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**MODELLING AND OPTIMISATION OF OXIDATIVE
DESULPHURIZATION PROCESS FOR MODEL
SULPHUR COMPOUNDS AND HEAVY GAS OIL**

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**MODELLING AND OPTIMISATION OF OXIDATIVE
DESULPHURIZATION PROCESS FOR MODEL
SULPHUR COMPOUNDS AND HEAVY GAS OIL**

Determination of Rate of Reaction and Partition Coefficient via Pilot Plant
Experiment; Modelling of Oxidation and Solvent Extraction Processes;
Heat Integration of Oxidation Process; Economic Evaluation of the Total
Process

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Keywords: Desulphurization, model sulphur compounds, heavy gas oil, oxidation, liquid-liquid extraction, partition coefficient, heat integration, solvent recovery, process economics

Abstract

Heightened concerns for cleaner air and increasingly more stringent regulations on sulphur content in transportation fuels will make desulphurization more and more important. The sulphur problem is becoming more serious in general, particularly for diesel fuels as the regulated sulphur content is getting an order of magnitude lower, while the sulphur contents of crude oils are becoming higher. This thesis aimed to develop a desulphurisation process (based on oxidation followed by extraction) with high efficiency, selectivity and minimum energy consumption leading to minimum environmental impact via laboratory batch experiments, mathematical modelling and optimisation.

Deep desulphurization of model sulphur compounds (di-n-butyl sulphide, dimethyl sulfoxide and dibenzothiophene) and heavy gas oils (HGO) derived from Libyan crude oil were conducted. A series of batch experiments were carried out using a small reactor operating at various temperatures (40 – 100 °C) with hydrogen peroxide (H₂O₂) as oxidant and formic acid (HCOOH) as catalyst. Kinetic models for the oxidation process are then developed based on ‘total sulphur approach’. Extraction of unoxidised and oxidised gas oils was also investigated using methanol, dimethylformamide (DMF) and N-methyl pyrrolidone (NMP) as solvents. For each solvent, the ‘measures’ such as: the partition coefficient (K_p), effectiveness factor (K_f) and extractor factor (E_f) are used to select the best/effective solvent and to find the effective heavy gas oil/solvent ratios.

A CSTR model is then developed for the process for evaluating viability of the large scale operation. It is noted that while the energy consumption and recovery issues could be ignored for batch experiments these could not be ignored for large scale operation. Large amount of heating is necessary even to carry out the reaction at 30-40 °C, the recovery of which is very important for maximising the profitability of operation and also to minimise environmental impact by reducing net CO₂ release. Here the heat integration of the oxidation process is considered to recover most of the external energy input. However, this leads to putting a number of heat exchangers in the oxidation process requiring capital investment. Optimisation problem is formulated using gPROMS modelling tool to optimise some of the design and operating parameters (such as reaction temperature, residence time and splitter ratio) of integrated process while minimising an objective function which is a coupled function of capital and operating costs involving design and operating parameters. Two cases are studied: where (i) HGO and catalyst are fed as one feed stream and (ii) HGO and catalyst are treated as two feed streams.

A liquid-liquid extraction model is then developed for the extraction of sulphur compounds from the oxidised heavy gas oil. With the experimentally determined K_p multi stage liquid-liquid extraction process is modelled using gPROMS software and the process is simulated for three different solvents at different oil/solvent ratios to select

the best solvent, and to obtain the best heavy gas oil to solvent ratio and number of extraction stages to reduce the sulphur content to less than 10 ppm.

Finally, an integrated oxidation and extraction steps of ODS process is developed based on the batch experiments and modelling. The recovery of oxidant, catalyst and solvent are considered and preliminary economic analysis for the integrated ODS process is presented.

Dedication

Dedicated to
My Parents, Wife
Brothers, Sisters
And
My Kids

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Nomenclature

A_r	Arrhenius factor, min^{-1}
A_C	Heat transfer area for cooler, m^2
A_E	Heat transfer area for exchanger, m^2
A_H	Heat transfer area for heater, m^2
A_t	Total heat transfer area, m^2
C_{A0}	Initial concentration of component A, mole/m^3
C_A	Concentration of component A at any time, mole/m^3
C_0	initial concentration of sulphur, ppm
C_S	Concentration of sulphur at any time, ppm
C_R	Cost of reactor, \$/yr
C_E	Cost of exchanger, \$/yr
C_{OP}	Operating cost, \$/yr
C_{PU}	Pumping cost, \$/yr
C_{PH2}	Heat capacity of oxidant, J/kg K
C_{PH}	Heat capacity of heavy gas oil, J/kg K
C_{PF}	Heat capacity of catalyst, J/kg K
C_{Pw}	Heat capacity of water, J/kg K
C_{TR}	Total cost of CSTR process, \$
d_s	Diameter of the separator, m
d_e	Diameter of the extractor, m
D_S	The percent desulphurization
H_t	Tray spacing, m
H_{min}	The additional column height, m
E_a	Activation energy, kJ/mol
e_0	Tray efficiency

E_f	Extraction factor
F_{A0}	Molar feed rate of component A, mole/hr
F	Feed flow rate, kg/hr
k	Reaction rate constant, min^{-1}
K_f	Solvent effectiveness
K_P	Partition coefficient
L	Length of the separator, m
M_S	Amount of steam, Kg/hr
M_w	Amount of water, kg/hr
M_{WS}	Molecular weight of the solvent, kg/mol
M_{Wmix}	Molecular weight of the mixture, kg/mol
N_A	Moles of reacting A
N_s	Number of stages
nc	number of compound
Q_C	Heat duty of cooler, kJ
Q_E	Heat duty of exchanger, kJ
Q_H	Heat duty of heater, kJ
Q_R	Heat recovery, kJ
Q_t	Total heating, kJ
R	Universal gas constant, J/mol k
S	Solvent flow rate, kg/hr
S_r	Splitter ratio
T_{F0}	Feed temperature, K
T_{F1}	Inlet temperature to heater (H1), K
T_{F2}	Inlet temperature to heater (H2), K
T_{F3}	Inlet temperature to heater (H3), K

T_O	Outlet temperature from exchanger (E1), K
T_{O1}	Outlet temperature from exchanger (E2), K
T_P	Temperature of product, K
T_r	Reaction temperature, K
T_W	Water temperature, K
T_S	Steam temperature, K
U_C	Over all heat transfer coefficient for cooler, W/m ² k
U_E	Over all heat transfer coefficient for exchanger, W/m ² k
U_H	Over all heat transfer coefficient for heater, W/m ² k
V	Volume of reactor, m ³
V_{HS}	Heavy gas oil loses, m ³
V_{OH}	Volumetric flow rate of heavy gas oil, m ³ /hr
V_{OH2}	Volumetric flow rate of oxidant, m ³ /hr
V_{OF}	Volumetric flow rate of catalyst, m ³ /hr
x	Conversion, %
X	Concentration of sulphur in the raffinate phase, mass ratio
Y	Concentration of sulphur in the extract phase, mass ratio

Greek letters:

ρ_D	Density of DMF, kg/m ³
ρ_M	Density of methanol, kg/m ³
ρ_N	Density of NMP, kg/m ³
ρ_H	Density of heavy gas oil, kg/m ³
ρ_{H2}	Density of oxidant, kg/m ³
ρ_F	Density of catalyst, kg/m ³

ρ_S	Density of the inlet solvent, kg/m ³
ΔT_{lm}	log mean temperature different
τ	Residence time, min
λ	Latent heat, kJ/kg
δ	Hildebrand solubility parameter

Abbreviations

AcOH	Acetic acid
ADS	Desulphurization by Adsorption
BDH	British Drug Hose
BDS	Biodesulphurisation
CED	Conversion Extraction Desulphurization
COS	Carbonyl Sulphide
CS	Cost saving
CSTR	Continuous Stirred Tank Reactor
DBDS	Dibutyl disulfide
DBT	Dibenzothiophene
DBTs	Dibenzothiophenes
DBDS	Dibutyl disulfide
DCA	Photosensitizer-9, 10-Dicyanoanthracene
DMF	Di-methyl Formamide
DMSO	Di-methylsulfoxide
DOE	Department of Energy
EDXRF	Energy-Dispersive X-Ray Fluorescence
EPA	Environmental Protection Agency
ES	Energy saving
FCC	Fluidized Catalytic Cracking
FP	Final Product
FT-IR	Fourier Transfer-Infra Red
gPROMS	general Process Modelling System
HDS	Hydrodesulphurization
HBP	2-hydroxybiphenyl

HCO	Heavy Cycle Oil
HEN	Heat Exchanger Network
HGO	Heavy Gas Oil
HP	Hydrogen Peroxide
LCO	Light Cycle Oil
LLE	Liquid-Liquid Extraction
LMTD	Log Mean Temperature Difference
MeCN	N-octane/acetonitrile
NAE	Nonlinear Algebraic Equation
NHT	Naphtha Hydro-Treating
NMP	N-methyl pyrrolidone
OATS	Olefinic Alkylation of Thiophenic Sulphur
OCR	Oxidant and Catalyst Recovery
ODS	Oxidative Desulphurization
ODE	Ordinary Differential Equation
OS	Oxidised Sulphur
PPM	Part Per Million
PT	Pinch Technology
SR	Solvent Recovery
TBHP	Tetrt-Butyl Hydro Per oxide
TMF	Total Mass Flow rate
TNF	2, 4, 5, 7 Tetranitro-9-Fluoren
TPA	Tungsto Posphoric Acid

List of Papers Published from this Work

1. Khalfalla, H.A., Mujtaba, I.M., El-Garni, M. and El-Akrami, H., 2007. Experimentation, Modelling and Optimisation of Oxidative Desulphurization of Heavy Gas Oil: Energy Consumption and Recovery Issues. *Chemical Engineering Transactions*, 11, pp. 53-58.
2. Khalfalla, H.A., Mujtaba, I.M., El-Garni, M. and El-Akrami, H., 2008. Optimisations with Energy Recovery for Oxidative Desulphurization of Heavy Gas Oil, In *Computer Aided Chemical Engineering*, vol. 25, Elsevier, pp.859-864, Eds. B. Braunschweig and X. Xoulia.
3. Khalfalla, H.A., Mujtaba, I.M., El-Garni, M. and El-Akrami, H., 2009. Oxidative Desulphurization of Heavy Gas Oil: Experimentation, Modelling and Optimisation of Extraction Step using gPROMS. Accepted in the 19th European Symposium on Computer Aided Process Engineering-ESCAPE19, Cracow, Poland 14-17 Jun 2009.

Chapter One

Introduction

1.1 Introduction

Energy production is one of the most pressing issues of modern times. Economic activity and energy usage are intimately linked. The production of useful goods and services require energy and more global economic output requires more energy usage. World energy usage increased by an average of 1.7% annually from 1997-2007 (Stacy et al., 2008). Over the coming decades, estimates of investment requirements in the energy sector are on an enormous scale never seen before. Published investment requirements total USD 20 trillion over the next 25 years and are likely to be considerably greater by 2050 (WEC, 2007). Although the percentage of energy obtained from fossil fuels declined over the same period, the share of world energy from fossil fuels is still over 82%, half of which comes from petroleum.

Unfortunately, the predominant modern technique for producing energy, the burning of fossil fuels, has a severe impact on the global environment. Some of this impact is the result of impure fuels. Sulphur is present in various organic and inorganic compounds that are naturally present in fossil fuels. When these compounds are oxidised in the combustion process, sulphur oxide gases are formed. These gases react with water in the atmosphere to form sulphates and acid rain which damages buildings, destroys automotive, paint finishes, forests and crops, changes the makeup of soil, ultimately leading to changes in the natural variety of plants and animals in an ecosystem (U.S. EPA, 2004). Sulphur emissions also cause respiratory illnesses, aggravate heart disease, trigger asthma and contribute to the formation of atmospheric particulates (Gokhale and Khare, 2004).

Electric utilities and other industrial sources are not the only source for atmospheric sulphur. Automobiles are also adversely affected by sulphur compounds. Sulphur levels in automotive fuels have a profound effect on the efficacy of catalytic converters. Sulphur affects these emission control devices by strongly adsorbing to the precious metal catalysts, preventing the adsorption and reaction of hydrocarbons, nitrogen oxides, and carbon monoxide. The EPA estimates that reducing sulphur levels from 400 ppm to 50 ppm reduces emissions of hydrocarbons by 45.9%, NO_x by 7.01%, and CO by 31.12%. Obviously, emissions of SO_x are also reduced by an amount equivalent to the sulphur reduction. The US national average sulphur level in automotive fuel in 2006 was 30 ppm (U.S. EPA, 1999).

Producing energy in a clean and responsible manner can be accomplished in a number of ways. The use of non-fossil fuel energy sources such as biofuel, solar, wind, and nuclear power will eventually replace fossil fuels. However, many of these technologies will require many years before they are able to provide the amounts of energy needed.

However, biofuel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable biological sources such as vegetable oils and animal fats. The remaining challenges are its cost and limited availability of fat and resources. With the increase in global human population, more land may be needed to produce food for human consumption. The problem already exists in Asia and the same trend will eventually happen in the rest of the world. The average prices of wheat, corn and soybeans raised by 136 %, 125 % and 107 % respectively, due in large part to both rising global populations and push for biofuels (Fangrui and Milford 1999). From this point of view, biofuel can be used as a supplement to other energy forms but not as primary source.

In the immediate future, fossil fuel-based energy production will continue, and new technologies need to be developed in order to produce clean fuels to power our societies.

1.2 Fuel Sulphur Specifications

Both the EPA (Environmental Protection Agency) and department of energy (DOE) have recommended significantly reduce the level of sulphur in gasoline and diesel fuels for meeting lower vehicle emission standards in the United States by 2007. In United States, EPA regulations will limit gasoline sulphur levels to 30 ppm and diesel sulphur levels to 15 ppm by 2006 (U.S. EPA, 1999; U.S. EPA, 2004).

The European has passed legislation to reduce sulphur levels in both gasoline and diesel to 50 ppm in 2005 and to 10 ppm in 2009 (DEPC, 2001). In Japan, sulphur levels in gasoline and diesel lows limited to 50 ppm by 2005 and further to 10 ppm by 2007, while more legislative action is forecasted for the near further (Eika, 2008).

1.3 Petroleum Refining

A typical petroleum refinery is a complex chemical processing and manufacturing plant, with crude oil feedstock going in and refined products. Refining begins by fractionating (distilling) crude oil into a series of streams with defined boiling ranges. Table 1.1 shows some of the fractions and their boiling ranges.

Fuels, including gasoline, diesel, and kerosene, are the most valuable products from petroleum. To enhance the quantity of these fuels produced from a single barrel of crude, heavier streams are cracked, or broken down into smaller molecules. The Fluid Catalytic Cracking (FCC) unit remains the primary hydrocarbon conversion unit in the modern petroleum refinery. The profitability of the FCC process depends largely on the type of feed being processed and the FCC catalyst employed.

Table 1.1 Petroleum distillate fractions and their boiling points (Pafko, 2000)

Distillate Fraction	Boiling Point (⁰C)	Carbon Number
Gases / LPG	<30	1-4
Straight-run gasoline	30-210	5-12
Naphtha	100-200	8-12
Kerosene	150-250	11-13
Diesel and fuel oil	160-400	13-17
Atmospheric gas oil	220-345	17-20
Heavy gas oil	315-540	20-45
Atmospheric residue	>450	30+
Vacuum residue	>615	60+

FCC typically utilizes a solid acid zeolite catalyst, often promoted with rare earth metals in a fluidized bed. Large molecules are broken down to create additional material in the naphtha range in order to produce more gasoline, a valuable product. The “cracked naphtha” stream often contains larger amounts of sulphur than virgin naphtha, since much of the sulphur in crude is in the form of heavy polynuclear aromatic molecules present in the FCC feed stream (Harding et al., 2001).

Two additional processes are used to improve the quality of the resulting fuels, particularly gasoline (Catalytic reforming and Alkylation processes). Reforming takes straight chain hydrocarbons in the C₆ to C₈ range from the gasoline or naphtha fractions and rearranges them into compounds containing benzene rings. Hydrogen is produced as a by-product of the reactions. Reforming uses Pt based catalysts to isomerise linear paraffin, such as *n*-hexane, to higher octane number branched paraffin like 2, 3-dimethylbutane. Pt supported on chlorided alumina, sulphated zirconia, and zeolites are all used (Fowler; Boock, 2002), the support alters the activity of the catalyst, with alumina being most active and zeolites being least active. However, high activity

catalysts are more susceptible to poisoning by sulphur and water (Fowler; Boock, 2002). Removal of sulphur compounds before reforming gasoline streams is therefore required.

The second process used to improve the quality of gasoline is alkylation process which involves the combination of small hydrocarbon molecules into larger molecules. Alkylation reacts *n*-butene with isobutane to create 2,2,4-trimethylpentane, also called isooctane, and other branched paraffin (Ackerman et al., 2002). Alkylation also uses an acid catalyst, but due to excessive coking, only liquid acid catalysts are currently used. Alkylation reactors blend either sulphuric or hydrofluoric acid with the butane/isobutene stream to create alkylate, a high quality gasoline that is blended into other gasoline streams.

The last major process used in oil refining is hydrotreating, or hydrodesulphurization (HDS). Crude petroleum typically contains from 0.1 wt% to 3.0 wt% sulphur, depending on the source. Table 1.2 shows the distribution of some aromatic sulphur species found in petroleum by boiling point. The most common light sulphur species, in “gasoline-range sulphur” (Table 1.2) are methane-, ethane-, and *t*-butanethiol, dimethyl sulphide, carbonyl sulphide (COS), and tetrahydrothiophene (Firor; Quimby, 2003).

1.3.1 Hydrodesulphurization Process

The hydrodesulphurization process (HDS) has been well established in refineries for many years and has supplied the bulk of the sulphur removal requirements for oil-derived fuels. HDS is a catalytic process that converts organic sulphur by reacting crude oil fractions with hydrogen to hydrogen sulphide gas that is then converted to elemental sulphur in Claus plant. HDS process is the primary desulphurization technology used

today (Shiflett; Krenzke, 2002). Most HDS operations also remove nitrogen compounds and some metal impurities.

Table 1.2 Aromatic sulphur species found in petroleum (Shiflett and Krenzke, 2002)

Sulphur Species	Boiling Point (⁰C)
Gasoline-range sulphur	218
Benzothiophene	221
C ₁ -benzothiophenes	221-260
C ₂ -benzothiophenes	260-279
C ₃ -benzothiophenes	279-307
C ₄₊ -benzothiophenes	307-332
Dibenzothiophene	334
C ₁ -dibenzothiophenes	335-363
2C ₂ -dibenzothiophenes	363-382
4,6-dimethyldibenzothiophenes	366
C ₃₊ -dibenzothiophenes	382

The operating conditions for the HDS reactor are 300-450°C and 35-270 bar depending upon the feed and level of desulphurization required (Gates et al., 1979). However, under these harsh conditions, olefins are also hydrogenated, leading to a loss of octane rating and excess hydrogen consumption. Under mild HDS conditions, H₂S can react with olefins in the reactor to create recombinant mercaptans which are linear or branched thiols of typically 5-12 carbons. An example of this reaction is shown in Figure 1.1. By far, the most common catalysts used in HDS are cobalt or nickel promoted molybdenum sulphide (Gates et al., 1979; Shiflett; Krenzke, 2002). The development of improved catalysts for HDS is the focus of virtually all research in HDS.

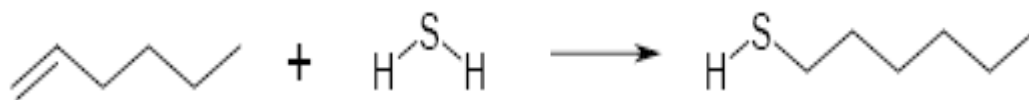


Figure 1.1: Recombination reaction producing an alkanethiol in HDS reactor

The effectiveness of HDS process depends on the type of sulphur compounds. The organic sulphur compounds in the lower-boiling fractions of petroleum, e.g., the gasoline range, are mainly thiols (RSH), sulphides (RSR) and disulfide (RSSR), which are relatively easy to remove in an inexpensive process. However, middle-distillate fractions, e.g., the diesel and fuel oil range, contain significant amounts of benzothiophenes and dibenzothiophenes (DBTs), which are considerably more difficult to remove by this process. Particularly, the strictly hindered ones, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene are the most resistant compounds in the current HDS processes (Table 1.2) and they retard the rate of HDS (Kabe et al., 1992; Baird et al., 2003).

Most of the sulphur contamination in diesel can be traced to the dibenzothiophene derivatives. In order to remove these compounds by HDS, it would require more hydrogen capacity and maintenance of high temperature and pressure for longer contact time. This would increase operating costs and enhance the likelihood that complete saturation of olefins and aromatics will occur resulting in losses of hydrocarbons. Thus, it is likely that HDS processing has reached a stage where increasing temperature and pressure are not economically justified to remove the residual sulphur without affecting the yield of diesel fuel from hydrotreatment processes (Yelda et al., 2002). This process also produces increased volumes of H₂S. Although HDS processes have dominated desulphurization of petroleum in the past, their cost and the requirements of strict fuel

specifications combine to motivate the development of innovative new technologies. A detailed explanation of HDS process is given in Chapter Two.

1.3.2 Oxidative Desulphurization Process

The ultra desulphurization of fuel has drawn increasing attention for new regulations requiring (<10 ppm sulphur) and it is difficult or very costly to use hydrodesulphurization process (as mentioned in the previous section) for reducing the sulphur in the fuels to less than 10 ppm.

In order to meet the new regulation, various alternative deep desulphurization approaches have been extensively investigated in the past few years, including metabolism of sulphur compounds using microbe, selective adsorption, and oxidative desulphurization. Among these new processes, oxidative desulphurization (ODS) appears to be particularly promising and is currently receiving growing attention (Gray et al., 2003; Chen et al., 2004; Garcia-Ochoa et al., 2004).

Oxidative desulphurization is based on the removal of heavy sulphides, usually in the form of polynuclear aromatics where one ring is a thiophene structure. In ODS, these compounds are oxidised by adding one or two oxygen atoms to the sulphur without breaking any carbon-sulphur bonds, yielding the sulfoxide and sulphones, respectively. These oxidised compounds can then be effectively extracted or adsorbed from down stream processing.

An ODS process has the significant advantage over HDS, namely the sulphur compounds that are the most difficult to reduce by HDS are the most reactive for ODS. In effect, the ODS process has the reverse order of reactivity as compared to the HDS process. This effect arises because the reactivity of sulphur compounds for oxidation is augmented with an increase of electron density on the sulphur atom (Otsuki et al.,

2000). The electron donating properties of methyl groups on the aromatic rings positively influences DBT derivatives and the one with the most electron rich sulphur atom will react fastest. Of significant importance is that this increased electron density at the sulphur upon methyl substitution overshadows their steric effects. The oxidation of thiophenes to sulphones increases their polarity, and molecular weight. The enhanced polarity makes it easier to be removed by adsorption on a solid material such as silica, alumina, clay or activated carbon. It also facilitates their separation by extraction, distillation or alkali treatment. Several peroxy organic (formic, acetic, propionic etc.) and inorganic as perboric, Caro's (peroxysulphuric) (Gore et al., 2003) acids have been used for selective oxidation of organic-sulphur compounds. The other oxidative processes involve nitrogen dioxide, transition metal-based catalysts in conjunction with organic hydro-peroxide as oxidant and photo – or ultra sound – induced oxidation.

The liquid phase oxidation process with hydrogen peroxide produces oxidised compounds that can be physically separated and may be easily downstream processed. The oxidation of thiophene derivatives with hydrogen peroxide is known to take place over various catalytic systems, such as formic acid, CCl_xCOOH ($x=1, 2, 3$) (Aida, 1993), CF_3COOH (Treiber et al., 1997), methyltrioxorhenium (VII) (Brown et al., 1996), and phosphotungstic acid (Collins et al., 1997).

However, the greatest advantage of the ODS is the mild reaction conditions (atmospheric pressure and temperature lower than $80\text{ }^\circ\text{C}$). Although the dibenzothiophenes can be removed by HDS process at high temperature, pressure and long reaction time these compounds can be effectively removed by ODS process at relatively low temperature and pressure. Oxidative desulphurization provides an important alternative to HDS, and it will be a particularly useful complementary process to HDS for deep desulphurization. A detailed explanation of ODS process, is given in Chapter Two.

1.4 Scope of This Research

To achieve the goal of reducing the sulphur content in fuel to 10 ppm with the current HDS process, using high temperature and pressure, large reactor volume and more active catalyst is indispensable but costly. Therefore, it is essential that a method that can operate under moderate conditions and has high efficiency in removing all kind of sulphur compounds be developed to produce ultra low sulphur products.

Various chemical process for thoroughly removing sulphur compounds have been investigated in the past (Gray et al, 2003; Chen et al., 2004; Garcia-Ochoa et al., 2004). One idea that has drawn wider attention, is referred as the oxidative desulphurization (ODS) which involves oxidizing sulphur compounds and then removing oxidised compounds by separation techniques (Yazu et al, 2001; Kabe et al., 2003).

Many studies on oxidative desulphurization have been reported and claimed. These include the use of various catalyst and oxidant system like hydrogen peroxide/formic acid, hydrogen peroxide/acetic acid, hydrogen peroxide/12-tungstophosphoric acid and hydrogen peroxide/polyoxometalates as shown in Table 1.3. From this table, it is found that the most of the researchers in this area studied the oxidation reactivity of DBTs compounds (by using toluene or octane as model oil). However, in this work, three different types of model sulphur compounds (Di-n-butylsulfide, Di-methylsulfoxide and Dibenzothiophene by using dodecane as model oil) and heavy gas oil are used to evaluate the reactivity of sulphur in the oxidation reaction.

The chemical and physical properties of the oxidised sulphur compounds are significantly different from the hydrocarbon compounds in petroleum fractions. Therefore, extraction is widely used to separate sulphur compounds from oxidised gas oil (Zannikos et al., 1995; Yen et al., 2003).

Table 1.3 Summary of the past work on ODS process

Reference	Type of feed	System, oxidant/catalyst Solvent	Objective
Paybarah et al., 1982	Model oil (DBT)	POB	Examine a system to oxidize selectively the thiophenic compounds
Tam et al., 1990	Diesel oil	Nitric acid/glacial acetic γ -butyrolactone	The effect of preoxidation of diesel fuel for sulphur reduction by solvent extraction
Zannikos et al., 1995	Gas oil	H ₂ O ₂ /acetic acid	Effects of solvent extraction on sulphur content of gas oil The sulphur content was reduced to 100 ppm
Collins et al., 1997	Gas oil	H ₂ O ₂ /PTA A [^] silica gel	Produce a highly selective, catalyst for the ODS process The sulphur content was reduced to 50 ppm
Otsuki et al., 2000	LGO and VGO	H ₂ O ₂ /formic acid DMF, MeCN, Methanol	Study, the relationship between the electron densities of sulphur atoms and reactivity The sulphur content was reduced to 100 ppm
Yazu et al., 2001	Model oil (DBTs in Octane) Diesel oil	H ₂ O ₂ /TPA acetonitrile	Immobilized TPA catalyzed the oxidation of DBT in the presence of H ₂ O ₂ and is effective for the ODS in the diesel/MeCN system The sulphur content was reduced to below 50 ppm
Fairbridge and Ring, 2001	Model oil (DBTs in toluene)	H ₂ O ₂ /polyoxometla	. Oxidation reactivity of DBTS H ₂ O ₂ /polyoxometla
Hulea et al, 2001	Kerosene	H ₂ O ₂ /Ti-beta acetonitrile	Oxidation with H ₂ O ₂ of several model molecules in both a two-phase The sulphur content was reduced to 80 ppm
Wang et al., 2003	Model oil (DBTs in toluene)	<i>t</i> -BuOOH/Mo-Al ₂ O ₃	Investigate the oxidative reaction mechanism The sulphur content was reduced to 25 ppm
This work	Model oil (DBT, Di-n-butyl sulphide, Dimethyl sulfoxide in Dodecane) and HGO	H₂O₂ /formic acid DMF, NMP, Methanol	Modelling of oxidation and extraction steps based on batch experiments Heat integration of oxidation step in ODS process Economic analysis of ODS process

POB: Peroxybenzoic acid, PTA: Phosphotungstic acid, HGO: Heavy gas oil, A: Adsorbent MeCN: Acetonitrile, LGO: Light gas oil, DMF: Dimethylformamide VGO: Vacuum gas oil, *t*-BuOOH: tert-butyl-hydroperoxide, DBTs: Dibenzothiophenes

However, there are two major problems associated with ODS process. First, some oxidants cause unwanted reactions that reduce the quantity and quality of the fuel. The second problem is the selection of suitable solvent for the extraction of oxidised sulphur compounds. There is also no detailed work to define the appropriate conditions in terms of the optimum reaction temperature, oxidants, catalysts, solvents, solvent to fuel ratio and the impact of such solvents extraction on fuel quality. So the ODS process still needs further research, especially in the area of designing the appropriate selective catalyst and solvent.

With this backdrop, the aim of this work is two fold. Firstly, the oxidation of three sulphur compounds in a model oil and sulphur present in two heavy gas oils (HGO) with hydrogen peroxide (H_2O_2) as oxidant and formic acid (HCOOH) as catalyst is studied. H_2O_2 and HCOOH are chosen due to the fact that HCOOH reacts with H_2O_2 to form more effective and selective oxidants oxo-or peroxy-acid complex, and results in high rate and high selectivity in oxidation of nucleophilic substrates such as organic sulphides or alkenes (Murahashi and Davies, 1999).

A series of batch experiments are carried out using a small reactor to define the appropriate operating conditions such as reaction temperature, reaction time and amounts of oxidant and catalyst. Kinetic model for the oxidation is also developed based on the experimental data. A point to note here that in the absence sophisticated equipment to measure and monitor what happens to individual sulphur compounds due to oxidation reaction, a 'total sulphur approach' (at the beginning and at the end of reaction) is adopted in this work. Therefore, throughout the thesis, conversion refers to total sulphur conversion. A CSTR model is then developed for evaluating the viability of a large-scale operation. To carry out the reaction even at low temperature i.e. 30-40 $^{\circ}C$, the large scale operation will demand large amount of heating therefore, the heat

integration model for the oxidation process is developed. Here, the modelling and optimisation are carried out by using gPROMS software (2005). Note, perfect mixing and perfect level control (no dynamics involved) are assumed in the CSTR model.

The extraction of sulphur compounds from unoxidised and oxidised heavy gas oils (HGO) was investigated in pilot plant experiments which were carried out using three solvents Methanol, Di-Methyl Formamide (DMF) and N-methyl pyrrolidone (NMP) as solvents. Adopting “total sulphur approach” as mentioned earlier, for each solvent, the partition coefficient (K_p), solvent effectiveness (K_f) and extractor factor (E_f) are determined at different heavy gas oil/solvent ratios. A liquid-liquid extraction model is then developed for the extraction of sulphur compounds from the oxidised heavy gas oil.

With the experimentally determined K_p , multi stage liquid-liquid extraction process is modelled using gPROMS software and the process was simulated for the three solvents at different solvent/heavy gas oil ratios to select the best solvent, and to obtain the optimal ratio of solvent to heavy gas oil and number of extraction stages to reduce the sulphur content level to less than 10 ppm. The model is employed with the following assumptions:

1. All the sulphur compounds present in HGO represented as one compound.
2. When the raffinate and extract phase are both dilute in the solute the partition coefficient K_p can be taken as constant at given temperature (Seader and Henley, 1998).

Finally, based on the CSTR and multi stage liquid-liquid extraction model, a continuous ODS process is developed and a preliminary economic analysis was conducted.

1.5 Aim and Objectives of the Research

The aim of the thesis is to develop an efficient and selective oxidative desulphurization process (ODS) using hydrogen peroxide as oxidant and formic acid as catalyst for three model oils and two heavy gas oils with minimum energy consumption leading to minimum environmental impact via laboratory experiments, mathematical modelling and optimisation.

The objectives of the thesis are summarised below:

- Extensive literature survey in the fields of sulphur removal from liquid petroleum products.
- Laboratory measurement of oxidation reaction rates for model sulphur compounds and sulphur present in heavy gas oils with emphasis on:
 - Amount of oxidant.
 - Amount of catalyst.
- Optimise the operating conditions, such as reaction temperature and reaction time.
- Testing and proposing reaction kinetics models.
- Laboratory measurement of separation efficiency data for solvent extraction of both non-oxidised and oxidised fuels with focus on:
 - Solvent type.
 - Solvent to fuel ratio.
- Development of CSTR model for the oxidation process for evaluating the viability of a large-scale operation and heat integration.
- Modelling of multi stage liquid-liquid extraction of ODS process using simulation software.
- Preliminary economic analysis of continuous of ODS process.

1.6 Thesis Layout

The layout of this thesis is presented below.

Chapter 1: Introduction

The thesis begins with an introduction, in which the background of U.S. EPA new sulphur rule and imposed technical challenges for refiners to meet the regulation are described. HDS and ODS technologies are also summarised and discussed. The scope of the research, aim and objectives of this research and the thesis layout are also presented.

Chapter 2: Literature Review

Chapter Two takes a look at past work in the fields of sulphur removal from petroleum and set the scene for this work. It also highlights briefly process modelling, simulation, optimisation and heat integration. Important features of gPROMS software package used for modelling, simulation and optimisation are also discussed in this chapter. A brief description for HYSYS software is also provided.

Chapter 3: Oxidation and Extraction-Experimental Work

Chapter Three describes the experimental procedures for oxidation and extraction and the equipment used for the task. The results of the oxidation and extraction experiments including the effects of reaction temperature, amounts of oxidant and catalyst on the oxidation reaction (of both model sulphur compounds and sulphur present in heavy gas oil) are presented. The kinetic study of both model sulphur compounds and sulphur present in heavy gas oil are also discussed.

Chapter 4: Heat Integration in Oxidation Process: Energy Consumption and Recovery Issue

Chapter Four provides a large scale oxidation process using a continuous stirrer tank reactor (CSTR) and heat integration of this process. In the absence of a real plant a process model for the system is developed here. Optimisation problem is formulated using gPROMS modelling tool to optimise some of the design and operating parameters of integrated process while minimizing an objective function which is a coupled function of capital and operating costs involving design and operating parameters. Two cases are studied where: (i) HGO and catalyst are fed as one feed stream and (ii) HGO and catalyst are treated as two feed streams.

Chapter 5: Modelling of Extraction Step of ODS Process

Chapter Five introduces the liquid-liquid extraction separation techniques and its applications are highlighted here. Use of these factors in determining/selecting the best solvent out of three solvents are discussed in detail. A multi stage liquid-liquid extraction model for the second stage of ODS process is then developed in this chapter using gPROMS software.

Chapter 6: Economic Analysis of Continuous Oxidative Desulphurization Process

A continuous ODS process is developed and a preliminary economic analysis is conducted in this chapter. Here three different cases are studied: In Case 1, the oxidant-catalyst recovery system was not considered in the ODS process. In Case 2, the oxidant-catalyst recovery system was considered in the ODS process. In Case 3, the amount of oxidant used less than that used in the Case 2.

Chapter 7: Conclusions and Future Recommendations

Chapter 7 concludes the thesis by highlighting what have been achieved and proposes some recommendations for future work.

Chapter Two

Literature Review

In this chapter (a) the removal of sulphur from petroleum and (b) process modelling, simulation, optimisation and heat integration are reviewed.

2.1 General

Sulphur compounds are perhaps the most important nonhydrocarbon constituents of petroleum and occur as a variety of structures (Figure 2.1) (Speight, 2000). During the refining sequences (converting crude oils to different grade products) a great number of the sulphur compounds that occur in any particular petroleum are concentrated in the residual and other heavy fractions.

The relative importance attached to sulphur compounds in petroleum may, at first, seem unwarranted, but the presence of sulphur compounds in any crude oil can only result in harmful effects. For example, the presence of sulphur compounds in finished petroleum products such as gasoline will cause corrosion of engine parts, especially under winter conditions when water containing sulphur dioxide (from the internal combustion engine) may collect in the crankcase. On the other hand, mercaptans cause the corrosion of copper and brass in the presence of air and also have an adverse effect on the colour stability of gasoline and other liquid fuels.

The distribution of sulphur compounds in crude oils has been studied extensively since the 1890s and it has become possible to note various generalities. For example, the proportion of sulphur will increase with the boiling point of the crude oil fraction. If the distillation is allowed to proceed at too high a temperature, thermal decomposition of the high molecular-weight sulphur compounds will ensue. Hence, the middle fractions

will contain more sulphur compounds than the higher-boiling fractions. The distribution of the various types of sulphur compounds varies markedly among crude oils of diverse origin. It is difficult to assign specific trends to the occurrence of compound types within the different crude oils other than an increase in boiling point of fractions from a particular crude oil, is accompanied by an increase in sulphur content.

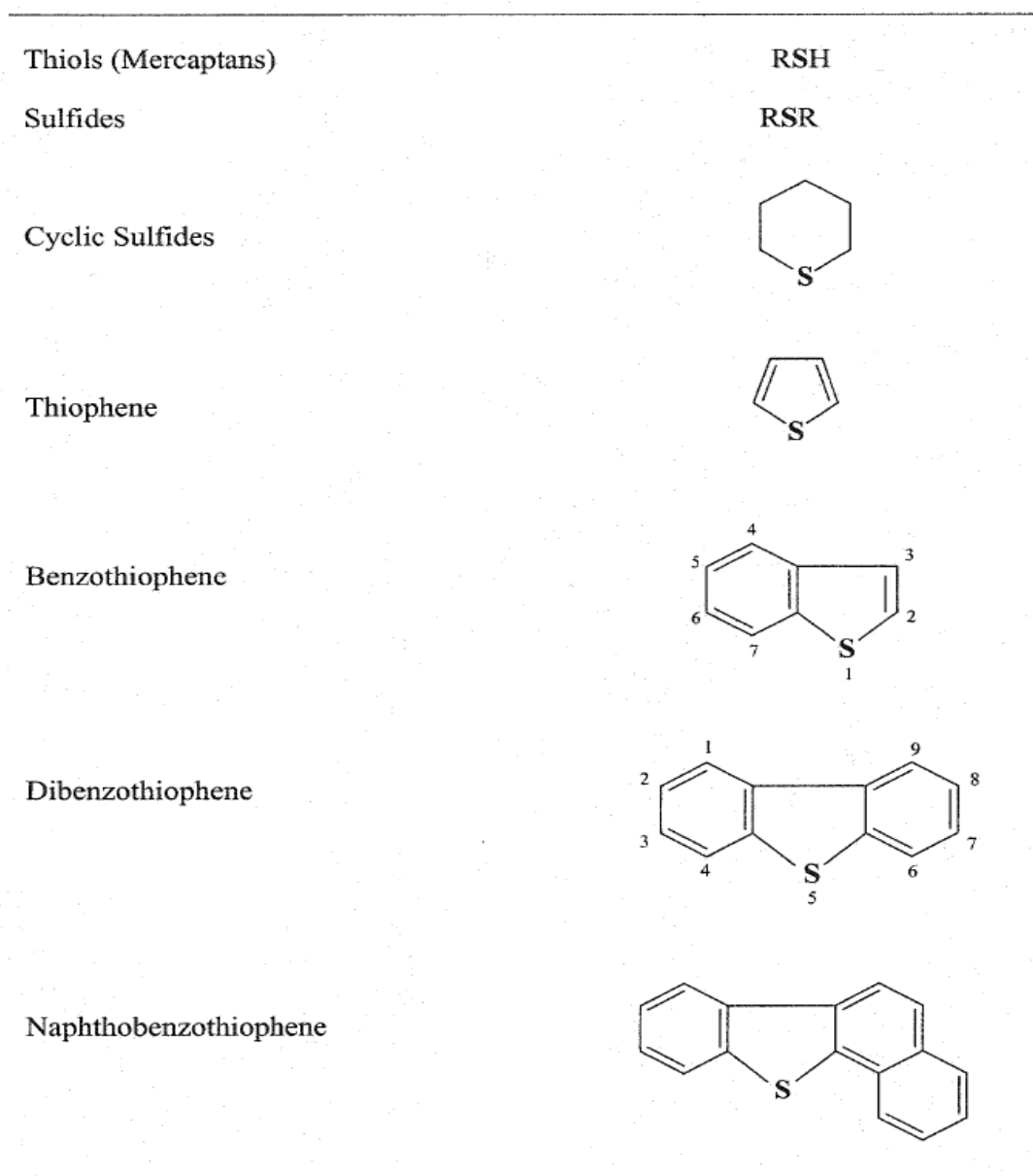


Figure 2.1 Representative sulphur compounds in crude oils

Sulphur is usually the only heteroatom to be found in the naphtha fraction, and then only at trace levels in the form of mercaptans (thiols, R-SH) thiophenols (C₆H₅SH), sulphides (R-S-R¹), alkyl sulphides, and five- or six-ring cyclic thiacyclane structures, and to a lesser extent, disulfides (R-S.S-R¹) (Speight, 2000).

The sulphur-heterocyclic compounds in the mid distillate range are primarily the thiacyclane derivatives, benzothiophene derivatives and di benzothiophene derivatives with lesser amounts dialkyl-aryl and aryl-alkyl sulphides. Sulphur compounds are significant contributors to the vacuum gas oil fraction. The major sulphur species are: alkyl benzothiophene derivatives, di benzothiophene derivatives, benzonaphthothiophene derivatives, and phenaphthro-thiophene derivatives (Quimby, 1998; Stumpf et al., 1998).

There are several valid reasons for removing sulphur from petroleum fractions, including:

1. Reduction, or elimination, of corrosion during refining, handling, or use of the various products.
2. Production of products having an acceptable odor.
3. Increasing the performance (and stability) of gasoline.
4. Decreasing smoke formation in kerosene.
5. Reduction of sulphur content in other fuel oils to a level that improves burning characteristics and is environmentally acceptable.

In order to accomplish sulphur removal, use is still made of extraction and chemical treatment of various petroleum fractions as a means of removing certain sulphur types from products, but hydrodesulphurization has been the only method generally applicable to removal of all types of sulphur compounds.

2.2 Classification of Desulphurization Technologies

Heavy hydrocarbon feed stocks that undergo catalytic refining processes generate products, such as gasoline and diesel with large amounts of sulphur containing organic compounds (James and Glenn, 1984). The associated organic sulphur compounds exist in several forms such as mercaptans, aliphatic and cyclic thioethers and thiophenes and their derivatives. The products containing sulphur compounds are usually hydrodesulfurized through several processes using well-established catalyst systems. There are two approaches used to reduce sulphur level in petroleum refining business (1) conventional hydrodesulphurization (HDS) and (2) non-hydrogen consuming desulphurization (non-HDS based).

2.2.1 Conventional Hydrodesulphurization

Catalytic HDS of crude oil and refinery streams carried out at elevated temperature and hydrogen partial pressure converts organic-sulphur compounds to hydrogen sulphide (H_2S) and hydrocarbons, Equation (2.1). The product gas is then separated and converted to elemental sulphur by the Claus process (Chan et al., 2000; Chan et al., 2004; Funakoshi and Aida, 1993).



The conventional HDS process is usually conducted over sulphide $CoMo/Al_2O_3$, $NiMo/Al_2O_3$ or other catalysts. Their performance in terms of desulphurization level, activity and selectivity depends on the properties of specific catalyst used (active species, concentration, support properties, synthesis route), the reaction conditions (sulfiding protocol, temperature, partial pressure of hydrogen and H_2S), nature and

concentration of the sulphur compounds present in the feed stream, reactor and process design (Murata et al., 2004). HDS with Mo, Ni or W-based catalysts are widely used to reduce sulphur content. Mercaptans, thioethers, and disulfide, for example, can be removed relatively easily using this process. Other sulphur bearing organic compounds such as aromatic, cyclic, and condensed multicyclic compounds are more difficult to remove (Funakoshi; Aida, 1998). Thiophene, benzothiophene, dibenzothiophene, other condensed-ring thiophenes and substituted forms of these compounds are particularly difficult to remove by hydrodesulphurization. The kinetic investigation into the behaviour of 4,6-alkyldibenzothiophene (4,6-DADBT) led to different explanations. First, the transformation of 4,6-DADBT is limited by the adsorption step via sulphur atom. The second hypothesis suggests that the adsorption occurs through π -electrons of the aromatic system (Jochen et al., 2004).

In general, the reaction mechanism of dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) through HDS process was suggested to proceed via two main pathways (Figure 2.2). One is a direct desulphurization pathway where sulphur is removed without affecting the aromatic rings. The other is via hydrogenation pathway, in which aromatic rings of DBT compounds are preferentially hydrogenated to 4H- or 6H-DBT intermediates and are subsequently desulphurized (Chan et al., 2000). Thus, the desulphurization rate of hindered compounds is greatly increased through the hydrogenation route. Without one or both of the rings, the molecule is much more flexible and the sulphur atom can approach the catalyst surface more easily. However the “hard sulphur compounds” like benzothiophene and its derivatives are the most satirically hindered compounds that have been identified in diesel fractions after conventional hydrodesulphurization (HDS) ranging in concentration 0.2-0.3 wt%. This would indicate that these catalysts are not efficient enough to desulphurization the most refractory sulphur-containing e.g. DBT and its derivatives (Chan et al., 2000; Murata et

al., 2004). However, the HDS is limited in treating benzothiophenes (BTs) and dibenzothiophenes (DBTs), especially DBTs having alkyl constituents on 4 and/or 6 positions. The production of light oil, with very low levels of sulphur-containing compounds therefore requires inevitably application of severe operating conditions and the use of especially active catalysts (Michael and Bruce, 1991; Rappas, 2002; Heeyeon et al., 2003).

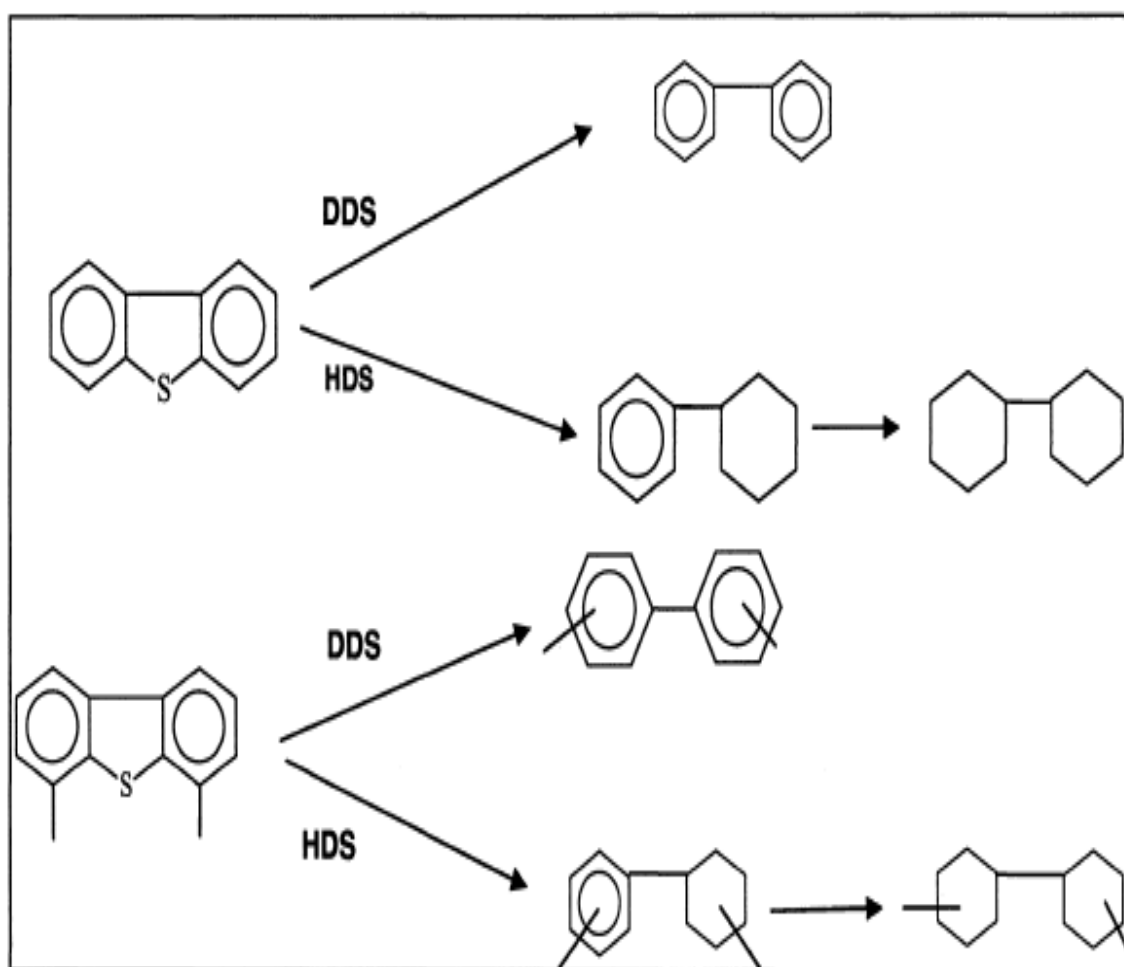


Figure 2.2 Direct desulphurization and hydrogenation path way for hydrodesulphurization of Benzothiophenes

HDS is a commercially proven refining process that passes a mixture of heated feed stock and hydrogen over catalysts to remove sulphur. Refiners can desulphurise distillate streams by hydrotreating the straight run streams that generated from direct

distillation from crude oil, hydrotreating streams coming out from conversion units such as fluid catalytic cracking (FCC) and hydrocracker units.

By controlling the hydrotreating conditions and selecting the appropriate catalysts, refineries may meet the ultra low sulphur diesel on fuels that are produced from straight runs streams. The difficulty however, arises in the desulphurization of other streams that come from the conversion units, which mostly include the refractory sulphur compounds. Meeting the sulphur requirement for gasoline is believed to be the greatest challenge for the refining business requiring substantial revamps to equipment or even construction of new units. This is due to the fact that most of the gasoline production in the market today is coming from cracked stocks that contain a large concentration of compounds with aromatic rings and high olefin content, thus making sulphur removal more difficult. The need to desulphurization the cracked stocks in addition to the straight-run streams will direct the refiners to choose the most cost-effective technology (Chan et al., 2000; Rappas 2002; Heeyeon et al., 2003; Murata et al., 2004).

In essence, refiners must desulphurize all diesel-blending components in order to meet the 10 ppm ULSD specification that will be take effect in 2010. In the case of diesel, a two-stage deep desulphurization process will most probably be sufficient to meet the 10 ppm sulphur target. The first stage can reduce the sulphur level to below 250 ppm with a second stage that could produce diesel product with 10 ppm sulphur or less. In some cases the first stage could be a conventional hydrotreating unit with moderate adjustment to the operating parameters. The second stage would require substantial modification of the desulphurization process, primarily through use of higher pressure, increasing hydrogen flow rate and purity, reducing space velocity, and choice of the catalyst. Such operation requirements to deep desulphurize cracked stocks also need a higher reactor pressure (Babich; Moulijn ,2003; Zhao et al. 2003).

2.2.2 Non-Hydrodesulphurization based

Technologies that do not use hydrogen for catalytic decomposition of organic-sulphur compounds can be categorized into six techniques: shifting the boiling point by alkylation, desulphurization via extraction, desulphurization by precipitation, desulphurization by adsorption on a solid sorbet (ADS), biodesulphurisation (BDS) and oxidative desulphurization (ODS).

2.2.2.1 Shifting the Boiling Point by Alkylation

When the boiling temperature of organic-sulphur compounds is shifted to a higher value, they can be removed from light fraction and concentrated in the heavy boiling part of the refinery streams. British Petroleum used this approach in a new advanced technology process for desulphurizing FCC gasoline streams by Olefinic Alkylation of Thiophenic Sulphur (OATS) (Burnett et al., 2000). The OATS technology consists of a pre-treatment section, an OATS reactor, and a product separation unit (Figure 2.3).

Thiophenic sulphur is alkylated in an OATS reactor employing acidic catalyst. After the alkylation, the feed is sent to a conventional distillation column where it is separated into light sulphur-free naphtha and a heavy sulphur-rich stream. The light naphtha is directly sent to the gasoline pool and the heavy stream is preferably hydrotreated. The hydrotreater is not an essential part of the OATS technology, but its application after the fractionator increases the product yield.

The process employs alkylation of thiophenic compounds via reaction with olefins present in the stream. As a result the boiling temperature of the sulphur compounds increases. In comparison with thiophenes, alkylated thiophenes have a much higher boiling point. This enables them to be easily separated from the main gasoline stream by distillation.

Experimental demonstration showed sulphur reduction in gasoline from 2330 ppm to less than 20 ppm with only two octane number losses (Burnett et al., 2000). The efficiency of the OATS process can be limited by competing process-alkylation of aromatic hydrocarbons and olefin polymerization. One of the disadvantages of the OATS process is that the alkylated sulphur compounds produced require more severe hydrotreating conditions to eliminate sulphur.

