PUPIL RESEARCHER INITIATIVE

# A Burning Problem

## Setting the Scene

*You will be working as a member of a team of new research students in a university chemistry department. The department is very interested in doing research into how to make diesel engines burn fuel more efficiently. It is about to put in a research proposal to the Research Council for a grant to fund the work.*

# Pupil Research Brief

## Study Guide

### Syllabus Targets *Science you will learn about in this Brief*

- ❑ unless waste is properly treated pollution will be caused
- ❑ most fuels contain carbon, and/or hydrogen, and sometimes sulphur
- ❑ when fuels burn the gases produced may include carbon dioxide and sulphur dioxide, which may harm animals and plants, and water vapour
- ❑ when fuels burn, energy is released as heat
- ❑ gases produced when fuels burn are released into the atmosphere
- ❑ high temperatures produced when fuels burn cause nitrogen and oxygen from the air to form nitrogen oxides

### Route through the Brief

**Memo**

**Paper 1** *Air pollution from road vehicles: is it getting worse?*

**Paper 2** *An investigation into pre-mixed and diffusion flames*

**Investigation**

**Paper 3** *The drive for clean exhaust diesel engines*

**Research Proposal**

### Outcome Checklist

You will produce a research proposal, written in three sections, outlining to the Research Council why it should support your research. A memo guides you through the Brief. It summarises the stages in writing the proposal. You should make sure you produce the following items as you work through the Brief.

**Paper 1**

- ❑ introduction and background for Section 1 of your research proposal, explaining why the research needs to be done, including:
  - a summary of the origins and effects of three pollutants
  - graphs showing how vehicle speed affects pollution
  - an explanation about how your research will benefit society and the economy

**Paper 2**

- ❑ investigation plans or designs
- ❑ investigation reports
- ❑ outline of department’s previous research and track record, including notes explaining complete combustion, for Section 2 of the research proposal

**Paper 3**

- ❑ list of suggestions for research topics
- ❑ outline of your plan for the research programme for Section 3 of the proposal

# School of Chemistry

Memorandum

**From:** Emma O'Brian, Chair of the Research Committee

**To:** Principal Investigator, Clean Technology Group

**Subject:** Submission of Research Proposal to Research Council
- *A case for support*

At our recent meeting we agreed to seek funding for a research project on reducing motor vehicle pollution. The Research Council has a clean technology research programme area. This is the programme we will apply to for the grant.

The application has to include a section called *A case for support*. This is where we have to persuade the Research Council that we are the right people to do the work, and that the work is worth doing. The research has to be new, timely and promising. I need a written report which covers the following sections in order for me to complete the Research Council Grant Application Form.

**Section 1. (Based on Paper 1)**
**Why we want to do the research.**
You will need to read the article called *Air pollution from road vehicles: is it getting worse?* (Paper 1) to get the background for this section. I have written some notes on it to help you work out what to write. I think this section should have three parts.

1. Introduce the topic in one or two sentences.

2. Explain the background, making reference, for example, to the origins and effects of pollutants and the effect of vehicle speed on pollution - 200 words maximum.

3. Explain how the results of our research will help to create wealth for the nation, and improve the quality of life. Emphasise the positive effect on people's health of improvements in engine technology - 100 words maximum.

**Section 2. (Based on Paper 2)**
**Outline of previous research and track record.**
Paper 2, *Investigation into pre-mixed and diffusion flames*, outlines some of our previous work in this field. I would like you to follow up this work, with your own investigation(s), so that we can talk about our recent experience in this area in the grant application. Have a look at Paper 2. I have made some notes on it which should help you. It may also be useful to include in this section brief notes explaining complete combustion and why it is important. Information on this topic is presented in Paper 2. When you have dealt with Paper 2, perhaps you would like to go on to Section 3.

**Section 3. (Based on Paper 3)**
**The Plan for the Research Programme.**
This section could be in the form of a flowchart. Paper 3 will give you some ideas about the possible research projects we could suggest to the Research Council. I have written some guidelines for the content of Section 3 at the end of Paper 3.

Paper 1

# Air pollution from road vehicles: is it getting worse?

I suggest you work through this paper in your research teams. I have written notes on each section to help you write section 1 of our research proposal.

