

University of Southern Queensland
Faculty of Engineering and Surveying

**Optimisation of biodiesel stationary engine
performance by modelling and simulating the
running conditions.**

A dissertation submitted by

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ABSTRACT

This dissertation analyses the use of biodiesel in the agricultural industry and the performance of biodiesel when used as a replacement fuel for conventional diesel. The performance characteristics that are focused on are the production of the greenhouse gas oxides of nitrogen and the fuels suitability for use in stationary engines. A computer model is developed to simulate the formation rate of nitric oxide (the main component of oxides of nitrogen) and analyse the affects of using biodiesel instead of the conventional diesel. It was found that biodiesel produces a higher initial formation rate of nitric oxide for the same temperature and has a higher adiabatic flame temperature across all the equivalence ratios analyse. It is also found that the characteristic time increases as the compression ratio of an engine increases, and increases as the temperature of the cylinder contents increases. From other experimental work it is found that biodiesel and biodiesel – diesel blends produce similar power outputs compared to the conventional diesel fuel. From these experiments it was also found that biodiesel lead to higher amounts of oxides of nitrogen being produced, but lower amounts of carbon monoxide and carbon dioxide. From these results it was established that biodiesel is a effective replacement for conventional diesel, with the formation of oxides of nitrogen possibly reduced with the retarding of the fuel injection timing to an optimal level, which should also reduce the brake specific fuel consumption as well as increasing the efficiency and power generated from the engine.

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Nomenclature

NO_x	<i>Oxides of Nitrogen</i>
NO	<i>Nitric oxide</i>
NO_2	<i>Nitrogen Dioxide</i>
CO	<i>Carbon Monoxide</i>
τ_{NO}	<i>Characteristic Time</i>
$\frac{d[NO]}{dt}$	<i>Initial Formation rate of Nitric oxide</i>
ϵ	<i>Molar fuel to air ratio</i>
φ	<i>Fuel to air equivalence ratio</i>
α	<i>Carbon atom concentration (in the fuel)</i>
β	<i>Hydrogen atom concentration (in the fuel)</i>
γ	<i>Oxygen atom concentration (in the fuel)</i>
δ	<i>Nitrogen atom concentration (in the fuel)</i>
v_i	<i>Moles of particular combustion product (i = 1 to 10)</i>
y_i	<i>Mole fraction of particular combustion product (i = 1 to 10)</i>
P	<i>Pressure in atmospheres</i>
T	<i>Temperature in Kelvin</i>

Chapter 1: Introduction

1.1 Project Background

Australia is a great land with great opportunity, as many people get to experience every day. However, in recent years some of these people have been made to struggle to make a living from day to day. One of main problems in recent past that has been causing this struggle has been the drought. Australia is the driest continent in the world (aside from Antarctica which is not permanently inhabited), and is also home to a very successful agricultural and horticultural industry. Over the past years many areas have been in there worst drought in one hundred years, causing severe problems for the agricultural and horticultural industries.

With Australia having sixty percent of its land area devoted to agriculture and horticulture, the drought has affected a huge amount of people, probably everybody if the rising price of produce is taken into consideration. There is little that can be done to make it rain in order to relieve a little of this pressure off the industry, but there is other ways of relieving some of this economical pressure. For instance the government have been offering aid, to support drought affected farmers through the drought, farmers have opted to be employed by other companies in order to fund their business, but this dissertation will focus on a smaller more specialised area. One of the main aspects all of the agriculture and horticultural industries have in common, as well as every other industry for that matter, is that they all require energy. One of common energies that are uses is petrochemical fuels. Over the past ten years, there has been quite a dramatic increase in the price of these fuels; due to many factors such as the increasing demand, decreasing supply and other external factors such as war. Almost every farm uses this type of fuel to generate electricity and power vehicles and machinery, so by giving the industry a way of decreasing these costs, there is a possibility of some relief for the economy of each business in the agricultural and horticultural industry.

A well known problem that has been known and contested against with the use of modern petrochemical fuels is there affect on the environment. Fossil fuels are the largest contributor to greenhouse gas emission to date. So the reduction in use of these fuels could greatly contribute to creating a healthier planet for our future generations. This has started to become of greater concern to all as the world is slowly convinced by the scientific evidence that is being produced around the world. This concern now has the world leaders starting to make a

change in the way we can generate power, many of these changes are currently in the form of blending renewable fuels with their fossil fuel based, non-renewable counterparts, such as ethanol and methanol. Other inclusions include the use of solar and wind energies where they are most beneficial, and the adaption of hydro electricity in convenient locations such as dam walls and river systems. Another addition that is slowly becoming better known is the commercial production of biodiesel. This is the area that the dissertation will focus on, as the fuel can become more economical viable than that of other alternative renewable energies.

In this dissertation the key points that will be focused on are:

- Analyse current literature on the use of biodiesel in internal combustion engines.
- Determine the current effectiveness of biodiesel use in the agricultural industry.
- Model and simulate the running conditions of biodiesel in an internal combustion engine.
- Alter specific engine parameters and determine the effect of this change in the performance of the engine, while comparing biodiesel to traditional diesel, and relating them to the affect on production of oxides of nitrogen and transient heat flux.
- Compare the modelled results with available data to determine the effectiveness of the model.
- Analyse the effectiveness due to modelled data and existing data, in using biodiesel in the agricultural industry for use in stationary engines and other engines.

These key points will be discussed in detail throughout this dissertation. But first it is important to understand where biodiesel comes from.

Biodiesel is a renewable replacement for the fossil fuel bases petro diesel. Biodiesel has three main components in its production, these are:

1. Oil or fat, produced from a renewable feedstock, these include palm, vegetable, canola oil and many others.
2. An alcohol, either methanol or ethanol
3. A catalyst, caustic soda (Sodium hydroxide) or caustic potash (Potassium hydroxide)

These ingredients are relatively easy to get a hold of so with the correct procedure, anybody is able to produce their own fuel. This makes it attractive to many do-it-yourselfers around

the world, ready for an interesting and challenging task, for this reason there are many people that currently make their own fuel for personal use.

1.2 Advantages and Disadvantages of Biodiesel

It is not only the cost that is the main advantage of the fuel, there is many other associated advantages in using biodiesel:

- Renewable energy source
- Many sources of feedstock's available for use in production
- Recycling of oils normally resorted to as "waste"
- Proven reduction in the production of most greenhouse gasses
- Biodegradable
- Can be used in existing compression ignition engines
- Can be made at home
- Can be blended with petro-diesel
- Utilises re-release of carbon emissions rather than new release of stored carbon

These are a few of the most well known advantages of the fuel, but as anything it is also suspect to disadvantages as well:

- Can cause an increase in the production of oxides of Nitrogen
- Produces slightly less power and torque when used in an unmodified compression ignition engine
- Commercially produced biodiesel can be more expensive than normal diesel
- Production of waste product, glycerine
- Can void warranty with some vehicle and machinery manufactures

Some of these disadvantages and advantages can vary from situation, for instance the production of oxides of nitrogen has been reported to change from each different, some experimental work has reported up to ten percent increase in the production of these gasses, while other experiments have noted reductions in their concentrations. Some of these experiments also have shown that the performance is also variable, depending on the experimental technique, loads and fuels used in their investigation. It is also noted that there is production of a waste product, glycerine. Glycerine is a by-product of creating biodiesel, but is also useful in other industries, for example is a key ingredient in making soap.

Therefore some of these advantages and disadvantages can be subjected to questioning, depending on the view and perception of the individual.

1.3 Making Biodiesel

As mentioned before, there are various ways of making your own biodiesel, with this option; it has opened up a new industry supplying these markets. There are many companies and organisations that are out there willing to share their knowledge in order to help expand their ideals. Companies such as Bio King, offer a range of products, 'recopies' and helpful hints to help make your own high quality fuel. In creating your own biodiesel there is quite a few different methods, a basic guide is explained below.

Making biodiesel:

1. The first step is to obtain you ingredients, for this example waste cooking oil, caustic soda, methanol, Isopropyl alcohol and Phenolphthalein-solution (ph indicator) will be used.
2. The next step is to perform titration. Titration is a process to determine how much extra catalyst you will need to neutralize the free fatty acids are present in your oil. This is an important step when using waste cooking oil, as the more the oil has been used, the more free fatty acids that are present. The common amounts are 200 to 220 ml of methanol to one litre of oil, and five grams of caustic soda for new oil, plus extra for used oil. The process for determining this amount (called titration) is started by dissolving one gram of caustic soda in one litre of distilled water; the caustic soda is prone to absorbing moisture and once this has happened is no longer useful. A small portion of oil is to be heated to forty-five degrees Celsius; one millilitre is then to be mixed with ten millilitres of the alcohol mixture made earlier, preferably in a small glass cup. The next step is to add two to three drops of the ph indicator. A small portion of the catalyst solution is then added to the mixture (the mixture is still swinging); the mixture should turn a light pink and after a short time will turn back yellow. Once the mixture stays pink for approximately thirty seconds, the amount is ample. A mixture containing less than three millilitres of the catalyst solution indicates high quality oil, between three and six millilitres means the oil is suitable to produce good biodiesel. A higher amount of catalyst solution means the oil is of a poor quality but may be suitable for biodiesel.

3. After titration is completed the next step is to produce a test batch. A test batch usually comprises of one litre of oil, as it is easy to produce. The test batch is produced by heating the oil (one litre) to forty-five degrees Celsius; separately the 220 ml of methanol is mixed with the amount of catalyst determined in the titration (five grams plus one gram for every extra millilitre of catalyst solution added). This mixture called meth oxide is then mixed with the oil and is stirred for approximately fifteen minutes (It should be noted that meth oxide is an extremely dangerous substance and proper precautions should be taken for the safety of all). The mixture is then allowed to rest, after one hour a layer of glycerine should be present on the bottom of the container. The mixture is good if there is a clear dividing line between the glycerine and the diesel, and if the amount of glycerine is approximately ten percent that of the total mixture. If there is less glycerine, more catalyst is probably needed, but if there is a clear layer of soap too much glycerine was probably used and action should be taken to resolve this with a new test batch.
4. It is now time to make a large batch. The process is similar to the test batch, but in a larger scale. The heating may be more difficult and a suitable heater should be used. It is also important to mix the solution well, so a pumping system may be employed. The same portions are used as in the test batch, but the solution is allowed to rest for one to two hours, with the initial glycerine drained after this period, the biodiesel is left for another eight hours when the last of the glycerine can be drained. With these steps now complete it is now possible to wash your biodiesel. Washing is an integral part in making high quality biodiesel. As there will be non used catalyst particles present in the fluid causing it to at a high ph level, washing will remove the lye and reduce the ph to neutral. Washing will also help remove excess methanol that will be present in the biodiesel, along with more soap, solid particles and pollutants that may be in the solution. Washing is achieved by misting a thin layer of water onto the top surface of the biodiesel mixture. This is then allowed to rest for approximately one hour allowing the water to flow through the biodiesel and clean it. The water is then drained from the bottom and the process is repeated for at least two more times to ensure the mixture returns to a neutral ph. It is advisable to test the ph of the biodiesel after washing to ensure a neutral ph, as the closer to neutral the less harm the fuel will do to anything it comes in contact with, as we all know what an acidic solution can do. The biodiesel should then be allowed to dry, by having it in an open container, allowing the water that has been mixed with the biodiesel to

evaporate, which should happen over one to two days. The biodiesel should now be fairly clear and have the odour of vegetable oil or the original oil that you have used, and should not smell like an alcohol. Another good test is to test the fuels miscibility with water, by adding five hundred millilitres with one cup of water and shaking the mixture, the water and biodiesel should separate, with no layer of soap between the two layers. If soap does form it is a good indication that the fuel has not been washed properly and should be washed again. Also if the fuel does not separate easily it is an indication of a poor quality fuel. If the fuel passes all of these tests, it quite assumable that a high quality fuel has been produced and your biodiesel is now ready for use.

5. Important points to note. When introducing the fuel into an existing fuel system that has been running on diesel, the fuel should not be used as a straight replacement and should be blended in. One of the good qualities of biodiesel is that it is a good solvent for deposits in the fuel system, which means that it will clean the fuel system as it is being used. This means that the fuel filter will need replacing as the fuel is blended in and the system is purged of these particles. It is also important to know that biodiesel will thicken easier due to lower temperatures compared to diesel. So in colder weather it is advisable to mix biodiesel with diesel to counteract this problem or engine complications such as not starting can result.

The procedure explained above is one of many ways of producing a high quality biodiesel at home, this information was obtained from the Bio King website (www.bioking.nl), but there are many more ways that a high quality fuel can be produced. One of the many differences that can occur in the production of biodiesel is the use of different oils, as many renewable oils can be used.

1.4 Agricultural advantage

It has become clearer over the years that using oil from grain or plant material that is not usually used for oil production has become more popular and proven to be effective. This is another major advantage for making this an alternative fuel in the agricultural industry. In agriculture, the choice of crops can be very versatile, depending on the location and conditions of the farm. This opens the door for many different grains to be produced throughout the year. It is now possible and practised currently, to produce grain with the normal crops and use this grain for the production of oil. Some grains depending on the conditions and quality of the yield can contain high amounts of oil content, some up to

approximately fifty percent, allowing oil to be obtained from the grain and used directly for the production of the renewable fuel. This opens an avenue for farmers to not only produce cheaper fuel, but also do it more economically by utilising their own produce to do so. The oil is normally extracted from the grain by means of pressing. This essentially squeezes the oil from the grain, leaving behind the highly nutritious solid material.

There are now machinery specially catered for this very purpose, for example Bio King in the Netherlands sell equipment for pressing and separating the oil from the seed. These units can range from a small capacity of twenty kilograms of seed an hour (Picture shown below):



(Figure 1.1: cold screw press manufactured by Bio King)

The range then extends from six hundred and thirty kilograms an hour to eighteen hundred kilograms per hour for larger more serious operations. Obviously this sort of large capacity equipment is expensive, and would probably not benefit the smaller agricultural businesses. But there is other machinery for a more cost effective set up available from other manufacturers across the globe that can cater for many different needs, not to mention building the equipment on site. This option is already utilised by many agricultural businesses around Australia and other parts of the world in order to lower fuel costs and reduce the reliance on fossil fuels. Oil can also be extracted by use of solvents, which comprises of a chemical reaction between the seed and an additional substance to extract the oil and further process it, but this option is much more complicated than the standard pressing operation. By using the pressing process, the oil can come out rather clean but will need clarification, by either allowing the oil to rest, leaving the contaminants separate from the oil where it is used, or by filtering the oil through appropriate filter material depending on the original condition of the fuel. Once these processes have been completed, the oil is then ready for processing into biodiesel in the same way any other oil is processed.

The other product that is created from the pressing of oilseeds is the solid cake material left from the grain. This product is not a waste product; in fact it adds further value to the use of self produced grain for the production of biodiesel. This cake as it is called is, in many cases, more valuable than that of the original seed. The cake makes an excellent food substitute for animal consumption and some human consumption, as depending on the grain used, it is usually high in nutrients such as protein. This opens an extra avenue for the sale of this cake material to different markets, adding additional income for the process, or used in house, reducing expenditures in other departments. It should be noted that with the extra processing of these materials that there is a higher safety risk associated, and appropriate rules and regulations should be followed in these areas to ensure the health and well being of all affected by the process.

1.5 Biodiesel: Things to Know

This overall process shows the attractiveness of adapting the industry from its current dependency on fossil fuels to the self producible biodiesel. There are many benefits listed earlier that can be obtained by each business willing to expand to this process. As one of the large benefits of moving from traditional diesel to biodiesel is the fact that it is a renewable fuel, the effects that the fuel will have on things such as the environment and the equipment that it will be used in should also be investigated and noted.

Biodiesel as noted before is a good solvent for deposits built up in the engine, which means that it will clean anything it comes on contact with. This means that the carbon deposits and other particulate matter will be cleaned from the inside of the cylinder and piston as well as the cylinder head, which is a good thing, but precautions such as changing of the fuel filter is advisable more often than specified, especially when first converting from diesel to biodiesel. There are also reports of the fuel degrading the condition of the original rubber fuel lines and it is advised that they be replaced with appropriate fuel lines that will withstand the composition of the biodiesel. This is usually not a large job, and has to be done on older vehicles due to age and heat damage. The seals in the injector pump and injectors are also of concern. Depending on the age of the engine and hardware, biodiesel will affect the natural rubber type seals due to its low sulphur content. This means that the seals may need to be replaced if there is a leak developed; this problem is highly specific to the situation, so each case should be treated independently.

It is also known that not all new car and machinery manufacturers will cover damage on equipment when the car is run on biodiesel. In Australia most manufacturers will allow (with respect to warranty) a blend of five percent or twenty percent biodiesel, but in places such as Europe where stricter standards exist the situation is different. Quite a lot of vehicle manufacturers offer warranty for their product running on one hundred percent biodiesel as long as the fuel meets the EN 14214 which is the proposed European standard (Department of Agriculture and Food). These companies include Audi, BMW, Case-IH, John Deere and Volvo just to name a few. This shows that the leading countries in this newly revived industry are in Europe, probably due to the concentrations of people and the lack of mainland supply of fossil fuels, making the renewable fuels more cost competitive and the realisation of the dim future if the technology is not invested in early enough.

1.6 Biodiesel Production

The absolute leader of commercial biodiesel production is Germany, with a production of 2,262 thousand tonnes, following behind is France with seven hundred and forty three thousand tonnes and Italy with four hundred and forty seven thousand tonnes out of a total four 4,890 thousand tonnes. This figure shows that the three leading countries produce seventy percent of Europe's biodiesel, with Germany itself producing forty six percent (European Biodiesel Board, 2006 figures). These figures show an increase of fifty four percent compared to the production of 2005, and have projected production of just over 10,000 thousand tonnes for the year of 2007. The United States of America is a little behind with an estimated 840 thousand tonnes produced in 2006 (Future Fuels, 2007). The difference between the production of Europe and the United States of America shows that both countries are heading in the same direction, but Europe has more dedication and a fair head start compared to the United States of America.

1.7 Topics of Concentration

Other points of concern for the use of biodiesel are the specific affects to the engine such as the affect on heat transfer, as well as the change in combustion emission concentrations when the alternative fuel is used. One of the main reasons for using biodiesel is that it is reported to have better emission products. One that will be focused on is the formation of Oxides of Nitrogen. This is an important combustion product to control, as it is one of the greenhouse gas components. Oxides of Nitrogen in the atmosphere lead to the formation of

photochemical ozone, known more commonly as smog, which is apparent in many cities every day. This gas also leads to increased effects of respiratory problems such as asthma and forms into acid rain due to its formation into nitric acid when present with moisture in the air. This is why it is important to understand the affect that the fuel will have on this particular matter, especially with the increasing problem of global warming. The other specific parameter that will be focused on will be the affect of using biodiesel in an engine and the related change in transient heat flux generated by the fuel. The change in heat flux is important in an engine due the affects that it will have on its components and combustion process. As the heat flux is increased or decreased, the auxiliary systems such as its cooling system will have more or less to do, which will affect the overall performance of the engine. The formation of combustion emissions is also heavily related to temperature, giving higher reason to predict the transient heat flux accurately.

Through this dissertation it is planned to develop a model in order to simulate the formation of the oxides of nitrogen dependent on the type of fuel. With this model the change in engine parameters such as the compression ratio and injection timing and investigate the predicted effects from the change in these parameters. Is also planned to develop a model to simulate the amount of transient heat flux, and investigate the affect when the mentioned engine parameters are altered and investigate the optimum combinations.

Once these models have been investigated, the advantages and disadvantages of running biodiesel in a stationary engine will then be stated, based on the work presented. These results will hopefully correlate with data that has been obtained and relevant theory valid for the combustion process. This should then be able to be applied to the use of biodiesel in the agricultural industry as a beneficial process that can be viable and effective for all involved.

Chapter 2: Literature Review:

2.1 Biodiesel in Australia

This dissertation is going to analyse the use of biodiesel in the agricultural industry, focusing on its benefits in singular applications, rather than the broader affects. This will be done by focusing on its compatibility when used in stationary diesel engines. Focusing on singular applications means that analysis will be carried out based on typical stationary engine applications and evaluating the expected theoretical performance. The evaluation of performance will be carried out by comparing the engine running on biodiesel as to conventional fossil fuel based diesel. The specific performance parameters that will be evaluated will be the transient heat flux during combustion, as well as the formation of NO_x for each fuel.

