Modeling Deposit Formation in Diesel Injector Nozzle

by

Chintoo Sudhiesh Kumar

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Submitted to the Department of Aeronautics and Astronautics
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Abstract

Formation of deposit in the diesel injector nozzle affects the injection behavior and hinders performance. Under running condition, deposit precursors are washed away by the ensuing injection. However, during the cool down process after engine shut down, fuel, detergent chemistry, and fluid transport (evaporation) compete to determine the magnitude of deposit. This project involves numerical modeling and simulation of these processes.

Thesis Supervisor: Wai K. Cheng
Title: Professor of Mechanical Engineering
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1. INTRODUCTION

Deposit formation in the diesel injector nozzle affects the injector performance. The process is influenced by the chemical properties of the fuel as well as its additives. The following is a description of the injection equipment to provide a background for the deposit formation process.

1.1 The Diesel Injector

The injector is the most important and one of the most complex components in a diesel engine. Its main objective is to atomize the metered fuel into a fine mist inside the combustion chamber so that it can effectively mix with the air. The nozzle at the tip of the injector has a needle that closes under a spring load, when it is not spraying.

The technical aspects of fuel injection may be divided into two categories, namely:

a) Metering – the supply of the desired quantity of fuel in each injection, at an acceptable rate and over an acceptable crank angle.

b) Spray formation – the control of the physical characteristics of the spray in order to secure proper mixing of fuel and air, both in time and space [1].

Fig 1.1 shows an electro-hydraulic injector fitted within a 17mm diameter body. The key to the operation is a nozzle needle hydraulic control system.
1.2 **Nomenclature**

*Nozzle* – The opening through which the fuel emerges into the combustion chamber.

*Nozzle assembly* – An assembly of parts containing the nozzle, which is removable from the engine as a unit.

*Needle* – A rod in the inner end which is used to open and close the nozzle passage. The needle is usually spring loaded. Most, but not all, high-pressure injection systems use some form of needle.

*Opening pressure* – The fuel pressure required to lift the needle under test-bench conditions, with the pressure applied gradually.

*Injection pressure* – The pressure on the upstream side of the nozzle.

*Injection volume* – The volume of fuel in one injection, measured at inlet pressure and temperature [1].

1.3 **Working of the Injector**

The fuel injection into the cylinder is controlled by the opening and closing of the nozzle using the needle. The needle opening and closing pressures are determined by the spring load and the projected area of the needle. The pressure to open the needle is greater than that required to maintain it open, since in the closed position the projected area of needle is reduced by seat contact area [2]. The differential pressures are controlled by the relative needle diameter and seat diameter (Fig. 1.2)

The cylinder pressure at injection is typically in the range of 50 to 100atm and the fuel injection pressures range from 200 to 1700atm depending on the engine size and type of combustion employed. These large pressure differences across the injector nozzle are required so that in the injected liquid fuel jet will enter the
chamber at sufficiently high velocity to atomize into droplets that are small enough to
enable rapid evaporation as well as to traverse the combustion chamber within the
available time, so as to fully utilize the air charge [3].

Fig 1.3 shows the various types of nozzle designs that are generally used. The plain-orifice
and pintle nozzle designs give *hard sprays*, i.e. sprays characterized by a rather solid
core of fuel surrounded by an outer layer of smaller drops. Most diesel engines require this type of spray for satisfactory performance. All the other types shown give *soft sprays*, which have no such core. They consist of wholly separate droplets. Such sprays are generally not used in diesel engines, but are used for injecting fuel into the inlet port, or into the cylinder during injection stroke, of spark ignition engines. Soft sprays have inadequate penetration into the very dense air in the cylinder at the time of injection, which is normally around 14-20 times the inlet density [1]. The core breaks up soon after ignition occurs; otherwise combustion of a good part of the spray would come too late in the expansion stroke, resulting in bulk of the fuel being unburnt, and leading to bad emissions.
1.4 Phenomenon of Deposit Formation

Fig 1.4 shows the sectional view of a general injector nozzle, used for automotive applications. It is of multi-holed type, which is more prone to blockage due to deposit formation than the single-holed type. The fuel will enter into the fuel gallery before injection. During the injection, the needle will rise, so that the high upstream pressure forces the fuel to enter into the nozzle holes and continue onto the combustion chamber. At the end of injection, there will be seepage of a small quantity of fuel downstream into the nozzle holes. Once the needle is seated, the combined effects of the cylinder pressure and surface tension (owing to minute diameter of nozzle) will be enough to hold that fuel in the nozzle hole. After the last injection, i.e. the final injection before the engine is shut off, this remaining fuel is subjected to the heat contained within the surrounding material. This causes chemical activity, which might lead to formation of substances that adhere to the inner nozzle surfaces. Some of these substances, upon cooling down, might stick to the walls strongly enough to resist being washed away by the next injection of fuel, when the engine is restarted. This is the phenomenon of deposit formation.

1.5 Mass Flow in One Injection

Accurate predictions of fuel behavior within the injection system require sophisticated hydraulic models. However, approximate estimates of the injection rate through nozzles can be made with the following assumptions. If the pressure upstream of the injector nozzle can be estimated or measured, and considering the flow through
the nozzle as quasi steady, incompressible, and one-dimensional,[3] the mass flow rate can be modeled as:

\[ \dot{m}_f = C_d A_n \sqrt{2\rho \Delta p} \]

where:

- \( \dot{m}_f \) - mass flow rate through nozzle in one injection
- \( C_d \) - discharge co-efficient
- \( A_n \) - nozzle flow area
- \( \rho \) - fuel density
- \( \Delta p \) - pressure drop across the nozzle

Fig 1.5 – Mass flow rate through injector over one cycle at idling condition taken at 1000rpm.
Fig 1.6 – Velocity profile of fuel injected over one cycle

Fig 1.7 – Velocity profile of fuel over one injection
Fig 1.5 gives the profile of the instantaneous mass flow rate of fuel through the injector nozzle over one cycle of engine operation. Fig 1.6 and Fig 1.7 depict the velocity profiles of the fuel injected over one cycle and one injection respectively. The average velocity of fuel is roughly around 200m/s. This is an important parameter with regards to modeling the system. Graphs were generated using GT – Fuel [Appendix A].

1.6 Consequences of Deposit Formation

The deposit formed that adheres to the inner walls of the nozzle holes effectively reduces the flow area, $A_n$. For a standard common-rail engine, the upstream injection pressure and the downstream combustion chamber pressure are generally quite uniform. Simple examination of the one-dimensional model for mass flow will prove that the fuel mass injected into the cylinder for specified injection time will be lower. This results in inaccurate air-fuel ratio in the cylinder at the time of combustion, leading to degraded working conditions such as:

- Lack of engine power
- Poor fuel economy
- Increase in smoke
- Higher noxious emissions level
- Rough idling
- Stalling
- Misfiring, etc.

Fig 1.8 gives a sectional view of the schematic representation of the phenomenon of deposit formation on the inner nozzle surfaces.

Fig 1.8 – Schematic representation of deposit
Fig 1.9 and Fig 1.10 clearly depict the difference in the mass of fuel injected between a clean injector (left) and a partially blocked injector (right) of multi-holed and single-holed types respectively. The clogged injector exhibits non-uniformity in the spray formed, which is more visible in the multi-holed instance; the single-holed example clearly shows the reduction in mass flow of the fuel to the combustion chamber.

1.7 **Mechanism of Deposit Formation**

Some of the fuel that seeps into the nozzle after the last injection will result in the final amount of deposit formed. The magnitude of this deposit will depend on several external factors, but it is directly affected by the rates of two competing phenomena:-

- **Evaporation of fuel** into the surroundings out of the nozzle.
- **Chemical activity** within the fuel resulting in final deposit.

Evaporation and convection of the fuel vapor away from the mouth of the nozzle will contribute to reduction of deposit, and it removes the fuel mass left inside the nozzle. The evaporative action must also take into account the differential diffusion rates of the various constituents in the fuel, which includes the actual components in the diesel as well as the additives used. The high temperature of the engine immediately after shutdown will instigate chemical activity between the fuel constituents leading to formation
of heavy compounds that settle on the inner nozzle surface. Some amount of this substance that does not get washed away at the next injection turns into the deposit. The relative rates of these two processes determine the actual amount of final deposit.

Another mechanism of critical importance at this juncture is the use of detergency in the fuel. This is the method of use of special additives in the fuel called "detergents" that aid in eliminating, or at least dramatically reduce, the amount of deposit formed on the surface. The chemical complexity of detergency will add a whole new dimension to this study. It will deal with the surface chemistry of the deposit, trying to pry out as much of the adhered compounds as possible and removing it from the site of settlement. It also aims at hindering the process of formation of the deposit precursors, impeding the rate of settlement.

1.8 Motivation

The purpose of this study is to come up with a method to model the amount of deposit and effectively reduce it with the use of proper detergency, as accurately as possible. The final model of this research will be able to predict the most viable and suitable configuration of the fuel and its additives to achieve minimum deposit in the nozzles. This will provide economic gains by decreasing fuel consumption and contribute to setting up much more enjoyable and smooth driving conditions along with facilitating usage of maximum engine power. More importantly, reducing deposits will directly bolster the environmentally friendly attribute of the vehicle by cutting down on harmful exhaust gases and smoke.
2. MODELING OF EVAPORATION

2.1 Working Phenomena

The two phenomena that are vital for the determination of magnitude of deposit formed are:

- Evaporation or Fuel Transport, and
- Fuel Chemistry

These are competing processes regarding the deposit formation. Fuel transport is the process that deals with diffusion of individual fuel constituents within the liquid bulk as well as the convection of vaporized fuel away from the mouth of the nozzle. Fuel chemistry deals with the chemical changes undergone by the fuel constituents with the intrusion of oxygen into the fuel from the surrounding through the mouth. The rate of these changes will vary with the falling engine temperature as it cools down.

![Diagram of fuel injector nozzle processes](image-url)

Fig 2.1 – Processes in fuel in injector nozzle
Fig 2.1 shows a single nozzle hole in the injector with fuel filled in it. Evaporation will occur at the mouth, with the fuel vapor moving away due to natural convection within the combustion chamber. The individual fuel components will diffuse among each other due to the concentration gradient. Simultaneously, they will undergo chemical changes, due to the oxygen intrusion into the fuel from outside. The relative rates of these processes, as well as temperature profile of engine cooling are major factors deciding material deposition on the nozzle walls.