**Every summer air pollution hits the headlines. Reports in the press and on TV claim that the problem is getting worse. Road traffic is being blamed, despite improvements in engine design and tighter controls of vehicle exhausts.**

This review describes the chief pollutants and their effects on the environment. It looks at improvements in engine design and at the measures being taken to control emissions from vehicles. Finally we look into the future. Government scientists predict an improvement in emissions from road transport by the year 2000.

## EFFECTS ON THE ENVIRONMENT

### The Pollutants

European Union (EU) regulations cover:

- carbon monoxide (CO)
- hydrocarbons (HCs)
- nitrogen oxides (NOx)
- lead
- particulates

Carbon dioxide is also produced when fuels burn but is not covered by regulations.

I would take one pollutant each - from those I've marked with an x. Each of you will need to explain where it comes from and why it is harmful.
You will each need to draw a graph to show the effect of car speed on the emission of your pollutant - based on the figures in Table 1 of this paper - and comment on the graph. It would be a good idea to pool your information to begin to write the background to section 1 of the proposal.

**i) Carbon monoxide (CO)** X
Carbon monoxide is produced when fuel does not burn completely . Road vehicles account for some 85% of total CO emissions in the UK. Most of this comes from petrol engines. The amount of carbon monoxide emitted varies with speed. The effect is shown in Table 1. It is high at low speeds and during a cold start. Stop-go driving around towns also produces high levels.

Carbon monoxide interferes with the way that red blood cells carry oxygen. It combines with haemoglobin and makes it unavailable for oxygen. This reduces the amount of oxygen the blood can transport. Once a red blood cell has been poisoned by CO it cannot be repaired, and must be replaced by the body. In a confined space, such as a garage, the effects of breathing in carbon monoxide can be lethal. The concentrations of the gas in the open air are not likely to affect the ordinary road-user. But they may be bad for people already suffering from respiratory and heart disorders.

**(ii) Oxides of nitrogen (NOx)** X
As the fuel burns inside the engine it produces very high temperatures. They are high enough for nitrogen oxides to form from the nitrogen and oxygen in the air. A mixture of nitrogen monoxide (NO) and nitrogen dioxide ($NO_2$) is made. The mixture is usually called 'NOx'. $NO_2$ is much more poisonous than NO and may be linked to respiratory problems such as chronic bronchitis.

**(iii) Hydrocarbons (HCs)**
Road traffic accounts for about 35% of hydrocarbon emissions in the UK. About two thirds of the hydrocarbon is unburnt fuel coming out of the exhaust. Another quarter is fuel which has evaporated and escaped into the air before reaching the engine. Some hydrocarbon vapour is lost from the fuel tank and from the warm engine when it is cooling down. This lost fuel increases the fuel consumption of the vehicle. Some hydrocarbons such as benzene are also linked to the occurrence of cancer.

$CO_2$ is important, but we can't do much research into this. All fuels produce it when they burn.

**(iv) Carbon dioxide ($CO_2$)**
Carbon dioxide is a product of efficient combustion. It is not the subject of EU regulations but nowadays we cannot assume that it is harmless. Scientists believe that increases in carbon dioxide levels in the atmosphere cause global warming.

The only method of reducing $CO_2$ emissions is to burn less fuel oil. This will mean fewer vehicles; vehicles which are more economical with fuel; vehicles travelling more slowly; or vehicles which do not use fossil fuels being more widely used.

Other research teams are looking at lead emissions.

**(v) Lead**
Lead is not the problem it was a few years ago. Modern blends of petrol have a much lower level of lead than older versions. Some petrols are completely 'lead free'. New cars must be fitted with 'three-way catalysts'. This is the only way cars can meet new laws on exhaust emissions. The catalysts do not work in the presence of lead. So leaded petrol will soon be doubly banished. It will go because it has bad effects on human health and because new cars do not use it.

You should all read through section (vi) - it is very important.
This information will be useful for the background section of the proposal, especially the information about where particulates come from.

**(vi) Particulates**
Particulates are particles of carbon (soot) and other matter which do not settle out of the air. They remain suspended because they are very small (around 10 microns ($\mu$m) or less in diameter - 1$\mu$m = $10^{-6}$m). They are less dense than lead particles, which tend to settle near roads.