As Australia has a large agricultural industry and approximately sixty percent of Australia's land mass is devoted to agriculture (ABARE, 2006), so if there is an advantage of using biodiesel, large benefits stand to be gained from moving from the conventional diesel to the alternative biodiesel. Every agricultural company in Australia that uses internal combustion engines would have at least a small amount of these consisting of diesel engines, either be it for machinery, pumping or generating electricity. With the evermore arising problem of global warming, it seems sensible to be trying to converge from more pollutant fossil fuels to greener, more renewable fuels. This means attacking every avenue of usage, to determine the most feasible areas to implement effectively. The agricultural industry is a prime example of these areas.

2.2 Biodiesel Feedstock's

The reason that the agricultural industry is a prime example is that, to make biodiesel, an organic source of oil needs to be available. Common sources of this organic oil are rapeseed, palm and in America, corn, flaxseed canola and soybean. Some of these crops however are not as feasible in Australian agriculture due to the different growing conditions that are necessary for successful crops. However, there are alternative grains that can be used to make oil. The key to making oil out of grain is the oil content in the grain. Obviously, if a grain has low oil content, then it is not a good candidate for this exercise. This means that it

is important to determine an appropriate grain which has a high oil content, and can be successfully grown in that specific area of Australia. The following figure (Figure 2.1) shows oilseeds that were part of research program carried out by the Department of Agriculture and Food in Western Australia do determine the effectiveness of such species for the use in biodiesel production.

Species	Common name	Type	% oil in seed
<i>Brassica juncea</i>	Indian Mustard	canola-like	35 – 40 %
<i>Brassica carinata</i>	Ethiopian Mustard	canola-like	38 – 42%
<i>Brassica nigra</i>	Black Mustard	hardy canola type	38 – 42%
<i>Sinapis alba</i>	White mustard	condiment mustard	36 – 40%
<i>Camelina sp.</i>	False Fax	low rainfall type	40%
<i>Eruca rucola</i>	Erucola	drought tolerant	?

(Table 2.1: Oil seeds studied by Department of Agriculture and Food, 2001)

There was also further research recommended for the oilseeds listed in Figure 2.2, which were identified as possible candidates for oil production, after the preliminary research had been completed on the oilseeds mentioned above, to determine their effectiveness in the dry environment of Western Australia.

Species	Common name	% oil in seed
<i>Lesquerella spp.</i>	Lesquerella	30
<i>Linum usitatissimum</i>	Linseed	38
<i>Seamun indicum</i>	Sesame	50
<i>Sapium sebiferum</i>	Tallow tree	55
<i>Limnanthes spp.</i>	Meadow Foam	24 - 30
<i>Lupine spp.</i>	Pearl Lupins	15
<i>Cannabis sativa</i>	Hemp	30 - 35
<i>Elaeis guineensis</i>	Palm oil (African spp.)	40 – 50%
<i>Salicornia bigelovii</i>	Glasswort (salt tolerant spp)	26 – 33%

(Table 2.2: Recommended candidates for oilseed production by Department of Agriculture and Food, Western Australia, 2001.)

Another important part of the correct grain selection, is crop rotation. In agriculture, it is important that different crops be grown on the same piece of land through the seasons. This provides the ground time to recover from one type of crop and let another grow with prosperity. This is required due to the type of nutrients each crop uses during growth; a good example of two crops that can be rotated is the canola plant and the wheat plant. The root system of the canola plant is different to that of the wheat crop, this allows the canola plant to break up the soil releasing nutrients and allowing better soil condition for the wheat. The

canola plant also fixes nitrogen into the soil, giving the wheat crop an advantage as it relies heavily on nitrogen to grow (Martin, P, Biodiesel Association of Australia Inc).

As biodiesel is made from organic oil that is able to be extracted from a grain, this also poses an advantage to the singular farmer to recoup costs, making the farm more viable. By this, it is realised that the farmer has the opportunity to make their own fuel for their private use. In this day and age, it is well proven that making your own fuel is a viable and a cost-effective option, one only has to Google the term “Make your own biodiesel” and there are many companies and organisations willing to send you in the right direction and set you up with the equipment required, or give you plans to create what you need to produce your own high quality fuel. Also, with the correct process of extracting the oil, the value of the grain may also be conserved. By extracting the oil using a screw press or similar machine, a good amount of the oil can be extracted. Once the oil is extracted from the grain, the meal that is left over can be made into a cake. This cake is a small pellet shape piece of compressed grain; with the nutritional value extremely high for feed. This cake can then be sold for feed for animals, with the value of the cake being higher than that of the original grain itself. This then means that there is little or no profit lost for a farmer using their own grain for producing their own fuel.

2.3 Classification and Production

Biodiesel is classified as an ester-based fuel that is created through the transesterification process. The transesterification is the reaction of a triglyceride (fat/oil, usually a vegetable oil, waste cooking oil or an animal fat) with an alcohol to form esters and glycerol. A triglyceride is made up of three long chain fatty acids attached to a glycerine molecule. The nature and characteristics of the biodiesel is determined by the fatty acids, as these make up the oil used. In the esterification process, the oil (or triglyceride) reacts with an alcohol in the presence of a catalyst. The catalyst is usually a strong alkaline like sodium hydroxide. The alcohol then reacts with the oil to produce biodiesel (mono-alkyl ester) and the bi-product crude glycerol. The most common alcohols used in the production of biodiesel are methanol and ethanol; methanol produces methyl esters, while ethanol produces ethyl esters. The most common catalysts used are potassium hydroxide and sodium hydroxide (NaOH, caustic soda). When using ethanol as the alcohol, it has been found that potassium hydroxide is more

suitable for the reaction; however both catalysts can be used for methanol (ESRU, Biodiesel production).

There are many reasons that biodiesel is becoming more popular and understood throughout the world. One that hits closest to home for many people is the ever rising cost of fossil fuels. In the recent years fuel prices have been on the rise, with no indication that this trend is not going to continue. This is mainly due to the slowly declining production of oil from our natural reserves. This means two things, first is that the problem of fuel cost from fossil fuels is only going to increase, and secondly that we are running out of supplies, giving reason to develop new technologies into the production of fuel sources that can replace our dependency on fossil fuels. In Europe, the total biodiesel production for 2006 was 4.89 million tonnes with Germany producing 2.662 million tonnes and France producing 743 thousand tonnes (EBB, 2007). These quantities are an increase of 54 % over the previous year's production, showing an increasing trend from previous years in Europe. This shows that there is a large industry in place in Europe and still growing. Another reason that biodiesel is becoming more popular is the environmental benefits. This day and age, society is heavily concentrated on the effects to our environment due to the increasing affects of global warming.

2.4 Oxides of Nitrogen

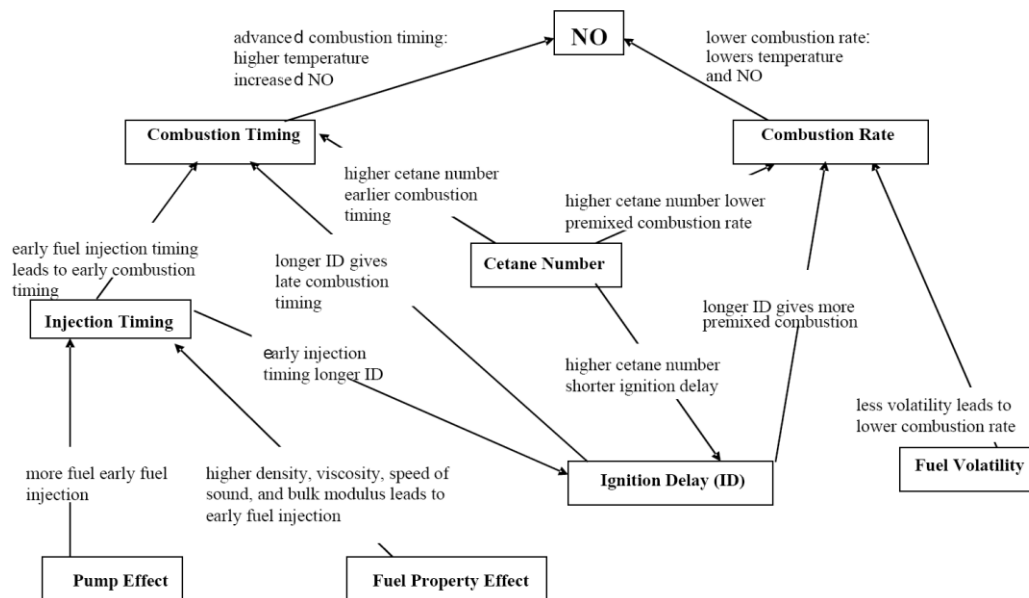
There is a high magnitude of information available on the affects of running biodiesel instead of conventional diesel with regards to emissions. Some of this information states conflicting results if unread carefully, as it is clear that each different test condition gives different results, which would be expected for most experimentation. In this dissertation, it is hopeful to gain a better understanding of results with variance to these conditions. As mentioned above, the two main parameters that will be focused on are the transient heat flux and the NO_x production from the two different fuels. The first parameter that will be discussed is the NO_x . NO_x is a molecule containing one atom of Nitrogen and multiple atoms of oxygen. NO_x is classed as a pollutant due to the effect it causes when in the atmosphere. The main problems with this pollutant is that it contributes to the formation of photochemical ozone, more commonly known as smog, it also impairs visibility and causes respiratory problems due to its formation into nitric acid when in contact with ammonia and moisture. NO_x is also a large contributor to acid rain, causing accelerated deterioration to cars buildings and historical monuments, as well as flowing into water resources contaminating and decreasing

the pH of the water, making it dangerous for the organisms that grow in and use this supply. NO_x also contributes to global warming by changing into the gas nitrous oxide (N_2O) which is a well known greenhouse gas known for getting trapped in the upper atmosphere, contributing to global warming (U.S.EPA 2007).

NO_x formation is dependent on many factors. The most prominent factors to affect the NO_x formation is the combustion temperature and injection timing, which in turn are both related together. There are many factors which affect the temperature of the combustion gases, which in turn affect the formation NO_x . The main factors that will be focused on are the chemical composition of the fuel, fuel to air ratio, compression ratio and the injection timing. These are important factors to consider due to the variation between different engines that are in use in the real world. As biodiesel is made from an alternative base oil, there is an expected and proven difference in the chemical composition of the fuel. A key indicator for the temperature of combustion is the adiabatic flame temperature. The adiabatic flame temperature is “the temperature of the products in the absence of heat transfer from the flow” (Energy Technology study book, 2007). Where the products described are the combustion products from the chemical reaction. In the determination of the adiabatic flame temperature of any fuel, the enthalpy of the reactants has to be equivalent to the enthalpy of the combustion products. Due to conservation of mass, the amount of atoms in the reactants has to be equal to that of the products; this therefore means that the composition of the fuel is a major determinant of the composition of the exhaust gases (products). This means that each fuel will have a different adiabatic flame temperature, hence affecting the formation of NO_x . The fuel to air ratio is also important for much the same reason described above. As the fuel to air ratio is altered, the amount of atoms in the fuel compared to that of the air is changed, this then causes a change in the enthalpy of the reactants and hence also the products, altering the adiabatic flame temperature and therefore the NO_x formation. Compression ratio is also another important factor that affects the formation of NO_x .

The compression ratio is a very large contributor to the temperature of the gases in the cylinder of the internal combustion engine. As work is done on a fluid, there is always heat generated. So during the compression stroke of the engine, work is done to the cylinder contents, which means that the temperature of the contents increases. This is exceptionally important in the case of a compression ignition engine. The compression engine works due to the fact that the cylinder contents are compressed sufficiently to get the contents to a high temperature. In a diesel engine, the only contents in the cylinder are air, unlike in a spark

ignition engine where fuel is mixed with air, prior to being inducted into the cylinder for compression. This means that the engine can have a higher compression as there is no risk of pre-ignition (also known as engine knock) like in the spark ignition engine. In a compression ignition engine, during the very late stages of compression, fuel is injected into the cylinder to create combustion. This is due to the very high temperature of the air in the cylinder, the fuel hits this hot air and combusts, increasing the temperature to create a chain reaction to burn all the fuel. This means that as the compression ratio is altered the temperature of the contents prior to combustion varies, changing the combustion temperature throughout the cycle, which will in turn affect the formation of NO_x . Van Gerpen, Tat and Wang developed a concept map to show the effects of various factors that affect the formation of NO_x and are shown below.



(Figure 2.1: Concept map of NO emission and combustion characteristics, Van Gerpen, Tat and Wang, 2004)

This figure shows the general effect of various fuel Injection parameters and fuel properties on the formation of NO_x . As seen it is evident that the above assumptions are correlated with this diagram. Another factor that has not yet been mentioned is the effect of engine speed and engine load. These parameters are of great concern especially when considering commercial use in machinery and other vehicles, as the engine speed and loads on the engine varies greatly through time and situation. It has been proven in experiments that the specific engine specifications and running conditions are highly important in the determination of

NO_x. It is shown by Ya-fen, Yo-ping and Chang-Tang the affects of engine speed are specific to mainly high to low engine speed. In this particular case engine speeds from 1400 to 2000 produce relatively consistent values, with traditional diesel having lower concentrations than all biodiesel blends, with a blend of B100 having the highest and B50 the lowest concentrations. At engine speeds of 1200 and 1000, traditional diesel again produced the lowest concentrations, while B20 produced the highest and B50 had the lowest concentrations. These tests were undertaken on a 4 cylinder water cooled diesel with a displacement of 2164cc (torque data unavailable) and a compression ratio of 21.6:1. The oil that was used for these tests were made from waste cooking oil, methanol, sodium hydroxide and was washed with water.

The affects of torque on the formation of NO_x has been investigated by comparing a fifty percent biodiesel blend made from waste cooking oil (palm oil), methanol and sodium hydroxide (Yusaf et al). This experiment was undertaken using a four cylinder direct injection Ford engine with a displacement of 2184cc. The engine was water cooled with a compression ratio of 22.9:1. The test for the exhaust emissions were carried out at a constant engine speed of 2000 rpm and torque gradually increased in increments of 20 from 20Nm to 80Nm and a final reading taken at 90Nm. The results showed that the brake specific fuel consumption of the biodiesel blend was higher from the lower torque settings but evened out for the last reading of 90Nm. The efficiency of the biodiesel was less than that of the traditional diesel from the lower torque settings but evened out at 60Nm and continued to improve on the diesels efficiency up to 90Nm. The emissions were also tested, from a torque of 0 to 120Nm. The fifty percent biodiesel blend showed an improvement in NO_x emissions from 0 to approximately 100Nm, after which the traditional diesel showed a lower emission level of NO_x. But in the case of this dissertation, stationary engines are the main focus of this research therefore the constant speed data will be of more importance to evaluate the effectiveness of the mathematical model being developed to predict the formation of NO_x.

It is commonly understood that when using biodiesel rather than traditional diesel, there will be an increase in NO_x emissions, but as Van Gerpen, Tat and Wang discovered, engines that have used a chassis dynamometer for testing have been observed to produce lower NO_x emission levels. In their research they discovered that when the two fuels were compared against their specific start of combustion timing, it was shown that biodiesel NO_x emissions were less than that of the traditional diesel. Van Gerpen, Tat and Wang's research reported that the actual injection timing was advanced by approximately 2.3° with the same injector

pump settings. This advance was then attributed to the difference in the fuels' physical properties. This effect seems reasonable as if the fuel is injected earlier, the combustion will start earlier and therefore give a higher in cylinder temperature due to the compression phase still in progress. This is stated in Heywood (1988), where it is explained that

...almost all of the NO is formed during the first 20° following combustion. As injection timing is retarded, so the combustion process is retarded; NO formation occurs later, and concentrations are lower since peak temperatures are lower.

Van Gerpen, Tat and Wang contributed the decrease in NO_x emission for the chassis dynamometer tests to the difference in average engine torque level, as the chassis dynamometer tests tend to have a much lower torque level compared with that of engine dynamometer testing procedures.

In agriculture, there are many different uses for diesel engines, mainly being for machinery, water movement and electricity generation. Two of these require steady speed engine operation, being water movement and electricity generation; the other requires variable speed as well as steady speed engine operation. As this dissertation is based on the performance of stationary engines which in turn correlate to steady speed operation, the parameters that affect a steady speed engine performance will take priority of focus. In summary the key factors that will affect the formation of NO_x in stationary engines are the physical properties of the fuel, the injection timing and the combustion temperature, all of which will be investigated to determine the performance of biodiesel compared to traditional diesel in reference to the formation of NO_x.

2.5 Transient heat flux

The other important parameter that will be focused on is the transient heat flux. Transient heat flux is the heat that is transferred from the flame to the cylinder contents and surroundings whose magnitude changes rapidly with time. This means that through one engine cycle, more specifically through the compression and combustion phase, the heat flux will vary greatly with the angular displacement. This condition is due to the high amounts of heat that is created during combustion and from continuing compression, giving higher in cylinder pressures and then decreasing cylinder pressures as more of the fuel is burnt and the volume is no longer in compression but in expansion. These conditions are extremely

important in the design characteristics in an engine. For example, an engine with a high compression ratio and larger cylinder capacity will create greater amounts of heat compared to an engine with a lower compression ratio and smaller cylinder capacity. This means that the cooling system of the larger engine will have to be able to exchange more heat between the surroundings and the engine.

Generation of heat in an engine is the key to maximising and optimising power and efficiency out of the product. It is ideal to predict the heat that an engine will create in order to create auxiliary systems to optimise its performance. By this it is meant that systems such as the cooling system for example should be designed to exchange the optimum amount of heat from the engine in order to keep its components at a desirable level to optimise the performance. For example, if the cooling system is designed so that it removes more heat than the ideal amount, the components of the engine will run cooler, meaning that more heat will be lost out of combustion to warm the cylinder walls and head, also meaning that the water pump has to pump more water, meaning that it will absorb more energy to function, energy that is usually created by the engine, decreasing the amount of power usable out of the engine. This shows that not only the thermal efficiency of the engine will decrease but also the overall power as well. On the other hand if the cooling system is under designed, the temperature of the engine will increase, which may lead to oxidation of the oil lubricant, increasing wear and friction, as well as an increase in engine component temperature leading to increased thermal stresses and component failure. This information is supported in Heywood (1988) where it is explained

...higher heat transfer to the combustion chamber walls will lower the average combustion gas temperature and pressure, and reduce the work per cycle transferred. Thus specific power and efficiency are affected by the magnitude of engine heat transfer.

Another factor that is affected by heat flux is emissions. As emission formation is highly dependent on temperature, increasing the temperature of the engine cylinder and exhaust system can cause afterburning of unburnt hydrocarbons and afterburning of CO and higher formation rates and concentrations of NO_x.

As shown above, it is highly desirable to be able to predict the engine heat transfer for design and performance purposes. The heat transfer rate can be estimated by the consideration of relevant factors such as the in-cylinder pressure, the temperature of the burnt and unburnt cylinder contents, the instantaneous cylinder surface area and wall temperature with the

assumption that gas velocities scale with mean piston speed (Heywood, 1988). There are three modes of heat transfer that are important, conduction, convection and radiation. Conduction is the transfer of heat through solids due to molecular motion where a temperature gradient exists. Heat transfer by conduction in an internal combustion engine is through the engine walls, block, cylinder head, piston and from the piston rings to the walls. Convection is important as it transfers heat through fluids to solid surfaces. The predominant heat transfer via convection is from the combustion gasses and the objects it comes in contact with. As the combustion gasses are the source of heat in an internal combustion engine, everything they come in contact will gain large amounts of heat due to the turbulence of the flow and temperature difference. The main components being, the cylinder walls, piston, cylinder head and valve(s), and the exhaust system. Convection is also important on the cooling side of the engine. The heat that is transferred between the engine block to the coolant medium is very important as discussed earlier. Radiation is also an important mode of heat transfer in compression ignition engines. In spark ignition engines, radiation is small in comparison with convective heat transfer, but for compression ignition engines, it can contribute twenty to thirty-five percent of the total heat flux (Heywood, 1988). The source of this radiation is from the highly luminous flame regions and soot particles. In a compression ignition engine, there are many flame regions due to the nature of the design. The flame regions tend to take the shape of the fuel spray then is dispersed by air motion. However, the majority of the irradiative component of the heat transfer is from the soot particles. These soot particles in the engine flame is approximately five times that of the flame regions. Soot particles mainly consist of carbon molecules.