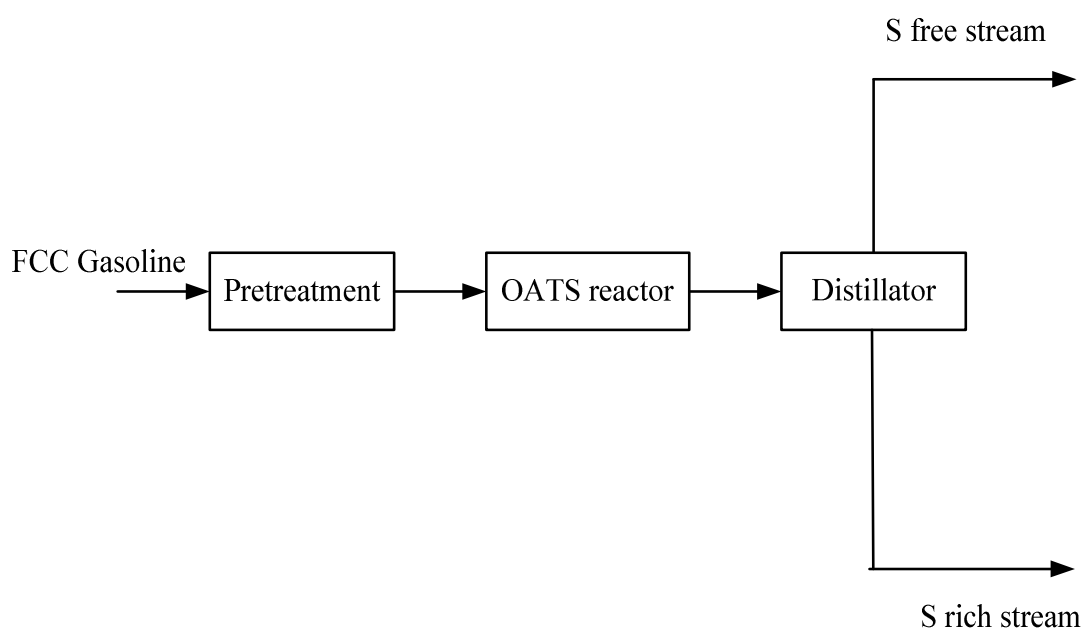


Figure 2.3 The OATS process flow diagram

2.2.2.2 Desulphurization via Extraction

The separation of sulphur compounds from fuel oil by extraction (extractive desulphurization) is based on the fact that sulphur compounds are more soluble than hydrocarbons in appropriate solvent. The general process flowsheet is shown in Figure 2.4. The most attractive feature of the extractive desulphurization is the applicability at low temperature and low pressure. The process does not change the chemical structure of fuel oil components. To make the separation of the process efficient, the solvent must

be carefully chosen to satisfy a number of requirements. The sulphur compounds must be highly soluble in the solvent. The solvent must have a boiling point different than that of the sulphur containing compounds, and it must be inexpensive to ensure economic feasibility of the process.

Solvents of different nature have been tried, among which acetone, ethanol (Funakoshi and Aida, 1998), polyethylene glycols (Forte, 1995), and nitrogen containing solvents (Horii et al., 1993). A reasonable level of desulphurization of 50–90% sulphur removal, depending on the number of extraction cycles, has been reported.

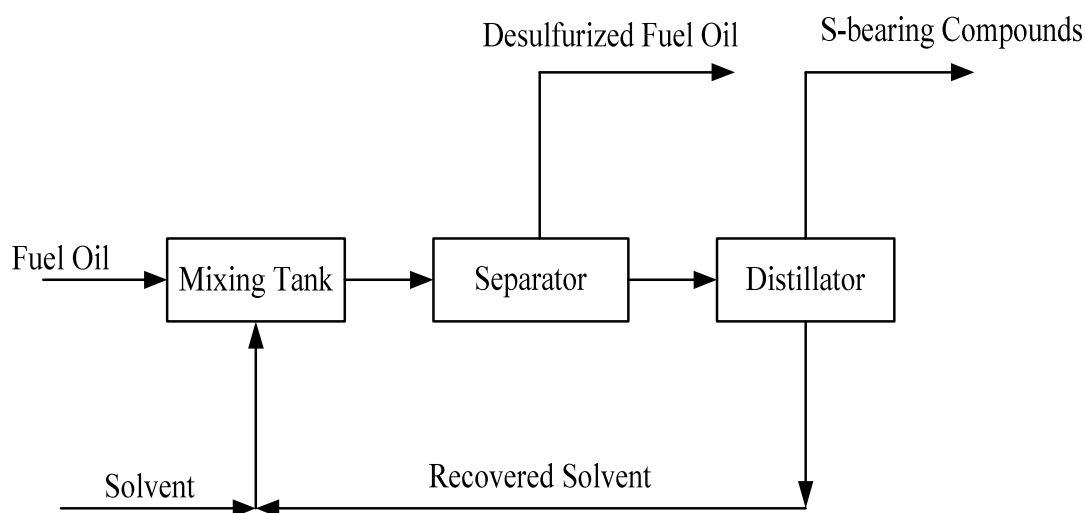


Figure 2.4 General process flow of extractive desulphurization

The efficiency of extractive desulphurization is mainly limited by the solubility of the organic sulphur compounds in the solvent. Solubility can be enhanced by selecting an appropriate solvent taking into account the nature of the sulphur compounds to be removed. This is usually achieved by preparing a ‘solvent cocktail’ such as acetone–ethanol or a tetraethylene glycol–methoxytriglycol mixture (Fankoshi and Aida, 1993). Preparation of such a ‘solvent cocktail’ is rather difficult and intrinsically non-efficient since its composition depends strongly on the spectrum of the organic sulphur compounds present in the feed stream.

The GT-DesulfSM process is an example of desulphurization technology based on organic sulphur compound extraction (Bonde et al., 2000). This process separates the organic sulphur compounds and aromatics from FCC naphtha by extractive distillation using a blend of solvents (Figure 2.5). A desulphurized-dearomatised olefin rich gasoline stream and an aromatic stream containing the sulphur compounds are formed after treatment in a GT-Desulf reactor. The first stream is directly used as a gasoline blend stock. Unfortunately, available literature does not contain any information on the level of sulphur removal from the treated stream. The aromatics fraction with the sulphur compounds is sent to a HDS reactor. After treatment in the HDS reactor, aromatics recovery is proposed as an additional option to increase economic efficiency of the process.

Bonde et al. (2000) pointed out that the GT-DesulfSM process is economically favourable due to an integrated approach to the refinery processing (segregated sulphur removal and aromatics recovery) and lower hydrogen consumption since less FCC naphtha is treated in the HDS reactor.

2.2.2.3 Desulphurization by Precipitation

Desulphurization by precipitation is based on the formation and removal of subsequent insoluble charge-transfer complexes. Preliminary experiments were reported for a model organic-sulphur compound (4, 6-DMDBT) in hexane and for gas oil, using 2,4,5,7-tetranitro-9-fluoren (TNF) as the most efficient π -acceptor. A suspension of the π -acceptor and sulphur-containing gas oil was stirred in a batch reactor where insoluble charge-transfer complexes between π -acceptor and DBT derivatives formed (Meille et al., 1998; Jefferies et. al., 1972). The consecutive steps include filtration to remove the complex formed from gas oil and the recovery of the π -acceptor excess using a solid adsorbent. Currently the efficiency is very low. One treatment results in the removal of

only 20% of the sulphur present. Moreover, there is a competition in complex formation between DBT compounds and other non-sulphur aromatics that result in low selectivity for DBT removal.

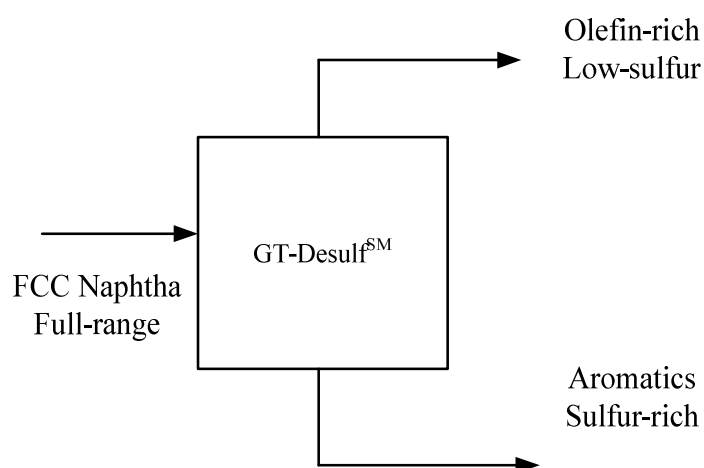


Figure 2.5 Desulphurization using GT-DeSulf

2.2.2.4 Desulphurization by Adsorption on a Solid Adsorbent

Desulphurization by adsorption (ADS) is based on the ability of solid adsorbent to selectively adsorb organic-sulphur compounds from refinery streams. Based on the mechanism of the sulphur compounds interaction with the adsorbent, ADS can be divided into two groups: “adsorptive desulphurization” and “reactive adsorption desulphurization”. Adsorptive desulphurization is based on physical adsorption of organic-sulphur compounds on the solid adsorbent surface. Regeneration is usually done by flushing the spent adsorbent with a solvent, resulting in a waste with high concentration of organic-sulphur compounds (Salem, 1994; Savage et al., 1997; Salem and Hamid, 1997).

Reactive adsorption desulphurization employs chemical interaction of the organic-sulphur compounds and the adsorbent. Sulphur is adsorbed, usually as sulphide, and the S-free hydrocarbon is released into the purified fuel stream. Regeneration of the spent adsorbent results in sulphur elimination as H₂S, S, or sulphur oxides, depending on the process applied. Efficiency of the desulphurization is mainly determined by the adsorbent properties: its adsorption capacity, selectivity for the organic-sulphur compounds, durability and regenerability (Salem, 1994; Savage et al., 1997; Salem and Hamid, 1997).

2.2.2.5 Biodesulphurisation

Biodesulphurisation (BDS) has been studied as an alternative to HDS for the removal of organic sulphur from fuels. BDS use bacteria as catalyst to remove sulphur from the fuel. In the BDS process, organosulphur compounds such as DBT and a variety of other organic sulphur compounds are oxidised with genetically microbes (selective oxidative pathway), and sulphur is removed as sulphate salt (Lizama and Scott, 1995; Gupta et al. 2005).

Generally, there are two pathways for BDS of alkyl-DBTs. However, most attention is given to the so-called 4S pathway of a few bacterial species, which can remove sulphur from DBT and its substituted, especially satirically compound 4,6-DMDBT that resist removal by HDS. Figure 2.6, shows that the enzymes involving “4S pathway” of DBT can selectively attack the sulphur atom without assimilation of the carbon content on fuels. In this pathway, DBT is stepwise oxidised to DBT sulfoxide and further to DBT sulphone and finally to 2-hydroxylebiphenyl (HBP) (Lizama and Scott, 1995; Magdalena et al., 1995; Ping and Steven, 1996; Folsom et al., 1999; Grossman et al., 2001; Monticello, 2000; Kimilko et al., 2003; Gupta et al. 2005).

Folsom et al. (1999) reported that the extensive biodesulphurisation of hydrodesulphurised diesel fuel led to a 67 % reduction in total sulphur from 1850 to 615 ppm and more importantly the sulphur content of 615 ppm cannot be further reduced.

However, to be commercially useful, biodesulphurisation must be able to remove the sulphur from fuels. Although considerable research on the desulphurization of model compounds via the sulphur selective oxidative pathway has been reported, little information on the desulphurization of fuel oils has been published.

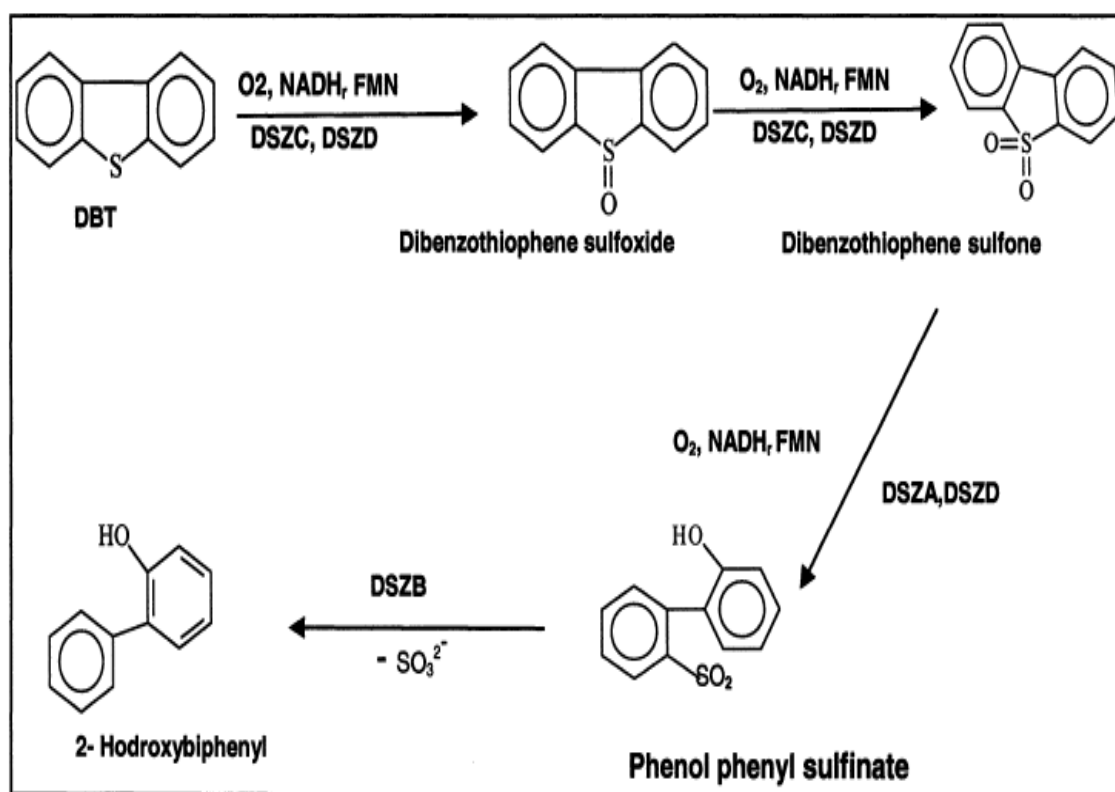


Figure 2.6 Biodesulphurisation pathways for DBT (Monticello, 2000)

2.2.2.6 Oxidative Desulphurization

The earliest study of oxidative desulphurization (ODS) was carried out in 1893 by Kayser using nitric acid as oxidant (Mei et al., 2003). The idea of ODS is actually quite

simple. Sulphur compounds are known to be slightly more polar than hydrocarbons of similar structure (Babich and Moulijn, 2003; Zhao et al., 2003). However, oxidised sulphur compounds such as sulphones or sulfoxides are substantially more polar than unoxidised sulphur compounds. This permits the selective removal of sulphur compounds from hydrocarbon by a combination process of selective oxidation and solvent extraction or solid adsorption.

Before 1980, the most popular oxidants in the study of ODS are nitric acid and nitrogen oxides and used largely because they have double effects of oxidizing sulphur compounds and nitrating the aromatic compounds to form nitroaromatics with high Cetane numbers (Collins et al., 1997). However, it has major drawbacks such as poor selectivity, low yield and loss of heating value of the treated oil (Long and Caruso, 1985; Gore, 2001). Other types of oxidants have also been used, including $\text{H}_2\text{O}_2/\text{AcOH}$, $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$, O_3 , KMnO_4 and BuOOH (Attar and Corcoran 1978; Mei et al., 2003; Aida, 1993).

In the ODS process, the sulphur containing compounds in oil are oxidised using appropriate oxidants to convert these compounds to their corresponding sulfoxides and sulphones. These are preferentially extracted from the oil due to their increased relative polarity (Long and Caruso., 1985; Gore, 2001; Babich and Moulijn 2003; Zhao et al., 2003). Any unused oxidant that remains in the oil can be removed by water washing and extracting. The oxidised compounds can be extracted from the oil by using non-miscible solvent. Depending on the solvents used for the extraction, the oxidised compounds and solvent are separated from the oil by gravity separation or centrifugation. The oil is water washed to recover any traces of dissolved extraction solvent and polished using other methods, such as absorption using silica gel and aluminium oxide. The solvent is separated from the mixture of solvent and oxidised compounds by a simple distillation for recycling and re-use. By using this process the

maximum sulphur removal is achieved with minimum impact on fuel quality (Paris-Marcono, 1992; Grossman et al. 1999; Vasile et al., 2000; Babich and Moulijn, 2003; Frank and Yuan, 2003).

Tam et al. (1990) described a process for purifying hydrocarbon aqueous oils containing both sulphur and nitrogen compounds by first reacting the oil with an oxidizing gas containing nitrogen dioxides and then extracting the oxidised oil with solvent in two stages (Gore, 2001; Babich; Moulijn 2003 and Zhao et al., 2003). The oxidation extraction process used by Patrick et al. (1990) operates at ambient pressure and low temperature (typically 30 °C), using nitrogen dioxides or nitric acid as oxidants, and any polar solvents for extraction (Gore, 2001; Zhao et al., 2003). In the petroleum industry, solvent extraction techniques have been used to remove sulphur and nitrogen compounds from light oil without any pre-treatment of petroleum feedstock. The solvent can be recovered and reused through a distillation (Gore, 2001 and Babich; Moulijn 2003).

2.2.3 Summary

The review in the previous section discusses some of the processes that have been, or are being, developed as an alternative/addition to hydrodesulphurization processes. These are summarized in Figure 2.7. The alternative technologies range from reactive adsorption, oxidative routes (especially for diesel) and other chemical conversion methods, to “simple” physical separation methods (adsorption, extraction, etc.). It appears that for the time being, as long as sulphur levels of 10 ppm are aimed at, the classical hydrotreating options and their off shoots still dominate the field of transportation-fuel desulphurization. However, a few possible alternatives do have achieved commercial status in the gasoline area as shown in Table 2.1. Some of these processes treat full range FCC gasoline, but others accomplish desulphurisation with

only a portion of FCC gasoline. It is extremely important in the latter processes that the column for the distillation of gasoline has to be optimally designed and the cut point well selected (Hancsok et al., 2002). Note, the focus of this thesis is on desulphurization by oxidation followed by extraction.

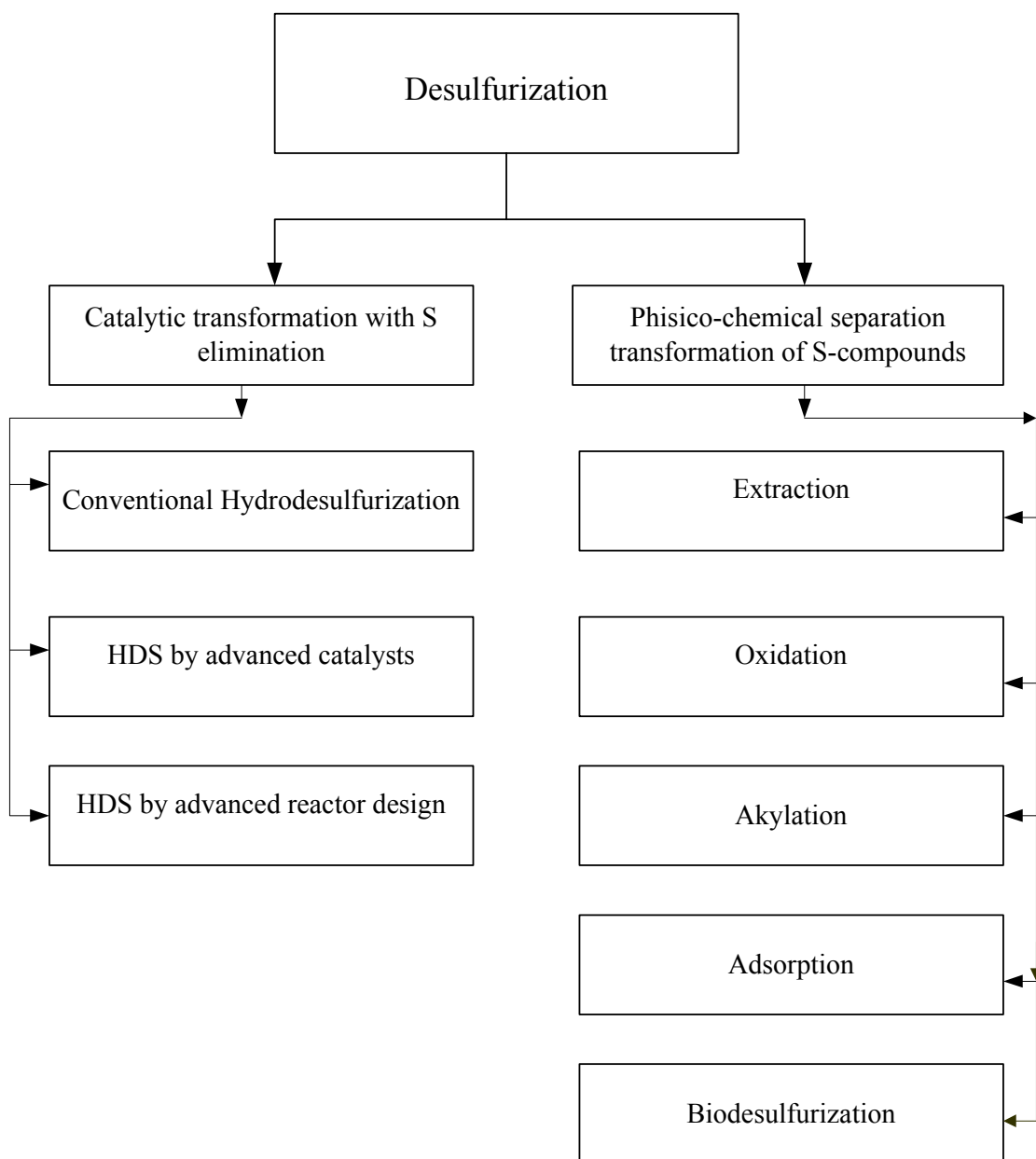


Figure 2.7 Alternative desulphurization processes

Table 2.1 Options for the desulphurization of FCC gasoline

Process	Key feature	Industrial application	H ₂ -consumption	Name of process	Licensors
Naphtha hydro-treating (N-HDT)	conventional	yes	high	various	a number of firms
N-HDT + octane increase	zeolite + isomerisation	yes	high	Octgain, Isal	ExxonMobil, UOP
Selective N-HDT	RT-225	yes	medium	SCANfining	ExxonMobil
	dual catalyst	yes	medium	Prime-G+	IFP
	catalytic distillation	yes	medium	CDHydro/CDHDS	CDTech
Selective N-HDT + octane increase	combination	yes	medium	SCANfining II	ExxonMobil
Adsorption (ADS)	Zn adsorbent	yes	low	S Zorb	Philips
	alumina adsorbent	pilot	low	Irvad	Alcoa
Extractive distillation	Selective solvent sys.	yes	none	GT-DeSulf	GTC
Alkylation	solid acid	pilot	low	OATS	BP
Bio processing	bio catalysis	no	none	--	Enchira
Oxidation	peroxyacid	pilot	none	CED	Petrostar
	ultrasound	pilot	none	SulphCo	Bechtel

2.3 Oxidation of Sulphur Contained in Petroleum Oils and Sulphur Compounds

2.3.1 Alternative Processes

Oxidation of petroleum oils has a long history. Different types of oxidants have been used, including various reactant gases as H₂, CO, CO₂, O₂ (Adschiri et al., 1998), HNO₃/AcOH, NO/NO₂, NO₂, HNO₃, H₂O₂ /H₂SO₄, BuOOH and O₃ (Collins et al., 1997).

In lab experimental H₂O₂ and formic acid systems were used to remove the sulphur containing compounds (Rappas, 2002). The amount of the hydrogen peroxide in the oxidizing solution is greater than about two times the stoichiometric amount of peroxide necessary to react with the sulphur in the hydrocarbon fuel. The reaction is carried out at temperature ranging from about 50 °C to 130 °C, at a pressure ranging from about 1 bar

to about 17 bar, for less than about 15 minutes contact time at optimum conditions (Rappas, 2001; Rappas et al., 2002). The authors achieved 2-15 ppm sulphur level. Earlier, Otsuki et al. (2000) used this system, but had only obtained 100 ppm sulphur.

Zaho et al. (2003) in their review of desulphurization (based on selective oxidation) has indicated that there are two main catalysts used for selective desulphurization. These are organic acid and polyoxometalates. Organic acids include formic acid, acetic acid and so on. Polyoxometalates have long been studied for oxidation reactions, particularly, polyoxometalate/hydrogen peroxide system for organic substrate oxidation. Little work however, has been reported on the detailed mechanistic and kinetic model for oxidation of organic sulphur compounds in a polyoxometalate/hydrogen peroxide system.

The oxidation of diesel oils with nitric acid in glacial acetic acid was studied in detail by Tam et al. (1990). They concluded that sulphur removal by oxidation is due to the formation of high-sulphur-containing residue, which results from the accelerated sedimentation of the oil from instability induced by nitric acid. Residues amounting to 6-13% of the feed gas oil were precipitated, containing 3% by wt sulphur. Extraction of the oxidised oil with γ -butyrolactone showed that the sulphur content could be reduced by up to 70% with a 90% (by volume) yield of extracted oil. In contrast, the oxidation with hydrogen peroxide and phosphotungstic acid in bi-physic system gave very little residue: less than 1% of the feed oil and containing just 1.9 wt% sulphur.

Zannikos et al. (1995) performed the oxidation of sulphur compounds by dissolving gas oil in equal volume (15 ml) of acetic acid, and heating the mixture to 90 °C. A solution of 30 % by wt. H_2O_2 is then added drop-wise and with stirring over a period of 30 minutes. The quantity of the oxidant used corresponded to three equivalents of 30 % by wt. H_2O_2 for each atom of sulphur in the gas oil.

Oxidation of dibenzothiophene with hydrogen peroxide using phosphotungstic acid as a catalyst and tetra-octylammonium bromide as phase transfer agent in a mixture of water and toluene has been studied by Collins et al. (1997). Catalyzed decomposition of hydrogen peroxide competes with dibenzothiophene oxidation by choice of suitable conditions. Conversion of dibenzothiophene approaching 100 % can be obtained. Treatment of gas oils with this technology shows that all the sulphur compounds present are oxidised by this catalyst system and highly substituted dibenzothiophenes are the most readily oxidised species containing a thiophene nucleus. Oxidised sulphur compounds can be separated from the oil by adsorption in silica gel.

Yazu et al. (2001) performed the oxidation of dibenzothiophenes with hydrogen peroxide in the presence of 12-tungstophosphoric acid (TPA) in n-octane/acetonitrile (MeCN) biphasic system to give their corresponding sulphones as the major product. For a typical run, TPA dissolved in 0.5 ml of 30 (wt %) aqueous solution of hydrogen peroxide and mixed with 50-200 ml of MeCN and 50 ml oil. The bi-phase mixture was heated to 60 °C with stirring. After the oxidation, the light oil phase was separated, washed with water, dehydrated, and the sulphur content had been measured. Table 2.2 shows that an increase in MeCN volume from 50 ml to 200 ml had enhanced the removal of sulphur compounds from 330 ppm to 12 ppm (Case 4). When oxidised light oil containing 12 ppm was treated with an equal volume of MeCN, the sulphur content further decreased to 3 ppm.

Hulea et al. (2001) investigated the sulfoxidation of aromatic sulphur compounds with hydrogen peroxide over Ti-containing molecular sieves. It has been shown that the large-pore catalytic materials, such as Ti-beta, and mesoporous Ti-HMS are active for the selective oxidation of thiophene derivatives to the corresponding sulphones, whereas the medium pore size zeolite TS-1 is totally inactive in the oxidation of polyaromatic

sulphur with H₂O₂. It has been also shown that thiophenes are less reactive than thioethers, and the reaction is first-order versus the organic substrates.

Table 2.2 Oxidative desulphurization of light oil* for 3hours (Yazu et al., 2001)

Case	TPA/30% H ₂ O ₂	Oil:MeCN(ml / ml)	Sulphur concentration (ppm)
1	0μmol/0ml	50/50	281
2	2.5μmol/0.5ml	50/50	44
3	2.5μmol/0.5ml	50/100	23
4	2.5μmol/0.5ml	50/200	12

*Initial sulphur content of light oil 330ppm.

The sulfoxidation reaction with hydrogen peroxide can be used as an interesting method for removing sulphur from kerosene without hydrogen consumption and high-pressure equipment utilization. The best results were obtained using acetonitrile as polar solvent, in the presence of both Ti-beta and Ti-HMS as catalysts. During the chemical treatment, the oxidised organic-sulphur compounds transfer integrally in the polar solvent, which is non-miscible with kerosene. The oxidised product can therefore be removed by simple liquid-liquid separation (Rabion et al., 1999).

2.3.2 Reaction Kinetics

Dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene are typical sulphur compounds that exists in diesel fuels. Model sulphur compounds are dissolved, in toluene to make up the model oil and experiments were carried out to compare the reactivity of the different dibenzothiophenes in oxidation reactions, a key step for oxidative desulphurization (Fairbridge; Ring, 2001). A series of

polyoxometalate/H₂O₂ systems were evaluated for the model compound oxidation, while their molybdenum counterpart systems were much less active. The H₂O₂ solutions of silicotungstic and silicomolybdic compounds were the least active catalyst systems for the reaction. Oxidation reactivity decreased in the order of dibenzothiophene > 4-methyldibenzothiophene > 4,6-dimethyldibenzothiophene, the same reactivity trend that exists in HDS. However, the oxidation of dibenzothiophenes was achieved under mild reaction conditions and it was easy to increase reaction temperature or reaction time to achieve high oxidation conversions, even for the least reactive 4,6-dimethyldibenzothiophene. Apparent activation energies of dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene were 53.8, 56.0 and 58.7 kJ/mol, respectively (Fairbridge; Ring 2001). These activation energies indicated a decrease in reactivity of dibenzothiophenes as methyl substituents increased at the 4 and 6 positions on dibenzothiophene rings. Interestingly, in a formic acid/H₂O₂ system, the oxidation reactivity of the dibenzothiophenes showed the reverse trend, suggesting that steric hindrance might play a role when bulky polyoxoperoxo species, which likely to form in hydrogen peroxide solution, act as catalyst.

Oxidation of dibenzothiophene with hydrogen peroxide using phosphotungstic acid as a catalyst and tetra-octylammonium bromide as phase transfer agent in a mixture of water and toluene has been studied by Collins et al. (1997). The researchers from BP Chemical have reported that dibenzothiophene could be 100% converted to sulphones by using a phosphotungstic acid/hydrogen peroxide system using mild conditions (Zhao et al., 2004). The results suggested that highly substituted dibenzothiophenes are the most readily oxidised species containing thiophenic nucleus. The results also show that there appear to be two competing reactions: the oxidation of dibenzothiophene and the non-productive decomposition of hydrogen peroxide. It was found that the decomposition of substrate was zero order in hydrogen peroxide, and non-linearly

dependent on catalyst and phase transfer agent. These results suggest that there is a fast reaction between the hydrogen peroxide and the catalyst to give a new species with a concentration independent of the hydrogen peroxide concentration and that the rate of peroxide decomposition is proportional to the concentration of new species (Collins et al., 1997).

The rate of oxidation of dibenzothiophene showed second order kinetics, and first order in hydrogen peroxide and dibenzothiophene: the second order rate constant at 25 °C was found to be $9 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$. In the presence of a large excess of hydrogen peroxide the reaction followed pseudo first order kinetics and the rate constant followed the Arrhenius equation with activation energy of 38 kJ mol^{-1} (Collins et al., 1997).

The oxidation of sulphur compounds in kerosene was conducted with *tert*-butyl hydroperoxide (*t*-BuOOH) in the presence of various catalysts (Wang et al., 2003). The oxidation activities of dibenzothiophene (DBT) in kerosene for a series of Mo catalysts supported on alumina with various Mo contents were estimated. The results show that the oxidation activity of DBT increased with increasing Mo content up to about 16 wt. % the addition of Co or Ni to the Mo/Al₂O₃ catalyst decreased the oxidation activity. Mo catalyst on alumina presented higher activity than that supported on titania or silica. The results indicated that the oxidation reactivity of model sulphur compounds decreased in the order of DBT > 4-MDBT > 4,6-DMDBT >> BT. It has also been found that the oxidative reaction of each sulphur compound can be treated as a first-order reaction. The apparent activation energies of the oxidative reaction were almost the same: $28 \pm 1 \text{ kJ mol}^{-1}$.

Desulphurization of organic-sulphur compounds by hydrogen peroxide in the presence of metal ions was studied in the oxidation of high sulphur coal (Borah et al., 2002). It has been suggested that the desulphurization by H₂O₂ due to the conversion of

sulphonic acids formed by the initial oxidation of organic-sulphur species to soluble sulphur, i.e. sulphate, by interaction with water. Qualitative detection of iron in the extracts obtained after desulphurization of coal indicated the leaching of organically bound iron. This metal ion catalyses the decomposition of H_2O_2 through the Fenton type reaction to produce OH^- and HO_2^- free radicals which are strong oxidants and participate in the desulphurization reaction. Externally added metal ions (iron), in some cases, remarkably affect the rate or level of desulphurization.

The highest desulphurization observed with Sb^{3+} ion at long reaction time (24 h) is largely due to some of the specific properties of SbCl_3 such as formation of π -complexes with aromatic sulphur compounds, cracking of macro sulphur compounds, and the large utilization of water, a decomposed product of H_2O_2 . The desulphurization reaction is an associated one and proceeds through the formation of an intermediate activated complex. The aromatic sulphur compounds can also form activated complexes; however, due to their loose binding forces prefer dissociation into reactants rather than decomposing to products. Therefore, the desulphurization reaction in coal is kinetically very slow, and it was not effective in case of DBTs (Borah et al., 2002).

2.3.3 Summary

In section 2.3, the desulphurization of hydrocarbon fuels, such as light gas oil, diesel oil and model oil (model sulphur compounds) using different oxidants and catalysts are presented. Several oxidation routes have been discussed. These studies show different levels of sulphur conversion which are due to the use of different systems (catalyst, oxidant and fuel oil).

Various studies on the ODS process have reported the use of differing oxidizing agents, such as H_2O_2 in combination with acetic acid (AcOH), H_2O_2 with formic acid, HNO_3 , polyoxometalate, 12-tungstophosphoric acid and *tert*-butyl-hydroperoxide. In these, the sulphur compounds in light oils are S-oxidised by the oxidizing agents, under relatively mild conditions at 303-373 K and atmospheric pressure, to give rise to the corresponding sulphones. These are highly polarized compounds, such that they are removed from the oil by subsequent extraction using water-soluble polar solvents such as Di-methylsulfoxide (DMSO) and Di-methyl formamide (DMF), or by adsorption using silica gel and aluminium oxide. By combination of the processes, the sulphur content of light oils can be reduced to <0.05 wt %. Although all the previous studies demonstrate these ODS processes to be highly effective, detailed studies of reactivity and selectivity of the desulphurization, in the presence of aromatic hydrocarbons, and the denitrogenation behaviour of light oils have so far not been investigated. Also note, among these studies the peroxyacid (mixture of an acid and H_2O_2 , e.g. mixture of formic acid and H_2O_2) seem to be most effective and so far have shown best results. Little work however, has been reported on the detailed mechanistic and kinetic model for oxidation of organic sulphur compounds in a formic acid/hydrogen peroxide system.

In this work, the kinetic model for oxidation of the model light oil (Dodecane solution, containing the pure model sulphur compounds) and sulphur presented in heavy gas oil have been studied using H_2O_2 as oxidant and formic acid as the catalyst. These kinetics model is very important and can be applied to evaluate the performance of ODS on fuels as well as to design a continuous ODS process. Also it aimed to examine the effect of various oxidation reaction parameters (reaction temperature, reaction time and amount of oxidant and catalyst), on the oxidation of sulphur presented in real fuel (heavy gas oil).

2.4 Extraction of Oxidised Organic-Sulphur Compounds

The second step of ODS process is the removal of the oxidised sulphur compounds by selective extraction with a solvent. As mentioned earlier solubility of organic sulphur compounds can also be enhanced by transforming the organic sulphur compounds to increase their solubility in a polar solvent. One way to do this is by selectively oxidizing the organic sulphur compound (thiophene, BTs, DBTs) to sulphones possessing higher polarity. However, besides extraction there may be other methods like distillation, adsorption or thermal decomposition for separating oxidised sulphur containing compounds from fuel (Babich and Moulijn, 2003).

Conversion Extraction Desulphurization (CED) technology began in 1996 when PetroStar Inc. combined conversion and extraction to remove sulphur from diesel fuel (Gentry and Lee, 2000; Dolbear and Skov, 2000). The oxidation requires a stoichiometric amount of the oxidant and proceeds at temperature below 100 °C at atmospheric pressure. Again, a solvent cocktail should be more suitable than an individual solvent, but additional investigations are required to determine the appropriate composition. The processes for deep extract treatment to recover sulphur from the concentrated sulphur-rich extract and to return most of the hydrocarbons to the product stream must be developed to enhance the CED process performance.

Diyarov et al. (1970) analyzed a whole row of different solvents. They found, that solvents with functional groups =NH, -OH, -COOH had the most selectivity to sulfoxidised compounds, because of H-bond formed with the sulfoxide. Solvents with short hydrocarbon chains are more selective. Solvent selectivity with the same hydrocarbon chain and different functional group decreases in order COOH>OH>NO₂. They found 2-chloro-ethanol and mono-ethanolamine as the best solvents for extraction.

Zannikos et al. (1995) reported results in oxidation and solvent extraction technique, using peroxyacetic acid for oxidizing diesel fuel and methanol, DMF and NMP as solvents in one-stage extraction. This combined process (oxidation/solvent extraction) is capable of removing up to 90% of the sulphur compounds in petroleum fractions using NMP as solvent (NMP/gas oil volume ratio = 4).

Ayala (1998) performed bio-catalytic oxidation of diesel oil. The reaction mixture (10 ml) was extracted three times by 2 ml of methylene chloride. The sulphur content of commercial light oil being reduced from 0.2 to 0.05 wt %.

Hulea et al. (2001) performed mild oxidation of kerosene with H₂O₂ over Ti-containing molecular sieves with simultaneous solvent extraction by acetonitrile, methanol or water. Otsuki et al. (2000) extracted vacuum gas oil by DMF, acetonitrile and methanol, but the solvent (DMF) for the removal of sulphur compounds gave the highest oil loss. The sulphur content of vacuum gas oil was reduced from 2.17 to 0.01 wt % by consecutive 10-time extractions.

Mei et al. (2003) had reported an ultrasound assisted oxidative desulphurization followed by solvent extraction. The solvent/oil ratio was set to 1/2 by weight (5gm acetonitrile/10 gm diesel). The best run indicated that the oxidation of diesel (0.1867 wt % sulphur) followed by solvent extraction with acetonitrile produced desulphurised diesel with sulphur content of 0.0012 wt % which corresponds to overall sulphur removal of 99.4 % after 10 minutes.

Anisimov et al. (2003) washed the diesel layer with water to extract the produced sulphones. Rappas et al. (2002) used oxidizer–extractor solution, containing formic acid, water and hydrogen peroxide. The total amount of sulphur in the fuel was reduced to 2000 ppm from 8600 ppm.

Oxidation of the organic sulphur compounds is the main limiting step of the CED technologies. Kinetics of the oxidation reaction can be improved by employing photons or ultrasound. This desulphurization method combines photochemical reactions with extraction of the organic sulphur compounds into an aqueous-soluble solvent (Adschiri et al., 1998). Polar compounds formed are rejected by the non-polar hydrocarbon phase and are concentrated in the solvent. Photochemical reaction is assisted by a photosensitizer—9,10-dicyanoanthracene (DCA). Acetonitrile, which provides relatively high solubility of initial and oxidised sulphur compounds, was found to be the most suitable solvent. After photo oxidation, the solvent and the hydrocarbon phases are separated, as in extractive desulphurization.

In addition, the recovery of aromatics and the photosensitizer from the solvent and desulphurised hydrocarbon stream must be done to increase product yield and economic efficiency. Aromatics are usually recovered by liquid–liquid extraction using light paraffin solvents and are subsequently blended into the desulphurised fuel stream. DCA is removed by adsorption, using a silica gel as an adsorbent. It can be returned to the process after desorption with aqueous solution of acetonitrile.

All of these processes are rather common refinery processes (though not all of the chemicals are common) that can be easily integrated into the refinery and do not require special equipment or condition (Salem and Hamid, 1997; Adschiri et al., 1998).

As reported in the literature, the liquid-liquid extraction technique using water-soluble solvents (DMSO, DMF and MeCN) is usually used for extraction of sulphur compounds from fuel (Paris-Marcono, 1992; Grassman et al. 2001; Vasile et al., 2000; Babich and Moulijn, 2003; Zhao et al., 2003). The former two solvents have a high selectivity for sulphones but also have a high boiling point at 300 °C. This is close to the boiling point of the sulphones, thus creating difficulties in separation and reuse for further extraction

(Gore, 2001, Babich and Moulijn, 2003; Zhao et al., 2003). Shiraishi et al. (2004) have used acetonitrile in their work as the extraction solvent, since it has a relatively low boiling point (82 °C) and can be easily separated from the sulphones by distillation. The extraction efficiency depends on the solvent's polarity, which have to be sufficient to remove sulphur compounds. Examples of polar solvents including those with high values of the Hildebrand solubility parameter (δ) are shown in Table 2.3. Liquids with a δ value higher than about 22 have been successfully used to extract these compounds (Gore, 2001; Zhao et al., 2003).

Polarity, however, is not the only criteria for the selection of suitable solvents. Methanol, for example has sufficient polarity, but its density, 0.79 g/cc, is about the same as that of typical light oil. Other properties such as boiling point and surface tension need to be considered carefully to evaluate the potential for separation and recovery of the solvent for recycling and reuse (Gore, 2001; Zhao et al., 2003).

2.4.1 Summary

Overall, with all of these developments, some work remains to be done to address suitability future approaches to meet the sulphur limit requirements. There are two major problems associated with ODS. First, the oxidants chosen do not always perform effectively and selectively. Some oxidants cause unwanted side reactions that reduce the quantity and quality of the light oil. The second problem is the selection of a suitable solvent for the extraction of the sulphur compounds. Using the wrong solvent may result in removing desirable compounds from the fuel or extracting less than a desired amount of the sulphur compounds from the fuel, in either case, the consequences can be costly.

There is also no detailed work to define the appropriate conditions in terms of the optimum solvents/fuel ratio for extraction, and the impact of such solvents extraction on fuel quality. So the oxidative desulphurization approach (ODS) still needs further research, especially in the area of designing the appropriate selective solvent.

Table 2.3 The Hildebrand solubility parameter δ for some solvents

Solvent	Hildebrand values (δ)
Acetone	19.7
Butyl Cello solve	20.2
Carbon disulfide	20.5
Pyridine	21.7
Cello solve	21.9
DMF	24.7
n-Propane	24.9
Ethanol	26.2
DMSO	26.4
n-Butyl alcohol	28.7
Methanol	29.7
Propylene glycol	30.7
Ethylene glycol	34.9
Water	48.0

For the separation of polar organo-sulphur compounds from heavy gas oils (HGO), especially sulphones, the selection of the solvent is very important. The general requirements for the solvent are as follows: (a) The solvent must have high polarity, (b) the solvent must be insoluble in fuel oil, (c) the solvent must have a substantially higher volatility than that of the solute (sulphones) and (d) the solvent should be thermally

stable. On the other hand, significant poor no polar organo-sulphur compounds removal has been observed in the solvent extraction of petroleum products.

In this work, the extraction of sulphur compounds presented in heavy gas oil (two heavy gas oils with different sulphur content) is studied with three polar solvents (methanol, DMF and NMP) for oxidised and un-oxidised heavy gas oil. The effect of solvent to heavy gas oil ratio on the sulphur removal was studied. Additionally, the solvent effectiveness, partition coefficients and extraction factor for three solvents were calculated and then the multi stage liquid-liquid extraction model is developed. From this model, it is possible to optimise the number of extraction stage and the heavy gas oil to solvent ratio.

2.5 Process Modelling, Simulation and Optimisation

2.5.1 Process Modelling

A mathematical model usually describes a system by a set of variables and a set of equations that establish relationships between the variables. The values of the variables can be practically anything; real or integer numbers, boolean values or strings, for example. The variables represent some properties of the system, for example, measured system outputs often in the form of signals, timing data, counters, event occurrence (yes/no). The actual model is the set of functions that describe the relations between the different variables.

Eykhof (1974) 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 many complex chemical processes, the models result to a set of non-linear equations requiring numerical solution.

Mathematical models are used particularly in the natural sciences and engineering disciplines (such as physics, biology, and electrical engineering) but also in the social sciences (such as economics, sociology and political science). Physicists, engineers, computer scientists, and economists use mathematical models most extensively. They are essential for understanding or controlling the system. Process models are commonly used for the optimisation of chemical processes because they allow for an estimate of the optimum operating conditions without making changes to the actual process. Process modelling plays a vital role in the optimisation of chemical processes in the chemical process industry. Process models are generally a complex set of algebraic and differential equations that can be solved on a computer (Leo and Rassadin, 1992)

A typical chemical engineering model includes the mass and energy balances, physical property correlations, chemical kinetics, etc. and can be described by a set of nonlinear algebraic equations (for steady state process) and differential and algebraic equations (for dynamic process). A steady state model ignores the changes in process variables with time whereas the dynamic model considers dynamic characteristics. The dynamic models are useful to understand the start-up and shutdown characteristics of the process and to study control (Leo and Rassadin, 1992).

2.5.2 Processes Simulation

Simulation is the technique for design validation; process integrity and operation study. Simulation helps to visualise the ultimate picture and trends of various conditions of existing plant as well as those of a new situation of the plant (Maniar and Deshpande, 1996).

Process simulation is an engineering tool used for the design and optimisation of steady state and dynamic chemical process. Process simulation offers many benefits. It is much

easier to incorporate actual process data into a simulation model instead of building a pilot plant and its economics (Iglesias and Paniagua, 2006).

Chemical process simulators simplify the process of evaluating the different design alternatives without the need of making too much process assumptions and considering the entire process structure (Iglesias and Paniagua, 2006). A process simulator has the capability to input and modify the configuration of the process flowsheet and to perform design calculations considering the complete process flowsheet, before they are tried on the actual plant. This way it is possible to model and predict the behaviour of the process flowsheet and to study different operation scenarios (e.g. higher flowrates, different feedstock, modified operating conditions, various levels of energy integration, etc.) in combination with evaluations of the process economics and potential environmental impacts.

2.5.3 Process Optimisation

The mathematical optimisation is the branch of computational science that seeks to answer the question 'What is best?' for problems in which the quality of any answer can be expressed as a numerical value. Such problems arise in all areas of business, physical, chemical and biological sciences, engineering, architecture, economics, and management. The range of techniques available to solve them is nearly as wide. Optimisation techniques specially provide an efficient way to minimise the cost of operation or maximise the profit by better operation and management. A typical chemical engineering problem has many solutions. Optimisation technique and along with computer software makes it efficient, feasible and cost effective to achieve better production, maximum profit and minimum cost and so on for an existing plant operation (Reklaitis et al., 1983).

For any optimisation problem we need to find a combination of parameters (independent variables), which optimise a given quantity, possibly subject to some restrictions on the allowed parameter ranges. The optimisation problem usually consists of the following terms (Edgar and Himmelblau, 1988):

- An objective function
- The controllable inputs are the set of decision variables which affect the value of the objective function.
- The uncontrollable inputs are called parameters.
- Constraints are relations between decision variables and the parameters.

A general optimisation problem (minimization) can be stated mathematically as follows:

$$\begin{array}{lll}
 \text{Minimize} & Z = f(x), & x = (x_1, x_2, \dots, x_n)^T \\
 \text{Subject to} & C_i(x) = 0, & i = 1, 2, \dots, m^* \\
 & C_i(x) \geq 0, & i = m^* + 1, 2, \dots, m
 \end{array}$$

Where $f(x)$ is the objective function, x is the vector of the n independent variables, and $C_i(x)$ is the set of constraint functions. Constraint equations of the form $C_i(x) = 0$ are termed equality constraints (e.g. model equations), and those of the form $C_i(x) \geq 0$ are inequality constraints (e.g. lower and upper bounds of the optimisation variables).

Optimisation problems are classified according to mathematical characteristics of the objective function, the control variables. Mainly, all optimisation problems are encountered into two types; linear optimisation (objective function and constraints are

linear) and non-linear optimisation (objective function and constraints are non-linear systems), and are classified as either unconstrained or constrained, single or multiple parameters optimisation (Edgar and Himmelblau, 1988).

2.5.3.1 Solutions Methods

A solution value for decision variables, where all of the constraints are satisfied, is called a feasible solution. Most solution algorithms proceed by first finding a feasible solution, then seeking to improve upon it, and finally changing the decision variables to move from one feasible solution to another feasible solution. This process is repeated until the objective function has reached its maximum or minimum. This result is called an optimal solution. Reklaitis et al. (1983), and Edgar and Himmelblau (1988) have discussed several solution methods for solving linear and non-linear optimisation problems with unconstrained or constrained, single or multiple parameters optimisation.

There are various methods which can be used for finding an optimum solution of unconstrained optimisation problems, such as Newton's method, Finite different approximation of Newton's method (Edgar and Himmelblau, 1988; Reklaitis et al., 1983).

For any function $f(x)$ with Nonlinear Algebraic Equation (NAE), the local minimum can be found by either direct or indirect methods of optimisation. The direct method is "search for the minimum by direct comparison" of function values of $f(x)$ at a sequence of trial points without involving analytical derivatives. The indirect method of finding x^* , the minimum of $f(x)$, is to set the gradient of $f(x)$ equal to zero.

There are various methods for solving non-linear programming optimisation problems with unconstrained such as iterative (linearization or quadratic) methods, penalty function method and Lagrange multiplier method (Edgar and Himmelblau, 1988).

Quadratic Programming (QP) is the name given to the procedure that minimize variables of a quadratic function of n variables to m linear inequality or equality, or both types of constrains (Edgar and Himmelblau, 1988).

In the course of this work, the constrained nonlinear optimisation problem is formulated and solved using Successive Quadratic Programming (SQP) algorithm. In the SQP, at each iteration of optimisation a quadratic program (QP) is formed by using a local quadratic approximation to the objective function and a linear approximation to the nonlinear constraints. The resulting QP problem is solved to determine the search direction and with this direction, the next step length of the decision variable is specified Reklaitis et al. (1983). See Edgar and Himmelblau (1988) for further details.

2.5.4 Summary

Process models are very useful. They can be used for operator training; safety analysis and design of safety systems; process design and process control systems designs. The development of faster computer and sophisticated numerical methods has enabled modelling and solution of complete system (process), while in the past one had to separate the system to its constituent parts. ‘Mathematical modelling’ of the process concerns with quantitative rather than a qualitative treatment of the process. Process optimisation is concerned with selecting the best among the entire set by efficient quantitative methods. Wide variety problems in the design, construction, operation and analysis of chemical plants (as well as other industrial processes) can be resolved by optimisation.

In this, work, the models of CSTR for oxidation process (first step in the ODS process) and heat integration of this process are developed in gPROMS software. The model includes mass, energy balances around each unit in the oxidation process (CSTR heat exchanger network) and chemical reaction kinetics (Chapter Four). The liquid-liquid extraction, oxidant-catalyst and solvent recovery models are also developed (Chapter Fiver) in gPROMS and HYSYS (Chapter Four). The softwares, are described in the next section. In this work, Successive Quadratic Programming (SQP) method is used to solve the optimisation problem formulated in gPROMS (Chapter Four).

2.6 Simulators Packages

A general-purpose simulator has wide application in process industry. These packages often have sophisticated languages and formalisms for model development that allow the description of complex models with differential/ algebraic equations.

Examples of commercially available process simulators that can be used to model chemical processes are ASPEN PLUS™ by Aspen Technology Inc., CHEMCAD™ by ChemStations, Inc., HYSYS™ by Hyprotech Ltd., gPROMS by Process Systems Enterprise Ltd. and PRO/II by Simulation Sciences Inc., etc. With the ever-increasing capabilities in computer power and accurate models for describing process units, process simulators make it possible to do rigorous analyses and exploring different design alternatives. In addition to the classical experimental approaches (e.g. bench scale, mini-plant, pilot plant, market development plant), the use of modelling and simulation tools is becoming increasingly popular and powerful.

Also there are many specific modelling packages that can be used to simulate some process. In general simulators can be classified in two categories: specific and general packages. Specific packages require and give detailed information. However, they can

be used only for the process for which it is developed. While the general one is used for any process.

In this work, gPROMS is used for modelling CSTR and LLE systems as the mathematical equations can be easily included in it. Also it has advanced optimisation algorithms. In addition to gPROMS, HYSYS was used to model the solvent, catalyst and oxidant recovery system of the ODS process. HYSYS was used due to availability of physical property for HGO and sulphur compounds which are not available in gPROMS. In the following two simulators (gPROMS and HYSYS) will be discussed.

2.6.1 gPROMS Simulator

The **general Process Modelling System** package commonly known as gPROMS is one of the modelling platform of Process System Enterprise (PSE) for both steady-state and dynamic simulation, optimisation, experiment design and parameter estimation of plant operation. The generality of gPROMS means that it has been used for a wide range of applications in petrochemical, food, pharmaceuticals, specialty chemicals and automation. Furthermore, it has the potential to be used for any processes that can be described by a mathematical model (Winkel et al., 1995; Oh and Pantelides, 1996; Georgiadis et al., 2005; Gosling, 2005). The gPROMS is a robust and open structure software (CAPE-OPEN, 2007; Gosling, 2005).

2.6.1.1 The gPROMS Model Builder Family Products

gPROMS Model Builder software has the following components:

- gPROMS Model Builder
- go: CFD
- go: Run
- go: Cap Open

- go: Simulink
- go: Matlab

go: CFD, go: Cap Open, go: Matlab, go: Simulink enable control engineers to deploy complex gPROMS process mode within other software environment. gPROMS model can be exported to the most of the modelling and solution engine in packages such as FLUENT, Aspen Plus, Matlab, Simulink, or various automation systems using the above mention package component. It has the capability of automatic generation of CAP-OPEN Unit Operation models can be exported as a CAP-OPEN Unit Operation model (Gosling, 2005).

2.6.1.2 Key Benefits of using gPROMS

gPROMS has been chosen by model developers for the following advantages:

- Reversible-irreversible, symmetric-asymmetric, continuities –discontinuities and direct system are handled by gPROMS simulators. These capabilities of gPROMS for solution of process makes more robust and faster.
- It can handle a large number of differential and algebraic equations (more than 100,000 differential and algebraic equations). In addition it can also handle PDE equations.
- Equations of physical system can be written as they appears or books i.e. without reformulation.
- Single or multi-dimensional arrays of both variables and equations can be described either implicitly or explicitly. All variables, other than those that are functions of time only, can be featured as distributions over one or more continuous and/or discrete domains.
- gPROMS allows using a single equipment model (described by several equations) for multiple operating procedures (process) and single process can be

used for several optimisation tasks. It provides greater flexibility and model development time is reduced.

