Advanced Studies of Catalytic Upgrading of Heavy Oil & Bio-Oil

By

Sam Derakhshan Deilami

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

DOCTOR OF PHILOSOPHY

School of Chemical Engineering
College of Engineering and Physical Science
University of Birmingham

September 2019

Abstract

Heavy oil and bio oil both have undesirable characteristics which makes them uneconomical to be used as a refinery feed stock. Therefore upgrading process is required to enhance their quality. Platinum group metals (PGM) are known for their high hydrogenation activity, and low coke formation in oil upgrading compares to other metal groups. However, it is significantly uneconomical to use virgin noble metals for oil upgrading processes. Since the introduction of autocatalysts in Europe in the 1980s there has been a clear link between their use and increasing concentrations of platinum group metals (PGMs) in the environment resulting in enhanced levels of these elements occurring in road dust and soils, particularly in urban areas and around major roads. Recent studies have shown development in technologies to recover these metals and produce a metal-rich concentrate that can either be smelted to recover the PGMs or leached into solution and used to produce new biological-based catalysts. The main purpose of this research is to compare the performance of bio-catalyst with commercial homogeneous catalyst in the application of heavy oil and bio oil upgrading. The results of the simulated distillation column (Sim-Dis), viscosity reduction, asphaltene, sulfur, and metals content after upgrading showed that the alternative bio-Pd nanoparticles have the potential of achieving a similar level of upgrading as obtainable with typical hydrodesulfurization (HDS) catalyst particles such as Pd supported on carbon and alumina, respectively. However, due to relatively high sulfur content of heavy oil, this catalyst experienced very fast deactivation. Additionally, less coke formation and slightly higher improvement of produced oil were observed in the case of lower Pd loading of the cell. The performance of bio-Pd in upgrading of bio-oil which is naturally low in sulfur in terms of Degree of Deoxygenation (DOD) at lower Hydrodeoxygenation (HDO) temperature (170 - 210 ^{o}C) was identical to the commercial catalyst, while at higher HDO temperature above 250 ^{o}C, bio-Pd performance in removing oxygen was decreased significantly because of decomposition of biomass support at higher reaction temperature.

Table of Contents

1 Introduction 1

1.1 Background and Motivation 1

1.2 Aim and Objectives of the Study 14

1.3 Thesis Organisation and Overview 15

2 Review of Heavy Oil and Bio-Oil Upgrading Processes 17

2.1 Crude Oil 17

2.1.1 Composition of Heavy Oils 19

2.2 Heavy Crude Oil Upgrading Technologies 22

2.2.1 Surface Upgrading Processes of heavy oil using dispersed catalysts 24

2.2.2 Catalytic aquaconversion Process 25

2.2.3 Heavy Oil Treating Process 26

2.2.4 Shell FCC Process 27

2.2.5 Hydroconversion in a Slurry Reactor 28

2.3 In-situ Upgrading Processes 30

2.3.1 Toe-to-Heel Air Injection (THAI) 30

2.3.2 Catalytic Upgrading Process In-situ (CAPRI) 39

2.4 Chemistry of Heavy Oil Upgrading 44

2.4.1 The Mechanism of Catalytic Upgrading 45

2.4.2 The Mechanism of Catalytic Upgrading 49

2.5 Pyrolysis Bio-Oil 52

2.5.1 History of Pyrolysis 52

2.5.2 Process of Pyrolysis 53

2.5.3 Main Components of Pyrolysis Oil 55

2.6 Properties of Pyrolysis oil 61

2.7 Upgrading of bio-oil 64

2.7.1 Catalytic cracking 64

2.7.2 Hydro-de-oxygenation (HDO) 65

2.8 Use of Solvent in hydrodeoxygenation 73
2.9 Bio Pd 76
3 Materials and Methods 80
3.1 Introduction 80
3.2 Oil Feedstock Properties 81
3.2.1 Heavy Oil 81
3.2.2 Bio-Oil 82
3.3 Materials 83
3.4 Experimental Set-Up and Procedure 84
3.4.1 Heavy Oil Reactor Set-Up 84
3.4.2 Bio-Oil Reactor Set-Up 88
3.5 Preparation of Bio-Pd 91
3.5.1 E. coli Growth and Pd Solutions Preparation 91
3.5.2 Metallisation of E.coli 92
3.5.3 Characteristics of catalyst 94
3.5.4 Catalyst Surface Morphology using SEM 95
3.6 Analytical Instruments 96
3.6.1 Density and API Gravity Measurement 96
3.6.2 Viscosity Measurement 97
3.6.3 True Boiling Point (TBP) Distribution of Heavy Oil 97
3.6.4 Qualitative and Quantitative Analytical Methods of Bio-Oil 99
3.6.5 Elemental Analysis 100
3.6.6 Thermogravimetric Analysis (TGA) 101
3.6.7 Refinery Gas Analyser (RGA) 102
3.7 Asphaltene Measurement 104
4 Effects of Catalyst on Heavy Oil CAPRI Upgrading 105
4.1 Introduction 105
4.2 Thermal Cracking Effect 106

4.2.1 Effect of Temperature........106

4.2.2 Effect of Time........109

4.3 CAPRI Process........111

4.3.1 Effect of Catalyst Type as a function of time........111

4.3.2 Effect of Catalyst on Physical Properties........112

4.3.3 Effect of Catalyst on Product Yield........115

4.3.4 Effect of Catalyst on Product Oil True Boiling Point (TBP) Distribution........119

4.3.5 Effect of Catalyst on Produced Gas Composition........121

4.3.6 Effect of Catalyst on Elemental Composition........123

4.4 Effect of Cyclohexane and Hydrogen Gas on Catalysts Performance........125

4.4.1 Effect of Cyclohexane to Oil Ratio........126

4.4.2 Effect of Cyclohexane on Mass Balance........130

4.4.3 Effect of Cyclohexane on API Gravity, Viscosity and Asphaltene content of Produced Oil........132

4.4.4 Effect on Elemental Composition........135

4.4.5 Effect on Produced Gas Composition........139

4.5 Effect of Bio-Palladium Catalyst versus Pd/C and Pd/Al_2O_3 Catalyst........140

4.5.1 Effect of Pd Support on Elemental Composition........141

4.5.2 Effect of Cell Metal Loading........145

4.6 Conclusion........148

5 Upgrading of Fast Pyrolysis Oil via HDO........151

5.1 Introduction........151

5.2 Effect of Time and Temperature on Product Phase Distribution........152

5.3 Effect of Time and Temperature on Produced Oil Quality........157

5.3.1 Product Water Content........157

5.3.2 Product Viscosity........158

5.3.3 Product Oxygen Content........161

5.4 Effect of Time and Temperature on Product Composition........164

5.5 Effect of Time and Temperature on Gas Composition........169

5.5.1 Hydrogen Consumption....171
5.6 Effect of Polar and Non-Polar Solvent on Improvement of HDO....173
5.6.1 Effects of Solvent on Product Phase Distribution....175
5.6.2 Physicochemical Properties of Liquid Products....178
5.7 Effect of Bio Pd versus Commercial Pd/C....181
5.7.1 Bio-Oil Characterisation Effect on DOD....181
5.7.2 Catalyst Characterisation....184
5.8 Conclusion....185
6 Conclusions and Recommendations....188
6.1 Conclusions....188
6.1.1 Heavy Oil....188
6.1.2 Bio-Oil....190
6.2 Recommendations....193
7 References....194

List of Figures

Figure 1.1 World oil demand (Mb/d).. 1
Figure 1.2 Routes of bio oil upgrading into biofuels... 11
Figure 2.1 the origin of heavy oil and tar sand 18
Figure 2.2 Photograph of (a) Light oil; (b) Heavy oil and (c) oil sand.................................. 19
Figure 2.3 Sectional view of the crude oil and SARA components 20
Figure 2.4 The molecular structure of asphaltenes 21
Figure 2.5 The molecular structure of heteroatoms in heavy oil. 22
Figure 2.6 Route to refinery for conventional and non-conventional oils. 23
Figure 2.7 Detailed schematic of an FCC process 25
Figure 2.8 Mobilised oil draining in conventional ISC Process 31
Figure 2.9 Mobilised oil draining in THAI Process 31
Figure 2.10 The effect of temperature on crude oil viscosity 32
Figure 2.11 Upgrading of Wolf Lake heavy oil conducted using THAI laboratory experiments.. 36
Figure 2.12 Temperature distribution of a 3-D laboratory THAI experiments using SLD configuration.. 36
Figure 2.13 Conventional CAPRI fixed-bed horizontal production well 39
Figure 2.14 Reaction pathways for Paraffins, Naphthenes and Aromatics 47
Figure 2.15 Reaction pathways for Paraffins, Naphthenes and Aromatics 47
Figure 2.16 Cellulose Structure 57
Figure 2.17 Bridge of hydrogen bonds 57
Figure 2.18 Main sugars of hemicellulose... 59
Figure 2.19 Main units of lignin 60
Figure 2.20 Major reactions occurring during bio-oil HDO.. 66
Figure 2.21 Biorefinery/Refinery integration 68
Figure 2.22 Comparison of different catalysts in the HDO process...................................... 71
Figure 2.23 Electron microscopy of native and palladised strains. 78
Figure 3.1Experimental and analytical method schemes of the heavy oil and bio-oil upgrading.. 80
Figure 3.2 100 ml batch reactor and cabin controller 84
Figure 3.3 The schematic diagram of the 100 ml Baskerville batch autoclave reactor. 85
Figure 3.4 The schematics diagram of the batch Parr reactor.. 89

Figure 3.5 Photograph of batch Parr instrument, heating jacket and a unit controller 89
Figure 3.6 Simplified steps of bio-Pd preparation using biomass 93
Figure 3.7 Photograph of Anton Paar digital density and API gravity meter..........................96
Figure 3.8 Schematic of the GC/FID system. 99
Figure 3.9 The simplified Schematic of the thermo-microbalance of the TGA 102
Figure 4.1 Mechanism of coke formation in upgrading reaction...110
Figure 4.2 TGA and DTG of the deposited coke and residue of upgraded heavy oil 118
Figure 4.3 Boiling-point fractions for feedstock and produced oil..119
Figure 4.4 Coke yield and asphaltene content after upgrading of heavy oil at different C/O ratio 128
Figure 4.5 Dehydrogenation of CH reaction scheme..131
Figure 4.6 Typical organosulphur compounds 137
Figure 4.7 TGA and DTG of the deposited coke and residue of upgraded heavy oil 143
Figure 4.8 TBP distribution curves of feedstock and produced oil 146
Figure 4.9 BSE images of bio-catalyst powders of a) 3wt%Pd/E. coli; b) 20wt%Pd/E. coli 147
Figure 5.1 Mild hydrodeoxygenation at 230 oC of bio-oil...153
Figure 5.2 Effect of temperature at different reaction time on product yield........................155
Figure 5.3 Effect of time and temperature on amount of organic, gas and coke 156
Figure 5.4 Effect of temperature and time on HDO products water content.........................157
Figure 5.5 Effect of time and temperature on products viscosity 160
Figure 5.6 Reaction network for the conversion of levoglucosan to hexadecanoic acid ethyl ester...161
Figure 5.7 Effect of time and temperature on DOD (%) 162
Figure 5.8 Degree of coking (%) as a function of degree of DOD (%)................................163
Figure 5.9 GC-MS chromatograms of a) raw bio oil and b) upgraded bio oil organic phase165
Figure 5.10 Effect of HDO temperature and time on the concentration of cyclopentanone. 166
Figure 5.11 Effect of HDO temperature on the concentration of Acetic acid 167
Figure 5.12 Effect of HDO temperature on the concentration of a) Guaiacols b) Syringol and Phenol 168
Figure 5.13 Effect of HDO temperature and time on the produced gas composition 169
Figure 5.14 Degree of Hydrogen Consumption (%) as a function of degree of DOD (%) ...171
Figure 5.15 Effect of temperature on DOD (%) 182
Figure 5.16 Effect of temperature on product oil viscosity 183
Figure 5.17 TGA of fresh and the deposited coke of bio-Pd and Pd/C 184

List of Tables

Table 2.1 Bond dissociation energy of hydrocarbon groups 45

Table 2.2 Key classes of catalytic upgrading reactions during CAPRI process 48

Table 2.3 Typical Lignocellulose Content of Some Plant Materials 55

Table 2.4 Comparison between biomass derived bio-oil and diesel 56

Table 2.5 Physical characteristics of pyrolysis bio-oil 61

Table 2.6 Summery of leading researchers on HDO of fast pyrolysis 69

Table 3.1 Properties of the THAI heavy feed oils. 81

Table 3.2 Properties of the pyrolysis bio-oil 82

Table 3.3 Commercial materials used in the experiments 83

Table 3.4 Heavy oil reaction conditions 86

Table 3.5 Bio-oil reaction conditions 90

Table 3.6 Physical characterisations of used catalysts 94

Table 3.7 RGA gas composition calibration 103

Table 4.1 Effect of thermal upgrading on API gravity, viscosity, coke and Asphaltene yield of heavy oil 107

Table 4.2 Effect of reaction time on API gravity, viscosity, coke and Asphaltene yield of heavy oil 109

Table 4.3 Effect of catalyst type at different reaction time on heavy oil upgraing 113

Table 4.4 Effect of catalyst type at different reaction time on product yield 117

Table 4.5 Produced gas composition for reactions under different catalysts 121

Table 4.6 Micro elemental analysis of feed oil, thermal, and different dispersed catalysts samples 124

Table 4.7 Effect of C/O ratio on API gravity, viscosity, liquid yield and gas yield of heavy oil 127

Table 4.8 Effect of different catalyst in the presence of cyclohexane versus hydrogen media on heavy oil upgrading 138

Table 4.9 Produced gas composition for Ru/C 140

Table 4.10 Effect of Pd catalyst on different support on heavy oil upgrading 144

Table 4.11 Effect of Pd loading of bio Pd catalyst on API gravity and coke yield of heavy oil 145

Table 5.1 Elemental composition of feed bio oil 153

Table 5.2 Main Components of bio-oil and upgraded bio-oil using labelled in Figure 5.9...166

Table 5.3 Critical Characteristics of Solvents....174
Table 5.4 Physiochemical, elemental analysis and mass balance of bio oil and collected organic phase 177
Table 5.5 Water content and acidity of the collected aqueous phase 181
Table 5.6 Product yield distribution of HDO....181

1 Introduction

1.1 Background and Motivation

There are wide ranges of forecast and projections regarding the future of global oil demand. Some estimate global oil demand peak soon after 2025, while other projections estimate continuity of growth in oil demand to 2040 and beyond (Bassam, 2018). Different projections from the same organisation can point to quite different estimates depending on the assumptions used. (Bassam, 2018). Figure 1.1 presents a range of organisations forecast for global oil demand over the next 20 years. Majority of the projections estimate a continuation of the rise of global oil demand by 2040. However, even those estimations that forecast a drop in oil demand, do not see a significant drop-off. The IEA (International Energy Agency), (2019) Sustainable Development scenario which forecasts the highest drop in global oil demand, estimates 15 Mb/d (million barrels per day) decrease of global oil demand by 2040 which is at 95 Mb/d today. Knowing that the IEA scenario considers tough climate change policies for reducing carbon emissions from the goals set out at the Paris COP21 meetings.

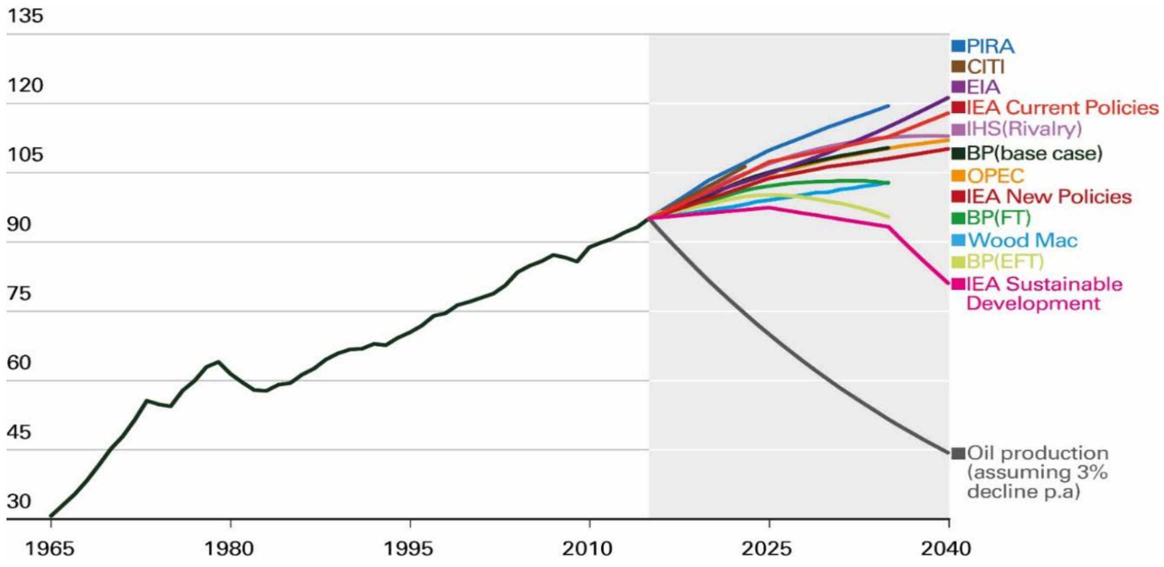


Figure 1.1 World oil demand (Mb/d)
Range of organisations forecast for global oil demand over the next 20 years (Bassam, 2018)

Throughout the forecast period to 2040, conventional crude oil is predicted to remain the fuel with the largest share in the energy market. (OPEC, 2017). OPEC (The Organization of the Petroleum Exporting Countries) annual World Oil Outlook (WOO) reports suggest countries such as China, India, Brazil and other emerging economies would drive this demand in long-term trends. The developing countries' oil demand is expected to increase, mainly due to stronger economic growth potential, an expanding middle class as well as high population growth rates. As today the world's conventional crude oil approaches its peak, exploitation and extraction of heavy oil still one of the answers to the rise in global oil demand (Hirsch et al., 2005). The International Energy Agency (IEA) has estimated the non-conventional-oil (heavy crude oil and bitumen) global reserve is to be about 6 trillion barrels (IEA, 2018), which has the potential of filling the market gap as the future demand increases.

Non-conventional oil resources make up about 70% of the world's total oil reserves which is between 10 to 13 trillion barrels (Zhang et al., 2012). On the other hand, non-conventional reserves are discovered in significantly larger amounts in more politically stable regions such as Europe (Difiglio, 2002). Therefore, non-conventional oils could potentially fulfil the global energy market needs for the next fifty years. Despite the vast deposits and long-term promising energy source, only very few attempts have been made by selected countries to develop extraction and upgrading methods and exploit the non-conventional oil resources. Countries, especially in Africa and the Middle East region, have still not made any real attempts at utilising non-conventional resources (Anderson, 2006). A crude oil reserve largely comprises heavy, viscous substances both arduous and expensive to extract. Non-conventional oil is characterised by low degree API (American Petroleum Institute) gravity, which is measured against a specific gravity relative to water, and exhibits high viscosity, low hydrogen to carbon ratio, is rich in sulfur, nickel, vanadium contents and high oxygen and nitrogen concentrations (Hoshyargar et al., 2013). Light oils have an API gravity higher than 31.1^{o} whereas heavy oils have an API of 22.3^{o} or less, with bitumen or oil sands possessing an API gravity of less than

10° (Conaway, 2000). Conversely, heavy oils have particularly high viscosities when contrasting lighter oils, making them more energy extensive in extraction and transportation process and more significantly, decreasing market product values (Rana et al., 2007). Therefore further surface treatment and upgrading are required for heavy oil to meet the market quality requirements, which will further increase the final product cost. For example, the global energy market experienced a significant change in conventional oil. According to the information available by OPEC, the price of average light crude oil dipped from 90 USD/bbl in 2014 to 28 USD/bbl in February 2016 which caused a significant problem for independent oil companies in non-OPEC countries, especially those with relatively higher extraction cost, e.g. heavy oil producers. On the other hand, heavy oil producer companies continued the extraction process even though the break-even cost estimation can be as high as 60-80 USD/bbl. Their prediction according to economic experts was that crude oil could potentially trade as high as 70 USD/bbl as early as the end of 2016 and crude oil is trading at around 70 USD/bbl today in 2019. Thus, the global crude oil price is the main factor which controls the commercial development of heavy crude oil resources (Atkins et al., 2011). Moreover, surface upgrading and conversion of heavy crude oil or bitumen into synthetic crude oil (or syncrude) are only economical during periods of high deviation between the heavy oil and light crude oil prices, which covers both the extraction and upgrading cost (Adib et al., 2015). The process of upgrading the heavy oil/bitumen into synthetic oil suitable for refining requires surface upgrading processes such as solvent deasphalting, catalytic cracking, delayed coking, etc. However, there are major disadvantages of low conversion and high yield of undesirable by-product coke in some surface upgrading processes such as delayed coking (Chen et al., 2004). Additionally, the use of surface upgrading processes could produce a significant amount of emission of greenhouse gases (GHG) which have a negative impact on the environment (Furimsky, 2009). Therefore, the development of efficient in-situ upgrading technologies, that are capable of converting the heavy crude oil to light oil before reaching the surface could significantly reduce the environmental impact as well as improving the economics of production of heavy oil and bitumen resources.

Conventional light oil is recovered by primary and secondary methods. The primary recovery, which is controlled by natural drive mechanisms, such as gas drive, water drive or gravity drainage. Only between 5 and 20% of the initial hydrocarbons in place are produced during primary recovery depending on natural drive mechanisms involved (Carcoana, 1992). The secondary production stage begins when the reservoir pressure is so low that the recovery rates are not economical, or when the high amount of water and energy are required for steam generation. The net efficiency of combined primary and secondary methods is below 40% of the Original Oil in Place (OOIP) (Stephen, 2013). On the other hand, heavy oils are generally extracted using tertiary recovery methods known as Enhanced Oil Recovery (EOR). EOR technologies endeavour to improve oil displacement efficiencies by increasing heavy oil flowrate. The various EOR technologies practised on oil reserves succeed primary and secondary techniques, which generally recover a small fraction of low viscosity conventional oil using pressurised gas and water, or pressures from the reservoir itself. EOR aims to recover adhering residual oils by utilising temperature to decrease viscosities, or using external constituents to lower interfacial tensions, holistically improving oil flow and reclamation (Shah et al., 2011). The EOR techniques consist of thermal and to a smaller extent non-thermal methods such as CO2 and microbial flooding. However, EOR methods involving the application of heat are generally more suited to heavy oil with an API gravity less than 20^o, due to increased energy demands requiring higher costs; thermal technologies, therefore, become economically viable when cold technologies are considered ineffective in recovering heavier oils (Speight et al., 2014). Thermal EOR techniques can be classified as steam-based and in-situ combustion. The Cyclic Steam Stimulation (CSS) also known by name of “huff-and-puff” and Steam Assisted Gravity Drainage (SAGD) are examples of implemented steam-based techniques for thermal EOR. However, CSS has a relatively low recovery factor (10-40% OOIP) because of the non-continuous nature of the process. The SAGD method, despite its relatively high recovery factor (50% OOIP), requires vast energy and is a cost-intensive process which involves a high amount of water consumption as well as electricity for steam generation. The process leads to a cost of 22 USD/bbl, which could be potentially comparable to mining as well as surface upgrading (Greaves et al, 2012). On the other hand, the in-situ combustion is the other classification of EOR processes which include; conventional in Situ Combustion (ISC) and the novel Toe-to-Heel Air Injection (THAI) and its add-on Catalytic upgrading process In-situ (CAPRI). The advantages of in-situ downhole upgrading are the production of relatively low-viscosity oil by the use of available heat and gases, which makes the produced oil transportable without requiring the addition of diluent and reduces the requirement of further surface upgrading (Xia, et al., 2002).

THAI and its catalytic add-on CAPRI have been developed over the last 15 years (Rogel et al., 2009). In the THAI process, a relatively limited amount of heavy oil in the reservoir is oxidised with its combustion front at the toe and it is prolonged by steady injection of air through a vertical well. Unlike ISC, in THAI, the combustion zone is anchored to the horizontal well at optimum operating temperature. The thermal cracking reactions in THAI technique happen in the mobile oil zone (MOZ) and extended upgrading by catalytic cracking (CAPRI) occurs as the hot mobilised oil flows across the layer of pelleted catalyst packed around an annulus surrounding the horizontal well. This causes further upgrading reactions as the mobilized heavy oil flows through the packed-bed of catalyst. Evaluations suggest that the THAI/CAPRI process costs three timess less than producing barrel using SAGD process as well as minimising water usage, environmental impact of the process and reducing the surface upgrading of the product oil. The amount of required commercial hydrodesulfurisation (HDS) catalyst in THAI/CAPRI process is estimated to be around 20 tonnes for a 500 m horizontal well, costing $70,000 to $100,000 (Shah et al, 2011). If THAI/CAPRI can potentially achieve 20^{o} API gravity this could add a $20–30/bbl margin of profit over conventional extraction. Additionally, Based on a production rate of about 800 bbl/d, the estimated payback time is less than10 days. However, previous studies suggest the fixed-bed system results in rapid catalyst deactivation due to deposition of carbonaceous materials such as asphaltenes and metal deposits at the mouth of the pores of the alumina during the process. Metal oxide catalysts are typically more resistant to deactivation by poisoning, but this still occurs through restricted access to active sites (Forzatti & Lietti, 1999). Further studies have supported the above findings where deposition from nickel and vanadium sulfides within heavy oil contribute to the plugging of pores and active sites, reducing catalyst activity (Marafi et al, 2008). This was suggested to be one of the main downsides of the CAPRI process with catalysts operating time being no longer than 90 hours. Recognising the mentioned drawback in the CAPRI and the problems of filling the horizontal production well with pelleted refinery catalyst, it was observed using ultrafine dispersed catalyst enables a once-through upgrading process. Much smaller particle size catalysts with nanometre range improves active sites compared to pellets, it potentially shorten the diffusion path and enhance mass and heat transfer (Ovalles et al., 2003). Furthermore the higher surface area of dispersed catalyst allows large complex molecules to reach active sites rather than plugging pores as is the case in the fixed-bed. However delivering the ultra-fine catalyst to the MOZ in the THAI process is still a major challenge.

There are two delivery methods being studied at the moment; the first method is accomplished by injecting the nanoparticle (NPs) catalysts into the oil-bearing, in the form of a slurry and transporting it into the MOZ. The other potential delivery method is using a suitable metal precursor for in-situ precipitation of the catalyst NPs (Ortiz-Moreno et al., 2012).

The comparative study conducted by Hart (2014) reported the superiority of dispersed ultrafine catalyst (batch reactor) over fixed-bed of pellets. The test was conducted at a temperature of 425 ^{o}C, the pressure of 20 bar, and 10 min residence time in the presence of Co-Mo/Al_2O_3 catalyst. The results showed that dispersed catalyst had a better upgrading performance than fixed-bed of the pelleted catalyst with 3.1^{o} API gravity improvement. On the other hand, it is challenging to simultaneously increase the amount and quality (API) of upgraded liquid product and also suppress coke yield. Heavy oil is hydrogen-deficient; hence carbon-rejection and/or hydrogen-addition are the two main routes of upgrading. Hydrogen source helps to terminate part of the active chain and limit the additional free radical reactions during C-C breakage which potentially lead to the formation of larger molecules. Ali et al (1999) and Biniwale et al (2005) determined that dehydrogenation solvent such as Cyclohexane, decalin and methylcyclohexane. Dehydrogenation of cycloalkanes, such as Cyclohexane, methylcyclohexane and decalin, can effectively limit the coke precursors generation by providing hydrogen supply during the catalytic cracking.