From the research above, it is planned to develop a model to simulate the formation of oxides of nitrogen, as well as the transient heat flux produced from the engine. With this data, it will then be correlated with relevant experimental data and findings determined.

Chapter 3: Methodology

3.1 Oxides of Nitrogen Formulation

The first main technical objective is to understand and model the formation of the greenhouse gases, oxides of nitrogen. This gas has been studied for many years and is well documented for the kinetics of formation. Oxides of nitrogen (NO_x) is formed of two predominant species, nitric oxide (NO) and nitrogen dioxide (NO_2). It is stated in Heywood 1988 that the predominant factor in the oxides of nitrogen is nitric oxide, this therefore means that the study and model will be focused on the formation of that particular species. The source of the nitrogen in this formation is mainly from atmospheric nitrogen, as the fuels produced these days contain insufficient nitrogen contents to warrant consideration, as shown in the chemical compositions where diesels are stated with only carbon and hydrogen atoms and biodiesels with carbon, hydrogen and oxygen. These assumptions then lead to following the general rule, that when combustion of near stoichiometric fuel air mixtures is considered, the principal reactions that govern the formation and destruction of nitric oxide from the molecular (atmospheric) nitrogen are as below:



By using these three equations a mathematical relationship can be developed in the form of:

$$\begin{aligned} \frac{d[NO]}{dt} = & [O][k_1^+ N_2] + k_2^+ [N][O_2] + k_3^+ [N][OH] - k_1^- [NO][N] + k_2^- [NO][O] \\ & + k_3^- [NO][H] \end{aligned} \quad (3.4)$$

Reaction	Rate constant cm ³ /mol.s	Temperature range, K	Uncertainty factor of or %
(1) O + N ₂ → NO + N	7.6 x 10 ¹³ exp [-38,000/T]	2000-5000	2
(-1) N + NO → N ₂ + O	1.6 x 10 ¹³	300-5000	± 20% at 300K 2 at 2000-5000K
(2) N + O ₂ → NO + O	6.4 x 10 ⁹ T exp [-3150/T]	300-3000	± 30% 300-1500K 2 at 3000K
(-2) O + NO → O ₂ + N	1.5 x 10 ⁹ T exp [-19,500/T]	1000-3000	± 30% at 1000K 2 at 3000K
(3) N + OH → NO + H	4.1 x 10 ¹³	300-2500	± 80%
(-3) H + NO → OH + N	2.0 x 10 ¹³ exp [-23,650/T]	2200-4500	2

(Table 3.1: rate constants for NO formation (Heywood, 1988))

Where the k_i^+ and k_i^- are the forward and reverse for their specific reactions. These constants have been developed from numerous experimental studies and the relevant constants taken by Heywood are given in table 3.1. The species enclosed in the [] denote concentrations is moles per centimetre cubic when related the given rate constants. By following the process in which (3.4) was developed, the formation of nitrogen can be shown as:

$$\frac{d[N]}{dt} = [O][k_1^+ N_2] + k_2^+ [N][O_2] + k_3^+ [N][OH] - k_1^- [NO][N] + k_2^- [NO][O] + k_3^- [NO][H] \quad (3.5)$$

From this it is known that the concentrations of [N] is much less than that of other species of interest, so we can apply the steady state approximation that $\frac{d[N]}{dt}$ is set to zero and is used to eliminate [N] in (3.4), therefore giving:

$$\frac{d[NO]}{dt} = 2k_1^+ [O][N_2] \frac{1 - \frac{[NO]^2}{K[O_2][N_2]}}{1 + \frac{k_1^- [NO]}{k_2^+ [O_2] + k_3^+ [OH]}} \quad (3.6)$$

Where:

$$K = \left(\frac{k_1^+}{k_1^-}\right) \left(\frac{k_2^+}{k_2^-}\right)$$

During combustion NO forms in both the flame front and the post flame regions. In engines this combustion occurs at high pressures, meaning that the flame reaction zone is extremely thin giving a short residence time. Also due to the mechanics of an engine, cylinder pressures

rise throughout most of the combustion process; this means that contents burned at the start of combustion are compressed to a higher temperature compared to that of when they were combusted. This leads to the conclusion that the NO formation almost always dominates in the post flame regions, compared to the flame front production. From these assumptions it is stated in Heywood 1988

It is, therefore, appropriate to assume that the combustion and NO formation processes are decoupled and to approximate the concentrations of O, O₂, OH, H and N₂ by their equilibrium values at the local pressure and equilibrium temperature.

With these approximations, it is now valid to introduce a new set of variables to aid in the introduction of the equilibrium assumption into the formation equation:

$$R_1 = k_1^+[O]_e[N_2]_e = k_1^-[NO]_e[N]_e \quad (3.7)$$

$$R_2 = k_2^+[N]_e[O_2]_e = k_2^-[NO]_e[O]_e \quad (3.8)$$

$$R_3 = k_3^+[N]_e[OH]_e = k_3^-[NO]_e[H]_e \quad (3.9)$$

In the above equations []_e denotes equilibrium concentrations, now substituting [O]_e, [O₂]_e, [OH]_e, [H]_e and [N]_e for [O], [O₂], [OH], [H] and [N₂] into (3.6) we obtain:

$$\frac{d[NO]}{dt} = \frac{2R_1 \left\{ 1 - \left(\frac{[NO]}{[NO]_e} \right)^2 \right\}}{1 + \frac{\left(\frac{[NO]}{[NO]_e} \right) R_1}{R_2 + R_3}} \quad (3.10)$$

The below table gives typical values for R_1 , $\frac{R_1}{R_2}$ and $\frac{R_1}{R_2+R_3}$ as given in Heywood 1988, the difference between $\frac{R_1}{R_2}$ and $\frac{R_1}{R_2+R_3}$ shows the importance of adding the final reaction equation (3.3) to the analysis.

Typical values of R_1 , R_1/R_2 , and $R_1/(R_2 + R_3)^*$

Equivalence			
ratio	R_1^{**}	R_1/R_2	$R_1/(R_2 + R_3)$
0.8	5.8×10^{-5}	1.2	0.33
1	2.8×10^{-5}	2.5	0.26
1.2	7.6×10^{-6}	9.1	0.14

* At 10 atm pressure and 2600K

** Units $\text{gmol/cm}^3 \cdot \text{s}$

(Table 3.2: Typical values for R_1 , $\frac{R_1}{R_2}$ and $\frac{R_1}{R_2+R_3}$ (Heywood, 1988))

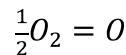
By considering the initial value of $\frac{d[NO]}{dt}$ when $\frac{[NO]}{[NO]_e} \ll 1$, the strong temperature dependence of the NO formation rate is demonstrated, then from (3.10):

$$\frac{d[NO]}{dt} = 2R_1 = 2k_1^+[O]_e[N_2]_e \quad (3.11)$$

The equilibrium oxygen atom concentration is given by:

$$[O]_e = \frac{K_{p(O)}[O_2]_e^{1/2}}{(\tilde{R}T)^{1/2}} \quad (3.12)$$

Where T is the temperature in Kelvin, \tilde{R} is the gas constant and $K_{p(O)}$ is the equilibrium constant for the reaction,



and is given by

$$K_{p(O)} = 3.6 \times 10^3 e^{\frac{-31090}{T}} \text{atm}^{\frac{1}{2}} \quad (3.13)$$

Now by combining equations (3.11) (3.12) and (3.13) with k_1^+ from Table 3.1, we get the following expression for the initial formation rate of NO:

$$\frac{d[NO]}{dt} = \frac{6 \times 10^{16}}{T^{1/2}} \exp\left(\frac{-69090}{T}\right) [O_2]_e^{1/2} [N_2]_e \quad \text{in } \frac{\text{mol}}{\text{cm}^3 \cdot \text{s}} \quad (3.14)$$

As shown in the above equation, the initial formation rate of nitric oxide has a strong temperature dependency, as the T is in the exponential term. This shows that when high

temperature situations result, high nitric oxide formation rates will exist. Also if there are high oxygen concentrations, or a combination of the two, there will be high initial formation rates of NO.

3.2 Characteristic Time Formulation

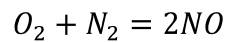
Also it is important to develop a relationship for the characteristic time for the reaction. This characteristic time is denoted by the symbol τ_{NO}^{-1} , and can be defined for the NO formation process by:

$$\tau_{NO}^{-1} = \frac{1}{[NO]_e} \frac{d[NO]}{dt} \quad (3.15)$$

By using the definition for the equilibrium constant for $[NO]_e$ of:

$$K_{NO} = 20.3 \times \exp(-21650/T)$$

For the reaction of:



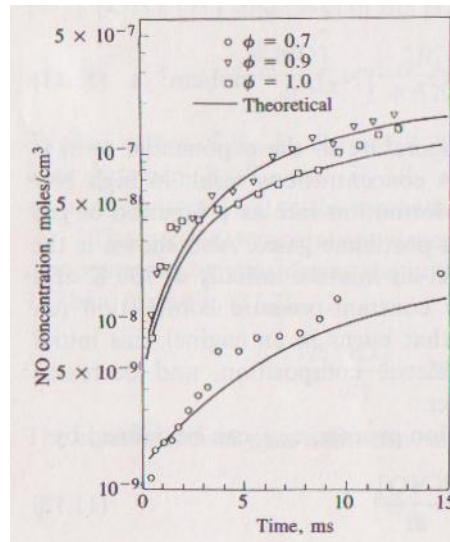
By making use of the fact that $[NO]_e = (K_{NO}[O_2]_e[N_2]_e)^{1/2}$ and combining Equations (3.14) and 3.15 we obtain:

$$\tau_{NO} = \frac{8 \times 10^{-16} T \exp(58300/T)}{p^{1/2}} \quad (3.16)$$

Where τ_{NO} is in seconds and p is in atmospheres, also in this equation, use has been made of the fact that $\tilde{x}_{N_2} \approx .71$. It is stated in Heywood 1988 that “For engine combustion conditions, τ_{NO} is usually comparable to or longer than the times characteristic of changes in engine conditions so the process is kinetically controlled.” This meaning that the time it takes for engine conditions to change are typical of the values of τ_{NO} . However the characteristic time becomes of the same order of typical combustion times for close to stoichiometric conditions at maximum burned gas temperatures and temperatures, giving the results of equilibrium NO concentrations.

This formulation has been backed up under conditions typically found in engines by the studies of Newhall and Shaded (as provided in Heywood 1988) in high pressure combustion bomb studies. The NO production was measured using the q-band absorption technique

behind hydrogen-air and propane-air planar flames with axial propagation in a cylindrical bomb. The graph below shows some of the results that were compared from these experiments and predictions made with the kinetic scheme.



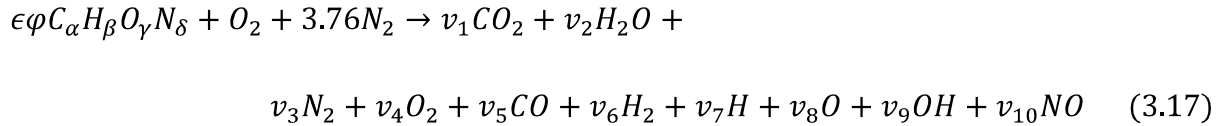
(Figure 3.1: Correlation between experimental and theoretical data (Heywood, 1988))

As shown in this figure the correlation between the experimental data and the predictions are excellent. This gives grounds for the analysis to be employed in the analysis of this work with confidence in the accuracy.

3.3 Equilibrium Combustion Products Formulation

From the derivation of the formation rate of nitric oxide, the relationship between the fuel and the rate of NO should be achieved by substituting the specific temperature and equilibrium products for that fuel. From this data, biodiesel and diesel can be compared in order to determine the effects of using the alternative fuel. From the characteristic time equation, the relationship between the engine parameters, such as compression ratio can be determined by evaluating the equation across a range of temperatures and pressures (related directly to compression ratio) in order to determine the affects of changing such parameters related to the formation of nitric oxide. In order to determine the formation rate of nitric oxide, the relevant equilibrium combustion products need to be determined, as well as the relevant temperatures. For this analysis, a range of temperatures will be used in order to analyse the affects that the temperature will have on the nitric oxide formation. The equilibrium combustion products now have to be determined in order to compare diesel and biodiesel fuels and its formulation will now be discussed.

The first step to determine the equilibrium combustion products of a combustion process is to determine the species that will be considered. This is done by considering all the species involved and eliminating the irrelevant ones. This process based on the work of Ferguson 1986, where the following equation represents the chemical reaction with the relevant species involved.



By utilising atom balancing we can obtain the following equations:

$$C \quad \epsilon\varphi\alpha \quad = (y_1 + y_5)N \quad (3.18)$$

$$H \quad \epsilon\varphi\beta \quad = (2y_2 + 2y_6 + y_7 + y_9)N \quad (3.19)$$

$$O \quad \epsilon\varphi\gamma + .42 \quad = (2y_1 + y_2 + 2y_4 + y_5 + y_8 + y_9 + y_{10})N \quad (3.20)$$

$$N \quad \epsilon\varphi\delta + 1.58 \quad = (2y_3 + y_{10})N \quad (3.21)$$

Where N is the total number moles ($N = \sum_{i=1}^{10} v_i$), now by definition and conservation of mass:

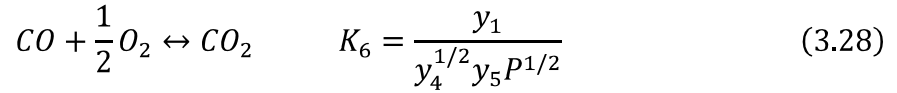
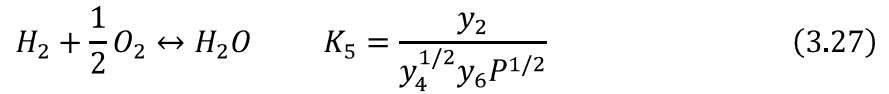
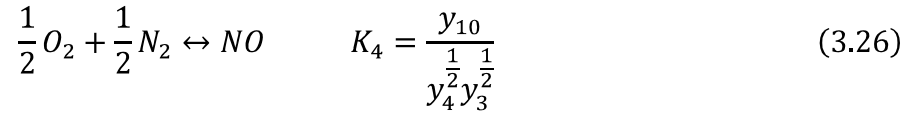
$$\sum_{i=1}^{10} y_i - 1 = 0 \quad (3.22)$$

With the introduction of six equilibrium constants, there will be eleven equations for the ten unknown mole fractions y_i , and the number of moles N . So we have:

$$\frac{1}{2}H_2 \leftrightarrow H \quad K_1 = \frac{y_7 P^{\frac{1}{2}}}{y_6^{\frac{1}{2}}} \quad (3.23)$$

$$\frac{1}{2}O_2 \leftrightarrow O \quad K_2 = \frac{y_8 P^{\frac{1}{2}}}{y_4^{\frac{1}{2}}} \quad (3.24)$$

$$\frac{1}{2}H_2 + \frac{1}{2}O_2 \leftrightarrow OH \quad K_3 = \frac{y_9}{y_4^{\frac{1}{2}} y_6^{\frac{1}{2}}} \quad (3.25)$$



This method is simpler when considering limited species lists such as the present case as the use of equilibrium constants is the same as maximising the entropy of the gas. The solution of these equations is based on a method developed by Olikara and Borman, as noted in Ferguson 1986. Olikara and Borman have curve fitted the equilibrium constants and derived a formula for their relationship of:

$$\log K_p = A \ln \left(\frac{T}{1000} \right) + \frac{B}{T} + C + DT + ET^2 \quad (3.29)$$

Where T is in Kelvin, and is valid for $600 < T < 4000$ K, the table below denotes values for their determination and use in the following set of equations:

	A	B	C	D	E
K ₁	0.432168E + 00	-0.112464E + 05	0.267269E + 01	-0.745744E - 04	0.242484E - 08
K ₂	0.310805E + 00	-0.129540E + 05	0.321779E + 01	-0.738336E - 04	0.344645E - 08
K ₃	-0.141784E + 00	-0.213308E + 04	0.853461E + 00	0.355015E - 04	-0.310227E - 08
K ₄	0.150879E - 01	-0.470959E + 04	0.646096E + 00	0.272805E - 05	-0.154444E - 08
K ₅	-0.752364E + 00	0.124210E + 05	-0.260286E + 01	0.259556E - 03	-0.162687E - 07
K ₆	-0.415302E - 02	0.148627E + 05	-0.475746E + 01	0.124699E - 03	-0.900227E - 08

(Table 3.3: Variable values for equation (3.29) (Ferguson, 1988))

$$y_7 = c_1 y_6^{1/2} \quad \text{where } c_1 = \frac{K_1}{P^{1/2}} \quad (3.30)$$

$$y_8 = c_2 y_4^{1/2} \quad \text{where } c_2 = \frac{K_2}{P^{1/2}} \quad (3.31)$$

$$y_9 = c_3 y_4^{1/2} y_6^{1/2} \quad \text{where } c_3 = K_3 \quad (3.32)$$

$$y_{10} = c_4 y_4^{1/2} y_3^{1/2} \quad \text{where } c_4 = K_4 \quad (3.33)$$

$$y_2 = c_5 y_4^{\frac{1}{2}} y_6 \quad \text{where } c_5 = K_5 P^{\frac{1}{2}} \quad (3.34)$$

$$y_1 = c_6 y_4^{\frac{1}{2}} y_5 \quad \text{where } c_6 = K_6 P^{\frac{1}{2}} \quad (3.35)$$

Now by re-evaluating equations (3.18) to (3.21), N can be eliminated by dividing (3.19), (3.20) and (3.21) by (3.18) to give the following equations:

$$2y_2 + 2y_6 + y_7 + y_9 - \frac{\beta}{\alpha}(y_1 + y_5) = 0 \quad (3.37)$$

$$2y_1 + y_2 + 2y_4 + y_5 + y_8 + y_9 + y_{10} - \left[\left(\gamma + \frac{0.42}{\epsilon\varphi} \right) \frac{1}{\alpha} (y_1 + y_5) \right] = 0 \quad (3.38)$$

$$2y_3 + y_{10} - \left[\left(\delta + \frac{1.58}{\epsilon\varphi} \right) \frac{1}{\alpha} (y_1 + y_5) \right] = 0 \quad (3.39)$$

To simplify these equations three ratios were determined, they are:

$$d_1 = \frac{\beta}{\alpha}; \quad d_2 = \frac{\gamma}{\alpha} + \frac{0.42}{\epsilon\varphi\alpha}; \quad d_3 = \frac{\delta}{\alpha} + \frac{1.58}{\epsilon\varphi\alpha} \quad (3.40)$$

By substituting equations (3.30) to (3.35) into equations (3.37) to (3.39) we obtain three equations and four unknowns, also using equation (3.22) and substituting equations (3.30) to (3.35), we obtain one more equation, making the system solvable. These four equations ((3.22) and (3.37) to (3.39)) can be represented in the form:

$$f_j(y_3, y_4, y_5, y_6) = 0 \quad \text{and } j = 1, 2, 3, 4 \quad (3.41)$$

An approximate solution vector can be determined by using Table 3.4 and is denoted by:

$$[y_3^{(1)}, y_4^{(1)}, y_5^{(1)}, y_6^{(1)}] \quad (3.42)$$

i	Species	$\varphi \leq 1$	$\varphi > 1$
1	CO ₂	$\alpha\epsilon\varphi$	$\alpha\varphi\epsilon - v_5$
2	H ₂ O	$\beta\varphi\epsilon/2$	$0.42 - \varphi\epsilon(2\alpha-\gamma) + v_5$
3	N ₂	$0.79 + \delta\varphi\epsilon/2$	$0.79 + \delta\varphi\epsilon/2$
4	O ₂	$0.21(1 - \varphi)$	0
5	CO	0	v_5
6	H ₂	0	$0.42(\varphi - 1) - v_5$