- It allows simultaneous optimisation of equipment sizes and operating procedures that saves capital and operational cost in long run.

All of the above features of gPROMS reduce both time and numerical expertise to perform model-based activities and assist the user. It can easily link to external components, for example, physical properties packages or control system software. In this work, gPROMS (version 2.3.4) is used to develop model for simulation and optimisation of ODS process.

2.6.1.3 Model Development using gPROMS

The gPROMS model builder makes it easy to construct and manage projects. Figure 2.8 shows all the currently opened project and cases.

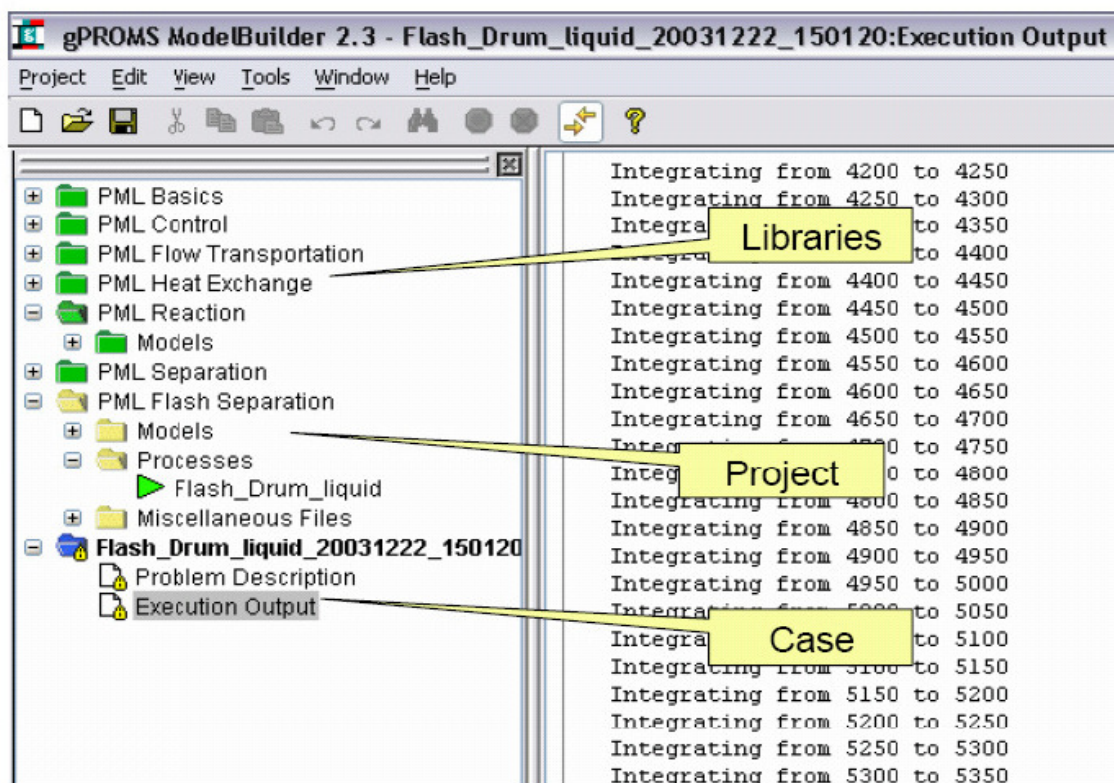


Figure 2.8 The Project Tree for building New Process Using gPROMS.

In gPROMS, the project has several subsections, among them the important sections are: Variables type, Model, Tasks, Process, Optimisation, Parameter estimation and Experimental design (Figure 2.9).

In VARIABLES TYPE section, the types and ranges of variables are specified for different models processes. In MODEL section, this is where the process model (which is described by a set of differential and algebraic the operation equations) is written. The model entity is divided into three sections: PARAMETERS, VARIABLES and EQUATIONS. PROCESS section contains specifications for simulating the process. Optimizing of the process is written in OPTIMISATION section. MODEL and TASK can be constructed in a hierarchy of arbitrary depth.

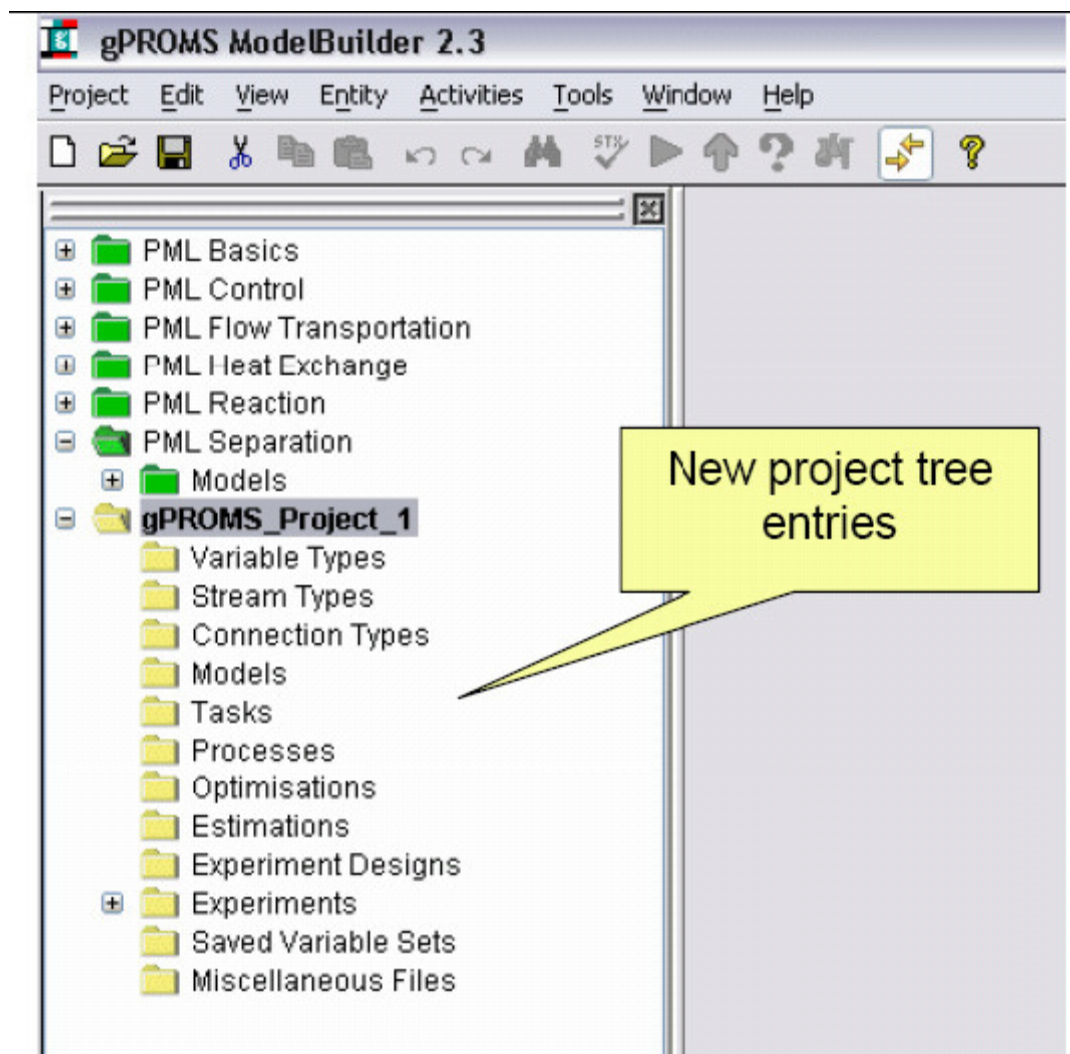


Figure 2.9 Subsection of a Project Tree

2.6.1.4 Defining a Model

In gPROMS, the model entity (see Figure 2.10) is where the process model is written out as stated in the previous section. The three sections of this entity (PARAMETERS, VARIABLE AND EQUATION) are clarified below:

PARAMETERS – this section declares the types and constants names used in the model. Parameter types include REAL, INTEGER AND LOGICAL. These are constant values used in the simulation and they are fixed which means that they cannot be calculated. Below are some examples of the parameters used in the CSTR program as declared in gPROMS model file as:

```
NoComp    AS    INTEGER
```

```
E          AS    REAL
```

These parameters describe the number of components (NoComp) and activation energy (E) respectively. In this model word REAL refers to the real values and word INTEGER refers to integer values.

The VARIABLE section declares the set of variables used in the model. This set of variables describes the time-dependent behaviour of the system. According to requirements in the model the variables values may or may not assigned. All variables types must be declared and defined in VARIABLE TYPE section. Concentration and reaction temperature are defined as variables type in the CSTR model and are declared within the model entity as:

```
C          AS    Conc.
```

```
Tr         AS    Rea.Temp
```

EQUATIONS – In this section the model equations (which are sets of differential and algebraic equations) are written out in gPROMS code. Equation 4.4 (Chapter 4) is illustrated here as an example of the model equation:

$$V = \frac{F_{A0} X_A}{-r_A}$$

This equation is declared in gPROMS model file as:

$$V = F_{A0} * X_a / -r_A ;$$

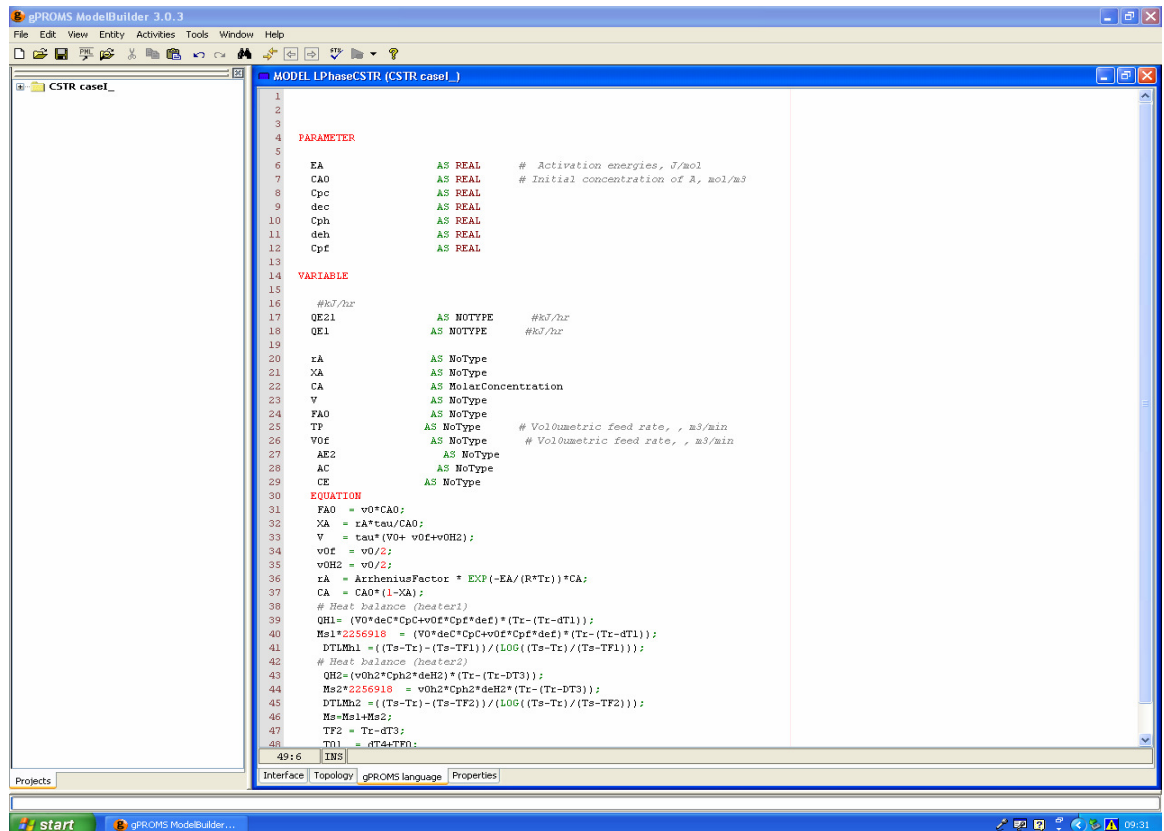


Figure 2.10 Snapshot of the Model Entity for the CSTR gPROMS model

2.6.1.5 Defining a Task/Process

TASK and PROCESS are defined as the modelling of operating procedure and control strategies. The process consists of the following sections:

- PARAMETER
- VARIABLE
- UNIT
- EQUATION
- SET

- ASSIGN
- INITIAL
- SOLUTION PARAMETER
- SCHEDULE

PARAMETER, VARIABLE, UNIT and EQUATION are described similarly to those in MODEL section (Section 2.6.1.4).

In SET section PARAMETER values are defined. In ASSIGN section, degrees of freedom are specified. In the INITIAL section the starting simulation values of the differential equations appearing in the model are specified.

The operator called SWITCH, CONTINUE and SEQUENCE is used to define the parallel, concurrent and sequential operation or tasks. The operator called RESET, REPLACE and REINITIALIZE is used to reinitialise different variables, parameter of the model.

The user defines mathematical solvers and output specifications for the process output, different solvers are available for simulation, optimisation, parameter estimation and experimental design (Tijl, 2005). Output specifications are used for display results in EXCEL and gRMS using the keyword gExcelOutput and gRMS respectively. Main mathematical solvers for simulation, optimisation and parameter estimation are DASOLV, DOSOLV and PESOLV respectively

2.6.1.6 Simulation in gPROMS

The SOLUTION PARAMETER section of the PROCESS in a project allows the specification of parameters of the results and the mathematical solvers for each type of activity (simulation, optimisation and parameter optimisation). Built-in solvers solution parameters take the default values unless user specifies any parameters.

There are three standard mathematical solvers for the solution of sets of nonlinear algebraic equations in gPROMS, namely BDNLSOL, NLSOL and SPARSE: BNDLSOL (Block Decomposition Non Linear solver). NLSOL is nonlinear solver, with and without block decomposition. SPARSE is sophisticated implementation of Newton-type method block decomposition.

Two mathematical solvers (DASOLV and SRADAU) solve mixed sets of differential and algebraic equations in gPROMS.

2.6.1.7 Optimisation in gPROMS

gPROMS provides a general numerical solver manager for the steady state and dynamic optimisation problem called DOSOLV. Mathematical solvers of the optimisation are specified in PROCESS entry SOLUTION PARAMETER subsection as:

DASolver="CVP_SS";

DASolver="CVP_MS";

PIECEWISE CONSTANT, PIECEWISE LINEAR and TIME INVARIANT must be assigned in the gPROMS PROCESS entity. The important parameters specified in the optimisation section are:

- Time horizon and its limits and different control interval

- Limits of the other variables and their limits called equality constraints and inequality constraints
- Interior point constraints variables and their limits different control interval

The limits of the control variables by default are the values specified in VARIABLE TYPE entities or in the PRESET section of the PROCESS entity unless user specifies the limits of those variables in the optimisation entry.

In summary gPROMS is particularly suitable for the modelling and simulation of any plant operation (steady state and dynamic) that is because this software package is an equation oriented general purpose modelling, simulation and optimisation tool for combined discrete and continuous processes. Due to robustness and flexibility of this software as mentioned in this chapter, gPROMS has been chosen to use for modelling, simulation and optimisation in this work.

2.6.2 HYSYS

HYSYS is computer software package developed by Hyprotech Ltd. The software package combines comprehensive data regression, thermodynamic database access and distillation technology to enable the design and analysis of separation systems, including isotropic and extractive distillation and non-ideal, heterogeneous and multiple liquid phase systems (HYSYS 2002). HYSYS helps process industries improve productivity and profitability throughout the plant lifecycle. The powerful simulation and analysis tools, real-time applications and the integrated approach to the engineering solutions in HYSYS enables the engineers to improve designs, optimise production and enhance decision-making. Some of the key benefits offered by HYSYS are listed below:

1. Improved process designs

2. Engineers can rapidly evaluate the most profitable, reliable and safest design
3. Ensure optimal equipment performance
4. HYSYS allows users to determine rapidly whether equipment is performing below specification.

2.6.2.1 HYSYS Features

HYSYS is built upon proven technologies, with more than 25 years experience supplying steady-state simulation tools to the oil & gas and refining industries and provides the following features (HYSYS, 2002):

- Easy to use windows environment
- Comprehensive thermodynamics foundation, accurate calculation of physical properties and transport properties of oil and gas contains an extensive component database and the ability to add components.
- Permits the integration of user created unit operations, proprietary reaction kinetic expressions, and specialized property packages and interfaces easily with programs such as Visual Basic and Microsoft Excel.
- Comprehensive unit operations, includes distillation, extractor, reactions, heat transfer operations, rotating equipment, and logical operations in the steady-state and dynamics environment.

2.6.2.2 HYSYS Options

HYSYS provides flexibility and power to users by using an open architecture which enables industry specific capabilities to be easily added by AspenTech. The following options are available for HYSYS to help users needs are met and enhance Process Lifecycle Management (PLM) (HYSYS, 2002).

- ACM Model Export™ Option

- Aspen WebModels™ Option
- HYSYS Crude Module™ Option
- HYSYS Data Rec™ Option
- HYSYS Dynamics™ Option
- HYSYS Neural Net™ Option
- HYSYS OLGAS™ Option
- HYSYS OLI Interface™ Option
- HYSYS Optimiser™ Option
- HYSYS PIPESYS™ Option
- HYSYS Upstream™ Option

Further information can be found in developers websites (www.aspentech.com) and HYSYS user guide (HYSYS 2002).

In this work, HYSYS (version 3.1) is used to develop oxidant-catalyst and solvent recover system for ODS process.

2.7 Process Integration

2.7.1 Introduction

Process plants, oil refineries, petrochemical complexes and gas plants generate large quantities of low grade heat. This energy is often rejected to atmosphere using either air or cooling water systems. There are, however, opportunities to recover some of this energy, and utilise it, either as part of a process integration scheme, or for heating in domestic and commercial properties by the installation of a hot water system.

Recovery of waste heat provides both financial and environmental benefits to process plant operators. From energy savings point view the important field of energy uses improvement are the heat exchanger network (HEN) retrofit projects to maximize the

existing heat recovery. The tool known as Pinch Technology (PT) for designing heat exchanger network was developed in the late 1970's by Linnhoff and Flower (1978).

Pinch Technology provides a systematic methodology for energy saving in processes. The application of PT in continuous process is becoming more attractive and providing a suitable tool for analyzing any processes at different stages of the design. The PT provides many helpful graphical representations that are to be used by the designer for analysis and for better understanding of the problem. It provides a systematic methodology for energy saving in processes and total sites. Using PT, it is possible to identify appropriate changes in the core process conditions that can have an impact on energy savings (Linnhoff and Flower, 1978).

To show the pinch technology concepts, Figure 2.11 shows a simple example of heat recovery (heat exchanger network) containing one hot stream and two cold streams (Floudas, 1995). The hot stream needs to be cooled to its target temperature T_{ht} , and both cold streams need to be heated to their target temperatures T_{ct} . The hot stream exchanges heat with cold streams in the heat exchangers, where the temperature of hot stream is decreased to a certain value, but to reach its target temperature a cooler is used to reduce the temperature of the hot stream to the target temperature. After heat exchange with the hot stream, the first cold stream requires extra heating to achieve its target temperature; a heater is employed for this purpose (Smith, 2005).

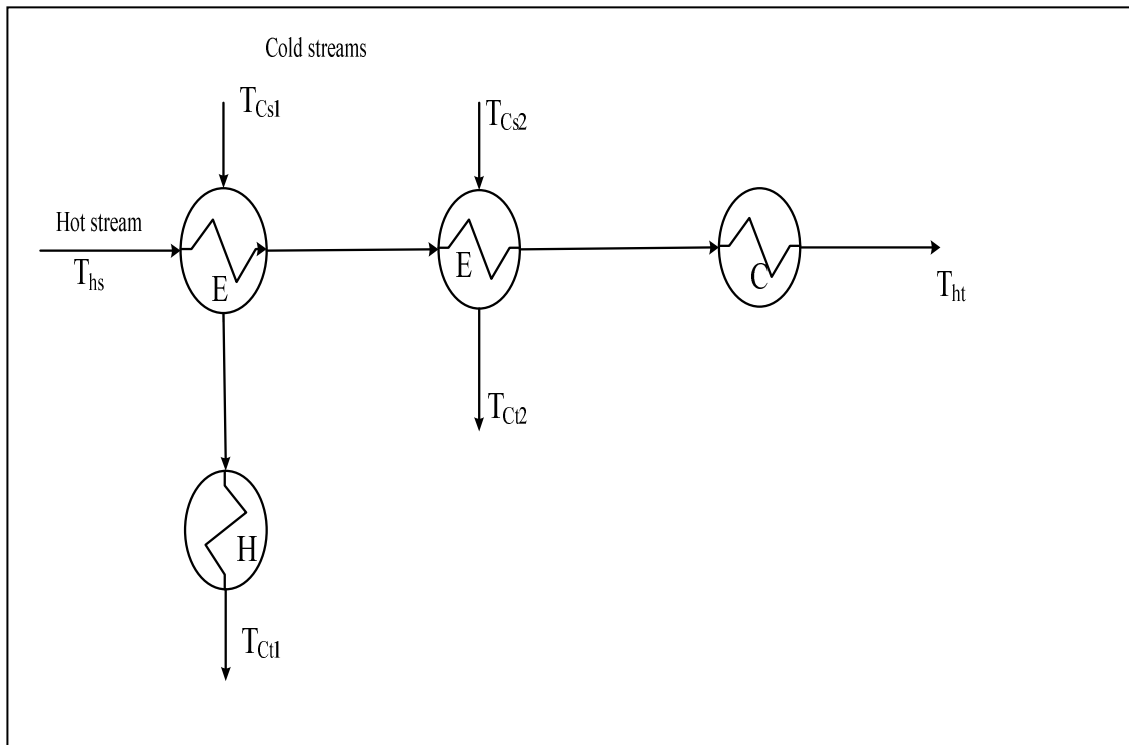


Figure 2.11 Heat recovery network (Smith, 2005)

A process plant generally consists of all or some of the following sections:

- A reactor, where the main chemical processes take place and impure product is formed from the raw materials.
- A separation system, that divides up the mixture of products, waste and unreacted raw materials emerging from the reactor using some separating agent, such as heat or a solvent.
- A heat exchanger network, that recovers heat from hot product streams to heat the cold feed streams.
- Utility system (Heater and Cooler).

Conventional design methods start by designing the reactor, then the separation system, then the heat exchanger network, and finally finish by using utilities to supply the residual needs (Douglas, 1988).

Process Integration goes a stage further by looking at how the reaction and separation systems fit in with the overall process. Often, changes to the process can be found (usually in the separation system) which increase overall heat recovery and give a better integrated system.

The utility system consists of hot and cold utility units. Typical hot utility units are turbines, generators, motors and boilers providing the required electricity, steam and hot water. Cold water from external sources is used as the cold utility, providing the necessary cooling in the processes. In the heat recovery system, the process streams exchange heat so as to reduce the hot and cold utility requirements. The only units in a heat recovery system are the heat exchangers.

Process Integration is a systematic method and the stages of any study can be clearly listed as following:

- Collect process data,
- Form heat and mass balances,
- Extract the Process Integration stream data,
- Select the minimum temperature approach between hot and cold streams,
- Calculate energy targets and the pinch point,
- Examine possibilities for process change and recalculate targets if necessary,
- Design an ideal heat exchanger network to achieve the targets,
- Relax this network to give a variety of practical energy-saving projects,
- Do an economic evaluation and select the best possibilities.

2.7.2 Heat Exchangers and Heat Exchanger Networks

A heat exchanger is a unit in which heat is transferred from a hot stream to a cold stream. A more correct term of reference is a heat exchange match between two

streams, as this makes no assumption regarding the type of exchanger or the number of units needed to fulfil a particular duty. A series of matches in the same process or serving a common set of streams is known as a heat exchanger network.

Heat exchanger network (HEN) has been one of the most well studied issues within process synthesis during the last three decades. Process synthesis, a part of process design, has the objective of developing systematically a flowsheet which describes the overall process system and which meets certain specified performance criteria and is ultimately able to transform the raw materials into the desired products (Floudas, 1995). The major challenge within the heat exchanger network synthesis problem is to identify the best pair of process streams to be connected with the heat exchangers, so as to maximize economical energy recovery.

The design problem is to devise a network that uses as little external energy as possible and as few matches as possible. Figure 2.12 shows a simple system consisting of two streams and a single heat exchanger (Smith, 2005). The top line is the hot stream being cooled from T_1 to T_2 , while the bottom line is the cold stream being heated from T_1 to T_2 . The match itself is shown as a dumb-bell shape of two circles joined by a vertical line, with the heat load of the match, Q , also marked. This representation is particularly convenient for comparing different arrangements of matches for the same process.

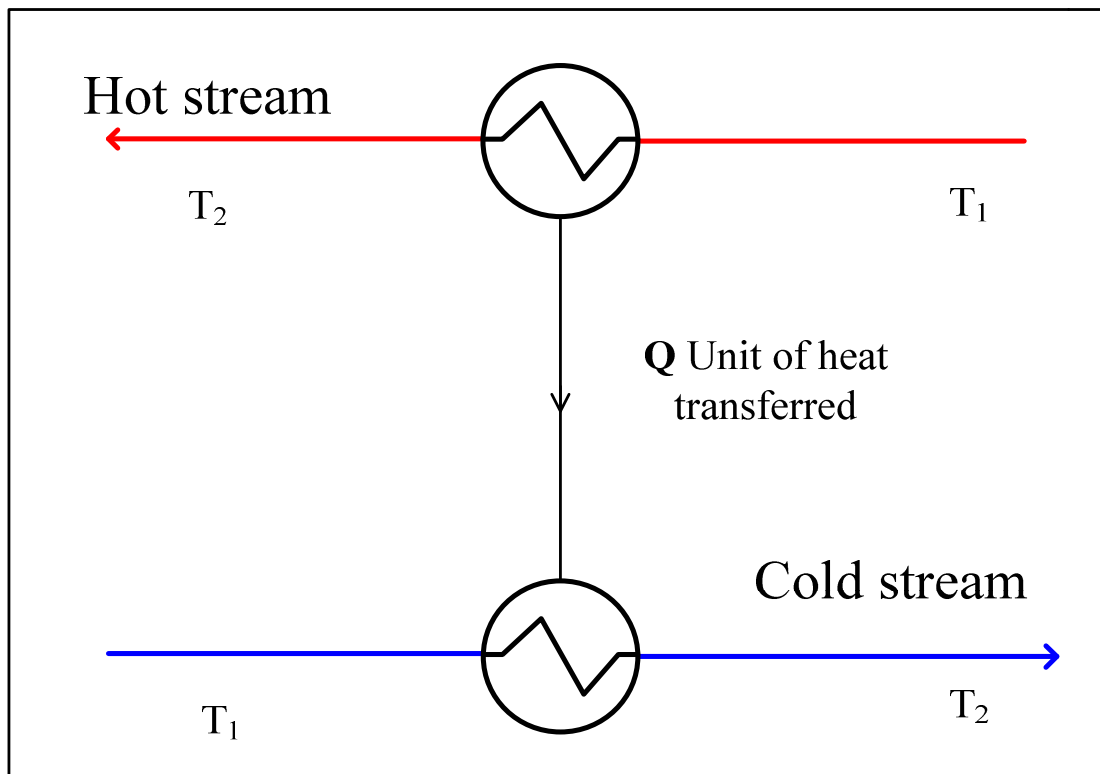


Figure 2.12 Grid notations for heat exchangers

2.7.3 Minimum Temperature Approach between Streams

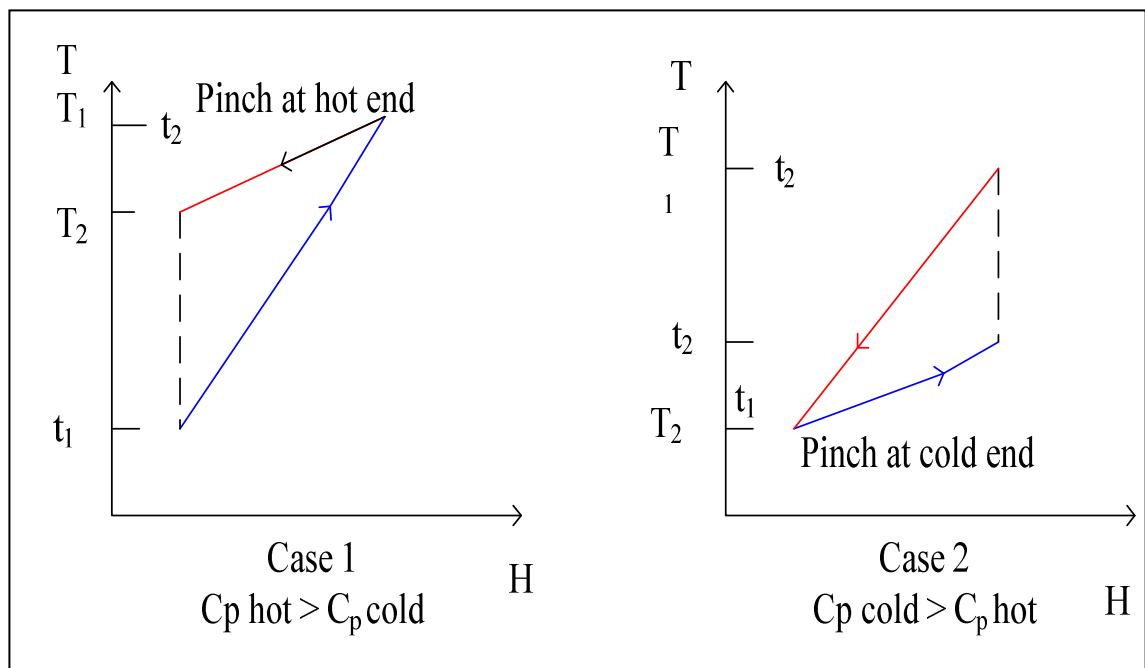
One of the key concepts to understand in Process Integration is that of the minimum allowable temperature approach or difference, ΔT_{min} . This is best illustrated by the use of temperature-enthalpy graphs as follows (Smith, 2005).

Consider a hot stream transferring heat to a cold stream. The C_p values of both streams are known, together with the supply temperatures T_1 and t_1 respectively. The maximum amount of heat that can be transferred and the temperature of each stream are shown in Figure 2.13 for two cases.

In Case 1 the hot stream has the larger C_p and therefore, given an infinitely large exchanger, the temperature of the cold stream will reach the initial temperature of the hot stream (pinch at hot end).

In Case 2, where the cold stream has the greater C_p value (the opposite occurs). The point at which the lines meet shows the limit of temperature change and heat recovery is constrained, or pinched, at this point (pinch at cold end).

The next step a finite minimum temperature difference, ΔT_{min} , must be selected, shown in Figure 2.13 by moving the lines for the hot and cold streams apart horizontally to create a temperature difference at the pinched end of the match. After that a real heat exchanger can be envisaged in each case, exchanging heat, Q , from the hot to the cold stream, where the minimum temperature difference, ΔT_{min} , has been specified for each match (www.cheresources.com).



Figur.2.13 Limiting heat transfer cases showing maximum energy recovery

In Case 1 of Figure 2.14, the limiting factor is the temperature difference at the hot end of the match, while in Case 2 it comes at the cold end. The practical design for heat recovery, and the constraining point, or pinch, is therefore dependent on the chosen value of ΔT_{min} . The concept of a pinch is extremely important within the wider context of heat exchanger network design. Its prime significance is as described here: the limit

of practical heat transfer enabling the maximum energy recovery to be found, and giving a target for heat exchange and residual heating and cooling (www.cheresources.com; Smith, 2005)

However, it is possible for a minimum temperature difference to be observed in the middle of a match, particularly if a phase change occurs, as shown in Figure 2.15 and not necessarily at one end of an exchanger. This indicates the importance of understanding the nature of the heat transfer operations and the physical states of the materials involved.

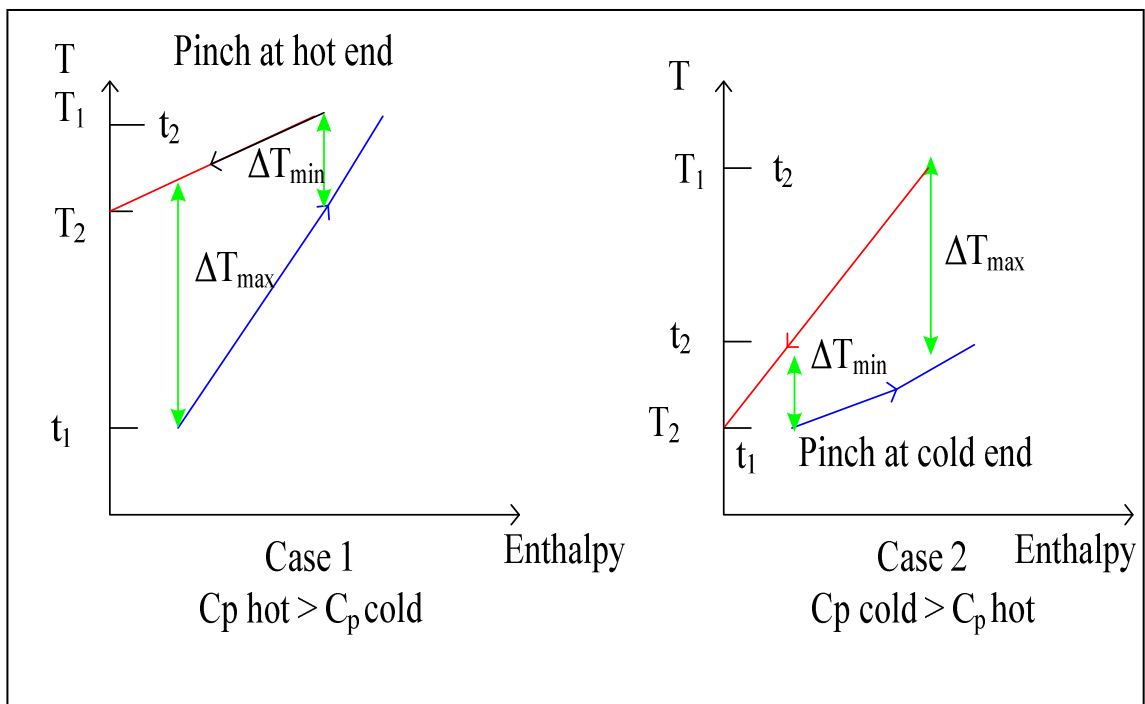


Figure 2.14 Maximum energy recovery with a real ΔT_{min}

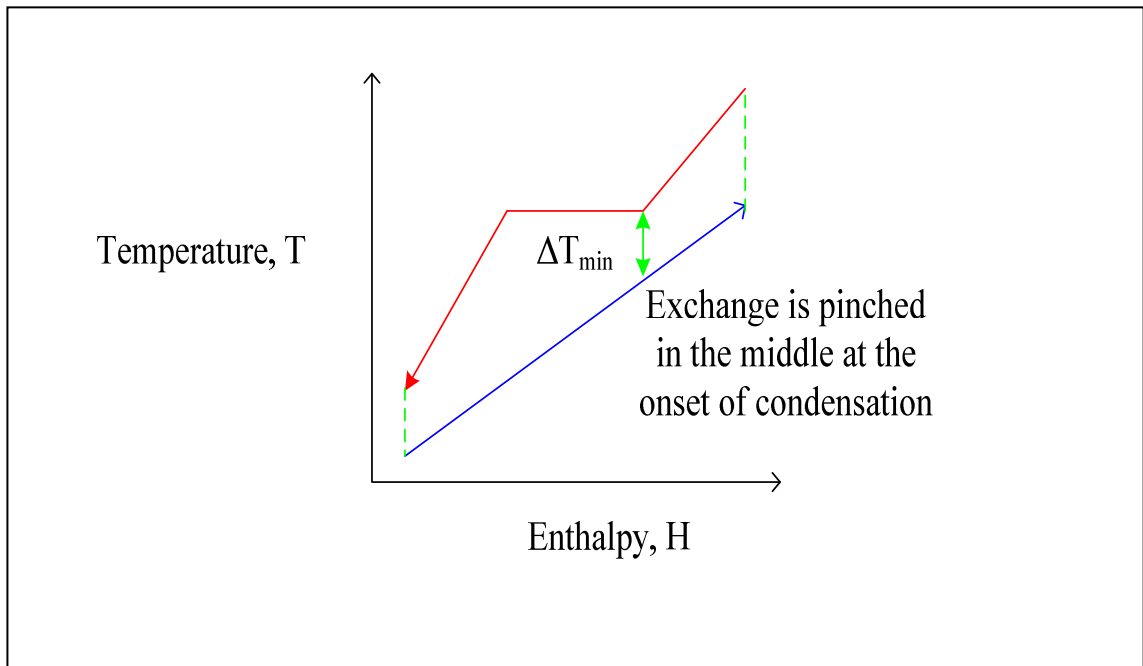


Figure 2.15 ΔT_{min} within a pinched exchanger

The value of ΔT_{min} should not be confused with the logarithmic mean temperature difference, $LMTD$, which is used to represent the average temperature difference throughout the match for the design of a pure counter-current, single pass exchanger.

The $LMTD$ is used in the equation:

$$Q = U \times A \times LMTD \quad (2.2)$$

where

Q is the total heat transferred from the hot stream to the cold stream.

A is total area of heat transfer.

U is the overall heat transfer coefficient.

$LMTD$ is the logarithmic mean temperature difference.

The equation for the log mean temperature difference is as follows:

$$\Delta T_{lm} = \frac{(T_{h,o} - T_{c,o}) - (T_{h,i} - T_{c,i})}{\ln\left(\frac{T_{h,o} - T_{c,o}}{T_{h,i} - T_{c,i}}\right)} \quad (2.3)$$

Where $T_{h,i}$, $T_{c,i}$ and $T_{h,o}$ and $T_{c,o}$ are the inlet and outlet temperatures of the hot and cold streams respectively.

In a real case, a factor usually between 0.8 and 1 would be included to allow for the fact that pure counter-current heat exchange is usually not attainable in practice. *LMTD* represents an average overall temperature difference, while ΔT_{min} is the minimum allowable temperature difference anywhere in the exchanger (Smith, 2005).

In order to achieve maximum energy recovery the following rules of Tjoe and Linnhof (1986) and Linnhof et al. (1982) should be followed:

- 1) No cold utility to be used above the pinch point.
- 2) No hot utility to be used below the pinch point.
- 3) No process heat to be transferred across the pinch.

2.7.4 Summary

In the pinch technology applications, the first step is the selection of data for streams (hot and cold) for performing technical analysis in which the supply temperature and target temperature as well as the enthalpy change and heat capacity and flow rate are to be identified. It is important to have all the required data for the existing energy consumption under the operating conditions to do the pinch analysis.

In this work the heat integration of oxidation process is developed applying Pinch technology and by matching cold feed streams with hot product streams to determine a retrofit design by putting a number of heat exchangers that can reduce the energy consumption, maximize energy recovery and minimize capital investment.

2.8 Conclusions

Sulphur removal from fuels sources is becoming more challenging and difficult due to shift in the global regulatory climate, increasing global demand for petroleum based products and deteriorating crude characteristics.

The very low levels of sulphur required in transportation fuels in the near future its difficult or high cost by current hydrodesulphurization process (HDS). Therefore, several alternative strategies to HDS are currently being explored, which include various oxidative desulphurization techniques (ODS) that not require the use of expensive hydrogen. The applicability of ODS process depends on the kinetics and selectivity of the oxidation of organic sulphur compounds to sulphones.

Various studies on the ODS process have reported the use of differing oxidant, such as H_2O_2 in combination with organic acids (i.e. formic acid), polyoxometlate, 12-tungstophosphoric acid and *tert*-butyl-hydroperoxide. There is no detailed work to define the appropriate oxidation reaction conditions in terms of the optimum reaction temperature, oxidants, catalysts, solvent, solvent to fuel ratio and the impact of such solvents extraction on fuel quality. Also there is no detailed work in the area of process modelling and scaling-up.

Much research is required for developing the oxidative desulphurization process. The two major tasks are to identify oxidant-catalyst systems with more selective oxidation capacity for sulphur containing compounds and to develop a more effective separation process such as extraction solvent, adsorption, etc. to cope with higher sulphur contents. In this work therefore, oxidative desulphurization of a model sulphur compounds and heavy gas oils (HGO) are conducted with hydrogen peroxide (H_2O_2) as oxidant and formic acid (HCOOH) as catalyst. The extraction of sulphur compounds from oxidised heavy gas oil (HGO) is investigated using three solvents methanol, dimethylformamide

(DMF) and N-methyl pyrrolidone (NMP) as solvents. For each solvent, the partition coefficients (K_p) are determined.

General process modelling, optimisation and heat integration aspects are presented in this chapter. The features of the gPROMS program used for the design, simulation and optimisation are highlighted. gPROMS has a wide range of application which can be used for steady state or dynamic simulation. It can also be used to perform parameter estimation calculations for complex system. Due to robustness and flexibility of this software as mentioned in earlier, gPROMS has been chosen to use for modelling, simulation and optimisation in this work.

In this work, kinetic models for the oxidation process are investigated based on the experiments described in Chapter Three. A CSTR model is then developed for the oxidation process for evaluating viability of the large-scale operation and heat integration of the process is conducted carrying out modelling and optimisation using gPROMS software (Chapter Four).

A liquid-liquid extraction model is developed for the extraction of sulphur compounds from the oxidised heavy gas oil. With the experimentally determined partition coefficient $K_p(s)$ (for methanol, NMP and DMF), multi stage liquid-liquid extraction process is modelled using gPROMS software (Chapter Five).

In addition to gPROMS HYSYS was used in Chapter Six to model and simulate solvent, catalyst and oxidant recovery system.

Chapter Three

Oxidation and Extraction: Experimental Work

3.1 Introduction

Sulphur compounds are known to be slightly more polar than hydrocarbon of similar structure. However, oxidised sulphur compounds such as sulphones or sulfoxide are substantially more polar than sulphide. More importantly, the oxidation of sulphides to sulphones is usually much easier and faster than the oxidation of most hydrocarbons (Campestrini et al., 1988; Ballistreri et al., 1991). This permits the selective removal of sulphur compounds from hydrocarbons by a combination process of oxidation and solvent extraction (or solid adsorption) (Aida et al., 1993; Otsuki et al., 2000).

The applicability of an oxidative desulphurization process (ODS) depends on the kinetics and selectivity of the oxidation of the sulphur compounds to corresponding sulphones. In organic syntheses the most common procedure to prepare sulphones is by oxidation of sulphides, generally by a reaction with peroxy-carboxylic acid generated in situ by hydrogen peroxide and the appropriate carboxylic acid (Cremllyn, 1996).

Recently, the activation of hydrogen peroxide with transition metal complexes such as $H_3PM_{12}O_{40}$ [M=Mo(VI), W(VI)] is of increasing interest in producing more effective and selective oxidants as peroxo-metal species for the oxidation of nucleophiles (such as olefins and organic sulphur compounds) under phase transfer conditions (Venturello et al., 1985; Ballistreri et al., 1991). Even sulphur compounds with less nucleophilicity such as dibenzothiophene can be oxidised under mild condition to sulphones in high yields (Collins et al., 1997).

In this chapter, an oxidative desulphurization (ODS) process operating at low temperature and atmospheric pressure was developed. The effectiveness of this process on model sulphur compounds and heavy gas oils were evaluated. Finally the kinetics study was conducted.

3.2 Materials Used

3.2.1 Materials

Three types of model sulphur compounds are selected to evaluate the reactivity of sulphur in an oxidation reaction. These are Di-n-butylsulfide, Di-methylsulfoxide and Dibenzothiophene (DBT) purchased from Aldrich. Dibenzothiophene (DBT), other corresponding-ring thiophenes and substituted forms of these compounds are particularly difficult to remove by hydrodesulphurization as mentioned in Chapter Two.

Hydrogen peroxide (30 wt% H₂O₂) was used as oxidant and supplied (Surechem Products Ltd.) Formic acid (99 wt % HCOOH) was used as a catalyst (supplied by British Drug House, BDH). Methanol, N-Methyl Pyrolidone (NMP), Di-Methyl Formamaide (DMF) and Dodecane, are used as solvents. These were supplied by Surechem Products Ltd. The boiling point and specific gravity of solvents are shown in Table 3.1.

Table 3.1 Boiling point and specific gravity of solvents

Component	Sp.Gr at 15.56/15.56 °C	Boiling point (°C)
N-Methyl Pyrolidone	1.028	205
Di-methyl formamaide	0.960	196
Methanol	0.800	64.65

3.2.2 Heavy Gas Oil

The real fuels used in this study (HGO) are obtained from Libyan crude oils and their properties are shown in Table 3.2, along with the standard methods that were used to determine them.

Table 3.2 Properties of original feeds

Physical property	HGO _A	HGO _B	Method
Specific gravity at 15.56/15.56 °C	0.8576	0.8820	ASTM D1298
K. viscosity at 50 C, cst	7.06	7.12	ASTM D445
Flash point closed cup, C	115	127	ASTM D93
Total sulphur, ppm	1560	1066	ASTM D4294
Copper corrosion 3 hrs at 50 C	1A	1A	ASTM D130
Cetane index	53.4	54.6	ASTM D976
Diesel index	60.2	52.8	IP21
Gross calorific value , MJ/Kg	45.213	45.305	ASTM D240
Total acidity KOH/ gr	0.04	0.1	ASTM D
Water content, % vol.	Nil	Nil	ASTM D95
Aniline point, C	>88	83	ASTM D611
Pour point °C	27	9	ASTM D97
API gravity	33.6	29.1	ASTM D1298
Distillation °C			ASTM D86
Initial boiling point	276	250	
10%	339	307	
20%	350	323	
30%	358	333	
40%	364	338	
50%	369	344	
60%	374	350	
70%	377	357	
80%	382	366	
90%	389	379	
Final boiling point	398	397	

3.3 Setup of Oxidation Experiments

A 500 ml 4-necked flask fitted with a mechanical stirrer, a thermocouple and a thermometer was used to carry out the oxidation reaction. The reaction flask was placed in a heating mantle equipped with a temperature controller. Figure 3.1 shows the assembled apparatus used for oxidation reaction.

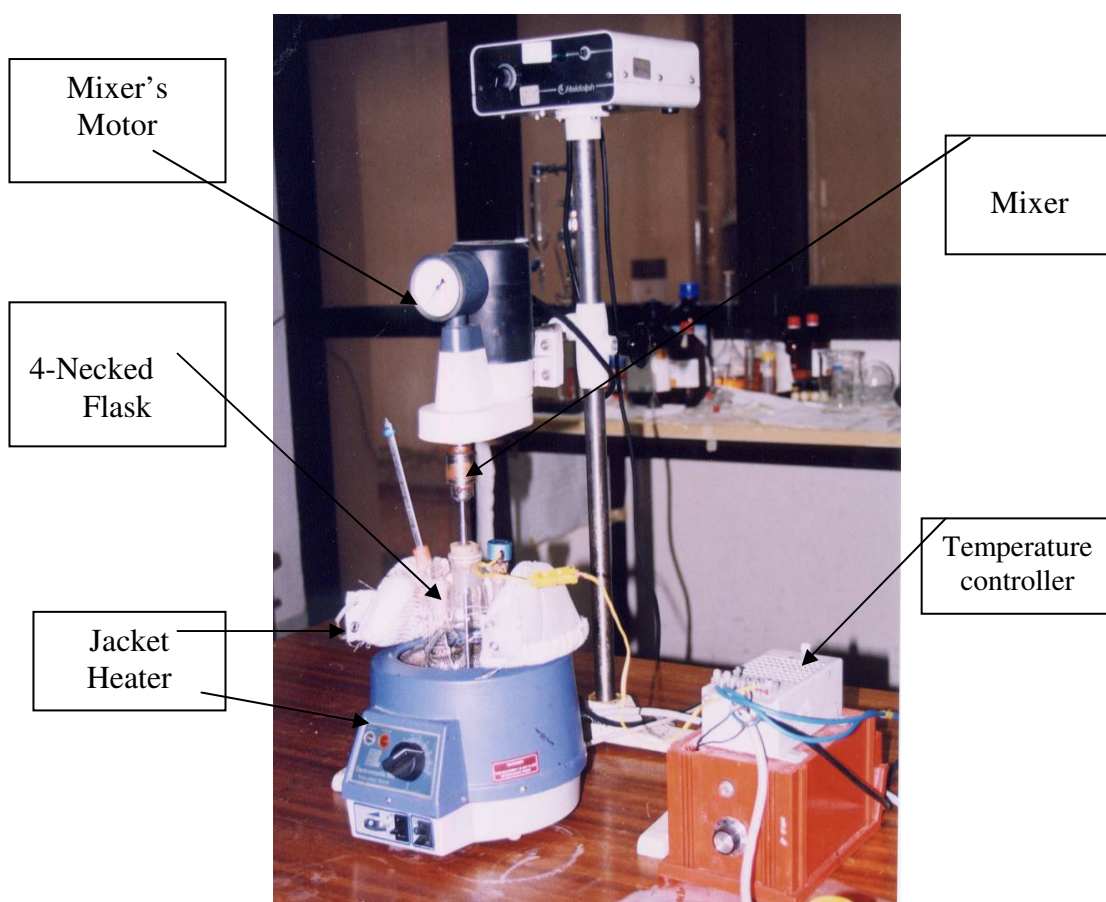


Figure 3.1 Experimental setup for oxidation

3.4 Procedure for Oxidation Experiments

3.4.1 Oxidation of Model Sulphur Compounds

The model sulphur compounds, Di-n-butylsulfide, Di-methylsulfoxide and Dibenzothiophene were dissolved in Dodecane as the model oil, resulting in initial

sulphur concentration of 1535, 1228 and 943 ppm respectively. The oxidation of model sulphur compounds (model oil) is conducted in a flask with a mechanical stirrer. A 1.25 ml of hydrogen peroxide is added to 30 ml of model oil in the flask. The flask is placed into the heating mantel and stirred at 750 rpm. When the required reaction temperature has been reached (approximately after 10 minutes) 30 ml of formic acid catalyst was added to the flask to initiate the reaction.

This procedure was carried out at different reaction temperatures (20, 40, 60 and 80 °C). Samples from the reactor are taken at different reaction time. The collected samples were left to settle for few minutes after which two layers were formed; the top layer (model oil) and the bottom layer (oxidised-catalyst). The top layer is analyzed by XRF in order to determine the sulphur content.

3.4.2 Oxidation of Heavy Gas Oil

The same procedure followed for the heavy gas oils using equal volumes of the formic acid and heavy gas oil (30 ml) and half volume of hydrogen peroxide (15 ml) at different reaction temperatures, 40, 60, 80 and 100 °C. Samples are taken for analysis at different time intervals. Note, 1.25 ml of hydrogen peroxide was used for oxidation of model sulphur compounds. However, this amount of hydrogen peroxide for oxidation of heavy gas oil was forming one phase (sludge). Therefore 15 ml was used for the oxidation of heavy gas oil.

After each run, the mixture is allowed to cool down to 25 °C whereupon two layers are formed by gravity. The top layer (oil) was separated, washed successfully with water, 5% aqueous sodium bicarbonate and water and was finally dried over anhydrous magnesium sulphate, then analyzed by XRF to measure the sulphur content.

3.5 Sulphur Measurement

Based on ASTM D4294 method, Energy-Dispersive X-Ray Fluorescence (EDXRF) was used to determine the total sulphur content in the model oil and real fuel (HGO). The Sulphur-in-Oil Analyzer (SLF A-1100, Horiba Inc., California), was employed to determine any sample with total sulphur content range from 0 to 5 wt. % of sulphur. Figure 3.2 shows the HORIBA model SLFA-1100H used in the current study.



Figure.3.2 HORIBA model SLFA-1100H sulphur-in-oil analyzer

3.5.1 Sample Cell

The sample cell used for the SLFA analyzer has been specially developed for the accurate measurement of the sulphur content in fuel oil by EDXRF spectroscopy method. The major part of the sample cell is made of plastic. It consists of the following parts: disposable cell, inner frame, five holder cell, and cells window.

3.5.2 Calibration of Equipment

The calibration of the setup is necessary to measure the sulphur content of oil fractions.

The calibration requires more than one sample of which sulphur concentration is known; this is called a standard sample.

In general, to measure the sulphur content in fuel oil, the following two types of standard samples are to be used.

1. Standard samples prepared by mixing tetralin, and dibutylidissulphide (DBDS).
2. Standard sample for sulphur content in oil, verified by the Japanese Petroleum Society.

3.6 Conversion and Reaction Rates

All the experiments carried out in this chapter were in a batch reactor with the following characteristics:

- There is no inflow or outflow of material
- The reactor is well mixed
- For most liquid-phase reactions, the density change is usually small and can be neglected.
- Since hydrogen peroxide is present in excess, and therefore the concentration of hydrogen peroxide at any time t is virtually the same as the initial concentration and the rate law is independent of the concentration of H_2O_2 .

With “total sulphur approach”, conversions (x) of sulphur present in model oil (di-n-butylsulfide, di-methylsulfoxide and dibenzothiophene) and sulphur present in heavy gas oils were calculated using their initial concentration (C_0) and concentration after certain reaction time (C_S):

$$x = \frac{C_0 - C_s}{C_0} \quad (3.1)$$

The oxidation reactions follow pseudo-first order reaction kinetics in the sulphur present in the model oil and heavy gas oil. The rate of unreacted sulphur, r_s can be described using the following equation:

$$-r_s = \frac{dC_s}{dt} = k C_s \quad (3.2)$$

$$\ln\left(\frac{C_0}{C_s}\right) = -kt \quad (3.3)$$

where

t is the reaction time (min).

k is the reaction rate constant (min^{-1}), which could be correlated by Arrhenius equation.

$$k = A_r e^{-E_a/RT} \quad (3.4)$$

where

A_r is the pre-exponential factor, E_a the apparent activation energy, R and T are the universal gas constant (kJ/mol) and the reaction temperature (K) respectively.

