

**KINETIC PARAMETER ESTIMATION OF DIESEL HDT
USING SEQUENTIAL QUADRATIC PROGRAMMING AND
GENETIC ALGORITHM**

A Project Report

Submitted by

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(With Specialization in Process Design Engineering)**

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DECLARATION BY THE SCHOLAR

I here by declare that this submission is my own and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other Degree or Diploma of the University or other Institute of Higher learning, except where due acknowledgement has been made in the text.

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CERTIFICATE

This is to certify that the thesis entitled “**Kinetic parameter estimation for Diesel HDT using Sequential Quadratic Programming**” submitted by **NAVNEET KAUR (R670215010)**, to the University of Petroleum and Energy Studies, for the award of the degree of **MASTER OF TECHNOLOGY** in Chemical Engineering with specialization in Process Design is a bonafide record of project work carried out by her under our supervision. The results embodied in this project review report are based on literature and the research in IOCL R&D. This data is based on research carried out in IOCL R&D, and hence only IOCL reserves all rights to patent, publish and present the data.

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ABSTRACT

Hydrotreating is one of the main processes of secondary processing of oil raw materials; it is directed on considerable reduction of the content of heteroatomic compounds in oil products. Hydrotreating process is applied for production and upgrading of various oil products: gasoline, kerosene, diesel fuel, vacuum gasoil, and oil fractions. The wide use of hydrotreating process is caused, first of all, by introduction of increasing volume of sulfur and high-sulfur oil to the production cycle. Toughening of ecological requirements to sulfur content in fuel, need of increase in oil refining depth necessitate improvement of hydrotreating process. Application of mathematical modeling methods allow predicting conditions of hydrotreating process and quality of products that will considerably increase the depth of oil refining and will provide observance of all existing environmental standards . The purpose of this work is to study the kinetics of various reactions involved in hydrotreating of diesel, develop the mathematical model of diesel fuel hydrotreating and development of Optimization code that minimizes the sum of square of error between experimental and computational results which in return calculates the constant values for the reaction rate of hydrodesulfurization of sulfur and hydrogenation of aromatics.

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Abbreviations

DHDT	diesel hydrotreating
GC	gas chromatography
HDS	Hydrodesulfurization
HDN	Hydrodenitrogenation
HDA	Hydrodearomatization
HDA _s	Hydrodeasphaltenization
HDM	Hydrodemetallization
HDO	Hydrodeoxygenation
HDC	Hydrocracking
HDT	Hydrotreating
ppm	parts per million
ULSD	Ultra Low Sulfur Diesel

CHAPTER ONE

Introduction

1.1 Background

Petroleum has remained an integral part of our lives and will do so for the next decades. The fuels that are produced from petroleum supply more than half of the world's total supply of energy. Gasoline, kerosene, and diesel oil provide fuel for transportation (automobiles, tractors, trucks, aircraft, and ships). Fuel oil, heavy oil and natural gas are employed for heating homes and commercial buildings in addition to generating electricity. Petroleum products represent the main raw materials utilized for production of synthetic fibers (for clothing), plastics, paints, fertilizers, insecticides, soaps, and synthetic rubber. These days the uses of petroleum as a source of raw material in manufacturing are central to the functioning of modern industry (Hsu and Robinson, 2006).

Petroleum refining is now in an important transition period. The industry has moved into the 21st century and the market demand for petroleum products has shown an immense growth in recent years. This means that the demand of transportation fuels will show an inclining trend in demand during the next decade, which can be fulfilled by the processing of heavier feedstock (Ancheyta and Speight, 2007).

As petroleum is the major source of energy over the coming years. In this respect, fossil fuels, heavy oils and residua are immensely important in any energy scenario, specifically those scenarios that relate to the production of liquid fuels (Ancheyta and Speight, 2007; Khalfallah, 2009). In recent years the average quality of petroleum has deteriorated that has triggered the nature of crude oil refining to change. This has led to the desire for managing of crude oil quality more effectively. The declining reserves of light oils in the world have resulted in an increasing need for developing choices to remove the impurities (such as sulfur, nitrogen, metals) and upgrade the heavy feedstock, specifically heavy oil and bitumen. This has resulted in a vast variety of operation choices that aims at removal of contaminants during refining.

The increase in supply of heavy oils is a serious issue and it is mandatory that refineries are able to refine these heavy oils. For meeting the changing pattern of product demand and profitably use these heavy oils, important investments in refining conversion operations is today's need.

The economical solution to this problem will depend on individual company situations and country also. However, the most promising technologies will likely include the conversion of heavy crude oil, vacuum bottom residua, asphalt from deasphalting processes, and bitumen from tar sand deposits (Hsu and Robinson, 2006). With all of the scenarios in place, there is no doubt that petroleum and its relatives (residua, heavy oils as well as tar sand bitumen) will be required for producing a considerable proportion of liquid fuels into the foreseeable future.

1.2 Petroleum Refining and Current Industrial Practice

A typical petroleum refinery is a complex chemical processing and manufacturing unit, with crude oil feedstock going in and refined fractions (products) coming out. Refining occurs by fractionation (distillation) of crude oil into a series of product streams based on boiling ranges for each fraction. Crude oil distillation is more complex than product distillation, in part due to the fact that crude oil contains water, salts, and suspended solids. These materials are removed from crude oil before the distillation process in order to reduce corrosion, plugging, and fouling in crude heaters and towers, and in order to prevent the poisoning of catalysts in downstream units by a process, which is called desalting. There are two typical methods that are commonly used for crude oil desalting: chemical and electrostatic separation, utilize hot water for dissolving the salts and collect suspended solids.

1.3 Impurities Problems in Crude Oil

Crude oil is a very complex material consisting of different hydrocarbon compounds in addition to sulfur, nitrogen, oxygen and some metallic compounds, containing nickel, vanadium, iron and copper (Ali and Abdul-Karim, 1986). Market demands for different crude oil derivatives are high. The average consumption of different fuels such as Gasoline, Kerosene, Jet fuels, etc is equivalent to 40-50% of crude oil consumption and the worldwide consumption will increase in the next years (Ray et al., 1995). Therefore, it is necessary to increase distillate production at high quality. The presence of sulfur, nitrogen, oxygen and metallic compounds in crude oil has a significant impact upon the quality of oil products in addition to the harm they can cause. Sulfur

Sulfur compounds lead to environmental pollution through atmospheric contamination by oxidation resulting from combustion forming sulfur dioxides, which will be oxidized later with ultraviolet rays to SO₃. These compounds react with atmospheric water to form sulfuric acid that causes many lung diseases, like asthma and shortness of breath. It also leads to soil pollution with acid materials, decreases the life of machinery, corrodes pipes, machines and equipment, affecting the additives used for the purpose of increasing the octane number, reducing the activity of Tetra Ethyl Lead (TEL) added to gasoline. As a result, the engine metal will erode, leading to the destruction of metallic parts. The same is true with gas oil and diesel fuel as well as lubricating oils. Also, their emissions are very dangerous to human safety and environment. In addition, these impurities cause catalyst poisoning and reduce the catalyst activity. Therefore, environmental regulations have enforced substantial decrease of sulfur compounds in fuels.

The presence of nitrogen compounds in crude oil or oil fractions has also a detrimental effect for refining industries. Nitrogen compounds are responsible for catalyst poisoning and reducing catalyst activity, where these impurities lead to dye formation that causes catalyst poisoning leading to reduced activity of the catalyst. Furthermore, nitrogen compounds have toxic effects on the storage stability of oil products and affect the color of oil products (Speight, 2000).

Andari et al. (1996) have demonstrated the impact of nitrogen and sulfur compounds through their studies of Naphtha, Kerosene and Diesel oils derived from Al-Kuwait crude oil and they proved that these compounds showed unwanted influence on the stability of fuel in addition to the environmental pollution. Kaernbach et al. (1990) confirmed that the nitrogen compounds significantly affect the catalyst activity through their works on the vacuum residue.

Metallic compounds in crude oil causes many problems so it is of great interest to researchers. The existence of metallic compounds in crude oil and its fractions has harmful effects. These compounds have a very bad influence on the hydrotreating (HDT) efficiency, plug the pores of catalysts used, cause rapid deactivation for the hydroprocessing catalyst, where they tend to deposit on the catalyst, and seem to act to reduce HDT activity by decreasing catalyst surface area (Abbas, 1999; Pereira et al., 1990; Bartholdy and Cooper, 1993). Also, the presence of vanadium and nickel in addition to iron and copper affects the activity of cracking catalysts and increase the level of coal deposited. The presence of these compounds, especially vanadium in

the fuel used in the high power machines as gaseous turbines, leads to the formation of some sediment on the turbine, which can lead to a change in the balance of the rotating parts of turbine (Ali and Abdul-Karim, 1986; Gary and Handwerk, 1994).

Many scientists have studied the probability of getting rid of such compounds by many approaches. One of the prominent methods was removing them with hydrogen, which is called the hydrotreating process (HDT) (Shimura, 1986). In the petroleum refining industry, HDT reactions that include

1. Hydrodesulphurization (HDS)
2. Hydrodenitrogenation (HDN)
3. Hydrodearomatization(HDA)
4. Hydrodeasphaltenization (HDAs)
5. Hydrodemetallization (HDM)
6. Hydrodeoxygenation (HDO) and
7. Hydrocracking (HDC)

are carried out in fixed bed tubular reactor.

1.4 Challenges

The hydrotreating process is one of the important processes in refineries for reducing the content of the sulfur, nitrogen, aromatics, oxygen, metallic and other contaminants from oil fraction. Conventionally, all hydrotreating processes are carried out on each oil cut separately and not on the full crude oil (i.e. after the separation of crude oil to its derivatives, such as gasoline, kerosene, light and heavy gas oil). This means that a large amount of the impurities, namely, sulfur, nitrogen, metals, aromatics and asphaltenes will be deposited at the bottom of the atmospheric and vacuum distillation column. In addition, hydrotreating each oil cut separately is fairly easy due to the ability to control the reaction, the knowledge of physical and chemical properties, the kind of reaction and its condition. Hydrotreating of crude oil is regarded as a difficult challenge since the crude oil involves a lot of compounds and multiple phases, in addition to difficult structures. Additionally, hydrotreating of crude oil in the existence of asphaltenes that contain a large amount of these impurities, especially metals that close the active sites on the catalyst is one of the more difficult and significant problems. The expected benefits

of directly hydrotreating crude oil are improvements of middle distillates productivity due to conversion of heavy compounds and long molecules that is concentrated in heavy fractions to light compounds. This is completely opposite to conventional processes that are carried out separately for each cut. This means that the heavy compounds and long molecules will settle down at the bottom of the atmospheric and vacuum distillation column. This makes it difficult to hydrotreat under normal operating conditions.