(Table 3.4: Low Temperature Combustion Products, v_i (moles/mole of air) (Ferguson, (1988))

Which should result in an estimation close to the solution vector:

$$(y_3^*, y_4^*, y_5^*, y_6^*) \quad (3.43)$$

By using Taylor series expansion on equation (3.41), we let:

$$\Delta y_i = y_i^* - y_i^{(1)} \quad (3.44)$$

And neglecting second order or higher derivatives we have:

$$f_j + \frac{\partial f_j}{\partial y_3} \Delta y_3 + \frac{\partial f_j}{\partial y_4} \Delta y_4 + \frac{\partial f_j}{\partial y_5} \Delta y_5 + \frac{\partial f_j}{\partial y_6} \Delta y_6 \approx 0 \quad j = 1,2,3,4 \quad (3.45)$$

Which solving this set of linear equations will give approximations to $\Delta y_i; i = 3,4,5,6$. This is done by employing matrix algebra and Gaussian elimination, which then means the second approximation is then:

$$y_i^{(2)} = y_i^{(1)} + \Delta y_i \quad i = 3,4,5,6 \quad (3.46)$$

This second approximation then replaces the first approximation, and the process is repeated until the changes are very small, according to the set tolerance

$$|\Delta y_i| \leq \xi \ll 1 \quad (3.47)$$

Where ξ is some specified tolerance. The next step is to define the following partial derivatives:

$$D_{ij} = \frac{\partial y_i}{\partial y_j} \quad \begin{matrix} i = 1,2,7,8,9,10 \\ j = 3,4,5,6 \end{matrix} \quad (3.48)$$

From equations (3.30) to (3.35) we derive the following non-zero derivatives:

$$\begin{aligned}
D_{76} &= \frac{1}{2} \frac{c_1}{y_6^{1/2}} & D_{103} &= \frac{1}{2} \frac{c_4 y_4^{1/2}}{y_3^{1/2}} \\
D_{84} &= \frac{1}{2} \frac{c_2}{y_4^{1/2}} & D_{26} &= c_5 y_4^{1/2} \\
D_{94} &= \frac{1}{2} \frac{c_3 y_6^{1/2}}{y_4^{1/2}} & D_{24} &= \frac{1}{2} \frac{c_6 y_6}{y_4^{1/2}} \\
D_{96} &= \frac{1}{2} \frac{c_3 y_4^{1/2}}{y_6^{1/2}} & D_{14} &= \frac{1}{2} \frac{c_6 y_5}{y_4^{1/2}} \\
D_{104} &= \frac{1}{2} \frac{c_4 y_3^{1/2}}{y_4^{1/2}} & D_{15} &= c_6 y_4^{1/2}
\end{aligned}$$

By evaluating equation (3.45) in the matrix notation $[A][Z] = [B]$, we have:

$$[B] = [-f], [Z] = [\Delta y] \text{ and}$$

$$A_{11} = \frac{\partial f_1}{\partial y_3} = 1 + D_{103}$$

$$A_{12} = \frac{\partial f_1}{\partial y_4} = D_{14} + D_{24} + 1 + D_{84} + D_{104} + D_{94}$$

$$A_{13} = \frac{\partial f_1}{\partial y_5} = D_{15} + 1$$

$$A_{14} = \frac{\partial f_1}{\partial y_6} = D_{26} + 1 + D_{76} + D_{96}$$

$$A_{21} = \frac{\partial f_2}{\partial y_3} = 0$$

$$A_{22} = \frac{\partial f_2}{\partial y_4} = 2D_{24} + D_{94} - d_1 D_{14}$$

$$A_{23} = \frac{\partial f_2}{\partial y_5} = -d_1 D_{15} - d_1$$

$$A_{24} = \frac{\partial f_2}{\partial y_6} = 2D_{26} + 2 + D_{76} + D_{96}$$

$$A_{31} = \frac{\partial f_3}{\partial y_3} = D_{103}$$

$$A_{32} = \frac{\partial f_3}{\partial y_4} = 2D_{14} + D_{24} + 2 + D_{84} + D_{94} + D_{104} + d_2 D_{14}$$

$$A_{33} = \frac{\partial f_3}{\partial y_5} = 2D_{15} + 1 - d_2 D_{15} - d_2$$

$$A_{33} = \frac{\partial f_3}{\partial y_5} = 2D_{15} + 1 - d_2 D_{15} - d_2$$

$$A_{34} = \frac{\partial f_3}{\partial y_6} = D_{26} + D_{96}$$

$$A_{41} = \frac{\partial f_4}{\partial y_3} = 2 + D_{103}$$

$$A_{42} = \frac{\partial f_4}{\partial y_4} = D_{104} - d_3 D_{14}$$

$$A_{43} = \frac{\partial f_3}{\partial y_5} = -d_3 D_{15} - d_3$$

$$A_{44} = \frac{\partial f_4}{\partial y_6} = 0$$

Using Gaussian elimination on the matrix equation:

$$[A][\Delta y] + [f] = 0 \quad (3.49)$$

The solution for Δy_i can be determined for use in equation (3.46). The solution of equations (3.46) through (3.49) is evaluated until the specified tolerance is met. With the mole fractions now known for the individual situation, the mole concentrations can then be determined by using equation (3.18):

$$N = \frac{\epsilon \varphi \alpha}{(y_1 + y_5)} \quad (3.50)$$

Giving:

$$v_i = y_i N \quad (3.51)$$

The concentrations $[O_2]_e$ and $[N_2]_e$ are then determined by:

$$[O_2]_e = \frac{v_4}{MW_{O_2}} \quad (3.52)$$

And

$$[N_2]_e = \frac{v_3}{MW_{N_2}} \quad (3.53)$$

Where MW_{O_2} and MW_{N_2} are the molecular weights Oxygen and Nitrogen.

With these variables now known, it is possible to evaluate equation (3.14) across a range of temperatures to determine the initial formation rates of nitric oxide. It will then be possible to alter the fuels chemical composition, simulating the change in fuel type and compare the affects of these changes in the equilibrium combustion products and the formation rate of nitric oxide. This will help analyse the first main objective of this project. The second however still needs to be discussed.

3.4 Transient Heat Flux

The second main technical objective is to determine the effect the fuel will have on transient heat flux produced. The first goal for this objective was to develop a computer model to simulate the transient heat flux in the engine, specific to the fuel properties. This could be achieved by analysing the combustion over one engine cycle and iteratively solving the heat flux. This however proved to be a lengthy process, and after the model for the formation rate of nitric oxide was completed, insufficient time remained to develop the second model so other means of evaluating this objective had to be introduced. One way of determining this affect is to analyse the change in the adiabatic flame temperature for the two fuels across a range of fuel air mixtures. As explained in earlier chapters, the adiabatic flame temperature is related to the temperature of the combustion, so the change in this parameter will give a very good indication of the heat flux's response to the change in fuel. As mentioned in chapter two, the adiabatic flame temperature is determined by evaluating the enthalpy of the combustion reactants (the unburnt air and fuel) and the enthalpy of the combustion products. These enthalpies change with respect to the temperature that they are at, this is how the adiabatic flame temperature can be determined, by evaluating the combustion products at different temperatures, and the temperature at which they are equal is the adiabatic flame temperature. To aid in the model development, a model that was previously developed by Dr David Buttsworth and Dr Talal Yusaf for the analysis of a spark ignition engine was donated for modification. This model follows the research and literature that was studied for the development of the theory for this project.

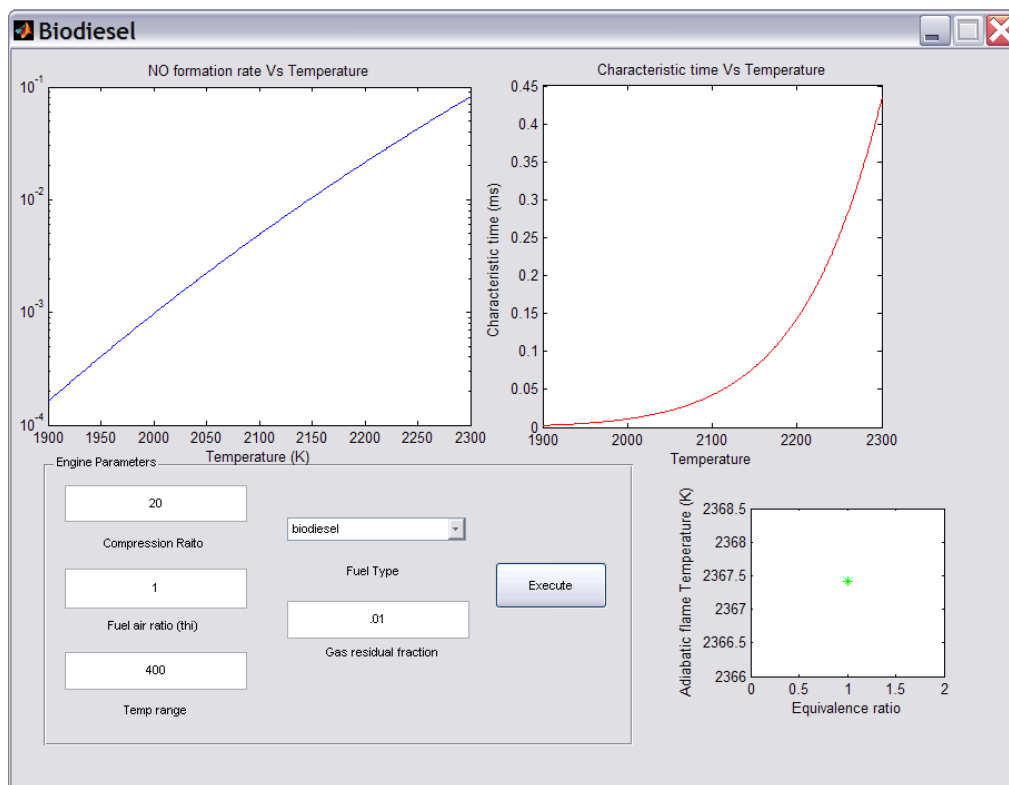
3.5 MATLAB Programmes

The model uses five main programmes for the solution of the problem. The model that was donated also comprised of a program to determine the equilibrium combustion products that was the same as the one developed from the theory above, but had an alternate format for synchronising between the four other programmes, this led to the decision to use this program in order to speed up the formulation of the model. The first program called “airdata” was used to specify the thermodynamic properties of the air and combustion products. The second program “fueldata1” was used to specify the specific properties for the fuel, such as the chemical composition, that was being evaluated in the model. The third program “farg1” is used to determine the enthalpy of the of the combustion reactants incorporating fuel-air residual gas as specified by the user.

The fourth program “ecp1” is used to determine the equilibrium state of combustion products. This program follows the solution of equations (3.46) through (3.49) and yields the solution of the mole fractions of all the species in the combustion products as shown in equation (3.17). The fifth program “Tadiabatic1” ties the above four programmes together in order to gain a solution for the adiabatic flame temperature. It does this by first specifying the user defined properties, these are the fuel type, the compression ratio, fuel to air ratio, and gas residual fraction (fraction of production gasses remaining in the cylinder from the previous engine cycle). The thermodynamic properties of the air and the combustion products are then specified by running “airdata”. The properties such as the enthalpy of the combustion reactants are then determined by running the program “farg1”. With the enthalpy of the reactants known the enthalpy of the products have to be determined iteratively. The program “ecp1” is then run, determining the enthalpy of the products at the specified temperature. If the enthalpies don't match, the program will alter the temperature that the combustion products are evaluated and the “ecp1” is run again with this new temperature.

This process continues until the enthalpies are approximately equal, the precision is dependent on the tolerance set in the program. This now gives all the information that is required for the solution of equations (3.14) and (3.16). Equation (3.14) is then programmed into “Tadiabatic1” after all the previous steps had been completed. This equation was solved iteratively across a specified temperature range. Equation (3.16) is also programmed in after equation (3.14) for analysis.

For ease of use, a graphical user interface (GUI) was developed to ease the control the specified inputs for the simulation. All the variable inputs were set to windows for variables to be typed in except the fuel type, as only diesel and biodiesel were to be considered into the simulation. Three graph areas were set up to display the results from the simulation, firstly the initial rate of formation of nitric oxide versus the temperature it was to be evaluated over. The second was the characteristic time for the formation displayed over the evaluated temperature range. Lastly the adiabatic flame temperature was shown against the equivalence ratio that is set by the user. This interface makes it easier for analysis when the user is unfamiliar with the programming logic of MATLAB, and simplifies the process to change the variable in the simulation. The figure below shows the layout of the graphical user interface.



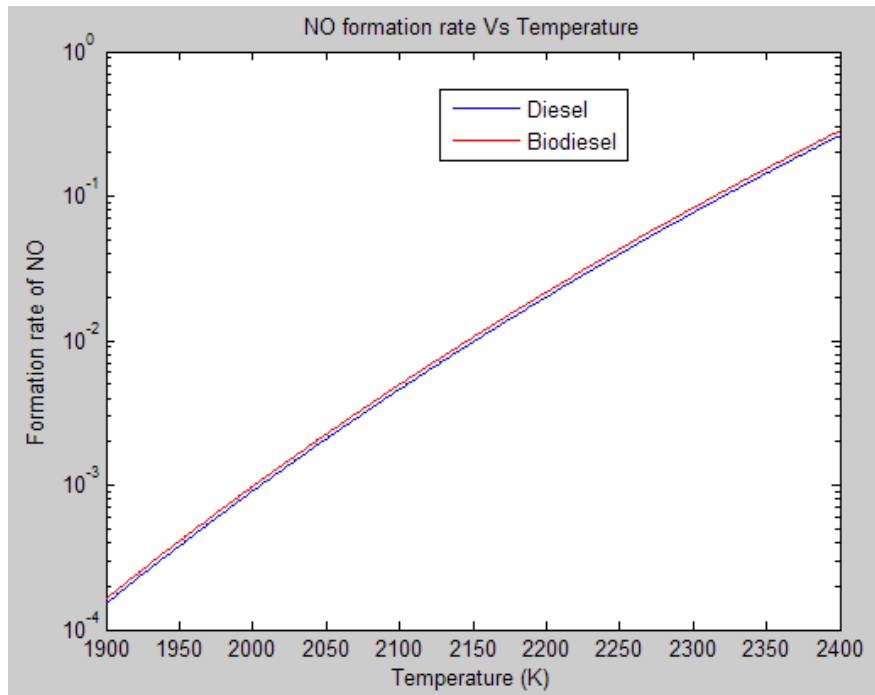
(Figure 3.2: Graphical User Interface developed for this simulation)

It is now possible to evaluate the formation rate of nitric oxide, the characteristic time for this reaction, and the adiabatic flame temperature change. These solutions can be evaluated across different gas residual fractions, temperature ranges that will be related to relevant temperatures experienced in the combustion. Also the compression ratio can be altered, which can simulate different engines as well as aging engines, as well as the fuel to air ratio, to aid in the analysis and optimisation recommendations for the use of biodiesel.

Chapter 4: Results and Discussion

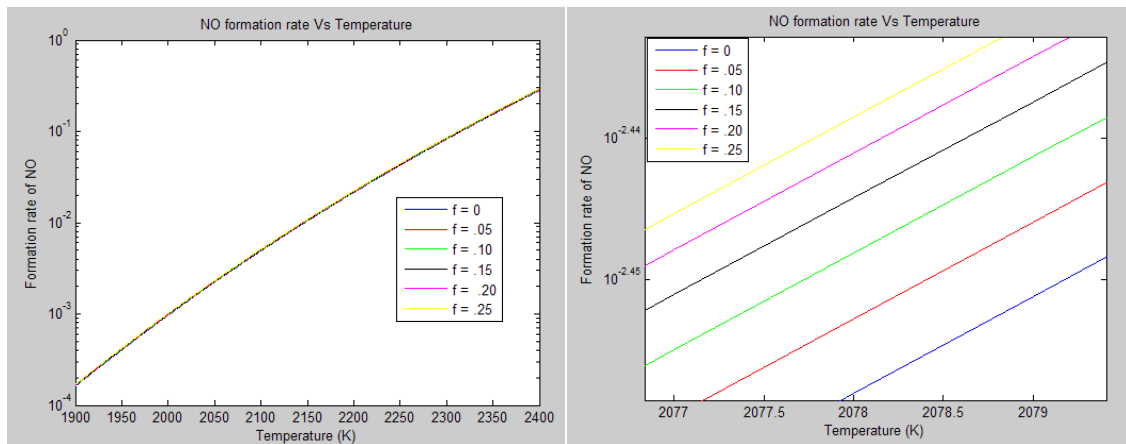
4.1 Results of Oxides of Nitrogen Analysis

The first set of results that will be analysed will be the formation rates of oxides of nitrogen.



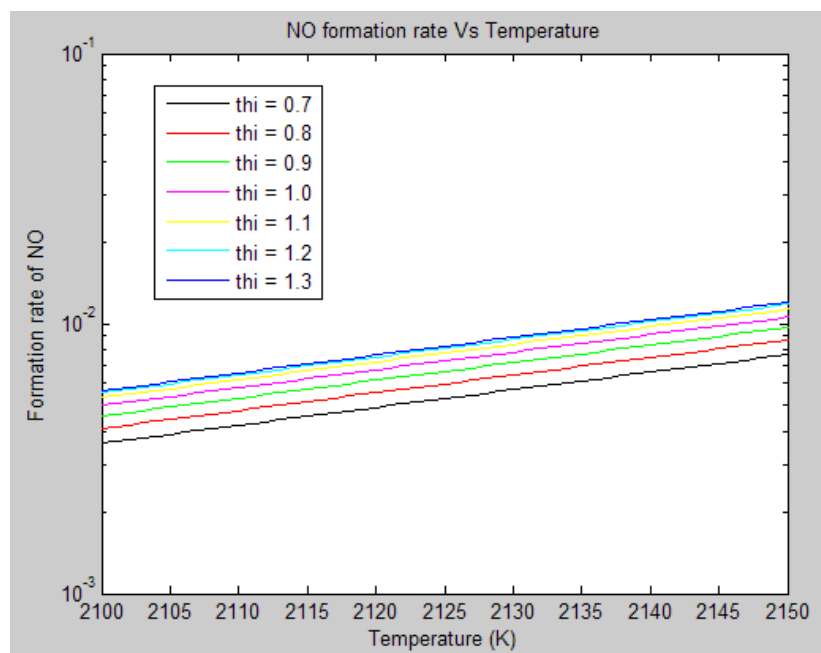
(Figure 4.1: Formation rate of NO, Diesel Vs Biodiesel)

Figure 4.1 shows the relationship between the initial formation rate of NO and biodiesel compared to diesel via the solution of equation (3.14). This figure is produced by a compression ratio of twenty, an equivalence ratio of one, a temperature range of five hundred and a residual gas fraction of .05. As shown in this graph, this figure shows a clear indication that biodiesel has a higher initial formation rate of oxides of nitrogen compared to the traditional diesel. This graph also shows that as the temperature increases, there is a dramatic increase in the formation rate of oxides of nitrogen for both biodiesel and diesel, as visible by the logarithmic scale of the y-axis representing the formation rate. This means that the higher the temperature of the combustion products and surroundings, there will be a much greater formation rate of NO. As equation (3.14) is dependent on temperature and the equilibrium products of $[O_2]_e$ and $[N_2]_e$, it is important to analyse the parameters that will directly affect these factors. Factors that affect the products are the chemical composition, which has been accounted for in the above figure, the next is the gas residual fraction.