Motor vehicles are responsible for about 40% of the particulate emission in the UK. Diesel vehicles produce at least 90% of this. It is sometimes visible as black smoke. The work of O'Brian in this area is interesting (O'Brian 1995). - Paper 2
The particles are black granules of carbon produced because the fuel has not burned completely. Particulates carry small amounts of other organic compounds including polycyclic aromatic hydrocarbons (PAHs), which are carcinogens, (cancer-causing chemicals).

At present there is great public concern over the effect of particulates on health. Small particles are thought to be the most dangerous. They are known as PM10 (particulate matter with a diameter of less than 10 $\mu$m). Because they are very tiny they tend to remain in the air for a long time. When people breathe in air these particles can be carried deep into their lungs. Recent research in the United States has shown that the death rate tends to increase on days when high air pollution is high and the PM10 is raised.

The above section on particulates is interesting. It may lead us towards a possible research project. Any ideas at this stage?

The next section also makes a few points we should take notice of.

## CONTROLLING EMISSIONS BY BETTER TECHNOLOGY

**All new petrol engine cars sold in Europe since the beginning of 1993 have three-way catalytic converters which reduce the levels of the three pollutant gases, CO, HCs and NOx, in exhaust emissions.**

Since 1993 new petrol and diesel cars also have devices called 'carbon canisters' to trap evaporating hydrocarbons. The canisters contain activated carbon to soak up the hydrocarbon vapour.

A new car in 1994 emits about 93% less carbon monoxide and about 85% less hydrocarbons and NOx per kilometre than a similar car in 1970.

Diesel cars generally produce lower levels of polluting gases than petrol cars. CO and HC emissions from diesel cars can be made even lower by fitting oxidation catalysts. Diesel vehicles also give out less $CO_2$ for each kilometre travelled than equivalent petrol vehicles. Sales of diesel cars rose from 5% of the UK market in 1990 to 25% in 1993. Diesel cars do not have all the advantages. They are unlikely to compete in terms of reduced NOx with petrol cars equipped with three-way catalysts. Particulate emission is much higher for diesel cars.

Modern engines will only behave in the way their designers intend if they have good fuel. Small amounts of active chemicals are added to petrol to boost its performance. Changes in engine technology are likely to have the most dramatic effects in reducing pollution.

## LAWS AGAINST MOTOR VEHICLE POLLUTION

Directives from the Parliament of the European Union set limits on vehicle emissions. Before a new design of car is put on the market it has to be tested to make sure it meets the regulations.

## HOW MOTORISTS CAN HELP

Vehicle speed influences pollutant emission rates. The results of a study of emissions from a car with a petrol engine are shown in Table 1.

It might be useful to comment on the effect of speed on emissions in your report.

*Table 1.*

| Speed / km per hour | Average emissions / g per km per vehicle | | |
|---|---|---|---|
| | CO | HCs | NOx |
| 10 | 33.02 | 4.47 | 2.53 |
| 25 | 21.20 | 2.60 | 2.17 |
| 50 | 9.80 | 1.30 | 2.13 |
| 75 | 6.40 | 0.93 | 2.24 |
| 100 | 7.83 | 0.86 | 2.97 |
| 125 | 11.04 | 0.87 | 4.15 |
| 150 | 13.97 | 0.92 | 6.07 |

Figure 1 on the next page is based on very recent unpublished data on carbon particulates from diesel vans.

As can be seen, the amount of PM10 increases with increasing speed. One of the easiest ways to reduce pollution would therefore be to enforce strict speed limits.

## THE FUTURE

There will be a time lag before the latest laws to control emissions take effect. It has only been compulsory to fit three-way catalysts to new cars since 1993. It will be several years before all non-catalyst vehicles are replaced by modern ones. Khan (1995) suggests the aim of future research should be to improve combustion rather than to clean up exhaust gases.