1.4.1 Diesel oil

Diesel oil is a carbonaceous compound of hydrocarbons typically in the range C₁₀ to C₂₅. It consists of normal, branched and cyclic paraffin and compounds consisting of single and fused aromatic rings. Aromatics are categorized as mono-, di- or polyaromatics. Some compounds consist of hetero atom (sulfur or nitrogen). Most of the sulfur compounds are either thiophenic compounds or sulfides. The nitrogen compounds are classified as basic or non-basic.

Important property of diesel is the cetane number. It is a measure of ignition properties of oil. cetane number of diesel fuel is measured by the delay in its ignition. Higher cetane number signifies that diesel fuel ignites more easily. Lesser cetane number signifies more aromatic content. Decreasing the content of aromatic compounds in diesel fuel increases its cetane value which in return improves its combustion properties. Cetane number of various refinery process streams used for production of diesel lies between 20 and 60. According to European Union a minimum value of cetane number should be 51 (and a cetane index of minimum 46) is acceptable for automotive diesel fuel.

Saturation of aromatics compounds can have a positive effect on the cetane number. It is therefore a significant way of controlling fuel quality.

Diesel fuel is most widely used type of transportation fuel. Large amount of sulfur content in diesel is harmful for the environment. Advanced technologies like nitrogen oxide adsorbers which is still under development to limit emissions. Sulfur present in the fuel is oxidized during combustion forming products such as sulfur dioxide and sulfur trioxide. In presence of water it rapidly converts to sulfuric acid which causes acid rain.

In the past, diesel fuel contained large quantities of sulfur. European emission standards and preferential taxation have forced oil refineries to drastically reduce the level of sulfur in diesel fuels. According to European Union the sulfur content has reduced dramatically during the past 20 years. Automotive diesel fuel is covered in the European Union by standard EN 590. In the 1990s the specifications allowed a maximum content of 2000 ppm of sulfur with the introduction of Euro 3 specifications this figure reduced to 350 ppm by the beginning of the 21st century. This upper value was further lowered with the introduction of Euro 4 by 2006 to 50 ppm (Ultra Low Sulfur Diesel). Currently the standard in force in European Europe for Diesel Fuel is the Euro 5, with a maximum content of 10 ppm.

Reducing pollution from the use of diesel oil as a transportation fuel is an important area of research. Addition of air pollutants into the atmosphere leads to depletion of ozone in the upper layers of stratosphere which in turn leads to global warming and acid rains, which are hazardous to public health. Concerns about the environment have resulted in tightened legislation regarding the sulfur content of diesel. Diesel that meet these specifications are often denoted as Ultra Low Sulfur Diesel (ULSD) or "sulfur-free" diesel.

The tightened legislations and the higher demand for transportation fuels has resulted in increased attention to refinery processes such as hydrotreating. In the hydrotreating process, the amounts of sulfur, nitrogen and aromatics are reduced, which limits the emissions of SO_x, NO_x and particles during combustion. Sulfur compounds act as poison for the catalysts used to limit the amount of particulates and NO_x released from the exhaust of diesel engines, and reducing the sulfur concentration in diesel is necessary in order to reduce the harmful emissions.

1.5 Hydrotreating reactions

The three main types of reactions taking place during the hydrotreating process are hydrodesulfurization (HDS), hydrodearomatization (HDA) and hydrodenitrogenation (HDN).

1.5.1 Hydrodesulfurization (Removal of sulfur content)

The refinery HDS feedstocks (diesel oil) contain a wide range of organic sulfur compounds, including thiols, thiophenes, organic sulfides and disulfides, and many others. These organic sulfur compounds are products of the degradation of sulfur containing biological components, present during the natural formation of the fossil fuel, petroleum crude oil.

When the HDS process is used to desulfurize a refinery naphtha, it is necessary to remove the total sulfur down to the parts per million range or lower in order to prevent poisoning the noble metal catalysts in the subsequent catalytic reforming of the naphthas.

When the process is used for desulfurizing diesel oils, the latest environmental regulations in the United States and Europe, requiring what is referred to as *ultra-low-sulfur diesel* (ULSD), in turn requires that very deep hydrodesulfurization is needed. In the very early 2000s, the governmental regulatory limits for highway vehicle diesel were within the range of 300 to 500 ppm by weight of total sulfur. As of 2006, the total sulfur limit for highway diesel is in the range of 15 to 30 ppm by weight.

The sulfur compounds present in gas oil covers a large range of reactivity. In order to produce ULSD it necessary to remove sulfur from the most refractive compounds, such as higher molecular weight dibenzothiophenes with side substituents at positions adjacent to the sulphur atom. Typical model molecules representing the most refractive sulfur compounds are 4-methyldibenzothiophene and 4, 6-dimethyldibenzothiophene.

Thiophenes

A family of substrates that are particularly common in petroleum are the aromatic sulfur-containing heterocycles called thiophenes. Many kinds of thiophenes occur in petroleum ranging from thiophene itself to more condensed derivative. Thiophene itself and its alkyl derivatives are easier to hydrogenolyse, whereas dibenzothiophene, especially its 4, 6-disubstituted derivatives, are considered the most challenging substrates. Benzothiophenes are midway between the simple thiophenes and dibenzothiophenes in their susceptibility to HDS.

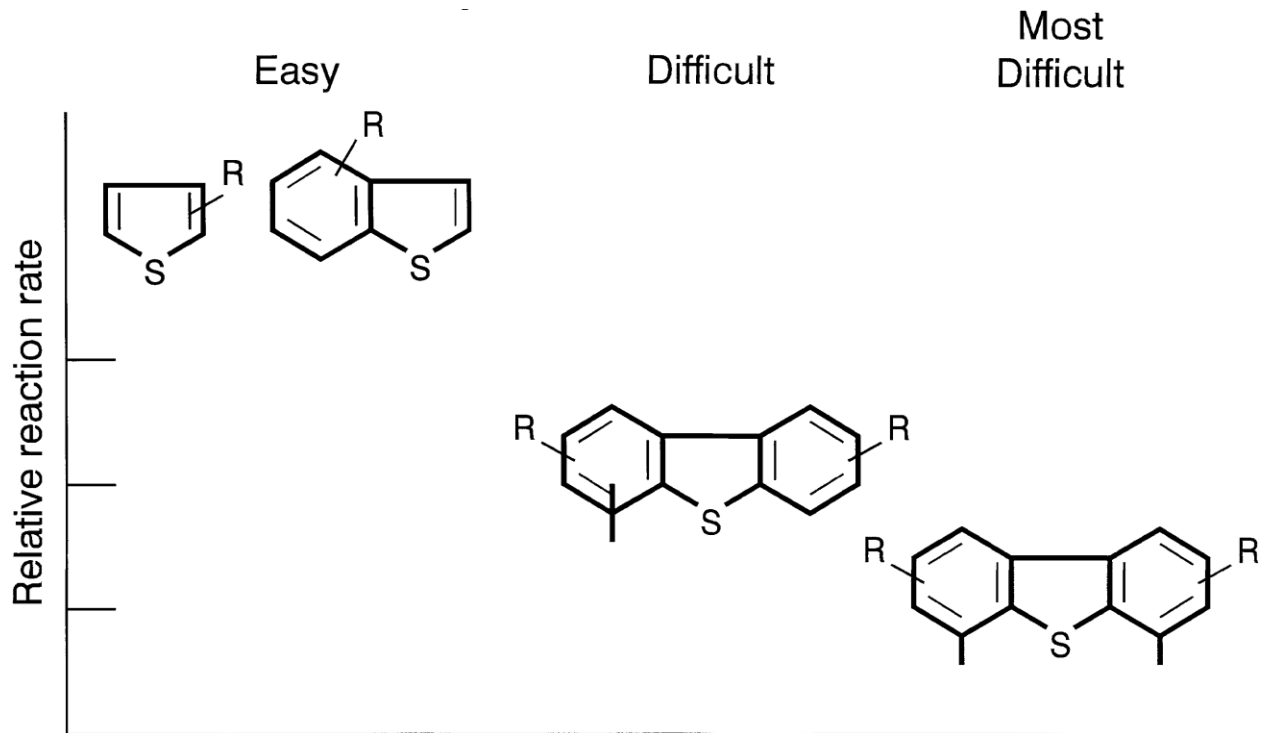


Figure 1. 1 Illustration of the difference in reactivity for typical sulfur compounds in gas oils

1.5.2 Hydrodearomatization

Hydrodearomatization reactions are reactions in which aromatic rings are saturated with hydrogen. For polycondensed aromatic hydrocarbons the hydrogenation of the first ring is in general the fastest, and the rate of hydrogenation for subsequent rings tend to be lower with the last ring being the least reactive. The reaction pathway for a typical diaromatic compound, naphthalene. The rate of hydrogenation of the last ring is significantly lower than of the first one.