Equation (3.2) now becomes

$$-r_s = A_r e^{-E/RT} C_s \quad (3.5)$$

Also from the Equations (3.1) and (3.2) the reaction rate as function of conversion is given by the following equation:

$$\frac{dx}{dt} = \frac{-r_s}{C_0} \quad (3.6)$$

According to Equation (3.2) the rate of sulphur reaction (r_s) at time $t = 0$ is the highest, therefore according to Equation (3.6) rate of conversion of sulphur to oxidised sulphur

is the highest. As the value of C_S decreases exponentially according to Equation (3.3), the value of r_S will also decrease exponentially. Therefore, the rate of conversion ($\frac{dx}{dt}$) will also decrease exponentially.

3.7 Reproducibility of Oxidation Experiments

The oxidation experiment is repeated several times to make sure the experiments are going in the right way. The reproducibility of HGO_B oxidation is studied at 60 °C, 750 rpm and for 90 minutes. These results are summarized in Table 3.3 and Figure 3.3. As shown from these results the conversion almost constant for all the runs.

Table 3.3 Reproducibility of the oxidation experiments for HGO_B

Run	S, ppm	Conversion (x)
1	609	42.9
2	601	43.6
3	607	43.06
4	605	43.2

Initial sulphur content (C_0) = 1066 ppm, amount of oxidant = 15 ml, amount of catalyst = 30 ml and amount of HGO = 30 ml

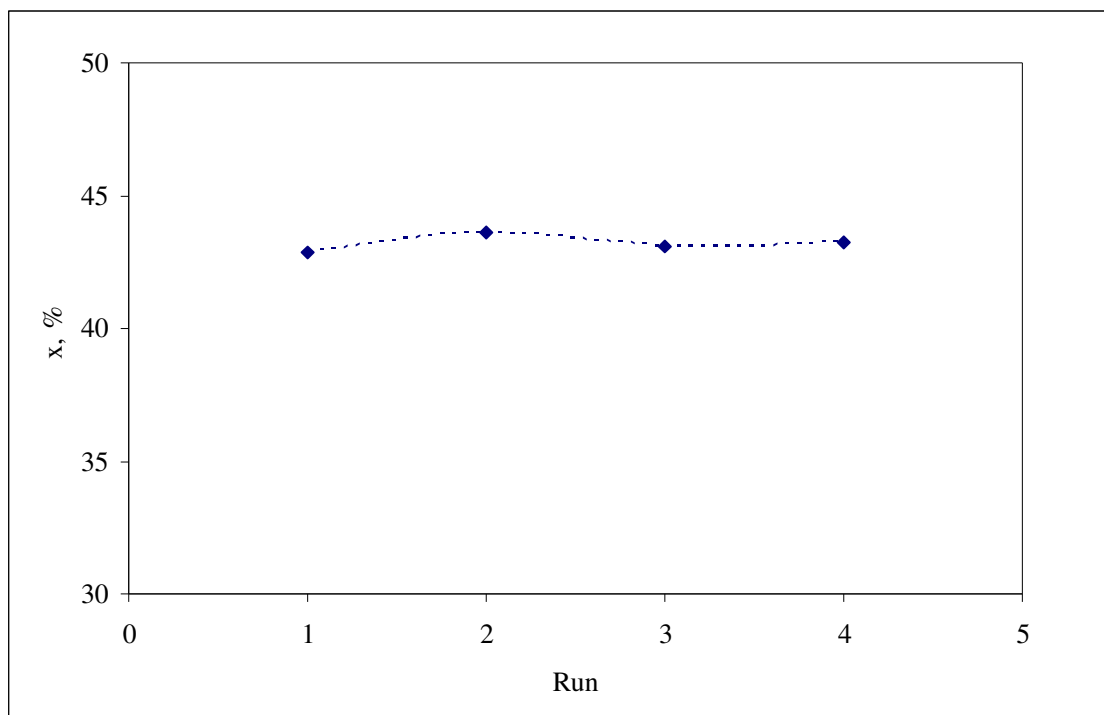


Figure 3.3 Reproducibility of the oxidation experiments for HGO_B, initial sulphur content (C_0) = 1066 ppm, amount of oxidant = 15 ml, amount of catalyst = 30 ml and amount of HGO = 30 ml

3.8 Results and Discussions

3.8.1 Effect of Operating Reaction Temperature

The sulphur compounds presented in the various oils are mostly aliphatic sulphides and dibenzothiophenes. A series of experiments were carried out using various organic sulphur compounds as mentioned earlier in the formic acid/H₂O₂ oxidation system. The reactions were carried out in the presence of organic solvents (mentioned earlier) fully miscible with organic sulphur compounds forming a single phase. Generally, increasing temperature will significantly accelerate most of the organic reactions.

Oxidation conditions were as follows: C_0 (sulphur as di-n-butylsulfide) = 1535 ppm, C_0 (sulphur as di-methylsulphoxide) = 1228 ppm C_0 (sulphur as DBT) = 943 ppm, amount of oxidant (H₂O₂ 30 wt %) = 1.25 ml, amount of catalyst (formic acid) = 30 ml and mixing speed = 750 rpm. The oxidation reactions were performed at temperatures of 20, 40, 60 and 80 °C.

3.8.1.1 Model Sulphur Compound 1 (di-n-butyl sulphide)

Figures 3.4a and 3.4b show the results of oxidation reaction of di-n-butyl sulphide with H_2O_2 /formic acid oxidant catalyst system as a function of reaction time over various temperatures. Following the discussions in section 3.6, it is clear from Figure 3.4a that the initial reaction rate of oxidation is high and conversion values above 75 % have been obtained within 5 minutes. This figure also shows that as the reaction temperature increases up to 60 °C, the initial reaction rate as well as the final conversion increase. As the temperature of the reaction increases, (Figure 3.4b) the concentration of sulphur (concentration of di-n-butylsulphide) in the model oil decreases, resulting in a lower final sulphur content in the model oil after 7.5 min. At 80 °C, the final sulphur content was 201 ppm, which represents a reduction of > 86 % in sulphur. At temperatures of 20, 40, and 60 °C, the final residual sulphur concentrations in the model oil were 344 ppm at 35 min, 310 ppm at 7.5 min and 201 ppm at 25 min respectively.

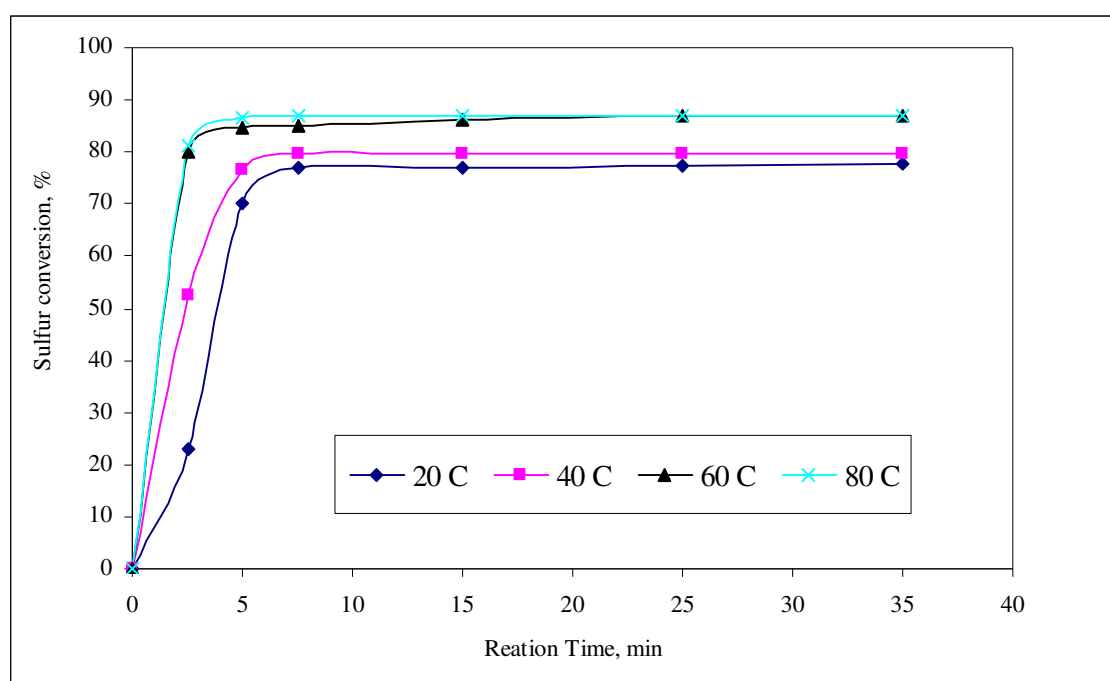


Figure 3.4a Oxidation of di -n-butyl sulphide in formic acid/ H_2O_2 system at different operating temperatures

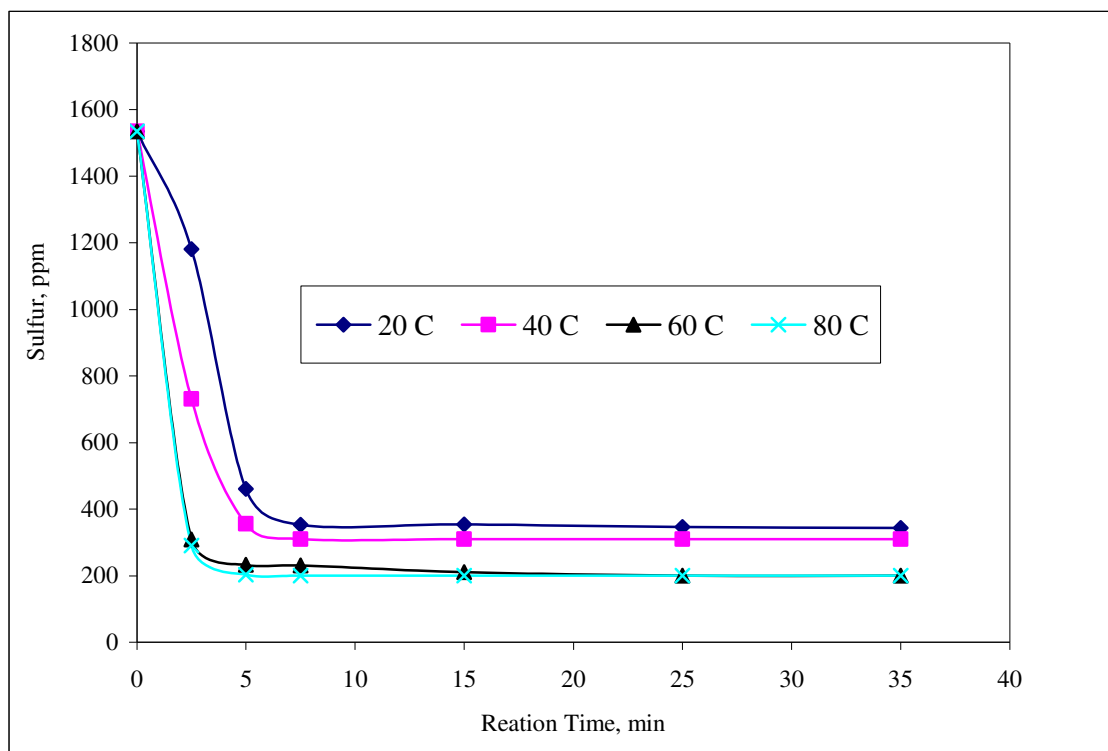


Figure 3.4b Oxidation of di -n-butyl sulphide in formic acid/ H₂O₂ system at different operating temperatures.

3.8.1.2 Model Sulphur Compound 2 (di-methylsulphoxide)

Figures 3.5a and 3.5b shows the oxidation of di-methylsulphoxide with H₂O₂/formic acid oxidant catalyst system as a function of reaction time over various operating temperatures. As shown in Figure 3.5a the initial rate of oxidation is less than that for di -n-butyl sulphide and the reaction rate strongly increases after 7.5 minutes. Both the initial reaction rate and the final conversion values increase upon increasing the reaction temperature, however above 60 °C levelling off to 97.8 % the apparent rate of reaction. This is probably due to mass transfer limitation as the kinetic curves fully overlap. The steps between 2.5 and 5 minutes require further investigation. This unusual behaviour can be due to (i) product solubility problem, (ii) partial poisoning by the product (product-substrate interaction).

The results in Figure 3.5b clearly show that the reaction is faster at higher temperatures, such as 40, 60 and 80 °C. At 80 °C, the final sulphur content was 25 ppm, which represents a reduction of 97.96 % in sulphur.

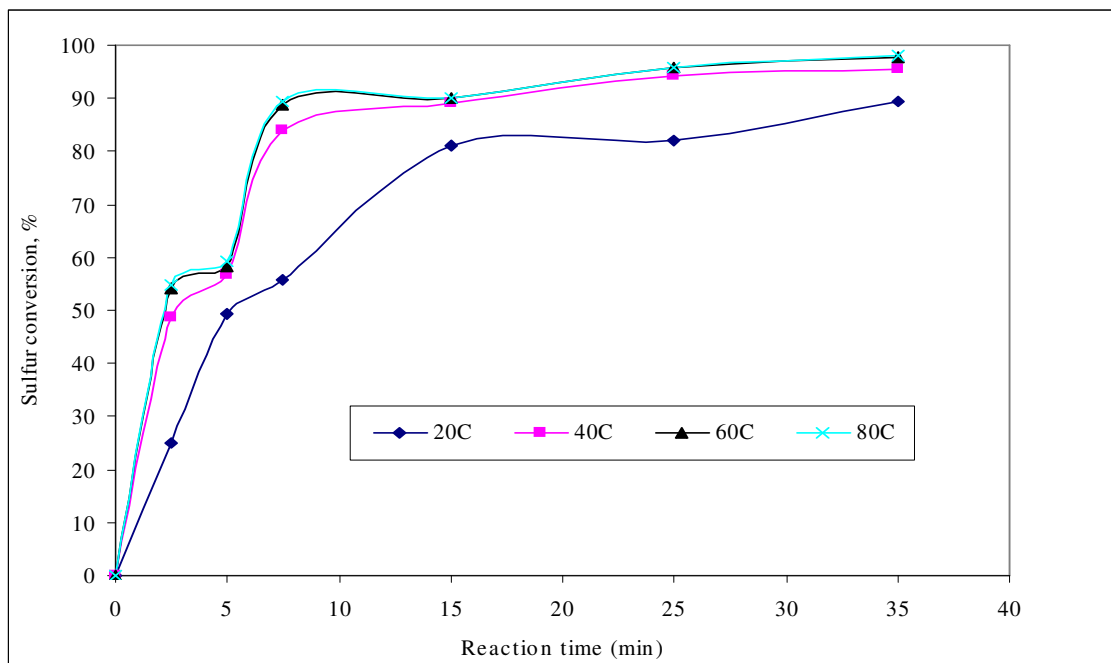


Figure 3.5a Oxidation of di-methylsulfoxide at different operating temperatures

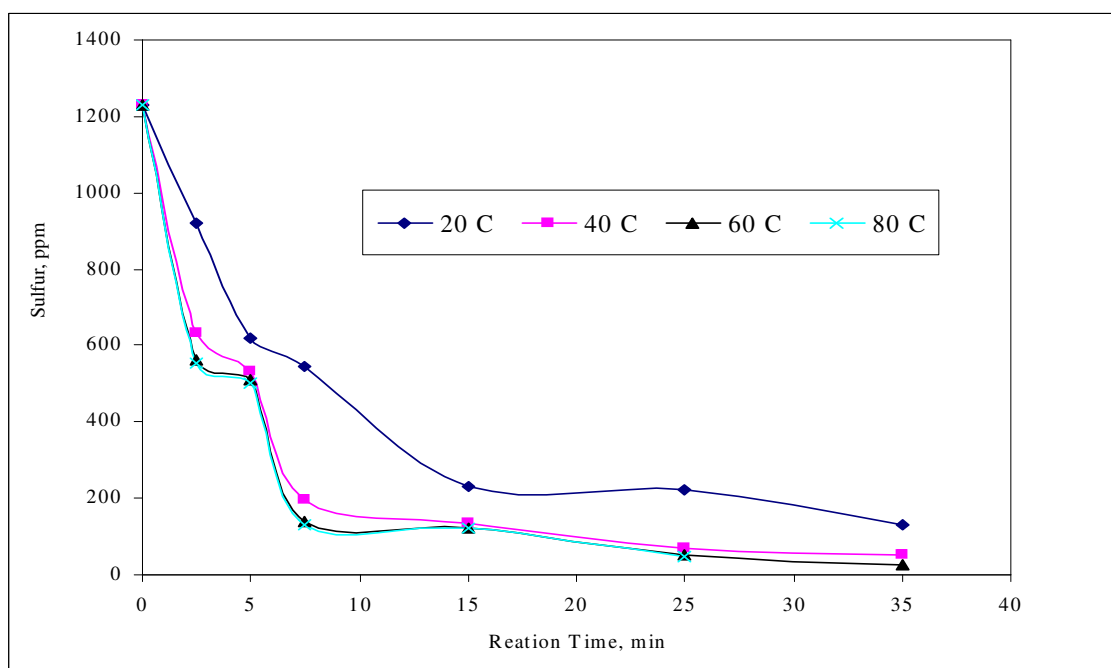


Figure 3.5b Oxidation of di-methylsulfoxide at different operating temperatures

3.8.1.3 Model Sulphur Compound 3 (Dibenzothiophene)

Figures 3.6a and 3.6b shows the results of oxidation of dibenzothiophene (DBT) with H₂O₂/formic acid oxidant catalyst system as a function of reaction time and operating reaction temperatures. It can be seen that as the reaction temperature increases (Figure 3.6a), the initial reaction rate increases at reaction time below 5 minutes whilst, 98 wt% conversion of DBT has been achieved after 5 minutes for all reaction temperatures. On other hand when the reaction temperature exceeds 40 °C and reaction time above 5 minutes, the reaction proceeds with constant conversion, or in other words the operating conditions have no significant influence on the oxidation of DBT.

The results in Figure 3.6b show that at temperatures 40, 60, and 80 ° the final residual of sulphur concentration in the model almost the same (< 18 ppm). At 80 °C, the final sulphur content was 5 ppm, which represents a reduction of 99.5 % in sulphur.

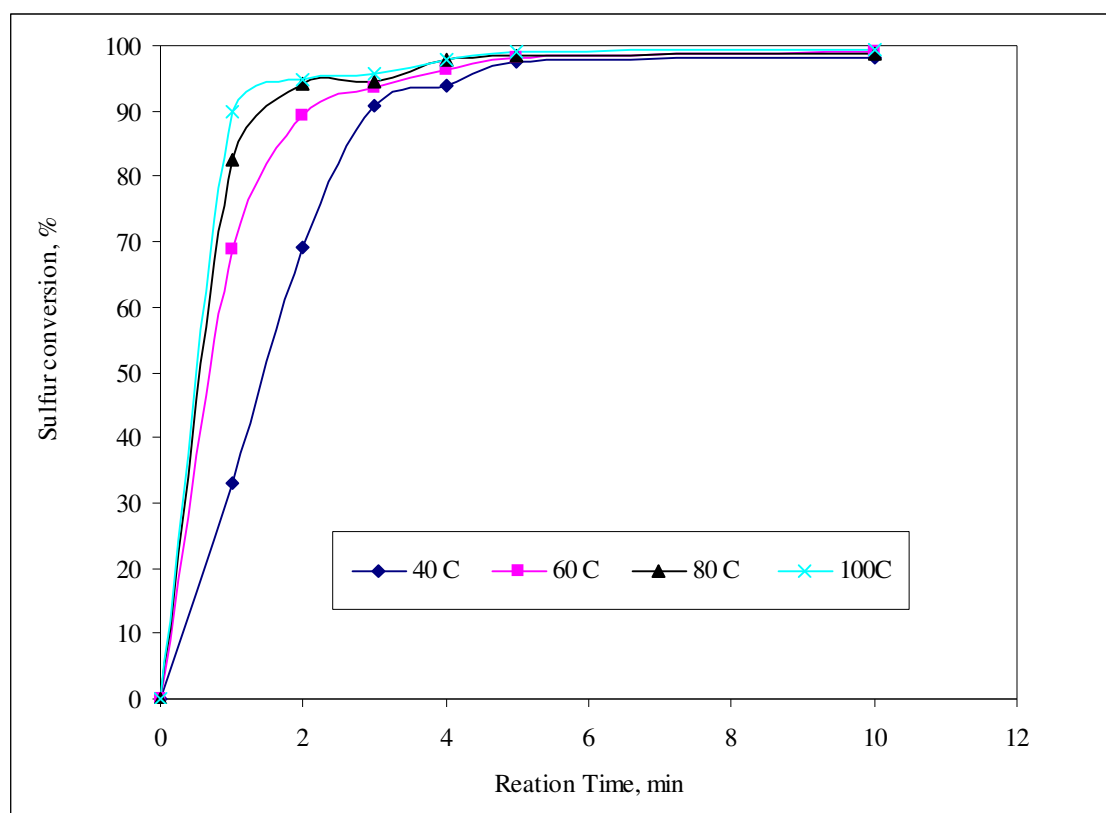


Figure 3.6a Oxidation of DBT at different operating reaction temperatures

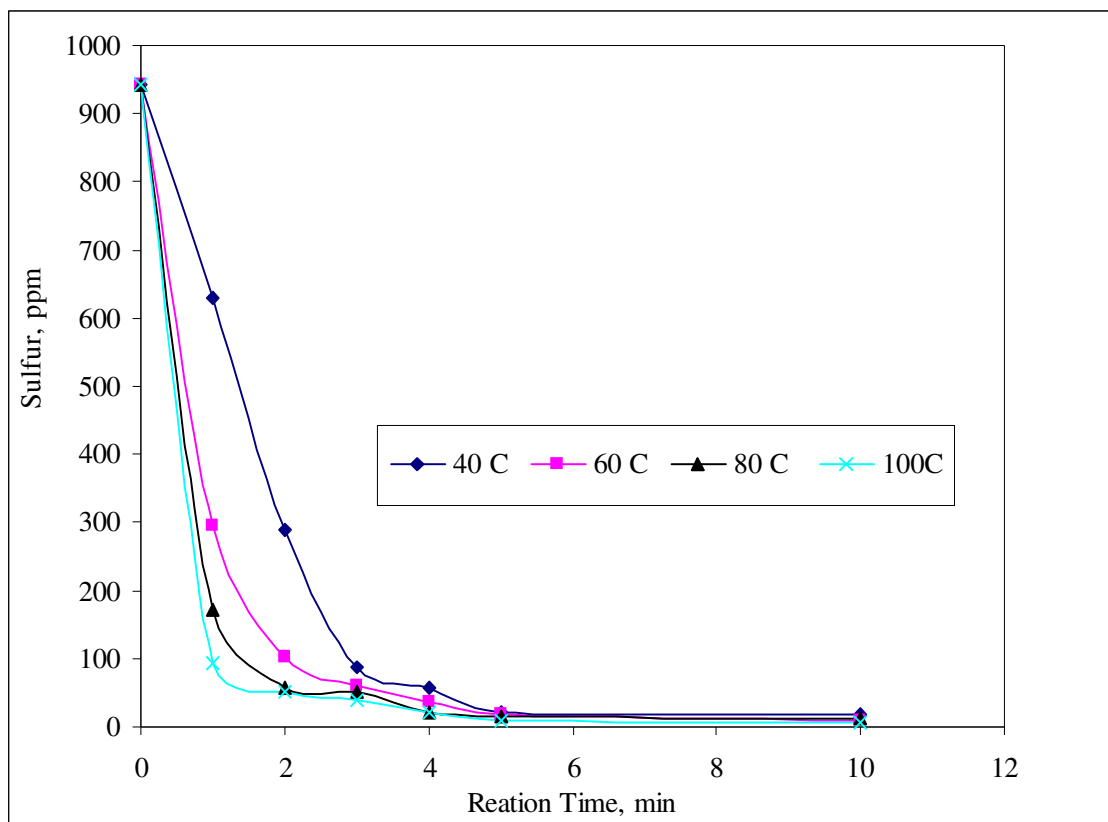


Figure 3.6b Oxidation of DBT at different operating reaction temperatures

It is obvious from the comparison of Figure 3.5 and Figure 3.6 that the initial rate of oxidation of DBT is faster than in case with n-dibutylsulfide. This can be due to electron density being higher in the case of DBT as reported by Otsuki et al. (2000). The higher the electron density of sulphur compound the higher is the reactivity. The oxidation of DBT with hydrogen peroxide and formic acid has been reported by Aide and Funakoshi (1983). They postulated that the divalent sulphur of DBT can be oxidised by the electrophilic addition reaction of oxygen atoms to the hexavalent sulphur of DBT sulphone. Hence, the reactivity of oxidation becomes higher for a sulphur atom with a higher electron density.

3.8.1.4 Heavy Gas Oils

The desulphurization of the actual heavy gas oils was then carried out using 15 ml H₂O₂ as oxidant and 30 ml formic acid as catalyst with stirring speed at 750 rpm, the reaction was conducted at temperatures 40, 60, 80, and 100 °C. Variation in the sulphur conversion and sulphur content with reaction time of the heavy gas oils (HGO_A and HGO_B) are shown in Figures 3.7 and 3.8 respectively.

Figure 3.7 shows the oxidation of HGO_A with H₂O₂/formic acid oxidant catalyst system as a function of reaction time over various operating reaction temperatures. The results indicated that at 40 °C there is a partial poisoning after 5 minutes of reaction but at 60, 80, and 100 °C the reaction stops after 25 minutes due to the poisoning effect of the reaction products. The concentration profiles of the sulphur in the oxidation reaction versus the reaction time at different temperatures are shown in Figure 3.7b. The remaining sulphur in HGO_A decreased with increasing temperature. For example at reaction time of 15 min and reaction temperatures, 40, 60, 80 and 100 °C, the remaining sulphur content were 1400, 1050, 1030 and 1020 ppm respectively.

As seen from Figure 3.8 the oxidation results of HGO_B also indicated that the oxidation activities increased with the increasing oxidation reaction temperature. The remaining sulphur in the HGO_B for 15 min at reaction temperatures, 40, 60, 80 and 100 °C were 765, 672, 645 and 644 ppm respectively. Since this amount of sulphur still remained in the heavy gas oil phase, the additional treatment is needed. Therefore, the solvent extraction of oxidised heavy gas oil is employed (Section 3.9) for further reduction of the sulphur content in the heavy gas oil.

However, the sulphur conversion for heavy gas oil is only about 40 % but for the model oil was about 98 %. This could be attributed to several reasons such as:

- Heavy gas oil is a complex mixture whereas the model oil consists of just two compounds mixed together (model sulphur compounds and dodecane). This reactivity mixture results in a different conversion.
- High molecular weight sulphones produced owing to oxidation of heavy gas oil. These compounds decrease the interaction between the oxidant and sulphur compounds content in heavy gas oils.

Note, the conversion of a particular sulphur compound in the HGO could be 100 % while for other sulphur compounds it could be close to zero leading to net sulphur conversion to about 40 %. Also note, that in this work “total sulphur approach” was adopted as mentioned in Chapter One (section 1.4).

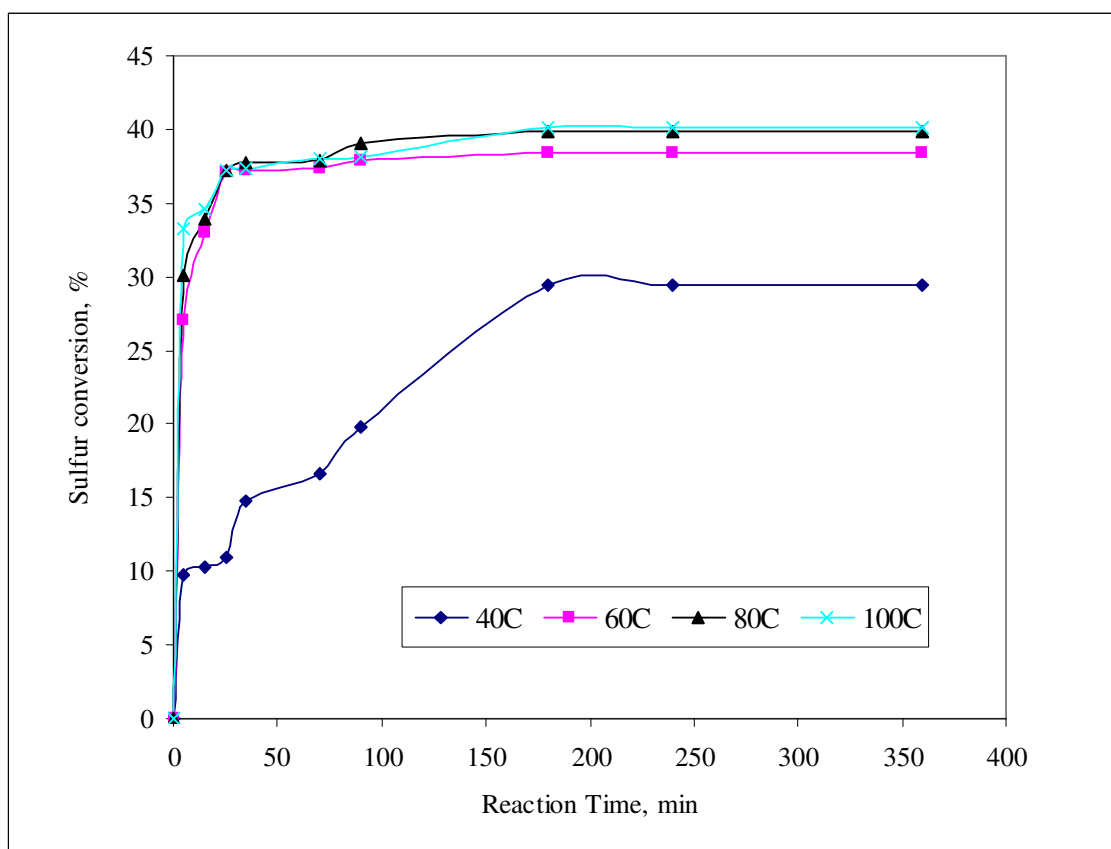


Figure 3.7a Oxidation of HGO_A at different reaction temperatures

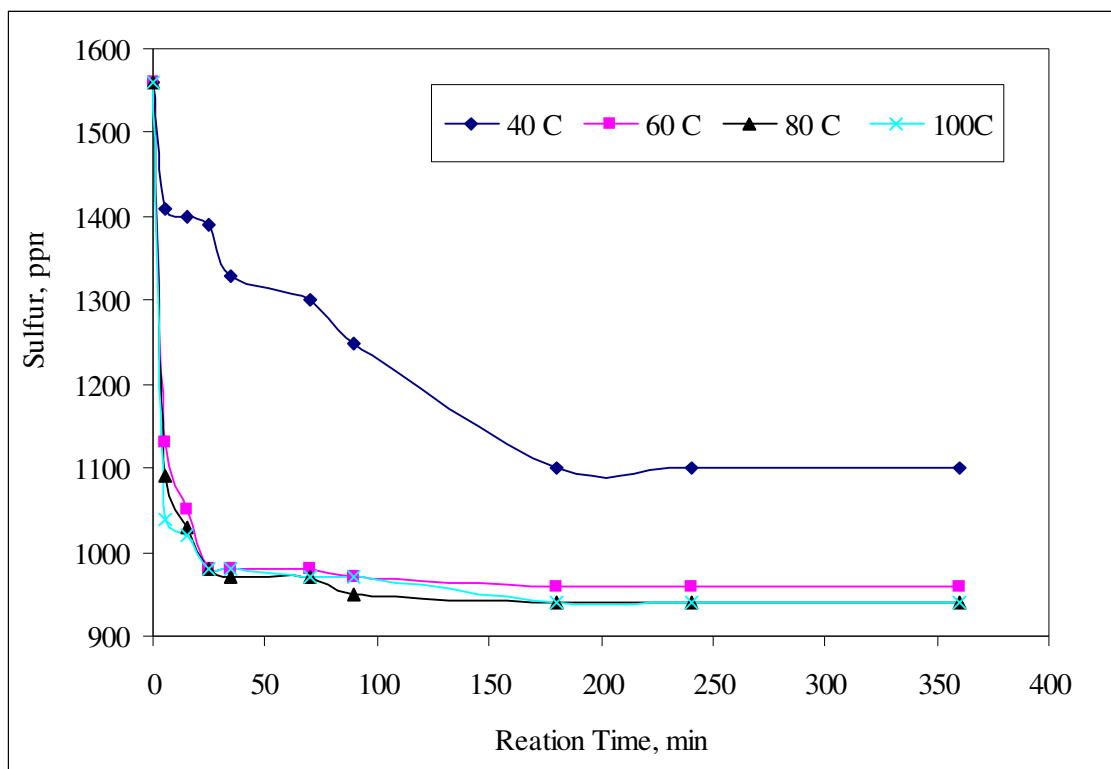


Figure 3.7b Oxidation of HGO_A at different reaction temperatures

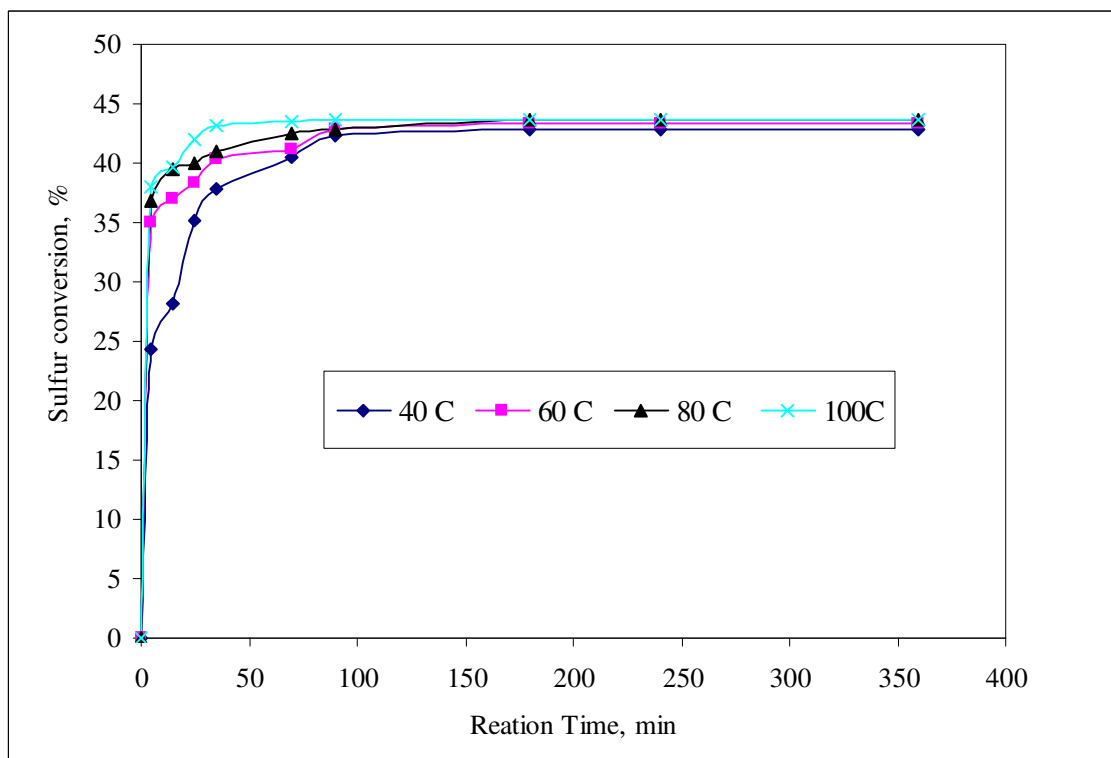


Figure 3.8a Oxidation of HGO_B at different reaction temperatures

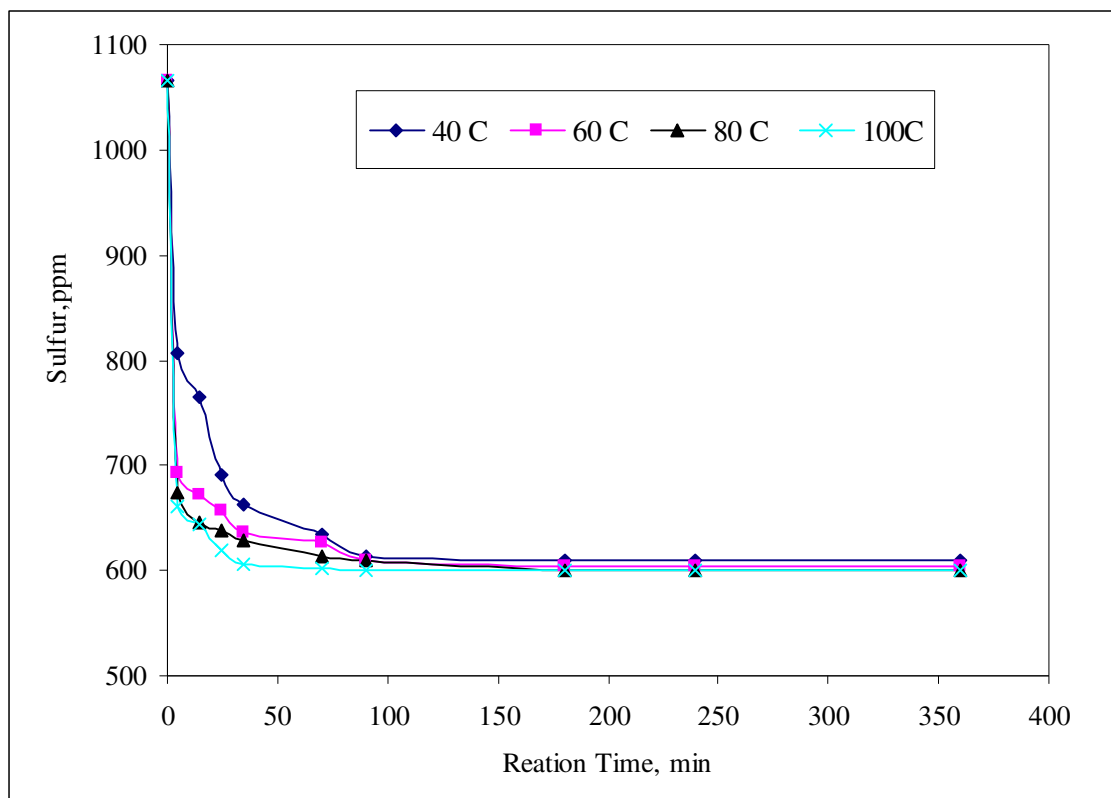


Figure 3.8b Oxidation of HGO_B at different reaction temperatures

3.8.2 Effect of Catalyst Amount

It has been well known that the addition of organic acid such as formic acid or acetic acid (as catalyst), which react with H₂O₂ to form more effective and selective oxidants oxo-or peroxy-acid complex, results in high rate and high selectivity in oxidation of nucleophilic substrates such as organic sulphides or alkenes (Sheldon and Kochi, 1981; Patai, 1983; Murahashi and Davies, 1999).

Different amounts of the catalyst (formic acid) were used in the oxidation of HGO_B to show its effect on the oxidation reaction at 60 °C. The results are summarized in Table 3.4 and Figure 3.9. It can be seen from the table and figure that increasing the amount of the catalyst increases both the initial rate and the final conversion. Higher amount of formic acid, gives higher conversion. Addition of more formic acid above 30 ml had no further improvement in the rate of reaction and final conversion.

Table 3.4 Effect of catalyst amount on the oxidation reaction for HGO_B at 60 °C

Reaction time (min)	Amount of catalyst							
	7.5 ml		15 ml		30 ml		40 ml	
	S, ppm	x %	S, ppm	x %	S, ppm	x %	S, ppm	x %
0	1066	0.00	1066	0.00	1066	0.00	1066	0.00
5	806	24.39	741	30.49	693	34.99	692	35.08
15	765	28.24	726	31.89	672	36.96	671	37.05
25	732	31.33	691	35.18	658	38.27	656	38.46
35	733	31.24	662	37.90	636	40.34	635	40.43
70	726	31.89	635	40.43	627	41.18	624	41.46
90	726	31.89	636	40.34	609	42.87	608	42.96
180	726	31.89	636	40.34	604	43.34	604	43.34

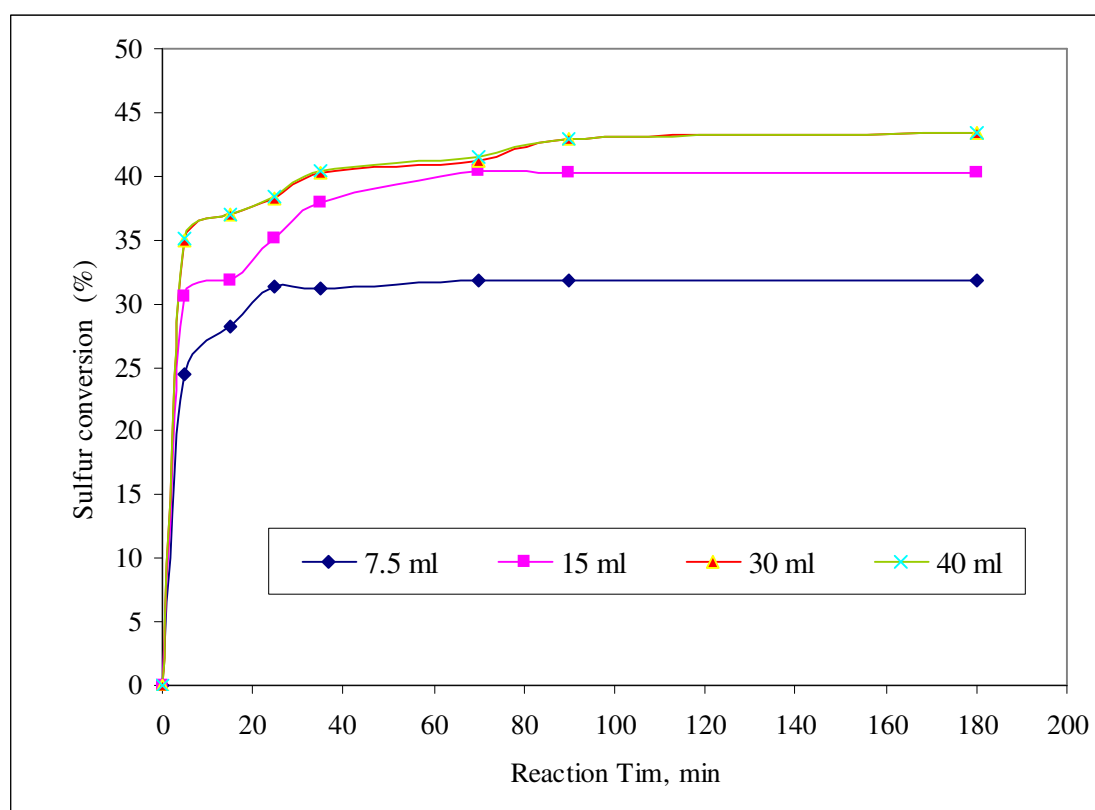


Figure 3.9a Effect of catalyst amount on the oxidation reaction of HGO_B at 60 °C

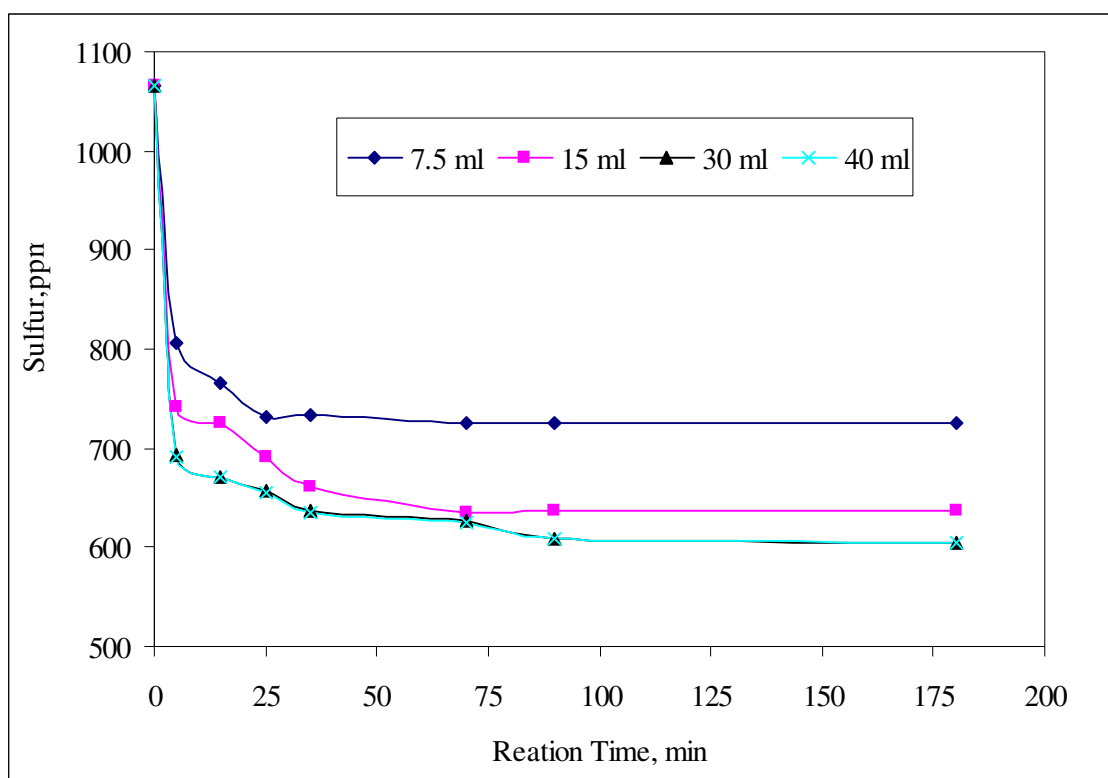


Figure 3.9b Effect of catalyst amount on the oxidation reaction of HGO_B at 60 °C

3.8.3 Effect of the Amount of Oxidant

Hydrogen peroxide is used as oxidant in the ODS process. The amount of aqueous H₂O₂ is an important variable in the process design consideration of oxidation rate, non-productive decomposition, cost and safety. Different amount of oxidant (hydrogen peroxide) were used in the different study of the oxidative sulphur removal for model sulphur compounds and real fuel. Zannikos et al. (1995) used three equivalents of hydrogen peroxide for each sulphur equivalent in the gas oil with acetic acid as catalyst. Otsuki et al. (2000) used 160 mole H₂O₂/mole sulphur for oxidation of light gas oil. With a H₂O₂/sulphur ratio > 3 mol/mol, more hydrogen peroxide decomposed to H₂O and O₂ (the H₂O₂ was not be utilized well, Zhao et al. (2007)). Here the effect of the amount of oxidant on the oxidation of sulphur in heavy gas oil under various amount of oxidant was studied at 60 °C. The results are summarized in Table 3.5 and Figure 3.10.

As shown in Table 3.5 and Figure 3.10, at oxidant amount equal to 0.625 ml there is no change in sulphur level (there is no reaction). The sulphur concentration levels off at 800 ppm within 5 minutes with 20 ml of oxidant while with 1.25 ml oxidant the concentration of sulphur riches to 400 ppm within 5 minutes. Clearly there is a strong negative effect of the oxidant both on the initial rate and the final conversion and the optimum amount of oxidant is 1.25 ml. The negative effect of H₂O₂ can be attributed to the presence of large amount of water. The larger the amount of water the less is the probability for the interaction between the sulphur compounds dissolved in the oil phase and H₂O₂ present in the water phase.

Table 3.5 Effect of oxidant amount on the oxidation reaction of HGO_B

Reaction time (min)	Amount of oxidant					
	0.625 ml	1.25 ml	2.5 ml	5 ml	15 ml	20 ml
	Sulphur content (ppm)					
0	1066	1066	1066	1066	1066	1066
5	1066	426	445	575	693	850
15	1066	420	446	506	672	834
25	1066	401	440	507	658	861
35	1066	401	431	505	639	850

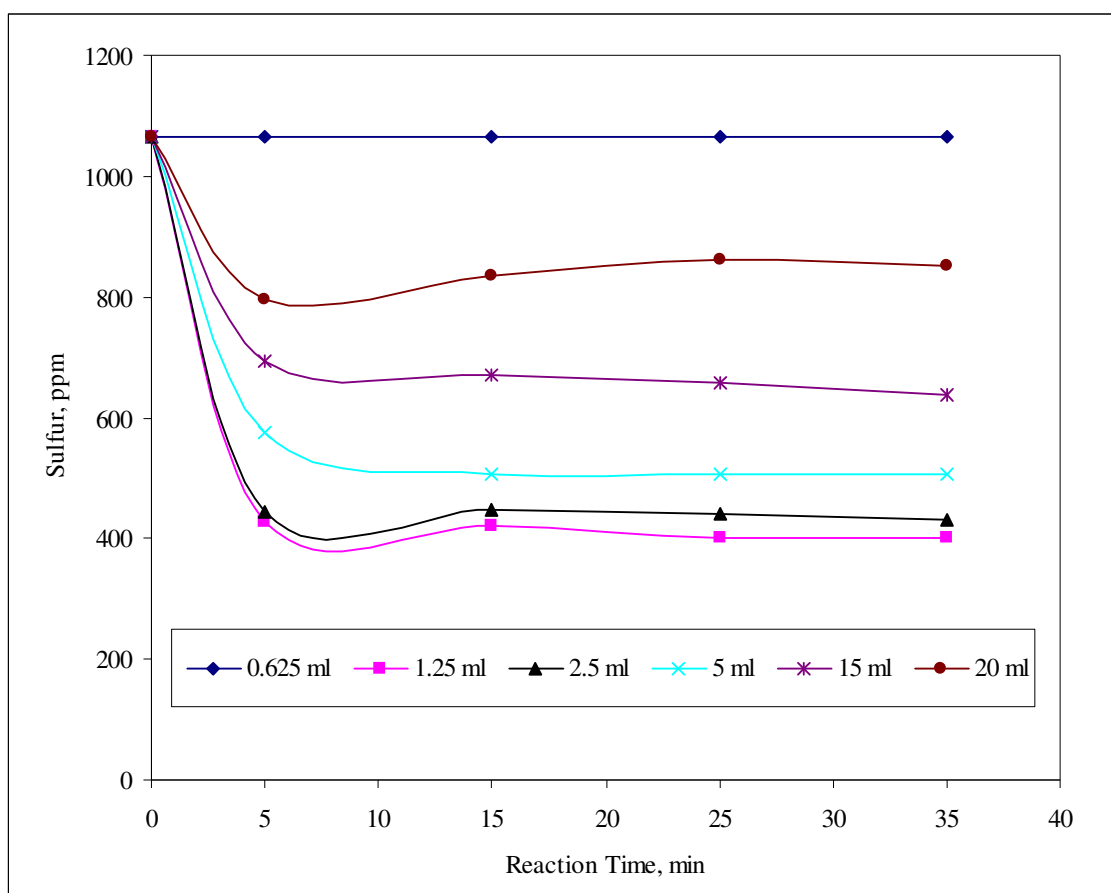


Figure 3.10 Effect of amount of oxidant on the oxidation reaction of HGO_B at 60 °C

3.8.4 Multi Step Oxidation

Multi step oxidation reaction was employed for HGO_B. The same procedure of experiment was done for the single step oxidation of heavy gas oil (Section 3.4.2). After each step the new catalyst and oxidant were used. The oxidation reaction conditions were as follows: initial sulphur present in HGO_B = 1066 ppm, amount of HGO_B = 30 ml, amount of oxidant (H₂O₂ 30 wt %) = 15 ml, amount of catalyst (formic acid) = 30 ml and mixing speed = 750 rpm. The oxidation reactions were performed at temperature of 60 °C for 90 min. The results are reported in Table 3.6 and Figure 3.11.

According to the data reported in Table 3.6 and Figure 3.11, the effectiveness of sulphur removal can be improved by up to 3 successive oxidation steps. There is no significant further improvement after the third step. The incremental conversion achieved after

third step is 15.5 %. This could probably be explained in view of the fact that oxidation by H₂O₂ is more effective for aromatic/dibenzothiophenic compounds which after 3 stages appears to have been removed. It may be attributed to solubility of various sulphur species in formic acid which acts as solvent for oxidised sulphur compounds. Further analysis of intermediates and products of reaction in this biphasing system using advanced analytical tools is highly suggested to absolutely clarify the causes of above mentioned phenomenon.

Table 3.6 Four steps oxidation reaction of HGO_B

Step	Sulphur, ppm	Sulphur conversion, %
1	609	42.87
2	508	52.35
3	445	58.44
4	436	59.1

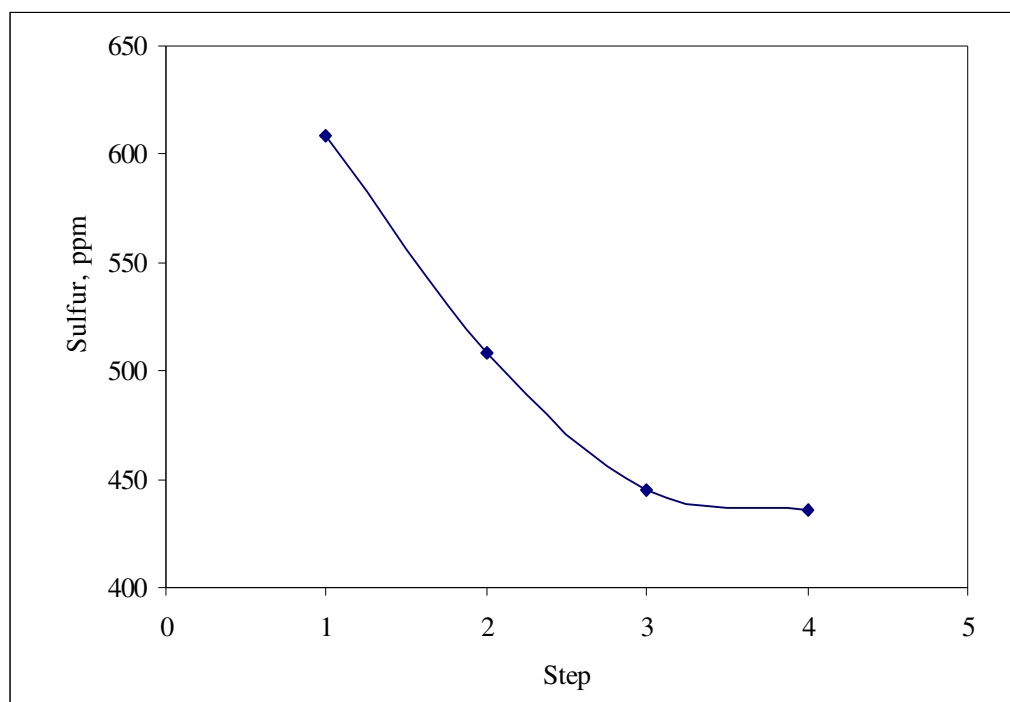


Figure 3.11 Four step oxidation reaction of HGO_B

3.9 Setup of Extraction Experiments

The extraction experiments were carried out in an apparatus designed to measure anti-rust of oils via ASTM D665 method. A view of assembled apparatus is shown in Figure 3.12. The components of the apparatus are described as follows:

I. Oil Bath

A thermostatically controlled liquid bath capable of maintaining the test sample at a required temperature.

