Experimental Optimization of the CAPRI Process

By

Amjad Ali Shah

A thesis submitted to
The University of Birmingham
for the degree of
Doctor of Philosophy

Department of Chemical Engineering
May 2011

THE UNIVERSITY
OF BIRMINGHAM

Abstract

The worldwide conventional crude oil demand is on the rise and because of the rising prices, unconventional oils are becoming more economically attractive to extract and refine. However, technological innovation is needed, if heavier oil supplies are to be further exploited. Toe-to-heel air injection (THAI), and its catalytic add-on (CAPRI) processes combine in-situ combustion with catalytic upgrading using an annular catalyst packed around the horizontal producer well. These techniques offer potentially higher recovery levels and lower environmental impact than alternative technologies, such as steam-based techniques. Information about CAPRI unlike THAI is limited. A number of parameters such as optimum catalyst, temperature, pressure and reaction media were investigated in this study and were optimised for the process. The upgrading processes that occur during catalytic cracking were also investigated.

An experimental study was carried out concerning the optimization of catalyst type, operating conditions, addition of water and hydrogen for use in the THAI-CAPRI process and is reported. Three feeds namely, THAI field oil, Combustion Cell Oil (CCO) and n-decane were used in the presence of catalyst or an inert medium for comparison.

The main feed oil was supplied from the Whitesands THAI pilot trial. Experiments were carried out using micro-reactors containing 5 g catalyst, with oil flow of 1 $ml.min^{-1}$ and gas flow of 0.5 $l.min^{-1}$, under different temperatures, pressures and gas environments. Catalysts tested included alumina supported CoMo, NiMo and ZnO/CuO, Bentonite clay, zeolites and Albemarle Corporation commercial catalysts. It was found that there was a trade-off in operation temperature between upgrading performance and catalyst lifetime. At a pressure of 20 bar, operation at 500 °C led to an average of 6.1 °API upgrading of THAI oil to 18.9 °API, but catalyst lifetime was limited to 1.5 hours. Operation at 420 °C was found to be a

suitable compromise, with upgrading by an average of 1.6 °API, and sometimes up to 3 °API, with catalyst lifetime extended to 77.5 hours. Coke deposition occurred within the first few hours of the reaction, such that the catalyst pore space became blocked. However, upgrading continued, suggesting that thermal reactions or reactions catalysed by hydrogen transfer from the coke itself play a part in the upgrading reaction mechanism. Some upgrading also occurred in the absence of active catalyst, suggesting that the upgrading of heavy oil is largely a thermal process. The addition of water did not add any upgrading value to the produced oils in terms of reduced viscosity and higher API gravity. The CAPRI process was relatively insensitive to changes in reaction gas medium, gas flow rate and pressure, suggesting that the dissolution of hydrogen or methane from the gas phase does not play a key role in the upgrading reactions. From the chemistry of upgrading, it was found that the produced oil mainly upgraded because of the side chain breaking from aromatics and cyclization of the aromatics into larger molecules. These results were further supported by the analyses of coke, where the presence of aromatics appeared in coke at relatively higher upgrading.

From the results of the current study it can be said that by careful control of the temperature and oil flow rate in the in-situ CAPRI process, additional upgrading compared with the THAI process alone may be effected, resulting in a more valuable produced oil, which is easier to transport and could be further processed into distillates.

To My Father and

Supervisor

Acknowledgments

I extend my deepest and heartiest thanks to the following individuals and organizations for their contribution to this work,

Dr. Joseph Wood, for his leadership in supervising my work with great patience and moral support. Dr. Robert Fishwick who assisted with the design and construction of the experimental upgrading rig and running of some experiments.

Dr. Gary Leeke for his encouraging comments and co-supervision. Project team members from Bath University, Navin Gopinathan, Dr. Sean Rigby and Professor Malcolm Greaves for their valuable comments and help. Professor Malcolm Greaves is also thanked for his ideas and management of the EPSRC project on In-Situ Catalytic Upgrading of Heavy Crude And Bitumen (EP/E057977/1), of which this work formed part of the investigation.

The Chemical Engineering and Biosciences Workshop teams, for their contribution in the construction and maintenance of the CAPRI experimental rig. Petrobank for providing the THAI field oil and analysing oil samples. Intertek Laboratories also for analysing oil samples. Albemarle Corporation for providing catalysts.

The Engineering and Physical Sciences Research Council (EPSRC), UK, are thanked for funding.

Finally, I would like to thank my dearest family members and my dedicated research group at Department of Chemical Engineering, University of Birmingham for their support in the successful completion of this work, without whom it would have been very hard.

Table of Contents

Chapter 1 Introduction

List of Figures

List of Tables

Nomenclature

BOC	Brin's Oxygen Company
CAPRI	Catalyst, Petroleum Research Institute
CCO	Combustion Cell Oil
CHOPS	Cold Heavy-Oil Production with Sand
CSS	Cyclic Steam Stimulation
CTO	Catalyst-To-Oil
DDS	Direct Desulphurization
DMDS	Di-Methyl Di-Sulphide
DMDBT	Dimethyl Dibenzo-Thiophene
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectra
DCM	DiChloro-Methane
EDX	Energy-dispersive X-ray spectroscopy
EOR	Enhanced Oil Recovery
ES-SAGD	Expanding Solvent Steam Assisted Gravity Drainage
ESR	Electron Spin Resonance
FCC	Fluid Catalytic Cracking
FID	Flame Ionization Detector

FTIR	Fourier Transform Infra Red
GC	Gas Chromatography
GC-FID	Gas Chromatography-Flame Ionization Detection
GOR	Gas to Oil Ratio
HC	Hydrocarbon
HCO	Heavy Cyclic Oil
HCR	Hydrocracking
HDA	Hydrodeasphaltenization
HDM	Hydrodemetallization
HDN	Hydrodenitrogenation
HPLC	High Pressure Liquid Chromatography
HDS	Hydrodesulphurization
HDT	Hydrotreating
HTO	High Temperature Oxidation
HYD	Hydrogenation
IEA	International Energy Agency
IFP	Institut Français du Pétrole
ISC	*In Situ* Combustion
LDOD	Long Distance Oil Displacement

LHSV	Liquid Hourly Space Velocity
LTO	Low Temperature Oxidation
MAT	Micro Activity Test
MEOR	Microbial Enhanced Oil Recovery
mbpd	Mbpd
MN	Methyl Naphthalene
MOZ	Mobile Oil Zone
OOIP	Original Oil In Place
PDVSA	Petróleos de Venezuela
RGA	Refinery Gas Analyzer
SAGD	Steam Assisted Gravity Drainage
SAGP	Steam and Gas Push
SARA	Saturates, Aromatics, Resins and Asphaltenes
SDOD	Short Distance Oil Displacement
SEM	Scanning Electron Microscopy
SG	Specific Gravity
SIMDIS	Simulated Distillation
STARS	Steam, Thermal and Advanced Processes Reservoirs Simulator
STEM	Scanning Transmission Electron Microscopy

TBP	True Boiling Point
TCD	Thermal Conductivity Detector
TEM	Transmission Electron Microscopy
TGA	Thermal Gravimetric Analysis (not in text)
THAI	Toe-to-Heel Air Injection
THSF	Toe-to-Heel Steam Flood
TTHW	Toe-To-Heel Waterflooding
TTH	Toe-to-Heel
TTHD	Toe-to-Heel Displacement
VAPEX	Vapour Extraction
VIVP	Vertical Injection Vertical Producer
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
NMR	Nuclear Magnetic Resonance
SEC	Size Exclusion Chromatography
UVF	Ultra-Violet Fluorescence
VGO	Vacuum Gas Oil

Symbols

β, γ	Beta and Gamma (Parameter)

η	Eta, Effectiveness Factor
μ	Micro, liquid measuring unit

Chapter 1

Introduction

1.1 Heavy Oil and Bitumen Recovery and Upgrading Background

The worldwide production of conventional crude oil is expected to reach its peak in the second decade of this century and subsequently enter a phase of permanent decline (Stosur *et al.*, 1998). This situation is further aggravated by the fact that the composition of the oil barrel is already getting heavier and diluent blending, assisted by very limited coke upgrading capacity will eventually be insufficient to cope with the increasing demand for light oil. The current strain on the supply and demand of light crudes can readily be met by Heavy oils and bitumen. With estimated reserves of heavy oil (estimated 3396 Billion Barrels Oil, BBO) and bitumen (estimated 5505 BBO) exist throughout the world (Meyer et al, 2007), with about 55–65% of these huge reserves are found in Canada and Venezuela (Curtis et al, 2002). These reserves may account for more than three times the remaining combined world reserves of conventional oil and gas.

Heavy oils are asphaltic, dense and viscous, having an American Petroleum Institute (API) gravity of between 10 and 20° and a viscosity of greater than 0.1 Pa.s. Bitumens or oil sands are yet more dense and viscous with API gravity less than 10° and viscosities usually greater than 10 Pa.s (Curtis *et al.*, 2002). The elevated viscosity and density of these non-conventional crude oils demand more energy intensive operations not only for their production and upgrading but also for transportation and consequently they are more costly to extract. Yet, with 6 trillion barrels of unexploited oil in place, they present a much under-used resource and with oil prices rising, production is becoming economically viable. To exploit heavy oil and bitumen reservoirs, the petroleum industry has in the past relied on cold production methods, predominantly surface mining. More recently a variety of Enhanced Oil

Recovery (EOR) technologies have been proposed and developed. Success has varied with recovery levels ranging from as low as 10% with Water Flooding, and up to 70% with Steam Assisted Gravity Drainage (SAGD) and potentially to greater than 80% with Toe-to-Heel Air Injection (THAI) (Shah et al, 2010). SAGD is the most commercialized technique at present, however, the use of large amounts of water and energy are potential disadvantages of SAGD (Donnelly and Pendergast, 1999).

With the exception of steam injection in the initial stages Toe-to-Heel Air Injection (THAI) is a novel in-situ combustion technique, where only air is injected once the process is started up. This is contrary to SAGD where steam is injected throughout the process life time, making it a more energy intensive technology. In THAI a small fraction of the oil in the reservoir (Less than 10%) is burnt in order to mobilize the heavy immobile oil towards the horizontal production well (Greaves and Xia, 2000). The thermally cracked heavy oil produced during the process, not only aids oil recovery but also has the added benefit of upgrading the oil (Xia *et al.*, 2002). This added side-effect of THAI is not only beneficial for the actual oil recovery but also aids transportation, downstream refining and subsequently increases the commercial value of the produced oil. Experimental and field pilot results indicate sulphur and heavy metal content is reduced in the produced oil with THAI (Petrobank, 2008).

Catalyst, Petroleum Research Institute (CAPRI) is the catalytic extension to THAI whereby placing an annular layer of catalyst around the perforated horizontal producer well, additional upgrading of heavy oils and bitumen can be achieved (Xia and Greaves, 2001; Greaves et al, 2000). A number of potential catalytic upgrading reactions including the water gas shift and/or gasification reactions and the resultant hydrogen production are believed to be responsible for the upgrading of heavy oil and bitumen (Hajdo *et al.*, 1985).

In summary, in situ combustion process such as THAI-CAPRI creates ideal conditions for in-situ catalytic upgrading (Weissman, 1997; Moore *et al.*, 1999), and the reactor-upgrader is virtually free by virtue of the reservoir conditions, which already establish the necessary high temperature and pressure (ca. 400-600°C, 20-40 bar for Athabasca Oil Sands). Previously, Xia and Greaves (2001) demonstrated the capability of THAI-CAPRI to upgrade a Wolf Lake Heavy Oil using 3D combustion cell tests. Even without a catalyst, thermal cracking conversion could upgrade Wolf Lake crude oil from 10.9°API to around 20° API. CAPRI tests using Hydrodesulphurization (HDS) catalyst (not pre-sulphided) showed that the THAI oil could be further upgraded by an additional 4-8 °API.

In previous 3D combustion cell tests (Xia and Greaves, 2001), the catalyst in the active part of the horizontal reactor section was only exposed to the reactant fluid for about one to two hours, during the overall run time of 10-15 hours. Whilst during the field scale the catalyst activity needs to be maintained over much longer operating periods than in the 3D combustion cell reactor, whilst the Mobile Oil Zone (MOZ) moves through the active section of catalyst. THAI has been extensively documented in the literature; however results with CAPRI are limited especially at reservoir conditions such as pressures of 20-50 bar. Therefore it is necessary to understand how process conditions can be optimized to avoid catalyst deactivation, and to maximize conversion. The above issues are addressed in the objectives of this work.

1.2 Objectives of the Present Study

The main objectives of the current study are as follow;

1. To test different types of refinery catalysts for the upgrading of THAI field oil, Combustion Cell Oil (CCO) and n-decane.
    a. Optimizing the best catalyst by testing a number of different catalysts and maintaining catalytic activity for as long as possible.

   b. Investigating the effect of catalyst in the upgrading of produced oil qualities in terms of viscosity, American Petroleum Institute Gravity (API) gravity, boiling point shift, hydrodesulphurization, hydrodemetallization and Saturates, Aromatics, Resins and Asphaltenes (SARA) distribution.
   c. Understanding the deactivation of catalyst by coke and heteroatoms
2. Optimizing reaction conditions, such as temperature, pressure, reaction gases, oil flow rate, gas flow rates, catalyst concentration
3. Effect of water gas shift reaction
4. Understanding the overall upgrading mechanism of the CAPRI process

1.3 Thesis Layout

An introduction and background information about the current work is provided in Chapter 1. Literature review is presented in Chapter 2, which covers details about heavy oils and bitumen, their chemistry, current technological challenges in their recovery and upgrading. Some of the current technologies currently used to recover these resources have also been presented. Emerging technologies such as THAI/CAPRI are presented in detail and their potential benefits compared with other technologies. The Chapter closes with some desirable catalyst and their respective properties along with deactivation challenges during heavy oil upgrading.

Chapter 3 describes the methods and materials used in this work. This chapter also provides detail information about the analytical methods used and their significance.

Results for the main feed used in this work i.e. the THAI field oil have been presented in Chapter 4. The Chapter provides almost all the experimental variables such as effect of catalyst type, temperature, pressure etc investigated in this work in detail. Chapter 5 presents experimental variables studied for the second feed i.e. the CCO.

Chapter 6 presents the chemistry of oil upgrading, where using a number of analytical techniques the chemistry of oil upgrading has been investigated.

In Chapter 7 analysis of coke on coked catalysts from THAI field oil have been presented. This is followed by the final Chapter of the thesis Chapter 8; where conclusions of the present work along with some future work recommendations have been provided.

Chapter 2 Literature Review

Chapter Overview

The chapter opens with an introduction about heavy oils and natural bitumens, their relative abundance and significance in Section 2.1. The chemistry of petroleum has been described in detail in Section 2.2. Current technological challenges in the recovery of heavy oils and bitumen are presented in Section 2.3. Recovery methods are divided in two sections of primary and secondary recovery techniques. Primary recovery techniques for heavy oils and bitumen are presented in Sections 2.4.1-2.4.4. Secondary or Enhanced Oil Recovery (EOR) techniques are presented in Sections 2.5-2.10. This section also includes emerging technologies THAI^{TM} and CAPRI^{TM}.

Some suitable catalysts for heavy oil and bitumen upgrading and their respective properties are provided in Section 2.11. Catalyst deactivation mechanism is presented in detail in Section 2.12.

Towards the end of the Chapter a comparison and evaluation of different EOR techniques is presented in Section 2.13. This is followed by some conclusions and a rational for the current work.

2.1 Introduction to heavy oils and natural bitumen

Despite the volatility in the energy market at present, the International Energy Agency has projected that demand for oil will continue to rise from 87.3 mbpd at present (IEA, 2010) to 96 mbpd by 2035 (IEA, 2010). To meet this demand, conventional light crude oils have been predominantly used due to their relative ease of production. However, this has resulted in light oils accounting for a declining share of the World's remaining oil reserves. Therefore, attention has switched to alternative sources, of which heavy crude oil and natural-bitumen are perhaps the most readily available to meet short- and long-term needs (Chen, 2006).

Unlike conventional light oils (typically having an API* gravity of greater than 25°), heavy oils are asphaltic, dense and viscous oils having an API gravity of between 10 and 20 °API and a viscosity greater than 0.1 Pa.s. Bitumens or oil sands share similar attributes to heavy oil but are yet more dense and viscous with API gravity less than 10 °API and viscosities usually greater than 10 Pa.s (Meyer *et al.,* 2007). The elevated viscosity and density of these non-conventional crude oils demand more energy intensive operations not only for their production and upgrading but also for transportation and consequently they are more costly to extract.

Light or conventional oils (Figure 2.1) are many times lower in viscosity than heavy oils or bitumen (Figure 2.2). However it is not possible to define natural bitumen on the basis of viscosity alone because much of it, defined on the basis of gravity, is less viscous than 10 Pa.s. Fundamental differences exist between natural bitumen, heavy oil, medium oil, and conventional (light) oil, according to the volatilities of the constituent hydrocarbon fractions: paraffinic, naphthenic, and aromatic. When the light fractions are lost through natural processes after evolution from organic source materials, the oil becomes heavy, with a high proportion of asphaltic molecules, and with substitution in the carbon network of heteroatoms

---

[*] API gravity stands for American Petroleum Institute gravity and is calculated by using the equation —— , where SG is specific gravity

such as nitrogen, sulphur, and oxygen. Therefore, heavy oil, regardless of source, always contains the heavy fractions, the asphaltics, which consist of resins, asphaltenes, and pre-asphaltenes (the carbene-carboids) (Yen, 1984). Geologically, several processes leading to the formation of heavy oil and bitumen have been proposed. Most heavy oil and natural bitumen is thought to be expelled from source rocks as light or medium oil and later converted to heavier components by bacterial degradation in subsurface reservoirs (Head *et al.,* 2003; Larter *et al.,* 2003 and 2006). Heavy oils are asphaltic, dense and viscous oils having an API gravity of between 10 and 20 °API and a viscosity greater than 0.1 Pa.s. Bitumens or oil sands share similar attributes to heavy oil but are yet more dense and viscous with API gravity less than 10 °API and viscosities usually greater than 10 Pa.s (Meyer *et al.,* 2007). The elevated viscosity and density of these non-conventional crude oils demand more energy intensive operations not only for their production and upgrading but also for transportation and consequently they are more costly to extract. Yet, with estimated reserves of 3,396 billion barrels of heavy oil [concentrated predominantly in Venezuela in the Orinoco heavy-oil belt, (Jayasekera and Goodyear, 2000)] and 5,505 billion barrels of bitumen (principally in Alberta, Canada), they present a much under-used resource and with oil prices rising, production is becoming economically viable. Some of the world's important geological basins of heavy oils and natural bitumen have been provided in Table 2.1 and 2.2 (Meyer *et al.,* 2007).

Figure 2.1 Light or Conventional Oil

Figure 2.2 Heavy Oil/Bitumen

Table 2.1 Heavy Oil Geological Basins

Heavy Oil		
Rank	**Region**	**Total BBO in place**
1	Arabian	842
2	Eastern Venezuela	593
3	Maracaibo	322
4	Compeche	293
5	Bohai Gulf	141

Table 2.2 Natural Bitumen Geological Basins

Bitumen		
Rank	**Region**	**Total BBO in place**
1	Western Canada Sed.	2330
2	Eastern Venezuela	2090
3	North Caspian	421
4	Volga-Ural	263
5	Maracaibo	169

2.2 The Chemistry of Petroleum

Petroleum is not a uniform material. In fact, its chemical and physical (fractional) composition can vary not only with the location and age of the oil field but also with the depth of the individual well. Indeed, two adjacent wells may produce petroleum with markedly different characteristics. On a molecular basis, petroleum is a complex mixture of hydrocarbons with small amounts of organic compounds containing sulphur, oxygen, and nitrogen, as well as compounds containing metallic constituents, particularly vanadium nickel, iron, and copper. The hydrocarbon content may be as high as 97% w/w, for example in the lighter paraffinic crude oil or as low as 50% w/w in heavy crude oil and bitumen. It will retain most of the essential characteristics of the hydrocarbons even though the non-hydrocarbon portion of the crude may actually consist of molecules containing one or perhaps two atoms of elements other than carbon and hydrogen (Gruse and Stevens, 1960). From ultimate elemental composition of a typical crude oil, it appears that the proportions of the elements in petroleum vary over fairly narrow limits; despite the wide variation in physical properties from the lighter, more mobile crude oils at one extreme to the heavier asphaltic crude oils at the other extreme (Charbonnier *et al.,* 1969; Draper *et al.,* 1977). The elemental analysis of oil sands bitumen has also been widely reported (Camp, 1976; Bunger *et al.,* 1979; Meyer and Steele, 1981). Like conventional petroleum, of the data that are available the elemental composition of oil sand bitumen is generally constant and, like the data for petroleum, falls into a narrow range (Table 2.3):

Table 2.3 Elemental Analysis of Light and Heavy Oils

Light Crude Oils		Oil Sand Bitumen	
Carbon	83.0– 87.0%	Carbon	83.4 %
Hydrogen	10.0– 14.0%	Hydrogen	10.4%
Nitrogen	0.1– 2.0%	Nitrogen	0.4-0.5%
Oxygen	0.05– 1.5%	Oxygen	1.0 0.2%
Sulphur	0.05– 6.0%	Sulphur	5.0 0.5%
Metals (Ni and V)	1000 ppm	Metals (Ni and V)	1000 ppm

The major exception to these narrow limits is the oxygen content of bitumen, which can vary from as little as 0.2% to as high as 4.5%.

Several generalities can be noted from the elemental composition; these can only give indications of how the material might behave during processing. The viscosity of bitumen is related to its hydrogen-to-carbon atomic ratio and hence the required supplementary heat energy for thermal extraction processes. An atomic hydrogen-to-carbon ratio of 1.5 is more typical. The higher the hydrogen-carbon ratio of bitumen, the higher is its value as refinery feedstock because of the lower hydrogen requirements. The occurrence of sulphur in bitumen as organic or elemental sulphur or in produced gas as compounds of oxygen and hydrogen is an expensive nuisance. It must be removed from the bitumen at some point in the upgrading and refining process (Speight, 1994).

The nitrogen content of tar sand bitumen, as high as 1.3% w/w, complicates the refining process by poisoning the catalysts employed in the refining process. Elements related to nitrogen content are sulphur content, hydrogen content, hydrogen-carbon ratio, bitumen viscosity, distillation profile, and viscosity (Speight, 1994).

2.2.1 The Chemical Constituents of Petroleum

The precise chemical composition of many of the heavier feedstocks is, despite the large volume of work performed in this area, largely speculative (Speight, 1999). In very general terms (and as observed from elemental analyses), petroleum, heavy oil, bitumen, and residua are a made of: (a) hydrocarbons; (b) sulphur compounds (c) nitrogen compounds; and (d) metallic constituents.

(a) Hydrocarbon Components: It has been well established that the hydrocarbon components of petroleum are composed of the following three classes:

1. Paraffins: These are saturated hydrocarbons with straight or branched chains, but without any ring structure. The proportion of paraffins in crude oils varies with the type of crude, but

within any one crude oil, the proportion of paraffinic hydrocarbons usually decreases with increasing molecular weight. Paraffins usually exist in the boiling range of 150– 350°C in crude petroleum (Speight, 1999).

2. Naphthenes: These are saturated hydrocarbons containing one or more rings, each of which may have one or more paraffinic side chains but generally five and six membered rings are the more common and stable in crude oils (more correctly known as alicyclic hydrocarbons). Their boiling range in crude oil is usually 150– 200°C. Cyclohexane, cyclopentane, and decahydronaphthalene derivatives are largely represented in oil fractions (Speight, 1999). Petroleum also contains polycyclic naphthenes, such as terpenes, and such molecules (often designated bridge-ring hydrocarbons) occur even in the heavy gasoline fractions. In the asphaltic (naphthenic) crude oils, the gas oil fraction can contain considerable amounts of naphthenic ring systems that increase even more in consideration of the molecular types in the asphaltenes. However, as the molecular weight of the fraction increases, the occurrence of condensed naphthene ring systems and alkyl-substituted naphthene ring systems increases. There is also the premise that the naphthene ring systems carry alkyl chains that are generally shorter than the alkyl substituents carried by aromatic systems. This can be reflected on hypothetical structures for the asphaltene constituents. In the asphaltene fraction, free condensed naphthenic ring systems may occur but general observations favor the occurrence of combined aromatic-naphthenic systems that are variously substituted by alkyl systems. There is also general evidence, that the aromatic systems are responsible for the polarity of the asphaltene constituents. The heteroatoms are favored to occur on or within the aromatic (pseudo-aromatic) systems.

3. Aromatics: These are hydrocarbons containing one or more aromatic nuclei, such as benzene, naphthalene, and phenanthrene ring systems, which may be linked up with (substituted) naphthene rings and/or paraffinic side chains. cyclohexane, cyclopentane, and

decahydronaphthalene derivatives are largely represented in oil fractions. The occurrence of monocyclic and polycyclic aromatic systems in natural product chemicals is well documented (Sakarnen and Ludwig, 1971; Durand, 1980; Weiss and Edwards, 1980). However, one source of aromatic systems that is often ignored is petroleum (Eglinton and Murphy, 1969; Tissot and Welte, 1978; Brooks and Welte, 1984). There is a general increase in the proportion of aromatic hydrocarbons with increasing molecular weight. In the higher molecular weight fractions, the rings are usually condensed together. In summation, all hydrocarbon compounds that have aromatic rings, in addition to the presence of alkyl chains and naphthenic rings within the same molecule are classified as aromatic compounds.

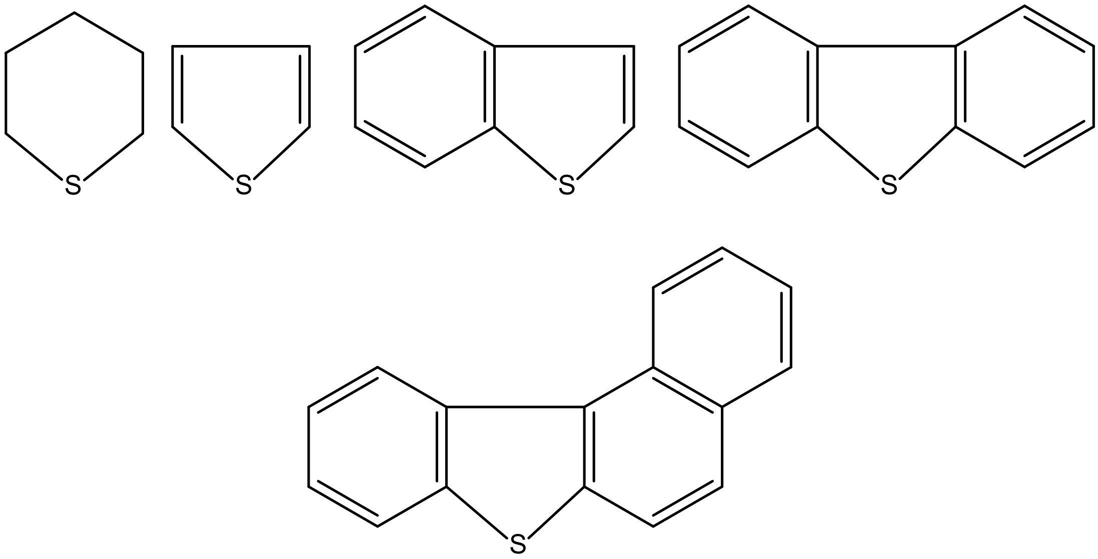
It should also be emphasized that in the higher boiling point petroleum fractions, many polycyclic structures occur in naphthenoaromatic systems. The naphthenoaromatic hydrocarbons, together with the naphthenic hydrocarbon series, form the major content of higher boiling point petroleum fractions. Usually the different naphthenoaromatic components are classified according to the number of aromatic rings in their molecules. Tetralin and methyl, dimethyl, methylethyl, and tetramethyltetralins have been found in several crude oils, particularly in the heavier, naphthenic, crude oils. Of special interest in the present context are the aromatic systems that occur in the nonvolatile asphaltene fraction (Speight, 1994b). These polycyclic aromatic systems are complex molecules that fall into a molecular weight and boiling range where very little is known about model compounds. There has not been much success in determining the nature of such systems in the higher boiling constituents of petroleum, i.e., the residua or nonvolatile constituents. In fact, it has been generally assumed that as the boiling point of a petroleum fraction increases, so does the number of condensed rings in a polycyclic aromatic system.

(b) Sulphur Compounds: Sulphur compounds are among the most important heteroatomic constituents of petroleum, and although there are many varieties of sulphur compounds

(Figure 2.3), the prevailing conditions during the formation, maturation, and even *in situ* alteration may dictate that only preferred types exist in any particular crude oil. In general, the higher the density of the crude oil or the lower the API gravity of the crude oil, the higher the sulphur content. The total sulphur in the crude can vary from 0.04% w/w for a light crude oil to about 5.0% w/w for a heavy crude oil.

The distribution of the various types of sulphur compounds varies markedly among crude oils of diverse origin, but fortunately some of the sulphur compounds in petroleum undergo thermal reactions at relatively low temperatures. If elemental sulphur is present in the oil, a reaction, with the evolution of hydrogen sulphide begins at about 150°C. This reaction becomes very rapid at 220°C, but organically bound sulphur compounds do not yield hydrogen sulphide until higher temperatures are reached. Hydrogen sulphide is, however, a common constituent of many crude oils, and some crude oils with 1% w/w sulphur are often accompanied by a gas having substantial properties of hydrogen sulphide. The identification of sulphur-containing constituents of crude oils has been the subject of many investigations with the result that many of the sulphur compound types that occur in crude oils are now known (Thompson *et al.,* 1976). These vary from the simple thiols (R-SH) to the simple sulphides (R-S-R) and the polycyclic sulphides, such as compounds with two condensed rings. Various thiophenes have also been isolated from a variety of crude oils; benzothiophene derivatives are usually present in the higher boiling petroleum fractions.

Figure 2.3 Various Verities of Sulphur Compounds found in Crude Petroleum



(c) Nitrogen Compounds Nitrogen in petroleum may be classified arbitrarily as basic and nonbasic. The basic nitrogen compounds (Figure 2.4), which are composed mainly of pyridine homologues and occur throughout the boiling ranges, have a decided tendency to exist in the higher boiling fractions and residua. The nonbasic nitrogen compounds, which are usually of the pyrrole, indole, and carbazole types, also occur in the higher boiling fractions and residua. In general, the nitrogen content of crude oil is low and generally falls within the range 0.1–0.9% w/w, although early work indicates that some crudes may contain up to 2% w/w nitrogen (Speight, 1999). In general the more asphaltic the oil, the higher its nitrogen content. In so far as an approximate correlation exists between the sulphur content and API gravity of crude oils there also exist a correlation between nitrogen content and the API gravity of crude oil.

It also follows that there is an approximate correlation between the nitrogen content and the carbon residue: the higher the carbon residue, the higher the nitrogen content. Nitrogen compounds can be responsible for the poisoning of cracking catalysts. The trend in recent years toward cutting deeper into the crude to obtain stocks for catalytic cracking has accentuated the harmful effects of the nitrogen compounds, which are concentrated largely in the higher boiling portions.

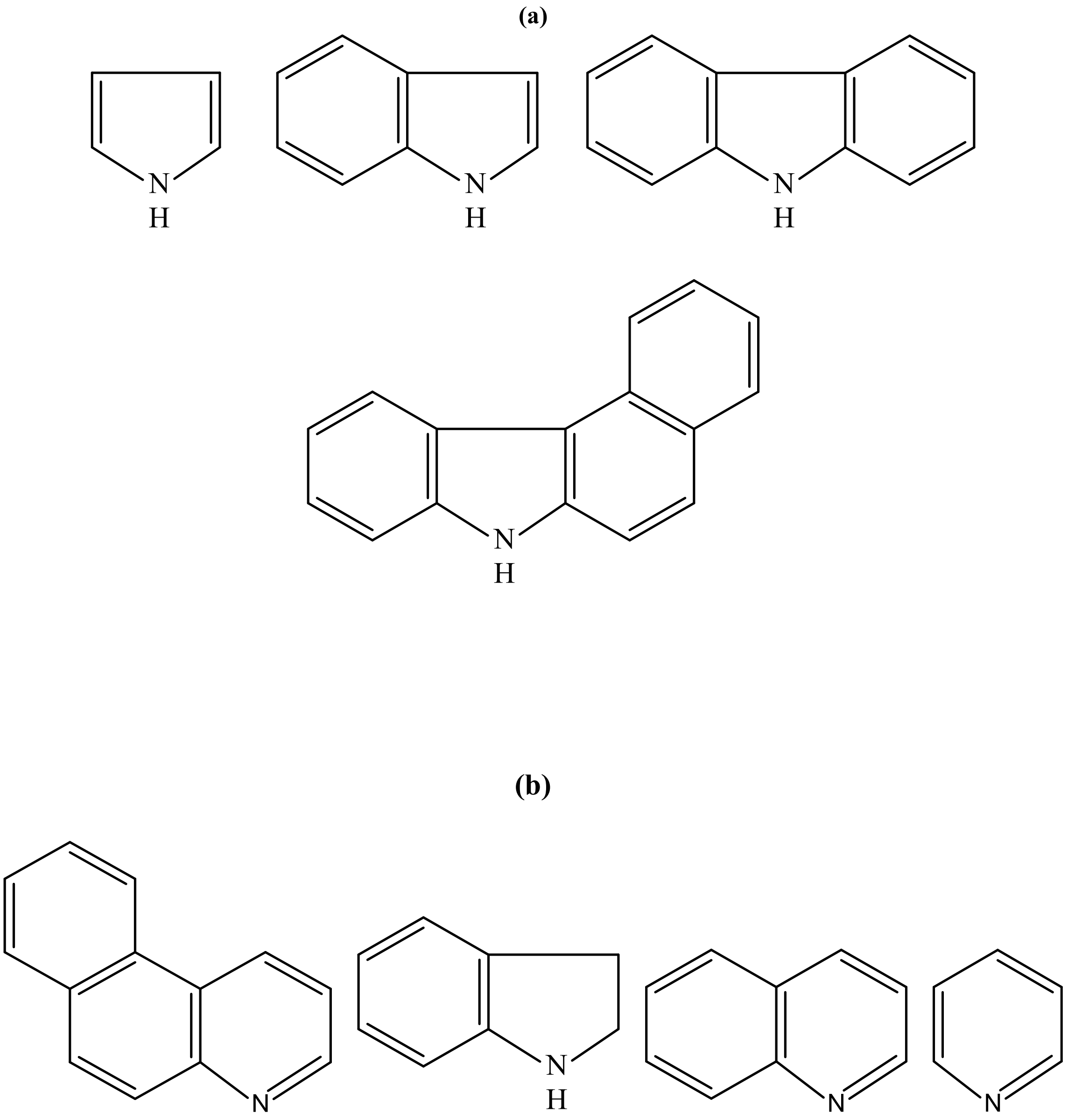
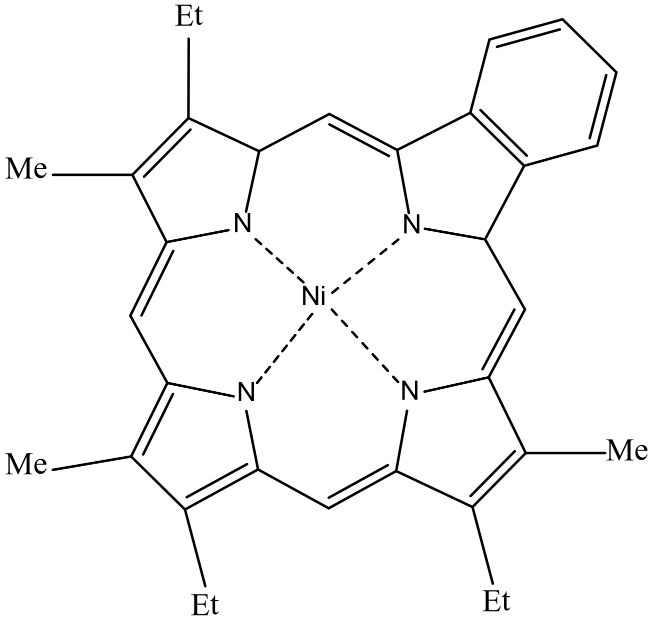


Figure 2.4 Nitrogenous Compounds found in Petroleum Crudes (a) Basic (b) Non-Basic

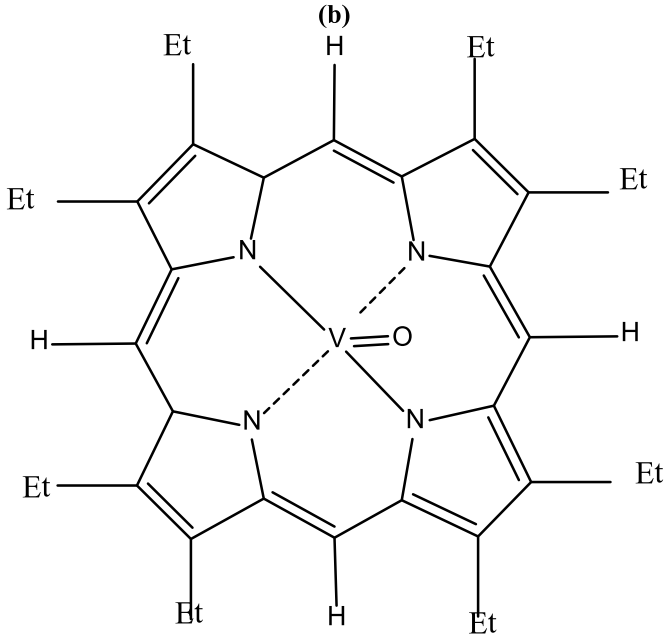
Porphyrins: Porphyrins usually occur in the non-basic portion of the nitrogen-containing concentrate. Almost all crude oils and bitumens contain detectable amounts of nickel and vanadyl porphyrins (Figure 2.5a and b). More mature, lighter crude oils usually contain only small amounts of these compounds. Heavy oils may contain large amounts of vanadyl and nickel porphyrins, while the absence of porphyrins chelated with metals other than nickel and vanadium in most crude oils and tar sand bitumen have been related to geochemical reactions during crude oil formation (Hodgson *et al.,* 1967; Baker, 1969; Baker and Palmer, 1978; Baker and Louda, 1986; Filby and Van Berkel, 1987; Quirke, 1987). Not all nickel and vanadium exists as porphyrins (Dunning *et al.,* 1960; Reynolds, 1997) and only rarely can all measured nickel and vanadium in a crude oil be accounted for as porphyrinic (Erdman and Harju, 1963).

Figure 2.5 Porphyrins (a) Nickel and (b) Vanadium

(a)



(b)



(d) Metallic Constituents: Metallic constituents are found in every crude. Metals affect many upgrading processes and cause particular problems because they poison catalysts used for sulphur and nitrogen removal as well as other processes such as catalytic cracking. Even minute amounts of iron, copper, and particularly nickel and vanadium in the charging stocks for catalytic cracking affect the activity of the catalyst and result in increased gas and coke formation and reduced yields of gasoline. More particularly, damage by corrosion may be very severe. Metals are generally found only in the non-volatile portion of crude oil (Altgelt and Boduszynski, 1994; Reynolds, 1997). Distillation concentrates the metallic constituents in the residues (Reynolds, 1997), although some can appear in the higher boiling distillates, but the latter may be due in part to entrainment.

2.3 Technology Challenges in Recovering Heavy oil/Bitumen

In spite of an immense resource base, heavy oil and natural bitumen accounted for only about 3 billion barrels of the 25 billion barrels of crude oil produced in 2000. Compared to light oil, these resources are generally more costly to produce and transport. Also, extra-heavy oil and natural bitumen must usually be upgraded by reducing their carbon content or adding hydrogen before they can be used as feedstock for a conventional refinery. The extra production, transportation, and upgrading costs explain why development and production of extra-heavy oil and bitumen are still limited. Even though recovery rates are still low and boosting production poses a range of technical challenges, the potential contribution to supply is just as impressive. Total net production (net bitumen plus synthetic crude oil) from Canadian oil sands was 1.1 mbpd in 2005 and has been projected to rise to 4.2 mbpd in 2020 (Govinda *et al.,* 2005).

Historically, heavy oil was found incidentally during the search for light oil and was produced by conventional methods when economically feasible. However, to sustain commercial well production rates, heavy and extra-heavy oil production almost always requires measures to reduce oil viscosity and to introduce energy into the reservoir. Extra-heavy oil commonly requires the addition of diluents (gas condensate, natural gas liquids, or light crude) to enable the oil to be transported by pipeline. Extra-heavy oil must also be chemically upgraded to reduce density and remove contaminants before it can be used as refinery feedstock. In recent projects in the Venezuelan Orinoco heavy oil belt, 1 barrel of diluents is required for every 3 or 4 barrels of extra-heavy oil produced. Natural bitumen is so viscous that it is immobile in the reservoir. For oil sand deposits less than 225 feet deep, bitumen is recovered by mining the sands, then separating the bitumen from the reservoir rock by processing it with hot waters, and finally upgrading the natural bitumen onsite to a synthetic crude oil. In deeper oil sand deposits, where the bitumen is commonly less viscous, various *in situ* techniques are used to mobilize the oil for recovery by production wells. The product may be upgraded on site or mixed with a diluent and transported to an upgrading facility (Meyer and Attanasi, 2003).

To exploit heavy oil and bitumen reservoirs, the petroleum industry has in the past relied on cold production methods, predominantly surface mining. More recently a variety of Enhanced Oil Recovery technologies have been proposed and developed. Success has varied with recovery levels ranging from as low as 10% (waterflooding) and up to 70% with steam assisted gravity drainage (SAGD) and potentially to greater than 80% with toe to heel air injection (THAI). Enhanced Oil Recovery or (EOR) techniques can be broadly classified into either thermal or non-thermal methods and their suitability to a particular project is usually dependent on the reservoir location as well as oil composition. This literature review aims to explore these diverse techniques and assess their relative advantages and disadvantages. In addition, the potential added benefit of upgrading heavy oils and bitumens by downhole catalytic processes is examined. Previous laboratory experimental works with *in situ* combustion (conventional and non-conventional processes) have been discussed in detail. Conclusions from the literature and objectives for this work have been derived at the end of the chapter.

2.4 Recovery Methods

Primary and Secondary Recovery Methods

Traditionally, the production of heavy oils and bitumens has been dominated by cold production from reservoirs that are either relatively close to the surface (as is in the case of Canadian oil sands) or easy to flow (as in the case of the lighter Venezuelan heavy oils). Since they are generally well understood techniques, they are seen as low-risk, primary or secondary production methods which may be followed up by alternative techniques to achieve higher recoveries.

2.4.1 Surface Mining

Surface mining has been operated extensively from open-cast mines in Canada (Figure 2.6 a) since 1967, although heavy oil has also been recovered by subsurface mining in Russia (Meyerhoff and Meyer, 1987). Canadian oil sands deposits are composed of sand, silt, clay, water and approximately 10-12% bitumen (Alberta Energy, 2004) and about 12% of the total reserves are located in sufficient quantity at shallow depths to make the process economical. In the Athabasca deposit, an area of 2,800 km^2 (about 53 x 53 km^2) has been identified as surface mineable (Alberta Energy and Utilities Board, 2004).

After excavation, hot water and caustic soda (NaOH) is added to the extracted material. The combination of hot water and agitation releases bitumen from the oil sand, and allows small air bubbles to attach to the bitumen droplets. The resulting bitumen froth can then be skimmed from the top (Oil discovery centre, 2010). Approximately four tonnes of material, including two tonnes of soil and rock above the deposit and two tonnes of oil sands, must be mined to produce one barrel of synthetic crude oil. In terms of recovery the process is very efficient though and around 90% of the bitumen found in the deposit is recovered (National Energy Board, 2004).

However, mining is strictly limited by the depth of the reservoir and it is estimated that approximately 80% of the Alberta oil sands and nearly all of the Venezuelan sands are too far below the surface to allow open-cast mining. In addition, the process is associated with severe environmental problems: Wetlands need to be drained, rivers diverted, and all trees and vegetation stripped from the surface (Figure 2.6 (b); Woynillowicz *et al.,* 2005). Many improvements are being implemented to reduce any environmental damage, but longer term exploitation of the vast oil sands deposits will require implementation of advanced *in situ* recovery methods.

Mining and certain *in situ* operations, such as SAGD, each use large volumes of water for extracting bitumen from the oil sands. Between 2 to 4.5 barrels of water are extracted, mainly from the Athabasca River, to produce each barrel of oil in a mining operation (National Energy Board, 2006). In 2006 approved oil sands mining projects were licensed to divert 370 million cubic metres of freshwater per year from the Athabasca River, and this could be increased to 529 million cubic metres with the addition of planned projects. Although processes such as SAGD use some recycling, most of the water ends up in tailings ponds. Despite requirements to utilise bird scaring devices, accidental contact with these tailing ponds has led to loss of wildlife, including the death of five hundred ducks (Nature Canada, 2008) due to the toxic nature of the water. Concerns have also been raised regarding air pollution from the tar sands. For example, in 2007 the Alberta government issued an order to Suncor Energy Inc. to take immediate steps to address unacceptable levels of hydrogen sulphide emissions at its site near Fort McMurray (Alberta Information Bulletin, 2007). A further concern regarding surface mining is the vast areas of land which need to be disturbed in order to extract the bitumen. The Alberta government figures stated that there are approximately 42000 hectares of disturbed land in the area, whilst 6500 hectares are undergoing reclamation (Alberta Govt. Information Bulletin, 2010).

Figure 2.6 (a) Bitumen is Extracted by Mining (Courtesy of National Geographic)

(b) A Stripped off Land to Allow the Mining of Bitumen (Courtesy of National Geographic)

2.4.2 Cold Production

Where the oil viscosity is sufficiently low to flow at reservoir conditions, heavy oils can be produced from boreholes by primary cold production. Much of the oil in the Orinoco heavy-oil belt in Venezuela is currently recovered in this way, as are reservoirs offshore of Brazil (Pinto *et al.,* 2003). Horizontal and multilateral wells are drilled in order to contact as much of the reservoir as possible (Stalder *et al.,* 2001) and diluents, such as naphtha, are injected to decrease fluid viscosity further. In order to lift the oil to the surface electrical submersible pumps and progressing cavity pumps, are employed (Robles, 2001).

The key advantage of the method is the considerably lower capital expenditure relative to thermally assisted techniques; however it is severely limited by the suitability of reservoirs. Significantly though, recovery factors are poor, typically in the region of 5-6% (Babusiaux, 2007) although that may be increased to 10% by the use of horizontal wells; that has to be weighed against the additional costs which are around 3 to 5 times higher than conventional vertical wells. In either case, a considerable quantity of unrecovered oil is left in place and reservoirs may be viable for further exploitation by more efficient methods.

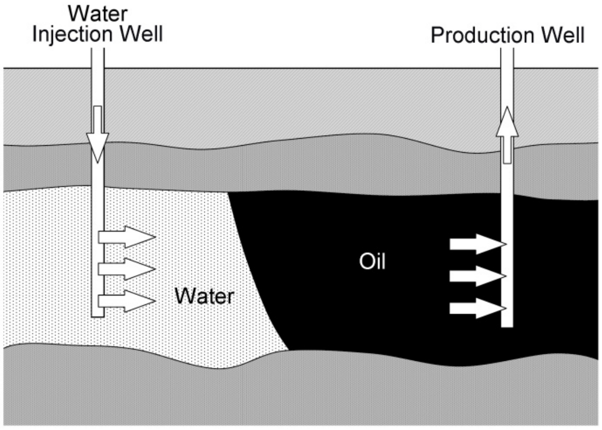
In order to utilise the bitumen produced in Venezuela, the company PDVSA developed Orimulsion fuel, which is a dispersion of bitumen and ~30% water, aimed specifically for boilers in applications such as power generation and industrial use (Bitumens Orinoco, 2010). In excess of 27 million tonnes were sold since 1990, with application in countries around the world. However, concerns about its environmental impact have been raised owing to the relatively high levels of sulphur, nickel and vanadium compared with other fuel oils. Miller and Srivastava (2000) carried out a survey, which showed that air emissions from the combustion of Orimulsion can depend upon plant-specific design and operational parameters, similar to emissions from other fossil fuels. Technologies such as Selective Catalytic Reduction, Flue Gas Desulphurisation and Electrostatic Precipitation are used to clean up the exhaust emissions from Orimulsion burning plants. However, concerns remain about the role of transition metals and particles that could be released from burning this fuel.

2.4.3 Water Flooding

Water flooding is more usually used as a secondary recovery process but has also been successfully employed as a primary technique in some heavy oil fields, notably on the UK Continental Shelf (Etebar, 1995; Jayasekera and Goodyear, 1999). Water is injected in a well and pushes the oil towards the producing wells where submersible pumps help raise the oil to the surface (Figure 2.7). Eventually the water front will reach the production well and increasingly larger quantities of water will be produced, making the process less economical until the producer well becomes watered-out. The use of horizontal injector and producer wells to allow in-line drive has improved the efficiency of the process by providing a more uniform pressure.

Unfortunately, water flooding tends to be less effective in reservoirs with an absence of underlying water as the injected water has a propensity to slump and channel along the base of the reservoir before coming into the producer (Babusiaux, 2007). Recovery factors of up to 20-40% have been achieved in light oil reservoirs, even up to 60%, but this decreases significantly with increasing oil viscosity due to channeling of the water flood front, resulting in poor sweep efficiency for all but the lightest heavy oils (Heavy oil info, 2010).

Figure 2.7 Cold Water Flooding



2.4.4 Cold Heavy-Oil Production with Sand (CHOPS)

Cold Heavy-Oil Production with Sand (CHOPS) modifies the more usual cold production technique where the completion zone of the well is designed to retain the crushed rock and sand which is carried to the well by the oil flow. This makes it easier to process the oil at the surface. Instead, CHOPS allows the sand to erode out of the well, thus extending highly permeable flow paths, or wormholes, through the reservoir to the well and thereby increasing production rates to 10 to 30 times that achieved in traditional cold production. The technique takes advantage of the fact that the World's heavy oil deposits are predominantly in high porosity (>28 %), unconsolidated sandstones that possess no tensile strength from grain-to-grain cementing and has been employed extensively in the Heavy Oil Belt straddling the Alberta-Saskatchewan border in Canada (Dusseault, 2002). Gas evolving from the depressurizing oil helps disturb and set the sand particles in motion and initially, a high percentage of sand is produced, as much as 40% sand by volume. However, this usually falls after a few months to 0.5 – 5 % by volume (Asghari, 2005). As sand and oil production continues, these wormholes continue to grow larger and extend further through the reservoir.

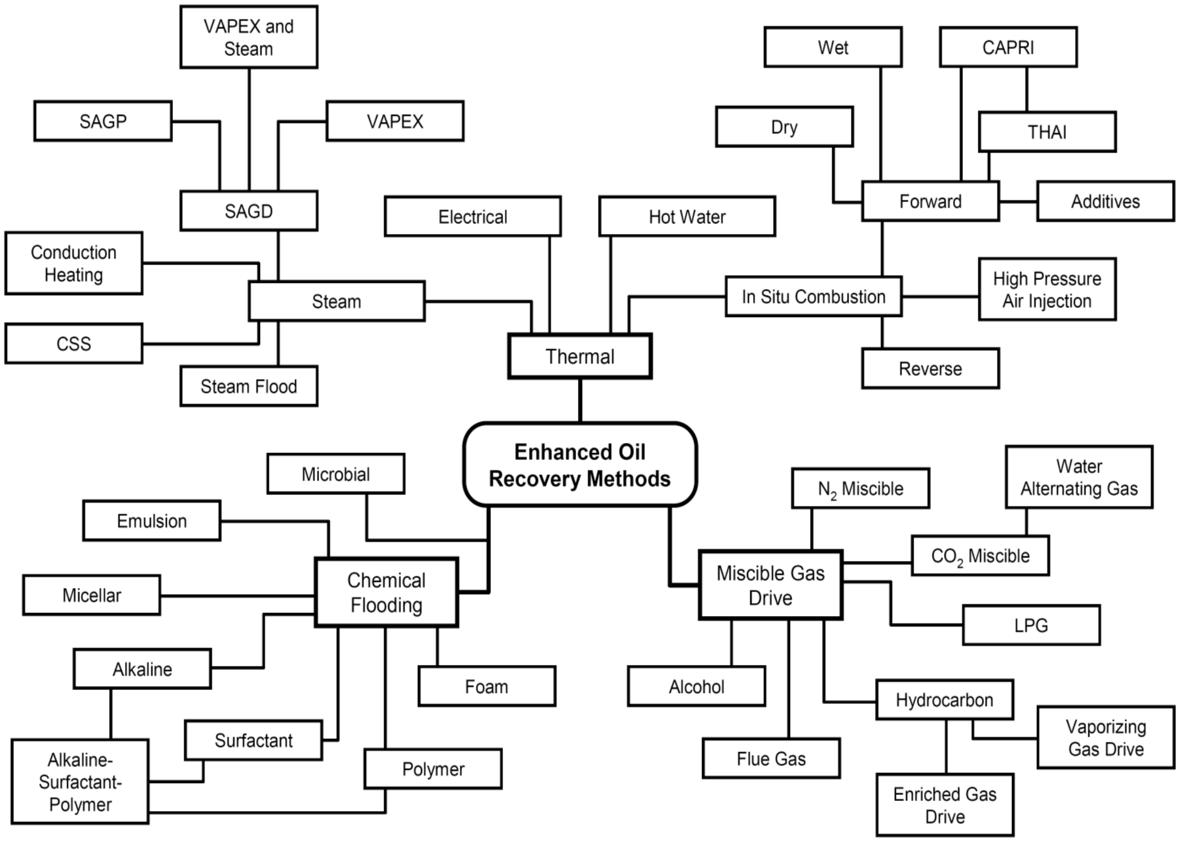
Typically, over 12% of oil in place can be recovered which is an improvement on traditional cold production. A major issue with CHOPS, however, is the separation of sand which is both mechanically and economically intensive due to the specialist fluid handling equipment necessary. The disposal of the large amounts of sand produced is also a problem and waste management can account for 15-35% of operating costs (Babusiaux, 2007). Moreover, if the expanding wormholes reach a water source, water will flow through these pathways and the production well will be filled of water, forcing its abandonment. A number of methods have been proposed to shut-off these watered-out wormholes by means of clay, polymer-gels and gel-foams with moderate success (Asghari, 2005).

2.5 Enhanced Oil Recovery (EOR) Technologies

Enhanced Oil Recovery or EOR is usually considered as the third stage of production where the oil left behind by the low risk primary and secondary methods is extracted. It is also commonly referred to as tertiary recovery or Improved Oil Recovery. In essence, EOR techniques improve oil displacement efficiency in the reservoir by reducing the viscosity of the oil to ease flow or by literally pushing it through the reservoir (Schumacher, 1980). A second objective is to improve sweep efficiency i.e. the more volume of oil inside the reservoir is contacted during extraction.

There are three major branches of Enhanced Oil Recovery: Miscible displacement, chemical flooding and thermal recovery, as illustrated in Figure 2.8. As a general guide, thermal processing is primarily intended for the highest viscosity oils and bitumens whereas fluid drive is most effective at the lighter end of the heavy oils with chemical processing sitting in between (Speight, 1999). However, reservoir geology and thickness also determine the suitability of a process.

Figure 2.8 Enhanced Oil Recovery (EOR) Technologies

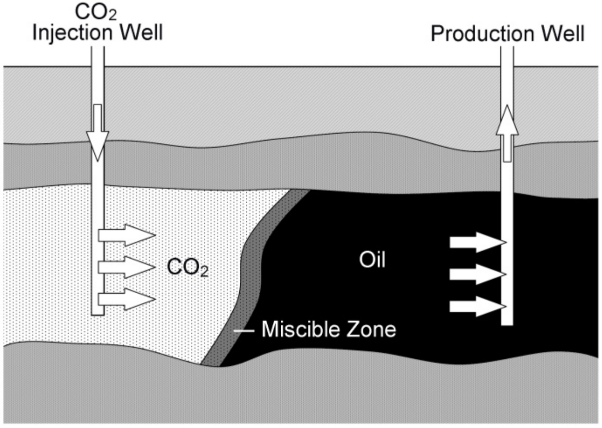


2.5.1 Miscible Displacement

Miscible displacement (also referred to as miscible flooding and miscible drive) involves injecting a fluid into the reservoir in a similar fashion to water flooding in that separate injector and producer wells are employed, as illustrated in Figure 6. However, a fluid is employed that dissolves in the oil either at first contact or after multiple contacts, significantly reducing interfacial tension and improving oil displacement on a microscopic level. In addition, reservoir pressure can be maintained, although allowing the expansion of dissolved gases can further aid oil flow. A narrow transition zone (mixing zone) develops between the displacing fluid and the reservoir oil, inducing a piston-like displacement. As the flood advances the mixing zone and the solvent profile spreads out.

Gases are generally used as the greater density difference between the oil and fluid improves sweep efficiency. Suitable injected gases include high pressure nitrogen, carbon dioxide, methane, methane enriched with light hydrocarbons and liquefied petroleum gas, such as propane. Process flue gas has also been employed as a low cost source of gas.

Figure 2.9 Miscible Gas Displacement



Gas displacement techniques are limited to relatively shallow deposits unless the deposit is sharply dipping as sweep efficiency is poor in the vertical plane. Furthermore, they need to be deep enough to allow high enough gas pressures, around 2,000 feet for the mildest techniques increasing to at least 5,000 feet for the highest pressure techniques (Leonard, 1986) The main problem, though, is that displacement efficiency decreases rapidly with increasing oil density and viscosity since fingering of the gas becomes problematic, hence the technique is only economical for the lighter end of heavy oils.

2.5.2 Carbon Dioxide Miscible Flooding

The use of carbon dioxide in the enhanced production of oil has been gaining prominence in recent years, partly due to the possibility of simultaneous sequestration of carbon dioxide (Holm, 1959) Carbon dioxide is a particularly attractive displacing agent because it has a relatively low minimum miscibility pressure in a wide range of crude oils. Strictly speaking, carbon dioxide is not truly miscible with the oil, instead the gas extracts light-to-intermediate components (C_5-C_{30}) from the reservoir oil and develops miscibility after multiple contacts. This leads to lowering of both the surface tension and viscosity of the oil to improve displacement.

Because of the very low viscosity of carbon dioxide, mobility control is poor and the gas tends to finger and break through to the producer well, leaving large areas of the reservoir unswept. To counter this, alternating volumes of gas and water (or brine) can be injected as slugs in what is known as the Water-Alternating-Gas (WAG) process. This approach tends to reduce the viscous instabilities. As well as the necessity of separating carbon dioxide from the oil, the main problems associated with carbon dioxide miscible flooding are the high gas requirements and the cost of repressurizing recycled gas (Picha, 2007). Asphaltene precipitation may also be a problem in some cases.

With increasing pressure for countries to reduce their emissions of greenhouse gases such as carbon dioxide, this method of oil recovery could potentially be a useful sink of carbon dioxide. This contrasts with other methods such as SAGD, which release significant quantities of carbon dioxide in the generation of steam. Lombardi *et al.,* (2006) reported pilot tests carried out in Russia to utilise carbon dioxide and combustion gases from different petrochemical plants to enhance heavy oil recovery in hydrocarbon fields. These combustion gases contain a mixture of components from partial and complete combustion, including carbon monoxide and dioxide, and could also contain inert gases such as nitrogen. The field data showed that much of the carbon monoxide injected in to oil reservoirs was recovered from the production wells during 1–1.5 years of the experiment. However the total amount of carbon dioxide which was irreversibly stored in the reservoir was not measured, illustrating that data regarding carbon dioxide flooding and storage are lacking in the public domain. More detailed studies of carbon dioxide interactions with oil, formation water and reservoir rocks are needed in order to understand mechanisms of carbon dioxide geological sequestration. Further studies of modeling carbon dioxide sequestration through EOR have been carried out, which have shown that project feasibility depends on a complex set of parameters including reservoir production profile, oil price, costs, capital and operating expenditures, carbon credits, depreciation time and fiscal assumptions (Ravagnani, 2009).

2.5.3 Nitrogen Miscible Flooding

This process is similar to the carbon dioxide process in principle although miscibility of nitrogen is poorer than carbon dioxide. However, the low cost of nitrogen can make the process more economical, allowing large quantities of gas to be injected at high pressure. At high pressures, lighter components in the oil (C_2 to C_6) are vapourized to generate miscibility. However, the necessity of high pressures limits the process to reservoirs at a depth of at least 4,500 feet. The Cantarell nitrogen flood project in Mexico is the largest of its kind at present, and is currently producing about 500,000 barrels per day of incremental oil (Sanchez, 2005).

2.5.4 Hydrocarbon Miscible Flooding

A number of gas drive methods make use of light hydrocarbons (Lyons and Zaba, 1996), the simplest of which are analogous to carbon dioxide and nitrogen flooding except that methane or liquefied petroleum gas (e.g. propane) is used. Enriched (or condensing) gas drive consists of injecting slugs of methane enriched with higher hydrocarbons (C_2 to C_6) dispersed by larger methane slugs. The enriching components are transferred from the gas to the oil, increasing miscibility but also decreasing the viscosity of the oil. The inverse of this process is called vapourizing gas drive and consists of injecting dry methane at high pressure to vapourize the C_2 to C_6 components. In this case the expanding vapour increases the mobility of the reservoir. In order to contain the high pressure of vapourizing gas drive, the process is limited to reserves at a depth of at least 5,000 feet.

2.5.5 Chemical Flooding

Chemical flooding is a general term for techniques involving the injection of chemicals to decrease interfacial tension and improve sweep efficiency (Thomas and Farouq Ali, 1993 and 1999). The three main groups are polymer, surfactant and alkaline flooding although they can be combined to obtain the best characteristics of each. Reservoir characteristics place a particular restriction as carbonates and clays absorb the chemicals. Recoveries up to 40% can be achieved but the technique is restricted by the high cost of the chemicals and is little used on large reservoirs with the exception of China. More recent developments include the use of emulsions, foams and microbes, the latter producing surfactants *in situ* as a result of their normal biological processes.

2.5.6 Polymer Flooding

Polymer flooding is by and large viewed as an improved waterflooding technique since it does not ordinarily recover residual oil that has been trapped in pore spaces and isolated by water, therefore is often referred as polymer-augmented water flooding. The injection of dilute water-soluble polymers, such as polyacrylamides and polysaccharides, can produce additional oil compared with that obtained by ordinary water flooding by improving the displacement efficiency and increasing the volume of reservoir that is contacted by increasing the viscosity of the water. This reduces the probability of the flood breaking through to the production well while also producing oil at a higher rate. In most cases, polymer flooding is applied as a slug process and is driven using dilute brine (Chang, 1978). Reservoir permeability needs to be higher than for gas displacement techniques although can be lower than that necessary for thermal methods (Picha, 2007). Recovery levels, however, are only a little higher than that achieved with just water and so thorough understanding of the reservoir is necessary to make the process profitable. Loss of polymer to the porous medium, particularly in reservoirs with high clay content, is particularly problematic as can be polymer degradation.

