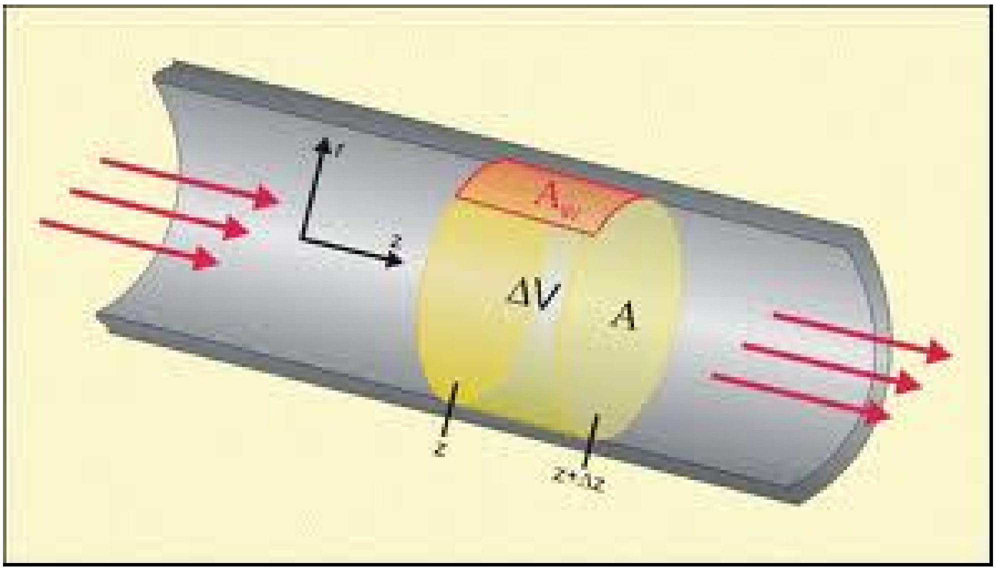

On Board Conversion of BioEthanol to Diethyl Ether

Master's Thesis in Innovative and Sustainable Chemical Engineering

TAPAS RAJKHOWA

Department of Chemical and Biological Engineering
Division of Chemical Reaction Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
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Cover:
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Chalmers Reproservice
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Abstract

The dehydration of Ethanol in the presence of a acidic catalyst in the right reaction condition can lead to the formation of Diethyl Ether (DEE). DEE can be a suitable substitute for diesel which can greatly prevent global warming. In this regard an on board reactor for the conversion of bio-ethanol to DEE is of great interest. In this study an effort has been made to develop a model to predict the performance of such an on board reactor and investigate the transient response of the same. In addition to this, literature reviews on the need and uses of such a reactor were also carried out.

A simple first order kinetics was used for the purpose of developing a model for predicting the performance of a packed bed reactor, which can be represented mathematically using a tank in seires model for the reactors. Sensitivity analysis of the reactor to various parameters were carried out with the model established.

First order kinetics for the liquid phase reaction shows a sensitivity to heat losses with very good response to transient flows. The transient behaviour of the reactor was investigated using an on/off cycle as well as a World Harmonized Stationary Cycle (WHSC). Simulations also show very good performance with water as well as gasoline like additives in the feed.

Keywords: Bioethanol, Reactor Design, Simulation, Diethyl ether

Contents

Preface

In this study the design and simulation of a small scale reactor for onboard conversion of bioethanol to diethyl ether was carried out. Both steady as well as unsteady state simulation was carried out using the reactor model herein derived. The work has been carried out from January 2011 to June 2011 at the Department of Chemical and Biological Engineering, Division of Chemical Reaction Engineering, Chalmers University of Technology, Sweden, with Tapas Rajkhowa as student and Professor Derek Creaser as supervisor.

Aknowledgements

I would like offer my sincere thanks to my supervisor, Derek Creaser at Chemical and Biological Engineering, for his relentless support and guidance towards the project. In addition to this I would like to thank Haldor Topsoe, especially Christophe Duwig and Par Gabrielsson, for the opportunity to work in such a challenging project and their continued assistance. A special thanks to my colleagues and teachers in the department for their constructive criticism and support.

Göteborg June 2011
Tapas Rajkhowa

1 Introduction

1.1 Background

Rapid urbanization and population growth has increased the consumption of fossil based fuels many folds since the onset of the industrial revolution. Since, the invention of the ignition engines, the importance of fossil fuels, especially petroleum fuels have increased drastically. The emissions of Green House Gases (GHG) from these fossil based fuels have influenced the climate change crisis not to mention the particulate matter and the NOx. In addition to that the fossil fuel reserves have been depleted significantly over the past decade. The search for alternate sources of energy is thus of prime importance towards sustainable development, environmental protection and preservation of human society and the eco system[1].

In this regard bio-based fuel provides a promising prospect at least in the near future, keeping in mind the fact that bio-based fuels like ethanol, bio-diesel, etc can be used in current motor vehicles with little or no modification. In addition to this, due to similarities in the properties of these fuels compared to current fuels namely Gasoline, Diesel, etc, the current established network and infrastructure can be used as well.

Ethanol in its pure form or in blends, with certain limitations, can be directly used in current vehicular engines. However, due to the physio-chemical properties of ethanol, the use of ethanol is limited only in the form is blends in internal combustion engine. For instance, in case of Compression Injection (or diesel) engines, the performance of ethanol is not good in lieu of its lower cetane number and in spark ignition engines due to higher flash temperature, start up problems occur at ambient temperatures below - 5 ^oC. These facts have stimulated the discussion on the use of diethyl ether (DEE) as fuel and/or additives to fuels in the engines.

DEE is a synthetic fuel with good ignition properties, low emissions and low soot formation. The advantages in using DEE as a fuel can be summarized as follows:

- Due to the higher volatility of DEE and lower flash temperature, start-up problems can be significantly reduced
- Due to higher Cetane number and low flash temperature, increases the efficiency of a Compression Ignition (or diesel) Engines. Note that cetane is a measure of the quality of a diesel engine fuel.

The question next then is why is it interesting to perform the conversion of Ethanol to Diethyl ether on board a vehicle rather than producing it in a large scale plant. In this regard, it has to be said that diethyl ether as does a lot of other ethers undergoes autooxidation in the presence of air or atmospheric oxygen to produce explosive organic peroxides. Studies[4] have shown ether especially DEE can decompose significantly to produce its corresponding peroxides at different atmospheric conditions. Such autoxidation reactions are both dangerous and harmful. This is why the on board conversion or production is important for the use of DEE as a vehicular fuel.

1.2 Purpose

The purpose of the current study is to develop a model for predicting the performance of a reactor for the conversion of ethanol to diethyl ether on board a motor vehicle. While the classical chemical engineering reactors are designed to be operated at steady state, a on board reactor will most usually be running in a transient state, do to the changing fuel flowrates in a car.

The focus herein in this study is to develop a simple reactor model and perform simulation using the same. At this point it has to be mentioned that the motivation here is not to develop a kinetic model which gives a quantitative representation of the reactor but rather a qualitative model which simply predicts the general trends that might be a representation of what might happen in a on board reactor. This initial trend study can then be used as a driving force for fueling future detailed studies.

The following qualitative analyses were performed:

- How sensitive is the conversion of the reactor to the heat loss from the reactor?
- How sensitive is the performance of the reactor to the dilution of ethanol?
- How sensitive is the performance of the reactor to contamination with a inert such as n-Octane?
- How does the reactor behave during the on-off cycle in a motor vehicle?
- How does the reactor the performance during a actual fuel (or driving) cycle for a diesel engine?

1.3 Limitations

As mentioned in the previous section, the purpose of the study is not to develop a quantitative model but rather a qualitative indication of the trends that might occur in the on board reactor. It is also worth mentioning here that pressure drop across the reactor is neglected for this study. Although the density of a liquid is a very weak function of pressure, the heat capacities can vary appreciably with pressure. Hence the model might deviate a lot if there is large pressure drop across. One of the other simplification in the model was to assume that the diethyl ether (liquid) would behave the same below or above the critical point. The model can be totally divergent from reality if the supercritical DEE is in the gas phase.

1.4 Approach

The approach adopted for the simulation of the reactor was as follows :

- To develop a model based on some basic assumptions for the reactor operation.
- Parameter fixation for replicating the behaviour of a pilot reactor.
- Simulate the reactor with different feed conditions and analyze the steady and unsteady response.

2 Theory

The reaction reaction is predominantly a liquid phase reaction at the reaction conditions of the study. The rates of liquid phase reactions are very slow. Hence it is reasonable to assume that the mass transfer limitations can be neglected and that the reaction is the rate limiting step. Other assumptions adopted for this study are:

- The physics of the reactor can be representated by a plug flow reactor (precisely tanks in series). Although tanks in series is not an exact representation of plug flow, it approaches a plug flow reactor as the number of tanks increases.

- Pressure drop in the reactor is neglected for the purpose of this study
- Volumetric flowrate in the reactor does not change along the reactor.
- The density of the liquid mixture is predominantly constant.

