 1.000$)

A large drop of NO concentrations was observed to occur from fuel-lean to stoichiometric conditions. At $\phi = 1.000$ the formation of NO peaks before the maximum flame temperature, between 200 and 250 mm, followed by a decrease which allows certain, although low, amounts of NO to be eventually emitted (see Figure 96).

Experimental results show that at $\phi = 1.000$ nitric oxide is not transformed into NO$_2$, as the concentrations of NO$_2$ also decrease sharply after reaching a maximum value at 250 mm, coincidental with the maximum flame temperature. NO formed in stoichiometric conditions is likely to be converted to HCN again by means of reactions with CH and CH$_2$ radicals, which may
be present. Another alternative mechanism is the reduction of NO to form N\textsubscript{2} with amine species, which is postulated as part of the fuel-NO mechanism in high concentrations of nitric oxide:

\[
\begin{align*}
\text{NH}_2 + \text{NO} & \rightarrow \text{N}_2 + \text{H}_2\text{O} & 39 \\
\text{NH} + \text{NO} & \rightarrow \text{N}_2 + \text{OH} & 87 \\
\text{N} + \text{NO} & \rightarrow \text{N}_2 + \text{O} & -2
\end{align*}
\]

The concentrations of NO\textsubscript{2} measured at short distances are larger than in fuel-lean conditions, possibly due to the greater influence of the RO\textsubscript{2} mechanism (see next paragraph) as the equivalence ratio increases.

The composite effect of low emissions of both NO and NO\textsubscript{2} is the low conversion of fuel-N to NO\textsubscript{x} at \(\varphi = 1.000\).

5.1.3.c. Fuel-rich conditions (\(\varphi = 1.200\))

As in stoichiometric mixtures, the peak of NO formation at \(\varphi = 1.200\) occurs before the maximum flame temperature, between 200 and 250 mm, with a subsequent decrease to the concentrations of NO that are eventually emitted.

The main nitrogenous compound emitted under fuel-rich conditions is NO\textsubscript{2}. At 900 °C furnace wall temperature and between 250 and 400 mm distance from the atomiser, NO\textsubscript{2} is formed at a steady rate of 0.33 ppm-wet/mm for fuel M1 and 0.24 ppm-wet/mm for fuel G1. This can be observed in Figures 46 and 47. However, for the large amounts of NO\textsubscript{2} formed at that equivalence ratio no similar transient amounts of NO are detected. Which is the mechanism for NO\textsubscript{2} formation in these conditions? Is NO\textsubscript{2} being formed through NO + HO\textsubscript{2} in a very fast reaction or via another mechanism such as reaction with hydrocarbon chains? In principle, it seems unlikely that NO\textsubscript{2} would be formed by means of the HO\textsubscript{2} reaction as the flame temperature is excessively high. In addition, the steady rates of formation observed suggest a mechanism that is not dependent on the flame temperature (the reaction rate constant for reaction 29, NO + HO\textsubscript{2} \(\leftrightarrow\) NO\textsubscript{2} + OH given by Glaenzer and Troe\textsuperscript{98} for the relevant temperature range is constant and
independent of temperature - see reaction 189 in “Appendix III” for a value of the reaction rate constant). Also, the conversion of fuel-N into NO\textsubscript{2} does not seem to depend on the fuel-N content at \( \varphi = 1.200 \). A similar effect relating the fuel-N content and the equivalence ratio was observed by Pfefferle and Churchill \textsuperscript{110} from ethane flames doped with various amounts of ammonia: Different dopant concentrations yielded comparable NO\textsubscript{X} emissions from fuel-rich flames.

High emissions of NO\textsubscript{2} in fuel-rich systems have been observed by other researchers. Courtemanche and Levendis \textsuperscript{32} found the ratio of \([\text{NO}_2/\text{NO}]\) emissions to increase when solid fuels were burned at fuel-rich conditions. Hori \textsuperscript{65} also found very high \([\text{NO}_2/\text{NO}_x]\) ratios in fuel-rich, air-cooled propane-air flames. The ratio was increased by two factors: The mixing of hot combustion gases with cold air and the sampling of gases with a water-cooled probe. NO\textsubscript{2} was presumed to form in the water-cooled sampling probe due to the rapid but steady cooling of the combustion gases, which causes the formation of HO\textsubscript{2} radicals. A similar explanation was given by Malte and Kramlich \textsuperscript{88}.

A graph showing the axial profile of the \([\text{NO}_2/\text{NO}_x]\) ratio and the flame temperature profile from experiments performed with fuels M1 and G1 at \( \varphi = 1.200 \) and 900 °C furnace wall temperature is shown in Figure 97. The profiles of \([\text{NO}_2/\text{NO}_x]\) ratio show similarities with those reported by Hori with a water-cooled probe at \( \varphi = 1.510 \) (gas sampling from the drop-tube furnace was also performed with a water-cooled probe). However, NO\textsubscript{2} is formed in the drop-tube furnace at a constant rate throughout the range of flame temperatures encountered from 150 to 500 mm, which includes zones of increasing, maximum and decreasing temperatures (see Figure 97). Constant formation of NO\textsubscript{2} is not consistent with a pattern of changing temperature.

An alternative hypothesis can be formulated. Irrespective of the axial flame temperature profile, the furnace walls are at a constant temperatur...
flame temperature profile, the furnace walls are at a constant temperature of 900 °C. Combustion gases near the furnace walls will be at a temperature which is more favourable for the formation of \( \text{HO}_2 \) and, consequently, \( \text{NO}_2 \). Also, oxygen needed to form \( \text{HO}_2 \) radicals is still available (albeit in low concentrations) up to 500 mm from the atomiser. \( \text{NO}_2 \) thus formed can subsequently diffuse back into the furnace central axis, giving place to the concentrations measured. Given the inverse relationship of \( \text{HO}_2 \) radicals with temperature, lower concentrations of \( \text{NO}_2 \) would be expected at higher furnace wall temperatures. However, the exhaust concentrations of \( \text{NO}_2 \) increased from 900 to 1,100 °C for fuel M1, whereas a very minor decrease was obtained from fuel G1.

Another likely source of high \( \text{NO}_2 \) concentrations is the reaction of NO with unburned hydrocarbons, present in fuel-rich systems such as that in the drop-tube furnace at \( \phi = 1.200 \). This possibility was contemplated by Jaasma and Borman \(^{69} \) to account for increased \( \text{NO}_2 \) levels in diffusion flames with hydrocarbon-doped combustion air. Numerical calculations were performed by Sano \(^{115} \) which yielded increased concentrations of \( \text{NO}_2 \) when a cool stream of air containing \( \text{CH}_4 \) was added to combustion gases containing nitric oxide. Methane is assumed to enhance the formation of H radicals which, in turn, would increase \( \text{HO}_2 \) concentrations. Bromly \textit{et al.} \(^{20} \) also found that concentrations of hydrocarbons could oxidise NO to \( \text{NO}_2 \) at relatively high temperatures. This effect was augmented by the presence of CO and \( \text{H}_2\text{O} \). The mechanism proceeds through the formation of hydroperoxyl radicals and other peroxides that can oxidise NO to \( \text{NO}_2 \). Later, Hori \textit{et al.} \(^{66} \) found that propane was most effective at promoting the oxidation of NO into \( \text{NO}_2 \). Also, it was favoured at relatively high temperatures where the formation of active species was sufficiently high.

The numerical model used in the present thesis shows that the concentrations of hydrocarbon fractions increased in fuel-rich mixtures (\( \phi = 1.200 \)) with respect to those under stoichiometric conditions (\( \phi = 1.000 \)). This could lead to greater concentrations of \( \text{NO}_2 \) via the hydroperoxyl mechanism.

At fuel-rich equivalence ratios the formation of \( \text{NO}_2 \) shows very little sensitivity to the furnace wall temperature. It is predictable that increasing furnace wall temperatures will
increase the flame temperature. Since NO₂ represents the largest proportion of nitro-
genous species formed, the concentrations of NOₓ are determined by those of NO₂.

5.1.4. Thermal-NO

Experimental results show that the conversion of fuel-N to NO was below 100 % in all
equivalence ratios investigated. In principle, no significant amounts of thermal-NO were
found even in the most favourable conditions, ie 1,200 °C furnace wall temperature and
\( \phi = 0.714 \).

Work carried out by other researchers shows that the dependence of thermal-NO with
temperature is strong and becomes significant above 1,400 °C \(^{56} \). The flame temperature
profiles obtained experimentally (see chapter V) show that such temperatures are ex-
ceeded in sections of the combustion chamber even when the furnace wall temperature
was set at 900 °C. However, thermal-NO seems unlikely to be a contributor to the for-
mation of NO as an evident direct relationship exists between fuel-N content and NO
formed and emitted from the fuels studied (see Figures 39 and 40). Although flame tem-
perature profiles were not obtained for fuel G1 it is deemed that they would not differ
greatly from those of fuel M1. Since thermal-NO is mainly dependent on flame tempera-
ture (and also on residence time), similar levels of NO formation would be expected from
both fuels, regardless their nitrogen content. In addition, the rates of formation of NO
are different for both fuels (higher for M1, which has the greater fuel-N content) in the
intermediate stages of the flame, between 100 and 400 mm. Thermal-NO would be
formed at similar rates.

Experimental work was performed during the course of this thesis in order to determine
the amount of thermal-NOₓ that is formed in the drop-tube furnace. This work is re-
ported in chapter IV. A low-nitrogen fuel was burned at the experimental conditions
used in this chapter. Only a minor amount of thermal-NO (approximately 4 ppm-wet)
was detected at 1,200 °C furnace wall temperature and \( \phi = 0.833 \) (see chapter IV).
5.2 \( \text{SO}_2 \)

A preliminary analysis of Figures 64 to 69 shows that the measured concentrations of \( \text{SO}_2 \) rise with the equivalence ratio. These increases are due to the reduced volume of gases associated with the smaller addition of combustion air. Calculations of the amounts of fuel-S transformed into \( \text{SO}_2 \) at \( \varphi = 0.714 \) and 0.833 show that in both cases the conversion of fuel-S into \( \text{SO}_2 \) was similar, at around 100%.

In fuel-lean conditions (\( \varphi = 0.714 \) and 0.833) the formation and emission of \( \text{SO}_2 \) seem to be independent of the furnace wall temperature. No increases were found when the furnace wall temperature was raised from 900 to 1,100 °C. With a large excess of oxygen available at these equivalence ratios, sulphur is likely to be fully oxidised to \( \text{SO}_2 \), regardless the furnace wall temperature. In some cases the fuel-S conversion is slightly lower at \( \varphi = 0.714 \) than at \( \varphi = 0.833 \), which may suggest the formation of \( \text{SO}_3 \).

When the combustion mixture becomes fuel-rich the rate of formation of \( \text{SO}_2 \) decreases. The shortage of oxygen at stoichiometric and fuel-rich conditions retards the formation of all \( \text{SO}_2 \) until most \( \text{O}_2 \) has been consumed. This can be seen in Figure 98.

![Figure 98: Formation of \( \text{SO}_2 \) and disappearance of \( \text{O}_2 \) for fuel M1 at \( \varphi = 1.200 \) and 900 °C furnace wall temperature](image)

SO\(_2\) reaches a maximum and then decreases when approximately only 0.5 % \( \text{O}_2 \) is left. Subsequently, the concentration of \( \text{SO}_2 \) decreases as the remaining oxygen disappears. Larger decreases were found at higher furnace wall temperatures, as the peaks of \( \text{SO}_2 \) concentration become more pronounced and the emissions lower. Results obtained by numerical modelling (see chapter VI for results of the numerical model) show that \( \text{SO}_2 \) is reduced to species such as COS, SO and H\(_2\)S in low-oxygen conditions. Furthermore, evidence was found in the drop-tube furnace of solid, yellow deposits, which can substantiate the formation of sulphur.
A survey of the literature reveals that unlike in fuel-lean conditions, SO₂ may not be the sole sulphur compound present in fuel-rich combustion environments. Other sulphur species such as H₂S, S, S₂, HS and SO may appear, as the relative importance of sulphur dioxide decreases. Figure 99 shows the calculated distribution of various predominant S compounds at various equivalence ratios.

The reduction of sulphur dioxide can take place through the following fast bimolecular reactions:

\[
\begin{align*}
    H + SO₂ & \rightarrow SO + OH & 92 \\
    H + SO & \rightarrow S + OH & 93 \\
    S + H₂ & \rightarrow HS + H & 94 \\
    HS + H₂ & \rightarrow H₂S + H & 95 \\
    HS + HS & \rightarrow S₂ + H₂ & 96 \\
\end{align*}
\]

together with reactions of the radical pool:

\[
\begin{align*}
    O + H₂ & \rightarrow OH + H & 5 \\
    H + O₂ & \rightarrow OH + O & 6 \\
    H₂ + OH & \rightarrow H + H₂O & 7 \\
\end{align*}
\]

6. Conclusions

1. NO is formed rapidly from both fuels at all equivalence ratios in the first 150 mm from the atomiser nozzle by means of the fuel-NO mechanism. The amounts of fuel-N converted to NO were dependent on the stoichiometry and the furnace wall temperature.
Although N₂O was also observed, the role of the prompt-NO mechanism was deemed to be of minor relevance.

2. As a result of the rapid formation of NO, significant amounts of NO₂ are also formed at short distances in stoichiometric and fuel-rich conditions. NO₂ is thought to be formed by means of the HO₂ and RO₂ mechanisms.

3. The extent of NO formation at longer distances depends mainly on the stoichiometry of the combustion system and the furnace wall (flame) temperature. Large amounts of NO are formed in fuel-lean conditions. The conversion of fuel-N into NO is greatest under these conditions. The fuel with the larger fuel-N content yields greater concentrations of NO, whereas conversion is higher for the fuel with lower fuel-N content. Raising the furnace wall temperature increases the conversion of fuel-N into NO.

4. Although significant amounts are formed, NO and NO₂ are emitted in small amounts in stoichiometric conditions. The concentrations of both species are reduced at relatively long distances from the atomiser nozzle.

5. Small amounts of NO are emitted at Φ = 1.200. NO₂ constitutes the largest nitrogenous emission in these conditions. NO₂ is thought to be formed by the reaction of NO with hydroperoxyl radicals (RO₂) that stem from unburned hydrocarbons. Although further work is needed at 1,200 °C furnace wall temperature, the conversion of fuel-N into NO₂ does not show a dependence on the furnace wall temperature nor the fuel-N content.

6. No significant amounts of thermal-NO were found even in the most favourable conditions, ie 1,200 °C furnace wall temperature and Φ = 0.714.

7. The measured concentrations of SO₂ rise with the equivalence ratio due to the reduced volume of combustion gases associated with high equivalence ratios.

8. In fuel-lean conditions the formation and emission of SO₂ seems independent from the furnace wall temperature.
9. In some cases the fuel-S conversion is slightly lower at $\varphi = 0.714$ than at $\varphi = 0.833$, which may indicate the formation of SO$_3$.

10. At stoichiometric and fuel-rich equivalence ratios the formation of SO$_2$ reaches a maximum and decreases subsequently. Larger decreases were found at the higher furnace wall temperatures. SO$_2$ is reduced into species such as COS, SO and H$_2$S in low concentrations of oxygen.
CHAPTER IV. EXPERIMENTAL DETERMINATION OF THERMAL-NO\textsubscript{X} IN THE DROP-TUBE FURNACE

1. Objective

One of the aims of the present PhD thesis is to study the processes and extent in which fuel-N is converted to NO\textsubscript{X}. Another objective is the possible effect that other fuel constituents may exert on emissions of oxides of nitrogen.

Three predominant processes for NO\textsubscript{X} formation and emission are accepted (see page 62 in chapter I):

1. From fixation of atmospheric nitrogen, known as thermal-NO\textsubscript{X}
2. From transformation of the nitrogen contained in the fuel: fuel-NO\textsubscript{X}
3. By reaction of hydrocarbon fragments with atmospheric nitrogen: prompt-NO\textsubscript{X}

Since all emissions are indistinguishable if concurrent, it is essential to determine the amounts of NO\textsubscript{X} formed in the thermal process in order to assess the quantities of NO\textsubscript{X} that are formed and emitted from the nitrogen in the fuel.

Thermal-NO\textsubscript{X} is formed solely from atmospheric nitrogen in a process that is strongly dependent upon flame temperature. A fuel with a low nitrogen content or no nitrogen at all would provide the adequate means of evaluating the formation of thermal-NO\textsubscript{X}.

2. Experimental procedure and results

The objective of the experiments reported in the present section is to estimate the maximum amounts of thermal-NO\textsubscript{X} emissions from the drop-tube furnace and also the conditions of equivalence ratio at which these are produced. An upper limit for thermal-NO\textsubscript{X} formation would thus be set and therefore lower amounts would be formed under any other conditions.

Experimental results reported in chapter III showed that maximum formation of NO\textsubscript{X} is attained at $\varphi = 0.833$. Experiments reported in this section were carried out by setting
three different stoichiometric ratios in the combustion chamber. The aforementioned equivalence ratio was investigated, as well as those adjacent, namely fuel-lean ($\varphi = 0.714$) and stoichiometric ($\varphi = 1.000$). This was accomplished by varying the amount of secondary air admitted in the combustion chamber whilst maintaining the same amount of atomisation air.

The fuel used in this section was a commercially available diesel fuel, purchased from Elf Oil UK Ltd. Typical physical and chemical characteristics of this fuel are reproduced in Table 9:

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density @ 15 °C, kg/l</td>
<td>0.8563</td>
</tr>
<tr>
<td>Kinematic viscosity @ 40 °C, cSt</td>
<td>2.0 - 4.5</td>
</tr>
<tr>
<td>Sulphur, % by mass</td>
<td>0.05</td>
</tr>
<tr>
<td>Nitrogen, ppm</td>
<td>230</td>
</tr>
<tr>
<td>Water, mg/kg (max.)</td>
<td>200</td>
</tr>
<tr>
<td>Carbon residue, % mass (max.)</td>
<td>0.30</td>
</tr>
<tr>
<td>Particulate matter, mg/kg (max.)</td>
<td>24</td>
</tr>
<tr>
<td>Gross calorific value, MJ/kg</td>
<td>45.72</td>
</tr>
</tbody>
</table>

Table 9: Typical chemical and physical characteristics of Elf diesel fuel

Although the fuel used was not N-free, its low nitrogen content allowed the estimation of an upper limit for the formation of thermal-NOx.

The experiments were carried out at three furnace wall temperatures, namely 900 °C, 1,100 °C and 1,200 °C. Higher furnace wall temperatures would result in higher flame temperatures, which, in turn, would cause greater formation of thermal-NOx. As in experiments in chapter VII, sampling of combustion gases was performed at 500 mm from the atomiser nozzle.

The experimental results are presented and discussed in the next paragraphs.

2.1. NO

The formation of NO from diesel fuel showed dependencies with both the flame temperature and the equivalence ratio (see Figure 100). Maximum amounts of NO were formed at approximately $\varphi = 0.833$ at all furnace wall temperatures investigated. At 900 °C the
maximum amount of NO emitted was 19.7 ppm-wet at $\varphi = 0.833$. Emissions of nitric oxide were lower at any other stoichiometric ratio. At $\varphi = 0.714$ the emissions of NO reached 13.8 ppm-wet, whereas at stoichiometric conditions only 4.6 ppm-wet were recorded.

As the furnace wall temperature was raised, the maximum formation of NO was also recorded at $\varphi = 0.833$, although the values obtained were greater. The maximum concentration of NO measured was 30.9 ppm-wet at $\varphi = 0.833$ and 1,200 °C furnace wall temperature.

2.2. $NO_2$

The experimental results on $NO_2$ emissions are shown in Figure 101. The values registered were low in all cases. At $\varphi = 0.714$ the furnace wall temperature, and thus the flame temperature seemed not to have an influence on the amounts of $NO_2$ emitted. However, under stoichiometric conditions the furnace wall temperature had an inverse effect on $NO_2$. Lower amounts of $NO_2$ were emitted as the furnace wall temperature was increased. Thus, the maximum values of $NO_2$ emission, 4 ppm-wet, were recorded at $\varphi = 1.000$ and 900 °C furnace wall temperature.
2.3. Total NO\textsubscript{x} and fuel-N conversion

Given the low amounts of NO\textsubscript{2} formed at all equivalence ratios the behaviour of total NO\textsubscript{x} emissions followed the same pattern as those of NO. The maximum amounts of NO\textsubscript{x} formed at 900 °C furnace wall temperature and $\varphi = 0.833$ were found to be 21.6 ppm-wet. At 1,200 °C and $\varphi = 0.833$, 32.4 ppm-wet of total NO\textsubscript{x} were emitted.