In order to improve the level of upgrading and maximizing the process economics, it is necessary to investigate alternative catalysts with high cracking performance, long life time and low-cost catalyst compared to refinery catalyst. Bennett et al. (2013) has investigated the immobilisation of metallic NPs upon micron-sized bacterial biomass as an alternative to commercial dispersed catalysts. Platinum group metals (PGM) are known for their high hydrogenation selectivity, and low coke formation compared to other metal groups. However, it is significantly uneconomical to use virgin noble metals for applications such as heavy oil upgrading. Therefore studies are in progress to find a sustainable technology which enables recovery of PGMs from secondary or waste sources (Murray, 2010). Road dust especially around major roads in urban areas contains high amount of PGMs since the autocatalysts were introduced in Europe from the 1980s (Jarvis et al., 2001). Murray, (2012) has developed technology to recover PGMs from road dust by leaching method to produce a palladium rich concentrate solution for production of biomass-based catalysts. Therefore bio-catalysts could potentially be an alternative and cheaper choice for commercial homogeneous catalysts, which has been shown to be active as a catalyst (Omajali et al., 2016).

Despite the popularity of supported palladium catalysts because of their high performance in the hydrogenation of organic chemicals (Huu et al., 2012), they often suffered from the deactivation which is a financial burden in the chemical industry (Albers et al., 2001). The major reason for deactivation of palladium catalysts is the strong chemisorption of impurities in the feed which decreases the active sites. Sulfur is one of the most crucial impurities that cause the deactivation of the palladium catalyst. Sulfur changes the catalytic properties of palladium catalysts (Meeyoo et al., 1998). Lampert et al. (1997) observed partial deactivation of palladium from sulfur-containing gases. A study by Trimm et al. (2001) showed the poison efficiency of sulfur to metal catalysts is: $SO_4^{2-} < SO_4 < H_2S$. Moreover in the catalytic combustion of methane to carbon dioxide and water and in oxidation reactions in the exhaust of lean-burn natural gas engines sulfur is identified as being a critical contaminant (Mowery et al, 1999).

On the other hand, noble metal catalysts, including Pd, have been shown to be effective in the upgrading of biomass which is naturally low in sulfur (Zhai et al., 2014; Capunitan et al,. 2014). Therefore part of this thesis concentrates on the application of Pd catalysts in bio-oil upgrading. Moreover, with considerable consumption of petroleum-derived fuels around the world, and concern about global climate change, the importance of producing fuels from renewable energy resources is rising and it has been the main concern of many researchers these days. Currently, 195 countries have ratified the United Nations Framework Convention on Climate Change (UNFCCC) as a way for countries to work together to limit global temperature increases and climate change (European Union Consilium, 2017). The convention contains the Doha amendment to the Kyoto Protocol (in force between 2013 and 2020), and the Paris Agreement (from 2020). For the countries involved, the implementation of a carbon-neutral alternative fuel assists in the fulfilment in a global reduction of carbon emissions (Kabir et al., 2017). Today, widespread attention has been drawn by Biomass among the most capable renewable resources of energy that are available on earth (Bu et al., 2012a). It can also be considered as the only fuel source available in solid, liquid and gaseous form. During the years 1979-2009, it has been reported by review of scientific research that altogether 56% of the renewable energy publications were related to research on biomass (Teella et al., 2011). According to the study of Lopes et al. (2013), there is a huge number of biomass feedstock including animal wastes, residues from the forestry and agriculture, vegetable oil and wood. Fuels that have been derived from the resources of biomass have shown a number of advantages over the fossil fuels. The first advantage is that as compared to the fossil fuels they are able to generate less emissions, almost they contain no emissions of sulfur and the emissions of NOx are also found to be low. The second advantage is that these fuels are sustainable. The third advantage is that the biomass is found to be carbon-neutral. In the growth of plants, it utilizes carbon and when the biomass is burned the carbon is returned. Hence, the loop of the carbon cycle is closed and does not cause any increase in the level of Carbon dioxide in the atmosphere. The fourth advantage is that biomass also has the geopolitical advantage as it has been distributed among several countries (Huber et al., 2006; Lopes et al., 2013; Xiu & Shahbazi, 2012). On the basis of the form of the energy that has been desired and the characteristics of the feedstock, a number of processes have been established for the conversion of biomass to different types of energy. Hence, a wide range of methods of conversion has been developed. For the production of liquid fuels, the thermochemical conversion is found to be suitable among all the conversion methods (Xiu and Shahbazi, 2012). For the conversion of biomass, the four major thermochemical methods include liquefaction, gasification, pyrolysis and direct combustion (Bridgwater, 1994). In order to convert biomass into bio-oil, fast pyrolysis is considered as the most effective method as it has a number advantages such as easy processing, increased bio-oil yield and short reactions with no pre-treatment required (Fisk et al., 2009; Bridgwater, 2012). It requires the thermal decomposition of the biomass in the absence of oxygen. In order to attain the liquid products, short vapor residence times and moderate temperatures are required (Bridgwater, 2003). Apart from the benefits of system

of fast pyrolysis, bio-oil is not found to be suitable for its direct application as a fuel of transportation due to high content of oxygen (35-50%) and water (15-30%) that results in the low calorific value of 17 MJ/kg as compared to the 40 MJ/kg calorific value of fossil fuel (Bridgwater, 2004). This prevents the direct use of bio-oil as a fuel of transportation and also makes the bio-oil unstable. Furthermore, clogging, stoppage of vehicle, low mobility, engine corrosion, high-pressure drop, fluidity and multiphase flow may occur (Czernik et al., 2004). Due to the aforementioned undesired characteristics of bio-oil, a process dealing with these problems is necessary to improve the liquid product and ensure of its quality consistency.

An upgrading process can be defined as any process that results in a higher-quality and improved-consistency product. By definition, this leads to numerous methods which can be classified mainly into three categories: Chemical, physical and catalytic upgrading processes. Figure 1.2 illustrates most of the possible upgrading routes for the production of chemicals and biofuels. However, examining closely the undesirable properties of bio-oil as well as its chemical composition, we notice that most of them are linked with each other, attributed to the presence of oxygen. As mentioned above, the high oxygen content of the bio-oil is either in the presence of water which results in the decrease of the heating value and causes acidity or in the presence of acids and phenols which cause material incompatibility and increase the polarity of the mixture causing non-miscibility with the non-polar petroleum fractions.

The direct blending with or replacement of petroleum and petroleum products, demands the removal of nearly all of the oxygen contained in the bio-oil (Mortensen et al., 2011). Thus, a feasible process to reduce the oxygen could lead to the solution of an alternative to crude-oil. The catalytic upgrading processes however, have been the most effective route in the reduction, of the oxygen in the bio-oils.

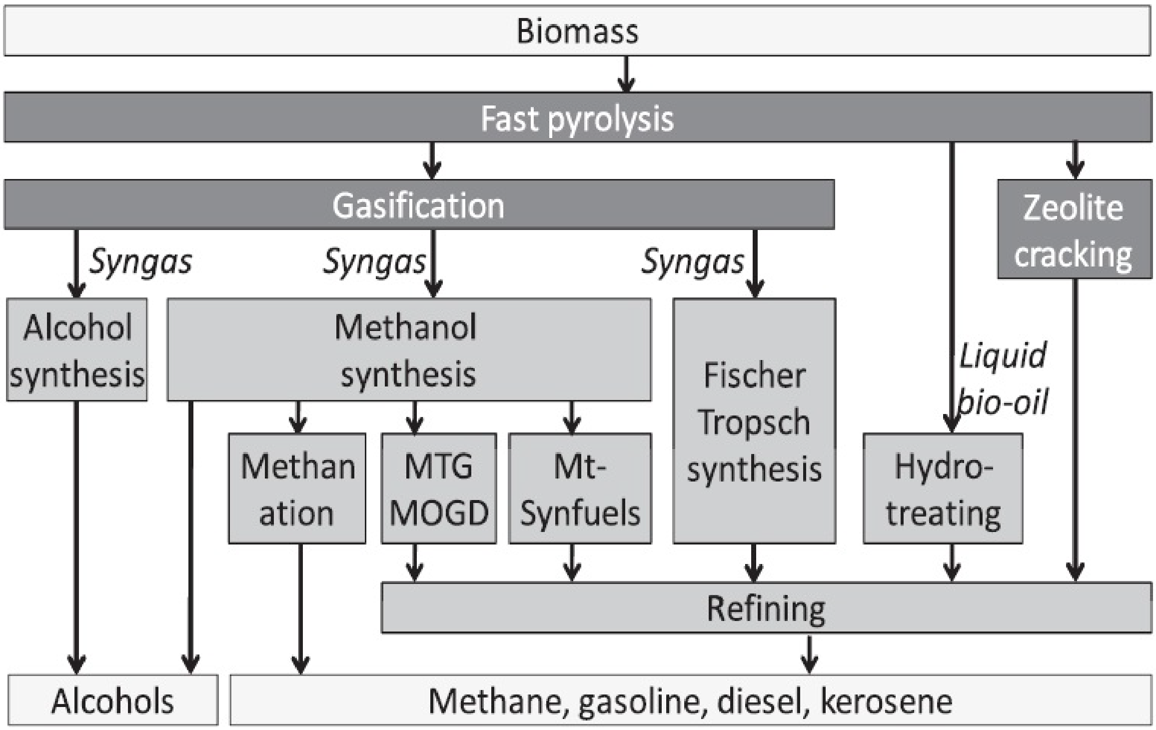


Figure 1.2 Routes of bio oil upgrading into biofuels
(Bridgwater. 2011)

The two major routes of catalytic upgrading are (1) hydrotreating and (2) cracking (zeolite cracking). Both of these processes have their counterparts in oil refinery industry. Bio-oil catalytic hydrotreating, rejects oxygen mainly as H2O in the presence of a catalyst and H2 and it is similar to the HDS process from the petroleum industry. The principal reaction during hydrotreating is hydrodeoxygenation, hence this process is also known as HDO. The other catalytic upgrading route is zeolite cracking which rejects the oxygen primarily as CO_2 in the absence of H_2, using zeolite catalysts since cracking is the main reaction as the name implies

(Mortensen et al., 2011). Bio-oil hydrotreating process has shown to be more effective than catalytic cracking in terms of oxygen removal with great research potential (Jones et al., 2013; Jones et al., 2009). In addition, fast pyrolysis/catalytic hydrotreatment (thereafter HC to produce light hydrocarbons) is considered as a milestone in the biorefinery-crude oil refinery integration (Jahirul et al., 2012; Elliott et al., 2009). In crude-oil refinery, hydrotreatment is used for the elimination of heteroatoms and different reactions occur like hydrodesulfurization, hydrodemetallation and hydrodenitrogenation for sulfur, metals and nitrogen respectively. Likewise, oxygen can be eliminated as H_2O, CO_2 or CO through a combination of hydrodeoxygenation, decarbonylation, decarboxylation, and dehydration reactions. However, the goal of catalytic hydrotreatment is to expel oxygen as water through HDO without though the saturation of aromatic rings (Arbogast et al., 2013; Jones et al., 2009). Thermal instability of bio-oil is the main disadvantage of the HDO process which increase the coke formation and lead to catalyst deactivation (Mortensen et al., 2011). Therefore solvents can be used in order to reduce coke formation and enhance the HDO process (Oasmaa et al., 2004). Hilten et al., (2009), found in use of solvent in the HDO process.For example, hydrogen-donor solvents such as decalin and tetralin, were used to reduce coke formation during the HDO process (Zhang et al, 2005). Subsequently, hydrocarbons solvents such as ethanol were used for bio-oil upgrading (Agblevor et al., 2012). However, hydrocarbons achieve only partial upgrading of bio-oil components because of their hydrophobicity.

Supercritical fluid has gas-like characteristics with significantly high diffusion rate and high density therefore can be used as a solvent in a HDO process. The characteristics of low viscosity and high density enhance the heat and mass transfer during the reaction as well as increasing concentrations of solvent around a solute (Mazaheri et al., 2010; Antal et al., 2000). Supercritical methanol, ethanol and acetone have been previously reported to be effective in esterification of biomass liquefaction leading to diesel production (Chen et al., 2015). Such solvents are effective in hydrogenation of unsaturated compounds, which makes them ideal to be used as hydrogen donors in the process such as HDO (Huang et al., 2014; Mazaheri et al., 2010). The aim and objectives of the research and thesis layout are listed below in Sections 1.2 and 1.3, respectively.

1.2 Aim and Objectives of the Study

The main the goal of utilising NPs catalysts with the THAI (crude oil) and HDO (bio-oil) process was to reduce the viscosity of the oil to enhance the pipeline transportation. Moreover, the catalysts are to remove metal impurities and increase the degree of API gravity of the oil in order to provide a feedstock that meets refinery specification and downstream processing. The specific objectives are listed below;

1. To investigate the effectiveness and performance of different catalyst under different conditions upon upgrading of heavy oil;

a. The extent of thermal upgrading versus catalytic cracking of heavy oil.

b. Effect of reaction time and temperature.

c. Effect of catalyst type at different reaction time.

d. Effect of hydrogen and cyclohexane upon the performance of different catalysts.

e. To compare of bio-Pd/*E. coli* with commercial Pd/Al_2O_3 and Pd/*C* in terms of the catalytic performance of the upgrading of heavy oil.

f. Effect of different metal loading of the bio-Pd catalyst.

2. To investigate upgrading of pyrolysis oil through Hydro-deoxygenation.

a. The effect reaction parameters such as reaction temperature and reaction time.

b. To compare the catalytic performance of bio-Pd/*E. coli* with Pd/*C* in bio-oil HDO Process.

c. To investigate the effect of methane and cyclohexane solvents upon bio-oil upgrading via HDO.

1.3 Thesis Organisation and Overview

The six Chapters in this thesis demonstrated the experimental technique of catalytic upgrading of heavy crude oil and bio-oil. The study examined the effect of bio-Pd NPs in comparison with commercial catalysts upon down-hole upgrading of heavy oil as well as bio-oil upgrading via HDO route. The study emphasizes controlling coke formation and catalyst deactivation while maximising the level of upgrading. The extent of upgrading for heavy crude oil was evaluated in terms of change in API gravity, viscosity, true boiling point (TBP) distribution, sulfur and metals removal, and change in asphaltenes content. While the upgrading of bio-oil was evaluated in terms of oxygen and water removal, viscosity and acidity.

Chapter 1 provides an in-depth introduction to the study and motivation. It also identified the need to sustain fuels, provides an overview of the world energy market, and identified considerable areas of challenges from previous studies that require further investigation. In Chapter 2, the different upgrading technologies available for heavy oil and bio-oil are reviewed. The Chapter provides the fundamental knowledge of CAPRI and HDO process. The experimental set- up and procedures used in this study are detailed in Chapter 3. Also, the instrumental techniques used to measure changes in upgraded oil samples properties; produced a gas composition, characterised fresh and spent catalysts after reactions are described in this Chapter.

Chapter 4 shows the effect of different reaction temperature and time in the presence of different catalysts. It examines the effect of hydrogen gas and hydrogen donor solvent upon the performance and deactivation rate of different catalysts. This chapter also studies the catalytic activity of biomass-supported Pd catalysts in comparison with another type of commercial Pd NPs.

Chapter 5, is devoted to finding the optimum reaction time and temperature for bio-oil HDO upgrading. The emphasis is on the effects of reaction temperature and time upon the degree of HDO, hydrogen consumption, viscosity and acidity of produced oil, followed by studying the effect of two different solvents on the HDO process. The chapter also studies the catalytic activity of bio-Pd catalysts in comparison with commercial Pd/C in HDO process. Finally, Chapter 6 presents some concluding remarks on the results of the studies and highlights various aspects of this study that still need further investigation.

2 *Review of Heavy Oil and Bio-Oil Upgrading Processes*

2.1 Crude Oil

Crude oil is defined as a chemical organic compound and is a fossil fuel that is formed from the remains of living organisms which have accumulated at sediment bottoms (Clarke, 2007). Bacterial actions and degradation over time transformed the accumulated deposits into hydrocarbons and other compounds. (Robinson, 2006). Geologically, crude oil undergoes compositional changes because of biological and physical degradation. The biological degradation consists of various hydrocarbons removal and formation of acidic compounds as well as selective degradation of specific isomers of a compound. These compositional changes are distinguishable from alterations caused by physical processes such as water-washing and evaporation and suggest in-situ biological degradation of oils inside the pore-space of the reservoir (Ian et al., 2003) (Figure 2.1). Oxidation of oil during biodegradation affects the composition and physical properties which leads to an increase in API (American Petroleum Institute) gravity, a measure that is associated with the economic value of the oil based on the specific gravity of degassed oil (Hunt, 1979). The decrease in API gravity correlates to increases in oil sulphur content, metal content, density and viscosity (Connan, 1984; Volkman 1984; Krejci, 1932). These changes have a negative effect on oil extraction and refinery operations and therefore reduce its market value.

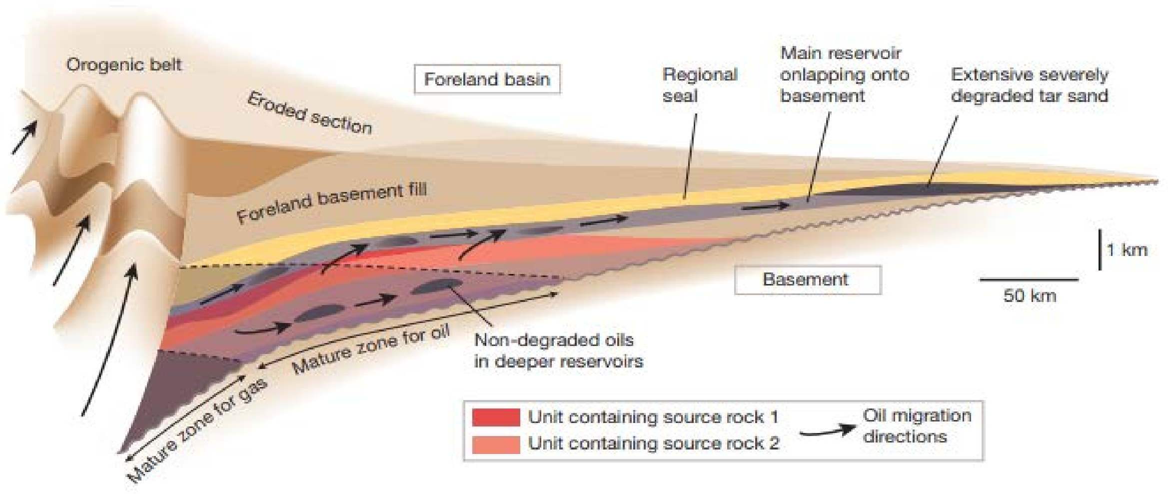


Figure 2.1 the origin of heavy oil and tar sand

(Ian et al., 2003)

The majority of world's oil reserves are biodegraded heavy and extra-heavy oils which are located in North (e.g. Canada) and South America (e.g. Venezuela) and elsewhere. The API gravity of heavy oils are at the range of 10-20^o. Oils with 10^o or less API gravity are classified as super-heavy oils, and a conventional light, non-biodegraded oil has an API gravity range between 35–38^o API (Figure 2.2.ab) (Roadifer, 1987; Hunt 1979). Tar sands are classified as another type of oils which consist of sandstones saturated with heavy and super-heavy oil with API gravity around 6-12^o (Figure 2.2.c). Microbial alteration is the main cause of appearance of vast majority of heavy oils in the reservoir (Demaison, 1977; Creaney et al., 1990), and accumulation of biodegraded heavy oil and tar sand makeover 50% of the Earth's oil inventory (Winters, 1969; Oil market report, 2019).

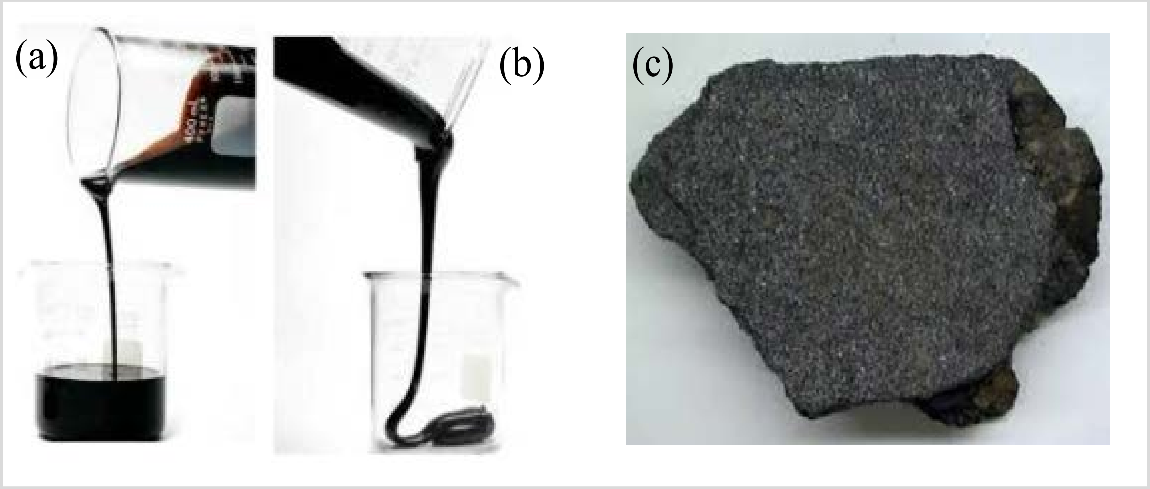


Figure 2.2 Photograph of (a) Light oil; (b) Heavy oil and (c) oil sand

2.1.1 Composition of Heavy Oils

Different models have been proposed depicting the molecular structure and components confined within the molecule of crude oil. Among these models, micro-emulsion model of crude oil molecule, presented by Wiehe and Liang (1996), incorporates the four main components called; saturates, aromatics, resins and asphaltenes shown in Figure 2.3.

The structure of saturates consists of non-polar hydrocarbons along with branched, linear moieties containing hydrogen such as naphthenes and paraffins; the branched or unbranched hydrocarbons. The volume percentage of naphthenes and paraffins may account for around 60% and 20% in crude oil respectively (Gray, 1994; Boduszynski, 1988).

The biodegradation of oil in the reservoir affects the composition of oil by reduction of thesaturates group of compounds through oxidation of oil (C6+ components). This increases the overall yield of the high molecular weights compound and overall boiling points of crude oil.

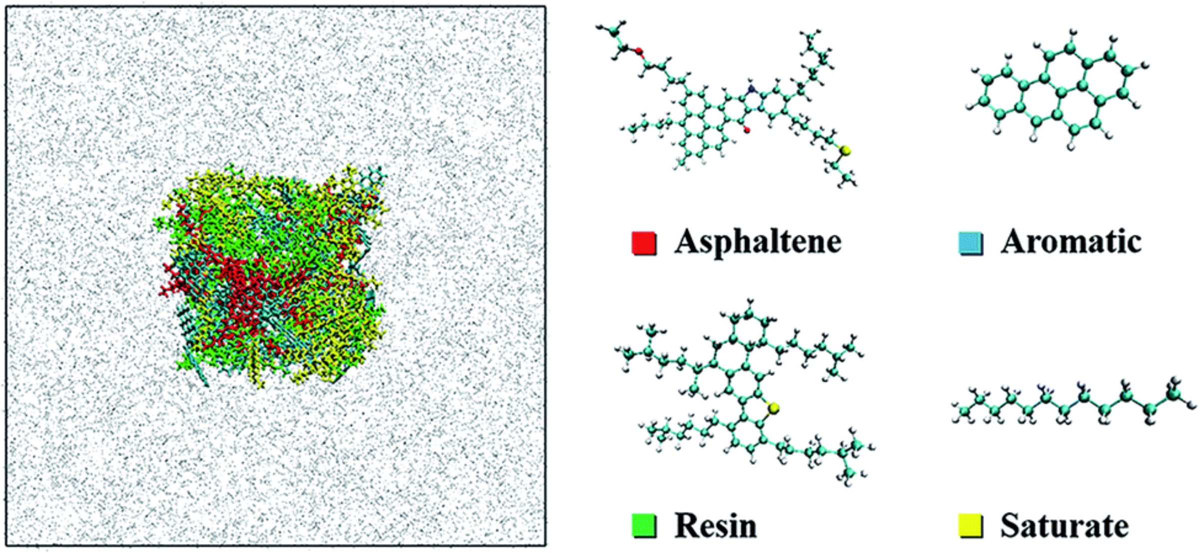


Figure 2.3 Sectional view of the crude oil and SARA components

Sectional view of the simulation setup for the oil (left) and the molecular structure of SARA components (right) (Liu et al., 2017)

Aromatics are hydrocarbons with sigma bonds and delocalized pi electrons between carbon atoms forming a circle. These benzene rings are unsaturated and in the case of multiple rings are bonded together. The benzene rings in aromatic hydrocarbons might be linked with naphthenic ring or paraffinic side chains. Aromatics are generally higher in concentration in heavy oil relative to light oil.

Resins contain heteroatoms including sulphur, nitrogen and oxygen and have been categorized among polar poly-aromatics. The solubility ratio of resins is higher in light alkanes such as solvents like n-heptane and n-pentane. Resins possess the molecular weight less than 1000 g/mol. Among all the other discussed components, resins and asphaltenes are the heaviest ones present in the crude oil. In this context, heaviness and denseness of heavy crude oils can be interlinked with the proportions of resins and asphaltenes present in them which are relatively higher than their proportions in light crude oil (Alvarez-Ramirez, et al., 2006). Composition of asphaltenes include multiple cyclic structures which are aromatic and bonded with either naphthenic or aliphatic moieties. The component asphaltene lies in the centre, residing in the core of micelle. Resins, adsorbed on the surface, disperse and spread the asphaltene due to their surfactant-like properties (Wiehe and Liang, 1996; Leyva, et al., 2007). The molecular structure of asphaltenes is shown in Figure 2.4

The properties of asphaltenes affect the properties of oil which consequently impact the oils' processing by modulations in pressure and temperature during extraction and upgrading. During the upgrading process and conversion of heavy crude oils to light hydrocarbon oils, production of CCR (Conradson Carbon Residue or coking tendency) takes place which is the major component of asphaltenes. Multiple sequential activities that initially convert saturates to aromatics, and finally from resins to asphaltenes, result in the formation of a large amount of coke (Sawarkar, et al., 2007). Crude oils also contain proportions of heteroatoms (Nitrogen,

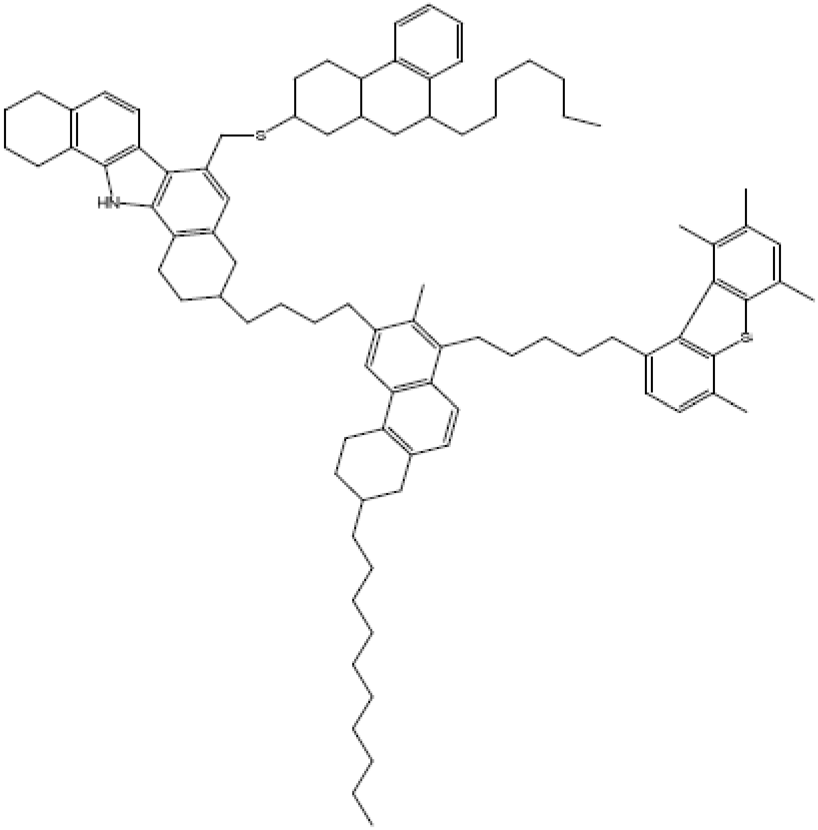
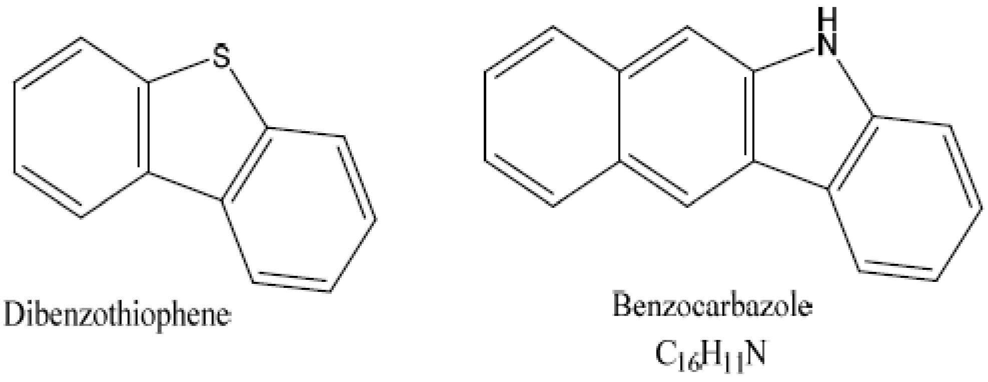


Figure 2.4 The molecular structure of asphaltenes

Sulfur and Oxygen) and heavy metals such as Nickel and Vanadium in their heavier components (resins and asphaltenes). These heavy metals increase the denseness and heaviness of heavy oils due to their higher concentration in resins and asphaltenes than in saturates and aromatics.