2.1 Reaction Kinetics

Studies have shown that the dehydration of ethanol happens in the presence of acidic catalysts [1, 2, 7]. Essentially, dehydration process can lead to predominantly two reactions, firstly direct dissociation of ethanol to form ethylene and water and secondly two molecules of ethanol loose a molecule of water to form diethyl ether as represented by equation (2.1) and (2.2) respectively. Having said this, it should be kept in mind that the extent to which the two equations and any other side reactions occur solely depends on the characteristics of the catalyst with some influence of the reaction conditions.

$$C_2H_5OH \xrightarrow[\text{Catalyst}]{Acidic} C_2H_4 + H_2O \tag{2.1}$$

$$2C_2H_5OH \xrightarrow[\text{Catalyst}]{Acidic} C_2H_5OC_2H_5 + H_2O \tag{2.2}$$

Although the rate equation can take up any form depending on the characteristics of the catalyst, a simple first order rate with respect to ethanol concentration was adopted in this study. This is because of the lack of enough experimental data available for the reaction to to determine the appropriate the kinetic expression for the reaction (2.2). To provide a qualitative analysis of the dehydration process and its sensitivity to different parametric changes, a first order rate expression was comnsidered adequate.The rate of production of DEE is as per the equation (2.3).

$$r_{DEE} = k_1 C_{EtOH} \left(1 - \frac{C_{DEE} C_{water}}{K_{eq} C_{EtOH}^2}\right) \tag{2.3}$$

Table 2.1: Explanation of variables for rate equation

r_{EtOH},r_{DEE},r_{water}	Rate of production, $\frac{mol}{(kg)(s)}$
k_1	Rate Constant, $\frac{m^3}{(kg)(s)}$
R	Universal Gas Constant,$\frac{J}{(mol)(K)}$
T	Temperature, K
C_{EtOH},C_{DEE},C_{water}	Effective Concentration, $C_i * \gamma_i$, $\frac{mol}{m^3}$

The rate constant for the reaction k_1 is often expressed with the help of the Arrhenius equation in the form:

$$k_1 = Aexp\left(-\frac{E_a}{RT}\right) \tag{2.4}$$

where E_a is the activation energy of the reaction, A is the pre-exponential term and R is the universal gas constant. Thus, the rate constants are strictly a function of Temperature.

From stoichiometry of the reaction (2.2) it can be established that the rate production/consumption of the other compounds involved in the reaction would then be related by (2.5).

$$\frac{r_{DEE}}{1} = \frac{r_{EtOH}}{-2} = \frac{r_{water}}{1} \tag{2.5}$$

The equilibrium constant for the reaction is given by:

$$lnK_{eq} = \frac{-\Delta G^o_{rxn}}{RT} \tag{2.6}$$

$$\text{Also by definition, } \Delta G^o_{rxn} = -\sum_i \nu_i G^o_i \tag{2.7}$$

Since G_o is a property of pure species i in its standard state at fixed pressure, it depends only on temperature. From equation (2.7) it follows that ΔG^o and hence K, is also a function of temperature only [6]. Combining the heat of reaction and the standard Gibbs Free Energy of reaction expressions gives an expression of the form as in equation (2.8).

$$K_{eq} = exp\left(5.9307ln\left(T\right) + \frac{1929.705}{T} - 34.0167 + 3.751T - 1.1463 * 10^{-5}T^2 + 1.3702 * 10^{-8}T^3\right) \tag{2.8}$$

Table 2.2: Explanation of variables for Equilibrium Constant

K	Equilibrium Constant
G^o_{rxn}	Standard Gibbs Free Energy, $\frac{mol}{m^3}$
R	Universal Gas Constant
T	Temperature, K

2.2 Reactor Model

One dimensional tanks in series as represented by figure 2.1 was selected for the purpose of reactor simulation [3]. The concentration of i^{th} component at the feed is C_{i0} with a volumetric flowrate of q and the concentration of the i^{th} component at the end of the reactor is C_i. The volumetric flowrate through the reactor is assumed to be constant. Now, if a differential section δx of the reactor at a distance x from the inlet of the reactor is considered, the concentration of i in at x is $C_i|_x$ and the concentration of i at x+dx is $C_i|_{x+dx}$. The Mole balance for the differential section is given by equation (2.9):

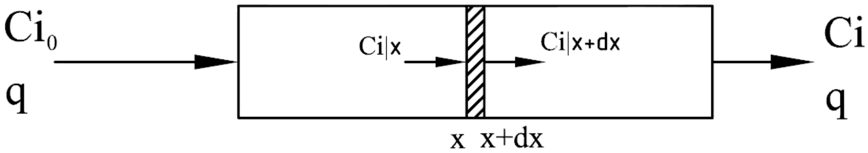

Figure 2.1: Plug Flow Reactor: Tank in Series

$$\text{Moles in - Moles out+Generation =Accummulation}$$

$$qC_i|_x - qC_i|_{x+dx} + r_i dW = \epsilon \delta V \frac{dC_i}{dt} \tag{2.9}$$

Table 2.3: Explanation of variables for Mole balance Equation

q	Volumetric flowrate of feed,$\frac{m^3}{s}$
$C_i\|_x$	Concentration of i at x, $\frac{mol}{m^3}$
dW	Weight of the differential section dx, kg
r_i	Rate of production of i, $\frac{mol}{kgs}$
ϵ	Void Fraction
δV	Differential Volume, m^3

2.3 Energy Balance

Consider the figure 2.1, the heat input to the reactor comes in the form of enthalpy of the reactants or feed to the reactor, heat generated by the reaction and the heat provided to the reactor from a heat source. Similarly, heat is consumed in the form of ethalpy taken away by the product from the reactor.

Energy in - Energy out+Generation+Heat Source =Accummulation

$$(FC_pT)\,|_x - (FC_pT)\,|_{x+dx} + r_i\Delta H_r dW + Q = (\tau FC_p + C_{pcat}\delta W)\,\frac{dT}{dt} \tag{2.10}$$

Table 2.4: Explanation of variables for Energy balance Equation

F	Molar flowrate of the liquid phase ,$\frac{mol}{s}$
C_p	Molar Heat capacity of the Fluid,$\frac{J}{molK}$
dW	Weight of the differential section dx, kg
r_i	Rate of production of i, $\frac{mol}{kgs}$
ΔH_r	Heat of Reaction, $\frac{J}{mol}$
Q	Heat Source term, $\frac{J}{s}$
τ	Residence Time, s
C_{pcat}	Heat capacity of Catalysts, $\frac{J}{KgK}$
δW	Weight of the differential section, kg

The Heat of reaction for the reaction was calculated using the equation:

$$\Delta H_r = \sum \nu_i \Delta H^o_{fi} + \sum \nu_i \int_{T_r}^{T} C_{pi} dT \tag{2.11}$$

Table 2.5: Explanation of variables for Heat of Reaction

ν_i	Stoichiometric coefficient
ΔH^o_{fi}	Standard Heat of formationof i, $\frac{J}{mol}$
C_{pi}	Heat capacity of i , $\frac{J}{molK}$
T_r	Reference Temperature, K

The heat of formation used in this study were as given in the table below:
The heat source term Q in equation (2.10) takes the form (2.12).

$$Q = q\delta A h_c\,(T - T_a) \tag{2.12}$$

The temperature at the outlet is controlled by varying the heat transfer coefficient.

Table 2.6: Tabulation of Heat of formation and Gibbs free energy

S.No	**Compound**	ΔH_f**x10^5, J/mol**	ΔG^o**x10^5**	T_c**, K**	P_c**, bar**
1	Ethanol(l)	-2.78	-1.75	516.1	63.1
2	Ethene(g)	0.523	0.682	282.7	50.5
3	DEE(l)	-2.73	-1.16	467.6	35.5
4	Ethanol(l)	-2.86	-2.37	647.15	218.4

Table 2.7: Explanation of variables for Heat Source Term

q	Volumetric flowrate of feed,$\frac{m^3}{s}$
δA	Differential heat transfer area, m^2
h_c	Heat transfer coefficient, $\frac{J}{m^2K}$
T	Temperature in the differential section of the reactor, K
T_a	Ambient Temperature, K

2.4 Activity Model

In an ideal solution, activity coefficients is equal to unity. However in real solutions, there ought to be deviations. These deviations can be quantified with the help of a parameter, γ_i, called the activity coefficient and/or ϕ_i, fugacity. In this study, γ_i is used as the indicator [5].

Although there are a number of two-three parameter models for solving for γ_i, UNIQUAC was used for this study because of the following advantages [5]:

- 2 adjustable parameters (rather than 3).
- UNIQUAC's parameters often have a smaller dependence on temperature.
- Because primary concentration variable is a surface fraction (rather than mole fraction), UNIQUAC is applicable to solutions containing smaller as well as large molecules, including polymers.

For correlating thermodynamic properties, it is often convenient to regard a molecule as an aggregate of functional groups; as a result properties like heat capacity etc. are calculated by summing up group contributions. An extension of this concept for an estimation of heat of mixing and for activity coefficient is called UNIFAC. The basic idea is to assume that a physical property of a fluid is the sum of contributions made by the molecule's functional groups. Like any group contribution method, UNIFAC is also an approximation because the contribution of one group in a molecule is not necessarily the same in another molecule.

The molecular activity coefficient is divided into two parts: part one takes into account the differences due to molecular sizes and shape and the other provides the contribution due to molecular interactions.