Paper 3

Projections show that emissions from road transport will decline through the rest of the 1990s. Although pollution could increase

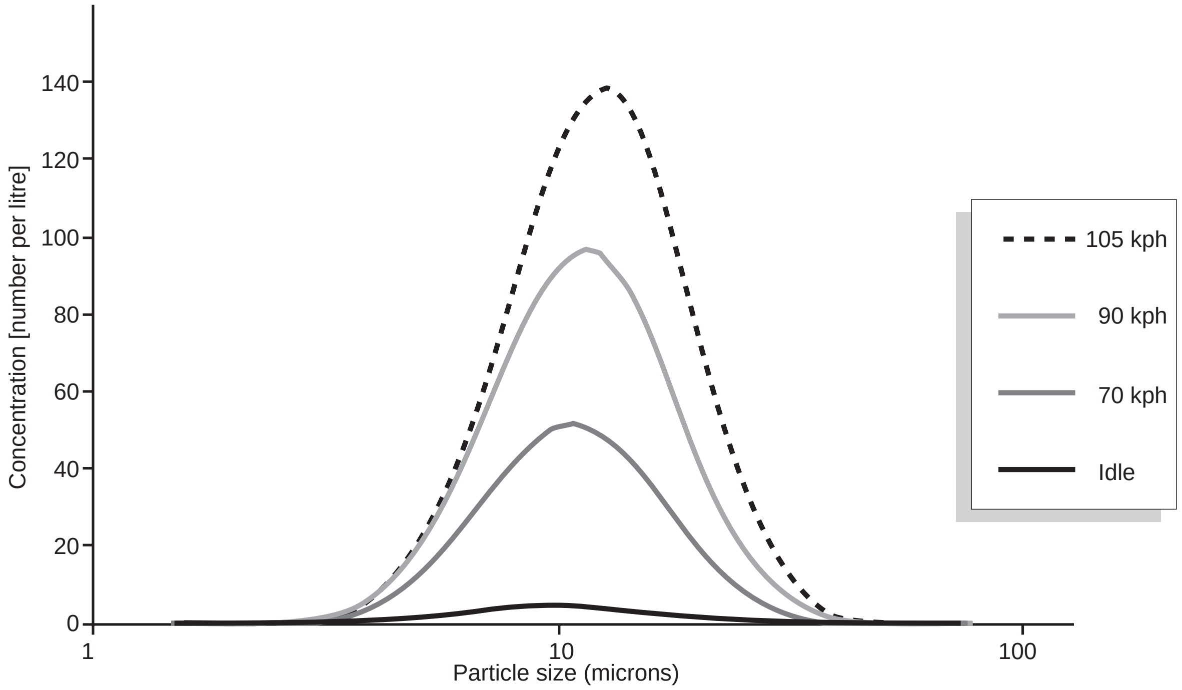


*Figure 1. Particle size distribution of emissions from a diesel van*

due to the continued rise in the number of cars on the road, it is thought that they will be used less and so produce fewer emissions in total.

The European automobile and oil industries have joined with the European Commission to fund a major research programme called the European Programme on Emissions, Fuels and Engine Technologies. The research will enable the three partners to make proposals on how to meet air quality standards in the year 2000 at the lowest possible cost. This, in turn, will lead to newer and better laws to protect the air we breathe.

**References**

**Khan M.** The drive for clean exhaust diesel engines, *Journal of Automotive Engineering* 1995, 122, 34-5

**O'Brian D.** An investigation into pre-mixed and diffusion flames, *Journal of Science and Technology*, 1995, 21, 156-6

I have copied these papers - they are Paper 2 (O'Brian) and Paper 3 (Khan)

Perhaps you would like to comment on how the particle size and concentration are affected by speed, in your report.

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This paper outlines some of our earlier work in this area. This, along with your own investigations on the link between different types of flame and the production of carbon particles, should help you to give an outline of our previous research and track record needed for Section 2 of the proposal.
I have written some suggestions on this paper for possible investigations you may wish to plan and carry out.

# An investigation into pre-mixed and diffusion flames

D. O'Brian

*In a recent letter to the Journal of Automotive Engineering, Khan (1995) put forward a case for increased research into reducing particulate emissions from burning diesel fuel in engines. He suggested that the focus of this work should be on improving combustion so that fewer particles are produced, rather than removing them from exhaust gases. This short paper describes some of the early work which has been carried out in this area. The work was funded by the Research Council.*


## Abstract

The paper gives details of some preliminary work done on pre-mixed and diffusion flames. Pre-mixed flames are produced when air and fuel are mixed before they ignite; in diffusion flames the flame gets its oxygen from air which diffuses into the flame as it burns. A basic comparison of the products of combustion of hydrocarbon fuels for the two types of flames is made.