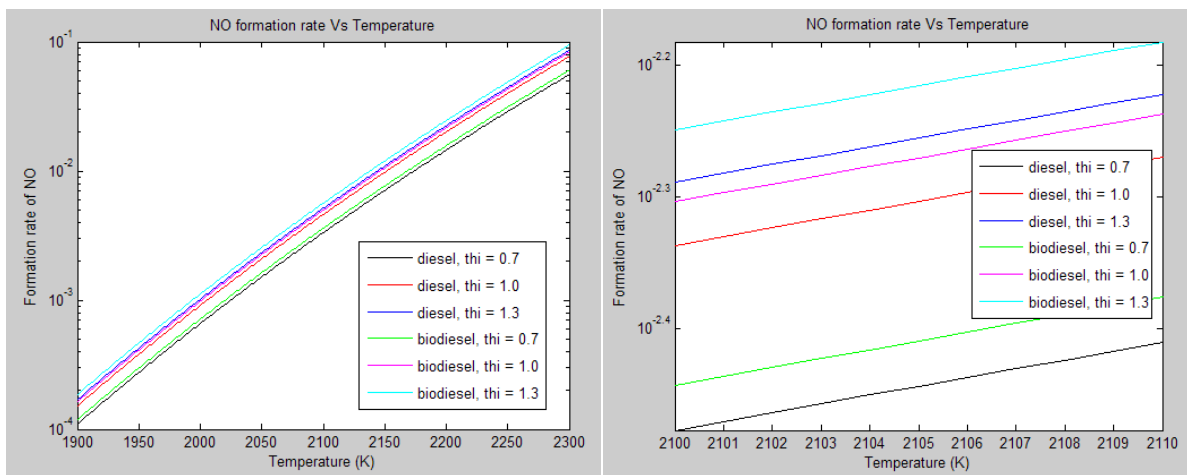
(Figure 4.2: Effect of gas residual fraction - Biodiesel fuel)

By evaluating the formation rate of NO of biodiesel with varying gas residual fractions (f), it is visible that the change in the formation rate is negligible. As visible in the left hand graph of figure 4.2, there is no possible distinction between the formation rate and the different residual fraction. By zooming in on one section (shown in right hand graph in figure 4.2) the higher residual gas fraction, the higher formation rate of nitric oxide, but this increase can be ignored due to the minuscule difference. As this effect is neglected, the next characteristic that can alter the combustion products is equivalence ratio. By varying the equivalence ratio, the amount of fuel to air is altered, altering the chemical composition of the combustion reactants. The following figure displays the change in formation rate of nitric oxide with the change in equivalence ratio.



(Figure 4.3: effect of change in equivalence ratio on formation rate)

This figure is generated with a compression ratio of twenty, gas residual fraction of .05 (5%) and biodiesel as the fuel type. The graph has been concentrated over a temperature range of fifty Kelvin. The graph shows that with a with lean mixtures (ϕ less than one), the initial formation rates of nitric oxide are lower for values further from the stoichiometric value (ϕ equal to one). With mixtures that are rich (ϕ greater than one) the greater the richness, the greater the formation rate of nitric oxide. It also shows that for leaner mixtures, the change in formation rate over the change in equivalence ratio is greater than that for richer mixtures; this is visible by the distance between the lines. The rich mixtures are closer together, especially for mixtures equal to 1.3 and 1.2 which has negligible difference, but the lean mixtures have a very visible difference ($\phi = 0.7, 0.8, 0.9$). Comparing the two fuels together with a different equivalence ratio gives the relationship shown below.

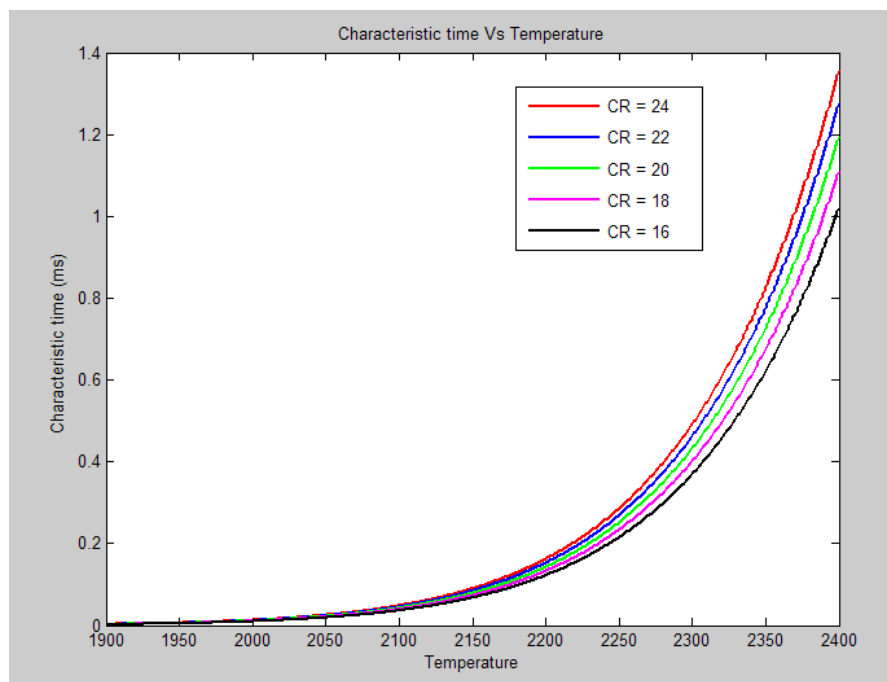


(Figure 4.4: Comparison between diesel and biodiesel with different equivalence ratio)

Figure 4.4 was created with a compression ratio of twenty, gas residual fraction of .05 and by altering the fuel type and equivalence ratio. The right hand graph shows the full comparison across the four hundred Kelvin. As these lines are relatively parallel, a graph with a smaller range was created to display more clearly the relationship for the variables. As shown by the right hand graph diesel follows the relationship of Figure 4.3, with richer mixtures having higher nitric oxide formation rates. This graph displays the change that the different fuel makes to the results. Each diesel mixture shows a lower formation rate compared to its biodiesel equivalent. It also shows that the rich diesel mixture is quite close to the formation rate of stoichiometric value for biodiesel, giving diesel an advantage as a richer diesel mixture can be used with minimal change in nitric oxide formation rate compared to a stoichiometric biodiesel mixture.

4.2 Results of Characteristic Time Analysis

From the results that have been obtained and discussed above, it is clear that from the solution of equation (3.14), there are clear differences between diesel and biodiesel. The first is that keeping all the engine parameters that are variable in this model the same, biodiesel will result in a high initial formation rate of nitric oxide compared to diesel. The second is that if the gas residual fraction is increased the model shows an increase in the formation rates, but it is so small so it could be neglected. The third is that a higher equivalence ratio gives a high initial formation rate of nitric oxide for both biodiesel and diesel. But keeping in mind the first outcome, biodiesel will result in a higher formation rate across the range. The fourth is that when increasing the equivalence ratio by the same increment for rich mixtures and lean mixtures, the lean mixtures will give a greater increase (or decrease depending on the direction of the change) in formation rate of nitric oxide. The next parameter that will be analysed will be the characteristic time. The characteristic time will change as the pressure will change. As the model for the transient heat flux was unable to be completed, the modelled pressure could not be incorporated into this equation. With this limitation, the isentropic compression pressure was used to estimate the cylinder pressure and therefore the characteristic time. The graph below represents the solution of equation (3.16).

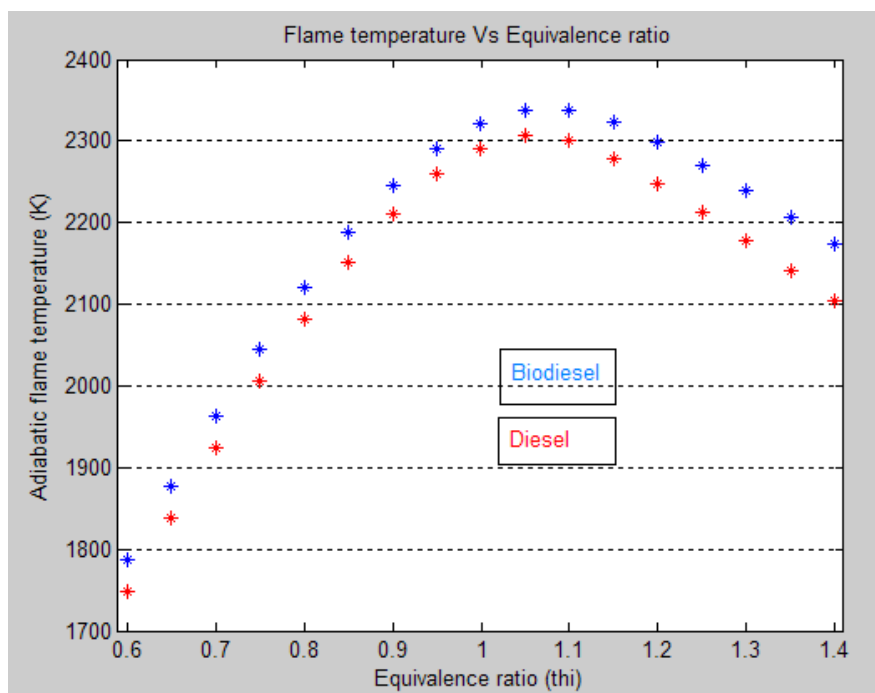


(Figure 4.5: Characteristic time Vs Temperature with varying compression ratio)

Figure 4.5 shows the effect of varying the compression ratio for the characteristic time. As the characteristic time is a good representation of the time it takes for engine conditions to change, it is important to understand how the cylinder temperature will affect this parameter. This graph shows that as the compression ratio is increased the characteristic time increases proportionally, as the equation is an exponential equation the higher the input variable, the greater the output variable will be. As shown in this figure, the higher temperatures result in much higher characteristic times, therefore meaning that as the cylinder temperatures increase, it will take longer for the engine conditions to change, giving longer amounts of time for the formation of nitric oxide to take place. This therefore means that the fuel that generates higher in cylinder as well as exhaust temperatures will generate higher amounts of nitric oxide. As mentioned above, as the compression ratio is increased, the pressure in the cylinder will increase, giving higher characteristic times, and longer for the reactions to occur, creating more nitric oxide emissions.

4.3 Results of Adiabatic Time Analysis

This also means that it is important to determine the parameters that will affect the temperature of the cylinder contents, one such parameter is the equivalence ratio, which can be related to the adiabatic flame temperature for each mixture as shown in the figure (4.6) below.



(Figure 4.6: Equivalence ratio Vs Adiabatic flame temperature)

Figure 4.6 was produced with a residual gas fraction of .05, and by altering the equivalence ratio for both diesel and biodiesel fuels. From this graph, it is easily noticeable that biodiesel results in a higher adiabatic flame temperature for all equivalence ratios considered. As a stoichiometric fuel-air mixture has an equivalence ratio of one, it is seen that fuel-air mixtures greater than stoichiometric (rich mixtures) tend to have greater flame temperatures compared to their counterparts that have mixtures lower than stoichiometric (lean mixtures). This indicates that mixtures that are rich will have higher formation rates of oxides of nitrogen. This graph also shows that the adiabatic flame temperatures for the same equivalence ratios are closer to together for leaner mixtures, and are further apart for richer mixtures. This indicates that that the difference between the formation rates of oxides of nitrogen will be greater for richer mixtures than in leaner mixtures.

4.4 Findings from Simulation

From the results that have been obtained from the simulation, quite a few relationships can be determined for both fuels.

1. With the same conditions such as equivalence ratio and residual gas fraction, the initial formation rate for nitric oxide will be greater for biodiesel compared to diesel.
2. There is negligible change in nitric oxide formation rates as the residual gas fraction is changed.
3. Higher equivalence ratios give slightly higher formation rates of nitric oxide.
4. As the compression ratio is increased, the characteristic time also increases, giving lengthier times for the oxides of nitrogen to form.
5. Adiabatic flame temperatures are higher across all equivalence ratios investigated.
6. Adiabatic flame temperatures are greater for rich mixtures compared to lean mixtures.

One factor that was planned to investigate was the injection timing, unfortunately as the transient heat flux model was not completed; this factor could not be investigated using the simulation. It is important however to link the results that have been found to evidence to support these findings.

4.5 External Experimental Results: Emissions

It has been found (Van Gerpen, Tat and Wang) that actual injection timing of an injection system is increased when biodiesel is substituted (or blended with) for diesel. It is stated in

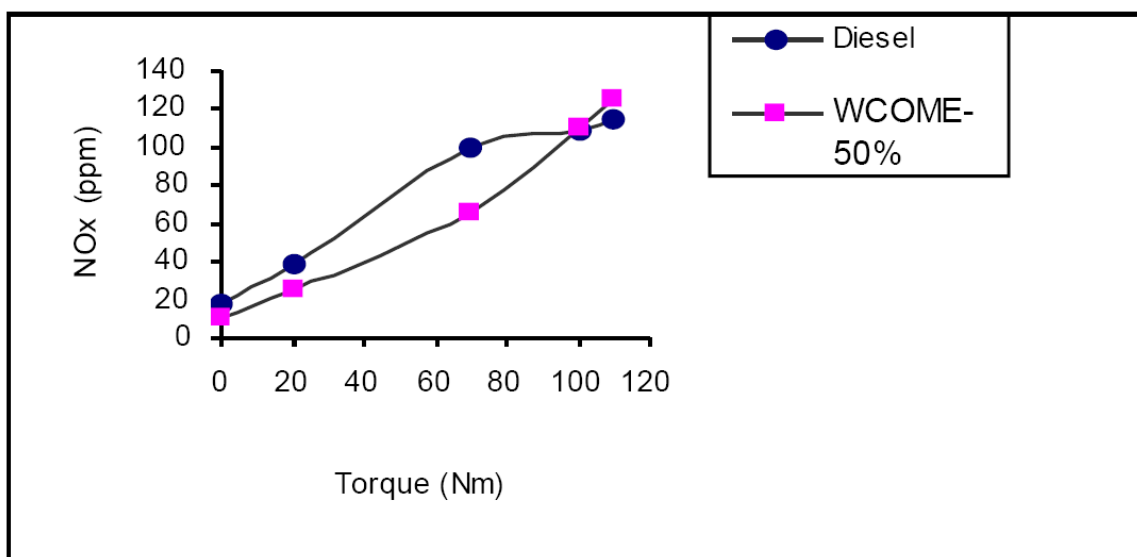
Heywood, 1988, that “As injection timing is retarded, so the combustion process is retarded; NO formation occurs later, and concentrations are lower since peak temperatures are lower.” This leads to conclusion that if the reverse were to occur, as to say the injection timing is advanced, the combustion process will also advance, causing higher peak temperatures and pressures which will lead to increased nitric oxide concentrations. As found in experimental work, with the natural advance in injection, there is a high possibility in increasing oxides of nitrogen concentrations with a change in fuel. It is also known that biodiesel has a higher cetane number compared to conventional diesel. As stated in Van Gerpen, Tat and Wang “Shorter ignition delay advances the start of combustion and the ignition delay time is mostly affected by the fuel’s cetane number.” This also leads to the conclusion that the use of biodiesel will result in an advance in combustion timing due to the higher cetane number. This means that biodiesel has two factors that will advance the combustion timing, leading to a much higher probability of an increase in oxides of nitrogen. It is also stated in Heywood, 1988, that “The 20 degrees after the start of combustion is the critical time period...almost all of the NO forms within the 20° following the start of combustion.” This draws the conclusion that the injection timing and combustion timing are critical in controlling the formation of oxides of nitrogen. Retarding the injection timing to counteract the effects of decreased ignition delay and advanced injection timing is a key step in correcting the ignition timing back to its designed value in every engine. Doing this will result in an equal ignition timing, decreasing the in cylinder temperatures and pressures, therefore decreasing the formation of oxides of nitrogen, making it possible for biodiesel to produce similar, if not lower values of oxides of nitrogen emissions.

As shown in figure 4.1, the simulation shows an increase in the formation rates of nitric oxide, there was no relevant data available to support the increase in formation rates in the same has been evaluated here. The only supporting evidence is that it was based on equation 3.14, also derived in Heywood, 1988, for the initial formation rate of nitric oxide. Comparison between the simulated results for the effect of increasing residual gas fraction and the theoretical relationship can also be made from making reference to Heywood. It is noted that an increase in diluents (such as exhaust gas residue) can effectively reduce the nitric oxide formation rate and hence the production of oxides of nitrogen. This is achieved by reducing the burnt gas temperatures in the combustion mixture. It should be noted that other diluents can be used to achieve this effect (such as N₂ and CO₂). The use of exhaust gas residue is effective as it is accomplished by the camshaft timing and is already contained in

the cylinder from the previous engine cycle. Figure 4.2 shows that for the same temperature, a higher residual gas fraction will result in a higher formation rate of nitric oxide, but as the temperature will decrease from the increase in diluents, the formation rate will be less for the equivalent situation. Figure 4.2 shows that with a drop in temperature of only one degree Kelvin or less for a concentration of five percent residual gas, the formation rate will be at worst equal, and will decrease from there, showing promising support to the evidence provided by Heywood.

From the work presented in this chapter, there has been moderate experimental work carried out on the performance of biodiesel compared to the traditional diesel. Firstly, the experimental data for emissions will be concentrated. Figure 4.7 shows the relationship between engine torque and the production of oxides of nitrogen in parts per million, as carried out by Yusaf et al.

This experiment was carried out on a 2.2 litre ford diesel engine running two fuels, conventional diesel and fifty percent blend of conventional diesel with fifty percent biodiesel made from waste cooking oil (palm oil) methyl ester. In this experiment, the engine torque level was varied to determine the corresponding effects on different parameters.

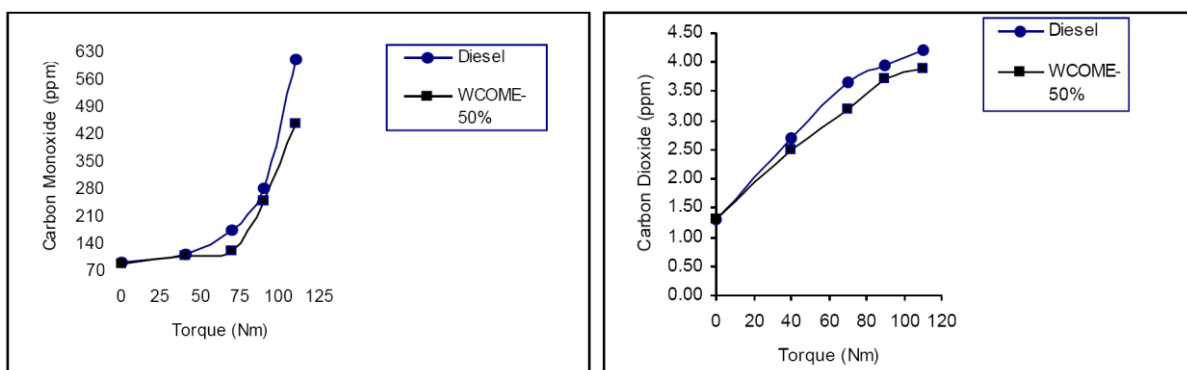


(Figure 4.7: Effect of torque on NO_x emissions using diesel and waste cooking oil biodiesel blend (Yusaf et al))

It is visible from this figure that under most loading conditions the waste cooking oil blend produces lower amounts of NO_x emissions. The oxides of nitrogen emissions seem to equal

at a load just under one hundred Newton-metres, after which the biodiesel blend has increased oxides of nitrogen emissions. This information does not directly support the results that have been discussed so far, as it has been generally understood and modelled that formation rates of oxides of nitrogen will be higher or biodiesel blends. The higher torque loading values, where the biodiesel blend has higher emission levels, do support the results that have been found. It should be noted that the model that was used to simulate the production of oxides of nitrogen did not utilise the affect of engine load, so this model does not necessarily contradict experimental results, as the model is relatively simple and should be improved to include such factors. This improvement is not possible however in the length of time that was available for the production of this dissertation. It should also be noted that production of oxides of nitrogen is also present in the exhaust system of the engine, so therefore the overall production of the oxides of nitrogen are heavily dependent on the design of the particular engine and exhaust system.