Calculations of the conversion of fuel-N to NO\textsubscript{x} are provided in Figure 103, where the dotted horizontal line denotes 100 % conversion.

The conversion of fuel-N is relatively low at 900 °C furnace wall temperature. Again the maximum values are achieved at $\varphi = 0.833$, with conversion close to 76 %, assuming that all NO\textsubscript{x} originate from nitrogen contained in the fuel. The conversion of fuel-N into NO\textsubscript{x} increases, as predicted, with increases of furnace wall temperature. The conversion reached a maximum value, 113.4 %, at $\varphi = 0.833$ and 1,200 °C. The fact that the conversion is higher than 100 % indicates that at least 3.8 ppm-wet thermal-NO\textsubscript{x} are formed in such conditions.
2.4. Conclusions from gas sampling experiments

From the results reported in the previous paragraphs it can be concluded that the emission of total-NO\textsubscript{x} from Elf diesel fuel is not greater than 22.6 ppm-wet at 900 °C furnace wall temperature and 0.833 equivalence ratio. Assuming that all nitrogenous emissions stem from the fuel-N (the fuel used contains 230 ppm fuel-N) is converted to NO\textsubscript{x}, and since fuel-NO\textsubscript{x} is formed at lower flame temperatures than thermal-NO\textsubscript{x}, it can be concluded that emissions of thermal-NO\textsubscript{x} are negligible at 900 °C furnace wall temperature.

A limited amount of thermal-NO\textsubscript{x} is formed at 1,200 °C furnace wall temperature and \( \varphi = 0.833 \). Assuming that all fuel-N is converted to NO\textsubscript{x}, the emissions of thermal-NO\textsubscript{x} were 3.8 ppm-wet.

3. Flame temperature profile

The similarity of the axial flame temperature from the diesel fuel compared to that obtained from the heavy gas oils used in this work is of great relevance. Comparable temperature traces in both flames would indicate the formation of similar amounts of thermal-NO\textsubscript{x} from the heavy gas oils, as thermal-NO\textsubscript{x} is mainly dependent upon flame temperature.

3.1. Experimental procedure and results

In order to assess this aspect of thermal-NO\textsubscript{x} formation, experiments were carried out to record the temperature profile of the flame produced by a diesel flame. The same experimental conditions as in experiments performed with the heavy coker gas oil M1 (see chapter V) were used. The equivalence ratio in this experiment was again 0.833, and the furnace wall temperature was 900 °C. Also the compensation of the temperatures recorded was performed according to the procedure reported in chapter V.

The experimental results of the flame temperature after corrections were applied can be seen in Figure 104. A graph showing the flame temperature profile obtained from the heavy coker gas oil M1 is adjacent (see Figure 105).
Both graphs show similar shapes of the temperature profile. Large scatter exists in the initial spray zone of the flame. Subsequently, the flame temperature rises rapidly, although at a rate which is slightly lower than that of fuel M1 (8.7 °C/mm vs 9.5 °C/mm). At 200 mm from the atomiser nozzle the temperature of the diesel fuel flame was 1,521 °C, whereas fuel M1 had almost reached its maximum temperature (1,691 °C). The maximum flame temperature from diesel fuel (1,780 °C) was recorded at a longer distance, approximately 259 mm, from the atomiser nozzle. Subsequently the flame temperature remained higher than that from fuel M1 for the remainder of the combustion chamber, with exit temperatures well above those of fuel M1.

3.2. Discussion of experimental results

The peak flame temperature can be used as an indication of thermal-NOX formation. Comparison of both flame temperature profiles shows that lower amounts of thermal-NOX would be formed from the combustion of the heavy gas oils as their maximum temperature is lower than that from Elf diesel fuel (1,691 °C vs 1,780 °C).

Also, the emission of total-NOX from the latter is 21.6 ppm-wet, which represents a conversion of fuel-N to NOX of 76 %. This may indicate that thermal-NOX formation is not relevant if compared to that from the nitrogen in the fuel.

Thus, it can be concluded that no appreciable amounts of thermal-NOX are formed in the drop-tube furnace at the furnace wall temperature of 900 °C.
CHAPTER V. EXPERIMENTAL DETERMINATION OF THE AXIAL FLAME TEMPERATURE PROFILES IN THE DROP-TUBE FURNACE

1. Objective

The flame temperature is an important variable when considering the processes occurring in a flame. The conversion of fuel-N and especially the formation of thermal-NO\textsubscript{X} are processes that are strongly influenced by the flame temperature, as is the interaction of nitrogen and sulphur species in the flame. Conversely, the flame temperature may also be affected by the interaction between these species.

In order to simulate numerically the formation of NO\textsubscript{X} from the fuel, and also the interaction of oxides of nitrogen with sulphur compounds it is necessary to have accurate measurements of the flame temperature in the path of the gas species.

Initial attempts were carried out to estimate the temperature profile by measuring the output power into the furnace zones. Since the flame radiates energy towards the furnace wall, less current would be needed in zones where the flame is located, thus indicating its approximate length. However, the information so obtained was purely qualitative and, although the length of the radiant part of the flame could be estimated with some accuracy, it did not provide absolute values of the flame temperature.

2. Experimental procedure and conditions

The flame temperature was measured by means of an Inconel sheath, K-type thermocouple inserted vertically in the sampling probe. The diameter of the thermocouple was 3 mm. Although the large diameter was disadvantageous with respect to radiation heat losses, a robust thermocouple was needed in order to endure the aerodynamic conditions in the furnace. Heat losses in radiation from the thermocouple were compensated for at a later stage.

Another source of heat losses from thermocouples is conduction to cooler surfaces. Great care was exercised to place the tip of the thermocouple at a minimum distance of
90 mm from the top of the water-cooled sampling probe so that conductive losses onto the probe were minimised. Thus it was also possible to measure the flame temperature at very short distances from the atomiser, which are not reached by the sampling probe.

The fuels used were Orimulsion and the heavy coker gas oil M1. It was deemed that the latter fuel would represent the group of heavy gas oils used in this thesis. No large differences in flame temperature are expected to be caused by the different N and S contents in other fuels of similar physical and chemical characteristics.

The experimental conditions in the drop-tube furnace were similar to those in experiments reported in other sections of this thesis. Three stoichiometric ratios were investigated by adjusting the amount of secondary air: Fuel-lean (\(\phi = 0.833\)), stoichiometric (\(\phi = 1.000\)) and fuel-rich (\(\phi = 1.200\)). The amount of atomisation air was maintained at 23.2 g/min. In the case of Orimulsion, only combustion in fuel-lean conditions was investigated. As in other experiments the furnace wall temperature was 900 °C.

The objective of both the numerical modelling and experimental runs was to measure the emissions at a distance of 500 mm from the atomiser nozzle. The temperature profiles were obtained by performing vertical traverses from approximately 500 mm up to the closest achievable distance to the atomiser nozzle. The signal from the thermocouple was collected by the Orion data-logger and plotted versus the thermocouple tip position.

3. Experimental results

The flame temperature traces obtained are shown in Figures 106 through to 109. These graphs show that the recorded values of the flame temperature were excessively low for the combustion systems considered. Thus, corrections for heat losses by radiation and convection were applied. The calculations were based on an algorithm reported by Bradley and Matthews 19. At steady-state conditions there should be no net gain or loss of energy in the thermocouple, and thus both convective and radiative effects would balance each other. Convective and radiative heat transfer are taken into account by means of the following formula:
Figure 106: Flame temperature profile recorded from Orimulsion at $\phi = 0.833$

Figure 107: Flame temperature profile recorded from fuel M1 at $\phi = 0.833$

Figure 108: Flame temperature profile recorded from fuel M1 at $\phi = 1.000$

Figure 109: Flame temperature profile recorded from fuel M1 at $\phi = 1.200$

$$h(T_F - T_{\infty}) - \sigma \varepsilon (T_{\infty}^4 - T_W^4) = 0$$

where:

$T_F$: flame temperature

$T_{\infty}$: infinite gas temperature, i.e., that recorded by the thermocouple

$T_W$: furnace wall temperature = 900 °C = 1,173 K

$\sigma$: Stefan-Boltzmann constant = $5.67 \times 10^{-8}$ W/m$^2$ K$^4$

$h$: convective heat transfer coefficient = \[ \frac{K}{D} \left( 0.42 \Pr^{0.2} + 0.57 \Pr^{0.33} \frac{\sqrt{\nu}}{D} \right) \] K

$K$: air thermal conductivity = $5.4874 \times 10^{-5}$ T$F$ - 0.001862, W/m K in the range of temperature considered

$D$: thermocouple diameter = 3 mm = $3 \times 10^{-3}$ m

$\Pr$: Prandtl number = 0.67314 - $3 \times 10^{-5}$ $T_F$, in the range of temperature considered
V: gas velocity, a function of the flame temperature $T_F$ and the mass flow rate

$\rho$: gas density $= \frac{404.42}{T_F}$, kg/m$^3$

$v$: gas viscosity, which is a function of the flame temperature $= 3.2143 \times 10^{-8} T_F + 1.2439 \times 10^{-5}$, kg/ms

$\varepsilon$: total hemispherical emissivity of the thermocouple. Information on this variable was obtained from INCO. A linear relationship was assumed between the total hemispherical emissivity $\varepsilon$ and the temperature recorded by the thermocouple (infinite gas temperature) in the form $\varepsilon = 1.9825 \times 10^4 T_\infty + 0.5734$

Thus the flame temperature can be calculated by:

$$T_F = T_\infty + \frac{\sigma \varepsilon}{h} (T_\infty^4 - T_W^4)$$

Since the Prandtl number, gas density, gas velocity and convection coefficient are, in turn, functions of the flame temperature, reiterative calculations were necessary in order to estimate those. The correct value of the flame temperature was achieved when the iterative correction procedure did not modify its value.

In all of the traces obtained there is considerable scatter in the data from the first 100 mm after the atomiser nozzle. Spurious readings are possibly caused by turbulence in this zone of high recirculation. Also in this zone, radiation from the furnace walls, set at 900 °C, would predominate over the cooler fuel-air mixture, thus providing inaccurate measurements of the gas temperature.

A precise temperature profile in the heating-up period (0 to 100 mm) was also needed as discrete values of the flame temperature are required to perform the numerical modelling of the CSTR region of the drop-tube furnace (see section "2.1. Representation of the flow dynamics in the drop-tube furnace" in chapter VI). The flame temperature in the heating-up period was calculated by means of a second order polynomial which related the flame temperature to the distance from the atomiser nozzle, so that the temperature traces obtained from experiments with the Single Suspended Droplet technique were re-
produced (see chapter II). Assuming that the fuel was injected at approximately 25 °C, at 100 mm the temperature calculated by the polynomial should match that in experimental runs.

The temperature profiles shown in the following graphs were obtained when these corrections were included:

![Flame temperature profile from Orimulsion at \( \phi = 0.833 \)](image1)

![Flame temperature profile from the heavy coker gas oil M1 at \( \phi = 0.833 \)](image2)

![Flame temperature profile from the heavy coker gas oil M1 at \( \phi = 1.000 \)](image3)

![Flame temperature profile from the heavy coker gas oil M1 at \( \phi = 1.200 \)](image4)

### 4. Discussion

In all cases the flame temperature increased steeply from the initial fuel temperature, ie 25 °C, up to a maximum value, decreasing subsequently to values close to those of the furnace wall at a slower rate. The maximum temperature and its location varied according to the equivalence ratio. In fuel-lean conditions \( (\phi = 0.833) \) the flame temperature has a maximum value of 1,691 °C at 201 mm from the atomiser nozzle. The maximum flame temperature decreased as the equivalence ratio was increased, and it was reached...
at longer distances from the atomiser nozzle. In stoichiometric conditions the maximum flame temperature was 1,599 °C at 262 mm from the atomiser nozzle, whereas at \( \varphi = 1.200 \) the maximum value of the flame temperature registered was 1,329 °C at 276 mm from the atomiser.

The temperature profile obtained from Orimulsion burned at \( \varphi = 0.833 \) showed a similar pattern to that of the heavy coker gas oil M1. The flame temperature rises more rapidly in the initial heating-up period than with fuel M1, since the flame temperature at 100 mm from the atomiser nozzle was higher than that of fuel M1. The water contained in the fuel evaporates shortly after entering the furnace. Micro-explosions produce secondary atomisation that enhance the combustion rates in these early stages of the flame. However, in the plug flow region the flame temperature increased at a lower rate than fuel M1 (7.9 °C/mm whereas the heating rate of fuel M1 was 9.5 °C/mm) until reaching the maximum flame temperature, 1,614 °C at 212 mm from the atomiser nozzle. This value is lower than that obtained from fuel M1 burned in similar conditions. A possible explanation for this phenomena is that the flame is cooled by the evaporation of water in the fuel. Also, radicals released by the water may have a similar effect.
CHAPTER VI. NUMERICAL MODELLING OF COMBUSTION IN THE DROP-TUBE FURNACE

1. Objectives of the numerical model

A literature survey of the experimental work carried out by other researchers shows that sulphur and nitrogen species interact to a significant extent. It is possible that the magnitude of such interaction can be predicted by a numerical model.

In an initial stage of the numerical simulation work performed in this thesis, the model was run to reproduce the experimental results from the combustion of fuels in air, with the main focus on NO\textsubscript{x} formation and emission. The results provided verification of the model and its implementation. Subsequently, the effect of the addition of sulphur to the combustion system was investigated by including SO\textsubscript{2} in the system input. The accuracy of the results obtained from the combustion in air ensured that calculations with the addition of SO\textsubscript{2} to the combustion environment would help predict the behaviour of the real combustion system in the drop-tube furnace.

By performing the numerical calculations at a residence time equivalent to 500 mm distance from the atomiser nozzle, it was expected that the results would aid the prediction of experimental readings at that position.

2. Simulation of the combustion system and code implementation

2.1. Representation of the flow dynamics in the drop-tube furnace

The extent and direction of the processes occurring in any combustion system are determined, amongst other variables, by the flow regime. A correct representation of the flow dynamics provides accuracy to a computer model. In the case of the drop-tube furnace, a simple combination of a CSTR (Continuous Stirred Tank Reactor) stage followed by a long PFR (Plug Flow Reactor) zone was deemed appropriate and has provided appropriate results in the previous work performed in this Research Group by Graville. However, it must be noted that these assumptions do not represent an exact representation of what must be a much more complex situation in reality.
The two different flow regimes can be identified in the drop-tube furnace: Subsequent to fuel injection a conical zone of high recirculation develops, caused not only by the atomisation process, but also by the ignition of the fuel-air mixture, which causes both turbulence and increase of the temperature. This zone can be likened to a continuous stirred tank reactor (CSTR) and it ends at the point of impingement of the fuel-air mixture on the furnace wall. This vertical distance was calculated geometrically to be 100 mm.

After the first 100 mm the ignited, hot, gaseous mixture moves downwards in motion similar to that of a plug flow reactor (PFR). This zone elapsed between 100 mm from the atomiser nozzle and the sampling point, that is 500 mm from the nozzle.

Although clearly separate in the numerical model, there is not a neatly defined boundary between the two zones in the experimental set-up, but they both overlap while the combustion products flow from the CSTR zone into the PFR zone.

2.2. Software, hardware and code implementation

The computer package used in the numerical simulation of the drop-tube furnace was CHEMKIN, by the Sandia National Laboratories. This suite is composed of various FORTRAN software codes, each adequate for a different flow regime, ranging from Plug Flow ("CONP" code), Continuous Stirred Tank Reactor ("PSR" code), Laminar Premixed Flame, etc. The codes can be readily modified to meet specific requirements and recompiled, so that executable files are easily generated after each modification.

The "PSR" code was used in the initial zone of the furnace, whereas the plug flow reactor zone was modelled by means of a "CONP" code. This code was originally written for adiabatic, constant pressure systems. However the drop-tube furnace, although of constant pressure, is not adiabatic. Thus, the "CONP" code was altered so that the experimental temperatures and thus, heat losses were taken into account in the calculations (the modified code is included in "Appendix IV"). Finally, minor modifications were performed to ease the post-processing of the output from both codes.
The "PSR" code was run in ten consecutive batches, each one representing 10 mm of the path of the fuel-gas mixture after exiting the atomiser nozzle. The outlet from a given batch served as the input for the following one. The temperature in each batch was set according to those calculated in chapter V, where the flame temperature was simulated by a second order polynomial with values ranging from that at the point of injection (25 °C) to that at exit of the CSTR zone (100 mm from the atomiser nozzle).

Subsequently, the "CONP" code simulated the plug flow section of the furnace. The outlet composition of the last CSTR batch was used as input to the "CONP" code. This code was run for the equivalent 400 mm, up to a total distance (ie CSTR plus PFR zones) of 500 mm, which was the sampling distance in the experimental work on N-S interactions reported in chapter VII.

The model was run on a PC computer equipped with a Pentium 75 microprocessor and 24 MB RAM. The running time varied according to the number of time step iterations taken by the "PSR" code and the temperature steps given in the input file of the "CONP" code; typical running times for the latter ranged from 15 to 20 minutes.

2.3. Chemical system in the drop-tube furnace

The model must represent the behaviour of fuel combustion at all different conditions encountered in the experimental work. As a result, the mechanism must encompass the same reactions in all conditions. Reaction rate coefficients must also be those applicable in the broad temperature range considered and will govern the extent of each reaction in different conditions of stoichiometry.

In this numerical model the fuel composition was simulated by a combination of simple species such as C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{6} for the hydrocarbon content, HCN for the fuel-nitrogen content and H\textsubscript{2}S for the fuel-sulphur content. Other compounds present in the combustion system, such as H\textsubscript{2}O in Orimulsion and SO\textsubscript{2} in sulphur addition trials were added as separate species.
One of the major limitations of the SANDIA CHEMKIN codes is that only species of up to six elements can be used. This poses restrictions to the form of the species in the fuel feed, which may not be totally representative of the actual ones. The representation of the fuel hydrocarbon content by means of \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{H}_6 \), although not illustrative of the complex hydrocarbon molecules in heavy distillate fuels, was deemed appropriate in the light of those restrictions. In addition, acetylene and ethane are intermediaries in the combustion of complex hydrocarbons and can be considered in gas phase reactions. HCN is accepted to be the most relevant fuel-N initial species in gas phase in combustion.  \( \text{H}_2\text{S} \) was used as a sulphur-containing compound because sulphur in fuel is normally in its reduced state.

Thus, mole fractions of \( \text{C}_2\text{H}_2 \), \( \text{C}_2\text{H}_6 \), HCN and \( \text{H}_2\text{S} \) were calculated to match the C, H, N and S contents and the values of the C/H ratio provided in the elemental analyses (see “Appendix II: Analyses of the fuels used in this thesis”, on page 265. The mole fraction compositions of the different fuels used are shown in the next Table:

<table>
<thead>
<tr>
<th>Species</th>
<th>M1</th>
<th>G1</th>
<th>Orimulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_2 )</td>
<td>0.8863</td>
<td>0.6721</td>
<td>0.5196</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6 )</td>
<td>0.0777</td>
<td>0.3065</td>
<td>0.0696</td>
</tr>
<tr>
<td>HCN</td>
<td>0.0061</td>
<td>0.0026</td>
<td>0.0066</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>0.0299</td>
<td>0.0189</td>
<td>0.0210</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.3832</td>
</tr>
</tbody>
</table>

Table 10: Mole fractions of species in fuel feed of the numerical model

The chemical species considered in the numerical model were composed of five elements, namely C, H, O, N and S. 61 species formed by these elements took part in a mechanism with 264 reactions, which are listed in “Appendix III” along with their reaction rate parameters. The reactions for nitrogen chemistry compiled by Miller and Bowman formed the core of the mechanism, which contains reactions for thermal, prompt and fuel-NO formation. In addition, sulphur species were catered for with a set of reactions previously reported by Crosley and Jeffries and Pfefferle and Churchill. These reactions have numbers 234 through to 264.