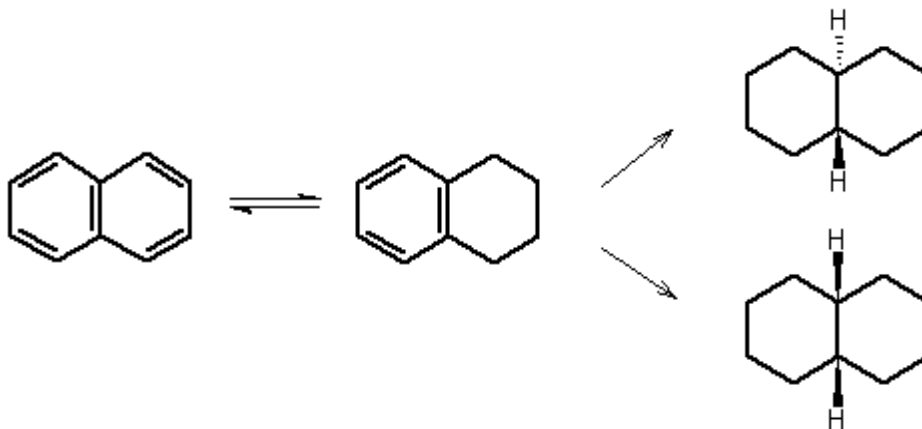


Figure 1.2 - Reaction pathway for naphthalene hydrogenation

1.5.3 Hydrodenitrogenation

Hydrodenitrogenation reactions are important, not only for their own sake, but also because nitrogen compounds can act as inhibitors for hydrogenation reactions. Nitrogen compounds are grouped into 2 different classes: Basic and non-basic. The non-basic species are compounds such as indoles and carbazoles, while the basic are compounds such as aliphatic amines, anilines, pyridines, quinolines and acridines. A common feature of HDN of aromatic nitrogen compounds, is that they are relatively slow reacting, and that hydrogenation of the aromatic ring has to happen prior to hydrogenolysis of the carbon-nitrogen bond. A possible reaction pathway for acridine, a basic nitrogen compound, is shown in figure 1.3.

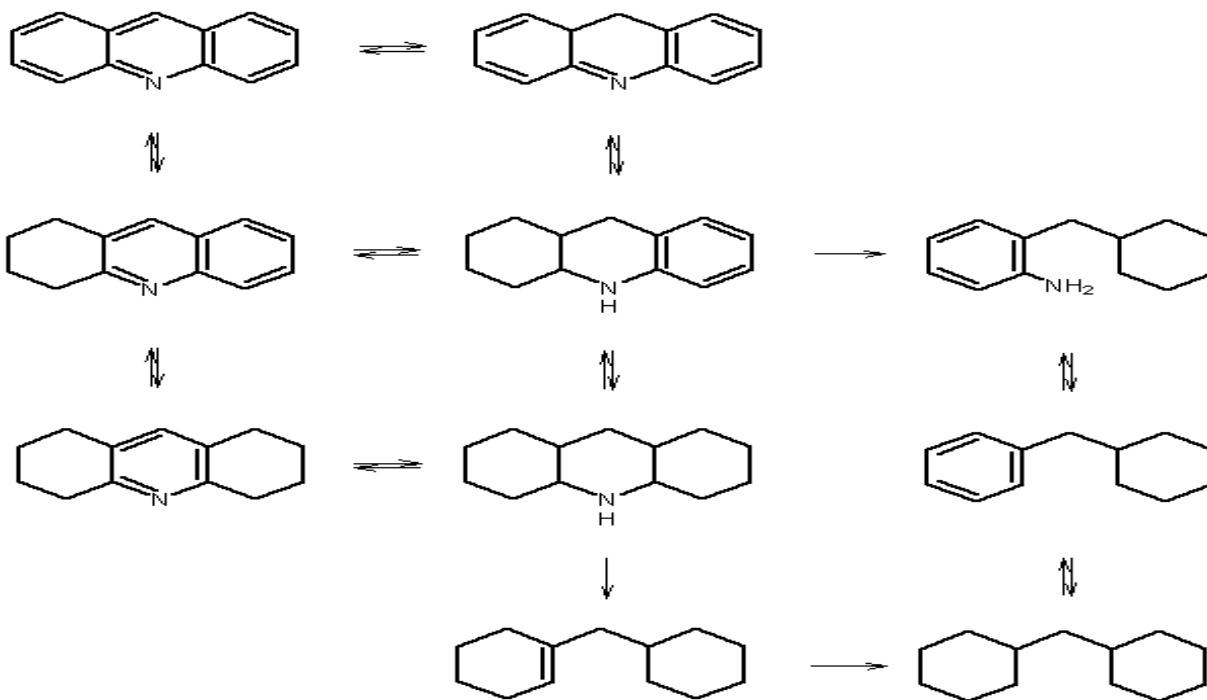


Figure 1.3 - Reaction network for acridine hydrodenitrogenation

Furthermore, the mathematical modeling of the hydrotreating of crude oil is a hard task in view of the intricate physiochemical changes that are undergone in the feed together with transport phenomena and mechanisms of catalyst deactivation in the reaction system. The major challenge is the accurate evaluation of the kinetic models, which can confidently predict the product compounds at different process conditions. For HDS, HDN, HDAs, HDV and HDNi reactions, the development of such kinetic models is a hard task due to the great variety of structures.

The world wide request for transportation fuel or middle distillates (such as car fuel, Jet fuel, diesel fuel) with fuel quality, which satisfies environmental legislations, is growing. This demand dictates the necessity for conversion capacity, which will be able to selectively produce oil fractions, especially middle distillates. Therefore, the petroleum refining industry has made efforts to find solutions for processing greater quantity of heavy oils for increasing the production of transportation fuels. In order to meet the challenges, a number of technologies have been developed to refine and improve heavy oils into more valuable transportation fuels beside content of the impurities such as, sulfur (S), nitrogen (N), metals (V and Ni) and

asphaltene (Asph). Catalytic hydrotreating process (HDT), has the potential for reducing the concentration of contaminants (S, N) simultaneously increase the productivity of distillate cuts. It is capable of increasing the quality as well as quantity of distillate fractions.

The HDT process includes contact of the oil feedstock with hydrogen at high temperature and pressure. The compounds in the oil feedstock are cracked to lower molecular weight compounds and saturated with hydrogen to produce distillate fractions with increasing hydrogen to carbon ratio and reducing the content of the impurities. This process is carried out by using high activity hydrotreating catalysts, which have the following main features:

- (a) Enhancing the removal of undesirable impurities (S, N, V, Ni, Asph) by promoting HDS, HDN, HDV, HDNi and HDAs reactions respectively
- (b) Conversion of the higher molecular weight compounds to lighter compounds
- (c) Hydrogenation of the cracked compounds that leading to increase of hydrogen to carbon ratio of the products
- (d) Reducing the formation of coke.

The hydrotreating process involves a number of reactions as mentioned in the previous section. Therefore first step is to find out the chemical reactions. Through the removal of the contaminants during HDT reactions, some conversion in the boiling range of the feedstock also takes place due to the impurities containing molecules which are cracked into lighter products. In addition, mild hydro cracking of the oil feedstock could occur through HDT process depending on the severity of the operation. All these reactions will bring some conversion for the heavy cuts into valuable derivative (lighter) cuts (Bej et al., 2001). For the purpose of achieving the target of removing the percentage of impurities as much as possible with the current HDT process, utilizing high temperature and pressure, high hydrogen consumption, large volume and more catalyst is indispensable but costly. Therefore it is important to find a method that can operate under moderate operating conditions and simultaneously has high efficiency to reduce all types of contaminant compounds to produce clean fuel.

This chapter presents literature for hydrotreating process modelling, the aspects of modelling, simulation and optimization processes, kinetic models of middle distillate yields and kinetic parameter estimation techniques.

The minimization of the sum of the squared errors (SSE) between the experimental and estimated concentrations of sulfur, nitrogen and aromatics is used as an objective function in optimization problem.

Optimization is an important tool in making decisions and analyzing of physical systems. In mathematical terms, an optimization problem is the problem of finding the best solution from the set of all feasible solutions.

1.6 CONSTRUCTING A MODEL

The first step in the optimization process is to construct an appropriate model. Modeling is the process of expressing the objective in mathematical terms, the variables in objective function, and the constraints of the objective function.

An objective is a quantitative measure of the performance of the system that we want to minimize or maximize. For example in manufacturing we want to maximize the profits or minimize the production cost. In fitting experimental data to a model it is required to minimize the total deviation of the observed data from the simulated data.

The variables or the unknowns are the components of the system for which we want to find values. In manufacturing, the variables may be the amount of each resource consumed or the time spent on each activity, whereas in data fitting, the variables would be the parameters of the model.

The constraints are the functions that describe the relationships among the variables and that define the allowable values for the variables. In manufacturing, the amount of a resource consumed cannot exceed the available amount.

1.6 .1 Process Modeling

A mathematical model is a set of variables and a set of equations that build relationships among the variables for describing some aspects of the behavior of the system under investigation. The variables describe some properties of the process, for instance, measured process outputs frequently in the shape of signals, timing data and counters.

The real model is the collection of functions which describe the relations among the various variables has defined a mathematical model as "a representation of the essential aspects of an existing system (or a system to be constructed) which presents knowledge of that system in usable form". However, for the complex systems encountered in several engineering contexts, the models are frequently sets of relations that exhibit highly non-linear equations. For several chemical engineering models, the non-linear behavior is further complicated by the exponential reliance of the reaction rates on the temperature (Arrhenius type equations) also by the severity of the rate expressions utilized within the mass and energy balance models.

Generally, there are three types of model:-

- 1- Data driven black box models.
- 2- Knowledge driven white box models.
- 3- Hybrid grey box models.

The derivation of black-box models is based on empirical observations of the process behavior. Black-box models are generally improved during an observation of the relation between various inputs and their corresponding outputs in a particular system. From this input-output data, a black box relation can be accomplished. Despite this, this type of model is easy to obtain, however, problems generally arise when it is employed to extrapolate as its exactness in such cases can be severely restricted. Another drawback is that data can only exist for measurable variables; hence no relation can be formed for variables that cannot be measured, such as heat of reaction. The problem with using a wide group of functions for describing a process is that calculating the variables becomes increasingly difficult when the number of variables increases.

Knowledge driven white-box models on the other hand are referred to as mathematical modelling, and are termed “mechanistic first principles models”. For a process, the model can be developed from stoichiometric and kinetic knowledge of the mass and energy balances of the process. In such a model the impact of temperature, concentration and any other control variables upon the rate of each reaction is reported by the kinetic model, and the reactor model relates the state variables of the process to other variables such as the composition of inlet streams and other system constraints.