Dibenzothiophene

Benzocarbazole
$C_{16}H_{11}N$

Figure 2.5 The molecular structure of heteroatoms in heavy oil.

During catalytic upgrading, these organometallic compounds, negatively impact the catalyst lifetime. As depicted in Figure 2.5, chelating complexes contain these heavy metals (V, Ni) in the form of porphyritic or non-porphyrenic moieties, which affect the upgrading and processing of crude oils (Yin, et al., 2009; Leyva, et al., 2007). Due to extreme temperature and pressure modulations, presence of rock minerals in the crude oil reservoirs results in formation of metallic forms of porphyrin and non-porphyrin structures, which must be minimized during refining.

2.2 Heavy Crude Oil Upgrading Technologies

Depletion of fossil fuel resources is one of the major concerns of the present day and the need to utilize eco-friendly resources is an emerging demand. Availability of abundant, more valuable and cleaner light oil is shifting the trends to upgrade the heavy oil more efficiently. The need for upgrading of heavy oil is the consequence of incompatibility of properties of heavy oil with those of refinery feedstock specifications. Heavy oils possess low viscosity, low API gravity due to high density, a high proportion of asphaltenes and heavy metals. Therefore, upgrading of heavy crude oil is performed with the aim of;

- Manufacture oil with specifications according to refinery feedstock (Diagram 2.6)
- To minimize viscosity and increase fluidity
- To facilitate easy transportation

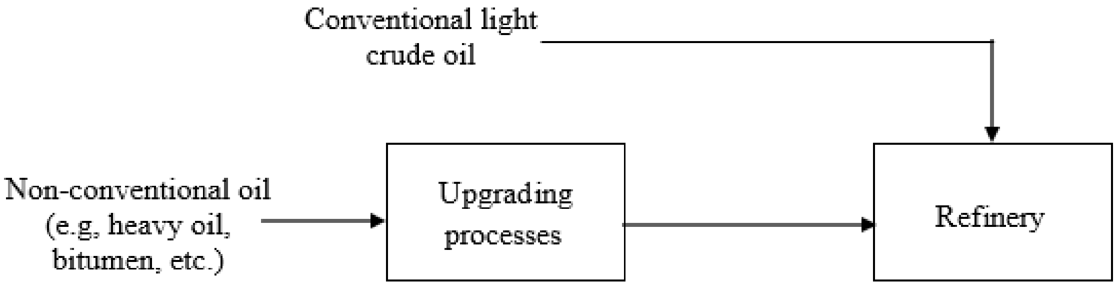


Figure 2.6 Route to refinery for conventional and non-conventional oils.

From economic perspectives, upgrading of heavy crude oil increases the profitability ratio. Moreover, upgrading of bitumen/ heavy oil is a function of market value which presents the price differential between the upgraded and heavy crude oil (Hedrick, et al., 2006; Leyva, et al., 2007).

2.2.1 *Surface Upgrading Processes of heavy oil using dispersed catalysts*

The non-conventional oil i.e. bitumen and heavy oil can help in compensating the shortage by fulfilling the energy demands of the world as they are available in huge amount. During the upgrading and treatment process, a number of hurdles are imposed by the physical and chemical nature of the heavy oil (Sahu et al., 2015; Bellussi et al., 2013). Fluidized catalytic cracking (FCC) technology is a well-stablished process in the industry for oil conversion which involves fine powder catalysts that when fluidised with hydrocarbon vapour, flows through the reactor and pipes resembling a liquid (Figure 2.7). Residuum fluidized catalytic cracking (RFCC) is an extension of the FCC process for heavier feedstocks involving highly contaminated residua. In the past decades, RFCC has become widely used in refineries for conversion and upgrading of oil heavier fractions into high-octane gasoline due to difficulties in the handling of such feedstocks.

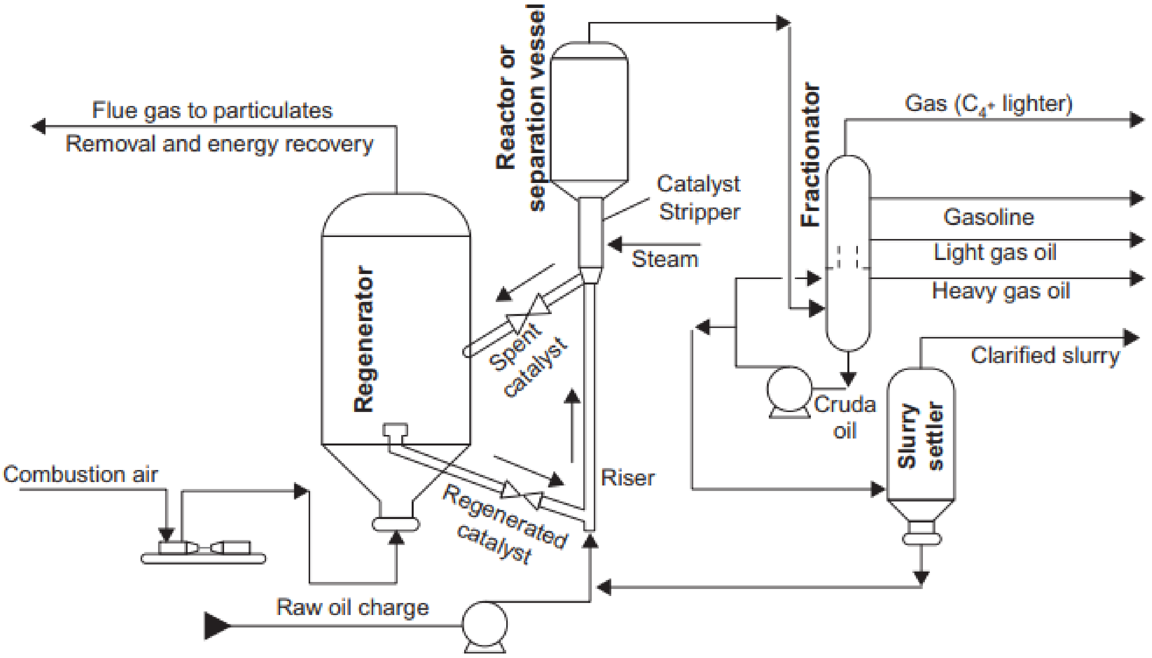


Figure 2.7 Detailed schematic of an FCC process

(Speight, 2007).

Unlike hydrotreating, the process of RFCC is based on redistribution of sulfur rather than removal of sulfur, even though sulfur is removed and retained on the catalyst by means of coke formation. As an integrated process, hydrotreating and RFCC can balance each other to offset many shortcomings such as operational cost of hydrotreating as well as sulfur oxide emissions of catalyst cracking related to residue conversion.

2.2.2 *Catalytic aquaconversion Process*

The catalytic aquaconversion process is considered as a hydrovisbreaking technique with the presence of a catalyst which enables the addition of hydrogen from its feed water source. The hydrogen source reduces the coke formation, however it doesn’t separate high molecular weight compounds such as asphaltene from feedstock (Marzin et al., 1998). Therefore the extent of conversion of residue is relatively low and external diluent are required for transport of product over large distances. The benefit of using such a process is its low operational cost since it doesn't require hydrogen from any other source and any high-pressure equipment.

The following works have shown noticeable upgrading of heavy oil in terms of viscosity with different catalysts; Li et al., (2007) used Nano-nickel catalyst for aquathermolysis at 280 °C and achieved 85.3% viscosity reduction for the Liaohe extra-heavy oil. Yanling et al., (2009) have tried nano-kegging catalyst for the extra-heavy oil Zhen 411 at 280 °C, G540 at 200 °C and 280 °C, and achieved 92.3%, 80% and 90% reduction in viscosity respectively. Another study by Dong et al., (2018) reported a reduction of heavy crude oil viscosity by 85 % using recyclable magnetic Fe_3O_4 catalyst at 280 °C for 6 h.

2.2.3 Heavy Oil Treating Process

Another catalytic process for the conversion of heavy oil is the heavy oil treating (HOT) process. The feedstocks which are generally used for this process include topped crude oils and vacuum residual (API 7-9^{o}). The process uses three fluidized bed reactors including; 1) A *cracker* which is packed with iron ore particles under the similar condition as thermal cracking where the cracking and the steam iron reaction occurs simultaneously. 2) *Regenerator*, coke deposited on the catalyst is partially burned to form carbon monoxide in order to reduce iron tetroxide and to act as a heat supply. 3) *Desulfurizer*, sulfur in the solid catalyst is removed and recovered as molten sulfur in the final recovery stage.

1) $3FeO + H_2O \rightarrow Fe_3O_4 + H_2$

2) $coke/Fe_3O_4 + O_2 \rightarrow 3FeO + CO + CO_2$ and $FeO + SO_2 + 3CO \rightarrow FeS + 3CO_2$

3) $3FeS + 5O_2 \rightarrow Fe_3O_4 + 3SO_2$

2.2.4 Shell FCC Process

The Shell FCC process is designed for heavy feedstocks such as residue and heavy oil for the production of more valuable distillates. The initial step of this process involves heavy feedstocks preheating and mixing with catalysts (often regenerated catalysts are used for significantly lower operating cost). The reaction of the feed oil and catalyst mixture takes place in the riser. The volatile material then separated from the catalysts which then goes through the regeneration process via a cyclone/swirl tube combination to a power recovery turbine. Shell Company claims that they have achieved a higher yield of naphtha because of its feedstock hydrogenation pretreatment prior to FCC.

The Shell FCC process is designed for heavy feedstocks such as residue and heavy oil for the production of more valuable distillates. The initial step of this process involves preheating heavy feedstocks and mixing with catalysts (often regenerated catalysts are used for significantly lower operating cost). The reaction of the feed oil and catalyst mixture takes place in the riser. The volatile material is then separated from the catalysts which then goes through the regeneration process via a cyclone/swirl tube combination to a power recovery turbine. Shell Company claims that they have achieved a higher yield of naphtha because of its feedstock hydrogenation pretreatment prior to FCC.

2.2.5 Hydroconversion in a Slurry Reactor

For the liquefaction of the coal, the VEBA-combi-cracking (VCC) was established in Germany. For catalysts, the combination of red mud (material that contains iron) and the fine coke powder obtained from the Bovey coal is used. According to the reports, the range of the coal conversion was found to be 90-94% and a total of 4000 barrels/day products were produced. The main drawbacks of this process include a large amount of catalyst (5 wt %) and high operating pressure (15-27 MPa) (Sahu et al., 2015; Ancheyta, 2013; Doehler et al., 1987). For the unconventional upgrading of the oil, M-coke process has been developed by the ExxonMobil. It has been found that 90% of the conversion was achieved at a pressure of 17 MPa and at an operating temperature of 440 °C. The molybdenum naphthenate and phosphor-molybdenum acid were present as dispersed catalysts. It has been observed by the ExxonMobil group that the utilization of the dispersed catalysts in the M-coke process displayed high production rate i.e. 1 drum/day in lab-scale and high activity. But, the usage of this process is prevented by the high cost of the catalysts (Schuetze and Hofmann, 1984; Bearden Jr and Aldridge, 1980; Bearden Jr and Aldridge, 1979). For heavy residues, the MICRO CART- RC process has also been developed by the ExxonMobil group. As the homogeneously dispersed catalysts, the oil-soluble manganese, and molybdenum were used in this process. The size of the particle was less than 1 µm. It was observed that there was an inhibition of the formation of the coke. On the other hand, the issue that has been reported in the MICRO CAT-RC process is the recovery of the catalyst (Castañeda et al., 2012; Bearden, 1997).

The Eni Slurry Technology (EST) was developed at ENI at the beginning of the 1990s by the R&D laboratories and the application of the hydroconversion of the heavy oil in a slurry reactor on the commercial scale started with it (Bellussi et al., 2013). The reaction for the upgrading was achieved at a temperature of 400-450°C and a pressure of 150 bar of hydrogen in the presence of an organic oil-soluble molybdenum compound (Bellussi et al., 2013; Montanari et al., 2003). It has been reported that the highly dispersed MoS_2 were formed in-situ under the operating conditions of EST and it was also found that with the long reaction time the size and shape of the catalysts that have been formed remained constant (Sahu et al., 2015; Bellussi et al., 2013). It has also been reported that the metals deposits, the coke precipitated and asphaltene that has been formed, inhibits the activity of the catalysts. In order to mitigate this problem, it has been recommended to remove the metals and the asphaltene before the reaction of hydrocracking (Sanfilippo, 2009; Marchionna et al., 2002). In order to upgrade the different types of heavy oil across the world, EST technology has been used. For the upgrading of the Athabasca bitumen and Venezuela Zuata, a reactor having a capacity of 1,200 Barrel per Stream Day (BPSD) was designed by the Eni in the year 2005 and the reactor capacity has been reached to 23,000 BPSD by the year 2012. Furthermore, since the initiation of the EST process in Italy in the year 2005, in the commercial demonstrating plant, around 23,000 bbl of the feedstock has been upgraded successfully (Sahu et al., 2015; Bellussi et al., 2013).

2.3 In-situ Upgrading Processes

2.3.1 Toe-to-Heel Air Injection (THAI)

THAI is an alternative thermal EOR method which uses a horizontal well and works according to a similar concept as conventional in-situ combustion, to achieve a relatively high oil recovery. The conventional ISC process's VIVP wells have some limitations that led to the concept of THAI. In the 1990's, a collaboration between the Petroleum Recovery Institute, Calgary, Canada, and the Improved Oil Recovery group allowed the development of the THAI technology at the University of Bath (Greaves, 2004). At the Christina Lake, Alberta, Canada, a field trial of the technology was later performed. For the stable propagation of the combustion front, the horizontal production well(s) and ISC were integrated by the technology.

Figure 2.8 shows the production of oil through conventional ISC, where mobilized oil passes through the cold heavy oil before flowing towards the producer well. However, the THAI process has an important feature of a short path for oil flow which is shown in Figure 2.9. This is associated with the location of the horizontal injection (close to the top of the oil layer) and horizontal producer well (close to the bottom of the oil layer). The placing of these wells causes the flow of oil, gas and water only in the MOZ from top to bottom by gravity force. Instead of passing through the cold region as it does in the conventional ISC process, the short oil path way helps to regulate the gas overriding and ensures a stable distribution of the combustion front through the reservoir (Xia et al., 2003).

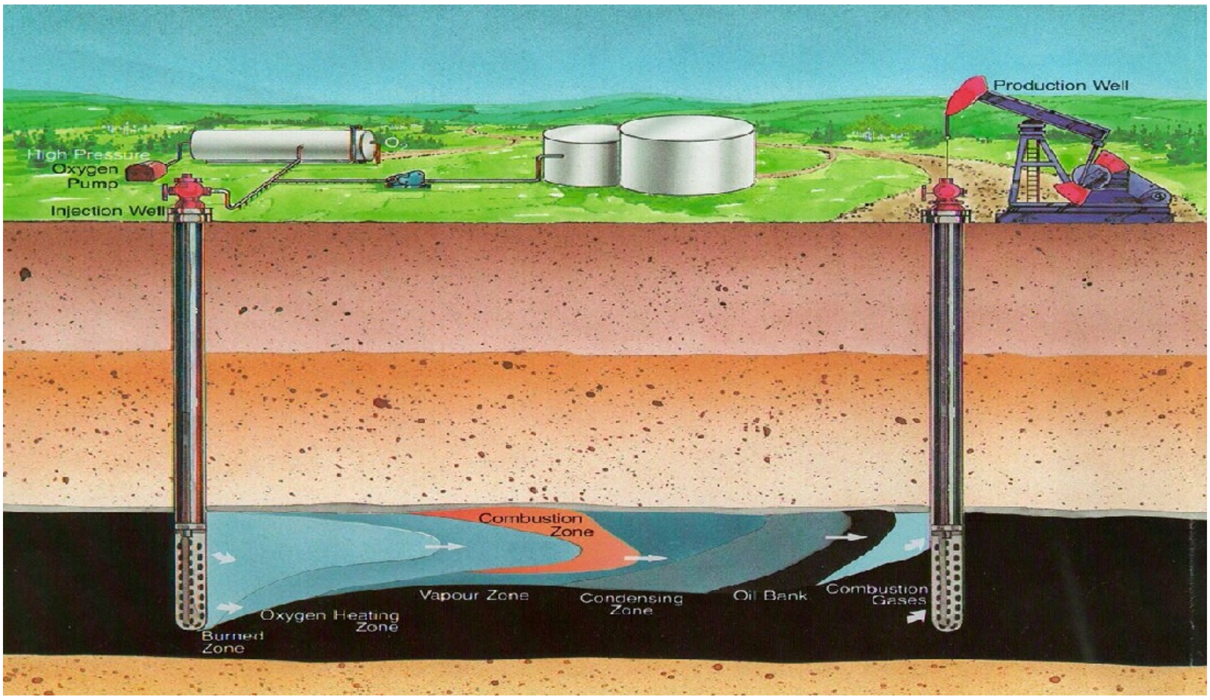


Figure 2.8 Mobilised oil draining in conventional ISC Process
(Speight et al., 2009)

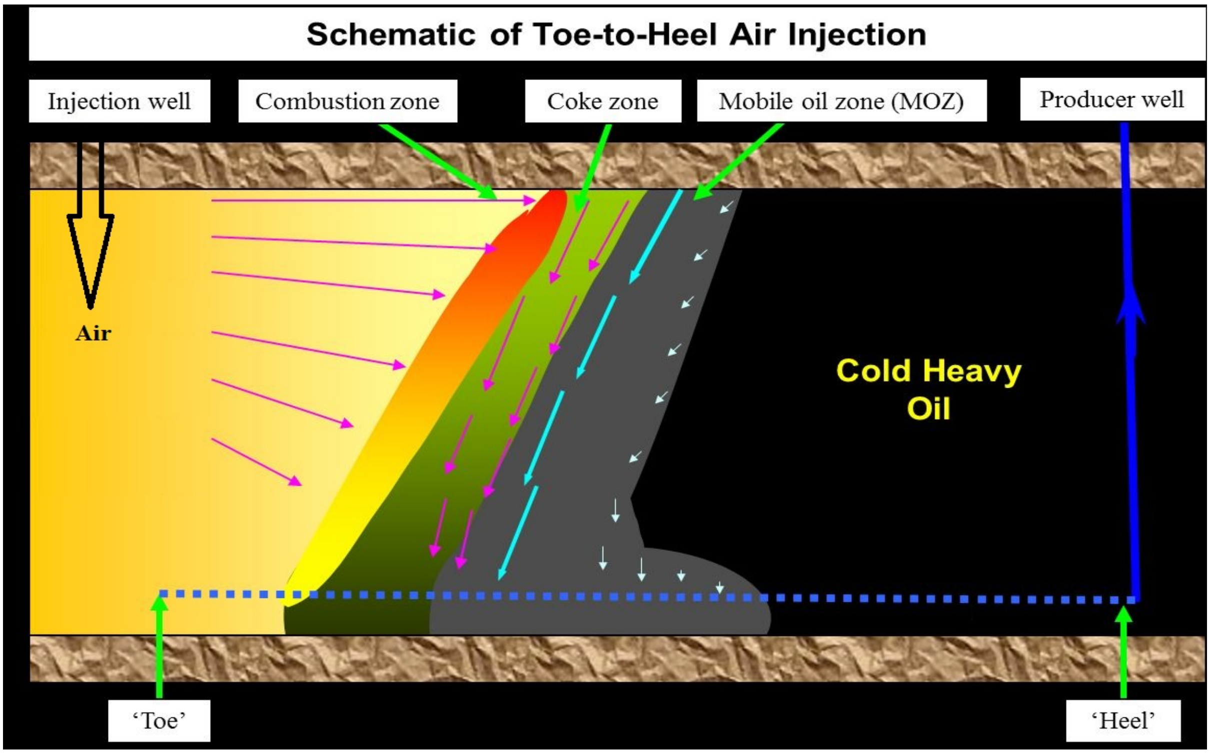


Figure 2.9 Mobilised oil draining in THAI Process

MOZ from narrow zone into exposed section of horizontal producer well in THAI process (Speight et al., 2009)

THAI enables high recovery of heavy oil because of its efficient access of the hot gas fronts to the reservoirs of heavy oil and bitumen. One of the main advantages of THAI is its in-situ thermal cracking, which enables the upgraded oil to be mobilized and flow from the combustion front along the horizontal well to the surface (Xia et al., 2001).

The Mobile Oil Zone (MOZ) is another important feature of the THAI technique which forms behind the combustion front and is shown in Figure 2.9. The MOZ is where the heavy oil in the reservoir has better mobility because of the higher temperature and lower viscosity compared to the extremely low mobility of the cold heavy oil in the rest of the reservoir.

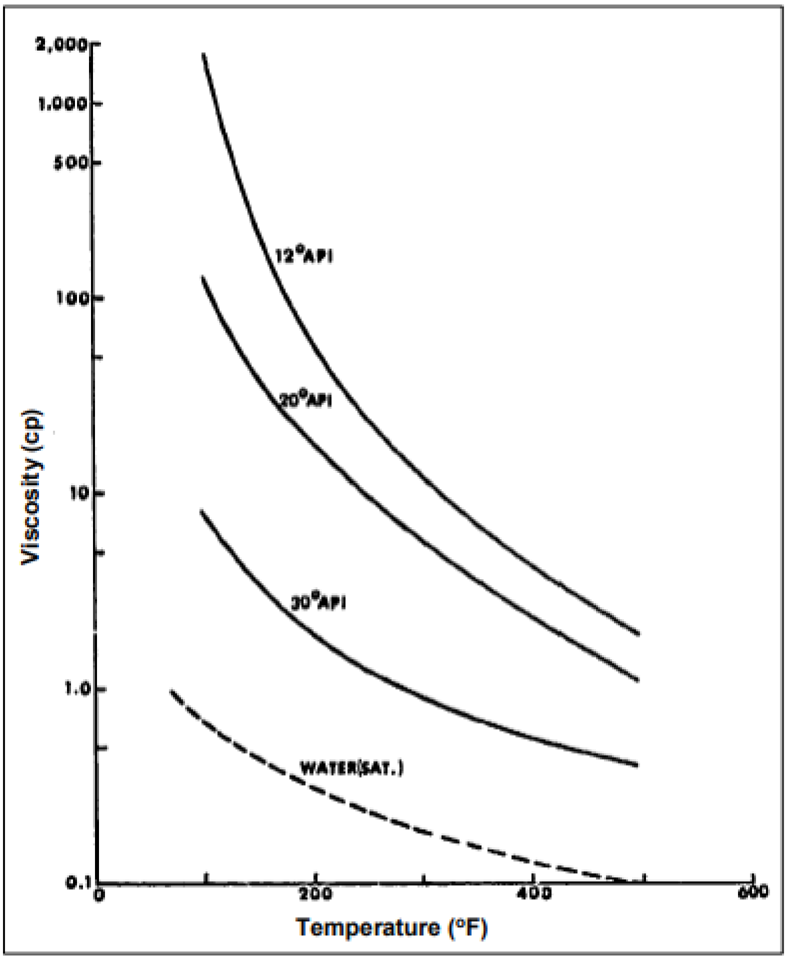


Figure 2.10 The effect of temperature on crude oil viscosity

(Wu, 1977)

The aim of the EOR processes, such as THAI technique, is to increase the reservoir temperature, in order to reduce heavy oil viscosity. This enhances the oil flow rate and its displacement. Figure 2.10 shows the viscosity behaviour of crude oil with different degrees of API gravity. Most of the reactions related to thermal upgrading occur in the mobile oil zone (MOZ), created behind the combustion front. While the combustion front causes an increase in temperature and mobility of heavy oil in the region of the MOZ, the cold heavy oil naturally seals along with the horizontal producer well to avoid gas bypassing and displacing into the horizontal producer well. This increases the efficiency of the combustion operation and therefore leads to higher recovery of oil (Greaves et al, 2000).

Figure 2.11 shows the production of oil through conventional ISC, where mobilized oil passes through the cold heavy oil before flowing towards the producer well. However, the THAI process has an important feature of a short path for oil flow. This is associated with the location of the horizontal injection (close to the top of the oil layer) and horizontal producer well (close to the bottom of the oil layer). The placing of these wells causes the flow of oil, gas and water only in the MOZ from top to bottom by gravity force. Instead of passing through the cold region as it does in the conventional ISC process, the short oil path way helps to regulate the gas overriding and ensures a stable distribution of the combustion front through the reservoir (Xia et al., 2003).

The temperature in the combustion zone ranges from 500-600 ^{o}C and the temperature in MOZ ranges from 300-500 ^{o}C. The high temperature of MOZ provides efficient thermal sweeping as well as thermal treatment of the oil layer ahead of the combustion zone for thermal cracking. The byproduct from thermal cracking of high molecular weight hydrocarbons, such as coke, works as a fuel for sustainable combustion front propagation (Xia and Greaves, 2006; Jinzhong, et al., 2012; Wenlong, et al., 2011).