UNIQUAC often gives good representation of vapour-liquid and liquid-liquid equilibrium for binary and multicomponent mixtures containing a variety of nonelectrolytes such as hydrocarbons, ketones, esters, water, amines, alcohols, nitriles, etc. In a multicomponent mixture, the UNIQUAC equation for the activity of component i is UNIQUAC in combination with UNIFAC for residual contribution

$$ln\gamma_i = ln\gamma_i^c + ln\gamma_i^r \tag{2.13}$$

$$\text{combinatorial part} = ln\gamma_i^c = ln\frac{\phi_i}{x_i} + \frac{z}{2}q_i ln\frac{\theta i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_j \frac{x_j}{l_j} \tag{2.14}$$

$$\text{Residual Part} = ln\gamma_i^r = q_i\left[1 - ln\left(\sum_j \theta_j \tau_{ji}\right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}}\right] \tag{2.15}$$

$$l_i = \frac{z}{2}\left(r_i - q_i\right) - \left(r_i - 1\right), z = 0 \tag{2.16}$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}, \phi_i = \frac{r_i x_i}{\sum_j r_j x_j}, \tau_{ji} = exp\left(-\frac{u_{ji} - u_{ii}}{RT}\right)$$

Table 2.8: Explanation of variables for UNIQUAC and UNIFAC Equations

x_i	mole fraction of i
θ_i	Area Function of i
ϕ_i	Segment fraction of i
r_i	Molecular van der waals volumes of i
q_i	Molecular Surface Areas of i
Γ_k	Residual activity of group of k

In the UNIQUAC, the two adjustable binary parameters τ_{ij} and τ_{ji} appearing equation (2.15) must be evaluated from experimental phase equilibrium data. No ternary (or higher) parameters are required for systems containing three or more components.

In UNIFAC method, the combinatorial part of the UNIQUAC activity coefficients (2.14) is used directly. Only pure component properties enter into this equation. Parameters r_i and q_i are calculated as the sum of group volume and area parameters R_k and Q_k given in table 2.10:

$$r_i = \sum_k \nu_k^{(i)} R_k \text{ and } q_i = \sum_k \nu_k^{(i)} Q_k \tag{2.17}$$

The residual part of the activity coefficient in equation (2.15) is replaced by the solution-of-group concepts. Instead (2.15), we can write

$$ln\gamma_i^r = \sum_{\substack{k \\ allgroups}} \nu^{(i)}\left(ln\Gamma_k - ln\Gamma_k^{(i)}\right) \tag{2.18}$$

Table 2.9: Explanation of variables for Equation (2.18)

Γ_k	Residual activity of group
$\Gamma_k^{(i)}$	Residual activity of group k in a ref solution containing only molecules of type i
$\nu_k^{(i)}$	Number of group k in molecule i

In equation (2.18) $\Gamma_k^{(i)}$ is necessary to attain the normalization that activity coefficient γ_i becomes unity as $x_i \to 1$. The activity coefficient for group k in molecule i depends on the molecule i in which k is situated. The group activity coefficient Γ_k is found from an expression similar to equation (2.15):

$$ln\Gamma_k = Q_k\left[1 - ln\left(\sum_m \theta_m \Psi_{mk}\right) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}}\right] \tag{2.19}$$

Equation (2.19) also holds for $ln\Gamma_k^{(i)}$. In eq (2.19), θ_m is the area fraction of group m, and the sums are over all different groups. θ_m is calculated as:

$$\theta_i = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{2.20}$$

where X_m is the mole fraction of group m in the mixture. The group interaction parameter Ψ_{mn} is given by:

$$\Psi = exp\left(\frac{-u_{mn} - u_{nn}}{RT}\right) = exp\left(\frac{-a_{mn}}{T}\right) \tag{2.21}$$

where U_{mn} is a measure of the energy of interaction between groups m and n. Note $a_{mn} \neq a_{nm}$. Parameter a_{mn} and a_{nm} are obtained from a database using a wide range of experimental results. Some of the values used in this study are tabulated in table 2.11 and taken from literature [5].

Table 2.10: Group contribution parameters used for the simulation

Molecule	**Name**	**Main No**	**Secondary No**	ν_j	R_j	Q_j
Ethanol	CH_3	1	1	1	0.9011	0.848
	CH_2	1	2	1	0.6744	0.54
	OH	5	14	1	1	1.2
Water	H_2O	7	16	1	0.92	1.4
DEE	CH_3	1	1	2	0.9011	0.848
	CH_2	1	2	1	0.6744	0.54
	CH_2O	13	25	1	0.9183	0.78
n-Octane	CH_3	1	1	2	0.9011	0.848
	CH_2	1	2	6	0.6744	0.54

Table 2.11: Group contribution parameters used for the simulation

Main Group	$n = 1$	**5**	**7**	**13**
m=1	0	986.5	1318	251.5
5	156.4	0	353.5	28.06
7	300	-229.1	0	540.5
13	83.36	237.7	-314.7	0

2.5 Heat Capacities

Heat capacity of a liquid is an important property in chemical process design. In liquid phase chemical reactions, liquid heat capacities are required to determine the energy necessary to bring the reactants up to reaction temperature. Although numerous correlations and forms of the heat capacities are available in literature, the series expansion as a function of temperature in [8, 56-58] was selected for this study for simplicity in computational manupulation and better fit to the actual heat capacity. The series expansion is of the form equation (2.22):

$$C_p = A + BT + CT^2 + DT^3 \tag{2.22}$$

Table 2.12: Explanation of variables in Heat Capacity Expansion

C_p	heat capacity of liquid, $\frac{J}{(molK)}$
A,B,C and D	regression coefficients for chemical compounds
T	Temperature, K

The regression coefficients for the four compunds in use in this study namely, Ethanol, Water, Diethyl and n-Octane are tabulated in table 2.13.

Table 2.13: Regression Coefficient of compounds in use

Compound	**A**	**B**	**Cx10^3**	**Dx10^6**
Ethanol	59.342	0.364	-1.216	1.803
Water	92.053	-0.0399	-0.211	0.5347
Diethyl Ether	75.939	0.773	-2.794	4.438
n-Octane	82.736	1.304	-3.825	4.646

3 Methodology

The theory behind the simulation is mentioned in section 2. The method adopted herein is to create logorithmically spaced tanks in series and solve the unsteady state equations mentioned in section 2 for the tanks in series in a coupled manner using the ode solver package 'odeint' in Scipy package in Python. The differential length of each tank is shown in figure 3.1.

The reason for the logorithmically spaced tanks is because of the fact that at the beginning of the reactor, the rate of reaction will be higher. So, to have a better resolution of the reaction, smaller tank sizes are needed at the beginning of the reactor.

The model kinectic parameters were adjusted such that at the conditions tabulated in table 3.1, the conversion of ethanol (in the feed) in the reactor is 75%.

Table 3.1: Feed Condition for the Base case

Parameter	**Value**
Pressure	45 bar
Temperature	210 ^oC
Mass Flowrate	14 kg
Composition	100% Ethanol

This is considered to be the base case for the model where a 5^oC loss in temperature was allowed.

The accuracy of the results also depend on the number of tanks in series that is used to resolve the reactor and solve the differential equation. The higher the number of tanks

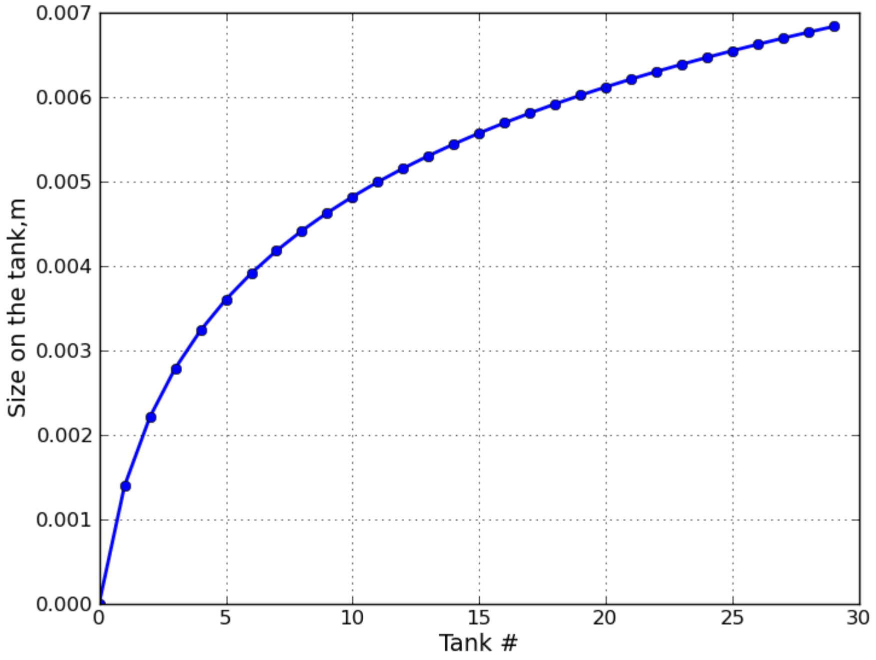

Figure 3.1: Differential Length of the Tanks

in series the more it replicates a plug flow reactor and the better is the results from the simulation. However, for the efficient use of computational capacity, a optimal number has to be selected.Figure 3.2 shows concentration profile of DEE along the reactor for various computaional grid sizes. Since there is not much difference between 30 tanks and 40 tanks, 30 tanks in series will be considered for the remaining simulations.