The reaction mechanism has been validated by Graville and other researchers against a wealth of previously published experimental data. Graville also confirmed the importance
of some relevant nitrogen reactions by calculating their sensitivity coefficients, which were in agreement with those reported by other authors.

Another limitation is that CHEMKIN cannot represent processes such as atomisation, droplet combustion and interaction, volatile release and fuel-air mixing. These aspects are of great importance in residual fuels, whereas their relative relevance decreases in more volatile ones such as the distillate fuels used in this thesis. In spite of these limitations, the results from the model showed that these restrictions can be omitted until a more complex model is developed.

Similar to the conditions set in the experimental work reported in chapter VII, three equivalence ratios were simulated, namely fuel-lean (φ = 0.833), stoichiometric (φ = 1.000) and fuel-rich (φ = 1.200). Since the fuel feed is constant at all conditions, the change of equivalence ratio involved only the alteration of the amounts of air included in the calculations.

3. Results

3.1. NO

Results of NO concentrations versus distance from the atomiser nozzle calculated by the numerical model with the heavy coker gas oil M1 are shown in Figure 114. The trends obtained for the heavy vacuum gas oil G1 show large similarities.

The formation of NO is almost negligible in the initial stages of the perfectly stirred zone, while the flame temperature is below 400 °C. The concentrations of NO begin to rise as the CSTR zone ends at a distance of 100 mm from the atomiser nozzle, more rapidly in fuel-lean and stoichiometric conditions, due to the presence of amounts of
oxygen-containing species.

The rise of NO concentration is arrested when the calculations progress into the PFR (plug flow reactor) zone, where calculations are performed by the modified "CONP" code (the code text can be found in "Appendix IV"). In fuel-lean conditions the concentrations of NO rise again and level off after a short decrease, whereas in stoichiometric and fuel-rich conditions there is a net decrease of the concentration of NO with distance, more pronounced in stoichiometric conditions.

The numerical model yielded final results of the same order of magnitude as the experimental ones in fuel-lean conditions. The largest concentrations of NO at exhaust are obtained at $\varphi = 0.833$, followed by stoichiometric conditions. The concentrations of NO are lowest at fuel-rich conditions.

The numerical model is also able to predict the decrease of NO concentrations observed experimentally in the latter part of the drop tube furnace at stoichiometric and fuel-rich equivalence ratios. However, the predictions are merely qualitative as the values of the emissions calculated do not match those obtained experimentally. Despite being most accurate among all results, the values of NO emissions obtained in fuel-lean conditions underestimated the experimental ones by 22%. At other equivalence ratios the calculated values were much higher than experimental ones. The following Table shows emissions of NO predicted by the model and those obtained experimentally from fuel M1 at 500 mm from the atomiser nozzle:

<table>
<thead>
<tr>
<th>Equivalence ratio ($\varphi$)</th>
<th>[NO], ppm-wet Experimental</th>
<th>[NO], ppm Numerical model</th>
<th>Percentage error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.833</td>
<td>206.7</td>
<td>156.9</td>
<td>-24.1</td>
</tr>
<tr>
<td>1.000</td>
<td>32.2</td>
<td>147.6</td>
<td>358.3</td>
</tr>
<tr>
<td>1.200</td>
<td>12.6</td>
<td>56.1</td>
<td>345.2</td>
</tr>
</tbody>
</table>

Table 11: NO emissions as calculated from the numerical model and obtained experimentally from fuel M1

Results from Orimulsion are discussed in the following paragraphs. As in experimental trials only one equivalence ratio (fuel-lean, $\varphi = 0.833$) was attempted with this fuel.
Many similarities to the patterns from fuel M1 were observed. Formation of NO was negligible until the flame temperature had reached 790 °C, attaining a maximum value (183 ppm-wet) on entering the PFR zone. Subsequently, the effect of the PFR flow regime is to cause a slight decrease of the NO concentrations followed by its stabilisation at exhaust. Eventually, the emissions of NO from Orimulsion at $\phi = 0.833$ and 500 mm sampling distance were 176 ppm-wet. The experimental value obtained at similar conditions was 269 ppm-wet. Thus, the calculation error was 34.6 %.

3.2. $NO_2$

The concentrations of $NO_2$ calculated by the numerical model from fuel M1 are shown in Figure 116.

In the low temperatures of the CSTR zone the formation of $NO_2$ is low, due to the similarly reduced concentrations of NO and the absence of HO radicals, which give rise to $NO_2$ formation mainly through reaction with NO.

As the flame temperature increases so does the concentration of $NO_2$, with higher values as oxygen is
consumed and the combustion conditions become fuel-rich. This process continues until the end of the CSTR zone. On entering the PFR zone the concentrations of NO$_2$ drop very rapidly, and its emissions become negligible at all equivalence ratios.

The results of NO$_2$ emissions calculations from Orimulsion are shown in Figure 117. The calculated values of NO$_2$ emissions were, again, much lower than those obtained experimentally. The PFR regime causes a decrease of the concentrations of NO$_2$, which leads to very low emissions. Emissions of nitrogen dioxide obtained experimentally were 33.5 ppm-wet.

Why are NO$_2$ emissions so different to experimentally obtained values?

The formation of HO$_2$ radicals according to the numerical simulation is high in the CSTR zone, particularly in fuel-rich conditions. However, virtually all HO$_2$ radicals are consumed rapidly in the PFR zone. Calculations of the contributions of individual reactions showed that reaction with H radicals (H + HO$_2$ $\rightarrow$ OH + OH) is responsible for the abrupt disappearance of HO$_2$ radicals, which are then no longer able to contribute to the formation of nitrogen dioxide, as can be seen in Figure 118.

Table 12 shows the reactions containing NO$_2$ comprised in the numerical model, whereas Figure 119 presents a graph of the evolution of species involved in the disappearance of NO$_2$ from fuel M1 in fuel-rich conditions:
NO$_2$ is consumed in stoichiometric and fuel-rich conditions predominantly by means of H and O radicals in reactions:

\[
\begin{align*}
\text{NO}_2 + \text{O} & \rightarrow \text{NO} + \text{O}_2 & 30 \\
\text{NO}_2 + \text{H} & \rightarrow \text{NO} + \text{OH} & 33 \\
\end{align*}
\]

The overall effect of these reactions with the high concentrations of H and O radicals shown in Figure 119 is a sharp drop of NO$_2$ concentrations in the PFR zone, which causes low values of NO$_2$ at exhaust.

Profiles of nitrogen dioxide similar to those obtained in this numerical model were experimentally obtained by Merryman and Levy$^{97}$ in stoichiometric and fuel-rich O$_2$/CH$_4$ flames. Relatively high concentrations of NO$_2$ were observed in the early stages of the flame, rapidly decaying subsequently. These researchers attributed the formation of NO$_2$ exclusively to reactions between NO and HO$_2$ radicals.

Several other researchers$^{20,65,69}$ have suggested in the past that large amounts of NO$_2$ can be formed in fuel-rich mixtures of hydrocarbon fuels. This is due to the presence of unburned hydrocarbons which may enhance HO$_2$ formation and may also supply hydroperoxyl radicals (RO$_2$). Experimental results obtained in this thesis$^{24}$ show that large amounts of NO$_2$ are emitted at stoichiometric and, especially, fuel-rich conditions (see page 151 in chapter III). Thus, a likely source of error in the estimation of NO$_2$ concen-
trations in stoichiometric and fuel-rich conditions may be the reactions of NO with hydrocarbon fractions (hydroperoxyl radicals, RO₂). These reactions were absent from the reaction scheme considered in this thesis, and they may also account for the erroneous concentrations of NO calculated at \( \varphi = 1.000 \) and 1.200.

Therefore, an extended set of species and reactions is necessary in order to accurately simulate the formation of NO\(_2\) in the drop-tube furnace at stoichiometric and fuel-rich equivalence ratios.

### 3.3. SO\(_2\)

The results of sulphur dioxide from fuel M1 are shown in Figure 120. The concentrations of SO\(_2\) increase with the equivalence ratio, due to the lower amounts of air present.

![Figure 120: Calculated concentrations of SO\(_2\) from fuel M1 in air at three equivalence ratios](image)

The concentrations of SO\(_2\) calculated by the numerical model, although 10% lower on average in the case of fuel M1, showed satisfactory agreement with those obtained experimentally, especially in the case of fuel G1. This can be seen by comparing Figures 64 and 65 (on page 159), and Figures 120 and 121.

Since the reactions that lead to the conversion of H\(_2\)S into SO\(_2\) are very rapid when oxygen is still available, the concentrations of sulphur dioxide are large from the very early stages of the combustion process.

The PFR zone exerts varying effects on the concentrations of SO\(_2\), according to the equivalence ratio. In fuel-lean conditions, they remain unchanged. Slight changes are observed at \( \varphi = 1.000 \), whereas in fuel-rich conditions the concentration of sulphur dioxide decreases as the distance from the atomiser (ie, the residence time) increases.
When calculations were performed with the simulated composition of fuel G1, the reduction of SO\(_2\) in fuel-rich conditions was more pronounced, as seen in Figure 121. This fuel had a lower sulphur content (1.74 % by weight) than M-013/95 (3.59 % by weight).

The reduction of SO\(_2\) in fuel-rich conditions was also observed in the experimental work performed in the drop-tube furnace, and it is reported in section "4.4.4. SO\(_2\)" of chapter III.

Results from the numerical model confirm that the disappearance of SO\(_2\) under fuel-rich conditions runs parallel to the increase of reduced sulphur species, such as SO, H\(_2\)S, HS and COS. Although SO\(_2\) remains as the predominant sulphur compound, eventually the concentrations of COS and H\(_2\)S become relevant whilst those of other sulphurous species decay in time. This can be seen in Figure 122. COS is formed via the reaction of CO and S, whereas H\(_2\)S is formed through a much more complex series of reactions involving several sulphurous species.

Under fuel-rich conditions the concentrations of NO\(_2\) are low, as seen in the previous section; thus the reaction between NO\(_2\) and SO\(_2\) may not be responsible for the disappearance of sulphur dioxide.
4. The influence of S on NO formation and emissions

Once the numerical model was verified with respect to experimental data on NO formation, it was used to predict the influence of fuel-S on the formation and emission of NO. To this end, SO$_2$ was included in the feed to the model in amounts that accounted for 0.5, 1.0, 1.5 and 2.0 % of sulphur in the fuel mass. These are the same concentrations of S that were used in the experimental work reported in chapter VII.

The model was run as detailed in paragraph "2.2. Software, hardware and code implementation". The same temperature profiles as in the previous section were used in these sets of runs. It was assumed that addition of SO$_2$ did not modify the flame temperature appreciably.

![Figure 123: Numerical model calculations of NO formation from fuel M1 at $\phi = 0.833$ and various degrees of fuel-S addition](image)

Sulphur dioxide exerted some effect over the formation and emission of nitric oxide at all equivalence ratios studied.

One example of such an influence can be seen in Figure 123. It depicts the profile of NO concentration from fuel M1 in fuel-lean conditions ($\phi = 0.833$) and five different amounts of SO$_2$ dopant.

According to the results from the numerical model the addition of SO$_2$ does not cause significant changes to the pattern of NO concentration in the CSTR zone. However, on leaving this stage the presence of added SO$_2$ was able to decrease the concentrations of NO. The decrease was larger for greater amounts of SO$_2$ dopant.

In the subsequent stages the PFR flow regime tended to enhance the differences in NO concentrations. After a relatively small decrease, the concentrations of nitric oxide levelled off in the latter part of the PFR zone. The values of the emissions ranged between
157.2 ppm-wet (without SO$_2$ addition) and 141.4 ppm-wet (with addition of 2.0 % fuel-S as SO$_2$). Thus, the numerical model predicted decreases of NO emissions at fuel-lean conditions ($\phi = 0.833$) of 9.9 % at 2.0 % fuel-S added. A reduction of 4.8 % was achieved in the experimental work reported in chapter VII.

At $\phi = 1.000$ the calculated emissions of NO differed from the experimental values, as explained in previous paragraphs. However, the numerical model was able to predict reductions of the emissions of nitric oxide, which were intermediate between other equivalence ratios. The concentration of NO was decreased by 5.5 %, whereas a reduction of 10.1 % was achieved in experiments.

Similar to experimental results the mathematical model predicts enhancements of NO emissions in fuel-rich conditions ($\phi = 1.200$), up to 11.7 % over the emissions in the absence of SO$_2$ dopant. However, the experimental readings of NO obtained at these conditions are very low, and thus the percentages do not represent a real change.

Comparison of the results from the numerical simulation of fuel M1 with the experimental results for the same fuel led to Figure 124 and Table 13.

The results obtained from Orimulsion were closer to those from experiments. Figure 125 shows the calculated and experimental percentage decrease of NO emissions. The model
predicted a decrease of 16.9 ppm-wet NO on addition of 1.5 % SO\textsubscript{2}. Although the calculated NO emission values were lower than experimental ones, similar percentage decreases were obtained from model and experiments.

Examination of the results obtained at \( \varphi = 0.833 \) from fuels M1 and Orimulsion show that the decrease of NO emissions on addition of SO\textsubscript{2} is concurrent with increases in the concentrations of reduced N species, such as HCN (9.5 % from fuel M1, 16 % from Orimulsion, with respect to the results without the addition of SO\textsubscript{2}), NCO (approximately 4.4 % from both fuels), NH\textsubscript{3} (23.7 % from both fuels) and NH\textsubscript{2} (by an average 18 % from both fuels). These are transient species in the process of fuel-NO formation, but they can also be formed in recycle processes, such as the reaction of NO with hydrocarbons to form HCN.

At the same time, species that take part in reactions of formation of NO are decreased by the addition of sulphur as SO\textsubscript{2}. These species are N\textsubscript{2}H (by approximately 4 %, with respect to results without addition of SO\textsubscript{2}), HNO (approximately 13 %), NH (11 %), N (by an average 9 %).

In addition, the concentrations of O, OH and H radicals are decreased on incorporation of SO\textsubscript{2} in the numerical model. The decrease was largest for OH radicals from Orimulsion, which were reduced by 30 % on addition of 1.5 % S with respect to the values obtained without addition of SO\textsubscript{2}. Decreases of O radicals were also obtained, which were of 2.8 % on addition of 1.5 % S to Orimulsion and 7.7 % on addition of 2 % S to fuel M1 over the values obtained without SO\textsubscript{2} addition.

Also, a large increase of the concentration of NS radicals was observed (by 55 %) on addition of SO\textsubscript{2}, which shows the feasibility of the reduction of NO via:
Figure 126 shows various paths for the formation of fuel-NO \(^{59,111}\). The effect that SO\(_2\) exerts on their concentrations is denoted by the blue arrows:

\[
\begin{align*}
\text{NS + NO} & \rightarrow \text{N}_2 + \text{SO} \\
\text{NH}_3 \downarrow & \text{OH, H} \\
\text{NH}_2 \downarrow & \text{NO} \\
\text{NNH + OH} \downarrow & \text{N}_2 \\
\text{HNO + N}_2 \downarrow & \text{NO + H} \\
\end{align*}
\]

\[
\begin{align*}
\text{HCN} \uparrow & \text{O} \\
\text{NCO} \uparrow & \text{H} \\
\text{NH + H}_2\text{O, CO} \uparrow & \text{OH, O}_2 \\
\text{N} \uparrow & \text{OH, H} \\
\text{HNO} \uparrow & \text{NO + H + M} \\
\end{align*}
\]

**Figure 126: Fuel-NO formation paths and the effect of SO\(_2\) on the concentration of the intermediate and final species at \(\varphi = 0.833\)**

The decrease of the concentrations of O and OH indicates that sulphur dioxide performs radical recombination under fuel-lean conditions. As a result, the concentrations of species that intervene in reactions prior to those with O and OH radicals, ie HCN, NCO, NH\(_3\) and NH\(_2\), are increased as channels for their reaction are blocked. The concentrations of species that are formed from reaction with O and OH radicals, ie \(\text{N}_2\text{H}, \text{HNO}, \text{NH, N}\) and, ultimately NO, are reduced.

The interaction of N and S species will be studied experimentally in chapter VII.

**5. Conclusions**

1. The numerical model was able to predict emissions of NO from fuel M1 and Orimulsion at \(\varphi = 0.833\) of the same order of magnitude as those obtained experimentally. However, the model was not accurate at calculating emissions at other equivalence ratios, where the calculated values were much larger than those observed experimentally. This results can be seen in Table 11, page 202.
2. The model predicted low emissions of NO\(_2\) at fuel-lean equivalence ratios. However, it failed to predict the high exhaust concentrations of NO\(_2\) measured from fuel M1 at \(\varphi = 1.000\) and 1.200. This inaccuracy was attributed to the model not including hydroperoxyl radicals (RO\(_2\)) and their reactions with NO, which can enhance the formation of NO\(_2\) in stoichiometric and fuel-rich systems.

3. The concentrations of sulphur dioxide calculated by the numerical model were in good agreement with the values obtained experimentally. These concentrations also increased with the equivalence ratio, as lower amounts of combustion air were present.

4. The model confirmed the transformation of SO\(_2\) into reduced sulphurous species in oxygen-deficient environments. The reduction was also observed experimentally.

5. On addition of SO\(_2\) to simulate fuel-S the numerical model calculated reductions of NO from fuel M1 in fuel-lean conditions. The reduction calculated was larger than that obtained experimentally. Although not accurate, the model also yielded reductions of NO concentrations in stoichiometric conditions.

6. Reductions of NO concentrations were also calculated from Orimulsion in fuel-lean conditions. The percentage reduction calculated by the model was similar to that obtained experimentally in the drop tube furnace on addition of various amounts of SO\(_2\).

7. The reductions of NO emissions were partly attributed to the radical recombination of O and OH radicals performed by SO\(_2\), which increased the concentrations of nitro­genous species such as HCN and those in the amine subsystem.

8. In addition, increased concentrations of NS radicals were found on addition of sulphur dioxide, which makes the reduction of NO by reaction of NS radicals viable.
CHAPTER VII. EXPERIMENTAL WORK ON NO\textsubscript{x}-SO\textsubscript{x} INTERACTIONS

1. Objective

The formation of nitrogenous species in the drop-tube furnace has been investigated in previous chapters. Also a literature review has been carried out which showed that NO\textsubscript{x} emissions can be notably affected by the presence of sulphurous species in the combustion system at all equivalence ratios. However, contradictory conclusions were drawn from the experimental work carried out in the past.

This chapter is dedicated to study such an effect on the fuels investigated in the drop-tube furnace. Two types of experiment were performed. In the first part of the work the change of NO\textsubscript{x} emissions with the addition of increasing amounts of SO\textsubscript{2} were investigated. Relevant parameters in this study were:

- The fuel composition, primarily the N, S and water contents
- The equivalence ratio, as the extent and orientation of the alteration seems to depend strongly on the combustion environment
- The amounts of SO\textsubscript{2} added to simulate increasing concentrations of fuel-S, in order to assess the extent of the effect of sulphur on NO\textsubscript{x} species.

Once the effect of S on NO\textsubscript{x} had been established, a second group of experiments was aimed to determine where the interaction between N and S species occurred along the gas path. The sampling distance from the atomiser was an essential parameter in these experiments.

2. Experimental procedure

The drop-tube furnace, as described in section “2. Description of the drop-tube furnace” of chapter III, was used in the experimental work to assess the effect of added S on the combustion of heavy fuels, with special emphasis on the emission of nitrogenous species.
Sulphur was added to the combustion system as SO₂ (gas). Spectrol range (long term stability) cylinders of 2 % vol. SO₂ (balance N₂) were supplied by BOC Special Gases. In order to obtain the desired increasing amounts of fuel-S (which, in turn, depend upon the mass flow rate of fuel), the necessary volumetric flow rates of SO₂ were calculated. Since additional nitrogen is introduced as a balance in the SO₂ cylinder, oxygen was also added to preserve the stoichiometry of the combusting mixture. Thus, an algorithm was devised to calculate the exact mass (volumetric) flow rates of sulphur dioxide, nitrogen, oxygen and atomisation air to be introduced in a given combustion system.