A study conducted by Greaves et al. (2000) aimed to understand the THAI process and improve its control system, as well as compare it to other conventional EOR processes. The study used Wolf Lake crude for its heavy oil sample and a 3D combustion cell with 60cm × 40cm × 20cm dimensions for combustion and MOZ simulation. CMG-STARS reservoir simulator was used for numerical simulation of the THAI process. The results show stable combustion is achieved in the THAI process through thermal cracking reaction and therefore it has high heavy oil recovery of up to 85 % OOIP (Original Oil In-Place). The author concluded that THAI provides a more robust process for heavy oil production compared to other EOR methods, it decreases the risk of reservoir heterogeneities from happening and therefore has higher ultimate oil recovery.

A similar method of the experiment using 3D combustion cell was applied in a study by Xia et al. (2000) in order to compare the THAI method to another EOR methods such as Toe-to-Heel Steam flood (THSF). Greaves et al. (2012) performed an experimental study on the basis of the results that have been obtained by the 3D combustion cell having dimensions 0.6×0.4×0.1 m respectively. The average temperature of the propagating front reached 500-550 ^{o}C. As compared to the 10.9 ^{o}API gravity for the feedback, the in-situ upgrading of the API gravity up to the 16-17^{o} was reported. In MOZ, the thermal cracking of the heavy fractions into the lighter components resulted in the increment of the API gravity. The host rock’s natural catalytic activity can also result in the upgrading reactions along with the oil that has been experiencing cracking. Jinzhong et al. (2012) and Wenlong et al. (2011) conducted a study of THAI fire-flooding process in which the 3D sand-pack cell having dimensions 0.4×0.4×0.15m comprising of the control system, production, measuring and injection. The experiment was conducted for the oil saturation of 84%, heavy oil having a viscosity of 12090 MPa at a temperature of 50 ^{o}C, the ratio of the injected air to oil 1400 m^3/m^3 and the 39% porosity of the sand-pack. It has been reported that the temperature of the combustion front could reach as high as 600 ^{o}C, having the range of average temperature as 450-550 ^{o}C, along with the recovery of 70% OOIP.

Prof Sean Rigby’s group at the University of Bath, and later the University of Nottingham, have conducted more than 100 3-D model cell combustion laboratory investigations over more than 13 years. The results in the majority of the experiments indicate more efficient volumetric sweep and oil recovery with use of a staggered line drive SLD (SLD-THAI process) well configuration. The results of CMGSTARS simulation of a 3D combustion cell test is shown in Fig 2.11. Furthermore, the results of characteristics of upgraded oil sample of Wolf Lake oil collected from experiments is shown in Figure 2.12

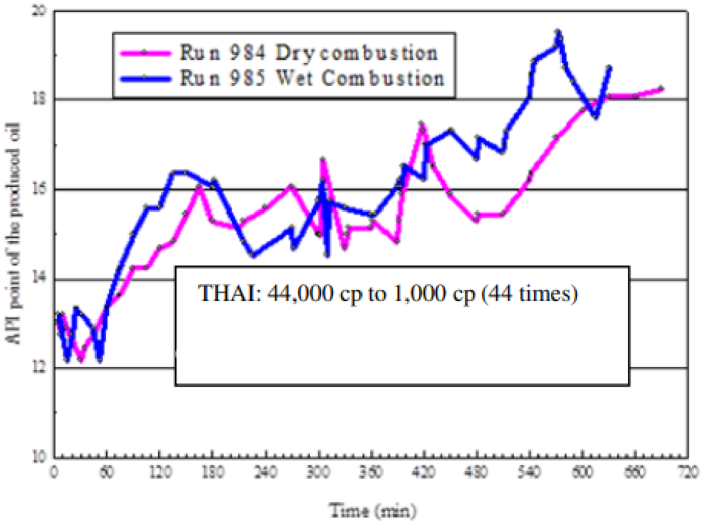


Figure 2.11 Upgrading of Wolf Lake heavy oil conducted using THAI laboratory experiments

(Greaves et al., 2012)

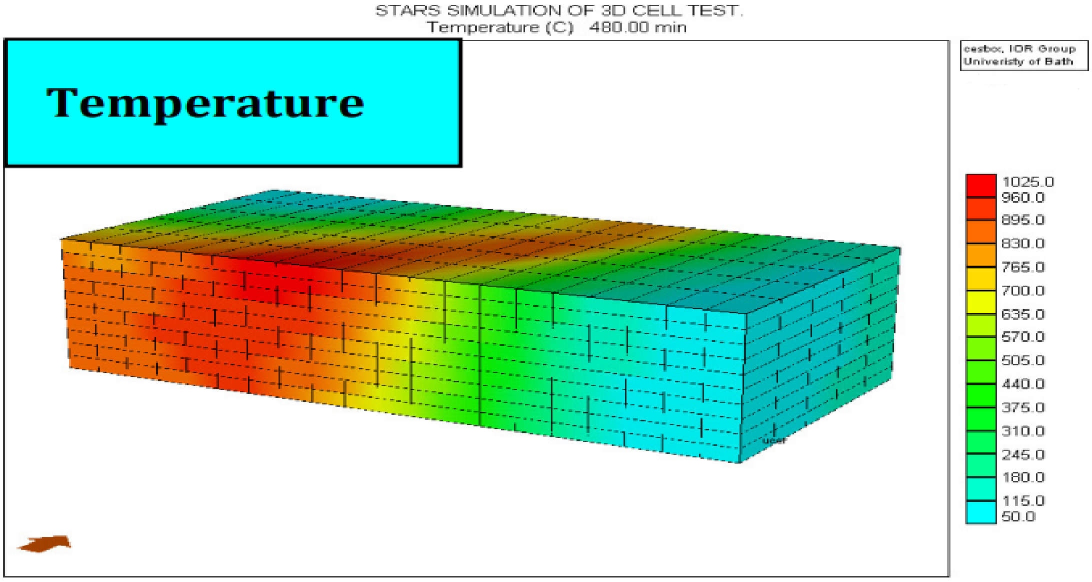


Figure 2.12 Temperature distribution of a 3-D laboratory THAI experiments using SLD configuration

(Greaves et al., 2012)

There have been a few pilot field tests of THAI heavy oil recovery in places such as Athabasca Oil Sands of Alberta and Wasseca in Canada, Shuguang and Fengcheng in China and also Balol and Lanwa Fields in India. Whitesands THAI Pilot consisted of three well pairs at an operational depth of 380m was under operation from 2006 to 2011. During operation consistent upgrading of heavy oil was reported, with partial upgrading of approximately 4 ^{o}API degrees. The composition of produced gas with 16% hydrogen confirmed high quality burning in the combustion zone. There were some operational problems such as sand influx and oil lifting, which were also reported. At the Wasseca Channel, the Kerrobert Project was started in 2009 and still ongoing, with initial 2 wells at a depth of 780m. The number of well pairs were then increased to 12 in 2011. The heavy oil reservoir at the Wasseca Channel is a bottom water (BW) reservoir with a BW zone thickness of 25 cm. BW reservoir configuration had a negative impact in production which caused more operational problems compared to the Athabasca project. The results from the Kerrobert pilot projects were reported to be consistent with the upgrading of 3-7 degree increase of API gravity of the produced oil.

Along with the emission of the gaseous pollutants, for example, H_2S, CO_2 and other pollutants and the stand-alone facilities of the buildings costs, the upgradation processes that are used commonly are also found to be unfriendly to the environment. Today the main focus of the petroleum industries is on the in-situ upgrading of the heavy oil. There are a number of advantages of the in-situ upgrading of the bitumen or heavy oil in the reservoir for example, during the extraction and upgrading in-situ, some of the impurities that are present in the heavy oil are left in the reservoir and that production of the oil has low viscosity which can be transported without adding any diluent.

As the in-situ upgrading of the heavy oil helps in minimizing the downstream processing that is demanding, it requires less capital, it can be applied on a well by the satisfactory basis and is able to produce valuable products. Therefore it is responsible to provide major environmental and economic advantages over the techniques for the surface upgrading before reaching the surface of the reservoir (Moore, et al., 1999). Consequently, the reservoir works as a reactor, indicating that it is not necessary to create a huge pressure vessel that is costly, as required in surface upgrading (Weissman, et al., 1996). For a successful in-situ or down-hole catalytic upgrading of the heavy oil in the reservoir, the requirements include the creation of the appropriate pressure and temperature conditions for the reaction in the catalyst bed and process. The in-situ catalyst bed in the formation of the oil-bearing reservoir must be pre-installed and in order to attain suitable catalytic upgrading and production of upgraded oil, the mobilization of co-reactants for example, carbon monoxide, hydrogen and water and the heavy oil over the catalyst have been sketched by Weissman et al., (1996) and Moore et al., (1999). The processes of the in-situ upgrading consist of THAI-CAPRI, ISC, and THAI.

2.3.2 *Catalytic Upgrading Process In-situ (CAPRI)*

Use of catalyst in the heavy oil production which is called “catalytic upgrading process in-situ” (CAPRI) was introduced to enhance ISC methods in terms of upgrading capability and therefore its oil production. Some studies were conducted using a catalyst-added version of THAI process in which a layer of active catalyst is placed between the horizontal production well’s concentric slotted liner shown in Figure 2.13 (Xia et al., 2001; Xia et al., 2002; Xia et al. 2006; Hart et al., 2013; Karimian et al., 2018).

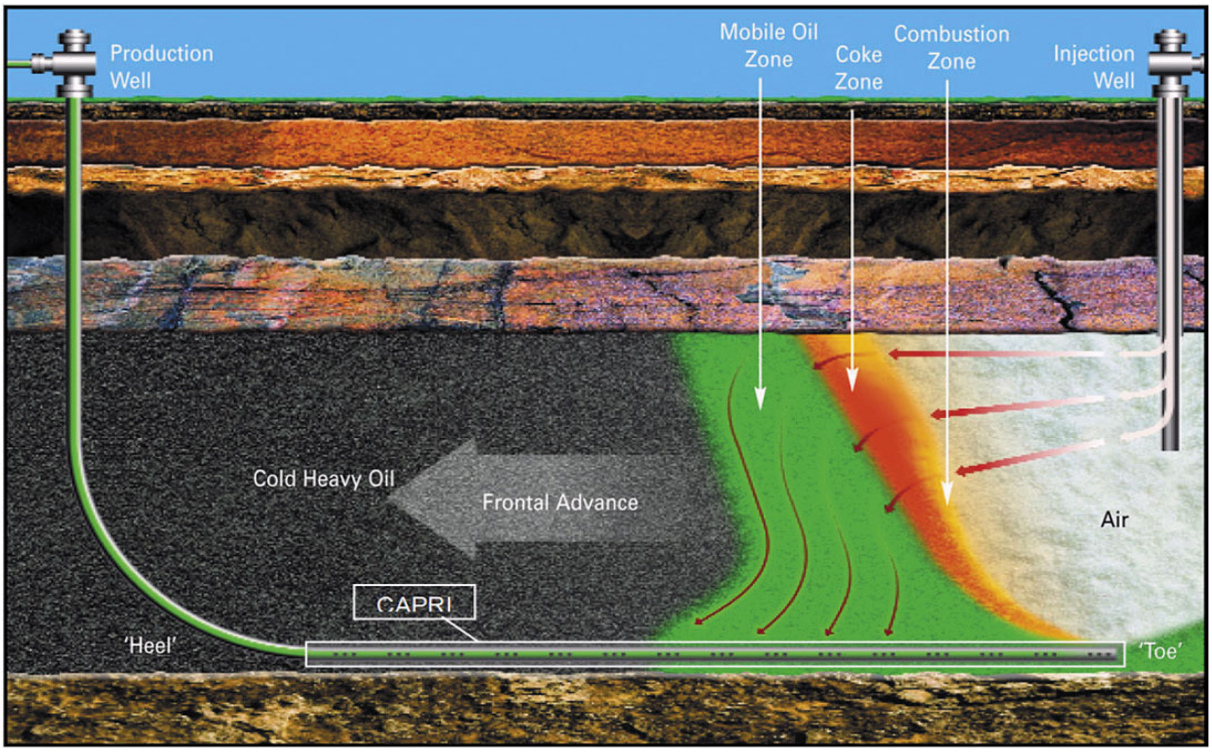


Figure 2.13 Conventional CAPRI fixed-bed horizontal production well
(Petroblogger 2011)

The CAPRI process was initially developed at the University of Bath, the UK, by the Improved Oil Recovery group in association with the Petroleum Recovery Institute (PRI), Calgary, Canada in the year 1998. A series of experiments were conducted by Xia and Greaves (2001) using Wolf Lake heavy oil to test the level of additional upgrading that can be achieved by CAPRI in addition to that already gained via THAI. It has been indicated in the results that alone THAI can attain an increment of about 10° in the API gravity of the oil that has been produced and on the addition of CAPRI, there was a further increment in the range of 4-7 ° API points. Also, the viscosity of the produced oil was recorded to be as low as 10 mPa at 20℃. Further experiments were carried out by Xia et al. (2002) using 3D combustion cell with feedstock from Lloydminster heavy crude oil with recorded 11.9° degree of API. The study used Co-Mo/alumina HDS catalysts in an operating condition of 500 to 550℃. It was found that the recovery factor of the oil was 79% OOIP and the upgraded oil has 23° API as compared to the 11.9° API of the feed and has a low viscosity range of 20-30 mPa. It has been indicated by the results that the heavy crude oil can be converted to the light crude oil within a single step by the THAI-CAPRI process and the range of the recovery factor is 79-85% OOIP, without the utilisation of expensive surface upgrading processes.

In a study conducted by Hart (2014) a fixed bed catalytic reactor was used in order to simulate the CAPRI process in heavy oil upgrading. The optimum reactor condition was found to be 425 °C, 20 bar nitrogen flow with the use of Ni catalyst supported on Zeolite-Alumina. The recorded upgrading of the produced oil was 6° API gravity increase and about 87% reduction in viscosity to the original feedstock. However, since the feedstock used was produced through THAI which was already partially upgraded through thermal cracking. The author argues the 6° API gravity increase represents further upgrading through catalytic cracking.

The first commercial production of heavy oil through THAI-CAPRI was announced by Petrobank Energy and Resources Limited on the 22nd of September 2008 (Petrobank, 2008).

In August 2008, the production by the well (P-3B) that was located at White Sands near Conklin, Alberta, Canada was started. The experiments conducted by Xia, et al. (2002) at laboratory scale reported the further upgrading ability of the CAPRI section as revealed by the P-3B well. Consequently, the P-3B well has an oil production level of 400 barrels per day on the low rate of injected air and is in continuous production. At White Sands, a limited amount of sand has been produced by the sandstone reservoir (Petrobank, 2008).The comparison of the THAI-CAPRI with other commonly used surface upgrading process has been made through some outline calculations by Shah et al (2010), from which it is clear that the capital cost of THAI-CAPRI projects is significantly less expensive. For example, in the UK a plant for surface upgrading was offered to have a cost of $ 2-3 billion. However, because of the relatively lower cost of the standard hydrotreating (HDT) catalysts, the process of THAI-CAPRI will cost only a fraction of the process of surface upgrading (Shah, et al., 2010).

For the in-situ catalytic upgrading, the hydro-processing catalysts that are being used are derived from group VIB transition metal oxides, for example, W, Mo and group VIII, such as Ni, Co that are being supported on the high-surface-area silica, alumina or silica-alumina (Hossian, et al., 2004). The acidic alumina supports are responsible for providing the cracking functions however the functions of hydrogenation are performed by Ni, Mo and Co metals.

In a 500 h study on the upgrading of bitumen conducted by Kim et al. (1997), NiMo alumina catalyst was used at the temperature range of 352–412 °C, and pressure of 13.7 MPa. The API gravity of the collected samples decreased from 16° to 13.5° as the time-on-stream increased from 0 to 500 h. A similar catalyst, NiMo alumina, was used in another heavy oil upgrading study by Hart et al. (2014) and the results also confirmed the decrease of catalyst activity with as the time-on-stream increased. During the 200 min heavy oil upgrading process, the API gravity increased from 13 (feedstock) to 19° and to 21° as the time-on-stream increased. The API gravity decreased to 16° when the reaction was carried out for a duration of 200 min.

Fukuyama et al. (2004) observed the catalysts with activated carbon support have better ability in terms adsorption of heavy molecules such as asphaltene, and therefore restrict coke formation.

Multiple studies have discussed the fast deactivation of the catalyst in the fixed bed reactor for heavy oil upgrading (Xia et al., 2006; Hart et al., 2013). The adsorption and deposits of heavy oil components and macromolecules, such as heteroatoms and heavy metals, on the catalyst surface, are the main cause of fast deactivation compared to conventional oil. Shah et al. (2011) found that in the CAPRI process, the deactivation of the catalyst is unavoidable and typically the catalyst is deactivated rapidly after the start of the process. Therefore the lifespan of the catalyst should be extended in order to improve the economy of the process. Because of the deposition of coke and asphaltenes, there is a risk of well-plugging that can be a reason for the loss of production stability along with the potential shutdowns (Hashemi, et al., 2013). Therefore alternative solutions such as dispersion of catalysts in the reservoir and the extension of catalyst lifespan can improve upgrading and also avoid catalysts replacement and ensure the production continuation for a reasonably long period.

In a study conducted by Castanier et al. (2014) dispersion of soluble catalyst salts by means of injection was investigated, while in another study, Hashemi et al. (2014) preferred dispersion of nanocatalysts through the MOZ. Nanocatalysts, compared to their pelleted counterpart have significantly more active sites per unit mass and larger surface-to-volume ratio. Therefore the chance of catalyst deactivation due to pore plugging is much less (Hashemi, et al., 2013). Moreover, nanocatalysts can be applied in a once-through process, therefore, the challenges associated with the pre-packing of the horizontal production well along with the pelleted HDT catalyst can be avoided.

In a study of heavy oil upgrading by Hart et al. (2015), pelleted and dispersed CoMo alumina catalysts were compared in fixed bed and batch reactor respectively. The performance of the catalyst in both forms was examined through the upgrading of feedstock heavy oil in terms of API gravity, viscosity and heteroatom removal. The experiments were carried out at 425 °C and 20 bar pressure for 10 min. The produced oil with dispersed catalyst resulted in 3.1° higher API gravity and 9 % less sulphur content compared to their pelleted counterpart.

Panariti et al. (2000) studied comparison of multiple dispersed catalysts in terms of their performance in the upgrading of petroleum residue feedstock which gave the following order of activity: Mo>Ni∼Ru>Co>V>Fe. Galarraga and Pereira-Almao (2010) studied the effect of tri-metallic (Mo-Ni-W) catalyst on heavy oil feedstock from Athabasca Bitumen using a batch reactor at 380℃ with a reaction time of 3-70 h. The API gravity of the produced oil samples increased from 9.5° to 16° and their viscosity decreased from 7680cP to 60cP at 40℃.

In another study conducted by Yusuf et al., (2016), NiMo and CoMo performance were also compared. They achieved up to 95% viscosity reduction in 24 h of reaction at 300 ºC in a batch reactor. Catalyst performance in terms of viscosity reduction was reported in the following trend: CoMo+NiMo > NiMo > CoMo. Fumoto (2015) used iron oxide-based catalyst for desulfurization of heavy oil under 2h of reaction at 500 ºC. They achieved a 50 % reduction in sulphur concentration of produced oil.

2.4 Chemistry of Heavy Oil Upgrading

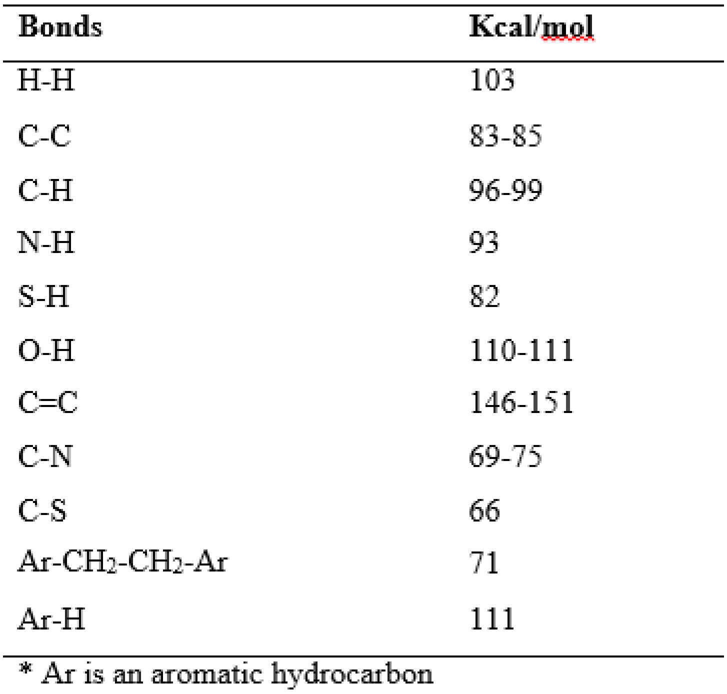
About 10^5-10^6 different components of hydrocarbons make up the complex mixtures of bitumen and heavy crude oil which makes its chemistry significantly complicated (Wiehe, 1999).

A large number of possible chemical reactions that may occur during the upgrading including ring growth, removal of heavy metals and heteroatoms, homolytic cleavage of the C-C bond, hydrogen shuttling, cleavage of side chains, ring-opening and cycloparaffin dehydrogenation or hydrogenation of aromatics, as discussed by Hsu and Robinson (2006). The free radical chain reactions are responsible for the dissociation of the C-C bond. During upgrading it is assumed that the mechanism of the reactions continues by the formation of the free radicals (Gray, 1994).

Gray (1994b) divided upgrading of heavy oil into *primary* and *secondary upgrading*, in order to better understand its chemistry. Primary upgrading is the initial breaking of large hydrocarbons into smaller molecules, mainly through a thermal process which causes the cleavage of (C-C) bonds. The dissociation of C-C bonds is considered as the major cleavage as it leads to upgrading (Gray, 1994). The term "secondary upgrading" refers to further treatment of hydrocarbons to higher quality products usually through dissociation of C-S and C-N bonds. Secondary upgrading generally occurs in the presence of catalysts and the availability of H_2. One of the most commonly used commercial processes of secondary upgrading is hydrotreating (Edwards et al., 1986, Tang et al., 2014).

Table 2.1 shows the required dissociation energies of the common bonds that are present in the crude oil. In order to enhance the cleavage of C-C bonds, the high reaction temperature is required, on the other hand, he C-S bond will easily break at low temperatures as it has the lowest energy for dissociation of the bond, as can be seen in Table 2.1.

Table 2.1 Bond dissociation energy of hydrocarbon groups
(Benson, 1976; Rahimi and Gentzi, 2006



Bonds	Kcal/mol
H-H	103
C-C	83-85
C-H	96-99
N-H	93
S-H	82
O-H	110-111
C=C	146-151
C-N	69-75
C-S	66
Ar-CH_2-CH_2-Ar	71
Ar-H	111

* Ar is an aromatic hydrocarbon

2.4.1 The Mechanism of Catalytic Upgrading

In this section, the catalytic upgrading mechanisms are discussed so that the experimental results that have been observed can be discussed later in the context of these mechanisms. The beta-scission and the carbenium ion intermediate helps the catalytic upgrading reactions to continue (Jian-hong, et al., 2008). The hydrocarbons ions in which the carbon atom has a positive charge are called as the carbenium ions. The mechanism is found to be similar to that of the mechanism of the chain reaction of the thermal cracking. On the other hand, there are three basic stages of this mechanism: 1) Initiation 2) Propagation of Chain and 3) Termination. The Bronsted acid sites attack the C-C bond directly or the presumption of a hydride ion (H-) form the C-H bond, starts the cracking of the paraffin on the catalyst's acid sites. This helps in the formation of the carbenium ion and hence is considered to start the step of initiation. Moreover, the carbenium ion can also be generated by other ways, for example, protonation of olefins by Bronsted acid sites, protolytic cracking and hydride abstraction of paraffin (Lee, et al., 2011).

In the stage of chain propagation, a series of the hydride ions are transferred to carbocations, from the hydrocarbon molecules resulting in the steady yield of carbenium ions. In order to stabilize the secondary or tertiary carbenium ion by alkyl shift or hydride shift, the carbenium ions that have been generated undergo the process of isomerization in some of the cases (Lee, et al., 2011). But, by cracking, isomerization, hydride transfer, protonation/deprotonation, cyclisation, β- scission, ring-opening (i.e. naphthenic) etc. the carbenium ion that has been produced can be split into a number of small hydrocarbons. The carbenium ions are deprotonated from the catalyst and in order to give tri-coordinated carbenium ions, light hydrocarbons, and hydrogen, they collapse in the termination stage (Jian-hong, et al., 2008). The cracking pathways for paraffin, naphthenes, and aromatics are shown in the figures 2.14 and 2.15 respectively.