2.5.7 Surfactant Flooding

With Surfactant Flooding, surface-active agents (e.g. petroleum sulphonates) are mixed with other compounds such as alcohol and salt in water and injected to mobilize the crude oil. These surface active materials are effective in lowering interfacial tension between oil and water. The major difficulty in the past has been due to excessive surfactant loss to the porous medium and the presence of clay minerals can be particularly problematic and therefore good understanding of the reservoir conditions is essential (Somasundaran and Hanna, 1979; Krumrine and Falcone, 1983). Treatment and disposal of emulsions were also of concern.

2.5.8 Alkaline Flooding

In alkaline flooding an aqueous solution of an alkaline, most usually a sodium hydroxide, sodium carbonate or sodium ortho-silicate, is injected in a slug form (Johnson, 1976; Mayer *et al.,* 1983). The alkali reacts with acidic components of the crude oil and generates the surfactant *in situ*; therefore a sufficiently high organic acid content is necessary. However, the process is not suitable for use in carbonate formations due to abundance of calcium which can react with the alkali to form precipitates that can damage the formation.

2.5.9 Micellar Flooding

Micellar flooding refers to a fluid injection process in which a stable solution of oil, water, and one or more surfactants along with electrolytes of salts is injected into the formation and is displaced by a mobility buffer solution (Gogarty and Tosch, 1968; Reed, and Healy, 1977; Dreher and Gogarty, 1979; Thomas and Farouq Ali, 1986). The main components of this method are a microemulsion slug (also known as a micellar slug) and a polymer slug. These two slugs are driven using brine. Microemulsions are surfactant-stabilized, oil-water dispersions with small drop size distributions (10-4 to 10-6mm) which are miscible with reservoir oil as well as water. The two chemical slugs are designed to promote very low interfacial to increase the mobility of the oil. Recovery factors have ranged between 35-50% of oil in place in field projects (Earlougher *et al.,* 1975). However, the downside is that the economics are unattractive due to a combination of the high cost of chemicals, the requirement of small well spacing, the high initial expense and the considerable delay in response. Moreover, the technique is unsuitable for reservoirs with high salinity, temperature and clay content.

2.5.10 Alkaline-Surfactant-Polymer (ASP) Flooding

Alkaline-Surfactant-Polymer flooding (Gao *et al.,* 1996; Wyatt *et al.,* 2002) takes advantage of the individual alkali, surfactant and polymer methods while lowering injection costs and reducing surfactant adsorption. The major mechanisms are interfacial tension reduction and improved reservoir sweep. Field results are encouraging (recovery factor 25-30% of oil in place) and the process holds potential; however, the economics are at best marginal.

2.5.11 Microbial Enhanced Oil Recovery (MEOR)

Microbial Enhanced Oil Recovery (MEOR) relies on microbes to ferment hydrocarbons and produce a by-product that is useful in the recovery of oil (Hitzman and Sperl, 1994; Bryant, 1994). Nutrients such as sugars, nitrates or phosphates are regularly injected to stimulate the growth of the microbes, which are indigenous to some reservoirs, and aid their performance. The microbes then generate surfactants and carbon dioxide that help to displace the oil in a similar way to other displacement methods. Since growth occurs at exponential rates, the process quickly generates considerable surfactant in a cost effective manner. Studies have shown that several microbially-produced bio-surfactants compare favourably with chemically synthesised surfactants.

MEOR has the advantage that microbes do not consume large amounts of energy and that they are independent of the price of crude oil, compared to other processes. However with increasing subsurface depth, temperature appears to be the principal factor limiting microbial life, besides availability of suitable nutrients. They are also susceptible to salinity which limits their use (Bernard *et al.,* 1992; Ridding and Awramik, 2000).

In a related study, Jones *et al.* (2008) investigated the probable mechanisms of hydrocarbon degradation in reservoirs by monitoring hydrocarbon composition of degraded oils and generated gases in the laboratory, together with carbon isotopic measurements at wellheads. They found that methanogenic degradation processes occur in the laboratory, similar to the field. Thus, a slow anaerobic degradation process takes place which leads to the sequential removal of different classes of compounds from the oil. Removal of n-alkanes generates methane, which could be artificially accelerated to provide a relatively clean gaseous fuel from oilfields where recovery by alternative methods would be difficult. This method is at the very early stages of development however, therefore extensive scale up and field trials would be required before it could be reliably used in practice. The production of oil from MEOR methods does not release significant amounts of carbon dioxide that would be generated through mining and upgrading, although the methane gas generated for use as a fuel is itself a greenhouse gas.

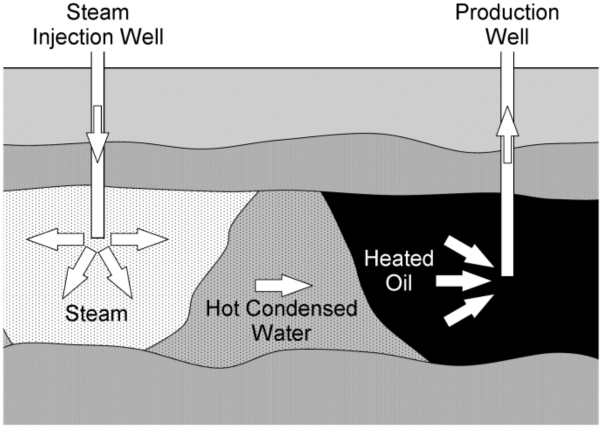
2.6 Thermal Methods

Thermal enhanced oil recovery processes add heat to the reservoir to reduce oil viscosity as well as vapourising lighter components, making the oil more mobile (Speight, 1999). Thermal methods can be used for most oils but the high energy costs normally only makes them an economical choice for the hard to extract, high viscosity heavy oils and oil sands. The use of electrical heaters or hot water in a process analogous to water flooding have been used but the two major groups use either steam or the *in situ* combustion of a proportion of the reservoir to heat the oil.

2.6.1 Steam Flooding

Steam Flooding (Stokes and Doscher, 1974; Farouq Ali and Meldau, 1979; Farouq Ali, 1982) or steam drive, is a process which requires continuous injection of steam into the oil layer to supply thermal energy and so to reduce the viscosity of the heavy oil to enhance the recovery of viscous crude oils. A suitable pattern of injection wells typically surrounding a production well is selected, with the pattern largely dependent on the geology of the formation to be flooded. Steam is continuously injected into the selected injection wells, forming a steam zone which both lowers the viscosity of the oil and also provides the pressure to drive the heavy oil towards the producer well, as illustrated in Figure 2.10. Typical recovery factors are in the range of 50-60% of oil in place although as high as 70% has been reported for parts of the Duri field in Indonesia (Clark *et al.,* 2007). The major drawback of the process is that excessive heat loss can be both problematic and expensive. Furthermore, steam flooding, like all the thermal techniques that employ steam, that it is very energy intensive adding a considerable cost to the project.

Figure 2.10 Steam Flooding

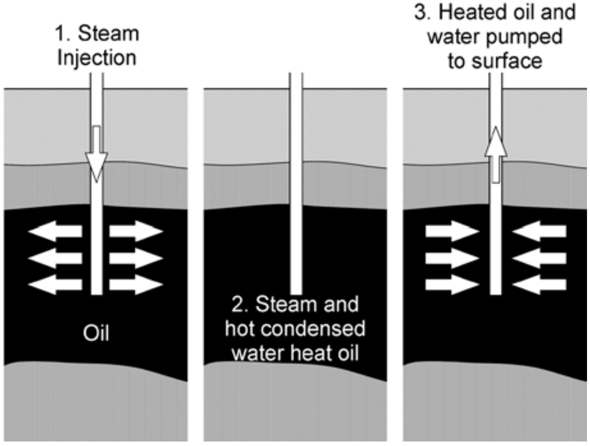


2.6.2 Cyclic Steam Stimulation (CSS)

In the 1960's, Shell Oil experimented with the injection of hot water and steam into heavy-oil reservoirs in Venezuela (Mut, 2006). However, when the injection pressure of one well exceeded the overburden pressure, a fissure opened in the ground releasing steam, hot water and oil. Injection was quickly abandoned and the well placed on production. Remarkably, hot oil flowed from the reservoir rather than the injected fluids. Shell came to know the process as 'steam soak' but the wider field gave it the moniker of 'huff and puff'.

Cyclic Steam Stimulation is a three-stage process starting with the injection of high pressure steam for around a month's duration. This is followed by the soak stage where the heat is left to distribute before the well is finally put in to production, as shown in Figure 2.11 (Owens and Suter, 1965). The oil production rate increases quickly to a high rate, staying at that level for a short time before gradually declining over several months. The cycle is then repeated when the oil rate becomes uneconomic. Steam to oil ratios are initially in the region of 2:1 but this increases as cycles are repeated and is typically in the range of 3:1 to 4:1 across the lifetime of the process (Alberta Chamber of Resources, 2002). For this reason, CSS is often used for the first cycle of production only before switching the reservoir to steam flooding.

Figure 2.11 Cyclic Steam Stimulation



In addition to heating the reservoir, the high pressure steam creates fractures in the formation thereby improving fluid flow but for this reason, an overburden cover of at least 300 metres is required to contain the pressure. The process is also sensitive to the geology near the well which should aid heat distribution as well as the capture of the mobilized oil. Cyclic Steam Stimulation is particularly attractive because it has quick payout; however, recovery factors are low compared with other thermal techniques, typically 10-40% of oil in place as are recovery rates due to the non-continuous nature of the process.

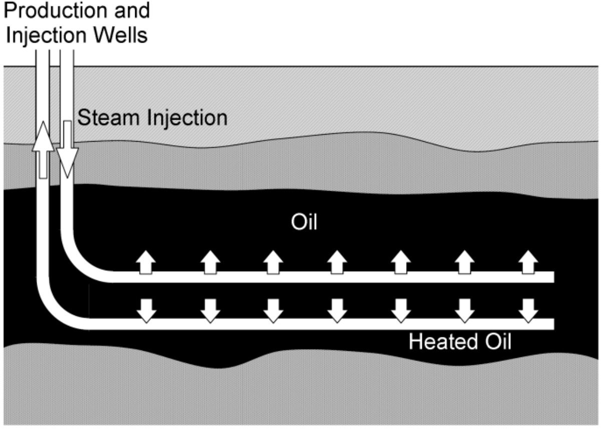
2.6.3 Steam Assisted Gravity Drainage (SAGD)

Steam Assisted Gravity Drainage (SAGD) was originally developed by Butler for *in situ* recovery of Alberta bitumen with Imperial Oil, who trialled the technique around 1980 at Cold Lake and Butler subsequently reported detailed investigation of the process (Butler and Stephens, 1981; Butler, 1985 and 1991). In a typical SAGD process, two horizontal wells running parallel to one another about 5 m apart are employed, as represented in Figure 2.12. Steam is injected into the upper injection well, reducing the viscosity of the oil which drains into the lower production well along with condensed steam and is then pumped to the surface. Continuous injection of steam causes a steam chamber to form and expand in the reservoir and for this reason the process performs better with bitumen and oils with low mobility, as steam channels are less likely to form.

SAGD is sensitive to operational and geometric reservoir parameters with high vertical permeability being particularly crucial to the process' success (Kamath *et al.,* 1993; Akin and Bagci, 2001; Kisman and Yeung, 1995; Queipo *et al.,* 2002). Rock permeability, reservoir heterogeneity, oil reservoir thickness, and operational conditions such as well separation and length and steam rate are also important. In addition, the process is not applicable to thin reservoirs which do not allow sufficient separation of the two wells. In the case of the

Canadian oil sands, 57% of reservoirs have been estimated to be inaccessible to the technique with reservoirs of less than six metres in thickness (PTAC, 2007).

Figure 2.12 Steam Assisted Gravity Drainage (SAGD)



Large volumes of water are needed to run SAGD with between two and ten barrels of water injected as steam for every barrel of oil produced (Gates and Chakrabarty, 2006). This water then has to be separated from the produced oil along with any formation water and water handling costs can amount to as much as half the cost of a project (E and P, 2007). However, it is the energy requirement that is the main limitation on the use of SAGD and other steam-based methods and this problem is amplified by the creation of significant quantities of green house gases, most notably carbon dioxide, during steam generation.

Assuming that three barrels of water are used to make steam per barrel of oil produced, the approximate amount of carbon dioxide generated to supply the latent heat requirement of steam generation was estimated to be ~0.092 tonnes. Calculation showed broad agreement with published estimates that approximately 0.1 tonnes of carbon dioxide are generated per barrel of oil produced (Donelly and Pendergast, 1999). Over 50 years projected from 1999, the emission of carbon dioxide from producing 20 billion barrels of oil using SAGD techniques would amount to 2 billion tonnes, which is four times Canada's estimated commitment to the Kyoto protocol with respect to total emissions, averaged over that period. Furthermore, SAGD operations have been identified as contributing up to 60% of the total greenhouse gas emissions from heavy oil extraction and processing, with mining, upgrader process energy and hydrogen consumption in upgrading being listed as other significant contributory factors (Flint, 2004). As one of the more extensively used and proven *in situ* extraction techniques, the economics of SAGD are fairly clearly established. The cost of purchasing natural gas can be reduced by combining the SAGD process with upgrading, incorporating gasification to convert a proportion of the produced bitumen in to gas suitable for generating steam required for the recovery process itself. It has been estimated that combining SAGD with co-generation of electricity and surface upgrading plants leads to a cost of ~$22/bbl (Nexen, 2009), which together with ongoing capital costs, is comparable to mining and surface upgrading. SAGD processes which require the purchase of external natural gas would be considerably less economically attractive.

A number of variations of SAGD have been developed, most notably Vapour Extraction or VAPEX, which strictly speaking isn't a thermal technique (Das and Butler, 1995; Curtis *et al.,* 2002). Instead of steam, a solvent gas, or a mixture of solvents, such as ethane, propane and butane, depending on the reservoir pressure and temperature, is injected along with a carrier gas such as nitrogen or carbon dioxide. Again, a vapour chamber is formed and propagates along the well as viscosities are reduced. However, the dispersion and diffusion of the solvents are relatively slow and therefore the process is much less efficient than thermal techniques. The high cost of solvent is the major economic concern and recovery of the solvent is therefore important. There are also worries about contamination of subterranean water (Gates, 2007).

Expanding Solvent Steam Assisted Gravity Drainage (ES-SAGD) is a hybrid of SAGD and VAPEX with the injection of both steam and solvent in order to increase the energy efficiency compared with VAPEX and reduce the energy costs with respect to SAGD (Gates, 2007). Recoveries of 40-60% of the oil in place have been reported along with high production rates. A further way to reduce the high demand of steam is to replace a proportion with a non condensable gas such as natural gas or nitrogen in what is termed Steam and Gas Push (SAGP) (Jiang *et al.,* 2000).

2.6.4 *In Situ* Combustion (ISC)

Conventional *in situ* combustion, or fire flooding as it is sometimes termed, is achieved by burning a small fraction of the oil by injecting air into the reservoir in order to enable flow of the unburned fraction and improve oil recovery (Cheih, 1977 and 1982; Lake, 1989; Sarathi, 1998). Because of the strong exothermal oxidation reactions between hydrocarbons and oxygen, oxygen is consumed to produce flue gases and, at the same time, the temperature of the oil-bearing matrix is greatly increased. ISC is particularly favourable for heavy oil reservoirs because the increase in temperature reduces the oil viscosity by several orders of magnitude. By generating the thermal energy *in situ* in the reservoir high energy efficiency is achieved along with an effective displacement drive mechanism, and reduced environmental impact compared with steam-based thermal recovery (Moore *et al.,* 1997). However, the conventional ISC process has not achieved wide acceptance largely due to the difficulty of controlling the process. In particular, gas overriding due to the difference between the gas and oil densities, channeling, due to the unfavourable rock heterogeneity and unfavourable gas/oil mobility ratios have hindered its application.

In general, ISC is the injection of an oxidising gas (air or oxygen enriched air) to generate heat by burning a proportion of the oil. Air is injected in to the target formation for a short time, usually from a few days up to a few weeks and the oil in the formation is then ignited either by using downhole gas burners, electrical heaters or in some cases auto-ignition may occur. Very high temperatures, in the range of 450-600°C, are generated in a narrow zone of the combustion front reducing viscosity and the process has high thermal efficiency, since there is relatively small heat loss to the overburden or underburden, and no surface or wellbore heat loss. After ignition, the combustion front is propagated by a continuous flow of air (Castanier and Brigham, 2003). In a typical conventional ISC as the front progresses into the reservoir, several zones can be found between the injector and the producer as a result of heat, mass transport and the chemical reactions occurring in the process. ISC is actually a gas displacement process, benefiting from oil viscosity reduction due to the heat generated and most of the oil is driven toward the producers by a combination of gas drive (from the combustion gases) and steam drive (either generated from formation or injected with the air). Therefore, as in any gas displacement process, the injectors should be located at the highest position in the reservoir. The process is illustrated in Figure 2.13.

Figure 2.13 Schematic Representation of ISC

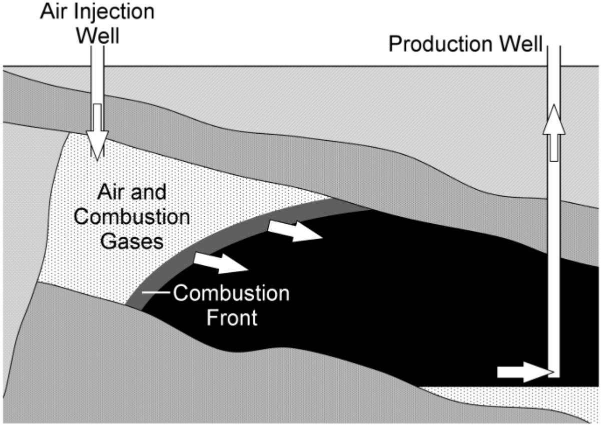
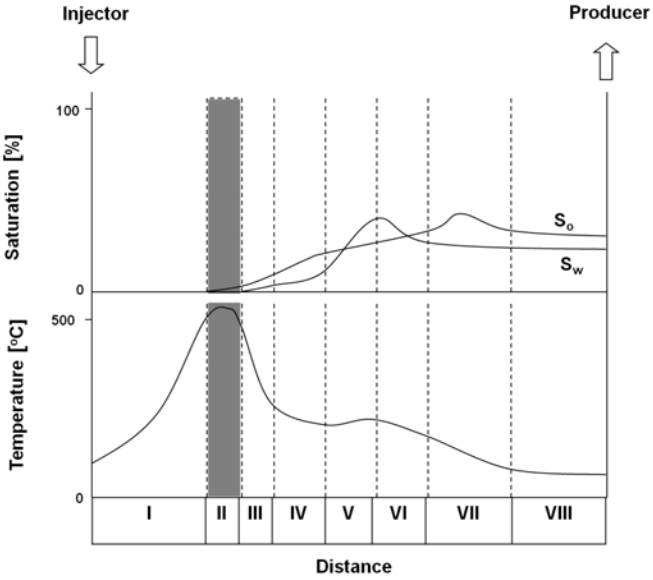


Figure 2.14 (after Wu and Fulton, 1971) shows a schematic representation of the locations of the various zones and temperature and fluid saturation distributions. In the field, there are however, transitions between these zones, so Figure 2.14 should only be treated as an idealized representation. Starting from the injector, seven zones can be defined.

(I) The burned zone is left with no oil as it is already burned. The temperature in this zone increases from air injector towards the combustion front because of the continuous air flow from injector towards the burned zone. This zone may contain small amounts of residual unburned organic solids and is mostly filled with air. (II) The combustion front is the highest temperature zone. In this region oxygen combines with the fuel and high temperature oxidation takes place. The fuel burned here is usually a mixture of heavy hydrocarbons formed in the thermal cracking zone ahead of the combustion front. The amount of fuel consumed determines how much air must be injected to burn a certain volume of reservoir. (III) and (IV) Downstream of the combustion front is the cracking/vapourization zone, where the high temperature of combustion modifies the crude. The light ends vaporize and are transported downstream where they condense and mix with the original crude. The heavy ends pyrolyse, resulting in hydrocarbon gases and solid organic fuel being deposited on the rock. (V) Steam plateau is next in downstream while most of the oil is displaced ahead of the steam. The immobile oil undergoes steam distillation. Depending on the temperature, the original oil may undergo a mild thermal cracking, often named visbreaking, in this zone, resulting in oil viscosity reduction. (VI) At the leading edge of the steam plateau, where the temperature is less than steam saturation temperature, a water bank forms that decreases in temperature and saturation as one looks downstream, with a resulting increase in oil saturation. (VII) An oil bank is next. This zone contains most of the oil displaced from upstream, including most of the light ends that resulted from the thermal cracking upstream. (VIII) Beyond lays the undisturbed original reservoir.

In a variation on the conventional forward combustion technique, reverse combustion can be employed where ignition occurs near the production well and the heated zone moves against the air flow the idea being that the low viscosity region will have an easier pathway to the producer well rather than being restricted by cold, viscous oil. However, it has not been successful in the field because of the consumption of oxygen in the air before it reaches the production well. High pressure air injection involves low temperature oxidation of the in place oil, although no ignition occurs and is analogous to the other gas displacement methods and not practical for use in bitumen and heavy oils (Wilson *et al.,* 1963; Burger and Sahuquet, 1971).

Figure 2.14 Schematic Diagram of Forward *ISC*:
A - Burned Zone; B - Combustion Zone; C - Cracking Region; D - Evapouration and Visbreaking Region; E - Steam Plateau; F - Water Bank; G - Oil Bank; H - Initial Zone
S_o and S_w represents, Saturation of oil and water respectively
(after Wu and Fulton, 1971)



Weissmann and Kessler (1996) investigated the kinetics mechanism of heavy Middle-Eastern crude oil upgrading. They noted that for this particular heavy crude oil hydrodesulphurization followed pseudo-first order kinetics and activity was not catalyst dependent but instead appeared to be limited by the reactivity of the feed. Additionally, from 20 to 30% of the sulphur contained in this particular crude oil consisted of thermally labile sulphur, the amount of which removed remained constant provided a minimum processing temperature was attained. Density of the product decreased almost linearly with increasing reaction temperature. Reduction of hydrogen partial pressure resulted in a decrease in hydrodesulphurization, probably due to hydrogen starvation. Upgrading reactions occurred in a sufficiently short contact time to allow conventional oil-well production rates. They indicated from their results that *in situ* hydroprocessing is feasible from reaction and catalyst standpoints.

2.7 "Toe-to-Heel" Air Injection (THAI™)

"Toe-to-Heel" Air Injection or THAI™, combines ISC with a horizontal production well (US Pat., 5, 626, 191, 1997). THAI is very robust and much more stable than conventional ISC, because it eliminates the tendency for gas override and also has a 'built-in' guidance mechanism, by virtue of the combustion front propagating along the horizontal producer well from the 'toe' position to the 'heel'. The objective is to add some control to the conventional ISC process since the combustion front propagates along the horizontal well, from the "toe" position, to the "heel" (Greaves *et al.,* 1993; Greaves, and Al-Shamali, 1995 and 1996) as shown schematically in Figure 2.15. A horizontal producer well is positioned in a line drive in the reservoir and air is injected via a vertical well, an arrangement that effectively solves the problem of gas overriding. Moreover, the horizontal well effectively self seals as coke is formed as the combustion front progresses, closing off the "toe" and preventing gas bypass. In laboratory experiments, the process has been demonstrated to achieve a stable combustion front propagation, once the combustion front has become 'anchored' on to the horizontal well (Greaves *et al.,* 2000) which leads to very high oil recovery (Xia and Greaves, 2000 and 2001; Xia *et al.,* 2002). Furthermore, compared to the conventional ISC process, in THAI™ the path of the mobilized oil to the producer well is much shorter, increasing production rates. Experimental modelling (using STARS^{TM} as discussed in Section 2.5.7.3) has suggested recoveries of up to 80–85% of oil in place may be feasible, significantly higher than other techniques (Greaves *et al.,* 2000). In addition, the process is potentially feasible over a wider range of reservoirs than other techniques including reservoirs that are low pressure, thinner, deeper, gas capped, those containing bottom water or which have been previously steamed. The partially upgraded oil produced with THAI is thought to occur because of the thermal cracking reactions taking place in the coke and mobile oil zone MOZ[†]. In the MOZ, the reactants are comprised of water (steam), oil and combustion gases. There is also some carbon monoxide and a small amount of unconsumed oxygen. All of these reactants, at high temperature, pass downwards through the MOZ into the horizontal producer well and travel a short distance, hence are referred to as short distance displacement methods. This is in contrast to conventional ISC, where the mobile oil has to pass through the cold zone covering longer distance and hence long distance displacement method, resulting in lower recovery levels and control problems[‡]. The temperatures generated by the combustion front are around 500 to 600°C or higher and the pressure is equal to the reservoir pressure around 30 to 50 bars. These severe conditions lead to the reservoir acting as a reactor. Oil upgrading occurs by (i) carbon rejection reactions (thermal cracking) and (ii) hydrogen addition. The source of *in situ* hydrogen is believed to be via gasification and/or water gas shift reactions (Hajdo and Vorndran, 1985). And added side-effect of THAI is the simultaneous upgrading of the oil which is not only beneficial for the actual oil recovery but also aids transportation, downstream refining and increases the value of the produced oil. Experimental and field pilot results indicate sulphur and heavy metal content is reduced (Petrobank Energy and Resources Ltd., 2008). THAI was initiated by Petrobank at their White sands pilot project in 2006, at Christina Lake, Alberta, Canada (Petrobank Energy and Resources Ltd., 2003). The test pilot well consists of three sections, with three injections (Ayasse *et al.,* 2005) and three horizontal production wells. Initially only steam was injected in both the vertical and horizontal wells for around three months (from March-July 2006). Air injection took place in July 2006,

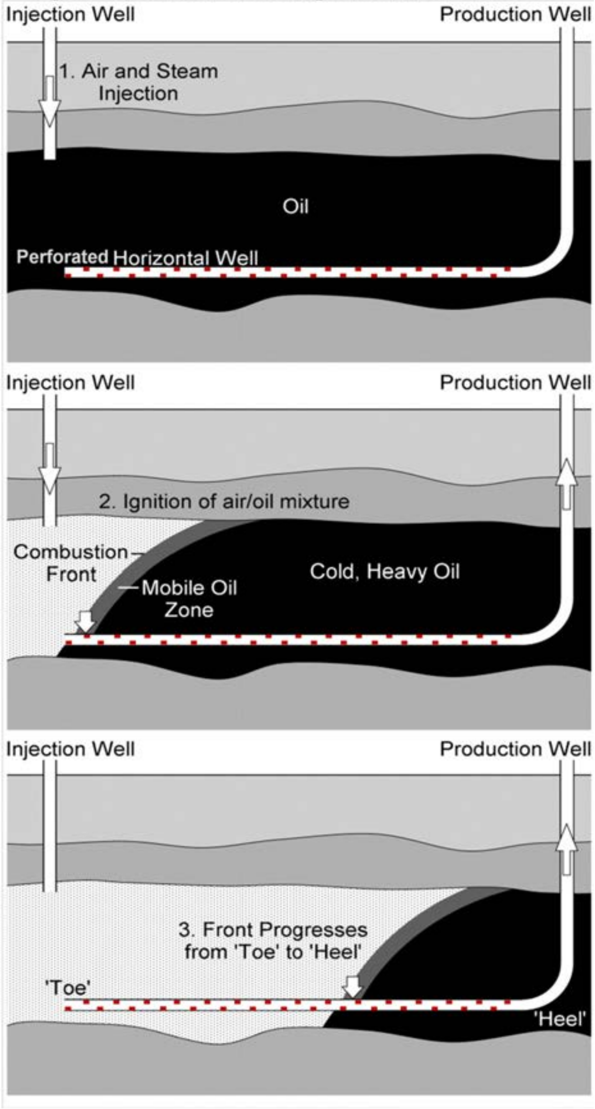
---

[†] The MOZ creates the precursor conditions for catalytic upgrading in which a catalyst is used wrapped around the THAI horizontal production well and the process is known as CAPRI

[‡] Alternatively these can contact with the catalyst layer in the CAPRI process

leading to spontaneous ignition in the reservoir. Peak combustion temperatures of 700 to 800°C were recorded. Currently three well pairs are in operation at different levels of production. Maximum gross fluids production per well pair is reported as 2000 barrels/day, with a bitumen cut at around 55%. The produced oil is partially upgraded in the range of 10.6 to 16.1 °API, compared to the original bitumen value of 7.9 °API. This means that only about 15% of diluent is needed to meet pipeline specifications, compared to 30–50% required for non-upgraded bitumen produced from SAGD and CSS operations. The small amount of sand co-produced with the oil (less than 1%) is easily separated due to the greatly reduced oil viscosity. The produced water is also of good quality so that it can be treated fairly simply for industrial re-use; for example in SAGD (Greaves and Xia, 2008).

Figure 2.15 Schematic Representation of THAI



Advantages of 'Toe To Heel' Processes over conventional ISC

Turta and Singhal (2004) have provided a detailed comparison of different types of 'toe to heel' processes versus conventional ISC processes. They classified the in situ processes into long distance oil displacement LDOD methods [like the conventional ISC process with vertical injection, vertical producer wells (VIVP) arrangement] and short distance oil displacement SDOD methods (like SAGD, VAPEX and TTH). They concluded that with SAGD and VAPEX processes the adverse effect of gravity segregation is almost eliminated (a typical problem usually associated with LDOD), but the negative effect of the lateral and vertical heterogeneity sill persists. On the other hand, in TTH processes, the negative effect of heterogeneity is significantly mitigated, while the gravity segregation effect, although mitigated, still exists, and it can impact the stability of the process, depending on the value of the injection rate. SAGD and VAPEX are only gravity controlled in contrast to TTH processes, which are controlled by pressure gradient and gravity, yet SAGD is by far the most commercialised processes. VAPEX was described to be more sensitive to permeability heterogeneity than SAGD and is equally useful along with TTH as both of these methods don't burn large quantities of natural gas or use water as is the case with SAGD. THAI was described in general and its ease of control and high oil recovery in particular. TTHW (Toe-To-Heel Waterflooding**)** another *in situ* non-thermal Toe-To-Heel Displacement (TTHD) processes was investigated for its vertical sweep in a Hele-Shaw model. The process was found useful in comparison to other conventional *in situ* processes with a VIVP scheme. Further schematic investigations were recommended for the creation of an initial communication link between the injection and producer wells. For TTH processes this phase was described as hugely important for their commercialized success in the field. Unlike other *in situ* methods like (SAGD) ISC methods are not only EOR processes but they upgrade the oil produced and Ramey *et al.,* (1992) has reported an upgrade from 2 to 6 °API. Table 2.4 summarises the different EOR techniques and their respective advantages and disadvantages.

Problems occurring in conventional oil displacement include gravity segregation, or gas overriding, causing overriding and severe channelling of gas through to the producer well. Oil banking in the cold region ahead of the combustion front occurs by switching the high temperature oxidation HTO to low temperature LTO by restricting the injection of air, and permeability heterogeneity has also been observed. These problems have not been observed with THAI after its intensive testing in the laboratory at the University of Bath.

Table 2.4 Generalized Screening Criteria for Oil Recovery Methods (Speight, 1999)

Recovery method	Viscosity centipoise	Gravity °API	Composition	Depth	Requirements	Limits
CO_2	<15	>26	C_2-C_{12}	>2000	Steep dip, anisotropic	Salinity, fissuring
N_2	<10	>35	High % of C_1-C_7	>4500	Steep dip, anisotropic	Fissuring
Hydrocarbon	<10	>35	C_2-C_7	>5000(H.P. Gas*)		
Polymer	<150	>25	N.C.	<9000	High permeability	Fissuring
Surfactants	<30	>25	Light intermediates desired	<8000	Low water-cut sand content	Clay content
fissuring						
Alkaline	<200	13-35	Some organic acids	<9000	Naphthenic acids, asphaltenes	Saline
Micellar					Low salinity	Fissuring
Steam Flood	>20	<25	N.C.¶	300-5000	Asphaltenes, paraffin	Hydrophobicity, water saturation
CSS			Asphaltic Component		Asphaltenes, paraffin	Hydrophobicity, water saturation
SAGD		>15		>3280	Thick reservoir	Depth more than 1000m
VAPEX		>15		>3280	Thick reservoir	Depth more than 1000m
ISC	<1000	N.C.		>500	Thin reservoir	Fissuring
THAI	>300	6-20		>300	Thin reservoir	Fissuring

¶N.C. = Not Critical *H.P. Gas = High Pressure gas

2.8 Downhole Catalytic Upgrading of Heavy Oil

The difficulties occurring during heavy oil production, transportation and surface processing can potentially be avoided by using in situ upgrading. Currently upgrading of bitumen from mining operations is carried out in special surface conversion units (delayed cokers and hydroconverters-hydrocrackers) to produce 'syncrude' of 25 to 35°API. Surface Upgraders are hugely expensive; indeed, one of 100,000–170,000 barrels/day capacity has been proposed for the UK/Europe, at a cost of £0.8–1.5 billion (Simons, 2006). By contrast, catalyst suitable for use in *in situ* upgrading process CAPRI is relatively cheap, if standard refinery HDS catalysts are used. By the authors' estimate, 20 tonnes of new HDS catalyst for 500 m horizontal producer well cost about $60– 100k (Xia *et al.,* 2002).

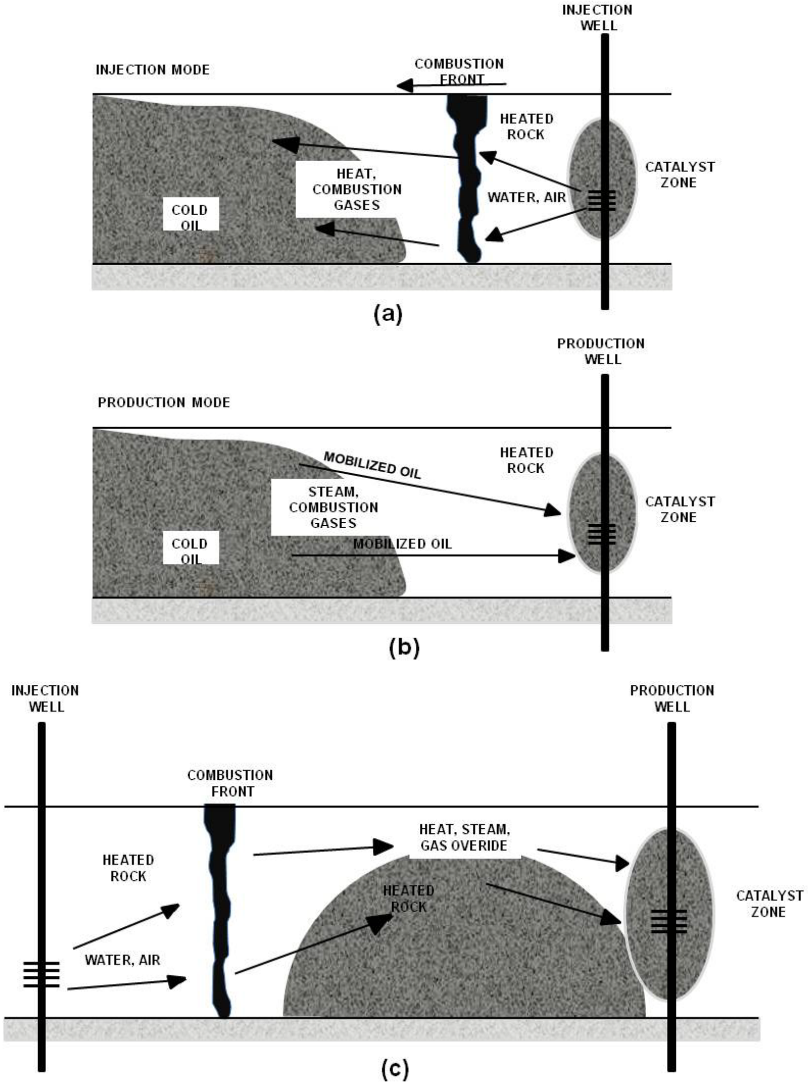
The concept of downhole catalytic upgrading of heavy oil using *in situ* combustion was proposed first by Moore *et al.,* (1999) and Weissmann *et al.,* (1996; Weissman and Kessler, 1996). The downhole catalytic upgrading process requires suitable placement of a catalyst bed in the reservoir, the flow of oil through the catalytic bed at a certain temperature and pressure, and finally drainage of the upgraded oil into the production well. Moore and Weissmann *et al.* (1996) placed a mixture of NiMo hydrotreating catalyst and sand (50/50 vol/vol) into the bottom section of a combustion tube at the production end to simulate the downhole catalytic upgrading reactor in a conventional ISC operation.

Figure 2.16 represents this arrangement of a "burn and turn" *in situ* catalytic upgrading production scheme. In the top part of the Figure 2.16 (a), air or a combustion-supporting gas is injected and a dry or wet combustion initiated in the oil-saturated catalyst bed; as the burn proceeds, the area adjacent to the well is heated. In the lower part of the Figure 2.16 (b), the well is brought onto production, reservoir fluids and combustion gases pass over the heated catalyst, and the produced oil is upgraded. Injection/production cycling is repeated to maintain the heated catalyst bed and remove coke deposits.

The authors reported substantial upgrading of the crude oil from 15.3 to 21.2° API by heating the catalytic processing zone to 325°C. They also noted that reactive hydrogen was supplied by gases produced by the combustion process, either as hydrogen or carbon monoxide. The heated catalyst was also found to be efficient at converting CO to additional H_2.

However, catalytic upgrading using conventional ISC is faced with two problems in that external heating of the catalyst bed is required and severe coking can foul the catalyst bed since the combustion front is not in contact with the production well and so oil flow over the catalyst is relatively cold.

Figure 2.16 Conventional *In Situ* Combustion (a) Injection Mode (b) Production Mode (c) The whole process in action



2.9 Downhole Catalytic Upgrading of Heavy Oil using THAI

THAI™ potentially allows the inclusion of a catalytic upgrading stage since it provides favourable operating temperatures at the production well as the combustion zone is ‘anchored’ to the horizontal well (Xia and Greaves, 2001; Xia *et al.,* 2002). The cracking reactions happening in the MOZ of THAI™ creates precursor conditions for CAPRI™. The reactants are usually water (steam) and combustion gases. All these reactants pass through the MOZ and in contact with the catalyst layer around the horizonta11 production well. The catalyst reacts with partially upgraded THAI oil and further upgrades it. The THAI-CAPRI™ upgrading mechanism can simply be represented by the following equations 1-9 (Xia and Greaves, 2001).

Thermal cracking (Pyrolysis):

$$\text{Heavy residue} \qquad \text{Light oil + Coke} \tag{1}$$

Oxidation of coke (high temperature oxidation):

$$\text{Coke} + O_2 \qquad CO + CO_2 + H_2O \tag{2}$$

Oxidation of heavy residue:

$$\text{Heavy residue} + O_2 \qquad CO + CO_2 + H_2O \tag{3}$$

Carbon rejection:

$$CHx \qquad CHx_1 + C\ (x_1 > x) \tag{4}$$

Hydrogen addition:

$$CHx + H_2 \qquad CHx_1\ \ (x_1 > x) \tag{5}$$

Upgrading of heavy oil/natural bitumen a very complex process, so, the hydrogen responsible for the upgrading the THAI-CAPRI produced oil is thought to be formed due to the water gas shift reaction, and is represented with the following simple equations (Xia and Greaves, 2001),

Gasification of hydrocarbon:

$CHx \qquad\qquad C + x/2H_2$ (6)

$C + H_2O$ (steam) $\qquad\qquad CO + H_2$ (7)

Boudouard reaction:

$C + CO_2 \qquad\qquad 2CO$ (8)

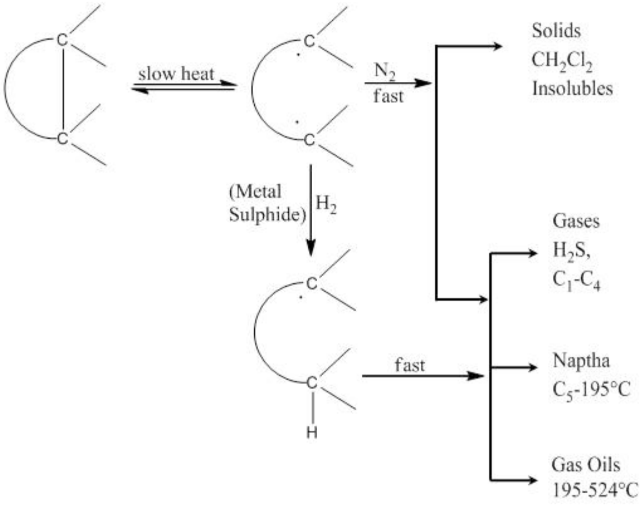
Water-gas shift:

$CO + H_2O \qquad\qquad CO_2 + H_2$ (9)

However, the chemistry of heavy oil upgrading is a very complex and the upgrading reaction scheme provided in equations 1-9 is an oversimplification of the processes occurring. Some of the previous attempts to unravel the chemistry of upgrading of heavy oils in the presence of catalyst have been provided in the following paragraphs.

Sanford (1994) has concluded that residuum conversion is a thermal reaction whose rate is largely unaffected by hydrogen and hydrotreating catalysts. He has proposed that, during the early stages of coking and hydrocracking reactions, residuum conversion is mainly the result of breaking labile carbon-to-carbon bonds, producing mainly distillate with very little coke and gas. As reaction proceeds, the unreacted residuum becomes highly condensed. Initial homolysis of the condensed ring system produces two radicals of different reactivity, an aliphatic-carbon radical and an aromatic carbon radical. The aliphatic-carbon radical undergoes fragmentation to produce distillate and gas. The aromatic carbon radical condenses with other similar species in coking reactions to eventually produce coke, whereas in the presence of hydrogen, the aromatic-carbon radical reacts with hydrogen to form a carbon-to-hydrogen bond and a hydrogen atom. The hydrogen atom adds to the aromatic ring leading to transformation of the aromatic ring system and eventually to the production of gases and distillate. Hydrogen transfer is almost exclusively to the distillate and gaseous products, and not to the residuum. Hydrocarbon gases are thought to arise from hydroaromatic structures, in keeping with the above bi-radical intermediate postulate. A general reaction mechanism representing the above concepts is provided in Figure 2.17.

Figure 2.17 General Mechanism for the Conversion of Athabasca Bitumen Residuum to Solids, Distillates, and Gases with and without Hydrogen (Sanford, 1994)

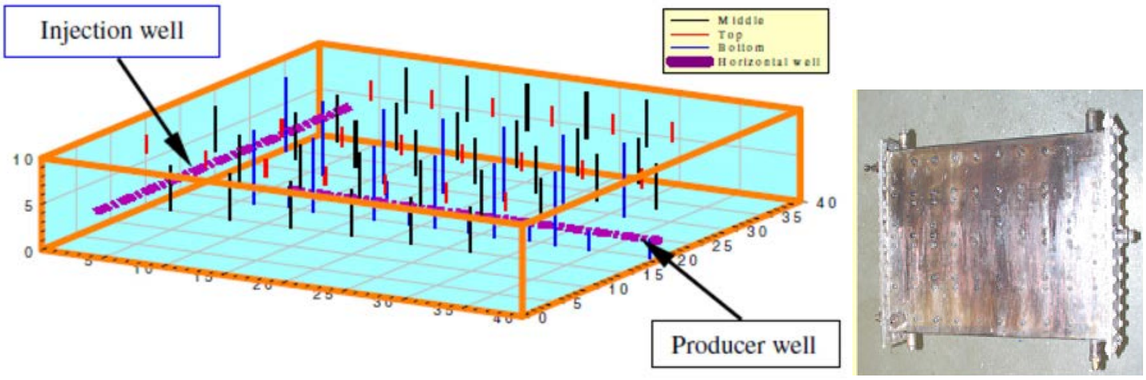


The effect of feed on Fluid Catalytic Cracking (FCC) of residuum has been investigated by Dupain *et al.* (2003). They demonstrated that the conversion of aromatic feed by cracking reactions is limited to the paraffinic fraction and the alkyl groups associated to the benzene ring in aromatic compounds. Benzene was found difficult to activate for cracking because of its resonance stability, and even if it were, β-scission would be unfavourable as the β-carbon–carbon bond can hardly be weakened. The probability for cracking of aromatics under the applied conditions of 525°C, catalyst to oil ratio of 5.5 $g_{cat}\ g_{oil}^{-1}$ were therefore found to be low. Formation of larger aromatics was found to occur due to self alkylation reactions of mono alkyl-aromatics or dealkylation of alkylated aromatics. Under the experimental conditions as described previously, approximately 19% of the feed was found to be uncrackable. This uncrackable fraction consisted predominantly of polycyclic aromatics, which are unable to crack under the applied FCC conditions, and remain in the Heavy Cyclic Oil (HCO) fraction. Coke was also found to occur at the first 50 ms of catalyst–oil contact. After which no more coke was formed.

2.10 THAI and CAPRI Previous Experimental Studies

All the previous experimental work presented in the following sections using THAI/CAPRI process was carried out in a standard stainless steel rectangular combustion cell, referred mostly as 3D Cell, measuring 0.4m square by 0.1 m deep at the University of Bath. The cell, which is shown in Figure 2.18 (a) and (b), was fitted with an array of 76 thermocouples arranged on three levels: Top, Middle and Bottom. These were placed, respectively, 0.02, 0.05 and 0.08 m from the top surface of the cell (Xia *et al.,* 2002).

Figure 2.18 3D Combustion Cell (a) Illustration (b) Actual 3D Cell (Xia *et al.*, 2002)



(a)

(b)

Mechanism of THAI High Oil Recovery

To understand the mechanisms governing the high oil recovery and thermal upgrading achieved by THAI, Xia *et al.,* (2003) carried out two three dimensional combustion cell tests (a dry and a wet combustion) of THAI on a wolf lake crude oil sample. They found that both the dry and wet combustion experiments were similar, though the level of upgrading was somewhat higher during the later stages of the wet combustion. Overall the upgrading was found to be 5-7°API above the original crude value. Using THAI, Greaves *et al.* (2001)

achieved recovery levels of as high as 85% of Original Oil In Place (OOIP). Also because of the simplicity of the technology and ease of control compared to any conventional ISC processes, THAI was found to be applicable to reservoir as thin as 6m.

Mechanism of THAI Stability

Xia *et al.* (2005) has investigated the main mechanism for the stability of THAI. They supported their work by taking help from the visual post-mortem results of two (previous) THAI experiments and reconfirmed their findings with help from numerical simulation of the experiment showing the distribution of coke and oxygen through the oil layer. In their conclusions they found that, THAI exhibits robust stability during start-up and steady operating phases. During ignition and start-up phase, the stability of THAI is governed by two factors: (i) maintenance of an expanding, high temperature combustion zone; and, (ii) a “controlled gas override” condition in the top part of the oil layer. This ensures that any oxygen flowing towards the “toe” of the horizontal well is at a very low, safe concentration. All of the combustion gas flows directly into the “toe” of the horizontal producer well during this period. The flow path of the combustion gas gradually changes as coke is deposited in the “toe part” of the horizontal producer well. The formation of coke inside the horizontal well acts as gas seal, so that combustion gas is forced to flow ahead of the advancing combustion front, and into the exposed section of the horizontal producer well downstream. The formation of a coke zone inside the horizontal producer well is a dynamic process, continuously forming and burning-off, as the combustion front approaches closer to the well. The gas seal mechanism was further reaffirmed by the post-mortem inspection of the contents of the horizontal producer well after it had been cut-open, and also by numerical simulation of a THAI experiment using the STARS. The combustion front was always found to be more advanced in the top part of the oil layer. This mechanism of “controlled gas overriding” was found to be contributing significantly to the overall stability of THAI.

THAI as Primary and Secondary Method for Athabasca Bitumen Recovery

Xia *et al.* (2006) investigated THAI as a primary and secondary recovery method, using Athabasca bitumen as feed in a series of 3D combustion cell experiments. Another type of the TTH method Toe-to-Heel Steam Flood (THSF) was also investigated in this work, in which steam was injected in place of hot air, as originally the case with THAI. They reported oil recovery efficiencies for THAI, using primary and secondary operations modes, 80% and 67% OOIP respectively (Table 2.4). The THSF recovery was much lower at only 23% of OOIP, which was thought to be due to the low steam temperature in the sandpack. Downhole upgrading of Athabasca Tar Sand bitumen was found to be very significant, with the API gravity of the produced oil increasing by an average of 8°API compared to the virgin bitumen. The produced oil viscosity was also found to be dramatically reduced from 1000 Pa.s at 15°C to less than 0.2 Pa.s with a minimum of 0.050 Pa.s. From Table 2.5 temperatures of as high as 700°C can also be observed produced by the combustion front. Fuel consumption of around 10% of the total oil in place can be observed, the majority of which seems to come from the asphaltene fraction as visible from Table 2.6. However the maximum duration of the experiment was less than 15 hours.

From Table 2.6 SARA (Saturates, Aromatics, Resins and Asphaltenes) analysis is used to assess the quality of the produced oil. The significant finding of the investigations was that the value of saturates increased significantly from only 15.5% to a notably high value of 72%. They proposed from their results that asphaltenes were the main donor compounds for the formation of the fuel needed to sustain stable combustion front propagation and thermal cracking was responsible for the significant increase of saturates. They also speculated that conversion of resin compounds might also have contributed to the overall upgrading effect achieved by THAI, in addition to being a fuel precursor.

Table 2.5 Experimental Result of 3-D Cell Tests

Run	2001-01	2000-03	2000-04
Recovery method	THAI (Primary)	THSF (Primary)	THAI (post-steam flooded)
Overall period (hrs)	14.5	14	14.5
Pre-ignition period (hrs)	3.5		3.5
Dry combustion phase (°C)	9		11.5
Peak Temperature (°C)	600-750		600-700
Fuel consumption (%OOIP)	8.2		9.5
Injected air (Sm^3)	5.37		8.28
Oil recovery (wt %OOIP)* (Vol. % OOIP)**	81.5 85.5	23	63.9 (83.0***) 66.7 (86.6***)
Residual oil (% OOIP)	11.0		8.2
Steam/oil ratio (m^3/m^3) overall		5	

*Oil recovery wt% OOIP is calculated from the weight of the initial oil in place
**Oil recovery volume % OOIP is based on the volume of the initial oil in place
*** The values are calculated based upon the residual oil after steam flooding

Table 2.6 SARA Analysis of Athabasca bitumen and Produced oil Samples from Run 200-01

Sample	**Crude Oil**					
Sampling Time (min)		0	75	210	420	570
Saturates (wt%)	14.52	49.0	62.0	69.7	61.0	69.7
Aromatics (wt%)	37.8	9.0	9.2	7.5	9.7	7.3
Resins (wt%)	38.0	38	26.4	21.0	26.0	21.4
Asphaltenes (wt%)	12.7	4.0	2.2	1.8	3.3	1.6

Effect of Oil Layer Thickness on THAI

Xia *et al.* (2002) investigated the effect of oil layer thickness on the effectiveness of THAI. In this work a number of 3-D combustion cell tests were performed to investigate the effect that oil layer thickness has on the dynamics of the THAI process. During these experiments 10.5°API Wolf Lake heavy oil was used. They found that the 3-D experiments exhibited very stable combustion front propagation through the sandpack, at all oil layer thicknesses of 0.1m, 0.2m and 0.4m. The combustion front peak temperature increased with increasing oil layer thickness, reaching 700 ~ 800°C. However, increasing the oil layer thickness had little effect on oil recovery, or the API gravity of the produced oil. Oil recovery was consistently very high, at 80~85 % OOIP. There was also an increase of 8 °API points in the gravity of the produced oil and a corresponding reduction in viscosity, from 24.4 Pa.s (20°C) for the original Wolf Lake crude oil, down to 0.03 Pa.s (20°C). They also found that THAI process works well for a heavy oil reservoir with an artificial gas cap above the oil layer, achieving the same level of oil recovery and upgrading as that for a reservoir without a gas cap. In the presence of a gas cap, oxygen utilization in THAI was reduced at an air flux above 22.5 $Sm^3.m^2h^{-1}$. However, changes in air flux resulted in little effect on the level of oil upgrading, or oil recovery. Oil layer thickness was observed to have a substantial effect on the air to oil ratio (AOR), but only at the greatest thickness (0.4m). The AOR was 980 Sm^3/m^3 (~4200 $scf.bbl^{-1}$), which was found low compared to values reported for the conventional ISC process.

Effect of Catalyst (CAPRI) on the Properties of Produced oils using THAI Process

Greaves and Xia (2001) investigated the produced oil properties and composition, produced from THAI-CAPRI experiments in their laboratory by using Wolf Lake crude oil in a 3-D combustion cell. Different analytical methods like Micro Activity Test[§] (MAT), Gas Chromatography (GC), elemental analysis, Simulated Distillation (SIMDIS), plus density and viscosity were employed. Standard HDS catalyst was “gravel packed” around the horizontal producer well, forming an annular radial inflow type reactor. The authors were of the opinion that though the analytical measurements made were necessarily selective in their scope, they nevertheless provided a good indication of what the potential might be for the downhole upgrading in the field. An overall increase of 4 to 6 additional API points was observed for the oil produced from Wolf Lake crude (produced from a prior steam flood operation) via *in situ* catalytic processing (CAPRI), compared to thermal upgrading alone with non-catalytic process (THAI). The produced oil viscosity was reduced by nearly 4 orders of magnitude. A micro activity test (MAT) on the ‘light oil’ produced from the CAPRI process, showed that it contained neither residue (+525°C), nor asphaltenes. This upgraded crude oil from a refinery

---

[§] ASTM method D3907: This test method covers determining the activity of equilibrium or laboratory-deactivated fluid catalytic cracking (FCC) catalysts, or both. This is evaluated on the basis of weight percent conversion of gas oil in a microactivity unit.

perspective was found to be readily convertible into gasoline and diesel fractions, with a higher conversion than obtained with normal virgin bitumen vacuum gas oil. The authors proposed very substantial environmental benefits by using CAPRI/THAI as removal of heavy metals (V, Ni) was greater than 90% (Table 2.7). They also suggested that these heavy metals are ‘trapped’ on the burned sand matrix in the actual reservoir. These findings were found to be a major breakthrough as majority of the tests using a non-presulphided, standard HDS catalyst only achieved about 30% reduction of the sulphur in the oil with only one test. By contrast using a partially spent presulphided catalyst achieved greater than 90% sulphur removal. From Table 2.8 SARA analysis of CAPRI processed oil shows that there is a very substantial increase in the saturate contents compared to the original Wolf Lake oil (>100%), accompanied by significant reductions in the aromatics (~ 25%), resins (> 35%) and asphaltenes (> 85%).

Table 2.7 Elemental Analysis of Wolf Lake Crude Oil, Catalytically Produced Oil and burned matrix

Element	**Wolf Lake Crude**			**Run 970**[a]	**Run 989**[b]	**Run 9903**[b]	**Run 9904**[b]	**Run 9905**[b]	**Solid Matrix**
	a	b	c						
C (%)		83.7	84.2		84.9				
H (%)		10.62	11.03		11.79				
N (%)		0.25	0.38		0.2				
S(ppm)	43.400	45.000		5.100	29.600	30.300	29.900	32.200	0.18%
N(ppm)									<0.01%
Ni(ppm)	73	75		3		12	<5	6.6	6.2
V (ppm)	195	192		8		30	<5	13	20
Fe(ppm)	5		<1						
H/C			1.573		1.64[c]				

[a] Analysis by BP Sunbury, UK

[b] Analysis by Medac Ltd, Surrey, U.K.

[c] University of Bath

Table 2.8 SARA Analysis for Produced Oil*

Fractions, Wt%	Saturates	Aromatics	Resins	Asphaltenes
Wolf Lake Crude	25.18	37.40	27.33	10.09
Run 9904	54.78	26.32	17.34	1.56
Run 9905 (dry mode)	53.5	28.1	16.4	2
Run 9905 (wet mode)	55	26.82	16.7	1.48

*Analysis by Chemical Engineering Unit, University of Salford, UK

Effect of Feed (Lloydminster Heavy Crude Oil) on THAI-CAPRI

Xia *et al.* (2002) conducted a series of 3-D combustion cell experiments using the THAI-CAPRI process on Lloydminster heavy crude oil (11.9 °API). In separate THAI and CAPRI experiments, high temperature combustion was sustained (500-550°C) achieving stable combustion front propagation. Oil recovery in excess of 79% OOIP for THAI and CAPRI were achieved. From Table 2.9, the first stage by the application of THAI (only thermal) alone and then with CAPRI (thermally/catalytically) in the second stage the API value is upgraded to 18.3° (on an average basis) and 23° (with a maximum value) respectively. The viscosity was significantly lowered for the subject crude oil from 14.6 Pa.s to as low as 0.02-0.03 Pa.s. The peak temperature achieved was 550°C and the maximum duration of the experiment was 17 hours. Some of gases produced during the experiment have also been provided in Table 2.9. This combination of gases in their respective percentage composition provided the bases to make a blended "THAI gas" mixture in a cylinder and was used as one of the reaction media in this work.

Table 2.9 Results for THAI and CAPRI Tests

Run	**2001-03**	**2001-04**
	THAI	CAPRI
Overall period (hrs)	13	17
Air injection (hrs)	8	13
Dry phase (hrs)	7	11.5
Wet phase (hrs)	1	1.5
Peak Temperature (°C)	500-550	500-550
Produced gases (% Average)		
CO_2	14.7	15.86
CO	5.3	4.39
O_2	3.8	0.035
$CO/(CO_2+CO)$	0.263	0.217
H/C	0.05	0.598
Oil recovery (wt% OOIP)	82.9	79.3
API gravity of the produced oil (average)	18.3	23.0
Combustion front velocity ($cm.hr^{-1}$)	6.8	4.2
Residual oil (%OOIP)	4.8	8.2

Upgrading levels of 4-6 API points was observed with both Wolf Lake crude and Lloydminster heavy oil. Similar level of upgrading in terms of viscosity within the lowest range of 0.02-0.035 Pa.s was achieved with both crudes. However the catalytic run duration of Wolf Lake and Lloydminster with 12 and 17 hours respectively was different. The pressure in both the experiment was also low with a maximum value of only 2 bars.

Apart from the THAI-CAPRI experimental studies in the laboratory, a field trial of the technologies is also underway by the Canadian oil company Petrobank. A brief insight into the latest results from the trial has been presented in the next section.

Petrobank Field Trail of THAI/CAPRI

Petrobank is started a field trial of the THAI/CAPRI process at Whitesands in Alberta, in 2008 (Petrobank, 2008). The project was announced to be producing 400 barrels per day for each well at a quality of approximately 12 °API, compared to the native 8 °API bitumen *in situ*. At the stage of reporting, it was too early to determine the catalyst effectiveness, partly as the well was only operating at 300°C, which is too low for the catalyst to be fully operational. Petrobank, predict a flow rate per horizontal well of 90 m^3 oil/day, of about 800 barrels/day. Allowing for the lower API gravity of CAPRI produced crude oil (say 22°), then at \$50/barrel, the catalyst cost represents only about 1½ to 2½ days' production. Early estimates suggest that the THAI/CAPRI process costs about one third per producing barrel of the equivalent SAGD process (Petrobank, 2009). In view of the fact that steam is only required during start up, electrical heating is not required, minimal water is used and less surface upgrading is necessary than mining, taking a balanced view the THAI/CAPRI process appears to be one of the most economically attractive EOR methods. However, further field data placed in the public domain is necessary to fully evaluate its economic viability.

Although further information regarding the catalyst optimization is necessary and results of field trials need to be evaluated, the technique has now been demonstrated in application. CAPRI^{TM} will have to overcome some significant challenges before it can be economically viable, as heavy crude oils are usually loaded with more than 5% sulphur and up to 1000ppm of nickel and vanadium, which can deactivate the catalyst very quickly. Moreover the pyrolysis of heavy oils or natural bitumen can produce coke which can cover the surface of the catalyst and hence prevent it from reacting with the oil in the reservoir leads to loss of upgrading (Bartholomew, 2001)

THAI STARS^{TM} Numerical Simulation Studies

Greaves *et al.,* (2000) studied numerical simulation of the THAI^{TM} process for heavy oil recovery using STARS^{TM} (Steam, Thermal and Advanced Processes Reservoirs Simulator by Computer Modelling Group, Canada). Because a 3-D cell was used as the physical model for the experiments, it is necessary to build a three-dimensional reservoir simulation model. The aim of the preliminary simulation study was to understand the mechanism of the oil displacement in THAI. The main features of the 3-D model used to carry out the simulation are listed in Table 2.10. From the simulation studies it was found that the combustion front propagates through the reservoir in nearly upright position, in a 'toe-to-heel' manner as presented in Figures 2.19 and 2.20. The temperature in the combustion zone is 700°C to

800°C, which is higher than that observed in the 3-D cell test. This is probably due to the fact that a perfect adiabatic condition was assumed in the simulation model. In the laboratory experiment, perfect adiabacicity cannot be realised. Heat loss from the sandpack to the surroundings occurs, even with apparently good temperature control. Figures 2.19 and 2.20, show that the combustion zone expands in three dimensions (i.e. x, y, z), as in the experiment (Run 984). Simulation studies predicted that there is no oxygen in the produced gas. The oil production initially was high at around 20 ml.min^{-1}. Afterwards, it falls rapidly to about 5 ml.min^{-1}. This oil recovery performance matches that obtained from the 3-D cell test. In the numerical run, oil production after 300 min is more stable, at a rate of 3.7 ml.min^{-1}. The average rate of oil production and overall oil recovery, which is about 85% OOIP, is the same as that obtained in the physical model.

The main findings from this preliminary numerical simulation study are:

- A stable combustion process is sustained. Nearly 100 per cent of the oil-bearing matrix is swept by the thermal front.
- By eliminating heat loss, the combustion temperature is higher by 100°C, compared to the experiment.
- Oxygen in the injected air is totally consumed.