II. Beaker

A 400 cm³, Berzelius-type, tall-form heat-resistant glass beaker, approximately 127 mm in height measured from the inside bottom center and approximately 70 mm in inside diameter measured at the middle.

III. Beaker Cover

A flat beaker cover of glass kept in position by suitable means such as a rim or groove.

IV. Stirring Apparatus

A convenient form of stirring apparatus capable of maintaining a speed of 1000±50 rpm.

3.10 Procedure for Extraction Experiments

The extraction of sulphur compounds from the oxidised oil layer and the original HGO were conducted with NMP, DMF and methanol at different solvent/oil ratios. Prior to the extraction the oxidation of HGO was performed at 60 °C for 90 minutes. The extraction was done at 25 °C for two hours. The phases are then allowed to separate and their volumes are measured, the hydrocarbon phases were washed with distilled water and then analyzed for their sulphur content.

Different ratios of solvent to heavy gas oil are applied. When the solvent to heavy gas oil ratio is less than 1 there is no effect of solvent extraction on the sulphur concentration in the raffinate layer therefore, the starting value of solvent to heavy gas oil ratio is chosen equal 1. above ratio of solvent to heavy gas oil of 5 is not economically feasible.

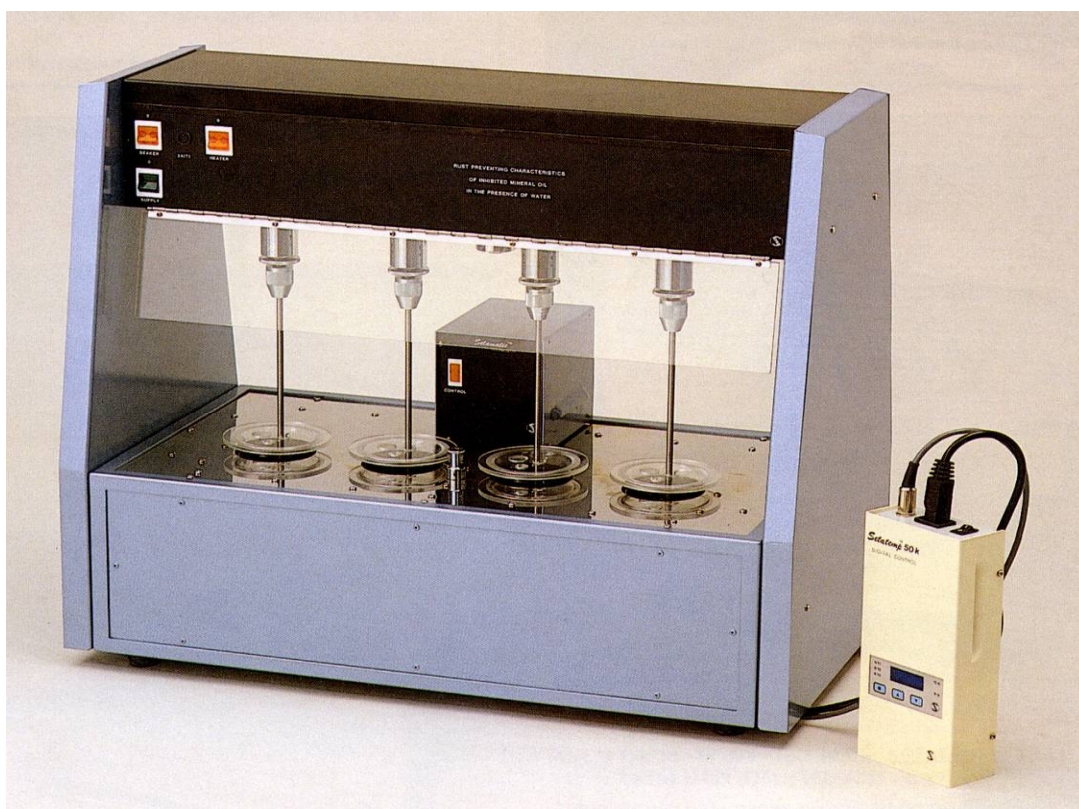


Figure 3.12 Setup of extraction experiment

3.11 Reproducibility of Extraction Experiment

The reproducibility of the extraction experiments of oxidised HGO_B with sulphur content 609 ppm is performed at 25 °C for two hours. In these experiments the methanol to oxidised oil ratio is 1:5 and NMP to oxidised oil ratio is 1:4. The results are

summarized in Figure 3.13. As shown in this figure the sulphur concentration is almost constant for all runs.

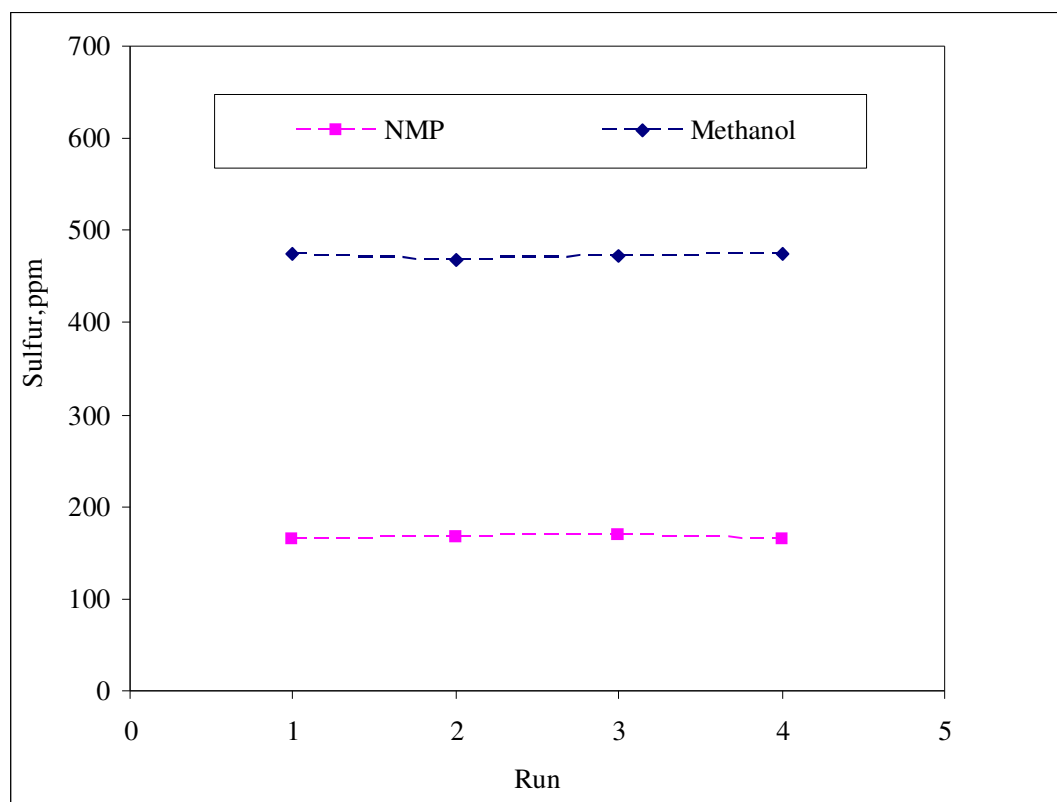


Figure 3.13 Reproducibility of extraction experiment

3.12 Results of Extraction Experiment

It was possible to study the selectivity of the solvent extraction on the model sulphur compounds. The oxidation of the model sulphur compounds result in a white precipitate that was completely soluble in different solvents such as methanol and N-methyl pyrrolidone (NMP). As a result, the mixture formed one layer which was difficult to separate.

The heavy gas oil (HGO_B) was used to relatively measure the efficiency of methanol, NMP and Di-methyl formamide (DMF) solvents extraction before and after oxidation.

The heavy gas oil losses (V_{HS}) was calculated according to the following equation

$$V_{HS}, \text{ vol\%} = 1 - \text{Yield} \quad (3.7)$$

$$\text{Yield, vol\%} = \frac{\text{Volume of the raffinate layer}}{\text{Volume of the feed (HGO)}} * 100 \quad (3.8)$$

Tables 3.7-3.9 shows the results of extraction of heavy gas oil before (Unoxidised HGO_B) and after (Oxidised HGO_B) oxidation by using methanol, NMP and Di-methyl formamide (DMF) at different solvent heavy gas oil ratio. It can be seen from these results that increasing the solvent heavy gas oil ratio decreases both the sulphur content and yield (oxidised and unoxidised HGO_B) for three solvents. For example with methanol (Table 3.7) the sulphur content for unoxidised HGO_B was reduced from 903 at methanol/HGO ratio of 3 to 790 ppm at methanol/HGO ratio of 5 and for oxidised HGO_B was reduced from 514 at methanol/HGO ratio of 3 to 475 ppm at methanol/HGO ratio of 5.

Table 3.7 Extraction of HGO_B by methanol

Methanol/HGO _B volume ratio		Unoxidised HGO _B		Oxidised HGO _B *	
		Initial S = 1066 ppm		Initial S = 609 ppm	
		S, ppm	Yield %	S, ppm	Yield %
(30/30) ml	1	982	98	584	97.5
(90/30) ml	3	903	96	514	97
(150/30) ml	5	790	95	475	96.5

*oxidation at 60 °C, 90 min. (S = 609 ppm), amount of H₂O₂:15 ml amount of formic acid: 30 ml

Table 3.8 Extraction of HGO_B by NMP

NMP/HGO volume ratio		Unoxidised		Oxidised *	
		Initial, S = 1066 ppm		Initial S = 609 ppm	
		S, ppm	Yield %	S, ppm	Yield %
(30/30) ml	1	733	80	307	78
(90/30) ml	3	652	79	243	77
(150/30) ml	5	614	74	155	70

*oxidation at 60 °C, 90 min. (S = 609 ppm), amount of H₂O₂:15 ml amount of formic acid: 30 ml

Table 3.9 Extraction of HGO_B oil by DMF

DMF/HGO volume ratio		Unoxidised		Oxidised *	
		Initial S = 1066 ppm		Initial S = 609 ppm	
		S, ppm	Yield %	S, ppm	Yield %
(30/30) ml	1	599	82.5	225	90
(90/30) ml	3	448	80	172	86
(150/30) ml	5	397	78	148	70

* Oxidation at 60 °C, 90 min.(S = 609 ppm) ,amount of H₂O₂:15 ml' amount of formic acid: 30 ml

Figure 3.14 shows the sulphur content of the raffinate as a function of the solvent/HGO ratio for unoxidised HGO. It can be observed that methanol is not an effective solvent in the case of extraction unoxidised HGO, whereas the NMP and DMF can achieve substantial desulphurization at the higher solvent ratios, albeit relatively low yields.

Figure 3.15 shows the sulphur content of the raffinate as a function of the solvent/HGO ratio for oxidised HGO. When the HGO was first oxidised and then treated with various solvents, a further substantial reduction of sulphur content could be obtained. In this particular case it was found that DMF is as effective as the very polar among the two solvents (NMP and methanol) (Figures 3.14 and 3.15). Furthermore DMF give better yields than NMP except at the solvent (DMF)/HGO ratio equal 5 for the oxidised HGO.

Figure 3.16 depicts the raffinate yield vs. percent desulphurization for the two-step oxidation/solvent extraction process in comparison with simple extraction of the unoxidised HGO with the same solvent. This figure makes it evident that superior yields can be obtained by the new process for the same degree of overall desulphurization. For example, at DMF/HGO_B ratio equals 3 the percent desulphurization of HGO about 58 % and the raffinate yield 78 % for unoxidised HGO whereas at same ratio for oxidised HGO the percent desulphurization of HGO about 82 % and the raffinate yield 85 %.

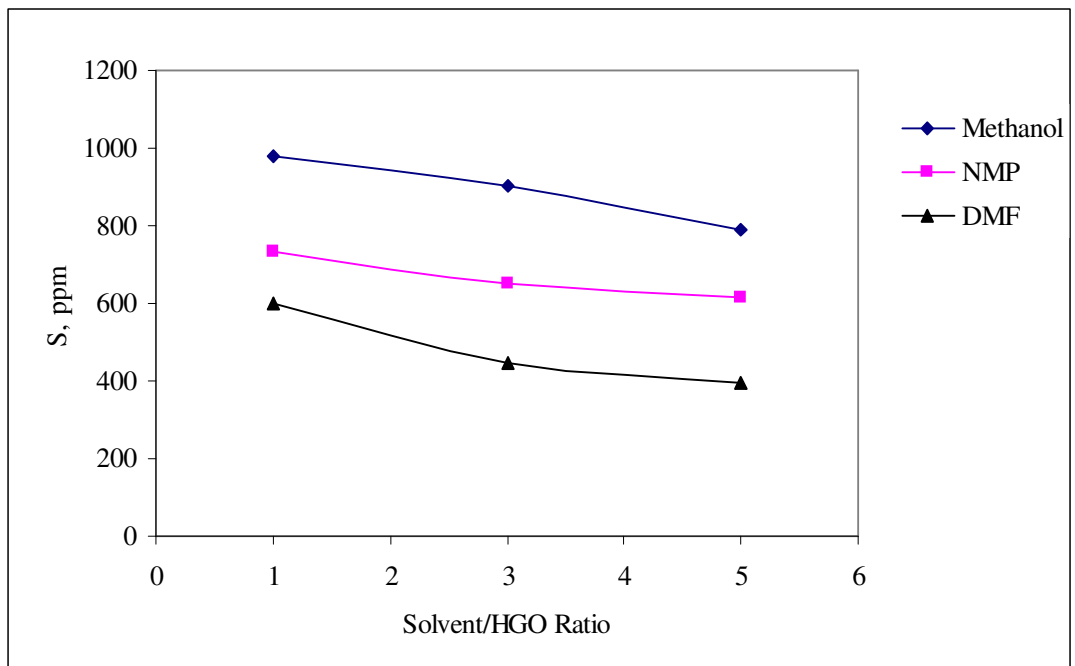


Figure 3.14 Sulphur removal by solvent extraction of Unoxidised HGO_B

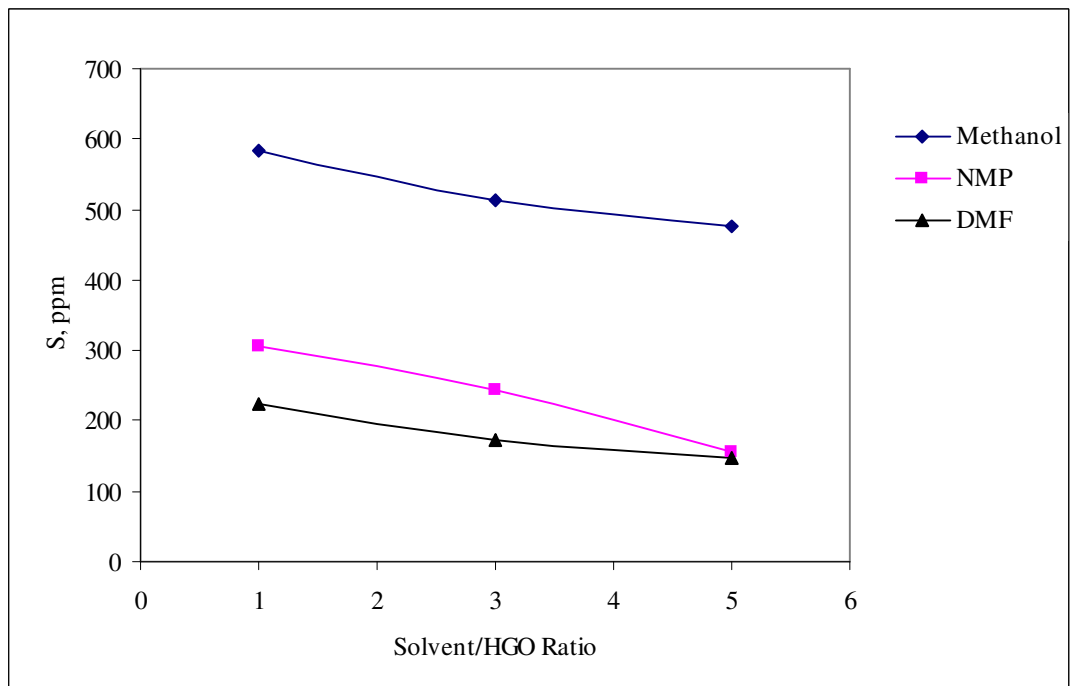


Figure 3.15 Sulphur removal by solvent extraction on oxidised HGO_B

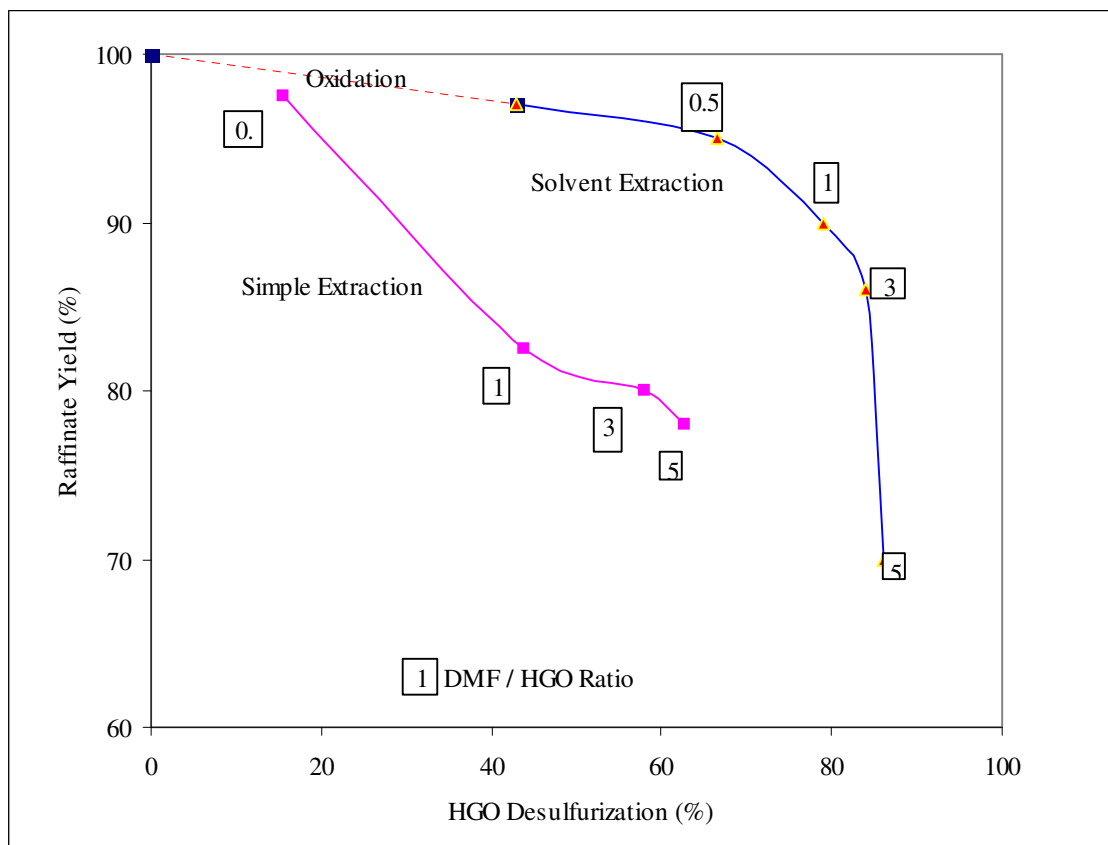


Figure 3.16 Comparison of oxidation/extraction with simple solvent extraction for HGO_B (solvent: DMF)

3.13 Effects of Oxidation and Extraction on HGO Properties

The physical properties of the original HGO_B and desulfurized HGO_B are listed in Table 3.10. As shown in this Table the oxidation and extraction processes lead to the removal of a substantial portion of the sulphur and nitrogen that are originally present without any negative effects on the other properties of fuel. In fact, important properties as cetane number has improved by at least 3 points. Furthermore, undesirable aromatics and poly nuclear aromatic (PNA) compounds had been reduced.

Table 3.10 Effects of oxidation and extraction on HGO_B physical properties

Physical property	HGO _B		Extraction	
	Original	Oxidised	Methanol	NMP
API	29.1	30	31.1	32.5
Cetane number	53.7	56.8	56.9	59.7
Cetane index	54.6	55.2	56.9	59.4
Total aromatic, Wt%	16.2	14.4	12.5	6.3
PNA	4.6	3.8	3	1.8
N ₂ , ppm	176	39	19	-----
S, ppm	1066	6.9	475	244
Yield, Vol %	-----	traces	96.5	77

3.14 Reaction Kinetics for Oxidation Step

In order to examine the kinetics of the oxidative reaction of model sulphur compounds and of sulphur compounds contained in HGO_B was carried out at 40, 60, 80 and 100 °C with 1.25 ml H₂O₂ for model sulphur compounds (15 ml for HGO_B) and 30 ml formic acid.

The plots of $\ln(C_S/C_o)$ versus time for the oxidative reaction of HGO_B and the model sulphur compounds conducted at 40 °C are shown respectively in Figures 3.17 to 3.19. C_S/C_o (fraction of sulphur unreacted) was defined as the ratio of sulphur concentration to initial sulphur concentration of each model sulphur compounds and total sulphur in HGO_B. A linear relationship of $\ln(C_S/C_o)$ versus time was obtained for each model sulphur compound and total sulphur in HGO_B. Similarly, the linear relationships were also obtained at 20, 60, 80, and 100⁰C for each sulphur compound and total sulphur in HGO_B. These results suggest that the oxidative reaction can be treated as a first-order reaction. Therefore, the reaction rate constants at various temperatures can be obtained from the slopes of $\ln(C_S/C_o)$ vs time. Similar results have been obtained for sulphur model compound in the literatures (Fairbridge; Ring, 2001 and Wang et al., 2003).

Figures 3.20 to 3.22 describe the Arrhenius plots of the reaction rate constants for the total sulphur contained HGO_B and model sulphur compounds respectively. The apparent activation energies of oxidation for all model sulphur compounds and total sulphur contained in HGO_B were obtained from the slopes of Arrhenius plots. Despite the variation in the sulphur compounds, the apparent activation energies of oxidative reaction were almost the same. This result suggested that there is essentially no difference in the mechanism of oxidative reaction for model sulphur compounds and actual sulphur compounds present in HGO when H₂O₂/HCOOH system is employed. On the other hand, the activation energies of oxidative reaction were much lower than those of HDS process. Oxidation using polyoxometalate/H₂O₂ gives activation energy 53.8 kJ/mol (Fairbridge and Ring, 2001) and oxidation using tetra-butyl hydroperoxide gives 28 kJ/mol (Wang et al., 2003). Obviously these systems employ different catalyst material and therefore reaction baths are different. As shown in this work oxidation reaction clearly showed much faster rates and hence lower activation energy is obtained. In fact H₂O₂/HCOOH system gave reverse order of reactivity for various thiophenic compounds in comparison with those obtained in other works (Fairbridge and Ring, 2001 and Wang et al., 2003).

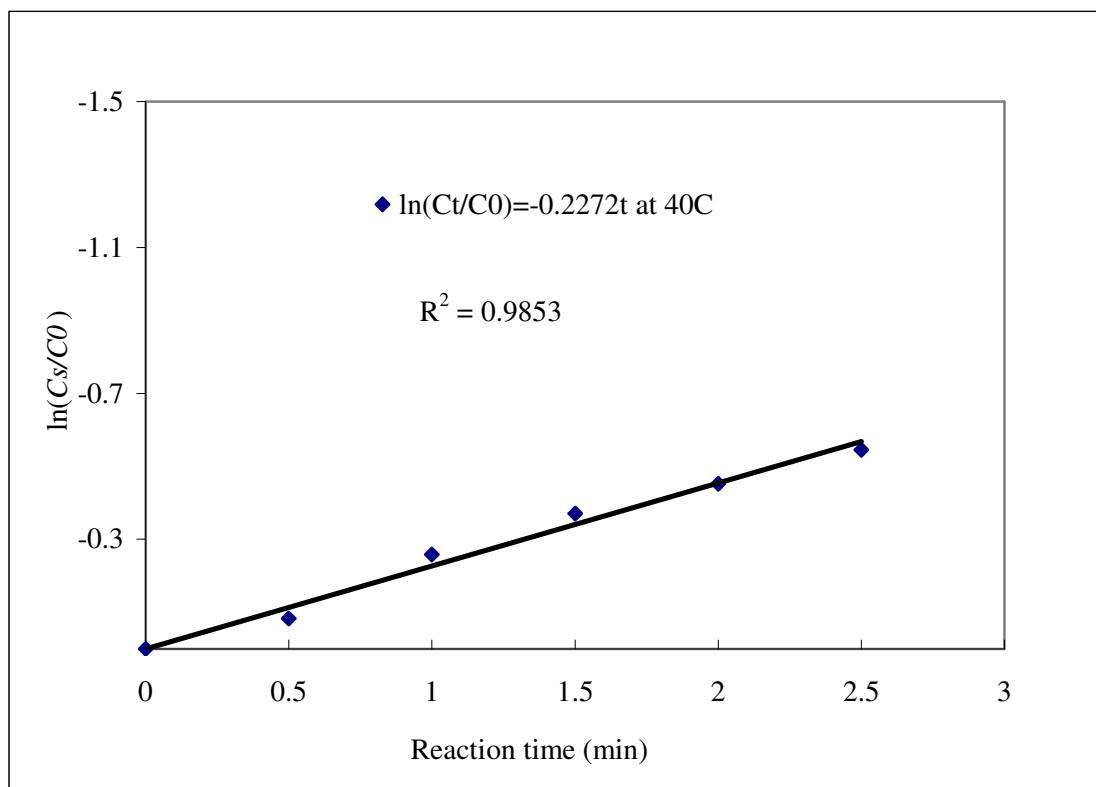


Figure 3.17 The first-order plots of $\ln(C_s/C_0)$ and reaction time for oxidation of HGO_B at 40 °C

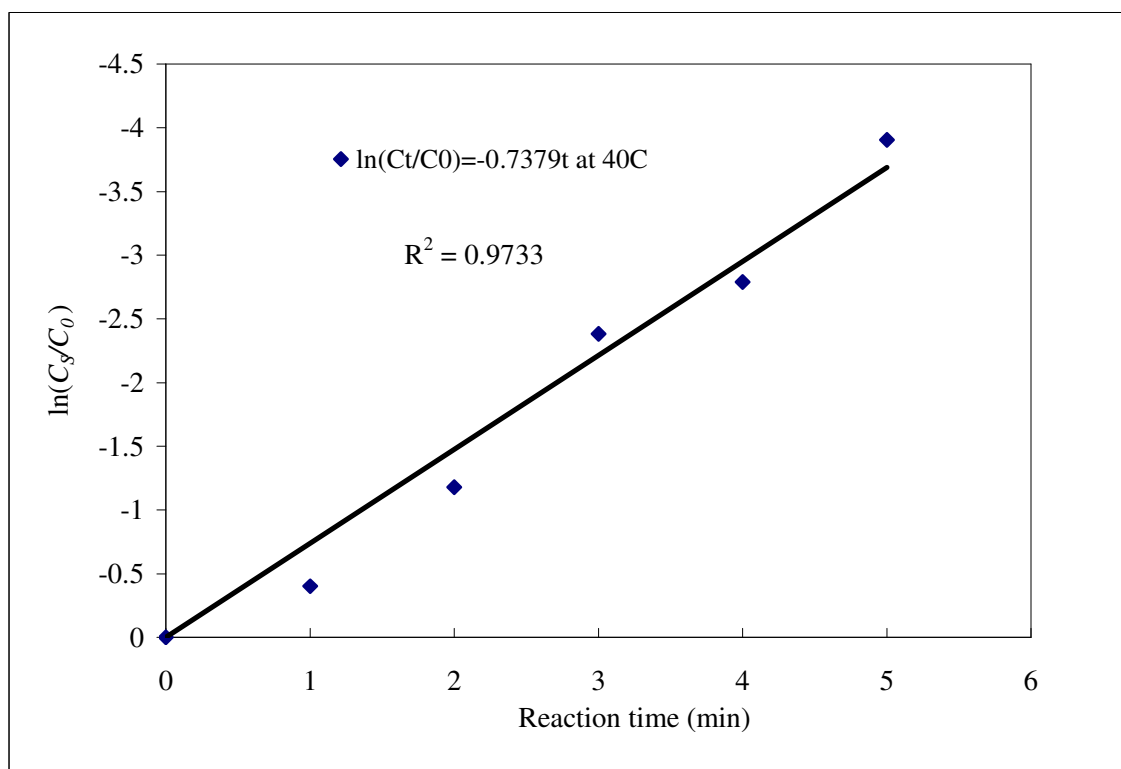


Figure 3.18 The first-order plots of $\ln(C_s/C_0)$ and reaction time for oxidation of DBT at 40 °C

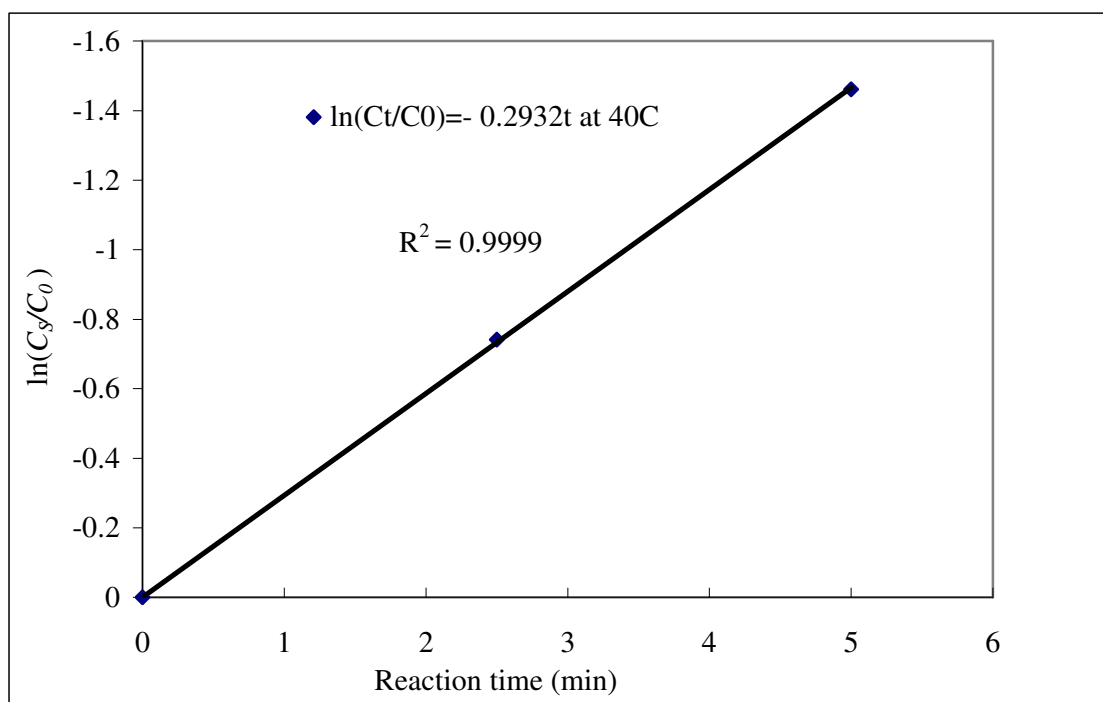


Figure 3.19 The first-order plots of $\ln(C_t/C_0)$ and reaction time for oxidation of di- n-butylsulfide at 40 °C

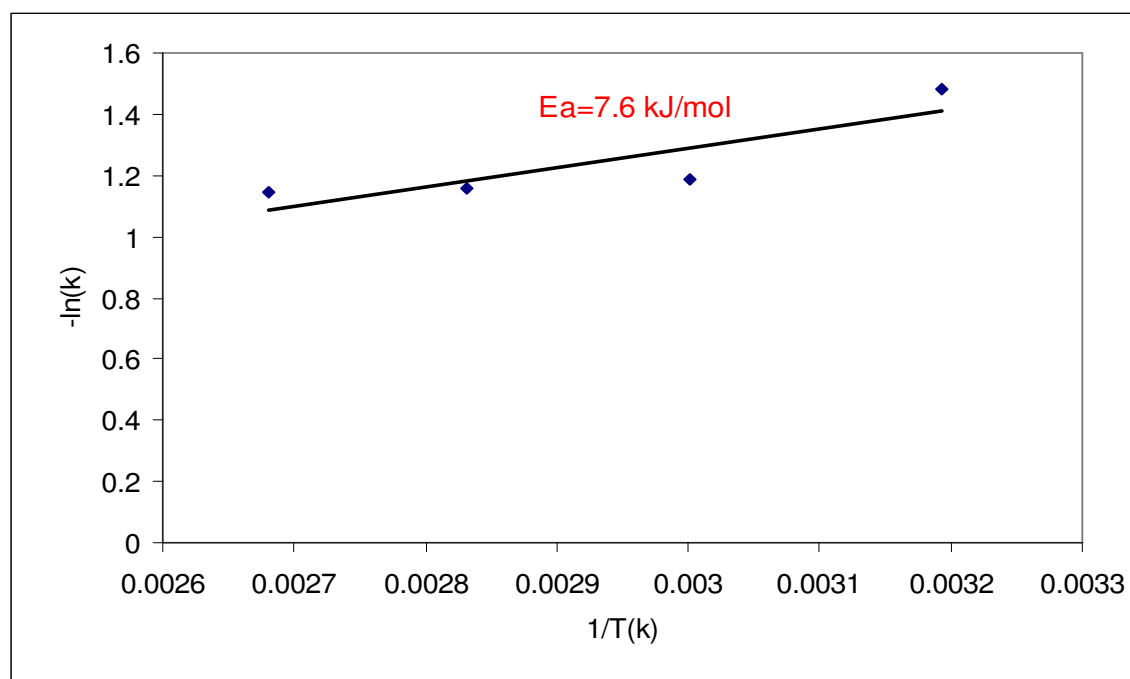


Figure 3.20 The Arrhenius plot of HGO_B

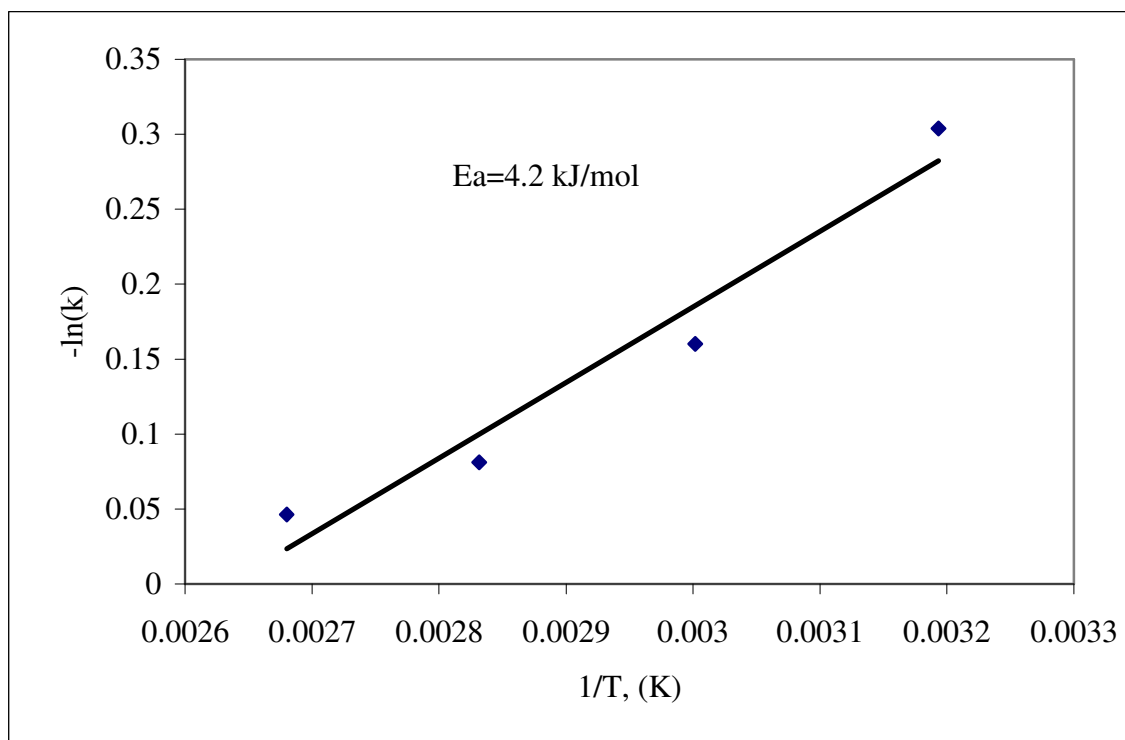


Figure 3.21 The Arrhenius plot of DBT

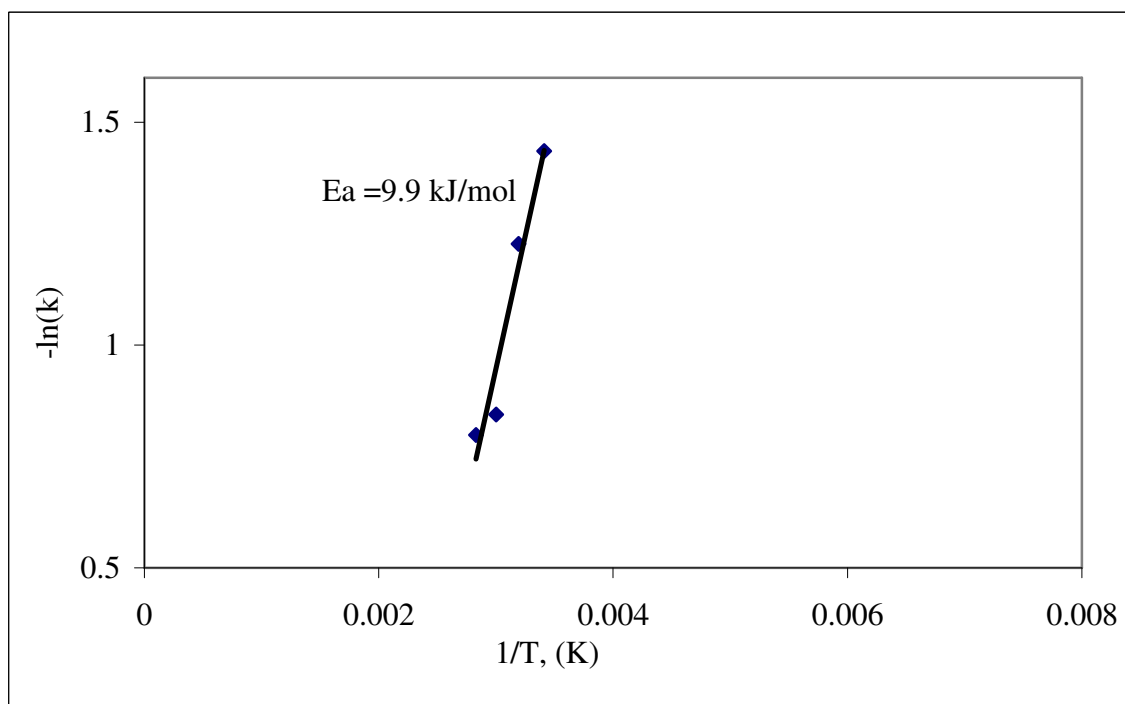


Figure 3.22. The Arrhenius plot of di-n-butylsulfide

3.15 Conclusions

This study aimed at developing an oxidative desulphurization process with high reaction rate and high selectivity. The process was designed to combine two complementary techniques: oxidation of organic sulphur compounds and solvent extraction of oxidised sulphur compounds.

The removal of model sulphur compounds (Di-n-butylsulfide, Di-methylsulfoxide and Dibenzothiophene) from dodecane and oxidative desulphurization of heavy gas oils with hydrogen peroxide have been investigated using formic acid as the catalyst. The sulphur removal is strongly affected by process parameters, such as operating reaction temperature, amount of oxidant and amount of catalyst.

In addition to the oxidative sulphur removal, extraction of unoxidised and oxidised heavy gas oils was also investigated using methanol, dimethylformamide (DMF) and N-methyl pyrrolidone (NMP) as solvents. It was found that the extractability of the sulphur compounds by polar solvents increased by oxidizing into their corresponding sulphones with higher polarity, therefore improving the yield of desulphurized raffinate and overall sulphur removal efficiency. DMF was the most effective polar solvent among the solvents used.

A model sulphur compounds and heavy gas oil were studied to evaluate the effectiveness of ODS process and to examine the kinetics of the oxidation reaction. In general the oxidation of organic sulphur compounds under ODS conditions follows pseudo-first-order kinetics. The apparent rates constant of DBT and sulphur contained in HGO are determined to be 0.737 min^{-1} at 40°C for DBT and 0.227 min^{-1} at 40°C for HGO. This information is very important to design a continuous ODS system as well as the process evaluation of ODS on HGO.

Chapter Four

Heat Integration in Oxidation Process: Energy Consumption and Recovery Issue

4.1 Introduction

One of the jobs with which chemical engineers are continually involved is the scale-up of laboratory experiments to pilot-plant operation or to full –scale production. In the past, a pilot plant would be designed based on the laboratory data. However, owing to the high cost of a pilot-plant study, this step is beginning to be surpassed in many instances by designing the full scale-plant from the operation of a laboratory-bench-scale unit called a microplant. To make this jump successfully requires a thorough understanding of the chemical kinetics and transport limitation. However, energy conservation is important in process design. In industrial experience, the calculation of the minimum heating and cooling requirements reveal significant energy savings. Specifically, ex. Imperial Chemical Industries in the United Kingdom and Union Carbide in the United States have both stated the results of numerous case studies that indicate 30% to 50% energy savings compared to traditional practice (Douglas, 1988).

Over a period of many years, the energy consumption of a chemical process can be reduced in successive designs. The learning curve thus obtained is typical of process plant development (Figure 4.1). However, if Process Integration techniques had been available initially, the target could have been found and the ultimate design could have been identified in one step. Process Integration, when eventually applied, still identified a practical and economic saving of 30 % (Vaselanak et al., 1986,). Therefore, energy integration is a very beneficial tool and is an important phase in determining the cost of preliminary design.

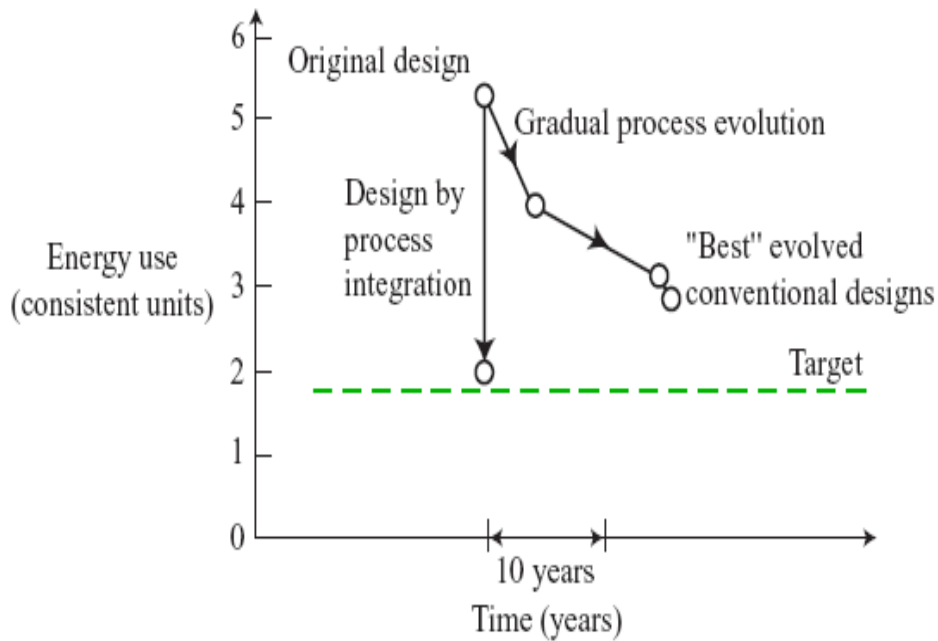


Figure 4.1 Process Integration vs. gradual development

Carbon dioxide concentrations in the atmosphere have risen from about 270 ppm before the industrial age to about 380 ppm by 2006, a 41% increase over pre-industrial values, and a 31% increase since 1870. U.S. Environmental Protection Agency (U.S. EPA) recently found carbon dioxide (CO₂), the most common greenhouse gas, a danger to human health, clearing the way for greater regulation of CO₂ emissions (<http://www.aip.org/history/climate/co2.htm>). The primary human source of CO₂ in the atmosphere is from the burning of fossil fuels for energy production and transport. In order to stop global warming, dramatic cuts in all CO₂ emissions must be achieved, 25 to 40 % below 1990 levels by 2020, and 80 to 95 % below 1990 levels by 2050 (<http://www.greenpeace.org>).

However, more efficient utilisation of energy consumption results in the reduction of the negative impacts of CO₂ emissions. Therefore, process integration is an efficient design methodology that addresses issues related to energy efficiency, waste minimisation and an efficient use of raw materials.

In this chapter a large scale oxidation process using a continuous stirrer tank reactor (CSTR) is developed. Large amount of energy is required to carry out the oxidation reaction at temperature same as the batch reactor experiment (Chapter Three). Therefore the heat integration of the oxidation process is considered. In the absence of a real plant a process model for the system is developed. The kinetic model for the CSTR is based on the batch reactor experiments. However, this leads to putting a number of heat exchangers in the system requiring capital investment.

4.2 Scale up from Batch to Continuous Stirred Tank Reactor

Batch reactor will not be suitable for reacting large amount of heavy gas oil therefore is not suitable for industrial scale. CSTR will be an attractive option.

4.2.1 Design of Continuous Stirred Tank Reactor

CSTRs are common in the chemical process industry because they are useful for both gas and liquid phase reactions and are ideal for continuous processes. CSTRs are used in a wide variety of process operations such as fermentation, chemical synthesis, polymerisation, crystallisation, liquid/liquid extraction, mixing, dissolution, evaporation and so on. Frequently, the same vessel can be used for multiple unit operations and for manufacturing a variety of different products.

Reactors are usually at the core of a chemical plant, thus optimizing the operating conditions of reactors is vital to the overall optimisation of the plant. An adiabatic CSTR is designed to oxidizing of heavy gas oil in a chemical process plant (ODS).

4.2.2 Continuous Stirred Tank Reactor Model

Reactor models are usually difficult to develop because the performance of a reactor can be influenced by temperature, pressure, species concentration, feed impurities, mixing and the geometry, etc.

The assumptions made in the model of a CSTR used in this study are:

1. Perfect mixing and perfect level control (no dynamics involved).
2. The temperature, pressure, and concentrations throughout the reactor are uniform.
3. Both specific heat capacities and densities are considered temperature independent (constant physical properties).
4. Heat will be generated due to reaction but the effect of it will be negligible as the volume of heavy gas oil is much larger compared to reactants.
5. Constant flow rate.

Due to the assumption of perfect mixing the temperature and composition in the reactor outlet are the same as in the reactor itself. Although these assumptions are never completely correct, they do allow for a reasonable model of a CSTR. For these assumptions to hold, the reactor must be well mixed. Figure 4.2 shows a CSTR with a single feed and a single product.

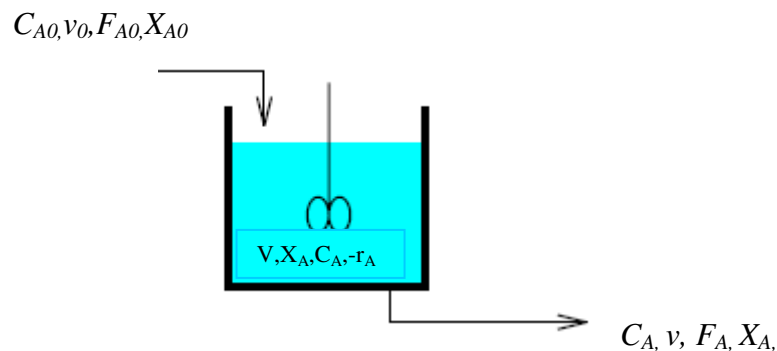


Figure 4.2 Schematic diagram of a CSTR

The material balance of CSTR is given by the following Equation:

$$\text{input} = \text{output} + \text{disappearance by reaction} \quad (4.1)$$

$$F_{A0} = F_A + (-r_A)V \quad (4.2)$$

Where

$$F_{A0} = \text{input flow rate}$$

F_A = out put flow rate and given by the following Equation:

$$F_A = F_{A0}(1 - X_A) \quad (4.3)$$

$-r_A$ = reaction rate described in Equation (4.5) (same as Equation 3.5 of Chapter 3).

For a first order, liquid phase, and irreversible reaction taken place adiabatically in a CSTR, the design equation and rate law can be written below.

$$V = \frac{F_{A0} X_A}{-r_A} \quad (4.4)$$

$$-r_A = A_r e^{-E/RT} C_A \quad (4.5)$$

4.3 Energy Consumption and Recovery Issues

Batch reactor experiment shows that oxidation reaction of model sulphur compound and total sulphur in heavy gas oil is favourable at higher temperature (>40 °C). Energy consumption for batch reactor (lab-scale) was negligible and natural cooling after the reaction was sufficient, no additional utility was required as the amount of reactants and products were small therefore heat recovery was not an issue in the lab-scale operation, but in the large scale operation even to raise the temperature to 40 °C, energy consumption will be a big issue and recovery must be considered. Therefore while scaling up a heat integrated CSTR process was considered to reduce overall energy consumption (thus reduce environmental impact). The CSTR process deals with the retrofit of a heat exchanger network. The objective is to determine a retrofit design that

can reduce the energy consumption, maximize energy recovery and then minimize of capital investment.

Often an exchanger operates in series with a cooler and a heater. The cooler regulates the final temperature of the hot fluid to requirements of the next step of the process (Extraction), and the heater adjusts the final temperature of the cooled fluid to requirements (reaction temperature). The exchangers, heaters and cooler are represented in Figures 4.3 and 4.6 by E, H and C respectively. The feed and product temperatures will be considered fixed and equal (T_{F0}). The temperatures of the steam and water will also be fixed. Only countercurrent flow heat exchangers are employed in this work.

4.4 Case I: Heavy Gas Oil and Catalyst as One Feed Stream

A heat-integrated CSTR system is depicted in Figure 4.3 In this case, feed stream S1 (cold stream) was containing HGO and catalyst (HCOOH). They were mixed in mixer M1 before preheating from T_{F0} to T_{F1} in heat exchanger E1. Then, the mixture was fed into heater H1 to preheat from T_{F1} to reaction temperature (T_r). The stream leaving the reactor S3 (hot stream) is divided into two streams (S4 and S5) according to the splitter ratio (S_r). Stream S4 is cooled from T_r to T_0 by in contact with feed stream S1 through heat exchanger E1. Stream S5 cooled from T_r to T_{01} by in contact with oxidant stream S2 in heat exchanger E2 and the oxidant stream was heated from T_{F0} to T_{F2} in heater H2. The product streams (S4 and S5) were mixed in mixer M2 and cooled to T_{F0} in cooler (C) by using water at T_{w1} . The energy balance equations for whole system are given below.