2.2 Fuel Transport

The two parts of fuel transport that are of importance here is diffusion of liquid fuel constituents and convection of vaporized fuel.

Diffusion is a net transport of molecules from a region of higher concentration to one of lower concentration by random molecular motion. Initially, the fuel that seeps into the injector nozzle will be more or less homogenous with respect to its individual constituents. But, the nozzle being open to the surroundings at the mouth, there will be vaporization and removal of mass at that site. The lighter components in the fuel tend to evaporate faster than the heavier ones. The same trend is applicable for the diffusion within the liquid mass. Lighter fuel constituents move towards the mouth and get depleted faster than the others. This generates the concentration gradient needed to force the mass diffusion.

The diffusion process is mathematically represented by two Fick’s Laws.

Fick's first law relates the diffusive flux to the concentration field, by postulating that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient (spatial derivative). In one dimension, this can be formulated as:

\[ J = -D \frac{\partial \rho}{\partial x} \]

where,

\( J \) – diffusion flux with units of \( \text{mol/m}^2 \text{sec} \)
D – co-efficient of diffusion with dimensions of \( m^2/sec \)

\( \rho \) – concentration of material with units of \( mol/m^3 \)

\( x \) – spatial co-ordinate

D is proportional to the squared velocity of the diffusing particles, which depends on the temperature, viscosity of the fluid and the size of the particles according to the Stokes-Einstein relation. In dilute aqueous solutions the diffusion coefficients of most constituents are similar and have values that at room temperature are in the range of \( 0.6 \times 10^{-9} \) to \( 2 \times 10^{-9} \) m\(^2\)/s [4, 5].

Fick's second law predicts how the concentration field in the fluid tends to change with time. It can be formulated as:

\[
\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}
\]

where 't' is the time co-ordinate. This equation is basically a compilation of the first law and mass balance in differential form.

Natural convection is the second phenomenon of interest with respect to fuel transport. This process occurs at the mouth of the nozzle, where the fuel evaporates and moves away from the injector farther into the combustion chamber. Mass convection is generally a combination of the vapor diffusion, due to random Brownian motion of the particles in the fluid, and advection, in which matter is transported by large-scale motion of currents in the fluid. The convection type in seen here is of natural type, which does not have any external agency forcing it. The flux of each component of a gaseous mixture is determined by its concentration and both the bulk fluid velocity (the average of all the components) and the diffusion velocity of the particular component.

A parameter of importance with respect to the convective mass transfer is the vapor diffusion length, \( L_v \), which is the length away from the mouth of the nozzle, where the convective effect becomes no longer quite important. It essentially describes the
boundary of the volume of scrutiny away from the nozzle. It is an important quantity with regards to the simulation. For the calculation, the rate of evaporation of fuel film from the mouth of the nozzle is matched to the rate of vapor convection away from it. This will pose as a constraint that is taken into account.

2.3 Estimation of Left Over Fuel

The quantity of residual fuel in the nozzle hole is a huge factor is deciding the amount of deposit left over once the whole process is completed. To quantify this, a model of the needle seating process is necessary. The common rail injector is designed such that fuel gallery pressure does not change appreciably in the needle closing process [6].

Fig 2.2 gives a view of the needle at its seated position in the injector. The geometrical nomenclature is as follows:

a – distance of spray hole from fuel gallery
h – gap between needle and seating surface
δ – spray hole diameter
L – spray hole length

Fig 2.2 – Details of needle seating geometry
N – number of spray holes
μ – fuel viscosity
ρ – fuel density
Δp_g – pressure drop along flow direction in the gap between needle and seating surface
Δp_n – pressure drop in nozzle spray hole
Δp_i – pressure difference between fuel gallery and combustion chamber; approximately equal to injector pressure p_i
U – velocity of fuel in the gap between needle and seating surface
V – velocity of fuel in the nozzle
Subscript ‘0’ – quantity at x = 0 (along co-ordinate ‘x’ as in figure 2.2)
Subscript ‘a’ – quantity at x = a

The gap ‘h’ between the needle and seating surface is of the order of a few microns to tens of microns. The generic needle closing speed for common rail engines is around 1 m/s. Simulation have shown that the nozzle hole fuel velocities are within the vicinity of 200 to 250 m/s. It can be argued using the continuity ideology that the velocity of fuel in the gap between needle and seating surface will be within a comparable range, due to approximate similarity in area of flow. Since this velocity is significantly higher than the needle seating velocity, the flow within this gap and the nozzle can be considered to be quasi-steady. Because of the conical geometry of the needle, the velocity U within the gap increases along co-ordinate x.

This velocity profile is given by:

\[ U(x) = U_0 \frac{d_0}{d(x)} \]

where d is needle diameter given by:

\[ d(x) = d_0 - x \sin(\theta) \]

The pressure drop in the hole is obtained from velocity U by integrating the pressure gradient:

\[ \Delta p_g = \int_0^a \frac{dx}{h} \frac{1}{2} \rho U^2 f \]

where ‘f’ is the friction factor given by the Moody chart [Appendix C]. For laminar flow, \( f = 64/Re \), where Re is the Reynold's number based on hydraulic diameter of the gap.
The solution is:

\[ \Delta p_g = 32 \ln \left( \frac{d_0}{d_a} \right) \frac{\mu a U_0}{h^2} \]

The pressure drop in the nozzle hole is:

\[ \Delta p_n = \frac{1}{2} \rho V^2 f \frac{L}{\delta} \]

Velocities \( V \) and \( U \) can be related using continuity of mass.

For \( N \) spray holes,

\[ V \frac{\pi \delta^2}{4} N = U_a \pi h d_a \]

The injection pressure provides the closure equation to solve for the nozzle velocity \( V \).

\[ \Delta p_i = \Delta p_g + \Delta p_n \]

For laminar flow in both gap and nozzle, the solution can be obtained analytically. For turbulent flow, however, the system of equations is implicit because friction factor ‘\( f \)’ depends in velocity through the Reynold’s number. This has to be solved numerically.

Fig 2.3 – Solution for fuel velocity
Fig 2.3 shows the graphical representation of the solution. The upper plot shows the variation of fuel velocity in the nozzle and the gap and the lower one gives the transit time of fluid in nozzle and the time to when the needle seats itself on the orifice. Needle closing velocity is taken to be 1 m/s and the hole length as 1 mm. Fuel injection pressure is assigned a realistic value of 1500 bar. It can be seen that the fuel velocity in the gap, $U$, is of the order of a few tens of meters per second when the gap is almost closed (around 1 µm gap). Thus, the quasi-static assumption is valid and as a result, the solution is independent of needle seating velocity. It is only used to translate needle lift position into the time to end of stroke.

The result can be interpreted as follows. As the injector needle closes (moving from right to left along the abscissa of the graph) the fluid velocity in the nozzle decreases due to the frictional pressure drop of the gap between the needle and the seat. However, the magnitude of the nozzle velocity is still substantial (more than 100 m/s). The time for this fluid to clear the nozzle is shown as the nozzle transit time in the lower graph. If this time is faster than the time to end of stroke of the needle, the nozzle fluid could still clear the nozzle as a continuous stream. If not (at 6.5 µm gap in figure), however, cavitation would occur and the liquid column would break off (Fig 2.4). The leakage flow after this break off...
would constitute the residual fuel. Thus the amount of residual fuel is equal to the cumulative fuel that leaks through the orifice in the last few micron of the seating process. In this specific example, the fuel would fill 40% of the nozzle passageway. Nevertheless, varied working conditions will affect the final amount of fuel seepage into the nozzle. Therefore, for the simulation, the nozzle will be assumed to be completely filled with fuel. This will constitute the worst case scenario which will potentially lead to maximum amount of deposit formed in the nozzle hole.

2.4 **Fuel Surrogate**

Diesel fuel comprises hundreds of components with a quite substantial range of physical and chemical properties. Therefore, to reduce the fuel properties to a more manageable set, the fuel will be represented by a surrogate consisting of a few compounds. The list of components of diesel fuel, determined by distillation, is given in Table 2.1. It essentially comprises aromatics and saturates, and the saturates are mostly paraffins. The aromatics are mostly alkyl benzenes and naphthenbenzenes at almost equal percentages, with the former having the slight edge over the latter. The composition is consistent with the typical modern diesel fuel composition [7]. In the selection of components to make up the surrogate fuel, it must be made sure that the selected mixture will more or less represent the actual diesel fuel in all its properties, so that the results obtained by

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</tr>
<tr>
<td>Alkyl benzenes ASTM D3239</td>
<td>vol%</td>
</tr>
<tr>
<td>Naphthenbenzenes</td>
<td>vol%</td>
</tr>
<tr>
<td>Dinaphthenbenzenes</td>
<td>vol%</td>
</tr>
<tr>
<td>Naphthalenes</td>
<td>vol%</td>
</tr>
<tr>
<td>Acenaphthenes</td>
<td>vol%</td>
</tr>
<tr>
<td>Fluorenes</td>
<td>vol%</td>
</tr>
<tr>
<td>Pyrenes</td>
<td>vol%</td>
</tr>
<tr>
<td>Crysenes</td>
<td>vol%</td>
</tr>
<tr>
<td>Phenanthrenes</td>
<td>vol%</td>
</tr>
<tr>
<td>Naphthene-phenanthrenes</td>
<td>vol%</td>
</tr>
<tr>
<td>Aromatic Thiophenes</td>
<td>vol%</td>
</tr>
<tr>
<td>Unidentified Aromatics</td>
<td>vol%</td>
</tr>
</tbody>
</table>

Table 2.1 – Constituents of diesel
simulation of the surrogate may reflect the behavior of the actual fuel.