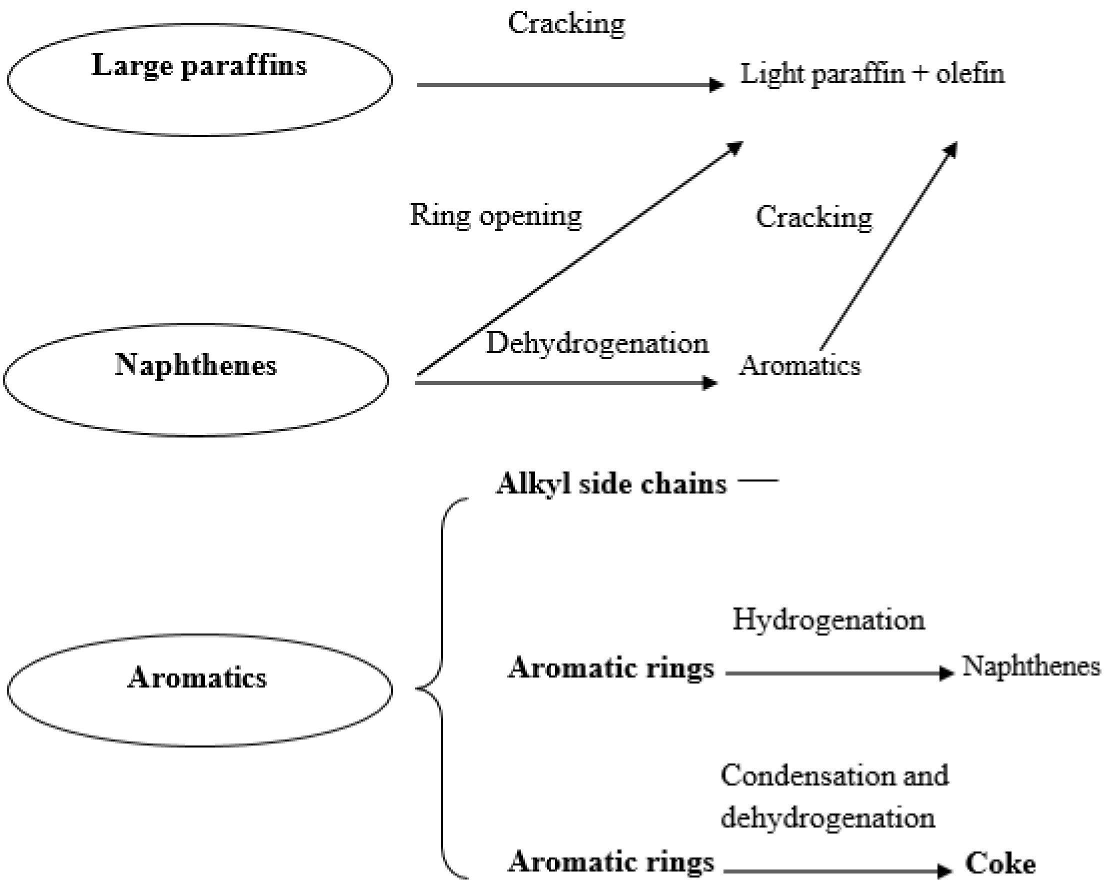


Figure 2.14 Reaction pathways for Paraffins, Naphthenes and Aromatics
(Hart, 2014)

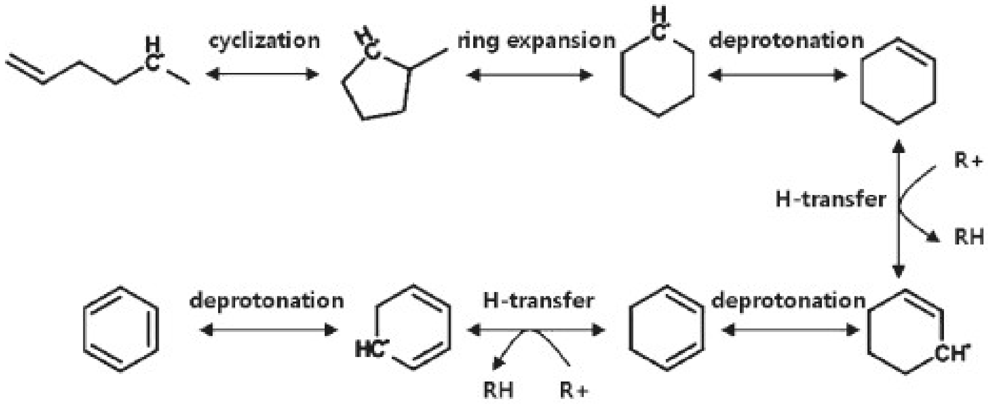
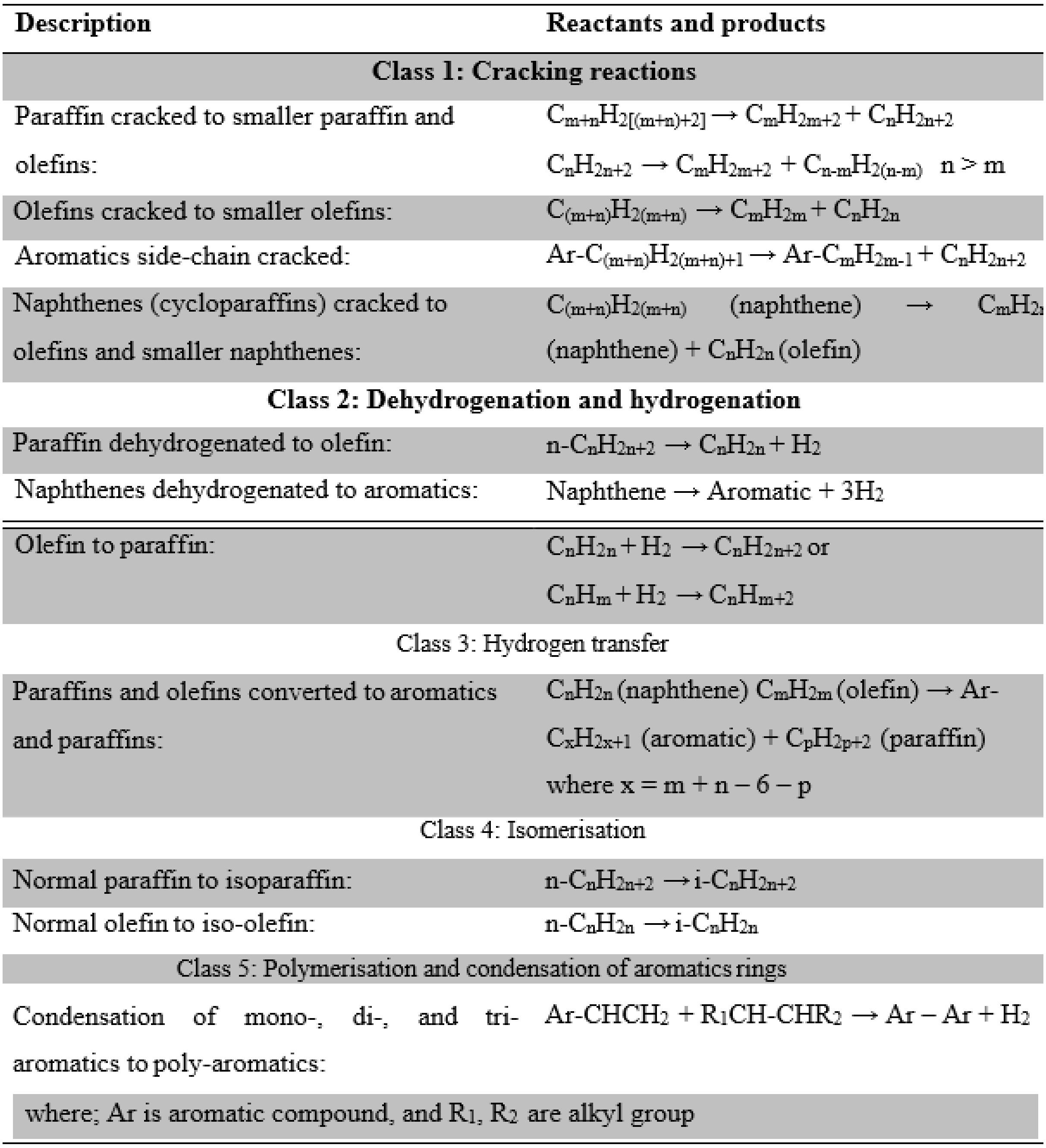


Figure 2.15 Reaction pathways for Paraffins, Naphthenes and Aromatics

Table 2.2 shows different classes of the reactions that occur. In the upgraded oil, the occurrence of the low boiling components may be due to these reactions (Pashikanti and Liu, 2011).

Table 2.2 Key classes of catalytic upgrading reactions during CAPRI process
(Hart, 2014)



Description	Reactants and products
Class 1: Cracking reactions	
Paraffin cracked to smaller paraffin and olefins:	$C_{m+n}H_{2[(m+n)+2]} \rightarrow C_mH_{2m+2} + C_nH_{2n+2}$ $C_nH_{2n+2} \rightarrow C_mH_{2m+2} + C_{n-m}H_{2(n-m)}$ n > m
Olefins cracked to smaller olefins:	$C_{(m+n)}H_{2(m+n)} \rightarrow C_mH_{2m} + C_nH_{2n}$
Aromatics side-chain cracked:	$Ar\text{-}C_{(m+n)}H_{2(m+n)+1} \rightarrow Ar\text{-}C_mH_{2m-1} + C_nH_{2n+2}$
Naphthenes (cycloparaffins) cracked to olefins and smaller naphthenes:	$C_{(m+n)}H_{2(m+n)}$ (naphthene) → C_mH_2 (naphthene) + C_nH_{2n} (olefin)
Class 2: Dehydrogenation and hydrogenation	
Paraffin dehydrogenated to olefin:	$n\text{-}C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2$
Naphthenes dehydrogenated to aromatics:	Naphthene → Aromatic + $3H_2$
Olefin to paraffin:	$C_nH_{2n} + H_2 \rightarrow C_nH_{2n+2}$ or $C_nH_m + H_2 \rightarrow C_nH_{m+2}$
Class 3: Hydrogen transfer	
Paraffins and olefins converted to aromatics and paraffins:	C_nH_{2n} (naphthene) C_mH_{2m} (olefin) → Ar-C_xH_{2x+1} (aromatic) + C_pH_{2p+2} (paraffin) where $x = m + n - 6 - p$
Class 4: Isomerisation	
Normal paraffin to isoparaffin:	$n\text{-}C_nH_{2n+2} \rightarrow i\text{-}C_nH_{2n+2}$
Normal olefin to iso-olefin:	$n\text{-}C_nH_{2n} \rightarrow i\text{-}C_nH_{2n}$
Class 5: Polymerisation and condensation of aromatics rings	
Condensation of mono-, di-, and tri-aromatics to poly-aromatics:	$Ar\text{-}CHCH_2 + R_1CH\text{-}CHR_2 \rightarrow Ar - Ar + H_2$
where; Ar is aromatic compound, and R_1, R_2 are alkyl group	

2.4.2 The Mechanism of Catalytic Upgrading

Approximately 30% wt of the heavy oil is produced as a result of the coking process however it experiences the disadvantages due to the subsequent lower yield of liquid and the handling of the coke stockpiles that have been generated (Hsu et al., 2006). Along with the upgrading of the heavy crude oil, the hydroconversion is also responsible to produce an increased yield of the liquid synthetic crude having a low number of impurities, for example, metals, nitrogen, and Sulphur (Longstaff et al, 1994). By reducing the amount of the originators of coke in the reacting media and preventing the dehydrogenation reactions, the hydrogen addition provides other reaction pathways that result in the formation of coke in fewer amounts and great yield of liquid (Liu et al., 2003). The sources of the smallest radicals that can be found in the reacting media are radicals of methyl and hydrogen that can help in reducing the free radical addition reactions that must be stopped in order to reduce the formation of coke and large molecules. In order to explain the formation of coke in the catalytic and thermal upgrading of the heavy oil, the phase separation reaction kinetic model (PSK) was suggested by Wiehe (1993) (refer to section 2.5, the formation of coke from the route (3)). the following stages are shown by the Wiehe (1993) model for the formation of coke:

$$A^{+} \xrightarrow{KA} aA^{*} + (1-a)\,(M^{*} + volatile) \qquad 2.1$$

$$M^{+} \xrightarrow{KB} bA^{*} + (1-b)\,(M^{*} + volatile) \qquad 2.2$$

Both the reactive asphaltene (A+) and reactive maltenes (M+) produces an asphaltene core (A*) and non-reactive maltenes (M*) where “a” and “b” are the stoichiometric constants and KA and KB are the rate constants as shown in equations 2.1 and 2.2. A portion of A* that has been produced can be dissolved by the mixture of oil (M+, M* and volatile). But, the excess amount of asphaltene core (A^{*}_{ex}) can be precipitated if the A* has exceeded the solubility limit, as follows:

$$A_{ex}^{*} = A^{*} - A_{max}^{*} = A^{*} - S_L \left(M^{+} + M^{*} + Volatile\right) \qquad 2.3$$

Where SL is the solubility constant and A_{max}^{*} is the maximum amount of A* that is soluble in the mixture of oil, finally, the A_{max}^{*} is transferred to the coke (C) as follows:

$$A_{ex}^{*} \overset{KC}{\rightarrow} C \qquad 2.4$$

In the THAI-CAPRI process, the temperature of the combustion zone can reach up to 450-700°C, to facilitate the generation of the steam by the water that is available from the combustion reaction and reservoir water. The hot water and the flooding steam banks that have resulted are moved towards the immobile cold bitumen (Xia et al., 2002; Wenlong et al., 2011). In order to moderate the number of free radicals that have been made during the pyrolysis of the heavy oil, the hydrogen that has been generated by the in-situ through the shift of water gas is not found to be enough. Therefore, it requires an external source of hydrogen, mainly because at the temperature ~400°C, the reaction of water gas shift is not found to be active in the well. The introduction of the hydrogen in the gaseous form from an external source into the oil reservoir can be dangerous as well as challenging. On the other hand, by injecting a suitable donor solvent, hydrogen can also be generated. In this regard, a hydrogen-donor solvent, for example, decline, cyclohexane and tetralin can be injected in order to increase the hydrogen that has been produced from the steam and hydrocarbons. In the literature, the vacuum residues have been recognized comprehensively by the utilization of hydrogen-donor solvents for example decalin, cyclohexane and tetralin for the liquefaction of the oil shale/coal and catalytic/thermal upgrading of the heavy oil (Fan et al., 2002; Biniwale et al., 2005; Alemán-Vázquez et al., 2012). In batch mode, at a reaction temperature 430 °C, the effect of the liquid solvents, for example, tetralin during the thermal upgrading of the heavy oil was tested by Rahmani et al (2002). Along with the PSK model the consistency reduction of the formation of the coke was observed (Rahmani et al., 2002). It has been shown by the results of the study that has been conducted by Alemán-Vázquez et al., (2012) that the combination of the reducing agents (H_2 and CH_4) and the Hydrogen donors causes a major decrease in the coke yield as compared to those that have been obtained by only making the use of the reducing agents provided the conditions are same. Liu et al., (2001) found in another study that the active chains that are present in the heavy oil that has reacted can connect to each other, therefore polymerization occurred and then directed to the viscosity regression. Then it was claimed by him that the active chains that are produced during the upgrading of the heavy oil can be terminated by the hydrogen additive donors, for example, tetralin and therefore can control the viscosity regression.

By making use of the solvents the rate of reactions of the equations 2.1, 2.2 and 2.4 can be slowed down by reducing the formation of coke during the catalytic and thermal upgrading of oil. The functions that have been fulfilled by the solvents include improvement of the hydrogen transfer reaction and increment in the solubility limits, thus inhibiting the formation of coke (Savage et al., 1988; Rahmani et al., 2003; Rahmani et al., 2002; Wiehe, 1993).

By making use of the solvents the rate of reactions of the equations 2.1, 2.2 and 2.4 can be slowed down by reducing the formation of coke during the catalytic and thermal upgrading of oil. The functions that have been fulfilled by the solvents include improvement of the hydrogen transfer reaction and increment in the solubility limits, thus inhibiting the formation of coke (Savage et al., 1988; Rahmani et al., 2003; Rahmani et al., 2002; Wiehe, 1993).

2.5 **Pyrolysis Bio-Oil**

2.5.1 *History of Pyrolysis*

Pyrolysis is an old method which was used thousands of years ago to create bio char to enhance and nutrient the soils of the rainforests. The product of the pyrolysis is solid called biochar and is similar to charcoal. The fire was initiated and in order to take the oxygen away, it was covered with soil. In the meantime, in the absence of oxygen, the high temperature became the cause of the breakdown of fuel and formed the biochar rather than ash (Magnum Group International Inc.).

In the absence of fossil fuels, the fuel for transportation was produced by waste feedstock of wood through pyrolysis during the two world wars. In transportation, an important role is played by the gases that were obtained from the biomass. Gasification was used to drive the agricultural machines and heavy vehicles for example buses and trucks by the year 1945. According to the reports, the bio-derived gases as fuel drove about 9,000,000 vehicles around the world (Magnum Group International Inc.).

2.5.1.1 The Modern Era

Bell Laboratories in 1958 based in the United States studied the effectiveness of pyrolysis for the production of an energy source. In the beginning, the research program was mainly concentrated on the waste material as a feedstock and its gas production through the pyrolysis process. Pyrolysis process initially conducted by Pyrolytic Gasification systems through firebrick ovens which provided indirect heat (Thomas, 2011). The system operated similar to a batch process in a low oxygen environment. In the early 1970s, the first commercial pyrolysis process was used in a hospital for gasification requirements. However, because of the limited capacity of the batch reactor and multiple mechanical problems, the project only had limited success. In the early 1980s, the pyrolysis system with continuous feed replaced the batch process in the UK, US, German and Canada respectively. The continuous system had overcome the limited reaction capacity of the batch system. Moreover, the con design improved the efficiency of the system by allowing better gas evacuation.

2.5.2 *Process of Pyrolysis*

Multiple steps conversion requires for the use of biomass as a precursor of fossil fuel in energy application such as heating, power and transportation (Collard et al., 2014). Therefore, processes and techniques such as pyrolysis and liquefaction are employed for the production of liquid fuel (Carrier et al., 2013). The feedstocks of these processes are lignocellulosic biomass from the forest, agricultural and agro-industries (Jahirul et al., 2014). A number of different factors, for example, heating rate, temperature, catalyst, type of reactor, feed material, etc. can affect the quality of the product (Bridgwater, 1994), depending on the desired pyrolysate (biochar or liquid oil), lignocellulosic matters on the basis of process conditions are divided into the fast process, slow process and intermediate process groups. The slow pyrolysis process produces primarily biochar. It has the residence of the vapour for a long period of time and it operates at a relatively low temperature of 400 ^{o}C using conventional heating element (Foo et al., 2011; Bridgwater, 1994). The residence temperature in the intermediate pyrolysis is found to be 10-30 s and the operating temperature is 500 ^{o}C (Bridgwater, 1994).

The fast pyrolysis is also called as the flash pyrolysis, unlike the slow process it allows the conversion of biomass to bio-oil. The fast pyrolysis process has a high temperature of more than 500 ^{o}C and a significantly short residence time of ~1s that is considered as ideal for the production of liquids. As it is more feasible and cheaper to store liquids compared to the solid biomass, and because of low yield of bio-oil at a high cost with the use of high-pressure liquefaction, the fast pyrolysis has been studied more than any other group of pyrolysis (Bridgwater, 2012, 2006; No SY, 2014). Czernik (2004) and Bridgwater (2004) have reported the overview for the power generation application of bio oil, in the area such as engines, boiler and turbines, as well as upgrading to potential transport fuel. Both scholars have concluded, using of bio oil as fuel in an application such as boiler, gas turbine and even diesel engine has been promisingly successful. However, in order to achieve higher quality bio-oil for transportation fuel, the upgrading process was not economically feasible because of technical challenges which are caused by the nature of biomass feedstock.

Since the residence time for fast pyrolysis is short, therefore, some of the phenomena, such as reaction kinetics and heat and mass transfer become more important. The reactor is considered as the most important part in the process of pyrolysis as 10-15% of the total cost of the entire plant is taken by it (Bridgwater, 2012). In order to achieve 70-80% of the high liquid yield, various reactors types including the transport reactor, bubbling fluid beds and the cyclonic reactor that is based on the dry biomass have been used in the process of pyrolysis (Oasmaa and Czernik, 1999). Non- condensable gas and solid char having a variable range of yields between 13-25% and 12-25% have also been acquired by the process of pyrolysis (Bridgwater, 2012). In the process of pyrolysis, basically, any kind of biomass can be used. In pyrolysis, a huge number of biomasses including nut shells, sorghum, leather wastes and straw has been used. On the basis of its repeatability and reliability during the experiments, wood is considered as the most interesting type (Mohan et al., 2006).

The examination of the effects caused by the rate of heating during the process of pyrolysis has been studied. It has been found that it is appropriate to apply high rates of heating at about 500°C, in order to cause an increment in the yield of liquid and reduction in the formation of char. More gas will be produced if the temperature is raised above 500°C (Bridgwater, 2012; Demirbas, 2009). It has been stated that under certain conditions there will be no production of char. Some transitional products that can rapidly condense have been formed by the reduction of vapours and the application of the fast rate of heating. As a result, no gaseous product is formed (Demirbas, 2005). On the other hand, the maximized gas yield is up to 80 wt.% at high rates of reaction having a short time of residence and a temperature above 700°C (Bridgwater and Ottam, 1992).

2.5.3 *Main Components of Pyrolysis Oil*

The main components of pyrolysis oil are very different from crude oil because of the nature and chemical composition of biomass. This is mainly due to the plant carbohydrate polymers that are significantly rich in oxygen which differs sharply from other fossil feeds (Danish et al., 2004). Plant biomass including wood is a composite material constructed from oxygen-containing organic polymers (Boucher et al., 2000). The major structural macromolecule substance of biomass are carbohydrate polymers and oligomers (65%-75%) and lignin (18%-35%). These components with relatively high molecular mass consist of cellulose, hemicelluloses, lignin and inorganic minerals. Some example of the weight per cent of lignocellulose contents of biomass with different plant source is presented in table 2.3. (Bridgwater, 2004; Huber et al., 2006).

Table 2.3 Typical Lignocellulose Content of Some Plant Materials
(Huber et al., 2006)

biomass component	Corn grain	Corn stover	Sugarcane	Pine
Celluloses wt%	3	36	22	46−50
Hemicelluloses wt%	6	23	15	19−22
Lignins wt%	2	17	11	21−29

Degradation and depolymerisation of the lignocellulosic biomass have been done in order to obtain the pyrolysis oil. After the pyrolysis of each block, the mixture of products that have been obtained is called pyrolysis oil. Hence, it can be said the elemental composition of the bio-oil is similar to that of the biomass (Czernik and Bridgwater, 2004). Table 2.4 shows the comparison of the elemental composition heavy oil, pyrolysis oil, and its biomass resource.

Table 2.4 Comparison between biomass derived bio-oil and diesel
Oasmaa and Czernik, 1999

Elemental Composition	Corn grain	Pine	Sugarcane	Diesel
C wt %	40	42	39	86
H wt%	8.1	7.5	7.6	13
O wt%	49	51	50	0.01
N wt%	0.61	0.1	0.1	0.001

The pyrolysis oil that has been derived from the birch and pine has an oxygen content of 44 wt% and 45.7% respectively, whereas 0.01 wt% oxygen content is used in the heavy petroleum fuel oil as depicted in Table 2.4. Therefore, the oxygen content of the bio-oil obtained through the process of pyrolysis is much higher as compared to fossil fuel oil. This serves as the reason for having a low heating value during the pyrolysis of bio-oil in comparison to the heavy crude oil (Zhang et al., 2013).

2.5.3.1 Cellulose

Figure 2.16 depicts the structure of cellulose. The basic structural framework of the cell walls of wood is the cellulose and consists of 40-50 wt% of dry wood. Cellulose is a crystalline material which comprises of monomers of glucose that is a ring sugar having six carbons (Parham et al., 1984). In order to obtain glucose anhydride, water from each glucose is removed. By the polymerization of the glucose anhydride, the chains of cellulose are obtained having 5000-10000 units of glucose (Huber et al., 2006; Mohan et al., 2006).

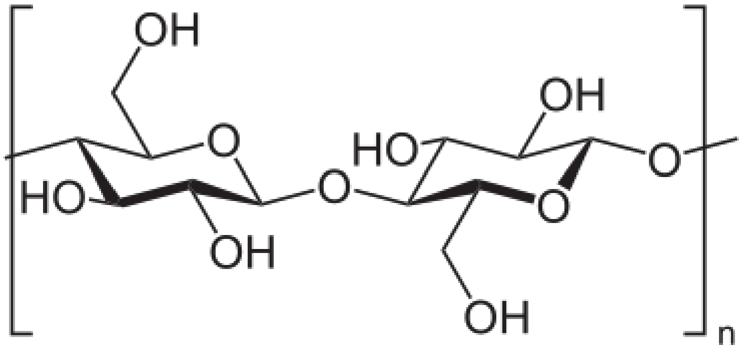


Figure 2.16 Cellulose Structure

As shown in Figure 2.17, the hydrogen bonds are used to join cellulose's long chains together. By the help of these hydrogen bonds, the chains of cellulose are preserved. The hydrophilic sides of the cellulose chains are used to make the hydrogen bonds. Cellulose is converted into cellotetraose, cellobiose, and cellotriose through the application of incomplete hydrolysis whereas complete acid hydrolysis is performed to obtain glucose (Huber et al., 2006).

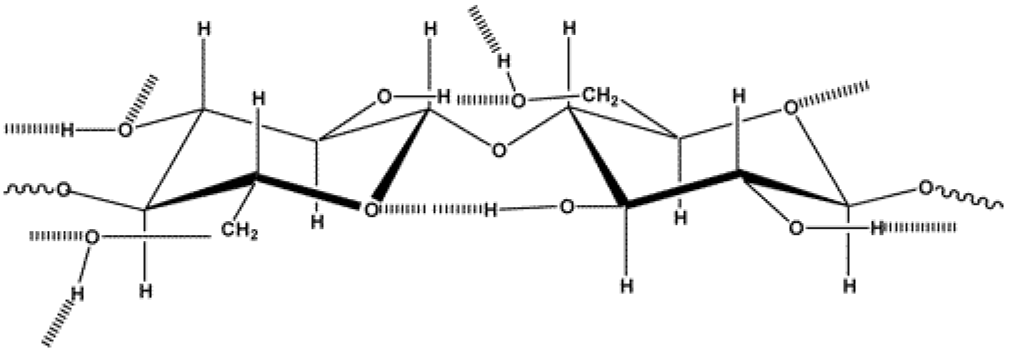


Figure 2.17 Bridge of hydrogen bonds
(Mohan et al., 2006). Copyright (2014) American Chemical Society

The cellulose conversion typically happens from 300 to 390 °C (Worasuwannarak et al., 2007; Patwardhan et al., 2011). Due to the high reactivity of glycosidic bond at a temperature above 300 °C, high number reactions occur, simultaneously (Wang et al., 2012). Depolymerization and conversion of Cellulose to volatile compounds are dominated significantly with yielding of 80% mostly condensable organic compounds (Shen et al., 2009; McGrath et al., 2003). On the other hand, the residue continues to become more aromatic at above 400 ^{o}C (Worasuwannarak et al., 2007). The cellulose char structure significantly changes at a temperature between 270 to 400 °C and at 320 °C the pyran rings conversion reaches its limit (Pastorova et al., 1994; Liu et al., 2013). As the temperature increases to 350 °C the furan rings increases continuously and at higher temperature the concentration starts to decrease (Pastorova et al., 1994) Moreover, the benzene rings occur at around 300 °C and become dominant in char structures at 400 °C (Pastorova et al., 1994; McGrath et al., 2003).

2.5.3.2 Hemicellulose

Hemicellulose is also called as polyose and it is the second main component of wood after cellulose. The composition of hemicellulose includes 35 wt% of hardwoods, 25-35 wt% of dry wood and 28 wt% of softwoods. As depicted in Figure 2.18, the hemicellulose is a polymer of various mannose, glucose, monosaccharides, xylose, galactose, 4-O-methyl glucuronic acid, arabinose and residues of galacturonic acids in spite of cellulose that is a polymer of glucose. In the structure of hardwood hemicellulose, the main sugar is found to be the xylan-xylose polymer. Due to its branched nature, the structure of hemicellulose is amorphous as compared to the crystalline structure of cellulose. As compared to the cellulose, hemicellulose can be hydrolyzed and broken into its monomers more easily. Hemicellulose has about 150 monomer units due to which its molecular weight is considered as low as compared to the cellulose. A study by Lv (2009) and Peng (2010) show that hemicellulose conversion generally occurs at a temperature between 200 to 350 °C which causes breaking and dehydration (release of H_2O) of some relatively less stable hemicellulose linkage (Widyawati et al., 2011). At a temperature of 200 °C, the dehydration of polysaccharides increases and from the fragmentation of the methoxy group, methanol is produced. Additionally, decarboxylation reactions of the carboxylic acid lead to the formation of CO_2 molecules at relatively low temperature (Shen et al., 2010). At a higher temperature of 240 °C rapid depolymerization of hemicelluloses linkages such as glucomannan and the glycosidic occurs. This reaction lead to the formation of a significant amount of unstable intermediaries which are highly likely to go through dehydration, fragmentation and secondary reactions causing a relatively high amount of CO, CO_2 and H_2O, formation (Worasuwannarak et al., 2007; Shen et al., 2010). At temperature above 300 °C, the residue structures becomes more stable and more aromatic, several methylphenols are formed and production of CH_4 increase through pyrolysis of hemicelluloses (Widyawati et al., 2011). It has been stated that during the process of pyrolysis, the application of a fast heating rate can help in the decomposition of the hemicellulose within few seconds. In comparison with the cellulose, less amount of tar and char and more number of volatiles produce during the hemicellulose decomposition. (Mohan et al., 2006).