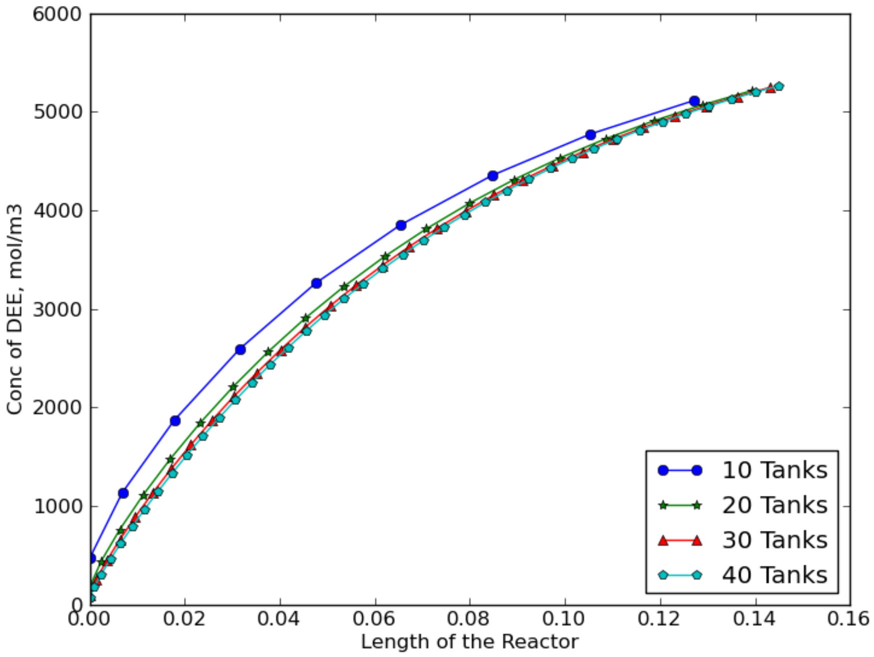

Figure 3.2: Concentration profile with number of tanks in series

The steady state results from the simulations of the base case are shown in figure 3.3 and 3.4.

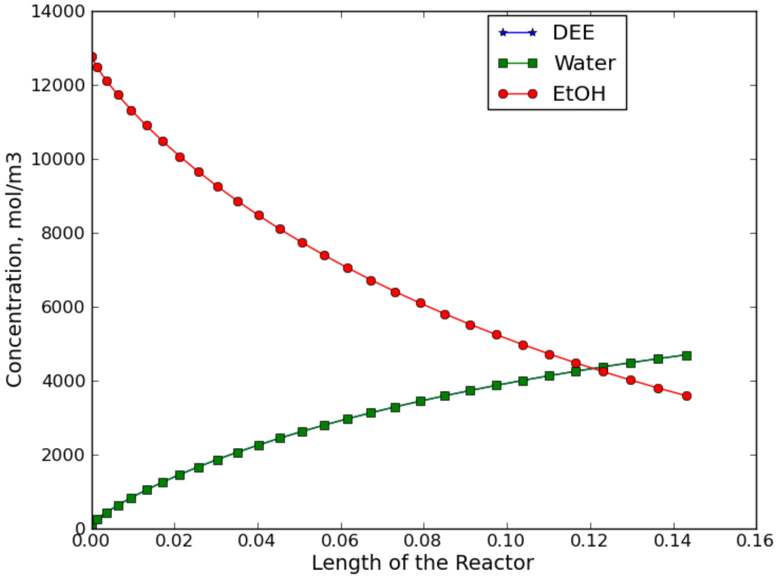

Figure 3.3: Concentration profiles along the reactor for the Base case

In figure 3.3 it is seen that the concentration of the ethanol decreases along the reactor and the concentrations of DEE and water increases. The shape of the curve also indicates that the reaction is not near equilibrium. Looking at the Temperature profile along the reactor in figure 3.4 it is seen that the temperature decreases upto 8 cm from the inlet and then starts to increase. The temperature profile for the reactor was obtained using the basic equation (2.10) with the other related equations linked to it. The activation energy E_a in equation (2.4) was taken as $51.7\frac{kJ}{mol}$. All the other parameters namely heat capacity, heat of reaction etc are obtained from the correlations mentioned in section 2 except for the pre-exponential term A in (2.4) and heat transfer coefficient h_c in equation (2.12). Thus, only two parameters were adjusted to achieve the desired conversion of the feed ethanol in the reactor.

The heat of reaction in the model is positive i.e. the reaction is endothermic, so heat has to be provided to keep the temperature upto 205^oC which is the temperature of the product from the pilot plant. Initially as concentration of ethanol is higher at the inlet of the reactor, the reaction rates are higher. Thus a net effect is consumption of heat. But gradually as the rate of reaction decreases at the end of the reactor, the temperature of the fluid/reactor increases.

Figure 3.5 shows the activity coefficients along the reactor for ethanol, diethyl ether and water for the steady state in the base case. It is seen from the figure that the activity coefficient of ethanol is approximately one and hence the effective concentration is the same as the concentration. However, for diethyl ether and water, the activity coefficients are significantly greater than one rendering the effective/apparent concentration to be more than the actual concentration.

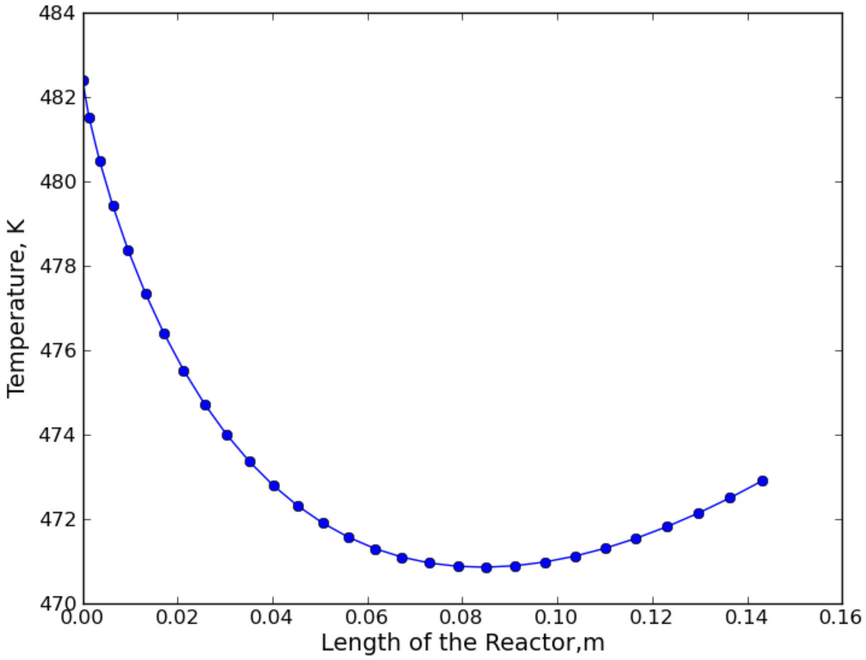

Figure 3.4: Temperature along the reactor for the Base case

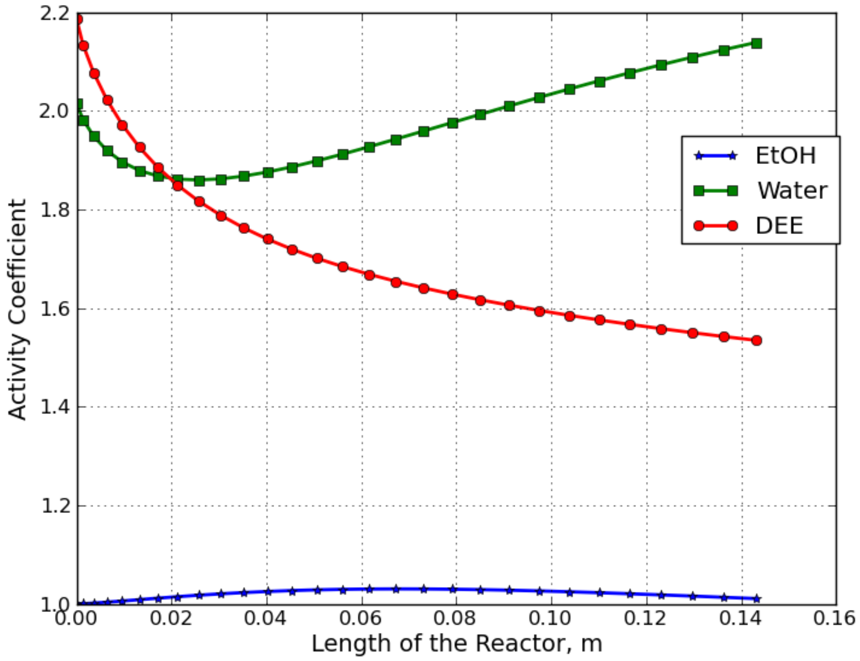

Figure 3.5: Activity coefficient along the reactor for the Base case

4 Simulations and Results

With the model setup in accordance with the steps in section 3, sensitivity of the reactor to different parameters were tested.

4.1 Sensitivity to Heat Loss

Insulation can be bulky and expensive and would add to the size of the reactor. This is very important for an on board reactor where reducing weight and space can have a huge impact on the overall efficiency of the vehicle. In this regard, it is of interest to investigate the effect of heat losses or decrease in temperature of the reactor. The reaction is endothermic according to thermodynamics in the operating temperature of the reactor. The simulations were conducted for three different cases where heat is supplied such that a temperature decrease of 5, 10, 15 ^oC was allowed.