<table>
<thead>
<tr>
<th>Name of compound</th>
<th>Carbon Atoms</th>
<th>NBP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Normal Paraffins</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n - pentane</td>
<td>5</td>
<td>36.1</td>
</tr>
<tr>
<td>n - hexane</td>
<td>6</td>
<td>68.7</td>
</tr>
<tr>
<td>n - heptane</td>
<td>7</td>
<td>98.4</td>
</tr>
<tr>
<td>n - octane</td>
<td>8</td>
<td>125.7</td>
</tr>
<tr>
<td>n - decane</td>
<td>10</td>
<td>174</td>
</tr>
<tr>
<td>n - dodecane</td>
<td>12</td>
<td>216.3</td>
</tr>
<tr>
<td>n - hexadecane</td>
<td>16</td>
<td>286</td>
</tr>
<tr>
<td>n - octadecane</td>
<td>18</td>
<td>316</td>
</tr>
<tr>
<td>n - eicosane</td>
<td>20</td>
<td>344</td>
</tr>
<tr>
<td><strong>Iso Paraffins</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2,3 - trimethylbutane</td>
<td>7</td>
<td>89</td>
</tr>
<tr>
<td>2,2,3 - trimethylpentane</td>
<td>8</td>
<td>99</td>
</tr>
<tr>
<td><strong>Olefins</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 – pentene</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>1 – heptene</td>
<td>7</td>
<td>93</td>
</tr>
<tr>
<td><strong>Aromatics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>6</td>
<td>80</td>
</tr>
<tr>
<td>Toluene</td>
<td>7</td>
<td>110</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>8</td>
<td>136</td>
</tr>
<tr>
<td>Meta Xylene</td>
<td>8</td>
<td>139</td>
</tr>
<tr>
<td>n – propyl benzene</td>
<td>9</td>
<td>159</td>
</tr>
<tr>
<td>Cumene</td>
<td>9</td>
<td>152</td>
</tr>
</tbody>
</table>

Table 2.2 – Normal boiling points of hydrocarbons

Table 2.2 gives the normal boiling points (NBP) of certain hydrocarbons. Fig 2.5 shows that NBP is approximately only a function of the number of carbon atoms in the compound. Therefore, this relation can be used to match up the distillation curve of real diesel.
For building up the surrogate, the first step is to use a collection of alkanes to overlap the distillation curve of diesel (Fig 2.6) with the use of NBP for alkanes from C10 to C22, which are present in actual diesel.

Five alkanes are selected to represent the distillation curve as shown in Fig 2.7 to as closely represent the curve as possible. The selected alkanes are n-undecane (C_{11}H_{24}), n-tridecane (C_{13}H_{28}), n-hexadecane(C_{16}H_{34}), n-nonadecane (C_{19}H_{40}) and n-heneicosane (C_{21}H_{44}). Each of the flats of the stepped curve represents one alkane. Further, to capture the essence of properties of aromatics, a 1-ring compound, n-decylbenzene (C_{16}H_{26}) with NBP of 300 °C, and a 2-ring compound, 1-methylnaphthalene (C_{11}H_{10}), with NBP of 241 °C are added on. Both are recommended species for diesel surrogate compilation [7]. The total aromatics to saturates ratio is tweaked to be 77:23 abiding by the results of dry distillation. For the same reason, the ratio of n-decylbenzene to 1-methylnaphthalane is adjusted to 1.1:1. These seven
compounds, summarized in Table 2.3, will comprise the fuel surrogate for our simulation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fraction by volume</th>
<th>Boiling point (°C)</th>
<th>CAS number</th>
<th>Carbon atoms</th>
<th>Hydrogen atoms</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-undecane</td>
<td>5%</td>
<td>195.6</td>
<td>1120-21-4</td>
<td>11</td>
<td>24</td>
<td>n-paraffin</td>
</tr>
<tr>
<td>n-tridecane</td>
<td>19%</td>
<td>235.0</td>
<td>1029-50-5</td>
<td>13</td>
<td>28</td>
<td>n-paraffin</td>
</tr>
<tr>
<td>1M-naphthalene</td>
<td>11%</td>
<td>241.0</td>
<td>90-12-0</td>
<td>11</td>
<td>10</td>
<td>2-ring aromatic</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>25%</td>
<td>286.0</td>
<td>544-76-3</td>
<td>16</td>
<td>34</td>
<td>n-paraffin</td>
</tr>
<tr>
<td>n-decylbenzene</td>
<td>12%</td>
<td>300.0</td>
<td>104-72-3</td>
<td>16</td>
<td>26</td>
<td>1-ring aromatic</td>
</tr>
<tr>
<td>n-nonadecane</td>
<td>18%</td>
<td>329.5</td>
<td>629-92-5</td>
<td>19</td>
<td>40</td>
<td>n-paraffin</td>
</tr>
<tr>
<td>n-heneicosane</td>
<td>10%</td>
<td>356.3</td>
<td>629-94-7</td>
<td>21</td>
<td>44</td>
<td>n-paraffin</td>
</tr>
</tbody>
</table>

Table 2.3 – Fuel surrogate components

Fig 2.8 shows how the seven selected compounds represent the distillation curve for the actual fuel. It is also to be noted that all these compounds are easily available in market, so that the simulation results could be justified by physical testing of such a blend.

2.5 **Modeling Strategy**

Having taken the nozzle to be completely filled with fuel, it can be argued that this residual fuel will be retained in it since the surface tension force is much higher than the hydrostatic force. For a nozzle of length L = 1mm and diameter δ = 200μm, the hydrostatic pressure, \( p g L \) (\( g \) – acceleration due to gravity), is approximately 10 N/m². The pressure generated by surface tension \( \sigma = 0.02 \text{N/m} \) is of the order of \( \sigma/\delta = 100 \text{ N/m}^2 \). Thus, it is seen that the surface tension force is greater by roughly one order of magnitude. The action of the detergent would be to keep the deposit precursors in the
liquid state so that they would be flushed out with the un-evaporated residual fuel in the next injection.

Fig 2.9 shows the processes occurring in the retained fuel after the engine is shut down. The aspect ratio of the liquid column ($L/\delta$) is of the order of 2 to 5. Since the axial to radial diffusion time ratio is $(L/(\delta/2)^2) \sim 16$ to 100, a simplified one-dimensional model (in the axial direction) will capture the underlying physics. In reality, the fuel will undergo the processes of evaporation and chemistry simultaneously. At the first stage of modeling, only the transport (diffusion and evaporation) is simulated. Since the lighter components get evaporated faster, the expected concentration profile is shown in Fig 2.9. At the mouth of the nozzle, density of lighter compounds will fall, while that of the heavier ones will increase.

Fig 2.10 gives a simplification of the 1-D model, where the details of the shape of the liquid-vapor interface are neglected. The interface profile would be quite complicated to model due to the strong influence of surface tension forces at the small length scales involved. Therefore, the receding interface is assumed to be flat, at a length $x_i$ from the inlet of the nozzle. Let the partial molar densities of each of the species in the fuel be represented by $\rho_i$ where 'i' goes from 1 to N for all species. (N=7 for the surrogate fuel).

If 'p' is average molar density of the fuel, then $\rho_i = p y_i$, where $y_i$ is the mole fraction of the species 'i'.
The molar densities would then be governed by the relation:
\[
\frac{\partial \rho_i}{\partial t} = D_i \frac{\partial^2 \rho_i}{\partial x^2} + \left( \frac{\partial \rho_i}{\partial t} \right)_{\text{chem}} - \left( \frac{\partial \rho_i}{\partial t} \right)_{\text{deposit}}
\]
where the chemical generation term must be modeled by kinetics, and the deposition term is the bulk reduction of the species concentration due to deposit formation on the inner walls. \(D_i\) is the diffusivity of the species 'i' in the mixture.

The boundary condition on the closed (left) side of the nozzle is:
\[
\left( \frac{\partial \rho_i}{\partial x} \right)_{x=0} = 0
\]

The boundary condition on the open (right) side is:
\[
D_i \left( \frac{\partial \rho_i}{\partial x} \right)_{x=x_1} + Q_i + \rho_i \left( \frac{dx_1}{dt} \right) = 0
\]
where \(Q_i\) is the surface flux of the species 'i' (considering both vapor diffusing out and oxygen diffusing in). The rate of regression of the interface, \(dx_1/dt\), is determined by overall conservation of fuel column. Since the fuel vapor concentrations in the combustion chamber are much more dilute than those at the fuel column surface, a single parameter, the vapor diffusion length \(L_v\) is used to determine the surface fluxes \(Q_i\) of the species from the surface vapor concentrations \(\rho_{v,i}\) and vapor diffusivities \(D_{v,i}\). A good estimate for the vapor diffusion length is the diameter of the nozzle.

\[
Q_i = D_{v,i} \frac{\rho_{v,i}}{L_v}
\]

Assuming the model of ideal gas for the vapor, the density can be represented as:
\[
\rho_{v,i} = \frac{P_{v,i}}{RT}
\]
where, \(P_{v,i}\) – partial pressure of vapor species 'i'
\(R\) – universal gas constant
\(T\) – temperature of the surroundings of the nozzle

To calculate the partial pressure of all the species, \textit{Raoult's law} is employed. It states that the partial pressure of a specific component vapor in a mixture is numerically
equal to the product of the saturation pressure of that component at that temperature and the molar fraction of that component in the mixture [8].

Raoult's Law is:

\[ p_i = p_{i,SAT}(T) \ y_i \]

where \( y_i \) is the mole fraction, given by

\[ y_i = \frac{\rho_i(x_1, t)}{\sum_{i=1}^{N} \rho_i(x_1, t)} \]

where \( x_1 \) represents the interface and \( t \) is time co-ordinate.

Therefore, the surface fluxes of the species can be written as:

\[ Q_i = \frac{D_{v,i} \ p_{i,SAT}(T)}{L_v RT} \ \frac{\rho_i(x_1, t)}{\sum_{i=1}^{N} \rho_i(x_1, t)} \]

The saturation pressure for each component is obtained using the Antoine equation. It is a vapor pressure equation that describes the relation of the saturated vapor pressure and the temperature for pure components. It is derived from the Clausius – Clapeyron relation.

The equation is:

\[ \log_{10} P = A - \frac{B}{C + T} \]

where \( T \) is the temperature of the vapor, and \( A, B \) and \( C \) are constants that are characteristic of the constituent. The values for these constants can be obtained from standardized tables [Appendix D].