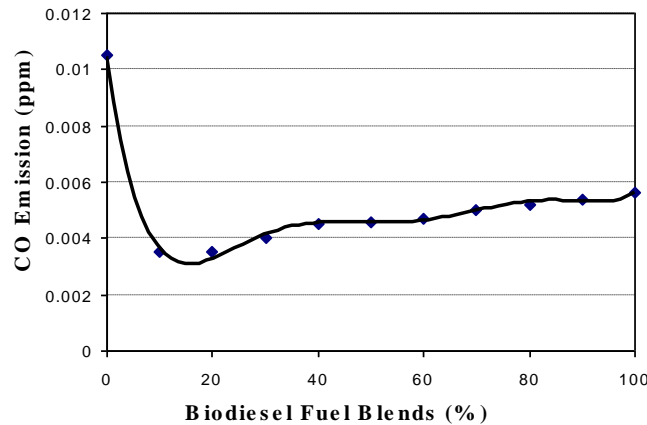
For the purpose of this dissertation to optimise the performance of a biodiesel stationary engine, other pollutants produced by internal combustion engines should also be analysed. The figure below (figure 4.8) shows the results of varying torque on the production of carbon monoxide and carbon dioxide.



(Figure 4.8: Carbon Monoxide and Carbon dioxide production levels (Yusaf et al.))

Figure 4.8 was generated under the same conditions and in the same test procedure as figure 4.7. This figure shows that with the use of the waste cooking oil methyl ester fuel, both carbon monoxide and carbon dioxide production levels were decreased across all torque loadings evaluated. In another experiment undertaken (Najafi, Pirouzpanah et al. (2007)), results supported the reduction in carbon monoxide production. Figure 4.9 shows carbon monoxide emission produced by a single cylinder direct injection diesel engine running on biodiesel – diesel fuel blends, with compressed natural gas as the inducted fluid from this

experiment. This experiment was used to investigate the use of a biodiesel – compressed natural gas engine combination.



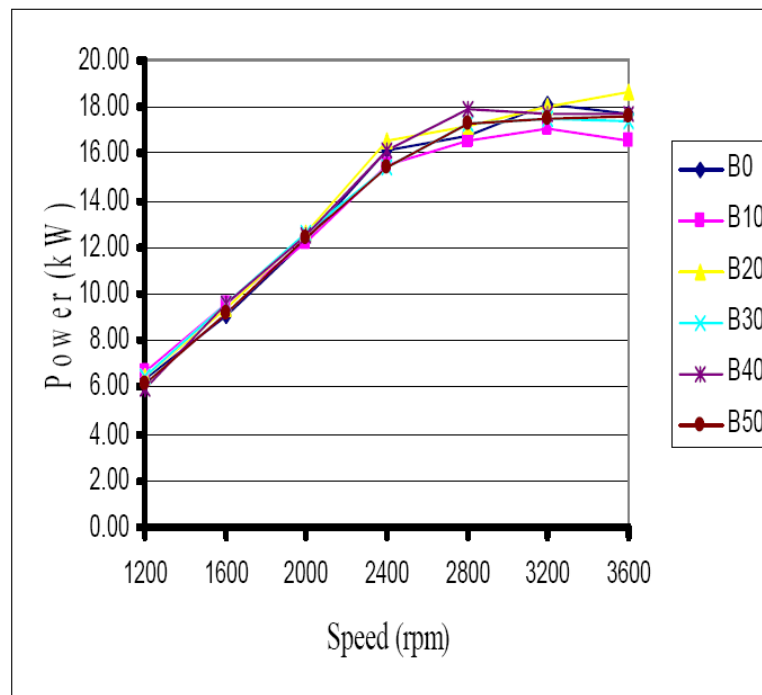
(Figure 4.9: Carbon monoxide emissions for biodiesel blends (Najafi et al, 2007))

This figure shows the carbon monoxide emissions produced for a variance of Biodiesel blends. The results show there is a dramatic reduction in carbon emissions when even a small amount (ten percent) of biodiesel is blended with diesel. It also shows that in this test, there was a gradual increase in carbon monoxide emissions from mixtures of ten percent biodiesel to a full biodiesel fuel blend. This increase is rather small compared to the overall decrease from each different mixture when compared to the full conventional diesel test. It should also be noted that when bio-fuels that are produced from a non fossil fuel based feedstock are burnt, the carbon that is released from these fuels is carbon that has been absorbed from the atmosphere by plants. Carbon emissions, however, that are released from fossil fuel based fuels release carbon that has been trapped under ground within the original material for millions of years, therefore releasing new carbon into the atmosphere, compared to the recycling affect from bio-fuels. This means that bio-fuels such as biodiesel further stop the release of new carbon, and therefore further reduce the carbon emissions.

4.6 External Experimental Results: Physical Performance

The affect on the performance of the stationary engine is also important when an alternative fuel is to be analysed. As diesel engines have many uses in the agricultural industry and many other industries, it is important to determine the effect it will have in these situations. The first parameter that needs to be considered is the brake power produced by the engine.

Figure 4.10 is the power analysis of a two cylinder diesel engine using blends of biodiesel produced from waste cooking oil (Najafi, Ghobadian et al, (2007)).



(Figure 4.10: Power analysis of a Stationary engine (Najafi, Ghobadian et al, (2007)))

Figure 4.10 shows under half speed running conditions the difference in power generation for the fuel blends is rather small. After half speed the power levels for the different fuel blends rank differently as the speed varies, with one notable consistency, which is that the fuel mixture of ten percent biodiesel produces the lowest power generation from 2400 rpm to the maximum speed of 3600 rpm. This experiment shows that there is a maximum power difference of approximately ten percent across the entire experimental data. But when comparing to the conventional diesel results, there is a power gain of approximately five percent at best for a twenty percent biodiesel blend and a maximum power loss of approximately five percent for the worst case for a ten percent biodiesel blend. These values are reduced depending on the engine speed and can change for different mixtures, which shows that the biodiesel fuel can cause minimal effect for the output on the engine depending on the situation.

A common use of stationary diesel engine is the use for electrical power generation. Experimental data for use on diesel generators has also been found. Table 4.1 shows the results of a constant load single cylinder direct injection diesel engine generator (Pereira et al, (2007)).

Parameters	Diesel	B20	B50	B75	B100
Power (W)	1584	1543	1572	1597	1593
Voltage (V)	102.4	100.9	101.7	102.9	102.6
Frequency (Hz)	58.8	58.2	58.7	58.7	58.9
Speed (rpm)	3490	3490	3500	3500	3500
Fuel consumption (L/h)	0.864	0.828	0.864	1.008	0.900

(Table 4.1: Stationary diesel engine generator results (Pereira et al, (2007)))

Table 4.1 shows that the maximum power from this test is gained from a seventy-five percent biodiesel mixture. But this table also shows that the engine speed has increased by ten revolutions per minute, which will cause the power to be increased with the increase in speed with the same engine torque produced. Taking this into consideration, if the torque is the same and the speed is reduced both the one-hundred percent and seventy-five percent biodiesel mixtures still generated higher power levels (as shown in Appendix B). Also from this table it is shown the fuel consumption per hour. To make these comparable for performance purposes, it is convenient to convert them to brake specific fuel consumption with the units' litres per kilowatt hours (as done in Appendix B). These results show that the twenty percent biodiesel blend has the best brake specific fuel consumption with the lowest power generation while the seventy-five percent biodiesel blend has the highest brake specific fuel consumption but produces the most power. These results show that there is always a compromise between the brake specific fuel consumption compared to the maximum power produced, as the lower the brake specific fuel consumption the more efficient, but the lower the power the lower the performance gained from the engine. Another set of results has also been obtained for the power production from a stationary engine as shown in table 4.2.

Speed RPM	Torque Nm	Power kW	BSFC (WCOME-diesel blend) g/kW.hr	BSFC (Diesel) g/kW.hr	Efficiency (WCOME) %	Efficiency (Diesel) %
2000	20	4.43	424.47	375.71	21.75	25.9
2000	40	8.87	298.41	289.04	30.93	33.62
2000	50	11.09	266.22	251.94	34.67	38.62
2000	60	13.31	259.17	254.94	35.62	35.16
2000	80	17.75	248.75	243.36	37.11	39.98
2000	90	19.97	245.26	245.31	31.64	39.66

(Table 4.2: Performance results from high speed diesel engine (Yusaf et al))

Table 4.2 is produced using a four cylinder ford engine, the same experiment that produced figure 4.7 and 4.8. This experiment used a fifty percent biodiesel/diesel blend made from waste cooking oil and conventional diesel mixture. These results use a varying load with a constant speed, and show that for the same power generation, the biodiesel mixture has a higher brake specific fuel consumption compared to the diesel fuel for all values except the last. The last torque of ninety Newton metres shows that the biodiesel blend has a slightly better brake specific fuel consumption compared to the diesel fuel with the same power rating, but shows that the efficiency is much lower than that of the diesel. All biodiesel blends have a lower efficiency than the diesel fuel except for a load of sixty Newton metres. This blend shows a .46 percent increase in efficiency over the conventional diesel, but at this point has a higher brake specific fuel consumption, causing a disadvantage for the fuel.

All the tests that have been discussed so far have been tested on a diesel engine specifically designed for running the conventional diesel fuel. As discussed earlier, modifications to the engine can permit better performance when running biodiesel fuel blends, giving the biodiesel an even playing fields in experimental work. These modifications can improve parameters such as the production of oxides of nitrogen, total power generated by the engine, brake specific fuel consumption rates and efficiencies.

Chapter 5: Conclusions

Conclusions from this dissertation

To date, there is only a small fraction of the agricultural industry using biodiesel. This use is mainly from self producing businesses, as this is the cheapest option at the current time. The current use of this fuel in the agricultural industry could be related to the lack of government incentives that is available for businesses to employ this strategy, compared to Europe where government initiatives are vast. This means that a great benefit is still available if the proper schemes are employed in Australia as in other countries where it has been tried and remarkably successful. The use of biodiesel however cannot be a direct introduction. As stated earlier, vehicle and machinery manufacturers are not at the stage of supporting warranties for the use of one hundred percent biodiesel. This however is linked to the lack of commercial production compared to fossil fuel based diesel, so together they are linked, and must both move forward together to implement the fuel effectively and most economically. As seen in the history of motor vehicles, when leaded fuel was slowly phased out, it took a long time to make the change, but it was for the best.

As shown, it is relatively easy to make small quantities of biodiesel for personal and small operation uses, and can be implemented effectively to reduce costs by the recycling of old oil. It is also possible to generate the feedstock from the agricultural business, by use of oil extraction from grain, to reduce costs without losing capital on the grain. The final problem was the performance characteristics of biodiesel compared to the conventional diesel. Due to the fact that most internal combustion engines produced up to the present time are based on the use of conventional diesel for the fuel type, this fuel has a performance advantage as the design is specific to its characteristics. That being said, biodiesel has performed remarkably well as a fuel extender or a direct replacement. Taking the results outlined in chapter four into consideration, biodiesel has great potential at fulfilling the power requirements set by diesel engines. As shown in figure 4.10 and table 4.1, the power generated by the biodiesel – diesel fuel blends is relatively equal and can be greater for some conditions. These results show great potential for the total replacement of conventional diesel over time as the same or greater performance can be gained with a fuel that is renewable and biodegradable.

Although it has been proven that biodiesel leads to greater amounts of oxides of nitrogen being produced, these readings are taken from experiments carried out on engines designed for the use of conventional diesel. This leads to the conclusion that with the proper design modifications, biodiesel can be made an effective replacement. The simulation carried out in this dissertation showed that biodiesel has a greater initial formation rate of nitric oxide (the main component of oxides of nitrogen) for the same temperature, design modifications made to the engine could produce lower in-cylinder temperatures resulting in lower formation rates of nitric oxide and hence oxides of nitrogen. Modifications such as retarding of injection timing were discussed and are an effective in lowering the peak cylinder temperatures, as well as improving the efficiency of biodiesel as it causes advanced injection timing and reduced ignition delay, which in turn lead to more fuel burnt during the compression stroke and hence higher peak cylinder temperatures. This higher quantity of fuel burnt in the compression stroke is one of the causes of lower efficiency levels for biodiesel when used on unmodified engines, so by modifying this characteristic, great advantages can be obtained.

It is also shown in figure 4.5 that by reducing the in-cylinder temperatures, the characteristic time can be reduced, therefore improving the amounts of oxides of nitrogen produced by decreasing the time for conditions to change in the cylinder. Reducing in-cylinder temperatures will also disadvantage the performance of the engine, as the more heat released the more power that is generated by the engine. The aim of this optimisation is to reduce the temperature of the cylinder contents during the compression stroke, as the more fuel burnt here unnecessarily the more fuel is wasted and the higher the brake specific fuel consumption and the lower the efficiency. So optimising the fuel burnt during the compression stroke for biodiesel engines can yield a great improvement in the brake specific fuel consumption, efficiency and power.

Biodiesel however does show remarkable results in the production of carbon monoxide and carbon dioxide. These gases are another large contributor to greenhouse gasses, probably the best known by everybody. As shown in figure 4.8 and even better in figure 4.9, the production of these gasses is greatly reduced for biodiesel blends. Also noting the fact that biodiesel is recycling carbon emissions, not releasing previously stored (for millions of years) carbon, this effect is practically having a zero increase in carbon emissions, as to say that no more carbon than that which is already there will be released, giving biodiesel a great advantage over conventional diesel.

With this said, it is important to note that the feedstock oil is generated from a large amounts of sources, many of which are grains, which are suitable for human consumption, so if all this grain is used for fuel, there may not be enough for food, which is another topic that needs to be analysed.

From the work set out in this dissertation, it is clear that biodiesel is an effective replacement for the conventional diesel fuel. Biodiesel will improve the carbon emissions from any engine it is used with properly but may cause increased oxides of nitrogen emissions. With modifications to the engine, the fuel can become even more effective and emissions can be reduced to previous if not improved levels. It has also shown that the fuel is able to be made by almost anyone who is willing to put in the effort, giving it a high attractiveness to many users. It is also a viable option for the use in agricultural and horticultural industries, and over time can be deeply integrated with the proper support and in turn will provide many benefits to the user.

Further work

There is many opportunities for the further study of biodiesel in the agricultural industry, as well as any other industry. Some topics that can be further analysed are:

- Feasibility of different grains for feedstock's
- Transient heat flux analysis of a biodiesel fuelled engine
- Practical engine testing analysing the affects of engine modifications
- Detailed economical study of biodiesel production in small applications
- Analysis and design of oil extraction techniques for feedstock's

These topics represent a small fraction of the further studies that can be carried out on this recently re-discovered energy source, all of which will carry great benefits if carried out effectively.

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Appendix A:

Project Specification

University of Southern Queensland

Faculty of Engineering and Surveying

ENG4111/4112 Research Project

Project Specification

For: Daniel Bichel

Topic: Optimisation of bio diesel stationary engine performance by modelling and simulating the running conditions.

Supervisor: Talal Yusaf

Enrolment: ENG4111 - S1, D, 2007
ENG4112 – S2, D, 2007

Sponsorship: USQ

Project aim: To determine the best operating conditions for a two cylinder stationary diesel engine running on biodiesel in respect to efficiency and power.

Programme: Issue B, 22 March 2007

1. Perform a literature review on the use of biodiesel in IC engines.
2. Research the current use and effectiveness of biodiesel in agricultural machinery and power sources.
3. Model and simulate the performance of the biodiesel using different compression ratios and different injection timing as the benchmark in an unmodified engine.
4. Compare the results of the simulated data such as (Q) and (NO_x) between diesel and biodiesel engines.
5. Compare the modelled results in point 4 with available data.

As time permits:

6. Extend the model to cover engine performance such as IMEP and IP (indicated power).

AGREED:

_____ Daniel Bichel

_____ Talal Yusaf

_____ Date

_____ Date

Co-examiner _____ Date _____

Appendix B:

Factoring change in speed for table 4.1

$$\text{As } P = 2\pi NT/60$$

Where: $P = \text{Power (W)}$

$$\pi = \text{pi } (\approx 3.14 \dots)$$

$$N = \text{Speen (revolutions per minute)}$$

$$T = \text{Torque (Nm)}$$

$$T = P60/2\pi N$$

From table 4.1, 75% Biodiesel mixture

$$T = (1597 \times 60)/(2 \times \pi \times 3500)$$

$$T = 4.357 \text{ Nm}$$

Assuming equal torque at 3490 rpm

$$P = (2 \times \pi \times 3490 \times 4.357)/60$$

$$P = 1592.36 \text{ W}$$

Using the same procedure for the 100% biodiesel mixture

$$T = (1593 \times 60)/(2 \times \pi \times 3500)$$

$$T = 4.346 \text{ Nm}$$

$$P = (2 \times \pi \times 3490 \times 4.346)/60$$

$$P = 1588.34 \text{ W}$$

Converting units to (L/kWh) for table 4.1

	Diesel	B20	B50	B75	B100
Power (kW)	1.584	1.543	1.572	1.597	1.593
Fuel consumption (L/h)	0.864	0.828	0.864	1.008	0.9
Fuel consumption (L/kWh)	0.546	0.537	0.55	0.631	0.565

Appendix C

Matlab Program scripts

M-file for airdata.m

```

function A=airdata(scheme);
%
%
% Written By Talal Yusaf
% A=airdata(scheme)
%
% Routine to specify the thermodynamic properties of air and
% combustion products.
% Data taken from:
% 1. Gordon, S., and McBride, B. J., 1971, "Computer Program for
% Calculation of Complex Chemical Equilibrium Composition, Rocket
% Performance, Incident and Reflected Shocks, and Chapman-Jouguet
% Detonations," NASA SP-273. As reported in Ferguson, C. R., 1986,
% "Internal Combustion Engines", Wiley.
% 2. Kee, R. J., et al., 1991, "The Chemkin Thermodynamic Data Base",
% Sandia Report, SAND87-8215B. As reported in
% Turns, S. R., 1996, "An Introduction to Combustion:
% Concepts and Applications", McGraw-Hill.
% *****
% input:
% scheme switch:
% 'GMcB_low' - Gordon and McBride 300 < T < 1000 K
% 'GMcB_hi' - Gordon and McBride 1000 < T < 5000 K
% 'Chemkin_low' - Chemkin 300 < T < 1000 K
% 'Chemkin_hi' - Chemkin 1000 < T < 5000 K
% output:
% A - matrix of polynomial coefficients for cp/R, h/RT, and s/R
% of the form  $h/RT=a_1+a_2*T/2+a_3*T^2/3+a_4*T^3/4+a_5*T^4/5+a_6/T$  (for
% example) where T is expressed in K
% columns 1 to 7 are coefficients a1 to a7, and
% rows 1 to 10 are species CO2 H2O N2 O2 CO H2 H O OH and NO
% *****

switch scheme
case 'GMcB_low'
    A=[ 0.24007797E+01  0.87350957E-02 -0.66070878E-05  0.20021861E-08 ...
        0.63274039E-15 -0.48377527E+05  0.96951457E+01
        0.40701275E+01 -0.11084499E-02  0.41521180E-05 -0.29637404E-08 ...
        0.80702103E-12 -0.30279722E+05 -0.32270046E+00
        0.36748261E+01 -0.12081500E-02  0.23240102E-05 -0.63217559E-09 ...
        -0.22577253E-12 -0.10611588E+04  0.23580424E+01
        0.36255985E+01 -0.18782184E-02  0.70554544E-05 -0.67635137E-08 ...
        0.21555993E-11 -0.10475226E+04  0.43052778E+01
        0.37100928E+01 -0.16190964E-02  0.36923594E-05 -0.20319674E-08 ...
        0.23953344E-12 -0.14356310E+05  0.29555350E+01
        0.30574451E+01  0.26765200E-02 -0.58099162E-05  0.55210391E-08 ...
        -0.18122739E-11 -0.98890474E+03 -0.22997056E+01
        0.25000000E+01  0.00000000E+00  0.00000000E+00  0.00000000E+00 ...
        0.00000000E+00  0.25471627E+05 -0.46011762E+00
        0.29464287E+01 -0.16381665E-02  0.24210316E-05 -0.16028432E-08 ...
        0.38906964E-12  0.29147644E+05  0.29639949E+01
        0.38375943E+01 -0.10778858E-02  0.96830378E-06  0.18713972E-09 ...
    ]