White-box models are not as simple to obtain as their black-box counterparts, and owing to the extreme non-linear behavior of several engineering processes, can be very difficult. In order to reduce some of complexity, assumptions are generally made and an easy to understand model which does not appropriately describe the process is sometime still preferred over a very detailed one that needs lot of computing time. In a white-box model, equations are generally derived based on the following considerations.

- Mass and energy balances.
- System constraints.
- Thermo-physical properties of the process.

1.7 Hydrotreating Kinetic Models (Literature Review)

The primary objective of this work is to develop a kinetic model that can accurately predict the hydrotreating performance of crude oil under different operating conditions. In order to develop a reliable catalytic hydrotreating model, it is important to fully understand the operation and all accompanied phenomena related to modelling aspects.

This part of the project presents some literature for the hydrotreating process modeling (includes HDS, HDN, HDM, HDAs, HDA and HDC). Rate equations are used to develop a one-dimensional heterogeneous non isothermal model in hydrotreating diesel oil fractions. A feedstock mixture consists of benzothiophene, di-benzothiophene and 4, 6 dimethyl dibenzothiophene as sulfur compounds and quinoline as nitrogen compounds. The model accounts for concentration gradient inside the catalyst particles. Integration in the axial direction was performed using a fourth order Runge-Kutta method and the intraparticle integration was carried out using the Orthogonal Collocation method.

Korsten and Hoffmann (1996) developed a three-phase reactor model for describing the hydrotreating reaction of vacuum gas oil in a trickle-bed reactor operated under high-pressure pilot plant and isothermal conditions. The model is based on two-film theory and involves correlations for estimating mass-transfer coefficients, gas solubilities and the gases and oils properties at operating conditions. The chemical reaction rate was described by Langmuir-Hinshelwood kinetics. The model equations were solved numerically by a Runge-Kutta method and the model presented (simulation process) shows good agreement with the experimental data that was carried out over a wide range of pressure, hydrogen to oil ratio, temperature and liquid hourly space velocity.

Tsamatsoulis and Papayannakos (1998) investigated a kinetic model for hydrodesulfurization of vacuum gas oil in a trickle-bed reactor using several catalysts. The kinetic model has been estimated by utilizing a plug-flow model for the liquid phase as well as by using non-ideal liquid flow. Differences in the chemical reaction rates and the mechanism parameters were discussed. The kinetic parameters of the model were determined using the fourth order Runge-Kutta method and the Marquardt Levenberg nonlinear regression algorithm to fit simultaneously the values of sulfur and hydrogen concentration predicted by the models to the experimental data. Van Hasselt et al. (1999) used a computer model to compare a conventional nonisothermal cocurrent trickle-bed reactor with two different configurations suggested for the process of the

reactor: counter current and semi-counter current, taking the hydrodesulfurization of vacuum gas oil as a case study. They found that the counter current flow application results in a significant increase of impurities conversion.

Bhaskar *et al.* (2002) reported on the effects of hydrodynamic parameters and reaction rates on reactor performance. They applied the three phase heterogeneous model for describing the performance of a pilot plant trickle-bed reactor used for atmospheric gas oil hydrodesulfurization. The developed model was compared with experimental observations. The algebraic equations were solved using Newton-Raphson algorithm for the given bulk phase concentration of receptive compounds. The differential equations were then solved simultaneously using Runge-Kutta method. The results obtained from pilot plant operated under wide range of operating conditions during HDS of atmospheric gas oil showed good agreement with the predicted results.

Chowdhury *et al.* (2002) developed a kinetic mathematical model for a two phase flow reactor, including both mass transfer and chemical reaction in the reactor. Diesel oil hydrodesulfurization and hydrogenation of mono-, di- and polyaromatics were investigated in a TBR operated under isothermal conditions. Model equations were solved with a 4th order Runge-Kutta method. Data obtained are compared satisfactorily with the experimental results.

1.8 TYPES OF OPTIMIZATION PROBLEMS

As noted in the Introduction to Optimization, an important step in the optimization process is classifying your optimization model, since algorithms for solving optimization problems are tailored to a particular type of problem.

1.8.1 Continuous Optimization versus Discrete Optimization

Some models only make sense if the variables take on values from a discrete set, often a subset of integers, whereas other models contain variables that can take on any real value. Models with discrete variables are **discrete optimization** problems; models with continuous variables are **continuous optimization** problems. Continuous optimization problems tend to be easier to solve than discrete optimization problems; the smoothness of the functions means that the objective function and constraint function values at a point x can be used to deduce information about points in a neighborhood of x . However, improvements in algorithms coupled with advancements in computing technology have dramatically increased the size and complexity of discrete optimization problems that can be solved efficiently. Continuous optimization algorithms are important in discrete optimization because many discrete optimization algorithms generate a sequence of continuous sub-problems.

1.8.2 Unconstrained Optimization versus Constrained Optimization

Another important distinction is between problems in which there are no constraints on the variables and problems in which there are constraints on the variables. Unconstrained optimization problems arise directly in many practical applications; they also arise in the reformulation of constrained optimization problems in which the constraints are replaced by a penalty term in the objective function. Constrained optimization problems arise from applications in which there are explicit constraints on the variables. The constraints on the variables can vary widely from simple bounds to systems of equalities and inequalities that model complex relationships among the variables. Constrained optimization problems can be further classified according to the nature of the constraints (e.g., linear, nonlinear, convex) and the smoothness of the functions (e.g., differentiable or non-differentiable).

Most optimization problems have a single objective function. There are interesting cases when optimization problems have no objective function or multiple objective functions. Feasibility problems are problems in which the goal is to find values for the variables that satisfy the constraints of a model with no particular objective to optimize. Complementarily problems are pervasive in engineering and economics. The goal is to find a solution that satisfies the complementarily conditions. Multi-objective optimization problems arise in many fields, such as engineering, economics, and logistics, when optimal decisions need to be taken in the presence of trade-offs between two or more conflicting objectives. For example, developing a new component might involve minimizing weight while maximizing strength or choosing a portfolio might involve maximizing the expected return while minimizing the risk. In practice, problems with multiple objectives often are reformulated as single objective problems by either forming a weighted combination of the different objectives or by replacing some of the objectives by constraints.

Deterministic Optimization versus Stochastic Optimization

In deterministic optimization, it is assumed that the data for the given problem are known accurately. However, for many actual problems, the data cannot be known accurately for a variety of reasons. The first reason is due to simple measurement error. The second and more fundamental reason is that some data represent information about the future (e. g., product demand or price for a future time period) and simply cannot be known with certainty.

In optimization under uncertainty, or stochastic optimization, the uncertainty is incorporated into the model. Robust optimization techniques can be used when the parameters are known only within certain bounds; the goal is to find a solution that is feasible for all data and optimal in some sense. Stochastic programming models take advantage of the fact that probability distributions governing the data are known or can be estimated; the goal is to find some policy that is feasible for all (or almost all) the possible data instances and optimizes the expected performance of the model.

1.9 CLASSIFICATION OF CONVENTIONAL TECHNIQUES

Classical optimization methods can be classified into two distinct groups:

- (1) Direct search methods and

(2) Gradient based methods.

In Direct search methods only the objective function and the constraint values are used to guide the search strategy. The direct search methods are usually slow, requires many function evaluation for convergence, since the derivative information is not used in the direct search method.

The gradient-based methods use the first –and /or second order derivatives of the objective function and/or constraints to guide the search process. The gradient based methods quickly converge to optimal solution if the objective function and the constraints are differentiable otherwise they fail to obtain even near optimal solution. Hence gradient based methods are not efficient for problems having non-differentiable or discontinuous functions and/ or constraint equations (Rao 2009).

The most common difficulties associated with classical methods are:

- The convergence depends on the chosen initial solution.
- Most of the algorithms tend to get stuck to a sub-optimal solution.

1.10 NON-TRADITIONAL OPTIMIZATION TECHNIQUES

Non-traditional optimization techniques are inspired from nature. They apply nature like processes to solutions, in order to serve as very flexible and robust tools for complex combinatorial optimization problems.

They are a class of approximate methods to search for an optimal solution out of all possible solutions. Some of the examples are Genetic Algorithms (GA) (Goldberg 1989), and Differential Evolution (DE) (Storn *et al* 1997).

1.10.1 GENETIC ALGORITHM

Genetic Algorithm was introduced by Holland in 1975. It is a search technique, which works on similar lines with the concept of Darwin's theory of natural evolution (Goldberg 1989). GA is a random search technique which works on natural selection and breeding. GA efficiently explores a large space of probable designs and find optimum solutions. The power of this algorithm starts from its ability to exploit historical information from previous solution. This is done to increase the performance of next solutions. When compared to traditional continuous optimization techniques GA has significant differences described below.

GA manipulates the coded versions of the parameters instead of the parameters themselves.

All conventional methods search from a single point where as GA operates on a whole population of points. This contributes to the robustness of genetic algorithm. This improves the chance of reaching the global optimum reducing the risk of getting trapped in a local stationary point.

Genetic algorithm does not use any auxiliary information about the objective function value such as derivatives. Therefore, they can be applied to continuous and discrete optimization problem.

GA uses probabilistic transition operators while conventional methods for continuous optimization apply deterministic transition operators. More specifically, the way a new generation is computed from the actual one has some random components.

Working principle of GA

GA maintains a population of individuals that represent candidate solutions. Each individual is evaluated to give some measure of its fitness to the problem from the objective function. In each generation, a new population is formed by selecting the fittest individuals based on a particular selection strategy. Some members of the new population undergo genetic operations to form new solution. The two commonly used operations are crossover and mutation. Crossover is a mixing operator that combines genetic material from selected parents. Mutation acts as a background operator and is used to search the unexplored search by randomly changing the values at one or more positions of the selected chromosome. After several generations, the algorithm converges to the best chromosome, which hopefully represents the

good strings that are already present in the mating pool, not all strings in the mating pool are used in crossover.