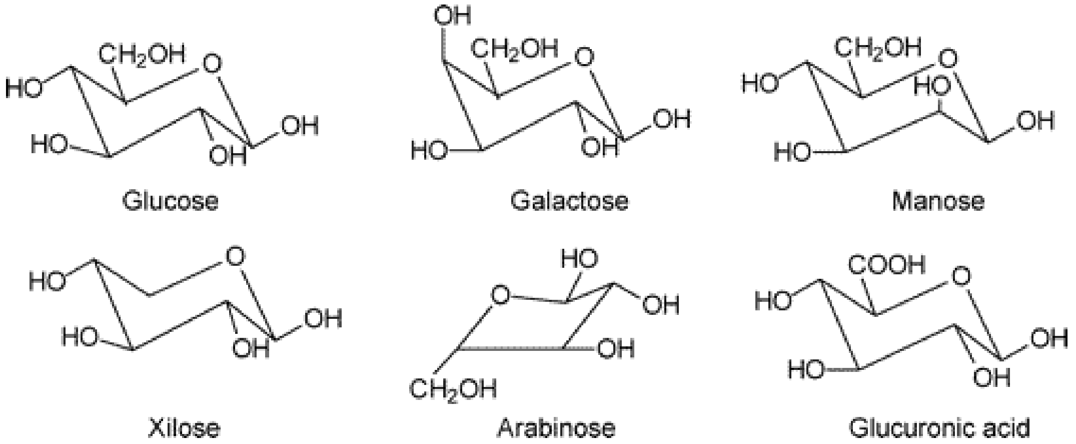


Figure 2.18 Main sugars of hemicellulose
(Mohan et al., 2006). Copyright (2014) American Chemical Society.

2.5.3.3 Lignin

The word lignin has been obtained from a Latin word lignum meaning wood (Jr. et al., 2001). It is considered as the third main component of wood consisting of 16-25 wt% of hardwood and 23-33 wt% of softwood. Lignin is present at the cell walls and is an amorphous, highly branched and polyphenolic material. For the formation of lignocellulose composites, it has been supplemented by cellulose and hemicellulose. Figure 2.19 depicts the skeletal units of lignin. The hardwood lignin consists of sinapyl and coniferyl alcohols whereas the softwood lignin comprises coniferly alcohols (Huber et al., 2006; Mohan et al., 2006). Lignin has a decomposition temperature in the range 280-500 °C. The cleavage of ether and C-C bonds help in the manufacture of phenol compounds in the process of pyrolysis. As compared to hemicellulose and cellulose it is more difficult to remove water from lignin. In comparison with the cellulose, the pyrolysis of lignin produces more char (Mohan et al., 2006).

Different species of biomass have a varied amount of lignin, cellulose and hemicellulose. Table 2.3 indicates the weight percentages of each constituent of different species of biomass.

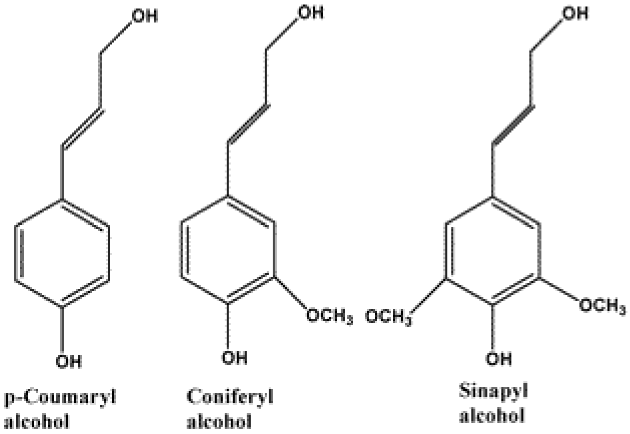


Figure 2.19 Main units of lignin

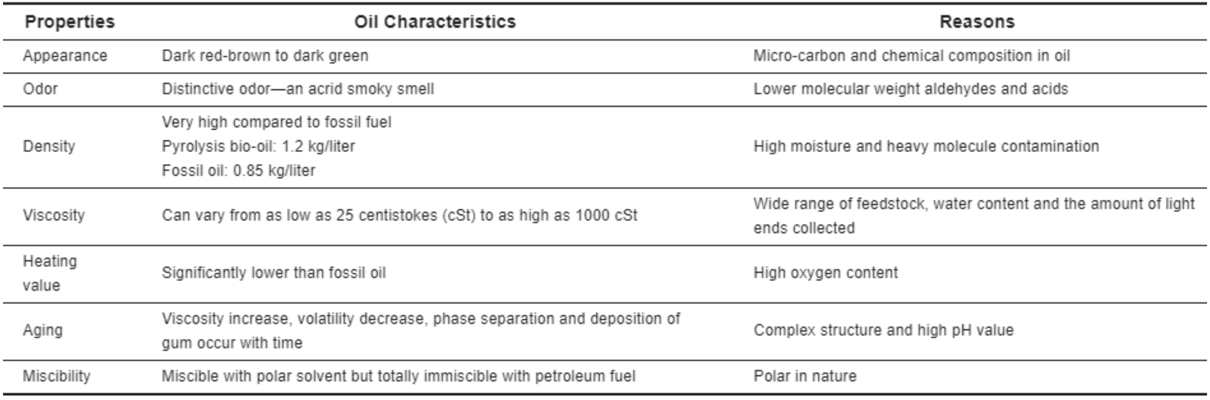
(Mohan et al., 2006). Copyright (2014) American Chemical Society.

2.6 Properties of Pyrolysis oil

Bio-oil is one of the highly viscous liquid, dark brown in colour and carries a smoky odor. During the pyrolysis process, various different reactions occur including dehydrogenation, aromatization, hydrolysis, condensation, and coking. Factors which influence the processing of bio-oils include temperature, pressure, mass transfer, the rate of heat, feedstock and time of pyrolysis. These factors pose a significant impact on the composition of bio-oils thus defining its physical properties (Huber et al., 2006; Jacobson et al., 2013a; Xiu and Shahbazi, 2012). Comparing the physical properties of bio-oils with fossil fuels, bio-oils possess lower heating value while higher values of oxygen, water, and ash contents unlike fossil fuels (Bu et al., 2012a).

More than 400 organic compounds are present in bio-oils. It can be observed from the illustration that bio-oils are composed of acids, alcohols, esters, aldehydes, ketones, sugars, phenols and similar other compounds. These compounds affect the physical and chemical nature of bio-oils by adding detrimental properties in them which include high water content, high oxygen content, poor ignition properties, low pH value, low heating value, higher viscosity, higher acidity, thermal and chemical instability, corrosiveness (Huber et al., 2006; Zhang et al., 2013). Table 2.5 describes the physical properties of bio-oil.

Table 2.5 Physical characteristics of pyrolysis bio-oil
Zhang et al., 2013



Properties	Oil Characteristics	Reasons
Appearance	Dark red-brown to dark green	Micro-carbon and chemical composition in oil
Odor	Distinctive odor—an acrid smoky smell	Lower molecular weight aldehydes and acids
Density	Very high compared to fossil fuel Pyrolysis bio-oil: 1.2 kg/liter Fossil oil: 0.85 kg/liter	High moisture and heavy molecule contamination
Viscosity	Can vary from as low as 25 centistokes (cSt) to as high as 1000 cSt	Wide range of feedstock, water content and the amount of light ends collected
Heating value	Significantly lower than fossil oil	High oxygen content
Aging	Viscosity increase, volatility decrease, phase separation and deposition of gum occur with time	Complex structure and high pH value
Miscibility	Miscible with polar solvent but totally immiscible with petroleum fuel	Polar in nature

During the pyrolysis process, different reactions take place which increases the water content of the bio-oils. This water content is obtained from the initial moisture of feedstock and successive dehydration reactions. Reaction conditions and influence of biomass type defines the overall range of water content in bio-oil i.e. 15 – 35 wt%. Certain hydrophilic compounds produced during carbohydrates decomposition affect bio-oil's water content miscibility properties with several lignin-derived oligomeric components. These hydrophilic compounds include hydroxy aldehydes, ketones, and alcohols. The water content in bio-oils negatively affects its chemical properties by decreasing the rate of combustion, reducing the heating value and delaying the process of ignition. However, the appropriate ratio of water also adds some significant values including lower NOx emissions and increased rate of bio-oil flow characteristics (Bridgwater, 2004a; Czernik and Bridgwater, 2004).

Oxygen range present in bio-oil is around 40 – 50 wt% comprising within the range of approx. 300 compounds in bio-oils including carboxylic acids, phenolics, hydroxy ketones, sugar, dehydrosugar and hydroxy aldehyde. The water content of bio-oils defines the ratio of oxygen content in them. For example, $CH_{1.9}O_{0.7}$ is the chemical formula for bio-oil which represents the overall content of oxygen i.e. 46 wt% in it while the oxygen content of wood is reported to be 42 wt%. This difference depicts the ratio variance of water and oxygen in bio-oil and wood (Mohan et al., 2006). Processing conditions which include temperature, heating rate and residence time along with the biomass species affect the distribution factor of these compounds in bio-oils. Temperature increase during pyrolysis results in the production of gaseous compounds but lower oxygen content is also one of the properties of certain liquid products (Bridgwater, 2004a).

Some undesirable properties of bio-oil such as low energy density, thermal instability, corrosiveness and less miscibility are attributed to the high oxygen content in them. These properties have been elaborated below.

Bio-oils produced through pyrolysis contain reactive organic compounds i.e. phenols and aldehydes which makes the bio-oils chemically unstable. These compounds were very reactive generate macromolecules by reacting with each other through polymerization reaction, the process which is further accelerated in acidic conditions. These reactions affect the physical properties of bio-oils such as increased molecular weight and viscosity while modifying the flow characteristics. The process has been termed ‘ageing' as it proceeds with time including the principal reactions esterification, polymerization, condensation and etherification (Diebold and Czernik, 1997; Zhang et al., 2013). Reactor plugging and coke formation are performed in order to inhibit the polymerization reaction (Elliott and Neuenschwander, 1996).

Due to high corrosiveness in bio-oils, the equipment in which the pyrolysis process is performed gets corroded (Zhang et al., 2013). Acids which lower the pH of bio-oils in range of 2 – 3 are formic and acetic acid. The acid content in bio-oil can lead to the corrosiveness of certain compounds such as aluminium and carbon steel but it will not affect stainless steel. Corrosive properties of bio-oils are further promoted by water content and at high temperature for storage purposes (Oasmaa and Czernik, 1999).

A large range of hydrophilic compounds is present in bio-oils, which increases the immiscibility of these oils with conventional hydrocarbons. These polar compounds are formed by non-bonded electrons in the functional groups of the bio-oils which possess oxygen and increase the polarity of these compounds.

Regardless of the detrimental properties of the bio-oils, these oils also possess certain promising characteristics which include less emission of NOx and low toxicity ratio. Due to low emission of NOx, less pollution is generated which is half of the ratio generated through fossil fuels. Moreover, bio-oils are CO_2 neutral, produce negligible amounts of SOx, offer easy handling practices and promote cost-effective transportation. After upgrading, bio-oils can be used engines and turbines in order to generate heat and electricity and are used in boilers (He and Wang, 2012; Tanneru and Steele, 2014; Zhang et al., 2013). Thus, bio-oil or pyrolysis oils must be upgraded through a specific process to generate the product with similar chemical and physical properties as that of petroleum generated fuels.

2.7 Upgrading of bio-oil

Upgrading of bio-oils requires catalytic thermal degradation in order to produce a compatible alternative for the present-day liquid fuels. Remove of almost all oxygen content is required from the bio-oils prior to direct blending with the crude oils and manufacturing of finished crude oil products. For achieving the finished, upgraded products, two methods have been devised, the counterparts of which exist in the petroleum refining. These processes include; catalytic cracking and catalytic hydroprocessing (Mohammad et al., 2012).

2.7.1 *Catalytic cracking*

Temperatures between 350 – 500 °C and atmospheric pressure are the conditions in which the process of catalytic cracking is carried out for bio-oils. For catalytic cracking, the different catalyst is used including alumina silicates and zeolites, depending on their catalytic properties. The high temperatures maintained during the cracking process breaks the bonds of the macromolecules while promoting the de-oxygenation of the bio-oils at the same time (Jacobson et al., 2013). Catalysts used are preferably water and oil-soluble organic compounds and hydrocarbon in nature where the removal of oxygen generates carbon dioxide and water. Due to low operation cost, less need for hydrogen and low operating pressure, the process of catalytic cracking has gained immense attention. However, certain facts limit the utilization of this process as an upgrading method which includes relatively low deoxygenation, catalyst deactivation, low carbon yield, and high coke formation. Thus, catalytic cracking requires continuous regeneration of catalyst at each interval (Bulushev and Ross, 2011; Huber et al., 2006).

The catalytic conversion of biomass has been studied by a number of workers (Sheu, 1988; Sharma et al., 1993). The catalytic cracking was usually carried out using typical hydrotreating and HZSM-5 catalysts. The silicalite (Sharma et al., 1993) silica-alumina (Adjaye et al., 1994), nickel-based catalysts (Koido et al., 2017), zeolite catalysts (Mohammed et al., 2017), transition metal catalysts (Fe) (Furusawa et al., 2005), and carbon-supported catalysts (Lee et al., 2017) have been investigated on conversion and tar removal in biomass pyrolysis. Silica-alumina and silica provide relatively high conversion rate however they also require high temperature operating conditions. Nickel-based catalysts are very good in terms of tar conversion, however, they rapidly deactivated through coking. Even though noble metal-based catalysts are a highly active catalyst and stabile against coking, they are considered as an expensive catalyst choice which is not economically feasible to be used. Zeolite and carbon-supported catalysts have a relatively intermediate performance in the conversion of tar and consider as cheap catalysts, additionally, zeolite has high thermal stability and unlike carbon-supported catalysts which simply become gasified, is relatively easy for regeneration.

2.7.2 *Hydro-de-oxygenation (HDO)*

Among the discussed upgrading processes, the other method is called hydro-de-oxygenation or HDO. This method also requires the addition of hydrogen as well as catalysts for extreme oxygen removal. High operating pressure is also required to avoid water to steam conversion. The presence of water is required to avoid extensive char formation in HDO (Goudriaan et al., 1990). During hydro-processing, other processes of hydro-de-sulfurization (HDS) and hydrodenitrogenation (HDN) occur at the same time with HDO and are quite similar to it. Hydrotreating or hydro-processing of bio-oils is majorly concerned with the removal of complete oxygen content form the oils while refinery hydro-treating eliminates nitrogen (HDN), sulfur (HDS) and metals (hydrodemetalation) from the stream (Elliott et al., 2013).

During removal of oxygen from the bio-oils, oxygen is expelled through a number of processes which include decarboxylation (DCO), hydrogenation, decarbonylation, dehydration reactions and HDO which result in the production of carbon dioxide, water, and carbon monoxide, as shown in the illustration 2.20. During DCO oxygen is released from the bio-oil in the form of

CO_2. Hydrogenation occurs by the addition of hydrogen to carbonyl groups and saturation of C-C double bonds to form alcohols. Moreover, during hydrogenolysis of bio-oil C-O bonds break up and oxygen is removed through water formation. The overall reaction stoichiometry of HDO may be generalized by:

$$-(CH_xO_y)- + c\ H_2 \rightarrow -(CH_x)- + (H_2O, CO_2, CH_4, CO)$$

The values for x (H/C) and y (O/C) depend on feedstock, operating conditions, any further treatment methods, water content and so on

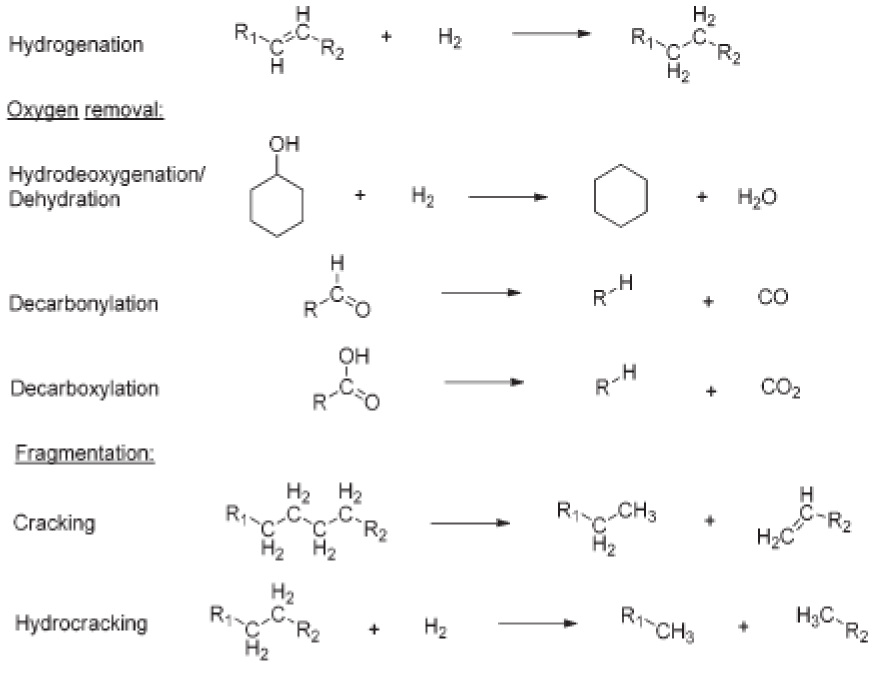


Figure 2.20 Major reactions occurring during bio-oil HDO
(Wang et al., 2013).

Removal of oxygen occurs at the expense of low amounts of carbon by the production of CO and CO_2 Identified by Jones et al. (2009) and Arbogast et al. (2013), low carbon yield negatively influences the yield of the upgrader. The improved upgrading path might also reduce the transportation cost to some extent. Although oxygen removal through water production is a preferable route but improvement in hydrogen efficiency is also required to be balanced, as the proportion of hydrogen is consumed during double bond saturation and cracking process. Thus, balancing the efficiency of H_2 is one of the main purposes in the process of hydrotreating. In the process of catalytic hydroprocessing, bond cleavage reactions at high temperatures are involved which process through formation of small constituents of bio-oil from a large bio-oil constituent.

Among the catalysts used for hydrotreating of bio-oils, the most common catalyst belongs to the category of petroleum hydrotreating including the sulfur-containing CoMo and NiMo (Elliott et al., 2007; Elliot et al., 2011). In some cases, the non-sulfur catalyst is also preferred and used for hydrotreating (Venderbosch et al., 2010; Wildschut et al., 2009; Ardiyanti et al., 2012). During the hydrotreating process of bio-oils, challenges are faced due to the higher amounts of acidic compounds as well as water content affecting the alumina support within petroleum refiners (Elliott et al., 2007).

For the purpose of hydrotreatment, a number of approaches have been suggested, for example, single-unit operations to a series of incremental processing steps for achieving the production of a liquid fuel that is compatible with the hydrocarbons that have been derived from the petroleum. As shown in Figure 2.21, these operations and the operations of the petroleum refinery run parallel to each other. From the processing of bio-oil, an integrative method is going to be involved in the refinery at multiple points specifically in the co-processing of the intermediate products obtained by the hydrotreatment of bio-oils along with the petroleum intermediate streams that are found to be compatible (Mercader et al., 2010) or dropped directly into the blending of finished products of petroleum and biofuels that are processed, for which the processing of the bio-oil products that is required should be more rigid and finished.

The methodologies, for example, finished HDO, in order to produce a suitable blendstock of refinery distillation or fuel blend stock and mild HDO that is found to be suitable for the purpose of co-processing should be grouped together in order to simplify the above-mentioned concept in a theoretical manner. On the basis of the requirements of the refinery distillation blend-stock, the requirements of oxygen for the finished HDO processing can be defined easily. Furthermore, for the successful co-processing of oxygen content along with the refinery streams that are integral, its ranges are still under study.

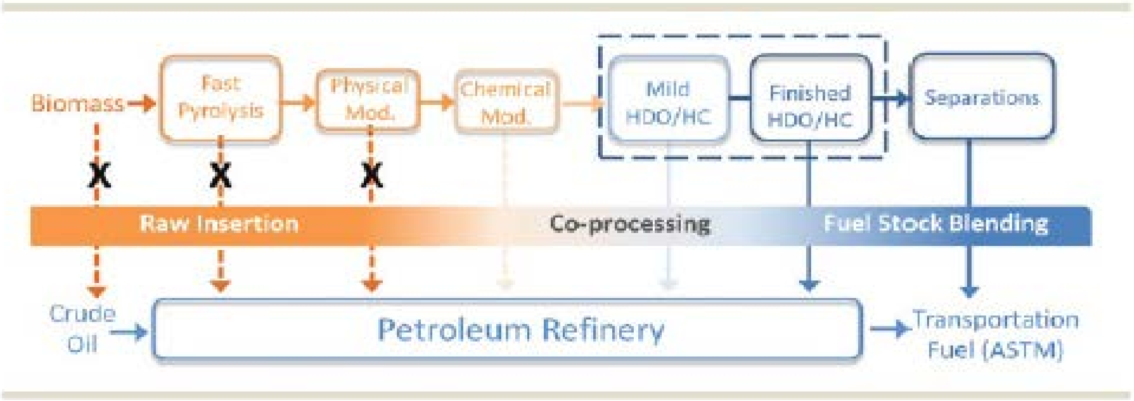


Figure 2.21 Biorefinery/Refinery integration
. Zacher et al (2013)

The use of conventional catalysts, for example, $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ in the process of HDO has been in focus of a number of researchers. In order to eliminate the sulfur and hydrogen in the HDS and HDN processes, the conventional catalysts are being used (Furimsky, 2000). A summary of important research on HDO upgrading of bio-oil is shown in Table 2.6

Table 2.6 Summery of leading researchers on HDO of fast pyrolysis

Authors	Yield (%-wt.)	DOD %-wt.	Reactor		Catalyst	Temperature (°C)	Pressure (bar)	LHSV/ Residence time	Remarks
			Type	Size (ml)					
Elliot, Baker (1984)	80	90-95	Continuous flow reactor	1000	NiMo and CoMo on Al_2O_3	350-450	138	0.1-0.6	Various Pyrolysis oils
Gagnon, Kaliagiune (1988)	-	75	Batch slurry reactor		5 %-wt. Ru/Al_2O_3	80-325	41-172	120 min	Vacuum pyrolysis oil feed. resulted in massive coking
Sheu, Anthony, Soltes (1988)	-	10-50	Trickle bed	157	$Pt/Al_2O_3/SiO_2$; sulphided CoMo, NiW& NiMo	350-400	53-104	WHSV 0.5- 3.0	Flash pyrolysis oil from pine sawdust & bark
Elliott (1988)			Up flow packed bed	1000	$CoMo/Al_2O_3$	stage 1:274; stage 2: 350-450	69-208	stage 1: LHSV =0.62; 2:LHSV=0.1	Various pyrolysis oils
Oasmaa (1992)	65	86	Batch		10 %-wt. CoO/Al_2O_3	390	215	2 hours	Peat pyrolysis oil
Samolada, Baldauf, Vasalols (1998)	30-55	88-99.9	Packed bed, up- and down flow	800	NiMo, CoMo	Up to 500	Up to 325	WHSV of 6-9 and 14-19 h^{-1}	*Eucalyptus* flash pyrolysis oil
Elliott, Neuenschwander (various)		31-99	2 Stage trickle bed	100; 425	NiMo, CoMo, sulphided; Ru/C and Ru/TiO_2	150-390	75-150	LHSV 0.5-1.5	Waterwashed and "whole" white wood, bagasse, eucalyptus, etc.
Su-Ping (2003)		90	Batch slurry reactor	500	CoMo sulphided	360-390	15-30 cold	5-60 min	Waterwashed bio-oil from fluidized bed reactor

In the Pacific Northwest National Laboratory (PNNL), a two-stage packed bed has been employed down the flow reactor for the process of HDO at 21 MPa by Elliott and Neuenschwander (1996). In both the stages same catalyst, sulfided NiMo/ Al_2O_3 or CoMo/spinel was used. The stabilization of the pyrolysis oil by HDO at a temperature of 150 °C was the aim of the first stage. In the second stage, at a higher temperature of300-400°C, the main process of HDO was performed. The main obstacle that was experienced during the process includes the formation of tar and char due to the which it was detected that there was plugging in the reactors lines and the catalyst got deactivated apart from achieving 99% removal of oxygen.

A continuous bench-scale reactor was proposed by Baldauf et al., (1994) for the HDO of pyrolysis oil. An option was also provided to either use an up or down flow. In this process, NiMo/ Al_2O_3 and sulfided CoMo/Al_2O_3 were used as catalysts. The conditions required for the reaction includes a pressure of up to 30 bar and a temperature range of 350-370 °C. Though the de-oxygenation yield was high approximately 88-99.9 wt% the yield of oil products was found to be 30-35 wt%. The deactivation of the catalyst and the plugging of the lines and beds of catalyst occurred rapidly because of the formation of a material that was gum-like in order to stop the operation of the reactor for a long period of time.

For the HDO of the fast pyrolysis oil, other catalysts that have been used include the bimetallic catalysts or the platinum group catalyst, for example, Ru, Pt, Rh, Pd. The features that have brought these catalysts into the light are their higher yield of the oil and lower yield of the coke (He and Wang, 2012).

Some catalysts, for example, Ru/Al_2O_3, Pt/C, Ru/C, Pd/C and Ru/TiO_2 in HDO process were studied by Wildschut et al. (2009). He also compared activities of the catalysts with the NiMo/ Al_2O_3 and sulfided CoMo/ Al_2O_3 that are the conventional catalysts, at two different pressures and temperatures in a batch reactor.

In order to hydrogenate the pyrolysis oil at 200 bar and 170°C, Ru/C was used as a catalyst by Elliot et al. (2012) in a fixed bed downflow reactor having two portions. The first portion of the bed contains Ru/C whereas the second portion contains the sulfided CoMo catalyst. The purpose of the first portion was partial upgrading. The second portion had a temperature of 400°C and pressure similar to that of the first portion. The pyrolysis oil's oxygen content reduced from 50 wt% to less than 3 wt% as shown in Figure 2.22

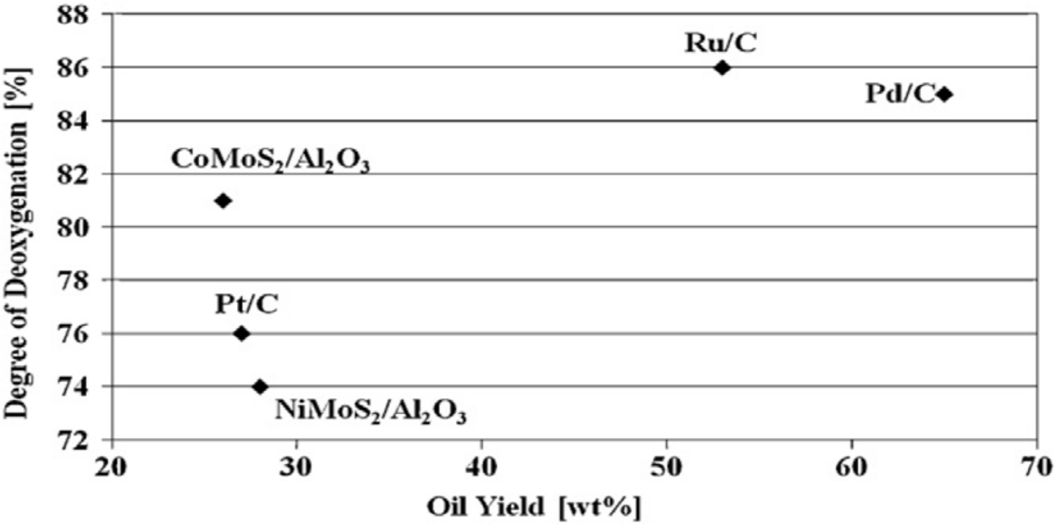


Figure 2.22 Comparison of different catalysts in the HDO process
Comparison of Ru/C, Pd/C, Pt/C, Co–MoS2/Al2O3 and Ni–MoS2/Al2O3 as catalysts for HDO, evaluated on the basis of the degree of deoxygenation and oil yield.