```

```

-0.22571094E-12  0.36412823E+04  0.49370009E+00
  0.40459521E+01 -0.34181783E-02  0.79819190E-05 -0.61139316E-08 ...
  0.15919076E-11  0.97453934E+04  0.29974988E+01];
case 'GMcB_hi'
A=[ 0.44608041E+01  0.30981719E-02 -0.12392571E-05  0.22741325E-09 ...
-0.15525954E-13 -0.48961442E+05 -0.98635982E+00
  0.27167633E+01  0.29451374E-02 -0.80224374E-06  0.10226682E-09 ...
-0.48472145E-14 -0.29905826E+05  0.66305671E+01
  0.28963194E+01  0.15154866E-02 -0.57235277E-06  0.99807393E-10 ...
-0.65223555E-14 -0.90586184E+03  0.61615148E+01
  0.36219535E+01  0.73618264E-03 -0.19652228E-06  0.36201558E-10 ...
-0.28945627E-14 -0.12019825E+04  0.36150960E+01
  0.29840696E+01  0.14891390E-02 -0.57899684E-06  0.10364577E-09 ...
-0.69353550E-14 -0.14245228E+05  0.63479156E+01
  0.31001901E+01  0.51119464E-03  0.52644210E-07 -0.34909973E-10 ...
  0.36945345E-14 -0.87738042E+03 -0.19629421E+01
  0.25000000E+01  0.00000000E+00  0.00000000E+00  0.00000000E+00 ...
  0.00000000E+00  0.25471627E+05 -0.46011763E+00
  0.25420596E+01 -0.27550619E-04 -0.31028033E-08  0.45510674E-11 ...
-0.43680515E-15  0.29230803E+05  0.49203080E+01
  0.29106427E+01  0.95931650E-03 -0.19441702E-06  0.13756646E-10 ...
  0.14224542E-15  0.39353815E+04  0.54423445E+01
  0.31890000E+01  0.13382281E-02 -0.52899318E-06  0.95919332E-10 ...
-0.64847932E-14  0.98283290E+04  0.67458126E+01];
case 'Chemkin_low'
A=[ 0.02275724E+02  0.09922072E-01 -0.10409113E-04  0.06866686E-07 ...
-0.02117280E-10 -0.04837314E+06  0.10188488E+02
  0.03386842E+02  0.03474982E-01 -0.06354696E-04  0.06968581E-07 ...
-0.02506588E-10 -0.03020811E+06  0.02590232E+02
  0.03298677E+02  0.14082404E-02 -0.03963222E-04  0.05641515E-07 ...
-0.02444854E-10 -0.10208999E+04  0.03950372E+02
  0.03212936E+02  0.11274864E-02 -0.05756150E-05  0.13138773E-08 ...
-0.08768554E-11 -0.10052490E+04  0.06034737E+02
  0.03262451E+02  0.15119409E-02 -0.03881755E-04  0.05581944E-07 ...
-0.02474951E-10 -0.14310539E+05  0.04848897E+02
  0.03298124E+02  0.08249441E-02 -0.08143015E-05 -0.09475434E-09 ...
  0.04134872E-11 -0.10125209E+04 -0.03294094E+02
  0.02500000E+02  0.00000000E+00  0.00000000E+00  0.00000000E+00 ...
  0.00000000E+00  0.02547162E+06 -0.04601176E+01
  0.02946428E+02 -0.16381665E-02  0.02421031E-04 -0.16028431E-08 ...
  0.03890696E-11  0.02914764E+06  0.02963995E+02
  0.03637266E+02  0.01850910E-02 -0.16761646E-05  0.02387202E-07 ...
-0.08431442E-11  0.03606781E+05  0.13588605E+01
  0.03376541E+02  0.12530634E-02 -0.03302750E-04  0.05217810E-07 ...
-0.02446262E-10  0.09817961E+05  0.05829590E+02];
case 'Chemkin_hi'
A=[ 0.04453623E+02  0.03140168E-01 -0.12784105E-05  0.02393996E-08 ...
-0.16690333E-13 -0.04896696E+06 -0.09553959E+01
  0.02672145E+02  0.03056293E-01 -0.08730260E-05  0.12009964E-09 ...
-0.06391618E-13 -0.02989921E+06  0.06862817E+02
  0.02926640E+02  0.14879768E-02 -0.05684760E-05  0.10097038E-09 ...
-0.06753351E-13 -0.09227977E+04  0.05980528E+02
  0.03697578E+02  0.06135197E-02 -0.12588420E-06  0.01775281E-09 ...
-0.11364354E-14 -0.12339301E+04  0.03189165E+02
  0.03025078E+02  0.14426885E-02 -0.05630827E-05  0.10185813E-09 ...
-0.06910951E-13 -0.14268350E+05  0.06108217E+02
  0.02991423E+02  0.07000644E-02 -0.05633828E-06 -0.09231578E-10 ...
  0.15827519E-14 -0.08350340E+04 -0.13551101E+01
  0.02500000E+02  0.00000000E+00  0.00000000E+00  0.00000000E+00 ...
  0.00000000E+00  0.02547162E+06 -0.04601176E+01
  0.02542059E+02 -0.02755061E-03 -0.03102803E-07  0.04551067E-10 ...

```

```

-0.04368051E-14  0.02923080E+06  0.04920308E+02
 0.02882730E+02  0.10139743E-02 -0.02276877E-05  0.02174683E-09 ...
-0.05126305E-14  0.03886888E+05  0.05595712E+02
 0.03245435E+02  0.12691383E-02 -0.05015890E-05  0.09169283E-09 ...
-0.06275419E-13  0.09800840E+05  0.06417293E+02];

```

End

M-file for Biodiesel.m

```

function varargout = Biodiesel(varargin)
%
% Written by Daniel Bichel
%
% Last edited 26 October 2007
%
% Purpose: File for opening Biodiesel Simulation Graphical User Interface
%
%
%BIODIESEL M-file for Biodiesel.fig
%   BIODIESEL, by itself, creates a new BIODIESEL or raises the existing
%   singleton*.
%
%   H = BIODIESEL returns the handle to a new BIODIESEL or the handle to
%   the existing singleton*.
%
%   BIODIESEL('Property','Value',...) creates a new BIODIESEL using the
%   given property value pairs. Unrecognized properties are passed via
%   varargin to Biodiesel_OpeningFcn. This calling syntax produces a
%   warning when there is an existing singleton*.
%
%   BIODIESEL('CALLBACK') and BIODIESEL('CALLBACK',hObject,...) call the
%   local function named CALLBACK in BIODIESEL.M with the given input
%   arguments.
%
%   *See GUI Options on GUIDE's Tools menu. Choose "GUI allows only one
%   instance to run (singleton)".
%
% See also: GUIDE, GUIDATA, GUIHANDLES

% Edit the above text to modify the response to help Biodiesel

% Last Modified by GUIDE v2.5 05-Oct-2007 14:28:33

% Begin initialization code - DO NOT EDIT
gui_Singleton = 1;
gui_State = struct('gui_Name',       mfilename, ...
                  'gui_Singleton',   gui_Singleton, ...
                  'gui_OpeningFcn',  @Biodiesel_OpeningFcn, ...
                  'gui_OutputFcn',   @Biodiesel_OutputFcn, ...
                  'gui_LayoutFcn',   [], ...
                  'gui_Callback',    []);
if nargin && ischar(varargin{1})
    gui_State.gui_Callback = str2func(varargin{1});
end

if nargout
    [varargout{1:nargout}] = gui_mainfcn(gui_State, varargin{:});
else
    gui_mainfcn(gui_State, varargin{:});

```

```

end
% End initialization code - DO NOT EDIT

% --- Executes just before Biodiesel is made visible.
function Biodiesel_OpeningFcn(hObject, eventdata, handles, varargin)
% This function has no output args, see OutputFcn.
% hObject    handle to figure
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
% varargin   unrecognized PropertyName/PropertyValue pairs from the
%           command line (see VARARGIN)
handles.biodiesel = 'biodiesel';
handles.diesel = 'diesel';

% Choose default command line output for Biodiesel
handles.output = hObject;

% Update handles structure
guidata(hObject, handles);

% UIWAIT makes Biodiesel wait for user response (see UIRESUME)
% uiwait(handles.figure1);

% --- Outputs from this function are returned to the command line.
function varargout = Biodiesel_OutputFcn(hObject, eventdata, handles)
% varargout  cell array for returning output args (see VARARGOUT);
% hObject    handle to figure
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Get default command line output from handles structure
varargout{1} = handles.output;

function edit5_Callback(hObject, eventdata, handles)
% hObject    handle to edit5 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of edit5 as text
%        str2double(get(hObject,'String')) returns contents of edit5 as a
double
function edittext5_Callback(hObject, eventdata, handles)

if isnan(user_entry)
    errordlg('You must enter a numeric value','Bad Input','modal')
end
set(handles.edit5,str2double(get(hObject,'string')));

% --- Executes during object creation, after setting all properties.
function edit5_CreateFcn(hObject, eventdata, handles)
% hObject    handle to edit5 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: edit controls usually have a white background on Windows.
%       See ISPC and COMPUTER.

```

```

if ispc
    set(hObject,'BackgroundColor','white');
else

set(hObject,'BackgroundColor',get(0,'defaultUicontrolBackgroundColor'));
end

%Fuel air ratio
function edit6_Callback(hObject, eventdata, handles)
% hObject    handle to edit6 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of edit6 as text
%         str2double(get(hObject,'String')) returns contents of edit6 as a
double

function edittext6_Callback(hObject, eventdata, handles)

if isnan(user_entry)
    errordlg('You must enter a numeric value','Bad Input','modal')
end
set(handles.edit6,str2double(get(hObject,'string')));

% --- Executes during object creation, after setting all properties.
function edit6_CreateFcn(hObject, eventdata, handles)
% hObject    handle to edit6 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: edit controls usually have a white background on Windows.
%         See ISPC and COMPUTER.
if ispc
    set(hObject,'BackgroundColor','white');
else

set(hObject,'BackgroundColor',get(0,'defaultUicontrolBackgroundColor'));
end

%gas residual fraction
function edit7_Callback(hObject, eventdata, handles)
% hObject    handle to edit7 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of edit7 as text
%         str2double(get(hObject,'String')) returns contents of edit7 as a
double
function edittext7_Callback(hObject, eventdata, handles)

if isnan(user_entry)
    errordlg('You must enter a numeric value','Bad Input','modal')
end
set(handles.edit7,str2double(get(hObject,'string')));

% --- Executes during object creation, after setting all properties.
function edit7_CreateFcn(hObject, eventdata, handles)

```

```

% hObject    handle to edit7 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: edit controls usually have a white background on Windows.
%         See ISPC and COMPUTER.
if ispc
    set(hObject,'BackgroundColor','white');
else

set(hObject,'BackgroundColor',get(0,'defaultUicontrolBackgroundColor'));
end

% --- Executes on button press in pushbutton1.
function pushbutton1_Callback(hObject, eventdata, handles)
% hObject    handle to pushbutton1 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

p = 101325;%atmospheric pressure
Tu = 400;%Unburnt air temperature
CR = str2double(get(handles.edit5,'string'));
phi = str2double(get(handles.edit6,'string'));
f = str2double(get(handles.edit7,'string'));
Trange = str2double(get(handles.edit8,'string'));
fueltype = handles.current_data;

[T,tou,Tb,dnodtvt]=Tadiabatic1(p,Tu,phi,f,Trange,CR,fueltype);

axes(handles.axes1)
semilogy(T,dnodtvt);
xlabel('Temperature (K)');
ylabel('Formation rate of NO')
title('NO formation rate Vs Temperature');

axes(handles.axes2)
plot(T,tou,'r');
xlabel('Temperature');
ylabel('Characteristic time (ms) ');
title('Characteristic time Vs Temperature');

axes(handles.axes3)
plot(phi,Tb,'g*');
xlabel('Equivalence ratio')
ylabel('Adiabatic flame Temperature (K)')

% --- Executes on selection change in popupmenu1.
function popupmenu1_Callback(hObject, eventdata, handles)
% hObject    handle to popupmenu1 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: contents = get(hObject,'String') returns popupmenu1 contents as
cell array
%         contents{get(hObject,'Value')} returns selected item from
popupmenu1
val = get(hObject,'Value');
str = get(hObject, 'String');

```



```

switch str{val};
case 'biodiesel'
    handles.current_data = handles.biodiesel;
case 'diesel'
    handles.current_data = handles.diesel;
end
guidata(hObject,handles)

% --- Executes during object creation, after setting all properties.
function popupmenu1_CreateFcn(hObject, eventdata, handles)
% hObject    handle to popupmenu1 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: popupmenu controls usually have a white background on Windows.
%         See ISPC and COMPUTER.
if ispc
    set(hObject,'BackgroundColor','white');
else

set(hObject,'BackgroundColor',get(0,'defaultUicontrolBackgroundColor'));
end

%Temp range
function edit8_Callback(hObject, eventdata, handles)
% hObject    handle to edit8 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of edit8 as text
%         str2double(get(hObject,'String')) returns contents of edit8 as a
double

function edittext8_Callback(hObject, eventdata, handles)

if isnan(user_entry)
    errordlg('You must enter a numeric value','Bad Input','modal')
end
set(handles.edit8,str2double(get(hObject,'string')));

% --- Executes during object creation, after setting all properties.
function edit8_CreateFcn(hObject, eventdata, handles)
% hObject    handle to edit8 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: edit controls usually have a white background on Windows.
%         See ISPC and COMPUTER.
if ispc
    set(hObject,'BackgroundColor','white');
else

set(hObject,'BackgroundColor',get(0,'defaultUicontrolBackgroundColor'));
end

```

M-file for ecpl.m

```

function
[x,h,u,v,s,Y,cp,dlvlT,dlvlp]=ecpl(p,T,phi,fueltype,airscheme,Yguess);
%
% Written By Talal Yusaf
%
% Modified By Daniel Bichel
%
% Last Modified 26 October 2007
%
%
% [h,u,v,s,Y,cp,dlvlT,dlvlp]=ecp(p,T,phi,fueltype,airscheme,Yguess)
%
% Routine to determine the equilibrium state of combustion products.
% Method closely follows that of:
% 1. Ferguson, C.R., 1986, "Internal Combustion Engines", Wiley, p122;
% which uses the method described by:
% 2. Olikara, C., and Borman, G.L., 1975, "A Computer Program for
% Calculating Properties of Equilibrium Combustion Products with
% Some Applications to I.C. Engines", SAE Paper 750468.
% *****
% input:
% p,T,phi - pressure (Pa), temperature (K), and equivalence ratio
% fueltype - 'gasoline', 'diesel', etc - see fueldata.m for full list
% airscheme - 'GMcB' (Gordon and McBride) or 'Chemkin'
% Yguess - (optional) initial estimate for mole fractions of the
% species CO2 H2O N2 O2 CO H2 H O OH and NO
% output:
% h - enthalpy (J/kg), u - internal energy (J/kg),
% v - specific volume (m^3/kg), s - entropy (J/kgK),
% Y - mole fractions of 10 species, cp - specific heat (J/kgK),
% dlvlT - partial derivative of log(v) wrt log(T)
% dlvlp - partial derivative of log(v) wrt log(p)
% *****

[alpha,beta,gamma,delta,Afuel]=fueldatal(fueltype);
switch airscheme
case 'GMcB'
    A0=airdata('GMcB_hi');
case 'Chemkin'
    A0=airdata('Chemkin_hi');
end

% Equilibrium constant data from Olikara and Borman via Ferguson
Kp=[ 0.432168E+00 -0.112464E+05 0.267269E+01 -0.745744E-04 0.242484E-08
     0.310805E+00 -0.129540E+05 0.321779E+01 -0.738336E-04 0.344645E-08
    -0.141784E+00 -0.213308E+04 0.853461E+00 0.355015E-04 -0.310227E-08
     0.150879E-01 -0.470959E+04 0.646096E+00 0.272805E-05 -0.154444E-08
    -0.752364E+00 0.124210E+05 -0.260286E+01 0.259556E-03 -0.162687E-07
    -0.415302E-02 0.148627E+05 -0.475746E+01 0.124699E-03 -0.900227E-08];

MinMol=1e-25;
tol=3e-12;

Ru=8314.34; % J/kmol.K
M=[44.01 18.02 28.008 32.000 28.01 2.018 1.009 16 17.009 30.004]'; %
kg/kmol

```

```

dcdT=zeros(4,1);
dcdp=zeros(4,1);
dfdT=zeros(4,1);
dfdp=zeros(4,1);
dYdT=zeros(10,1);
dYdp=zeros(10,1);
B=zeros(4,1);

% check if solid carbon will form
eps=0.210/(alpha+0.25*beta-0.5*gamma);
if phi>(0.210/eps/(0.5*alpha-0.5*gamma))
    error('phi too high - c(s) and other species will form');
end

if nargin==5 % no Yguess so estimate the composition using farg
    [h,u,v,s,Y,cp,dlvlT,dlvlp]=farg1(p,T,phi,1,fueltype,airscheme);
    Y(7:10)=ones(4,1)*MinMol; % since farg only returns first 6 species
else
    Y=Yguess;
end

% evaluate constants
patm=p/101.325e3; % convert Pa to atmospheres
TKp=[log(T/1000) 1/T 1 T T^2]';
K=10.^(Kp*TKp);
c=K.*[1/sqrt(patm) 1/sqrt(patm) 1 1 sqrt(patm) sqrt(patm)]';
d=[beta/alpha (gamma+0.42/eps/phi)/alpha (delta+1.58/eps/phi)/alpha]';

if abs(phi-1)<tol
    phi=phi*(1+tol*sign(phi-1));
end

i=find(Y<MinMol);
Y(i)=ones(length(i),1)*MinMol;

DY3to6=2*tol*ones(4,1);
MaxIter=500;
MaxVal=max(abs(DY3to6));
Iter=0;
DoneSome=0;

while (Iter<MaxIter)&((MaxVal>tol)|(DoneSome<1))
    Iter=Iter+1;
    if Iter>2,
        DoneSome=1;
    end

    D76=0.5*c(1)/sqrt(Y(6));
    D84=0.5*c(2)/sqrt(Y(4));
    D94=0.5*c(3)*sqrt(Y(6)/Y(4));
    D96=0.5*c(3)*sqrt(Y(4)/Y(6));
    D103=0.5*c(4)*sqrt(Y(4)/Y(3));
    D104=0.5*c(4)*sqrt(Y(3)/Y(4));
    D24=0.5*c(5)*Y(6)/sqrt(Y(4));
    D26=c(5)*sqrt(Y(4));
    D14=0.5*c(6)*Y(5)/sqrt(Y(4));
    D15=c(6)*sqrt(Y(4));
    A(1,1)=1+D103;
    A(1,2)=D14+D24+1+D84+D104+D94;
    A(1,3)=D15+1;

```

```

A(1,4)=D26+1+D76+D96;
A(2,1)=0;
A(2,2)=2*D24+D94-d(1)*D14;
A(2,3)=-d(1)*D15-d(1);
A(2,4)=2*D26+2+D76+D96;
A(3,1)=D103;
A(3,2)=2*D14+D24+2+D84+D94+D104-d(2)*D14;
A(3,3)=2*D15+1-d(2)*D15-d(2);
A(3,4)=D26+D96;
A(4,1)=2+D103;
A(4,2)=D104-d(3)*D14;
A(4,3)=-d(3)*D15-d(3);
A(4,4)=0;
B(1)=- (sum(Y)-1);
B(2)=- (2*Y(2)+2*Y(6)+Y(7)+Y(9)-d(1)*Y(1)-d(1)*Y(5));
B(3)=- (2*Y(1)+Y(2)+2*Y(4)+Y(5)+Y(8)+Y(9)+Y(10)-d(2)*Y(1)-d(2)*Y(5));
B(4)=- (2*Y(3)+Y(10)-d(3)*Y(1)-d(3)*Y(5));

invA=inv(A);
DY3to6=invA*B;
MaxVal=max(abs(DY3to6));
Y(3:6)=Y(3:6)+DY3to6/10;
i=find(Y<MinMol);
Y(i)=ones(length(i),1)*MinMol;

Y(7)=c(1)*sqrt(Y(6));
Y(8)=c(2)*sqrt(Y(4));
Y(9)=c(3)*sqrt(Y(4)*Y(6));
Y(10)=c(4)*sqrt(Y(4)*Y(3));
Y(2)=c(5)*sqrt(Y(4))*Y(6);
Y(1)=c(6)*sqrt(Y(4))*Y(5);
end

if Iter>=MaxIter
    warning('convergence failure in composition loop');
end

TdKdT=[1/T -1/T^2 1 2*T]';
dKdT=2.302585*K.*(Kp(:, [1 2 4 5])*TdKdT);
dcdT(1)=dKdT(1)/sqrt(patm);
dcdT(2)=dKdT(2)/sqrt(patm);
dcdT(3)=dKdT(3);
dcdT(4)=dKdT(4);
dcdT(5)=dKdT(5)*sqrt(patm);
dcdT(6)=dKdT(6)*sqrt(patm);
dcdp(1)=-0.5*c(1)/p;
dcdp(2)=-0.5*c(2)/p;
dcdp(5)=0.5*c(5)/p;
dcdp(6)=0.5*c(6)/p;
x1=Y(1)/c(6);
x2=Y(2)/c(5);
x7=Y(7)/c(1);
x8=Y(8)/c(2);
x9=Y(9)/c(3);
x10=Y(10)/c(4);
dfdT(1)=dcdT(6)*x1+dcdT(5)*x2+dcdT(1)*x7+dcdT(2)*x8+ ...
    dcdT(3)*x9+dcdT(4)*x10;
dfdT(2)=2*dcdT(5)*x2+dcdT(1)*x7+dcdT(3)*x9-d(1)*dcdT(6)*x1;
dfdT(3)=2*dcdT(6)*x1+dcdT(5)*x2+dcdT(2)*x8+dcdT(3)*x9+ ...
    dcdT(4)*x10-d(2)*dcdT(6)*x1;
dfdT(4)=dcdT(4)*x10-d(3)*dcdT(6)*x1;