Table 2.10 Numerical Model of THAI Experiment

• 2100 Grid blocks (20*21*5)
• 6 components: Water, Heavy oil, Light oil, Inert gas, Oxygen and Coke
• Four chemical reactions: Heavy oil cracking; Light oil burning; Heavy oil burning; Coke burning
• Horizontal Injection well and a horizontal producer well arranged in 'Toe-to-Heel' placement in the reservoir
• Initial conditions: Oil saturation: 72% Water saturation: 20% Gas saturation: 5% Reservoir temperature: 25°C Reservoir pressure: 30psig
• Reservoir porosity: 38.5% • Permeability: 1040mD
• Air injection rate: 6.0 l.min^{-1}
• Using external electric heating element as the igniter
• No heat loss to the environment

Figure 2.19 STARS Simulation of 3D Cell Test -- Dry Combustion Run 984, Temperature (°C) 360 min

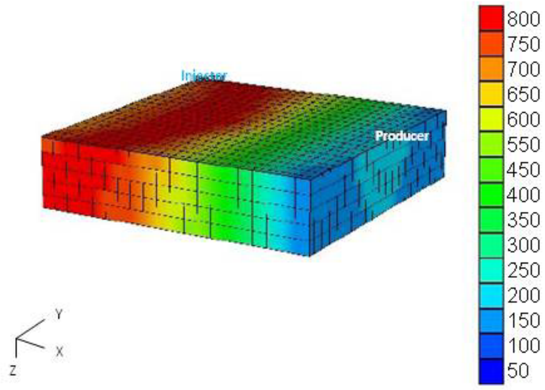
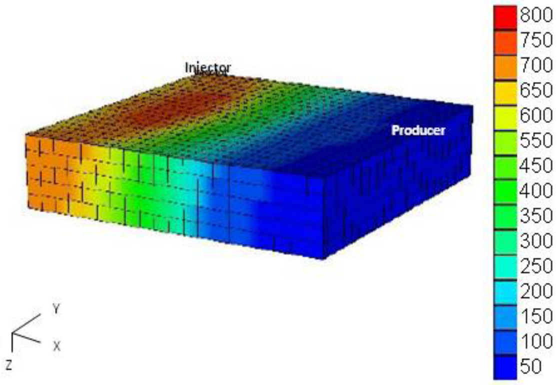


Figure 2.20 STARS Simulation of 3D Cell Test -- Dry Combustion Run 984, Temperature (°C) 660 min



2.11 Catalyst Properties and Composition for Heavy Oil Upgrading

The catalysts used for residue hydroprocessing are sulphides of Co, Ni, W and Mo supported catalysts, which have a variety of pore structure and active metal dispersion or active sites. The most important property for residue hydroconversion catalyst is pore diameter because feedstock contains large molecules of asphaltene, metal chelated, etc (Rana *et al.,* 2007). Broadly the bottom fraction or residuum of distillates crude is typically processed in trickle-bed reactors at temperatures of 350–450°C and pressures of 5–15 MPa. Under these conditions, much of the metals such as Ni, V and Fe, which are present as porphyrin or chelating compounds, are deposited as metal sulphides (Ni_3S_2, V_3S_2 and V_3S_4, having 2–30 nm crystal size) over the catalyst (Rana *et al.,* 2007). These deposited transition metal sulphides poison the catalyst by decreasing catalytic sites, hinder the transport of reacting molecule or eventually plugging the pores. The deposited metal sulphides have been characterized by Smith and Wei (1991a and b) using Transmission Electron Microscopy (TEM), Energy-dispersive X-ray spectroscopy (EDX), Scanning Transmission Electron Microscopy (STEM) and X-ray Photoelectron Spectroscopy (XPS) for the HDM of model molecules on deactivated catalyst and by Takeuchi *et al.* (1985) X-ray Diffraction (XRD), Electron Spin Resonance (ESR) and SEM, on the catalysts used in Hydrodemetallization (HDM) of heavy oil. The V_2S_3 phase was observed in a circular or rod shaped crystallites about 100 nm in length. Toulhoat *et al.* (1987) reported that nickel is always associated with vanadium [$Ni(V_3S_4)$] and its crystallite grew perpendicular to the support surface. Apart from these metals, Ca, Mg and Fe sulphides are also possible to deposit on the exterior surface of the catalyst (Gosselink, 1998). The major problem in residue oil is to eliminate asphaltene with respect to conversion as well as characterization due to its complex nature (Absi-Halabi *et al.,* 1991; Furimsky and Massoth, 1999). Additionally, the chemistry of asphaltene is not totally understood and its molecules are precursor to the most problematic organic deposits in residue e.g. sediment formation. During the reaction these huge molecules are allowed to diffuse into the catalyst pore and their metal atoms (V and Ni) are removed from the ring structures. These results will lead to instability and finally to dry sludge, which is the dead point for any kind of catalyst stability. Therefore, the preferred catalyst design will result in the large quantity of metal deposition with time-on-stream, which will represent the catalyst life or stability. Catalyst cracking activity can be improved by modifying the supports, by using more acidic (zeolites) material than conventional catalyst (supported γ-Al_2O_3), this however, also may increase the rate of coke formation (Rana *et al.,* 2007). Properties of supports are crucial for defining the desirable porosity and surface area of catalysts. Therefore the performance of catalysts can be modified by chemical composition of these supports, in this sense it is well established that mixed oxide support can be prepared with acid–base sites (Rana *et al.,* 2005a,b and c; Caloch *et al.,* 2005), which improve cracking functionality of the catalyst (Maity *et al.,* 2003; 2005 and 2006). It is believed that during hydroprocessing of heavy feeds, catalyst life can be further prolonged by applying balanced (high pore volume and low surface area) textural properties of catalyst.

2.12 Catalyst Deactivation Mechanism

It is inevitable that all catalysts will decay eventually, however catalyst deactivation mechanisms need to be understood and reduced in view of the costs involved in replacing the catalysts or process shutdowns. In this part of the literature review, some of these mechanisms are reported.

The mechanisms of catalyst deactivation are many; nevertheless, they can be grouped into six intrinsic mechanisms of catalyst decay: (i) poisoning, (ii) fouling, (iii) thermal degradation, (iv) vapour compound formation accompanied by transport, (v) vapour–solid and/or solid–solid reactions, and (vi) attrition/crushing. As (i), (iv), and (v) are chemical in nature while

(ii) and (v) are mechanical, the causes of deactivation are basically three-fold: chemical, mechanical and thermal (Bartholomew, 2001).

(i) Poisoning is the strong chemisorption of reactants, products or impurities on sites otherwise available for catalysis. Depending upon the poison concentration, poisoning may be rapid or slow; depending on the strength of poison adsorption, poisoning may be reversible or irreversible. Mechanistically, poisoning is a complex process involving some or all of the following: (a) physical blockage of one or more catalytic sites by the strongly adsorbed poison, (b) electronic modification of nearest neighbour atoms and sometimes even next-nearest neighbour atoms, (c) restructuring of the adsorbent surface, and (d) hindering surface diffusion of adsorbed reactants, thereby preventing reaction. A conceptual model of how sulphur poison a metal catalytic surface has been provided in Figure 2.21. Since a number of common poisons such as coke, sulphur and arsenic compounds are strongly and irreversibly adsorbed, poisoning is best prevented through purification of the reactant stream by means of scrubbers or guard beds, rather than attempting to remove the poison from the catalyst after the fact. However in case of THAI-CAPRI processes where the feed can’t be purified the only option is to better design the catalyst to resist coking or working under optimum reaction conditions to prolong the catalyst life. Some of the common poisons relevant to its reactions have been presented in Table 2.11 of which cracking reactions and hydrotreating of the residue are very relevant to this work.

Figure 2.21 Conceptual Model of Poisoning by Sulphur Atoms of a Metal Surface during Ethylene Dehydrogenation (Bartholomew, 2001)

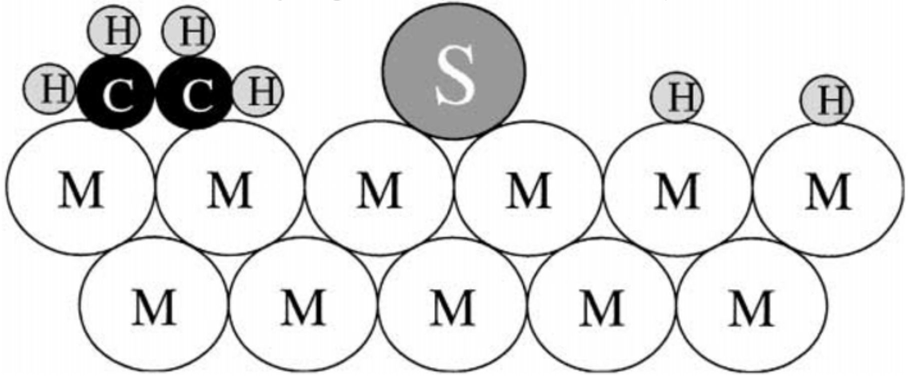
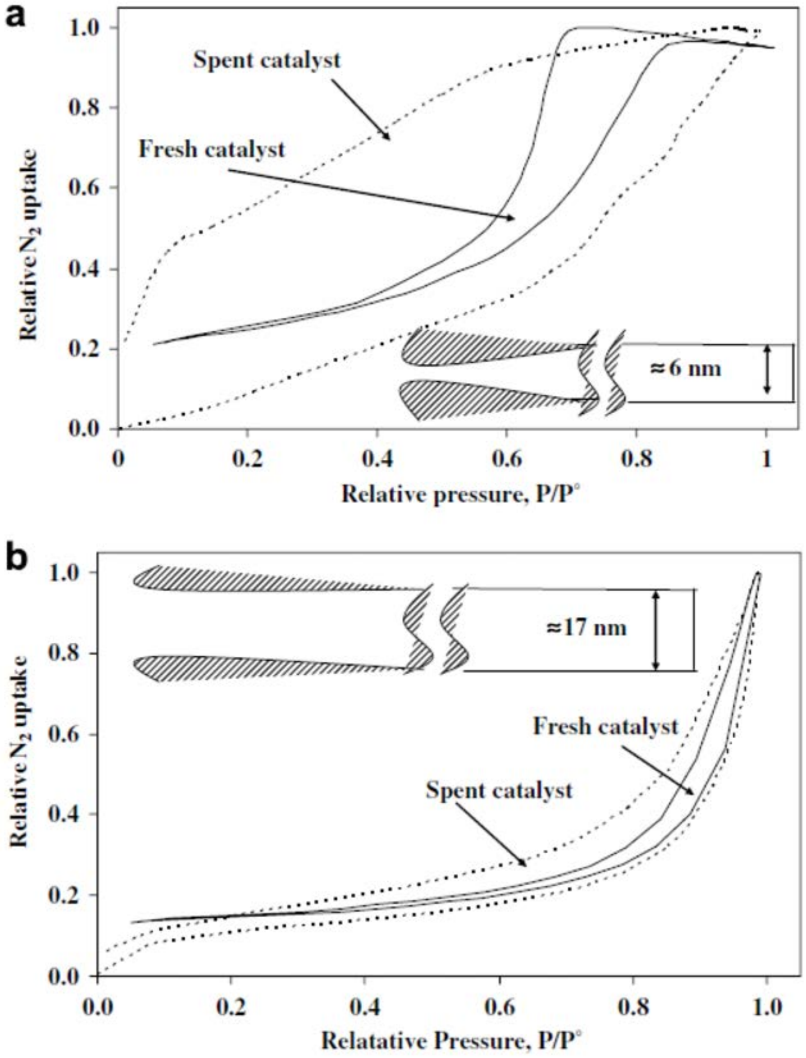


Table 2.11 Poisons for Selected Catalysts in Important Representative Reactions (Bartholomew, 2001)

Catalyst	**Reaction**	**Poison**
Silica-alumina, zeolites	Cracking	Organic bases, hydrocarbons heavy metals
Nickel, platinum, palladium	Hydrogenation dehydrogenation	Compounds of S, P, As, Zn, Hg, halides, Pb, NH_3, C_2H_2
Nickel	Steam reforming of methane, naphtha	H_2S, As
Iron, ruthenium	Ammonia synthesis	O_2, H_2O, CO, S, C_2H_2, H_2O
Cobalt, and iron	Fischer–Tropsch synthesis	H_2S, COS, As, NH_3, metal carbonyls
Noble metals on zeolites	Hydrocracking	NH_3, S, Se, Te, P
Silver	Ethylene oxidation to ethylene oxide	C_2H_2
Vanadium oxide	Oxidation selective catalytic reduction	As, Fe, K, Na from fly ash
Platinum, palladium	Oxidation of CO and hydrocarbons	Pb, P, Zn, SO_2, Fe
Cobalt and molybdenum sulphides	Hydrotreating of residue	Asphaltenes, N compounds, Ni, V

(ii) Fouling is the physical (mechanical) deposition of species from the fluid phase onto the catalyst surface, which results in activity loss due to blockage of sites and/or pores. In its advanced stages it may result in disintegration of catalyst particles and plugging of the reactor voids. In reactions involving hydrocarbons, coke may be formed in the gas phase and on both non-catalytic and catalytic surfaces. Nevertheless, formation of coke on oxides and sulphides (refer to Chapter 7 for detailed discussion about coking on supported catalysts and zeolites) is principally a result of cracking reactions involving coke precursors (typically olefins or aromatics) catalyzed by acid sites (Rostrup-Nielsen, 1974; Gates *et al.,* 1979). Generally, in the catalytic upgrading of heavy residues/oils when the ratio of the intrinsic HDM activity to the asphaltene diffusion into and through the catalyst pore structure is too high, the metals will be removed from their organic environment towards the pore mouth, thus, restricting diffusion of reactant species into the pores. Since pore diameter plays an important role to control the heavy fraction Hydrotreating HDT catalyst activity, therefore, the deposition of metal will depend on the pore diameter of catalyst as shown in Figure 2.22 (a, b and c). This figure also indicates the deposition of metal around the pore mouth Figure 2.22(c), which increases with decreasing the pore diameter. Catalysts having high cracking activity usually have smaller average pore diameters, sharp pore distribution, high surface area, and high HDT activities. As these catalysts are more susceptible to pore mouth plugging, they have to be “protected” by the guard-bed catalyst, which should have large pore diameter, low surface area and high metal retention capacity. The effect of surface area and pore diameter and/or pore volume on catalyst deactivation and their applicability are different e.g. high surface area is expected to have high dispersion of active sites (high activity) while pore diameter controls the diffusion of complex molecule into the pores or the catalytic sites. Therefore, there is an optimum balance of surface area and pore diameter of the catalyst (Ancheyta *et al.,* 2005; Rana *et al.,* 2005) as shown in Figure 2.23, which balances the activity, diffusion properties and dispersion of active metals. Catalyst stability is improved as the macro-pores remain accessible to large molecules even after significant Ni and V deposition. The characteristic bi-modal pore structure provides high activity or metals retention capacity and stability.

Figure 2.22 Fresh and Spent Catalysts Adsorption–Desorption Isotherms. (a) CoMo/γ-Al_2O_3 (6 nm Average Pore Diameter), (b) CoMo/ γ -Al_2O_3 (17 nm Average Pore Diameter) and (c) (Rana *et al.*, 2005)



(c) Spent catalyst XRD and deposited metal sulphides (Maya crude, temperature of 380°C, pressure of 5.4 MPa and LHSV of 1 h^{-1}, 60h, Time on Stream; average pore diameter of catalyst of 17.3 nm (Rana *et al.*, 2004)

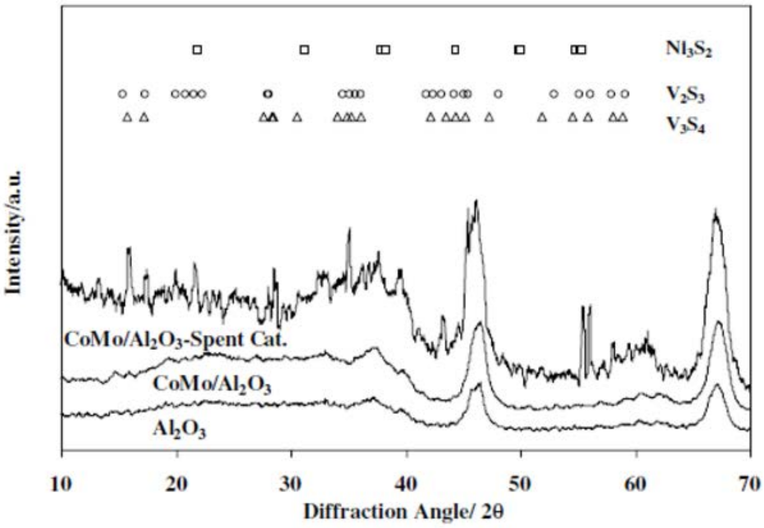
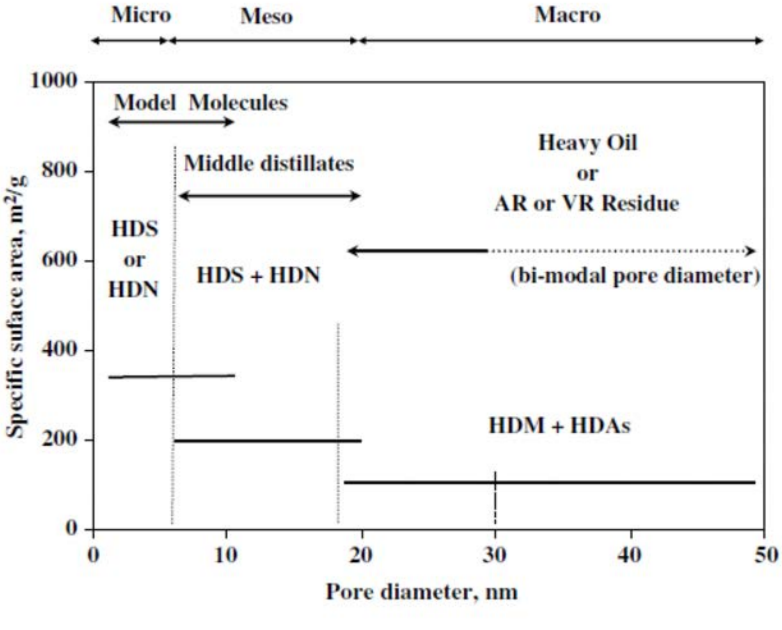
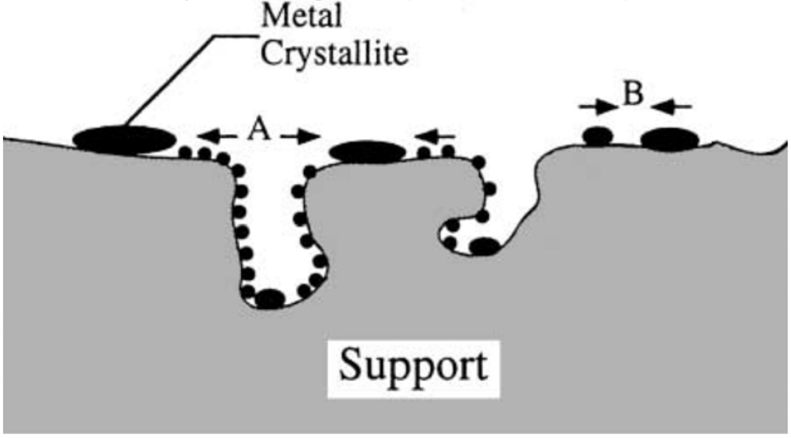


Figure 2.23 Effect of Pore Diameter and Specific Surface Area on Hydrotreating Catalyst Activities (Ancheyta *et al.*, 2005)



(iii) Thermally-induced deactivation of catalysts result from (a) loss of catalytic surface area due to crystallite growth of the catalytic phase, (b) loss of support area due to support collapse and of catalytic surface area due to pore collapse on crystallites of the active phase, and/or (c) chemical transformations of catalytic phases to non-catalytic phases. The first two processes are typically referred to as "sintering". Sintering processes generally take place at high reaction temperatures (e.g. >500°C) and are generally accelerated by the presence of water vapour. Three principal mechanisms of metal crystallite growth have been advanced: (1) crystallite migration, (2) atomic migration, and (3) (at very high temperatures) vapour transport. A Conceptual model of the first two types has been illustrated in Figure 2.24.

Figure 2.24 Two Conceptual Models for Crystallite Growth due to Sintering by (A) Atomic Migration (B) Crystallite Migration (Bartholomew 2001)



Redispersion, the reverse of crystallite growth in the presence of O_2 and/or Cl_2, may involve (a) formation of volatile metal oxide or metal chloride complexes which attach to the support and are subsequently decomposed to small crystallites upon reduction and/or (b) formation of oxide particles or films that break into small crystallites during subsequent reduction. Growth of metal crystallites on a support could in principle involve a combination of all three sintering mechanisms operating simultaneously, although relative rates will depend upon reaction conditions. Temperature, atmosphere, metal type, metal dispersion, promoters/impurities and support surface area, texture and porosity, are the principal parameters affecting rates of sintering and redispersion. Sintering rates increase exponentially with temperature; activation energies are on the order of 15–100 kJ.mol^{-1} (Bartholomew 1992; Bartholomew and Fuentenes 1997). Metals sinter relatively rapidly in oxygen or water vapour and relatively slowly in hydrogen. Promoters such as MgO or BaO lower sintering rates by decreasing metal atom mobility, while support surface defects or pores impeded surface migration of metal particles. In general, sintering processes are slow at moderate reaction temperatures and either irreversible or difficult to reverse. Thus, sintering is more easily prevented than cured; the key is to maximize catalytic activity enough to enable operation at temperatures low enough that sintering rates are negligible.

Key areas to minimize coking include; operating under conditions that minimize formation, e.g. at sufficiently high H_2/CO ratios, optimizing catalyst design, e.g. in the case of zeolites optimizing acidity to minimize coke formation; and purifying the feed to remove precursors that accelerate carbon or coke formation, e.g. removal of polynuclear aromatics from the feed of a hydrocracking or hydrotreating process which otherwise react readily on acid sites to form coke. Purifying the feed however is not practical with *in situ* technologies such as THAI-CAPRI.

2.13 Comparison and Evaluation of Different Enhanced Oil Recovery Techniques

The unconventional resource base is vast and current projections on global unconventional oil production of 2.5 MMbbls/d for Canadian oil sands and 2 MMbbls/d for Venezuelan heavy oil in 2015 and 9 MMbbls/d in 2030 do not appear unrealistically high. Mining is the major heavy oil and bitumen recovery technique at present, however is severely limited to shallow deposits. Cold production is a low-cost, low-risk method for the recovery of heavy oils but suffers from low recovery rates and is not applicable to the most viscous heavy oils and bitumen. EOR techniques must be therefore applied to extract further oil from sources.

The suitability of the various EOR techniques are summarised in Table 2.4. The geology of the reservoir is important but most significant is the properties of the oil and only thermal techniques are feasible for the most viscous oils and bitumens. ISC has largely fallen out of favour as a thermal technique in preference to steam methods such as Steam Flooding and SAGD which are easier to control (Butler and Stephens, 1981; Butler, 1985 and 1991). However, in a similar way that the use of horizontal wells in SAGD has made Steam Flooding a more controllable process, their use in THAI has reinvigorated interest in ISC methods which benefit from using low-cost air instead of steam and offer potentially higher recovery levels. Furthermore, the process is attractive for coupling with downhole catalytic upgrading to produce a lighter product at little extra cost when compared with surface upgrading facilities. The role of the emerging technologies such as THAI and CAPRI becomes particularly important as present commercial technologies like SAGD need comparatively more investment to increase the extraction, upgrading, transportation (pipelines and trucking) facilities, and infrastructure.

Producing and upgrading heavy oil and natural bitumen with present technologies (mainly thermal such as SAGD and CSS) requires considerable energy input. Currently natural gas provides mostly the energy for steam generation and is a source of hydrogen production for upgrading processes. The present natural gas reserves of North America at least are not enough to sustain the projected growth of heavy oil and natural bitumen production levels (Oil and Gas J., 2008).

Increasing production from heavy oil and natural bitumen with present commercial technologies could have a huge impact on the environment. Increased carbon dioxide emissions are of prime concerns and especially if carbon intensive alternatives like coke or coal are burnt to supplement natural gas (Flint, 2004). Large quantities of water usage e.g. SAGD currently uses between two to ten barrels of water injected as steam for every barrel of oil produced, (Gates and Chakrabarty, 2006) and soil contamination, land reclamation and reforestation are some of the very important issues to be taken into consideration. Moreover, upgrading at the production site or *in situ* upgrading in the future will be of added help, as this will save on the costs, e.g. solvents (used as diluents to ease heavy oil/natural bitumen flow through pipelines) and refinery upgrading.

The benefits of emerging technologies like THAI-CAPRI are yet to become a reality on a commercial scale. However, the Canadian oil company, Petrobank, has recently made an application to the Alberta Energy and Utilities Board for a commercial project of 100,000 barrels per day, called the May River project. THAI technology is also being tested on heavy oil at Dawson Creek in the Peace River district of Alberta, and there is also the likelihood of another heavy oil project in North West Saskatchewan, by True Energy. As conventional oil resources become scarcer, there will be greater reliance on these new technologies being developed now. Alternative technologies such as electrical heating, developed by Shell and the Electrofrac process developed by ExxonMobil could also present promising methods of producing and upgrading heavy oils. However these methods require large inputs of electrical energy, which will necessitate difficult decisions about the source of supply, including evaluation of whether nuclear power has a role to play in extraction of oil from the tar sands.

Conclusions

Some of the following conclusions can be made from the above discussion;

Unused huge reserves of heavy oils and bitumen are vital to keep up the future supplies of crude oil worldwide.

Despite extensive research and modifications the current EOR technologies for the recovery and upgrading of heavy oils and bitumen are not efficient and not sustainable.

Reliance on the current EOR technologies will mean, ruling out more than 50% of the huge reserves of heavy oil and bitumen as unrecoverable.

THAI as a new EOR method has the potential of recovering up to 85% OOIP and its produced oil have been found to be upgraded in comparison to oil produced using methods such as SAGD or VAPEX.

THAI is also very easy to operate due to its simplicity of technology and is potentially applicable to reservoirs as thin as 6m previously ruled out to be unrecoverable.

CAPRI can potentially further upgrade the produced oil in terms of API gravity and reduce harmful ingredients such as Sulphur, Vanadium and Nitrogen by almost 90%.

Rationale for Current Studies

Unlike THAI, information about CAPRI is limited. Xia and Greaves (2001) have listed the effectiveness of some refinery catalysts for heavy oil upgrading, yet these catalysts and/or other catalysts, needs further optimization before they can be applied in the field. THAI has been previously observed to improve the saturate contents possibly because of hydrogenation and reduction in harmful contents such as heavy metals V, N and Sulphur of up to 90%. However, the mechanism involved through which all these processes operate (during THAI or CAPRI), needs to be better understood. Moreover, catalysis of heavy oils and bitumen suffers from severe coking and catalyst life needs to be optimized for THAI-CAPRI process, as previous studies only lasted for a maximum of 17 hours. In order to know how THAI-CAPRI will work at different reservoir pressures the technology needs to be optimized as in previous laboratory studies a maximum of 2 bar g of pressure has been used. Effect of water, temperature, oil flow rates and reaction media also needs to be optimized.

Chapter 3

Experimental and Analytical Methods

3.1 Introduction

In this Chapter, the experimental CAPRI rig and parameters used are described, together with the methodologies which have been developed and used to analyse both the produced oil liquid fraction and flue gases. §3.1 contains a detailed description of the development of the experimental CAPRI rig. Descriptions of how the CAPRI experimental rig is simulated at laboratory scale from field scale, the selection of gases used as reaction media, detailed description of the rig, accessories attached for the addition of steam and pre-sulphiding of the catalyst are included. The rig commissioning and modifications, the mixing chamber, the CAPRI reactor and its packing, main separating vessel, standard operating procedure of the rig along with clean up procedure, pre-sulphiding of the catalyst (procedure), pre-reduction (procedure) and the properties of different type of oils used are also described in §3.1.1 to 3.1.14. §3.1.3 details the different analytical methods used to analyse produced oils, gases and coke. These methods and instruments include density and API gravity, viscosity, simulated distillation, refinery gas analysis, TGA, NIR, SARA analysis, sulphur and metal analysis (§3.2.1-3.2.9).

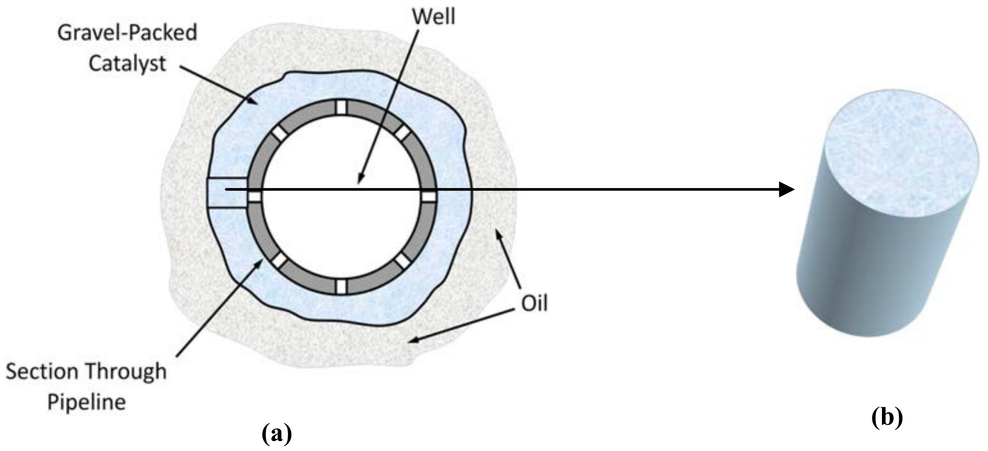
Appendix 9.1 provides the detailed calculations for gas and oil flow rates used in this work. Appendix 9.2 provides the list of steel tubes deemed feasible to be used CAPRI reactors. Appendix 9.3 provides the list of all experiments being conducted (letter P stands for Pilot oil, C for Combustion Cell Oil and D for n-decane experiment). Appendix 9.4 provides the health and safety assessment needed as part of the health and safety regulations.

3.2 In-situ CAPRI Reactor

3.2.1 Simulating *in situ* CAPRI Conditions in the Experimental Rig

In the *in situ* THAI-CAPRI process the catalyst is packed with gravel around the horizontal producing well. The thickness of the annular packing in the well create an annular of this dimension in the laboratory, a cylindrical core was taken as the catalyst in a packed bed micro-reactor oil flowing downwards through the micro-reactor simulates oil in the field flowing in to the well through the annular catalyst layer. The CAPRI experimental reactor tube is based on a cylindrical core as represented in Figure 3.1 (a) and (b), from this packed catalyst.

Figure 3.1 (a) and (b) The CAPRI Reactor based on a Cylindrical Core from the Gravely Packed Catalyst around the Horizontal Production Well



3.2.2 Scaling down of the CAPRI reactor to laboratory scale, the selection of gases (reaction media) and oil flow rates

It was desired to scale the experimental micro-reactor according to the same ratios of superficial velocity being used in the field trial at the Whitesands well in Alberta, Canada.

Petrobank, the Canadian oil company carrying out the pilot studies of THAI technology, is using 20 tonnes of new HDS catalyst for 500 m horizontal producer well with a superficial velocity of 14.19 mm.min^{-1}, which costs about \$60- 100k. Petrobank predicts a flow rate per horizontal well of 90 m^3 oil/day, about 800 barrels/day. A similar figure is obtained by scaling directly from the University of Bath 3D experiments, with a volumetric ratio between pilot and experiment of 30 million: 1 (Greaves et. al. 2001).

In order to replicate the conditions in the well it was decided to maintain the same superficial velocity of oil. In order to practically implement this velocity, calculations of flow and velocity were performed for a range of different diameters of steel tubing in Table 3.1 (calculations provided in Appendix 9.1). To scale down the horizontal producer well from field to the laboratory scale, a number of steel tubing diameters were taken into consideration (full list provided in Appendix 9.2), keeping the superficial velocity closer to 14.19 mm.min^{-1}, predicted at field scale. The steel tube selected for this work was a ½” tubing from Swagelok, with an internal diameter of 10.2 mm. As per the following calculations the superficial velocity of 12.2 mm.min^{-1} was found achievable with an oil flow rate of 1 ml.min^{-1} and gas flow rate of 0.5 l.min^{-1} at STP and temperature of 400°C and pressure of 20 bar g (superficial velocities of gas and oil, at different conditions have been provided in Table 3.1). These conditions were therefore selected as being sufficiently close to the actual superficial velocity in the oil well, based on the available tube sizes.

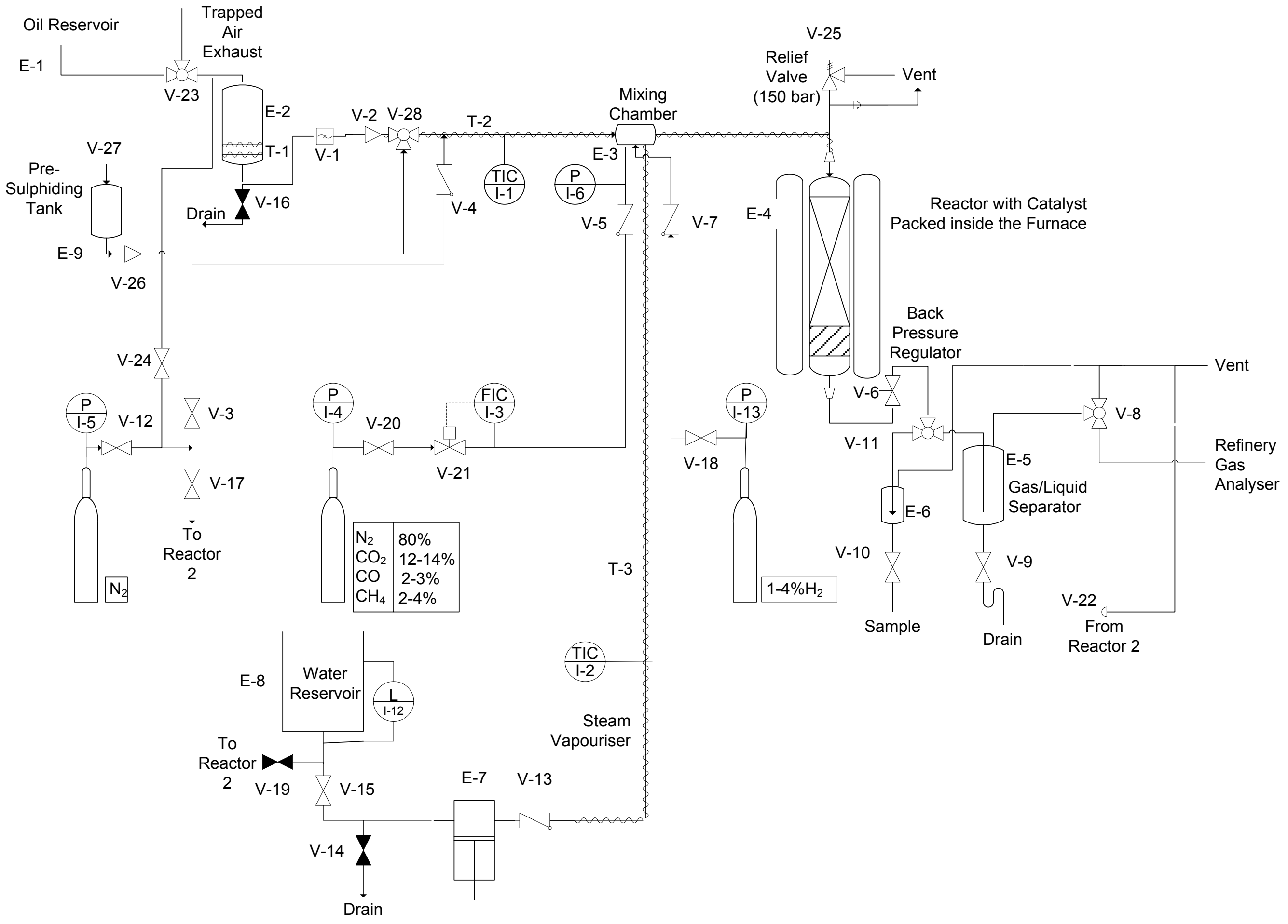
Table 3.1 Superficial Velocity of Gas and Oil at Different Temperatures and Pressures at 1 l.min^{-1} and 1 ml.min^{-1} of Flow Rates Respectively

Temperature [°C]	Pressure [bar g]	Velocity of Gas [m^3.min^{-1}]	Velocity of Oil [mm.min^{-1}]
380	20	1.478	12.2
400	20	1.520	12.2
425	20	1.579	12.2
450	20	1.636	12.2
475	20	1.694	12.2
500	20	1.750	12.2
425	40	0.790	12.2
425	60	0.526	12.2

3.2.3 Detailed Rig Description

A state of the art CAPRI rig was developed, consisting of two identical micro-reactors for the purpose of simulating *in situ* catalytic oil upgrading conditions in the horizontal producer well. Figure 3.2 shows the flow diagram of one of the two identical reactors. Initially in the experimental setup a syringe pump was used. However, the inlet and outlet of the pump consistently got blocked with the viscous THAI field oil and its inherent contaminants. Afterwards a peristaltic pump was used; however the same problem of clogging continued to occur. These blocking also caused inconsistent feed rate than the target level of 1 $ml.min^{-1}$ to the reactor. Eventually, pressurised vessels were used successfully to achieve the target oil flow rate of 1 $ml.min^{-1}$. The pressurised vessel with a maximum capacity of 3.59 l (E-2) is used as the feed reservoir and can be filled with either THAI field oil, Combustion Cell Oil (CCO) or n-decane using a three way valve (V-23) which is connected to the crude oil tank [(E- 1), Figure 3.2]. The vessel (E-2) is pressurised 5 bar (g) above the set experimental pressure, using nitrogen gas by opening (V-24). The furnace around the catalyst (E-4) houses the experimental reactor. Trace heating around the bottom of the pressurised vessel (T-1) provides heat of 50°C to keep the THAI field oil mobile. Trace heating around the channels feeding the reactor from the pressurised vessel and water reservoir (T-2 and T-3) both provides a temperature of 300°C and vaporizes the oil/water before it enters the reactor. Reaction gases either nitrogen or THAI gas can be initiated using (V-20). V-18 can be used for hydrogen addition. The back pressure regulator (V-6) keeps the experimental pressure in the reactor.

Figure 3.2 CAPRI Experimental Rig Schematic



The manual metering valve (V-2) used to open oil flow into the reactor is kept protected from any possible sediment contamination in the crude oil by a filter of 15 micron (V-1). Oil and reaction gas (nitrogen, THAI or a combination of the two with hydrogen) are mixed in a mixing chamber (E-3) before fed into the reactor, with all the components in vapour state.

The gas liquid separator (E-5) is designed to separate gases from liquid, where the flue gases are either sent to the vent or to the Refinery Gas Analyser RGA using (V-8).

As a safety feature to prevent the CAPRI experimental rig accidently being pressurised beyond the maximum designed pressure capacity of 150 bar (g), a relief valve (V-25) was set to 150 bar (g), which vents off any excess pressure automatically. Any excess temperature at the furnace around the reactor is checked automatically by the alarm system of the furnace control unit made by Severn Thermal Solutions Ltd.

3.2.4 THAI Gas, Nitrogen and Hydrogen as Reaction Gases

In the field well the gases flowing through the catalyst bed are produced by combustion of oil in the THAI process and thus consist of nitrogen from the injected air, together with by products of the combustion process. In the 3D chamber THAI process experiments Greaves *et al.* (2001) detected the THAI gas combination (N_2 80%, CO_2 13-14%, CO 3%, CH_4 4%) in the flue gases using GC. Though a small amount of oxygen (2.24% on average) was observed during the laboratory experiments, it was not considered significant, as at laboratory scale the conditions are not truly adiabatic compared with the adiabatic nature of the reservoir conditions. In the reservoir close to 100% oxygen consumption was predicted, as THAI-CAPRI process operates by high temperature oxidation mode. For this reason the THAI gas combination was pre-blended specially as per the above composition by BOC gases and used in some of the experiments in this work. It was also desired to determine whether the CO_2/CH_4/CO components of THAI gas have significantly beneficial effect upon upgrading performance compared with nitrogen only. Therefore, oxygen free nitrogen (99% pure) prepared by BOC gases was primarily used apart from THAI gas as the reaction media to investigate heavy oil upgrading in the THAI CAPRI process. Upto 4% (16 $ml.min^{-1}$) of hydrogen was also used in some of the selected experiments, as Petrobank has observed some hydrogen in its pilot scale studies (Petrobank, 2008).

3.2.5 Chemicals, Gases and Catalysts

The subsequent commercial chemicals were used as received without further purification: Carbon disulphide ($\geq$99%, Sigma), Di-Methyl Di-Sulphide (DMDS) ($\geq$99%, Sigma), marble chips (for general use, Fisher scientific), n-decane anhydrous ($\geq$99%, Sigma), potassium bromide (>99.5%, Fluka), standard automotive diesel (Esso Petroleum), White Spirit used for cleaning (Commercial grade by BandQ).

Air (>99.9%), oxygen free nitrogen, zero grade nitrogen (>99.9%), THAI gas [N_2 80%, CO_2 13%, CO 3%, CH_4 4%], hydrogen (>99.9%) and helium (>99.9%) were all supplied by BOC Gases. All the catalysts were provided by Akzo chemicals and Albemarle Corporation.

3.2.6 Addition of Steam and Pre-sulphiding the Catalyst

To investigate the effect of water gas shift reaction in heavy oil upgrading, water was fed to the CAPRI reactor mixing chamber (E-3) using a standard High Pressure Liquid Chromatography (HPLC) pump (E-7). The pump was fed with water from a water reservoir (E-8). The flow rate of water to the pump was controlled using (V-15).

It was assumed that there could be enough sulphur in the crude to pre-sulphide the catalyst during catalytic upgrading of heavy oil. To confirm this assumption pre-sulphiding of the catalyst prior to the experiment was tried in two experiments. For this reason a small pressurised vessel was fitted to the main oil line just after the manual metering valve (V-2). The new three way valve (V-28) now offered the facility to feed the reactor with either 5%

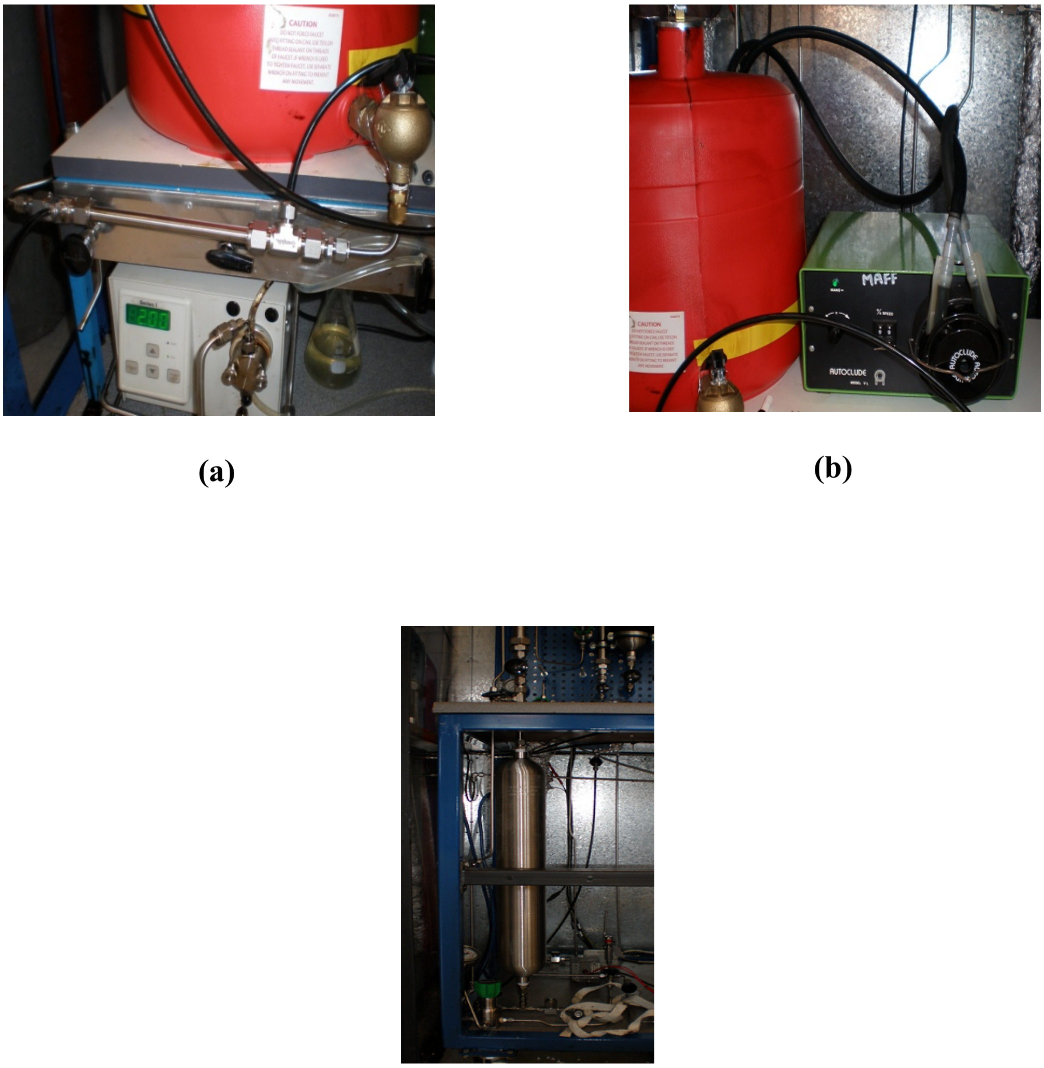
dimethyl disulphide DMDS solution in diesel from a 1 l pre-sulphiding tank (E-9) or the usual oil flow from the main pressurised vessel (E-2).

During the pre-sulphiding experiments, the pre-sulphiding tank (E-9) was first filled (from top using a simple valve, V-27 and then closed) with 5% DMDS solution in diesel and then pressurised to 5 bar (g). The reactor was operated at atmospheric pressure under a small purge of nitrogen (16ml.min^{-1}) to keep the catalyst bed air free. The pre-sulphiding solution of DMDS was allowed to pass through the catalytic bed at a rate of 1ml.min^{-1}. Once the pre-sulphiding of the catalyst was complete the three way valve (V-28) was shut to the pre-sulphiding tank and the reactor was made available for normal operation.

3.2.7 Commissioning and Modifications

Initially, it was planned to install three reactors and all of them to be fed with oil using standard HPLC or peristaltic pumps Figure 3.3 (a) and (b). However, it proved very hard to pump any oil at all into the reactor using either HPLC pump or peristaltic pumps. To resolve this issue, the CAPRI reactor was equipped with two pressurised vessels Figure 3.3 (c). The two 3.59 l steel vessels were filled with THAI heavy oil to feed two reactors running simultaneously. The oil vessels were pressurised from the top using nitrogen gas. A pressure drop of 5 bar g was maintained between the experimental pressure in the reactor and the reservoir pressure, to feed oil in to the CAPRI reactor. The oil flow rate was controlled manually using a Swagelok volumetric flow meter. This however proved difficult throughout the experimental work, as the flow rate has to be checked and adjusted with regular interval of at least every 5 minutes at the beginning of experiment and every 30 minutes during the experiment once the desired flow rate of 1 ml.min^{-1} was achieved.

Figure 3.3 (a) Standard HPLC Pump (b) Peristaltic Pump (c) Pressurised Vessel



(a)

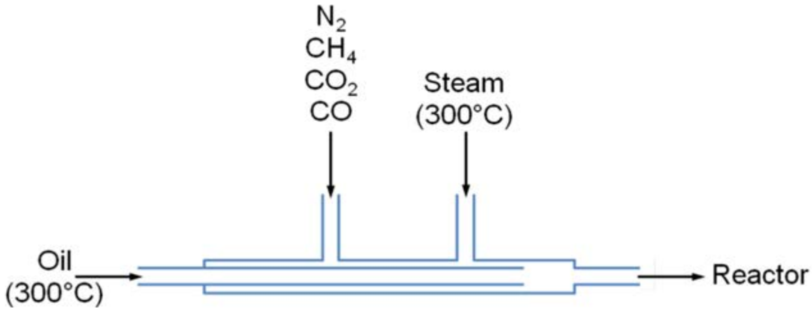
(b)

(c)

3.2.8 The Mixing Chamber (E-3)

Figure 3.4 provides a detailed sketch of how the mixing chamber works in the CAPRI reactor. THAI crude oil pre-heated (T1 and T2 from Figure 2) to 300°C enters the mixing chamber and THAI gas or Nitrogen (some-times in combination with hydrogen) enters from the first of the two inlets. This gas is blended with high temperature steam from the other inlet in some experiments. Once oil and reaction gases (with or without steam) leave the mixing chamber, they are thoroughly mixed and are all in the vapour state before entering the reactor.

Figure 3.4 The Mixing Chamber



3.2.9 The CAPRI Reactor and Catalyst Packing

The CAPRI reactor is a steel tube of ½” made by Swagelok (Figure 3.5 and Table 2). A new reactor was used for every experiment. After the experiment, the reactor was usually cut open in the middle to retrieve the spent catalyst for further analysis.

Figure 3.5 The CAPRI Reactor

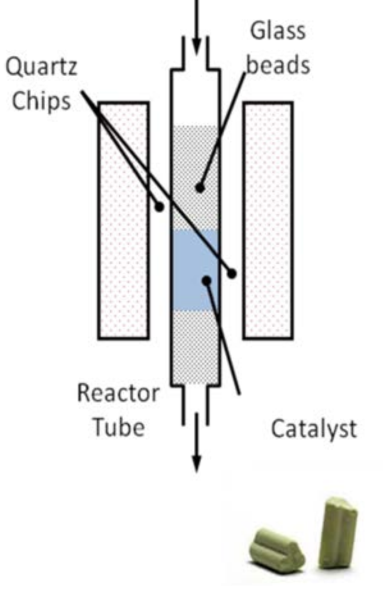
Figure 3.6 shows how the reactor is packed inside the furnace. The middle of the reactor was packed with a catalytic bed of 5 g in all experiments except one, where a bed of 2.5 g was

used. The top and the bottom of the reactor were packed with glass beads of 5mm diameter. The empty spaces between the furnace walls and the reactor were filled with quartz chips for effective thermal conductivity.

Table 3.2 The CAPRI Reactor Dimensions

Diameter	Length	Volume
10.2 mm	110 mm	8.99 cm^3

Figure 3.6 The CAPRI Reactor



3.2.10 The Gas Liquid Separator and Sample Collecting Vessel (E5 and E6)

Two cylinders, one large and one small, were used to separate the gas and liquid products after collected at the bottom of the CAPRI reactor (Figure 3.7 and Figure 3.8). The smaller of the sample vessels was readily used to take small samples at regular intervals while the larger vessel was used to store produced oil sample during longer runs and drained at regular intervals. The larger vessel was equipped with a three way valve which can divert the produced gases to either the vent or the RGA for gas analysis.

Figure 3.7 The Gas Liquid Separator

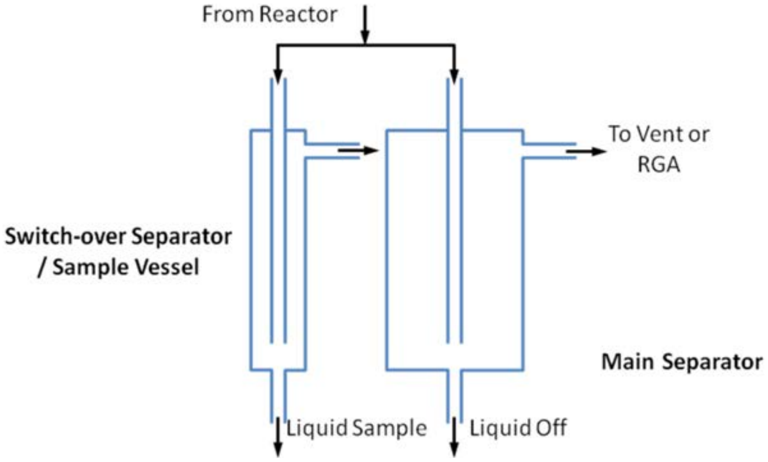
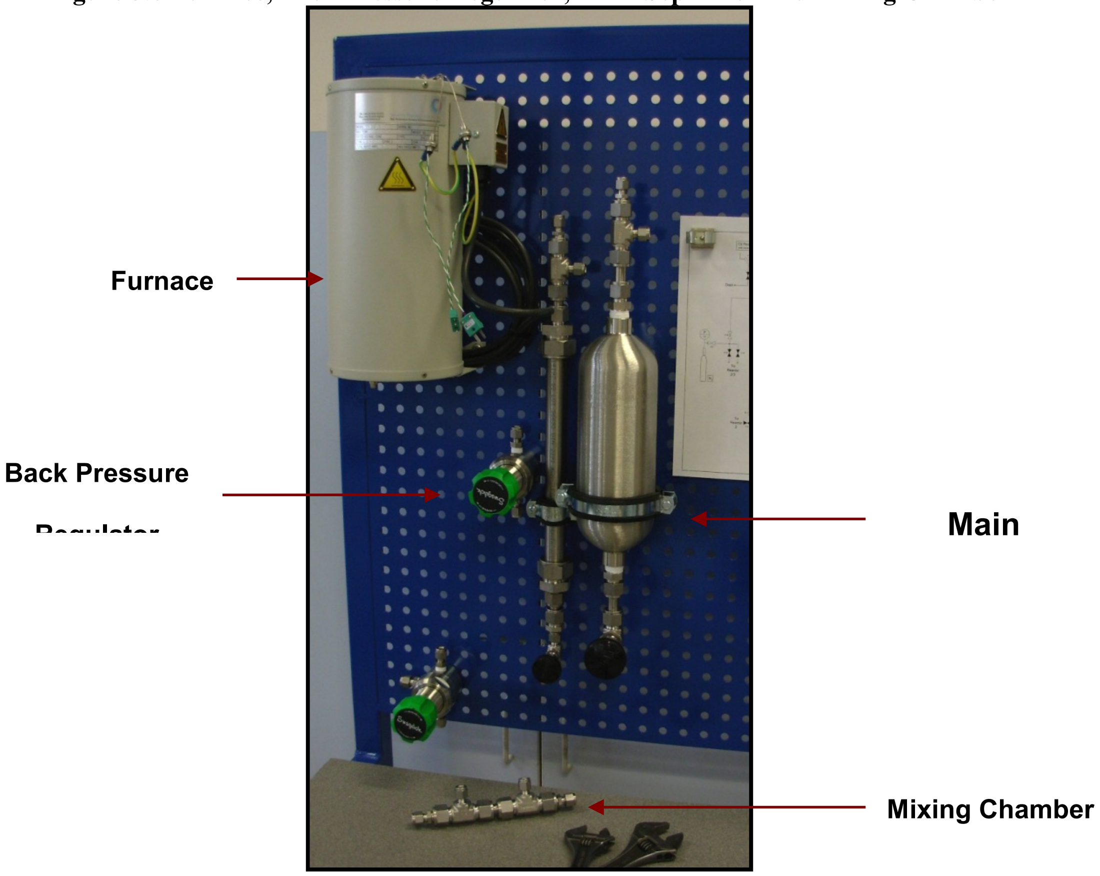


Figure 3.8 Furnace, Back Pressure Regulator, Main Separator and Mixing Chamber



3.2.11 Standard Method of Operation

The CAPRI rig as pictured in Figure 3.9 is complicated and potentially dangerous due to the high temperatures and pressures used. Therefore, a safe standard procedure is needed to run it. For this reason all the experiments were performed using the following procedure.

All the valves were closed except the vent. 160 $ml.min^{-1}$ of nitrogen gas was then used to constantly purge the catalyst while it is heated to reach the desired experimental temperature. The furnace around the reactor tube was set to the experimental temperature and heated at a rate of 5 $°C.min^{-1}$. In the mean time THAI crude oil was pre heated to a temperature of 60°C in the oil reservoir using trace heating to enable it to flow easily through the lines of the rig into the reactor once the experiment is initiated. The trace heating around the lines feeding the reactor from the oil reservoir were also heated to 300 °C. The oil reservoir pressure was always kept 5 bar g higher than the experimental pressure to maintain a pressure drop and ensure the oil flowed to the reactor. Once the desired temperatures and pressures were achieved at the reactor, the oil flow was initiated using the manual metering valve. The gas/liquid separator was used to store produced oil samples. This vessel was always emptied at the end of every experiment and before each new experiment to make sure that it only contains the produced oil from the current experiment. Initially produced oil samples were taken every five minutes (though not recorded and are not included in the results) to ensure that the oil is flowing at the rate of $1ml.min^{-1}$. Once the flow rate was achieved the flow rate was checked at 30minutes interval and the oil flow rate was adjusted if necessary. Mass balance was calculated using the following formula

The CAPRI rig is also equipped with emergency shutdown.

After every experiment the shut down procedure was followed, which is as follows; first the oil flow was terminated, then the furnace and trace heating was turned off. A small purge of nitrogen gas (16 ml.min^{-1}) was used until the reactor bed reached room temperature.

The CAPRI rig was cleaned regularly during the whole length of the project as crude oil proved to be very contaminating towards the experimental rig causing blockages. The clean up was performed according to the following procedure;

The pressurised vessel (E-2) was filled with white spirit the whole system was flushed with white spirit repeatedly, until the collected liquid at the gas liquid separator was colourless.

Cleaning for n-decane experiment was performed exactly the same way as explained above followed by rinsing with 600 ml hexane.

Figure 3.9 The CAPRI Rig

3.2.12 Oil types used and their properties

Two different types of oils were used during the CAPRI process optimisation. Extensive tests were carried out on the THAI pilot oil from Canada. This oil is partially upgraded after being recovered from Christina Lake using THAI technology. The properties of the Athabasca Bitumen inside the reservoir and after being recovered by THAI process are provided in Table 3.3. Since it has been upgraded by 5 API° points and greatly reduced in viscosity by the THAI process alone, further processing using the CAPRI technique was envisaged to improve further the resultant oil as proved in the previous experimental runs.

Table 3.3 Physical Properties of THAI Oil

Origin of Sample	Viscosity Pa.s at 20°C	API°
Athabasca Bitumen	10*	8
THAI Oil	0.577	13
Experimental THAI Oil		19

*(Xia and Greaves, 2000)

A much lighter version of THAI oil (called the experimental THAI oil in this thesis) was also tested in order to check the effect of catalysts applied to THAI pilot oils. This oil was from previous experiments conducted on heavy oils using THAI technique in the Bath University labs. Some of its properties are provided in Table 3.3.

n-Decane was also tested in one experiment to see whether a relatively small chain hydrocarbon mix will provide better upgrading results in comparison to high viscous THAI oil.

The experimental conditions and ranges investigated in this work have been provided in Table 3.4. Table 3.4 also details the catalysts properties used in this work with their respective shapes, surface areas and metal loading.

Table 3.4 Experimental Conditions and Ranges Investigated

Temperature Range		380 °C	400 °C	425 °C	450 °C	500 °C	
Pressure Range bar (g)		20	40	60			
Reaction Media Used		Nitrogen		THAI gas[1]		Hydrogen[2]	
Catalyst	**Manufacturer**	Akzo			Albemarle		
	Active Metals	CoMo	NiMo	ZnO/CuO	CoMo/Bo	NiMo	NiMo
	Shape	Extrusions	Extrusions	tablets	Extrusions	Extrusions	Cylindrical
Wt % metal loading		11	16	70	50	40	30
Surface Area $m^2.g^{-1}$		125 - 175	-	60-100	-	-	-
GOR[3]		250	500	750	-		
THAI Oil Flow Rate		1 ml.min^{-1}					
Gas Flow Rate		0.5 l.min^{-1}					

[1] THAI gas a mixture of [N_2 80%, CO_2 12-14%, CO 2-3%, CH_4 2-4%]

[2] 4% hydrogen was used and the rest of the reactant gas was either nitrogen or THAI gas

[3] GOR, The gas to oil ratio fed into the reactor

3.2.13 Pre-Reducing the Catalyst

In order to further optimise the catalyst effect, the influence of the pre-treatment of the catalyst was investigated. Experiments were carried out with and without pre-reducing the catalyst in hydrogen. The pre-reduction of the catalyst involved, flowing 0.1 l.min^{-1} of hydrogen over the catalytic bed at a temperature of 425 °C for a period of 30 or 60 minutes. Thereafter the oil flow and THAI gas, nitrogen or 4% (16 ml.min^{-1}) hydrogen (in either THAI gas or nitrogen) flows were started.

3.2.14 Pre-Sulphiding the Catalyst

The catalyst was presulphided for two experiments, according to the following procedure; a flow amount of nitrogen (16 ml.min^{-1}) was used as purge gas, to remove air from the catalyst. 5% solution of dimethyl disulphide DMDS in standard automobile diesel was prepared and this solution was passed through the CoMo catalyst bed for 30 minutes at room temperature at the rate of 1 ml.min^{-1}. Then the catalyst was heated to 140 °C and the DMDS solution was again passed over the catalyst at a rate of 1 ml.min^{-1} for 30 more minutes. The catalyst was heated to 280°C and 1ml.min^{-1} of DMDS solution was passed through it for 30 minutes. The catalyst was heated to a final temperature of 340°C and the DMDS solution was passed through it for 30 minutes at a rate of 1 ml.min^{-1}. After this treatment the catalyst was heated to the experimental temperature in the presence of purge gas nitrogen and the experiment carried out according to the procedure listed.

3.3 Analytical Methods

3.3.1 Density and API Gravity

Density of the THAI and CAPRI oils were measured using an Anton Parr digital density meter (Figure 3.10) at 15 °C and reported in kg.m^{-3}.

Figure 3.10 The Anton Parr Digital Density Meter

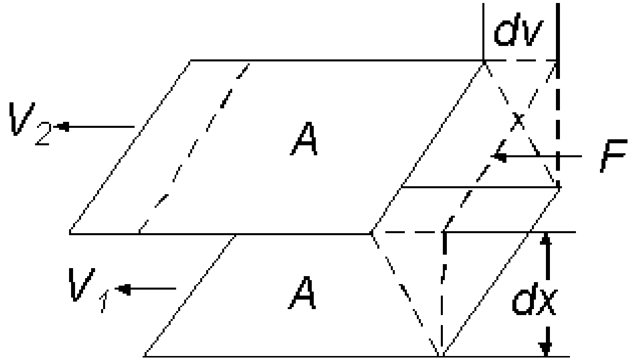
API stands for American Petroleum Institute gravity and is a criteria widely used to measure the crude grades, so, the higher the API gravity, the lighter and more desirable the crude oil. API was calculated using the following equation,

Where SG is specific gravity.

3.3.2 Viscosity

Viscosity is the measure of the internal friction of a fluid. This friction becomes apparent when a layer of fluid is made to move in relation to another layer. The greater the friction, the greater the amount of force required to cause this movement, which is called *shear*. Shearing occurs whenever the fluid is physically moved or distributed, as in pouring, spreading, spraying, mixing, etc. Highly viscous fluids, therefore, require more force to move than less viscous materials.

Figure 3.11 Viscosity measurements as defined by Newton



Isaac Newton defined viscosity by considering the model represented in Figure 3.11 (Goldschmidt and Streitbeger, 2003). Two parallel planes of fluid of equal area *A* are separated by a distance *dx* and are moving in the same direction at different velocities *V1* and *V2*. Newton assumed that the force required maintaining this difference in speed was proportional to the difference in speed through the liquid, or the velocity gradient.

The velocity gradient, *dv/dx*, is a measure of the change in speed at which the intermediate layers move with respect to each other. It describes the shearing the liquid experiences and is thus called *shear rate S* and is measured in *reciprocal second* (s^{-1}).