The dopant gases were added in the atomisation air stream. The amount of compressed air was progressively reduced to accommodate increasing amounts of dopant gases so that a constant total mass flow rate of 23.2 g/min was maintained. This ensured that no dilution was caused by the addition of dopant gases.

The volumetric flow rates of the gases were controlled by means of Chell Instruments Ltd. “Tele-Hastings” digital mass flowmeters. Monitoring the flowmeters enabled adjustment to the set-point values within ± 5 % deviation. The flowmeters also produced an output of the gas flow rates expressed in standard conditions (ie 0 °C and 1 atm), which was directed to the Orion 3561 D data-logger for recording purposes.

The fuels used in these experiments were the heavy coker gas oil M1, the heavy vacuum gas oils G1 and G2, supplied by Repsol Petróleo S.A., and Orimulsion. This latter fuel was provided by National Power plc. Their specifications are reproduced in “Appendix II”, page 265. The introduction of other fuels widened the scope of fuel-N and S contents, so that comparative studies of the influence of these variables could be made. Unlike the heavy gas oils used in this thesis, Orimulsion is a [heavy fuel oil:water] emulsion with approximately 30 % water.

Increasing mass flow rates of SO₂ gas were added in order to simulate concentrations of fuel-S increasing in steps of 0.5 % by weight, up to a maximum of 2 % wt fuel-S added. For Orimulsion the maximum addition of sulphur was 1.5 % by weight.
Experiments with heavy gas oils were carried out at three equivalence ratios, namely 0.833 (fuel-lean), 1.000 (stoichiometric) and 1.200 (fuel-rich). Experiments with Orimulsion could only be performed at $\varphi = 0.833$ (fuel-lean). Sampling of gases was not feasible at other equivalence ratios as extensive formation of particulates blocked the filters and coalescers in the sampling lines.

The furnace wall temperature was set at 900 °C to ensure that no thermal-NOX was formed. It has been shown in chapter IV that the formation and emission of thermal-NOX is minimum at these experimental conditions (see page 190). The fuel mass flow rate was kept constant at 3.5 g/min for heavy gas oils and 5 g/min for Orimulsion as this fuel contains 29.8% of water, which maintained the equivalent fuel oil flow rate of 3.5 g/min.

Sampling of gaseous species was performed at a distance of 500 mm from the atomiser. Previous experimental work showed that no relevant changes in gas species concentrations occurred beyond this distance from the atomiser nozzle at all equivalence ratios. The experimental readings lasted for eight minutes for all gases, except for NO and NO$_2$, which were recorded during alternative periods of four minutes each. The logged values were averaged and standard deviation was calculated, except for nitrogen dioxide, as explained in chapter III. Finally, experimental values were plotted versus the percentage of fuel-sulphur added as SO$_2$ dopant.

Finally, the Thermo-Electron chemiluminescence NOX analyser was tested for possible interference by SO$_2$. No interference occurred.

3. Experimental results

3.1. NO

3.1.1. Fuel-lean conditions ($\varphi = 0.833$)

Emissions of NO were higher under fuel-lean conditions ($\varphi = 0.833$) than at any other equivalence ratio. Large concentrations of oxidising species favour the formation of NO over other compounds (see NO formation mechanism on page 62 and subsequent pages).
A net reduction of NO emissions was observed from all fuels investigated when \( \text{SO}_2 \text{gas} \) was added to the combustion system at fuel-lean equivalence ratios.

The largest reduction of NO emissions was obtained from Orimulsion, by 23.4 ppm-wet (ie 8.71 % of the initial emissions) on addition of 1.5 % fuel-S.

The nominal and percentage reductions obtained from the heavy gas oils (both coker and vacuum) were within a narrow range, between 5 and 7 % on addition of 2 % fuel-S. The percentage decreases of NO emissions from these fuels were lower than those from Orimulsion, and seemingly independent of the initial nitrogen and sulphur contents (see analyses of fuels in “Appendix IF”, page 265). This effect can be observed in Figure 128, which shows the percentage change of NO emissions from all fuels investigated.

3.1.2. Stoichiometric conditions \( (\varphi = 1.000) \)

The emissions of nitric oxide at stoichiometric conditions were intermediate to those at other equivalence ratios.
Addition of sulphur dioxide caused a decrease of NO emissions from all of the fuels studied at this equivalence ratio (see Figure 129). The decrease was maximum for fuel G1, from which a reduction of 11.5 ppm-wet was obtained on addition of 2 % fuel-S. This represented a 50 % drop from the emissions of NO in absence of sulphur dopant. Decreases from other fuels were smaller, i.e. 6.3 ppm-wet (10.1 %) for fuel M1, and 9.5 ppm-wet (19.4 %) for fuel G2.

3.1.3. Fuel-rich conditions ($\varphi = 1.200$)

Emissions of NO at fuel-rich conditions were minimum among those at all equivalence ratios studied, caused by the absence of oxidising species. Only fuel G2 showed significant emissions of NO. Experimental readings were 9 ppm-wet (fuel M1), 2.5 ppm-wet (fuel G1) and 20.9 ppm-wet (fuel G2).

Measured concentrations of NO$_2$ at this equivalence ratio were much higher and accounted for the largest portion of the emissions of nitrogenous species.

The addition of fuel-S to the combustion system had little effect on NO emissions at fuel-rich conditions. Most readings increased by 2 ppm-wet which, added to the fact that NO readings were almost negligible, resulted in an irrelevant effect of sulphur.

3.2. NO$_2$

3.2.1. Fuel-lean conditions ($\varphi = 0.833$)

Emissions of NO$_2$ at fuel-lean conditions were much lower than those of NO for all of the fuels burned. Emissions from heavy gas oils were as little as 2 ppm-wet or lower,
whereas those of Orimulsion were more significant at 33.5 ppm-wet. However, addition of SO\(_2\) exerted no effect on emissions of NO\(_2\) from Orimulsion at fuel-lean conditions.

3.2.2. Stoichiometric conditions (\(\varphi = 1.000\))

Experimental readings of NO\(_2\) in stoichiometric conditions were intermediate between those at other equivalence ratios.

Maximum readings of NO\(_2\) were obtained from fuel G1 (68.3 ppm-wet without SO\(_2\) injection), whereas fuel M1 produced intermediate values (35.6 ppm-wet) and fuel G2 gave the lowest readings (31.4 ppm-wet). A graph of the experimental readings can be seen in Figure 130.

The effect of addition of sulphur dioxide in stoichiometric conditions is to cause a drastic increase of NO\(_2\) emissions from all fuels investigated. The nominal increases of NO\(_2\) emissions can be seen in Figure 131. This graph clearly shows that the largest increases of NO\(_2\) emissions were obtained from fuel M1, whereas smaller reductions were obtained from the heavy vacuum gas oils.

Emissions from fuel G1 increased by 31.7 ppm-wet (ie 46.4 % of the emissions without addition of S) whereas G2 produced the smallest nominal increases of NO\(_2\) (16.3 ppm-wet, ie 52 %). The extent of the increase followed the order of nitrogen content of the fuels. The nitrogen content of fuel M1 is 0.32
%2C whereas it is 0.13 % for fuel G1 and 0.06 % for fuel G2.

3.2.3. Fuel-rich conditions (\( \varphi = 1.200 \))

The experimental readings of nitrogen dioxide at fuel-rich conditions were highest among all conditions investigated. Fuel M1 (0.32 % N) produced 253 ppm-wet NO\(_2\) without the addition of SO\(_2\), whereas lower amounts were obtained from other fuels with lower nitrogen contents: 149 ppm-wet from fuel G1 (0.13 % N) and 98 ppm-wet from fuel G2 (0.06 % N). The experimental results are shown in Figure 132.

The effect of SO\(_2\) addition to the combustion system had varying results, according to the fuel. Fuels M1 and G2 experienced increases of NO\(_2\) emissions, whereas fuel G1 did not change its emissions appreciably.

Figure 133 shows this effect in greater detail. Fuel M1 showed increases of up to 37 ppm-wet on addition of 2 % fuel-S as SO\(_2\). This represented a 14.6 % increase over the figures in absence of SO\(_2\). Fuel G2 exhibited a smaller increase of NO\(_2\) emissions, 12.1 ppm-wet (6.4 % per 1 % S added), whereas fuel G1 had a negligible variation of NO\(_2\) emissions with SO\(_2\) addition.
3.3. NO\textsubscript{x}

3.3.1. Fuel-lean conditions ($\varphi = 0.833$)

All fuels investigated showed a net decrease of NO\textsubscript{x} emissions when sulphur was added as SO\textsubscript{2}-gas. The experimental readings are shown in Figure 134.

In the absence of sulphur addition, Orimulsion yielded the largest NO\textsubscript{x} emissions, followed by fuels M\textsubscript{1}, G\textsubscript{2} and G\textsubscript{1}.

Orimulsion also had the largest nominal reduction of NO\textsubscript{x} emissions among all fuels studied, from 302.7 ppm-wet in air to 281.5 ppm-wet with 1.5 % sulphur added (approximately 5 % of the initial NO\textsubscript{x} emissions per 1 % fuel-S added). It is expected that a larger addition of sulphur would cause a further reduction of NO\textsubscript{x} emissions.

Smaller reductions of NO\textsubscript{x} emissions were achieved from the other fuels studied, the heavy coker and vacuum gas oils M\textsubscript{1}, G\textsubscript{1} and G\textsubscript{2}. In general, nominal values of the decrease of NO\textsubscript{x} concentrations were similar for these fuels, regardless their initial nitrogen and sulphur content. Thus, after almost no change at 0.5 % of S addition, the readings of NO\textsubscript{x} were decreased almost uniformly by 7 to 11 ppm-wet with addition of 2 % fuel-S, which can be seen in Figure 135.

Figure 134: Experimental readings of NO\textsubscript{x} from experiments of sulphur addition from all fuels investigated at $\varphi = 0.833$

Figure 135: Change in NO\textsubscript{x} emissions with addition of fuel-S at $\varphi = 0.833$ from all fuels investigated
The percentage change of NO\textsubscript{x} emissions can be seen in Figure 136. Reductions of NO\textsubscript{x} emissions are obtained at almost all additions of sulphur investigated. However, no correlation could be established between the percentage of sulphur added and the reduction of NO\textsubscript{x} concentrations obtained. The percentage change is larger for Orimulsion (N content = 0.40 %) and fuel G1 (N content = 0.13 %).

### 3.3.2. Stoichiometric conditions (\(\varphi = 1.000\))

Only three fuels were studied in these conditions, namely M1, G1 and G2. The experimental readings are shown in Figure 137.

In the absence of sulphur addition, the largest emissions of NO\textsubscript{x} corresponded to fuel M1 (97.7 ppm-wet), which also has the largest fuel-N content (0.32 %) among these fuels. Both heavy vacuum gas oils G1 and G2 caused lower emissions of NO\textsubscript{x} (91.1 and 80.3 ppm-wet, respectively).

The effect of the addition of sulphur on oxides of nitrogen at stoichiometric conditions is that of increasing emissions from all fuels investigated. This effect can be observed in Figures 137 and 138.

The increase of NO\textsubscript{x} emissions is largest for fuel M1, although it seems to stabilise after the initial
increase of 0.5% fuel-S. The maximum increase was 23.6 ppm-wet (24.2% of the initial SO\textsubscript{2} emissions) obtained on addition of 2% fuel-S.

Moderate increases of NO\textsubscript{X} were obtained from fuels G1 and G2. These were approximately 10 ppm-wet per 1% fuel-S added for fuel G1 and 3.5 ppm-wet per 1% fuel-S added to fuel G2.

It is worth mentioning the change of the relative amounts of NO and NO\textsubscript{2} found at stoichiometric conditions. Unlike at other equivalence ratios, significant amounts of both NO and NO\textsubscript{2} are formed at $\varphi = 1.000$. However, the percentages of NO and NO\textsubscript{2} vary as increasing amounts of fuel-S are added to the combustion environment. Emissions of NO decrease as those of NO\textsubscript{2} increase.

Figure 138 shows a graph of the [NO]/[NO\textsubscript{2}] ratio vs percentage of fuel-S addition.

The [NO]/[NO\textsubscript{2}] ratios was similar for fuels M1 and G2, ranging between 1.7 in air and 0.9 with addition of 2% S. Fuel G1 showed much lower ratios, between 0.3 and 0.1, denoting larger amounts of NO\textsubscript{2} than those of NO at all sulphur additions investigated.
3.3.3. Fuel-rich conditions (\(\varphi = 1.200\))

The effect of addition of sulphur to the combustion system at fuel-rich conditions is to increase \(\text{NO}_x\) emissions.

Emissions of \(\text{NO}_x\) were highest from fuel M1 (262 ppm-wet in combustion in air), whereas they were intermediate from fuel G1 (151 ppm-wet) and lowest from fuel G2 (119.1 ppm-wet).

Calculations of the percentage increase of \(\text{NO}_x\) emissions when \(\text{SO}_2\) was added to the combustion system yielded the results shown in Figure 141. This graph shows that maximum increases of \(\text{NO}_x\) emissions were presented by fuel M1, whose emissions increased by 15 % (39 ppm-wet) with addition of 2 % fuel-S. Intermediate increases of \(\text{NO}_x\) emissions were obtained from fuel G2 (11.4 %, ie 13.6 ppm-wet), whereas the lowest increases were obtained from fuel G1 (3.5 %, ie 5.4 ppm-wet).

Figure 140: Experimental readings of \(\text{NO}_x\) from experiments of sulphur addition from the fuels investigated at \(\varphi = 1.200\)

Figure 141: Percentage change of \(\text{NO}_x\) emissions at \(\varphi = 1.200\) from experiments of sulphur addition from the fuels investigated
3.4. \(O_2\)

The concentrations of residual oxygen were significant at fuel-lean conditions only (\(\phi = 0.833\)) as all oxygen supplied at other equivalence ratios was consumed. As a result, only fuel-lean conditions will be considered in this section.

3.4.1. Fuel-lean conditions (\(\phi = 0.833\))

A common feature observed in experiments with SO\(_2\) addition from all fuels was a decrease of the exit concentrations of oxygen as increasing amounts of sulphur dioxide were added. This effect can be observed in Figure 142.

A shortage of \(O_2\) added as compensation for the \(N_2\) balance can be ruled out as a reason for this decrease. Preliminary tests performed by injecting gas species (air, SO\(_2\), \(N_2\) and \(O_2\)) in the absence of combustion showed the concentration of oxygen not to change appreciably. It can be concluded that the decrease of oxygen concentrations is caused by the addition of SO\(_2\) to the combustion system.

The decrease of oxygen concentration with addition of SO\(_2\) was most accentuated from Orimulsion, with a decrease of 0.43 % per 1 % sulphur. It was intermediate for fuel M1 (0.3 % per 1 % S) and lowest for fuels G1 and G2 (0.11 and 0.16 % per 1 % S, respectively).
3.5. $SO_2$

3.5.1. Fuel-lean conditions ($\varphi = 0.833$)

In absence of $SO_2$-gas addition the amounts of sulphur dioxide formed in combustion are directly proportional to the sulphur content of the fuels. Thus, Orimulsion (2.90 % S, ie 4.14 % when compensated for its 30 % water content) produced 2,365 ppm $SO_2$. Fuel M1 (3.59 % S) generated 2,019 ppm; 1,014 ppm were formed from fuel G1 (1.74 % S), whereas 585 ppm of $SO_2$ were formed from fuel G2 (1.15 % S). The readings of $SO_2$ obtained in these experiments are shown in Figure 143.

As expected, the measured concentrations of $SO_2$ increase with the injection of $SO_2$-gas to the combustion system. Concentrations of $SO_2$ rose by an average 472 ppm with every 0.5 % fuel-S increase to Orimulsion. The increases were lower with the heavy gas oils investigated, between 316 and 363 ppm for each 0.5 % fuel-S increase, due to smaller additions of $SO_2$ being required to meet the percentage of fuel-S.

However, in all cases the increases of $SO_2$ concentrations were greater than the values estimated prior to experiments. Calculations showed that injection of 0.5 % fuel-S as $SO_2$ should cause an increase of 418 ppm from Orimulsion, whereas only 296 ppm are to be expected from heavy gas oils in fuel-lean conditions.

3.5.2. Stoichiometric conditions ($\varphi = 1.000$)

The values of $SO_2$ emissions measured in stoichiometric conditions in absence of dopant addition were higher than those in fuel-lean conditions, as would be expected due to lower amounts of combustion air being used. This can be observed in Figure 144.
For the same reason, it is foreseeable that addition of identical masses of SO$_2$ dopant would cause higher increases of the concentration of sulphur dioxide.

Calculations showed that the measured concentration of SO$_2$ should rise by 350 ppm with an increase of 0.5 % S dopant. However, the increases of SO$_2$ concentration measured on addition of sulphur dioxide were similar to those obtained in fuel-lean conditions and lower than calculated ones in most cases. Values of SO$_2$ emissions increased by an average 340 ppm for each 0.5 % fuel-S equivalent added.

3.5.3. Fuel-rich conditions ($\phi = 1.200$)

The concentrations of SO$_2$ measured in fuel-rich conditions were highest among all equivalence ratios considered.

However, increases of SO$_2$ emissions with increasing amounts of dopant, although slightly higher, remained similar to those in fuel-lean and stoichiometric conditions. The average increase of SO$_2$ emissions per 0.5 % fuel-S increase was 384 ppm, whereas calculations indicate that these should be increased by 414 ppm.

The disparity between these figures denotes that SO$_2$ may be reacting after injection into the combustion chamber. A possible explanation could be the reduction of SO$_2$ to other
sulphurous species, which was discussed in chapter III. Once again, this is substantiated by yellow solid deposits found in the exhaust system of the drop-tube furnace. Also, not all sulphur contained in the fuel is transformed into SO\textsubscript{2} during combustion in fuel-rich conditions. As shown in chapter III, the conversion of fuel-S into SO\textsubscript{2} decreases with the increase of the equivalence ratio.

3.6. \textit{N}_2\textit{O}

3.6.1. Fuel-lean conditions ($\varphi = 0.833$)

Addition of SO\textsubscript{2} dopant did not seem to have a large effect on N\textsubscript{2}O emissions from any of the fuels studied at fuel-lean equivalence ratio (see Figure 146).

Emissions from Orimulsion reached 14 ppm in absence of SO\textsubscript{2}, whereas 12.8 ppm were measured when the dopant was added. However, both values are within the range of instrumental error.

Other fuels studied showed lower emissions of N\textsubscript{2}O. Fuel M1 produced 4.6 ppm without addition of SO\textsubscript{2}. Fuel G\textsubscript{1} produced 4.9 ppm of N\textsubscript{2}O in similar conditions, whereas 5.4 ppm were formed from fuel G\textsubscript{2}. Minimum changes in N\textsubscript{2}O emissions were observed when SO\textsubscript{2} was added to the combustion of these fuels. Only fuel G\textsubscript{2} showed a somewhat significant decrease of 0.8 ppm on addition of 1 % fuel-S and greater.

3.6.2. Stoichiometric conditions ($\varphi = 1.000$)

Readings of N\textsubscript{2}O at stoichiometric conditions were negative from the three fuels studied. This is likely to be due to large amounts of CO formed in these conditions, which interact with the N\textsubscript{2}O gas analyser by lowering its output. Since the actual amounts of carbon
monoxide cannot be established as they lay were greater than the CO gas analyser detection limit (1 %), the real values of N$_2$O concentrations cannot be calculated. A graph showing all experimental readings of N$_2$O at stoichiometric conditions is shown in Figure 147.

The instrumental readings of N$_2$O decreased on addition of sulphur dopant in most cases. The rate of the decrease was inversely proportional to the initial sulphur content of the fuels. Thus, fuel M1 (3.59 % fuel-S) had its readings decreased from -5 ppm at a rate of 1.6 ppm per 1 % fuel-S added. Measurements from fuel G1 (2.20 % fuel-S) decreased from -26.9 ppm at a rate of 1.9 ppm per 1 % fuel-S added. Finally, values from fuel G2 (1.54 % fuel-S) decreased from -15.8 ppm at a rate of 2.8 ppm per 1 % fuel-S added.