The last equation which provides closure to the system is one that will depict that all mass loss from the fuel that is retained in the injector nozzle exhibits itself as the vapor that is removed from the system at the interface. It is represented as:

\[ \sum_{i=1}^{N} D_i \frac{\partial \rho_i(x_1, t)}{\partial x} = 0 \]

where \( N \) is the number of species in the fuel.
The chemistry, evaporation and diffusion processes are all temperature dependent. Since the thermal diffusion time along the nozzle metallic wall is much shorter than that along the liquid, the fluid temperature is assumed to be in thermal equilibrium with the nozzle wall. The wall temperature will be uniform in the x direction throughout the nozzle, but with a time dependence governed by the cooling characteristics of the nozzle through heat transfer to the head of the cylinder. For the convenience of modeling, at this stage, the temperature is assumed to be a constant. Although this isothermal assumption does not reflect reality, it will serve as a good standard to compare simulation results to experimental values, which are also carried out at similar conditions. The cooling profile of engines will depend on several factors ranging from atmospheric condition at the time to the size and material for the structures that encapsulate it. Quite intuitively, this will vary from engine to engine. Nevertheless, at a later time, the temperature variation should also be accounted for to reflect the actual conditions of cooling down of an automobile after engine shut-down.

2.6 Discretization

Solving the four sets for equations prescribed above for the fuel surrogate of seven components \((i = 1 \text{ to } 7)\) will represent the complete fuel transport in the system, with no chemistry involved. This is accomplished by numerical means.

![1-D discretization into M layers](image.png)

Figure 2.11 – Discretization of domain

The first step is to discretize the fuel domain as shown in Fig 2.11. Since 1-dimensional assumption is employed, the fuel column can be divided into M layers longitudinally. If \(L\) is the length of the fuel column, each layer has a width \(dx = L/M\) units. The assumption is that each layer is homogenously filled (or empty) at all times during
the evaporation process, i.e. there is no concentration gradient for any species within one layer in any direction. Time discretization is carried out by Crank-Nicolson method which gives it second order accuracy [9, 10] [Appendix B].

The equations are discretized as follows:

**Equation 1**

\[
\frac{\partial \rho_i}{\partial t} = D_i \frac{\partial^2 \rho_i}{\partial x^2}
\]

with the chemistry and deposition terms removed, so that only transport is taken into account.

\[
\frac{\rho_{i,j}^n - \rho_{i,j}^{n-1}}{\Delta t} = D_i \frac{1}{2} \left[ \frac{\rho_{i,j-1}^n - 2\rho_{i,j}^n + \rho_{i,j+1}^n}{(\Delta x)^2} + \frac{\rho_{i,j-1}^{n-1} - 2\rho_{i,j-1}^n + \rho_{i,j+1}^{n-1}}{(\Delta x)^2} \right]
\]

where,

- \(\Delta x\) – spatial discretization (= L/M units)
- \(\Delta t\) – time discretization step
- \(n\) – current time step
- \(n-1\) – previous time step
- \(i\) – represents species number
- \(j\) – represents layer number (which goes from 2 to M-1 in the above equation)

The terms can be grouped as follows:

\[
- \frac{D_i \Delta t}{2 (\Delta x)^2} \rho_{i,j-1}^n + \left(1 + \frac{D_i \Delta t}{(\Delta x)^2}\right) \rho_{i,j}^n - \frac{D_i \Delta t}{2 (\Delta x)^2} \rho_{i,j+1}^n - \frac{D_i \Delta t}{2 (\Delta x)^2} \rho_{i,j-1}^{n-1} + \left(-1 + \frac{D_i \Delta t}{(\Delta x)^2}\right) \rho_{i,j}^{n-1} - \frac{D_i \Delta t}{2 (\Delta x)^2} \rho_{i,j+1}^{n-1} = 0
\]

N being the number of species in the surrogate and M the number of layers into which the fuel is discretized. The above equation represents N(M-2) distinct equations with 'i' running from 1 to N and 'j' running from 2 to M-1.
**Equation 2**

\[
\left. \left( \frac{\partial \rho_i}{\partial x} \right) \right|_{x=0} = 0
\]

The discretized version is:

\[
\rho^n_{i,1} - \rho^n_{i,2} = 0
\]

This represents N equations with 'i' running from 1 to N.

**Equation 3**

\[
D_i \left( \frac{\partial \rho_i}{\partial x} \right)_{x=x_1} + \frac{D_{v,i} \rho_{i,SAT}(T)}{L_v RT} \frac{\rho_i(x_1, t)}{\sum_{i=1}^{N} \rho_i(x_1, t)} + \rho_i \left( \frac{dx_1}{dt} \right) = 0
\]

for convenience, assign:

\[
C_i = \frac{D_{v,i} \rho_{i,SAT}(T)}{L_v RT}
\]

The discretized version is:

\[
D_i \left( \frac{\rho^n_{i,M} - \rho^n_{i,M-1}}{\Delta x} \right) + C_i \frac{\rho^n_{i,M}}{\sum_{i=1}^{N} \rho^n_{i,M}} + \rho^n_{i,M} \left( \frac{-\Delta x}{\Delta t} \right) = 0
\]

Grouping up terms leads to:

\[
\left( \frac{D_i \Delta t}{(\Delta x)^2} - 1 \right) \rho^n_{i,M} \sum_{i=1,N}^{N} \rho^n_{i,M} - \frac{D_i \Delta t}{(\Delta x)^2} \rho^n_{i,M-1} \sum_{i=1,N}^{N} \rho^n_{i,M} + \left( \frac{\Delta t}{\Delta x} \right) C_i \rho^n_{i,M} = 0
\]

This represents N equations with 'i' running from 1 to N.

**Equation 4**

\[
\sum_{i=1}^{N} D_i \frac{\partial \rho_i(x_1, t)}{\partial x} = 0
\]
This is discretized to:

\[
\sum_{i=1}^{N} D_i \left( \rho_{i,M}^n - \rho_{i,M-1}^n \right) = 0
\]

The above relation represents one equation which closes the system with a total of \((N*M + 1)\) equations to be solved.

2.7 **Solution Strategy**

The set of equations assembled will be solved implicitly with respect to time coordinate. Contrary to traditional time marching scheme, \(\Delta t\) here is treated as an unknown, while \(\Delta x\) is fixed to be numerically equal to length of nozzle divided by number of layers. Initially, the concentrations \(p_i\) of each component has to be obtained. The whole nozzle is assumed to be filled with the fuel homogenously. Therefore, from the equations, the unknowns are the concentrations of all constituents at the next time step, which accounts to \(N*M\) terms and \(\Delta t\). In other words, concentration of each component in each layer is known at time step \((n-1)\), while those at time step \(n\) are unknowns.

![Fuel Layer Removal](image)

Figure 2.12 – Fuel layer removal

The solution simulates evaporation of each layer one at a time off from the front. Over the first iteration, concentrations of all components for the proceeding time step and the time step itself, \(\Delta t\), is calculated. At the end of this time period, all fuel in the front layer has been removed (as shown in Fig 2.12), by evaporation into the air as well as by diffusion into the rest of the fuel. For the next iteration, only \((M-1)\) layers are left and the concentrations of all components for these \((M-1)\) layers have already been
calculated as the result of the previous time step. This process is continued until all the fuel has been completely evaporated. Adding up each individual $\Delta t$ will give the total time taken for fuel transport to completely remove the fuel in the nozzle. Multi-dimensional Newton solution using Jacobian is employed to solve this set of equations [9, 10]. The equations are set up to provide second order accuracy in time.

The initial concentration of fuel, before the simulation begins, is obtained from the software, Supertrapp that employs the NIST (National Institute of Standards and Technology) database to carry out flash calculations of the components in the fuel surrogate at the prescribed pressure and temperature. These values are given in Table 2.4.

<table>
<thead>
<tr>
<th>Component</th>
<th>Initial concentration (mol/liter)</th>
<th>Percentage in mixture (by volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-undecane</td>
<td>3.817</td>
<td>5%</td>
</tr>
<tr>
<td>n-tridecane</td>
<td>3.159</td>
<td>19%</td>
</tr>
<tr>
<td>1M-naphthalene</td>
<td>3.710</td>
<td>11%</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>2.522</td>
<td>25%</td>
</tr>
<tr>
<td>n-decylbenzene</td>
<td>2.604</td>
<td>12%</td>
</tr>
<tr>
<td>n-nonadecane</td>
<td>2.049</td>
<td>18%</td>
</tr>
<tr>
<td>n-heneicosane</td>
<td>1.799</td>
<td>10%</td>
</tr>
</tbody>
</table>

Table 2.4 – Initial concentrations in surrogate fuel
2.8 Results and Inferences

The simulation was carried out for the seven component diesel surrogate. The initial fuel column, \( L = 0.5 \text{ mm} \), which was divided into \( M = 100 \) layers. Diameter of the nozzle is 0.1mm. The temperature of a generic engine as it shuts down is about 130 °C. Therefore, the calculation is set to have an isothermal temperature of 130 °C throughout the fuel transport process. Figs 2.13 – 2.19 represent the progression of the concentration profile of each of the surrogate components. In each figure, the x-axis represents the layers in the fuel column. For each profile, the x value of the end point is the position of the liquid/vapor interface. The first curve (the top curve) is the profile after one layer has evaporated. As the computation progressed, the end point recessed one layer at a time until 4 layers were left. At this point, computation stopped because the formulation would be singular if it tries to model the condition where no fuel was left.