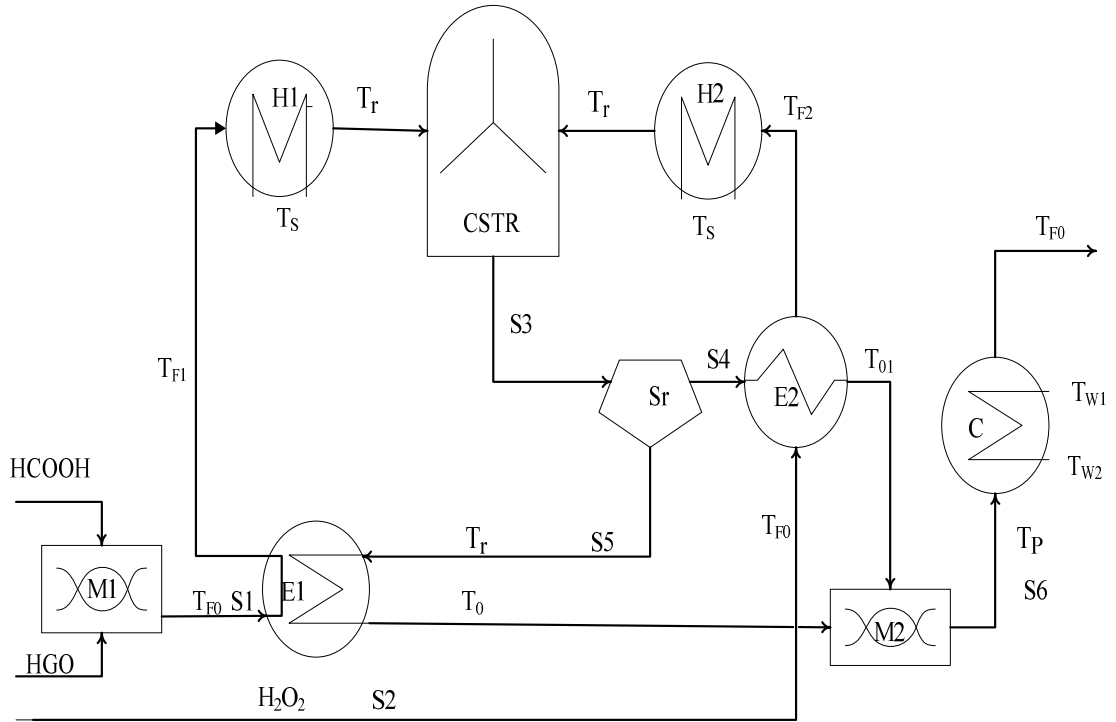


Figure 4.3 Process flowsheet of heat- integrated reaction system case I

4.4.1 Model Equations

a) Heat exchanger (E1)

S_r % of the product (S5) was used to preheat the feed (S1) from T_{F0} to T_{F1} through the heat exchanger (E1) and in the same time the S_r % of the product is cooled from T_r to T_0 (Figure 4.4). The equations of heat duty for these streams are shown below:

$$Q_{1E1} = (V_0 \rho_H C_{PH} + V_{0F} \rho_F C_{PF}) (T_{F1} - T_{F0}) \quad (4.6)$$

$$Q_{2E1} = S_r (V_0 \rho_H C_{PH} + V_{0F} \rho_F C_{PF} + V_{0H2} \rho_{H2} C_{PH2}) (T_r - T_0) \quad (4.7)$$

where:

T_{F0} = inlet temperature of the cold fluid.

T_{F1} = outlet temperature of the cold fluid.

T_r = inlet temperature of the hot fluid (reaction temperature).

T_0 = outlet temperature of the hot fluid.

S_r = splitter ratio

ρ_F = density of catalyst

ρ_H = density of heavy gas oil

ρ_{H_2} = density of oxidant

V_0 = volumetric flow rate of heavy gas oil

V_{0F} = volumetric flow rate of formic acid

V_{0H_2} = volumetric flow rate of oxidant

C_{PH} = heat capacity of heavy gas oil

C_{PF} = heat capacity of catalyst

C_{PH_2} = heat capacity of oxidant

$$\Delta T_1 = (T_r - T_{F1}) \quad (4.8)$$

$$\Delta T_2 = (T_0 - T_{F0}) \quad (4.9)$$

The log mean temperature difference (LMTD) for countercurrent flow in tubular heat exchangers is:

$$\Delta T_{lm1} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)} \quad (4.10)$$

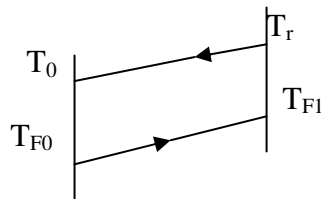


Figure 4.4 Heat exchanger E1 Case I

Substituting Equation (4.8) into Equation (4.6) and Equation (4.9) into Equation (4.7), the following equations are obtained:

$$Q_{1E1} = (V_0\rho_H C_{PH} + V_{0F}\rho_F C_{PF})(T_r - T_{F0} - \Delta T_1) \quad (4.11)$$

$$Q_{2E1} = S_r(V_0\rho_H C_{PH} + V_{0F}\rho_F C_{PF} + V_{0H2}\rho_{H2} C_{PH2})(T_r - T_{F0} - \Delta T_2) \quad (4.12)$$

$$Q_{1E1} = Q_{2E1} \quad (4.13)$$

The heat transfer area for heat exchanger E1 is

$$A_{E1} = \frac{Q_{1E1}}{U_{E1}\Delta T_{lm1}} \quad (4.14)$$

Where, U_{E1} is the overall heat transfer coefficient.

b) Heater (H1)

The feed stream (S1) leaves the heat exchanger E1 at T_{F1} and is to be used in a reactor at T_r ($T_{F1} < T_r$). Heating will be achieved by steam in the heater H1. The heat balance equations can be written below:

$$Q_{H1} = (V_0\rho_H C_{PH} + V_{0F}\rho_F C_{PF})(T_r - T_{F1}) \quad (4.15)$$

By substituting Equation (4.8) into Equation (4.15), the following equation is obtained

$$Q_{H1} = (V_0\rho_H C_{PH} + V_{0F}\rho_F C_{PF}) \Delta T_1 \quad (4.16)$$

$$Q_{S1} = M_{S1}\lambda \quad (4.17)$$

$$Q_{H1} = Q_{S1} \quad (4.18)$$

Where M_{S1} and λ are the amount of steam (kg/hr) and latent heat respectively.

The log mean temperature difference is:

$$\Delta T_{lmH1} = \frac{(T_S - T_r) - (T_S - T_{F1})}{\ln\left(\frac{T_S - T_r}{T_S - T_{F1}}\right)} \quad (4.19)$$

The heat transfer area for heater H1

$$A_{H1} = \frac{Q_{H1}}{U_{H1} \Delta T_{lmH1}} \quad (4.20)$$

c) Heat exchanger (E2)

The oxidant stream S2 is heated from T_{F0} to T_{F2} by in contact with (1-Sr %) of the product stream S4 (hot stream) through the heat exchanger E2 and the product stream is cooled from reaction temperature T_r to T_{01} (Figure 4.5). The heat balance equations are:

$$Q_{1E2} = (1 - S_r)(V_0 \rho_H C_{PH} + V_{0F} \rho_F C_{PF} + V_{0H2} \rho_{H2} C_{PH2})(T_r - T_{01}) \quad (4.21)$$

$$Q_{2E2} = V_{0H2} \rho_{H2} C_{PH2} (T_{F2} - T_{F0}) \quad (4.22)$$

where

T_{F2} = outlet temperature of the cold fluid.

T_{01} = outlet temperature of the hot fluid

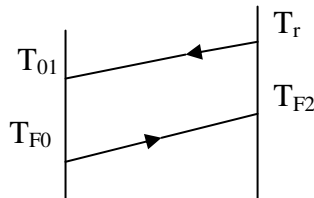


Figure 4.5 Heat exchanger E2 Case I

$$\Delta T_3 = (T_r - T_{F2}) \quad (4.23)$$

$$\Delta T_4 = (T_{01} - T_{F0}) \quad (4.24)$$

The log mean temperature difference (LMTD) is:

$$\Delta T_{lm2} = \frac{\Delta T_3 - \Delta T_4}{\ln \left(\frac{\Delta T_3}{\Delta T_4} \right)} \quad (4.25)$$

By substituting Equation (4.24) into Equation (4.21) and Equation (4.23) into Equation (4.22), result the following equations.

$$Q_{1E2} = (1 - S_r)(V_0\rho_H C_{PH} + V_{0F}\rho_F C_{PF} + V_{0H2}\rho_{H2} C_{PH2})(T_r - T_{F0} - \Delta T_4) \quad (4.26)$$

$$Q_{2E2} = V_{0H2}\rho_{H2} C_{PH2}(T_r - \Delta T_3 - T_{F0}) \quad (4.27)$$

$$Q_{1E2} = Q_{2E2} \quad (4.28)$$

The heat transfer area for heat exchanger E2 is

$$A_{E2} = \frac{Q_{1E2}}{U_{E2}\Delta T_{lm2}} \quad (4.29)$$

d) Heater (H2)

The feed stream (S2) leaves the heat exchanger E2 at T_{F2} and is to be used in a reactor at T_r ($T_{F2} < T_r$). Heating will be achieved by steam in the heater H2. The heat balance equations as shown below:

$$Q_{H2} = V_{0H2}\rho_{H2} C_{PH2}(T_r - T_{F2}) \quad (4.30)$$

Substituting Equation (4.23) into Eq (4.30), result the following equations:

$$Q_{H2} = V_{0H2}\rho_{H2} C_{PH2} \Delta T_3 \quad (4.31)$$

$$Q_{S2} = M_{S2}\lambda \quad (4.32)$$

$$Q_{S2} = Q_{H2} \quad (4.33)$$

Where M_{S2} and λ are the amount of steam (kg/hr) and latent heat respectively.

The log mean temperature difference is:

$$\Delta T_{lmH2} = \frac{(T_S - T_r) - (T_S - T_{F2})}{\ln\left(\frac{T_S - T_r}{T_S - T_{F2}}\right)} \quad (4.34)$$

The heat transfer area for heater H2 is

$$A_{H2} = \frac{Q_{H2}}{U_{H2}\Delta T_{lmH2}} \quad (4.35)$$

The total amount of steam used (M_S) is

$$M_S = M_{S1} + M_{S2} \quad (4.36)$$

e) Cooler (C)

The product streams S4 and S5 were mixed in the mixer M2 to produce stream S6 at temperature T_P and then cooled from this temperature (T_P) to the feed temperature T_{F0} in the cooler by using water at T_{w1} . The heat balance equations as shown below:

$$Q_c = (V_0 \rho_H C_{PH} + V_{0F} \rho_F C_{PH} + V_{0H2} \rho_{H2} C_{PH2}) (T_P - T_{F0}) \quad (4.37)$$

$$Q_c = m_w c_{pw} (T_{w2} - T_{w1}) \quad (4.38)$$

Where

T_P = product temperature, K

$$T_P = S_r T_0 + (1 - S_r) T_{01} \quad (4.39)$$

m_w = Amount of cooling water, (Kg/hr)

c_{pw} = Heat capacity of water, (J/kg K) and

T_{w2}, T_{w1} = Outlet and inlet temperatures of cooled water, K

The log mean temperature difference is:

$$\Delta T_{lmc} = \frac{(T_P - T_{w2}) - (T_{F0} - T_{w1})}{\ln \left(\frac{T_P - T_{w2}}{T_{F0} - T_{w1}} \right)} \quad (4.40)$$

The heat transfer area for heat exchanger C is

$$A_C = \frac{Q_c}{U_c \Delta T_{lmc}} \quad (4.41)$$

Where, U_c is the overall heat transfer coefficient.

The total heat transfer area is given in the following equations

$$A_t = A_{E1} + A_{E2} + A_{H1} + A_{H2} + A_C \quad (4.42)$$

The total heating (Q_t) and total heat recovery (Q_r) are given in the following equations

$$Q_t = Q_{H1} + Q_{H2} \quad (4.43)$$

$$Q_r = Q_{1E1} + Q_{1E2} \quad (4.44)$$

f) CSTR

The Equation (4.4) is re-organized in to:

$$X_A = \frac{-r_A \tau}{C_{A_0}} \quad (4.45)$$

$$F_{A_0} = V_0 H C_{A_0} \quad (4.46)$$

$$C_A = C_{A_0} (1 - X_A) \quad (5.47)$$

$$\tau = \frac{V}{v} \quad (4.48)$$

Where

τ = the residence time

v = total volumetric flow rate of the feed

V = volume of the reactor

F_{A_0} = molar flow rate

The reaction rate equation was described in Equation (4.5).

4.4.2 Degree of Freedom Analysis for Case I

The final set of model equations for Case I is:

Equations (5), (8)-(14), (16)-(20), (23)-(29), (31)-(35), (37)-(41) and (45)-(48). There are thirty four equations and forty three variables (thirty nine unknown and four specified) and seventeen fixed parameters in these equations and they are:

$$\Delta T_1, \Delta T_2, \Delta T_3, \Delta T_4, \Delta T_{lm1}, \Delta T_{lm2}, \Delta T_{lmH1}, \Delta T_{lmH2}, \Delta T_{lmC}, T_r, T_{F0}, T_{F1}, T_{F2}, T_O, T_{O1}, T_P, T_{w1}, T_{w2}, T_s, Q_{1E1}, Q_{2E1}, Q_{1E2}, Q_{2E2}, Q_{H1}, Q_{H2}, Q_{S1}, Q_{S2}, Q_C, A_{E1}, A_{E2}, A_{H1}, A_{H2}, A_C, M_{S1}, M_{S2}, X_A, -r_A, \tau, F_{A_0}, V, v, C_A, \text{ and } S_r$$

Therefore, the degree of freedom is given by:

$$\text{d.f.} = \text{total number of variables} - \text{total number of equations} = 43 - 34 = 9$$

Accordingly, the values of parameters and variables that must be specified are:

1) Fixed parameters

$R, A_r, E_a, C_{A_0}, C_{PH_2}, C_{PF}, C_{PH}, C_{Pw}, \lambda, \rho_H, \rho_{H_2}, \rho_F, U_{E1}, U_{E2}, U_{H1}, U_{H2}$ and U_C

2) Specified variables

T_{F0}, T_{w1}, T_s and $v = 4$

The following variables can be relaxed and optimised

$\Delta T_2, \Delta T_4, T_r, \tau$ and $S_r = 5$

4.5 Case II: Heavy Gas Oil and Catalyst as Two Feed Streams

In this case, three feed streams were fed into the reactor. The first stream $S1$ (cold stream) was containing HGO preheating from T_{F0} to T_{F1} in heat exchanger $E1$, and then fed into the heater $H1$ to preheat from T_{F1} to reaction temperature (T_r). The second stream $S2$ (cold stream) was containing HCOOH preheating from T_{F0} to T_{F2} in heat exchanger $E2$, and then from T_{F2} to T_r through the heater $H2$. The third stream $S3$ was containing oxidant (H_2O_2) fed into heat exchanger $E3$ to preheat from T_{F0} to T_{F3} and then heat up to reaction temperature in heater $H3$ by using steam at T_s . The stream which leaving the reactor $S4$ (hot stream) divided into two streams ($S5$ and $S6$) according to the splitter ratio (S_r). Stream $S5$ was cooled from T_r to T_0 by heat exchanger $E1$, and stream $S6$ cooled from T_r to T_{01} by heat exchanger $E2$. The product streams ($S5$ and $S6$) mixed in mixer M and cooled from T_p to T_A in heat exchanger $E3$ and then from T_A to feed temperature T_{F0} in the cooler by using cooled water at T_{w1} . Figure 4.6 is a flowchart of these performance streams.

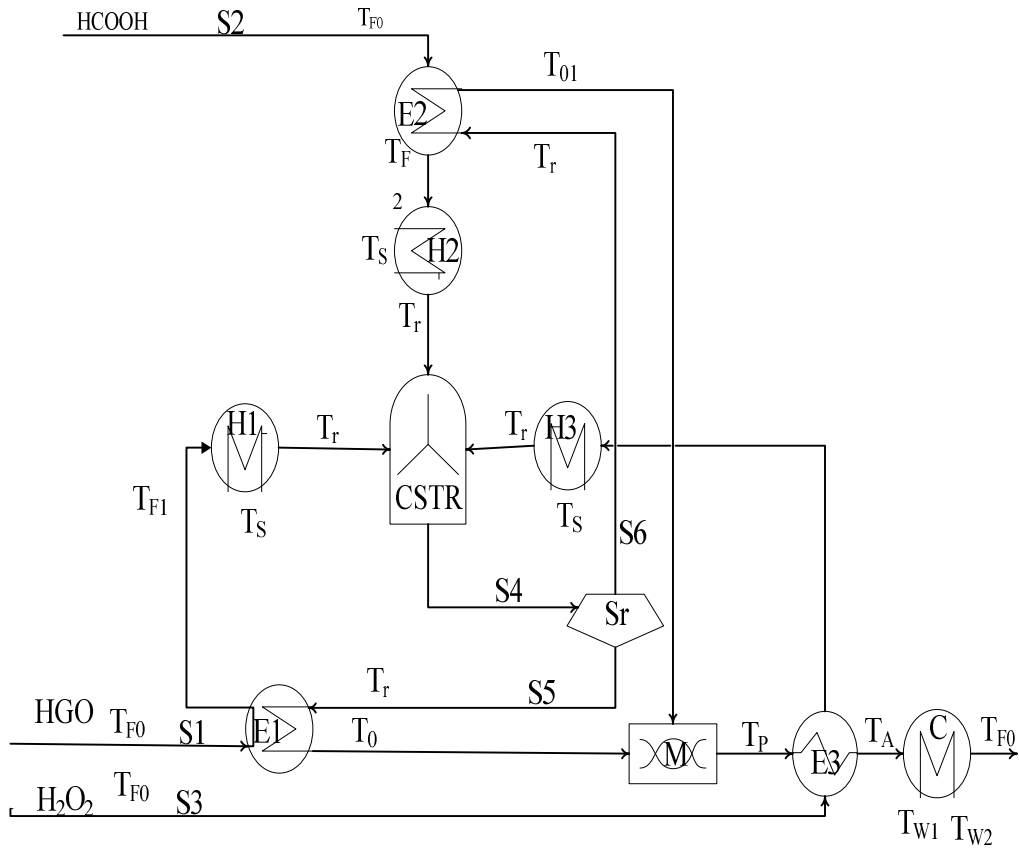


Figure 4.6 Process flowsheet of heat- integrated reaction system case II

4.5.1 Model Equations

a) Heat exchanger (E1)

The feed stream (S1) was heated by S_r % of the product stream (S4) from T_{F0} to T_{F1} and it's cooled from T_r to T_0 in heat exchanger E1 (Figure 4.7). The heat balance equations for these streams are shown below:

$$Q_{1E1} = V_0 \rho_H C_{PH} (T_{F1} - T_{F0}) \quad (4.49)$$

$$Q_{2E1} = S_r (V_0 \rho_H C_{PH} + V_{0F} \rho_F C_{PF} + V_{0H2} \rho_{H2} C_{PH2}) (T_r - T_0) \quad (4.50)$$

$$Q_{1E1} = Q_{2E1} \quad (4.51)$$

$$\Delta T_1 = (T_r - T_{F1}) \quad (4.52)$$

$$\Delta T_2 = (T_0 - T_{F0}) \quad (4.53)$$

The log mean temperature difference (LMTD) for countercurrent flow in tubular heat exchangers is:

$$\Delta T_{lm1} = \frac{\Delta T_1 - \Delta T_2}{\ln \left(\frac{\Delta T_1}{\Delta T_2} \right)} \quad (4.54)$$

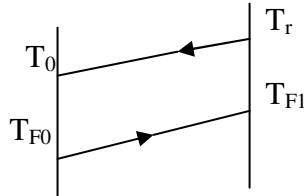


Figure 4.7 Heat exchanger E1 Case II

By substituting Equation (4.52) into Equation (4.49) and Equation (4.53) into Equation (4.50), the following equations are obtained.

$$Q_{1E1} = V_0 \rho_H C_{PH} (T_r - \Delta T_1 - T_{F0}) \quad (4.55)$$

$$Q_{2E1} = S_r (V_0 \rho_H C_{PH} + V_{0F} \rho_F C_{PF} + V_{0H2} \rho_{H2} C_{PH2}) (T_r - T_{F0} - \Delta T_2) \quad (4.56)$$

The heat transfer area for heat exchanger E1 is

$$A_{E1} = \frac{Q_{1E1}}{U_{E1} \Delta T_{lm1}} \quad (4.57)$$

b) Heater (H1)

The first feed stream (S1) enters the heater H1 at temperature T_{F1} and is heated to the reaction temperature T_r , using a steam. The heat balance equations as following:

$$Q_{H1} = V_0 \rho_H C_{PH} (T_r - T_{F1}) \quad (4.58)$$

Substituting Equation (4.52) into Equation (4.58) obtained the following equation:

$$Q_{H1} = V_{0H} \rho_H C_{PH} \Delta T_1 \quad (4.59)$$

$$Q_{S1} = M_{S1} \lambda \quad (4.60)$$

$$Q_{H1} = Q_{S1} \quad (4.61)$$

$$\Delta T_{lmH1} = \frac{(T_S - T_r) - (T_S - T_{F1})}{\ln\left(\frac{T_S - T_r}{T_S - T_{F1}}\right)} \quad (4.62)$$

The heat transfer area for heater H1 is

$$A_{H1} = \frac{Q_{H1}}{U_{H1} \Delta T_{lmH1}} \quad (4.63)$$

c) Heat exchanger (E2)

The second feed stream (S2) is heated from T_{F0} to T_{F2} by in contact with (1-Sr %) of the product stream S6 (hot stream) through the heat exchanger E2 and the product stream is cooled from T_r to T_{01} (Figure 4.8). The equations of heat balance are shown below:

$$Q_{1E2} = V_{0F} \rho_F C_{PF} (T_{F2} - T_{F0}) \quad (4.64)$$

$$Q_{2E2} = (1 - S_r)(V_{0H} \rho_H C_{PH} + V_{0F} \rho_F C_{PF} + V_{0H2} \rho_{H2} C_{PH2}) (T_r - T_{01}) \quad (4.65)$$

$$Q_{1E2} = Q_{2E2} \quad (4.66)$$

$$\Delta T_3 = T_r - T_{F2} \quad (4.67)$$

$$\Delta T_4 = T_{01} - T_{F0} \quad (4.68)$$

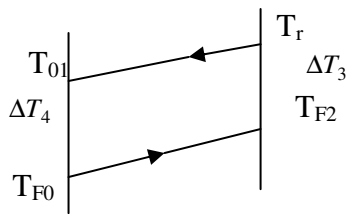


Figure 4.8 Heat exchanger E2 Case II

The log mean temperature difference (LMTD) for countercurrent flow in tubular heat exchangers is

$$\Delta T_{lm3} = \frac{\Delta T_3 - \Delta T_4}{\ln\left(\frac{\Delta T_3}{\Delta T_4}\right)} \quad (4.69)$$

Substituting T_{F2} into Equation (4.64) and T_{0I} into Equation (4.65), resulting the following equations:

$$Q_{1E2} = V_{0F} \rho_F C_{PF} (T_r - \Delta T_3 - T_{F0}) \quad (4.70)$$

$$Q_{2E2} = (1 - S_r)(V_0 \rho_H C_{PH} + V_{0F} \rho_F C_{PF} + V_{0H2} \rho_{H2} C_{PH2})(T_r - T_{F0} - \Delta T_4) \quad (4.71)$$

The heat transfer area for heat exchanger E2 is

$$A_{E2} = \frac{Q_{1E2}}{U_{E2} \Delta T_{lm1}} \quad (4.72)$$

d) Heater (H2)

The second feed stream (S2) enters the heater H2 at T_{F2} and is heated to T_r by using the steam. The heat balance equations are shown below:

$$Q_{H2} = V_{0F} \rho_F C_{PF} (T_r - T_{F2}) \quad (4.73)$$

From Equation (4.67), we get

$$Q_{H2} = V_{0F} \rho_F C_{PF} (\Delta T_3) \quad (4.74)$$

$$Q_{S2} = M_{S2} \lambda \quad (4.75)$$

$$Q_{S2} = Q_{H2} \quad (4.76)$$

$$\Delta T_{lmH2} = \frac{(T_S - T_r) - (T_S - T_{F2})}{\ln\left(\frac{T_S - T_r}{T_S - T_{F2}}\right)} \quad (4.77)$$

The heat transfer area for heater H2 is:

$$A_{H2} = \frac{Q_{H2}}{U_{H2} \Delta T_{lmH2}} \quad (4.78)$$

e) Heat exchanger (E3)

The third feed stream (S3) is heated from T_{F0} to T_{F3} by the product stream (hot stream) in the heat exchanger E3 and the product stream is cooled from T_P to T_A (Figure 4.9).

The heat balance equations are shown below:

$$Q_{1E3} = V_{0H2} \rho_{H2} C_{PH2} (T_{F3} - T_{F0}) \quad (4.79)$$

$$Q_{2E3} = (V_0 \rho_{Hh} C_{PHh} + V_{0F} \rho_{Fh} C_{PFh} + V_{0H2} \rho_{H2} C_{PH2}) (T_P - T_A) \quad (4.80)$$

$$Q_{1E3} = Q_{2E3} \quad (4.81)$$

Where

T_P product temperature, K

$$T_P = S_r T_0 + (1 - S_r) T_{01} \quad (4.82)$$

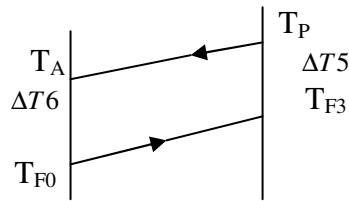


Figure 4.9 Heat exchanger E3 Case II

$$\Delta T_5 = T_P - T_{F3} \quad (4.83)$$

$$\Delta T_6 = T_A - T_{F0} \quad (4.84)$$

The log mean temperature difference (LMTD) for countercurrent flow in tubular heat exchangers is

$$\Delta T_{lm4} = \frac{\Delta T_5 - \Delta T_6}{\ln\left(\frac{\Delta T_5}{\Delta T_6}\right)} \quad (4.85)$$

Substituting T_{F3} into Equation (4.79) and T_A into Equation (4.80) resulting the following equations:

$$Q_{1E3} = V_{0H2} \rho_{H2} C_{PH2} (T_P - \Delta T_5 - T_{F0}) \quad (4.86)$$

$$Q_{2E3} = (V_{0H} \rho_H C_{PH} + V_{0F} \rho_F C_{PF} + V_{0H2} \rho_{H2} C_{PH2}) (T_P - T_{F0} - \Delta T_6) \quad (4.87)$$

The heat transfer area for heat exchanger E3 is:

$$A_{E3} = \frac{Q_{1E3}}{U_{E3} \Delta T_{lm3}} \quad (4.88)$$

f) Heater (H3)

The feed stream (S3) leaves the heat exchanger E3 at T_{F3} and is to be used in a reactor at T_r ($T_{F3} < T_r$). Heating will be achieved by steam in the heater H3. The heat balance equations are shown below:

$$Q_{H3} = V_{0H2} \rho_{H2} C_{PH2} (T_r - T_{F3}) \quad (4.89)$$

Substituting T_{F3} into Equation (4.89)

$$Q_{H3} = V_{0H2} \rho_{H2} C_{PH2} (T_r - T_P + \Delta T_5) \quad (4.90)$$

$$Q_{S3} = M_{S3} \lambda \quad (4.91)$$

$$Q_{H3} = Q_{S3} \quad (4.92)$$

Where M_{S3} and λ are the amount of steam (kg/hr) and latent heat respectively.

The log mean temperature difference is:

$$\Delta T_{lmH3} = \frac{(T_S - T_r) - (T_S - T_{F3})}{\ln \left(\frac{T_S - T_r}{T_S - T_{F3}} \right)} \quad (4.93)$$

The heat transfer area for heater H3 is

$$A_{H3} = \frac{Q_{H3}}{U_H T_{lmH3}} \quad (4.94)$$

The total amount of steam used (M_S) is

$$M_S = M_{S1} + M_{S2} + M_{S3} \quad (4.95)$$

g) Cooler (C)

The product streams were mixed in the mixer M and cooled from T_A to the feed temperature, T_{F0} in the cooler by using water at T_{w1} . The heat balance equations are shown below:

$$Q_c = (V_{0H}\rho_H C_{PH} + V_{0F}\rho_F C_{PF} + V_{0H2}\rho_{H2} C_{PH2}) (T_A - T_{F0}) \quad (4.96)$$

$$Q_c = m_w c_{pw} (T_{w2} - T_{w1}) \quad (4.98)$$

Where

m_w = Amount of cooling water, (Kg/hr)

c_{pw} = Heat capacity of water, (J/kg K) and

T_{w2}, T_{w1} = Outlet and inlet temperatures of cooled water, K

The log mean temperature difference is:

$$\Delta T_{lmc} = \frac{(T_A - T_{w2}) - (T_{F0} - T_{w1})}{\ln\left(\frac{T_A - T_{w2}}{T_{F0} - T_{w1}}\right)} \quad (4.98)$$

The heat transfer area for heat exchanger C is

$$A_C = \frac{Q_C}{U_c \Delta T_{lmc}} \quad (4.99)$$

The total heat transfer area is given in the following equations

$$A_t = A_{E1} + A_{E2} + A_{E3} + A_{H1} + A_{H2} + A_{H3} + A_C \quad (4.100)$$

The total heating (Q_t) and total heat recovery (Q_r) are given in the following equations

$$Q_t = Q_{H1} + Q_{H2} + Q_{H3} \quad (4.101)$$

$$Q_r = Q_{1E1} + Q_{1E2} + Q_{1E3} \quad (4.102)$$

4.5.2 Degree of Freedom Analysis for Case II

The final set of model equations for Case II is:

Equations: (5), (45)-(48), (51)-(57), (59)-(63), (66)-(72), (74)-(78), (81)-(88), (90)-(94) and (96)-(99). There are forty six equations and fifty seven variables (fifty three unknown and four specified) and nineteen fixed parameters in these equations and they are:

$$\Delta T_1, \Delta T_2, \Delta T_3, \Delta T_4, \Delta T_5, \Delta T_6, \Delta T_{lm1}, \Delta T_{lm2}, \Delta T_{lm3}, \Delta T_{lmH1}, \Delta T_{lmH2}, \Delta T_{lmH3}, \Delta T_{lmC}, \\ T_r, T_{F0}, T_{F1}, T_{F2}, T_{F3}, T_O, T_{O1}, T_P, T_A, T_{w1}, T_{w2}, T_s, Q_{1E1}, Q_{2E1}, Q_{1E2}, Q_{2E2}, Q_{1E3}, Q_{2E3}, \\ Q_{H1}, Q_{H2}, Q_{H3}, Q_{S1}, Q_{S2}, Q_{S3}, Q_C, A_{E1}, A_{E2}, A_{E3}, A_{H1}, A_{H2}, A_{H3}, A_C, M_{S1}, M_{S2}, \\ M_{S3}, m_w, X_A, C_A, -r_A, \tau, F_{A0}, V, v \text{ and } S_r$$

Therefore, the degree of freedom is given by:

$$\text{d.f.} = \text{total number of variables} - \text{total number of equations} = 57 - 46 = 11$$

Accordingly, the values of parameters and variables that must be specified are:

1) Fixed parameters

$$R, A, E_a, C_{A0}, C_{PH2}, C_{PF}, C_{PH}, C_{Pw}, \lambda, \rho_H, \rho_{H2}, \rho_F, U_{E1}, U_{E2}, U_{E3}, U_{H1}, U_{H2}, \\ U_{H3} \text{ and } U_C$$

2) Specified variables

$$T_{F0}, T_{w1}, T_s \text{ and } V_{0H} = 4$$

The following variables can be relaxed and optimised

$$\Delta T_2, \Delta T_4, \Delta T_6, T_r, T_{w2}, \tau, S_r = 7$$

4.6 Optimisation Problem Formulation

The optimisation problem for two cases can be described as follows.

Given feed and product temperature (T_{F0}), steam temperature (T_s),
water temperature (T_w) and volumetric flow rate of feed (v);

Optimise residence time, reaction temperature, splitter ratio, $\Delta T_2, \Delta T_4$ (for Case I and Case II) and ΔT_6 (for Case II);

So as to

Minimize total cost of the process;

Subject to constraints on the conversion and linear bounds on all optimisation variables.

Mathematically, the optimisation problem can be written as

$$\begin{aligned}
 & \mathbf{Min} && C_{TR} \\
 & && T_r, T_w, \Delta T_2, \Delta T_4, (\Delta T_6), \tau, S_r \\
 & \mathbf{s.t.} && X_{AL} \leq X_A \leq X_{AU} \\
 & && S_{rL} \leq S_r \leq S_{rU} \\
 & && \tau_L \leq \tau \leq \tau_U \\
 & && T_{rL} \leq T_r \leq T_{rU} \\
 & && T_{wL} \leq T_w \leq T_{wU} \\
 & && \Delta T_{2L} \leq \Delta T_2 \leq \Delta T_{2U} \\
 & && \Delta T_{4L} \leq \Delta T_4 \leq \Delta T_{4U} \\
 & && \Delta T_{6L} \leq \Delta T_6 \leq \Delta T_{6U} \\
 & && f(x, u, v) = 0 \text{ (model)}
 \end{aligned}$$

Where C_{TR} is the total cost of the process, T_r is the reaction temperature, X_A is the conversion, S_r is the splitter ratio, τ is the residence time, ΔT is the temperature difference, T_{rL} and T_{rU} are the lower and upper bounds of reaction temperature, T_{wL} and T_{wU} are the lower and upper bounds of cooling water temperature, ΔT_L and ΔT_U are the lower and upper bounds of temperature difference, τ_L and τ_u are the

lower and upper bounds of residence time, X_{AL} and X_U are the lower and upper bounds of conversion and S_{rL} , and S_{rU} are the lower and upper bounds of splitter ratio.

4.6.1 Cost Function

The objective function is the overall annual plant cost (C_t) that considers equipments cost (reactor C_R , heat exchangers C_E and a three-year constant amortization) and operating cost (C_{OP}) (Fernando and Pedro, 1998).

a) Reactor Cost (C_R)

$$C_R, \$ / yr = 4.18 \left(\frac{900}{280} \right) \left(\frac{937.7}{3} \right) \left(\frac{V}{\pi} \right)^{0.6227} \quad (4.103)$$

with the volume expressed in m^3 .

b) Heat Exchanger Cost (C_E)

$$\log_{10} C_E, \$ / yr = K_1 + K_2 \log_{10} A + K_3 (\log_{10} A_E)^2 \quad (4.104)$$

Where:

$K_1 = 4.8306$, $K_2 = -0.8596$, $K_3 = 0.3187$ and A_E is the heat exchanger surface area, m^2

c) Operating Costs (C_{OP})

The operating costs include heating/refrigeration costs:

$$C_{OP}, \$ / yr = \frac{900}{760} (7896 - 6327 q + 47640 q^2 - 10220 q^4) \quad (4.105)$$

Where $q = (Q_H + Q_C) / Q^N$ and $Q^N = 2.54 * 10^7$ J/min.

d) Pumping Cost (C_{pu})

$$C_{pu}, \$ / yr = \left(\frac{900}{834} \right) \left(\frac{38.6}{3} \right) (264 .2 F_{A0})^{0.8050} \quad (4.106)$$

With F_{A0} expressed in m^3/min .

The total cost of the oxidation process is:

$$C_{TR} = C_R + C_E + C_{OP} + C_{PU} \quad (4.107)$$

4.7 Results and Discussions

The values of constant parameter and specified variables for two cases are listed in Table 4.1.

Table 4.1 Values of constant parameters and specified variables used in the model

Parameter	Symbol	Unit	Value
Initial concentration	C_{A0}	mol/ m ³	20
Activation energy	E_a	J/mol	7622
Arrhenius Factor	A_r	min ⁻¹	0.227866
Heat capacity of H ₂ O ₂	C_{PH2}	J/kg K	3517
Density of H ₂ O ₂	ρ_{H2}	kg/m ³	1400
Heat capacity of HGO	C_{PH}	J/kg	1988.73
Heat capacity of HCOOH	C_{PF}	J/kg	1730
Heat capacity of water	C_{Pw}	J/kg	4181.3
Density of HGO	ρ_H	kg/m ³	882
Density of HCOOH	ρ_F	kg/m ³	1220
Gas constant	R	J/mol K	8.314
Latent heat	λ	J/kg	2256918
Over all heat transfer coefficient for exchanger	$U_{E1}, U_{E2},$ * U_{E3}	W/m ² K	321
Over all heat transfer coefficient for heater	$U_{H1}, U_{H2},$ * U_{H3}	W/m ² K	851
Over all heat transfer coefficient for cooler	U_C	W/m ² K	638
Feed temperature,	T_{F0}	K	300
Cooling water temperature	T_{w1}	K	298.15
Steam temperature	T_S	K	373.15
Feed flow rate	v	m ³ /min	0.1

* For Case II

The results of optimisation problem for the Case I (summarized in Table 4.2) show that, the minimum total cost (C_{TR}), amounts of steam and cooling water with heat integration of the oxidation process are less than those without the heat integration at specified variables. The cost saving is around 36 % compared with without heat integration.

The results for this case show that the cold utility and minimum energy requirement were reduced by 77 %. Therefore, the CO₂ emission will be reduced by 77 % leading to significant reduction in environmental impact.

Table 4.2 Results of optimisation problem Case I

Variable	With heat integration	Without heat integration	Decision variable type	Optimised value
A, m ²	133	66.15	ΔT_2 , K	9.128
C_{TR} , \$	53965	84454.7	ΔT_4 , K	11.200
CS*, %	36	--	S_r , %	0.5149
M _S , kg/min	2.30	12.47	τ , min	44
M _W , kg/min	178	356.46	T_r , K	343.467
Q_C , kJ	5212	2.21E04	T_{w2} , K	305.15
Q_t , kJ	5212	2.21E04	X _A	0.410
Q_r , kJ	1.71E04	0.0	-----	-----
ES, %	77	0.0	-----	-----

*CS = Cost saving, ES= Energy saving

The results of Case II listed in Table 4.3 show that, the minimum total cost (C_{TR}), amounts of steam and cooling water with heat integration of the oxidation process are less than those without the heat integration at specified variables ($T_{F0} = 300$ K, $T_{w1} = 298.15$ K, $T_s = 373.15$ K and $v = 0.1$ m³/min). The total cost of the process is reduced by 22%. The results also show that cold utility and energy consumption are reduced by 57 %. Note the minimum approach temperatures for the heat exchangers E1, E2 and E3 (ΔT_2 , ΔT_4 and ΔT_6) are within 19-30 K which is quite practical.

Table 4.3 Results of optimisation problem Case II

Variable	With heat integration	Without heat integration	Decision variable type	Optimised value
A, m ²	86.11	66.15	ΔT_2 , K	27.1613
C_{TR} , \$	65887.8	84454.7	ΔT_4 , K	30.842
CS [*] , %	22	0.0	ΔT_6 , K	19.000
M _S , kg/min	4.30	12.47	S_r , %	0.5932
M _W , kg/min	334	356.46	τ , min	44
Q_C , kJ	9770	2.21E04	T_r , K	343.5
Q_r , kJ	9770	2.21E04	T_{W2} , K	305.15
Q_r , kJ	1.26E04	0.0	X_A	0.410
ES, %	56	0.0	-----	-----

*CS = Cost saving, ES= Energy saving

Comparison between two cases clearly show that the cold utility, total cost and energy requirement for the Case I are less than those for the Case II. The cold utilities are reduced by 77 % for the Case I and by 56 % for the other case. The results also show that the cost savings for two cases are 36 % and 22 % respectively and the reduction of energy for Case I is 77 % and for Case II is 56 %. However reducing energy consumption means that is not only generating maximum savings in operating costs, but has the added benefit of significantly reducing environmental impact. Therefore, the Case I give less environmental impact compared with the other case.

4.8 Sensitivity of Design and Operating Parameters

Further simulation is carried out to study the sensitivity of feed temperature (T_{F0}) and feed flow rate (v) on the temperature of each stream and energy requirement for Case I. The results are summarized in Table 4.4.

With the increase of flow rate, the temperatures of each stream are almost constant but the energy requirement increases (Cases 1-3 in Table 4.4).

If the feed temperature is decreased (say by 10 %) (Case 4), the temperatures of each stream are changed and the energy requirement increases to very high value. If the feed temperature is increased by 10 % the gPROMS program fails (Case 6) (numerical failure due to probably in calculating log mean temperature).

However, a small change in the temperature as shown above will make the system unstable therefore, to avoid this the feed temperature must be fixed all time (when the system is running) thus, the temperature controller should be added to the process (which was beyond the scope of this thesis).

Table 4.4 Sensitivity of feed temperature (T_{F0}) and feed flow rate (v) on Q_t

Case	v	T_{F1}	T_O	T_{F2}	T_{O1}	T_P	T_r	Q_t , kJ
1	0.09	333.86	309.54	332.2	311.33	310.4	343.45	4814
2	0.1	333.92	309.13	332.69	311.21	310.14	343.47	5212
Base Case								
3	0.11	333.97	309.08	332.88	311.01	310.02	343.46	5666
T_{F0}								
4	295	312.08	328	301	330	328	335	1.45E ⁰⁵
5	300	333.92	309.13	332.69	311.21	310.14	343.47	5212
Base Case								
6	315	-----	-----	-----	-----	-----	-----	-----

4.9 Conclusions

A CSTR model is developed for the process for evaluating viability of large-scale operation for oxidation step in ODS process. It has been found that while the energy consumption and recovery issues could be ignored for batch experiments that are certainly not the case for the lab-scale operation. Large amount of heating is necessary even to carry out the oxidation reaction to 40 °C, the recovery of which is very important for maximizing profitability of operation. In industrial experience, the

calculation of the minimum heating and cooling requirements reveal significant energy savings (Douglas; 1988).

Optimisation problem was formulated to optimise some of the design and operating parameters (such as reaction temperature, residence time and splitter ratio) of integrated process while minimizing an objective function which is a coupled function of capital and operating costs involving design and operating parameters. Two cases are studied: Case I HGO and catalyst are fed as one feed stream and Case II HGO and catalyst are treated as two feed streams. The product stream from the reactor was split in to two streams according to splitter ratio (S_r) to maximize heat recovery. The model equations were implemented in the gPROMS software and were solved using the built in numerical methods.

Optimal minimum energy requirement, heat recovery and cost saving in CSTR reactor heat exchangers network system for oxidation sulphur compounds in HGO were obtained using optimisation techniques. Optimisation problems for two cases were formulated and the solutions of such problems were presented, the first case where HGO and catalyst are fed as one feed stream and the other case where HGO and catalyst are treated as two feed streams. The results show that the cost saving for the first and second case are 36 %, 22 % respectively and the energy consumption are reduced by 77 % for the first case and 56 % for the second case. However, the first case provides better minimum energy requirement thus reducing environmental impact and maximum heat recovery than the second case.

The sensitivity of feed temperature (T_{F0}) and feed flow rate (v) on the temperature of each stream and energy requirement for Case I were studied. The results show that a small change in temperature will make the system unstable therefore, the temperature controller should be added to the process (which was beyond the scope of this thesis) to

fixed the feed temperature. However, with the change the flow rate the temperature of each stream of the process almost constant but the energy requirement increases.

Chapter Five

Modelling of Extraction Step of Oxidative Desulphurization Process

5.1 Introduction

Liquid-liquid extraction is an important chemical/biochemical engineering operation employed in many industrial processes such as processing of nuclear fuels (Drew et al, 2001), refining of crude petroleum, extraction of penicillin, biochemical separations (Blomquist and Alberston, 1972; Johansson, 1974; Likidis and Schagrel. 1988; Xinghua et al., 2006), treatment of dilute waste streams for metal recovery and hazardous waste elimination (Tavlarides et al.,1987), hydrometallurgical production of nonferrous metals and food processing (Feltt, 1981).

Extraction techniques are also commonly employed in many of the downstream operations to separate inhibitory fermentation products such as ethanol and acetone-butanol from a fermentation broth. Antibiotics are also recovered by these techniques (using amylacetate or isoamylacetate) (Kalaichelvi and Murugesan, 1997). Further, liquid-liquid extraction plays major role in traditional separation such as hydrodesulphurization in petroleum industry.

Extraction processes are well studied in the petroleum industry because of the need to separate heat-sensitive liquid feeds according to chemical type (e.g., aliphatic, aromatic, naphthenic) rather than by molecular weight or vapour pressure. There are many examples of liquid-liquid extraction process, Table 5.1 shows some representative industrial extraction process (Seader and Henley, 1998). Other major applications exist

in the biochemical industry, where emphasis is on the separation of antibiotics and protein recovery from natural substrates.

In general, extraction is preferred to distillation:

- In the case of separation of a mixture according to chemical type rather than relative volatility.
- In the case of the separation of close-melting or close boiling liquids, where solubility differences can be exploited.
- In the recovery of heat sensitive materials, where extraction may be less expensive than vacuum distillation.
- When a high-boiling component is present in relatively small quantities in waste stream, as in the recovery of acetic acid from cellulose acetate.
- In the case of mixtures that form azeotropes.
- For removal of a component present in small concentrations such as sulphur compounds from heavy gas oil.
- In the case of dissolved or complex inorganic substances in organic or aqueous solutions.

Table 5.1 Industrial extraction processes

Solute	Carrier	Solvent
Acetic acid	Water	Ethyl acetate
Acetic acid	Water	Isopropyl acetate
Aromatics	Paraffin	Sulphur dioxide
Aromatics	Kerosene	Sulphur dioxide
Asphaltenes	Hydrocarbon oil	Furfural
Butadiene	1-Butene	Cuprmonium acetate
Benzoic acid	Water	Benzene
Formic acid	Water	Tetrahydrofuran
Fatty acid	Oil	Propane
Phenol	Water	Benzene

Petroleum oils used as feedstock for diesel oils are middle distillates in the 180-440 °C boiling range. Due to the higher boiling range, the sulphur compounds in diesel flues are mostly alkylbenzothiophenes (BTs) and alkyldibenzothiophenes (DBTs). Recent studies (Marcelis et al.; 2003; Quimby, 1998; Stumpf et al., 1998) indicated that when the sulphur level was reduced to lower than 1000 ppm, the major sulphur compounds remaining in diesel fuels are the dibenzothiophenes with alkyl substituted at the 4- and/or 6-position. These compounds are lower in HDS reactivity and are classified as the most refractory compounds in conventional HDS process. Even though ODS is capable of oxidizing model sulphur compounds such as DBT and 4,6-DMDBT into corresponding sulphones with high efficiency as demonstrated in Chapter Three, it is essential to evaluate the effectiveness of this process on heavy gas oil.

As mentioned in Chapter Three, ODS process consists of two steps: selective oxidation of sulphur compounds and separation of the oxidised sulphur compounds from the heavy gas oil. The separation methods of ODS could be selected among distillation, low temperature separation, solvent extraction and solid adsorption through utilization of differences in the boiling points and solubility (polarity) between organic sulphur compounds and oxidised sulphur compounds. Solvent extraction was used as the separation method in this study by using three solvents, namely methanol, Di Methyl Formamide (DMF) and N-Methyl Pyrolidone (NMP).

Kinetics and selectivity of the oxidation of organic sulphur compounds as well as the selective separation of oxidised sulphur compounds from heavy gas oil by solvent extraction was investigated in Chapter Three. In this chapter the solvent effectiveness (K_f), extractor factor (E_f) and partition coefficients (K_p) are determined for each solvent at different heavy gas oil/solvent ratios and finally a liquid-liquid extraction model is developed for the extraction of sulphur compounds from the oxidised heavy gas oil.

5.2 Fundamentals of Liquid-Liquid Extraction

In liquid-liquid extraction, a liquid feed of two or more compounds to be separated is contacted with a second liquid phase (solvent), which is immiscible or only partial miscible with one or more compounds of the liquid feed and completely or partial miscible with one or more of the other compounds of the liquid feed.

The simplest liquid-liquid extraction involves only a ternary system (Figure 5.1). The feed consist of two miscible compounds, the carrier, B, and the solute, A. Solvent, S, is a pure compound. Components B and S are only partially soluble in each other. Solute A is soluble in B and completely or partially soluble in S. During the extraction process, mass transfer of A from the feed to the solvent occurs, with less transfer of B to the solvent or S to the feed stream. Accordingly, the two immiscible phases are called the raffinate (R) and the extract phases (E) are created.

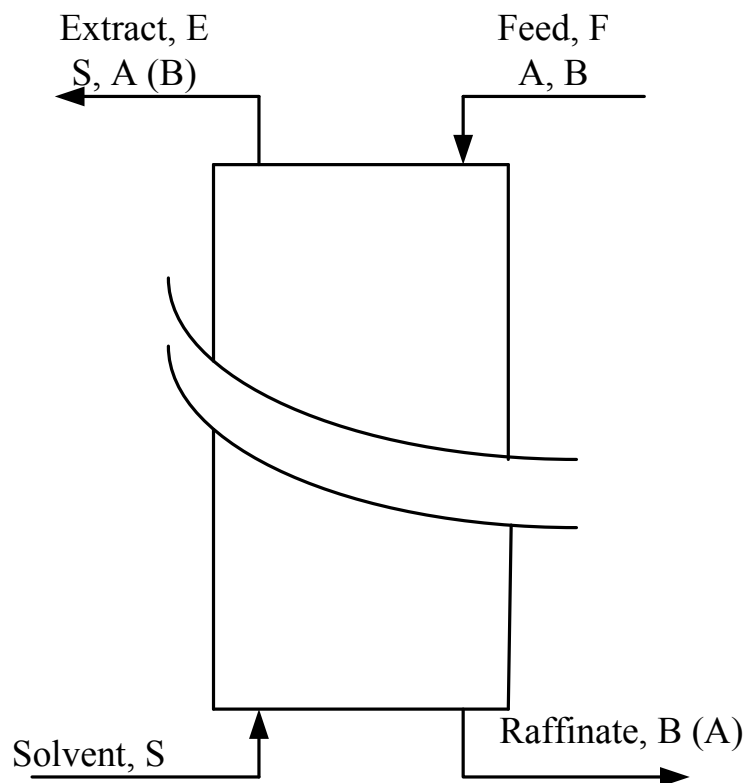


Figure 5.1 Basic extraction system

5.2.1 Solvent Selection

Solvent selection is a major consideration in the design of an extraction system (Skelland and Culp, 1989). The key to an effective extraction process is the discovery or design of a suitable solvent. In addition to being non toxic, inexpensive and easily recoverable for recycling, a good solvent should be relatively immiscible with feed components other than the solute and have different density from the feed to facilitate phase separation. If the recovery of the solvent is more expensive than the distillation of the original mixture is to be considered, extraction will not be a viable alternative. Properties which can be determined by analysing liquid-liquid equilibrium of the system, such as solute selectivity and solubility, are often used to initially screen solvents. However, the difficulty of solvent recovery is not necessarily reflected in the liquid –liquid equilibrium behaviour of the system.

Physical properties which control the operability of the system play a major factor in the overall efficiency of the extractor. The interfacial tension between the raffinate phase and extract phase dictates whether formation of a dispersed phase will occur. At an interfacial tension greater than 50 dyne/cm, the phases do not mix or emulsions form at an interfacial tension less than 1 dyne/cm, the extractor may become inoperable (Cusack et al., 1991). Other properties such as solvent viscosity, chemical stability and reactivity must also be considered.

The goal of adding solvent to the system is to treat a difficult separation by distillation for a set of easier and less expensive separations in the solvent recovery system. However, the complete recovery of solvent is often economically impractical. The cost of solvent-makeup must be considered during the selection process.

5.2.2 Solvent Recovery

A liquid extraction process consists of both the extraction step along with a solvent recovery step. In fact, the solvent recovery cost is often a large fraction of the total cost of the process. A systematic method for generating and evaluating feasible solvent flowsheet alternative is therefore, useful in the design of the separation of these systems. A simplified flowsheet is given in Figure 5.2. A feed stream is contacted with a solvent stream in the extractor. The extractor may be a mixer/settler cascade (Cusack and Fremeaux, 1991) or a column (e.g. packed or pulsed).

An extract stream contains the solvent and extract components (i.e. extracts), and a raffinate stream contains unextracted components exit the extractor. The extract stream is then sent to solvent recovery which is performed in a distillation column, crystallization, and / or extraction trains. Solvent may be recovered from the raffinate stream if it is only partially miscible with raffinate components

5.3 Fundamentals of Distillation

In distillation, a feed mixture of two or more components is separated into two or more products, and often limited to, an overhead distillate and bottom, whose compositions differ from that of the feed. The separation requires that a second phase be formed so that both liquid and vapour phases are present and can contact each other on each stage within a distillation column. The components have different volatilities so that they will partition between two phases to different extents. Distillation differs from extraction in that the second fluid phase is created by thermal means (vaporization and condensation) rather than by introduction of a second phase that usually contains an additional component or components not present in the feed mixture. The distillation process can be carried out in continuous and batch mode.

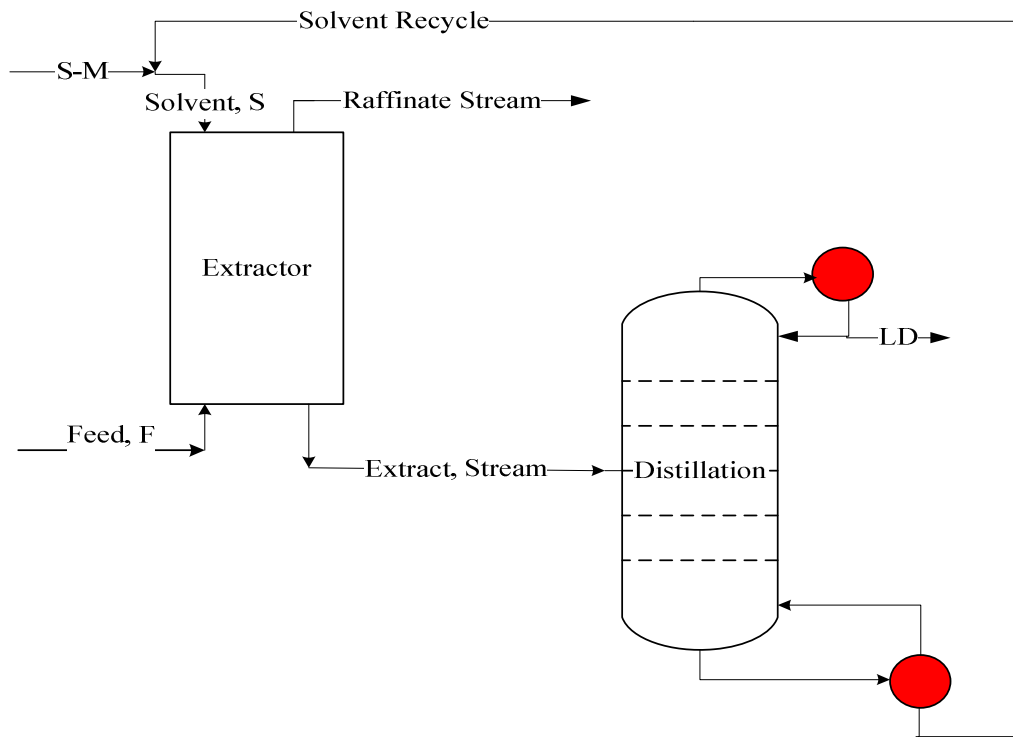


Figure 5.2 Simplified extraction flowsheet

Separation of a mixture into two or more products through distillation is very common in the process industry such as in petroleum refining where distillation is used to separate crude oil into petroleum fractions, light hydrocarbons (C_2 to C_5) and aromatic chemical.