However, the origin of these decreases remains unclear since the exact amounts of CO emitted are not known. Thus, the apparent decreases of N$_2$O may be due either to the direct action of SO$_2$ or to lower amounts of CO formed, also as a result of the addition of SO$_2$. Although the CO and N$_2$O gas analysers are equipped with a compensation setting, this is not sufficient to account for the interaction caused by very large amounts carbon monoxide, above 1 %.

3.6.3. Fuel-rich conditions ($\varphi = 1.200$)

The readings of N$_2$O at fuel-rich conditions showed a similar scenario to that at stoichiometric conditions. Moderate decreases were registered on addition of SO$_2$ from all fuels (approximately 3 ppm on addition of 2 % S as SO$_2$). However, as in stoichiometric conditions, the reason for the decrease has not been established as measurements of carbon monoxide exceeded the instrumental scale.
3.7. Summary of N-S interactions at various equivalence ratios

The qualitative effect of the addition of SO₂-gas on NOₓ emissions (as NO, NO₂ and total NOₓ) is summarised in the following Table:

<table>
<thead>
<tr>
<th>Equivalence ratio (φ)</th>
<th>NO</th>
<th>NO₂</th>
<th>Total NOₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.833</td>
<td>┴</td>
<td></td>
<td>┴</td>
</tr>
<tr>
<td>1.000</td>
<td>┴</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>1.200</td>
<td></td>
<td>↑</td>
<td>↑</td>
</tr>
</tbody>
</table>

Table 14: Qualitative effect of SO₂ addition on emissions of nitrogenous species at various equivalence ratios (font size denotes relative extent of interactions)

- NO emissions are decreased by SO₂, strongly at fuel-lean and less intensely at stoichiometric conditions, but emissions are negligible at fuel-rich conditions.

- NO₂ emissions are increased by SO₂, strongly at fuel-rich and stoichiometric conditions, but emissions are negligible at fuel-lean conditions.

- Total NOₓ emissions are strongly decreased at fuel-lean conditions, but increased at both stoichiometric and fuel-rich conditions, although more strongly in the latter conditions.

4. The location of sulphur-nitrogen interactions

The previous sections have shown that sulphur can appreciably modify the emissions of nitrogenous compounds. However, emissions are the final result of various different processes occurring in different conditions of temperature, stoichiometry and flow dynamics along the furnace duct. Therefore, a knowledge on where and to what extent sulphurous species are able to modify the concentrations of nitrogenous species along the combustion chamber is advisable.

The following set of experiments aimed at determining the location at which N-S interactions occur in the drop-tube furnace. Sampling of combustion gases from a heavy
coker gas oil was performed at selected probe positions and with and without the addition of 2 % S as SO$_2$-gas.

4.1. Experimental procedure

The experimental conditions were similar to those in previous paragraphs (see page 213 in this chapter). However, only the heavy coker gas oil M1 was burnt with and without the addition of 2 % S as SO$_2$-gas only (see “Appendix II”, page 265 for analyses of this fuel). This fuel was deemed to be representative of the family of heavy gas oils used in other sections of this thesis.

Sampling of the combustion gases was performed at various positions along the furnace duct, from 100 mm to 500 mm distance from the atomiser block in steps of 100 mm.

The handling of the experimental results was performed in a similar way to other sections. Graphs showing the concentrations of the various species measured at the points of sampling are presented in the following paragraphs.

4.2. Experimental results

4.2.1. NO

The concentrations of NO measured in these experiments decreased as the equivalence ratio increased. The formation and emission of nitric oxide was lowest in fuel-rich conditions, intermediate at stoichiometric and highest in fuel-lean conditions (see Figure 148), which agreed with other experimental results shown in this chapter and in chapter III.

The addition of sulphur caused decreases in the exhaust concentrations of NO in fuel-lean and stoichiometric conditions only. However, unlike in previous experiments of SO$_2$ addition, in this case the largest reduction of NO emissions was achieved at $\varphi = 1.000$. Addition of sulphur had almost no effect on NO emissions at $\varphi = 1.200$. 

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In fuel-lean conditions the decrease of NO concentrations caused by SO₂ addition starts at an early stage of the combustion process. Gas samples withdrawn at 100 mm from the atomiser nozzle already reveal a reduction of 9 ppm-wet with the injection of 2 % sulphur on an initial concentration of 152 ppm-wet. Although the concentration of nitric oxide increases subsequently up to a maximum of 266 ppm-wet, the reduction of NO caused by SO₂ addition remains almost invariable throughout the combustion process.

In stoichiometric conditions the decrease of NO concentrations occurs progressively. Sampling at 100 mm reveals no change with addition of SO₂. As combustion progresses downstream the concentration of NO rises to a maximum value at 300 mm, followed by a slight decrease and a new increase. Along the gas path SO₂ is able to reduce the concentration of NO by increasing amounts; eventually a decrease of 16 ppm-wet from 100 ppm-wet is achieved at 500 mm from the atomiser nozzle.

Fuel-rich conditions provide the environment for the lowest formation of nitric oxide. In these conditions the concentration of NO is maximum at 200 mm from the atomiser (67 ppm-wet), followed by a decline and the final emission of 11 ppm-wet. SO₂ modifies the concentration of NO only at the point of maximum concentration, and then only with a reduction of 7 ppm-wet. Experimental results at other sampling locations revealed no effect of sulphur on NO formation.
As reported in section "4.4.2. NO₂" of chapter III, the formation and emission of NO₂ was maximum in fuel-rich conditions, intermediate at stoichiometric and almost negligible in fuel-lean conditions. Such a pattern was obtained in the present experiments. Whenever formed, the effect of SO₂ addition was to increase the concentrations of NO₂. This can be seen in Figure 149.

At 0.833 equivalence ratio (fuel-lean) small amounts of NO₂ were formed at short distances from the atomiser nozzle (41 ppm-wet). However, it disappeared rapidly within the ensuing 100 mm. SO₂ increased NO₂ concentrations by 8 ppm-wet, but after 200 mm the amounts of NO₂ remaining were negligible and thus sulphur could no longer exercise any effect.

In stoichiometric conditions the formation and emission of NO₂ is significant. At the closest distance investigated (100 mm) 60 ppm-wet NO₂ were measured, but no S-N interaction was observed as sulphur was not able to modify that amount. The concentration of NO₂ decreased as the sampling probe was displaced away from the atomising nozzle, but the interaction with sulphur raised as sulphur addition increased the concentration of nitrogen dioxide at all other sampling locations. Eventually, emissions of NO₂ were raised by 7 ppm-wet, which represents 33% of the emissions without SO₂ addition.

The effect of sulphur is most intense at fuel-rich equivalence ratio. At 100 mm there is no difference in the amounts of NO₂ found with or without addition of SO₂. However, within the following 100 mm an increment of 23 ppm-wet was established by the addition of SO₂. More nitrogen dioxide is formed subsequently, but the increase of NO₂ con-
centration is sustained steadily up to the point of exhaust. NO₂ concentrations were increased by 26 ppm-wet from 247 ppm-wet on exhaust at \( \phi = 1.200 \).

4.2.3. \( NO_X \)

A graph of concentrations of \( NO_X \) measured at all equivalence ratios, selected sampling distances and sulphur addition is presented in Figure 150.

In fuel-lean conditions (\( \phi = 0.833 \)) there was a small 2 ppm-wet decrease in the concentration of NO₂ at short distances when SO₂ was added. This is the result of opposed effects encountered by NO and NO₂. Whilst nitric oxide is decreased by sulphur, nitrogen dioxide is increased. As the concentration of NO₂ falls at longer distances the decreasing effect of S on NO prevails. The final outcome was a moderate decrease of total \( NO_X \) of approximately 10 ppm-wet over a total 267 ppm-wet in absence of SO₂.

In stoichiometric conditions the final effect was similar, although it evolved at a later stage in the gas path. No net change in \( NO_X \) concentration was seen in the first 200 mm of the sampling path. At 100 mm there is no change in the concentrations of NO and NO₂ as an effect from SO₂ addition. Thereafter, sulphur decreases nitric oxide whereas nitrogen dioxide is increased. As the concentration of \( NO_X \) peaked and decreased at longer distances from the atomiser, both effects intensify. The result on \( NO_X \) is dictated by the larger decrease of NO. A decrease of 9 ppm-wet was measured on exhaust.

Marked increases of total \( NO_X \) concentrations were obtained in fuel-rich conditions, although not from the earliest stages investigated. Whereas a small decrease of 4 ppm-wet
was registered at 100 mm from the atomiser, a pronounced increase was obtained subsequently, mainly as a result of the large increase of NO₂ caused by the addition of sulphur dioxide.

5. Discussion

5.1. Fuel-lean conditions ($\phi = 0.833$)

The results shown in previous sections demonstrate that sulphur (as SO₂ in the experiments reported) is able to reduce the emissions of NOₓ under fuel-lean conditions. Emissions of NO were reduced, whilst those of NO₂ were low from all fuels except Orimulsion. However, nitrogen dioxide formed by the heavy gas oils was also detected in significant amounts at very short distances, and in this case it was increased to a similar extent as the decrease of NO concentrations.

![Figure 151: Nominal reduction of NO emissions at $\phi = 0.833$ from experiments of sulphur addition from all fuels investigated](image)

No large differences were found in the nominal reductions of the NO emissions from the heavy gas oils studied on addition of SO₂, which can be observed in Figure 151 (emissions from Orimulsion were reduced further and they will be discussed in subsequent paragraphs). However, the fuels have very different fuel-N and -S contents. No correlation seems to exist between these and the decreases achieved. This suggests that the interaction of S with NO occurs at a stage or by a mechanism which is independent from the amounts of sulphur and nitrogen in the fuel and also of the amounts of NO formed, but somehow dependent on the amount of dopant added. Also, experimental results shown in Figure 148 indicate that the interference of S with NO occurs before 100 mm from the atomiser nozzle, where the concentration of NO was decreased by 9 ppm-wet on addition of SO₂.

It was postulated in section “5.1.1. Formation of NO at short distances” that NO was formed at short distances predominantly via the fuel-NO mechanism. In addition, Figure

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148 shows that the presence of sulphur is not able to modify the concentration of NO in later stages of the flame at $\varphi = 0.833$.

Experimental measurements also indicate that a certain proportion of the sulphur dioxide injected as dopant at $\varphi = 0.833$ is not detected in the early stages of the fuel-air atomisation stage. This is demonstrated by the increase of SO$_2$ concentrations at 100 mm from the atomiser when SO$_2$ dopant is added, which is significantly lower than that at longer distances. This suggests that SO$_2$ is recombined shortly after injection and regenerated at longer distances.

No one single mechanism so far proposed in the literature reviewed, which is summarised in section “4.3. Interactions between S and N species: Their effect on NO$_x$ formation and emission” of chapter I, can justify the experimental results obtained in the drop-tube furnace. It is likely that they are the outcome of various processes operating concurrently.

In the early stages of the (fuel - atomisation air) cone, fuel-rich pockets may be formed in which SO$_2$ may be reduced to other sulphurous species. These reduced sulphur species may reduce the concentrations of nitric oxide via reactions such as those proposed by Chagger et al. $^{26}$:

$$\text{SH} + \text{NO} \rightarrow \text{SO} + \text{NH}$$  
$$\text{SH} + \text{NO} \rightarrow \text{S} + \text{HNO}$$  
$$\text{SH} + \text{NO} \rightarrow \text{NS} + \text{OH} \rightarrow \text{NS} + \text{NO} \rightarrow \text{N}_2 + \text{SO}$$  
$$2 \text{NS} \rightarrow \text{N}_2 + \text{S}_2$$

A peculiar feature of the experimental results obtained at $\varphi = 0.833$ is an increase of NO$_2$ concentrations concurrent with the decrease of nitric oxide, as shown in Figure 149. However, the final emissions of NO$_2$ in fuel-lean conditions were negligible as it disappears after 200 mm from the atomiser nozzle. The nominal increase of NO$_2$ concentrations is similar to the reduction of the amounts of NO, which may suggest a relationship between both events.
NO\textsubscript{2} is a nitrogenous compound that has traditionally been overlooked in studies of N-S interactions, even in systems where its formation is likely. A very small number of reports have investigated the interconversion of NO and NO\textsubscript{2} aided by sulphur compounds.

Armitage and Cullis\textsuperscript{13} proposed a mechanism for the simultaneous decrease of NO and increase of NO\textsubscript{2}. At low NO concentrations its oxidation proceeds through reaction with SO\textsubscript{2} to form NO\textsubscript{2} and SO\textsubscript{3}:

\[
\text{NO} + \text{O}_2 \rightleftharpoons \text{NO}_3 \quad 74
\]

which is a transient stage, followed by

\[
\text{NO}_3 + \text{SO}_2 \rightleftharpoons \text{NO}_2 + \text{SO}_3 \quad 75
\]

implying the disappearance of NO and SO\textsubscript{2} and the formation of NO\textsubscript{2} and SO\textsubscript{3}. According to Lyon et al.\textsuperscript{85}, the optimum temperature range for these reactions seems to be between 700 and 900 °C. This range of flame temperatures can be encountered in the injection zone of the drop-tube furnace.

Sulphur trioxide could be transformed to SO\textsubscript{2} subsequently by means of the reaction

\[
\text{SO}_3 \rightleftharpoons \text{SO}_2 + \frac{1}{2} \text{O}_2 \quad 51
\]

which is known to be displaced to the right at temperatures above 1,000 °C\textsuperscript{34}.

Formation of SO\textsubscript{3} could partly explain the reduction of the concentration of oxygen observed on addition of SO\textsubscript{2} in fuel-lean conditions. The decrease is more sustained and pronounced for Orimulsion, which also presents the highest concentrations of residual O\textsubscript{2} among all fuels investigated at $\phi = 0.833$.

The reduction of NO and the increase of NO\textsubscript{2} concentrations in fuel-lean conditions could also be explained in terms of the radical recombination originated by SO\textsubscript{2}.\textsuperscript{136,152}
which takes place according to the following reactions (a complete mechanism is shown on page 86):

\[
X + SO_2 + M \rightleftharpoons XSO_2 + M \quad 60
\]

\[
X + YSO_2 \rightleftharpoons SO_2 + XY \quad 61
\]

where \(X = O, OH\) or \(H\) and \(Y = O\) or \(H\).

As a result, the concentrations of both \(OH\) and \(H\) radicals will decrease. The formation of \(NO\) via the fuel-\(NO\) mechanism is thus depleted in the early stages by the lower amounts of \(OH\) radicals. Conversely, \(NO_2\) formed at low temperatures by reaction of \(NO\) with \(HO_2\) or \(RO_2\) radicals will be increased as the \(H\) radicals necessary for its reduction are removed by \(SO_2\).

Reductions of \(NO\) concentrations in zones of high superequilibrium concentrations were also explained by Tseregounis and Smith \(^{135}\) in terms of radical recombination, which can alter the amine reaction subsystem:

\[
NH_i + X \rightleftharpoons NH_{i+1} + HX \quad 97
\]

where \(X: O, H, OH\) and \(i: 1, 2, 3\), by removing \(X\) radicals. This would shift the balance of this reaction to the left. \(NO\) formation would be impeded as it is formed from \(N\) (less \(N\) radicals would be formed), and \(NO\) recombination would be promoted as it forms \(N_2\) with \(NH_i\) via reaction 87 (more \(NH_i\) radicals would be available).

Chen \textit{et al.} \(^{27}\) found large decreases of \(OH\) radicals when \(SO_2\) was added to a propane flame. The decrease of \(OH\) concentrations was most accentuated under fuel-lean conditions. Durie \textit{et al.} \(^{41}\) reviewed the feasibility of the recombination of \(OH\) radicals by \(SO_2\) by reactions:

\[
OH + SO_2 + M \rightleftharpoons HOSO_2 + M \quad 98
\]

\[
HOSO_2 + OH \rightleftharpoons H_2O_2 + SO_2 \quad 99
\]
but deemed it to be unlikely in C\textsubscript{2}H\textsubscript{8} fuel-rich flames as the product, H\textsubscript{2}O\textsubscript{2}, is unstable. However, enhanced H\textsubscript{2}O\textsubscript{2} concentrations in the drop tube furnace could lead to higher HO\textsubscript{2} concentrations (for instance, by reaction of H\textsubscript{2}O with oxygen or OH radicals\textsuperscript{153}). This could, in turn, promote the formation of NO\textsubscript{2} in the early stages of the combustion process, where the temperature is still low.

In addition to the heavy gas oils, Orimulsion was studied under fuel-lean conditions. The reduction of NO emissions from this fuel was much larger than that from the heavy gas oils. This suggests that the mechanism for NO removal is greatly affected by the presence of water from the fuel or by the inherent characteristics of this heavy fuel. However, the addition of sulphur did not cause, in this case, an increase of the emissions of NO\textsubscript{2}.

Although in small amounts, it has been suggested that the introduction of water in a combustion system leads to the enhanced production of OH radicals by means of\textsuperscript{39}:

$$\text{H}_2\text{O} + \text{H} \leftrightarrow \text{H}_2 + \text{OH}$$

$$\text{H}_2\text{O} + \text{O} \rightarrow \text{OH} + \text{OH}$$

This would lead to lower concentrations of H and O radicals, as the higher amounts of OH radicals displace the radical pool in such a direction. Higher concentrations of OH could be counteracted partly by recombination by SO\textsubscript{2}. However, this would lead to increased concentrations of NO\textsubscript{2}, which did not occur. If H and O radicals are more effective than OH in the formation of NH\textsubscript{3} and NO, respectively, their recombination could cause a larger proportional effect on those species.

Decreases of OH radical concentrations have been observed by Tang \textit{et al.}\textsuperscript{130} in fuel-lean hexane flames doped with pyridine and S as tertiary butyl mercaptan. Reduced OH concentrations accounted for reductions in the concentrations of nitric oxide.

N\textsubscript{2}O emissions were also measured at $\varphi = 0.833$. Orimulsion generated higher emissions of nitrous oxide than the heavy oils, but addition of SO\textsubscript{2} did not have a marked effect on them from any of the fuels studied.
5.2. Stoichiometric conditions ($\varphi = 1.000$)

In general, the emissions of NO were observed to decrease under stoichiometric conditions. Again the reductions achieved in this case bore no relation with the S or N contents of the fuels. However, the reductions were proportional to the amounts of S dopant added, as presented in Figure 152. Although the nominal reductions were lower than in fuel-lean conditions, the percentage reductions were larger as less NO is formed initially.

Increases in the measured concentrations of SO$_2$ when increasing amounts of dopant were added were lower than those calculated from the flow of SO$_2$ dopant, as sulphur dioxide was reduced to other species in this oxygen-deficient conditions.

Experiments showed no change of NO concentrations at 100 mm (see Figure 148). The interaction of sulphur with NO$_x$ species occurs later in the gas path, with concentrations of NO decreasing gradually after 100 mm, and increases of those of NO$_2$. The extent of both interactions was different as NO$_2$ was increased to a larger extent than NO was reduced. This may show that the mechanisms for NO formation and NO$_2$ disappearance apply separately. Figure 139 shows the change of the [NO]/[NO$_2$] ratio with increasing amounts of SO$_2$ under stoichiometric conditions. Whilst NO$_2$ is reduced by reaction with H radicals, NO is formed in reactions with O and OH radicals. As the amounts of SO$_2$ increase NO will be prevented from being formed to a larger extent whereas NO$_2$ will be not reduced. As a result, the ratio [NO]/[NO$_2$] will decrease.

Figures 148 and 149 show that the reduction of NO and the increase of NO$_2$ concentrations occur gradually along the flame path. As the formation of fuel-NO is delayed in
lower concentrations of oxygen than those at $\varphi = 0.833$, the radical recombination by $\text{SO}_2$ acts by withdrawing H and OH radicals.

Tseregounis and Smith point out that NO can be reduced to $\text{N}_2$ by the action of amine species. Withdrawal of H radicals by means of $\text{SO}_2$ addition would result in lower amounts of $\text{N}$ radicals and higher amounts of $\text{NH}_3$ radicals.