![Fig 2.13 – Concentration profiles for n-undecane](image)
Fig 2.14 – 
Concentration profiles for n-tridecane

Fig 2.15 – 
Concentration profiles for 1-methylnaphthalene
Fig 2.16 – Concentration profiles for n-hexadecane

Fig 2.17 – Concentration profiles for n-decylbenzene
Fig 2.18 — Concentration profiles for n-nonadecane

Fig 2.19 — Concentration profiles for n-heneicosane
For n-undecane, the lightest fuel component, evaporation depleted the concentration adjacent to the liquid-vapor interface (Fig 2.13). As evaporation progress, the concentration of the species in the whole fuel column was depleted. This component gets completely removed when around 45 layers of fuel are left in the nozzle. The next two fuel components, n-tridecane (Fig 2.14) and 1-methyl naphthalene (Fig 2.15) are less volatile; therefore the depletion adjacent to the interface is less severe; otherwise, the behavior is similar to that of the n-undecane. For n-hexadecane (Fig 2.16), the species with the next higher NBP, the concentration profiles are very different from the previous ones. As the high volatility components evaporated, the low volatility components became more concentrated at the top layer and there was significant back diffusion from the top layer back to the bulk. As time progresses, the n-hexadecane concentration at the top layer first increases due to the distillation of the higher volatility fuel components, and then decreases as the higher volatility components runs out. At the latter transition, the n-hexadecane has become the de-facto “high volatility” component because all the higher volatility components were depleted. For the remaining components, n-decylbenzene (Fig 2.17), n-nonadecane (Fig 2.18) and n-heneicosane (Fig 2.19), the behaviors are similar. Note that for n-heneicosane, the species with the highest NBP (356.3 °C), at 130 °C wall temperature, the vapor pressure is sufficiently low that it is the only fuel component left at the end of the computation when the fuel column is reduced to 4 layers.

Fig 2.20 - Expected concentration progression

Fig 2.20 shows the expected progression of the concentrations of the components with respect to their relative weights. As the fuel column evaporates, the concentrations of the three lightest components decreased monotonously. The
concentrations of the middle two components first increased, and then stay almost constant for some time before decreasing. For the heaviest two components, the concentrations increased substantially as the lighter components had escaped.

![Graph showing concentrations at fuel-vapor interface.](image)

Fig 2.21 – Concentrations at fuel-vapor interface.

Fig 2.21 shows the concentrations of each component at the interface, as it recedes backwards (from right to left as seen in graph). This clearly depicts the heavier constituents getting more and more concentrated in the left over fuel, while the lighter ones get depleted.

At a grid resolution of 100 layers, the time taken for the fuel to get completely depleted (down to 4 layers in this numerical calculation) at a temperature of 130°C was 1.3708 hours. Higher grid resolutions yielded very similar result.
Fig 2.22 shows how the total time required for evaporation of the fuel column varies with the temperature. Since the saturation vapor pressure is extremely sensitive to temperature, the time scale for evaporation is a strong function of temperature. A 30 °C increase in temperature will decrease the time for evaporation by roughly one order of magnitude, as seen in Fig 2.23, which depicts the progression of time as the fuel gets depleted. It can also be seen that the first few layers (85-100) are removed much faster than the inner ones, which take substantially longer.
3. MODELING OF CHEMISTRY

3.1 Incorporation of Chemistry

The study of fuel transport gives a clear idea of the liquid recession profile and related times for the fuel within the nozzle. In order to understand and predict the effects of fuel detergents on deposit formation in diesel injector nozzles, a detailed model describing both the physical and chemical processes involved in the deposit formation is necessary. During the first stage of incorporating chemistry into the physical fuel transport process, detergent materials are avoided. Such components will be added to the fuel surrogate at a later stage. Therefore, the aim here is to understand the chemical changes that occur in the fuel surrogate at the existing conditions within the injector nozzle, during the time scale set by evaporation. The methodology is to develop the chemical model theoretically so that they could reproduce quantitatively the results observed in the bench scale experiments (Section 4).

The process of chemical modeling comprises the following steps:

- Building a chemical model consisting of appropriate chemical reactions.
- Coupling of the chemical kinetics into the fuel transport model.
- Estimating physical properties and kinetic parameters for the fuel and intermediate species.
- Improve estimates of chemical kinetic and physical property parameters based on physical experimentation.
- Applying the model to injector nozzle environment.

3.2 The Chemical Model

Many systems of interest to chemical engineers include very complicated chemistry. The auto-oxidation of hydrocarbons is one of them. The reaction has complicated radical reaction pathways [11]. These reaction networks may contain thousands of reactions and species. Reacting system like this may also have complicated temperature dependencies, where the dominant reaction pathway may change at different temperatures leading to a change in reaction order. The typical way
to model these systems is to choose a simple chemistry model such as $A + B \rightarrow C$ based on the understanding of the system, compile it into a reactor model, and fit the parameters for the rate expressions to measurements from experiments. However, even if the model can be made to fit the data, this does not prove that the underlying understanding is accurate; the fitted parameters may not be physically meaningful. Moreover, these models are not reliably predictive for conditions outside the range covered by experimental data, due to the possibility of complex temperature-dependency mentioned above. There are numerous other species and reactions, typically involving competing catalytic cycles, and these complicated reaction networks cannot be described by a sequential linear kinetics model except in a very narrow range of conditions. Fortunately, in this case, the ability to perform experiments in the same temperature range as that of a slowly cooling diesel engine is an actuality, so temperature extrapolation is unnecessary. However, so as to extend the model to include detergency effects, oxidation and degradation of detergent, and other attempts to mitigate deposit formation, a physically meaningful understanding of reaction pathways and intermediate species will become important. The simple model of fuel $\rightarrow$ intermediate $\rightarrow$ deposit, with parameters tuned to fit bench experiments may not be sufficient.

A detailed kinetic model consists of two parts: a list of species and a list of reactions. For each species there is thermochemical data ranging over all temperatures covered by the model; the standard enthalpy of formation, standard entropy, and heat capacity as a function of temperature are sufficient to calculate all other thermodynamic properties. For each reaction is a forward rate coefficient for all temperatures (the reverse rate is calculated from the chemical equilibrium constant, derived from the thermochemistry). For elementary reactions this is usually given as a function of temperature in Arrhenius form:

$$k = A \, e^{-E_a/RT}$$
Where, $k$ – rate constant
$A$ – pre-exponential factor
$E_a$ – activation energy
$R$ – gas constant
$T$ – temperature

Since complex kinetic models may contain thousands of species and reactions, manual generation of the model would be tedious and error-prone. Automatic generation of kinetic models would allow for modeling arbitrarily complicated chemistry systems without too much effort. Several research groups are working on computational tools to automate the process [12-14]. All these tools have common requirements: (1) a method for representing molecules in the computer memory, and of uniquely identifying the molecules and recognizing equivalents; (2) a method for creating reactions and their product species; (3) a method for predicting thermochemical and kinetic parameters for each of the species and reactions.

3.3 **Reaction Mechanism Generator (RMG)**

RMG is an automatic chemical reaction mechanism generator that constructs kinetic models composed of elementary chemical reaction steps using a general understanding of how molecules react [15, 16]. Molecules are represented as graphs, with atoms as nodes and bonds as edges connecting the nodes. Standard graph-theory methods are used to identify equivalent graphs and ensure uniqueness. RMG uses "reaction families" to generate all the possible reactions that a species can undergo in the presence of the other species in the chemical mechanism. Every reaction family represents a particular type of elementary chemical reaction, such as bond breaking, or radical addition to a double bond. Each reaction family has a recipe for mutating the graph, and a library of rate expressions for different functional groups. There are currently over 30 primary reaction families in RMG. Because the model can contain thousands of species and rates, the estimation of thermochemical and kinetic parameters must be very fast. As with most mechanism generating tools, RMG uses a database of known values wherever possible to find thermochemical data for species, but usually it estimates parameters using a group contribution method. The functional groups are recognized using a graph-theory matching algorithm. A similar method is
used to estimate the rate coefficients for the reactions. RMG uses a rate-based termination criterion; the reaction network is expanded until the rates of all reactions going to species not included in the network fall below a certain threshold.

The following steps were used to build a detailed kinetic model for the auto-oxidation of diesel fuel using RMG:

- Define the conditions, define the surrogate components, and run RMG to create a first reaction network.
- Modify the thermochemistry estimates to account for solvation effects.
- Modify the kinetics estimates to account for diffusion and solvation effects.
- Add reaction families for solution-specific reactions.
- Reduce the size and stiffness of the resulting kinetic models.

RMG is used to simulate the diesel surrogate oxidation. To do this, the surrogate fuel components are defined in terms of their molecular structure graphs, and appropriate conditions for the simulation are chosen. Until the internal chemistry solver is modified to explicitly handle liquid phase simulations, RMG uses the ideal gas law to calculate the total molar concentration. Therefore, a pressure of 210 bars which produces roughly the same molar concentration as that of liquid diesel, is made use of. The initial concentrations were determined according to the volume fractions of the chosen surrogate mixture, and the temperature was 150 °C. The resulting kinetic model contains temperature and concentration dependence, so it is valid for a range of conditions beyond the conditions at which the model is generated. Some additional modifications are also made to RMG for these surrogate diesel simulations. First, the concentration of oxygen is held constant at its solubility limit throughout the simulation. Without this modification the dissolved oxygen is quickly used up and reaction slows down. Secondly, the volume change due to chemical reactions (usually determined by the ideal gas law) is removed to better simulate the liquid phase.
3.4 Application of RMG to Diesel Surrogate

Several kinetic models were generated in the same way using RMG. The accuracy tolerance or termination criterion was varied to yield kinetic models of different sizes and complexities. Eventually it would be preferable to generate a large kinetic model to ensure all relevant reaction pathways have been captured, then to reduce it to a more manageable size afterwards for computational efficiency. Smaller mechanisms are made by relaxing the tolerance in the generation stage.

Table 3.1 shows the typical size of the model (in terms of the number of species and of reactions) generated by RMG in relationship to the termination criterion.

<table>
<thead>
<tr>
<th>Termination Criterion</th>
<th>Number of Species</th>
<th>Number of Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>14</td>
<td>13</td>
</tr>
<tr>
<td>0.1</td>
<td>31</td>
<td>142</td>
</tr>
<tr>
<td>0.01</td>
<td>83</td>
<td>2146</td>
</tr>
</tbody>
</table>

Table 3.1 – Sizes of mechanisms generated by RMG

To facilitate bookkeeping of the chemistry terms in the numerical integration of the kinetics scheme, it is best to use specialized chemistry libraries. One such library is Chemkin [17], which has had extensive use over the last 20 years. A newer alternative is Cantera, an open-source suite of object-oriented software tools for problems involving chemical kinetics, thermodynamics, and/or transport processes. Although Cantera itself is written in C++, it can be used from MATLAB, Python, C++, or even Fortran. RMG outputs chemistry kinetic models in the format required by Chemkin, but these are easily converted by Cantera. The kinetic model input file specifies the elements and species to be included in the simulation, along with the thermochemical information for each species in the form of polynomial coefficients, and a list of all the reactions with their rate expressions. The Cantera routines are called from within MATLAB or Python.