Ru/C was also used as a catalyst in a fixed bed reactor, in another HDO process study that was conducted by Venderbosch et al. (2010). Different reactions, for example, the process of hydrocracking, oil polymerization through the high-pressure thermal treatment, HDO at a higher temperature of up to 400°C and the hydrogenation of the oil at 250 °C temperature was studied by them. It has been found by them that at temperatures up to 250 °C, parallel reactions, for example, hydrotreating, re-polymerization and decarboxylation occurred and as compared to the hydrotreating reactions, the previous reaction took place at a faster rate (Venderbosch et al., 2010).

De Miguel Mercader et al. (2011) used Ru/C as a catalyst in the HDO of pyrolysis oil in a batch reactor. There was a continuous addition of hydrogen so that the pressure of the reactor remains constant. For the process of HDO, a retention time of 4h and different temperatures such as 220,270 and 310 °C were applied. It was stated that removal of oxygen was promoted by the increment in temperature from 220 °C to 310 °C. Moreover, there was a reduction in the molar mass of the oil and formation of coke due to the increase in temperature.

In an autoclave reactor, at three different factors of reaction including reaction time of 40-120 min, loading of Pd/C catalyst under the atmosphere of hydrogen and temperature of 250-370 °C, the process of HDO was performed by Kim et al., (2014). At the end of the HDO process, char, two immiscible products of liquids i.e. heavy oil and light oil and gas were attained. As compared to crude bio-oil, the liquid products contained less water and were found to be less acidic. The range of the water content in the heavy oil was 0.4 wt% to 1.9 wt%. The estimated heating values of 28.7 and 37.4 MJ/Kg of the heavy oil were found to be twice higher as compared to the crude bio-oil.

In HDO of Furfural, Acetic acid and Guaiacol model compound, the catalysts Ru/C and Pd/C were compared by Elliot et al., (2009) over a temperature range of 150-300 °C. Following points were found by them: (1) Ruthenium can be used as a catalyst at lower temperatures of 50-100 °C. (2) For the efficient hydrogenation chemistry, the use of the ruthenium catalysis of the aqueous-phase methanation and reforming reactions is limited to less than 250 °C. (3) The aqueous-phase gasification reactions are not catalyzed by palladium, therefore for the purpose of hydrogenation, it can be used at a higher temperature to overcome its lesser activity. (4) Pd/C is able to provide higher yields of oil as compared to Ru/C. Onwudili and Williams (2016) investigated the effect of Ru/Al_2O_3 (5–20 wt.%) catalyst on HDO using a batch reactor at more extreme conditions. They have carried out the reaction at a temperature range of 400 to 500 °C and pressure of 265 to 400 bar with a residence time of up to 1 hr. The finding suggests the heating value as well as O/C of upgraded oil sample rapidly with increasing of the holding time and reaction temperature. Moreover, the gas production increased because of carbon gasification and upgraded oil yield reduced at higher HDO temperature. Higher Ru loadings led to higher CH_4 production rather than carbon gasification and a significant decrease in char yields.

2.8 Use of Solvent in hydrodeoxygenation

In order to reduce the formation of coke and to enhance the bio-oils HDO, the utilization of the solvent is considered as a favourable methodology. In the upgrading processes of bio-oil, the usage of solvents actually has been discussed before (Sheu et al., 1988). Alcohol that was highly boiling, for example, n-butanol, was used to treat the flash pyrolysis oil at 50-80 ^{o}C under reduced pressure (<10kPa) in the presence of a solid acid catalyst. Mahfud et al. (2007) utilized this approach and found out that there was a considerable improvement in the acidity, upgraded pyrolysis oils product properties and heating value, and there was a significant reduction in the water content of the pyrolysis oil. When the pressure and temperature of fluids cross the critical point then it is called supercritical. The specific transport characteristics of the supercritical fluids (SCF’s) includes dissolving ingredient similar to a liquid (high density similar to liquids) and effusing through a solid that is similar to gas (low diffusivity and viscosity). The materials that do not usually are soluble in the gas or liquid phase of solvent reactions can be dissolved by it (Xiu and Shahbazi, 2012; Xu and Etcheverry, 2008). The advantages of unique and supercritical reaction media’s great properties including the better dissolving, diffusivity, faster rates of heat and mass transfer and gas-like viscosity are possessed by this technique (Zhang et al., 2007). In order to produce and upgrade oils, the supercritical fluids are utilized. It is able to produce bio-oils along with the reduced formation of coke and low viscosity (Xiu and Shahbazi, 2012). For the enhancement of the yield and quality of the oils, supercritical fluids have been used today. It has been recognized that supercritical fluids (SFC’S) have an increased potential to produce bio-oils having low viscosity and high quality (Zhang et al., 2013).

The liquefaction and gasification reactions can be improved by supercritical fluids (Xiu and Shahbazi, 2012; Xu and Etcheverry, 2008). For the process of liquefaction, water is used as a solvent. Due to its less cost, water has been used as a supercritical fluid, however, it also has some negatives, for example, resulting in the oil products having a low yield that cannot be soluble in the water phase and high viscous oil having a high content of oxygen. A number of organic solvents, for example, acetone (Heitz et al., 1994; Liu and Zhang, 2008), ethanol (Street, 2010), 1, 4-dioxane (Cemek and Ku, 2001; Mazaheri et al., 2010), methanol (Yang et al., 2009), n-hexane (Street, 2010) and hydrocarbons, for example, tetralin (Sheu et al., 1988) and decalin (Zhang et al., 2005) have been used to increase the yield and quality of oil. The significant effects of these solvents on the yields and quality of bio-oils have been stated.

In a number of advanced research reports, some of the solvents that have been described above, for example, methanol (Cui et al., 2011; Li et al., 2011), ethanol (Peng et al., 2009a, 2008; Tang et al., 2010, 2009; Zhang et al., 2012), CO_2 (Cui et al., 2010) and water (Duan and Savage, 2011) have been applied.

The difference between the simple addition of the solvent and its addition in a supercritical state is the extreme conversion of the compounds that are unwanted into the compounds that are required, resulting in the improvement in the properties of the bio-oils (Butler et al., 2011). The esterification in the supercritical ethanol can improve these conversions (Peng et al., 2009a; Tang et al., 2009). One more benefit of the catalyzed esterification includes the milder conditions of the reaction as compared to catalytic cracking and hydro-processing. The upgrading of the oligomers derived from lignin in supercritical ethanol was studied by (Tang et al., 2009). He evaluated that the quality of oil, for example, viscosity, heating value, and pH has been improved. In order to produce stable compounds, the quantity of aldehyde and ketones were reduced. A huge number of acids have been converted to esters. The formation of coke or tar can be avoided by preventing the condensation and polymerization reactions, as compounds having unsaturated carbon bonds and aldehydes encourage the reactions of condensation and polymerisation and cause an increase in the phase separation and viscosity (Tang et al., 2009).

Phenol was considered as a model compound in the process of hydro-de-oxygenation in supercritical hexane at a temperature of 300-450 ℃ under the atmosphere of hydrogen in the presence of CoMoP/MgO and CoMo/MgO and was evaluated by Yang et al. (2009). For the upgrading of phenol in supercritical hexane above 350 ℃ temperature, both the catalysts were found to be effective and showed excellent resistance to the formation of coke.

Esterification upgrading of a few acids, for example, acrylic acid and acetic acid under atmospheric pressure in supercritical methanol was investigated by Cui et al. (2011). In regards to the removal of acid, the performance of the supercritical esterification was found to be better than the normal esterification as shown by the results.

2.9 Bio Pd

Platinum group metals (PGMs) are widely used in petrochemical and chemical manufacturing industries for catalytic processes because of their outstanding catalytic activity. Platinum group metals (PGMs) are include Osmium, ruthenium, platinum, rhodium, iridium and palladium. The most widely used metal among the six PG metals is Palladium, for example, in both the inorganic and organic oxidation reaction, reforming reactions in the petroleum refining industry and hydrogenation and dehydrogenation reactions in the pharmaceutical industry (Bernardis et al., 2005). Since the development pollution control devices with the use of PGM-based catalysts and other outstanding properties such as high stability, electrical conductivity and excellent resistance to high temperature and corrosion PGM importance and market price have increased (Deplanche. et al., 2014).

Due to limited global resources and the high market value of PGM, their recovery often takes priority over environmental concerns. In the case of platinum, each kg of Pt, generated more than 14 tonnes CO_2 (Anon, 2008) Traditional PGM recycling methods (electrochemical recovery, solvent extraction) are energy-demanding or rely on the use of aggressive chemicals (Edward et al., 1986). The process of transition metals reduction with the help of bacteria has significant impact on the environment (Lovley et al., 1991). The bacteria microbial ability can be used in decontamination of bioremediation of metal as well as metal biorecovery (Lovley et al., 1991; Lloyd et al., 2003).

The reduction of transition metals by some bacteria is believed to exert a considerable impact on the ecology of the environment. This microbial ability can be harnessed for biotechnological applications such as bioremediation of metal contaminants and metal biorecovery (Lovley et al., 1991; Lloyd et al., 2003) Biorecovery of PGMs demonstrated in the recent studies shows the efficacy of recovery methods from metal salts solutions and also from secondary waste sources. (Deplanche. Et al., 2014; Taylor, 2012). Moreover Yong et al., (2002) was first to perform continuous recovery of Pd and Pt from spent automotive catalyst leachates) using an electrobioreactor coated with a biofilm of the sulfate-reducing bacterium (SRB) *Desulfovibrio desulfuricans*.

In an attempts to Pd deposition on the bacteria cell and NP synthesis, Lloyd et al., (1998) found that the bacteria has a role in hydrogenases in Pd(II) Later, Mikheenko et al. (2008) constructed strains of *Desulfovibrio fructosovorans* deficient in its periplasmic hydrogenases, observing relocation of the Pd(0) deposits to the cytoplasmic membrane, the site of the remaining hydrogenase. Similar results were obtained with hydrogenase-deficient *E. coli* mutants (Mikheenko et al., 2008). Bennett et al., (2013) studied electron microscopy of native and palladised strains. Figure 2.23 shows TEM micrographs of bacteria cell and arrangement of Pd particles on its interface. which showed unique Pd atomic arrangements at the interface. Effect of Accumulation of Pd NP forming bulk NP compared to interface is not yet known (Deplanche. et al., 2014).

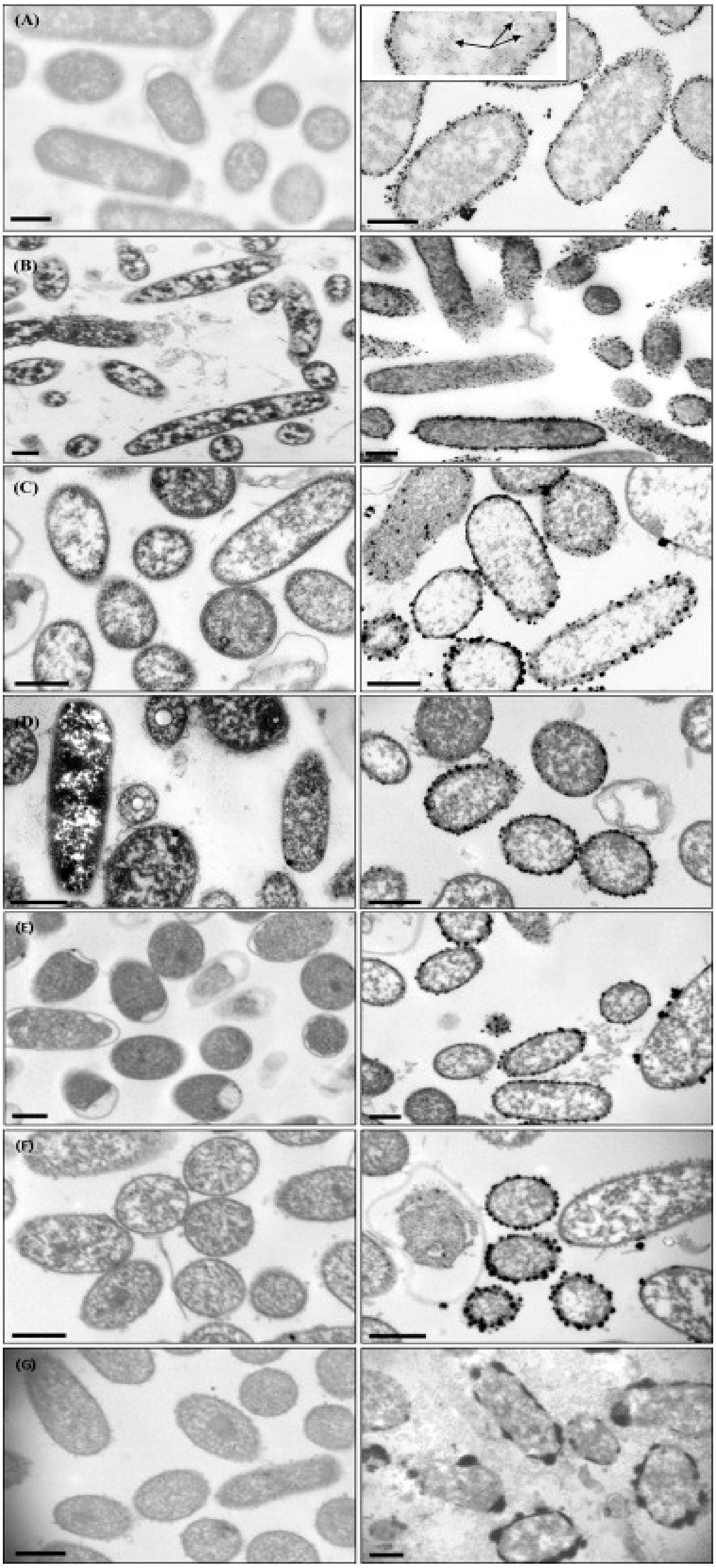


Figure 2.23 Electron microscopy of native and palladised strains.
TEM micrographs of native (left panel) and palladised (right panel) cells of (A) E. coli MC4100 (inset; magnified area of a cell transect), (B) D. desulfuricans, (C) C. metallidurans, (D) S. oneidensis, (E) Serratia sp., (F) M. luteus and (G) A. oxydans. Cells were loaded at 1:3 Pd

There are different types of bacteria with the ability of reduction of metallic elements to reduce. *Desulfovibrio fructosovorans* was shown for reduction of Tc (VII) (Luke et al., 2001) While D. *desulfuricans* showed ability for reduction of Au(III), Pd(II) and Fe(III).(Lloyd, 2003). Moreover, *Escherichia* coli (E.coli) cell was shown for reduction of Au(III) and Pd(II) (Deplanche. Et al., 2010). These bacteria carry out dissimilatory metal reduction whereby the oxidation of substrates such as H_2 or formate is coupled to the reduction of metallic ions by redox-active enzymes such as periplasmic hydrogenases (Lloyd, 1993).

The produced bacteria cell coated with reduced PGM metals on the surface was compared in multiple studies in different reactions compared to commercially available catalysts. Deplanche et al.,(2009) reported selectivity of Au, Pd metal loaded on E.coli bacteria for its performance in selectivity of oxidation of alcohols and glycerol. In another study, Yong et al. (2010) tested bio-Pd D. *desulfuricans* and bio-Pd E. coli for application of proton exchange membrane (PEM) within fuel cell electrocatalyst for power production. The results showed ~68% of the power output as commercial Pd(0). In another study of using bio-Pd conducted by Bennett et al. (2010) showed the successful selection of hydrogenation of 2-pentyne using 5wt% Pd/ D. *desulfuricans*.

3.1 Introduction

An overview of materials used is provided in this chapter including properties of heavy and bio-oil feedstock and nano-particle dispersed catalysts. Additionally, details of the experimental set up for the upgrading of heavy oil and bio-oil, and methods of products yield calculations are described in detail. Analytical methods used to determine the level of heavy oil and bio-oil upgrading and quality of produced oil are explained in detail. Moreover, the method of microbial manufacturing bio-catalyst is described in chapter 3

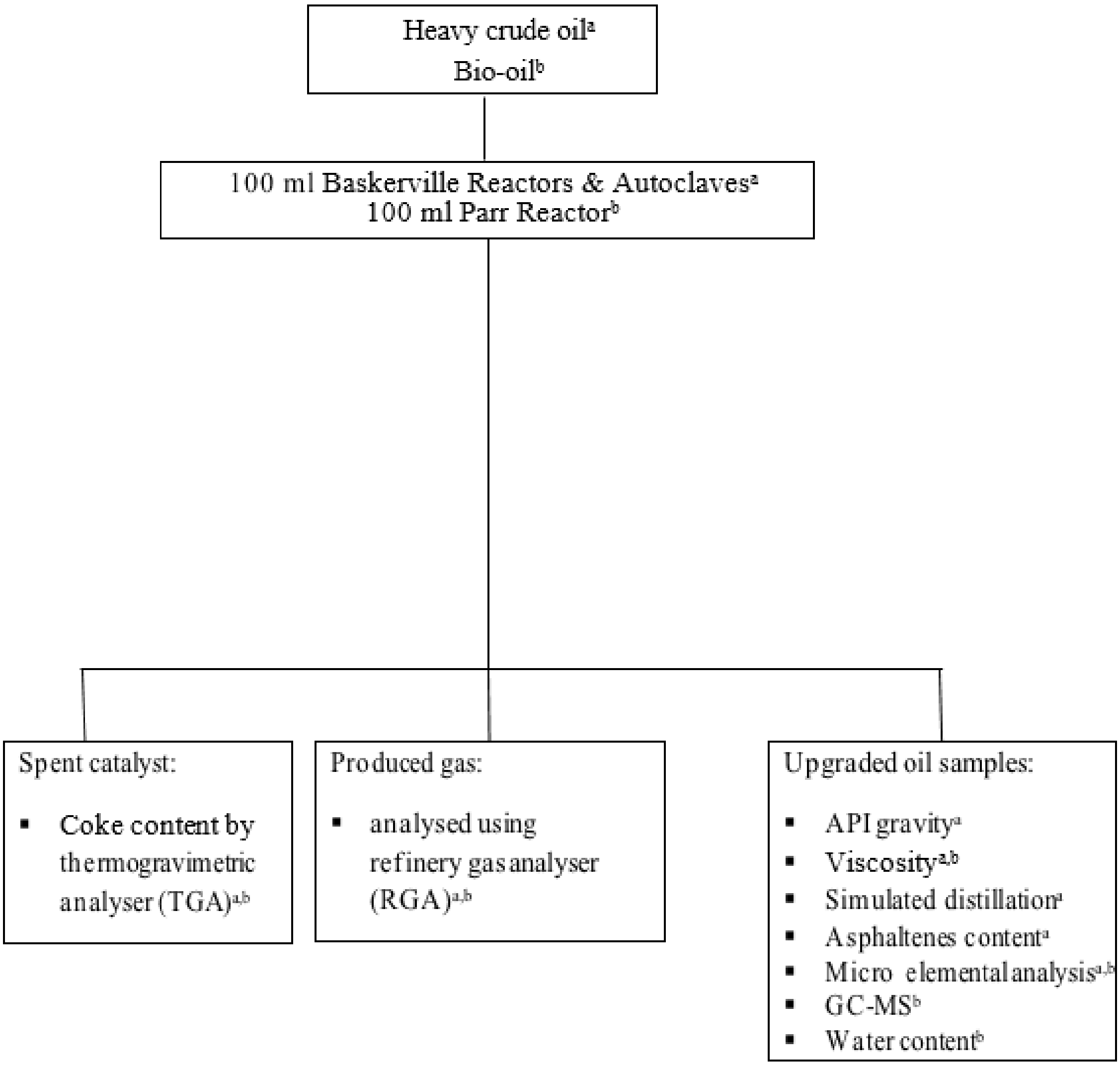


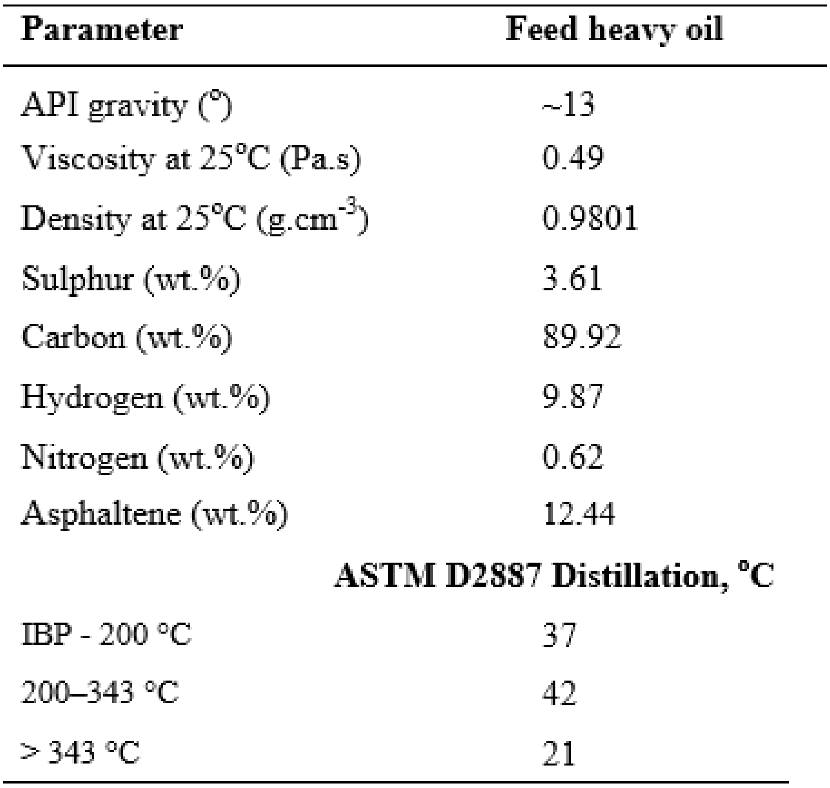
Figure 3.1Experimental and analytical method schemes of the heavy oil and bio-oil upgrading
Heavy oil - [b] Bio oil

3.2 Oil Feedstock Properties

3.2.1 *Heavy Oil*

The heavy oil feedstock used for upgrading process was supplied by Petrobank Energy and Resources Ltd, from its WHITESANDS THAI Pilot, at Conklin, Alberta, Canada. The feedstock was, in fact, a blend of oils from eight wells, produced by field THAI trials (the feed crude gravity was 10.9^{o} API which was increased to 13.8^{o} API during the extraction under THAI process); with properties summarised in Table 3.1

Table 3.1 Properties of the THAI heavy feed oils.

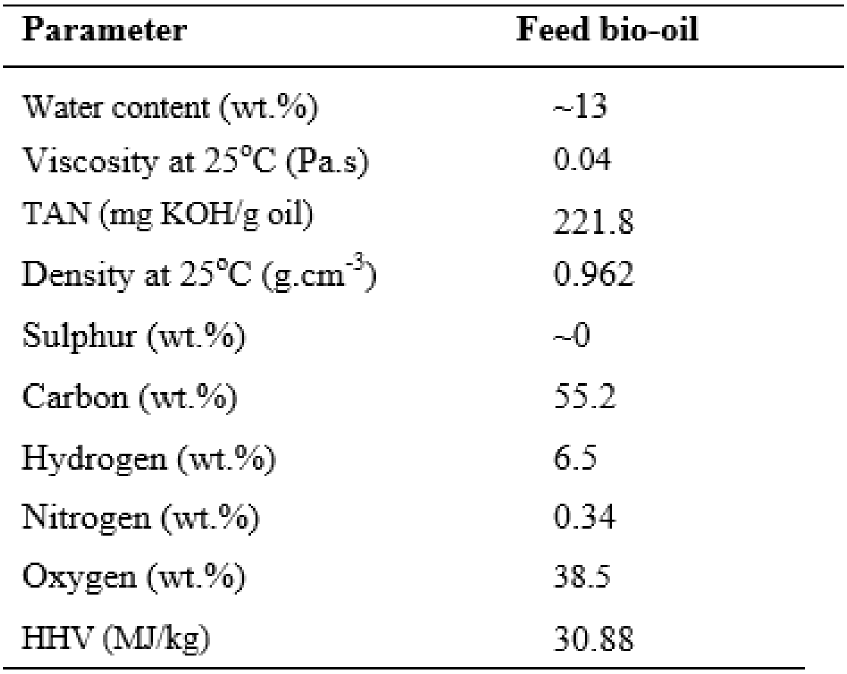


Parameter	**Feed heavy oil**
API gravity (°)	~13
Viscosity at 25°C (Pa.s)	0.49
Density at 25°C (g.cm^{-3})	0.9801
Sulphur (wt.%)	3.61
Carbon (wt.%)	89.92
Hydrogen (wt.%)	9.87
Nitrogen (wt.%)	0.62
Asphaltene (wt.%)	12.44
ASTM D2887 Distillation, °C	
IBP - 200 °C	37
200–343 °C	42
> 343 °C	21

3.2.2 *Bio-Oil*

The bio-oil feedstock used for the upgrading process was purchased from Biomass-to-liquid (btg-btl) direct online shop www.btg-btl.com (Netherlands). The bio-oil was produced using fast pyrolysis, the liquid condensate recovered by thermal treatment of lignocellulosic biomass, at short vapour residence time (~ 10s), at between 450-600 °C, at near below atmospheric pressure, in the absence of oxygen. The details of the bio-oil properties are summarised in Table 3.2.

Table 3.2 Properties of the pyrolysis bio-oil

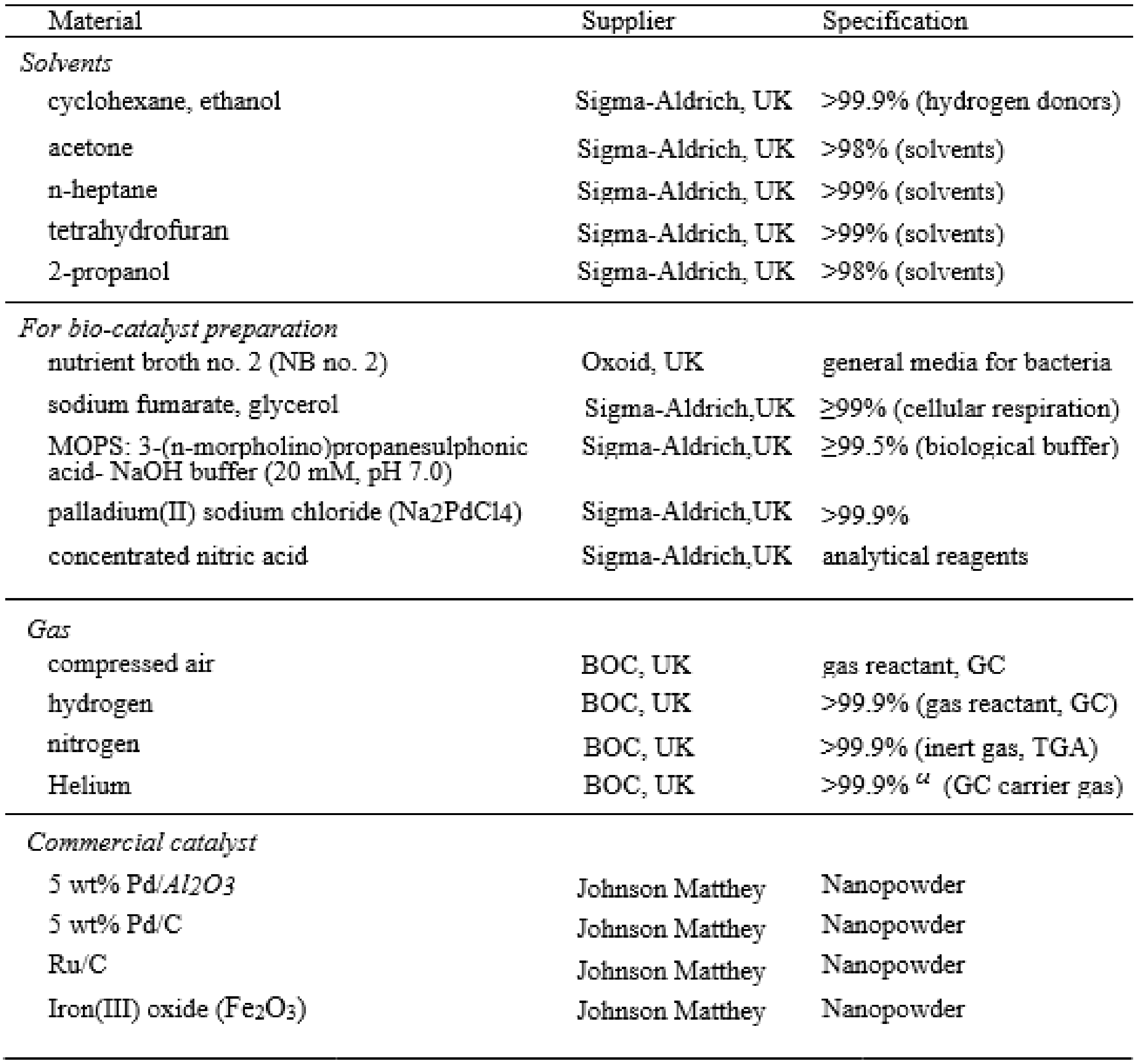


Parameter	**Feed bio-oil**
Water content (wt.%)	~13
Viscosity at 25°C (Pa.s)	0.04
TAN (mg KOH/g oil)	221.8
Density at 25°C ($g.cm^{-3}$)	0.962
Sulphur (wt.%)	~0
Carbon (wt.%)	55.2
Hydrogen (wt.%)	6.5
Nitrogen (wt.%)	0.34
Oxygen (wt.%)	38.5
HHV (MJ/kg)	30.88

3.3 Materials

Table 3.3 provides a full list of all the commercial gases, solvents, chemicals and catalysts used in the experiments. It should be noted that all the chemicals were used without further purification.