In a similar way the increase of $\text{NO}_2$ concentrations can be explained by the radical recombination assisted by $\text{SO}_2$. $\text{NO}_2$ is known to disappear by reaction with radicals such as O and H, although the amount of O radicals is expected to be low in these conditions. Thus, further reduced concentrations of these radicals will lead to higher concentrations of $\text{NO}_2$.

5.3. Fuel-rich conditions ($\varphi = 1.200$)

Under fuel-rich conditions the emissions of total-$\text{NO}_x$ were observed to increase on addition of $\text{SO}_2$. This was due to the increase of $\text{NO}_2$ emissions, as those of NO were unaltered by the inclusion of the sulphur dopant.

Another effect observed under fuel-rich conditions was a lower increase of the measured concentrations of sulphur dioxide than those calculated. This is due to the transformation of $\text{SO}_2$ to other reduced sulphur species in this oxygen-deficient environment (see page 181 for a graph detailing the distribution of sulphur species according to the equivalence ratio).

The emissions of NO were low from all fuels studied. However, a better understanding of the influence of sulphur on nitric oxide is given by the sampling at various distances from the atomiser, as shown in Figure 148 in page 231. $\text{SO}_2$ affected NO only at and around 200 mm distance, where it is still undergoing formation or is reaching its maximum concentration. The concentration of nitric oxide was reduced by 7 ppm-wet at 200 mm distance. For the next 100 mm $\text{SO}_2$ reduced the rate at which NO disappeared.
Only a very limited number of papers studied the interaction of sulphur with NO in fuel-rich hydrocarbon flames have been published. In most cases, the effect reported was that of increasing NO concentrations by adding sulphur. Such is the case of the report by Corley and Wendt. Although the equivalence ratios studied were higher than those considered in this thesis (φ = 1.74 and 2.18), they reported a large increases of NO concentrations from methane flames which used Ar as a diluent. Decreases of NO concentrations were observed only when Ar was replaced by He (N2 was the diluent in the drop tube furnace, which has similar heat transfer properties to He). However, the concentrations of CO2 were observed to rise with SO2, whereas they decreased in the drop tube furnace.

Similar results obtained by other researchers were attributed to reactions of NO with reduced sulphur species such as SH (Chagger et al. or a shift in the amine subsystem on reduction of radicals by SO2 (Chen et al.).

Enhancement of NO2 in the presence of hydrocarbon species has been documented previously, and is discussed in section “5.1.3.c. Fuel-rich conditions (φ = 1.200)” of chapter III. However, no previously published report has been found on the effect of SO2 on NO2 in fuel-rich, hydrocarbon systems. Two possible processes may be altered in order to cause the increment of NO2 concentrations measured (see Figure 149):

a. The enhancement of radical species that form NO2, such as HO2 or RO2

b. The withdrawal of H radicals that contribute to the disappearance of NO2, possibly by SO2 radical recombination.

Interaction between hydrocarbons and S and N species were also studied by Corley and Wendt in the report previously mentioned. In fuel-rich conditions they observed a certain degree of interference between nitrogen and sulphur compounds and soot, as soot particles analysed contained amounts of nitrogen. The amounts of soot collected decreased on addition of SO2. Experimental results on Orimulsion combustion at φ = 1.200 obtained concurrently to this experimental work showed a decrease of solid matter.
emissions with the addition of SO$_2$, which confirms the existence of interactions between S and hydrocarbon species. In stoichiometric and fuel-rich conditions the measured concentrations of CO$_2$ decreased on addition of SO$_2$, as can be observed in Figure 153. This may suggest that combustion is less complete in the presence of SO$_2$. Reduced sulphur species and carbon monoxide may compete for oxidising compounds in this oxygen-deficient atmosphere. As the amounts of CO$_2$ decrease, those of carbon monoxide and remaining hydrocarbons will therefore increase. It is also likely that the concentrations of hydroperoxyl radicals (RO$_2$) will also rise, thus increasing the concentrations of NO$_2$. However, more information about the process of NO$_2$ formation by RO$_2$ radicals must be known before a thorough rationale could be established. Although a number of papers have been published about this process at low temperature, no information is available at the temperatures found in combustion operation.

A practical application that could be derived from the enhancement of NO$_2$ concentrations by sulphur is that it may facilitate NO$_x$ removal, as nitrogen dioxide can be removed by the same scrubbers that remove sulphur compounds from combustion gases.

6. Conclusions

1. The effect of SO$_2$ on NO$_x$ emissions was reported in paragraph “3.7. Summary of N-S interactions at various equivalence ratios”, and extended here:

a. NO emissions are decreased by SO$_2$, more strongly under fuel-lean than under stoichiometric conditions; emissions of NO are negligible under fuel-rich conditions;
i. In fuel-lean conditions the decrease of NO concentrations caused by SO₂ occurs at an early stage of the combustion process, and remains invariable subsequently. It was thought that this is the outcome of the combined action of intercombination of SO₂ and NO₃ to form SO₂ and NO₂, a shift of the amine subsystem by radical recombination and, to a lesser extent, direct reactions with reduced S species.

ii. In stoichiometric conditions the reduction of NO concentrations occurs progressively along the combustion path. Lower amounts of radicals available after radical recombination can cause a decrease of NO concentrations. Also, the amine subsystem is expected to be altered by reaction with reduced S species.

iii. Under fuel-rich conditions the concentrations of nitric oxide are reduced by SO₂ locally at the point of maximum NO concentration, and then only to a very small extent.

b. NO₂ emissions are increased by SO₂, strongly under fuel-rich and stoichiometric conditions, but its emissions are negligible under fuel-lean conditions:

i. Under fuel-lean conditions SO₂ increased the measured concentrations of NO₂ at short residence times, but disappeared subsequently. The increases may be explained by the reaction of NO₃ with SO₂ to form NO₂, and the radical recombination that slowed the NO₂ reduction reactions. In addition, enhanced concentrations of HO₂ radicals caused by the recombination of OH radicals may promote the formation of NO₂.

ii. At φ = 1.000 a gradual increase of NO₂ concentrations was seen along the combustion path. Lower amounts of radicals can act by depleting NO and promoting NO₂.

iii. The concentration of NO₂ was drastically increased by sulphur dioxide in fuel-rich conditions at a given distance from the atomiser nozzle, but no further effect was recorded thereafter. Higher concentrations of NO₂ may be due to
lower amounts of radicals available for its reduction or to enhanced concentrations of HO₂ or hydroperoxyl radicals (RO₂) caused by SO₂. Sulphur dioxide was seen to interact with hydrocarbons present in the system, which may substantiate the presence of larger concentrations of RO₂ radicals.

c. Total-NOₓ emissions are strongly decreased under fuel-lean conditions, but increased at both stoichiometric and fuel-rich conditions, although more strongly in the latter conditions:

i. In fuel-lean conditions Orimulsion showed the largest reduction of NOₓ emissions, whereas the heavy gas oils had similar nominal reductions regardless their fuel-N and -S contents. The water contained in the Orimulsion fuel and the radical recombination caused by SO₂ are thought to play an important role in this feature.

ii. In stoichiometric conditions the ratio \([NO]/[NO₂]\) decreases on addition of SO₂, signalling enhanced transformation of NO into NO₂.

iii. Emissions of total-NOₓ were largely enhanced under fuel-rich conditions due to increased NO₂ emissions.

2. The amounts of residual oxygen were seen to decrease on addition of SO₂ in fuel-lean conditions. This may be due to the transformation of SO₂ into SO₃ in conditions of excess oxygen. The decrease was most accentuated for Orimulsion as larger amounts of SO₂ were added.

3. At \(\varphi = 1.000\) and 1.200 the exhaust concentrations of SO₂ were lower than calculated from the amounts of SO₂-dopant added, which indicates that SO₂ is recombined into reduced S species in conditions of low oxygen availability. This is confirmed by yellow sulphur deposits on the injection probe.

4. Addition of SO₂ did not seem to have an effect on the emissions of N₂O at \(\varphi = 0.833\) from any of the fuels investigated. However, at other equivalence ratios they de-
creased as higher concentrations of CO were caused by the addition of sulphur diox-
ide and the competition for oxidising species with CO₂.
CONCLUSIONS

The results reported in this thesis have provided further information about the processes of formation of oxides of nitrogen from the nitrogen contained in fuels during combustion and their interaction with sulphur, also originated from the fuel. Although a significant number of studies has been made previously with respect to thermal-NOX, the literature review carried out found very few reports on the interaction of both groups of species when they originate from the fuel. The literature survey also covered related topics of the combustion of heavy liquid fuels for power generation, such as NOX, SOX, ash, particulate formation and the use of gas turbines for the generation of electricity.

A number of heavy distillate gas oils, in addition to Orimulsion, have been studied. The former fuels are by-products of refining operations (vacuum distillation and delayed coking), and contain varying amounts of nitrogen and sulphur. Orimulsion also contains 30 % water by weight.

In the first part of the experimental work, the ignition characteristics of the range of heavy distillate fuels studied were investigated with the single suspended droplet technique. The fuels were found to comply with the correlations that relate the ignition properties of a fuel droplet to its initial dimensions. However, no direct correlation was found between their pre-ignition delays and the data available for their distillation ranges. The groups of fuels studied (heavy vacuum gas oils and heavy coker gas oils) were also found to have different ignition temperatures. The single suspended droplet technique also helped determine other characteristics of their combustion, such as large soot formation, absence of coke particulates, or the size variation of fuel droplets prior to ignition, the latter assisted by video recordings.

In the next part of the experimental work, the formation of pollutants from two selected heavy distillate fuels was studied in the drop-tube furnace. This study was performed at various conditions of stoichiometry, furnace wall temperature and residence time. Oxides of nitrogen were found to be formed by the fuel-NOX mechanism in amounts that varied with the flame temperature, the equivalence ratio and the distance from the atomiser. The thermal-NOX and prompt-NOX mechanisms were considered to be of lesser importance.
The concentrations of NO detected were maximum under fuel-lean conditions, decreased in stoichiometric mixtures, and reached a minimum under fuel-rich conditions. Conversely, large amounts of nitrogen dioxide were detected in stoichiometric and especially fuel-rich conditions, but not under fuel-lean conditions. Hydroperoxyl radicals were thought to have a significant role in the formation of NO$_2$ under stoichiometric and fuel-rich conditions. SO$_2$ was the most important sulphur combustion product and accounted for almost 100% of the total sulphur in fuel-lean conditions. However, in oxygen-deficient, fuel-rich conditions, SO$_2$ was transformed into other reduced sulphur species.

The preliminary information thus obtained about NO$_X$ and SO$_X$ formation was instrumental in choosing criteria for the subsequent study of fuel-N and -S interactions. It also provided experimental data for the validation of the numerical model used to study these interactions. The formation of negligible amounts of thermal-NO$_X$ was confirmed with the use of a low-nitrogen diesel fuel. Also, information about the axial flame temperature was obtained by performing thermocouple traverse measurements.

Numerical simulation was performed with the CHEMKIN suite of FORTRAN codes. Two flow regimes in the furnace were simulated by different codes, namely “PSR” for the initial short CSTR zone and “CONP” for the subsequent long PFR zone. The reaction system comprised reactions for the three NO$_X$ formation mechanisms, i.e., fuel, thermal and prompt. The model was able to reproduce the experimental results of NO and NO$_2$ emissions at fuel-lean equivalence ratios. However, at stoichiometric or fuel-rich conditions the model failed to simulate the experimental measurements. It was thought that significant reactions for the formation of NO$_2$ in these conditions were absent from the model. The reduction of SO$_2$ under fuel-rich conditions, previously found in experiments, was also reproduced by the model.

Finally, the interaction of fuel-sulphur with oxides of nitrogen originating from the fuel-N content were investigated both experimentally and numerically. Orimulsion was included in this study. Experiments were performed with increased amounts of fuel-S simulated by the addition of SO$_2$-gas. The extent and direction of the interactions depended on the amount of sulphur dopant, the equivalence ratio and the residence time in the combustor. Addition of SO$_2$-gas yielded reductions of NO and increases of NO$_2$ concentrations at
short residence times under fuel-lean conditions. The reduction of NO emissions was particularly effective in Orimulsion. Possible mechanisms include radical recombination, direct N-S interactions and interconversion of NO and SO\textsubscript{2} to yield NO\textsubscript{2} and SO\textsubscript{3}. Reductions of fuel-NO\textsubscript{x} at fuel-lean conditions were also calculated by the numerical model, and the results were most accurate for Orimulsion. The emissions of NO\textsubscript{2} were largely increased in fuel-rich conditions by addition of SO\textsubscript{2}. Recombination of H radicals by SO\textsubscript{2} can act by preventing the disappearance of NO\textsubscript{2}. Also, SO\textsubscript{2} was found to interact with hydrocarbons present in the system, which may be related to increased efficiency of the formation of NO\textsubscript{2} by hydroperoxyl radicals.

_Further work proposed_

Further work to continue that reported in this thesis could comprise the effect of flame temperature on N-S interactions, as the experiments reported in this work were confined to one value of the furnace wall temperature. Detailed measurements of the flame temperature in the first 200 mm of the furnace and at higher furnace wall temperatures would also be beneficial for the numerical model.

The study of fuels of a heavier nature than those in this thesis may also provide useful information. Residual fuels may present a larger potential for NO\textsubscript{x} reduction by SO\textsubscript{x}, as the release of nitrogen during combustion is progressive.

Although SO\textsubscript{2} is the major sulphur combustion product, sulphur in fuel is normally in its reduced state. Experiments with addition of sulphur as H\textsubscript{2}S or as an organic additive to the fuel, under similar conditions to those investigated in this thesis could provide comparative information and further insight into their interactions with fuel-NO\textsubscript{x}. The analysis of gas samples for reduced sulphur species formed at stoichiometric and fuel-rich conditions could be instrumental at quantifying the reduction of sulphur dioxide in such conditions.

Since the numerical model was not able to reproduce experimental results obtained under stoichiometric and fuel-rich conditions, an extension including larger species and reactions of hydroperoxyl radicals (RO\textsubscript{2}) would be useful to widen its range of applicability.
APPENDIX I: LIST OF REFERENCES


25. CERNANSKY N.P., SAWYER R.F. 1974. NO and NO\textsubscript{2} formation in a turbulent hydrocarbon/air diffusion flame. *15\textsuperscript{th} Symposium (International) on Combustion*. The Combustion Institute, Pittsburgh (USA), 1,039-1,050.

26. CHAGGER H.K., GODDARD P.R., MURDOCH P., WILLIAMS A. 1991. Effect of SO\textsubscript{2} on the reduction of NO\textsubscript{X} by reburning with methane. *Fuel*, **70**, 1,137-1,142.


32. COURTEMANCHE B., LEVENDIS Y.A. 1997. NO-NO\textsubscript{2} emissions from the combustion of solid fuels. *Proceedings of the 22\textsuperscript{nd} International Technical Conference on Coal Utilisation & Fuel Systems*, Clearwater (USA), 827-838.

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49. GILLS BG. 1973. Production and emission of solids, SO\textsubscript{X} and NO\textsubscript{X} from liquid fuel flames. *Journal of the Institute of Fuel*, 46, 71-76.


106. NIMMO W., HAMPARTSOUMIAN E., SEDIGHI K., WILLIAMS A. 1991. Control of NO\textsubscript{x} emissions by combustion-air staging: the measurement of NH\textsubscript{3}, HCN, NO and N\textsubscript{2}O concentrations in fuel-oil flames. *Journal of the Institute of Energy*, 64, 128-134.


110. PFEFFERLE L.D., CHURCHILL S.W. 1986. NO\textsubscript{x} production from the combustion of ethane doped with ammonia in a thermally stabilised plug flow burner. *Combustion Science and Technology*, 49, 235-249.


120. SINGH P.P., MULIK P.R., COHN A. 1983. Effect of using emulsions of high N containing fuels and water in a gas turbine combustor on NO\textsubscript{X} and other emissions. *Journal of Engineering for Power*, 105, 430-437.


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139. URBAN D.L., DRYER F.L. 1990. Relationship of the Coke Formation Index to heavy fuel oil properties. *Joint Meeting of the Western States and Canadian Section of the Combustion Institute*, The Combustion Institute, Banff (Canada), 1-5.


153. ZAMANSKY V. M., HO L., MALY P.M., SEEKER W.R. 1996. Gas phase reactions of hydrogen peroxide and hydrogen peroxide/methanol mixtures with air pol-
**APPENDIX II: ANALYSES OF THE FUELS USED IN THIS THESIS**

<table>
<thead>
<tr>
<th>Analysis</th>
<th>M1</th>
<th>M2/M3</th>
<th>G1</th>
<th>G2</th>
<th>G3/G4/G5</th>
<th>Orimulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density @ 15 °C, kg/l</td>
<td>0.9627</td>
<td>0.9644</td>
<td>0.9114</td>
<td>0.8869</td>
<td>0.9214</td>
<td>--</td>
</tr>
<tr>
<td>Viscosity @ 40 °C, cSt</td>
<td>31.72</td>
<td>56.49</td>
<td>--</td>
<td>--</td>
<td>71.80</td>
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</tr>
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<td>Viscosity @ 100 °C, cSt</td>
<td>4.73</td>
<td>6.51</td>
<td>8.30</td>
<td>10.10</td>
<td>7.60</td>
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</tr>
<tr>
<td>Gross calorific value, MJ/kg</td>
<td>42.58</td>
<td>44.36</td>
<td>44.70</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Net calorific value, MJ/kg</td>
<td>40.69</td>
<td>42.94</td>
<td>43.37</td>
<td>--</td>
<td>30.40</td>
<td>--</td>
</tr>
<tr>
<td>Flammability point, °C</td>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Nitrogen, ppm</td>
<td>3.231</td>
<td>4.100</td>
<td>1.300</td>
<td>600</td>
<td>1,619</td>
<td>4,000</td>
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<tr>
<td>Sulphur, % by weight</td>
<td>3.59</td>
<td>3.07</td>
<td>1.74</td>
<td>1.10</td>
<td>1.504</td>
<td>2.90</td>
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<td>Carbon, % by weight</td>
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<td>85.43</td>
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<tr>
<td>Hydrogen, % by weight</td>
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<td>--</td>
<td>11.71</td>
<td>11.83</td>
<td>--</td>
<td>6.50</td>
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<td>Water, % by weight</td>
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<td>--</td>
<td>--</td>
<td>--</td>
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<td>29.8</td>
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<tr>
<td>C/H ratio</td>
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<td>--</td>
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<td>--</td>
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<tr>
<td>Aromatic carbon, %</td>
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<td>23.40</td>
<td>--</td>
<td>--</td>
<td>32.99</td>
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<td>Asphaltene content, % by weight</td>
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<td>0.10</td>
<td>0.00</td>
<td>0.00</td>
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<td>Ash content, % by weight</td>
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<td>0.0014</td>
<td>0.0014</td>
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<td>Conradson residue, % by weight</td>
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<td>0.18</td>
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<td>Ramsbottom residue, % by weight</td>
<td>--</td>
<td>0.54</td>
<td>--</td>
<td>--</td>
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<tr>
<td>Metals, ppm</td>
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</tr>
<tr>
<td>Iron</td>
<td>2.7</td>
<td>0.14</td>
<td>--</td>
<td>--</td>
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</tr>
<tr>
<td>Nickel</td>
<td>&lt;0.2</td>
<td>0.20</td>
<td>--</td>
<td>--</td>
<td>1.90</td>
<td>--</td>
</tr>
<tr>
<td>Vanadium</td>
<td>&lt;0.2</td>
<td>0.30</td>
<td>--</td>
<td>--</td>
<td>3.60</td>
<td>460</td>
</tr>
<tr>
<td>Magnesium</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>734</td>
</tr>
<tr>
<td>Sodium</td>
<td>5.2</td>
<td>0.14</td>
<td>--</td>
<td>--</td>
<td>1.70</td>
<td>48</td>
</tr>
<tr>
<td>Distillation range, °C</td>
<td></td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Initial point</td>
<td>253</td>
<td>345</td>
<td>--</td>
<td>--</td>
<td>260</td>
<td>--</td>
</tr>
<tr>
<td>5 % vol</td>
<td>325</td>
<td>351</td>
<td>--</td>
<td>--</td>
<td>317</td>
<td>--</td>
</tr>
<tr>
<td>10 % vol</td>
<td>346</td>
<td>382</td>
<td>--</td>
<td>--</td>
<td>346</td>
<td>--</td>
</tr>
<tr>
<td>20 % vol</td>
<td>376</td>
<td>409</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>30 % vol</td>
<td>390</td>
<td>418</td>
<td>--</td>
<td>--</td>
<td>406</td>
<td>--</td>
</tr>
<tr>
<td>40 % vol</td>
<td>405</td>
<td>430</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>50 % vol</td>
<td>419</td>
<td>437</td>
<td>--</td>
<td>--</td>
<td>441</td>
<td>--</td>
</tr>
<tr>
<td>60 % vol</td>
<td>433</td>
<td>443</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>70 % vol</td>
<td>449</td>
<td>451</td>
<td>--</td>
<td>--</td>
<td>484</td>
<td>--</td>
</tr>
<tr>
<td>80 % vol</td>
<td>465</td>
<td>464</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>90 % vol</td>
<td>489</td>
<td>477</td>
<td>--</td>
<td>--</td>
<td>568</td>
<td>--</td>
</tr>
<tr>
<td>95 % vol</td>
<td>514</td>
<td>488</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Final point</td>
<td>522</td>
<td>500</td>
<td>--</td>
<td>--</td>
<td>581</td>
<td>--</td>
</tr>
</tbody>
</table>

These analyses, except those for Orimulsion, were provided by Repsol Petróleo S.A. and performed according to the following standard practices:

(1) Density: ASTM-D-4052
(2) Viscosity: ASTM-D-445 a
(3) Gross calorific value and net calorific value: ASTM-D-240
(4) Flammability point: ASTM-D-93
(5) Sulphur content: ASTM-D-4924
(6) Asphaltene content: IP 143
(7) Ash content: ASTM-D-4530
(8) Conradson Residue: ASTM-D-189
(9) Distillation range: ASTM-D-1160

Analyses of Orimulsion were provided by National Power plc.
The abbreviated designations correspond to the following samples provided by Repsol Petróleo S.A.:
M1 = M-013/95
M2 = GOPK B 58/91
M3 = GOPC B 54/93
G1 = GOPV B 48/93
G2 = GOPV B 51/93
G3 = GOPV B 74/91
G4 = GOPV B 49/93 (mayoritariamente maya)
G5 = GOPV B 52/93 (minoritariamente maya)
APPENDIX III. REACTION MECHANISM USED IN THE NUMERICAL MODEL

The following is a description of the chemical scheme used in the numerical model reported in chapter VI.