## Methods

It is known that the fuel in a diesel engine burns with a mixture of pre-mixed and diffusion flames. It is thought that the smoky diffusion flame leads to particulate formation. The aim was to find out why diffusion flames produce carbon particles.

In an internal combustion engine the flame only lasts for a fraction of a second. Steady flames, such as a Bunsen flame are useful models. The Bunsen burner flame with the collar open can be used as a typical pre-mixed flame. When the air hole is open, air is drawn in and mixes with the fuel as it travels up the barrel. A Bunsen flame with the collar closed and a candle flame are good examples of diffusion flames.

The Bunsen burner burns natural gas, which is almost pure methane, and belongs to a class of hydrocarbon compounds called alkanes. Butane, petrol, diesel and paraffin are other examples of alkanes. The molecules in candle-wax also contain hydrocarbon (alkane) chains. The chains of linked carbon atoms are each about 30 atoms long.

### 1. The products of burning alkanes and the combustion process: investigation details

When natural gas was burned in a Bunsen flame with the air hole fully open and the products of burning collected, it was found that the main substances detected were carbon dioxide and water vapour. This was to be expected since with the air hole fully open and the hottest flame produced, it was assumed that there was complete combustion of the methane gas fuel. Fuels are substances that react with oxygen to produce a large amount of heat energy very quickly. This reaction is known as combustion or burning. The fuel is in fact being oxidised. When a hydrocarbon such as methane burns the carbon combines with oxygen to form carbon dioxide, and the hydrogen combines with oxygen to form water. The equation for the complete combustion of methane is:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{heat energy}$$

All fuels need oxygen to burn. If there is not enough oxygen the combustion is incomplete. In the case of methane there may not be enough oxygen to convert all the fuel into carbon dioxide and water. Some carbon monoxide (CO), which is poisonous, is produced, along with carbon (soot particles) and unburnt fuel. Soot particles are responsible for smokey, yellow flames.

The more complete the combustion, the more efficient is the burning and the more heat energy is produced by the flame. If there is insufficient oxygen, and thus incomplete combustion, the heat energy produced by the flame will be less. The flame will also give off more soot particles.

It might be useful if you produce a design for an experimental set up to show that the main products of burning are $CO_2$ and $H_20$ - include how you would detect the presence of these two substances. You can include this information and a brief description of complete combustion in Section 2 of our proposal.

**2. The supply of oxygen to the flame.**

*(i) Pre-mixed flames*

As its name suggests in this type of flame the oxygen is pre-mixed with the fuel before it is ignited. This is the case with a Bunsen burner flame, when the air hole is open. The further it is open, the more oxygen will be pre-mixed with the fuel.

*(ii) Diffusion flames*

With a Bunsen burner when the air hole is closed, or with a candle, oxygen has to come from the surrounding air (see Figure 1 on the next page). This process limits the rate at which oxygen can be supplied to the flame and leads to soot formation. Not enough oxygen reaches the inner cone for the complete combustion reaction to occur. Instead, fragments of fuel break down to give carbon atoms. Groups of carbon atoms then grow to make soot particles.

This paper suggests that the more complete the combustion, the less soot (and therefore less particulate pollution) is produced. It also suggests that pre-mixing oxygen with the fuel leads to more efficient and more complete combustion. Also, the more complete the combustion, the more heat energy is produced by the flame. Could you carry out the following investigations to check these claims?

1. Show that a diffusion flame produces more soot than a pre-mixed flame (for the same amount of fuel).

2. How does varying the amount or rate of oxygen pre-mixing with the fuel affect the combustion process and the heat energy output of the flame.? (Think about how you would measure the heat energy output of a flame as the amount of oxygen pre-mixing with the fuel is raised). Comment also on how the amount of carbon particulates (soot) produced changes as you vary the oxygen input to the flame.