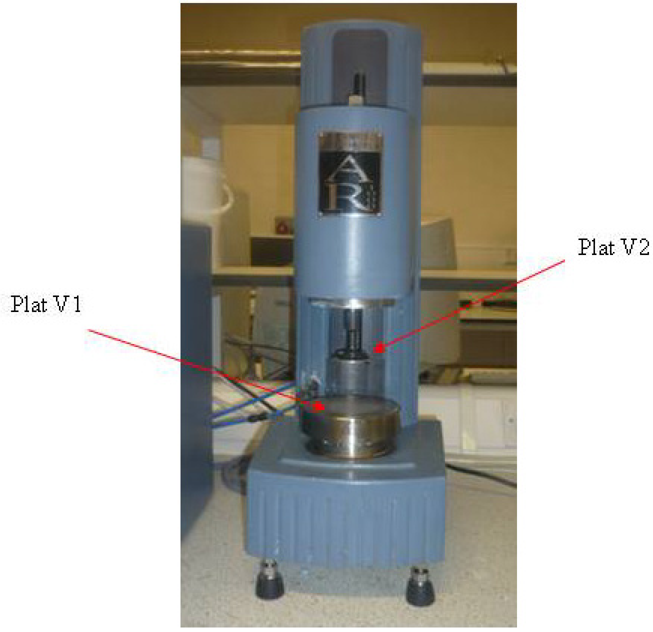
Using these simplified terms, viscosity may be defined mathematically by this formula:

$$\eta = \text{Viscosity} = \frac{F}{A}\,\frac{\text{shear stress}\,(Pa)}{\text{shear rate}\left(\frac{1}{s}\right)}$$

Viscosity was measured using an AR 1000 Rheometer (Figure 3.12) at the School of Chemical Engineering, University of Birmingham and is reported in Pa.s. The method for measuring viscosity was as follow,

About 1 ml of oil was needed to be placed on top of plat *V1* and than plat *V2* was lowered. Any excess oil outside the edges of *V2* was wiped off using a standard paper tissue. The gap between *V1* and *V2* was usually 1000 µm, however some time when the viscosity of any oil was too low it caused error in the measurements and resulted in over spin of the instruments. This gap was than lowered to suit these oils and hence forth a variable gap was used in viscosity measurements. Experiments were repeated three times and they were found to be repeatable to ± 0.4 Pa.s.

Figure 3.12 AR 1000 Rheometer



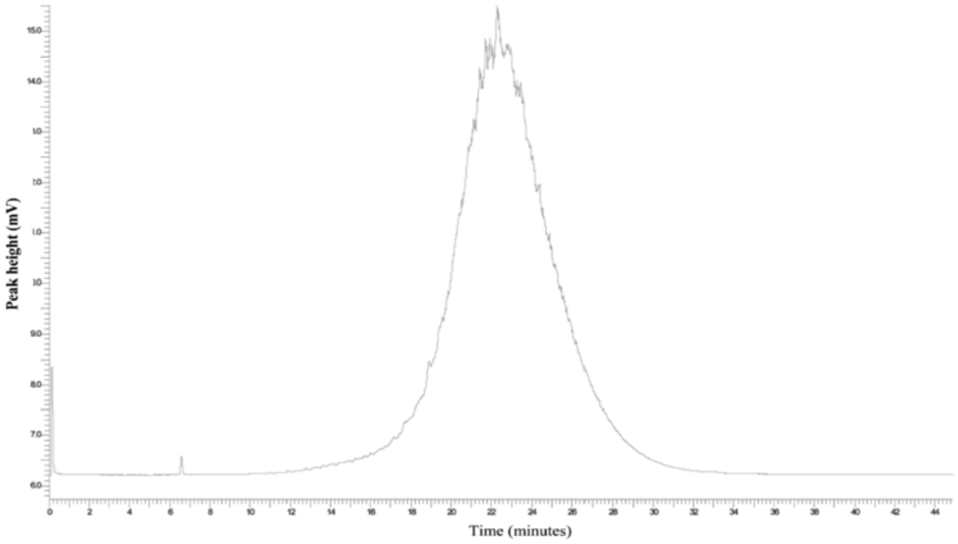
3.3.3 Simulated Distillation Analysis SIMDIS

ASTM (American Standard of Testing Materials) D2887 is widely used in the refining industry (ASTM, 2011). This method is designed to determine the boiling range distribution of petroleum products and fractions having a final boiling point of 538 °C or lower. Agilent has developed a Simdis system including an easy to use software package where the Simdis software is coupled with the GC chemstation (the standard software of the Agilent GC based on 6850 model). First the GC is calibrated with a known mixture of hydrocarbons from C_5 to C_{40} using a DB1 column (10 m x 0.53 mm x 2.65 μm). The software then compares the retention time of the injected sample and the known standards from the calibration samples and generates an engineering report of boiling point ranges for petroleum products. The rest of the Gas Chromatography is standard and is equipped with a Flame Ionization Detector (FID). The FID uses hydrogen and air to partially burn the organic constituents that are carried by helium through a retention column.

Unlike True Boiling Point (TBP) distillation, Simulated Distillation (SD) is a low resolution chromatographic method that has been developed to simulate true boiling point or physical distillation. It is based on the fact that hydrocarbons elute from a non-polar adsorbent or liquid phase in order of their boiling points. In simulated distillation analysis, the components are not separated as individual peaks but as one large Gaussian-shaped peak that resembles a lump. Figure 3.13 illustrates a typical simulated distillation chromatogram.

SD is based on the correlation of the normal boiling point and retention time data for a normal paraffin mixture, often referred to as the calibration mixture. The retention time data for the normal paraffins are gathered using a specified temperature program. A mathematical relationship between the boiling points of the normal paraffins and retention or elution time is determined.

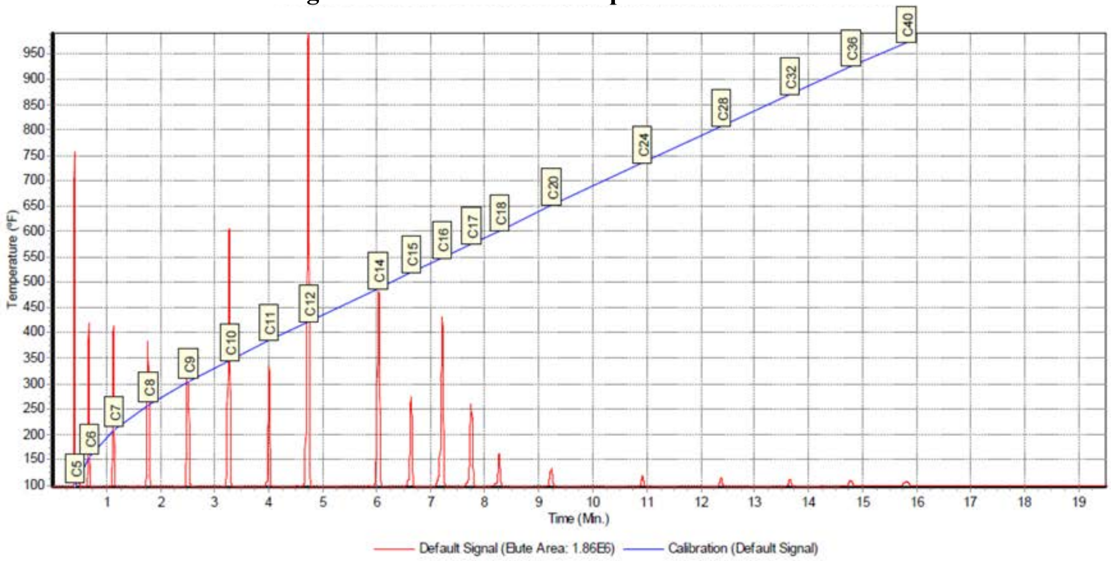
Figure 3.13 A Typical Simulated Distillation Chromatogram



This relationship is essentially linear for the hydrocarbons that are retained by the column. The output from a sample chromatogram, analyzed under the same conditions, is divided into equal individual area slices and compared to the calibration equation. Each area slice has a retention time associated with it and therefore a boiling point is determined from the calibration equation (boiling point versus retention time). The area slices are then summed to generate the area or weight percent off by temperature report. Therefore, the amount at any interval on the chromatogram can be determined. Normal paraffin calibration chromatograms are shown in Figure 3.14.

In this work, 1 part of oil sample was first mixed with 10 parts of carbon disulphide, than 1 µl of the mixture was injected each time a SIMDIS measurement was made using the Agilent 6850 GC. Each graph was then opened in the special SIMDIS software and the boiling point curves reported.

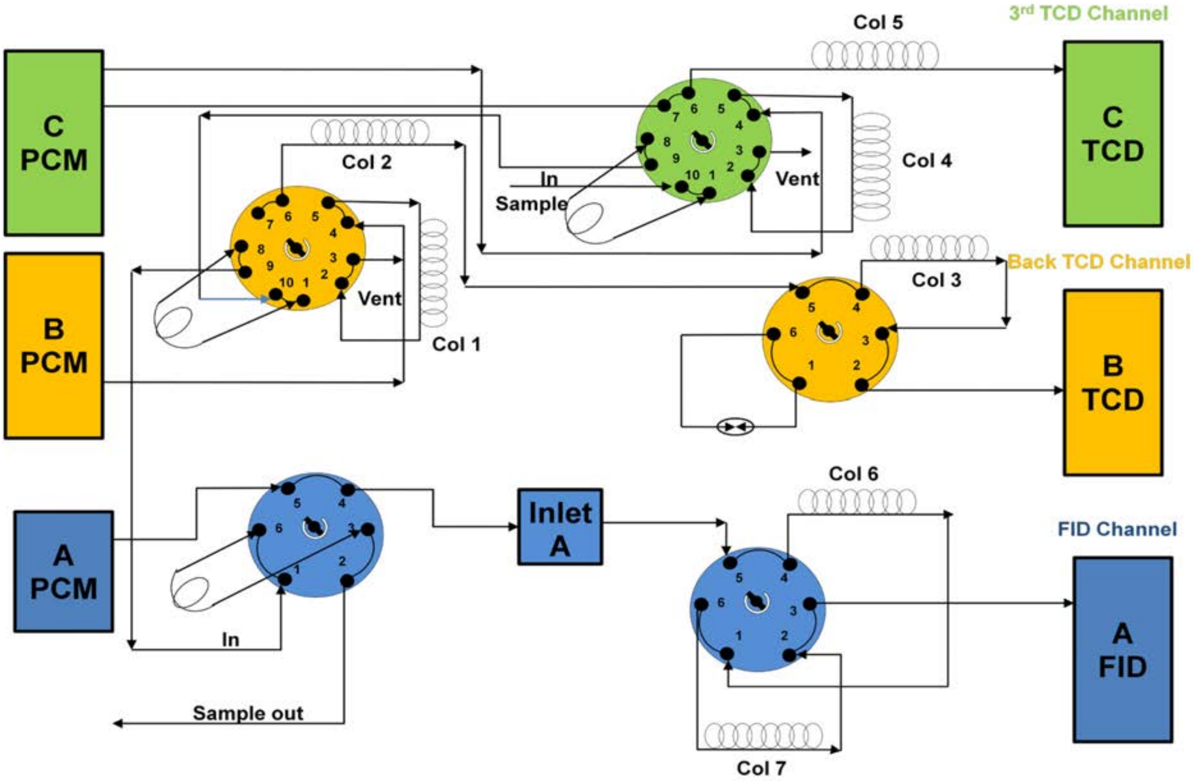
Figure 3.14 SIMDIS normal paraffin calibration curve



3.3.4 Refinery Gas Analyser RGA

During the cracking of petroleum crudes, a number of different reactions happen, especially in the presence of a catalyst. To precisely identify these gases Agilent has designed a Refinery Gas Analyzer based on 7890A model which is equipped with 7 columns, five valves and 3 detectors including an FID and two TCD (thermal conductivity detectors) detectors. The combination of TCD's with FID offers the advantage to identify gases like helium, carbon dioxide, carbon monoxide and nitrogen too, which an FID detector cannot identify, as these gases cannot be ionised. This GC was exclusively used to identify the different gases produced during the CAPRI process apart from the reaction gases like nitrogen or THAI gas. A schematic of the RGA has been given in Figure 3.15. A gas mixture sample is injected which is split by the five valves and the different gases are split to their respective columns and detectors as follows; All the hydrocarbons are diverted on to column 6 and 7 and the separated products are detected by the FID channel (the whole group represented by blue colour). Gases such as CO_2, O_2, CO, CH_4 and N_2 are diverted to the orange set of columns and detected by the 'Back TCD Channel. The third TCD channel detected the zero grade N_2 which is used as the carrier/reference gas.

Figure 3.15 Schematic of RGA Valves and Columns



3.3.5 TGA

Thermal Gravimetric Analysis (TGA) is a simple analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature. As materials are heated, they can lose weight from a simple process such as drying, or from chemical reactions that liberate gasses. TGA was performed for selected coke samples using a specially designed method and employing NETZSH TG 209F1 model. In this method, first the coke sample was placed in an alumina crucible and the chamber evacuated, then slowly heated up to 200 °C in the presence of nitrogen and this temperature was held for 30 minutes. The temperature was than raised to 1000 °C and held there for 30 minutes. The last stage was burning the sample at 1000 °C in the presence of air for a further 30 minutes.

3.3.6 DRIFTS

Diffuse Reflectance Infrared Fourier Transform Spectra (DRIFTS) is a powerful tool for the study of materials such as polymers and catalysts. Diffuse Reflectance occurs when light impinges on the surface of a material and is partially reflected and transmitted. Light that passes into the material may be absorbed or reflected out again. Hence, the radiation that reflects from an absorbing material is composed of surface-reflected and bulk re-emitted components, which summed are the diffuse reflectance of the sample. DRIFTS of the crushed catalysts were obtained with a Bruker Tensor 37 spectrometer. A background spectrum was recorded with KBr powder in air. The catalyst was crushed in a pestle and mortar, sieved and loaded in to the sample cup of a thermo collector diffuse reflectance accessory. Room temperature spectra were recorded in the mid-IR range (550 - 4000 cm^{-1}). For each spectrum, 2400 scans were accumulated with a nominal 2 cm^{-1} resolution.

3.3.7 UVFS

Ultra-Violet Fluorescence Spectroscopy (UVFS) is commonly used to characterize fluorescence effects in the UV and visual range of the electromagnetic spectrum. Such fluorescence is caused by the fact that the absorption of UV or visible light of specific wavelengths causes excitation of electrons within a molecule. If radiating relaxation occurs directly from the singlet S_1 state, the process is called fluorescence. Readily measurable fluorescence intensities are found for molecules having aromatic and heteroaromatic rings (widely present in petroleum), in particular when annulated rings are present, and in the case of conjugated Π-electron systems. If the polymer molecules contain such fluorescence active subunits they can be characterized by this technique, either directly via their fluorescence spectrum or via fluorescence quenching experiments (for polymers with appropriate quencher groups). It is also possible to introduce a very small amount of fluorescent-active groups (as comonomer units, “fluorescence marker”) into a polymer.

3.3.8 SARA Analysis

Saturates, Asphaltenes, Resins and Aromatics are the usual constituents of petroleum oils. SARA analysis is performed on crude oils to check the increase or decrease of any constituent. Asphaltenes are usually the least desirable, so, a decrease in their quantity indicates the crude’s improvement in quality. The analysis is performed using a number of proven techniques but the most common is dissolving these fractions in different solvents and then removing the solvents. For example, asphaltenes could be pentane or heptane-insolubles. Resins may be classified as a solubility fractions, such as heptane-soluble and pentane-insoluble or heptane-soluble and acetone or ethyl acetate insoluble, or as the polar fraction eluted from a polar adsorbent with a polar solvent, such as pyridine, toluene or methanol.

Saturates and Aromatics are determined by adsorption chromatography, typically from silica or silica/alumina. Saturates are eluted with a paraffinic solvent, such as pentane or heptane. Aromatics are eluted either with paraffinic or moderately polar solvents, such as toluene or Di-Chloro Methane (DCM).

In this work SARA analysis was performed by HPLC by an external laboratory service (of Intertek laboratory Sunbury) including asphaltene content by the Institute of Petroleum method IP-143.

3.3.9 Analysis for Sulphur

Analysis for sulphur was performed by Petrobank Canada, using the American Standard for Testing materials (ASTM) method D4294 for sulphur in petroleum and petroleum products by energy dispersive X-ray Fluorescence Spectrometry. In this method the sample is placed in the beam emitted from an X-ray tube. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with counts from previously prepared calibration samples to obtain the sulphur concentration in mass % and/or mg.kg^{-1}. Usually a minimum of three groups of calibration samples are required to span the concentration range: 0.0 to 0.1 mass %, 0.1 to 1.0 mass % and 1.0 to 5.0 mass % sulphur.

3.3.10 Analysis for Metals

To analyse for metals in produced and THAI oils, the standard ASTM D5185 was used by Petrobank Canada. This method is a well established practice to determine additive elements, wear metals, and contaminants in used lubricating oils and determination of selected elements in base oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). In this method a weighed portion of thoroughly homogenized used oil/base oil (such as THAI oil) is diluted tenfold by weight with mixed xylenes or other suitable solvent. Standards are prepared in the same manner. An optional internal standard can be added to the solutions to compensate for variations in test specimen introduction efficiency. The solutions are introduced to the ICP instrument by free aspiration or an optional peristaltic pump. By comparing emission intensities of elements in the test specimen with emission intensities measured with the standards, the concentrations of elements in the test specimen are calculable.

Chapter 4

CAPRI Process Optimization: "THAI Field Oil as Feed"

Chapter Overview

In this chapter the results and discussion for the experimental optimization of the CAPRI process with THAI field oil as feed are presented. The chapter starts with a brief introduction describing why it is important to optimize the CAPRI process for the parameters discussed in the subsequent sections. A number of variables have been optimized for the CAPRI process, namely effects of; Catalyst type, liquid hourly space velocity LHSV or residence time, catalyst pretreatment, thermal versus catalytic runs, short run times, pre-sulphiding the catalyst, temperature, pressure, gas: oil ratio, gas composition and hydrogen content, steam and alternative catalysts are presented in Sections 4.1 to 4.13 respectively.

THAI field oil produced in the Whitesands trial in Alberta, Canada was selected to represent a realistic feed to the CAPRI process and the results for processed oils were mainly produced using analytical methods like viscosity, density and API gravity, SIMDIS 2887 and RGA analysis.

4.1 Introduction

Heavy oils and bitumen with large reserves are readily available alternative resource to replace the conventional crude oil supplies which are expected to reach its peak in the second decade of this century and subsequently enter a phase of permanent decline (Stosur et al, 1998). However as discussed in Chapter 2, heavy oils and natural bitumen are usually asphaltic, dense and viscous and their elevated viscosity and density demand more energy intensive operations not only for their production and upgrading but also for transportation and consequently they are more costly to extract. Until recently the petroleum industry has relied on cold production methods, predominantly surface mining. With high oil prices and the increased demand for oil production, a number of Enhanced Oil Recovery (EOR) technologies have been proposed and developed. Success has varied with recovery levels ranging from as low as 10% (water flooding) and up to 70% with Steam Assisted Gravity Drainage (SAGD) and potentially to greater than 80% with Toe-to-Heel Air Injection (THAI) (Shah et al, 2010). However the use of large amounts of water and energy are potential disadvantages of SAGD (Donnelly and Pendergast, 1999). Emerging technology like Toe-to-Heel Air Injection (THAI) (which is an *in situ* combustion technique) offers alternative to energy intensive techniques like SAGD or cyclic steam stimulation (CSS) etc. The thermally cracked heavy oil, produced during the process, not only aids oil recovery but also has the added benefit of upgrading the oil (Xia et al, 2002). This added side-effect of THAI is not only beneficial for the actual oil recovery but also aids transportation, downstream refining and subsequently increases the commercial value of the produced oil. Experimental and field results indicate sulphur and heavy metal content is reduced in the produced oil with THAI (Petrobank, 2008). Petrobank has been able to extract partially upgraded oil with their first field studies of THAI in the range of 10.6 to 16.1°API, compared to the original bitumen value of 7.9°API. This means that only about 15% of diluent is needed to meet pipeline specifications, compared to 30–50% required for non-upgraded bitumen produced from SAGD and Cyclic Steam Stimulation (CSS) operations. The produced water is also of good quality so that it can be treated fairly simply for industrial re-use, for example in SAGD (Greaves and Xia, 2008). CAPRI the catalytic extension to THAI, further upgrades the heavy oil obtained with THAI alone (Xia and Greaves, 2001; Greaves et al, 2000) to create a downhole catalytic reactor. The thermal cracking reaction of THAI, taking place in the coke and Mobile Oil Zone (MOZ), creates the precursor for CAPRI. The MOZ comprises water (steam), oil and combustion gases as well as some carbon monoxide and a small amount of unconsumed oxygen at high temperatures of around 500 to 600°C and at reservoir pressure (typically 30-50 bar g). Oil upgrading is thought to occur by a combination of carbon rejection reactions (thermal cracking) and hydrogen addition at the surface of a hydroconversion or hydrotreating catalyst. The source of hydrogen is believed to be due to gasification and/or water gas shift reactions (Hajdo et al, 1985). In summary, *in situ* combustion or THAI-CAPRI creates ideal conditions for *in situ* catalytic upgrading (Weissman, 1997; Moore et al, 1999), and the reactor-upgrader is virtually free by virtue of the reservoir conditions, which already establish the necessary high temperature and pressure (ca. 400-600°C, 20-40 bar for Athabasca Oil Sands). Xia and Greaves (2001) demonstrated the capability of THAI-CAPRI to upgrade a Wolf Lake Heavy Oil using 3D combustion cell tests. Even without a catalyst, thermal cracking conversion could upgrade Wolf Lake crude oil from 10.9°API to around 20° API. CAPRI tests using HDS catalyst (not pre-sulphided) showed that the THAI oil could be further upgraded by an additional 4-8°API.

In previous 3D combustion cell tests (Xia and Greaves, 2001), the catalyst in the active part of the horizontal reactor section was only exposed to the reactant fluid for about one to two hours, during the overall run time of 10-15 hours. Whilst during the field scale the catalyst activity needs to be maintained over much longer operating periods than in the 3D combustion cell reactor of perhaps eventually a few days, or longer, whilst the Mobile Oil Zone (MOZ) moves through the active section of catalyst. THAI has been extensively documented in the literature; however results with CAPRI are limited especially at reservoir conditions such as pressures of 20-50 bar g. Therefore it is necessary to understand how process conditions can be optimized to avoid catalyst deactivation, and to maximize conversion. This chapter presents a detailed investigation in to the optimum catalyst, catalyst pre-treatment, temperature, pressure, gas-to-oil ratio and gas composition upon the upgrading performance of CAPRI.

4.2 Effect of Catalyst Type

Selection of catalyst types is one of the important decisions to find a material that promotes cracking of larger molecules such as asphaltenes or polar molecules held together in clusters by either sulphur centres such as thiophenes or metals porphyrins. In the industry efforts have been long centred in removing sulphur (Hydrodesulphurization, HDS) and metals (Hydrodemetallization, HDM) from these large agglomerates. The latter are largely responsible for the undesirable higher viscosity and other properties of heavy crude oils and will crack in the process to smaller Hydrocarbon (HC) chains (Grey *et al.*, 1992; Kressmann, 1998). However as sulphur conversion increases, the most refractory species – alkylated dibenzothiophenes are left as residue. Under idealized conditions, the conversion of molecules that are sterically hindered mainly proceeds by first hydrogenating the molecules before desulphurization takes place (Topsoe *et al.*, 1996; Landau, 1997; Whitehurst *et al.*, 1998; Knudsen *et al.*, 1999; Song 2003). Since NiMo catalysts are generally more active for the indirect hydrogenation route and CoMo catalysts more active for the direct route, NiMo is the preferred option for ultra deep desulphurization. However, at low hydrogen pressures and high space velocities CoMo catalysts are often seen to outperform NiMo catalysts (Knudsen *et al.*, 1999). At high hydrogen partial pressure, the indirect hydrogenation route is favoured, as occurs with NiMo, where the sulphur molecules are hydrogenated before desulphurization occurs.

To maintain oil production rates of up to 100000 bbl/day using THAI-CAPRI, the process will need to operate at relatively high space velocities through the catalytic bed (Petrobank, 2008). THAI-CAPRI uses only air as the injected gas, which means the absence of higher partial pressure of hydrogen; therefore the process favours the use of CoMo catalyst. For this reason in this study, CoMo with or without pre-treatment and with different shapes has been investigated as the preferred catalyst to NiMo or other types of catalysts such as iron or nickel oxides etc. Apart from CoMo and NiMo low cost ZnO/CuO (the low temperature water gas shift catalyst) was also investigated. The three different types of catalysts possess different properties, for example CoMo is preferred for hydrocracking compared with NiMo and the latter catalyst is better in hydrodemetallization. Similarly ZnO/CuO is a low temperature water gas shift reaction catalyst, so better in releasing hydrogen from water dissociation (detailed catalysts properties used in this study can be found in Table 4, chapter 3).

The experiments conducted using these different types of catalysts have been listed in Table 4.1. All the experiments listed in Table 4.1 were carried out at 400°C and 20 bar g pressure. The gas flowrate was 0.5 $l.min^{-1}$ and an oil flowrate of 1 $ml.min^{-1}$ except in P11 where these quantities were twice as high (Refer to Appendix 1 for full list of all experimental conditions with P numbers). The reaction gas was oxygen free nitrogen except for P86, where it was THAI gas (N_2 80%, CO_2 12-14%, CO 2-3%, CH_4 2-4%), in order to get the best possible results in one run because of the limited quantity of the catalyst.

Table 4.1 List of Experiments Effect of catalyst in the upgrading of THAI heavy crude

Expt. No.	**Catalyst**	**Gas**
P11	ZnO/CuO	Nitrogen
P12	Akzo NiMo	Nitrogen
P13	Akzo CoMo	Nitrogen
P15	Presulphided CoMo	Nitrogen
P86	Bentonite Clay	THAI

Figures 4.1a) and b) and Table 4.2 show the upgrading of oil in terms of viscosity and API gravity for the different catalysts tested. Amongst the three types of catalysts, it was observed that NiMo displayed the highest level of upgrading in terms of average viscosity reduction, followed by CoMo and ZnO/CuO. CoMo catalyst displayed the best upgrading in terms of average API gravity, with very similar performance to NiMo, whilst ZnO/CuO showed a poorer level of upgrading. The catalytic reactors were shut down when oil flow declined, which was thought to be due to bed blockage caused by coke deposition. It was observed that CoMo catalyst continued for the longest period of operation of up to 95 hours. The propagation front in the THAI process propagates at 0.25 m/day (Greaves *et al.*, 2008), while the length of the catalytic bed in this work was 0.11m. This will mean that the catalyst life time needed at any one point in the THAI-CAPRI horizontal well is less than a day. However, the volume of oil passing through at any one point of the catalytic bed in the actual well could be more than a 1000 bbl/day (Greaves *et al.*, 2008); while in this work it was a few litres at maximum.

ZnO/CuO displayed the poorest upgrading therefore was shut down after 32.5 hours. The data in Figures 4.1a) and b) show some scatter, particularly for ZnO/CuO, in which a number of samples showed higher viscosity than the starting material, indicating undesirable degradation of the oil rather than upgrading. This is probably because ZnO/CuO has a lower surface area than the other catalysts (Table 4, Chapter 3).

Hydrocracking or hydrodesulphurization catalysts need to be pre-sulphided (activated) prior to their use in residue upgrading processes as metallic sulphides, especially MoS_2, as these are usually the active states of any residue upgrading catalyst (Topsøe *et al.*, 1996). The presulphiding of the catalyst may be carried out using one of two methods. Either the catalyst is sulphided itself by the sulphur present in the feed or an external source of sulphiding such as dimethyl disulphide (DMDS) may be passed over the catalyst prior to start up. Both of these methods were investigated in the present study. Presulphided CoMo catalyst samples previously used in the industry were used to assess their suitability in the upgrading of THAI field oil, then in later experiments (Section 4.9) sulphiding of catalysts was carried out by passing DMDS over them prior to start up. Results shown in Table 4.2 and Figure 4.1 were compared to the processed oils from Akzo CoMo as a base case. It is noted in Figure 4.1 that the THAI oil viscosity and API gravity are marked with a dotted line, so that the results can be readily compared with the properties of the feed oil. The final oil viscosity of 0.286 Pa.s with presulphided CoMo (Table 4.2) was found to be lower in viscosity than the non-treated Akzo CoMo processed oil, with a final value of 0.357 Pa.s. The API gravity of this processed oil with the presulphided catalyst with a final value was 14.26° and is relatively lower than the 14.7° for the CoMo base case.

Table 4.2 Average and Standard Deviation Viscosity and API Gravity after Upgrading of Heavy Oil with Different Catalysts

THAI oil starting material has a viscosity of 0.58 Pa.s and an API gravity of 13°. Experiments were carried out at 400 °C and 20 bar (g) pressure, with a flow of 1 $ml.min^{-1}$ oil and 0.5 $l.min^{-1}$ nitrogen (except for Bentonite Clay where it was THAI gas) except for ZnO/CuO which was 2 $ml.min^{-1}$ oil and 1 $l.min^{-1}$ nitrogen

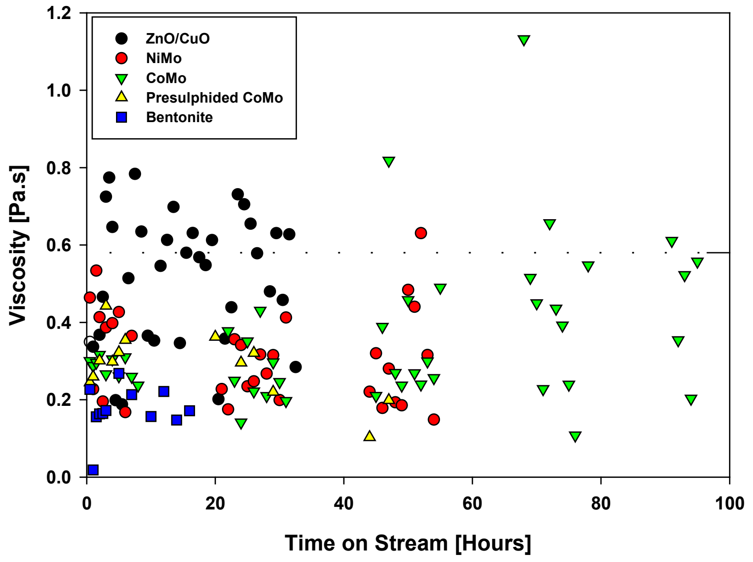
	ZnO/ CuO	**NiMo**	**CoMo* Akzo**	**CoMo Pre-sulphided**	**Bentonite Clay**
Average flowrate $ml.min^{-1}$	1.74	1.32	1.14	0.86	1.00
Standard deviation flowrate $ml.min^{-1}$	0.83	1.10	0.68	0.321	0.180
Average viscosity Pa.s	0.514	0.315	0.357	0.286	0.173
Standard deviation viscosity Pa.s	0.169	0.120	0.185	0.523	0.061
Average API gravity	13.6	14.5	14.7	14.26	14.03
Standard deviation API gravity	0.619	0.503	0.640	0.546	0.314
Operation time (hours)	32.5	54	95	47	16

*Used as a base case to compare all other catalysts with

Figure 4.1. Effect of Catalyst upon a) Viscosity and b) API Gravity (c) SIMDIS[**]

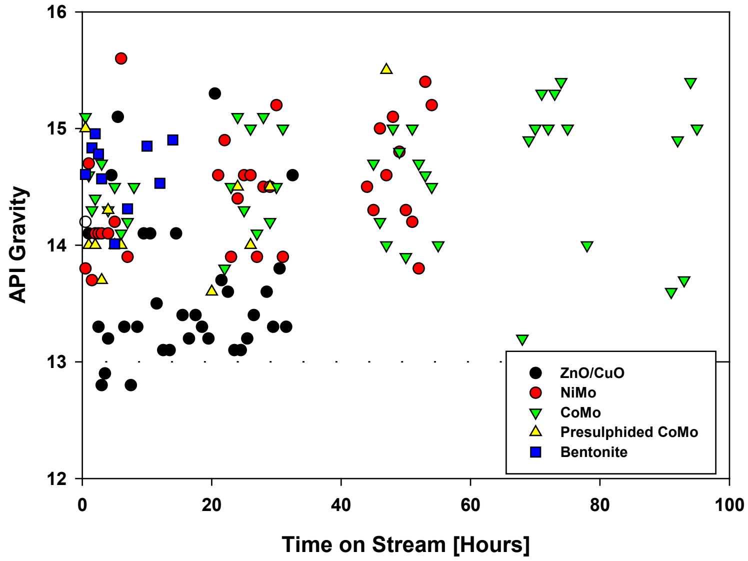
THAI oil viscosity of 0.58 Pa.s. 400 °C, 20 bar (g), 1 $ml.min^{-1}$ oil flowrate and 0.5 $l.min^{-1}$ nitrogen, except for ZnO/CuO which was 2 $ml.min^{-1}$ oil and 1 $l.min^{-1}$ nitrogen. Dotted lines in this and other figures represent the measured viscosity or API value of the field THAI oil prior to upgrading in the experimental CAPRI reactor.

(a)

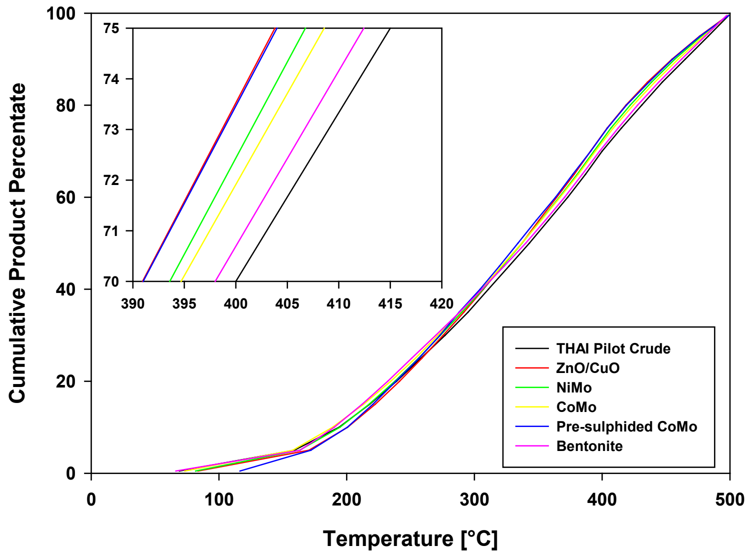


[**] All SIMDIS analysis presented in this work have been done using ASTM D2887 except where stated otherwise

(b)


API Gravity
Time on Stream [Hours]
16
15
14
13
12
0
20
40
60
80
100
ZnO/CuO
NiMo
CoMo
Presulphided CoMo
Bentonite

(c)


Cumulative Product Percentate
Temperature [°C]
0
20
40
60
80
100
0
100
200
300
400
500
70
71
72
73
74
75
390
395
400
405
410
415
420
THAI Pilot Crude
ZnO/CuO
NiMo
CoMo
Pre-sulphided CoMo
Bentonite

The catalytic effect of alumino silicates in the upgrading reactions of heavy oils and bitumens is well documented (Shakirullah *et al.*, 2006 and 2008). Their low prices and slow deactivation in the absence of metals like Co or Mo make them attractive to be investigated as a catalyst in the upgrading of THAI field oil. For this reason Bentonite clay was used as an alternative catalyst. Bentonite clay catalysts were prepared from corresponding powder in the laboratory by mixing it with water and then making small pellets of approximately 1 mm in diameter by 10 mm in length, then calcining it in the presence of nitrogen at a temperature of 400°C for 2 hours prior to experiment. Results show an upgrading to values of 0.173 Pa.s and 14.03° viscosity and API gravity respectively (Table 4.2). The viscosity reading is significantly lower than either Akzo CoMo leading to viscosity of 0.357 Pa.s or NiMo with a value of 0.315 Pa.s at the same time on stream. However API upgrading with Bentonite clay is slightly lower than Akzo CoMo. The higher reduction in viscosity over Bentonite clay is thought to occur because of less coke precursor formation and more of physical effects such as suppressing coalescence of larger particle etc and a lower chemical effect as there are no active metals like CoMo and NiMo. This could occur if the catalyst acts as a filter to remove heavy molecules, without actually causing catalytic upgrading. Such an effort would also explain why the extent of upgrading in terms of API gravity is lower than the equivalent change in viscosity over Bentonite clays.

In similar work to the experimental studies reported in the thesis, Sanaie *et al.* (2001) observed, that the native solids in Athabasca bitumen did not easily disperse in water unlike both kaolin and Southern Alberta clay which were much more hydrophilic. They hypothesized that the higher carbon content and partially hydrophobic character of native clays leads them to, disperse much more readily in bitumen than do the hydrophilic clays and, therefore, interfere more strongly with the developing coke phase. This implies that the surface character of the added solids plays a major role in their interaction with the coke phase hence less coke. Tanabe and Gray (1997) also argue that clays which adhere to the coke particle would inhibit their coalescence, thereby reducing coke yield. Their data, taken at higher temperatures and shorter times, also appears to rule out an effect on chemical reactions. Rahimi *et al.* (1999) have shown in hot stage microscopy studies of Athabasca vacuum bottoms that clay mineral additives do suppress coalescence and mesophase growth[††].

As shown on Figure 4.1 (a) the superior decrease in viscosity in the presence of Bentonite clay in comparison to CoMo catalyst is largely because of the absence of larger or suspended particles in the produced oil. From Figure 4.1 (b) relatively lower upgrading in terms of API gravity indicates little or no role of chemical change in the processed oil. These findings are consistent with earlier work (Tanabe and Gray, 1997; Rahimi *et al.* 1999).

It was also found that during the upgrading with Bentonite clays, the oil flow could be maintained at a more steady value than with the metal supported catalysts, possibly because the bed was not blocked by coke deposits over the clay catalysts.

Average boiling point shift towards lower hydrocarbons is another analysis technique used to assess the role of the catalysts in the upgrading of THAI field oil. Figure 4.1 (c) presents the average SIMDIS graphs for the whole of the experimental duration. Although the experiments were carried out for different durations, the average values were used to smooth out experimental errors in the data. From Figure 4.1(c) a visible shift of about 10°C towards the lighter end products for ZnO/CuO and pre-sulphided catalysts in comparison to the THAI crude oil is evident. For CoMo and NiMo the change in temperature are about 6 and 8°C respectively and the lowest change of about 2-3°C is for Bentonite clay. This might further

---

[††] A complex mixture of essentially aromatic hydrocarbons containing anisotropic liquid-crystalline particles (carbonaceous mesophase). The carbonaceous mesophase particles are formed from the aromatics of high molecular mass in mesogenic substances.

suggest that the bifunctional active catalysts used for hydrocracking and hydrogenation, improves the quality of produced oils superior to the clay catalyst having no active metals.

Analysis of the possible sources of error and scatter in the data showed that the viscosity measurement was repeatable to within ± 4.6 %, and API gravity within ± 1 %. However, control of the flowrate to the reactor proved to be difficult, due to the highly viscous nature, presence of sand particles, and tendency to foul both pipework and the catalyst bed. Consequently, the actual flowrate in the bed fluctuated during the experiment, with the actual average values shown in Table 4.2, determined by collecting and measuring the volume of oil. These fluctuations led to associated changes in residence time, may have resulted in the observed scatter in the upgrading data. Whilst it is undesirable for such fluctuations in flow to occur experimentally, similar effects may also occur in the downhole CAPRI process due to the MOZ passing through regions of oilsands of different permeability and uneven depositions of coke within the catalyst bed. The intended operation of the reactor with a gas flowrate of 0.5 l.min^{-1}(‡‡) and an oil flowrate of 1 ml.min^{-1} through the 11 cm length of the catalyst bed with 10.2 mm tube diameter would lead to a mean residence time of gas in the reactor of approximately 0.27 seconds. The calculated liquid hourly space velocity (LHSV) would be 8.89 h^{-1}, with mean residence time of 6.74 minutes. However, the actual residence time of the oil will depend upon whether the vaporized droplets are carried through the reactor with the gas flow or impact upon the catalyst particles and are retained there.

4.3 Alternative Catalysts (Albemarle and Zeolite Catalysts)

Apart from the upgrading behaviour of a catalyst for heavy oil, a number of other considerations have to be taken in to account. For example any type of catalyst for heavy oil

---

[‡‡] ZnO/CuO experiment was performed at 1 l.min^{-1} gas and 2 ml.min^{-1} oil flow rates but in order to conserve both gases and oil the flowrate was reduced for all other experiments to 0.5 l.min^{-1} gas and 1 ml.min^{-1} of oil, which doesn't change the gas to oil ratio but only the quantity of the gas and oil used.

upgrading must have good coke resistivity, as coking is the biggest cause of deactivation of any heavy oil upgrading catalyst. In addition to catalyst deactivation by coke and metal deposit, vacuum residue HDS in fixed-bed reactors such as the CAPRI reactor used in this study, involves typical problems such as Hot spot occurrence and pressure drop buildup can also occur in the CAPRI reactor, similar to vacuum residue HDS in fixed bed reactors. Good liquid flow distribution across the catalytic bed is essential to avoid hot spots which generally originate from an initial poor distribution of the liquid flow (Kressmann, 1998). The use of good liquid distribution is therefore necessary, but unfortunately the effect of this good distribution is limited to a certain depth of the bed, which varies with catalyst particle shape and size. In addition, the flowing of the liquid phase is related to the orientation of the catalysts particles in the reactor, hence the loading method is important in order to control this orientation. Moreover, the shape of the catalyst is of importance e.g. beads lead to more homogeneous liquid flow (Kressmann, 1998). The Institute Francais du Pétrole (IFP) Energies Nouvelles has developed its residue upgrading catalysts in various sizes and shapes and, in particular, in the shape of beads and cylinders. Conditions which necessitate the reactor to be shut down can arise due to an increase in pressure drop above the maximum design conditions (Kressmann, 1998). Combining catalysts with different sizes and shapes in the reactor have been found to limit the rate of pressure drop buildup (Kressmann, 1998).

From the above discussion it is clear that shape and size of catalyst particles are essential for selecting an optimum catalyst for heavy oil upgrading. For this reason commercial catalysts from Albemarle Corporation and molecular sieves having different shapes and pellet sizes were used as alternative catalysts to the typical HDS CoMo and NiMo as described in Section 4.2 of this work. These properties are particularly important because in spite of the significant advances of macro-porous or bi-modal pore catalyst development, diffusion problems encountered during hydroprocessing of residue cannot be entirely eliminated.

The three different types of Albemarle Corporation catalysts and a molecular sieve used in this work have been listed in Table 4.3. These catalysts are specifically designed for the processing of heavy oils by the petroleum refining industry and have tailored metal composition, support and shapes for this application. Detailed characteristics of these catalysts have been provided in Table 4, chapter 3.

Zeolites are another class of catalysts, which have been used extensively in the refining industry as catalysts of choice, preferably for Hydrocracking (HCR) activity (Lapinski, 1998; Otterstedt *et al.* 1986; Degnan, 2007). Having extensive network of active acidic sites available to accommodate and crack molecules such as asphaltenes in heavy oils and residue, it definitely offered advantages to be used as an alternative catalyst in this work. However, they are prone to deactivation. For this reason, a calcium form of molecular sieve (zeolite) provided by sigma Aldrich and having a pore diameter of $5x10^{-10}$ m was used for the upgrading of THAI field oil.

Results from these catalysts are presented in Table 4.4 and Figures 4.2 (a) and (b), from which none of the Albemarle catalysts show any superior upgrading of THAI crude to that of the benchmark Akzo CoMo catalyst, in terms of viscosity reduction or API increase. Therefore, they were not used for any further investigation. This lack of activity was thought to be due to similar problems occurring, as was the case with the other three types of catalysts i.e. Akzo CoMo, NiMo and ZnO/CuO. Deactivation of the active sites of these metal catalysts by coking and other types of poisoning. These deactivation reactions occurred as soon as the upgrading process began. An important factor in the quick deactivation of the catalyst is the absence of high partial pressure of hydrogen, as explained previously in section 4.2. In a typical oil refinery operation, high hydrogen partial pressures are used as an essential tool in the upgrading of any residual feed to prevent coke formation and stabilize the produced oils. However, since the addition of high partial pressure to a CAPRI in situ reservoir will be impractical hence not the objective of this study.

Table 4.3 Average and Standard Deviation Viscosity and API Gravity after Upgrading of Heavy Oil with Different Catalysts

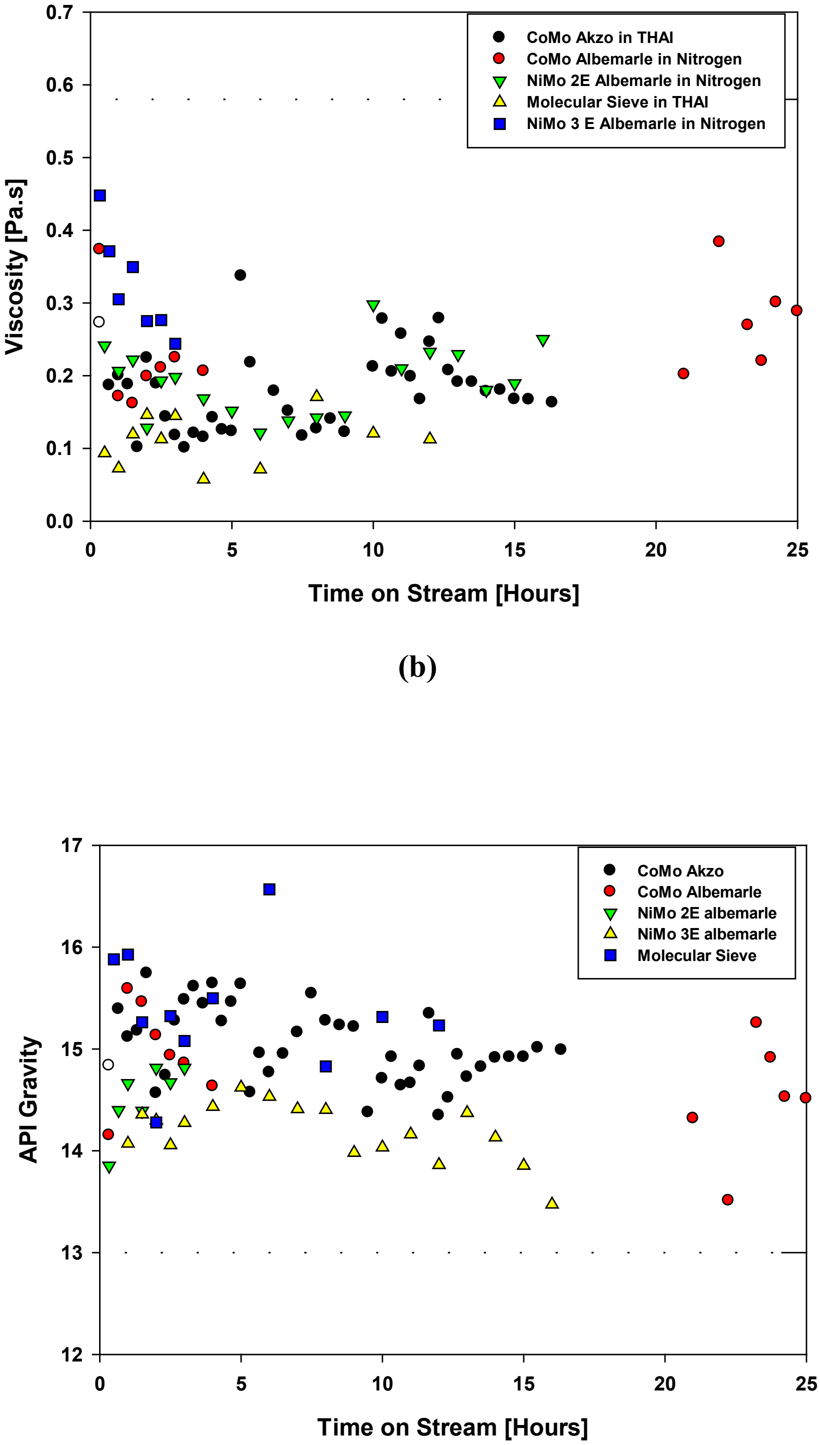
Exp. No.	Catalyst	Reaction Media
P66	CoMo Akzo	THAI Gas
P51	Albermarle CoMo APC-1E	1% H_2 in N_2
P53	Albemarle NiMo APC-2E	1% H_2 in N_2
P75	Albemarle NiMo APC-3E	N_2
P84	Molecular Sieves	THAI

Table 4.4 Effect of Albemarle and Zeolite Catalysts; Average and Standard Deviation Viscosity and API Gravity after Upgrading of Heavy Oil with Alternative Catalysts

	CoMo Akzo	CoMo 1E Albemarle	NiMo 2E Albemarle	NiMo 3E Albemarle	Molecular Sieves
Average flowrate ml.min^{-1}	1	1.06	1.15714	0.9384	0.904
Standard deviation flowrate ml.min^{-1}	0.044	0.642	0.34208	0.0940	0.101
Average viscosity Pa.s	0.180	0.246	0.324	0.192	0.111
Standard deviation viscosity Pa.s	0.055	0.071	0.07024	0.0471	0.035
Average API gravity	15.04	14.75	14.5145	13.437	15.38
Standard deviation API gravity	0.365	0.569	0.3398	0.284	0.601
Operation time (hours)	16	25	3	16	12

Figure 4.2 Alternative Catalyst; Albemarle HDS Catalysts and Zeolites upon (a) Viscosity (b) API
Experiment conducted at 425°C, 20 bar g pressure of N2 except for Zeolite which was THAI gas

(a)



(b)

To get the best possible results with zeolites, the experiment was carried out at the optimum temperature of 425°C as was found to be the case in the temperature study in Section 4.10. With the zeolite catalyst a final viscosity value of 0.11 Pa.s for the produced oil was achieved against a final value of 0.18 Pa.s for Akzo CoMo, showing more upgrading compared to base case CoMo. The results were more valuable because in both the experiments the experimental control was relatively smooth. A steady flowrate of oil was maintained in each case, rather than fluctuations in flow that occurred in some other experiments due to coke deposition and blocking the void structure of the bed. However the duration of the experiment with the molecular sieves (zeolites) was limited to only 12 hours. To fully evaluate this catalyst, their use for longer term durations together with consideration of their higher cost in comparison to typical HDS catalysts needs to be further investigated.

From the above results the enhanced activity of the molecular sieve versus the supported CoMo or NiMo catalysts could be explained by a number of reasons. Supported metal catalysts such as NiMo/Al_2O_3 usually have relatively low total average acidities compared to those of zeolites or zeolite supported catalysts. A value of 0.12 mmol.g^{-1} was observed for the alumina based NiMo catalyst by Ding *et al.*, (2007). When alumina was exchanged for zeolite Y as support an increase in HDS, Hydrodenitrogenation (HDN) and HDA activities was observed, with a single model component as feed. This could be due to the much higher acidity of zeolite Y, with typical average acidity value of 0.21 mmol.g^{-1}. Although zeolite pores may become easily blocked by coke after an initial period of inevitable coking on both types of catalysts, those containing zeolite Y still showed higher hydrogenation activity than NiMo/Al_2O_3. This is because it has previously been demonstrated that HDS of organic sulphur compounds generally proceeds by two parallel reaction pathways, one by direct desulphurization (DDS) via hydrogenolysis of the C–S bond, and one via hydrogenation

(HYD) of the aromatics ring followed by hydrogenolysis of the C–S bond (Vrinat, 1983; Houalla *et al.* 1978). The two reaction pathways are believed to take place on different active sites. Due to the steric hindrance of the methyl constituents, the reactivity of 4,6-DMDBT (dimethyl dibenzo-thiophene) HDS is very slow, and preferentially proceeds via HYD. The HDS activity of 4,6-DMDBT can be enhanced by adding acidic zeolite, which can lessen or eliminate the hindrance through hydro-isomerizing or dealkylating the methyl groups at 4 and 6-positions (Meille *et al.*, 1997; Kabe *et al.*, 1993; Bataille *et al.*, 2000). Therefore, it is not surprising to see that the HDS activity of NiMo/Y was higher than that of NiMo/Al_2O_3. Another possible reason could be because of the higher hydrogenation activity of the zeolite containing catalysts, e.g. the acidity of the support favours the migration of the hydrogen spillover[§§] from the donor phase (Ni_2S_3) up to the acceptor phase (MoS_2) (Ding *et al.*, 2007). It has been previously demonstrated (Baeza, 2006) that the mobility of the spillover hydrogen occurred even if Co_9S_8 (or NiS_x in case of a NiMo catalyst) and MoS_2 were separated by 10 mm in successive beds of Co, Ni and Mo-supported catalysts rather than dispersed over the same catalyst support. The higher activity of zeolite containing catalysts may be caused by the easy migration of spillover hydrogen over acid surfaces (Ding *et al.*, 2007).

Moreover, HDS of 4,6-DMDBT occurs mainly via HYD route over NiMo/Al_2O_3, while on the zeolite containing catalysts, HDS can proceed not only via HYD, but also via DDS. In the work of Ding *et al.* (2007), it was observed that the conversion of 1-methylnaphthalene (MN) can be enhanced by the shift of chemical equilibrium due to the cracking of the hydrogenated products of 1-MN, methyltetralin, on zeolite containing catalysts. Therefore, the influence of hydrogen partial pressure on HDS and HDA becomes more pronounced on NiMo/Al_2O_3 than

---

[§§] 'Hydrogen Spillover' is the dissociative chemisorption or adsorption of hydrogen on the metal part for the catalyst and migration of atomic hydrogen to the surface of the support such as alumina, silica, and zeolites.

on zeolite containing catalysts. This could perhaps explain that under the same conditions in the absence of any hydrogen, zeolites outperformed supported CoMo and NiMo catalysts.

Although hydrogen would not be added externally in the THAI-CAPRI process, the gas environment within the well is reported to contain some hydrogen, which possibly is liberated by thermal and catalytic processes (Petrobank, 2008). Therefore to investigate this effect in the experimental study, 4% hydrogen was blended with either nitrogen or THAI gas flow, by metering both gases through Brooks mass flow controllers (Refer to Section 4.12 for hydrogen addition to the base case CoMo). Results from this experiment with Albemarle CoMo and Akzo CoMo in the presence of 4% added hydrogen in nitrogen are presented in Table 4.5 and Figures 4.3 (a) and (b). From these results it can be observed that the viscosity reduction is only 0.044 Pa.s lower with Albemarle CoMo than with the base case Akzo CoMo. This difference is relatively small and could be considered to be within the experimental error range of the measurement. Similarly from Figure 4.3 (b) the API value is 0.29° higher for the Akzo CoMo than the Albemarle CoMo, which is also within the experimental error. This experimental error is also visible from Figure 4.3 (a) and (b) the scatter and could explain the Albemarle CoMo poor performance in comparison to Akzo CoMo.

Another possible reason for the general apparent lack of catalytic activity, as observed in Section 4.2, could be that these catalysts were designed for an optimum residence time of 30 minutes and in the presence of high partial pressure of hydrogen, where they may be active for almost a year (Personal Communication from Dr. Hiro Toshima, Albemarle Corporation, 2009). However in this work the target residence time was just over 6 minutes and in the presence of largely nitrogen or THAI gas.

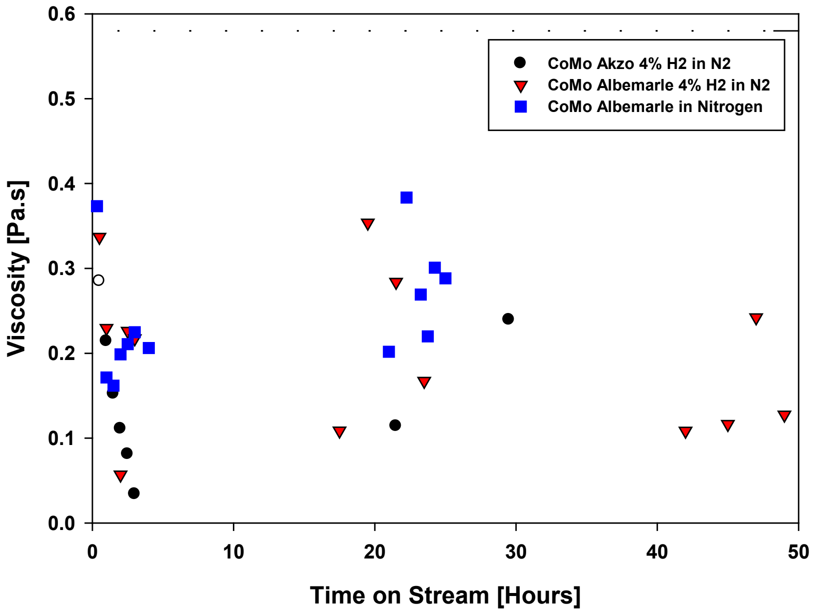
Table 4.5 Average and standard deviation viscosity and API gravity after upgrading of heavy oil with different catalysts

	CoMo Akzo	CoMo 1E Albemarle	CoMo 1E Albemarle
Reaction Media	4% H_2 in N_2		N_2
Average flowrate ml.min^{-1}	1.01	1.10	1.06
Standard deviation flowrate ml.min^{-1}	0.321	0.498	0.642
Average viscosity Pa.s	0.154	0.198	0.246
Standard deviation viscosity Pa.s	0.086	0.093	0.071
Average API gravity	15.90	15.00	14.75
Standard deviation API gravity	1.233	0.99	0.569
Operation time (hours)	29.5	49	25

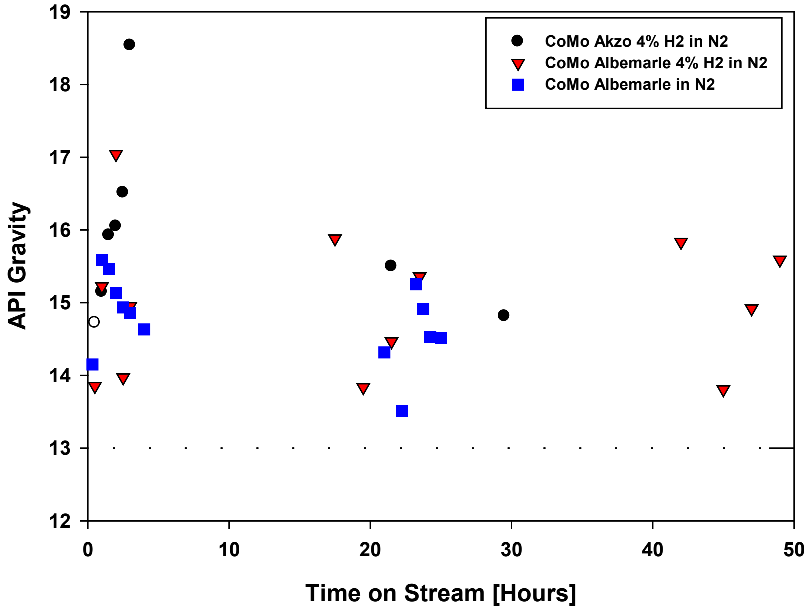
Figure 4.3 Alternative Catalyst; Effect of Hydrogen addition Albemarle CoMo vs Akzo CoMo (a) Viscosity (b) API

Experiment conducted at 425°C, 20 bar g pressure of 4% H2 in N_2

(a)



(b)



Zeolite catalyst was exceptional in providing higher level of upgrading, possibly because of higher support acidity than the other catalysts comprised of metals supported upon alumina. Clay catalyst on the other hand possibly reduced only the formation of larger molecules and hence only reducing viscosity. Akzo and Albemarle catalysts more or less equally upgraded the produced oils to within the margins of experimental errors. The biggest challenge during the catalysis was the formation of coke over the catalysts early in the reaction. A favourable reaction medium such as high partial pressures of hydrogen have been found to increase the formation of liquid yields during upgrading of heavy oils in the presence of catalysts (Ding *et al.*, 2007). However, since adding hydrogen or controlling it is not practical with CAPRI process hence not a useful optimization parameter.

The addition of smaller flowrates of hydrogen at low partial pressure did not produce any upgrading effect in terms of viscosity reduction or API gravity increase. The use of a guard bed before the active catalyst in fixed bed reactors has been strongly recommended in the literature to prevent metals deactivating the active surfaces (Rana *et al.*, 2007). The guard bed is usually highly porous substance with neutral support, low surface area but large pores to accommodate the crude metals on its surface. Most of the metals present in the crude are left on the guard bed and the feed is relatively clean to be processed using typical HDS catalysts such as CoMo or NiMo (Rana *et al.*, 2007). This could be used in future investigations.

As explained earlier that the optimization of the catalyst size and shape for fixed bed reactors requires a number of considerations. For instance spheres may offer improved abrasion resistance and lower pressure drop. In terms of lowering pressure drop, rings are currently the most common shape favoured as they have greater geometric surface area and improved diffusion of the reactants to the catalytic surface (Rana *et al.*, 2007). Multi-lobed shapes, consisting of central core surrounded by lobes (Ancheyta, *et al.*, 2005; Macias and Ancheyta, 2004) have been developed to reduce mass transport distances from the outside to the centre of the pellet. The tri-lobe and penta-lobe extrudates shapes also provide lower pressure drop compared with the traditional cylindrical extrudates (Cooper *et al.*, 1986). Most of these modifications and improvements in catalyst design were applied in this work. However despite using tablets, cylinders and tri-lobe catalysts, none of these changes in shape or sizes helped in significantly upgrading the THAI field oil.

4.4 Catalytic versus Thermal Upgrading

In order to investigate the extent of catalytic versus thermal upgrading, comparisons were made between upgrading over a metal supported catalyst (run P13), alumina support without metals (run P19) and inert glass bead packing (run P17). The latter run was important to investigate the role of thermal upgrading and its significance in comparison to catalytic upgrading of THAI field oil. From the results as shown in Table 4.6 and Figure 4.4 (a) and (b) it is evident that the Akzo CoMo is not significantly active in reducing the viscosity of

THAI field oil in comparison to its acidic support alumina or glass beads (GB). However, the average values of 0.35 Pa.s of viscosity for CoMo have more than twice as high standard deviation (0.16) in comparison to alumina and GB (0.07). The same is true for API with average value of 14.4° for CoMo the standard deviation is 0.37 while that of GB is only 0.26. Thus perhaps viscosity reduction and API improvement will be higher in comparison to GB if the scatter (or less standard deviation) in data for CoMo catalyst is not taken into account. In the absence of higher partial pressures of hydrogen the bifunctional metal of the HDS catalyst CoMo did not raise the upgrading levels by hydrogenating the processed oils compared with just the cracking activity of alumina. This may represent a role for the acidity of alumina support. This point is also supported by the fact that the alumina run shows a relatively higher upgrading in comparison to the CoMo catalyst in terms of reduction in viscosity initially in the experiment, though the CoMo and alumina equally decrease viscosity later in the run. Moreover, alumina runs were also blocking the reactor rapidly due to sever coking and hence was found not suitable for further investigations.

Since heavy crude contains oils, resins and asphaltenes, it is the amount of asphaltenes which are the main concern as these compounds are the primary cause of catalyst deactivation. This very large complex molecule is the principal coke precursor and is held in suspension by the resins or polar fraction of the heavy crude oil. During hydroprocessing of heavy crude, oil and resin fractions are converted to smaller fragment very fast compared to the asphaltene fraction (Trimm, 1990). Solubility of asphaltenes decreases during conversion of resin. Therefore, asphaltenes are precipitated on the catalyst surface and block the pore mouth (Trimm, 1990). Coke deposition is the main cause of the initial loss of micro-pore and hence surface area of catalyst. It is reported in the literature that coke equivalent to up to 25 wt.% of the original catalyst is deposited within few hours of run and this can decrease surface area of up to 50–60% of the original catalyst (Absi-Halabi *et al.*, 1991). Grey *et al.*, (1992) also found that hydrocracking activity in the presence of γ-alumina caused severe coking right from the beginning in comparison to alumina supported CoMo or NiMo catalyst. This possibly means that the initial higher activity of alumina was caused by the reduction of carbon in the produced oil (which deposited on the alumina surface as coke) leading to upgrading of the density and lowering viscosity. A similar trend was observed in this work.