To characterize the kinetic model, a simple batch reactor simulation was created using Cantera in Python. For the graphs shown, the initial mass fractions were set according to the surrogate composition, the mole fraction of oxygen was replenished at
each time step to 0.2 mol% (an estimate of the solubility limit) [18], the temperature was fixed at 408 K and the total mass density was maintained at 850 kg/m³ (approximately the density of diesel). The kinetic model with 83 species and 2146 reactions was used. Cantera uses a variable time step for the ODE solver and took 534 steps overall to simulate 46 minutes of reaction time.

![Graph showing mass fractions of surrogate fuel components](image1)

**Figure 3.1 – Evolution of surrogate components**

Fig 3.1 shows the mass fractions of the surrogate fuel components and oxygen throughout the simulation. Very little reaction can be seen on this plot – the mass fractions essentially “flatlined”.

![Graph showing evolution of sum of mass fractions](image2)

**Figure 3.2 - Evolution of the sum of mass fractions of fuel components**

Fig 3.2 shows the mass fraction of the fuel components summed together. It starts out at 99.97 wt% because there is a small amount of dissolved oxygen.
within the mixture. After 46 minutes the amount of fuel that has reacted reaches 0.08 wt%. This was the observed deposit formation amount in the flat plate experiments (Section 4.3), so was used as the criterion to terminate the simulation. In the experiments the fuel evaporated from the plate in the order of magnitude of an hour, so the agreement is considerably good.

Figure 3.3 - Carbon flux through the large reaction network

Scale = 9.8e-05

Figure 3.4 - Carbon flux through the small reaction network

Scale = 1e-05
Fig. 3.3 shows the carbon flux through the large (83 species, 2146 reactions) reaction network towards the end of the simulation. The size of the arrow represents the size of the flux. Only fluxes above a certain threshold are shown, which is why only the most reactive surrogate component appears: n-decylbenzene. A diagram with all 2146 reactions would be hard to read. Fig. 3.4 shows the carbon flux through the small (14 species, 13 reactions) reaction network towards the end of the simulation. By comparing Figures 3.3 and 3.4, one can see that the major pathways are captured by the smaller kinetic model. However, because the reactions on the major pathways are driven by the pool of radical species, every reaction that creates a radical, however slowly, will increase the rate of the major pathways. By missing many of these low-flux reactions, the smaller kinetic model predicts a lower overall rate.

Figure 3.5 shows that the small kinetic model takes 75 minutes to reach 0.08 wt% conversion whereas the large kinetic model (Figure 2.2) took 46 minutes. This is why it will be preferable to build a large model and reduce it rather than just build a small model. However, the small model has been used in the coupled chemistry/transport model with regard to calculation times.

3.5 Estimation of Physical Properties

While undergoing the chemical changes, diesel generates and passes through numerous distinct intermediate species. Therefore, in order to accurately couple the chemical kinetics to the physical transport, it would be necessary to determine physical properties of each of these intermediaries such as the liquid and vapor phase diffusivities and their vapor pressures as functions of temperature. Predictive methods
that allow for approximation of physical properties based on molecular structure will have to be used for some of these species since experimental measurements may not be available.

3.5.1 Vapor Pressure

Vapor pressure (equilibrium vapor pressure) is the pressure of a vapor in equilibrium with its non-vapor phases. All liquids and solids have a tendency to evaporate to a gaseous form, and all gases have a tendency to condense back into their original form (either liquid or solid). At any given temperature, for a particular substance, there is a pressure at which the gas of that substance is in dynamic equilibrium with its liquid or solid forms. This is the vapor pressure of that substance at that temperature. In the transport model, vapor pressure relations are used to determine gas/liquid phase interfacial concentrations using Raoult’s law, so a substance with a higher vapor pressure will evaporate more quickly. Prediction of vapor pressure as a function of temperature is a well studied problem leading to several correlations like the Antoine and Riedel equations. Most vapor pressure correlations require other information about a species (heat of vaporization, normal boiling point, critical properties etc.) besides its molecular structure. Prediction of vapor pressure using these correlations would require the prediction of these auxiliary properties first. In the interest of simplicity, the Antoine approach is assumed to be sufficient (see Section 2.5).

3.5.2 Diffusivity of Species in Liquid Phase

The transport model for the deposit formation process involves diffusive fluxes in the liquid phase. The liquid phase contains many species, each having a different diffusion coefficient with respect to every other species, apart from a self-diffusion coefficient. Modeling binary diffusivities between each pair of components would be a very complex task. To simplify things, the Stokes-Einstein (SE) equation to estimate the diffusivity of a single species in the liquid phase. The SE equation is:

\[ D_i = \frac{k_b T}{6\pi \eta r_i} \]
where,
- $D_i$ - diffusion co-efficient of species $i$
- $T$ - temperature
- $\eta$ - fluid viscosity
- $r_i$ - effective molecular radius of species $i$
- $k_b$ - Boltzmann constant

By using the SE equation an implicit assumption of pseudo-binary diffusion can be made. Species 'i' is assumed to diffuse in a mixture of all the other components. The effect of the presence of these other components can best be captured by determining the viscosity of the medium as a function of composition. Another assumption made is that of treating each species as a sphere of effective radius $r_i$, which is essentially an indicator of the size of the species in question. There are several ways in which one may estimate the size of a particular species. In this model, $r_i$ is approximated as the hard sphere Lennard-Jones parameter $\sigma$ using a correlation by Amotz and Herschbach:

$$\sigma = 1.244 \left( V_{hs} \right)^{1/3}$$

Where,

$$V_{hs} = 0.1973 \left( V_c - 44.28 \right)$$

in which $V_c$ is the critical volume of the species under consideration. All lengths in the above correlation are in the units of angstrom and volumes in (angstrom)$^3$. The critical volume, $V_c$, can be estimated using the JOBACK group contribution method which allows for the calculation of several species properties as a linear superposition of contributions made by individual molecular groups present in the species [19].

3.6 **Reduced Kinetic Model**

As the first stage of the combination of transport and chemistry, the smallest kinetic model consisting of 14 species and 13 reactions is used. This reduced model was derived from the more detailed chemical model using RMG as explained in Section 3.4. So as to simulate the deposit formation, an additional pseudo species, $C_{32}H_{52}O_4$ by name of 'deposit' is added to the set, and a pseudo reaction is appended to the reaction list to generate this species. The list of species is given in Table 3.2.
Table 3.2 – List of species in reduced kinetic model.
Compounds in italics are the surrogate components.
‘J’ denotes that the compound is an active radical species

It is to be noted that n-decylbenzene, being the most active component in the fuel surrogate, is the only compound that figures in this smallest chemical kinetic model.

The list of reactions in relation to this model is given below:

Disproportionation estimate
\[ \text{H}_2\text{O}_2 (J) + \text{C}_{16}\text{H}_{25} (J) \leftrightarrow \text{O}_2 + \text{C}_{16}\text{H}_{26} \]

Radical Addition for Multiple bond estimate
\[ \text{O}_2 + \text{C}_{16}\text{H}_{25} (J) \leftrightarrow \text{C}_{16}\text{H}_{25}\text{O}_2 (J) \]

Radical Recombination estimate
\[ \text{H}_2\text{O}_2 (J) + \text{C}_{16}\text{H}_{25} (J) \leftrightarrow \text{C}_{16}\text{H}_{26}\text{O}_2 \]

Disproportionation estimate
\[ \text{H}_2\text{O}_2 (J) + \text{C}_{16}\text{H}_{25} \leftrightarrow \text{O}_2 + \text{C}_{16}\text{H}_{26}\text{O}_2 \]

Hydrogen Abstraction estimate
\[ \text{C}_{16}\text{H}_{26} + \text{C}_{16}\text{H}_{25}\text{O}_2 (J) \leftrightarrow \text{C}_{16}\text{H}_{25} (J) + \text{C}_{16}\text{H}_{26}\text{O}_2 \]

Disproportionation estimate
\[ 2 \text{H}_2\text{O}_2 (J) \leftrightarrow \text{O}_2 + \text{H}_2\text{O}_2 \]

Hydrogen Abstraction estimate
\[ \text{C}_{16}\text{H}_{25} (J) + \text{H}_2\text{O}_2 \leftrightarrow \text{C}_{16}\text{H}_{26} + \text{H}_2\text{O}_2 (J) \]

Hydrogen Abstraction estimate
\[ \text{C}_{16}\text{H}_{25}\text{O}_2 (J) + \text{H}_2\text{O}_2 \leftrightarrow \text{H}_2\text{O}_2 (J) + \text{C}_{16}\text{H}_{26}\text{O}_2 \]

Disproportionation estimate
\[ \text{H}_2\text{O}_2 (J) + \text{C}_{16}\text{H}_{25} (J) \leftrightarrow \text{H}_2\text{O}_2 + \text{C}_{16}\text{H}_{24} \]

Disproportionation estimate
\[ 2 \text{C}_{16}\text{H}_{25} (J) \leftrightarrow \text{C}_{16}\text{H}_{26} + \text{C}_{16}\text{H}_{24} \]
Disproportionation estimate
\[ O_2 + C_{16}H_{25} \ (J) \iff H_2O_2 \ (J) + C_{16}H_{24} \]

Disproportionation estimate
\[ C_{16}H_{25} \ (J) + C_{16}H_{25}O_2 \ (J) \iff C_{16}H_{26}O_2 + C_{16}H_{24} \]

\[ H_2O_2 \ (J) \ \text{Elimination from Peroxy Radical estimate} \]
\[ C_{16}H_{25}O_2 \ (J) \Rightarrow H_2O_2 \ (J) + C_{16}H_{24} \]

Artificial Deposit Formation reaction
\[ 2C_{16}H_{26}O_2 \Rightarrow C_{32}H_{52}O_4 \ (Deposit) \]