The temperature at the outlet is controlled by varying the heat transfer coefficient in equation (2.12). In this case any temperature gradient in the radial direction and the inside and outside of the reactor is neglected. The results of the simulations are reflected through figure 4.1, where x-axis represents the temperature decrease in K and y-axis represents the percentage conversion of the feed ethanol in the reactor. It is seen that the conversion decreases as the temperature is allowed to fall. The decrease in the conversion can be attributed to the decrease in reaction rate as the temperature of the reactor is allowed to fall, as evident from (2.4).

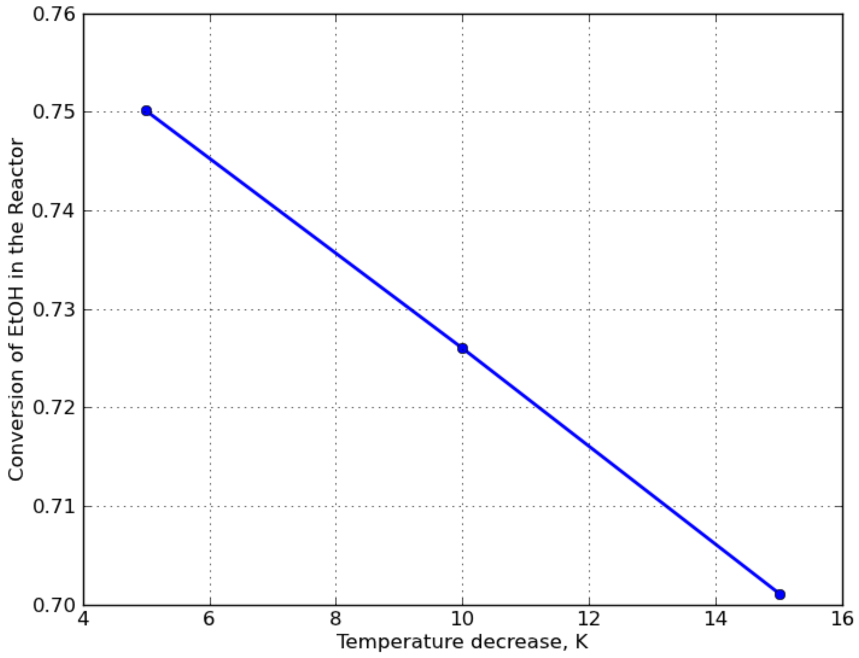

Figure 4.1: Sensitivity to heat Losses

4.2 Dilution of Ethanol with Water

The reactor is designed to fuel a 105 kW engine, so the flowrate of the feed along with all the other parameters are set so that a power output of 105 kW is achieved in the base case mentioned is section 3. Thus, when the concentration of water in the feed is increased, the flowrate of the feed has to be increased to ensure a constant power output of the engine. Table 4.1 shows the five simulation cases and their corresponding feed flowrates.

Table 4.1: Variation in Mass Flowrate with % water in Feed

S.No	**% Water**	**MF,kg/hr**
1	0	14
2	1	14.14
3	5	14.74
4	10	15.56
5	15	16.475

Figure 4.2 shows the concentration profiles of ethanol and diethyl ether along the reactor. The concentration of ethanol decreases with the increase in percentage of water and also along the reactor. The concentration of DEE increases as the feed passes through the reactor.

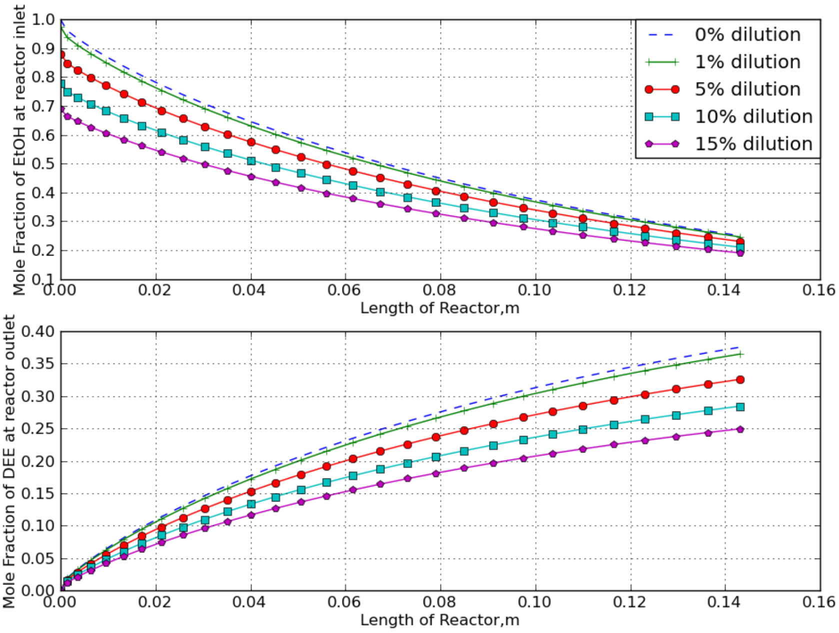

Figure 4.2: Concentration profile for the cases in table 4.1

The conversion of the feed ethanol in the reactor decreases as the concentration of water is increased in the feed. This is mostly because the increase in the flowrate of the feed reduces the residence time of the fluid in the reactor thus giving it less time to reactor. This is represented in figure 4.3. The reaction in the reactor is far from equilibrium with a very high equilibrium constant, K_{eq} of the order of 250 at the operating temperature. This is the reason for a very minute change in the conversion as the percentage water in the feed is increased from 0 to 15%. If however, the $K_{eq} \sim 20$, which is the value suggested for the gas phase reaction, the conversion would more drastically change with water percentage in the feed.

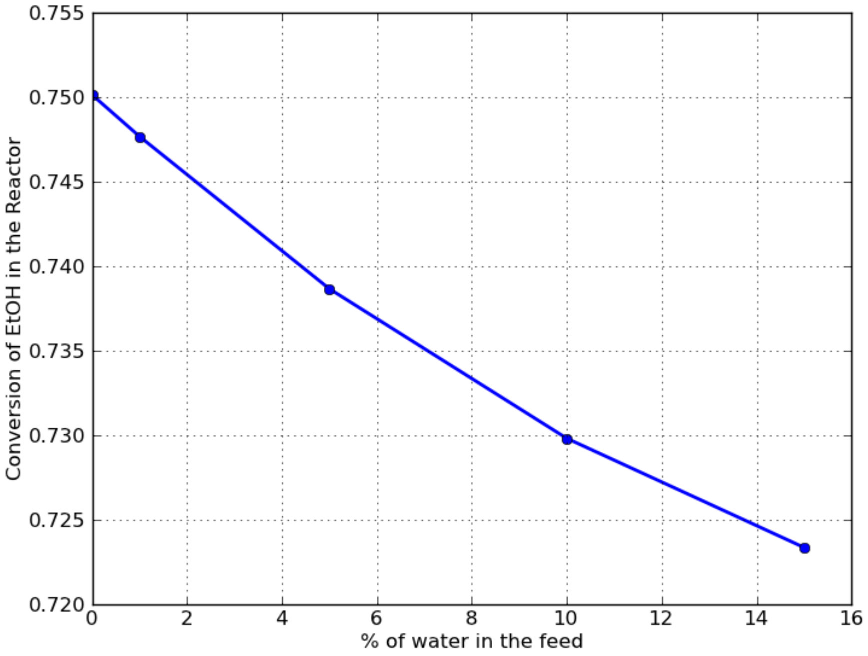

Figure 4.3: Sensitivity to % water in Feed

4.3 Dilution with C8

Commercially, ethanol for motor vehicle fuel is available in blends as E85 or similar variants. It is henceforth essential to test the performance of the reactor with varying amounts of Gasoline or similar compounds in the feed to check its compatibility with the more commercially available ethanol blends. Gasoline is predominantly octance or more so its isomers, so it is safe to use n-Octane in the simulation as a representative of Gasoline. One assumption in this study is to consider n-Octane inert i.e. it does not take part in any reaction in this particular case.

The Lower Heating value of Octane is almost twice that of DEE. Thus, when the concentration of octane in the feed is increased, the flowrate of the feed has to be decreased to ensure a constant power output of 105 kW from the engine. Table 4.2 shows the four simulation cases and the corresponding feed flowrates.

Table 4.2: Variation in Mass Flowrate % n-Octane in Feed

S.No	**% n-Octane**	**MF,kg/hr**
1	0	14
2	10	13.16
3	15	12.77
4	25	12.06

Figure 4.4 shows the effect of conversion of the feed ethanol in the reactor with the percentage n-Octane in the feed. It is seen from the graph that the conversion actually increases with the increase in the percentage of octane in the feed. This is beacause of the fact that with the increase in octane percentage the feed flowrate has to be decreased (to obtain a constant power output). This in turn increases the residence time of the fluid in the reactor, giving it more time to react and hence a higher conversion.