Mutation:

A crossover operator is mainly responsible for the search of new strings, even though a mutation operator is also used for this purpose. The mutation operator changes 1 to 0 and vice versa in a bit position with a small mutation probability, p_m . Changing bit with probability p_m can be simulated by choosing a number between 0 to 1 at random. If the random number is smaller than p_m , the randomly selected bit is altered; otherwise the bit is kept unchanged. The need for mutation is to create a point in the neighborhood of the current point, thereby achieving a local search around the current solution. The mutation is also used to maintain diversity in the population. For example, consider the following population having four eight-bit strings:

0 1 1 0 1 1 0 0

0 0 1 0 0 0 1 1

0 1 0 1 1 1 1 1

0 1 1 1 0 0 0 0

Notice that all four strings have a 0 in the left-most position. If the true optimum solution requires 1 in that position, then neither reproduction nor crossover operator described above will be able to create 1 in that position. The inclusion of mutation introduces some probability of turning 0 into 1.

Advantages of GAs :

As seen from the above description of the working principles of GAs, they are radically different from most of the traditional optimization methods. However, the general advantages are described in the following paragraphs.

GAs work with a string-coding of variables instead of the variables. The advantage of working with a coding of variables is that the coding discretizes the search space, even though the function may be continuous. On the other hand, since GAs require only function values at

various discrete points a discrete or discontinuous function can be handled with no extra cost. This allows GAs to be applied to a wide variety of problems.

Another advantage is that the GA operators exploit the similarities in string-structures to make an effective search.

The most striking difference between GAs works with a population of points instead of a single point. Because there is more than one string being processed simultaneously, it is very likely that the expected GA solution may be a global solution. Even though some traditional algorithms are population-based, like Box's evolutionary optimization and complex search methods, those methods do not use previously obtained information efficiently. In GAs, previously found good information is emphasized using reproduction operator and propagated adaptively through crossover and mutation operators. Another advantage with a population-based search algorithm is that multiple optimal solutions can be captured in the population easily, thereby reducing the effort to use the same algorithm many times.

In discussing GA operators or their working principles in the previous section, nothing has been mentioned about the gradient or any other auxiliary problem information. In fact, GAs does not require any auxiliary information except the objective function values.

Although the direct search methods used in traditional optimization methods do not explicitly require the gradient information, some of those methods use search directions that are similar in concept to the gradient of the function. Moreover, some direct search methods work under the assumption that the function to be optimized is unimodal and continuous. In GAs, no such assumption is necessary.

One other difference in the operation of GAs is the use of probabilities in their operators. None of the genetic operators work deterministically. The basic problem with most of the traditional methods is that they use fixed transition rules to move from one point to another. For instance, in the steepest descent method, the search direction is always calculated as the negative of the gradient at any point, because in that direction the reduction in the function value is maximum. In trying to solve a multimodal problem with many local optimum points, search procedures may easily get trapped in one of the local optimum points. But in GAs, an initial random population is

used, to start with, the search can proceed in any direction and no major decisions are made in the beginning.

Later on, when the population begins to converge in some bit positions, the search direction narrows and a near optimal solution is achieved. This nature of narrowing the search space as the search progresses is adaptive and is a unique characteristic of genetic algorithms.

CHAPTER TWO

EXPERIMENTAL WORK

2.1 Equipment and procedure

Experimental Setup

The Microactivity-Reference unit is an automated and computer-controlled laboratory reactor for catalytic microactivity tests. The system consists of a fixed-bed tubular reactor, with the catalyst bed placed inside. The flow inside the reactor is up-down, whereby the reactant mixture is fed through the upper part of the reactor and the reaction products are obtained through the lower part. The reactant gas streams are fed into the reactor by means of a system of mass flow controllers that provide a known and controlled flow of gases. In order to stop the products flowing back through the lines, the controllers are protected with check-valves. Once the gases have been preheated and liquids evaporated, these streams merge and flow to a 6-port valve. This valve is operated by remote pneumatic control through the computer or by means of the touch screen and allows for selecting from two possible alternatives for the flow path: either towards the reactor or rerouting it towards the system's gas outlet (by-passing the reactor). When the flow of reactants is directed towards the reactor, it passes through filters, at both the inlet and outlet of the reactor, thereby protecting the arrangement of valves from possible finely-separated catalyst particles.

The Microactivity-Reference consists of :

- An integrated unit, whose interior houses the hot box and the reaction system, as well as all the system's control elements and valves.
- A pump (optional) for feeding liquids into the reactor.
- A PC

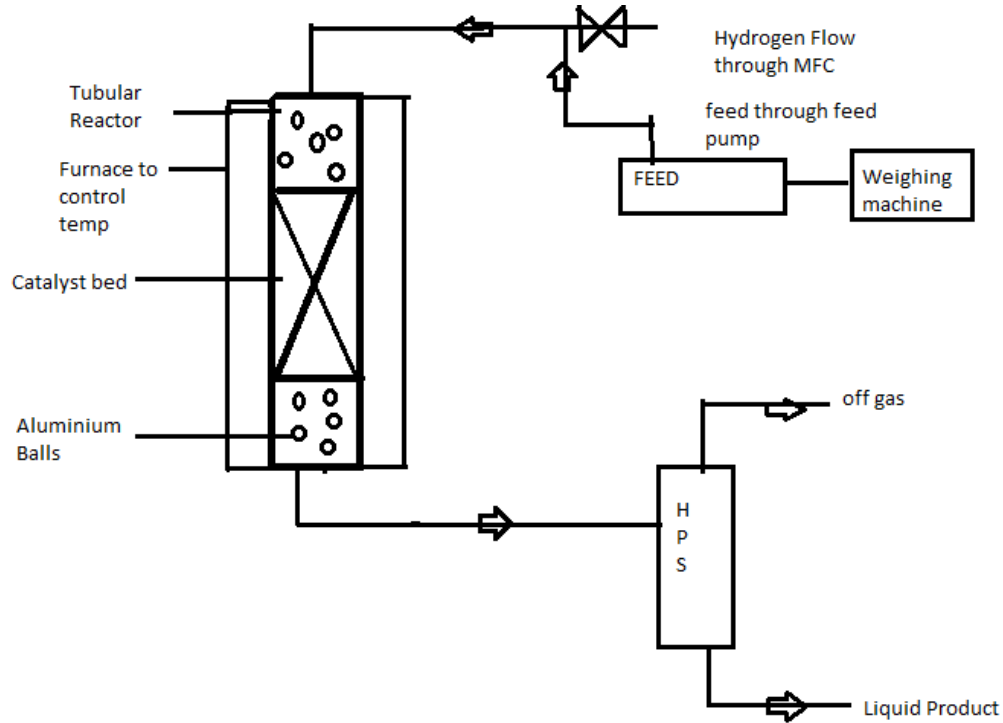


Figure 2.1 :- Experimental setup

THE CONTROLLERS

THE REGULATION PARAMETERS

The Microactivity-Reference unit uses P-I-D controllers for the following control loops:

Reaction temperature: The signal from the thermocouple located in the catalyst bed is analysed by the controller, whose output signal is relayed to a solid-state zero-switching relay that regulates the power supplied to the oven proportionally to the control signal.

Hot box temperature: The signal from the thermocouple located inside the hot box is analysed by the controller, whose output signal is sent to a relay that regulates the power supplied to the box's heater proportionally.

Pressure control: The signal from the pressure transmitter installed upstream of the reactor is analysed by the controller, whereby its output signal determines the position of the pressure control valve.

Level control: The signal from the capacitive level sensor installed in the liquid – gas separator is analysed by the controller, whereby its output signal determines the position of the level control valve located in the base of the separator.

2.2 Materials Used

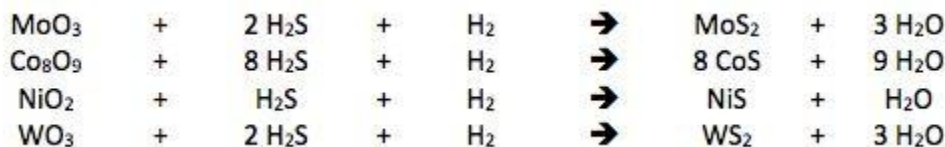
Feed oil

Refinery DHDТ feed was used in all the experiments carried out.

Catalyst

Catalyst used for hydrotreating of diesel was commercial one. Before the actual process of hydrotreating, the catalyst is activated through sulfiding process. The sulfiding process involves passing feed spiked with a sulfiding agent over the catalyst bed in a controlled procedure that includes several temperature holds. As the feed and spiking agent are heated in the presence of hydrogen, the sulfur compound will readily decompose to form the H₂S required to complete the sulfiding reactions.

Catalyst sulfiding involves the following chemical reactions:



2.3 Hydrotreating process conditions

Hydrotreating of atmospheric gas oils has typically been carried out at temperatures between 315 and 400°C, and pressures between 30 and 100 bar. The hydrogen flow is set to be 3-4 times the theoretical required in chemical hydrotreating reaction. The ratio of hydrogen to liquid feed can typically be in the range of 70-1000 Nm³ hydrogen per m³ liquid feed. Contact time between the reaction mixture and the catalyst is expressed in terms of the Liquid Hourly Space Velocity (LHSV), which is defined as the ratio between the volumetric liquid feed flow, v₀, in m³/hr divided by the volume of the catalyst in m³.

2.4 Sample Analysis

Table 2.1 - CHARACTERIZATION OF FEED AND PRODUCT

Characteristics	Method	Instrument	Repeatability
Sulfur	UV	ASTM 6453	±5%
SIMTBP	FID	ASTM D2887	±5%
Nitrogen	chemiluminescence	ASTM4629	±5%
Aromatics	HPLC	ASTM 6591	±5%
H ₂ Content	NMR	WI-AD-47	0.089
PONA	NMR	AD032/NMR06	±10%

Aromatics are further classified into mono, di and poly aromatics. Additional tests carried out on feed and product are density and cetane number.

All NMR spectra has been recorded in a 500 MHZ(in frequency). NMR spectrometer is under optimized condition for quantitative analysis.

/

CHAPTER THREE

Results and Discussions

3.1 OPERATING CONDITIONS

The main purpose of hydrotreating process is to improve the quality of diesel by removing impurities. Diesel consists of impurities which can affect the quality of end product and also it is important to meet environmental specification to be marketable. The effectiveness of DHDT reactions depends on process parameters. In this experimental work, the sensitivity of temperature and pressure are studied towards Sulfur and Aromatics conversion. All other process parameters such as LHSV, hydrogen to oil ratio, feed rate and quality are maintained same.