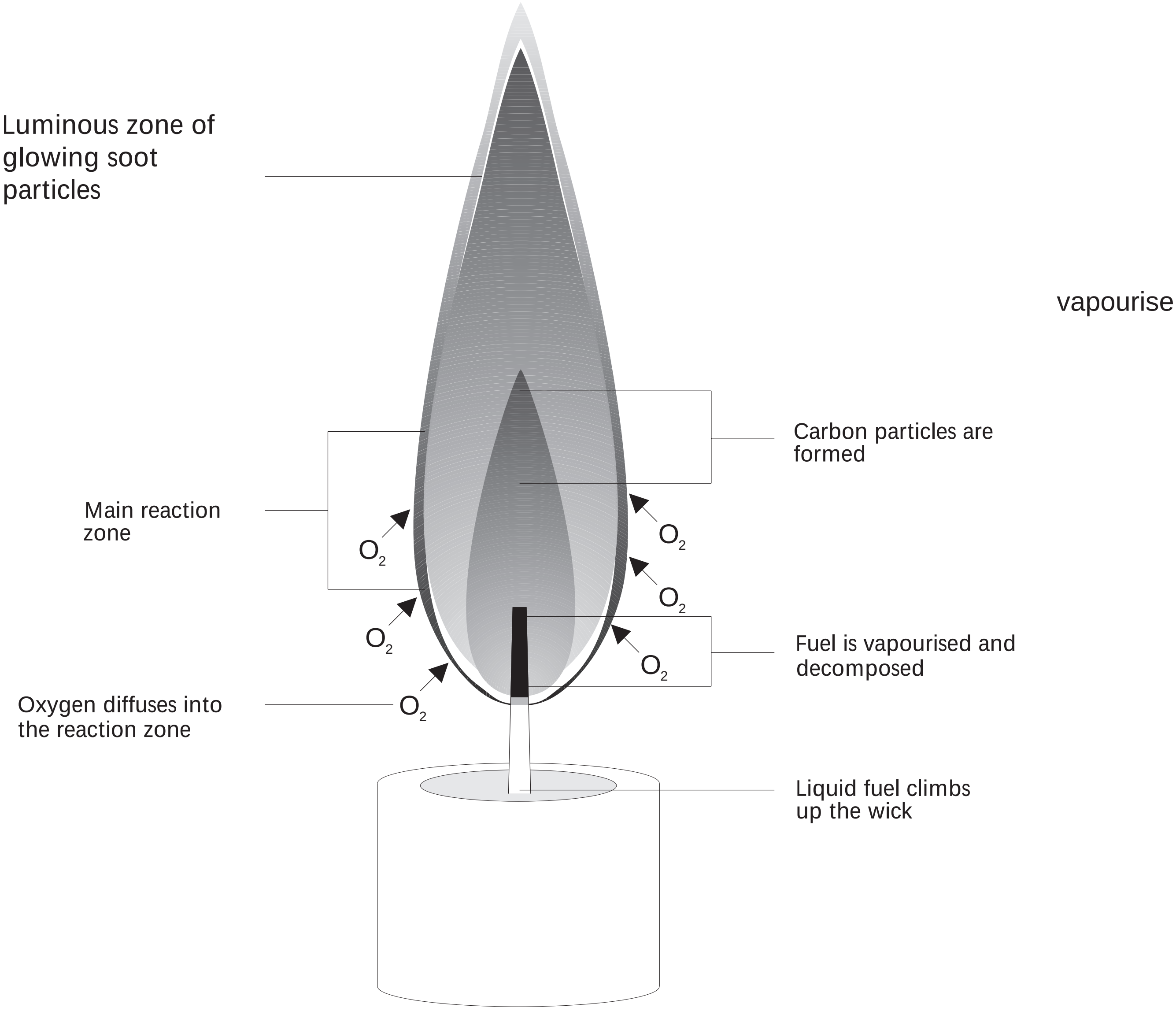


*Figure 1. A candle flame - an example of a diffusion flame*

## Further Work

More research is needed to allow us to understand what happens when a flame burns. In particular, the effect of varying the amount of oxygen that is pre-mixed with the fuel on the amount of soot produced. This will help engineers to design diesel engines which produce less particulate pollution.

## References

Khan, M. The drive for clean exhaust diesel engines, *Journal of Automotive Engineering,* 1995, 122, 34-5

Did your investigation show any link between the amount of oxygen pre-mixed with the fuel, and soot formation? Based on information in this paper and your findings we should be able to complete section 2 of our proposal and also to start thinking about the focus of our research proposal.

Journal of Automotive Engineering Vol 41 page 122 1995

# The drive for clean exhaust diesel engines

The research you did following up paper 2 should provide us with a good understanding of the link between oxygen/fuel mixing and soot production. Khan's paper outlines some of the possible ways forward for researchers trying to make diesel engines produce less pollutants. I suggest you read it - I have written some notes to help you write Section 3 of the research proposal.