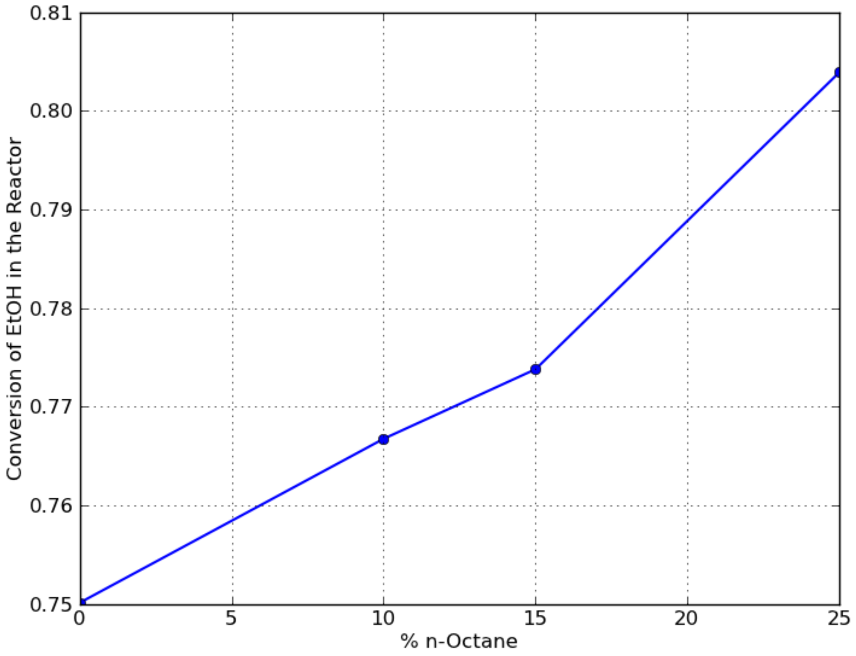

Figure 4.4: Sensitivity to % n-Octane in Feed

4.4 Variation in Void Fraction

The size of the reactor is a very important parameter to consider while designing a reactor. In the case of an on board reactor as is the case in this study the sizing of the reactor plays an important role especially because of the space constraint in a motor vehicle. An oversized reactor would add to the weight of the car and would reduce the overall efficiency of the vehicle. However, since the reactor used herein is a packed bed reactor, a predominantly more effective way to change the conversion of the reactor is to change the amount of catalyst in the reactor.

The void fraction can depend on the catalyst structure and how it is supported. For example typically a packed bed has a lower void fraction than a monolith supported catalyst. The void fraction not only influences the size of the reactor but also the pressure drop. The overall conversion of the reactor for a catalytic reactor of the kind used in this study predominantly depends on the weight and type of catalyst used in the reactor. Having said this, it is of interest to study the effect of change in void fraction of the reactor keeping the weight of the catalyst constant. A change in the diameter or the length of the reactor will effect a change in the void fraction to maintain the same total amount of catalyst.

Both these cases were studied for the sake of completeness of the study. Table 4.3 presents the five different lengths and their corresponding void fraction. The weight of the catalyst in the reactor being constant at 1.7 kg for the five instances. Figure 4.5 presents the simulation results for these five cases. It is seen from the graph that the conversion of ethanol in the reactor is not affected by the change in the void fraction of the reactor.

Similarly, table 4.4 presents the cases considered for the change in diameter with the same amount of catalyst as the previous case. The results are analogous to the ones for the change in length as can been seen from figure 4.6. Both these results reflect that the conversion of ethanol in the on board catalytic reactor does not have a dependence on the void fraction of the reactor.

Table 4.3: Change in ϵ with Length, Weight of catalyst= 1.7 kg

S.No	**Length, cm**	**Void Fraction**
1	15	0.5
2	9	0.167
3	12	0.375
4	20	0.625
5	30	0.75

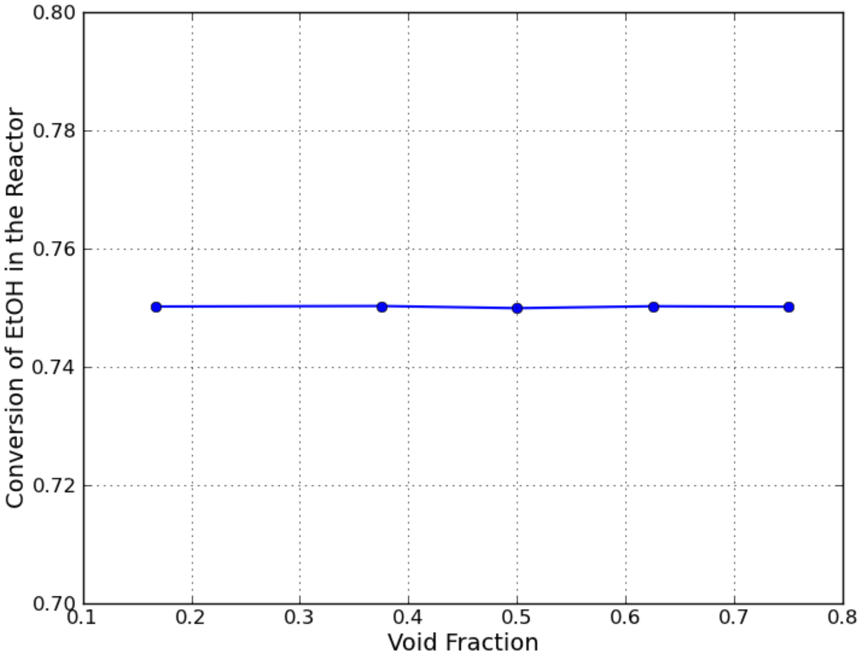

Figure 4.5: Sensitivity to change in Length of the reactor

Table 4.4: Change in ϵ with Diameter, Weight of catalyst= 1.7 kg

S.No	**Dia, cm**	**Void Fraction**
1	18	0.5
2	14	0.17
3	16	0.367
4	25	0.74

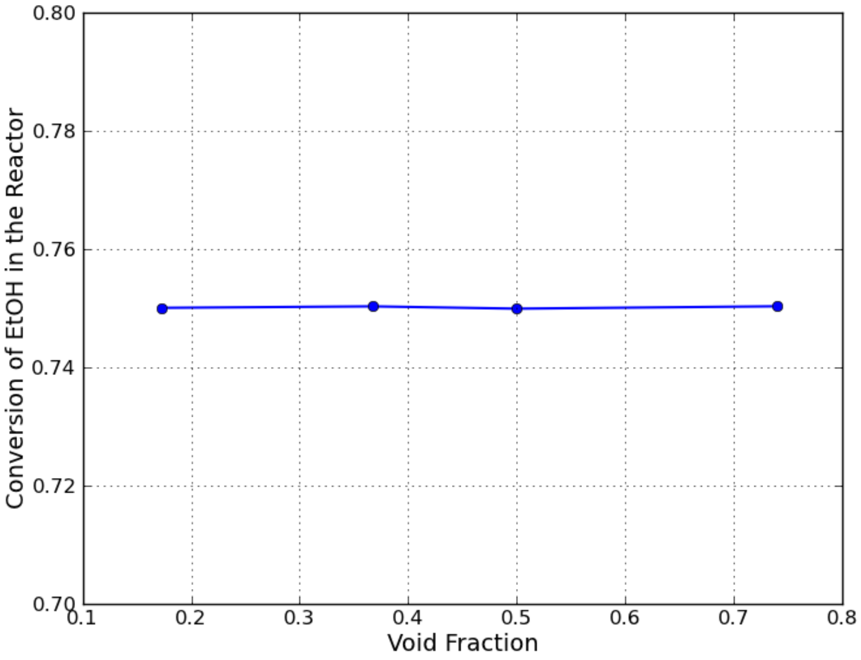

Figure 4.6: Sensitivity to change in Diameter of the reactor

4.5 On/Off Cycle

As compared to most industrial reactors which run in steady state conditions or at least near steady states with little or no fluctuations in feed and/or operating conditions, a reactor on board a motor vehicle would rarely be operated operated at steady state conditions. This is because of the transient nature of the fuel flow cycles in such a system. Hence, it is of interest to study the transient behavior of the reactor. In this regard it is utmost interest to study two cases below:

- The transient response to an on off cycle.
- The transient response to a fuel cycle such as a World Harmonized Stationary Cycle.

The on off cycle considered in the current study is tabulated in table 4.6. At time t=0, the reactor is at 100% load (volumetric flowrate of the feed) which then is switch to 0 load for 200 seconds. At t=200, the load is again set to 100% and so on. A hyperbolic function of the form as in equation (4.1) with a ramp size of 20 sec was used to achieve the transition between steps.

$$q = q\left(L_{old} + (L_{new} - L_{old})\,0.5\left(1 + tanh\left(\frac{t - t_c}{t_{ramp}}\right)\right)\right) \tag{4.1}$$

Table 4.5: Explanation of variable of the Hyperbolic Function

L_{old}	Old Load (Fractional)
L_{new}	Old Load (Fractional)
t	Time, s
t_c	Change Time, s
t_{ramp}	Ramp size, s

Table 4.6: On/Off Cycle

S.No	**%Load**	**Time,s**
1	100	0
2	0	200
3	100	200
4	0	400
5	100	300
6	0	100
6	100	100

Simulations were performed for the base case i.e. 100% ethanol in the feed and for a 5 ^oC loss in the temperature. The response from the on off cycle in table 4.6 is presented in figure 4.7. The graph at the bottom shows the variation in ethanol molar flowrate in the feed with time while the figure at the top shows the product or the diethyl ether molar flowrate with time at the reactor outlet. Comparing both the graphs, it is seen that the response to the change in the flowrate of the feed is almost instantenous replicated by the flowrate of the DEE with some overshoot after the reactor is started from an off step. The overshoots are because of the fact that as the flowrate of the feed is set to zero, the fluid inside reactor continues to react producing water and DEE in the process. Thus, when the feed is started again, a sudden overshoot of DEE is seen at the outlet of the reactor. It is also be pointed out that as expected, the overshoot after the second on step is greater than the first. This is because the second off cycle is longer than the first.