The same pattern is evident from SIMDIS results in Figure 4.4 (b). CoMo showed a shift of only 5°C of the SIMDIS curve towards the left or lower end hydrocarbons HC in comparison to alumina or GB. Alumina also showed a very slight shift towards lighter end more than the GB, suggesting acidic sites contributing towards catalytic upgrading reactions of the THAI crude.

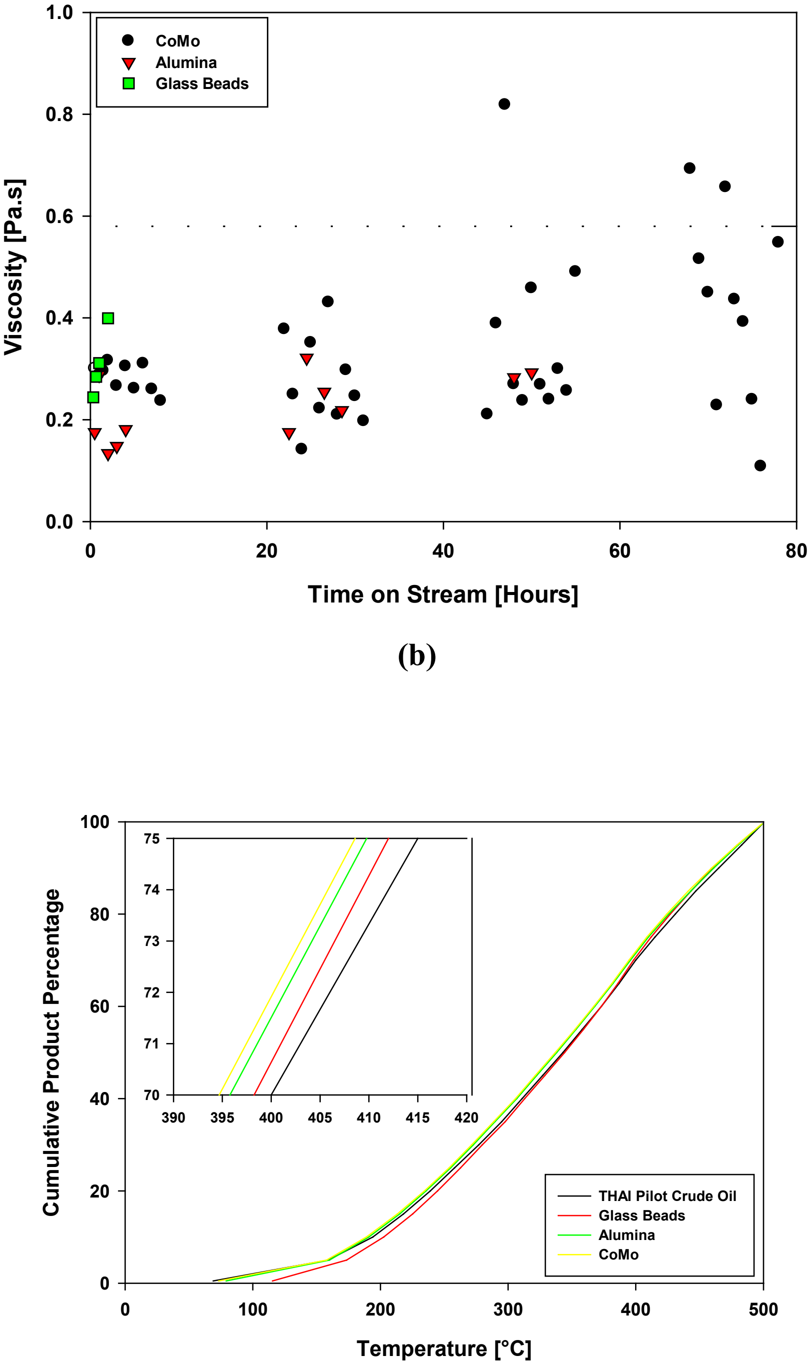
These findings are consistent with the literature as the properties of the supports are crucial for defining the desirable porosity and surface area of catalysts and the catalyst performance can be modified by chemical composition of supports. For example, in this sense it is well established that mixed oxide support can be prepared with acid–base sites (Rana *et al.*, 2005a, b and c; Caloch *et al.*, 2005), which improve cracking functionality of the catalyst (Maity *et al.*, 2003; 2005; 2006).

Table 4.6 Effect of Catalyst versus Thermal Upgrading

	CoMo	**Alumina**	**GB**
Average viscosity Pa.s	0.353626	0.224609	0.309675
Standard deviation viscosity Pa.s	0.158496	0.065671	0.065797
Average API gravity	14.40204	14.87182	14.72
Standard deviation API gravity.	0.371225	0.321864	0.263186

Figure 4.4 CoMo comparison to Alumina and GB (a) viscosity (b) SIMDIS;
At 400°C, 20 bar g of pressure in nitrogen gas

(a)

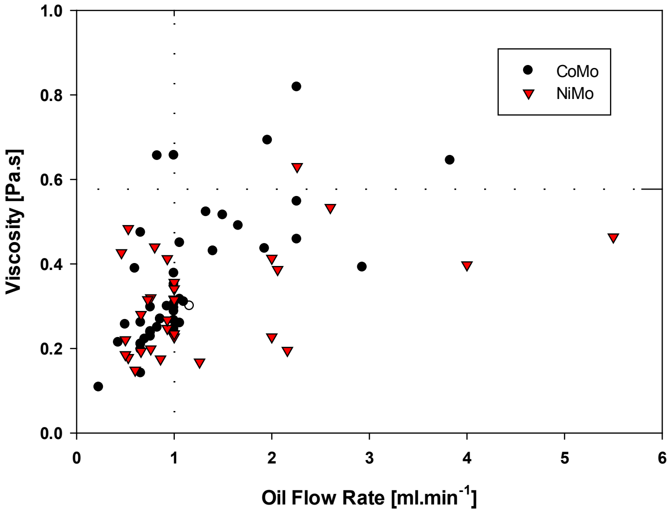


4.5 Effect of LHSV

Figure 4.5 shows the viscosity of upgraded oil as a function of the actual oil flowrate, indicating a "cone shaped" correlation, whereby lower flowrates led to lower viscosity of upgraded oil due to increased residence time in the catalyst bed, whilst higher oil flowrates gave higher viscosities due to insufficient residence time for further upgrading to occur.

From this observation it was evident that residence time over the catalyst or LHSV is a major factor in effecting the upgrading of THAI crude oil. Hence two experiments were conducted to investigate this effect in detail. Figures 4.6 (a) and (b) and Table 4.7 further illustrates the effect of oil flowrate upon upgrading when different oil flowrates were used under constant conditions in experiment P71. The lowest flowrates led to higher upgrading in API gravity and reduction in viscosity in comparison to higher flowrates.

Figure 4.5 Viscosity of the Upgraded Oil Versus Oil Flowrate
Experimental conditions as for Figure 4.1.



This was particularly evident for the oil flow of 0.2ml.min^{-1}, which led to API gravities in the range of 18-20° and viscosities below 0.1 Pa.s. In Figures 4.6 (a) and (b) and Table 4.7 the results of the CoMo catalyst have also been compared with a controlled run carried out in the presence of the inert packing material GB. This investigation will provide evidence whether the influence of oil flowrate is a thermal upgrading effect or specific to catalytic runs.

From Table 4.7, it can be observed that at the highest LHSV favours more reduction in viscosity for the catalytic run in comparison to the GB. The same is true about API gravity too. With the reduction in LHSV the viscosity reduction and rise in API gravity in the catalytic run is almost twice as much as with the non-catalytic i.e. GB. This is particularly evident at the lowest LHSV of 0.18 h^{-1} LHSV where the API gravity was 19.9° for the CoMo versus 15.3° with the GB, whilst the viscosity was 0.03 Pa.s for CoMo versus 0.10 Pa.s for GB. These trends indicate the role of catalyst in the improvement of produced oil quality in terms of viscosity and API gravity.

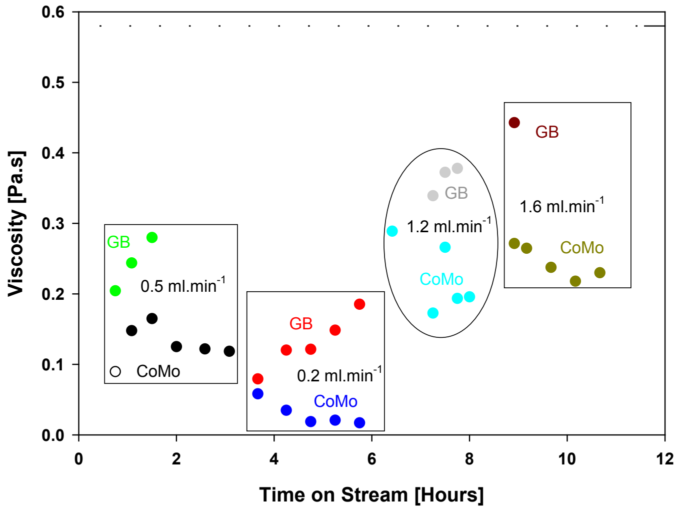
From the above discussion and Figures 4.6 (a) and (b) it is clear that the viscosity reduction and API upgrading of the processed oil with the GB are markedly inferior to the oil processed with Akzo CoMo at all flowrates. It is also evident that as the time on stream increases, the viscosity reduction increases almost linearly in the presence of CoMo in comparison to GB. This effect is more visible at 0.2 ml.min^{-1} of oil flowrate than the 0.5 ml.min^{-1}. At 0.5 ml.min^{-1} oil flowrate, the viscosity reduction with CoMo slightly rises and then drops down as the time on stream increases. There is a slight scatter in the 1.2 ml.min^{-1} in the catalytic run, yet the level of upgrading is higher in the presence of the catalyst than the GB. Consequently, it is concluded that lower oil flowrate or LHSV is an important variable in the control of the CAPRI process and this is specific to the catalyst.

Table 4.7 Effect of LHSV or Residence Time

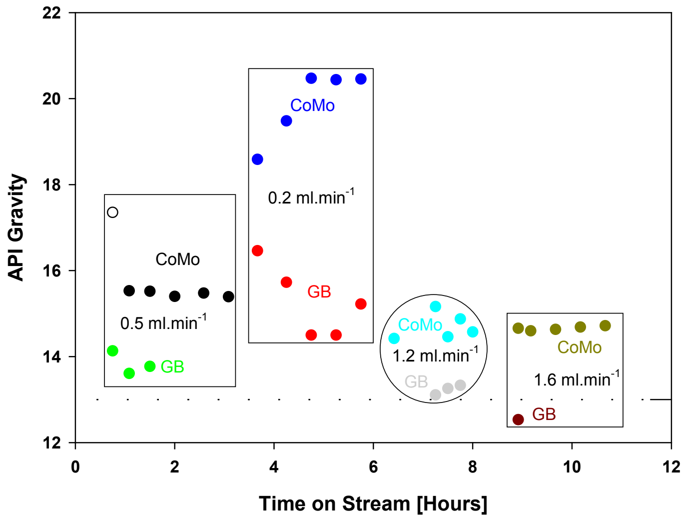
Oil flowrate ml.min^{-1}	1.6		1.2		0.5		0.2	
LSHV	1.43		1.07		0.45		0.18	
Residence Time (min^{-1})	0.699		0.9346		2.22		5.56	
	GB	CoMo	GB	CoMo	GB	CoMo	GB	CoMo
Average viscosity Pa.s	0.44	0.24	0.36	0.22	0.24	0.13	0.10	0.03
Average API gravity	12.5	14.7	13.9	14.7	13.8	15.8	15.3	19.9

Figure 4.6 Viscosity and API of Upgraded Oil Versus Variable Oil Flowrate.
THAI oil viscosity of 0.58 Pa.s and an API gravity of 13°. 425 °C, 20 bar (g), with a flowrate of 0.2-1.6 ml.min^{-1} oil and 0.5 l.min^{-1} THAI gas (a) Viscosity (b) API values

(a)



(b)



4.6 Effect of Gas:Oil Ratio.

After investigating the effect of LHSV or the oil flowrate in section 4.5 this section reports investigation of the effect of gas to oil ratio upon the upgrading behaviour. For this reason experiment P68 was conducted using a fixed oil flowrate of 1 ml.min^{-1} while the gas to oil ratio (GOR) (or gas flowrate) was varied within a range of 250-750 rather than the usual 500 kept for all the other experiments. Table 4.8 shows the average viscosity and API gravities at different gas-to-oil ratios (GOR). The viscosities of the upgraded oil lie within a narrow band of values of 0.24 ± 0.4 Pa.s. Although the viscosity is slightly lower at the smallest and highest GOR, all of the values are within the margin of error of the experiment. Similarly the average API gravities lie within the band of 14.7 ± 0.3. The lack of effect of GOR upon the upgrading performance suggests that it is only the residence time of the oil upon the catalyst which influences the upgrading performance, rather than interactions between the gas and liquid phases.

Table 4.8 Effect of Gas-To-Oil Ratio Upon Viscosity and API Gravity of Upgraded Oil
CoMo catalyst, 1ml.min^{-1} oil flowrate, 0.25 – 0.75 l.min^{-1} gas flowrate (4% hydrogen in THAI gas), 425 °C, 20 bar (g)

GOR	**235.5**	**375**	**500**	**641.4**	**744**
Average viscosity Pa.s	0.202	0.276	0.249	0.247	0.200
Standard deviation viscosity Pa.s	0.054	0.034	0.036	0.055	0.046
Average API gravity	15	14.56	14.52	14.43	14.46
Standard deviation API gravity.	0.524	0.169	0.129	0.288	0.228

4.7 Effect of Pre-reduction of Catalyst in Hydrogen

In order to further check the catalytic effect, the influence of the pre-treatment method of the catalyst during start up was investigated. Experiments were carried out with and without pre-reducing the catalyst in hydrogen. The pre-reduction of the catalyst consisted of, flowing 25% hydrogen over the catalyst at a temperature of 425°C for a period of 30 and 60 minutes. Thereafter the oil flow and THAI gas, nitrogen or 4% hydrogen in either THAI gas or nitrogen flows were started. Average values of the viscosity of the upgraded oil were 0.154 Pa.s with catalyst pre-activation and 0.176 Pa.s without pre-activation. API gravity values were 15.9 with pre-activation and 15.04 without pre-activation. The upgraded oil that was passed over the pre-activated catalyst showed very slightly lower viscosity and higher API gravity, compared with non pre-treatment. However this difference was within the experimental error of ± 0.1 Pa.s in viscosity and ± 1°API gravity and therefore the pre-treatment of the catalyst did not appear to significantly influence the upgrading performance.

4.8 Effect of Short Run Times

Short runs were repeated for different times on stream of 1, 2, 4, 8 and 18 hours (Table 4.9). The purpose of carrying out the short runs was two-fold. Firstly, repeating the early part of the experiment would provide several sets of results run under the same conditions to determine whether the experimental results are repeatable. Secondly, stopping the reactor at different lengths of time would enable the catalyst to be recovered for coke analysis[***]. Catalytic runs at different operation times showed that viscosity results were repeatable to within ± 0.1 Pa.s, whilst the API gravity results were repeatable to within ± 1°API. Visual inspection of the catalyst bed after each run showed considerable coke deposition, even at the shorter reaction times of 2 and 4 hours, illustrating that coke deposition occurred early in the reaction. This finding is consistent with the literature as generally in fixed bed reactors, deactivation occurs in three steps: a rapid initial deactivation, slow gradual deactivation at the middle of the run and very rapid at the end of the run (Oelderik *et al.*, 1989; Tamm *et al.*, 1981; Al-Dalama and Stanislaus 2006; Kam *et al.*, 2005; Thakur and Thomas 1985).

Table 4.9 Effect of Short Runs; List of Experiments
at 400°C, 20 bar g, 0.5 l.min and 1ml.min^{-1}
of nitrogen gas and oil flowrates respectively

Exp. No.	Catalyst	Time [Hours]
P18	CoMo	2
P20	CoMo	4
P21	CoMo	1
P22	CoMo	18
P23	CoMo	8

4.9 Effect of Pre-sulphiding the Catalyst

Hydrodesulphurization HDS catalysts containing CoMo and NiMo are produced in oxidic form. The activation is carried out under pressure by reducing and sulphiding agents at moderate temperatures (300-400°C). The activation phase is important as it produces active states of sulphided metals such as MoS_2, CoMoS like structures, which are essential for HDS

[***] Results and discussion about coke analysis has been presented in Chapter 7

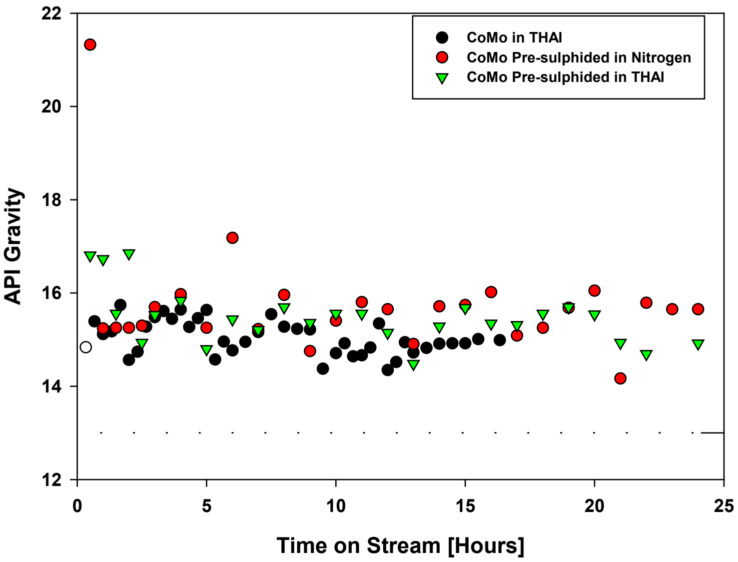
activity (Silvy *et al.* 1989). It was therefore apparent that pre-sulphiding the catalyst may be a more effective means of activating the catalyst.

As discussed in section 4.2 that there are two ways to presulphide a catalysts, firstly where the catalyst becomes sulphided itself while being operated in the processing of a higher sulphur feed or secondly by an external sulphiding agent such as DMDS. In this section results with the catalyst presulphided using the second method are presented.

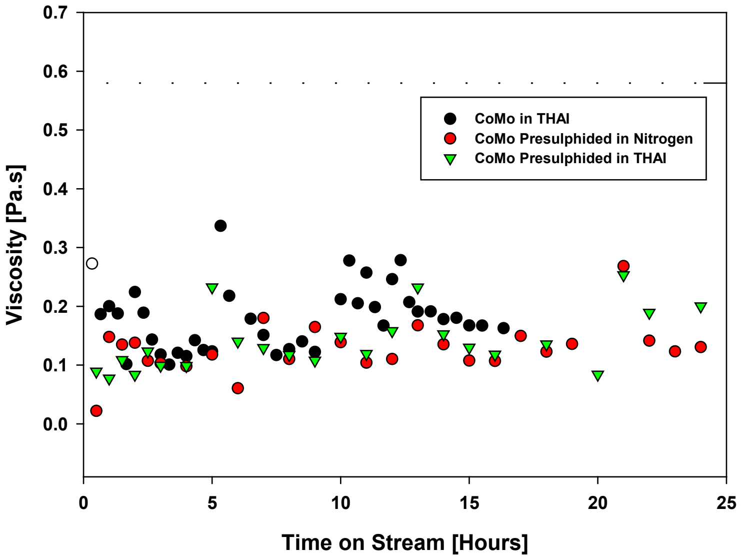
CoMo catalyst was pre-sulphided prior to experiments P77 and 78 using the method described in Section 3.1.15. Viscosity and density analysis of the collected oil samples are illustrated in Figure 4.7 (a) and (b), with both nitrogen and THAI Gas (13% CO_2, 3% CO, 4% CH_4 in N_2) employed as the reaction gas. A slight improvement in upgrading is apparent for the pre-sulphided catalysts with the produced oil generally presenting lower viscosity and density in comparison to a non-sulphided CoMo. In terms of density this is only an improvement of around 0.5°API compared with the non-pre-treated catalyst and this small change in API may be considered to be within the experimental error.

Figure 4.7 Effect of Pre-sulphiding Stage on (a) Viscosity and (b) API Gravity
CoMo catalyst, 425°C, 20 bar g, 500 $ml.min^{-1}$ N_2 or THAI gas and 1.0 $ml.min^{-1}$ oil

(a)



(b)



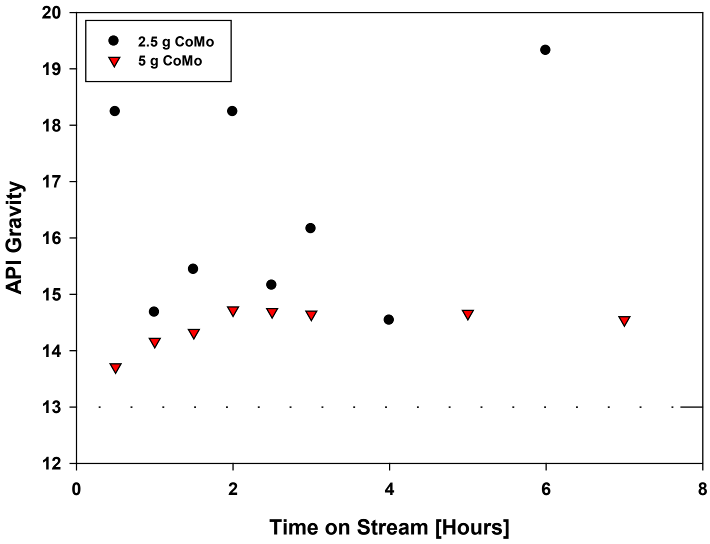
4.10 Effect of Catalyst Bed Length/Concentration

The amount of catalyst in the reactor bed was varied in order to simulate the effect of different thicknesses of annular catalyst in the field process. Two different catalytic beds lengths of 10 cm (the usual length employed in all other experiments) and 5 cm depth with a catalyst quantity of 5 and 2.5 g respectively were used. Both of them were supported above and below by GB in the usual manner. The resultant oil upgrading in terms of viscosity and API gravity is shown in Figure 4.8 (a) and (b), which does not show any conclusive difference in upgrading behaviour. At the beginning of the two experiments, the 2.5 g catalytic bed seems to perform better in reducing viscosity and improving API gravity than the 5 g catalytic bed; however with time on stream increases the 5 g catalytic bed viscosity reduction and API improvement becomes level. This is not unexpected given that the coking of the catalyst bed happens initially at the start of the experiment and the smaller catalytic bed cokes up more slowly than the larger one. The scatter in the results also suggests this may be because of the poor control of the process. Generally, the presence of low amounts of molybdenite can significantly reduce coke formation during hydrotreatment (Perchec, 1993). Panariti *et al.*, (2000) reported that the presence of 1000 ppm of molybdenite decreases the amount of coke; at higher catalyst concentration (5000 ppm of molybdenum) the amount of solids tends to increase again. This behaviour was found to occur both at mild and severe operating conditions and similar trends were found to occur elsewhere (Bearden and Aldridge (Bearden and Aldridge, 1981; Kennepohl and Sanford, 1996). The trend of increasing coke formation at higher molybdenum concentrations can be explained by two different phenomena occurring simultaneously. On one side, the MoS_2 microcrystals dispersed in the vacuum residue may be responsible for seeding the precipitation of solids. On the other side, the high level of hydrogenation of the feedstock achieved in the presence of significant amounts of catalyst reduces asphaltene stability (Shew and Mullins, 1995) thus promoting coke formation (Wiehe, 1993). These two phenomena are in competition with the well-known mechanism of coke inhibition through hydrogen transfer due to the dispersed catalyst. The level of MoS_2 concentration determines which process prevails.

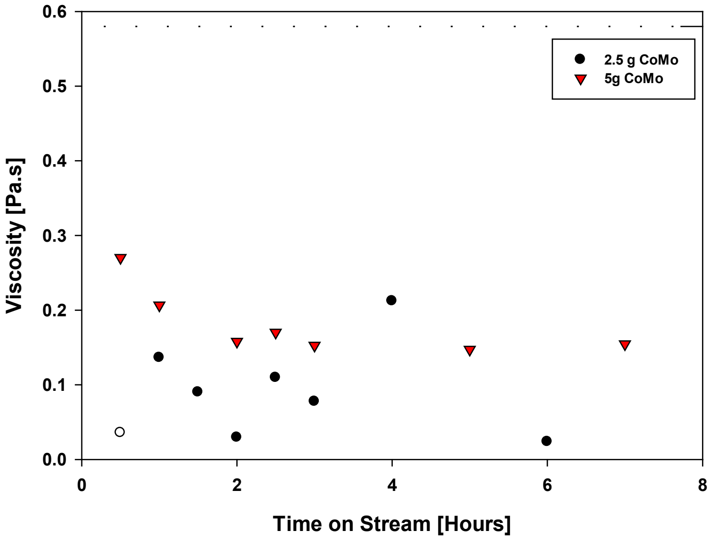
The scatter in the 2.5 g CoMo catalyst experiment indicates that poor control of the feed rate may largely be responsible for the difference of activity in between the two catalytic beds.

Figure 4.8 Effect of Catalyst Bed Length on (a) Viscosity and (b) API Gravity
CoMo catalyst, 425°C, 20 bar g, 500 ml.min^{-1} N_2 or THAI gas and 1.0 ml.min^{-1} oil

(a)



(b)



4.10 Effect of Temperature

Table 4.10 lists the experiments conducted to investigate the effect of temperature. Figures 4.9a) and b) and c) and Table 4.11 show the effect of temperature upon upgrading performance. At lower temperatures of 380-420°C, moderate levels of oil upgrading were observed, with viscosity reduction of approximately 0.3 Pa.s and API gravity increase of 1.5-2 points. However, the data at 400ºC and 420ºC/425 ºC show some scatter, with occasionally poorer upgrading results being achieved. Upgrading levels improved with increasing temperature, with viscosity of the upgraded oil processed at 475°C being decreased by 0.57 Pa.s (96 %) from the THAI oil value, and the API increased by 5.7 points, and similar upgrading performance occurring at 500°C. However, catalyst operation time was severely limited with operation at 475 – 500°C, since the oil flowrate declines and pressure drop increases sharply due to bed blockage by coke. Greaves and Xia (2001) obtained upgrading of 4-6 API points with CAPRI above that achieved using only THAI (non-catalytic process), with final viscosities decreasing to below 0.1 Pa.s, or as low as 0.02Pa.s in selected runs, which is comparable with the upgrading performance observed in the experiments reported in this work at temperatures of 475-500°C. SIMDIS analysis of the product liquid oil samples further confirms that the higher temperature favoured lighter end products in liquid fractions in comparison to the partially upgraded THAI oil, where approximately 10-15°C shift was observed towards the lighter end products (Figure 4.9 c).

Figure 4.9 (d) shows a photo of the cross-section of the catalyst bed after coke deposition when operating at the higher temperature of 475°C with the CoMo catalyst illustrating that the pore space is almost completely filled with coke.

Millan et al (2008) studied catalytic activity in heavily coated hydrocracking catalysts and found that, although a large coke deposit was observed to form earlier on in the runs, catalyst samples recovered from the initial coking experiment displayed continued activity despite a large drop in surface area and a complete apparent pore blockage. Similarly, attempts to characterize the pore structure of spent catalysts using gas sorption methods in the experiments reported here showed that almost complete pore blockage occurred. However, even towards the end of the run, some upgrading of the oil still occurred. This suggests that either the catalyst retains its activity despite a heavy coke deposition, which could occur because of exchange of carbonaceous deposits with the oil, such that catalyst activity continues. A second possible effect would occur if the coke itself were acting as a catalyst, through exchanging hydrogen with the oil molecules in the liquid phase. Alternatively, it could be because of thermal reactions, which are not dependent on catalytic activity. It is noted that if classical catalyst deactivation effects occurred, the extent of upgrading would be likely to follow exponential decay behaviour, with the exact deactivation function depending on the way in which the network of pores becomes plugged by coke (Beeckman and Froment, 1979). However, in most of the runs the viscosity and API were scattered around a band of values, but did not show a clear decline with time on stream. This suggests that some thermal reactions occur, leading to carbon rejection and deposits upon the catalyst surface, but that catalytic hydroconversion reaction do not predominate the upgrading. With hydrogen pressure of 13.7 MPa and LHSV of 0.41 h^{-1} Kim *et al.* (1997) investigated the effect of temperature on the conversion of residuum, sulphur, nickel and nitrogen removal using a NiMo catalyst supported on alumina while working on PR spring bitumen. They observed that the API increased from 12.4° to 22.1° with temperature increase from 635 K to 685 K. The levels of sulphur, nitrogen and nickel also dropped from 0.26, 0.80 wt. % and 29 ppm to 0.17, 0.22 wt. % and 18 ppm respectively with the same level of increase in temperature.

The above results suggest that there is a trade-off between catalyst operation time and upgrading performance. The higher temperatures lead to high rates of reaction, but large deposits of carbon upon the catalyst limit the useful lifetime in the absence of any media e.g.

hydrogen to sweep away the coke precursors. In the CAPRI process, the catalyst within a particular section of the horizontal well must be active for sufficient time for the MOZ to pass through it. The width of the MOZ may depend upon many factors such as the rate of combustion, oil quality etc. Yet any catalyst will be required to remain active for long enough until the MOZ passes through a section of the horizontal well and hence through the gravel packed catalyst. Thus, any catalyst to be applied in the CAPRI process in the field would have to be active for tens of hours, up to several days. For this reason a trade off between the catalyst life and activity was found to be 425°C, with acceptable upgrading and a catalyst lifetime sufficiently long to be comparable to the time required for the MOZ to pass through it. This temperature is consistent with the temperature range suggested elsewhere for the upgrading of crude and residues in the presence of HDS catalysts (Weisser and Lands, 1973).

Temperature is perhaps the most critical variable because hydrotreating (HDT) and deactivation rates are directly proportional to this variable as found in this study. Generally hydroprocessing reactions are exothermic by nature, so an appropriate temperature control system is required, however in this study no temperature monitoring of the catalytic bed was carried out yet the furnace temperature was kept to controlled experimental temperature. Temperature runaways beyond acceptable limits boost catalyst deactivation and change selectivity toward undesirable products (Yan, 1980; Furimsky and Massoth, 1999) and perhaps this is the main reason that at higher temperatures the deactivation is very fast and at the same time the number of aromatics also increases significantly. This is also visible from the material balance as presented in Table 4.12, where the highest temperature gives the highest amount of coke and the liquid fraction varies with in a range of 92.32-97.5 %, where the lowest temperature yields the highest amount of liquid.

Alvarez and Ancheyta (2008) studied experimentally the hydroprocessing of residue upgrading in the presence of typical HDS and HDM catalysts. They observed that temperature effect was greater when temperature was increased from 400 to 420°C than from 380 to 400°C. This behavior of temperature effect has been attributed to a change in reaction selectivity from being hydrogenation dominated at low temperature to hydrocracking dominated at high temperature (Ancheyta *et al.*, 2003). However the major exception to this work is that Alvarez and Ancheyta (2008) used around 100 bar g of hydrogen pressure to sweep off any coke precursor and the conditions were favourable for HDS, HDM, while in this work no higher hydrogen partial pressure was added, so, it can be concluded that majority of the reactions were hydrocracking rather than hydrodesulphurization.

Table 4.10 Effect of Temperature; List of Experiments

Exp. No.	Catalyst	Temperature [°C]	Time [Hours]
P27	CoMo	380	29
P13	CoMo	400	95
P26	CoMo	420	78
P74	CoMo	425	10
P32	CoMo	475	1
P30	CoMo	500	1.5

Table 4.11 Upgrading Performance at Different Temperatures

Using a CoMo catalyst with oil flowrate of 1 ml.min^{-1} and gas flowrate of 0.5 l.min^{-1} at pressure 20 bar

Temperature (°C)	380	400	420	475	500
Average viscosity Pa.s	0.339	0.290	0.353	0.024	0.039
Standard deviation viscosity Pa.s	0.039	0.087	0.195	0.006	0.048
Average API gravity	14.5	14.9	14.43	18.54	18.92
Standard deviation API gravity	0.149	0.429	0.728	0.325	2.985
Operation time (hours)	28.5	18	77.5	1.0	1.5

Table 4.12 Material Balance at

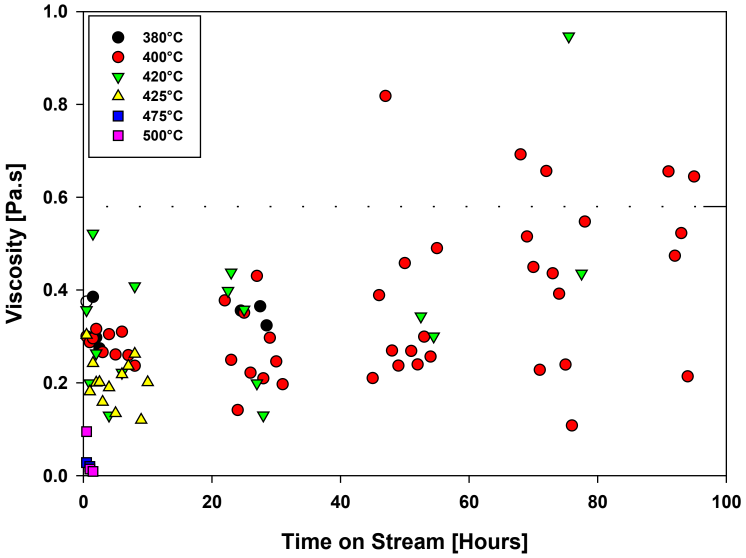
CoMo Catalyst, 20 bar g pressure, THAI gas as feed

%	400°C	425°C	450°C
Gases	1.40	1.72	4.98
Liquid	97.5	96.21	92.32
Coke	1.07	2.08	2.70

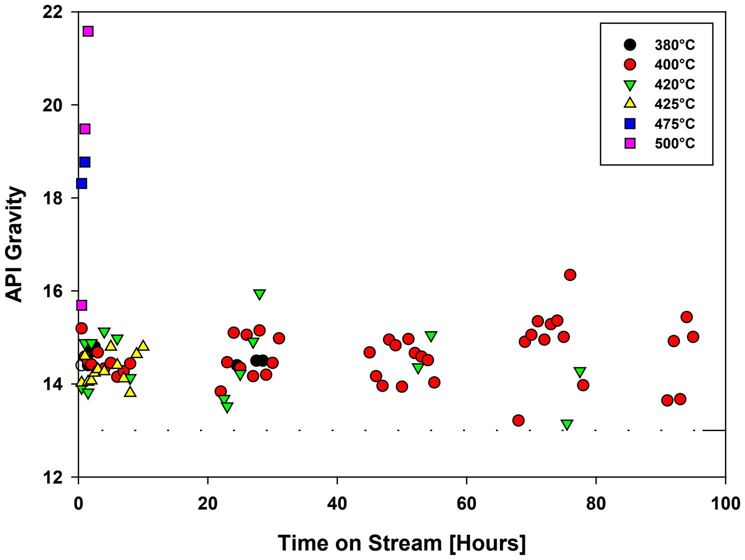
Figure 4.9 Effect of Temperature on (a) Viscosity and (b) API Gravity (c) SIMDIS (d) Coked Catalyst inside a Used Catalytic Bed at 475°C

CoMo catalyst, 425°C, 20 bar g, 500 ml.min^{-1} N_2 or THAI gas and 1.0 ml.min^{-1} oil

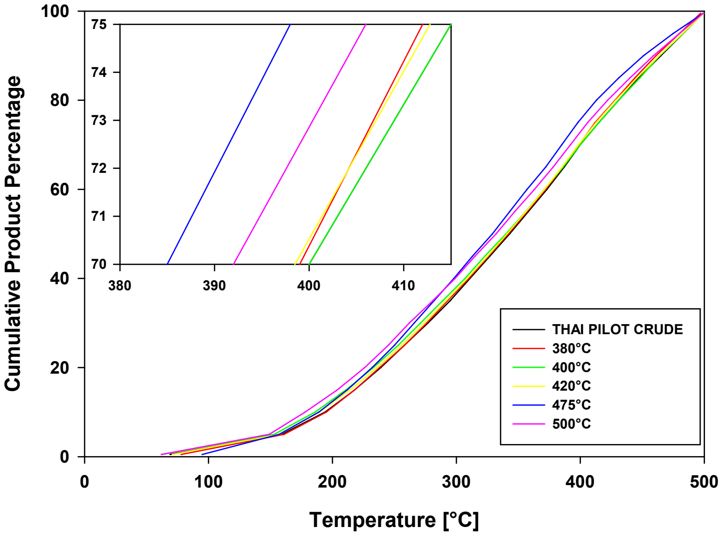
(a)



(b)


API Gravity
Time on Stream [Hours]
22
20
18
16
14
12
0
20
40
60
80
100
380°C
400°C
420°C
425°C
475°C
500°C

(c)


Cumulative Product Percentage
Temperature [°C]
100
80
60
40
20
0
0
100
200
300
400
500
75
74
73
72
71
70
380
390
400
410
THAI PILOT CRUDE
380°C
400°C
420°C
475°C
500°C

(d)

4.11 Effect of Pressure

Experiments P65-67 were carried out to investigate the effect of pressure at 20, 40 and 60 bar g respectively. Average experimental viscosities and API gravities recorded at different upgrading pressures are shown in Table 4.13 and Figure 4.10 (a) and (b). Although the highest API gravity occurred at 20 bar and the lowest viscosity at 40 bar, the measurements at all three pressures tested lay within a similar range. However, a difference in the SIMDIS measurements in Figure 4.10 (c) is discernable, where the 20 bar line shows an improvement of about 20°C towards the lighter end products. The 40 bar and 60 bar lines indicate a shift towards the heavier fractions, suggesting a decrease in the quality of the produced oil. In the case of catalytic hydroconversion, the effect of pressure would be expected to have the effects of increasing the rate of reaction through increased concentration of reactants presented at the catalyst surface, improving the penetration of oil into the catalyst pores and increasing the solubility of gases such as hydrogen and methane within the liquid oil. However, the relative insensitivity of the upgrading results to pressure, suggests that the dissolution of gas phase components such as hydrogen or methane in the oil do not play a significant role in the reaction. This observation is consistent with thermal reactions, or the possible transfer of hydrogen from the coke layer to the upgrading oil molecules to leave behind a carbon rich deposit.

Weissman and Kessler (1996) achieved significantly lower degrees of upgrading, when processing with lowered hydrogen partial pressures. Upgrading equivalent only to thermal processing was obtained when the oil was processed over a catalyst in the presence of nitrogen, indicating that the catalyst does not contribute any intrinsic upgrading activity; that is, the catalyst does not promote visbreaking or cracking reactions under the processing conditions employed. One reason they suggested for the lowered upgrading for the synthesis gas runs was that as the reaction proceeded, consumed gas was not replenished, as in the 100% hydrogen experiments, so that the extent of hydrogenation may have been limited by insufficient hydrogen, in addition to lower hydrogen partial pressure providing less of a driving force for the reaction to proceed.

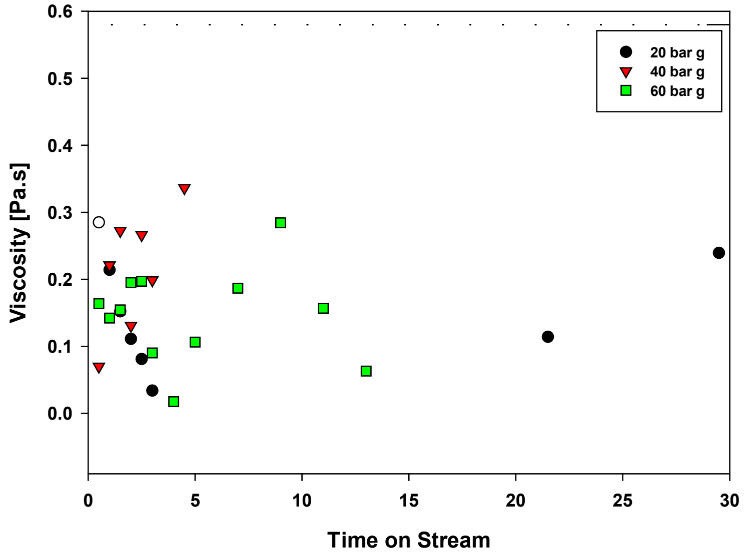
Table 4.13 Effect of Pressure Upon Viscosity and API Gravity of Upgraded Oil

CoMo catalyst, 425 °C upgrading temperature, 1 ml.min^{-1} oil flowrate, 0.5 l.min^{-1} gas flowrate (4 % H_2 in N_2)

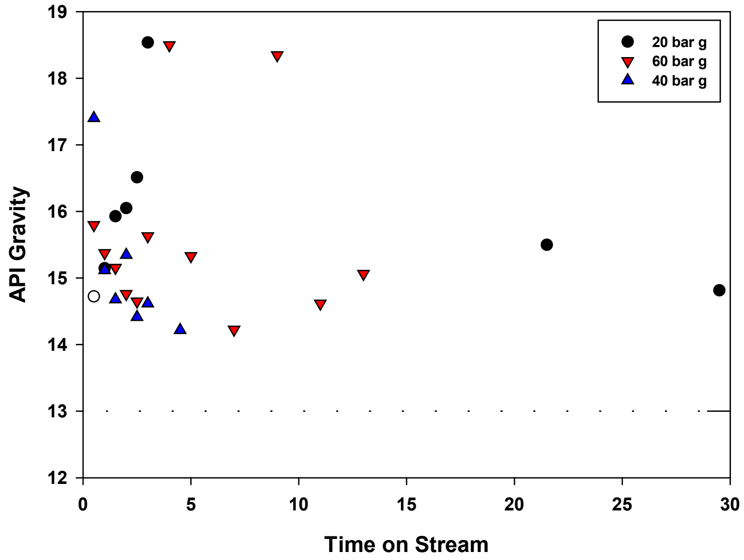
Pressure (bar)	20	40	60
Average viscosity Pa.s	0.154	0.146	0.213
Standard deviation viscosity Pa.s	0.085	0.07	0.090
Average API gravity	15.9	15.6	15.1
Standard deviation API gravity	1.20	1.38	1.08
Operation time (hours)	29.5	13	4.5

Figure 4.10 Effect of Pressure on (a) Viscosity (b) API (c) SIMDIS
CoMo catalyst, 425°C, 20 bar g, 500 ml.min^{-1} 4% in N_2 gas and 1.0 ml.min^{-1} oil

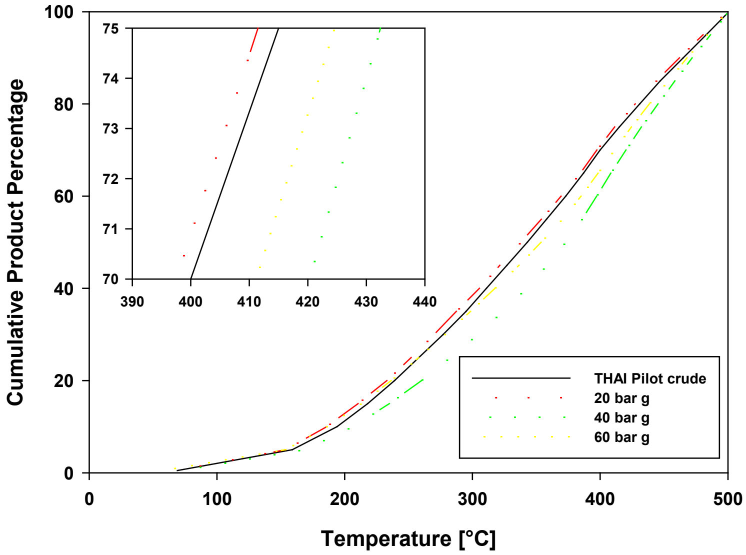
(a)



(b)



(c)



4.12 Effect of Gas Composition and Hydrogen Content

During the THAI process the burning of oil produces a number of gases inside the reservoir. The reaction of these gases with the free radicals produced during the cracking of large molecules could be potentially important (Clark and Hyne 1984). In particular, gases such as hydrogen or methane could potentially participate in the upgrading reactions, for example in the case of hydrogen, through hydroconversion processes. To understand how the CAPRI process performs under different reaction media, three different types of gases were used in the optimization of the CAPRI process namely, nitrogen, THAI gas and nitrogen/hydrogen mixture. Figures 4.11a) and b) show the viscosity and API of the upgraded oil in the presence of nitrogen, THAI gas, 4% hydrogen in nitrogen and 4% hydrogen in THAI gas respectively. The reduction in viscosity with the 4% hydrogen/nitrogen mixture was the highest, leading to the lowest viscosity reading of 0.034 Pa.s, from a value of 0.58 with THAI oil. Upgrading with nitrogen and THAI gases led to minimum viscosity readings of 0.21 Pa.s and 0.12 Pa.s respectively (Figure 4.11a). The API gravity results show similar upgrading trends, with the highest levels of upgrading being achieved by nitrogen/hydrogen mixture (Figure 4.11b). Averaged upgrading parameters are shown in Table 4.14, also showing 4% hydrogen/nitrogen to achieve the most significant upgrading. However SIMDIS curves for the product oil shows little difference in the composition of the liquid fractions (Figure 4.11 c), which means that the addition of hydrogen did not significantly improve the quality of the produced oil. Although in theory it may be expected that the smaller concentration of hydrogen could stabilise the free radical and lead to less coke and lighter end products. However, in practice the addition of gaseous hydrogen was found to have minimal effect upon the quality of the produced oil. This result confirms earlier findings that the gas phase variables such as pressure and GOR do not significantly influence the quality of the produced oil.

These findings are similar to the work of Weissman and Kessler (1996) who observed significantly lower degrees of upgrading when processing under lowered hydrogen partial pressures in comparison to nitrogen or a 50/50 mixture of CO/H_2. Although in all cases where hydrogen and catalyst were used, sulphur removal above the thermal background was obtained. They also noticed that upgrading equivalent only to thermal processing was obtained when the oil was processed over a catalyst in the presence of nitrogen, indicating that the catalyst does not contribute any intrinsic upgrading activity; that is, the catalyst does not promote visbreaking or cracking reactions under the processing conditions employed here. This is very relevant here, as in this work all of the experiments were performed in the presence of nitrogen and that perhaps explains why catalytic upgrading is not very high in comparison to the thermal run with inert material GB.

Hydrogen quenching is practiced in most hydrotreating (HDT) processes. In fact its role is so important that according to a recent comprehensive review about the advantages and disadvantages of hydrogen and liquid quenching in fixed-bed hydroprocessing reactors, large volumes of hydrogen (hydrogen-to-oil ratios of ∼1800 std $m^{-3}.m^{-3}$) have to be handled, when processing heavy-feed [residue and vacuum gas oil (VGO)] in HDT/HCR fixed-bed units, where the target conversion is high. This increases hydrogen availability for quenching and the considerable heat release (Alverez *et al.*, 2007).

Analysis of the gas product stream reveals small amounts (0.02-0.38%) of light hydrocarbons, as shown in Table 4.15 for an experiment conducted with hydrogen in the THAI Gas feed. These gases are most probably generated during the reaction as no gases were detected by the refinery gas analyzer (RGA) when the THAI field oil was heated to 50°C and the flue gases diverted to RGA apart from the carrier gas nitrogen. The predominant products are unbranched alkanes with smaller amounts of branched alkanes and unsaturated compounds and in total around 1.7-1.8% of the outlet gas stream consists of produced hydrocarbons. This suggests cracking of larger molecules to produce gas phase alkanes and alkenes together with higher molecular weight compounds which remain in the liquid phase is occurring. Interestingly, the net change in hydrogen content is negligible while a small but significant fraction of carbon monoxide is also generated. Possibly the reverse water gas shift reaction could lead to the consumption of hydrogen and carbon dioxide to produce carbon monoxide. Alternatively, gasification reactions could include the Bouduard reaction, which leads to the production of carbon monoxide from the reaction of carbon dioxide with coke.

Table 4.14 Effect of Reaction Media Upon Viscosity and API Gravity of Upgraded Oil

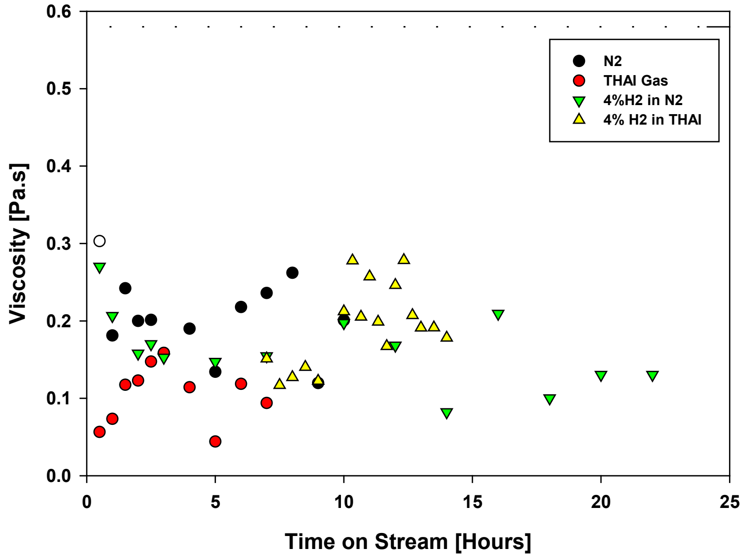
Temperature of 425 °C and 20 bar (g) pressure with a flowrate of 1 ml.min^{-1} oil and 0.5 l.min^{-1} gas

	N_2	THAI gas	4 % H_2 in N_2	4 % H_2 in THAI gas
Average viscosity Pa.s	0.353	0.195	0.154	0.163
Standard deviation viscosity Pa.s	0.196	0.042	0.086	0.061
Average API gravity	14.4	15.0	15.9	15.1
Standard deviation API gravity	0.728	0.331	1.233	0.383
Operation time (hours)	77.5	16.3	29.5	10.7

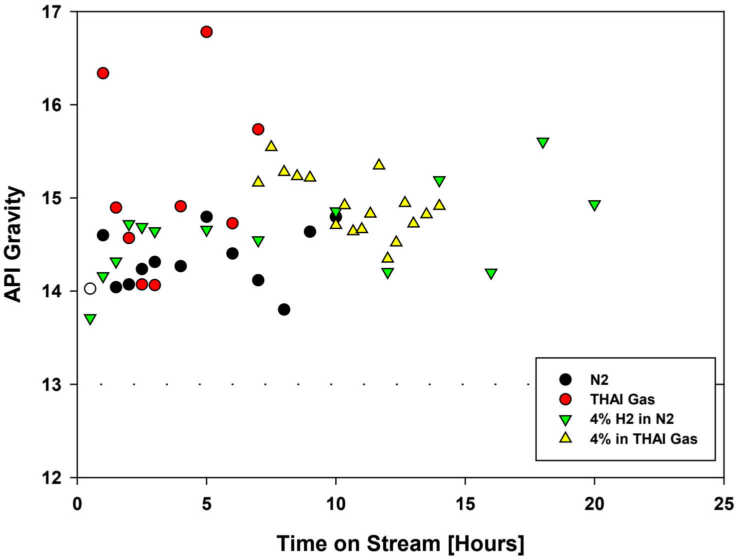
Figure 4.11 Effect of Reaction Media on (a) Viscosity (b) API Gravity (c) SIMDIS

Temperature of 425 °C and 20 bar (g) pressure with a flowrate of 1 ml.min^{-1} oil and 0.5 l.min^{-1} gas

(a)



(b)


API Gravity
17
16
15
14
13
12
0
5
10
15
20
25
Time on Stream [Hours]
N2
THAI Gas
4% H2 in N2
4% in THAI Gas

(c)

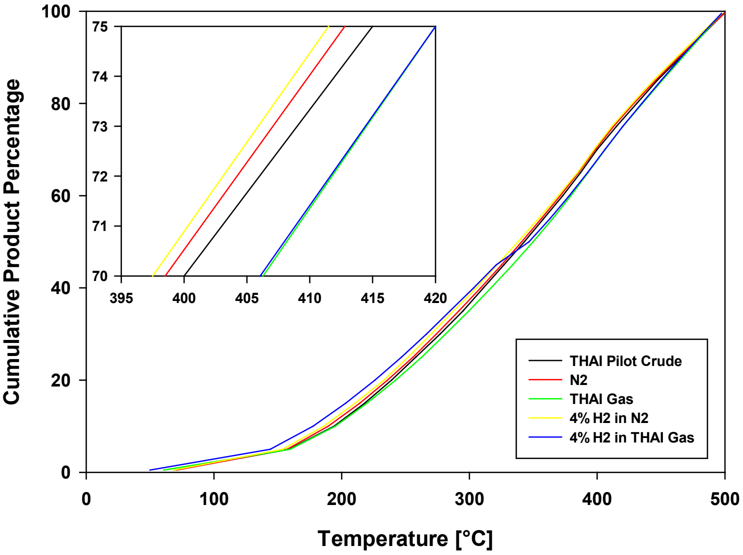

Cumulative Product Percentage
100
80
60
40
20
0
0
100
200
300
400
500
Temperature [°C]
75
74
73
72
71
70
395
400
405
410
415
420
THAI Pilot Crude
N2
THAI Gas
4% H2 in N2
4% H2 in THAI Gas

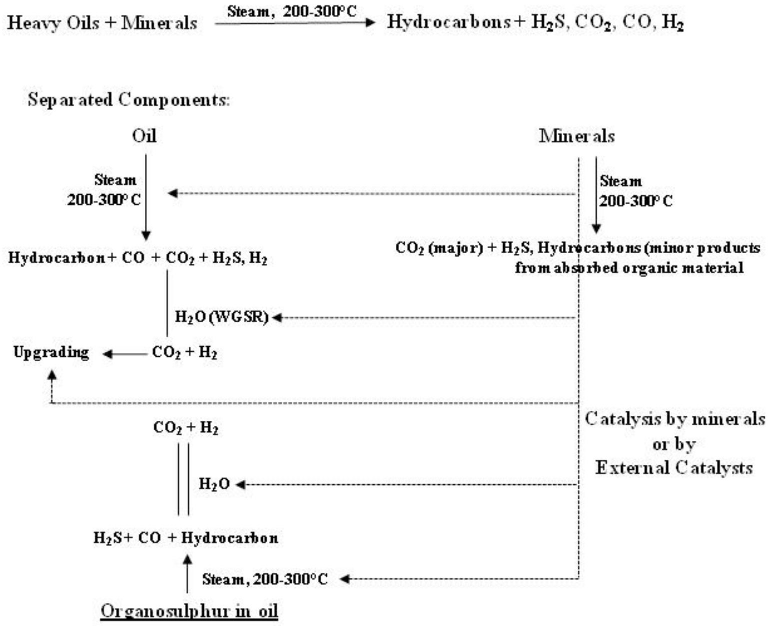
Table 4.15 Typical Outlet Gas Composition as Measured by Refinery Gas Analyser for CoMo Catalyst at 425 °C, 20 bar g and feed gas composition of 4% Hydrogen in THAI (4% H_2, 76.8% N_2, 12.48% CO_2, 3.84% CH_4, 2.88% CO).

Compound	Volume Fraction	Compound	Volume Fraction
Methane	4.24-4.27 %	*cis*-2-Butene	0.02 %
Produced Methane	0.35-0.38 %	i-Pentane	0.10 %
Ethane	0.20 %	n-Pentane	0.17-0.19 %
Ethene	0.04 %	Total Hydrocarbon Produced	1.69-1.79 %
Propane	0.23-0.24 %	Carbon Dioxide	12.51-12.59 %
Propene	0.19-0.21 %	Carbon Monoxide	3.09-3.10 %
i-Butane	0.04 %	Produced Carbon Monoxide	0.17-0.18 %
n-Butane	0.20 %	Hydrogen	3.89 %
1-Butene	0.07-0.08 %	Consumed Hydrogen	0.01 %
trans-2-Butene	0.07-0.08 %	Nitrogen	74.73%

4.13 Effect of Water (steam) Addition

The comprehensive effects of water and heat mostly during heavy oil stimulation processing have been associated not only with change in their physical properties but also to chemical reactions (Clark and Hyne 1983, 1990; Gould 1983; Hongfu *et al.* 2001). Hyne (1986) has termed all the chemical reactions between oil, sands and steam “aquathermolysis”. Researchers also indicated that hydrolysis of the sulphur bridge of organosulphur compounds in heavy oils is the important step of aquathermolysis (Clark *et al.* 1983 and 1984; Hyne *et al.* 1988). The cleavage of S-C bond of the sulphide compounds may reduce the molecular weights, decrease the amount of asphaltenes and then reduce the viscosity of heavy oils (Hongfu *et al.*, 2002). This aquathermolysis not only produce H_2S gas but also CO and CO_2 and most important of all some H_2 gas as a result of water gas shit reaction (WGSR). Clark and Hyne (1984) have provided some possible reactions (Figure 4.12), responsible for this upgrading mechanism in the presence of steam, heat and minerals present in the heavy oils catalysing these reactions. To assess the role of water/steam addition in the upgrading of THAI field oil experiments P8 and P72 were carried out in the presence of steam. However the addition of water made it difficult to control the experiment mainly because the mixture of oil and water caused fluctuations in the reactor pressure, especially during experiment P8. Moreover after the experiment in the presence of water the analysis of the processed oil mixed with water also proved very hard because of the dispersion of water in oil, despite attempts to remove water by centrifuging. Viscosity and density readings proved almost impossible because water was still present in the centrifuged oil in shape of fine droplets. This problem was overcome later in P72, when a very fast centrifuge of 13000 rpm (using equipment not available during P8 experiment) was used to remove the water droplet from the processed oil. Hence results from experiment P72 are only presented here. In P72 water was injected at rates of 0.3 and 0.6 ml.min^{-1} and mixed with oil, which was flowing at a fixed flowrate of 1.0 ml.min^{-1}, in the mixing chamber at the reaction inlet.

Figure 4.12 Reaction Mechanism of Heavy Oil Upgrading in the Presence of Steam and Heavy Oil Inherent Minerals



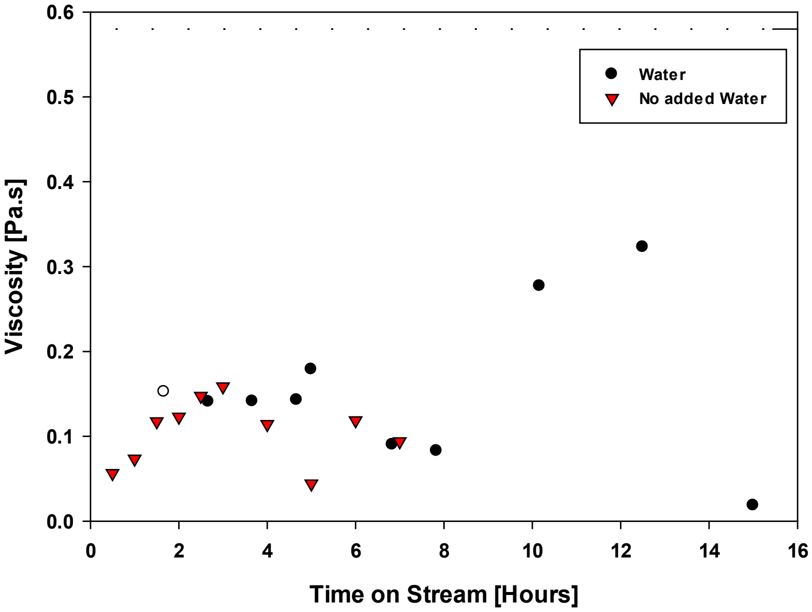
Results for viscosity and API gravity measurements are presented in Figures 4.13a) and b). There appears to be a slight decrease in upgrading in the presence of water, with viscosity only reduced to around 0.15 Pa.s while density is only improved by around 1-1.5°API. To investigate the effect of water flowrate, a flowrate of 0.3 ml.min^{-1} was maintained up to 8 hours and than 0.6 ml.min^{-1} from 8 hours onwards. The density improvement showed little dependence on the quantity of water added although at the higher water flowrate there was more scatter observed in the viscosity measurements (Figure 4.13 a). This may have been due to a small amount of water still dispersed in the oil sample which makes it difficult to measure the viscosity of the biphasic mixture.

Hongfu *et al.*, (2002) reported 28-42% reduction in viscosity while processing a Chinese heavy oil (and any minerals present naturally within) in the presence water at 240°C. They also reported an increase of saturates at the expense of naphthenes and asphaltenes. They concluded that the upgrading in the properties of the processed oil was because of the water gas shift reaction and the possible role of alumino silicates reacting with water and activating minerals to act as Bronsted acids to and [H^+], and hence upgrading the processed oil. The reason the addition of water did not make any improvements in the upgrading of THAI field oil in contrast with the work of Hongfu *et al.*, (2002) is because their work involved placing the heavy oil in an autoclave along with water at 240°C for up to 72 hours and then studying the effect of upgrading. While in this work water/steam contacts the oil for a very short time period and perhaps the much shorter contact time between oil and water may limit the reaction with the oil or any minerals inherent in bitumen or heavy oil. This would be an interesting effect to observe in the real reservoir with THAI-CAPRI in action, as it takes several years for it to complete and may give enough time for the minerals and water to react. At the elevated reaction temperatures of upto 750°C as reported by Xia and Greaves (2006), the water gas shift reaction may be more predominant as sufficient heat is available to overcome the activation energy of the reaction. Xia and Greaves (2006) also reported a rise in the level of saturates while processing Athabasca bitumen using ‘Toe-to-Heel-Steam-Flood’ technique which could be due to the addition of hydrogen from water to unsaturated oil molecules. This again however needs to be investigated in longer experiments as these runs were only for a few hours and at relatively lower pressures of 2-3 bar g and very high temperatures of upto 750°C.

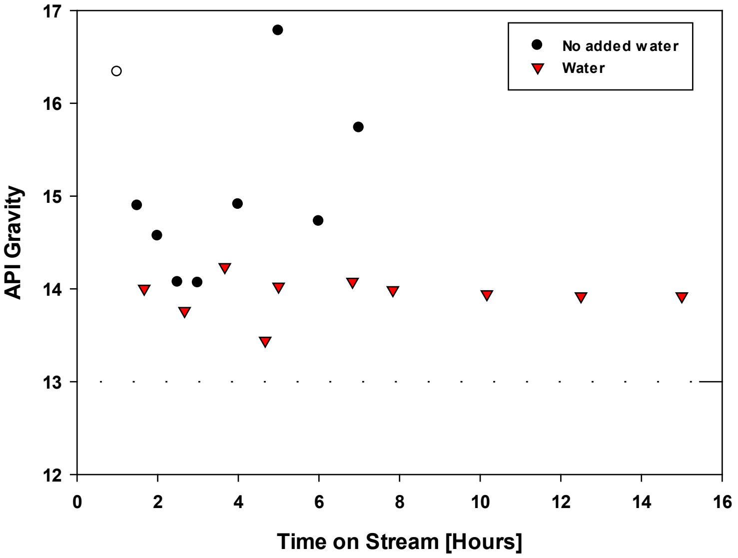
The THAI-CAPRI process is also different from the widely used Cyclic Steam Stimulation (CSS) process which is a three stage process. High pressure steam is injected into the reservoir in the first stage for a month or so, which is left inside the reservoir to soak and afterwards production. This process may therefore provide more time and energy for the oil and steam/water to react. On the other hand CAPRI process used in this work, the oil interacts with water for a matter of seconds and this provides low time and activation energy for the oil to react with water and get upgraded in the process. CAPRI process used alone (as was the case in this work) is different from a THAI-CAPRI in a real reservoir. As in a real reservoir the THAI-CAPRI process are in action together. The high temperatures generated by THAI process may provide more activation energy and time for the mobilized oil from the mobile oil zone (MOZ) to the horizontal production well and can react with water present inside the reservoir during these favourable conditions, a process not practical to simulate in this study.