3.7 **Collaborating Fuel Transport and Chemical Kinetics**

![Diagram of fuel transport and chemical processes](image)

Figure 3.6 – All processes within entrapped fuel

Fig 3.6 shows the complete scenario experienced by the fuel that is trapped within the nozzle. Since the chemical kinetics is complex, especially if the larger models are considered for the simulation, complete incorporation in terms of using rate equations for each of the reactions is extremely tedious and practically impossible. For this purpose, transport and chemistry are essentially decoupled and simulated one following the other. This is achieved by first carrying out calculation of removal of the fuel in the front-most layer (by the combination of evaporation as well as diffusion into the rest of the fuel) resulting in a particular \( \Delta t \). Secondly, chemical activity is simulated in each of the layers individually using the model prescribed above, for a time span of \( \Delta t \). During this action, there will be no inter-layer transport of fuel species, i.e. mass conservation can be employed in each layer individually. These two steps are repeated over and over, until all the fuel has disappeared. This strategy would prove to be comparatively accurate of the grid discretization is considerably fine, thus ensuring as small value of \( \Delta t \) for each iteration.
The above described methodology may be formulized as follows. The complete diffusion equation including chemical activity and deposit formation is:

\[
\rho_i^n - \rho_i^{n-1} = \Delta t \frac{D_i}{2} \left\{ \frac{\rho_{i+1}^n - 2\rho_i^n + \rho_{i-1}^n}{(\Delta x)^2} + \frac{\rho_{i+1}^{n-1} - 2\rho_i^{n-1} + \rho_{i-1}^{n-1}}{(\Delta x)^2} \right\} \\
+ \int_t^{t+\Delta t} \left\{ \left( \frac{\partial \rho_i}{\partial t} \right)_{\text{chem}} - \left( \frac{\partial \rho_i}{\partial t} \right)_{\text{deposit}} \right\} \, dt
\]

This step can be split up into two:

\[
\rho_i^* - \rho_i^{n-1} = \int_t^{t+\Delta t} \left\{ \left( \frac{\partial \rho_i}{\partial t} \right)_{\text{chem}} - \left( \frac{\partial \rho_i}{\partial t} \right)_{\text{deposit}} \right\} \, dt
\]

\[
\rho_i^n - \rho_i^* = \Delta t \frac{D_i}{2} \left\{ \frac{\rho_{i+1}^n - 2\rho_i^n + \rho_{i-1}^n}{(\Delta x)^2} + \frac{\rho_{i+1}^{n-1} - 2\rho_i^{n-1} + \rho_{i-1}^{n-1}}{(\Delta x)^2} \right\}
\]

Where,

- \( \rho \) – concentration of fuel species
- \( \Delta x \) – spatial discretization (= L/M units)
- \( \Delta t \) – time discretization step
- \( n \) – current time step
- \( n-1 \) – previous time step
- \( i \) – species number
- \( j \) – layer number

Fig 3.7 shows the profiles of oxygen that intrudes into the fuel. This calculation was done by adding oxygen as an extra species in the transport simulation model, assuming there is will be no chemical activity. The
assumption made is that oxygen content available at the mouth of the nozzle remains at the solubility limit in the fuel. The figure shows that oxygen molecules will reach the furthest layer from the mouth within the first solution step time, \( \Delta t \). Also, it may be noted that it will completely fill the fuel up to solubility limit with a few solution steps, although in a realistic environment, this oxygen will be used up for chemical activity.

3.8 Results

The combined process simulation was carried out at 130 °C assuming that the fuel is in thermal equilibrium with the nozzle walls. Starting with a 100 layer grid, the calculation was stopped at the point where 7 layers were left in the fuel column, so as to maintain numerical integrity of the Jacobian matrix during solution. The total time taken for the simulation up to the removal of all but seven layers of fuel is 51 minutes. Fig 3.8 shows the profile of deposit formed within the nozzle. Since the model was set up such that the deposit does not diffuse within the fuel or evaporate, whatever amount formed will remain at the same location. Therefore, the envelope of these profiles, which were generated by the combination of concentration profiles over each of the iterations, will represent the amount and even the shape of deposit settled on the nozzle walls. The total mass of deposit generated is 1.8827e-011 kg, which accounts for 0.0838 % of the total mass of initial fuel. This value is very close to the results obtained from the bench experiments conducted on diesel, which will be described in the following section.
4. EXPERIMENTAL WORK

Physically running an engine for a considerably long time in an effort to fathom the amount of deposit formed at the injector nozzle is an expensive and difficult process. Moreover, it is quite difficult to control the thermal environment in the nozzle at stable conditions. Therefore, a bench scale experiment was devised that would emulate the deposit formation under a more controllable atmosphere, and at a much accelerated rate. To serve this purpose, the thin film reactor is employed. The results of the experiments will prove to validate the numerical model of the process and also provide a bench mark on which the chemical kinetics can be based. Since the experiments are comparatively quick, it can be used to test different blends of diesel and the surrogate, with and without detergents. This will also help in selection of proper detergent selection since the results will be very evident and conclusive.

4.1 Apparatus

4.1.1 Thin Film Reactor

The thin film reactor is a cylindrical trough which can confine a thin layer of fuel the thickness of which can be obtained from the trough diameter and the amount of fuel metered using a micro-pipette.

![Thin Film Reactor Design](image)

Figure 4.1 – Thin Film Reactor Design
a) Cylindrical trough with vertical walls
b) Trough with groove defining liquid film

Fig 4.1 shows two designs of the reactor that were considered. Fig 4.1(a) shows the first design, which was unsuccessful because the meniscus took up a large bulk of the fuel, needing the fuel film to be unrealistically thick if a measurable and properly defined thickness is to be obtained. Therefore, so as to reduce the meniscus effect, a
grooved trough as seen in Fig 4.1(b) was used. In this case, the surface tension force would be exactly balanced by the normal reaction on the surface, leading to the generation of a well defined film of fuel.

The parameters regarding the reactor used for the experiment are:

Substrate: Aluminum (6061-T6)
Fuel film area: 4.05 cm² (2.27 cm diameter)
Fuel metered: 200 μL (162 mg)
Initial film thickness: 494 μm

Fig 4.2 shows the substrate used as the thin film reactor.

4.1.2 Heating Element

Fig 4.3 shows the instrument employed to maintain the substrate at the required constant temperature. The top plate has affixed screws that will bolster the substrate on the surface while the surface gets heated from a hot coil underneath. A feedback control system ensures proper maintenance of temperature. The experiments are carried out under controlled conditions such that there is no considerable air flow over the surface, which might affect the temperature.
4.1.3 *Micropipette*

Fig 4.4 shows the micro-pipette which is used to meter accurate volumes of fuel onto the substrate before each cycle. The instrument used has a capacity of 200μL.

4.1.4 *Weighing Balance*

Fig 4.5 shows the weighing balance that was used to measure the mass of deposit after each unit of fuel is administered. The resolution of the instrument is 0.1mg. Practically, using a balance with this resolution turned out to be insufficient. The error in the values reported is also within the range of the resolution. This hinders the maintenance of proper accuracy. However, for the time being, several measurements of the same subject are taken and a mathematical average is considered. Before moving into more rigorous experimental work, a device with a resolution of 0.01mg will be acquired.

4.2 *Procedures*

Three different procedures were made use of in the experiments, each of them simulating a different real physical scenario. In all of them, the fuel is metered in several units of 200μL each, one after the other. The mass of deposit formed is weighed after the concerned procedure is completed following each unit addition.
Dry Procedure – In the dry procedure, after adding each unit of fuel, the trough is allowed to stand for a long time, until all the fuel has been completely evaporated, before the ensuing unit is administered. This process will give a measure of the amount of deposit that can possibly be formed by that specific blend of fuel.

Dry Wash Procedure – In this method, the unit of fuel is allowed to completely evaporate, but before the addition of the next unit, the dried samples are rinsed with an organic solvent, n-hexane (boiling point – 69 °C). This process will examine whether the formed deposit is soluble in the organic solvent. It emulates the condition at which the engine is switched on after having been shut down for a considerable amount of time. In that situation, the ensuing injections of fuel in the nozzle will act as the solvent. After the rinse, the samples are air dried before being weighed.

Rinse Procedure – The rinse procedure is very similar to the wash procedure explained above, with the exception that the metered fuel is not allowed to dry up completely. The samples are washed with the solvent after a certain fixed time interval, irrespective of whether there is still liquid fuel left in the sample or not. This process will emulate the restarting of the engine a short time after it has been shut off, without allowing all the fuel in the injector nozzle to dry up, so that some of the precursors of the deposits will be washed away by the next fuel injection. Rinse procedures were carried out at 2 hour, 1 hour and 30 minute intervals between fuel unit administrations. After the rinse in the solvent, the samples are air dried and weighed following each unit addition.

4.3 Results

The experiments were conducted mostly for a temperature of 135 °C. This is in accordance with the fact that the highest injector tip temperature is generally around 200 °C. Tests were also conducted at this higher temperature, but it was observed that smoke appeared to emanate from the fuel film and the film dried up quickly, within an hour. At lower temperatures, around 100 °C, the film took over 10 hours to dry up
completely. Therefore, the primary choice is 135 °C at which the film evaporates completely within a more realistic time frame of 4 to 6 hours.

![Graph showing deposit accumulation history for diesel at 135 °C](image)

**Figure 4.6 – Deposit accumulation for dry procedure**

Fig 4.6 shows the deposit accumulation history for diesel at 135 °C for 11 unit additions of fuel (each unit 200 μL). The deposit was weighed multiple times at each data point due to limited resolution of the weighing balance (0.1 mg). The cumulative mass equivalent to eleven units of fuel is 1.815g. The final mass of deposit at the end of the experiment is 0.0016g. Therefore, the deposit formed accounts for 0.088% by mass of the fuel. This data was used as the criterion for the end point of simulation for the chemical kinetic model in Section 3.4.