Following seven sets of experiments were performed by varying temperature and pressure:-

Table 3.1 Details of Experimental Runs

CASE NO.	Temperature	Pressure
1(base case)	T	P
2	$T+\Delta T$	P
3	T	$P-\Delta P$
4	T	$P-2*\Delta P$
5	$T-\Delta T$	P
6	$T-\Delta T$	$P-\Delta P$
7	$T+\Delta T$	$P-\Delta P$

3.2 Effect of operating conditions on removal of impurities

3.2.1 Sulfur removal

Effect of process conditions namely temperature of the reactor and pressure of the reactor is shown in the figure below. It is observed from the figure that with increase in reactor temperature and pressure the concentration of the sulfur in the exit stream decreases. The rate of an irreversible HDS reaction increases with increase in temperature because for an irreversible reaction rate constant increases with increase in temperature, in turn, responsible for smaller concentration of sulfur in the exit stream.

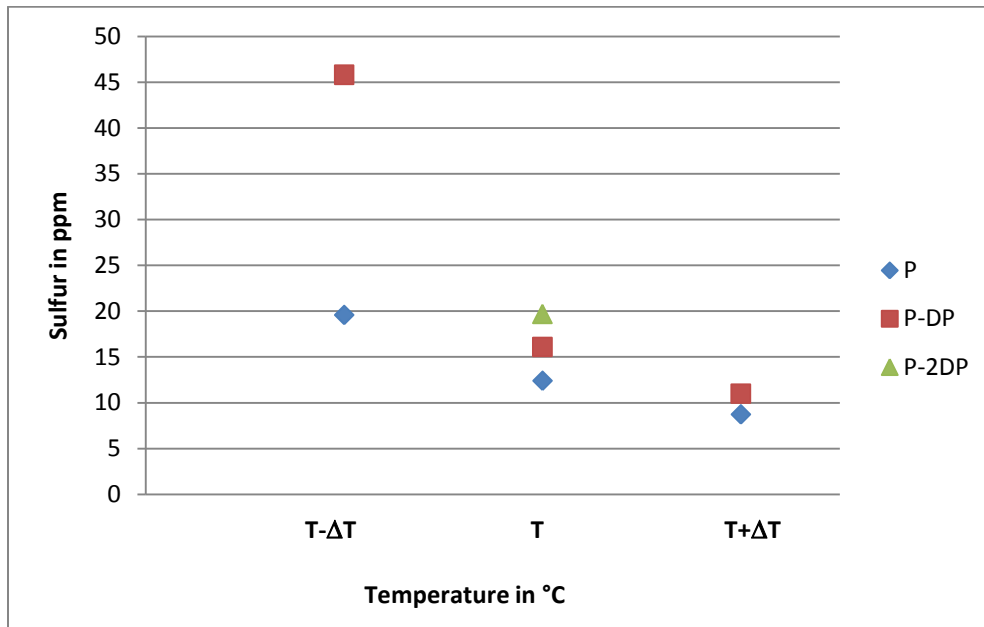


Figure 3.1:-Experimental data variation of sulfur in product with temperature and pressure

3.2.2 Nitrogen removal

The hydrodenitrogenation (HDN) reaction is considered to be one of the hardest HDT reactions owing to the complexity of nitrogen compounds. The rate at which the denitrogenation reaction happens depends upon the saturation rate of aromatic rings. The hydrodenitrogenation reaction increases the hydrogen consumption and the amount of heat generated. The experimental results for HDN reactions showed that the amount of nitrogen decreases with increase in temperature and pressure.

3.2.3 Aromatic conversion

High aromatic content in diesel decreases the cetane value and also contributes to formation of environmentally harmful emissions. Therefore government regulations call for production and use of environmental friendly transportation fuels with lower content of sulfur and aromatics.

It is observed that with increase in operating pressure the conversion of aromatics increases. This is because with increase in pressure the solubility of hydrogen in diesel oil increases which in turn increases the conversion of aromatics. The conversion of aromatics increases with increase in temperature but till certain temperature (360°C) above which it falls sharply. This behavior is explained by the approaching of chemical equilibrium by the reversible hydrogenation reactions of the aromatics at higher temperature.

Conversion is defined as the ratio of reacting amount of component to its initial amount.

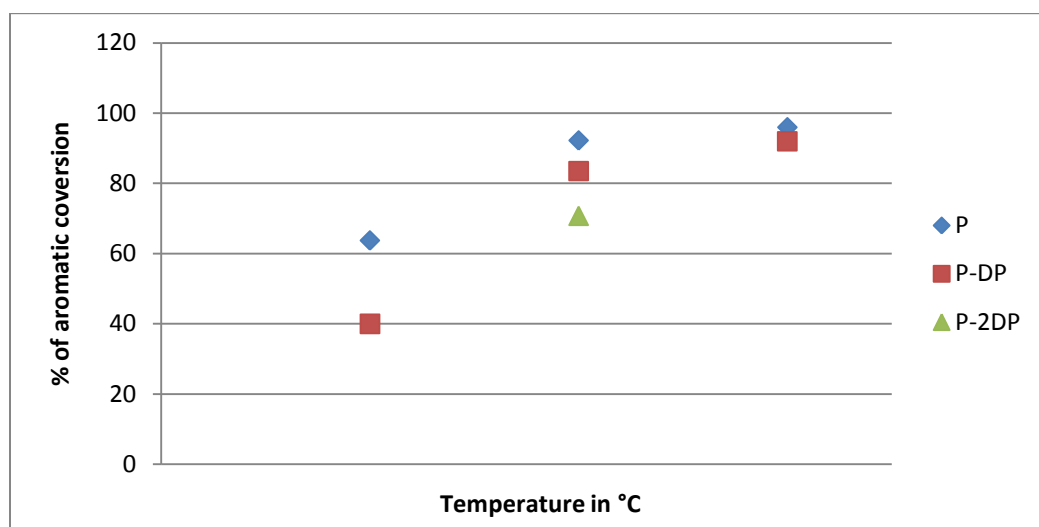


Figure 3.2:- Experimental data variation of aromatic conversion with temperature and pressure

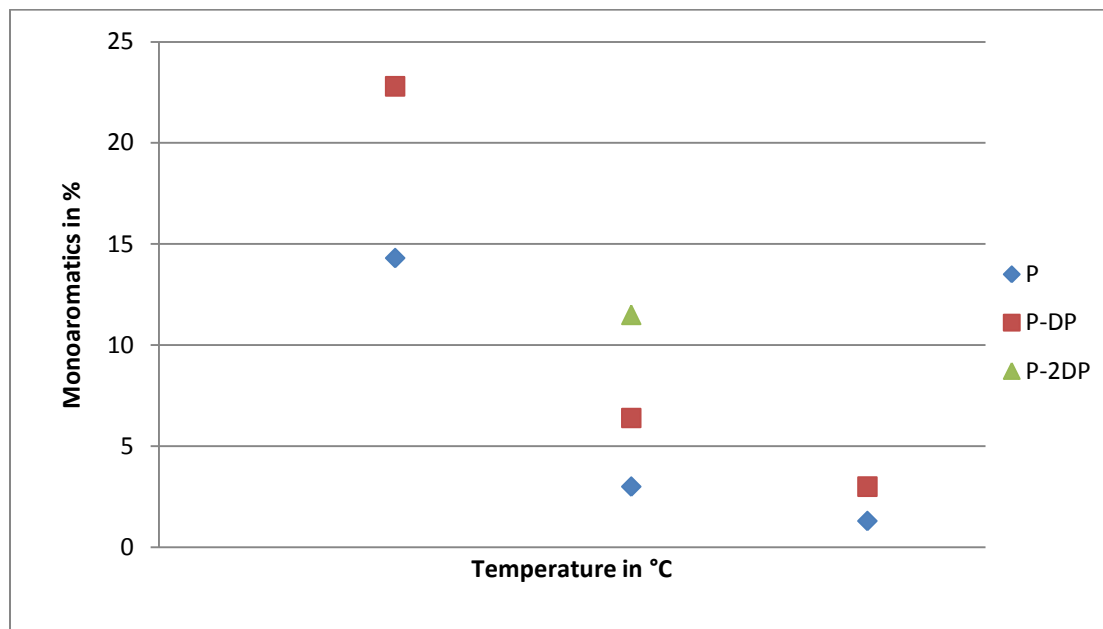


Figure 3.3:- Experimental data variation of mono-aromatics in product with temperature and pressure

It is observed from the graph that with increase in temperature and pressure the amount of mono aromatics decreases leading to saturation.

3.2.4 Hydrogen consumption

Hydrogen is consumed during saturation of olefins and aromatics, hydrodesulphurization, hydrodenitrogenation. Hydrotreating is a process that consumes hydrogen. Therefore hydrogen balance is of significant interest for refiners as its availability dictates operation policy of plants. Hydrogen consumption depends on the properties of feedstock, operating conditions, catalyst and the level of impurities removed. Heavier feedstock requires more hydrogen to reach fixed level of up gradation.

The common approach to calculate hydrogen consumption is by the difference between the hydrogen entering the system and hydrogen leaving the system. Chemical hydrogen consumption is calculated from hydrogen content in feed and product measured through NMR technique. Hydrogen balance is applied to both liquid and gas streams. The application of this method requires data of flow rates of the gas streams entering and leaving the reactor, which are frequently reported in volumetric basis as well as the gas stream composition measured by gas chromatography (GC). Hydrogen is consumed for conversion of sulfur present

in diesel to H_2S , nitrogen to NH_3 and in the hydrogenation of aromatics. Hydrogen consumption is calculated on the basis of feed.