The design of distillation columns involves determination of the number of plates, feed-plate location, reflux ratio, and vapour load. Preliminary values of these design variables are often determined by trial and error using the McCabe-Thiele method (McCabe and Thiele, 1925).

Since distillation is an energy intensive process, it is desirable to determine the values of these design variables corresponding to a minimum in terms of cost of investment and operation. Rigorous simulation and optimisation are commonly employed to determine the optimal design.

The solvent recovery in the extraction step of the oxidative desulphurization process (ODS) is considered by using continuous distillation column in Chapter Six.

5.4 Extractor Design and Model

The design and analysis of liquid-liquid extractor involves more factors than vapour liquid separation because of complications introduced by the two liquid phases. Classical methods for design of extractor involve graphical techniques combining material and energy balances with liquid-liquid equilibrium relations. Some of these methods are given in standard text (Sherwood and Pigford 1952; Tribal, 1963; Partt, 1967; Wankat, 1988). These approaches involve use of triangular diagram and y-x diagram which are similar to the McCabe-Thiele diagrams used in binary distillation. However these methods for liquid-liquid extraction are restricted to ternary system. A more general geometric method for design of extractors for multicomponent systems was presented by Minotti et al. (1996) and Minotti et al. (1998). This method is similar to a new approach for the design of nonideal multicomponent systems (Fidkowski et al., 1991).

The extractor consists of two partially miscible liquid streams in countercurrent or concurrent flow; solvent-rich extract stream and the solvent-lean raffinate. The extractor design equations that follow are for the separation of a single feed stream by contact with a single solvent stream in a countercurrent cascade (Figure 5.3). The assumption that the cascade operates at constant temperature and pressure can easily be relaxed if temperatures and pressures on each stage of the cascade are specified. The liquid phases leaving each stage of the cascade are in equilibrium and thus have compositions which lie on liquid-liquid equilibrium equation.

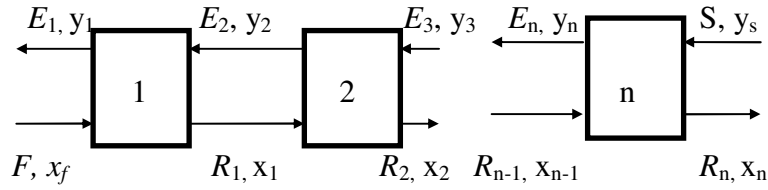


Figure 5.3 Continuous countercurrent extraction cascade

The steady state model for the countercurrent cascade with a feed stream molar flow rate F and composition x_f , a solvent stream molar flow rate S and composition y_s , an extract stream molar flow rate E and composition y_n , and a raffinate stream molar flow rate R and composition x_n is described below:

The composition and flow rates of the liquid phases on each stage within the cascade are related by the material balance and equilibrium equations.

- **The material balance around the first stage $j=1; i=1, n_c$**

$$Fx_{if} + E_2y_{i2} = R_1x_{i1} + E_1y_{i1} \quad (5.1)$$

The phase equilibrium relationship

$$y_{i1} = k_{i1}x_{i1} \quad (5.2)$$

where k_{i1} is the phase equilibrium ratio at first stage.

$$k_{i1} = k_{i1}\{T, P, x_{i1}, y_{i1}\}$$

In addition, the mole fractions of each stream are required to sum to unity.

$$\sum_{i=1}^{n_c} y_{i1} = 1 \quad (5.3)$$

$$\sum_{i=1}^{n_c} x_{i1} = 1 \quad (5.4)$$

- The material balance around any stage, $j=2$ to N_s ; $i=1$ to n_c

$$S y_{ij+1} + R_{j-1} x_{ij-1} = R_j x_{ij} + E_j y_{ij} \quad (5.5)$$

where $y_{i,j+1} = y_{is}$.

The phase equilibrium relationship

$$y_{i1} = k_{ij} x_{ij} \quad (5.6)$$

where k_{ij} is the phase equilibrium relationship:

$$k_{ij} = k_{ij} \{T, P, x_{ij}, y_{ij}\}$$

$$\sum_{i=1}^{n_c} x_{ij} = 1 \quad (5.7)$$

$$\sum_{i=1}^{n_c} y_{ij} = 1 \quad (5.8)$$

5.5 Performance Measure of Solvents

5.5.1 Solvent Effectiveness Factor

The solvent effectiveness combines both the efficiency of a given solvent to extract the sulphur species and the amount of oil or hydrocarbon that will be extracted with the sulphur species. It is a very useful tool or measure to determine the best solvent which will desulphurise the oil as well as minimize the oil loss.

The solvent effectiveness factor, K_f , is defined as:

$$K_f = \frac{D_s}{(100 - Y)} \quad (5.9)$$

Where D_s is the percent desulphurization in the raffinate phase and Y is the percent raffinate yield (oil yield). For example, in Figure 5.4, 100 ml of heavy gas oil with

initial sulphur content 1000 ppm is mixed with 100 ml of solvent. After extraction, let say the volume of the raffinate stream is 95 ml with sulphur content of 800 ppm. The percent desulphurization of HGO (D_s) is equal to 20 % (i.e. $\frac{1000 - 800}{1000} \times 100$) and the percent oil yield (Y) equal to 95 % (i.e. $\frac{95}{100} * 100$). Substituting the values of D_s and Y in Equation (5.9) the effectiveness factor (K_f) equals to 4 (i.e. $\frac{20}{100 - 95}$).

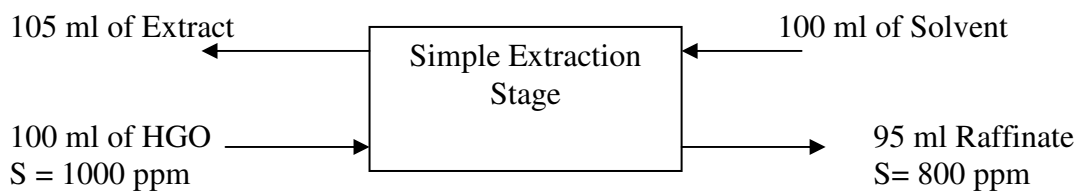


Figure 5.4 Simple extraction stage

The larger the value of effectiveness factor, the greater the extent to which the solute (sulphur) is extracted with the minimum oil loss. K_f will increase with increasing percent of desulphurization, D_s and decreasing oil loss.

In this following section solvent effectiveness has been studied for extraction of unoxidised heavy gas oil with initial sulphur content 1066 ppm (Case 1) and oxidised heavy gas oil with sulphur content 609 ppm (Case 2) by using three solvents (methanol, DMF and NMP).

The results of solvent effectiveness as a function of solvent to heavy gas oil ratio for three solvents (Methanol, NMP and DMF) for Case 1 are given in Table 5.2 and Figure 5.5. As shown from these results the K_f values of NMP and DMF is almost constant for all solvent to HGO_B ratios and DMF appear better than NMP (where K_f values of DMF is higher than that for NMP). For methanol when solvent/HGO ratio increases from 1 to

3 the solvent effectiveness factor decreases but for solvent/HGO_B ratio of 3 to 5 K_f increases. Also K_f values of methanol are higher than that for DMF and NMP at all solvent/HGO_B ratios.

Table 5.2 K_f for unoxidised HGO_B (Case 1)

Solvent/ HGO Volume Ratio		K_f		
		NMP	Methanol	DMF
(30/30) ml	1	1.5	4	2.5
(90/30) ml	3	1.8	3.8	2.9
(150/30) ml	5	1.6	5.2	2.8

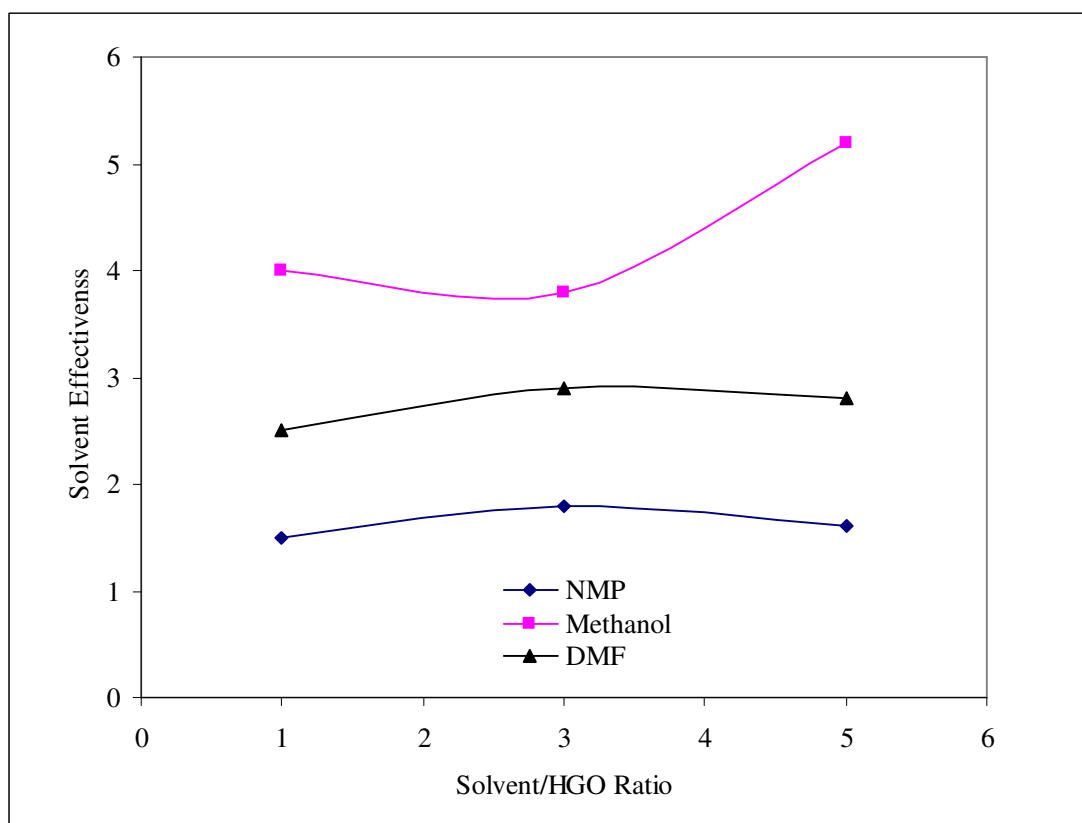


Figure 5.5 Solvent effectiveness factor for unoxidised HGO_B (Case 1) initial S = 1066 ppm

For Case 2 (Table 5.3 and Figure 5.6) the solvent effectiveness factor of NMP is almost constant for all the solvent/HGO ratios whereas, for the solvent effectiveness of DMF decreases with an increase of the solvent/HGO ratio and for methanol solvent effectiveness factor increases with increase in the solvent/HGO ratio.

The increase of solvent effectiveness factor indicates that the solvent gives good separation of sulphur from heavy gas oil (high percent desulphurization) with low heavy gas oil loss (high percent oil yield). The separation of sulphur is low (percent desulphurization is low) and oil loss is high when solvent effectiveness factor decreases. Therefore, the results clearly show that methanol is the most effective of these solvents for both Case 1 and Case 2, however at the expense of increasing amount of solvent. At solvent/HGO ratio of 1, still methanol is the best for Case 1 but NMP and DMF are best for Case 2. At solvent/HGO ratio of 3 methanol and DMF solvents are comparable in Case 2 but methanol is still the best for Case 1.

The ultimate type of solvent selected for extraction can only be considered with respect to the solvent with minimum cost and the one has least environmental impact.

Table 5.3 K_f for oxidised HGO_B (Case 2)

Solvent/ HGO Volume Ratio		K_f		
		NMP	Methanol	DMF
(30/30) ml	1	2.3	2	6
(90/30) ml	3	2.6	5	5
(150/30) ml	5	2.5	6	2

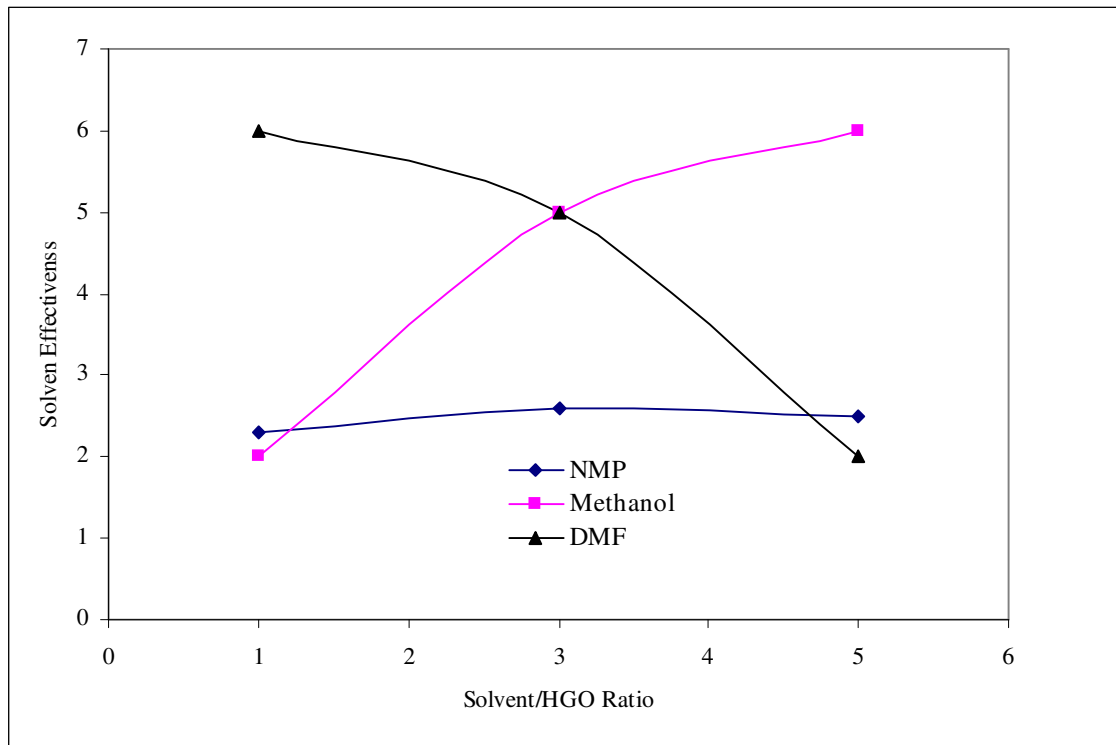


Figure 5.6 Solvent effectiveness factor for oxidised HGO_B (Case 2) S = 1066 ppm

5.5.2 Partition Coefficients and Extraction Factor

The distribution law or partition law states that if a substance is added to a system of two liquid layers, made up of two immiscible or slightly miscible components, then the substance will distribute itself between the two layers so that the ratio of the concentration in the first layer (phase) to the concentration in the second layer (phase) remains constant at constant temperature. At equilibrium, the partition coefficient is described by the mathematical expression:

$$K_p = \frac{\text{Concentration of sulfur in solvent layer (Y)}}{\text{Concentration of sulfur in HGO layer (X)}} \quad (5.10)$$

The extraction factor, E_f for the solute (sulphur) is given by the following equation:

$$E_f = K_p \frac{S}{F} \quad (5.11)$$

Where:

S is the flow rate of solvent.

F is the flow rate of HGO_B.

The sulphur distribution ratios were calculated from experimental data to evaluate solvent extraction capacity according to the above equation. For example, the sulphur concentration in heavy gas oil layer (raffinate phase, X) equals to 0.0307 wt% (g/g) and for solvent layer (extract phase, Y) equals to 0.0266 wt% (g/g) when NMP is used as solvent in NMP/heavy gas oil ratio of 1. The partition coefficient for this case will be

$$K_p = \frac{Y}{X} = 0.867.$$

The larger the value of E_f , the greater the extent to which the sulphur is extracted by solvent. Large values of E_f result from values of the distribution coefficient, K_p , or large ratios of solvent to feed.

For the oxidised HGO_B (Case 2 of Section 5.5.1) the partition coefficients and extraction factors using three solvents are shown in Table 5.4 and Figures 5.7 and 5.8. As shown from these results, the partition coefficients of sulphur decrease with an increase of the solvent heavy gas oil ratio for NMP and DMF. For methanol, the partition coefficient is almost constant (slight increase) for all cases and smaller compared with those of NMP and DMF. For all solvents, the oxidised organic sulphur compound can be separated from the heavy gas oil effectively at high solvent heavy gas oil ratios. These partition coefficients data will be useful in studying model based extraction process in the ODS system.

Comparison between the values of extraction factor, E_f (Figure 5.8) for the solvents show larger values of E_f for DMF for all solvent heavy gas oil ratios. Thus, DMF is the most attractive solvent for sulphur removal from heavy gas oil compared with other solvents.

Table 5.4 Partition coefficients and extractor factor of sulphur for solvent/ HGO_B system

Solvent/ HGO Volume Ratio	NMP		Methanol		DMF	
	K_P	E_f	K_P	E_f	K_P	E_f
(30/30) ml 1	0.867	0.867	0.073	0.073	1.528	1.528
(90/30) ml 3	0.646	1.938	0.079	0.237	0.791	2.373
(150/30) ml 5	0.526	2.63	0.096	0.480	0.598	2.99

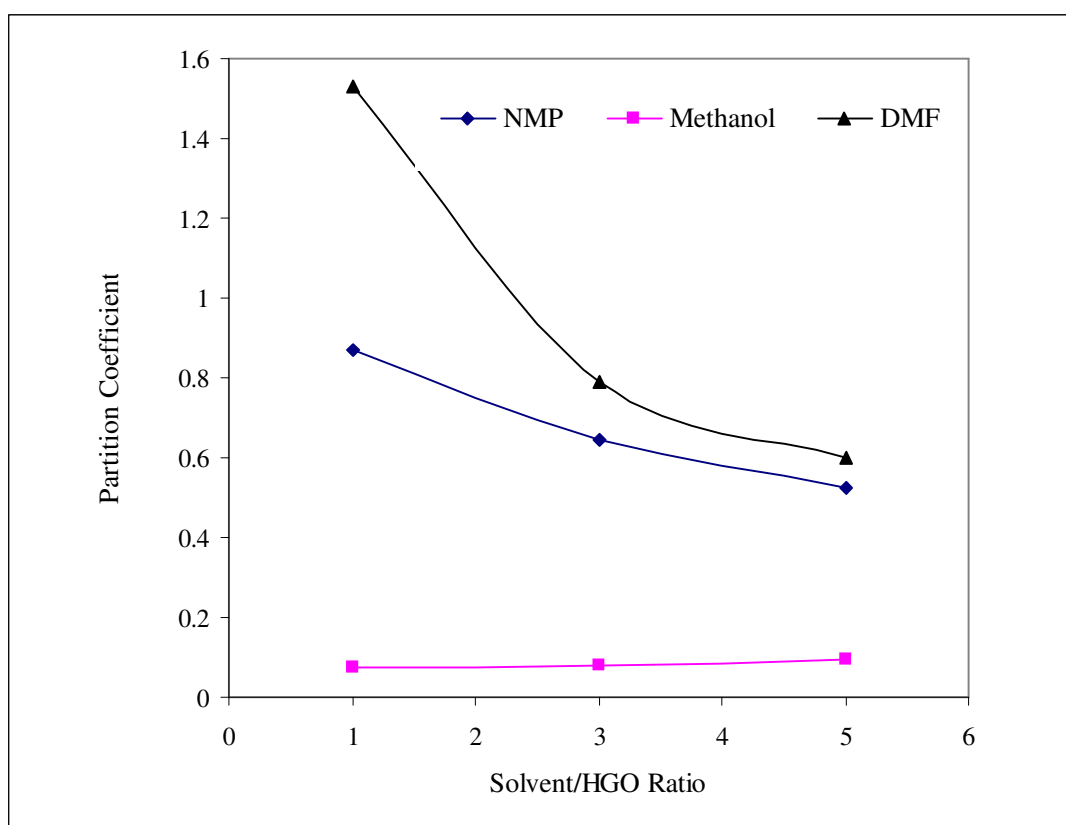


Figure 5.7 Partition coefficients of sulphur as a function of solvent/ HGO_B ratio

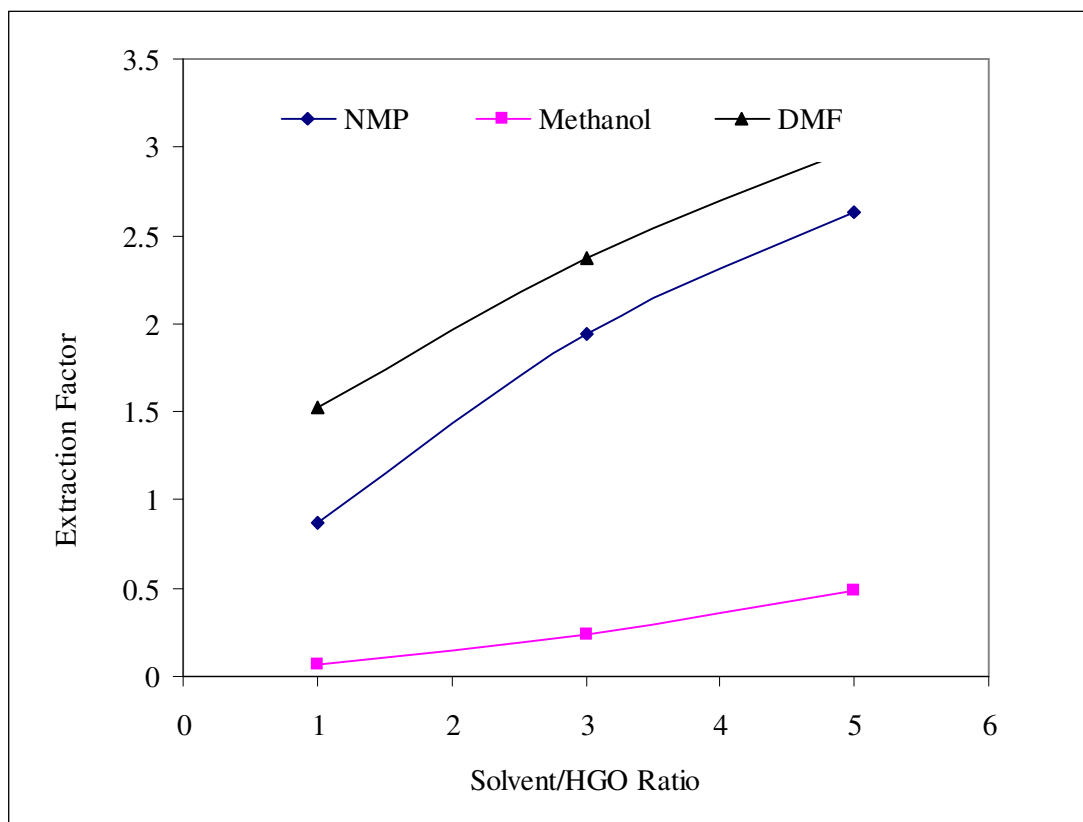


Figure 5.8 Extractor factor of sulphur as a function of solvent/ HGO_B ratio

Use of K_f “measure” selects DMF as the best solvent at low solvent/HGO ratio and the methanol was the best solvent at high solvent/HGO ratio (Table 5.3 oxidised case). On the other hand use of K_p “measure” selects DMF as the best solvent for all solvent/HGO ratios. Therefore, in this work “ K_p ” is suggested as the “tool” for selecting the best solvent.

5.6 Multi Stage Liquid-Liquid Extraction Model

The steady state model for the countercurrent cascade presented in Section 5.4 (Figure 5.3) is used here for extraction of sulphur compounds from oxidised heavy gas oil. The concentrations of sulphur and flow rates of the liquid phases in each stage within the cascade are related by the material balance and equilibrium equations. As mentioned in earlier Chapter, due to absence of tracking and measuring extraction of individual

sulphur from their mother compounds a “total sulphur approach” is adopted in this work. This means that estimation of K_i of each sulphur compound present in the HGO will be difficult. K_p (based on total sulphur content) is therefore used for defining equilibrium relationship in this work. The model is employed with the following assumption and consideration:

1. All the sulphur compounds (solute) present in HGO represented as one compound with initial concentration x_f (mass fraction) and all mixtures of heavy gas oil also represented as one compound.
2. The equation of the phase equilibrium relationship ($y = kx$, refer to general model in Section 5.4) will be

$$Y = K_p X \quad (5.12)$$

Where

K_p = the partition coefficient and given by Equation (5.10).

X = the ratio of mass of solute (sulphur) to the mass of HGO in the raffinate phase.

Y = the ratio of mass of solute (sulphur) to the mass of solvent in extract phase.

Values of mass ratios, X_i are related to the mass fractions, x_i by the following equation:

$$X_i = \frac{x_{if}}{(1 - x_{if})} \quad (5.13)$$

3. When the values of x_{if} are small (as in this case, $x_{if} = 0.0609$ wt % of sulphur in the oxidised heavy gas oil), X_i approaches x_{if} ie $X_i = \frac{0.000609}{(1 - 0.000609)} \approx 0.000609 = 609$ ppm sulphur.

4. When the raffinate and extract phase are both dilute in the solute (as in this case), the partition coefficient K_p can be taken as constant at given temperature (Seader and Henley, 1998).

5. The countercurrent liquid-liquid extraction is applied due to higher degree of extraction than other arrangements (crosscurrent and co-current) (Seader and Henley, 1998).

The model equations were implemented in the gPROMS software and were solved using the built in numerical methods.

5.7 Problem Description

In the following section the multi stage liquid-liquid extraction model was employed for desulphurization of oxidised heavy gas oil (HGO_B, initial sulphur content 609 ppm) by using three solvents, methanol, DMF and NMP at different solvent heavy gas oil ratios.

The description and specification of the problem are shown in Figure 5.9 and Table 5.5.

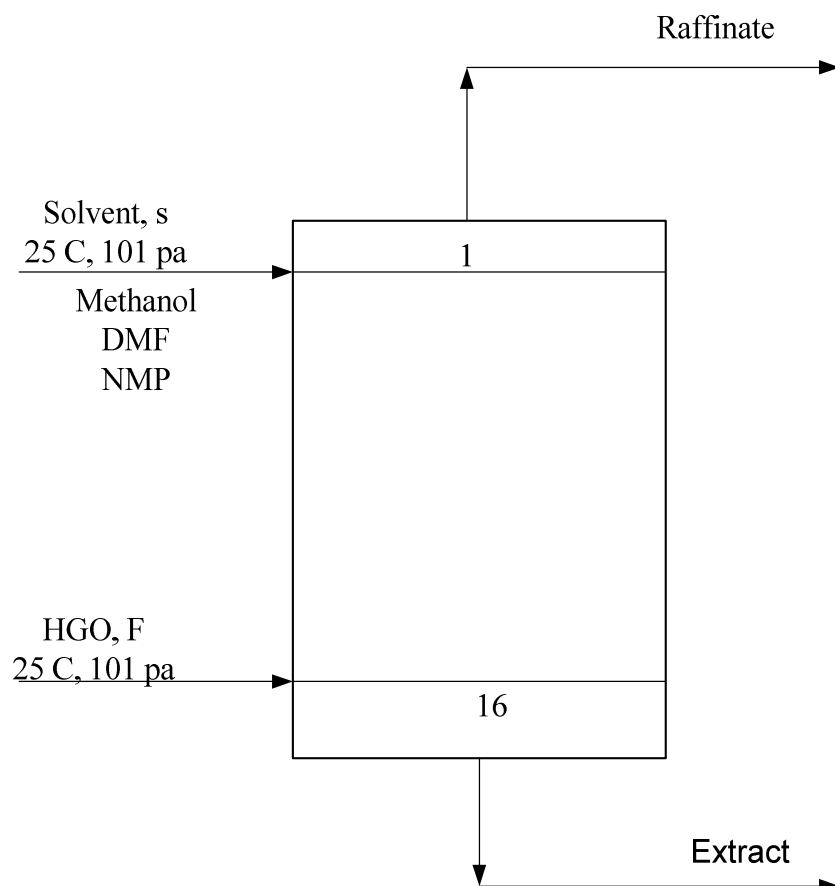


Figure 5.9 Continuous countercurrent extraction column

Table 5.5 Values of constant parameters and specified variables used in the model

Parameter	Symbol	Unit	Value
Initial sulphur concentration	X	wt %	0.0906
Density of OHGO _B	ρ_H	kg/m ³	882
Density of methanol	ρ_M	kg/m ³	800
Density of DMF	ρ_D	kg/m ³	960
Density of NMP	ρ_N	kg/m ³	1028
Number of extraction stage	Ns	--	16
Partition coefficient, K _p			
Solvent to HGO _B ratio, S/F Volume ratio	DMF	NMP	Methanol
1	1.528	0.867	0.073
3	0.791	0.646	0.079
5	0.598	0.526	0.096

5.8 Results of Multi Stage Extraction Model

The results of multi stage liquid-liquid extraction process are shown in Figures 5.10-5.12 and Tables 5.6-5.8 for three solvents (DMF, NMP and methanol respectively) at different solvent to heavy gas oil volume ratios. As shown in Figures 5.10-5.11 and Tables 5.6-5.7, the concentration of sulphur in raffinate phase decreases with increasing number of extraction stages for all solvent/heavy gas oil ratio (1, 3 and 5) when DMF and NMP solvents are used. Also it can be seen from these results that the sulphur present in raffinate phase is almost zero ppm sulphur level. For solvent DMF the sulphur level equals to zero ppm at all ratios (1, 3 and 5). For ratio 1:1 the sulphur level equals to zero ppm at stage 14, for ratio 1:3 at stage 8 and for ratio 1:5 at stage 6 (Figure 5.10 and Table 5.6). In case of solvent NMP with ratio 1:3 the sulphur level equals to zero ppm at stage 9, for ratio 1:5 at stage 5 and for ratio 1:1 the minimum sulphur level (17 ppm) at stage 16 (Figure 5.11 and Table 5.7). For methanol (Figure 5.12 and Table 5.8) the

concentration of sulphur remains almost constant with an increasing number of extraction stages up to 12 for all solvent/HGO ratios (1, 3 and 5). After stage 12, the sulphur level slightly decreases with increasing of number of stages. The lower values of K_P results in the lower values of extraction factor, E_f . Also, in case of methanol sulphur never reaches to zero ppm but at stage 16 and with methanol/HGO ratio of 5 the sulphur concentration goes down to 192 ppm (Figure 5.12 and Table 5.8).

From the above discussions, it is found that DMF is the most attractive polar solvent for reducing the organic sulphur compounds from heavy gas oil with less of solvent/heavy gas oil ratio and numbers of extraction stages compared to those with the methanol and NMP. The results also indicate that the extraction step for oxidative desulphurization (ODS) process was able to reduce the total sulphur content to less than 10 ppm for HGO_B (within the regulation) with only three or four extraction stages when NMP or DMF are used as solvents.

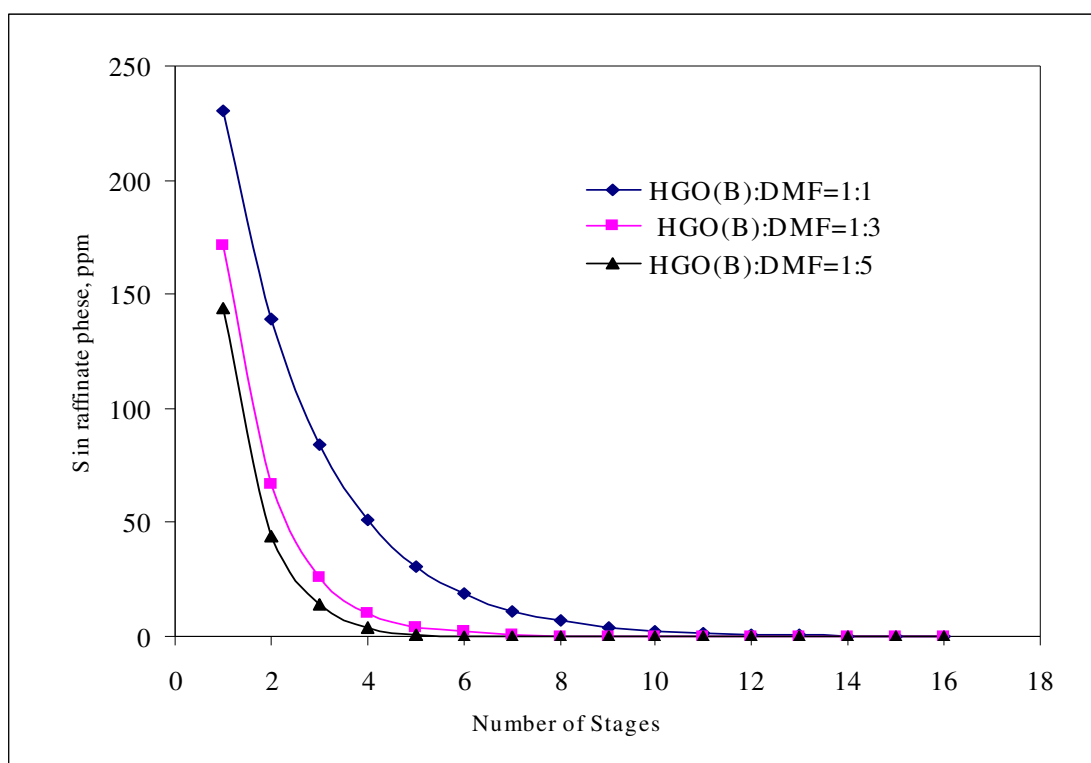


Figure 5.10 Multi stage extraction at different HGO_B/DMF volume ratios

Table 5.6 Concentration of sulphur in the raffinate phase (Solvent, DMF)

OHGO/Solvent Volume Ratio	1:1	1:3	1:5
Ns	S, ppm	S, ppm	S, ppm
1	230	171	144
2	139	67	44
3	84	26	14
4	51	10	4
5	31	4	1
6	19	2	0
7	11	1	0
8	7	0	0
9	4	0	0
10	2	0	0
11	1.4	0	0
12	1	0	0
13	1	0	0
14	0	0	0
15	0	0	0
16	0	0	0

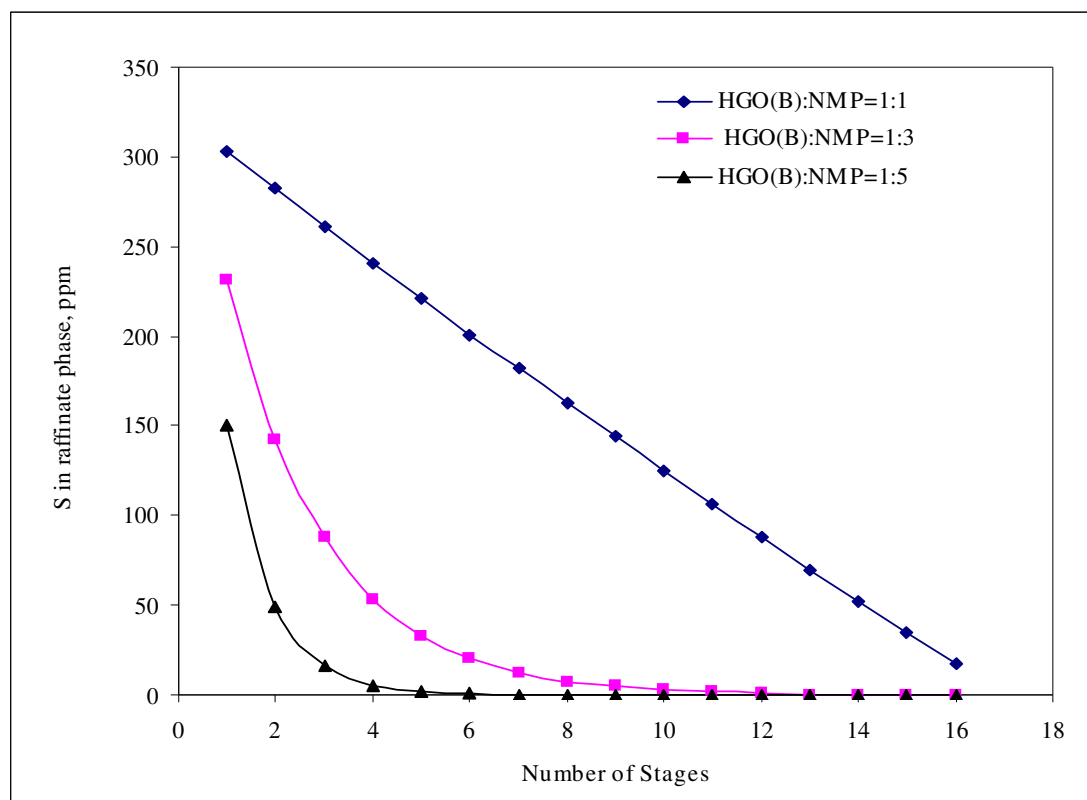


Figure 5.11 Multi stage extraction at different OHGO_B /NMP volume ratios

Table 5.7 Concentration of sulphur in the raffinate phase (Solvent, NMP)

OHGO/Solvent Volume Ratio	1:1	1:3	1:5
Ns	S, ppm	S, ppm	S, ppm
1	303	231	150
2	282	142	49
3	261	88	16
4	241	53	5
5	221	33	2
6	201	20	1
7	182	12	0
8	163	7	0
9	144	5	0
10	125	3	0
11	106	2	0
12	88	1	0
13	70	0	0
14	52	0	0
15	35	0	0
16	17	0	0

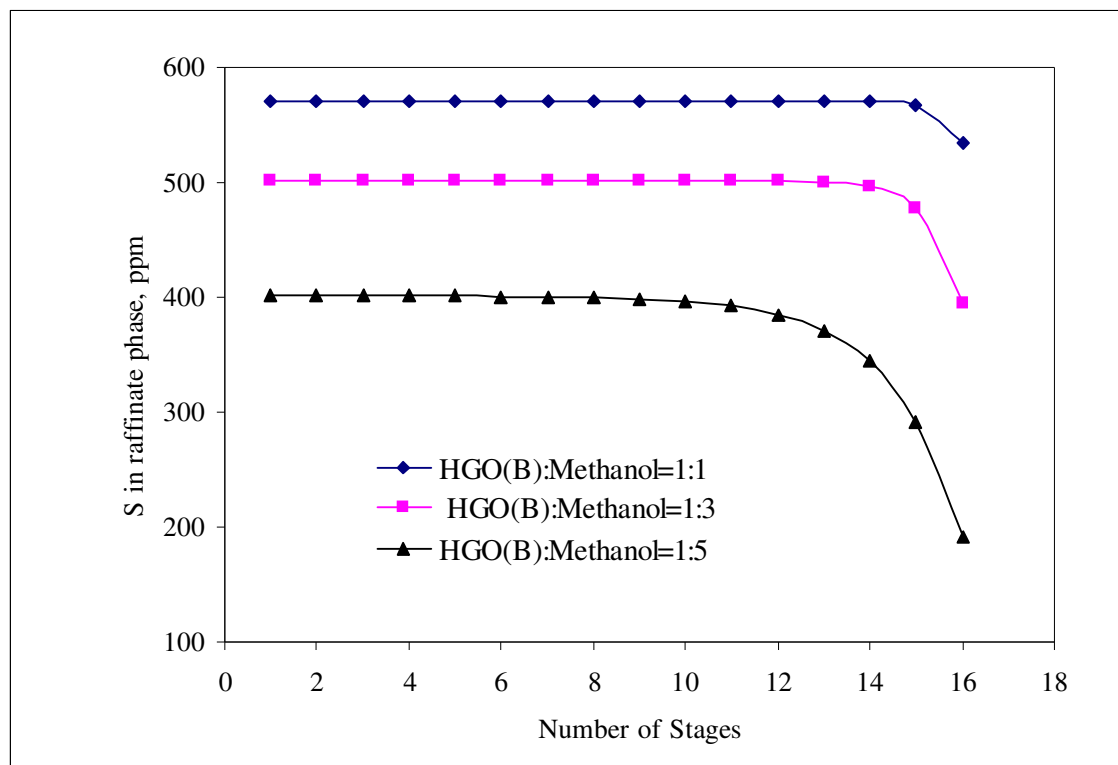


Figure 5.12 Multi stage extraction at different HGO_B/methanol volume ratios

Table 5.8 Concentration of sulphur in the raffinate phase (Solvent, methanol)

OHGO/Solvent Volume Ratio	1:1	1:3	1:5
Ns	S, ppm	S, ppm	S, ppm
1	571	501	401
2	571	501	401
3	571	501	401
4	571	501	401
5	571	501	401
6	571	501	400
7	571	501	400
8	571	501	400
9	571	501	398
10	571	501	397
11	571	501	393
12	571	501	385
13	571	500	371
14	571	497	344
15	568	478	292
16	534	394	192

5.9 Conclusions

Liquid-liquid extraction is a reasonably mature separation operation however, considerable experimental effort is often needed to find a suitable solvent. Solvent selection is facilitated by consideration of a number of chemical and physical factors.

Based on the experimental results in Chapter Three the solvent effectiveness factor (K_f), partition coefficient (K_p) and extraction factor (E_f) were calculated for organic sulphur compounds present in heavy gas oil at different solvent to heavy gas oil ratio for three solvents namely methanol, Di-methyl formamide (DMF) and N-Methyl Pyroledon (NMP). A counter-current multi stage liquid-liquid extraction process was then developed using gPROMS software and the process was simulated for the three solvents at different heavy gas oil/solvent ratios. DMF is the most effective polar solvent for reducing the sulphur level of the heavy gas oil within the regulation with minimum of

solvent/HGO ratio and number of extraction stages compared to those with methanol and NMP. The results also indicated that the oxidation/extraction process to be a promising approach for the reduction of sulphur to less than 10 ppm from the original value of 1066 ppm.

Chapter Six

Economic Analysis of Continuous Oxidative Desulphurization Process

6.1 Introduction

The objective of the oxidative desulphurization process (ODS) is to convert straight run middle distillate containing various organosulphur compounds to a blending stock with less than 10 ppm of sulphur for addition to a refinery diesel pool. For this research project, the middle distillate considered is heavy gas oil (HGO_B). The process scheme utilized to meet this objective is based on the oxidation of sulphur containing species, followed by removal of the resulting polar organosulphur compounds using solvent extraction in liquid-liquid extraction and recovery of solvent using a distillation process.

In essence, the ODS process alters the physical properties of the thiophenic compounds in heavy gas oil via oxidation. These physical property changes result in higher polarities and higher boiling points. The process then takes advantage of these changes in the physical properties to separate the oxidised organosulphur compounds from the balance of hydrocarbon fuel. The primary objective of developing ODS process is to produce ultra low sulphur heavy gas oil with high efficiency and high selectivity under low temperature (40 to 80 °C) and atmospheric pressure. In Chapter Three, the experimental data of batch ODS process on both model sulphur compounds and heavy gas oil demonstrates that ODS is technically feasible to reach this goal.

However, batch reactor (large scale) operates discontinuously with cyclic operation of charging, reaction, and discharging. In contrast a continuous flow reactor operates continuously at steady state with reactants continuously coming to the reaction vessel

and products continuously leaving from the reactor. The continuous nature of a flow reactor permits itself to large productivities and great economics of scale than cyclic operation of a batch reactor (Nauman, 2001). The development of a new chemical process that involves major technical and economical effort should meet a defined and practical need of an industry. The nature of petroleum refining prefers the use of continuous-flow reactors for long production runs of high volume fuel streams. Furthermore, as compared with batch reactors, continuous-flow reactors tend to be easier to scale up and control, the product is more uniform, materials handling problems are lessened and the capital cost for the same annual capacity is lower (Mizrahi, 2002).

In this chapter, the integrated oxidation and extraction steps of ODS process was developed based on the batch experiment. For the oxidation step, the continuous-flow reactor was chosen. The recovery of oxidant, catalyst and solvent were also considered. Finally, preliminary economic analysis for the development of an integrated ODS process was conducted.

6.2 Continuous Oxidative Desulphurization Process for Heavy Gas Oil

The ODS process developed here is based on the experimental results obtained from the batch experiment in Chapter Three and the model equations of a continuous stirred tank reactor and liquid-liquid extraction column presented in Chapters Four and Five.

A feed capacity of 1000 barrel per day (bpd) of heavy gas oil (HGO) with initial sulphur content of 1066 ppm was chosen for the pilot scale ODS. Referring to Chapter Three the amount of oxidant (H_2O_2) is 500 bpd and the amount of catalyst (HCOOH) is 1000 bpd. In the extraction step of ODS process in Chapter Five, DMF solvent with solvent to heavy gas oil ratio of 3 and number of extraction stages of 4 was found to be the best solvent. In this Chapter, the amount of DMF solvent used was 3000 bpd.

6.3 Process Description

There are four major unit operations in the ODS process: Oxidation, Oxidant and Catalyst Recovery (OCR), Extraction and Solvent Recovery (SR), (Figure 6.1). In the oxidation system, the sulphur compounds in heavy gas oil stream (S_1) are oxidised at oxidation reaction temperature in the continuous stirred tank reactor. The oxidation reaction is accomplished with hydrogen peroxide as oxidant and formic acid as catalyst (Stream, S_2). The formic acid, oxidant and oxidised sulphur compounds (S_4) are separated from oxidised heavy gas oil (OHGO) in a separator (L-L separator) and fed to the distillation column (D1) for recovery of oxidant and catalyst. In the catalyst oxidant recovery system most of the catalyst and oxidant are recovered as the top product from the distillation column (S_5). The temperature of recycled oxidant and catalyst stream is higher than the oxidation reaction temperature therefore, this stream is accompanied with the make-up oxidant catalyst stream (S_7) and cooled to the reaction temperature in the cooler (C1, S_8).

The oxidised heavy gas oil stream (S_9) is cooled to the extraction temperature by contacting with cooled fluid (water) in the cooler (C2) and fed to the extraction column where most of the organosulphur compounds are removed by contacting with dimethylformamide (DMF). The resulting extract stream (S_{12}) that contains most of organosulphur compounds, heavy gas oil and solvent is fed to the solvent recovery system (distillation column, D2). The raffinate stream, S_{11} , consists of treated heavy gas oil (final product).

In solvent recovery system, DMF is removed from the extract phase in a distillation column (D2) as top product stream (S_{13}) and most of the solvent was recovered. The temperature of the recycled solvent stream (S_{13}) is higher than the extraction

temperature therefore, this stream is accompanied with a make-up solvent stream (S_{15}) and cooled to the extraction temperature in the cooler ($C3, S_{10}$).

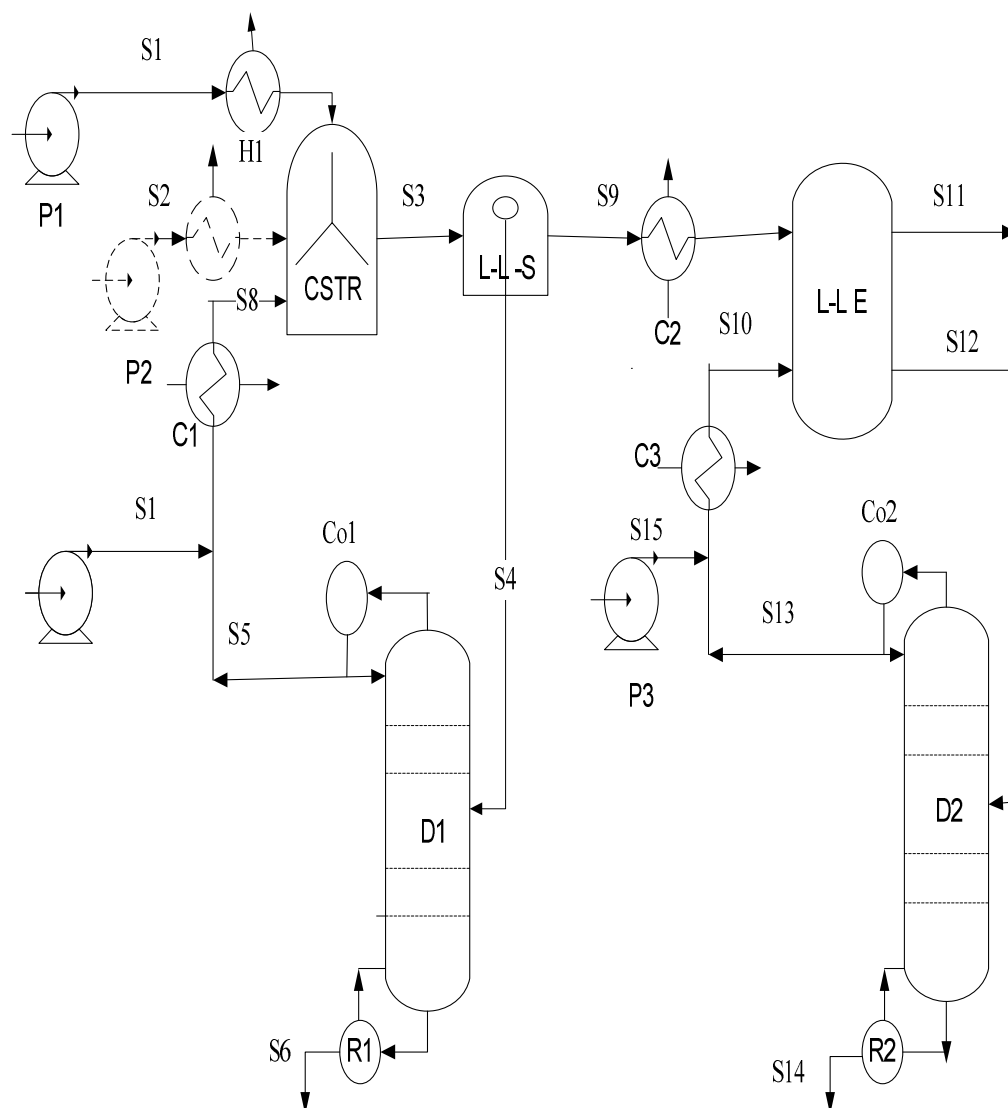


Figure 6.1 Block flow diagram of oxidative desulphurization process

6.4 Process Simulation

The model equations for oxidation and extraction steps of ODS process (presented in Chapters Four and Five) are simulated in gPROMS software. The solvent and catalyst-oxidant recovery system were simulated in the HYSYS software. HYSYS instead of gPROMS was used due to availability of physical property for HGO and sulphur

compounds. The values of constant parameters and specified variables used in the continuous ODS process are listed in Table 6.1. The results of process material and energy balances are shown in Tables 6.2 and 6.3, more details of material balance were presented in Appendix A.

Table 6.1 Values of constant parameters and specified variables used in the process

Parameter	Unit	Value
Initial concentration of S	ppm	1066
Activation energy	J/mol	7622
Arrhenius Factor	min ⁻¹	0.228
Heat capacity of H ₂ O ₂	J/kg K	3517
Heat capacity of HGO	J/kg K	1988.73
Heat capacity of HCOOH	J/kg K	1730
Heat capacity of water	J/kg K	4181.3
Gas constant	J/mol k	8.314
Feed temperature,	K	300
Cooling water temperature	K	298.15
Steam temperature	K	373.15
HGO flow rate	Kg/hr	4372.954
Solvent flow rate	Kg/hr	14175.88
Oxidant flow rate	Kg/hr	2704.77
Catalyst flow rate	Kg/hr	6049.17
Partition coefficient	--	0.791
Number of extraction stages	--	4
Number of plates, D1	--	8
Number of plates, D2	---	10

As shown from these results the initial amount of sulphur in the HGO equals to 4.663 kg (in S1 Table 6.2) and the final sulphur amount was 0.038 kg (in S11 Table 6.2) which represents a reduction of 99.18 % in sulphur. The fractional recovery of solvent is equals to 99.99 % (amount of solvent recovered, S13/ amount of solvent inlet to the extractor, S10) and for oxidant catalyst is equals to 99.96 % (amount of oxidant-catalyst recovered, S5/ amount of oxidant-catalyst to inlet to the reactor, S2). The percent of heavy gas oil loses is equals to 14.1 wt % (amount of HGO in S14/ amount of HGO in S1).

The bold numbers shown in Table 6.3 (results of process energy balance) is the duties of heaters and coolers. The sample calculations for these are in Appendix A.

Table 6.2 Results of material balance of ODS process

Stream	HGO	Sulphur	O S	Catalyst	Oxidant	Solvent	TMF
	(Kg/hr)						
1	4368.29	4.663	0.000	0.00	0.000	0.000	4372.95
OC,2	0.00	0.000	0.000	6049.17	2704.77	0.000	8753.94
3	4368.29	2.658	2.353	6049.17	2704.42	0.000	13126.89
4	0.00	0.000	2.353	6049.17	2704.42	0.000	8755.94
OCR,5	0.00	0.000	0.000	6049.16	2701.55	0.000	8750.71
6	0.00	0.000	2.353	0.010	2.87	0.000	5.23
7	0.00	0.000	0.000	0.010	3.22	0.000	3.23
8	0.00	0.000	0.000	6049.17	2704.77	0.000	8753.94
9	4368.29	2.658	0.000	0.000	0.000	0.000	4370.95
10	0.00	0.000	0.000	0.000	0.000	14175.88	14175.88
FP,11	3756.73	0.038	0.000	0.000	0.000	0.000	3756.77
12	611.56	2.62	0.000	0.000	0.000	14175.88	14790.06
SR,13	0.00	0.000	0.000	0.000	0.000	14174.63	14174.63
14	611.56	2.620	0.000	0.000	0.000	1.25	615.43
15	0.00	0.000	0.000	0.000	0.000	1.25	1.25

TMF = Total Mass Flow rate, OS = Oxidised Sulphur, OCR = Oxidant Catalyst Recovery, SR = Solvent Recovery, FP = Final Product

Table 6.3 Results of energy balance of ODS process

Stream	TMF, (Kg/hr)	T, °C	-H×10 ⁻² , J/Kg	-Q×10 ⁻⁴ , kJ/hr
1	4372.95	25	20.60	900.83
H1		67	19.75	863.66
2	8753.94	25	99.82	8738.18
H2		67	98.89	8656.77
3	13126.89	67	72.52	9519.62
4	8755.94	67	98.86	8656.12
5	8750.71	109.4	97.94	8570.44
6	5.23	156.3	23.23	1.21
7	3.23	25	55.86	1.80
8	8753.94	109.4	97.93	8572.73
C1		67	98.89	8656.77
9	4370.95	67	19.77	864.14
C2		25	20.62	901.29
10	14175.88	149.3	29.76	4218.74
C3		25	32.60	4621.34
11	3756.77	25	20.62	774.65
12	14790.06	25	32.09	4746.13
13	14174.63	152.8	29.67	4205.61
14	615.43	171.4	22.12	136.13
15	1.25	25	32.60	0.41

Heaters and coolers duties are in bold

6.5 Equipment Cost Models

In this section the design of equipment and cost models for extractor, distillation column, separator and heat exchangers are described which are based on Douglas (1988) and Guthrie (1969). The cost for the reactor and pumping are estimated based on Fernando and Pedro (1998) and are presented in Chapter Four.