Elements:

C  H  N  O  S

Species:

H₂ H₂O HO₂ OH CH CH₂ CH₂(S) CH₃ CH₄ C₂H C₂H₂ C₂H₃ C₂H₄ C₂H₅ C₂H₆ C₃H₂ C₃H₃ C₄H₂ C₄H₃ HCO CH₂O CH₂O HCO HCCO HCOH CH₂CO CH₂OH CO CO₂ O₂ HCN HNO H₂O₂ HCN H₂CN NH CN C₂N₂ NCO COS CS SO SO₂ SO₃ SH H₂S HSO₂ SN

CH₂(S) stands for the singlet form of CH₂.

The Sandia thermodynamic data-base does not include reaction rate coefficients for HSO₂. They are necessary to calculate the various thermodynamic parameters used in the model. Such data was taken from Zachariah and Smith¹², and their values are:

\[ A₁ = 4.081 \quad A₂ = 8.375 \times 10^{-3} \]
\[ A₃ = -4.722 \times 10^{-6} \quad A₄ = 9.349 \times 10^{-10} \]
\[ A₅ = 0 \quad A₆ = -31.56 \]
\[ A₇ = 8.610 \]

Reactions:

The reactions included in the mechanism are listed below.

The mechanism described includes some reactions with third-body efficiency ⁵⁵, denoted by the inclusion of a so-called M reactant. For such reactions lines are included that identify the elements that may act as third bodies. Their corresponding efficiency coefficients are given.

The Arrhenius parameters of the reactions were provided for calculation of the reaction rate coefficients by the numerical simulation package in the form:

\[ K_r = A T^n \exp\left(-\frac{E}{RT}\right) \]
In the case of reactions 254, 255 and 256, different values of the Arrhenius parameters have been published. Since CHEMKIN allows the use of both sets of values, duplicate reactions have been declared.

<table>
<thead>
<tr>
<th>Reaction no.</th>
<th>Reaction</th>
<th>Pre-exponential factor A (mol/cm^2 K)</th>
<th>Temp. exponent n</th>
<th>Act. energy E (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CH₃+CH₃=CH₂H₆</td>
<td>3.16E+36</td>
<td>-7.2</td>
<td>750.0</td>
</tr>
<tr>
<td>2.</td>
<td>CH₃+H=CH₄</td>
<td>2.08E+25</td>
<td>-4.0</td>
<td>665.0</td>
</tr>
<tr>
<td>3.</td>
<td>CH₄+O₂=CH₃+HO₂</td>
<td>7.90E+13</td>
<td>0.0</td>
<td>560000.0</td>
</tr>
<tr>
<td>4.</td>
<td>CH₃+H=CH₃+H₂</td>
<td>2.20E+04</td>
<td>3.0</td>
<td>8750.0</td>
</tr>
<tr>
<td>5.</td>
<td>CH₂+OH=CH₂+H₂O</td>
<td>1.60E+06</td>
<td>2.1</td>
<td>2460.0</td>
</tr>
<tr>
<td>6.</td>
<td>CH₂=CH₂+OH</td>
<td>1.02E+09</td>
<td>1.5</td>
<td>8604.0</td>
</tr>
<tr>
<td>7.</td>
<td>CH₂+O₂=CH₃+H₂O₂</td>
<td>1.80E+11</td>
<td>0.0</td>
<td>187000.0</td>
</tr>
<tr>
<td>8.</td>
<td>CH₂=CH₂+OH</td>
<td>2.00E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9.</td>
<td>CH₃+O=CH₂+OH</td>
<td>2.05E+19</td>
<td>-1.57</td>
<td>29229.0</td>
</tr>
<tr>
<td>10.</td>
<td>CH₂=O=CH₂+OH</td>
<td>8.00E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>11.</td>
<td>CH₂=O+CH₂+OH</td>
<td>1.00E+14</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>12.</td>
<td>CH₂+OH=CH₂+OH</td>
<td>1.00E+14</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>13.</td>
<td>CH₂+OH=CH₂+H₂O</td>
<td>7.50E+06</td>
<td>2.0</td>
<td>5000.0</td>
</tr>
<tr>
<td>14.</td>
<td>CH₂+H=CH₂+H₂</td>
<td>9.00E+13</td>
<td>0.0</td>
<td>15100.0</td>
</tr>
<tr>
<td>15.</td>
<td>CH₂+O=M=CH₂O+H+M</td>
<td>1.00E+14</td>
<td>0.0</td>
<td>25000.0</td>
</tr>
<tr>
<td>16.</td>
<td>CH₂+OH=CH₂O+H+M</td>
<td>1.00E+14</td>
<td>0.0</td>
<td>25000.0</td>
</tr>
<tr>
<td>17.</td>
<td>CH₂+O=CH₂+H₂</td>
<td>2.00E+14</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>18.</td>
<td>CH₂=O+CH₂+H₂</td>
<td>2.00E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>19.</td>
<td>CH₂+O=CH₂+H₂O</td>
<td>1.00E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>20.</td>
<td>CH₂+OH=CH₂+H₂O</td>
<td>1.00E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>21.</td>
<td>CH₂+O=CH₂O+OH</td>
<td>1.00E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>22.</td>
<td>CH₂+OH=CH₂O+OH</td>
<td>1.00E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>23.</td>
<td>CH₂+O₂=CH₂+HO₂</td>
<td>6.30E+10</td>
<td>0.0</td>
<td>2600.0</td>
</tr>
<tr>
<td>24.</td>
<td>CH₂O=CH₂O+HO₂</td>
<td>1.48E+13</td>
<td>0.0</td>
<td>1500.0</td>
</tr>
<tr>
<td>25.</td>
<td>CH₂+H=CH₂+H₂</td>
<td>1.00E+18</td>
<td>-1.56</td>
<td>0.0</td>
</tr>
<tr>
<td>26.</td>
<td>CH₂+OH=CH₂+O₂</td>
<td>1.13E+07</td>
<td>2.0</td>
<td>3000.0</td>
</tr>
<tr>
<td>27.</td>
<td>CH₂+OH=CH₂+O₂</td>
<td>2.50E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>28.</td>
<td>CH₂+OH=CH₂+O₂</td>
<td>3.30E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>29.</td>
<td>CH₂O=CO+H</td>
<td>5.70E+13</td>
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</tr>
<tr>
<td>30.</td>
<td>CH₂O=CO+H</td>
<td>3.00E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>31.</td>
<td>CH₂CO₂=HCO+CO</td>
<td>3.40E+12</td>
<td>0.0</td>
<td>690.0</td>
</tr>
<tr>
<td>32.</td>
<td>CH₂+H=CH₂+H₂</td>
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<td>0.0</td>
<td>0.0</td>
</tr>
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<td>33.</td>
<td>CH₂+H₂O=CH₂+O₂</td>
<td>1.17E+15</td>
<td>-0.75</td>
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<tr>
<td>34.</td>
<td>CH₂+H₂O=CH₂+O₂</td>
<td>9.46E+13</td>
<td>0.0</td>
<td>-515.0</td>
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<tr>
<td>35.</td>
<td>CH₂+H₂O=CH₂+H₂</td>
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<td>0.0</td>
</tr>
<tr>
<td>36.</td>
<td>CH₂+H₂O=CH₂+H₂</td>
<td>4.00E+13</td>
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<td>0.0</td>
</tr>
<tr>
<td>37.</td>
<td>CH₂+H₂O=CH₂+H₂</td>
<td>3.00E+13</td>
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<td>0.0</td>
</tr>
<tr>
<td>38.</td>
<td>CH₂+H₂O=CH₂+H₂</td>
<td>6.00E+13</td>
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</tr>
<tr>
<td>39.</td>
<td>C+O₂=CO+O</td>
<td>2.00E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>40.</td>
<td>C+O₂=CO+O</td>
<td>5.00E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>41.</td>
<td>C+CH₂=CH₂+H₂</td>
<td>5.00E+13</td>
<td>0.0</td>
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</tr>
<tr>
<td>42.</td>
<td>C+CH₂=CH₂+H₂</td>
<td>5.00E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>43.</td>
<td>CH₂+CO₂=CH₂O+CO</td>
<td>1.10E+11</td>
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<td>1000.0</td>
</tr>
<tr>
<td>44.</td>
<td>CH₂+CO₂=CH₂O+CO</td>
<td>1.10E+11</td>
<td>0.0</td>
<td>1000.0</td>
</tr>
<tr>
<td>45.</td>
<td>CH₂+H=CO+H</td>
<td>5.00E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>46.</td>
<td>CH₂+H₂O=CH₂+H₂</td>
<td>3.00E+13</td>
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<td>0.0</td>
</tr>
<tr>
<td>47.</td>
<td>CH₂+O₂=CO₂+H</td>
<td>1.80E+12</td>
<td>0.0</td>
<td>1000.0</td>
</tr>
<tr>
<td>48.</td>
<td>CH₂+O₂=CO₂+H</td>
<td>5.00E+13</td>
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<td>9000.0</td>
</tr>
<tr>
<td>49.</td>
<td>CH₂+O₂=CO₂+H₂O</td>
<td>8.60E+10</td>
<td>0.0</td>
<td>-500.0</td>
</tr>
<tr>
<td>50.</td>
<td>CH₂+O₂=CO₂+H₂O</td>
<td>4.30E+10</td>
<td>0.0</td>
<td>-500.0</td>
</tr>
<tr>
<td>51.</td>
<td>CH₂+O₂=CO₂+H₂O</td>
<td>3.43E+09</td>
<td>1.18</td>
<td>-447.0</td>
</tr>
<tr>
<td>Reaction</td>
<td>Rate Constant</td>
<td>Preexponential Factor</td>
<td>Activation Energy (kJ/mol)</td>
<td>Reaction Type</td>
</tr>
<tr>
<td>----------</td>
<td>---------------</td>
<td>-----------------------</td>
<td>---------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>52. CH₂O+M=HCO+H+M</td>
<td>3.31E+16</td>
<td>0.0</td>
<td>81000.0</td>
<td>CO enhanced by 1.9</td>
</tr>
<tr>
<td>53. CH₂O+OH=H₂O+CO</td>
<td>1.80E+13</td>
<td>0.0</td>
<td>3080.0</td>
<td>CH₄ enhanced by 1.9</td>
</tr>
<tr>
<td>54. HCO+OH=H₂O+CO</td>
<td>1.00E+14</td>
<td>0.0</td>
<td>0.0</td>
<td>CO₂ enhanced by 2.8</td>
</tr>
<tr>
<td>55. HCO+M=H+CO+M</td>
<td>2.50E+14</td>
<td>0.0</td>
<td>16802.0</td>
<td>H₂O enhanced by 3.0</td>
</tr>
<tr>
<td>56. HCO+H=CO+H₂</td>
<td>1.19E+13</td>
<td>0.25</td>
<td>0.0</td>
<td>CO enhanced by 1.9</td>
</tr>
<tr>
<td>57. HCO+O=CO+OH</td>
<td>3.00E+13</td>
<td>0.0</td>
<td>0.0</td>
<td>H₂ enhanced by 1.9</td>
</tr>
<tr>
<td>58. HCO+O=CO₂+H</td>
<td>3.00E+13</td>
<td>0.0</td>
<td>0.0</td>
<td>CH₄ enhanced by 2.8</td>
</tr>
<tr>
<td>59. HCO+O₂=HO₂+CO</td>
<td>3.30E+13</td>
<td>-0.4</td>
<td>0.0</td>
<td>CO₂ enhanced by 3.0</td>
</tr>
<tr>
<td>60. CO+O+M=CO₂+M</td>
<td>6.17E+14</td>
<td>0.0</td>
<td>0.0</td>
<td>H₂O enhanced by 5.0</td>
</tr>
<tr>
<td>61. CO+OH=CO₂+H</td>
<td>1.51E+07</td>
<td>1.3</td>
<td>-758.0</td>
<td>CO enhanced by 1.9</td>
</tr>
<tr>
<td>62. CO+O₂=CO₂+O</td>
<td>1.60E+13</td>
<td>0.0</td>
<td>41000.0</td>
<td>H₂ enhanced by 1.9</td>
</tr>
<tr>
<td>63. HO+CO=CO₂+OH</td>
<td>5.80E+13</td>
<td>0.0</td>
<td>22934.0</td>
<td>CH₄ enhanced by 2.8</td>
</tr>
<tr>
<td>64. C₂H₆+CH₃=C₂H₅+GH₄</td>
<td>5.50E-01</td>
<td>4.0</td>
<td>8300.0</td>
<td></td>
</tr>
<tr>
<td>65. C₂H₄+H=C₂H₂+H₂</td>
<td>5.40E+02</td>
<td>3.5</td>
<td>5115.0</td>
<td></td>
</tr>
<tr>
<td>66. C₂H₂+CH₂=C₂H₂+H₂</td>
<td>1.10E+14</td>
<td>1.2</td>
<td>746.0</td>
<td></td>
</tr>
<tr>
<td>67. C₂H₂+O₂=CH₂+CO</td>
<td>1.60E+09</td>
<td>1.2</td>
<td>5955.0</td>
<td></td>
</tr>
<tr>
<td>68. C₂H₂+O₂=CH₂+CO</td>
<td>5.80E+13</td>
<td>0.0</td>
<td>50.0</td>
<td></td>
</tr>
<tr>
<td>69. C₂H₂+O₂=CH₂+CO</td>
<td>1.00E+14</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>70. C₂H₂+O₂=CH₂+CO</td>
<td>1.10E+13</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>71. C₂H₂+O₂=CH₂+CO</td>
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<td>72. C₂H₂+OH=CH₂+H</td>
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<td>73. C₂H₂+O₂=CH₂+H₂</td>
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<td>74. C₂H₂+O₂=CH₂+H₂</td>
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<td>75. C₂H₂+O₂=CH₂+H₂</td>
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<td>76. C₂H₂+O₂=CH₂+H₂</td>
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<td>77. C₂H₂+O₂=CH₂+H₂</td>
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<td>78. C₂H₂+O₂=CH₂+H₂</td>
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<td>79. C₂H₂+O₂=CH₂+H₂</td>
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<td>81. C₂H₂+O₂=CH₂+H₂</td>
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<td>84. C₂H₂+O₂=CH₂+H₂</td>
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<td>85. C₂H₂+O₂=CH₂+H₂</td>
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<td>86. O+H₂=C₂H₂+H₂</td>
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<td>87. O+H₂=C₂H₂+H₂</td>
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<td>89. O+H₂=C₂H₂+H₂</td>
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<td>94. C₂H₂+O=C₂H₂+H₂</td>
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<td>101. O+HCO=H₂O+CO</td>
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<td>103. CH+HCO=C₂H₂+CO</td>
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<td>104. HCO+HCO=C₂H₂+CO+CO</td>
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<td>105. CH₂(S)+M=CH₂+M</td>
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<td>C₂H₂ + HCCO = C₂H₃ + CO</td>
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<td>C₂H₂ + H₂ = C₂H₃ + H</td>
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<td>C₂H₂ + OH = C₂H₃ + HCO</td>
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<td>C₂H₂ + O₂ = HCCO + HCO</td>
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<td>C₂H₂ + O₂ = CH₃CO + HCO</td>
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<td>C₂H₂ + O₂ = CH₃CO + C₂H</td>
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<td>C₂H₂ + OH = C₂H₃ + H₂O</td>
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<td>C₂H₂ + CH₂ = C₂H₃ + H</td>
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<td>C₂H₂ + M = C₂H₂ + H + M</td>
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<td>C₂H₂ + OH = C₂H₃ + H + M</td>
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<tr>
<td>C₂H₂ + O₂ = HCCO + OH</td>
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<td>C₂H₂ + H₂ = C₂H₃ + H + M</td>
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<td>C₂H₂ + H₂ = C₂H₃ + H + M</td>
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<td>H₂ + O₂ = OH + OH</td>
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<td>OH + H₂ = H₂O + H</td>
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<td>O + OH = O₂ + H</td>
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<td>O + H₂ = OH + H</td>
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<td>H₂O + M = HO₂ + M</td>
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</tbody>
</table>

H₂O enhanced by 1.86
CO₂ enhanced by 4.2
H₂ enhanced by 2.9
CO enhanced by 2.1
N₂ enhanced by 1.3

134. OH + HO₂ = H₂O + O₂       | 7.50E+12      | 0.0  | 0.0  |
135. H + HO₂ = OH + OH         | 1.40E+14      | 0.0  | 1073.0 |
136. O + HO₂ = O₂ + OH         | 1.40E+13      | 0.0  | 1073.0 |
137. OH + OH = O = H₂O         | 6.00E+08      | 1.3  | 0.0  |
138. H + H₂ + M = H₂ + M       | 1.00E+18      | -1.0 | 0.0  |

H₂ enhanced by 0.0
H₂O enhanced by 0.0
CO₂ enhanced by 0.0

139. H + H₂ + H₂ = H₃ + H₂      | 9.20E+16      | -0.6 | 0.0  |
140. H + H₂ + O₂ = H₂ + H₂O    | 6.00E+19      | -1.25| 0.0  |
141. H + CO₂ = H₂ + CO₂        | 5.49E+20      | -2.0 | 0.0  |
142. H + OH + M = H₂O + M      | 1.60E+22      | -2.0 | 0.0  |