M. Khan

**The legal controls on diesel exhaust emissions are becoming tighter. New European regulations on diesel exhaust limits are due to be introduced in 1996. The next stage in reducing emissions is likely to be in the year 2000. It is thought that both NOx and particulate limits will be cut yet again.**

The Automotive Industry is striving to design engines which perform within these limits. Companies will capture new markets if they can succeed where their competitors fail. They may also be able to sell expertise to other manufacturers.

We could emphasise this in the research proposal.

The ratio of air to fuel in a diesel engine is much higher than in a petrol engine. Because oxygen is in excess, diesel engines tend to emit smaller amounts of the polluting gases CO and HCs. Modern diesel engines are also more efficient in that they use less fuel. Diesel engines produce higher NOx emissions than petrol engines equipped with a three-way catalyst. It was once thought that reducing NOx meant losing fuel economy. Recent developments suggest that improvements will be possible without this drawback.

In spite of the high ratio of air to fuel the exhaust from a diesel-powered vehicle contains carbon particulates. The emissions of particulate matter from diesel cars has received a lot of publicity over the last year or so. Public concern has been reflected in a significant drop in sales. The Automotive Industry is taking this very seriously. Developments that reduce particulates are advancing rapidly. The best solution is to improve combustion. To do this we need a better understanding of what happens in the combustion chamber.

This shows we really must concentrate on particulate emission in our research. We don't want to be left behind!

Although the diesel fuel is injected as a liquid, it can only burn efficiently when it has been vapourised and mixed with the hot, compressed air in the cylinder. The key to making cleaner diesel engines lies in controlling combustion.

To get the best mixing, the air must swirl through the incoming fuel stream. The combustion patterns are very complex.

Ideally, the air and the fuel vapour swirl together to produce a pre-mixed flame. But there will be some areas in the cylinder where the droplets have vapourised but not yet mixed with the air. These fuel-rich pockets will burn with diffusion flames. Diffusion flames do not have enough oxygen for the fuel to burn completely and fuel particles decompose to give carbon. At first very tiny particles of carbon, only 1 - 2 nanometres (1nm = $10^{-9}$m)across, are produced. They are called nuclei. They grow to form particles of soot which are 20 - 30 nanometres across. These soot particles enter the exhaust pipe but they are not yet 'particulates'. Unburnt hydrocarbon material from traces of lubricating oil in the engine stick to the surfaces of the soot particles in the exhaust pipe.

These coated soot particles stick to each other to make bigger particles of 10 -15 microns in diameter. The result, when it leaves the exhaust pipe and enters the air, is called 'particulate'.

Particulates carry small amounts of other organic compounds including polycyclic aromatic hydrocarbons (PAHs). Some sulphate and water are also present in the particulate. The sulphate comes from the sulphur that is present in diesel fuel.

Treating the exhaust gases after they have left the engine is one way to meet new emission standards. Probably a better approach is to improve the combustion process itself to prevent the soot particles from forming.

Engines used in this research have quartz windows in their cylinders. This makes it possible to use laser beams to study reactions in the combustion chamber. Special techniques make burnt regions visible and high speed images of the combustion process allow engineers to carry out detailed studies. They hope to understand more fully how pollutants form. Their conclusions are likely to lead to changes in engine design.

This fundamental research will eventually give us cleaner and more efficient engines.

We could base our proposal on looking at particulates produced by diesel engines under different circumstances, such as by improving the mix between the air (oxygen) and the vapourised fuel, or by finding better ways to turn the liquid fuel into a vapour. Thus it would mix better with the air, reducing the amount of diffusion flame burning which takes place in the engine cylinders.

Have you any ideas about how we could go about this?

What factors should we look at?

Could you outline a possible research programme (section 3 of the proposal). I suggest the following headings.

- Aim (what are we going to target, from all the ideas you have had so far?)
- Background science (you should try to explain the importance of complete combustion - see Paper 2)
- Description of factors to be researched (such as improving air supply, better fuel vaporisation etc)
- Brief description of how we might go about the research (don't spend too much time on this, I can add details to your outline)
- Predictions about what we expect to find (based on your investigations and understanding of the background science).