6.5.1 Distillation Column

6.5.1.1 Height of the Column

The height of the column is calculated as follows

$$H_e = H_{\min} + H_t \frac{N_s}{e_0} \quad (6.1)$$

where

H_t the tray spacing

H_{\min} the additional column height

N_s the number of stages

e_0 the tray efficiency

The tray spacing, number of plates and diameter for each distillation column (catalyst-oxidant recovery column, D1 and solvent recovery column, D2) in the ODS process are taken from the simulation results in the HYSIS software. The values of these design parameters are presented in Appendix A.

The cost of the distillation column shell is given by:

$$C_S (\$/yr) = \left(\frac{M \& S}{M \& S_{base}} \right) C_{0,S} (F_m F_p - 1.0 + F_I F_D) \left(\frac{d_e}{d_0} \right) \left(\frac{H_e}{H_0} \right)^{a_S} \quad (6.2)$$

The cost of the distillation column trays is given by:

$$C_t (\$/yr) = \left(\frac{M \& S}{M \& S_{base}} \right) C_{0,t} (F_s + F_t + F_m) \left(\frac{H_e}{H_0} \right) \left(\frac{d_e}{d_0} \right)^{a_s} \quad (6.3)$$

where for both above equations, H_e is the height and d_e is the diameter of the column.

The values of factors and coefficients used in the cost models are given in Table 6.4.

The total cost of distillation column is given:

$$C_D = C_S + C_t \quad (6.4)$$

6.5.2 Extractor Column

6.5.2.1 The height of the column

The height of the column (H_e) is calculated as follows:

$$H_e = H_{min} + H_t \frac{N_s}{E_0} \quad (6.5)$$

where

H_t the tray spacing

H_{min} the additional column height

N_s the number of stages

E_0 the tray efficiency

6.5.2.2 The column cross-sectional area

The column cross-sectional area (A_e) is calculated as follows

$$A_e = 0.033 S \frac{MWS}{\rho_S} \quad (6.6)$$

where

S The inlet solvent flow rate

M_{WS} The molecular weight of the inlet solvent stream

ρ_S The density of the inlet solvent

$$A_e = \frac{\pi}{4} d_e^2 \quad (6.7)$$

The cost equations of the extractor column shell (Cs) and trays (Ct) are same as that for the distillation column (Equations 6.2 and 6.3)

The total cost of extractor is given by:

$$C_{Ex} = C_S + C_t \quad (6.8)$$

6.5.3 Liquid-Liquid Separator

The separator is sized using a method described by McCabe et al. (1985). A decantation time, t_{dec} is calculated as follows:

$$t_{dec} = \frac{100 \mu_{HGO}}{\rho_{oc} - \rho_{HGO}} \quad (6.9)$$

where μ_{HGO} is the heavy gas oil viscosity and $(\rho_{oc} - \rho_{HGO})$ is the density difference between the density of mixture (oxidant -catalyst phase) and heavy gas oil phase.

The separator volume which is assumed equivalent to the separator liquid hold-up (i.e. the separator is full) is then determined.

$$V_S = F_s t_{dec} \frac{M_{Wmix}}{\rho_{mix}} \quad (6.10)$$

where

F_s the total molar flow rate

M_{Wmix} the molecular weight of the mixture

The separator length was then calculated by assuming that the tank length is three times the diameter. The cost estimate for the separator is given by:

$$C_{Se} (\$ / yr) = \left(\frac{M \& S}{M \& S_{base}} \right) C_{0,S} (F_m F_p - 1.0 + F_I F_D) \left(\frac{d_s}{d_0} \right) \left(\frac{L}{L_0} \right)^{a_S} \quad (6.11)$$

where L is the length and d_s is the diameter of the separator. The values of the factors and coefficients used in the separator cost model are given in Table 6.4.

Table 6.4 Factors and coefficients for the distillation and extraction columns

Parameter, Units	Value
d_0, m	1
H_0, m	6.1
L_0, m	6.1
F_D, m	3.00
F_I, m	1.38
Shell Costs	
a_s	0.82
F_p	1.0
F_m	1.0
Tray Costs	
a_t	1.8
F_s	1.0
F_t	0.0
F_m	0.0

6.5.4 Condenser

The utilities requirement for the condensers used in the distillation columns of the process is calculated from the process energy balance. Cooling water is used as the utility in the condenser and its flow, F_c , is given by the following equation:

$$F_c = \frac{Q_c}{C_{p_w} \Delta T_c} \quad (6.12)$$

The area of heat exchange in the condenser is calculated by :

$$A_c = \frac{Q_c}{U_c \Delta T_{avg}} \quad (6.13)$$

Where U_c is the overall heat transfer coefficient and ΔT_{avg} is an average temperature driving force of the condenser.

6.5.5 Reboiler

The utilities requirement for the reboilers used in the ODS process was estimated from the process energy balance.

Steam is used as the utility in the reboiler and flow, F_h , is determined by:

$$F_h = \frac{Q_r}{\Delta H_s} \quad (6.14)$$

The area of heat exchange in the reboiler is calculated by following equation

$$A_r = \frac{Q_r}{U_r \Delta T_{avg}} \quad (6.15)$$

where U_r is the overall heat transfer coefficient and ΔT_{avg} is an average temperature driving force of the reboiler.

6.5.6 Heat Exchanger

The coolers, heaters are designed using the following equations for shell and tube heat exchangers. Constant values for the overall heat transfer coefficients are assumed which depend on the type of system. The heat transfer area required for heat exchange, A_E (cooler A_{Co} or heater A_H), is calculated by the following equation.

$$A_E = \frac{Q}{U\Delta T_{avg}} \quad (6.16)$$

where Q is the heat duty, U is the overall heat transfer coefficient and ΔT_{avg} is an average temperature driving force of the exchanger.

The cost estimate for the heat exchangers (condensers, reboilers, coolers and heaters) is given by:

$$C_E (\$/yr) = \left(\frac{M \& S}{M \& S_{base}} \right) C_{0,E} \left((F_d + F_p) F_m^{-1} + F_I F_D \right) \left(\frac{A_t}{A_0} \right)^{a_e} \quad (6.17)$$

where,

$$A_t = A_{Co} + A_C + A_r + A_H \quad (6.18)$$

The values of the factors and coefficients used in the exchanger cost model are given in Table 6.5.

Table 6.5 Factors and coefficients used for the heat exchanger

Parameter, Units	Value
A_0, m^2	93
a_e	0.65
F_d	1.0
F_p	0.0
F_m	1.0
F_D	2.3
F_I	1.38

6.6 Total Annualised Cost of the Process

The total annualized cost of the process, TAC , is given by:

$$TAC = (2.43K_{Cap} + 0.19)C_{Cap} + C_{Op} \quad (6.19)$$

where the capital charge factor $K_{Cap} = 0.333$ (Minotti et al., 1996).

C_{Cap} is the total capital cost of the process is the sum of the equipment costs (reactor, extractor, distillation columns, heaters, condensers, reboilers, separator and pumps). The total operating cost (C_{Cop}) is the sum of the costs associated with heating, cooling (utilities cost) and raw material cost (oxidant, catalyst and solvent) in the process.

6.7 Process Economics

In this section the economic analysis for ODS process is studied by using the previous cost models for three cases:

Case 1: Economics of ODS process without catalyst - oxidant recovery system.

Case 2: Economics of ODS process with catalyst - oxidant recovery system.

Case 3: Economics of the ODS process with less oxidant amount.

For all cases the price of hydrogen peroxide (oxidant) is 1.1 \$/kg (Skov and Dennis, 2007) and prices of catalyst (formic acid) and solvent (DMF) are 0.451 \$/kg, 1.39 \$/kg respectively (John, 2000).

Cooling water is used as the utility in the coolers and condensers. A difference between inlet and outlet temperatures, ΔT_C , of the cooling water of 20 °C is assumed. The utility cost of the cooling water is calculated using a price of \$ 0.0305 per 1000 kg of water (Sinnott, 2005).

Steam at 689.5 kpa is used as the utility in the reboilers and heaters. The latent heat of steam, ΔH_{steam} at this pressure is 2067 kJ/kg. The utility cost of the steam at 689.5 kpa is calculated using a price of \$ 5.27 per 1000 kg of steam (Sinnott, 2005).

Constant values for the overall heat transfer coefficients are assumed which depend on the type of the system. For the hot organic liquid/cooling water systems in the condensers and coolers, the $U = 800 \text{ W}/(\text{m}^2 \text{ K})$. For the systems involving condensing steam in the reboilers, the $U \Delta T_{\text{avg}} = 3550 \text{ W}/\text{m}^2$. The utilities of condensers, reboilers, heaters and coolers were extracted from the process energy balance.

6.7.1 Case 1: Economics of the ODS Process without Catalyst - Oxidant Recovery System

The excess oxidant and catalyst recovery system was not considered in the oxidative desulphurization process. Figure 6.2 shows the block flow diagram for this case.

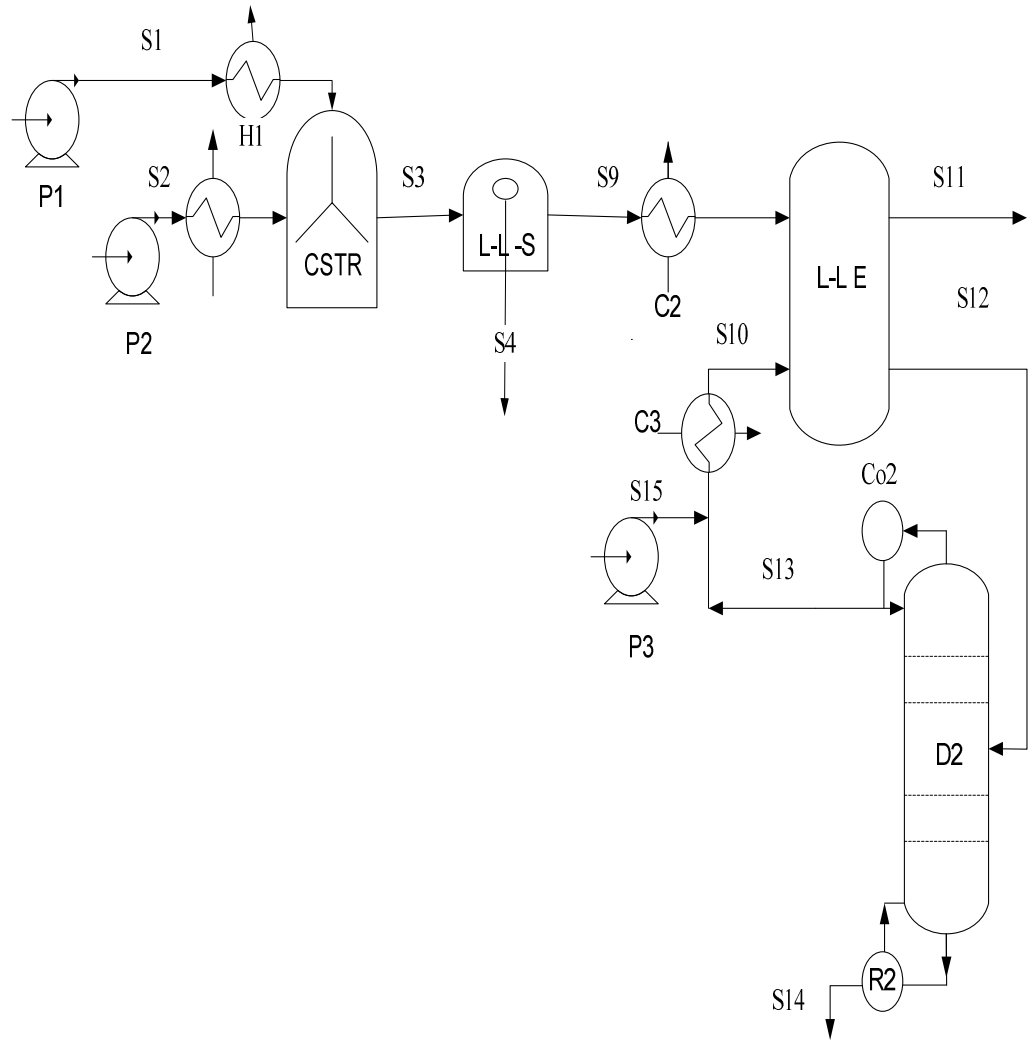


Figure 6.2 Block flow diagram of oxidative desulphurization process (Case 1)

The results of process material and energy balances for this case are listed in Tables 6.6 and 6.7. The economic results of this case are based on the consumption of raw material and utilities summarized in Table 6.8 and total capital cost presented in Table 6.9.

The economic results of this case shown in Table 6.10 indicate that the total cost is most sensitive to hydrogen peroxide consumption (55.53 % of total cost) and formic acid (38.80 % of total cost) and the total cost based on per bbl feed is 38.5817 dollar per barrel feed. This means that the excess oxidant and catalyst must be recovered otherwise the ODS process in terms of cost will not be economically viable.

Table 6.6 Results of material balance of ODS process (Case 1)

Stream	HGO	Sulphur	O. Sulphur	Catalyst	Oxidant	Solvent	T.M.F
	(Kg/hr)						
1	4368.29	4.663	0.000	0.000	0.000	0.000	4372.95
2	0.000	0.000	0.000	6049.17	2704.77	0.000	8753.94
3	4368.29	2.658	2.35	6049.17	2704.42	0.000	13126.89
4	0.000	0.000	2.35	6049.17	2704.42	0.000	8755.94
9	4368.29	2.658	0.00	0.000	0.000	0.000	4370.95
10	0.000	0.000	0.00	0.000	0.000	14175.88	14175.86
11	3756.73	0.038	0.00	0.000	0.000	0.000	3756.77
12	611.56	2.620	0.00	0.000	0.000	14175.88	14790.06
13	0.000	0.000	0.00	0.000	0.000	14174.63	14174.63
14	611.56	2.620	0.00	0.000	0.000	1.25	615.43
15	0.000	0.000	0.00	0.000	0.000	1.25	1.25

Table 6.7 Results of energy balance of ODS process (Case 1)

Stream	M.F, (Kg/hr)	T, °C	-H×10 ⁻² , J/kg	-Q×10 ⁻⁴ , kJ/hr
1	4372.95	25	20.60	900.83
H1		67	19.75	863.66
				37.17
2	8753.94	25	99.82	8738.18
H2		67	98.89	8656.77
				-81.41
3	13126.89	67	72.52	9519.62
4	8755.94	67	98.86	8656.12
9	4370.95	67	19.77	864.14
C2		25	20.62	901.29
				-37.15
10	14175.88	149.3	29.76	4218.74
C3		25	32.60	4621.34
				-402.6
11	3756.77	25	20.62	774.65
12	14790.06	25	32.09	4746.13
13	14174.63	152.8	29.67	4205.61
14	615.43	171.4	22.12	136.13
15	1.25	25	32.60	0.41

Heaters and cooler duties in bold

Table 6.8 Raw material and utility consumption of the ODS process (Case 1)

Feed Material	
	Usage, kg/hr
Hydrogen peroxide	2704.77
Formic acid	6049
Dymetylformamied	14171
Utilities	
Steam	9503
Cooling water	226485

Table 6.9 Equipment cost of the process (Case 1)

Equipment	Cost, \$/yr
Reactor	10903
Extractor	114912
Distillation Columns (D1)	186235
Coolers (C2, C3)	58063
Heaters (H2, H2)	58062
Condensers (Co2)	58072
Reboilers (R2)	29049
Pumping	6592
Separator	176799
Total capital cost (C_{Cap})	698686

Table 6.10 E economics of the ODS process (Case 1)

Technical basis	Cost basis			
Plant capacity	1000	bpd	H ₂ O ₂ (100%)	1.1 \$/kg
	4373	kg/hr	Formic acid (100%)	0.451 \$/kg
On-stream time	300	Days/Year	DMF	1.39 \$/kg
Sulphur in feed	1066	ppm	Cost of steam	5.27 \$/t
HGO Yield	86	%	Cost of C- water	0.0305 \$/t
Sulphur in product	10	ppm		
	Quantity		Cost	% of Total
	Unit/hr	Unit/bbl feed	\$/bbl feed	
Feed material				
Heavy gas oil	4373 kg	105 kg		
Oxidant	2075 kg	20 kg	21.424	0.5553
Catalyst	6049 kg	33 kg	14.972	0.3880
Sol. Make-up	1.25 kg	0.03 kg	0.0417	0.0011
Utilities				
Steam	9503 kg	228.06 kg	1.2019	0.0312
Cooling water	226485 kg	5435.36 kg	0.1658	0.0043
Capital charges			0.7763	0.0201
Total cost based /bbl feed			38.5817	1.0000
Actual total capital, C_{cap} , \$/yr			698686	
Actual total Operating, C_{op} , \$/yr			11341620	
Total Annual Cost, TAC			12044394	

6.7.2 Case 2: Economics for Oxidative Desulphurization Process with Oxidant Catalyst Recovery System

The amount of excess oxidant and catalyst are considered here and most of these amounts were recovered. Figure 6.1 show the block flow diagram for this case and the results of process material and energy balances are listed in Tables 6.1 and 6.2 (section 6.3.1).

The economic results for this case are shown in Table 6.13. These results are based on the raw material and utility consumptions presented in Table 6.11. The amount of oxidant used were based on the batch experiment in Chapter Three (oxidant to sulphur molar ratio, H/S=150). The total capital cost of the process is listed in Table 6.12.

The results show that both the cost of utility consumption (2.486 \$/bbl feed) and the capital cost (0.9864 \$/bbl feed) are increased compared to those in the Case 1 (1.368 \$/bbl feed). This increase is due to increase in the cost for the catalyst and oxidant recovery system (capital and operating cost for OCR column). Although the utility consumption cost and capital cost of the process increase, the total cost of this Case (3.5991 \$/bbl feed) is less than that for Case 1.

The total cost of the process in this Case is sensitive to steam consumption (60.49 % of total cost) and capital cost (27.41 % of total cost).

Table 6.11 Raw material and utility consumption of the ODS process (Case 2)

Feed Material	
	Usage, kg/hr
Hydrogen peroxide	2704.77
Formic acid	6049
Dymetylformamied	14171
Utilities	
Steam	15962
Cooling water	421663

Table 6.12 Equipment costs of the process (Case 2)

Equipment	Cost, \$/yr
Reactor	10903
Extractor	114912
Distillation Columns (D1, D2)	346242
Coolers (C1, C2, C3)	87094
Heater (H1)	29031
Condensers (Co1,Co2)	58072
Reboilers (R1, R2)	58096
Pumping	6592
Separator	176799
Total capital cost (C_{Cap})	887741

Table 6.13 Economics of the ODS process (Case 2)

Technical basis	Cost basis				
Plant capacity	1000	bpd	H ₂ O ₂ (100%)	1.1	\$/kg
	4373	kg/hr	Formic acid (100%)	0.451	\$/kg
On-stream time	300	Days/Year	DMF	1.39	\$/kg
Sulphur in feed	1066	ppm	Cost of steam	5.27	\$/t
HGO Yield	86	%	Cost of C- water	0.0305	\$/t
Sulphur in product	10	ppm			
	Quantity		Cost	% of Total	
	Unit/hr	Unit/bbl feed	\$/bbl feed		
Feed material					
Heavy gas oil	4373	kg	105	kg	
Oxidant	3.219	kg	0.0773	kg	0.0236
Catalyst	0.01	kg	0.0002	kg	0.0000
Sol. Make-up	1.25	kg	0.0300	kg	0.0116
Utilities					
Steam	15962	kg	413.14	kg	2.1773
Cooling water	421663	kg	10119.9	kg	0.3087
Capital charges			0.9864		0.2741
Total cost based / bbl feed			3.5991		1.0000
Actual total capital, C_{Cap} , \$/yr			887741		
Actual total Operating, C_{op} , \$/yr			783814		
Total Annual Cost, TAC			1670836		

6.7.3 Case 3: Economics of the Oxidative Desulphurization Process with less Oxidant Amount

The amount of oxidant (the oxidant to sulphur mole ratio, H/S =3) used in this case is less than that was used in the Case 2 (the oxidant to sulphur mole ratio, H/S = 150) and most of the oxidant, catalyst and solvent are recovered and reused in the process. The results of this case are based on the consumption of raw material and utilities summarized in Table 6.14 and total capital cost shown in Table 6.15. The results of material balance of this case are given in Appendix A.

Table 6.16 shows the results of Case 3. It can be seen from this result, the cost of utility consumption (1.506 \$/bbl feed) and capital cost decrease compared to those with Case 2 (2.486 \$/bbl feed). Moreover, the total cost (2.5 \$/bbl feed) is less than those in the other cases (due to the decrease oxidant mass flow rate and thus, lower operating and capital cost).

The total cost is sensitive to steam consumption (52.82 % of total cost) and capital cost (36.41 % of total cost) follow the same trend as in Case 2.

Table 6.14 Raw material and utility consumption of the ODS process (Case 3)

Feed Material	
	Usage, kg/hr
Hydrogenperoxide	49.549
Formic acid	6049
Dymetyl formamied	14171
Utilities	
Steam	10441
Cooling water	253833

Table 6.15 Equipment costs of the process (Case 3)

Equipment	Cost, \$/yr
Reactor	9515
Extractor	114912
Distillation Columns (D1, D2)	346242
Coolers (C1, C2, C3)	87093
Heater (H1)	29031
Condensers (Co1, Co2)	58068
Reboilers (R1, R2)	58084
Pumping	5528
Separator	110799
Total capital cost (C_{Cap})	819272

Table 6.16 Economics of the ODS process (Case 3)

Technical basis	Cost basis			
Plant capacity	1000	bpd	H ₂ O ₂ (100%)	1.1 \$/kg
	4373	kg/hr	Formic acid (100%)	0.451 \$/kg
On-stream time	300	Days/Year	DMF	1.39 \$/kg
Sulphur in feed	1066	ppm	Cost of steam	5.27 \$/t
HGO Yield	86	%	Cost of C- water	0.0305 \$/t
Sulphur in product	10	ppm		
	Quantity		Cost	% of Total
	Unit/hr	Unit/bbl feed	\$/bbl feed	
Feed material				
Heavy gas oil	4373 kg	105 kg		
Oxidant	1.577 kg	0.0378 kg	0.0416	0.0166
Catalyst	0.0118 kg	0.0004 kg	0.0002	0.0001
Sol. Make-up	1.25 kg	0.0300 kg	0.0417	0.0167
Utilities				
Steam	10441 kg	251.59 kg	1.3206	0.5282
Cooling water	253833 kg	6091.98 kg	0.1858	0.0743
Capital charges			0.9103	0.3641
Total cost based /bbl feed			2.5002	1.0000
Actual total capital, C_{Cap} , \$/yr	819272			
Actual total Operating, C_{op} \$/yr	476979			
Total Annual Cost, TAC	1295588			

6.8 Comparison between Oxidative Desulphurization and Hydrodesulphurization Processes

Referring to Chapter Two HDS process essentially removes the sulphur atoms from the hydrocarbon fuel, producing hydrogen sulphide that is then converted to elemental sulphur in Claus plant. The ODS process instead convert the sulphur compounds present in the hydrocarbon fuel to corresponding sulphones and then remove a by-product mixture containing sulphones and hydrocarbons. However, the oxidative desulphurization process can be considered not to be a competitor of the traditional HDS one. It appears to be complementary since hydrotreatments not only remove sulphur from refinery streams but also improve the quality of the fuels.

The ODS process is specially designed to be integrated in the final processing steps to decrease remaining sulphur compounds in the fuel to the level fixed by the environmental regulations. Thus, it seems appropriate to compare the oxidative desulphurization process with modification HDS unit able to perform a deep desulphurization and reach the same low sulphur levels which can be achieved with the coupled standard HDS and ODS processes (Table 6.17).

A modification of HDS unit involves high investment costs and an increase in operation costs in the order of 4.59 \$/bbl (Skof and Deniss, 2007). Such a cost is still higher than that required in the ODS process (2.5 \$/bbl feed, Table 6.16). However, a true cost comparison between ODS and HDS processes would require a definition of how hydrogen and Claus sulphur plant capital costs are accounted for. Also in the future perhaps the cost associated with carbon dioxide emissions should be considered.

Table 6.17 Comparison between ODS and HDS processes

Criteria	ODS process	HDS, hydrotreating
Feedstock	Gas oil and HDS product	Gas oil LCO, HCO
Feedstock sulphur, ppm	<4500	500-9000
Product sulphur, ppm	<10	<10
Byproduct	High sulphur oil	Elemental sulphur
Peroxide	Proportional to feed-S content	Non required
Hydrogen	Non required	450-550 ft ³ /bbl
Operating T, °C	40-80	280-350
Operating P, atm	atmospheric	45-80
Ancillary units required	Non	Syngas and H ₂ Plant, Claus sulphur plant
LCO, Light Cycle Oil, HCO Heavy Cycle Oil		

6.9 Conclusions

The continuous oxidative desulphurization process for heavy gas oil is developed based on batch experiment (oxidation and extraction), and the model equation of a continuous stirred tank reactor and multi stage liquid-liquid extraction model are presented in the previous chapters. In this chapter the cost model for the whole process is developed.

The feed capacity of 1000 barrel per day of heavy gas oil was chosen with initial sulphur content 1069 ppm for a pilot scale ODS process. The total annualized cost of ODS process is calculated and economics of the process are analysed by using three different Cases.

In Case 1, the oxidant-catalyst recovery system was not considered in the ODS process.

In Case 2, the oxidant-catalyst recovery system was considered in the ODS process.

In Case 3, the amount of oxidant used is less than that used in the Case 2.

For each case the material and energy balances around each unit operation in the process are calculated and primary designs of each unit in the process are estimated.

For Case 1, result of this case clearly shows the total cost is very sensitive to hydrogen peroxide consumption (55.53 % of total cost) and formic acid (38.80 % of total cost) and the total cost based on feed is much higher compared with the other cases (\$38.58 per bbl feed). Therefore, without recovery of excess oxidant and catalyst ODS process in terms of costing is not viable.

The results in Case 2 indicate that the total cost is most sensitive to steam consumption (60.49 % of total cost) and capital cost (27.41 % of total cost). The total cost based on feed is equal to 3.599 \$/bbl feed which is significantly lower compared to Case 1.

In Case 3 where the amount of oxidant used less than that used in Case 2, the results indicate that the total cost of the process is sensitive to utility consumption and capital cost. The total cost (2.50 \$/bbl) based on feed is less than that found in the other cases.

Oxidative desulphurization process appears to be technically and economically viable for processing ultra low sulphur fuel from gas oil feedstock. It can be considered in conjunction with or as substitute for hydrodesulphurization process (HDS). Notably, ODS does not require hydrogen for desulphurization, but instead converts the sulphur compounds present in the gas oil to corresponding sulphones that are then extracted from the gas oil. Prospectively, it is expected that capital cost and operating cost with ODS would be significantly lower than with HDS.

Chapter Seven

Conclusions and Future Work

7.1 Conclusions

Sulphur in fuel leads directly to emission of SO₂ and sulphate particulate matter which endanger public health and welfare therefore regulatory limitations on sulphur levels in automotive fuels, particularly diesel have led to a renewed interest in alternative desulphurization technologies. The achievement of very low levels of sulphur required in transportation fuels in the near future which will be difficult and/or will be highly costly by current hydrodesulphurization process (HDS). As highlighted in Chapter 2, several alternative strategies to HDS process are currently being explored, which include various oxidative desulphurization techniques (ODS) that do not require the use of expensive hydrogen. Various studies on the ODS process have reported the use of differing oxidant, such as Hydrogen Peroxide (H₂O₂) in combination with organic acids (i.e. formic acid), polyoxometalate, 12-tungstophosphoric acid and *tert*-butylhydroperoxide.

This study aimed at developing an oxidative desulphurization process with high reaction rate and high selectivity. The process was designed to combine two complementary techniques: oxidation of organic sulphur compounds and solvent extraction of oxidised sulphur compounds. The oxidation of model sulphur compounds (Di-*n*-butylsulfide, Dimethylsulfoxide and Dibenzothiophene) and sulphur present in heavy gas oils (HGO_A and HGO_B) with H₂O₂ in the presence of a catalyst Formic Acid (HCOOH) are studied in Chapter Three. A series of batch experiments are carried out using a small reactor (500 ml) operating at various temperatures ranging from 40 °C to 100 °C. The effectiveness of sulphur removal is found to be proportional to the reaction temperature

in the range of 40 to 60 °C and maximum 30 ml of formic acid. It is found that, increasing the amount of hydrogen peroxide leads to the reduction in both conversion of sulphur compound as well as initial reaction rate. Through the oxidation, the sulphur content in HGO_A and HGO_B were reduced from 1550 to 970 ppm and from 1066 to 609 ppm respectively and that for the model compounds, Di-n-butylsulfide, Dimethylsulphoxide and DBT were also reduced from 1535 to 201 ppm, from 1228 to 25 ppm and from 943 ppm to 5 ppm respectively. Kinetic models for the oxidation reaction of model sulphur compounds and sulphur content in heavy gas oil are investigated further. In general the oxidation of organic sulphur compounds under ODS conditions follows pseudo-first-order kinetics. The apparent rates constant of DBT and sulphur present in HGO_B are determined to be 0.737 min⁻¹ at 40 °C for Dibenzothiophene (DBT) and 0.227 min⁻¹ at 40 °C for HGO_B. This information is very important to design of continuous flow ODS system as well as the process evaluation of ODS on HGO.

In addition to the oxidative sulphur removal, extraction of unoxidised and oxidised heavy gas oils were also investigated using methanol, dimethylformamide (DMF) and N-methyl pyrrolidone (NMP) as solvents. The results showed that the removal of sulphur compounds by solvent extraction became more effective for oxidised samples than for unoxidised samples. DMF was the most effective polar solvent among the solvents used. Through oxidation and extraction the sulphur content in the heavy gas oil (HGO_B) is reduced from 1066 to 148 ppm sulphur.

Simulation and optimisation help achieving better design and operation of desulphurization processes leading to low-cost for production fuel with low sulphur. To carry out meaningful simulation and optimisation to create alternative design and operation scenarios cheaply, development of a reliable process model is the first step (in the absence of a real plant).

In Chapter Four, a CSTR model is developed for the oxidation process for evaluating viability of large-scale operation. In this process, a large amount of energy is required to carry out reaction at temperature close to that of the batch reactor, the recovery of which is very important for maximizing the profitability of operation and reducing environmental impact. Therefore a heat integration of oxidation process is considered. In the absence of a real plant a model for the system is developed. The kinetic model for the CSTR is based on the batch reactor experiments reported in Chapter Three.

The optimisation problem is formulated to optimise some of the design and operating parameters (such as reaction temperature, residence time and splitter ratio) of integrated process while minimizing an objective function which is a coupled function of capital and operating costs involving design and operating parameters. Two cases were studied: (i) HGO and catalyst were fed as one feed stream and (ii) HGO and catalyst were treated as two feed streams. The product stream from the reactor was split into two streams according to splitter ratio (S_r) to maximize heat recovery. For simplicity a simple CSTR model with the assumption of perfect mixing was used carrying out the modelling and optimisation in gPROMS software.

Optimal minimum energy requirement, heat recovery and cost saving in heat exchangers network system for oxidation of sulphur compounds in HGO_B were obtained. The first case provided better minimum energy requirement and maximum heat recovery compared to the second case. However reducing energy consumption means reducing CO₂ emission thus significantly reducing environmental impact. The cost savings for the first and second case were 36% and 22% respectively and the energy consumption was reduced by 77 % for the first case and by 57 % for the second case.

The sensitivity of feed temperature (T_{F0}) and feed flow rate (v) on the temperature of each stream and energy requirement for Case I were studied. The results show that a small change in temperature will make the system unstable therefore, the temperature controller should be added to the process (which was beyond the scope of this thesis) to fix the feed temperature. However, with the change the flow rate the temperature of each stream of the process almost constant but the energy requirement increases.

With the batch experiments the solvent effectiveness (K_f) factor, partition coefficients (K_p) and extraction factor (E_f) (for methanol, NMP and DMF) at different solvent to heavy gas oil ratio were determined in Chapter Five. A multi stage liquid-liquid extraction process model was then developed using gPROMS modelling tool. The simulation results showed that, the DMF was the most effective polar solvent for reducing the sulphur level of the heavy gas oil within the regulation with minimum solvent/HGO ratio and number of extraction stages compared to those with other solvents (methanol and NMP). The results also indicated that the oxidation/extraction process could be a promising approach for the reduction of sulphur to less than 10 ppm from the original value of 1066 ppm.

Finally, in Chapter Six a continuous ODS process for heavy gas oil was developed based on the models of a continuous stirred tank reactor and multi stage liquid-liquid extraction. The total annualized cost of ODS process is then calculated and economics of the process were analysed by using three different Cases. In Case 1, the oxidant-catalyst recovery system was not considered in the ODS process. In Case 2, the oxidant-catalyst recovery system was considered in the ODS process. In Case 3, the amount of oxidant used was less than that used in Case 2. The simulation result of Case 1 showed that the total cost was very sensitive to hydrogen peroxide consumption and formic acid and the total cost was much higher compared with those for the other cases. Therefore,

recovery of oxidant and catalyst was important. The results of Case 2 and Case 3 indicate that when the oxidant-catalyst recovery system was considered the total cost of the process was sensitive to utility consumption and capital cost. The total cost of the Case 3 (2.50 \$/bbl feed) was less than those obtained in the other cases.

The results show that the ODS process is capable of scaling up from a lab-scale (batch system) to a continuous flow system followed by a solvent extraction. To make this jump successfully requires a thorough test of the continuous ODS process (integrated process) in the lab (possibly with a micro-plant).

7.2 Future Work

One of the objectives of this research is to reduce the sulphur content of heavy gas oil to less than 10 ppm sulphur. By using the proposed method of desulphurization it is possible to ease the huge demand for hydrogen gas and energy that are required by the current refining technology (HDS). The experimental data illustrates that the method described in this thesis are feasible to reach the goal. Further work, however, is required to enhance the overall efficiency of this method. Suggestions for future research work are summarized as follow:

- Application of different catalyst systems such as supported metallic-acidic catalyst (heterogeneous) with the objectives to improve reactivity and simplify regeneration of deactivated catalysts. Other types of homogenous catalysts that may improve reactivity such as 12-tungstophosphoric acid (TPA) or selenius acid can be used.
- Improve recovery of heavy gas oil loses in extraction step.

In Chapter Six about 14.1 % of oil loses in extraction step was noted and recovery of it was not considered in this study. The concentrated extract form

solvent recovery system (S14 in Figure 6.1) contains heavy gas oil, solvent and oxidised sulphur compounds (sulphones). Considering the cost of the fuel and environmental impact recovery of the oil losses should be recovered.

- Investigating various oxidants is suggested. Possible oxidant include; oxygen, pure or with air to improve oxidation reaction rates with the aim to minimize mass transfer limitation that may result due to the bi-physic liquid system and also to reduce waste disposal problem.
- In Chapter Four, it was noted that the heat recovery of intergraded oxidation process is very sensitive to operating parameters (feed temperature and feed flow rate). However a small change in the temperature will make the system unstable. Considering safety and heat recovery efficiency of the process control of oxidation process should be further studied.

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Appendix A

A.1 Mass Balance Calculation

The feed capacity of ODS process is 1000 bpd. The densities of the feed (HGO, hydrogenperoxide, formic acid and dimethylformamide) were taken at atmospheric pressure and 25 °C. The material balance around each unit in the oxidation step and extraction step of ODS process (Case 2) are shown in the Figure A.1a and Figure A.1b and for the Case (3) are shown in Figure A.2

The following are sample calculation for Case (2) (Figure A.1)

1) Mass Flow Rate of HGO and Sulphur (Feed stream, S1)

$$M_{mix} = V_{mix} \times \rho_{mix}$$

where

M_{mix} is the mass flow rate of mixture HGO and sulphur (Feed, stream S1)

$V_{mix} = 1000 \text{ bpd} = 119.00 \text{ m}^3/\text{day} = 4.958 \text{ m}^3/\text{hr}$ (Plant feed capacity)

$\rho_{mix} =$ Liquid density of mixture (HGO and sulphur) = 882 Kg/m³ (Measurement)

$$M_{mix} = 4.958 \times 882 = 4372.954 \text{ Kg/hr}$$

$$M_{Sulfur} = \text{wt \% of sulfur} \times M_{mix}$$

Wt % of sulphur = 0.001066 (Measurement) = 1066ppm

$$M_{Sulfur} = 0.001066 \times 4372.954 = 4.663 \text{ Kg/hr}$$

$$M_{HGO} = M_{mix} - M_{Sulfur}$$

$$M_{HGO} = 4372.954 - 4.663 = 4368.292 \text{ Kg/hr}$$

2) Mass Flow Rate of Oxidant Feed (H₂O₂, S2)

$$M_{Oxi} = V_{Oxi} \times \rho_{Oxi}$$

where

M_{Oxi} is the mass flow rate of oxidant (Oxidant Feed)

$$V_{Oxi} = 500 \text{ bpd} = 59.5 \text{ m}^3/\text{hr} = 2.47916667 \text{ Kg/hr}$$

$$\rho_{Oxi} = \text{Liquid density of oxidant} = 1091 \text{ Kg/m}^3$$

$$M_{Oxi} = V_{Oxi} \times \rho_{Oxi} = 2704.771 \text{ Kg/hr}$$

3) Mass Flow Rate of Catalyst Feed (HCOOH, S2)

$$M_{Cat} = V_{Cat} \times \rho_{Cat}$$

where

M_{Cat} is the mass flow rate of catalyst (Reactant Feed)

$$V_{Cat} = 1000 \text{ bpd} = 119.00 \text{ m}^3/\text{day} = 4.958 \text{ m}^3/\text{hr}$$

$$\rho_{Cat} = \text{Liquid density of oxidant} = 1220 \text{ Kg/m}^3$$

$$M_{Cat} = V_{Cat} \times \rho_{Cat} = 6049.167 \text{ Kg/hr}$$

$$\text{Total feed stream, S2} = M_{Cat} + M_{Oxi} = 8753.938 \text{ Kg/hr}$$

4) Mass Flow Rate of Solvent Feed (DMF, S10)

$$M_S = V_S \times \rho_S$$

where

M_S is the mass flow rate of solvent (Solvent feed to the extractor column)

$$V_S = 3000 \text{ bpd} = 375.00 \text{ m}^3/\text{day} = 14.875 \text{ m}^3/\text{hr}$$

$$\rho_S = \text{Liquid density of solvent} = 953 \text{ Kg/m}^3$$

$$M_S = V_S \times \rho_S = 14175.875 \text{ Kg/hr}$$

A.2 Design Variable of Distillation Columns used in the ODS Process

The specification and results of the design variable for oxidant-catalyst, solvent recovery distillation columns (D1 and D2) used in the ODS process (Case 2) are shown in Table A.1. For the mass flow rates and composition of feed, top and bottom products are shown in Figure A.1.

Table A.1 Design variable of oxidant-catalyst and solvent recovery distillation columns

Variable	C-O Column (D1)	S.R Column (D2)
Number of stages	8	10
Feed temperature, °C	67	25
Top stage temperature, °C	109.6	152.8
Bottom stage temperature, °C	149.2	194.8
Top stage pressure, kPa	100	100
Bottom stage pressure, kPa	100	100
Stage column diameter, m	3	3.5
Stage space, m	0.5	0.5

Table A.2. Design variable of extraction column

Variable	Extractor
Number of stages	4
Feed temperature, °C	25
Top stage temperature, °C	25
Bottom stage temperature, °C	25
Top stage pressure, kPa	100
Bottom stage pressure, kPa	100
Stage column diameter, m	2
Stage space, m	0.4

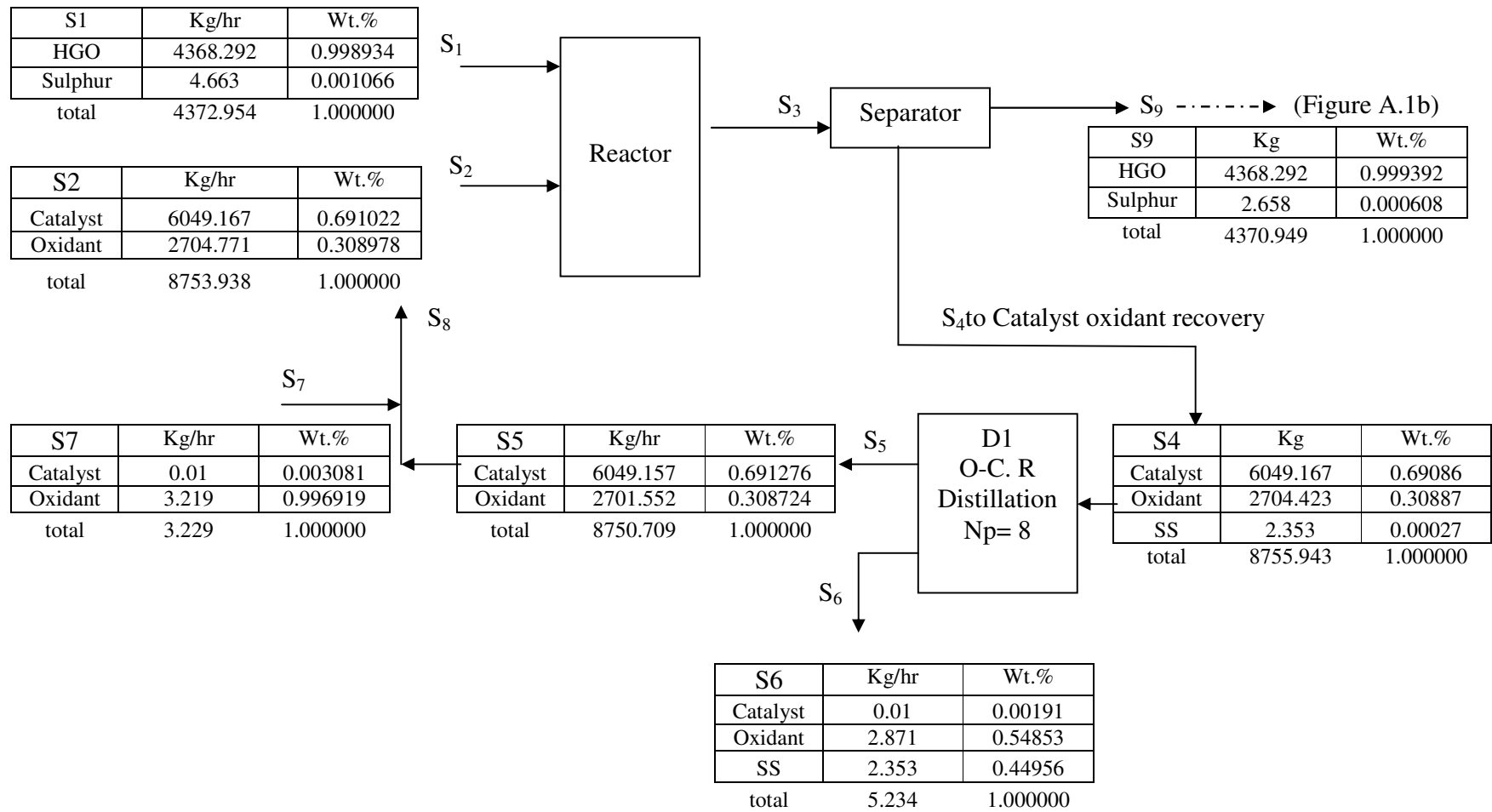


Figure A.1a Results of material balance in oxidation step and oxidant-catalyst recovery system (O-C.R) of ODS process (Case 2)

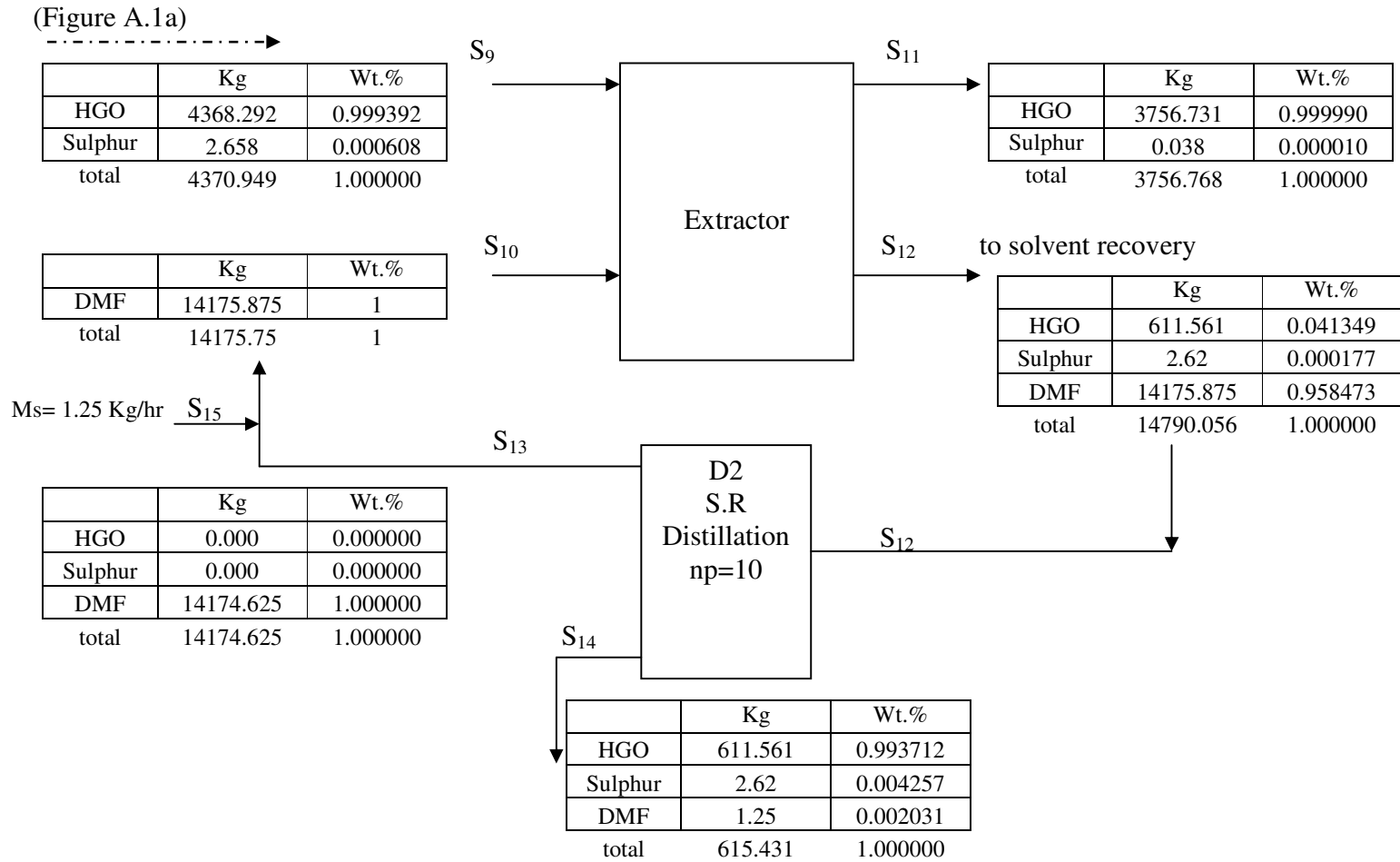


Figure A.1b Results of material balance in extraction step and solvent recovery system of ODS process (Case 2)

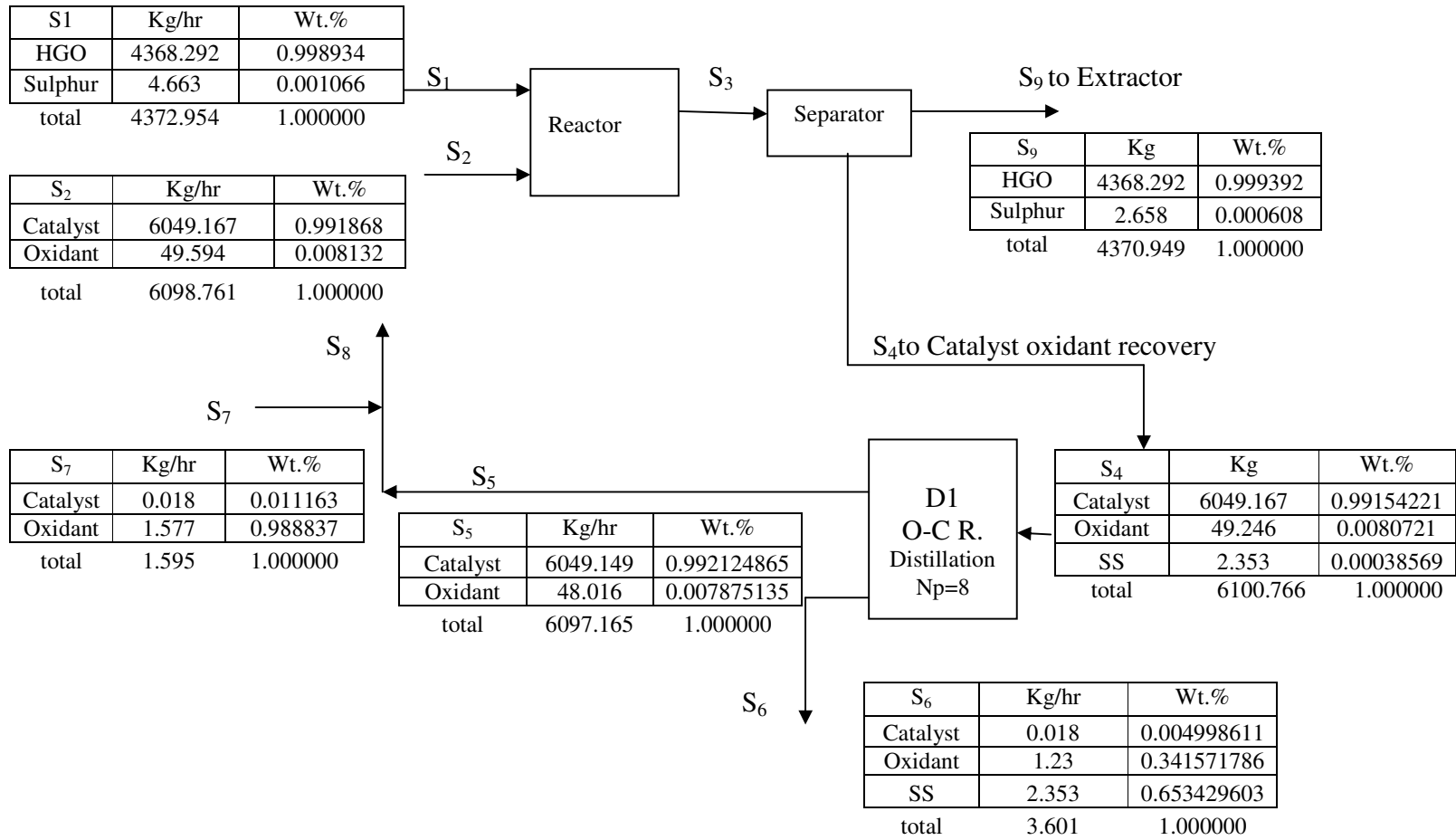


Figure A.2 Results of material balance in oxidation step of ODS process (Case 3)

A.3 Heating and cooling Duties

The bold numbers shown in Table 6.3 (results of process energy balance for Case 2) is the duties of heaters and coolers. The following are the sample calculations for the heater (H1) at stream, S₁ and cooler (C1) at stream, S₈:

Heating Duty of (H1 at S1)

$$Q_{H1} = Q_{S1} \text{ at } 67^{\circ}C - Q_{S1} \text{ at } 25^{\circ}C$$

$$Q_{S1} = \text{TMF} * H_{S1},$$

where Q_{S1} is the heating amount of stream S₁, H_{S1} is the mass enthalpy of stream S₁ and TMF is the total mass flow rate of this stream (S₁). From Table 6.2 $H_{S1} = -6020$ kJ/Kg and TMF = 4368.292 Kg/hr hence, $Q_{S1} = -900.83 \times 10^4$ kJ/hr at 25 °C and at 67 °C $Q_{S1} = -863.8 \times 10^4$ kJ/hr. Therefore, $Q_{H1} = -863.66 \times 10^4 - (-900.83 \times 10^4) = 37.17 \times 10^4$ kJ/hr

Cooling Duty (C1 at S8)

$$Q_{C1} = Q_{S8} \text{ at } 109.4^{\circ}C - Q_{S8} \text{ at } 67^{\circ}C$$

$$Q_{S8} = \text{TMF} * H_{S8},$$

where Q_{S8} is the heating amount of stream S₈, H_{S8} is the mass enthalpy of stream S₈ and TMF is the total mass flow rate of this stream (S₈). From Table 6.2 $H_{S8} = -7993$ kJ/Kg and TMF = 8753.94 Kg/hr

hence, $Q_{S8} = -8572.73 \times 10^4$ kJ/hr at 109.4 °C and at 67 °C $Q_{S8} = -8656.77 \times 10^4$ kJ/hr.

Therefore, $Q_{C1} = -8572.73 \times 10^4 - (-8656.77 \times 10^4) = 84.04 \times 10^4$ kJ/hr.