Figure 4.13 Effect of Steam on (a) Viscosity (b) API Gravity
CoMo catalyst, 425°C, 20 bar g, 500 ml.min^{-1} THAI gas and 1.0 ml.min^{-1} field oil Water flowrate of 0.3 ml.min^{-1} used up to 8 hours and 0.6 ml.min^{-1} after 8 hours

(a)



(b)



Discussion and Conclusions

The optimization studies showed that the variables which most influenced upgrading in the CAPRI process were temperature, oil flowrate and to a lesser extent the addition of hydrogen. The effect of gas flowrate, gas composition and pressure all showed relatively little effect upon the upgrading performance. Several types of reaction may be occurring during the CAPRI process. Early in the reaction, catalytic cracking and hydroconversion process may start to occur as a result of the catalytic activity. This may for example be the case in the early stages of the tests with nitrogen/hydrogen mixtures, in which the lowest product viscosities were observed at short reaction times. Sanford (1994) studied the reactions occurring during residuum conversion, and concluded that during the early stages of coking and hydrocracking reactions, the main reactions occurring involve the breaking of carbon-carbon bonds. However these reactions are accompanied by carbon rejection reactions at the surface of the catalyst pellets similar to the reactions occurring in the THAI process, which would be responsible for the heavy coke deposit upon the catalyst. Thereafter the pores of the catalyst become completely blocked and there is also a heavy deposit upon the outside surface of the pellet.

In the next stage of the reaction, because the catalytic metals become completely covered with coke, further catalytic reactions involving the metal are limited. Therefore further reactions could occur through thermal cracking, further carbon deposition, or catalytic effects of the coke itself. The latter reactions could occur if the coke contains hydrocarbons which could release hydrogen to react with the oil, thus increasing their carbon fractional content. Reyniers *et al.* (2000) studied coke formation on the conversion of alkanes over USY-zeolite and found that an increase in the molar H/C ratio of the products as a function of coke yield was observed due to hydride transfer reactions with coke. Coke molecules could not be considered as being inert with respect to the cracking reactions and their formation led to the occurrence of reactions that strongly influence the catalyst performance. These reactions occur through the ability of the coke to act as a hydride donor towards carbenenium ions at the surface and facilitate reaction pathways towards paraffinic reaction products. Sanford (1994) postulated that initial homolysis of aromatic rings in the oil produces two radicals of different reactivity, an aliphatic-carbon radical and an aromatic carbon radical. The aliphatic carbon radical undergoes fragmentation to produce distillate and gas, which would explain the aliphatic components detected by refinery gas analysis in this study. The aromatic component can condense with other similar species to produce coke, or the aromatic-carbon radical can react with hydrogen to form a carbon-to-hydrogen bond and a hydrogen atom. The hydrogen atom adds to the aromatic ring leading to the production of gases and distillate. The most logical source of the hydrocarbon gases was the breaking of side chains from naphthenic rings. Such reaction mechanisms would be consistent with the experimental observations reported in this work. Dupain *et al.* (2003) made similar observations to the results reported in this study for the aromatic gas oil cracking in FCC conditions (575°C and with a catalyst-to-oil (CTO) ratio of 4.8 gcat goil^{-1}) within a microriser reactor. Coke was formed early in the reaction, cracking reactions involved the paraffinic fraction of the feed and alkyl groups associated with the benzene ring, and were accompanied by complex dealkylation and hydrogen transfer reactions. Gas phase alkenes and alkanes were produced by thermal cracking reactions. This is further supported by the SARA analysis of some of the selected produced oil samples. In all of the samples analysed regardless of the level of upgrading, the concentration of aromatics increased and the level of naphthenes decreased. This resulted in the release of hydrogen by the breaking of side chains attached to naphthenes and upgrading the produced oils in the process.

The variables which showed greater influence upon the process upgrading in this study were temperature and oil flowrate. Operation at temperatures in the range of 475 – 500°C led to the highest levels of upgrading, but heavy coke deposition occurred leading to premature reactor shut down. This effect is thought to be because the higher temperatures provide sufficient activation energy to accelerate carbon rejection reactions rather than hydroconversion, leading to complete plugging of the catalyst inter-particle pore space. The high temperature can also be responsible for ring opening and desulphurization, but as majority of the experiments were carried out in the presence of nitrogen and no hydrogen to sweep away the coke precursors such as sulphur, metals and condensed HC, the level of hydrodesulphurization and hydrodemetallization was less significant. Even in the experiments where 4% of hydrogen was used the H_2/HC ratio was probably far less than the typical crude processing requirement levels of hydrogen-to-oil ratios of ~1800 std $m^{-3}.m^{-3}$ (Alverez *et al.*, 2007). Due to this reason the catalysts quickly became deactivated with condensed aromatics deposited upon its surface (Jones and Pujadó, 2006). These findings considerably agree with the reaction mechanism provided in Figure 4.13, where polar (naphthenic) constituents of the heavy oils in the absence of hydrogen reacts with a Brønsted acid, which are present upon the support material of the catalyst, and after a number of reactions (Figure 4.13) accumulates as condensed ring aromatics.

The high temperature has been known to favour the condensation reactions between aromatic clusters, which lead to the formation of mesophase, and consequently coke. Also, under these reaction conditions, the C–C and C–heteroatoms bonds cracking reactions are favoured, bringing about the formation of low molecular weight compounds, such as C_1–C_4 hydrocarbon gases and concentrating more of the high molecular weight products in the liquid fraction (Gray, 1994).

The addition of externally added hydrogen did not upgrade the produced oils in terms of API gravity or viscosity to a significant level. However from detailed chemical analysis (Refer to SARA and SEC analysis, Chapter 5), it is evident that the role of reaction media is very important and the addition of even smaller levels of hydrogen did affect the properties of produced oils. Weissman and Kessler (1996) also observed significantly lower levels of upgrading when processing heavy crude oils with lowered hydrogen partial pressures, although in all cases where hydrogen and catalyst were used, sulphur removal above the thermal background was obtained. Upgrading equivalent only to thermal processing was observed to be attainable when the oil was processed over a catalyst in the presence of nitrogen alone, indicating that the catalyst does not contribute any intrinsic upgrading activity; that is, the catalyst does not promote visbreaking or cracking reactions under the processing conditions employed. Miki *et al.* (1983) concluded that the main role of the catalyst in hydrocracking is to supply hydrogen to large oil molecules. Which otherwise become deficient in hydrogen and will result in the condensation of the aromatic fraction deactivating the catalyst severely. Moreover, hydrogenation of aromatic rings would also result in a more reactive oil.

The effect of oil flowrate is to simply increase or decrease the residence time of oil in the bed, with longer residence times leading to improved upgrading, as evidenced by lower product viscosity. This effect is also similar to the upgrading operations in a typical refinery where the lower flowrate of the feed or LHSV and higher residence time over the catalyst in the presence of high partial pressure of hydrogen results in higher level of upgrading. Kim *et al.* (1997) studied the effect of temperature and LHSV using an HDN NiMo catalyst supported on alumina. To investigate the effect of LHSV a fixed temperature of 664 K and 13.7 MPa of hydrogen partial pressure were used. They observed from their studies that the API gravity of the total liquid product increased significantly from 13.3° to 25.5° as the residence time (reciprocal LHSV) increased from 1.25 to 7.14 h. Hydrogen consumption relative to the H/C atomic ratio of the total liquid product also increased from 58 to 155 $l.l^{-1}$ as the residence time increased. The fractional conversion of residuum, nitrogen and sulphur increased from 9.8, 0.64, 0.23 wt. % to 5.4, 0.18, 0.14 wt. % respectively with decrease in LHSV from 0.8 h^{-1} to 0.14 h^{-1}.

The different types of catalysts had only a limited effect upon the upgrading properties of the produced oils mostly because, the major role of the catalyst has been described to be hydrogen transfer to the heavy fractions, to help suppress coke formation, hydrogenation and heteroatom removal from the distillate fractions (Grey *et al.*, 1994). However in this work no or only 4% hydrogen was added to hydrogenate the heavy oil. This made the case for selecting the optimum catalyst all the more challenging as CoMo and NiMo are better HDS and HDM catalysts, yet zeolites are better for hydrocracking usually in the catalysis industry.

Moreover, the hydroprocessing of heavy feeds presents many difficulties because of the complex composition of oil. Heteroatoms such as sulphur and nitrogen leave the reactor as gaseous products; metals are deposited on the catalyst causing irreversible deactivation (Ancheyta *et al.*, 2001). Asphaltene molecules undergo a series of complex physicochemical processes that result in fouling and coking (Speight, 1994). This was indeed a major problem in this research that all the catalysts were fouled with coke in the reaction and there activity was not differentiable from one another. Commonly, downflow fixed-bed reactors sequentially loaded with a series of catalysts with different functionalities are employed for heavy feed hydroprocessing (Furimsky, 1998). However, the objective of this work was to optimize the THAI-CAPRI process under real reservoir conditions unlike the refinery processing in a series of reactors, packed with different types of catalyst.

Quality of the feed is another factor, which strongly influences the selection of catalyst type and reactor technology in any catalytic hydroprocessing (Rana *et al.*, 2007). Usually the catalyst system is selected on the basis of activity, selectivity, and cycle life and is composed of catalysts designed for specific objectives such as hydrodesulphurization (HDS), hydrodemetallization (HDM), hydrodenitrogenation (HDN), hydrodeasphaltenization

(HDAs), and hydrocracking (HCR) (Marafi *et al.*, 2003; Rana *et al.*, 2007). However, since the selection of the feed is not practical in THAI-CAPRI process as the process has to handle different feeds with various properties depending upon origin in the *in situ* reservoir. This makes the selection of any particular catalyst for processes such as HDS, HDM, HDN and HCR very hard and therefore this approach is not the objective of this study (Refer to Section 6.3 and 6.4 of Chapter 6 for results of HDS and HDM). This perhaps will explain why, unlike typical refining processing, none of the different types of catalysts employed in this work, showed any significant difference in activity to one another, leaving the optimization study for the optimum catalyst inconclusive.

Acidity of any HDS catalyst or its support is largely responsible for the cracking reactions (Occelli and Anthony, 1989) and its optimization in detail for CAPRI process will be of interest. From the results in Section 4.4, upgrading of the processed THAI oil with alumina was comparable to the supported CoMo base case, indicating a role for support acidity. Significant residue conversion was observed by Grey *et al.*, (1994) in the absence of a hydrogenation catalyst, i.e., during runs with y-alumina, but severe coking occurred during these experiments.

The results presented in this chapter demonstrate that the CAPRI add-on to the THAI process can achieve moderate levels of upgrading over up to 95 hours of operation, but that coke deposition presents a limitation to the lifetime of the catalyst. Control of the *in situ* process in the oil well could possibly be affected by adjusting the air injection rate in order to achieve a controlled rate of combustion, and thus operating temperature in the MOZ.

Chapter 5

CAPRI Process Optimization: “CCO as Feed”

5.1 Introduction

In this chapter results have been presented for produced oils using a different feed than the heavy THAI field oil discussed in chapter 4. Combustion cell oil (CCO) is a collection of processed oils from previous University of Bath THAI experiments carried out in the laboratory. This processed oil hence has known processing history. The feed with relatively lower viscosity and API gravity was subjected to catalytic cracking in this study and two main variables, namely the effect of temperature and reaction media were investigated. These variables have been presented in sections 5.2 and 5.3 respectively.

n-decane was used as a model compound in one experiment and details of the experiment have been presented and discussed at the end of this chapter.

CCO was denoted as feed oil processed under controlled conditions in laboratory combustion cell tests (Refer to Table 5.1 for typical experimental conditions). This feed was used in a different set of CAPRI micro-reactor experiments as feed rather than the THAI field oil. The rationale behind using different oil as a feed was that with a viscosity of 0.0340 Pa.s and API gravity of 19° this oil was much lighter than THAI field oil and hence was expected to offer more control of the flow rate with less variability in the data than the viscous THAI field oil. Being THAI processed oil, CCO is already low in metal contents in comparison to the bitumens used as feed by Xia and Greaves (2002). Metal analysis of the CCO and THAI field oil is presented in Table 5.2 from which it is clear that it is indeed low in heavy metals like nickel + vanadium. However iron was significantly higher than in the THAI field oil along with the presence of aluminum and silicon which were absent in THAI field oil. These may have come from the packaging material from the 3D combustion cell used in the THAI process.

Table 5.1 Experimental Conditions for CCO††† (Xia and Greaves, 2006)

3D Combustion Cell Dimensions	0.6 m x 0.4 m x 0.1 m
Temperature °C	Upto 750
Reaction Gas	Air
Pressure	Upto 2 bar g

[†††] Experimental conditions for the production of CCO may differ in other experiments, as CCO is a mixture of produced oils from different experiments. Especially the feed properties, as a number of feeds were used e.g. Athabasca and Wolf Lake bitumens.

Table 5.2 Metal Analysis of CCO THAI oil

	CCO Crude	**THAI Field Oil Crude**
Metals content¶	**ppm**	**ppm**
Tin	0	0
Lead	0	0
Copper	0	0.3
Aluminium	29	6
Silicon	55	0.4
Iron	148	10
Chromium	0.4	0
Silver	0	0
Zinc	9	2
Magnesium	4	0
Nickel	18	54
Barium	0	0
Sodium	0	0
Calcium	2	0
Vanadium	50	144
Phosphorous	0.6	0.3
Molybdenum	3	6
Boron	1.3	0.6
Manganese	0	0
Total Sulphur¶**, wt%;**	**3.7**	**3.8**

¶ Metals analysed by Petrobank Canada using ASTM D5185 and Sulphur by ASTM D4294

From THAI field oil two variables showed a significant effect upon the quality of the produced oil, namely temperature and the liquid residence time over the catalyst. However the addition of small partial pressures of external hydrogen did not result in significant improvements in the properties of the processed oil. These variables were selected for further investigations with the CCO, since more precise flow rates closer to the target oil flow rate of 1 ml.min^{-1} was expected to be achieved with this lighter oil. However the number of experiments that could be carried out was limited by the quantity of this oil. Also some contaminations such as plastics and other inorganic substances were found in the oil, of which the plastic may have resulted from the disintegration of the container lining during storage following shipping from Bath University. The presence of contaminants in the oil led to some experimental difficulties owing to restricted flow and severely blocked the CAPRI reactor in some cases. Therefore only two variables were investigated in detail, which were the effects of temperature and reaction media, as reported in the following sections. The effect of liquid residence time could not be investigated in detail owing to the above difficulties. Effect of catalyst types especially the comparison of Albemarle Corporation CoMo and NiMo with Akzo CoMo and NiMo were also tried but due to repeated reactor blockages and poor control during the experimental work, they are not reported here.

5.2 Effect of Temperature

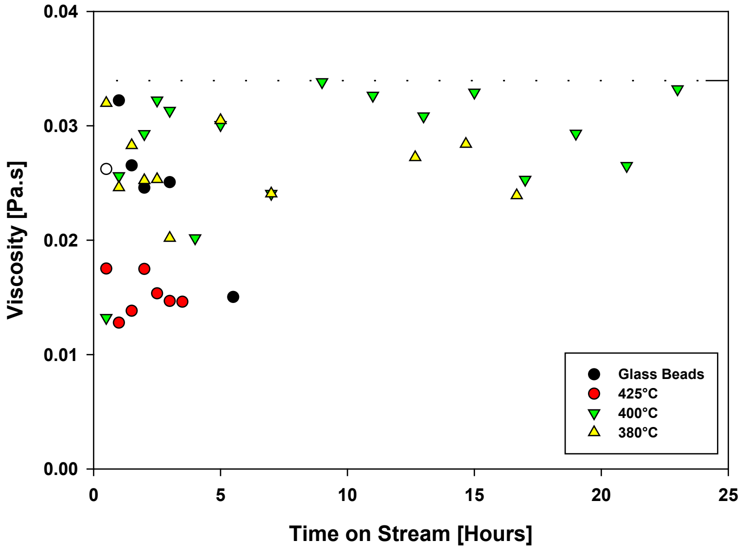
The effect of temperature upon upgrading is presented in Table 5.3 and Figures 5.1 (a) and (b) in terms of viscosity and API gravity respectively. Similar to the trend observed in the THAI field oil upgrading (Chapter 4), elevated temperature was also found to favour enhanced upgrading of CCO, with highest temperature leading to the largest reductions in viscosity and increase in API gravity. However the higher temperature again resulted in severe coking of the catalyst. The experiments carried out at 380°C and 400°C do not show significant upgrading, with average viscosities of 0.028 and 0.026 Pa.s and API gravities of 19.2° and 19.4° respectively, yet these viscosity and API readings are hardly changed from the CCO feed viscosity of 0.034 Pa.s and 19° respectively. However it is noted that a small amount of upgrading occurs in the run carried out at 425°C having final viscosity of 0.0152 and API gravity of 20.72°. The experiments conducted at 380°C and 400°C only upgraded the viscosity of the feed crude oil by a difference of only 0.0058 and 0.0077 Pa.s respectively. In some cases degrading of the processed oil is apparent especially at longer durations of the experiment this effect is more evident. This was not unexpected as the effect of temperature was the major variable that affected the upgrading behaviour of THAI field oil. The higher temperature was able to supply more heat to overcome the activation energy for the breaking of hydrocarbon (HC) chains and led to increased upgrading in terms of lower viscosity and higher API gravity. This was indeed the case when the temperature was raised to the optimum temperature of THAI field oil 425°C. At this temperature the decrease in viscosity is 0.018 Pa.s and a rise of 1.72° in API gravity from the CCO feed values of 0.034 Pa.s and 19°. These results are comparable to those achieved with THAI field oil experiment under similar conditions, where the reduction in viscosity of 0.3764 Pa.s and increase of 1.32° API from the THAI field oil values of 0.58 Pa.s and 13° API were achieved.

Table 5.3 Effect of Temperature Upon Viscosity and API Gravity of Upgraded Oil
CoMo catalyst, 20 bar g pressure of N_2, 1 ml.min^{-1} oil flow rate, 0.5 l.min^{-1} gas flow rate

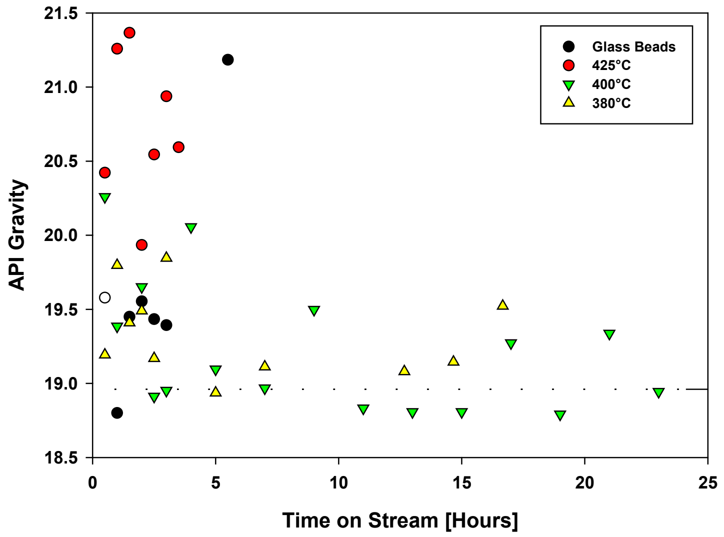
Pressure (bar)	380°C	400°C	425°C
Average viscosity Pa.s	0.026	0.028	0.015
Standard deviation viscosity Pa.s	0.0033	0.0055	0.0018
Average API gravity	19.34	19.22	20.72
Standard deviation API gravity	0.30	0.45	0.50
Operation time (hours)	16.7	23	3.5

Figure 5.1 Effect of Temperature on (a) Viscosity (b) API Gravity Experiment Conducted at 20 bar g pressure of N_2 in the presence of CoMo catalyst, oil flow rate of 1 ml.min^{-1} and gas flow rate of 0.5 l.min^{-1}

(a)



(b)



5.3 Effect of Reaction Media

The effect of reaction media is much more apparent in the catalytic upgrading of the THAI CCO than the THAI field oil. For example, the average viscosity of the processed CCO was 0.0047 Pa.s and API gravity was 26° for 4% H_2 in N_2. These values showed much greater upgrading than with nitrogen gas alone, for which viscosity was 0.0152 Pa.s and API gravity 21°. Similarly, addition of 4% H_2 to THAI gas led to viscosity of 0.0025 Pa.s and API gravity of 27°, which again shows a significant improvement in upgrading performance compared with nitrogen gas only.

The base qualities of the CCO both physically and chemically were superior to that of the THAI field oil as feed and hence potential for more upgrading. Indeed the CCO feed is lighter in viscosity and has higher API gravity or is lower in longer and heavier HC chains. Another possible reason why the CCO shows a larger degree of upgrading than the THAI field oil could be because the former is richer in paraffins, having a saturates level of as high as 72% and aromatics of as low as 1.6% (Xia and Greaves, 2006), while the later having saturate and aromatics levels of 15.38 and 57.04 % respectively (Table 6.3, Chapter 6). This has been proved previously that the crackability of feedstock having higher normal paraffins is more compared to naphthenes and aromatics, where naphthenes are relatively more susceptible to cracking than aromatics (Behera *et al.*, 2007). Cracking becomes easier with normal paraffins having longer chains. It is shown in literature that tertiary carbons are 10 times as reactive as secondary carbons and 20 times as reactive as primary carbons (Greensfelder, 1955; Woijciechowski and Corma, 1986; Decrooocq, 1984; Gates *et al.*, 1979). THAI field oil was also found to be richer in aromatic contents than the CCO and aromatics have been found to be generally stable under normal cracking conditions i.e. at a temperature of 450°C (Speight, 1999; Behera *et al.*, 2007). The presence of more amounts of aromatics in the feedstock also causes more coking and hence leads to deactivation of catalysts, which was a major problem with THAI field oil processing as discussed in Chapter 4. Principal reactions involved in catalytic cracking reactions to different types of hydrocarbons have been provided in Table 5.5.

Detailed viscosity and API gravities of the three experiments have been presented in Table 5.4 and Figure 5.2 (a) and (b) respectively.

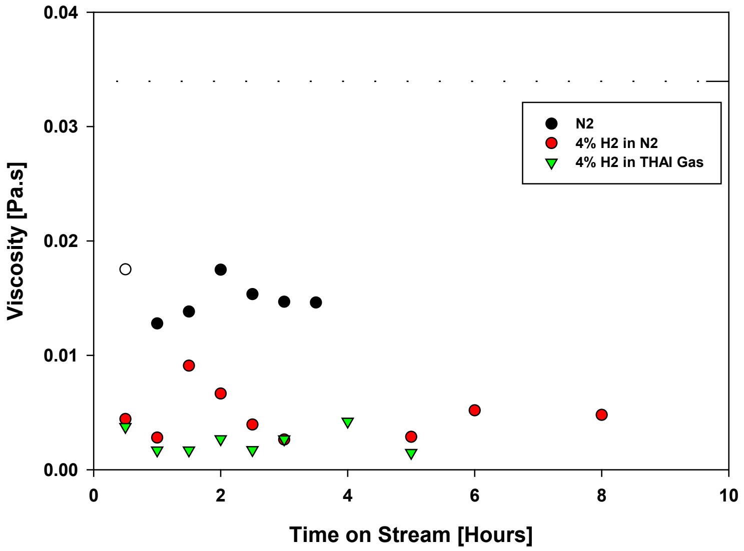
Table 5.4 Effect of Reaction Media Upon Viscosity and API Gravity of Upgraded Oil

CoMo catalyst at 425°C, 20 bar g pressure in N_2, 1 $ml.min^{-1}$ oil flow rate, 0.5 $l.min^{-1}$ gas flow rate

Pressure (bar)	**N_2**	**4% H_2 in N_2**	**4% H_2 in THAI Gas**
Average viscosity Pa.s	0.015	0.0047	0.0025
Standard deviation viscosity Pa.s	0.0018	0.0021	0.0010
Average API gravity	20.72	25.88	27.03
Standard deviation API gravity	0.50	1.38	0.52
Operation time (hours)	3.5	8	5

Figure 5.2 Effect of Reaction Media on (a) Viscosity (b) API Gravity Experiment conducted at 425°C Temperature, 20 bar g Pressure in the presence of CoMo Catalyst, Oil Flow Rate of 1 $ml.min^{-1}$ and Gas Flow Rate of 0.5 $l.min^{-1}$

(a)



(b)

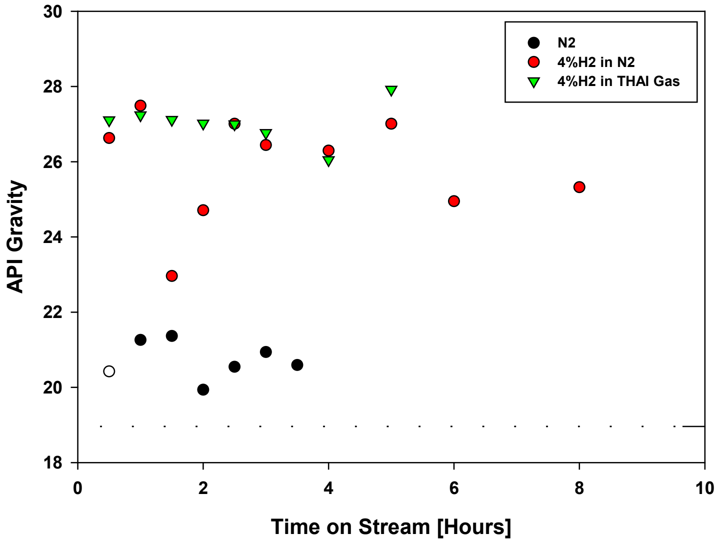
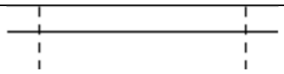
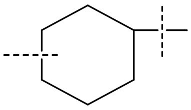
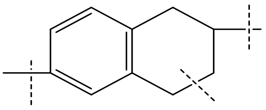
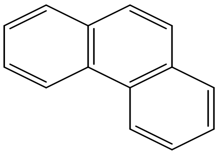
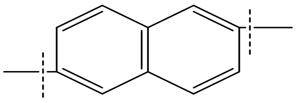
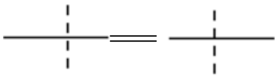


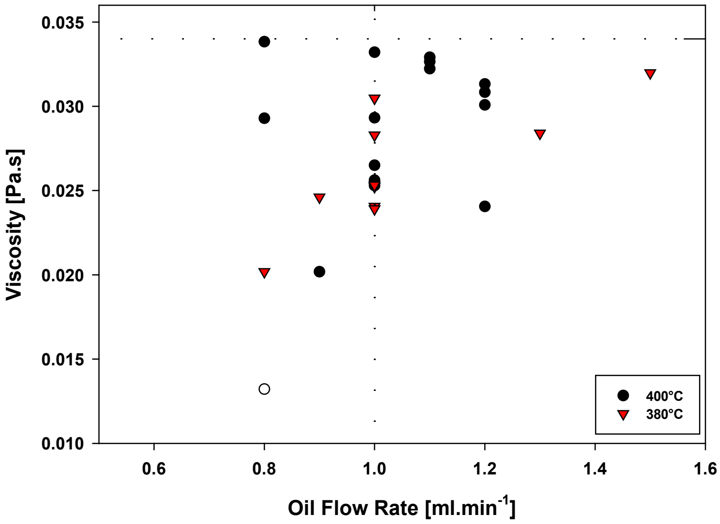
Table 5.5 Principal Reactions involved in Catalytic Cracking of Various Classes of Hydrocarbons (Voge, 1958)

Hydrocarbon class	Schematic chemical reactions	Principal reactions	Principal products
n-Paraffins and isoparaffins		Cleavage of hydrocarbon at different points: cleavage of terminal C-C bonds are unusual	Branched paraffins and olefins with not less than 3 carbon atoms: small amounts of methane
Naphthenes		Cleavage of rings and lateral chains	Paraffins and olefins: a small amount of aromatic compounds
Naphteno-aromatic compounds		Opening of naphthenic ring: cleavage of lateral chains of aromatic rings	Paraffins, olefins and aromatic compounds
Aromatic compounds without side chains		Cracking is negligible	Coke
Aromatic compounds with side chain		Cleavage of lateral chains of aromatic rings	Olefins and aromatic compounds
Olefins		Cleavage of hydrocarbon chains at various points	Branched olefins; small amounts of paraffins

Although no separate investigations were carried out to determine the effect of oil flow rate or LHSV, upon upgrading some fluctuations in the oil flow rate during different experiments were noted. From these readings it was apparent that lower flow rates or higher residence time favours higher upgrading, a finding similar to the more viscous THAI field oil processing. The viscosity of upgraded oils versus oil flow rates for experiments conducted at

380 and 400 °C have been plotted in Figure 5.3. If the scatter in the data is ignored the higher flow rates usually shows higher viscosity, though there are some exceptions.

Figure 5.3 Viscosity of Upgraded Oil Versus Oil Flow Rate



5.4 n-Decane as Feed

One experiment was carried out using n-decane to determine the effect of upgrading on a model substance and to produce coke samples for further analysis, with a view the model feed would cause less deactivation. It was found that the density of n-decane feed was 738.3 kg.m^{-3} (API 59.72), whilst that of the produced oil was quite similar, with a value of 741.68 kg.m^{-3} (API 59.28°). Clearly these densities are much lower than those of heavy oil from the THAI field trial.

However, it was found that the viscosity of n-decane and the produced samples were too low to measure using available rheometer.

Since some liquid products showed an increase in density, with lower API gravity than the n-decane feed, this showed that some degradation occurred. Possibly this effect could result from cracking of light hydrocarbons from the liquid accompanied by dehydration to yield volatile gases together with a heavier more carbon rich liquid product. Therefore, due to the above reasons, only a limited trial was carried out and further experiments under different conditions were not carried out.

Conclusions

Comparing the upgrading studies with CCO and THAI field oil some similar trends were observed, for example in the effect of temperature upon upgrading. However some significant differences were also observed as summarized below:

The introduction of hydrogen has a larger effect upon upgrading of CCO than THAI field oil. It is thought that the addition of hydrogen to the CCO causes hydrogenation of unsaturated double and triple carbon-carbon bonds, produced as a result of the cracking of more easily crackable paraffinic crude under normal cracking conditions than the more aromatic crude THAI field oil. CCO contains a larger fraction of unsaturated hydrocarbons than THAI oil and thus there is more potential for hydrogenation to produce saturated hydrocarbons, and leading to greater improvements in quality of the upgraded oil. The addition of hydrogen to the feed caused more upgrading of CCO than THAI field oil, possibly because the feed of CCO contained lower amounts of coke precursors such as asphaltenes and other heteroatoms (Xia and Greaves, 2006). These impurities may have poisoned the catalyst to a greater extent when exposed to THAI oil than when exposed to CCO, thus explaining the higher level of upgrading occurring with the latter feed. The major role of these HDS catalysts have been described to hydrogenate the produced oils and since the CCO is already rich in saturates, the majority of the possible reactions may be cracking of large straight chain HC’s and then the external hydrogen can stabilize the newly formed smaller molecules.

Chapter 6

The Chemistry of Oil Upgrading

6.1 Introduction

As described in detail in Chapter 2, Section 2.1.1, the chemistry of petroleum crudes is very complex and varies significantly depending upon origin. Upgrading processes such as CAPRI bring a number of physical and chemical changes into the produced oils. Viscosity and API gravity along with SIMDIS using D2887, as presented in Chapter 4, provides useful information about these physical and chemical changes. However in order to gain deep insight into the chemistry of upgrading of the processed oil, it needs to be analysed in detail for upgrading processes such as hydrodesulphurization, hydrodemetallation and hydrodeaspaltenization. For this reason the services of independent laboratories from Canada and UK were used. The analyses performed for selected samples by Petrobank Canada and Intertek laboratories UK were; residue reduction and simulated distillation (SIMDIS) analysis by D5307, metals and sulphur analysis, Saturates, Aromatics, Resins and Asphaltenes (SARA) analysis, Size Exclusion Chromatography (SEC), Gas Chromatography-Flame Ionization Detection (GC-FID) and Ultra-Violet Fluorescence (UVF), and are presented in sections 6.2-6.8 respectively.

6.2 Residue reduction and SIMDIS analysis by D5307

In order to independently verify the SIMDIS results presented in this work and to know the level of residue conversion, a number of selected samples were sent to Petrobank Canada for analysis. Their laboratory is especially equipped to analyse THAI field oil, being the pioneer company to run the first THAI field project. The SIMDIS method used by Petrobank was ASTM method D5307, a method providing more detailed analysis of heavier crudes or processed oils than D2887, employed at Birmingham. It also provided the advantage that method D5307 is able to determine reside reduction; a measure cannot be investigated using method D2887.

SIMDIS methods D2887 and D5307 are both suitable for the measurement of crude petroleum boiling range distribution up to a maximum temperature of 538°C. However D5307 has the added advantage that it can provide further details about materials above 538°C, which are classified as residue. The residue contained in the crude oil, the lower its quality in terms of having high viscosity, lower API gravity and is more concentrated in undesirable heavy hydrocarbons. Therefore, for any processed oil e.g. from catalytic cracking process such as CAPRI, the level of upgrading can be calculated from the conversion of residue. SIMDIS curves from method D2887 for selected samples have been presented in Figure 6.1; and results from method D5307 for the same samples are presented in Figure 6.2 and Table 6.1. The new data provides more detailed evidence for the upgrading role of the CAPRI process in improving the quality of processed oils than method D2887.

From Figure 6.1, the SIMDIS curves are closely packed and a shift towards the lower product range to the left of the graph is not clearly visible in any run except for the high temperature run of 500°C. Detailed discussion about the selected samples using method D2887 has been provided in Chapter 4. However, the major difference between Figures 6.1 and 6.2 is at the high temperature end. Whereas in Figure 6.2 the SIMDIS curves for method D5307 provides more detailed information about the quality of the processed oil in terms of a shift towards the left. This difference is because in D5307 the column temperature is relatively higher than the D2887 and the method can simulate for higher HC's. Also, the added advantage is that the method provides the level of residue wt. %.

From Figure 6.2 it is clear that in all of the experiments, except for P13 and P17, the SIMDIS curves are shifted to the left relative to the feed oil, indicating that there is a marked improvement in oil quality with increased fraction of lighter end products. Table 6.1 also shows the temperatures at the cumulative product percentage of 70%. With increased upgrading, this temperature decreases. This shift in temperature is very clear in experiments P30 and P37 where at a cumulative product percentage of 70%, significant improvements of 147.1 and 138.4°C respectively can be observed, relative to the temperature for the THAI feed oil.

Figure 6.1 SIMDIS Analysis using D2887 of the selected samples

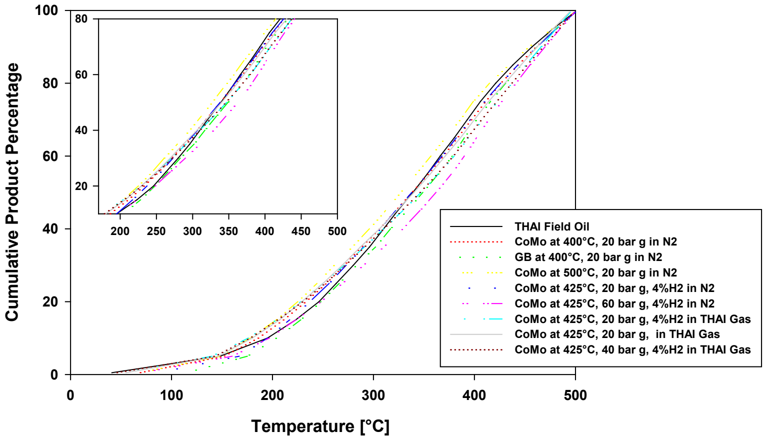


Figure 6.2 SIMDIS Analysis using D5307 of the Selected Samples

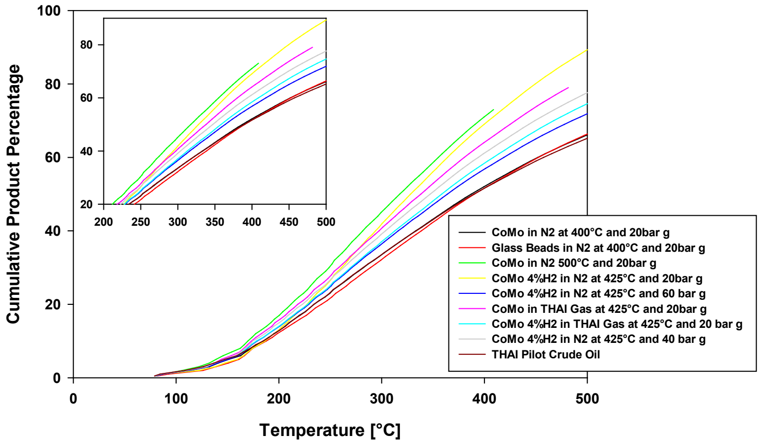


Table 6.1 Cumulative Product Percentage at 70% and Residue Reduction Comparison of Selected Samples

Experiment No.	**THAI Field Crude Oil**	**P13**	**P17***	**P30**	**P37**	**P65**	**P66**	**P66**	**P67**
Time of Sample [Hrs]		**53**	**1**	**1**	**21.5**	**3**	**6.5**	**14.5**	**2.5**
Temperature [°C]		**400**	**400**	**500**	**425**	**425**	**425**	**425**	**425**
Pressure [bar g]		**20**	**20**	**20**	**20**	**60**	**20**	**20**	**40**
Gas Composition		**N_2**	**N_2**	**N_2**	**4%H_2 in N_2**	**4%H_2 in N_2**	**4%H_2 in THAI**	**THAI**	**4%H_2 in N_2**
Temperature at which Cumulative Product Percentage of 70% occurs	542.3	534.2	530.0	395.2	403.9	485.2	430.0	467.3	448.9
Residue wt. %	29.7	28.9	28.3	4.9	3.9	22.8	12.0	19.7	16.6

*In all the experiments Akzo CoMo was used as catalyst except for P17 where only GB were used

From Figure 6.2 the curves most shifted towards the left correspond to CAPRI experiments carried out at higher process temperature or the addition of 4% hydrogen, indicating that these conditions lead to a dramatic improvement in the quality of oil. These findings are in agreement with data provided in Sections 6.5 and 6.6. Previously from Section 4.10, Chapter 4, it is evident that the highest reaction temperatures lead to the largest amounts of upgrading but are associated with high coke deposits. However the addition of 4% hydrogen and the resulting shift towards the left in the SIMDIS analysis using D5307 is much more prominent than with method D2887 (Figure 6.1). This could be because of the fact that method D5307 accounts for higher HC's closer to residue both in the feed i.e. THAI field crude and in the processed oil in more detail while D2887 does not. Therefore the difference between the feed and produced oil is more prominent as the feed contains more residue or heavy HC's. This is further supported by the level of reduction in residue for the different runs. From Figure 6.2 it is evident that the SIMDIS curves make an "S" shape curve, where the higher end products are cracked and reduced to lighter end products. These findings also indicate that the use of D5307 is more suitable for quantitative analysis and providing residue values, while the analysis results for the processed oil using D2887 are qualitative at best.

As defined in standard ASTM D5307, "Any fraction of crude petroleum having a boiling point above 538°C is classified as residue" (ASTM, 2011). Usually called "bottom of the barrel" in the refining industry, residue conversion into cleaner and more valuable liquid products is highly sought after. Residue represents a significant portion up to 85% vol. of a barrel of crude and it is difficult and wasteful to dispose of this fraction (Rana *et al.*, 2007). Thus, residue must be converted into more valuable products in any efficient oil upgrading process.

Table 6.1 displays the residue reduction values, from which it can be observed that the catalyst does not show any significant effect at 400°C. When the temperature rises to 500°C the final value of residue drops down to only 4.9 wt. % from a starting value of 29.7 wt. %. This could be because high temperatures usually favour the condensation reactions between aromatic clusters, which lead to the formation of mesophase, and consequently coke. Furthermore, at the highest reaction temperature, the C–C and C–heteroatoms bonds cracking reactions are favoured, bringing about the formation of low molecular weight compounds, such as C_1–C_4 hydrocarbon gases (Gray, 1994).

The effect of gas composition was investigated, and with the addition of 4% H_2 in N_2 at 425°C, the produced oil residue level was reduced to only 3.9 wt. % from a base value for THAI field oil of 29.7 wt. %. This also compares favourably even to the produced oil from the high temperature experiment conducted at 500°C. The role of hydrogen is again evident from the two P66 samples. When only THAI gas was used as the reaction medium, the final residue level was 19.7 wt. %. However when 4% H_2 was added to the THAI gas, the residue level dropped to only 12 wt. %. These results are similar to what would be expected in industrial catalytic processes, where a CoMo catalyst is required to favour hydrogenation over cracking reactions (Niemann and Wenzel, 1993) and interferes with the coalescence of the mesophase[‡‡‡] as well (de Bruijn *et al.*, 1993). This was new evidence that the addition of hydrogen externally does effect the upgrading of THAI field oil, not evident from viscosity and API gravity measurements presented in Section 4.12, Chapter 4. These results are consistent with residue upgrading processes used elsewhere, where the addition of hydrogen or hydrogen donor solvents has been found to be essential in the upgrading of heavy oils (Aaarts *et al.*, 1978). Rana *et al.*, (2007) has associated the process economy of residue conversion to the amount of hydrogen in-put requirements.

[‡‡‡] A complex mixture of essentially aromatic hydrocarbons, containing anisotropic liquid-crystalline particles (carbonaceous mesophase). The carbonaceous mesophase particles are formed from the aromatics of high molecular mass in mesogenic substances.

In terms of the effect of pressure upon the residue conversion, the final residue contents of the processed oil for experiments carried out at 60 and 40 bar g were 22.8 and 16.6% respectively. These values were significantly lower than the 29.7% residue of THAI crude, but were not as low as observed in some experiments, such as P37 which was carried out at the same temperature but lower pressure of 20 bar g. Therefore the effect of pressure alone does not seem to significantly influence the residue conversion.

6.3 Metal Analysis

Metals and sulphur analysis were performed for selected samples, details of which have been provided in Table 6.2. A number of metals were detected in the THAI crude oil, however most of these are in trace quantities and the metals of primary interest to this work were nickel, vanadium and iron, as these are present in highest quantities. As described in the Chapter 2, Section 2.2.1 (d), metals can seriously damage a typical refinery operation by corrosion and fouling or deactivating the catalysts. These metals may exist in either the metallic state or in organic structures like metal porphyrins. Xia and Greaves (2002) employed THAI process for the upgrading of Athabasca bitumen and observed above 90 % reduction in the level of Ni+V. Therefore with the application of THAI and the resulting thermal cracking, the majority of the metals such as Ni+V in their metallic state would be expected to have already been removed from the THAI field oil. Typical Athabasca bitumen may contain up to 1000 ppm of Ni+V, while metals analysis showed that THAI oil contained only 198 ppm of these components. These levels indicate that THAI field oil may be concentrated in harder to remove metal structures e.g. chelates in metallic porphyrins compared to Athabasca bitumen. To remove these organically bound metals relatively severe experimental conditions are required, where higher temperatures and pressure of hydrogen favours more hydrodemetallization and less fouling or poisoning of the catalyst. Referring to

Table 6.2, most of the experimental conditions studied did not lead to a substantial decrease in Ni+V content with exception of experiment P30 at a temperature of 500°C, in which the level of Ni+V left in the produced oil was only 79 ppm in comparison to 198 ppm in the THAI crude oil. This indicates that the severe temperature of 500°C may have favoured HDM reactions compared with lower temperatures. The addition of 4% hydrogen in experiment P37 led to a slight decrease of 12 ppm in the Ni+V concentration in comparison to THAI field oil. This moderate decrease suggests that the addition of low flow rates or partial pressures of hydrogen may improve the removal of metals. Ancheyta *et al.*, (2002) also found that hydrogen addition helps in hydrodemetallization, when typical HDS and HDM catalysts such as CoMo and NiMo were used. The addition of hydrogen in THAI gas however did not reduce any metal contents. The rest of the samples did not show any decrease in metal levels or displayed a slight increase, illustrating that other variables such as the effect of pressure did not significantly influence the metal removal. Iron levels were reduced more than three times in comparison to the THAI field oil levels, providing further evidence that the CoMo catalyst did perform well for HDM activity. The demetallization was higher for iron than Ni+V as unlike Ni+V, iron is usually not found in organically bound form due to geochemical reasons (Hodgson *et al.*, 1967; Baker, 1969; Baker and Palmer, 1978; Baker and Louda, 1986; Filby and Van Berkel, 1987; Quirke, 1987). Although Franceskin *et al.* (1986) has claimed that iron does exist in metal chelates in some crude oils. Thus the metallic iron in the THAI oil was more removed than organically bound metals such as Ni+V reported earlier in this chapter.

6.4 Sulphur Analysis

CoMo and NiMo catalysts are typical HDS catalysts and are primarily used to desulphurise crudes or distillate products by breaking up large molecules attached to aromatic or naphthenic structures (Morel *et al.*, 1997). However as detailed in the Chapter 2, Section 2.1.1 (c), sulphur can exist in many forms in crude oil and different levels of desulphurisation occur with increased severity of processing conditions. For example, elemental sulphur can be removed at a temperature as low as 150°C, leaving the crude as H_2S gas. However to remove organically bound sulphur higher temperatures and partial pressure of hydrogen are needed. At these conditions first the complex molecules are catalytically cracked to which sulphur is attached and then stabilised with the help of hydrogen, which will escape eventually as H_2S gas (Speight, 1999). A sulphur level as high as 4.54 wt. % has been reported for Athabasca bitumen though it can widely vary depending on the origin (Jacques *et al.*, 1978). THAI field oil was already thermally cracked whilst being processed inside the reservoir. Therefore most probably all the loosely bound or elemental sulphur, bonded to small hydrocarbon chains may have been removed. This will mean that the crude is left more concentrated in organic or harder to remove sulphur. Selected samples from different experiments were analysed for sulphur and results are presented in Table 6.2. The selected experiments were assessed to investigate whether CoMo catalyst used in experiment P13 has any significant effect in comparison to P17 where GB were used for desulphurisation. The effect of 4% hydrogen addition, pre-sulphiding the catalyst, increasing pressure and temperature were also compared by analysing experiments P37, P77, P65, P67 and P30 respectively for HDS. None of these changes in the reaction conditions or catalysts showed an increased level of desulphurisation except for experiment P30, where a larger amount of hydrodesulphurisation was observed. Typically the amount of sulphur removed was below 3%, although in P30 the removal increased to 16 %, showing that the higher processing temperature was able to overcome the significant activation energy required for sulphur removal. This level of upgrading is lower in comparison to 51% hydrodesulphurisation achieved elsewhere (Speight and Moschopedis, 1979) under the conditions of hydrogen pressure of as high as 75 bar g. The higher pressure of hydrogen used in their study is thought to be responsible for the increased sulphur removal, compared with the inert atmosphere or low hydrogen pressures used in this study. It must be noted however that the 51% HDS level reported by Speight Moschopedis (1979) referred to a crude oil feed which may have contained various forms of sulphur, including elemental sulphur. The elemental sulphur would have been relatively easy to remove when compared with the THAI field oil used in this work. The processing of THAI oil underground may have already removed elemental and easy to remove sulphur, leaving more difficult organically bound sulphur in the oil. This would explain why the removals observed in this work could be lower than those reported by Speight and Moschopedis (1979). Assuming that the THAI field crude is more concentrated in organic sulphur, which only starts to react with hydrogen to dissociate from crude petroleum at higher temperatures and higher partial pressure of hydrogen, it is thought that the level of hydrodesulphurisation would have been more significant if the hydrogen partial pressure was high. Once sulphur is dissociated from larger hydrocarbon petroleum chains it can quickly be stabilised as H_2S and with the continuous flow of gases, swept out of the catalyst bed without adsorbing significantly on the surface of the catalyst causing poising. In this work, the highest processing temperature of 500°C led to the greatest removal of sulphur of up to 16%, as mentioned earlier. The addition of up to 4% hydrogen at a temperature of 425°C led to a sulphur removal of only 6% (Table 6.2), showing that this processing temperature and hydrogen partial pressure were not high enough to cause substantial sulphur removal observed at higher temperatures or as observed in the work of Speight and Moschopedis (1979). However, without the use of hydrogen at 425°C the sulphur removal was only 3%, suggesting that even a low partial pressure of hydrogen does contribute towards a small removal of sulphur. This hypothesis is supported from the work of Weissman and Kessler (1996), who observed that 30% of the sulphur from heavy crude oils can be removed without using any catalyst and the use of HDS catalyst such as CoMo in the presence of high partial pressures of hydrogen always resulted in more hydrodesulphurisation than thermal hydrodesulphurisation.

Another possible reason for the lower HDS or HDN activities of the CoMo or NiMo in comparison to reduced levels reported elsewhere (Panariti *et al.*, 2000) is because of the presence of nitrogenous compounds in the THAI oil. It has been observed that nitrogenous compounds may inhibit the hydrogenative pathway (Nagai and Kabe, 1983; Nagai *et al.*, 1986; Looij *et al.*, 1998; Zeuthen *et al.*, 2001). Zeuthen *et al.*, (2001) conducted detailed studies into the influence of such effects under real feed conditions and found that specific basic nitrogenous compounds have a profound effect on HDS and HDN activity. This is presumably a result of competitive adsorption. These nitrogen compounds inhibit both direct and indirect desulphurization but the effect is largest for the latter. In this work the role of nitrogen was not assessed and this may need to be investigated in future work. In addition, issues such as hydrogen availability and other product properties may play a role (Tippet, 1999).

Table 6.2 Metals and Sulphur Analysis of Selected Samples

In all the experiments Akzo CoMo catalyst was used except in P17 and P77, where glass beads and pre-sulphided CoMo were used respectively

Sample Description →	**Experiment No.**	**THAI Field Crude Oil**	**P13**	**P17**	**P30**	**P37**	**P65**	**P66**	**P66**	**P67**	**P77***
	Time of Sample [Hrs]		**53**	**1**	**1**	**21.5**	**3**	**6.5**	**14.5**	**2.5**	**18**
	Temperature [°C]		**400**	**400**	**500**	**425**	**425**	**425**	**425**	**425**	**425**
	Pressure [bar g]		**20**	**20**	**20**	**20**	**60**	**20**	**20**	**40**	**20**
	Gas Composition		**N_2**	**N_2**	**N_2**	**4% H_2 in N_2**	**4% H_2 in N_2**	**4% H_2 in THAI**	**THAI**	**4% H_2 in THAI**	**N_2**
Metals content[¶]		**ppm**	**ppm**	**ppm**	**ppm**	**Ppm**	**ppm**	**ppm**	**ppm**	**ppm**	
Tin		0	0	0	0	0	0	0	0	0	0
Lead		0	0	0	0	0	0	0	0	0	0
Copper		0.3	0	0	0	0	0	0	0	0	0
Aluminum		6	7	7	1	6	7	7	6	6	0
Silicon		0.4	2	2	0	0.4	1	0.4	0.1	0.2	0
Iron		10	3	5	0	4	4	4	3	4	3
Chromium		0	0.2	0.2	0	0.3	0.1	0.1	0.1	0.1	0
Silver		0	0	0	0	0	0	0	0	0	0
Zinc		2	0.6	0.7	0	0.3	0.5	0.5	0.5	0.5	0
Magnesium		0	0	0.1	0	0	0	0	0	0	0
Nickel		54	56	56	21	50	55	55	54	54	57
Vanadium		144	149	150	58	136	148	150	146	146	147
Ni+V		198	205	206	79	186	203	205	200	200	204
Barium		0	0	0	0	0	0	0	0	0	0
Sodium		0	2	5	0	0	0	0	0	0	0
Calcium		0	0.7	0.6	0	0	0	0	0	0	0
Phosphorous		0.3	0.6	0.5	0.2	0.1	0.3	0.2	0.4	0.3	0
Molybdenum		6	5	6	0	3	4	5	4	4	0
Boron		0.6	1.1	1	0.6	0.8	1	0.8	0.7	0.7	0
Manganese		0	0	0.1	0	0	0	0	0	0	0
Total Sulphur[¶]**, wt%;**		**3.8**	**3.7**	**3.6**	**3.2**	**3.6**	**3.6**	**3.6**	**3.6**	**3.6**	**3.79***

*Samples analysed by Interteck Laboratories Sunbury Technology Centre, UK, using HPLC for SARA analysis and IP 143 for Sulphur

[¶] Metals analysed by Petrobank Canada using ASTM D5185 and Sulphur by ASTM D4294

6.5 SARA Analysis

Saturates, Aromatics, Resins and Asphaltenes are the usual constituents of petroleum oils. SARA analysis is used as an indicator of whether any of these particular components increase or decrease during a petroleum processing operation such as catalytic cracking. Of these four components, asphaltenes are usually the least desirable as they increase the viscosity of the heavy oils and contain heteroatoms such as sulphur, Ni and V. A decrease in their quantity is indicative of improvement in oil quality. The analysis is usually performed using fractions in different solvents and then evaporating the solvents. For example, asphaltenes could be pentane- or heptane-insolubles and saturates pentane or heptanes soluble etc. Hence SARA analysis helps to explain any chemical changes in the processed oil. In order to check whether any of these changes occurred, selected samples of the processed oils were analysed using SARA analysis, and then compared with SARA analysis of THAI field oil.

The results are shown in Table 6.3, from which it is clear that the amount of saturates have increased from 15.38 wt. % for the THAI field oil in to the range of 16.17-20.59 wt. %, depending on processing conditions. The rise in saturates was greatest for the high temperature experiment at 500°C and 20 bar g pressure of nitrogen, where an increase of 5.21 wt. % represented a 34% rise. The second highest rise in saturates of about 12% relative to THAI oil was evident in the lower oil flow rate experiment (P71) indicating that the residence time over the catalyst does increases the saturates level in the processed oils. Lower flowrate leads to higher residence time in the catalyst bed, with increased levels of saturates formation. The addition of 4% hydrogen in P37 and the presulphided catalysts in P77 showed a 6% increase in the level of saturates which was slightly higher than the 5% rise with nitrogen alone in the presence of a fresh CoMo.

Table 6.3 SARA Analysis of Selected Samples
Akzo CoMo catalyst was used in all experiments, Oil flow rate was 1 ml.min^{-1}

Sample Description →	**Experiment No.**	**THAI Field Crude Oil**	**P20**	**P30**	**P37**	**P74**	**P71***	**P77¶**
	Temperature [°C]		**400**	**500**	**425**	**425**	**425**	**425**
	Pressure [bar g]		**20**	**20**	**20**	**20**	**20**	**20**
	Reaction Gas		**N_2**	**N_2**	**4% H_2 in N_2**	**N_2**	**THAI**	**N_2**
SARA Analysis by HPLC		**% mass**						
Saturates		15.38	16.6	20.59	16.37	16.17	17.18	16.35
Aromatics		57.04	68.87	72.38	67.62	69.34	68.47	68.09
Polars (Naphthenes or Resins)		20.18	7.73	4.53	9.11	7.29	6.25	8.16
Asphaltenes Content by IP143		7.4	6.8	2.5	6.9	7.2	8.1	7.4

*Oil flow rate was 0.5 ml.min^{-1}
¶Catalyst was presulphided prior to experiment using DMDS

The amount of aromatics increased significantly from 57.04 wt. % for THAI field oil to a range of 67.62 and 72.38 for the processed oils. The highest rise of 26.8% in the level of aromatics relative to THAI oil was observed in the experiment conducted at a high temperature of 500°C, followed by a rise of 21.6% in the experiment conducted at 425°C, with both the experiments conducted in the presence of nitrogen. The level of aromatics rise for the low oil flow rate experiment (P71) was 20%, slightly lower than the experiments conducted at the standard oil flow rate of 1 ml.min^{-1}. However the lowest level of aromatics rise was in the experiment where 4% of hydrogen was used in nitrogen. In this experiment the level of aromatics rose by only 18.6% relative to THAI oil followed closely by the presulphided catalyst experiment with only 19% rise. This might be an indication that though the level of 4% hydrogen addition did not improve the produced oils significantly in terms of reduction of viscosity or a rise in API gravity (Section 4.12, Chapter 4), it brought changes in their chemical composition by virtue of lowering the aromatics production.

The amount of resins decreased in all experiments analysed. The level of resins for THAI field oil was 20.18 wt. %, and was significantly reduced within a range of 4.53 to 9.11 wt. % for the produced oils.

The decrease in asphaltenes is a key indicator of upgrading behaviour, since asphaltenes are highly undesirable in quality produced oils. The amount of asphaltenes changed from 7.4 wt. % for THAI field oil to within a range of 2.5 to 8.1 wt. %. The level of asphaltenes however was most significantly reduced to 2.5 wt. % only in the high temperature run of 500°C and all the rest of experiments did not show any significant HDA activity. This however is not surprising, as the level of asphaltenes in THAI field oil are already comparatively low as this feed has already been de-asphalted once in the reservoir using THAI processes. Secondly, similar findings were observed by Ding *et al.* (2007) while investigating the hydrocracking activity of NiMo catalysts, that when hydrogen pressure was increased from 1.52 to 2.54 MPa, HDA activity was considerably increased. This is due to the limitation of thermodynamics, as at high temperature and low hydrogen pressure hydrogenation reactions of aromatic rings are not favoured. On the contrary, high hydrogen pressure can enhance the hydrogenation of aromatic rings, and consequently increase HDS and HDA activities.

The above results in Table 6.3 indicate that the amount of saturates and aromatics have increased while a decrease in naphthenes occurred, as did asphaltenes at the high temperature of 500°C. These changes in composition are typical of classical catalyst deactivation reactions over oxides and sulphide catalysts (Gates *et al.*, 1979; Naccache, 1985). At low partial pressure of hydrogen and at relatively short residence time, as represented in Figure 6.3 (reactions 1-14), smaller naphthenic or aromatic ring structures condenses into larger multi ring aromatic structures. Reactions 1–3 in Figure 6.3 illustrate the polymerization of olefins, reactions 4–8 illustrate cyclization from olefins, and reactions 9–14 illustrate chain reaction formation of polynuclear aromatics, which condense as coke on the catalyst surface.

Because of the high stability of the polynuclear carbocations (formed in reactions 10–13), they can continue to grow on the surface for a relatively long time before a termination reaction occurs through the back donation of a proton. From this mechanistic scheme (Figure 6.3) it is clear that olefins, benzene and benzene derivatives, and polynuclear aromatics are precursors to coke formation.

These findings are also consistent with earlier similar work by Speight and Moschopedis (1979). They noticed the increased level of aromatics in the produced oil with increase in time on stream, while processing the Athabasca bitumen in the presence of CoMo catalyst supported on alumina. In experiment P37, the addition of a small flow of hydrogen led to a slightly lower increase in aromatics content than the other experiments presented in Table 6.3. This may indicate that even a low partial pressure of hydrogen inhibits the formation of aromatics and is thus important in the upgrading reactions. However to maintain catalytic activity for longer durations, higher hydrogen pressure is required to perform hydrogenation and inhibit polymerization (Jones and Pujado, 2006). In this work it is thought that the relatively low hydrogen pressures may have limited the extent of upgrading, in comparison with the high pressures that would typically be used in refinery hydroprocessing.

Figure 6.3 Coke-Forming Reactions of Alkenes and Aromatics on Oxide and Sulphide Catalysts: (a) Polymerization of Alkenes; (b) Cyclization from Alkenes; (c) Formation of Polynuclear Aromatics from Benzene (Farrauto and Bartholomew, 1997).