```

```

dfdp(1)=dcdp(6)*x1+dcdp(5)*x2+dcdp(1)*x7+dcdp(2)*x8;
dfdp(2)=2*dcdp(5)*x2+dcdp(1)*x7-d(1)*dcdp(6)*x1;
dfdp(3)=2*dcdp(6)*x1+dcdp(5)*x2+dcdp(2)*x8-d(2)*dcdp(6)*x1;
dfdp(4)=-d(3)*dcdp(6)*x1;

B=-dfdT;
dYdT(3:6)=invA*B;
dYdT(1)=sqrt(Y(4))*Y(5)*dcdT(6)+D14*dYdT(4)+D15*dYdT(5);
dYdT(2)=sqrt(Y(4))*Y(6)*dcdT(5)+D24*dYdT(4)+D26*dYdT(6);
dYdT(7)=sqrt(Y(6))*dcdT(1)+D76*dYdT(6);
dYdT(8)=sqrt(Y(4))*dcdT(2)+D84*dYdT(4);
dYdT(9)=sqrt(Y(4)*Y(6))*dcdT(3)+D94*dYdT(4)+D96*dYdT(6);
dYdT(10)=sqrt(Y(4)*Y(3))*dcdT(4)+D104*dYdT(4)+D103*dYdT(3);

B=-dfdp;
dYdp(3:6)=invA*B;
dYdp(1)=sqrt(Y(4))*Y(5)*dcdp(6)+D14*dYdp(4)+D15*dYdp(5);
dYdp(2)=sqrt(Y(4))*Y(6)*dcdp(5)+D24*dYdp(4)+D26*dYdp(6);
dYdp(7)=sqrt(Y(6))*dcdp(1)+D76*dYdp(6);
dYdp(8)=sqrt(Y(4))*dcdp(2)+D84*dYdp(4);
dYdp(9)=D94*dYdp(4)+D96*dYdp(6);
dYdp(10)=D104*dYdp(4)+D103*dYdp(3);

% calculate thermodynamic properties
Tc0=[1 T T^2 T^3 T^4]';
Th0=[1 T/2 T^2/3 T^3/4 T^4/5 1/T]';
Ts0=[log(T) T T^2/2 T^3/3 T^4/4 1]';
cp0=A0(:,1:5)*Tc0;
h0=A0(:,1:6)*Th0;
s0=A0(:,[1:5 7])*Ts0;

% Y(1) and Y(2) reevaluated
Y(1)=(2*Y(3)+Y(10))/d(3)-Y(5);
Y(2)=(d(1)/d(3)*(2*Y(3)+Y(10))-2*Y(6)-Y(7)-Y(9))/2;
i=find(Y<MinMol);
Y(i)=ones(length(i),1)*MinMol;

% properties of mixture
h=sum(h0.*Y);
s=sum((s0-log(Y)).*Y);
cp=sum(Y.*cp0+h0.*dYdT*T);
MW=sum(Y.*M);
MT=sum(dYdT.*M);
Mp=sum(dYdp.*M);

R=Ru/MW;
v=R*T/p;
cp=R*(cp-h*T*MT/MW);
dlvlT=1+max(-T*MT/MW,0);
dlvlp=-1-max(p*Mp/MW,0);
h=R*T*h;
s=R*(-log(patm)+s);
u=h-R*T;

%by using eq3.56 of Furguson (1986)
N=(eps*phi*alpha)/(Y(1)+Y(5));
N1=(eps*phi*beta)/(2*Y(2)+2*Y(6)+Y(7)+Y(9));
x=Y*N;

```

M-file for farg1.m

```

function [h,u,v,s,Y,cp,dlvlT,dlvlp]=farg1(p,T,phi,f,fueltype,airscheme);
%
% Written By Talal Yusaf
%
%
% [h,u,v,s,Y,cp,dlvlT,dlvlp]=farg(p,T,phi,f,fueltype,airscheme)
%
% Routine to determine the state of mixtures of fuel, air
% and residual combustion products at low temperatures.
% Method closely follows that of:
% 1. Ferguson, C.R., 1986, "Internal Combustion Engines", Wiley, p108;
% who uses the results of:
% 2. Hires, S.D., Ekchian, A., Heywood, J.B., Tabaczynski, R.J., and
% Wall, J.C., 1976, "Performance and NOx Emissions Modeling of a Jet
% Ignition Pre-Chamber Stratified Charge Engine", SAE Trans., Vol 85,
% Paper 760161.
% *****
% input:
% p,T,phi - pressure (Pa), temperature (K), and equivalence ratio
% f - residual mass fraction; set f=0 if no combustion products
% are present and f=1 if only combustion products are present
% fueltype - 'gasoline', 'diesel', etc - see fueldata.m for full list
% airscheme - 'GMcB' (Gordon and McBride) or 'Chemkin'
% output:
% h - enthalpy (J/kg), u - internal energy (J/kg),
% v - specific volume (m^3/kg), s - entropy (J/kgK),
% Y - mole fractions of 6 species: CO2, H2O, N2, O2, CO, and H2,
% cp - specific heat (J/kgK),
% dlvlT - partial derivative of log(v) wrt log(T)
% dlvlp - partial derivative of log(v) wrt log(p)
% *****

[alpha,beta,gamma,delta,Afuel]=fueldatal(fueltype);
switch airscheme
case 'GMcB'
    A=airdata('GMcB_low');
case 'Chemkin'
    A=airdata('Chemkin_low');
end

Ru=8314.34; % J/kmolK
table=[-1 1 0 0 1 -1]';
M=[44.01 18.02 28.008 32.000 28.01 2.018]'; % kg/kmol

MinMol=1e-25;

dlvlT=1; dlvlp=-1;
eps=0.210/(alpha+0.25*beta-0.5*gamma);

if phi <= 1.0 % stoichiometric or lean
    nu=[alpha*phi*eps beta*phi*eps/2 0.79+delta*phi*eps/2 ...
        0.21*(1-phi) 0 0]';
    dcdT=0;
else % rich
    z=1000/T;

```

```

K=exp(2.743+z*(-1.761+z*(-1.611+z*0.2803)));
dKdT=-K*(-1.761+z*(-3.222+z*0.8409))/1000;
a=1-K;
b=0.42-phi*eps*(2*alpha-gamma)+K*(0.42*(phi-1)+alpha*phi*eps);
c=-0.42*alpha*phi*eps*(phi-1)*K;
nu5=(-b+sqrt(b^2-4*a*c))/2/a;
dcdT=dKdT*(nu5^2-nu5*(0.42*(phi-1)+alpha*phi*eps)+ ...
    0.42*alpha*phi*eps*(phi-1))/(2*nu5*a+b);
nu=[alpha*phi*eps-nu5 0.42-phi*eps*(2*alpha-gamma)+nu5 ...
    0.79+delta*phi*eps/2 0 nu5 0.42*(phi-1)-nu5]';
end

% mole fractions and molecular weight of residual
tmoles=sum(nu);
Y=nu/tmoles;
Mres=sum(Y.*M);

% mole fractions and molecular weight of fuel-air
fuel=eps*phi/(1+eps*phi);
o2=0.21/(1+eps*phi);
n2=0.79/(1+eps*phi);
Mfa=fuel*(12.01*alpha+1.008*beta+16*gamma+14.01*delta)+ ...
    32*o2+28.02*n2;

% mole fractions of fuel-air-residual gas
Yres=f/(f+Mres/Mfa*(1-f));
Y=Y*Yres;
Yfuel=fuel*(1-Yres);
Y(3)=Y(3)+n2*(1-Yres);
Y(4)=Y(4)+o2*(1-Yres);

% component properties
Tcp0=[1 T T^2 T^3 T^4]';
Th0=[1 T/2 T^2/3 T^3/4 T^4/5 1/T]';
Ts0=[log(T) T T^2/2 T^3/3 T^4/4 1]';
cp0=A(1:6,1:5)*Tcp0;
h0=A(1:6,1:6)*Th0;
s0=A(1:6,[1:5 7])*Ts0;
Mfuel=12.01*alpha+1.008*beta+16.000*gamma+14.01*delta;
a0=Afuel(1); b0=Afuel(2); c0=Afuel(3); d0=Afuel(6); e0=Afuel(7);
cpfuel=Afuel(1:5)*[1 T T^2 T^3 1/T^2]';
hfuel=Afuel(1:6)*[1 T/2 T^2/3 T^3/4 -1/T^2 1/T]';
s0fuel=Afuel([1:5 7])*[log(T) T T^2/2 T^3/3 -1/T^2/2 1]';

% set min value of composition so log calculations work
if Yfuel<MinMol
    Yfuel=MinMol;
end
i=find(Y<MinMol);
Y(i)=ones(length(i),1)*MinMol;

% properties of mixture
h=hfuel*Yfuel+sum(h0.*Y);
s=(s0fuel-log(Yfuel))*Yfuel+sum((s0-log(Y)).*Y);
cp=cpfuel*Yfuel+sum(cp0.*Y)+sum(h0.*table*T*dcdT*Yres/tmoles);
MW=Mfuel*Yfuel+sum(Y.*M);

R=Ru/MW;
h=R*T*h;
u=h-R*T;
v=R*T/p;

```

```
s=R*(-log(p/101.325e3)+s);
cp=R*cp;
```

M-file for fueldata1.m

```
function [alpha,beta,gamma,delta,Afuel]=fueldata1(fuel);
%
% Written By Talal Yusaf
%
% Modified By Daniel Bichel
%
% Last Modified 26 October 2007
%
%
% [alpha,beta,gamma,delta,Afuel]=fueldata(fuel)
%
% Routine to specify the thermodynamic properties of a fuel.
% Data taken from:
% 1. Ferguson, C.R., 1986, "Internal Combustion Engines", Wiley;
% 2. Heywood, J.B., 1988, "Internal Combustion Engine Fundamentals",
%    McGraw-Hill; and
% 3. Raine, R. R., 2000, "ISIS_319 User Manual", Oxford Engine Group.
% *****
% input:
% fuel switch
% from Ferguson: 'gasoline', 'diesel', 'methane', 'methanol',
% 'nitromethane', 'benzene';
% from Heywood: 'methane_h', 'propane', 'hexane', 'isooctane_h',
% 'methanol_h', 'ethanol', 'gasoline_h1', 'gasoline_h2', 'diesel_h';
% from Raine: 'toluene', 'isooctane'.
% output:
% alpha, beta, gamma, delta - number of C, H, O, and N atoms
% Afuel - vector of polynomial coefficients for cp/R, h/RT, and s/R
% of the form h/RT=a1+a2*T/2+a3*T^2/3+a4*T^3/4-a5/T^2+a6/T (for
% example) where T is expressed in K.
% *****

% Set values for conversion of Heywood data to nondimensional format
% with T expressed in K
SVal=4.184e3/8.31434;
SVec=SVal*[1e-3 1e-6 1e-9 1e-12 1e3 1 1];

switch fuel
case 'biodiesel' %AESE meeting
    alpha=18.74; beta=34.51; gamma=2; delta=0;
    Afuel=[7.9710 1.1954E-01 -3.6858E-05 0 0 -1.9385E+04 -1.7879];
    %co-eficients from diesel
case 'gasoline' % Ferguson
    alpha=7; beta=17; gamma=0; delta=0;
    Afuel=[4.0652 6.0977E-02 -1.8801E-05 0 0 -3.5880E+04 15.45];
case 'diesel' % Ferguson
    alpha=14.4; beta=24.9; gamma=0; delta=0;
    Afuel=[7.9710 1.1954E-01 -3.6858E-05 0 0 -1.9385E+04 -1.7879];
case 'methane' % Ferguson
    alpha=1; beta=4; gamma=0; delta=0;
    Afuel=[1.971324 7.871586E-03 -1.048592E-06 0 0 -9.930422E+03 8.873728];
case 'methanol' % Ferguson
```



```

    alpha=1; beta=4; gamma=1; delta=0;
    Afuel=[1.779819 1.262503E-02 -3.624890E-06 0 0 -2.525420E+04
1.50884E+01];
case 'nitromethane' % Ferguson
    alpha=1; beta=3; gamma=2; delta=1;
    Afuel=[1.412633 2.087101E-02 -8.142134E-06 0 0 -1.026351E+04
1.917126E+01];
case 'benzene' % Ferguson
    alpha=6; beta=6; gamma=0; delta=0;
    Afuel=[-2.545087 4.79554E-02 -2.030765E-05 0 0 8.782234E+03
3.348825E+01];
case 'toluene' % Raine
    alpha=7; beta=8; gamma=0; delta=0;
    Afuel=[-2.09053 5.654331e-2 -2.350992e-5 0 0 4331.441411 34.55418257];
case 'isooctane' % Raine
    alpha=8; beta=18; gamma=0; delta=0;
    Afuel=[6.678E-1 8.398E-2 -3.334E-5 0 0 -3.058E+4 2.351E+1];
case 'methane_h' % Heywood
    alpha=1; beta=4; gamma=0; delta=0;
    Afuel=[-0.29149 26.327 -10.610 1.5656 0.16573 -18.331
19.9887/SVal].*SVec;
case 'propane' % Heywood
    alpha=3; beta=8; gamma=0; delta=0;
    Afuel=[-1.4867 74.339 -39.065 8.0543 0.01219 -27.313
26.4796/SVal].*SVec;
case 'hexane' % Heywood
    alpha=6; beta=14; gamma=0; delta=0;
    Afuel=[-20.777 210.48 -164.125 52.832 0.56635 -39.836
79.5542/SVal].*SVec;
case 'isooctane_h' % Heywood
    alpha=8; beta=18; gamma=0; delta=0;
    Afuel=[-0.55313 181.62 -97.787 20.402 -0.03095 -60.751
27.2162/SVal].*SVec;
case 'methanol_h' % Heywood
    alpha=1; beta=4; gamma=1; delta=0;
    Afuel=[-2.7059 44.168 -27.501 7.2193 0.20299 -48.288
31.1406/SVal].*SVec;
case 'ethanol' % Heywood
    alpha=2; beta=6; gamma=1; delta=0;
    Afuel=[6.990 39.741 -11.926 0 0 -60.214 8.01623/SVal].*SVec;
case 'gasoline_h1' % Heywood
    alpha=8.26; beta=15.5; gamma=0; delta=0;
    Afuel=[-24.078 256.63 -201.68 64.750 0.5808 -27.562 NaN].*SVec;
case 'gasoline_h2' % Heywood
    alpha=7.76; beta=13.1; gamma=0; delta=0;
    Afuel=[-22.501 227.99 -177.26 56.048 0.4845 -17.578 NaN].*SVec;
case 'diesel_h' % Heywood
    alpha=10.8; beta=18.7; gamma=0; delta=0;
    Afuel=[-9.1063 246.97 -143.74 32.329 0.0518 -50.128 NaN].*SVec;
End

```

M-file for Tadiabatic1.m

```

function [T,tou,Tb,dnodtvt]=Tadiabatic1(p,Tu,phi,f,Trange,CR,fueltype);
%
% Written By Talal Yusaf
%
% Modified By Daniel Bichel
%

```

```

% Last Modified 26 October 2007
%
%
% Tb=Tadiabatic(p,Tu,phi,f,fueltype,airscheme)
%
% Routine for calculating the adiabatic flame temperature.
% Method involves iteratively selecting flame temperatures until
% the enthalpy of the combustion products (in equilibrium) matches
% the enthalpy of the initial gas mixture.
% farg.m is used to determine the enthalpy of the unburned mixture,
% and ecp.m is used to determine the enthalpy of the burned gas.
% Also used to determine the initial formation rate of NO and the
% characteristic time.
% *****
% input:
% p - pressure (Pa)
% Tu - temperature of the unburned mixture (K)
% phi - equivalence ratio
% f - residual mass fraction; set f=0 if no combustion products
% are present and f=1 if only combustion products are present
% fueltype - 'gasoline', 'diesel', etc - see fueldata.m for full list
% airscheme - 'GMcB' (Gordon and McBride) or 'Chemkin'
% CR - compression ratio
% Trange - temperature range for the evaluation of NO formation and
% characteristic time
% output:
% Tb - temperature of the burned gas (K) - adiabatic flame temperature
% Formation rate of NO graph across the evaluated temperature
% Characteristic time graph across the evaluated temperature
% *****
clc

airscheme='Chemkin';%airscheme type
thi=phi;
P1=1;%inlet pressure in BAR
MWN2=28.013;%Molecular weight of N2
MWO2=31.999;%Molecular weight of O2\

MaxIter=50;
Tol=0.00001; % 0.001% allowable error in temperature calculation
Tb=2000; % initial estimate
DeltaT=2*Tol*Tb; % something big
Iter=0;
[hu,u,v,s,Y,cp,dlvlT,dlvlp]=farg1(p,Tu,phi,f,fueltype,airscheme);

while (Iter<MaxIter)&(abs(DeltaT/Tb)>Tol)
    Iter=Iter+1;
    [x,hb,u,v,s,Y,cp,dlvlT,dlvlp]=ecp1(p,Tb,phi,fueltype,airscheme);
    DeltaT=(hu-hb)/cp;
    Tb=Tb+DeltaT;
end

if Iter>=MaxIter
    warning('convergence failure in adiabatic flame temperature loop');
end

x3=x(3,1)/MWO2;%O2 fraction (Y) in mol/g
x2=x(2,1)/MWN2;%N2 fraction
x8=x(8,1);%NO fraction
P=P1*(CR)^1.4;
MWN0=.5*MWO2+.5*MWN2;

```

```

x10=x(10,1)/MWNO;

for k=1:(1+Trange)
    T=(k+1899);%temperature range from 1900 to 1900+Trange

    %initial formation rate of NO (dondtvt)
    dnodtvt(k)=((6*10^16)/(T^(1/2)))*exp(-69090/T)*x3^(1/2)*x2;

    %characteristic time (tou)
    tou1=(8*10^(-16)*T*exp(58300/T))/(P^(1/2))*100;%time is in seconds, so
    divide it by 100 as P is in BAR ie 1000/100000
    tou(k)=1/tou1;

end
T=[1900:1:(1900+Trange)];

%Optional Graphing commands
% figure(1);
% semilogy(T,dnodtvt,'y');
% xlabel('Temperature (K)');
% ylabel('Formation rate of NO');
% title('NO formation rate Vs Temperature');
% hold on
%
% % figure(2);
% plot(T,tou,'k');
% xlabel('Temperature');
% ylabel('Characteristic time (ms) ');
% title('Characteristic time Vs Temperature');
% hold on
%
% figure(3);
% plot(phi,Tb,'r*');
% hold on
% xlabel('Equivalence ratio (thi)');
% ylabel('Adiabatic flame temperature (K)');
% title('Flame temperature Vs Equivalence ratio');

```