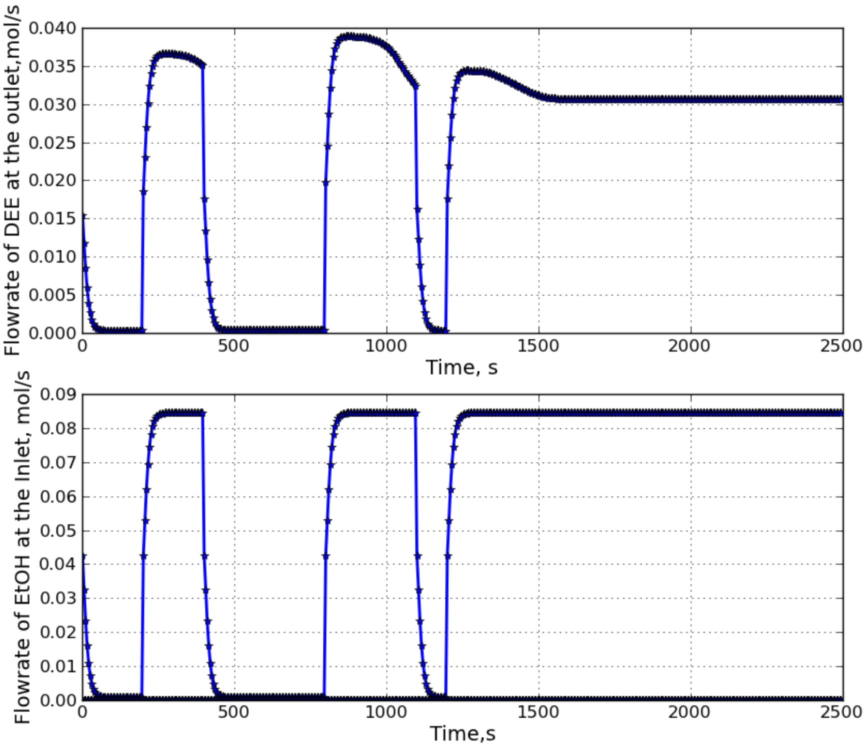

Figure 4.7: Response to on/off cycle

Figure 4.8 shows the temperature at the end of the reactor for the on off cycle in table 4.6. It is seen from the graph that as the feed is turned off, the temperature of the fluid in the reactor starts to fall. This is because of the consumption of heat by the reaction without the supply of heat as the enthalpy of the feed plus the heat source term (**??**) which is a function of volumetric flowrate in the model. Endothermic reactions are especially low risk because of their self extinguishing nature.

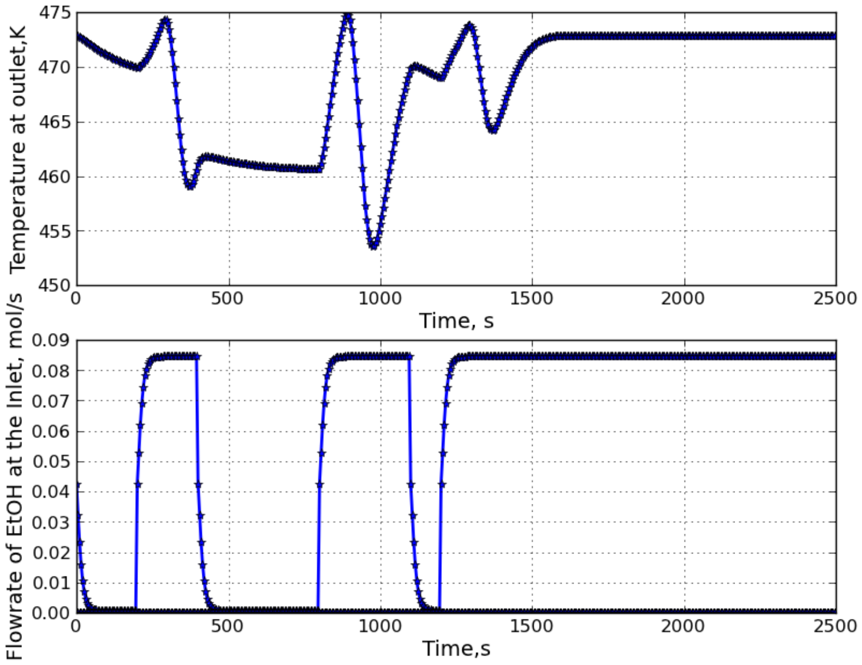

Figure 4.8: Temperature for a on off cycle

4.6 Fuel Cycle

As mentioned in the previous section 4.5, it is of interest to study the transient response of the reactor to a World Harmonized Stationary Cycle (WHSC). A typical WHSC is tabulated in table 4.7. At time t=0, the load on the reactor is 100% which is reduced to zero for 210 seconds and switched back again to 100% for 50 seconds and so forth. A hyperbolic function of the form similar to equation (4.1) was used for the transition.

Simulations were performed for the base case i.e. 100% ethanol in the feed and for a 5 ^oC loss in the temperature. The response to a WHSC as in table 4.7 is presented in figure 4.9. The graph at the bottom shows the variation in ethanol molar flowrate in the feed with time while the figure at the top shows the product or the diethyl ether molar flowrate with time at the end of the reactor. It is seen from graph that the flowrate of the diethyl ether at the end of the reactor follows the exactly as the inlet flowrate of ethanol.

Figure 4.10 shows the temperature at the end of the reactor for the WHSC as in table 4.7. The temperature profile shows similar trends as in the on off cycle in the previous section 4.5 with a fall in temperature as and when the flowrate is decreased.

Table 4.7: WHSC Fuel Cycle

S.No	**Load**	**Time,s**
1	100	0
2	0	210
3	100	50
4	25	250
5	70	75
6	100	50
7	25	200
8	70	75
9	25	150
10	50	125
11	100	50
12	50	200
13	25	250
14	0	210

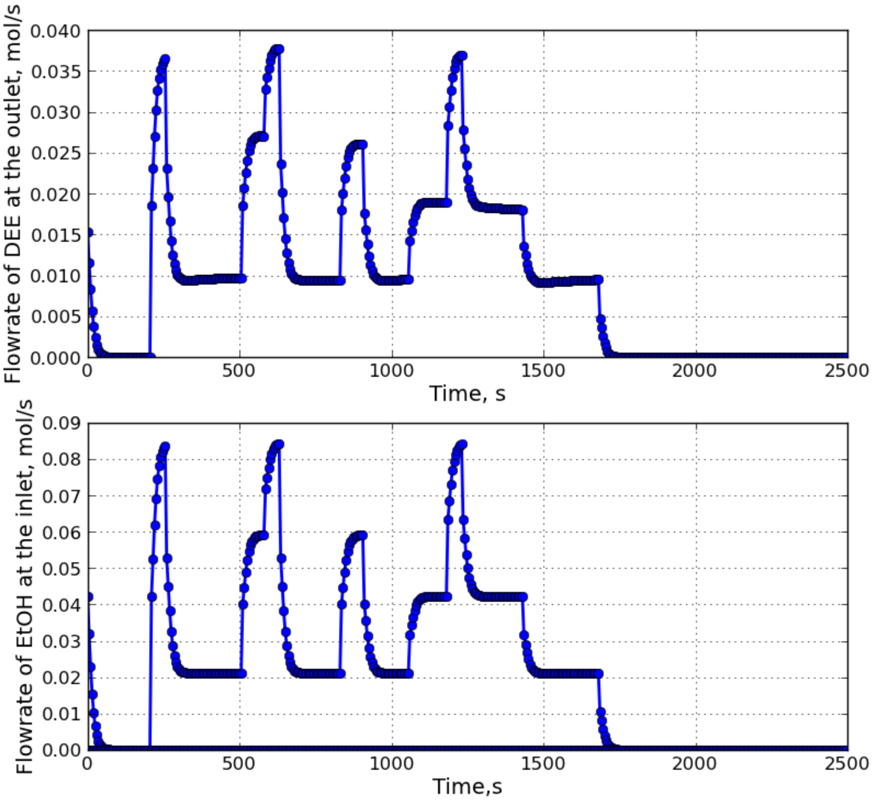

Figure 4.9: Response to a fuel cycle (WHSC)