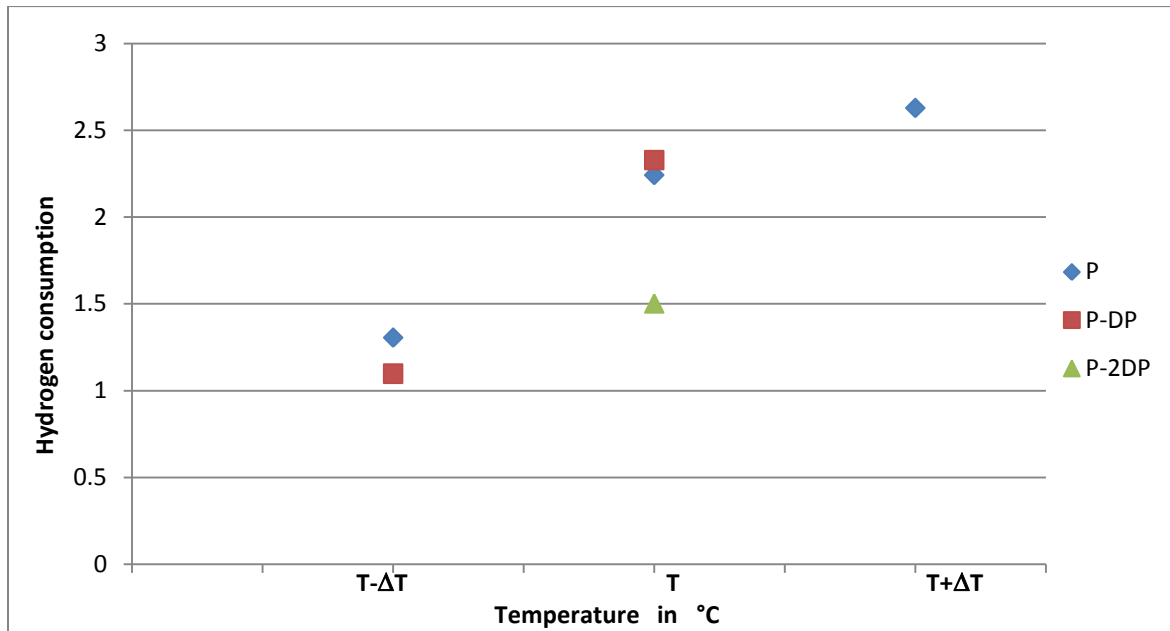


Figure 3.4:- Experimental data variation of Hydrogen consumption with temperature and pressure

Chapter Four

Hydrotreating modeling

Estimation of kinetic parameters is a challenging task because of presence of number of compounds in diesel. It has been investigated that different compounds have different reactivity. When kinetic parameters are estimated the aim is to minimize the error between experimental results and simulated (from mathematical model) results. Experimental data are required to estimate the best kinetic parameters, to validate the model under different operating conditions, to design and predict the expected behavior of crude oil hydrotreating processes with increasing the productivity of oil distillates at commercial or industrial scale, and to facilitate adequate reactor modeling. Although the models reported in the literature were used successfully to describe the behavior of pilot plant reactors, little effort has been made towards scaling up to an industrial reactor. Furthermore, several of the models presented (on different oil fractions and not on full crude oil) have not considered all of the significant reactions taking place in a hydrotreating unit. In the present investigation, efforts are made for developing adequate mathematical models that can account for all of the main reactions, and can simulate the behavior of both pilot plant and commercial scale.

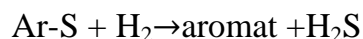
4.1 Parameter estimation

To analyze performances of the physical and chemical systems under different conditions, one has to model these systems. Typically, Physical or chemical systems are modeled mathematically, and the model parameters are estimated using the experimental data. The resulting models then are used for design, scale up, control and optimization purpose. Parameter estimation is a crucial part of the modeling process. Without estimating the model parameters, the system model would be of little use, because it cannot predict the system behavior under different conditions. However, parameter estimation is not a straightforward process at most of the times. First, the model has to be checked for identifiability. A model is structurally identifiable if all the model parameters can be determined uniquely having the ideal data set. Second, the model has to be tested for estimability, which means that the model parameters can be estimated accurately using the current experimental design and data set in hand. Finally, if the model was both identifiable and estimable, the parameters can be estimated without any modifications made

to the model. However, that is not the case most of the times, and model parameters can be unidentifiable, or even identifiable but in-estimatable.

Assumptions used in deriving mathematical model

1. The reactor is operated isothermally under constant temperature and steady-state conditions.
2. The reactor behaves like a plug flow reactor. There is no axial diffusion of concentration and temperature. Their variation along the radial direction within the reactor is neglected.
3. Gas and liquid flows are cocurrent. Gas and liquid velocities are considered constant throughout the reactor. Density of gas and liquid phases along the length of the reactor is assumed to be constant.
4. Evaporation of diesel oil occurs instantaneously only at the entrance of the reactor. The evaporation of the reacting components can be neglected due to their high molecular weights.
5. The aromatics consist of three groups namely mono-, di- and polyaromatics.
6. The desulfurization reaction is considered to be irreversible under normal hydrotreating reactions.



7. Each of the aromatic groups undergoes different hydrogenation reactions that are all reversible under normal hydrogenation conditions.
8. The forward reactions of reversible hydrogenation of aromatics are pseudo first order with respect to aromatics only as the hydrogen has been used in excess. And backward reactions are considered first order with respect to products.

Hydrotreating process is used to reduce sulfur, nitrogen, aromatics and other impurities to meet stringent environmental regulations. Various chemical reaction involved in hydrotreating of diesel are reduction of sulfur (HDS), aromatics (HDS). The untreated diesel feedstock contains large number of organic sulfur compounds, and the overall HDS reaction is usually represented by a single generalized stoichiometric equation, which lumps all the HDS reactions into one expression. It is assumed that concentration of hydrogen and sulfur has positive effect on the rate

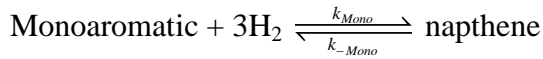
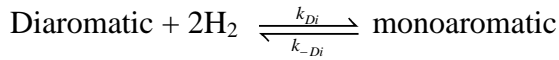
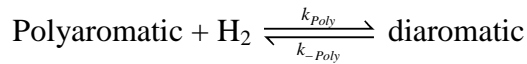
of reaction where as hydrogen sulfide adsorbed on the catalyst inhibits the rate of reaction. The objective function for optimization is summation of square of error between experimental and predicted values of the concentration of sulfur and aromatics. Kinetic parameters are estimated by minimizing the objective function.

Single objective problem is solved using inbuilt subroutine available in MATLAB namely GA and SQP.

Langmuir type rate equation has been considered for desulfurization reaction [22]

$$r_{Ar-S} = \frac{k C_{Ar-S}^{1.6} C_{H_2}^{0.56}}{1 + k_{ad} C_{H_2S}} \quad 4.1$$

The generalized form of hydrogenation reactions of aromatics can be represented in following manner:



$$r_{Poly} = -k_{Poly} C_{Poly} P_{H_2}^{n_3} + k_{-Poly} C_{Di} \quad 4.2$$

$$r_{Di} = -k_{Di} C_{Di} P_{H_2}^{n_2} + K_{-Di} C_{Mono} \quad 4.3$$

$$r_{Mono} = -k_{Mono} C_{Mono} P_{H_2}^{n_1} + K_{-Mono} C_{Naph} \quad 4.4$$

Equilibrium constants are defined as following

$$K_{Poly} = \frac{k_{Poly}}{k_{-Poly}} \quad 4.5$$

$$K_{Di} = \frac{k_{Di}}{k_{-Di}} \quad 4.6$$

$$K_{Mono} = \frac{k_{Mono}}{k_{-Mono}} \quad 4.7$$

As an example optimization routine was carried out using open literature

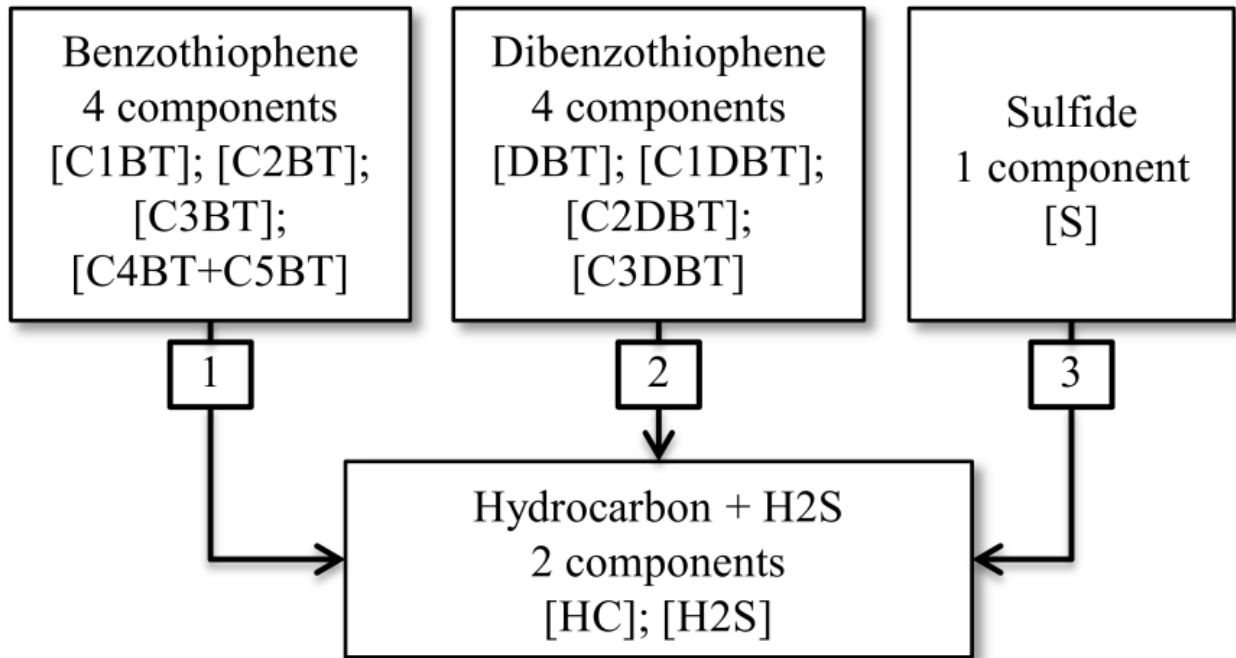


Figure 4.1 - The formalized kinetic scheme of diesel fuel hydrotreating process

Table 4.1 - Molar concentration(mol/l) of components in feed and product of experiment

	Feed(mol/l)	Temperature		
		340°C	360°C	380°C
S	0.00681	0.000546	0.000548	0.000460

C1BT	0.001063	0.00058	0.000054	0.000065
C2BT	0.006313	0.000390	0.0004	0.000474
C3BT	0.010969	0.000686	0.000695	0.000713
(C4+C5)BT	0.011688	0.000688	0.000738	0.000585
DBT	0.00125	0.000094	0.00011	0.000087
C1DBT	0.002750	0.000220	0.000298	0.000203
C2DBT	0.0025	0.000243	0.000326	0.000228
C3DBT	0.000531	0.000148	0.000148	0.000121

Code written in matlab for optimization is coupled with model equations which are first order differential equations with respect to sulfur compounds. Upper and lower bounds are given for every kinetic parameter to be estimated. In this optimization there are three cases here temperature is the operating parameter rest all are kept constant that is pressure and lhsv.