Polymerization of Olefins

Step 1: Reaction of olefin with Bronsted acid to form secondary carbenium ion:

$$H_2C{=}CH{-}CH_2 + HX \rightleftharpoons H_3C{-}\overset{+}{C}H{-}CH_2 + X^- \qquad (1)$$

Step 2: Condensation reaction of a C_3 carbocation with a C_3 olefin to form a condensed, branched C_6 product with a carbenium ion:

$$H_3C{-}\overset{+}{C}H{-}CH_2 + H_2C{=}CH{-}CH_3 \rightleftharpoons H_3C{-}\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{C}H}{-}CH_2{-}\overset{+}{C}H{-}CH_3$$

(2)

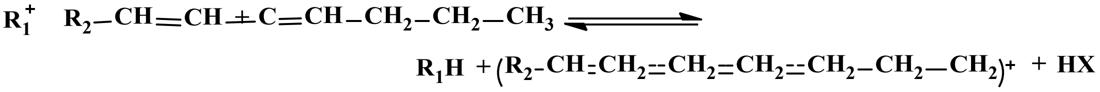
Step 3: Reaction of carbenium ion with Bronsted base to form olefin:

$$H_3C{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}CH_2{-}\overset{+}{C}H{-}CH_3 \rightleftharpoons H_3C{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}CH_2{-}CH_2{-}CH_2 + HX$$

(3)

Cyclization from Olefins

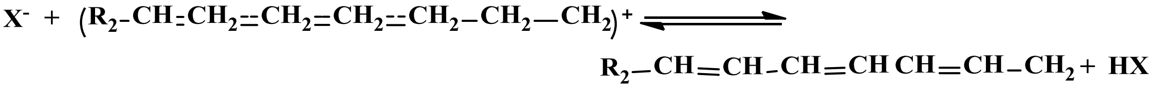
Step 1: Formation of an allylic carbocation ion by reaction of diene with a primary carbocation ion:



$$R_1^+ \quad R_2{-}CH{=}CH{\pm}C{=}CH{-}CH_2{-}CH_2{-}CH_3 \rightleftharpoons R_1H + (R_2{-}CH{\doteq}CH_2{\doteq}CH_2{=}CH_2{\doteq}CH_2{-}CH_2{-}CH_2)^+ + HX$$

(4)

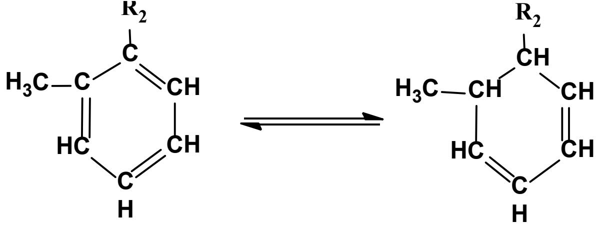
Step 2: Reaction of an allylic carbocation with a Bronsted base to form a triene:



$$X^- + (R_2{-}CH{\doteq}CH_2{\doteq}CH_2{=}CH_2{\doteq}CH_2{-}CH_2{-}CH_2)^+ \rightleftharpoons R_2{-}CH{=}CH{-}CH{=}CH\;CH{=}CH{-}CH_2 + HX$$

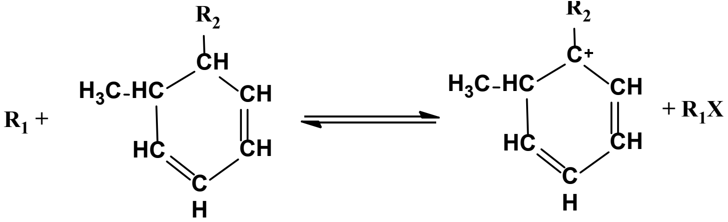
(5)

Step 3: Cyclization of a triene to form a substituted cyclohexadiene:



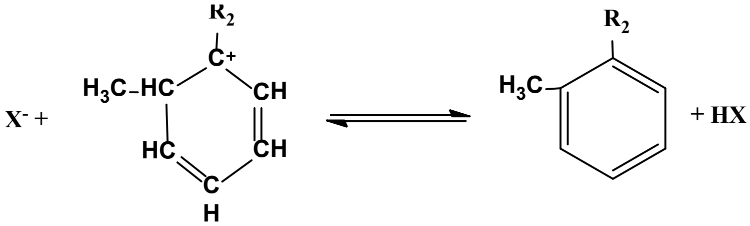
(6)

Step 4: Formation of a tertiary carbocation ion:



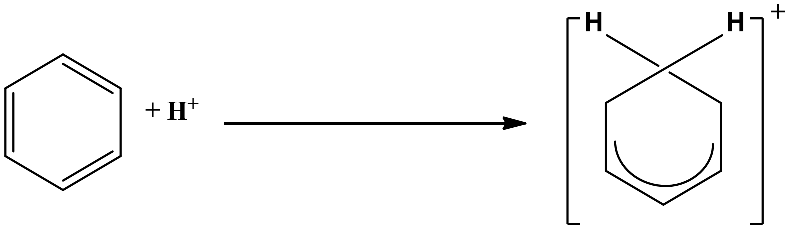
(7)

Step 5: Reaction of a tertiary carbocation ion with Bronsted base to form a substituted benzene:



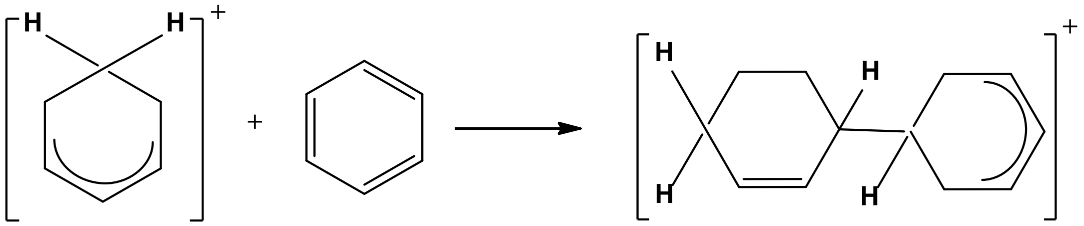
(8)

Step 1: Initiation (protonation of benzene):

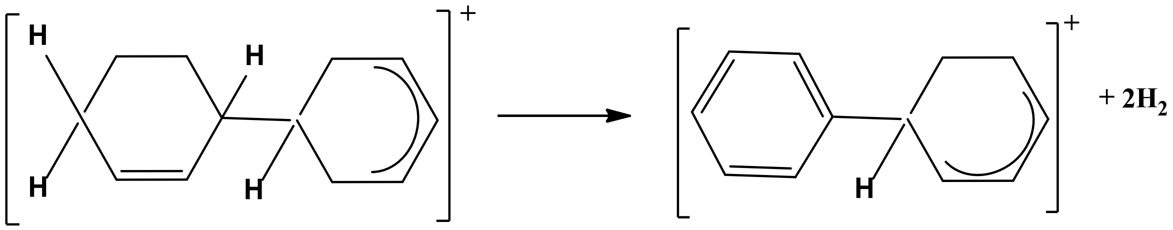


(9)

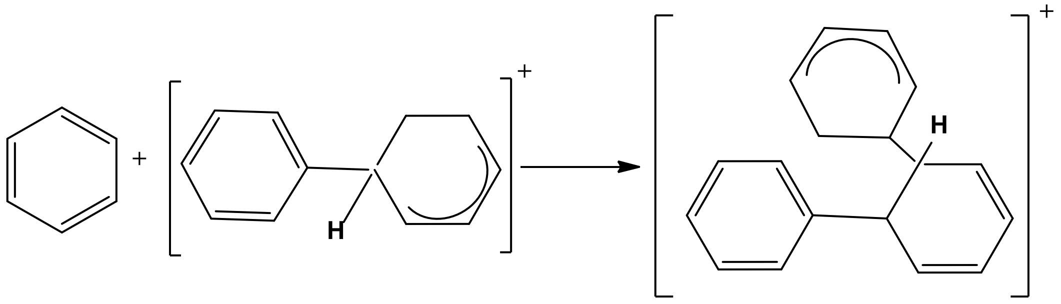
Step 2: Propagation (condensation reaction of carbocation with benzene followed by H abstraction):



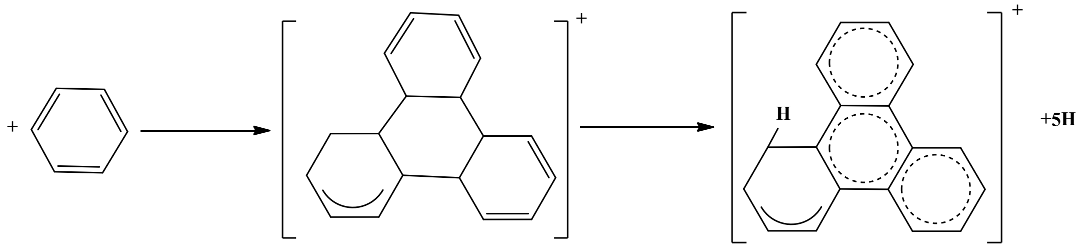
(10)



(11)

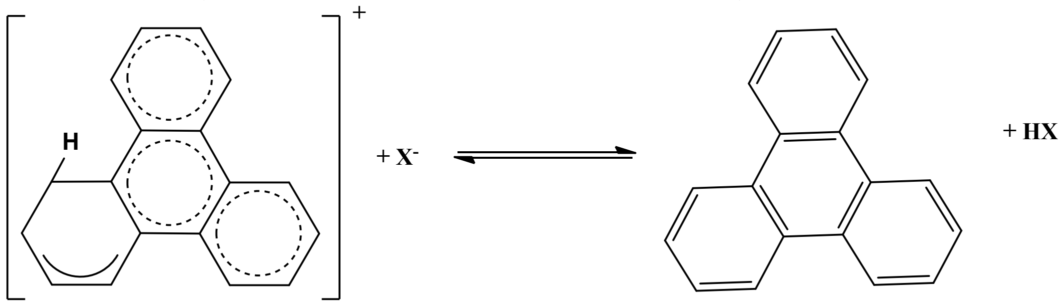


(12)



(13)

Step 3: Termination (reaction of carboction with Bronsted base):



(14)

Since no significant HDS, HDM or HDA activity from the above analysis is evident, along with no significant uptake of added hydrogen, it is a strong indication that majority of the CAPRI upgrading reactions are hydrocracking rather than hydrodemetallization, hydrodesulphurization or hydrodeasphaltenization. This finding is also supported by the fact that in all the selected experiments analysed for HDS, HDM and HDA activity; only the high temperature experiment resulted in the reduction of asphaltenes, metals as well as some level of sulphur. It is also evident that due to the lower H_2/HC molar ratio and lower hydrogen partial pressure, the effect of external hydrogen addition (P37) did not affect the upgrading of CAPRI processed oil. Alvarez and Ancheyta (2008) also attributed the lower HDS, HDM, HDA, HDN activity of their catalyst to lower uptake of H_2 by comparing their HDS, HDM, HDA and HDN activity to those achieved in the industry under similar conditions. However, the addition of high partial pressure hydrogen externally is not practical with CAPRI, and therefore not the objective of this study.

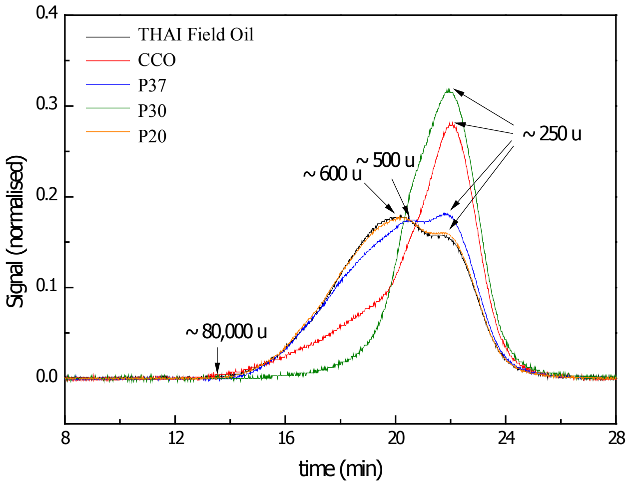
6.6 Size Exclusion Chromatography (SEC)

In order to further confirm the effect of hydrogen addition in P37 and what effect it has on molecular weight distribution in comparison to higher temperature experiment P30, size exclusion chromatography SEC was performed on these samples by the laboratories of

School of Chemical Engineering, Imperial College London. Results for these tests are presented in Figure 6.4.

From Figure 6.4 all chromatograms except for P30 showed lift-off around 13.9 min, which corresponds to a mass of about 80,000 u[§§§] according to a calibration made with polystyrene standards. THAI field oil, P37 and P20 present a bimodal distribution of signal with maximum peaks of intensity at 600 u (THAI field oil, P20), 500 u (P37) and 250 u (combustion cell oil CCO and P30). The experiment with 4% hydrogen addition to nitrogen (P37) shows certain shift towards smaller sizes relative to the THAI field oil (non-treated) and the run conducted at 400°C in the presence of nitrogen only. On the other hand the experiment conducted at 500°C in the presence of nitrogen (P30) show a lighter and narrower molecular mass distribution with a single maximum peak centred at about 250 u.

Figure 6.4 SEC Chromatograms[*]



[*]Key for Experimental Conditions

Exp. No.	Temperature °C	Pressure bar g	Reaction Media
P20	400	20	N_2
P30	500	20	N_2
P37	425	20	4%H_2 in N_2

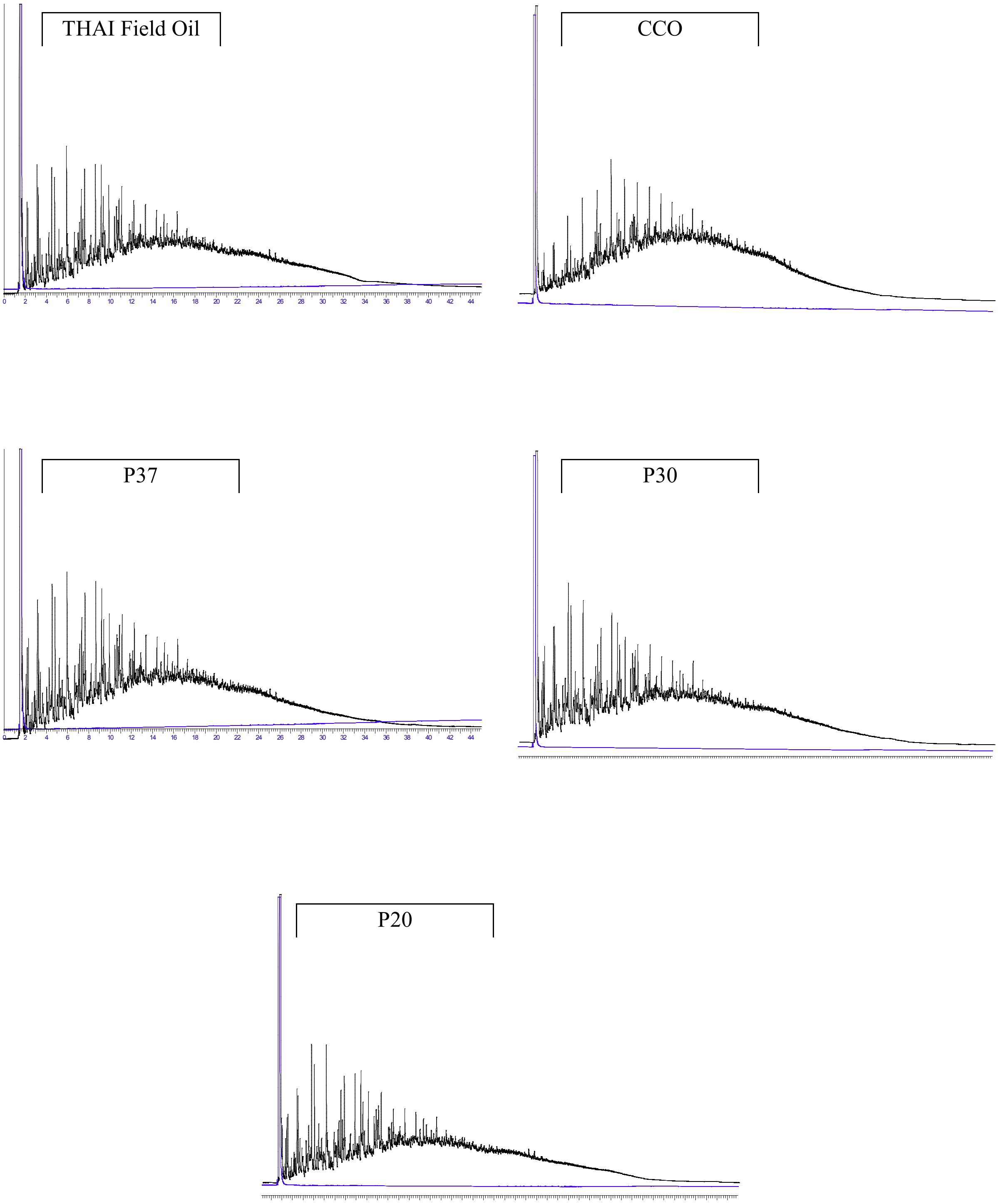
[§§§] Arbitrary unit

The samples showed differences outside the mass range detectable by GC. Significantly smaller molecular sizes and smaller aromatic rings clusters have been observed in P30 in comparison with the other samples. The THAI field oil and the reaction products at 400°C (P20) were undistinguishable by the techniques employed. The products from reaction with hydrogen at 425°C (P37) showed a small but noticeable shift towards smaller molecular sizes by SEC, which further cements the earlier conclusion that a small amount of hydrogen makes the difference in the upgrading of THAI heavy oil.

6.7 Gas Chromatography-Flame Ionization Detector GC-FID

GC-FID chromatograms of the selected samples are presented in Figure 6.5. In all the cases, a series of resolved compounds can be identified in the low molecular weight region (up to around 300 u). The resolved peaks appear superimposed on an unresolved complex mixture which makes the comparison among the samples difficult. The percentage of sample analysed by the GC was estimated for each chromatogram, from the total area under the curve and using the mean response factor of n-alkanes. The values of these percentages were found to be around 50% for samples THAI field oil, 4% hydrogen addition to nitrogen experiment (P37) and the 400°C experiment in the presence of nitrogen only (P20) and around 60% for CCO and the experiment conducted at 500°C in the presence of nitrogen (P30). Therefore only a 10% rise can be observed for the high temperature experiment conducted at 500°C.

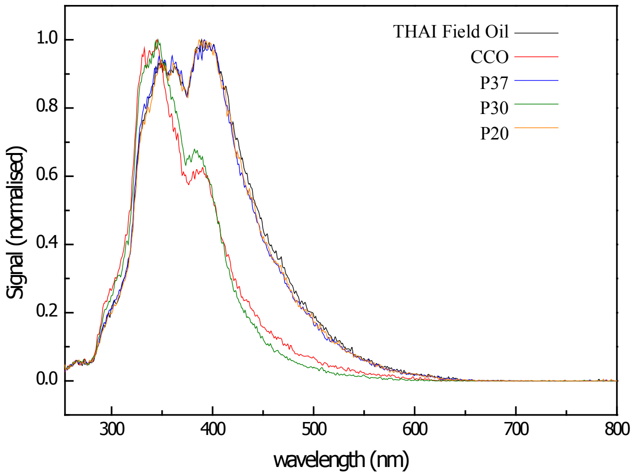
Figure 6.5 GC-FID of Selected Samples



6.8 UV-fluorescence spectroscopy (UVF)

The synchronous UV-fluorescence spectra (height normalized) are shown in Figure 6.6.

Figure 6.6 UV-fluorescence of Selected Samples



No significant differences in the range of chromophores detected can be seen between THAI field oil, and the experiments P37 and P20. Regarding samples CCO and P30, it can be observed a clear shift in the spectra towards shorter wavelengths, in comparison with the other samples. This shift is related to smaller aromatic chromophore sizes in these samples. These findings are not unexpected, given the fact that all other tests indicated earlier that at 500°C the highest level of upgrading of the processed oil happened in the presence of CoMo catalyst. The spectra for the CCO oil displayed closer similarity to the processed THAI oil from experiment P30 rather than the THAI feed oil, since the CCO oil was originally much lighter than the THAI feed oil. This result is in line with the SEC results.

The samples showed differences outside the mass range detectable by GC. Significantly smaller molecular sizes and smaller aromatic rings clusters have been observed in CCO and P30 in comparison with the other samples. The THAI field oil and the reaction products at

400°C (P20) were undistinguishable by the techniques employed suggesting that at 400°C the catalytic upgrading in terms of the chemical properties of the produced oils were not significant. The products from reaction with the added 4% hydrogen in nitrogen at 425°C (P37) showed a small but noticeable shift towards smaller molecular sizes by SEC. P37 was also different from the 400°C temperature experiment that in this experiment 4% of external hydrogen was also added during the experiment. From the refinery gas analysis (Table 4.13, Chapter 4) there was not any evidence that the added hydrogen has been consumed during the processing of the THAI field oil, however results from SEC does suggest that even at the relatively smaller hydrogen flow rates, its presence does affect the properties of the produced oils.

Conclusions

From fractional distillation of selected processed oil samples analysed using ASTM method D5307, it is clear that the processed oil samples have been upgraded more than previously observed by using the qualitative method D2887 at Birmingham. The added advantage of using D5307 was to produce quantitative conversion data of residue. From both enhanced fractional distillation and residue data it is clear that the CAPRI process offers the advantage of upgrading the processed oils in terms of improving their chemical properties. This was also confirmed by the SARA analysis that at the optimum temperature of 425°C and the addition of 4% H_2 there was a slight reduction in the asphaltenes contents as well as increase in the fraction of saturated HC’s. However, the biggest reduction in asphaltenes contents was only achieved at 500°C. These results were also supported by SEC, where both the aforementioned experiments provided low molecular weight products. The level of HDS was not substantial except at high temperature experiment at 500°C, owing probably to the presence of difficult to remove organically bound sulphur. Similar was the case with demetallization. Only at high temperature of 500°C was significant demetallization achieved. From all the results the most probable reactions appear to be cracking rather HDS, HDM or HDA.

Chapter 7

Analysis of Coke and CAPRI Reaction Upgrading Mechanism

Chapter Overview

In this chapter, an introduction has been provided about the coking of catalysts in Section 7.1. The section describes how the coking of catalysts happens and why the study of this phenomenon is so instrumental in efforts to design optimum catalysts and processes to minimize coking.

Section 7.2 describes the analysis of coke: effect of temperature, where the coked catalysts during the processing of THAI field oil in a number of specially designed experiments. The effect of temperature upon the production of different types of coke and some of the possible explanations of these effects are discussed. The analysis have been performed by two instrumental techniques namely thermogravimetric analysis TGA and Diffuse Reflectance Infrared Fourier Transform (DRIFTS).

In Section 7.3 TGA and DRIFTS results are presented for samples coked under different conditions of reaction media and temperature. The effect of catalyst pre-treatment upon the results is also presented.

A discussion about the analysis of coke provided in sections 7.2 and 7.3 has been provided followed by some conclusions of the chapter.

7.1 Coking of Catalysts: Introduction

In hydroprocessing of petroleum products, catalyst deactivation by coke deposition is one of the major concerns, both from economic and technological perspectives (Wolf and Alfani, 1982; Thakur and Thomas, 1985; Abasi-Halabi *et al.*, 1991; Furimsky and Massoth, 1999; Bartholmew, 2002). The coke deposition occurs in the pores and/or on the surface of the catalysts, and generally leads to loss of activity and product selectivity (Bhatia *et al.*, 1989; 1990). Thus, the first remedy of deactivation has always been linked to the development of coke resistant catalysts. However, understanding the mechanism of catalyst deactivation is critical to identify the reactions happening during heavy oil upgrading, and is a foundation for modelling deactivation processes, designing stable catalysts, and optimizing processes to prevent or slow catalyst deactivation. An additional benefit of studying the chemistry of coke also provides an insight into the reactions responsible for the upgrading of heavy oils. However, coking reactions in processes involving heavy hydrocarbons are very complex. Different kinds of coke may be formed and cokes may range in composition from CH to C and have a wide range of reactivates with oxygen and hydrogen depending upon the time-on-stream and temperature to which they are exposed. For example, coke deposits occurring in hydrodesulphurization of residue have been classified into three types, the first two types fall within the category of soft and the third type of hard coke (Beuther *et al.*, 1980):

1. Type I deposits are reversibly adsorbed normal aromatics deposited during the first part of the cycle at low temperature.

2. Type II deposits are reversibly adsorbed asphaltenes deposited early in the coking process.

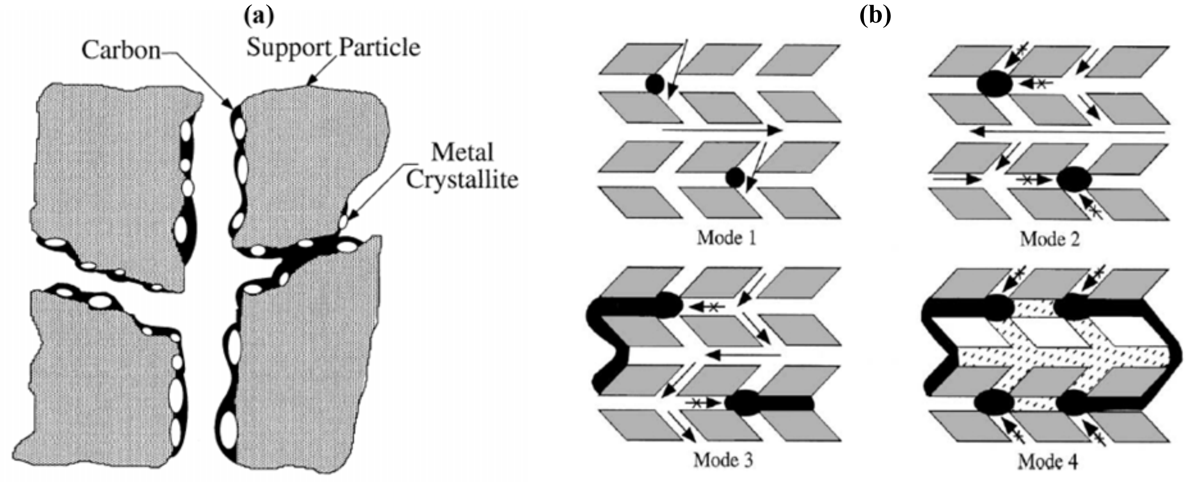
3. Type III deposits result from condensation of aromatic concentrates into clusters and then crystals which constitute a “mesophase”. This crystalline phase is formed after long reaction

times at high temperature. This hardened coke causes severe deactivation of the catalyst (Beuther *et al.*, 1980).

The principal chemical loss of activity in oxides and sulphides is due to the strong adsorption of coke molecules on acidic sites. Strong acid sites also play an important role in the formation of coke precursors which subsequently undergo condensation reactions to produce large polynuclear aromatic molecules that physically coat catalytic surfaces as represented in Figure 7.1 (a). Physical loss of activity also occurs as coke accumulates, ultimately partially or completely blocking catalyst pores as in supported metal catalysts. For example, in isomerisation of cis-butene on SiO_2/Al_2O_3 (Gayubo *et al.*, 1993) catalyst deactivation occurs by rapid, selective poisoning of strong acid sites; coke evolved early in the reaction is soluble in dichloromethane and pyridine and is slightly aromatic. Apparently, the blocking of active sites does not significantly affect porosity or catalyst surface area, as SiO_2/Al_2O_3 contains relatively large mesopores.

In zeolite catalysts, the formation of coke and the manner of deactivation are shape-selective processes, deactivation is mainly due to heavy aromatic clusters in pores and pore intersections, and both acid-site poisoning and pore blockage participate in the deactivation as represented in Figure 7.1(b). Thus, pore size and pore structures are probably more important than acid strength and density under typical commercial process conditions (Naccache, 1985; Guisnet and Magnoux, 1989; Bauer *et al.*, 1989; Grotten *et al.*, 1992; Bellare and Dadyburjor, 1993; Uguina *et al.*, 1993; Li *et al.*, 1994; Buglass *et al.*, 1995; Chen *et al.*, 1996; Guisnet *et al.*, 1997; Masuda *et al.*, 1999; Cerqueira *et al.*, 1999). Indeed, deactivation is typically more rapid in zeolites having small pores or apertures and/or a monodimensional structure (Guisnet *et al.*, 1997).

Figure 7.1 (a) Coke Formation on Metal Supported Catalysts (b) Coke Deactivation of Zeolite Catalysts



Thermogravimetric and Fourier Transform Infra Red (FTIR) analysis have been extensively used to characterise coke and ascertain the different types of reactions responsible for the deactivation of catalysts (Karge *et al.*, 1996; Binghui and Gonzalez, 1997). Kondo *et al.*, (2007) used infrared spectroscopy to study n-heptane isomerization over Pt/H-beta zeolites and the resultant coke. Matsushita *et al.*, (2004) studied the initial coke deposition on hydrotreating catalysts using TGA and FTIR. These two techniques have therefore been employed to characterize the coke and results are reported in the subsequent sections.

7.2 Analysis of Coke: Effect of Temperature

Catalyst samples were prepared specifically for coke analysis by running different experiments (P79-83) under various conditions for 3 hours in order to produce catalyst under similar conditions. Samples were prepared under reaction conditions of 400 - 450°C alongside a presulphided catalyst and a catalyst operated with hydrogen in the feed gas in order to assess the effect of the catalyst treatment on coke formation.

Figures 7.2 and 7.3 show the results of Thermogravimetric Analysis (TGA), as a function of temperature and time respectively, for catalysts operated at 400, 425 and 450°C compared with the original fresh CoMo catalyst (not used and treated). A constant purge of nitrogen was used to remove any volatile gases. For the original CoMo catalyst, which had undergone no other treatment before analysis, the loss of two types of water molecule can be distinguished. Firstly, the absorbed water leaves the catalyst below 200°C followed by the loss of hydroxyl groups from the alumina support at 800°C.

Figure 7.2 Thermogravimetric Analysis of Catalysts Run at Various Temperatures as a Function of Temperature

CoMo catalyst, 400-450°C, 20 bar g, 500 $ml.min^{-1}$, THAI gas and 1 $ml.min^{-1}$ oil

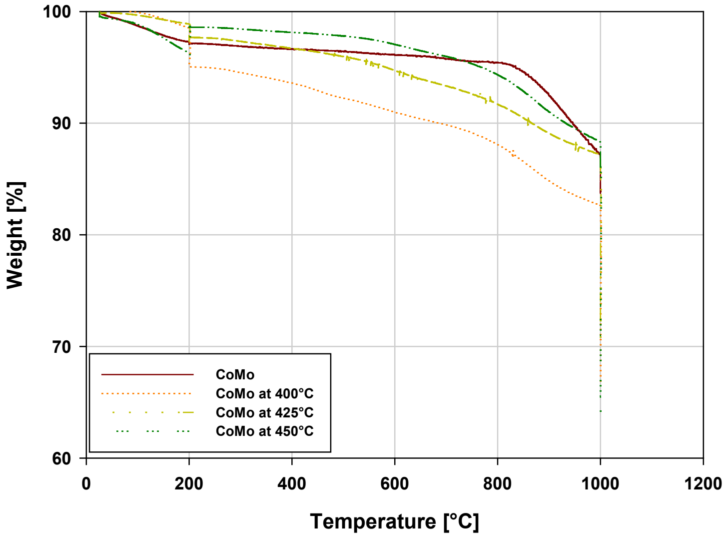
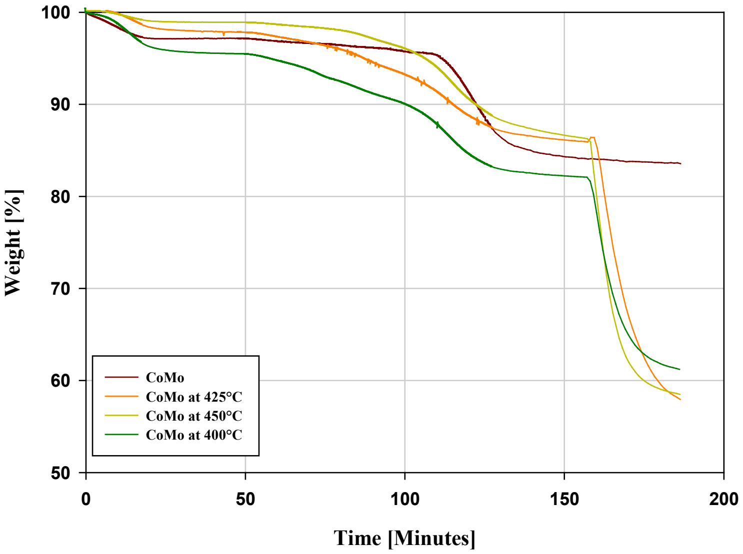


Figure 7.3 Thermogravimetric Analysis of Catalysts Run at Various Temperatures as a Function of Time
CoMo catalyst, 400-450°C, 20 bar g, 500 ml.min^{-1}, THAI gas and 1.0 ml.min^{-1} oil



In case of the three used catalysts, an earlier weight loss begins to occur after around 50 minutes or 200°C (Figure 7.2 and 7.3) which is expected to be associated with the loss of so-called 'soft' (chloroform-extractable) coke. The loss of the hydroxyl groups from the support is less obvious with the used catalyst, being most apparent in the catalyst run at the lower temperature. The overall weight loss appears similar whether from hydroxyl groups alone in the case of the original catalyst or from a loss of a combination of soft coke and hydroxyl groups. This suggests that either the surface hydroxyl groups have been modified during the reaction or that the hard coke on the catalyst is offering some shielding to the surface.

Table 7.1 Weight loss by CoMo Catalyst either Fresh or Coked at Different Temperatures
All catalysts except the Fresh CoMo were used for three hours in the CAPRI reactor under 20 bar g of THAI gas at an oil flow rate of 1 ml.min^{-1}

Pre-treatment	Wt. % loss at 200°C	Wt. % loss at 800°C*	Wt. % loss at 1000°C*
Fresh	2.85	1.72	11.72
400°C	4.96	5.22	9.74
425°C	2.31	4.27	9.37
450°C	1.41	2.54	18.48

*Values adjusted by subtracting the fresh CoMo values at similar temperature

After around 160 minutes, the gas supply was switched from nitrogen to air, with the sample maintained at 1000 °C. This led to the final weight loss observed in the used catalyst and can be attributed to the loss of 'hard' coke burnt off in the oxidising atmosphere. Hard coke, which is associated with a carbon aromaticity as opposed to the aliphatic soft coke, was in higher concentrations in the catalyst operated at 450°C. In the sample processed at 450 °C around 18.48% of the weight was lost after oxidation compared with around 10% for the two lower temperature runs (Table 7.1). In this case, assuming no loss of hydroxyl groups, hard coke composed around two-thirds of the total coke on the catalyst.

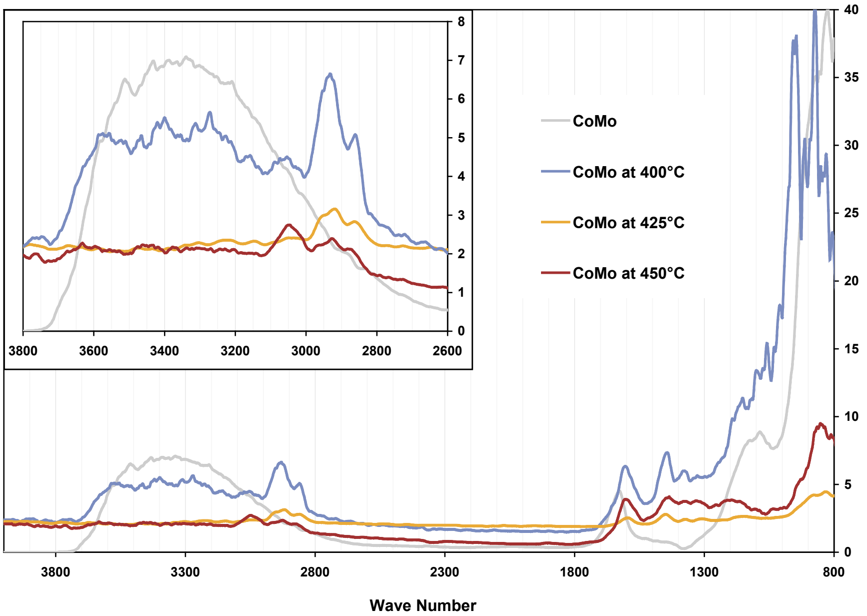
Similar findings were observed by Snape *et al.*, (1995) while characterizing coke on HDS catalysts using ^{13}C NMR. They found that soft coke accounts for typically about one-third of the carbon on deactivated catalysts from gas oil hydrotreating units. The soft coke is highly polar in nature, but possesses significant aliphatic character. The hard coke obtained in normal operating situations (5-7 % carbon) has a carbon aromaticity of not much more than 50% and comprises of small clusters. However, prolonged usage of catalysts with carbon content greater than 15% leads to a vast increase in aromaticity and ring cluster size.

Further analysis of the samples was conducted using DRIFT Spectroscopy in order to ascertain the nature of the carbon compounds deposited on the catalyst.

Referring to Figure 7.4, for the fresh $CoMo/Al_2O_3$ catalyst, the most noteworthy feature is the broad absorption band at around 3200-3400 cm^{-1} which is associated with hydroxyl groups and which is due to surface water and hydroxyl groups on the alumina support. It is notable that this broad band is absent from the two catalysts operated at higher temperatures (425 and 450°C) suggesting that the hydroxyl groups have indeed been lost as suggested by the thermal analysis. The broad band is partially observed for the sample operated at 400°C and explains why in TGA data the loss of hydroxyl groups at above 800°C appears to be superimposed on top of the loss of coke. Extrapolating from the TGA analysis, this suggests that around 5% of the weight lost from the 400°C sample is due to hydroxyl group loss and around 5% due to soft coke (Table 7.1).

A number of key absorption peaks are observed. The peak at around 3070 cm^{-1} and most prominent on the 450°C sample is associated with aromatic C-H bonds, supporting the indication of hard coke formation from the TGA data. The catalysts operated at 400 and 425°C show clear peaks at 2870, 2960 (methyl stretching) and 2925 cm^{-1} (methylene stretching) which result from C-H stretching in aliphatic chains. This is suggestive of soft coke and supports the findings noted with TGA above. In a similar study Matsushita *et al.* (2004) also observed peaks between 2845- 2970 cm^{-1} region and these aliphatic fractions were found soluble in tetrahydrofuran (THF), confirming that they belonged to the more softer coke.

Figure 7.4 DRIFT Spectroscopic Analysis of Catalysts Run at Various Temperatures
CoMo catalyst, 400-450°C, 20 bar g, 500 ml.min^{-1} THAI gas and 1.0 ml.min^{-1} oil



7.3 Analysis of Coke: Effect of Catalyst Pre-treatment and Reaction Media

Figures 7.5 and 7.6 illustrate the thermal analysis for three used catalysts: The first underwent pre-sulphiding as described previously in Section 3.1.15 of Chapter 3, the second was operated with 4% hydrogen in the gas feed (THAI) in an attempt to induce reduction of the catalyst while the third underwent no additional treatment and is shown for comparative purposes. Detailed experimental conditions can be found in Table 7.2.

Similar to the temperature studies (above), from Table 7.2 there is a weight loss observed between 200 and 800°C linked with the loss of soft coke and again there is a small indication that hydroxyl group loss occurs above 800°C, a feature perhaps most apparent with the pre-sulphided catalyst. When the gas stream is changed to air at 1000°C, the hard coke is once again burnt off and at this point significant differences between the three catalysts are evident. The catalyst operated with a hydrogen supplemented feed shows the highest degree of coking with around 17% of the original mass lost as hard coke, almost twice as much as the catalyst operated without hydrogen and otherwise identical reaction conditions. On the other hand, the pre-sulphided catalyst displayed the lowest quantity of hard coke – just 9% of the original sample weight.

Again, DRIFT Spectroscopy in Figure 7.7 supports these observations with an absorption peak at around 3070 cm^{-1} for the hydrogen supplemented catalyst indicative of aromatic C-H bonds and hard coke. Moreover, aliphatic absorption peaks at 2870, 2960 (methyl stretching) and 2925 cm^{-1} (methylene stretching) were observed in the spectra for the pre-sulphided catalysts. However, strong peaks are also observed at this wave number for the catalyst run in hydrogen which suggests that besides aliphatic content in the hard coke that more soft coke was also produced. This result is supported by the thermal analysis from which it was determined that an additional 4% total sample mass is made up of soft coke for the run carried out with 4% hydrogen compared with the non-treated catalyst.

Figure 7.5 Thermogravimetric Analysis of Catalysts Subjected to Different Treatments as a Function of Time

CoMo catalyst, 425°C, 20 bar g, 500 ml.min^{-1} gas and 1.0 ml.min^{-1} oil

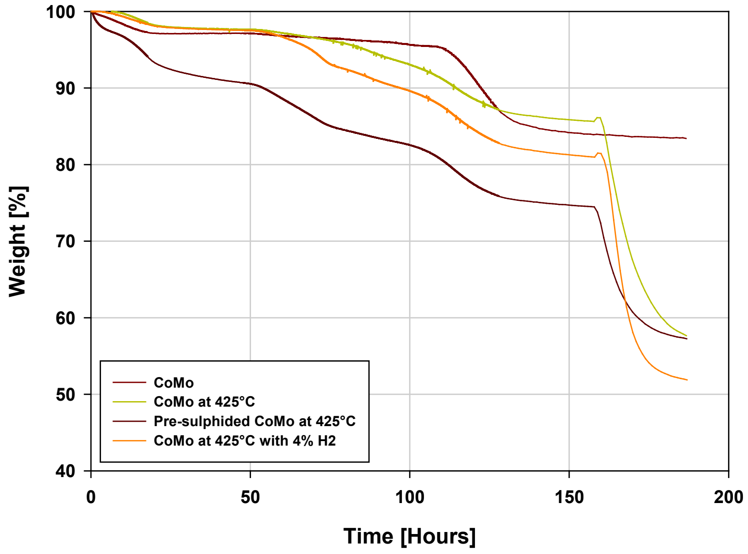


Figure 7.6 Thermogravimetric Analysis of Catalysts Subjected to Different Treatments as a Function of Temperature

CoMo catalyst, 425°C, 20 bar g, 500 ml.min^{-1} gas and 1.0 ml.min^{-1} oil

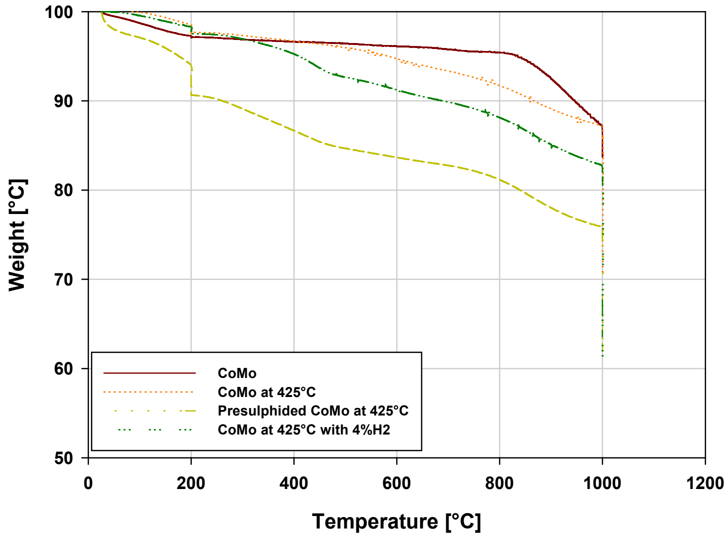


Table 7.2 Weight loss by CoMo Catalyst either Fresh or Coked under Different Reaction Media or Pre-Treated before Experiment

All catalysts except the Fresh CoMo were used for three hours in the CAPRI reactor
At 425°C and 20 bar g of THAI gas at an oil flow rate of 1 ml.min^{-1}

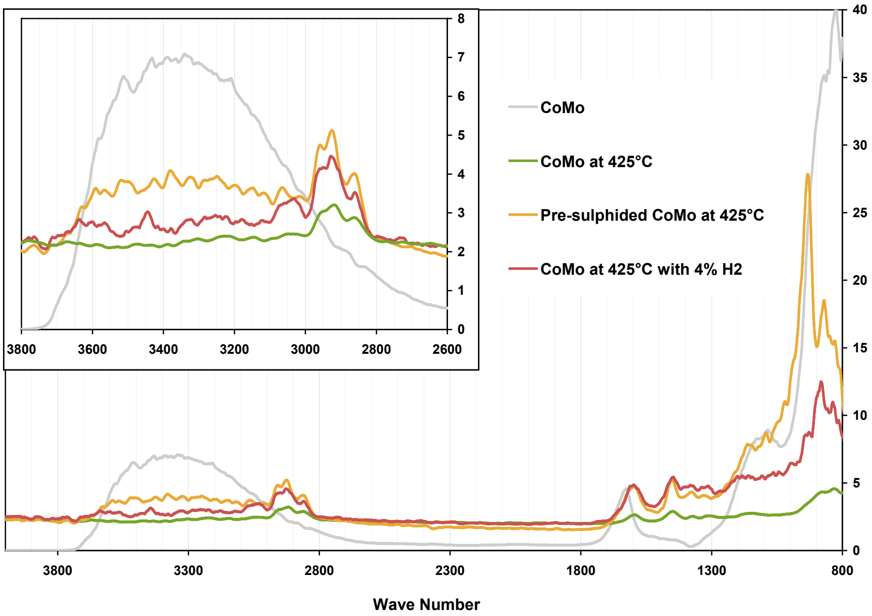
Pre-treatment	Wt. % loss at 200°C	Wt. % loss at 800°C*	Wt. % loss at 1000°C*
Fresh	2.85	1.72	11.72
-	2.31	4.27	9.37
Presulphided	9.33	7.79	9.17
4%H_2 in THAI	2.47	7.69	16.76

*Values adjusted by subtracting the fresh CoMo values at similar temperature

As already noted from Figure 7.7, there appears to be a suggestion of hydroxyl loss from all the runs except for the pre-sulphided catalyst, in fact the spectrograph shows a weak but broad absorption band at around 3200-3400 cm^{-1} symptomatic of hydroxyl groups. Topsoe and Topsoe (1993) reported that sulphidation of Mo/Al_2O_3 catalyst regenerated hydroxyl groups lost during the calcining stage. It can therefore be surmised that the basic hydroxyl groups on the alumina support may play a role in inhibiting the formation of hard coke. This is also supported by the fact that the pre-sulphided catalyst has the most coke content liberated under 200°C during the TGA experiment in comparison to the non-treated CoMo and the run with 4%H_2 added to THAI gas (Table 7.2). The pre-sulphided run also has the highest amount of soft coke indicating a further loss of more OH groups at 800°C.

Figure 7.7 DRIFT Spectroscopic Analysis of Catalysts Subjected to Different Treatments

CoMo catalyst, 425°C, 20 bar g, 500 $ml.min^{-1}$ gas and 1.0 $ml.min^{-1}$ oil



5.4 Discussion:

As discussed above, in a similar study Sahoo *et al.*, (2004) also observed three distinct regions, while characterizing coke using TGA. Region I (T < 200°C) was ascribed to the loss of water and volatile species in the sample, and the presence of volatile matter was put forward as a possible explanation why there is more loss of weight from the spent catalyst per gram. Region II (200 °C < T < 1000 °C) in the presence of nitrogen was ascribed to desorption of coke as CO or CO_2. The coke desorbed in region II was found to be more mobile carbonaceous residues or physisorbed products or side products and was termed as ‘soft coke’ altogether. In region III (T < 1000 °C in the presence of air), the more bulky carbonaceous compounds were termed as ‘hard coke’.

Shamsi *et al.*, (2005) observed that coke formed in reactions such as catalytic reforming, coke appears to be deposited on both the metal and support, with the more easily oxidized coke (soft coke) being on the metal. In current study though there is no direct evidence available to confirm this trend, however the appearance of aromatic peak at 3070 cm^{-1} at the support OH loss region (Figure 7.7) in the 4%H_2 addition experiment, indicates that this might be the case in the current study too.

In previous studies with supported bifunctional metal/metal oxide catalysts (e.g. CoMo or NiMo oxides supported on alumina), different kinds of coke were formed on the metal and the acidic oxide support, e.g. soft coke (high H/C ratio) on Pt or Pt-Re metals and hard coke (low H/C ratio) on the alumina support in catalytic reforming (Augustine *et al.*, 1989). In this case, coke precursors may be formed on the metal via hydrogenolysis, following which they migrate to the support and undergo polymerization and cyclization reactions, after which the larger molecules are dehydrogenated on the metal and finally accumulate on the support causing loss of isomerisation activity. Mild sulfiding of these catalysts (especially Pt-Re/alumina) substantially reduces the rate of hydrogenolysis and the overall formation of coke on both metal and support; it especially reduces the hard coke, which is mainly responsible for deactivation. Similar trends were also observed in this work, where harder coke was formed mostly on those catalysts surfaces where the support acid strength was high (e.g. the non treated catalyst at 425°C) and comparatively less hard coke or more soft coke was observed on catalysts which were sulphided.

Conclusions

In CAPRI process, the majority of the reactions are hydrocracking when the catalyst is used without pre-treatment and some other hydrotreating processes, such as HDS, may be happening when the catalyst is pre-sulphided or occur with the addition of small amounts of hydrogen. This finding further confirms that hydrogen addition does have a role in the upgrading of heavy oils resulting in some HDS activity and improving the quality of produced oil and producing relatively smaller amounts of hard coke. DRIFT spectroscopy confirms that at higher temperatures the coke is more aromatic and at lower temperatures less aromatic.

Chapter 8

Conclusions and Future Study Recommendations

8.1 Conclusions

CAPRI technology is an emerging heavy oil extraction and upgrading technology and the current work has demonstrated some of its key strengths and some weaknesses, which are listed as follows:

Effect of Operating Conditions

- CAPRI can effect further upgrading of partially upgraded THAI oil, with upgrading levels of viscosity and API gravity dependent upon temperature and oil flow rate. However majority of the upgrading observed in this work seems to result from thermal upgrading.
- There is a trade-off in operation temperature between upgrading performance and catalyst bed lifetime. For example, at 500 °C, upgrading of up to 6 °API occurs, but catalyst bed lifetime is reduced to 1.5 hours. Catalytic activity can be maintained for up to 95 hours at a relatively low operation temperature of 400 °C and 20 bar pressure.
- The optimum temperature was determined to be 425 °C at a pressure of 20 bar, for which additional upgrading by up to 3 °API of partially upgraded THAI oil was observed with operation time of 77.5 hours. This temperature represents a compromise between extending catalyst lifetime and achieving satisfactory upgrading.
- Upgrading of heavy oil is relatively unaffected by the pressure of the experimental system and the gas flow rate in the absence of higher concentrations of hydrogen.

Effect of Reaction Media and Properties of the Produced Products

- Addition of a small amount of hydrogen can lead to different reactions compared with feeds that do not contain hydrogen. Up to 15% hydrogen has been claimed to be present during THAI process, which may lead to improved upgrading of the THAI crude oil. Further investigation is needed to confirm this.
- Boiling fractions of the produced oil show a reduction of up to 140 °C as determined by SIMDIS analysis, and therefore the product would be expected to have greater commercial value than the THAI oil starting material. This effect is more prominent with the residue reduction by the high temperature experiment and with the addition of hydrogen.
- The gases evolved from the CAPRI process contains trace amounts of lighter hydrocarbons, which suggests that cracking of hydrocarbons, including side chains of naphthenic rings may be taking place in the process.
- From chemical analysis of the processed oil, the main mechanism of upgrading of the THAI field crude is by the condensation of the naphthenic and aromatic structures in the feed into larger condensed aromatic structures and therefore increasing the amount of aromatics in the processed oils. Small amounts of hydrogen release may also have been a result of this mechanism.
- From SARA analysis, the majority of the upgrading appears to be because of the change in naphthenic contents, whilst previous THAI and CAPRI experiments carried out at Bath University demonstrated that upgrading was largely because of the change in asphaltenes content. This may have been because most of the asphaltenes contents are consumed as fuel in the THAI process and the feed becomes more concentrated in conversion resistive asphaltenes, a fact also established from previous Bath laboratory

studies. Upgrading of a non-treated feed such as Athabasca bitumen may provide more HDA activity in this regard.

- HDM and HDS activities were negligible with most of the produced THAI field oil samples except in the produced oil samples at higher temperatures of 500°C. Being processed oil, THAI field oil may have been more concentrated in harder to remove metals and sulphur and experiments with non-treated feed such as Athabasca bitumen may be of interest.

Effect of Catalyst and Pre-treatment

- Without the presence of a dilating medium for example the high partial pressure of hydrogen, typical HDS catalyst are prone to severe coking and modified catalyst with non-acidic support may be of interest.
- The use of clays like Bentonite showed increase in the upgrading of THAI field crude and their optimization in future studies may be of interest.
- Pre-treatment of the catalyst does not seem to have a significant effect on the catalyst activity which includes pre-reducing the catalyst with hydrogen, pre-sulphiding the catalyst.

Addition of Water

- The addition of water did not show significant increase in the upgrading of the THAI field crude, however the use of water together with ionic salts has attracted significant attention in the past (Thomas *et al.*, 1989; del Bianco *et al.*, 1993) and whilst its role in this work did not show much improvement with the simple addition in the presence of the HDS catalyst CoMo, its use with ionic salts may be of interest for future studies.

Effect of Feed and Types of Coke

- Change in feed from THAI field oil to CCO did affect the upgrading behaviour of the catalytic cracking, in terms of higher upgrading under nitrogen or THAI gas. However CCO being the more paraffinic crude, responded more to 4% hydrogen addition in the reaction media than the THAI field oil, with a higher change of upgrading quality being observed when hydrogen was added to the feed.
- Catalyst coking occurs relatively early in the process and rapidly leads to complete pore plugging in the absence of any dilating media to remove the coke precursor and prolong the catalyst life. The effect is particularly severe at temperatures in the range 475 – 500 °C.
- The use of pre-sulphided catalysts showed relatively smaller amounts of refractory or hard coke and its role in future upgrading studies may be of interest.

8.2 Future Study Recommendations

Further developments of the CAPRI process will seek to extend further the catalyst lifetime, improve its activation, and reduce coke deposition. Use of a guard bed to remove heavy molecules from the feed, or use of large-pore catalysts which are more resistant to coke deposition are possible ways in which the process may be further improved in future studies. The guard bed should be a large pore structure and neutral in character to quench majority of the heavy metals like Ni and V, largely responsible for severe deactivation of hydroprocessing catalysts (Rana *et al.*, 2007).

The majority of the catalysts used in the current study were standard refinery catalysts, and in future studies tailored catalysts with varying porosity of support are strongly recommended. A combination of large pore supported catalysts at the surface for HDM, HDS and small pore catalysts just underneath the large pore catalyst is recommended for hydrocracking.

Operation under less severe conditions may also be of help in minimizing the deactivation of the catalyst. These measures may include reduced space velocity or reduced temperature (Thakur and Thomas, 1984; Shi *et al.*, 1980). In both cases, coking could be reduced but conversion would also be reduced. However, coking can be reduced and conversion increased by increasing the operating pressure of hydrogen (Thakur and Thomas, 1984). Pyrolysis reactions are free radical in nature and increased hydrogen pressure leads to increased free radical capping (Semenov, 1958). As a result, free radical intermediates are removed before polymerisation/condensation/coking can occur. This however may be not very practical to the THAI-CAPRI processes. The addition of sodium or potassium salts in water has been the subject of many investigations in the past, based on the assumption that the presence of catalyst will dissociate H_2O and release [H+]. The presence of oil soluble catalyst and water prevents the coke formation and deposition of sediment that often occurs during visbreaking (Thomas *et al.*, 1989; del Bianco *et al.*, 1993) or other hydrogen donor solvents addition could help minimize the catalyst deactivation of coke (Doyle, 1976).

From the effect of the reaction media on the CCO, it is clear that more paraffinic crudes respond well to even smaller amounts of hydrogen available. THAI field oil as discussed in Chapter 4 and 5 was relatively richer in aromatics in comparison to the CCO. However, if Athabasca bitumen is used as feed, this may potentially provide more upgrading with the use of catalyst and lesser amounts of hydrogen available by virtue of less aromatics. This bitumen may not be representative of THAI-CAPRI process in the field oil, yet will provide more insight into the upgrading behaviour of different feeds.

The effect of presulphiding the catalyst will also be of interest if used in combination with a hydrogen source.

The refinery gas analyser RGA could be fitted with a sulphur detector and calibrated for H_2S detection which will indicate the level of hydrodesulphurization readily and costly sulphur analysis can be avoided.

Bibliography

Aaarts J.J.B., Ternan, M. And Parsons, B.I. (1978) Catalytic desulphurization of Athabasca bitumen using hydrogen donors. *Fuel,* 57, 8, 473.

Augustine, S.M., Alameddin, G.N., Sachtler, W.M.H., (1989) The effect of Re, S, and Cl on the deactivation of Pt/γ-Al2O3 reforming catalysts. *Journal of Catalysis,* 115, 1, 217.

Absi-Halabi M, Stanislaus A, Trimm DL. (1991) Coke formation on catalysts during the hydroprocessing of heavy oils. *Applied Catalysis,* 72, 193.

Altgelt, K.H., and Boduszynski, M.M. (1994) *Compositional Analysis of Heavy Petroleum Fractions*. Marcel Dekker Inc., New York.

Ancheyta, J., Betancourt, G., Marroquı´n, G., Pe´rez, A., Maity, S. K., Cortes, M. T., del Rı´o, R. (2001) An Exploratory Study for Obtaining Synthetic Crudes from Heavy Crude Oils via Hydrotreating. *Energy and Fuels,* 15, 120.

Akin S. and Bagci, S. (2001) A laboratory study of single-well steam-assisted gravity drainage process, *Journal of Petroleum Science Engineering*, 32, 23.

Ancheyta, J., Betancourt, G., Marroquı´n, G., Centeno, G., Castan˜eda, L.C., Alonso, F., Mun˜oz, J.A., Go´ mez, M.T., Rayo, P., (2002) Hydroprocessing of Maya heavy crude oil in two reaction stages. *Applied Catalysis A: General*, 233, 159.

Alberta Chamber of Resources (2002) *Oil Sands Technology Roadmap.*

Ancheyta, J., Centeno, G., Trejo, F., Marroquı´n, G., (2003) Changes in Asphaltene Properties during Hydrotreating of Heavy Crudes. *Energy and Fuels*, 17, 1233.

Alberta Energy and Utilities Board (2004) *Alberta's Reserves and Supply/Demand Outlook/Overview 2005, Statistical Series* (ST), 2.

Ancheyta J., Rana M.S., Furimsky E. (2005) Hydroprocessing of heavy petroleum feeds: Tutorial. *Catalysis Today*, 109, 3.

Asghari, K., Taabboddi, L., Dong, M., (2005) A New Gel-Foam System for Water Shutoff Purposes in Wormhole Reservoirs, *Proceedings of the SPE/PSCIM/CHOA International Thermal Operations and Heavy Oil Symposium*, Calgary, Canada.

Al-Dalama K, Stanislaus A. (2006) Comparison between deactivation pattern of catalysts in fixed-bed and ebullating-bed residue hydroprocessing units. *Chemical Engineering Journal,* 120, 33.

Annual Reference Guide, (2007) *Unleashing the Potential of Heavy Oil, A supplement to EandP*. www.eandp.info. Accessed 8/1/2010.

Alberta Energy, *What is oil sands*? http://www.energy.gov.ab.ca/OilSands/793.asp.

Alberta Information Bulletin (2007) *Province Orders Suncor to Address Excessive H_2S Emissions*. http://alberta.ca/home/NewsFrame.cfm?ReleaseID¼/acn/

20071222769EEFBE725-9D96-985A-E4143B1351544456.html. Accessed 7/1/2010.

Alvarez, A., Ancheyta, J., Mun˜oz, J. A. D. (2007) Comparison of Quench Systems in Commercial Fixed-bed Hydroprocessing Reactors. *Energy and Fuels*, 21, 1133.

Alvarez, A., Ancheyta, J. (2008) Modeling residue hydroprocessing in a multi-fixed-bed reactor system. *Applied Catalysis A: General,* 351, 148.

Alberta Government Information Centre, (2010) *Frequently Asked Questions – Oil Sands.* http://environment.gov.ab.ca/info/faqs/faq5-oil_sands.asp. Accessed 7/1/2010.

ASTM Standards (2011) www.astm.org/standards.

Baker, E.W., (1969) *Organic Geochemistry*. Springer-Verlag, New York.

Burger, J. and Sahuquet, B. (1971) DP 14 (4) Basic Research on Combustion in situ and recent results on field, *Rev. Inst. Franc. Du Petrole*, 26, 399.

Baker, E.W., and Palmer, S.E. (1978) *In The Porphyrins. Volume I. Structure and Synthesis. Part A.* D. Dolphin Editor). Academic Press, New York.

Bunger, J.W., Thomas, K.P., and Dorrence, S.M. (1979) Compound types and properties of Utah and Athabasca tar sand bitumens. *Fuel*, 58, 183.

Beeckman, J.W. and Froment, G.F. (1979) Catalyst Deactivation by Active Site Coverage and Pore Blockage. *Industrial Engineering Chemistry Fundamentals,* 18, 3, 245.

Binghui Li, Gonzalez, R.D. (1997) TGA/FT-IR studies of the deactivation of sulphated zirconia catalysts. *Applied Catalysis A: General*, 165, 291.

Beuther, H., Larson, O.H., Perrotta, A.J., in: Delmon, B., Froment, G.F. (Eds.), (1980) Catalyst Deactivation, *Studies in Surface Science and Catalysis,* Vol. 6, Elsevier, Amsterdam, 271.

Bearden, R., Aldridge, C.L., (1981) Novel catalyst and process to upgrade heavy oils. *Energy Programme,* 1, 1-4, 44.

Butler, R.M. and Stephens, D. J. (1981) The Gravity Drainage of Steam Heated to Parallel Horizontal Wells, *Journal of Canadian Petroleum Technology*, 20, 90.

Brooks, J., and Welte, D.H. (1984) *Advances in Petroleum Geochemistry.* Academic Press Inc., New York.

Butler, R. M. (1985) A New Approach to the Modeling of. Steam-Assisted Gravity Drainage, *Journal of Canadian Petroleum Technology*, 24, 42.

Baker, E.W., and Louda, J.W. (1986) *Biological Markers in the Sedimentary Record*. R.B. Johns (Editor). Elsevier, Amsterdam.

Bauer, F., Karazirev, V., Vlaev, C., Hanisch, R., Weiss, W. (1989) Design aspects of MOS controlled thyristor elements. *Chemische Technik*, 41, 297.

Bhatia, S., Beltramini, J., Do, D.D., (1989–1990) Deactivation of zeolite catalysts. *Catalysis Reviews, Science and Engineering,* 31, 431.

Butler, R. M. (1991) *Thermal Recovery of Oil and Bitumen*, Prentice Hall, New Jersey USA, 7, 285.

Bernard, F. P., Connan, J., Magot, M., (1992) Indigenous microorganisms in connate water of many oil fields: a new tool in exploration and production techniques. *Proceedings of the SPE Annual Technical Conference and Exhibition*, Washington, D.C, 2, 467.

Bartholomew, C.H. (1992) *Catalysis, Specialist Periodical Report*, Vol. 10, Royal Society of Chemistry.

Grotten, W.A., Wojciechowski, B.W., Hunter, B.K. (1992) On the relationship between coke formation chemistry and catalyst deactivation. *Journal of Catalysis,* 138, 343.

Bellare A., Dadyburjor D. B. (1993) Evaluation of Modes of Catalyst Deactivation by Coking for Cumene Cracking over Zeolites. *Journal of Catalysis,* 140, 510.

Bryant, R. S., (1994) Microbial Enhanced Hydrocarbon Recovery and Its Potential for Application to North-Sea Reservoirs, *Chemical Engineering Research and Design*, 72, 144.

Buglass, J.G., Jong, K.P.D., Mooiweer H.H. (Eds.), (1995) in: *Proceedings of the 120th National Meeting of the American Chemical Society on Analytic Studies of the Coking of the Zeolite Ferrierite*, 20–24 August, 631.

Bartholomew, C.H., Fuentes, G.A. (1997) Catalyst Deactivation, *Studies in Surface Science and Catalysis,* Vol. 111, Elsevier, Amsterdam.

Bataille, F., Lemberton, J.-L., Michaud, P., Perot, G., Vrinat, M., Lemaire, M., Schulz, E., Breysse, M.E., Kasztelank, S. (2000) Alkyldibenzothiophenes Hydrodesulfurization-Promoter Effect, Reactivity, and Reaction Mechanism. *Journal of Catalysis*, 191, 409.

Bartholomew C. H. (2001) Mechanisms of catalyst deactivation. *Applied Catalysis A: General*, 212, 17.

Bartholmew, C., (2002) *Catalyst Deactivation/Regeneration*, Encyclopedia of Catalysis, Wiley, New York.

Baeza, P., Villarroel, M., Avila, P., Lspez-Agudo, A., Delmon, B., il-Llambmas, F.J., (2006) Spillover hydrogen mobility during Co–Mo catalyzed HDS in industrial-like conditions *Applied Catalysis*, 304, 109.

Babusiaux, D., (2007) *Oil and Gas Exploration and Production, Reserves, Costs and Production*, Paris, TECHNIP edn, chap. 1, 51.

Behera, B., Ray S.S., and Singh I.D., (2007) NMR studies of FCC feeds, catalysts and coke. *Studies in Surface Science and Catalysis,* 166, 163.

Bitumenes Orinoco, S.A. Orimulsion, (2010) ‘‘*Natural Energy For a Brighter World*’’, http://www.sovereign-publications.com/bitumene.htm. Accessed 7/1/2010.