Fig 4.7 shows the cumulative deposit accumulation data for all three different procedures at 135 °C. The dry procedure was also conducted at 200 °C. It can be noted that deposit formation profiles for the dry procedure at both temperatures are not materially different, although the film dried up in less than an hour at the higher temperature and took 4-6 hours for the lower one. This points out that the total deposit yield is independent of substrate temperature as well as the evaporation time. The data for the dry wash procedure seems to be higher than the dry procedure, but this can be
accounted to experimental error owing to limited resolution of weighing balance, since the dry procedure marks the upper limit of deposit accumulation. Nevertheless, this seems to indicate that the deposit formed is insoluble in the organic solvent n-hexane.

The accumulation patterns for the dry wash procedure and the 2-hour rinse procedure are very similar, their difference falling within experimental error limit. This indicates that most of the deposit was formed primarily within two hours of soak time. Substances left over after this time period was either evaporated, for the former, or washed away, for the latter, thus not affecting further deposition significantly. For rinse procedures with lesser time intervals, 1 hour and 30 minutes, deposit accumulation was considerably lower. This is expected as a substantial amount of deposit precursors are washed away before reaching the final compound. However, the data was insufficient to discern the
difference in deposit accumulation rates for these quicker rinse experiments, although it indicates critical deposit growth within the first two hours of hot soak.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Deposit Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry procedure</td>
<td>11 units added</td>
</tr>
<tr>
<td>Rinse procedure</td>
<td>2 hour soak &amp; rinse, 7 units added</td>
</tr>
<tr>
<td>Rinse procedure</td>
<td>1 hour rinse, 12 units added</td>
</tr>
</tbody>
</table>

Figure 4.8 – Appearance of deposits at the end of testing

Fig 4.8 shows the appearance of some of the substrates at the end of testing. The brown deposit from the dry procedure and 2-hour rinse procedures looked very similar. However, the 1-hour rinse substrate shows considerably lesser amount of deposit indicating that much of the potential deposit forming precursors were washed away during rinses.
5. CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The diesel engine has undergone numerous advances over the past few years. But there are still several areas of possible improvement to boost overall performance, the injector being one of them. Considering the competitive market, engineers would strive for betterment of all aspects of the engine, aiming at optimum working at all times. Designing an injector such that it does not foul up too fast is vital, since it impacts the driving comfort and fuel efficiency directly. This factor also opens up a new dimension to selection of fuel and detergent such that their chemistry is compatible with mitigation of deposits as well as economic and environmental aspects. As the size of the nozzle hole reduces further, the effect of fouling would be more amplified. Scrutinizing the trend of nozzle diameters over the past few years, it can only be expected to drop further in an effort to increase fuel spray consistency and thus obtain better mixing with the air in the combustion chamber.

At this juncture of the project, it is clearly evident that significant amount of deposit can be accumulated at the injector nozzle without having to transcend the boundaries of general automotive working conditions. From the data available, it can be discerned that, without the presence of detergents to suppress the deposit formation, it is practically unavoidable. Available literature suggested that maximum susceptibility to this issue if during short drives, such as a city drive that lasts for less than fifteen minutes, followed by hot soak in the sun for over an hour [20, 21]. The obtained results seem to point to the same fact as the experimental results clearly depict that most of the deposition process occurs within the first two hours after the engine is shut down.

In the absence of detergents in the fuel, results shows that a deposit magnitude to the tune of 0.08% by mass of fuel penetrating into the nozzle after shut down can be expected. The cumulative effect of this phenomenon is highly undesirable. Ideally, changes should be made with respect to the injector design as well as attuned
detergent chemistry to bring this down considerably. The future of this project will be aimed mainly at the latter.

5.2 Future Work

5.2.1 Temperature Variation

So as to capture the technicalities of the fuel within the nozzle, the combined transport and chemical kinetic model must be associated with a realistic temperature variation as experienced by a real injector in the engine, rather than the isothermal conditions that are used at the current stage. Since it might be difficult to accurately predict how the change will progress, it would be considerably easier to use experimental methods to calculate this. A properly controlled experiment with a generic diesel engine and a well calibrated thermocouple should provide reliable data. This would also depend on the size of the engine and the other parts of the automobile surrounding it as well as the atmospheric conditions of the location.

5.2.2 Physical Properties of Intermediaries

Starting at the surrogate diesel, the fuel will undergo several chemical changes, passing through several intermediate species before reaching the final set of products. Even with just seven starting compounds, there would be hundreds of intermediaries along the path to complete depletion. To properly map this effect, some of the physical properties of these components should be accurately predicted, such as density, vapor pressure and diffusivity, accounting for the variation in temperature as well. A model for this prediction is being worked on currently. It will comprise data for around one thousand intermediate species within a considerable temperature range. Incorporation of this into the numerical model will increase the accuracy of deposit prediction and therefore provide for a more realistic model of the actual injector working. It should be noted that physical compilation of data for each of these constituents is practically impossible. Therefore, some estimative methods are also employed.
5.2.3 Detergency

Detergents are additives introduced into the fuel which inhibits the process of deposit formation as well as remove settled deposits. Detergent chemistry is very closely dependent on the nature of the nozzle wall surface as well as the fuel blend. Therefore, there is no universal detergent that would work under all situations. The working hypothesis is that the detergent suspends some or most of the oxidized deposit precursors into a non-polar liquid phase without allowing it to continue on reacting to reach the final deposit. Ideally, this detergent-fuel concoctive compound will be able to endure the ensuing hot soak and be removed by the next injection of fuel. However, care must be taking for the analysis of oxidation of the detergent itself, since non-volatile oxidized detergent might contribute to the deposit. Also, oxidation of the detergent might also render it less effective at its intended utility.

Analysis and testing on detergent blends will be one of the prime focuses of this project in the near future. Achieving the proper combination of compounds to act as detergent for the fuel under consideration is the easiest path to reach the goal of reduction of deposit formation, or ideally, eradicate the issue completely.
References


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APPENDICES

A – **GT-FUEL**

GT-FUEL, from Gamma Technologies Inc ©, is a simulation tool for design and analysis of fuel injection and general hydraulic systems. It is based on one-dimensional, compressible, unsteady fluid dynamics and two-dimensional (translational and rotational) mass dynamics. This allows modeling of the flow and heat transfer in the piping and volumes, as well as mass dynamics and the combined interaction of the mechanical and hydraulic systems. It also features an object-based code design that provides a powerful model building facility. This tool was made use of to simulate the dynamics of the fuel in the injector close to the end of injection.

Two lumped parameter models were used in this calculation. The first one is that of the complete common rail engine and the second one is a more detailed design of the generic common rail injector. Simulations from these designs gave a clear idea of the behavior of the fuel within the flow path of the whole engine. GT-FUEL is capable of predicting parameters such as flow rates and flow velocities in passages, injection duration, injection rate with respect to crank angle/time, pressure wave dynamics, temperature and pressure of the fuel, among others. The results are quite reliable over a considerable range of operating conditions, since the whole program has been validated against experimental data.

The simulator was used to obtain the accurate mass flow rates and velocities of fuel within the passages. The predictions were quite consistent with theoretical values that had been previously formulated. The two lumped models used are shown in the following figures.
Model of Common Rail Diesel Engine
Model of Diesel Injector
B – Crank-Nicolson Method

The Crank-Nicolson scheme is a finite difference solution method used for partial differential equations. It is an implicit second order method in time and is unconditionally stable for diffusion equations. It was formulated by John Crank and Phyllis Nicolson. It is based on a central difference in space, and the trapezoidal rule in time, giving second-order convergence in time. In other words, it essentially is an average of the Forward Euler and the Backward Euler schemes in time.

Consider the simple linear diffusion equation,

\[
\frac{\partial u}{\partial t} = a \frac{\partial^2 u}{\partial x^2}
\]

The Crank-Nicolson discretization is:

\[
\frac{u_i^{n+1} - u_i^n}{\Delta t} = a \frac{1}{2} \left\{ \frac{u_{i+1}^{n+1} - 2u_i^{n+1} + u_{i-1}^{n+1}}{(\Delta x)^2} + \frac{u_{i+1}^n - 2u_i^n + u_{i-1}^n}{(\Delta x)^2} \right\}
\]

Where,
- \(\Delta x\) – space discretization
- \(\Delta t\) – time discretization
- \(n\) – represents time step
- \(i\) – represents space step

This scheme was employed in the discretization of the diffusion equations for the modeling of fuel transport (Section 2.6)
The Moody Chart is used to obtain friction factor \( f \) which is employed in the calculation of fuel left over the nozzle (Section 2.3)

**Moody Diagram**

Friction Factor vs. Reynolds Number

- **Laminar Flow**
- **Transition Region**
- **Complete Turbulence**

**Friction Factor**

\[
\text{Friction Factor } = \frac{2\Delta P}{\rho V^2} \frac{d}{L}
\]

**Material**

- Concrete, course: 0.25
- Concrete, new smooth: 0.025
- Drawn tubing: 0.0025
- Glass, plastic, Perspex: 0.0025
- Iron, cast: 0.15
- Sewers, old: 3.0
- Steel, mortar lined: 0.1
- Steel, rusted: 0.5
- Steel, structural or forged: 0.025
- Water mains, old: 1.0

**Relative Pipe Roughness**

- Smooth Pipe

**Reynolds Number**

\[
Re = \frac{\rho V d}{\mu}
\]
**D – Antoine Constants**

Antoine Constants are used for determination of the vapor pressure of the surrogate components at any specified temperature (Section 2.5)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
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<tr>
<td>n-undecane</td>
<td>C\textsubscript{11}H\textsubscript{24}</td>
<td>6.97220</td>
<td>1569.570</td>
<td>187.700</td>
</tr>
<tr>
<td>n-tridecane</td>
<td>C\textsubscript{13}H\textsubscript{28}</td>
<td>7.00756</td>
<td>1690.670</td>
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<td>1M-naphthalene</td>
<td>C\textsubscript{11}H\textsubscript{10}</td>
<td>7.03592</td>
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<td>195.002</td>
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<td>C\textsubscript{16}H\textsubscript{34}</td>
<td>7.02867</td>
<td>1830.510</td>
<td>154.450</td>
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<tr>
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<td>n-nonadecane</td>
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<td>137.600</td>
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<td>n-heneicosane</td>
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<td>7.08420</td>
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<td>120.100</td>
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