H₂O enhanced by 5.0

143. H + O + M = OH + M        | 6.20E+16      | -0.6 | 0.0  |

H₂O enhanced by 5.0

144. O + O + M = O₂ + M        | 1.89E+13      | 0.0  | -1788.0 |
145. H + HO₂ = H₂ + O₂         | 1.25E+13      | 0.0  | 0.0  |
146. HO₂ + HO₂ = H₂O₂ + O₂     | 2.00E+12      | 0.0  | 0.0  |
147. H₂O₂ + M = OH + OH + M    | 1.30E+17      | 0.0  | 45500.0 |
148. H₂O₂ + H₂ = H₂O + H₂      | 1.60E+12      | 0.0  | 38000.0 |
149. H₂O₂ + OH = H₂O + HO₂     | 1.00E+13      | 0.0  | 18000.0 |
150. CN + N₂ = CH₄ + N         | 3.00E+11      | 0.0  | 13600.0 |
151. CN + N₂ = C + N₂          | 1.04E+15      | -0.5 | 0.0  |
152. CN + N₂ = CH₄ + NH        | 1.00E+13      | 0.0  | 74000.0 |
153. CN + N₂ = N₂ = CH₂        | 2.00E+13      | 0.0  | 0.0  |
154. CN + N₂ = CH₄ + N₂ + CH₂  | 3.00E+14      | 0.0  | 22000.0 |
155. CN + NO = CN + O          | 6.60E+13      | 0.0  | 0.0  |
156. CN + NO = HCN + O         | 1.10E+14      | 0.0  | 0.0  |
157. CN + NO = HCN + H         | 1.39E+12      | 0.0  | -1100.0 |
158. CN + NO = HCN + HO        | 1.00E+11      | 0.0  | 15000.0 |
159. CN + NO = HCN + HO + M    | 1.00E+11      | 0.0  | 15000.0 |
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<th>Reaction</th>
<th>Rate Constant</th>
<th>Reaction</th>
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<td>C₂N⁺+O=NO+CN</td>
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<td>NO₂⁺M⁺=NO⁺O⁺M</td>
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<td>NCO⁺H⁺≡NH⁺CO</td>
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<td>NCO⁺+O⁺≡NO⁺CO</td>
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<td>NCO⁺+N₂⁺=N₂⁺+CO</td>
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<td>NCO⁺+OH⁺=NO⁺CO⁺H</td>
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<td>NH₂⁺O⁺≡N⁺OH</td>
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<td>NH₂⁺OH⁺≡NH⁺H₂O</td>
<td>4.00E+06</td>
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<td>NH₂⁺NO⁺≡NNH⁺OH</td>
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<td>M</td>
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<td>-----</td>
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<tr>
<td>222. $\text{NNH} + \text{H} = \text{N}_2 + \text{H}_2$</td>
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<td>223. $\text{NNH} + \text{OH} = \text{N}_2 + \text{H}_2\text{O}$</td>
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<td>224. $\text{NNH} + \text{NH}_2 = \text{N}_2 + \text{NH}_3$</td>
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<td>225. $\text{NNH} + \text{NH} = \text{N}_2 + \text{NH}_2$</td>
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<td>226. $\text{NNH} + \text{O} = \text{N}_2 + \text{OH}$</td>
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<td>227. $\text{HNO} + \text{O} = \text{H} + \text{NO} + \text{M}$</td>
<td>1.50E+16</td>
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- H$_2$O enhanced by 10.0
- O$_2$ enhanced by 2.0
- N$_2$ enhanced by 2.0
- H$_2$ enhanced by 2.0

<table>
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<th>Equation</th>
<th>Value</th>
<th>P</th>
<th>M</th>
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<td>228. $\text{HNO} + \text{OH} = \text{NO} + \text{H}_2\text{O}$</td>
<td>3.60E+13</td>
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<td>229. $\text{HNO} + \text{H} = \text{H}_2 + \text{NO}$</td>
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<tr>
<td>230. $\text{HNO} + \text{NH}_2 = \text{NH}_3 + \text{NO}$</td>
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<td>231. $\text{N} + \text{NO} = \text{N}_2 + \text{O}$</td>
<td>3.27E+12</td>
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<td>232. $\text{N} + \text{O}_2 = \text{NO} + \text{O}$</td>
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<td>233. $\text{N} + \text{OH} = \text{NO} + \text{H}$</td>
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<td>234. $\text{SO}_3 + \text{O} = \text{SO}_2 + \text{O}_2$</td>
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<td>238. $\text{SO} + \text{OH} = \text{SO}_2 + \text{H}$</td>
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<td>239. $\text{SO} + \text{NO}_2 = \text{SO}_2 + \text{NO}$</td>
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<td>240. $\text{SO} + \text{O} + \text{M} = \text{SO}_2 + \text{M}$</td>
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<td>242. $\text{SO} + \text{SO} = \text{SO}_2 + \text{S}$</td>
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<td>243. $\text{SH} + \text{O} = \text{OH} + \text{S}$</td>
<td>1.00E+14</td>
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<td>244. $\text{CO} + \text{O} = \text{CO}_2 + \text{O}$</td>
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<td>245. $\text{S} + \text{O}_2 = \text{SO} + \text{O}$</td>
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<td>246. $\text{SH} + \text{H}_2 = \text{H}_2\text{S} + \text{H}$</td>
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<tr>
<td>247. $\text{SH} + \text{O} = \text{SO} + \text{H}$</td>
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<td>248. $\text{OH} + \text{H}_2\text{S} = \text{H}_2\text{O} + \text{SH}$</td>
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<td>249. $\text{O} + \text{H}_2\text{S} = \text{OH} + \text{SH}$</td>
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<td>250. $\text{S} + \text{H}_2 = \text{SH} + \text{H}$</td>
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<tr>
<td>251. $\text{S} + \text{OH} = \text{SH} + \text{O}$</td>
<td>3.00E+13</td>
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<td>252. $\text{S} + \text{H}_2\text{O} = \text{SH} + \text{OH}$</td>
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<td>253. $\text{H} + \text{SO}_2 = \text{OH} + \text{SO}_2$</td>
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<td>254-1. $\text{H} + \text{SO}_2 + \text{M} = \text{HSO}_2 + \text{M}$</td>
<td>1.40E+06</td>
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<td>254-2. $\text{H} + \text{SO}_2 + \text{M} = \text{HSO}_2 + \text{M}$</td>
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<td>255-1. $\text{H} + \text{HSO}_2 = \text{H}_2 + \text{SO}_2$</td>
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<td>257. $\text{S} + \text{NH} = \text{SH} + \text{N}$</td>
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<td>259. $\text{SH} + \text{NH} = \text{SN} + \text{H}_2$</td>
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<td>260. $\text{SN} + \text{NO} = \text{N}_2 + \text{SO}$</td>
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<td>261. $\text{NO} + \text{CS} = \text{SN} + \text{CO}$</td>
<td>1.00E+13</td>
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<td>262. $\text{CS} + \text{O} = \text{CO} + \text{S}$</td>
<td>1.00E+13</td>
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<td>263. $\text{CO} + \text{S} + \text{M} = \text{COS} + \text{M}$</td>
<td>1.00E+13</td>
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<tr>
<td>264. $\text{CH} + \text{SO} = \text{CO} + \text{SH}$</td>
<td>1.00E+13</td>
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**APPENDIX IV. MODIFIED “CONP.FOR” SOURCE CODE USED IN NUMERICAL MODEL**

PROGRAM CONP
C Integration of adiabatic, constant pressure kinetics problems
C Modified by Javier Molero. July 1995
C Modified February 1997 for input of temperatures and residence times
C
C****precision > double
IMPLICIT DOUBLE PRECISION (A-H,0-Z), INTEGER(I-N)
C*****END precision > double
C
PARAMETER ( LENIWK=5000, LENRWK=13000, LENCWK=500, NK=5, NLMAX=55,
1 LIN=5, LOUT=6, LINKCK=25, KMAX=61, ITOL=1, IGPT=0,
2 RTOL=1.0E-6, ITASK=1, ATOL=1.0E-15)
C
DIMENSION IWORK(LENIWK) , RWORK( LENRWK) , X(KMAX), Z(KMAX)
CHARACTER CWORK(LENCWK)*16, KSYM( KMAX)* 16, LINE*80
LOGICAL KERR, lERR
EXTERNAL FUN
C
COMMON /RCONS/ P , RU, TT2, T
COMMON /ICONS/ KK, NWT, NH, NWDOT
C
DATA KERR/.FALSE./ , X/KMAX*0.0/, KSYM/KMAX*" '/
C
C*****open statements included (cif)
OPEN (LIN, FILE='INP',  STATUS=' OLD' )
OPEN (LOUT, FILE='CONP.OUT',  STATUS=' UNKNOWN' )
C*****end of open statements !  !  (cif)
C
WRITE (LOUT, 15)
15 FORMAT (1 ' CONP: CHEMKINII Vers 1.2 Aug. 1992',
C**  *  *'precision > double
2' DOUBLE PRECISION')
C*****END precision >  double
C
C Open the CHEMKIN LINK file
C
C*****OPEN statement > unix
OPEN (LINKCK, FORM=' UNFORMATTED' ,  file=' cklink' )
C*****END OPEN statement > unix
C
C*****Initialize CHEMKIN
C
CALL CKLEN (LINKCK, LOUT, LENI, LENR, LENC)
CALL CKINIT (LENIWK, LENRWK, LENCWK, LINKCK, LOUT, IWORK,
1 RWORK, CWORK)
CALL CKINDX (IWORK, RWORK, MM, KK, II, NFIT)
NEQ = KK + 1
LRW = 22 + 9*NEQ + 2*NEQ**2
NVODE = LENR + 1
NWT = NVODE + LRW
NH = NWT + KK
NWDOT = NH + KK
NTOT = NWDOT+ KK - 1
LIW = 30 + NEQ
IVODE = LENI + 1
ITOT = IVODE + LIW - 1
C
IF (KK .GT. KMAX) THEN
WRITE (LOUT, *)
1 ' Error...KMAX too small...must be at least ',KK
KERR = .TRUE.
ENDIF
C
IF (LENRWK .LT. NTOT) THEN
KERR = .TRUE.
WRITE (LOUT, *)
1 ' Error...LENRWK too small...must be at least ', NTOT
273
IF (ILENK .LT. ITOT) THEN
    KERR = .TRUE.
    WRITE (LOUT, *) ' Error...LENIVIK too small...must be at least', ITOT
ENDIF

IF (KERR) STOP

CALL CKSYMS (CWORP, LOUT, KSYM, IERR)
IF (IERR) KERR = .TRUE.
CALL CKWT (IWORK, RWORK, RWORK(NWT))
CALL CKRP (IWORK, RWORK, RU, RUG, PATH)

C** Read initial non-zero moles from input file
40 CONTINUE
LINE = ' ',
READ (LIN, '(A)', END=45) LINE
ILEN = INDEX (LINE, '!')
IF (ILEN .EQ. 1) GO TO 40

ILEN = ILEN - 1
IF (ILEN .LE. 0) ILEN = LEN(LINE)
IF (INDEX(LINE(:ILEN), 'END') .EQ. 0) THEN
    CALL CKSNUM (LINE(:ILEN), 1, LOUT, KSYM, KK, KNUM,
    VAL, 1ERR)
    IF (IERR) THEN
        WRITE (LOUT,*) ' Error reading moles...' 
        KERR = .TRUE.
    ELSE
        X(KNUM) = VAL
    ENDIF
ENDIF
GO TO 40
ENDIF
GOTO 40

C** Normalize mole fractions
XTOT = 0.00
DO 50 K = 1, KK
    XTOT = XTOT + X(K)
50 CONTINUE
DO 55 K = 1, KK
    X(K) = X(K) / XTOT
55 CONTINUE

C** Set time interval for integration constant at 0.001 s
C Initialise accumulated residence time
C Set system pressure constant at 1.15 bar
DT = 0.001
RTIME = 0.0
PA = 1.15
P = PA*PATM

C** Read first set of conditions, T and T2
60 READ (LIN, *) T, T2

C** Convert mole fractions to mass fractions
CALL CKXTY (X, IWORK, RWORK, 2(2))

C** Print spreadsheet heading and first set of conditions
WRITE (LOUT, 7020) ( K, K=l, KK+2)
WRITE (LOUT, 7000) (KSYM(K)(:10), K=1, KK)
WRITE (LOUT, 7010) RTIME, (10**6 * Z(K), K=2, KK+1), T

C*****Integration loop begins here
C*****Read new temperature and final time from input file
C
100 READ (LIN, *) T, T2
C
C*****End of computation
C
IF (T .EQ. 0.0 .AND. T2 .EQ. 0.0) THEN
STOP
ENDIF

C*****Sets initial conditions and mass fractions and integration
parameters for DVODE
C
TT1 = 0.0
TT2 = TT1
Z(1) = T
MF = 22
ISTATE= 1
N LINES= NLMAX + 1
C
C 250 CONTINUE
C
C*****Calculate accumulated residence time and
print solution of present stage to output file
C
IF (TT2 .GE. T2) THEN
RTIME = RTIME + T2
WRITE (LOUT, 7010) RTIME, (10**6 * Z(K) , K=2 , KK+1), T
GOTO 100
ENDIF

C*****Increase computation time
C
TT2 = MIN(TT2 + DT, T2)
C
C*****Call the differential equation solver
C
350 CONTINUE
C*****precision > double
CALL DVODE
C*****END precision > double
C
IF (ISTATE .LE. -2) THEN
IF (ISTATE .EQ. -1) THEN
ISTATE = 2
GO TO 350
ELSE
WRITE (LOUT,*) ' ISTATE=',ISTATE
STOP
ENDIF
ENDIF
GO TO 250
C
C FORMATS
C
7000 FORMAT (4X, 'Time/ss', IX, 61(IX,All), 2X, ' Temperat')
7010 FORMAT (100E12.4)
7020 FORMAT (100I12)
END
C
SUBROUTINE FUN (N, TIME, Z, ZP, RPAR, IPAR)
C
C****precision > double
IMPLICIT DOUBLE PRECISION(A-H,O-Z), INTEGER(I-N)
C****END precision > double
C
275
COMMON /RCONS/ P, RU, TT2, T
COMMON /ICONS/ KK, NWT, NH, NWDOT
DIMENSION Z(*), ZP(*), RPAR(*), IPAR(*)

Variables in Z are: Z(1) = T, Z(K+1) = Y(K)

Call CHEMKIN subroutines

CALL CKRHOY (P, T, Z(2), IPAR, RPAR, RHO)
CALL CKWYP (P, T, Z(2), IPAR, RPAR, RPAR(NWDOT))

Form governing equation

DO 100 K = 1, KK
   WDOT = RPAR(NWDOT + K - 1)
   WT = RPAR(NWT + K - 1)
   ZP(K+1) = WDOT * WT / RHO
100 CONTINUE

RETURN
END
MEMORIA EXPLICATIVA

La calidad de los combustibles fósiles líquidos continúa decreciendo en todo el mundo. Aunque los recursos disponibles son grandes, no sólo como resultado de operaciones de refino sino en forma de recursos naturales, las dificultades de su uso se deben no sólo a los inconvenientes de su proceso, sino también como resultado de las emisiones contaminantes, fundamentalmente de NO\textsubscript{X}, SO\textsubscript{X} y partículas. Debido a las altas cantidades de compuestos de nitrógeno y azufre que contienen, estos combustibles son grandes contribuyentes de los procesos de acidificación y eutrofización asociados a la contaminación transfronteriza. Como resultado, se está introduciendo legislación que limita el contenido de azufre en ciertos combustibles líquidos pesados.

En esta tesis se ha estudiado la capacidad de formación de NO\textsubscript{X} y SO\textsubscript{X} de varios combustibles destilados pesados destinados a turbinas de gas. Los combustibles investigados son subproductos de operaciones de refino, y se clasifican en dos tipos: gasóleos pesados de vacío y gasóleos pesados de coker. Los primeros son destilados obtenidos durante la destilación a vacío del crudo. La destilación a 30-40 mmHg permite que los hidrocarburos más pesados se vaporicen a temperaturas mucho más bajas que los puntos de ebullición correspondientes a presión atmosférica, evitándose así el cracking térmico. Por el contrario, los gasóleos pesados de coker se obtienen como una corriente de destilado en la etapa de coking retardado. En este proceso de cracking térmico los hidrocarburos son precalentados a 520 °C y pasados por un tambor de coking a 4 o 5 atm, donde se rompen para producir hidrocarburos más ligeros a una velocidad baja.

Orimulsion es otro combustible estudiado en esta tesis. Esta emulsión (combustible:agua) es un recurso natural de la cuenca del río Orinoco en Venezuela. A pesar de su polémica reputación, esta emulsión al 30 % ofrece varias ventajas con respecto a otros combustibles convencionales, tales como su facilidad de manejo, transporte y procesamiento, y emisiones medioambientales comparables a las de otros combustibles pesados.

Todos los combustibles estudiados contienen grandes cantidades de azufre y nitrógeno que forman NO\textsubscript{X} y SO\textsubscript{X}, y que pueden interaccionar durante su combustión, a veces de forma impredecible. La investigación sobre las interacciones entre NO\textsubscript{X} y SO\textsubscript{X} realizada hasta la fecha ha sido limitada. Es más, una gran parte de estos trabajos se ha enfocado en la interacción de los óxidos de azufre y NO\textsubscript{X}-término. Sin embargo, pocos y contradictorios resultados se han publicado sobre los efectos de los óxidos de azufre y NO\textsubscript{X}-fuel, es decir, óxidos de nitrógeno originados a partir de los compuestos de nitrógeno en el combustible.

Aparte de facilitar información sobre los procesos fundamentales de formación de óxidos de nitrógeno, el conocimiento de las interacciones de NO\textsubscript{X} y los compuestos de azufre pueden propiciar el desarrollo de técnicas de reducción de contaminantes, de forma similar a la que el conocimiento detallado de los procesos de formación de NO\textsubscript{X} ayudó al desarrollo de los quemadores de bajo NO\textsubscript{X}. 

1
Es el objeto de esta tesis el facilitar información experimental y análisis de los procesos por los cuales el NOx-fuel (NO y NO2) y los óxidos de azufre interactúan en la combustión de los hidrocarburos líquidos pesados.

La mayor parte del trabajo experimental se llevó a cabo en un horno vertical de escala semi-industrial. Aunque las condiciones de combustión en el horno vertical difieren de las de las turbinas de gas (es de prever que en éstas se encuentren mayores intensidades de combustión, presión, y tiempos de residencia más reducidos), se pueden obtener conocimientos significativos a partir del estudio de los procesos básicos de interacción entre NOx y SOx a presión atmosférica.

Además, un modelo numérico es una herramienta que puede facilitar información adicional sobre las interacciones estudiadas. El grupo de códigos Sandia CHEMKIN puede simular diferentes regímenes de flujo, y adaptarse a las condiciones experimentales, combustible y sistema de reacciones químicas. El efecto de la variación de la cantidad de fuel-S y -N se puede simular modificando los datos de entrada del código.

Se consideraron cinco variables a la hora de determinar los efectos de interacción entre NOx y SOx:

- La estoichiometría del sistema de combustión, que se alteró variando las cantidades de aire presentes en el horno.
- La temperatura de llama, que se alteró variando la temperatura de pared del horno y la relación de equivalencia.
- El tiempo de residencia en la cámara de combustión, mediante el muestreo en diversos puntos a lo largo de la cámara de combustión
- La cantidad total de azufre presente en el sistema de combustión: se estudiaron combustibles con diferentes contenidos de azufre, y se aumentó la cantidad total de azufre en el sistema mediante la adición de SO2-gas.
- La cantidad de nitrógeno presente en el combustible, mediante el estudio de combustibles con diferentes contenidos de nitrógeno.

También se utilizaron otras técnicas complementarias para obtener mayor información sobre los combustibles estudiados. Por ejemplo, se realizaron experimentos mediante la técnica de gota suspendida que permitieron la determinación de las características básicas de ignición. Además, la variación del tamaño de gota previo a la ignición, la formación de hollín o partículas de coke en estos experimentos se observó mediante el uso de grabaciones de vídeo.

Información adicional, tal como la capacidad de formación de NOx y SOx de los combustibles utilizados, el perfil longitudinal de temperatura de llama, la formación y emisión de otros compuestos como resultado de la combustión y de NOx-térmico, también ayudó a establecer y validar el modelo numérico y a completar el estudio de las interacciones investigadas.