Three different files are created, one is the optimization routine second one is the .out file where user can give inputs such as operating conditions, initial guess of the parameters to be estimated, concentration of compounds in feed and length of the reactor.

Results and conclusion

	From Literature	Estimated (SQP)	Estimated (GA)
S	1.9779	1.9123	1.9149
C1BT	2.1921	2.0000	2.0001
C2BT	2.0512	2.0279	2.0262
C3BT	2.1114	2.0827	2.0717
(C4+C5)BT	2.2975	2.1100	2.1100
DBT	1.9534	2.2446	2.0000
C1DBT	1.9929	2.2147	2.0001
C2DBT	1.8802	2.2062	2.0000
C3DBT	1.1226	2.2417	2.0001

SSE		4.1801 E-07	3.6298 E-07
Tol fun		1E-19	1E-5
TolX(kinetic parameter)		1E-22	1E-5
No. of iterations		18	4

GA is more time consuming as compared to SQP. But GA has an advantage that it does not require initial guess of the parameter to be estimated.

APPENDIX

MATLAB CODES

```
function bestk = kpe_examp()
%one exp ,9 response
%this will be no.of cases * no. of lumps
%it will be equal to number of lumps
% Initial values for the 9 components present in feed
% Initial guess
A=[];
b=[]';
Aeq=[];beq=[]';

% Set up optimization
fileID=fopen('scanfcode_input.out','r');
formatSpec='%f';
Lreact =fscanf(fileID,formatSpec,1)
nlump =fscanf(fileID,formatSpec,1)
cases =fscanf(fileID,formatSpec,1)
nvars =fscanf(fileID,formatSpec,1)
formatSpec='%f %f %f %f %f %f %f %f %f';
sizelb =[9 1];
lb =fscanf(fileID,formatSpec,sizelb)
sizeub =[9 1];
ub =fscanf(fileID,formatSpec,sizelb)
sizek0 =[9 1];
k0 =fscanf(fileID,formatSpec,sizek0)
sizeT =[3 1];
T =fscanf(fileID,formatSpec,sizeT)
sizeexpY =[9 3];
expY =fscanf(fileID,formatSpec,sizeexpY)
sizez0 =[9 1];
z0 =fscanf(fileID,formatSpec,sizez0)
sizeLSpan =[2 1];
```

```

LSpan      =fscanf (fileID,formatSpec,sizeLSpan)

fclose(fileID);
lb=lb'
ub=ub'
k0=k0'
T=T'
expY=expY'
z0=z0'
LSpan=LSpan'

disp('k0=')
disp(k0)
disp('expY=')
disp(expY)
%x means updating of kinetic parameters
myObjective = @(x) objFcn(x, Lreact, expY,LSpan,z0,T,cases,nlump);
options = optimset('Algorithm','SQP','Display','iter');
[k,feval]=fmincon(myObjective,k0,A,b,Aeq,beq,lb,ub,@nonlcon,options)

function cost = objFcn(x, Lreact, expY,LSpan,z0,T,cases,nlump)
for i=1:3
    Temp=T(i);
    disp('Temp=')
    disp(Temp)
ODE_Sol = ode45(@(L,z)updateStates(L,z,x,Temp), LSpan, z0);
simY = deval(ODE_Sol, Lreact);
simY=simY'
%disp('simY=')
    % disp(simY)
for j=1:nlump
    %disp('simY(j)=')
    %disp(simY(j))
    simP(i,j)=simY(j);
    % disp('simY(i,j)=')
    % disp(simY(i,j))

```

```

    end
end
m=cases;
%no of rows = no.of cases
n=nlump;
%no of coumns = no of lumps
cost=0;
for i=1:m
    for j=1:n
        cost=cost+(simP(i,j)- expY(i,j))^2;
    end
end
%cost = (simY(1)-expY(1))^2+(simY(2)-expY(2))^2+(simY(3)-expY(3))^2+(simY(4)-
expY(4))^2+(simY(5)-expY(5))^2+(simY(6)-expY(6))^2+(simY(7)-
expY(7))^2+(simY(8)-expY(8))^2+(simY(9)-expY(9))^2;

function [C,Ceq]=nonlcon(x)
C=[];      % no nonlinear inequality constraint
Ceq=[];    % no nonlinear equality constraint

```

Function file saved as updatestates.m

```

function f = updateStates(L, z, k,Temp)
%disp('Temp in fun=')
%disp(Temp)
f(1,1) = -k(1)*exp(-2.11/Temp)*z(1);
f(2,1) = -k(2)*exp(-11.534/Temp)*z(2);
f(3,1) = -k(3)*exp(-6.591/Temp)*z(3);
f(4,1) = -k(4)*exp(-9.598/Temp)*z(4);
f(5,1) = -k(5)*exp(-27.17/Temp)*z(5);
f(6,1) = -k(6)*exp(-15.23/Temp)*z(6);
f(7,1) = -k(7)*exp(-17.69/Temp)*z(7);
f(8,1) = -k(8)*exp(-32.655/Temp)*z(8);
f(9,1) = -k(9)*exp(-46.59/Temp)*z(9);
%disp('z(1)=')

```

Results

>> dhdsscancode

Lreact = 1.3500

nlump = 9

cases =3

nvars = 9

lb =

1

2

2

2

2

2

2

2

2

ub =

2.0000

2.1100

2.1100

2.1100

2.1100

2.3300

2.3300

2.3300

2.3300

k0 =

1.9000

2.0300

2.0300

2.0300

2.0300

2.2500

2.2500

2.2500

2.2500

T =

613

633

653

expY =

1.0e-03 *

0.5460 0.5480 0.4600

0.5800 0.0540 0.0650

0.3900 0.4000 0.4740

0.6860 0.6950 0.7130

0.6880 0.7380 0.5850

0.0940 0.1100 0.0870

0.2200 0.2980 0.2030

0.2430 0.3260 0.2280

0.1480 0.1480 0.1210

z0 =

0.0068

0.0011

0.0063

0.0110

0.0117

0.0013

0.0027

0.0025

0.0005

LSpan =

0

1.3500

lb = 1 2 2 2 2 2 2 2 2

ub = 2.0000 2.1100 2.1100 2.1100 2.1100 2.3300 2.3300 2.3300 2.3300

k0 = 1.9000 2.0300 2.0300 2.0300 2.0300 2.2500 2.2500 2.2500 2.2500

T = 613 633 653

expY = 1.0e-03 *

0.5460 0.5800 0.3900 0.6860 0.6880 0.0940 0.2200 0.2430 0.1480

0.5480 0.0540 0.4000 0.6950 0.7380 0.1100 0.2980 0.3260 0.1480

0.4600 0.0650 0.4740 0.7130 0.5850 0.0870 0.2030 0.2280 0.1210

z0 = 0.0068 0.0011 0.0063 0.0110 0.0117 0.0013 0.0027 0.0025 0.0005

LSpan = 0 1.3500

k0 = 1.9000 2.0300 2.0300 2.0300 2.0300 2.2500 2.2500 2.2500 2.2500

expY =

1.0e-03 *

0.5460 0.5800 0.3900 0.6860 0.6880 0.0940 0.2200 0.2430 0.1480

0.5480 0.0540 0.4000 0.6950 0.7380 0.1100 0.2980 0.3260 0.1480

0.4600 0.0650 0.4740 0.7130 0.5850 0.0870 0.2030 0.2280 0.1210

Temp = 613

simY = 1.0e-03 * [0.5287 0.0722 0.4195 0.7387 0.8495 0.0646 0.1438 0.1403 0.0318]

Temp= 633

simY = 1.0e-03 *[0.5285 0.0721 0.4192 0.7377 0.8464 0.0644 0.1434 0.1397 0.0316]

Temp= 653

simY = 1.0e-03 *[0.5284 0.0720 0.4188 0.7368 0.8435 0.0643 0.1430 0.1390 0.0314]

Temp= 613

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Norm of First-order

Iter	F-count	f(x)	Feasibility	Steplength	step optimality
------	---------	------	-------------	------------	-----------------

0	10	5.026976e-07	0.000e+00		1.156e-06
---	----	--------------	-----------	--	-----------

Temp=613

simY = 1.0e-03 * [0.5287 0.0722 0.4195 0.7387 0.8495 0.0646 0.1438 0.1403 0.0318]

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Temp= 653

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Temp= 613

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Temp= 633

simY=1.0e-03 *[0.5285 0.0721 0.4192 0.7377 0.8464 0.0644 0.1434 0.1397 0.0316]

Temp= 653

simY = 1.0e-03 * [0.5284 0.0720 0.4188 0.7368 0.8435 0.0643 0.1430 0.1390 0.0314]

1 20 5.026961e-07 0.000e+00 1.000e+00 1.197e-06 1.156e-06

Local minimum possible. Constraints satisfied.

fmincon stopped because the size of the current step is less than

the default value of the step size tolerance and constraints are

satisfied to within the default value of the constraint tolerance.

<stopping criteria details>

k=[1.9000 2.0300 2.0300 2.0300 2.0300 2.2500 2.2500 2.2500 2.2500]

feval = 5.0270e-07

with GA results

k=[1.9149 2.0001 2.0262 2.0717 2.1100 2 2.0001 2 2.0001]

feval =3.6354e-07

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