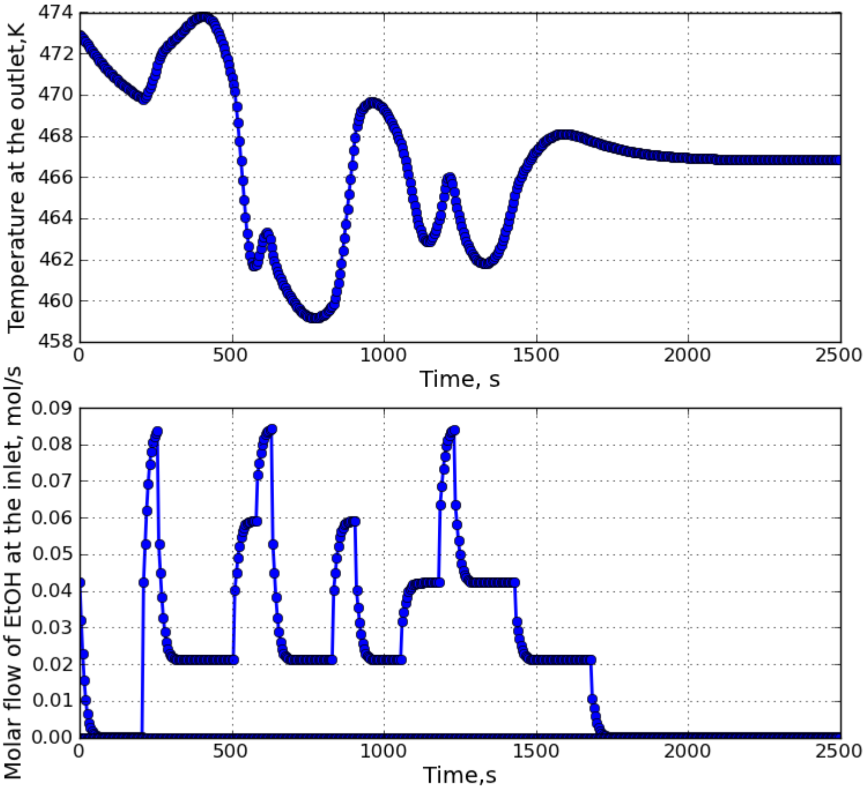

Figure 4.10: Temperature for a fuel cycle(WHSC)

5 Conclusions

From the results of this study it is clear that the temperature and overall the thermodynamics of the system plays an important part in the performance of the reactor. It is seen that lower the heat losses higher is the performance of the reactor. Heat losses can be atmospheric heat losses or due to consumption of heat by the reaction itself. It is of prime importance to check heat losses. In terms of the model, it is seen that the thermodynamics especially the heat capacity correlations have a huge impact on the results of the simulations. This is because both the heat of reaction as well as the equilibrium constants for the reactions are derived from them. Thus, the correlations used should fit well atleast in the spectrum of temperature range of the simulation. In this regard, it has to be kept in mind that the correlations used for this study as in table 2.13 have a validity up to the critical temperature. However, DEE is supercritical in the operating condition of the reactor which throws some uncertainity into the validity of the results. Having said that, it can be argued that even though the model is not adequate to quantify the performance of the on board reactor, it can still be valid for a qualitative analysis of the reactor.

The reactor performs well with feeds containing water as well as n-Octane with very low reduction in conversion in the case of water in the feed and an increase in conversion when n-Octane is added to the feed. These results are a very strong driving force for further studies regarding the performance of such a reactor for the production of DEE. A well performing reactor at a higher percentage of water in the feed implies that the energy requirement in the purification of Ethanol from a Ethanol-water solution can drastically be reduced. Thus, increasing the overall energy efficiency of a system running on such a fuel if the whole life cycle is considered.

Additionally, the response of the reactor to the on/off as well as the WHSC fuel cycle justifies the cause of the reactor. It is seen from sections 4.5 and 4.6 that the reactor responds very well to the fluctuations in the feed flowrates with little or no overshoots. Thus, such a reactor can be directly installed in a motor vehicle.

6 Future Studies and Modifications

As discussed in section 5, the results from the simulations show that the predicted performance of the reactor appears satisfactory with good responses to transient flows. However, there are some areas of concerns that require further investigations.

The biggest concern is the validity of the heat capacity correlations which are essential for the better understanding of the thermodynamics as well as quantification of the results of the simulations. Hence, further study and experimental investigation is recommended in this area. The kinetic model used in this study was a first order reaction with respect to Ethanol. However, for a better understanding and quantification of the liquid phase reaction of the catalyst used herein, literature as well as experimental studies can be pursued.

One simplication in the model was to neglect the transport limitations. However, an investigation of transport limitations can be of interest and should henceforth be pursued. And lastly experiments should be performed to validate the experimental results and consolidate the model if necessary.

Appendix

Program

The simulation was performed using Python 2.6.5. In addition to this the additional packages used for the simulation were:

- Scipy 0.7.0-2ubuntu0.1 for scientific computing
- Numpy 1:1.3.0-3ubuntu1 to add multi dimensional array to Python
- Matplotlib 0.99.1.2-3ubuntu1 for ploting and figures

The algorithm for the model used for the simulation can be represented with the help of the figure 6.1

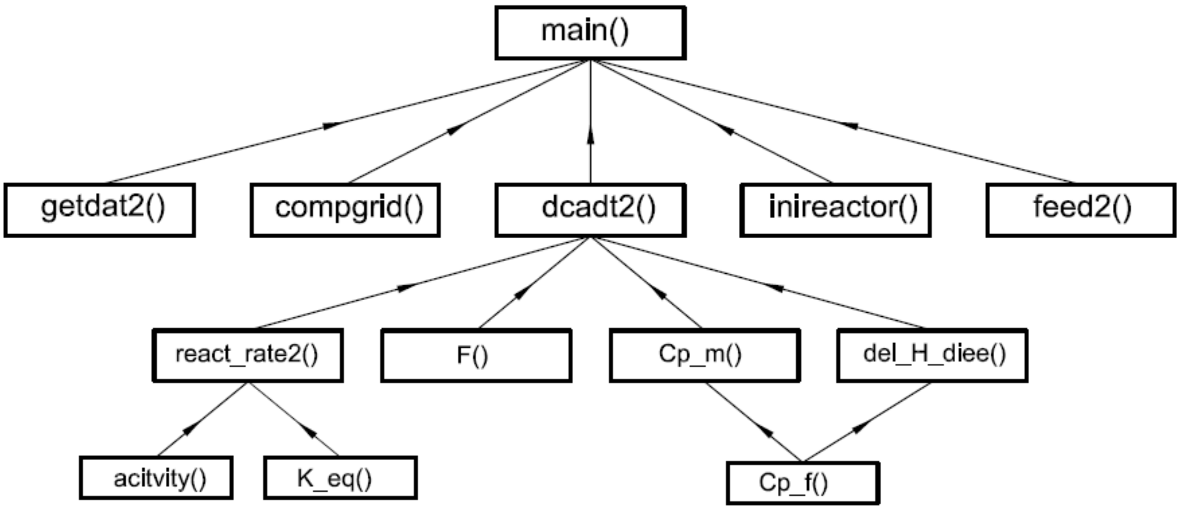

Figure 6.1: Flow chart for the model

The block main() represents the main function area, call area and the post processing routines. It calls different routines depending on what is being solved for. The coding is conducted in layers with different layers representing different purposes in the code. For example, the top most layer where main() resides is the layer where the calling of different functions take place. The second layer represents the setup layer where the reactor conditions, the inlet conditions as well as the computational grid is setup. The third layer represents the computational layer which is directly related to the calls by the function for the ode solver and the last layer represents the sub-routine for property calculations that assist in the calculations made by the third layer.

Table 6.1: Input-Return structure for the functions used in the simulation

Block	**Inputs**	**Returns**	**Remarks**
main()	Time and time step	Results from the simulation	Function call area
getdata2()	L, Dia, Cp_cat, void_f	L, A, Sp, Cp_cat, void_f, Dia	Reactor data
compgrid()	L, n	dx, x, n	Computational grid setup
dcadt2()	Ca, t, tau, Ca_0, T_f, q, Q, dV, Sp, Cp_cat, Dia, dx, void_f	dcadt	Function for ode solver
inireactor()	dx, Ca_0, A, q, T_f, void_f	Conc_T, tau, dV	
feed2()	M, T_f, P_f, massfrac	q, Conc0, T_f, P_f, Q	Feed Condition
react_rate2()	Ca	R_etoh, R_h2o, R_diee,	Reaction rate
F()	Ca, q	mf_t	Total molar flowrate
Cp_m()	Ca, q, T	Cp_mix	Heat capacity of the mixture
del_H_diee()	T	H_r	Heat of reaction at temperature, T
activity()	mol_x, T	lamda	Activity coefficient
K_dee2()	T	K	Equilibrium constant
Cp_i()	T,Cp_f	Cp	Heat capacity

Table 6.2: Explanation of notations used in 6.1

L	Length of the Reactor, m
Dia	Diameter of the reactor, m
Cp_cat	Heat Capacity of Catalyst
void_f	Void fraction of the catalyst
A	Cross sectional Area of the Reactor, m^2
Sp	Catalyst Mass per reactor volume, $\frac{kg}{m^3}$
n	Number of Tanks in series
dx	differential length array
x	Length array
Ca	Linearized array containing concentration and temperature for each tank in
t	Time, s
tau	Residence Time, s
Ca_0	Feed Concentration array containing concentration of all the components
T_f	Temperature of the Feed, K
q	Volumetric Flowrate, $\frac{m^3}{s}$
Q	Heat Source term, J
dV	Differential volume array
dcadt	Function return for ode solve
Conc_T	Initial condition of the reactor, linearized array
M	Mass Flowrate, $\frac{kg}{s}$
P_f	Feed Pressure, Pa
massfrac	Feed mass fraction array
Conc0	Feed concentration array
R_etoh, R_h2o, R_diee	Rate of production of EtOH, H_2O and DEE
mf_t	Total molar flowrate, $\frac{mol}{s}$
Cp_mix	Heat capacity of the solution
H_r	Heat of Reaction
mol_x	Mole fraction
lamda	Activity coefficient
K	Equilibrium Constant
Cp_f	Array containing the regression coefficients as in table 2.13

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