Charbonnier, R.P., Draper, R.G., Harper, W.H., and Yates, A. (1969) *Analyses and Characteristics of Oil Samples from Alberta*. Information Circular IC 232. Department of Energy Mines and Resources, Mines Branch, Ottawa, Canada.

Clark P.D., Hyne J.B., Tyrer J.D. (1983) Chemistry of organosulphur compound type occurring in heavy oil sands. 1. High temperature hydrolysis and thermolysis of tetrahydrothiophene in relation to steam stimulation processes. *Fuel,* 62, 959.

Clark P.D., Hyne J.B., (1984) Steam-Oil chemical reactions: mechanisms for the aquathermolysis of heavy oil. *AOSTRA J Researcher*, 1, 15.

Cooper B.H., Donnis B.B.L., Moyse B. (1986) *Oil and Gas Journal*, 84:39.

Clark P.D., Hyne J.B. (1990) Studies on the chemical reactions of heavy oils under steam stimulation condition. *AOSTRA J Researcher*, 6, 29-39.

Chen, D., Rebo, H.P., Moljord, K., Holmen, A. (Eds.), (1996) Effect of coke deposition on transport and adsorption in zeolites studied by a new microbalance reactor, in: *Proceedings of the 14th International Symposium on Chemical Reaction Engineering*, Part B, 5–9 May, 2687.

Caloch B, Rana M.S., Ancheyta J. (2005) Improved hydrogenolysis (C–S, C–M) function with basic supported hydrodesulfurization catalysts. *Catalysis Today*, 98, 91.

Clark, B., Graves, W. G., Lopez-de-Cardenas, J. E., Gurfinkel M. E., and Peats, A. W. (2007) *Heavy oil, Working Document of the NPC Global Oil and Gas Study.*

Camp, F.W. (1976) *The Tar Sands of Alberta*. Cameron Engineers, Denver, Colorado.

Cheih, C. (1977) A Study of Fireflood Field Projects, *Journal of Petroleum Technology*, 29, 111.

Chang, H. L. (1978) Polymer Flooding Technology – Yesterday, Today and Tomorrow, *Journal of Petroleum Technology*, 30, 1113.

Cheih, C. (1982) State-of-the-Art Review of Fireflood Field Projects, *Journal of Petroleum Technology,* 34, 19.

Clark P.D., Hyne J.B., Tyrer J.D., (1984) Chemistry of organosulphur compound type occurring in heavy oil sands. 2. Influence of pH on the high temperature hydrolysis of tetraothiophene and thiophenes. *Fuel*, 63, 125.

Cerqueira, H.S., Magnoux, P., Martin, D., Gusinet, M., in: Delmon, B., Froment G.F. (Eds.), (1999) Catalyst Deactivation, *Studies in Surface Science Catalysis,* 126, Elsevier, Amsterdam, 105.

Curtis, C., Kopper, R., Decoster, E., Guzm_an-Garcia, A., Huggins, C., Knauer, L., Minner, M., Kupsch, N., Linares, L. M. Rough, H., and M. Waite, (2002) Heavy Oil Reservoirs, *Oilfield Review*, 14, 42.

Castanier L. M. and Brigham, W. E. (2003) Upgrading of crude oil via in situ combustion. *Journal of Petroleum Science and Engineering*, 39, 125.

Chen, Z. J. (2006) Heavy Oils Part I. *SIAM News*, 39, 3.

Doyle, G. (1916) *American Chemical Society, Preprints, Division of Petroleum Chemistry,* 21, 1,165.

Dunning, H.N., Moore, J.W., Bieber, H., and Williams, R.B. (1960) Porphyrin, Nickel, Vanadium, and Nitrogen in Petroleum. *Journal of Chemical Engineering Data*, 5, 547.

Draper, R.G., Kowalchuk, E., and Noel, G. (1977) *Analyses and Characteristics of Crude Oil Samples Performed Between 1969 and 1976*. Report ERP/ERL 77-59 (TR). Department of Energy Mines and Resources, Ottawa, Canada.

Dreher K. D. and Gogarty, W. B. (1979) An overview of mobility control in micellar - polymer enhanced oil recovery. *Journal of Rheology,* 23, 209.

Durand, B. (1980) *Kerogen: Insoluble Organic Matter from Sedimentary Rocks*. Editions Technip, Paris, France.

Decrooocq, D. (1984) *Catalytic Cracking of Heavy Petroleum Fractions*, Gulf Publishing Co., Houstan, TX.

Del-Bianco, A., Panariti, N., Prandini B., Beltrame, P.L., Carnita, P. (1993) Thermal Cracking of Petroleum Residues: 2. Hydrogen-Donor Solvent Addition. *Fuel*, 72, 81.

De-Bruijn, T.J.W., Ikura, M., Ternan, M., Patmore, D.J., Hogan, C.M. (1993) *Proceedings of the Oil Sands our Petroleum Future Conference, Edmonton, Canada*, 4–7 April, 357.

Das S. K. and Butler, R. M. (1995) Extraction ofHeavy Oil andBitumen. Using Solvents at Reservoir Pressure. *Proceeding of the Sixth Petroleum Conference of the South Saskatchewan Section of the Petroleum Society of CIM*, Regina, Sask.

Donelly J. K. and Pendergast. D. R. (1999) *Nuclear Energy in Industry: Application to Oil Production*. http://www.ecolo.org/documents/documents_in_english/oil-sands-nuke-Donnelly-05.pdf (Accessed 7/1/2010).

Dusseault, M., (2002) *Oil Sands - Reports - CHOPS Study*, Govt. of Alberta,Canada.

Dupain, X., Gamas, E.D., Madon, R., Kelkar, C.P., Makkee, M., Moulijn, J.A. (2003) Aromatic gas oil cracking under realistic FCC conditions in a microriser reactor. *Fuel*, 82, 1559.

Degnan, T. F. Jr (2007) Recent progress in the development of zeolitic catalysts for the petroleum refining and petrochemical manufacturing industries. *Studies in Surface Science and Catalysis*, 170, 54.

Ding, L., Zheng, Y., Zhang, Z., Ring, Z., Chen, J., (2007) HDS, HDN, HDA, and hydrocracking of model compounds over Mo-Ni catalysts with various acidities. *Applied Catalysis A: General,* 319, 25.

Erdman, J.G., and Harju, P.H. (1963) Capacity of Petroleum Asphaltenes to Complex Heavy Metals. *J. Chem. Eng. Data.,* 8, 252.

Eglinton, G., and Murphy, B. (1969) *Organic Geochemistry: Methods and Results*. Springer-Verlag, New York.

Earlougher, R. C., O'Neal, J. E., Surkalo, H. (1975) Micellar Solution Flooding: Field Test Results And Process Improvements. *Proceedings of the Rocky Mountain Regional Meeting of the Society of Petroleum Engineers*, Denver, CO, USA.

Etebar, S. (1995) *Proceedings of the SPE Offshore Europe Conference*, Aberdeen, http://www.ecolo.org/documents/documents_in_english/oil-sands-nuke-Donnelly-05.pdf. Accessed 7/1/2010.

EandP, Annual Reference Guide, (June 2007) Unleashing the Potential of Heavy Oil, *A supplement to EandP*, www.eandp.info.

Expanding Heavy Oil and Bitumen Resources While Mitigating GHG Emissions and Increasing Sustainability (Accessed 8/1/2010).

Farouq Ali S. M. and Meldau, R. F., (1979) Current Steamflood Technology. *Journal of Petroleum Technology,* 31, 1332.

Farouq Ali S. M., (1982) *Steam Injection Theory – A Unified Approach*, paper SPE 10746, California Regional Meeting of the Society of Petroleum Engineers, San Francisco, March 24–26.

Franceskin, P.J., Gonzalez-Jiminez, M.G., DaRosa, F., Adams, O., and Katan, L. (1986) *Hyperfine Interactions*. 28, 825.

Filby, R.H. and Van Berkel, G.J. (1987) *Metal Complexes in Fossil Fuels.* Symposium Series No. 344. American Chemical Society, Washington, DC, 2.

Farrauto, R.J., Bartholomew, C.H. (1997) *Fundamentals of Industrial Catalytic Processes*, Chapman & Hall, Kluwer Academic Publishers, London.

Furimsky, E. (1998) Selection of catalysts and reactors for hydroporcessing. *Applied Catalysis A: General,* 171, 177.

Furimsky E., Massoth F.E. (1999) Deactivation of hydroprocessing catalysts. *Catalysis Today,* 52, 381.

Flint. L. (2004) *Bitumen and Very Heavy Crude Upgrading Technology. A Review of Long Term RandD Opportunities*. LENEF Consulting Limited.

http://www.ptac.org/links/dl/osdfnlreport.pdf. Accessed 7/1/2010.

Greensfelder, B. S. (1955) *The Chemistry of Petroleum Hydrocarbons*, Brooks, Rainhold Publishing, New York, 2, 137.

Gruse, W.A., and Stevens, D.R., (1960) *The Chemical Technology of Petroleum*. McGraw-Hill, New York.

Gogarty W. B. and Tosch, W.C. (1968) Miscible-type Waterflooding: Oil Recovery with Micellar Solutions. *Journal of Petroleum Technology,* 20, 1407.

Gates, B.C., Katzer, J.R., Sch uit, G.C.A. (1979) *Chemistry of Catalytic Processes*, McGraw-Hill, New York.

Gould, K.A. (1983) Influence of thermal processing on the properties of Cold Lake asphaltene. 2. Effect of stream treatment during oil recovery. *Fuel,* 62, 370.

Gray, M.R. Khorasheh, F., Wanke, S.E., Achia, U., Krzywicki, A., Sanford, E.C., Sy, O.K.Y., Ternan, M., (1992) Role of Catalyst in Hydrocracking of Residues from Alberta Bitumens. *Energy & Fuels,* 6, 4.

Gayubo, A.G., Arandes, J.M., Aguayo, A.T., Olazar, M., Bilbao, J. (1993) Calculation of the kinetics of deactivation by coke of a silica-alumina catalyst in the dehydration of 2-ethylhexanol, *Industrial and Engineering Chemistry Research*, 32, 588.

Gao, S. T., Li, H. B., Yang, Z. Y., Pitts, M. J., Surkalo H., and Wyatt, K. (1996) Alkaline-Surfactant-Polymer Pilot Performance of the West Central Saertu, Daqing Oil Field. *SPE Reservoir Engineer*, 181.

Guisnet, M., Magnoux, P., Martin, D. in: Bartholomew, C.H., Fuentes G.A. (Eds.), (1997) Catalyst Deactivation, *Studies in Surface Science and Catalysis*, 111, 1.

Gosselink JW. (1998) Metal sulphides and refinery processes. *CatTech.*, 22, 127.

Greaves, M., El-Saghr A. and Xia T.X. (2000) *CAPRI Horizontal Well Reactor for Catalytic Upgrading of Heavy Oil.* Presented at the ACS Symposium, Division of Petroleum Chemistry, on Advances in Oil Field Chemistry: Downhole Upgrading, 20-25 Washington DC, August. ACS Preprints, 45, 4, 525.

Greaves, M., Xia, T.X., Turta, A.T., and Ayasse, C., (2001) THAI-New Air Injection Technology for Heavy Oil Recovery and In Situ Upgrading. *Journal of Canadian Petroleum Technology*, 40, 3.

Goldschmidt A. and Streitbeger H. J. (2003) *Basf Handbook on Basics of Coating Technology* (American Coatings Literature) Vincentz Publishers.

Govinda R. Timilsina, Nicole LeBlanc and Thorn Walden (2005) Economic Impacts of Alberta's Oil Sands, *Canadian Energy Research Institute, Study No.* 110 ISBN 1 896091-47-

Guisnet, M., Magnoux, P. (1989) Coking and deactivation of zeolites: Influence of the Pore Structure. *Applied Catalysis,* 54, 1.

Gates I. D. and Chakrabarty, N. (2006) *Journal of Canadian Petroleum Technology*, 45, 54.

Gates, I. D. (2007) Oil phase viscosity behaviour in Expanding-Solvent Steam-Assisted Gravity Drainage. *Journal of Petroleum Science Engineering*, 59, 123.

Greaves M. and Xia T. X. (2008) Stability of THAI ™ Proces – Theoretical and Experimental Observations. *Journal of Canadian Petroleum Technology,* 47, 9, 65.

Greenpeace Canada, (2010) *Stop the Tar Sands: Threats: Water Depletion*. http://www.greenpeace.org/canada/en/campaigns/tarsands/threats/water-depletion. Accessed 7/1/2010.

Holm, L. W., (1959) *Transactions of the American Institute of Mining and Metallurgical Engineers*, 216, 225.

Hodgson, G.W., Baker, B.L., and Peake, E. (1967) *Fundamental Aspects of Petroleum Geochemistry*. B. Nagy and U. Columbo (Editors). Elsevier, Amsterdam.

Houalla, M., Nag, N.K., Sapre, A.V., Broderick, D.H., Gates, B.C. (1978) Hydrodesulfurization of dibenzothiophene catalyzed by sulphided CoO-$MoO_3\gamma$-Al_2O_3: The reaction network. *AIChE J.,* 24, 1015.

Hajdo, L.E., Hallam R.J. and Vorndran L.D.L. (1985) *Hydrogen Generation During In-Situ Combustion*. PSE Paper No 13661, presented at the SPE California Regional Meeting, Bakersfield California (March) 27-29.

Hyne J.B., (1986) Aquathermolysis. A synopsis of work on the chemical reactions between water on the chemical reactions between water and heavy oil sands during simulation steam stimulation. *AOSTRA synoposis No. 50*.

Hyne J.B., Greidanus J.W., Tyrer J.T., *et al.* (1988) Aquathermolysis of heavy oil and tar sands. *The second UNITAR international conference on heavy crude oil and tar sands. Petroleum Industrial Press*, Beijing, 278-86.

Hitzman, D.O., Sperl, G.T., (1994) A New Microbial Technology for Enhanced Oil Recovery and Sulphide Prevention and Reduction. *Proceedings of the SPE/DOE ninth Symposium on Improved Oil Recovery*, Tulsa, OK, USA.

Hongfu, F., Yongjian, L., Xiaofei, Z., (2001) Downhole aquathermolysis catalytic upgrade heavy oils. *Oilfield Chem. (Chin)*, 18, 1, 13.

Hongfu, F., Yongjian, L., Liying, Z., and Xiaofei, Z., (2002) The study on composition changes of heavy oils during steam stimulation processes. *Fuel,* 81, 13, 1733.

Head, I.M., Jones, D.M., and Larter, S.R. (2003) Biological activity in the deep subsurface and the origin of heavy oil: *Nature*, 426, 20, 344.

Head, I., Riediger, C. And Fowler, M., (2006) The controls in the composition of biodegraded oils in the deep subsurface: part II. Geological controls on subsurface biodegradation fluxes and constraints on reservoir-fluid property prediction: *American Association of Petroleum Geologists Bulletin*, 90, 6, 921.

Highlighting Heavy Oil (2010) http://www.heavyoilinfo.com/feature_items/article-downloads/copy_of_heavy-oil-article_en.pdf. Accessed 8/1/2010.

IEA (International Energy Agency) (2010) *Oil Market Report,* www.oilmarketreport.org.

IEA (2010) *World Energy Outlook*, www.wouldenergyoutlook.org.

Johnson, C. E., (1976) Status of Caustic and Emulsion Methods. *Journal of Petroleum Technology*, 1, 85.

Jayasekera, A. J. and Goodyear, S. G., (1999) The Development of Heavy Oil Fields in the U.K. Continental Shelf: Past, Present and Future. *Proceedings of the SPE Western Regional Meeting*, Anchorage, USA.

Jiang, Q., Butler R. and Yee, C. T. (2000) The steam and gas push (SAGP)-2: mechanism analysis and physical model testing. *Journal of Canadian Petroleum Technology*, 39, 52.

Jayasekera, A. T. and Goodyear, S. G. (2000) The development of heavy oil fields in the United Kingdom continental shelf: past present and future. *Reservoir Evaluation and Engineering*, 3, 371.

Jones, D.S.J., and Pujadó, P.P., (2006) *Handbook of Petroleum Processing*. Springer; 1 edition.

Jones, D. M., Head, I. M., Gray, N. D. , Adams, J. J., Rowan, A. K., Aitken, C. M., Bennett, B., Huang, H., Brown, A., Bowler, B. F. J., Oldenburg, T., Erdmann M. and Larter, S. R.

(2008) Crude-oil biodegradation via methanogenesis in subsurface petroleum reservoirs. *Nature,* 451, 176.

Krumrine, P. H., Falcone, J. S., (1983) *Proceeding of the SPE International Symposium on Oilfield and Geothermal Chemistry*, Denver, CO.

Kamath, V. A. Sinha, S., Hatzignatiu, U. (1993) Simulation study of steam-assisted gravity drainage process in Ugnu Tar Sand reservoir. *Proceedings of the SPE Western Regional Meeting Held in Anchorage*. SPE, Alaska U.S.A, pp. 26–28.

Kabe, T., Ishihara, A., Zhang, Q. (1993) Deep desulfurization of light oil. Part 2: hydrodesulfkrization of dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. *Applied Catalysis A: General*, 97, L1.

Karge, H.G., NieBen, W., Bludau, H. (1996) In-situ FTIR measurements of diffusion in coking zeolite catalysts. *Applied Catalysis A: General*, 146, 339.

Kennepohl, D., Sanford, E. (1996) Conversion of Athabasca Bitumen with Dispersed and Supported Mo-Based Catalysts as a Function of Dispersed Catalyst Concentration. *Energy and Fuels*, 10, 1, 229.

Kim, J.W., Longstaff D.C. and Hanson F. V. (1997) Upgrading of bitumen-derived heavy oils over a commercial HDN catalyst. *Fuel*, 76, 12.

Kressmann S., Morel F., Harle´ V., Kasztelan S. J. (1998) Recent developments in fixed-bed catalytic residue upgrading. *Catalysis Today,* 43, 203.

Knudsen, K.G., Cooper, B.H., Topsøe H. (1999) Catalyst and process technologies for ultra low sulfur diesel. *Applied Catalysis A: General*, 189, 205.

Kisman, K. E. and Yeung, K. C. (1995) Numerical study of the SAGD process in the Burnt Lake oil sands lease. Proceedings of the SPE International Heavy Oil Symposium Held in Calgary, Canada International heavy oil symposium : Calgary AB, 19-21 June.

Kam, E.K.T., Al-Simali, Juraidan M., Qabazard H. A. (2005) Hydroprocessing Multi catalyst Deactivation and Reactor Performance Model−Pilot-Plant Life Test Applications. *Energy and Fuels*, 19, 753.

Kondo, J.N., Yang, S., Zhu, Q., Inagaki, S., and Domen, K., (2007) In situ infrared study of n-heptane isomerization over Pt/H-beta zeolites, *Journal of Catalysis,* 248, 1, 15, 53.

Leonard, J., (1986) Increased rate of EOR brightens outlook. *Oil Gas J.*, 84, 71.

Lake, L. W. (1989) *Enhanced Oil Recovery, Prentice Hall*, Englewood Cliffs, New Jersey.

Li, C., Chen, Y., Yang, S., Yen, R., (1994) In-situ FTIR investigation of coke formation on USY zeolite. *Applied Surface Science,* 81, 465.

Lyons W. C. and Zaba, J. (1996) *Standard Handbook of Petroleum and Natural Gas Engineering,* Gulf Professional Publishing, vol. 2.

Landau, M. V., (1997) Deep hydrotreating of middle distillates from crude and shale oils. *Catalysis Today,* 36, 393.

Lapinski M. P. (1998) *Catalytic cracking process with Y zeolite catalyst comprising silica binder containing silica gel*. United States Patent 5788834.

Looij, F.V., Van der Laan, P., Stork, W.H.J., DiCamillo D.J., and Swain J., (1998) Poisoning of thiophenes hydrodesulphurization by nitrogen compounds. *Journal of Applied Catalysis A*: *General*, 170, 1.

Larter, S, Whilhelms, A., Head, I., Koopmans, M., Aplin, A., Di Primio, R., Zwach, C., Erdmann, M., and Telnaes, N. (2003) The controls on the composition of biodegraded oils in the deep subsurface – part 1: biodegradation rates in petroleum reservoirs: *Organic Geochemistry,* 34, 3, 601.

Larter, S., Huang, H., Adams, J., Bennett, B., Jokanola, O., Oldenburg, T., Jones, M., Head, I., Riediger C. and Fowler, M. (2006) *American Association of Petroleum Geologists Bulletin*, 90, 921.

Lombardi, S., Altunina, L. K. and Beaubien, S. E., (2006) Advances in Geological Storage of Carbon Dioxide: International Approaches to Reduce Anthropogenic Greenhouse Gas Emissions, *NATO Science Series IV Earth and Environmental Sciences,* 65, 271.

Meyer, R.F., and Steele, C.F (Editors) (1981) *The Future of Heavy Crude and Tar Sands*, McGraw-Hill. New York.

Miki, Y., Yamadaya, S., Oba, M., Sugimoto, Y. (1983) Role of catalyst in hydrocracking of heavy oil. *Journal of Catalysis*, 83, 371.

Mayer, E. H., Berg, R. L., Carmichael J. D. and Weinbrandt, R. M. (1983) Alkaline Injection for Enhanced Oil Recovery - A Status Report. *Journal of Petroleum Technology*, 209.

Meyerhoff, A. A. and Meyer, R. F. (1987) *Proceedings of the 12th World Petroleum Congress*, Houston, USA.

Meille, V., Schulz, E., Lemaire, M., Vrinat, M., (1997) Hydrodesulfurization of Alkyldibenzothiophenes over a NiMo/Al_2O_3 Catalyst: Kinetics and Mechanism. *Journal of Catalysis,* 170, 29.

Moore, R. G., Laureshen, C. J., Belgrave, J. D. M., Ursenbach M. G. and Methta, S. A. (1997) In-situ combustion heavy-oil reservoirs: problems and perspectives. *In situ,* 21, 1.

Moore, R.G., Laureshen, C.J., Mehta, S.A., Ursenbach, M.G., Belgrave, J.D.M., Weissman, J.G. and Kessler R.V. (1999) A Downhole Catalytic Upgrading Process for Heavy Oil Using In Situ Combustion, *Journal of Canadian Petroleum Technology,* 38, 13, 96.

Masuda, T., Tomita, P., Fujikata, Y., Hashimoto, K. in: Delmon, B., Froment G.F. (Eds.), (1999) Catalyst Deactivation, *Studies in Surface Science Catalysis,* 126, 89.

Miller C. A. and Srivastava, R. K., (2000) The combustion of Orimulsion and its generation of air pollutants. *Progress in Energy and Combustion Science*, 26, 131.

Microbial Sediments, ed. R. E. Ridding, S. M. Awramik, (2000) *Springer-Verlag Berlin and Heidelberg GmbH and Co. KG*, illustrated edition, 118.

Meyer, R. F. and Attanasi, E. D. (2003) Heavy Oil and Natural Bitumen-Strategic Petroleum Resources*, U.S. Geological Survey*, Fact Sheet 70-03 - Online Version 1.0.

Maity S.K., Ancheyta J., Soberanis L., Alonso F., Llanos M.E. (2003) Alumina–titania binary mixed oxide used as support of catalysts for hydrotreating of Maya heavy crude. *Applied Catalysis A: General,* 244, 141.

Marafi, A., Fukase, S., Al-Marri, M., Stanislaus, A. (2003) A Comparative Study of the Effect of Catalyst Type on Hydrotreating Kinetics of Kuwaiti Atmospheric Residue. *Energy and Fuels*, 17, 661.

Matsushita, K., Hauser, A., Marafi, A., Koide, R., and Stanislaus, A. (2004) Initial coke deposition on hydrotreating catalysts. Part 1. Changes in coke properties as a function of time on stream. *Fuel*, 83, 7-8, 1031.

Maity S.K., Ancheyta J, Rana M.S. (2005) Support Effects on Hydroprocessing of Maya Heavy Crude. *Energy and Fuels*, 19, 343.

Maity SK, Ancheyta J, Rana MS, Rayo P. (2006) Alumina−Titania Mixed Oxide Used as Support for Hydrotreating Catalysts of Maya Heavy Crude-Effect of Support Preparation Methods. *Energy and Fuels,* 20, 427.

Mut, S., (2006) *MarketWatch*, Available at http://www.tellshell.net/blog/MarketWatch

/_archives/2006/8/12/2223600.html.

Meyer, R. F., Attanasi, E. D. and Freeman, P. A. (2007) Heavy Oil and Natural Bitumen Resources in Geological Basins of the World. *US Geological Survey*, Virginia, http://pubs.usgs.gov/of/2007/1084/OF2007-1084v1.pdf. Accessed 8/1/2010.

Nagai, M. and Kabe T., (1983) Selectivity of molybdenum catalyst in hydrodesulphurization, hydrodenitrogenation, and hydrodeoxygenation: Effect of additives on dibenzothiophenes hydrodesulphurization. *Journal of Catalysis*, 81, 440.

Nagai, M., Sato T., and Aiba. A., (1986) Effect of solvents and acridine on dibenzothiophene hydrodesulphurization. *Journal of Catalysis*, 97, 52.

National Energy Board, (2004) *Canada's Oil Sands – Opportunities and Challenges* to 2015, 25.

National Energy Board, Canada's Oil Sands (2006) Opportunities and Challenges to 2015: An Update, http://www.neb.gc.ca/clf-nsi/rnrgynfmtn/nrgyrprt/lsnd/

pprtntsndchllngs20152006/pprtntsndchllngs20152006-eng.pdf. Accessed 7/1/2010.

Millan, M., Adell, C., Hinojosa, C., Herod, A.A. and Kandiyoti, R. (2008) Mechansims of Catalytic Activity in Heavily Coated Hydrocracking Catalysts. *Oil Gas Sci Technol.,* 63, 1, 69.

Naccache, C. in: Oudar, J., Wise H. (Eds.), (1985) *Deactivation and Poisoning of Catalysts*, Marcel Dekker, New York.

Niemann, K., Wenzel, F (1993) The Veba-Combi Cracking Technology: An update. *Fuel Process Technology*, 35, 1.

Nature Canada, (2008) Bird Deaths in Tailings Ponds Renews Questions About Tar Sands Impact on Environment. http://www.naturecanada.ca/enews_may08_ oiledbirds.asp, Accessed 7/1/2010.

New Estimates Boost Worlwide Oil, Gas Reserves, Worldwide Look at Reserves and Production. (2008) *Oil and Gas Journal*, 106, 48, 22.

Nexen, *SAGD and Upgrader Integration*, (2009). http://www.nexeninc.com/

Operations/Athabasca_Oil_Sands/Long_Lake/SAGD.asp. Accessed 7/1/2010.

Owens W. D. and Suter, V. E. (1965) Steam Stimulation – Newest Form of Secondary Petroleum Recovery, *Oil and Gas Journal*, 90, 82.

Otterstedt, J. E.; Gevert, S. B.; Jaras, S. G.; Menon, P. G. (1986) Fluid Catalytic Cracking of Heavy (Residual) Oil Fraction: A Review. *Applied Catalysis,* 22, 159.

Oelderik J.M., Sie S.T., Bode D. (1989) Progress in the catalysis of the upgrading of petroleum residue: A review of 25 years of R&D on Shell's residue hydroconversion technology. *Applied Catalysis,* 47, 1.

Occelli, M.L., Anthony R.G., (1989) Hydrotreating Catalysts (Studies in Surface Science and Catalysis) Elsevier Science Ltd.

Perchec, P. Le., Fixari, B., Elmouchnino, J., Peureux, S., Vrinat, M., Morel, F. (1993) New developments in deep hydroconversion of heavy oil residues with dispersed catalysts. Thermocatalytic analysis of the transformation with various catalyst precursors. *ACS Div. Petroleum Chem., Preprints,* 38, 2, 401.

Panariti N., Bianco, A. Del., Del Piero, G., Marchionna, M., Carniti, P., (2000) Petroleum residue upgrading with dispersed catalysts Part 2. Effect of operating conditions. *Applied Catalysis A: General,* 204, 215.

Pinto, A. C. C., Branco, C. C., Matos, J. S., Vieira, P. M., Guedes, S. D. S., Pedroso, C. J. Coelho A. C. D., and Ceciliano, M. M., (2003) Offshore Heavy Oil in Campos Basin: The Petrobras Experience. *Proceedings of the Offshore Technology Conference*, Houston.

PTAC, http://www.ptac.org/osd/dl/osdp0601a07.pdf.

Picha, M. S., (2007) Enhanced Oil Recovery by Hot CO2 Flooding. *Proceedings of the 15th SPE Middle East Oil and Gas Show and Conference*, Kingdom of Bahrain.

Petrobank updates (2008) www.Petrobank.com.

Petrobank updates (2009) www.Petrobank.com

Quirke, J.M.E. (1987) *Metal Complexes in Fossil Fuels.* R.H. Filby and J.F. Branthaver (Editors). Symposium Series No. 344. American Chemical Society, Washington, DC, p. 74.

Queipo, N. V., Goicochea J. V. and Pintos, S., (2002) Surrogate modeling-based optimization of SAGD processes. *Journal of Petroleum Science and Engineering*, 35, 83.

Rostrup-Nielsen, J.R. (1974) Coking of nickel catalysts for steam reforming of hydrocarbons. *Journal of Catalysis,* 33, 184.

Reed, R. L. and Healy, R. N. (1977) *Improved Oil Recovery by Surfactant and Polymer Flooding,* ed. D. O. Shah and R. S. Schechter, Academic Press, New York.

Reynolds, J.G. (1997) *In Petroleum Chemistry and Refining.* J.G. Speight (Editor). Taylor & Francis Publishers, Washington, DC,

Rahimi, P., Gentzis, T., and Fairbridge, C. (1999) Interaction of Clay Additives with Mesophase Formed during Thermal Treatment of Solid-Free Athabasca Bitumen Fraction, *Energy & Fuels*, 13, 817.

Reyniers, M.F., Berinaert, H., Marin, G.B. (2000) Influence of coke formation on the conversion of hydrocarbons. I. Alkanes on a USY-zeolite. *Applied Catalysis A: General*, 202, 49.

Robles, J., (2001) *Proceedings of the SPE International Thermal Operations and Heavy Oil Symposium*, Porlamar, Marguerita Island, Venezuela.

Rana M.S., Ancheyta J, Maity S.K., Rayo P. (2005) Characteristics of Maya crude hydrodemetallization and hydrodesulphurization catalysts, *Catalysis Today,* 104, 86.

Rana M.S., Ancheyta J, Rayo P. (2005) A comparative study for heavy oil hydroprocessing catalysts at micro-flow and bench-scale reactors. *Catalysis Today*, 109, 24.

Rana M.S., Ancheyta J, Maity S.K., Rayo P. (2005) Maya crude hydrodemetallization and hydrodesulphurization catalysts: An effect of TiO_2 incorporation in Al_2O_3. *Catalysis Today,* 109, 61.

Rana, M.S., Samano, V., Ancheyta J., Diaz, J.A.I. (2007) A review of recent advances on process technologies for upgrading of heavy oils and residua. *Fuel*, 86, 1216.

Ravagnani, A. T. F. S. G., Ligero E. L. and Suslick, S. B., (2009) CO_2 sequestration through enhanced oil recovery in a mature oil field. *Journal of Petroleum Science and Engineering*, 65, 129.

Semenov, N.N. (1958) Some Problems of Chemical Kinetics and Reactivity, Pergamon, New York.

Sakarnen, K.V., and Ludwig, C.H. (1971) *Lignins: Occurrence, Formation, Structure and Reactions*. John Wiley & Sons Inc., New York.

Stokes D. D. and Doscher, T. M. (1974) Shell Makes a Success of Steam Flood at Yorba Linda. *Oil and Gas Journal*, 72, 71.

Somasundaran P and Hanna, H. S., (1979) Adsorption of Sulfonates on Reservoir Rocks. *Soc. Petroleum Engineering Journal*, 19, 221.

Speight J.G. and Moschopedis S.E. (1979) The production of low-sulphur liquids and coke from Athabasca bitumen, *Fuel Processing Technology,* 2, 295.

Shi, S.S.. Angevine, P.J., Heck, R.H. and Sawruk, S. (1980) Catalyst Assessment for Upgrading Short-Contact-Time SRC to Low Sulfur Boiler Fuels. *American Chemical Society, Preprints, Division of Fuel Chemistry,* 25, 152.

Schumacher, M. M., (1980) *Enhanced Recovery of Residual and Heavy Oils*, Noyes Data Corp., Park Ridge, Noyes Data Corporation, Park Ridge , New Jersey, 50, 112.

Silvy, R.P., Grange P., and Delmon, B. (1989) Activation of CoMo HDS catalysts: influence of the sulphidation procedure on the physic-chemial properties and catalytic activity.

Catalysts in petroleum refining, proceedings of the Conference on Catalysts in Petroleum Refining, Kuwait, March 5-8.

Speight, J. G., (1999) *Chemistry and Technology of Petroleum*, New York, NY, USA, 3rd Edition, pp. 202.

Smith, B.J., Wei, J. (1991a) Deactivation in catalytic hydrodemetallation II. Catalyst characterization. *Journal of Catalysis*, 132, 41.

Smith BJ, Wei J. (1991b) Deactivation in catalytic hydrodemetallation I. Model compound kinetic studies, *Journal of Catalysis,* 132, 21.

Sanford, E.C. (1994) Molecular Approach to Understanding Residuum Conversion. *Industrial and Engineering Chemistry Research,* 33, 1, 109.

Shew, E.Y., Mullins, O.C. (1995) *Asphaltenes: Fundamentals and Applications*, Plenum Press, New York, p. 97.

Snape, C.E., Diaz, M.C., Tyagi, Y.R., Martin, S.C., and Hughes, R. (2001) Characterisation of coke on deactivated hydrodesulphurisation catalysts and a novel approach to catalyst regeneration. *Studies in Surface Science and Catalysis*, 139, 359.

Stosur, G. J., Waisley S. L., Reid T. B., and Marchant L. C. (1998) Tar Sands – Technology, Economics and Environmental Issues for Commercial Production beyond the Year 2000, Paper No 1998-002 *presented at the 7th. UNITAR International Conference on Heavy Oil and Tar Sand, Beijing*, China, 27-30th October, 11-18.

Sarathi, P. S. (1998) “Nine Decades of Combustion Oil Recovery– A Review of In situ Combustion History and Assessment of Geologic Environments on Project Outcome”, Paper

No 1998-124 *presented at the 7th. UNITAR International Conference on Heavy Oil and Tar Sand,* Beijing, China, 27-30 October 1189-1200.

Speight, J.G. (1994) *In Asphaltenes and Asphalts. I. Developments in Petroleum Science*, 40. T.F. Yen and G.V. Chilingarian (Editors). Elsevier, Amsterdam, The Netherlands.

Speight, J. G., (1999) *Chemistry and Technology of Petroleum*, Marcel Dekker Incorporated, New York, NY, USA, 3rd edn, p 192.

Stalder, J. L., York, G.D., Kopper, R. J., Curtis, C. M., Cole, T. L. And Copley, J. H. (2001) Multilateral Horizontal Wells Increase Rate and Lower Cost Per Barrel in the Zuata Field. *Proceedings of the SPE International Thermal Operations and Heavy Oil Symposium*, Porlamar, Marguerita Island, Venezuela, March 12-14.

Sanaie, N., Watkinson, A. P., Bowen, B. D., Smith, K. J. (2001) Effect of minerals on coke precursor formation. *Fuel*, 80, 1111.

Song, C., (2003) An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catalysis Today*, 86, 211.

Sanchez, L., Astudillo, A., Rodriguez, F., Morales J., and Rodriguez, A. (2005) Nitrogen Injection in the Cantarell Complex: Results after Four Years of Operation. *Proceedings of the Latin American and Caribbean Petroleum Engineering Conference*, Rio de Janeiro, Brazil.

Shakirullah, M., Ahmad, I., Rahman, H., Khan, M.A., Ishaq M. and Shah, A.A. (2006) Spectral analysis of some distillates from asphalt cracking and evaluation of UTIMAC as cracking catalyst. *Journal of Chinese Chemical Society*, 53, 5, 1059.

Shakirullah, M., Ahmad, I., Khan, M.A., Shah, A.A., Ishaq M. and Rahman, H., (2008) Conversion of asphalt into distillate products, *Energy Conversion Management*, 49, 107.

Shah, A., Fishwick, R., Wood, J., Leeke, G., Rigby, S., Greaves, M. (2010) A Review of Novel Techniques for Heavy Oil and Bitumen Extraction and Upgrading, *Energy and Environmental Science*, 3, 700.

Thompson. C.J., Ward. C.C., and Ball, J.S. (1976) *Characteristics of World's Crude oils and Results of API Research Project 60*. Report BERC/RI-76/8. Bartlesville Energy Technology Center, Bartlesville, Oklahoma.

Tissot, B.P., and Welte, D.H. 1978. *Petroleum Formation and Occurrence.* Springer-Verlag, New York. Treibs, A. 1934. Analen. 509, 103.

Tamm P.W., Harnsberger H.F., Bridge A.G. (1981) Effects of feed metals on catalyst aging in hydroprocessing residuum. *Industrial and Engineering Chemistry Process Design and Development,* 20, 262.

Takeuchi C, Asaoka S, Nakata Shin-ichi, Shiroto Y. (1985) Characteristics of Residue Hydrodemetallation Catalysts. American Chemical Society Preprints-Division of Petroleum Chemistry, 30, 1, 96.

Thakur D.S., Thomas M.G., (1985) Catalyst deactivation in heavy petroleum and synthetic crude processing: a review. *Applied Catalysis,* 15, 197.

Thomas, S., Farouq Ali, S.M. (1986) *Proceedings of the 37th Annual Technical Meeting of the Petroleum Society of CIM,* Calgary, Alberta.

Toulhoat H, Plumail JC, Houpert C, Szymanski R, Bourseau P, Muratet G. (1987) Modelling RDM catalysts deactivation by metal sulphides deposits: An original approach supported by HREM investigations and pilot tests results. *American Chemical Society Division of Petroleum Chemistry*, 32, 2, 463.

Thakur, D .S. and Thomas, M.G. (1984) Catalyst deactivation during direct coal liquefaction: a review. *Industrial and Engineering Chemistry Product Research and Development,* 23, 349.

Thomas, M., Fixari, B., Perchec, P.L., Princic, Y., Lena, L., (1989) Visbreaking of Safaniya Vacuum Residue in the Presence of Additives. *Fuel*, 68, 318.

Trimm, D.L., (Ed.), (1989) *Catalysts in Petroleum Refining*, Elsevier, Amsterdam, 1990, pp. 41.

Thomas S. and Farouq Ali S. M., (1993) Field Experience with Chemical Oil Recovery Methods. *Proceeding of the 21st Australian Chemical Engineering Conference (Chemeca 93)*, Melbourne, Australia, Sept. 26-29, 45-3-49-3.

Topsoe, N. Y. and Topsoe H. (1993) FTIR Studies of Mo/Al_2O_3-Based Catalysts: I. Morphology and Structure of Calcined and Sulfided Catalysts, *Journal of Catalysis*, 139, 631.

Topsøe, H.; Clausen, B.S.; Massoth, F.E. (1996) *Hydrotreating Catalysis – Science and Technology*, Vol., 11, Ed. Anderson, J.R and Boudart, M.; Springer Verlag Berlin.

Tanabe, K., Gray, M. R. (1997) Role of Fine Solids in the Coking of Vacuum Residues. *Energy and Fuels,* 11, 1040.

Tippet, T., Knudsen, K. G., Cooper, B. C. (1999) Proc. NPRA Annual Meeting, Paper AM-99-06.

Thomas S. and Farouq Ali S. M., (1999) Status and Assessment of Chemical Oil Recovery Methods. *Energy Sources*, 21, 177.

US Pat., 5, 626, 191, 1997.

The oil sands story: extraction, (Accessed 8/1/2010) *Oil Sands Discovery Centre* http://www.oilsandsdiscovery.com/oil_sands_story/extract.html.

Uguina, M.A., Serrano, D.P., Grieken, R.V., Venes, S. (1993) Adsorption, acid and catalytic changes induced in ZSM-5 by coking with different hydrocarbons. *Applied Catalysis,* 99, 97.

Voge, H. H. (1958) *Catalytic Cracking, Catalysis*, Vol., VI, p. 407. Reinhold Publishing Co., New York.

Vrinat, M.L. (1983) The kinetics of the hydrodesulphurization process; A review, *Applied Catalysis,* 6, 137.

Wilson, L. A, Reed, R. L., Reed, W. D., Clay R. R. And Harrison, N. H. (1963) Some effects of pressure on forward and reverse combustion. *Society Petroleum Engineering Journal,* 32, 127.

Wu C. H. and Fulton, F. P. (1971) Experimental Simulation of the Zones Preceding the Combustion Front of an In-situ Combustion Process. *Society Petroleum Engineering Journal*, 11, 38.

Weiss, V., and Edwards, J.M. (1980) *The Biosynthesis of Aromatic Compounds*. John Wiley & Sons, Inc., New York.

Wolf, E.H., Alfani, A. (1982) Catalysts Deactivation by Coking Catalysis Reviews: Science and Engineering. *Catalysis Reviews, Science and Engineering,* 24, 3, 329.

Woijciechowski B. W. and Corma, A. (1986) *Catalytic Cracking Catalysts, Chemistry and Kinetics*, Marcel Dekker, New York.

Wiehe, I.A. (1993) A phase separation kinetic model for coke formation. *American Chemical Society, Preprints-Division of Petroleum Chemistry,* 38, 2, 428.

Weisser and Lands, L. (1973) *Sulphide Catalysts: Their Properties and Applications*, Pergamon, Oxford.

Weissman, J.G. and Kessler, R.V. (1996) Downhole heavy crude oil hydroprocessing. *Applied Catalysis A: General*, 140, 1, 16.

Weissman, J.G. (1997) Review of Processes for Downhole Catalytic Upgrading of Heavy Crude Oil. *Fuel Process Technology,* 50, 2-3, 199.

Whitehurst, D. D., Isoda, T., Mochida, I. (1998) Present state of the art and future challenges in the hydrodesulfurization of polyaromatic sulfur compounds. *Advances in Catalysis*, 42, 345.

Wyatt, K., Pitts, M. J., Surkalo, H., (2002) Mature Waterfloods Renew Oil Production by Alkaline-Surfactant-Polymer Flooding. *Proceedings of the SPE Eastern Regional Meeting*, Lexington, Kentucky.

Sahoo, S.K., Ray, S.S., Singh, I.D. (2004) Structural characterization of coke on spent hydroprocessing catalysts used for processing of vacuum gas oils. *Applied Catalysis A: General,* 278, 83.

Shamsi, A., Baltrus, J.P., Spivey, J.J., (2005) Characterization of coke deposited on Pt/alumina catalyst during reforming of liquid hydrocarbons. *Applied Catalysis A: General,* 293, 145.

Woynillowicz, D., Baker, C., Raynolds, M. (2005) *Oil sands fever*, The Pembina Institute.

Xia T.X. and Greaves M. (2000) Upgrading Athabasca Tar Sand Using Toe-to-Heel Air Injection. *SPE/Petroleum Society of CIM International Conference on Horizontal Well Technology held in Calgary*, Alberta, Canada, 6-8 November.

Xia, T. X., and Greaves M. (2001) 3-D Physical Model Studies of Downhole Catalytic Upgrading of Wolf Lake Heavy Oil Using THAI. Paper number 2001-017, *Presented at the Petroleum Society, Canadian International Petroleum Conference*, Calgary, Alberta, Canada, June 12-14.

Xia, T.X., Greaves M., Werfilli M.S., Rathbone R.R. (2002. THAI Process—Effect of Oil Layer Thickness on Heavy Oil Recovery. *Presented at the Petroleum Society, Canadian International Petroleum Conference*, Calgary, Alberta, Canada, June 11 – 13.

Xia, T.X., Greaves, M., Turta, A.T., and Ayasse, C., (2003) THAI-A 'Short-Distance displacement' In situ combustion process for the recovery and upgrading of Heavy oil, *Trans IChemE*, 81, Part A.

Xia, T.X., and Greaves, M.,(2006) In Situ Upgrading of Athabasca Tar Sand Bitumen using THAI, Trans IChemE, Part A, *Chemical Engineering Research and Design*, 84, A9, 856.

Yan, T. Y. (1980) Dynamics of a Trickle-Bed Hydrocracker with a Quenching System. *Canadian Journal of Chemical Engineering*, 58, 259.

Yen, T.F. (1984) *Characterization of heavy oil*, New York, McGraw-Hill, p. 412.

Zeuthen, P., Knudsen, K.G., Whitehurst D.D. (2001) Organic nitrogen compounds in gas oil blends, their hydrotreated products and the importance to hydrotreatment. *Catalysis Today,* 65, 307.

Chapter 9

Appendices

9.1 Calculation of Oil and Gas Flow Rates

Gas and Oil flow rate at STP

400°C = 673K and

20 bar g = 20 Atm

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$1\,L.min^{-1}\ x\frac{T_2}{T_1}x\frac{P_1}{P_2}$$

$$1\,x\frac{673}{273}x\frac{1.01}{20} = 0.1245\ l.min^{-1}$$ gas flow rate

For $10.2\,m^3.min^{-1}$ internal diameter tubing

Area $= \frac{\pi d^2}{4} = 81.72\,mm$

Velocity of gas $= \frac{Q}{A} = \frac{1.245x10^{-4}}{81.72x10^{-6}} = 1.52\,m^3.min^{-1}$

Oil flow rate $1ml.min^{-1} = 1x10^{-3}\ L.min^{-1}$

$= 1x10^{-6}\ m^3.min^{-1}$

Velocity of oil $= \frac{1x10^{-6}}{81.72\,10^{-6}} = 0.0122\,m^3.min^{-1}$

$= 12.2\ mm.min^{-1}$

9.2 Steel tubes considered for CAPRI reactor

Tubing	**O.D.**	**Wall**	**I.D.**	**I.D. [mm]**	**Area [mm^2]**	**Superficial Velocity [mm.min^{-1}]**	**Flowrate [ml.min^{-1}]**	**Volume (24 hours) [l]**	**Volume (100 hours) [l]**	**Allowable Working Pressure**	
1"	1	0.083	0.834	21.18	352.44	***14.19***	***5.00***	7.20	30.00	214	bar
3/4"	0.75	0.049	0.652	16.56	215.40	14.19	3.06	4.40	18.34	165	bar
3/4"	0.75	0.065	0.620	15.75	194.78	14.19	2.76	3.98	16.58	228	bar
5/8"	0.625	0.049	0.527	13.39	140.73	14.19	2.00	2.87	11.98	200	bar
5/8"	0.625	0.065	0.495	12.57	124.16	14.19	1.76	2.54	10.57	276	bar
1/2"	0.5	0.035	0.430	10.92	93.69	14.19	1.33	1.91	7.97	179	bar
1/2"	0.5	0.049	0.402	10.21	81.89	14.19	1.16	1.67	6.97	255	bar
1/2"	0.5	0.065	0.370	9.40	69.37	14.19	0.98	1.42	5.90	352	bar
1/2"	0.5	0.083	0.334	8.48	56.53	14.19	0.80	1.15	4.81	462	bar
3/8"	0.375	0.035	0.305	7.75	47.14	14.19	0.67	0.96	4.01	228	bar
3/8"	0.375	0.049	0.277	7.04	38.88	14.19	0.55	0.79	3.31	331	bar
3/8"	0.375	0.065	0.245	6.22	30.42	14.19	0.43	0.62	2.59	448	bar
1/4"	0.25	0.035	0.180	4.57	16.42	14.19	0.23	0.34	1.40	352	bar
1/4"	0.25	0.049	0.152	3.86	11.71	14.19	0.17	0.24	1.00	517	bar
1/4"	0.25	0.065	0.120	3.05	7.30	14.19	0.10	0.15	0.62	703	bar
1/8"	0.125	0.028	0.069	1.75	2.41	14.19	0.03	0.05	0.21	586	bar
1/8"	0.125	0.035	0.055	1.40	1.53	14.19	0.02	0.03	0.13	752	bar
20mm	20	2.0		16.00	201.06	14.19	2.85	4.11	17.11	260	bar
18mm	18	1.0		16.00	201.06	14.19	2.85	4.11	17.11	120	bar
18mm	18	1.5		15.00	176.71	14.19	2.51	3.61	15.04	200	bar
18mm	18	2.0		14.00	153.94	14.19	2.18	3.14	13.10	290	bar
16mm	16	1.0		14.00	153.94	14.19	2.18	3.14	13.10	140	bar
16mm	16	1.5		13.00	132.73	14.19	1.88	2.71	11.30	230	bar
16mm	16	2.0		12.00	113.10	14.19	1.60	2.31	9.63	330	bar
12mm	12	1.0		10.00	78.54	14.19	1.11	1.60	6.69	200	bar
12mm	12	1.5		9.00	63.62	14.19	0.90	1.30	5.42	330	bar
12mm	12	2.0		8.00	50.27	14.19	0.71	1.03	4.28	470	bar
10mm	10	1.0		8.00	50.27	14.19	0.71	1.03	4.28	240	bar
10mm	10	1.5		7.00	38.48	14.19	0.55	0.79	3.28	400	bar
8mm	8	1.0		6.00	28.27	14.19	0.40	0.58	2.41	310	bar
8mm	8	1.5		5.00	19.63	14.19	0.28	0.40	1.67	520	bar
6mm	6	1.0		4.00	12.57	14.19	0.18	0.26	1.07	420	bar
6mm	6	1.5		3.00	7.07	14.19	0.10	0.14	0.60	710	bar

9.3 Full List of Experiments

Expt.	**Catalyst**	**Mass [g]**	**Gas**	**Pre-reduced**	**Flow Rate [ml.min^{-1}]**			**Temperature [°C]**	**Pressure [bar g]**
					Gas	Oil	Water		
P3	CoMo	5	THAI Gas	No	1000	2		450	20
P4	NiMo	5	THAI Gas	No	1000	2		500	20
P5	ZnO/CuO	5	THAI Gas	No	1000	2		500	20
P6	ZnO/CuO	5	THAI Gas	No	1000	2		500	20
P7	ZnO/CuO	5	Nitrogen	No	1000	2		500	20
P8	ZnO/CuO	5	Nitrogen	Water	1000	2	0.6	500	20
P9	ZnO/CuO	5	Nitrogen	No	1000	2		500	20
P11	ZnO/CuO	5	Nitrogen	No	1000	2		400	20
P12	NiMo	5	Nitrogen	No	500	1		400	20
P13	CoMo	5	Nitrogen	No	500	1		400	20
P14	Alumina	5	Nitrogen	No	500	1		400	20
P15	Presulphided CoMo	5	Nitrogen	No	500	1		400	20
P17	Glass beads	5	Nitrogen	No	500	1		400	20
P18	CoMo	5	Nitrogen	No	500	1		400	20
P19	Alumina	5	Nitrogen	No	500	1		400	20
P20	CoMo	5	Nitrogen	No	500	1		400	20
P21	CoMo	5	Nitrogen	No	500	1		400	20

P22	CoMo	5	Nitrogen	No	500	1		400	20
P23	CoMo	5	Nitrogen	No	500	1		400	20
P26	CoMo	5	Nitrogen	No	500	1		420	20
P27	CoMo	5	Nitrogen	No	500	1		380	20
P28	Glass beads	5	Nitrogen	No	500	1		500	20
P29	Alumina	5	Nitrogen	No	500	1		500	20
P30	CoMo	5	Nitrogen	No	500	1		500	20
P31	Alumina	5	Nitrogen	No	500	1		475	20
P32	CoMo	5	Nitrogen	No	500	1		475	20
P33	CoMo	5	Nitrogen	30 min	500	1		400	20
P34	Large Glass Beads	5	Nitrogen	No	500	1		400	20
P35	Presulphided CoMo	5	5% H_2 in N_2	30 min	500	1		400	20
P36	Presulphided CoMo	5	Nitrogen	No	500	1		400	20
P37	CoMo	5	5% H_2 in N_2	60 min	500	1		425	20
P38	CoMo	5	5% H2 in N2	60 min	500	1		400	20
P39	CoMo	5	5% H_2 in N_2	60 min	500	1		450	20
P40	Albermarle CoMo APC-2E	5	5% H_2 in N_2	60 min	500	1		425	20
P41	Albermarle CoMo APC-2E	5	5% H_2 in N_2	60 min	500	1		400	20
P42	Albermarle CoMo APC-2E	5	5% H_2 in N_2	60 min	500	1		400	20
P43	Albermarle CoMo APC-2E	5	Nitrogen	60 min	500	1		425	20
P44	Albermarle CoMo APC-2E	5	THAI Gas	No	500	1		425	20

P50	Glass Beads	5	1% H_2 in N_2	No	500	1		425	20
P51	Albermarle CoMo APC-2E	5	1% H_2 in N_2	60 min	500	1		425	20
P52	Albermarle CoMo APC-2E	5	2% H_2 in N_2	60 min	500	1		425	20
P53	Albemarle NiMo APC-3E	5	1% H_2 in N_2	60 min	500	1		425	20
P54			2% H_2 in N_2						
P55			4% H_2 in N_2						
P56			8% H_2 in N_2						
P57			1% H_2 in N_2						
P58			1% H_2 in THAI						
P59	CoMo	5	4% H_2 in THAI	No	500	1		425	20
P60			4% H_2 in THAI						
P61			H_2 off from P60						
P62			P61 cont.						
P63			H_2 on from P60						
P64			P63 cont.						
P65	CoMo Bath	5	4% H_2 in N_2	60 min	500	1		425	60
P66	CoMo Bath	5	0-4% in THAI	No	500	1		425	20
P67	CoMo Bath	5	4% H_2 in N_2	60 min	500	1		425	40
P68	CoMo Bath	5	4% H_2 in THAI	60 min	250-750	1		425	20
P69	CoMo Bath	2.5	4% H_2 in N_2	60 min	500	1		425	20

P70	CoMo Bath	5	1% H_2 in N_2	No	500	1		425	20
P71	CoMo Bath	5	THAI	No	500	0.2-1.6		425	20
P72	CoMo Bath	5	THAI	No	500	1	0.3-0.6	425	20
P73	CoMo Bath	5	4% H_2 in N_2	No	500	1		425	20
P74	CoMo Bath	5	N_2	No	500	1		425	20
P75	Albemarle NiMo APC-3E	5	N_2	No	500	1		425	20
P76	CoMo Bath	5	THAI	No	500	1		425	20
P77	Presulphided-CoMo Bath	5	N_2	No	500	1		425	20
P78	Presulphided-CoMo Bath	5	THAI	No	500	1		425	20
P79	Presulphided-CoMo Bath	5	THAI	No	500	1	Experiments carried out only to get coke at a 3 hour mark	425	20
P80	CoMo Bath	5	THAI	No	500	1		425	20
P81	CoMo Bath	5	4% H_2 in THAI	No	500	1		425	20
P82	CoMo Bath	5	THAI	No	500	1		450	20
P83	CoMo Bath	5	THAI	No	500	1		400	20
P84	Molecular Sieves	5	THAI	No	500	1		425	20
P85	CoMo Bath	5	THAI	No	500	1		425	40
P86	Clay	5	THAI	No	500	1		400	20
E1	CoMo Bath	5	N_2	No	500	1		380	20
E2	CoMo Bath	5	N_2	No	500	1		400	20
E3	CoMo Bath	5	N_2	No	500	1		425	20

E4	CoMo Bath	5	4% H_2 in N_2	No	500	1		425	20
E5	CoMo Bath	5	4% H_2 in THAI	No	500	1		425	20
D2	CoMo Bath	5	THAI	No	500	1		425	20

9.4 Hazardous Substances Policy - Assessment

CHEMICAL HAZARD AND RISK ASSESSMENT

School/Dept	School of Chemical Engineering	Assessment Number	
Assessor	Amjad Shah/Rob Fishwick	Date of Assessment	10/01/2008

Notes Guidance on making an assessment is given in *Chemical Hazard and Risk Assessment (GUIDANCE/22/CHRA/05)*. Guidance is also available from the attached *Guidance on Completing the Chemical Hazard and Risk Assessment Form*. Substance data is available in HAZDAT. Use a continuation sheet or word processor to expand any section of this form. An *MS Word* file for this form is available from http://www.hsu.bham.ac.uk/univ/hspolicy/hs15/HS2ASSFM.DOC.

1	LOCATION OF THE WORK ACTIVITY	Room 215, Chemical Engineering Building

2	PERSONS WHO MAY BE AT RISK

List names where possible

Amjad Shah/ Rob Fishwick/ Joe Wood/ Reaction Engineering Group

3	ACTIVITY ASSESSED	Heavy oil up-gradation/CAPRI Reactor

4	MATERIALS INVOLVED	Attach copies of data sheet(s)

NAME and CAS NUMBER	AMOUNT and FORM	HAZARD	RISK PHRASES	REPORTABLE
Crude Oil (Representative Compounds) n-PENTANE CAS No. 109-66-0	Liquid	highly flammable, harmful	At long or repeated contact with skin it may cause dermatitis due to the degreasing effect of the solvent. Has a narcotizing effect. R 12 Extremely flammable. R 51/53 Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. R 65 Harmful: may cause lung damage if swallowed. R 66 Repeated exposure may cause skin dryness or cracking. R 67 Vapours may cause drowsiness and dizziness.	No
n-Hexane CAS No.73513-42-5	Liquid	flammable, harmful, irritant	R 11 Highly flammable. R 38 Irritating to skin. R 48/20 Harmful: danger of serious damage to health by prolonged exposure through inhalation. R 62 Possible risk of impaired fertility. R 51/53 Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. R 65 Harmful: may cause lung damage if swallowed. R 67 Vapours may cause drowsiness and dizziness.	No
n-Heptane CAS No. 142-82-5	Liquid	flammable, harmful, irritant	R 11 Highly flammable. R 38 Irritating to skin. R 50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. R 65 Harmful: may cause lung damage if swallowed. R 67 Vapours may cause drowsiness and dizziness.	No
n-Hexadecane CAS No. 544-76-3	Liquid	irritant	R 36/38 Irritating to eyes and skin.	No

Benzene	Liquid	flammable, toxic	R 46 May cause heritable genetic damage. R 11 Highly flammable. R 36/38 Irritating to eyes and skin. R 48/23/24/25 Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed. R 65 Harmful: may cause lung damage if swallowed.	No
Nitrogen Gas CAS No. 7727-37-9	Gas	Asphyxiant	Can cause asphyxia. High pressure. Keep container in a well-ventilated place.	No
Carbon dioxide, CAS No. 124-38-9	Gas	Asphyxiant	Can cause asphyxia. High pressure. S9 Keep container in a well-ventilated place.	No
Carbon Monoxide CAS No. 630-08-0	Gas	Fire and Inhalation	Compressed gas. Extremely flammable. Toxic by inhalation.	No
Methane 74-82-8	Gas	Fire and High Pressure	May cause harm to the unborn child. Compressed gas. Extremely flammable.	No
CoMo (or the catalysts to be used)			Data needed	
NiMo				
Crude Oil data needed as well				

If substance is reportable, have you reported it to the Health and Safety Unit? YES/NO (see Note 4)

5 INTENDED USE and JUSTIFICATION (where appropriate)

Give brief details and attach protocol/instructions. Justification is needed for exceptionally hazardous substances(see Note 5)

Partially treated Crude oil vaporized blended with steam and gaseous mixture of N_2, CO_2, CO and CH_4. Reacted over catalyst at pressure of 2-100 bar and temperature of 300-600 ^oC. Reaction gas provided as a dilute blend in Nitrogen. Product stream separated as gas (direct feed to vet or Refinery Gas Analyser) and liquid collected.

n-pentane, n-hexane, n-heptane, hexadecane and benzene used in the experiments are all part of the crude oil and will not be used in the refined stage and in this form are just representative of the main constituents groups present in crude oil. Crude oil will be used in a continuous reactor system at 1-100 bar and from 200-500 ^oC. Nitrogen will be used as the purge gas along with a BOC gas mixture of Nitrogen, Carbon dioxide, Carbon monoxide and methane as the reaction gas. The reaction pressure and temperature will be 1-100 bar and 200-500 ^oC.

6 RISKS to HEALTH and SAFETY from INTENDED USE

From personal exposure or hazardous reactions. Refer to WELs, flash points, etc., as appropriate. Are pregnant women, breast-feeding mothers especially at risk?

Release of Nitrogen, or the BOC gas (composed of Nitrogen, Carbon dioxide, Carbon monoxide and methan) can cause asphyxiation or may result in fire or injury.

High Pressure- Pressure relief from reactant mixture chamber and product sampling vessel

High Temperature- Ensure adequate insulation

Accidental Release of Vapour or Gas- Use fume cabinet

7 CONCLUSIONS ABOUT RISKS

Is level of risk acceptable? Can risk be prevented or reduced by change of substance/procedure? Are control measures necessary?

Alarms and automated shutdown necessary.

Power failure (and return in absence) Valves arranged in a way that it will shut the whole system automatically in case of power breakdown

8 CONTROL MEASURES

Additional to *Good Chemical Practice*, e.g., fume cupboard, etc. Any special requirements, e.g., glove type, etc.

Protective clothing must be worn in all operations, including safety glasses, gloves and lab coat.

Temperature alarm and shut down for trace heating.
Reaction gas control valve, furnace and other flows by pump to shut in the event of power failure automatically

Pressure relief and alarm

9 INSTRUCTION/TRAINING

Specify course(s) and/or special arrangements.

Gas cylinder handling training and high pressure safety course are necessary.

10 MONITORING

Performance of control measures,

Leak and pressure testing. To be repeated before each experiment using N_2 as purge gas.

Full monitoring during initial use

Personal exposure	Health Surveillance, specify measures agreed with Health and Safety Unit

11 WASTE DISPOSAL PROCEDURE

Include name, 6-digit code and H numbers if to be sent away for disposal

Waste oil (mostly used oil) will be collected in a drum and will be disposed off according to set procedure.

12	REVIEW

Enter the date or circumstances for review of assessment (maximum review interval 5 years)

13	EMERGENCY ACTION

TO CONTROL HAZARDS	To stabilize situation eg spread absorbent on liquid spill; eliminate sources of ignition, etc.
Evacuate area. Wear breathing apparatus. Wash burns with water and call medical assistance. Eliminate sources of ignition.	
TO PROTECT PERSONNEL	Evacuation, protection for personnel involved in clean-up, Special First Aid
Ventilate area	
TO RENDER SITE OF EMERGENCY SAFE	Clean-up/decontamination

14	EMERGENCY CONTACT	NAME	Joe Wood	PHONE	

9.5 Publications

Shah, A. Fishwick, R.P., Gary A. L., Wood, J., Rigby S.P. and Greaves, M., (2010) Experimental Optimization of Catalytic Process In-Situ for Heavy Oil and Bitumen Upgrading, accepted and to be presented at *SPE-CURIPC conference, October 2010 at Calgary in Canada and accepted for publication in the Journal of Canadian Petroleum Technology*.

Shah, A. Fishwick, R.P., Gary A. L., Wood, J., Rigby S.P. and Greaves, M., (2010) A review of novel techniques for heavy oil and bitumen extraction and upgrading, *Energy Environ. Sci.*, 3, 700–714.