Table 3.3 Commercial materials used in the experiments



Material	Supplier	Specification
Solvents		
cyclohexane, ethanol	Sigma-Aldrich, UK	>99.9% (hydrogen donors)
acetone	Sigma-Aldrich, UK	>98% (solvents)
n-heptane	Sigma-Aldrich, UK	>99% (solvents)
tetrahydrofuran	Sigma-Aldrich, UK	>99% (solvents)
2-propanol	Sigma-Aldrich, UK	>98% (solvents)
For bio-catalyst preparation		
nutrient broth no. 2 (NB no. 2)	Oxoid, UK	general media for bacteria
sodium fumarate, glycerol	Sigma-Aldrich,UK	≥99% (cellular respiration)
MOPS: 3-(n-morpholino)propanesulphonic acid- NaOH buffer (20 mM, pH 7.0)	Sigma-Aldrich,UK	≥99.5% (biological buffer)
palladium(II) sodium chloride (Na_2PdCl_4)	Sigma-Aldrich,UK	>99.9%
concentrated nitric acid	Sigma-Aldrich,UK	analytical reagents
Gas		
compressed air	BOC, UK	gas reactant, GC
hydrogen	BOC, UK	>99.9% (gas reactant, GC)
nitrogen	BOC, UK	>99.9% (inert gas, TGA)
Helium	BOC, UK	>99.9% $^{\alpha}$ (GC carrier gas)
Commercial catalyst		
5 wt% Pd/Al_2O_3	Johnson Matthey	Nanopowder
5 wt% Pd/C	Johnson Matthey	Nanopowder
Ru/C	Johnson Matthey	Nanopowder
Iron(III) oxide (Fe_2O_3)	Johnson Matthey	Nanopowder

3.4 Experimental Set-Up and Procedure

3.4.1 *Heavy Oil Reactor Set-Up*

A stirred batch autoclave reactor of 100 mL capacity (Baskerville, UK) with the maximum operating condition of 550 °C and 100 bar was used to carry out the upgrading of heavy oil with dispersed catalyst nanoparticles (NPs). A photograph and a schematic diagram of the batch autoclave reactor are shown in Figure 3.2 and Figure 3.3 respectively. As shown in the schematic diagram (Figure 3.2), the batch reactor is equipped with a temperature thermocouple, a pressure gauge, a relief valve and an inline agitator with three round-shaped pitched blades impeller (5.84 cm diameter). Additionally, a 60-mL stainless steel sleeve with baffles was designed to fit inside the reactor to allow easier access to the final product to perform mass balance. Furthermore, Figure 3.2 shows a control cabinet connected to the batch reactor which controls the heating rates and the speed of agitator during the reaction.

Figure 3.2 100 ml batch reactor and cabin controller

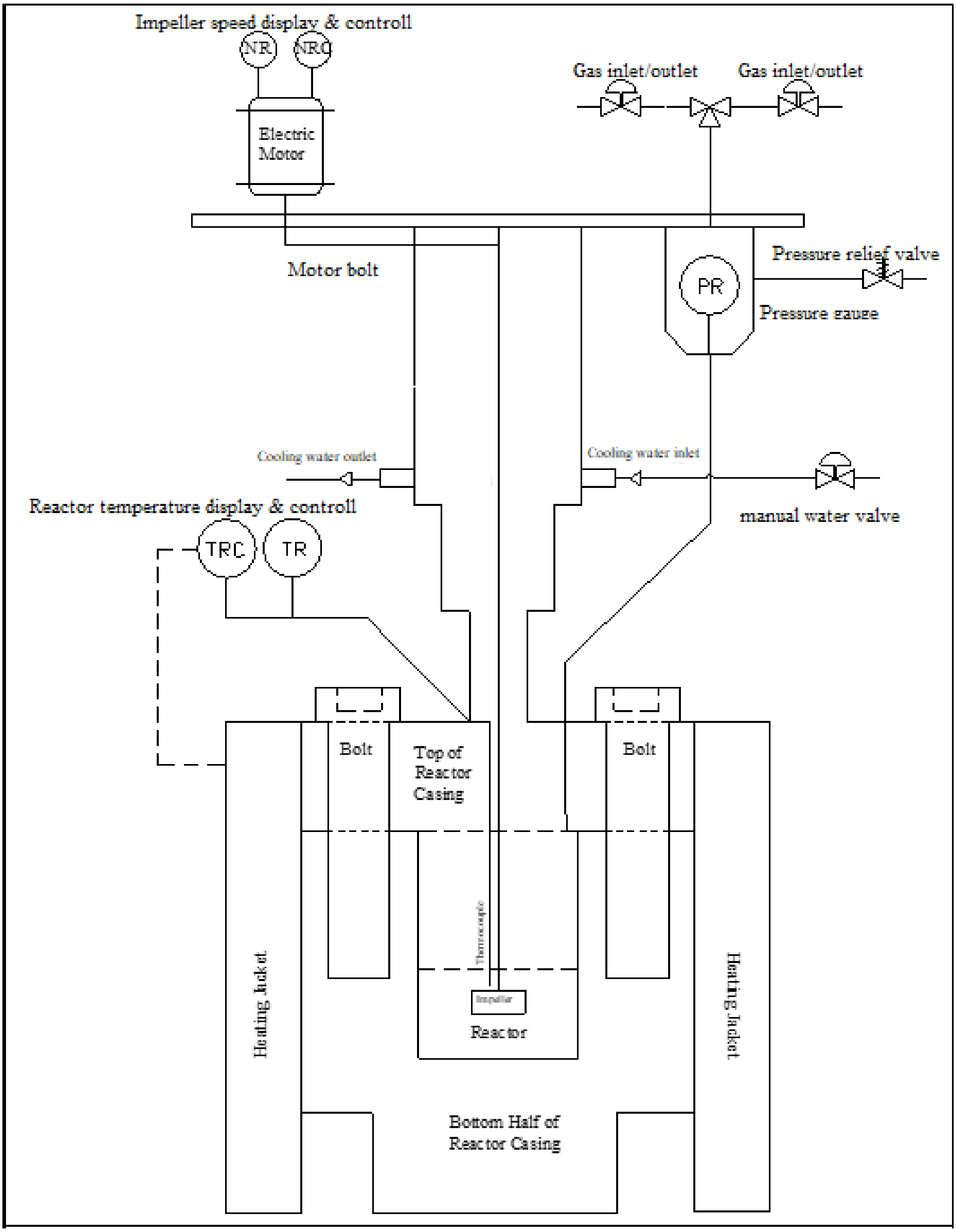


Figure 3.3 The schematic diagram of the 100 ml Baskerville batch autoclave reactor.

3.4.1.1 Experimental Procedure and Mass Balance

In preparation for each experimental reaction run, THAI feedstock oil was prepared in the 60 ml reaction sleeve along with a given catalyst and a known amount of a hydrogen-donor solvent. The subsequent sleeve weight and its contents were recorded to allow for the mass balance calculation. The known catalysts and hydrogen-donor solvents used in each experiment are listed in table 3.4. The sleeve and its contents were slotted into the bottom half of the batch reactor, before securing the top half manually using 10 stainless steel bolts and a rotary ratchet tool. To achieve a seal capable of containing pressures of up to 80 bar, 10 bolts surrounding the reactor casing are tightened uniformly to a value of 5.5 and then 7.5-inch pounds using a torque wrench, ensuring the reactor casing is set as level. The sealed reactor was then purged with commercial nitrogen gas to check for leakage before being flushed to ensure clear pipes. The batch reactor was then pressurised to 20 bar, with an inert feed gas (nitrogen or hydrogen) and placed inside a controlled ducted fume cupboard.

Table 3.4 Heavy oil reaction conditions

Parameter	Value
Feed oil	20 g
Catalyst weight	0.5 g
Solvent weight	0.6-2.4 g
Agitation Speed	750 RPM
Reaction time	30-120 min
Reaction temprature	350-450 ^{o}C
Initial pressure	20 bar

The agitator motor was adjusted to provide the required rotational speed, allowing for adequate dispersion of the known catalyst. The proportional-integral-derivative controller (PID controller) was programmed to adjust the input and output power of the furnace to quickly obtain the desired temperature. The total heating time takes approximately 1 h, allowing for full catalyst activation (Kinzel et al., 2010). With the reaction temperature meeting the desired value from the PID controller, the reaction time initiates. Once complete, the reactor is cooled using a 230 W high-efficiency 18” industrial fan. During the reaction, the heavy fraction converts into light oil, light ends and coke fractions. The sample of reaction gas formed during the reaction was collected in a gas syringe for GC injection, and the remaining is released within the fume cupboard, allowing for the reactor to be opened and the sleeve contents recovered and weighed. The upgraded oil and the suspended catalysts/coke were separated by vacuum filtration using Whatman filter paper grade 6 with 6 µm pore size and 4.5 cm diameter. The deposit left in the wall and bottom of the sleeve was recovered. The deposits consist ofultrafine dispersed catalysts which generally are encapsulated with residual oil and coke. Remainder oil refers to encapsulated and residual oil which has been trapped, not able to flow freely, under the heavy residue and/or coke deposits. Although remainder oil could potentially contribute to light oil production, this fraction cannot be easily obtained. Therefore, TGA (Thermogravimetric Analysis) and DTG (Differential Thermogravimetric) were used to determine the amount of actual coke formed during the reaction by calculating the mass difference after burning off the remainder oil of the sample of deposited materials inside the sleeve. The mass of gas produced during the reaction was calculated by subtracting the masses of the liquid oil, catalysts and coke fraction after the reaction from the total mass of feed oil and catalyst. Equation 3.1 used for calculating the overall mass balances of individual phases

$$Y_{product}\,(\%) = M_{product}\,(g) / M_{bio\text{-}oil+solvent}\,(g) \times 100 \qquad (3.1)$$

Where $Y_{product}$ is the yield and $M_{product}$ is the mass of the product. For the reaction with the presence of cyclohexane, the upgraded oil and cyclohexane were a homogeneous mixture, and trying to separate them will affect the upgraded oil composition. Therefore, the physical properties (API° gravity and viscosity) reported here are those of the produced mixture (upgraded oil and cyclohexane).

3.4.2 *Bio-Oil Reactor Set-Up*

A stirred batch reactor of 100 mL capacity (Parr reactor) with the maximum operating condition of 350 °C and 200 bar was used to carry out the upgrading of bio-oil with dispersed catalyst nanoparticles (NPs). This reactor is a cylindrical vessel with the inside diameter of 3.30 cm and height of 11.68 cm. The schematic diagram and a photograph of the batch reactor are shown in Figure 3.4 and Figure 3.5 respectively. As shown in the schematic diagram (Figure 3.4), the batch reactor is equipped with a temperature thermocouple, a pressure gauge, a relief valve and an inline gas entrainment impeller with a four-bladed impeller (2.06 cm diameter). Furthermore, Figure 3.4 shows a control unit connected to the batch reactor which controls the heating rates and the speed of agitator during the reaction.

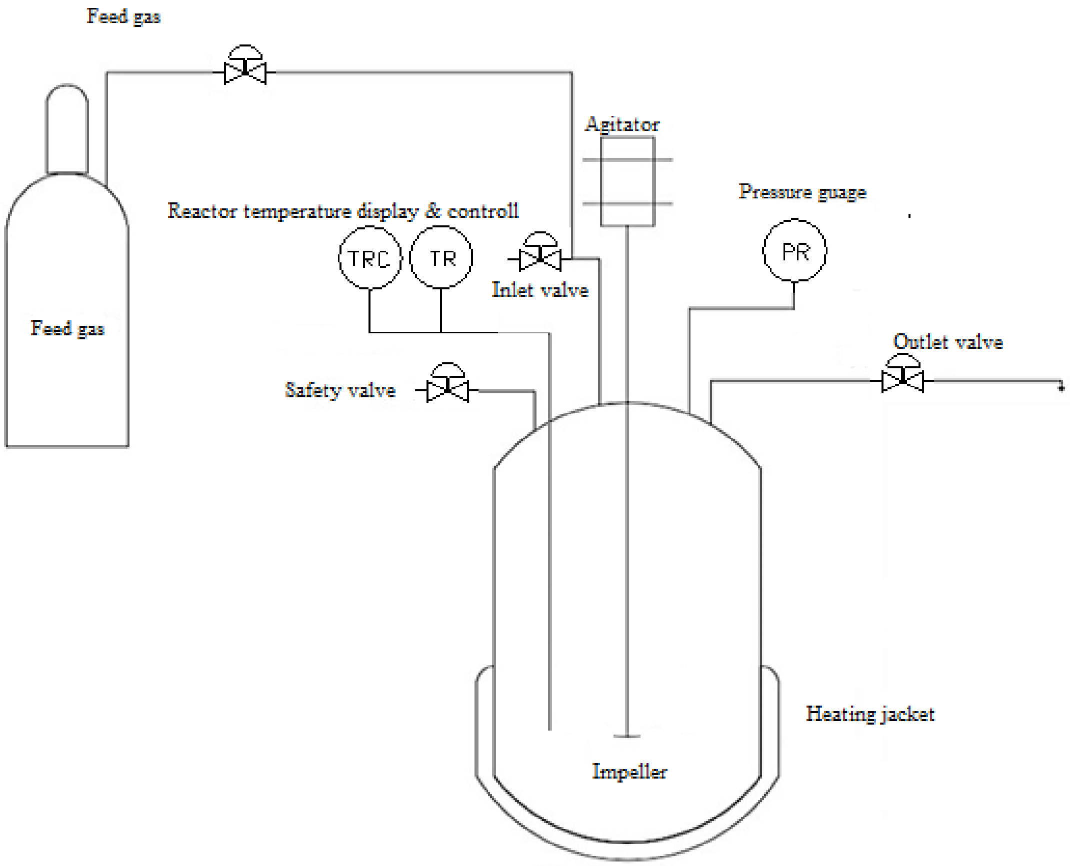


Figure 3.4 The schematics diagram of the batch Parr reactor

Figure 3.5 Photograph of batch Parr instrument, heating jacket and a unit controller
(Parr Instrument 2018)

3.4.2.1 Experimental Procedure and Mass Balance

BTG pyrolysis bio-oil was prepared in the 100 ml Parr reactor along with a given catalyst and a known amount of a hydrogen-donor solvent. The subsequent sleeve weight and its contents were recorded to allow for the mass balance calculation. The known bio-oil, catalysts and solvents used in each experiment are listed in table 3.5. The reactor than was sealed and pressure purged with hydrogen twice, to remove either the remaining oxygen in the headspace of the reactor or the dissolved oxygen in the liquid. The reactor was then pressured to 100 bar with H_2 at room temperature. Agitation occurred for 5 min to ensure dispersion of catalyst in bio-oil, and the reactor was checked for leaks.

Table 3.5 Bio-oil reaction conditions

Parameter	Value
Feed oil	20 g
Catalyst weight	0.6 g
Solvent weight	5 g
Agitation Speed	900 RPM
Reaction time	0-300 min
Reaction temprature	160-350 ^{o}C
Initial pressure	100 bar

The reactor was then heated up to the desired temperature with constant heat up time of 30 min for every reaction, with the timer starting from the beginning of the addition of heat. When the desired reaction time had completed, the reactor system was cooled with ice to room temperature, and the final pressure was noted. The gas sample was extracted from the system using a syringe for the gas chromatograph analysis. Once an adequate gas sample had been analysed, the remainder of the gas was released from the system, reducing the pressure to atmospheric. The reactor sleeve was removed from the system, and any products were dripping from the agitator or probes were collected before the separation of the aqueous phase and organic phase using a separating funnel. The mass of both phases was weighed for mass balance calculations. The organic phase was subject to dilution with Acetone and vacuum filtered to separate the catalyst and solid deposits (coke). A double layer of Whatman filter paper grade 6 with 6 µm pore size and 4.5 cm diameter was used to ensure the collection of all the particles. Duplicate experiments were conducted for all the conditions, and the yields of the coke and organic, aqueous and gas phases were calculated using the following equations:

$$Y_{product}\ (\%) = M_{product}\ (g) / M_{bio\text{-}oil+solvent}\ (g) \times 100 \qquad (3.2)$$

$$Y_{gas}\ (\%) = 100 - [Y_{aqueous} + Y_{organic} + Y_{coke}] \qquad (3.3)$$

where $Y_{product}$ is the yield and $M_{product}$ is the mass of the product.

3.5 Preparation of Bio-Pd

Section 3.4.1 and 3.4.2 describes the biochemical method to produce novel biomass-supported Pd nanoparticles (NPs) with a strain of Escherichia coli (*E. coli*) using the sacrificial hydrogen strategy.

3.5.1 *E. coli Growth and Pd Solutions Preparation*

Escherichia coli MC4100 frozen precultures in glycerol (-80 °C) initially was defrosted and then grown in Postgate's Medium of NB no. 2 with 0.4% sodium fumarate (w/v) and 0.5% glycerol (v/v) under anaerobic respiratory conditions (nitrogen atmosphere) at 37 °C (Deplanche et al., 2010). The precultures were then transferred into Durham bottles of 2 litres filled with degassed Postgate's medium, sealed and grown anaerobically in the same way. The day after the cells were harvested using centrifuge with 10,000 rpm speed and duration of 10 min at 5 °C, washed for two times and re-suspended in the degassed 20 mM MOPS (3-(N-morpholino) propanesulfonic acid) buffer to a pH of 7.0.

Optical density (OD) measurements were used to estimate the cell concentration in the suspension. A spectrophotometer operating at 600 nm wavelength by reference to a pre-determined optical density (OD) was used for this measurement. The OD_{600} of 1 for an E.*coli* biomass concentration is 0.482 $g.l^{-1}$ (Deplanche et al., 2008). The concentrated cell solution then stored at 4 °C for bio-Pd preparation.

- Pd (II) solutions

2 mM Pd(II) aqueous solution was prepared through dissolving of 0.01 M of HNO_3 in a required amount of sodium tetrachloropalladate (Na_2PdCl_4) to a pH of 2.3. Yong et al. (2002) found this concentration to be an optimal solution for the production of the active biomass supported catalyst.

3.5.2 *Metallisation of E.coli*

The stored concentrated cell was transferred into a calculated volume of 2 mM Pd(II) degassed solution anaerobically depending on the required metal loading of the catalysts. For example for 5 wt% or 20 wt% Pd catalyst the weight of Pd: cells was 1:20 or 1:4 respectively. For allowing of biosorption of Pd(II) complexes, the cell/Pd(II) mixture was kept for 30 mins at 30 °C (Yong et al., 2002). In order to allow the biosorption of Pd(II) complexes, the biomass/Pd(II) mixture was left to stand for 30 mins at 30 °C (Yong et al., 2002). Hydrogen gas was then introduced by sparging through the suspension as the electron donor for reduction at a flow rate of 200 $ml.min^{-1}$ for 20 min (Lloyd et al., 1998). During hydrogen sparging, the observed colour of the mixture changed from yellow to dark grey, which confirmed the reduction of cell surface-bound Pd(II) to Pd(0) (Deplanche et al., 2011). The Pd loaded biomass were stored overnight to settle and harvested using centrifuge with 4,000 rpm for 15 min at 4 °C. The harvested product was then washed in distilled water for three times, finally washed with acetone and left in a fume cupboard to be dried prior to grinding. Figure 3.6 shows the simplified procedure of bio-Pd preparation steps and Pd reduction.

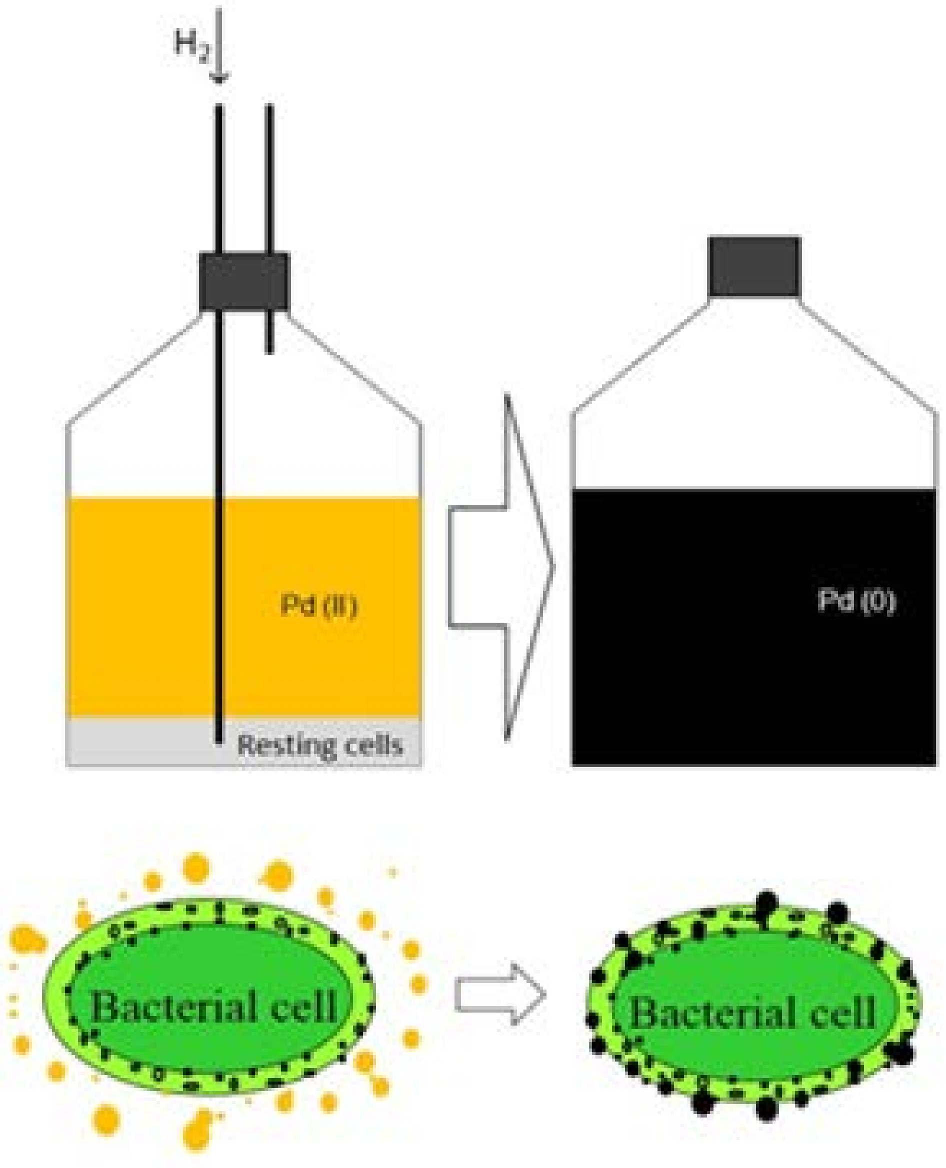


Figure 3.6 Simplified steps of bio-Pd preparation using biomass

3.5.3 *Characteristics of catalyst*

The microstructural properties and physical characterisation of catalysts used in upgrading reaction of heavy oil and bio-oil including specific surface area, pore volume particle size were measured using Brunauer – Emmett – Teller (BET) method and laser diffraction particle size analyser. These properties are presented in Table 3.6.

Table 3.6 Physical characterisations of used catalysts.

Catalyst	BET area (m^2/g)	Pore volume (cm^3/g)	Particle size (μm)
5 wt% Ru/C	808 ± 0.1	0.4	2.2
5 wt% Pd/$Al2O3$	227.7 ± 1.5	0.55	2.5
5 wt% Pd/C	818.7 ± 12	0.42	2.2
5 wt% bio-Pd	65.5 ± 0.1 [a]	0.02	4.8
Fe_2O_3	2321 ± 1.5	0.84	0.05

Particle size analyser manufactured by Helos-Rodos, model T4.1, Sympatec was used to determine the size of the catalyst particles. A Micromeritics Analytical Instrument was used to perform the BET method according to ASTM C1274 to calculate the catalysts surface area and pore size. The method includes measurement of adsorption isotherm of nitrogen on the catalyst particles at -196 ^oC.

The ratio of adsorbed nitrogen and the monolayer volume coverage at given partial pressure was determined using the BET equation 3.4. The specific surface area was estimated by the gas molecules monolayer formation on the surface of the catalyst, and the particle pore volume determined by the principle of capillary condensation of the nitrogen gas.

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C\, P_0} \qquad (3.4)$$

where P is the partial pressure of nitrogen, V is volume adsorbed at P, P_o is the saturation pressure at -196 ^oC and V_m adsorbed monolayer volume coverage, and C is a constant value of 101.5.

Equation 3.5 was then used to calculate the BET surface area (S_{BET}) of catalyst particles.

$$S_{BET} = \frac{V_m n_a a_m}{m_V} \tag{3.5}$$

where m_v is the value of the gram-molecule volume with the value of 22.414 mL, n_a is the Avogadro's number with the value of 6.022 x 10^{23} mol^{-1} and, a_m is each adsorbate molecule cross-sectional area at -196 ^oC which is 0.162 nm^2

3.5.4 *Catalyst Surface Morphology using SEM*

The catalysts particles morphology and metal NPs dispersion of bio-Pd were displayed using a Scanning Electron Microscope manufactured by Philips, model XL30 ESEM-FEG. In this type of microscope, a high-energy beam of secondary electrons used in to create an image of the catalyst particles. The image could potentially reflect the 5~50 nm thick surface topography information. Back-Scattered Electron (BSE) is another type of signal produced by an SEM which is used for image compositional contrast. In the BSE technique high atomic number elements have stronger backscatter electrons and appear brighter than low atomic number elements in the produced SEM image. This is because of the linear monotonic relation of the BSE signal intensity to the chemical composition of the sample atomic number (Z) (Goldstein et al., 1981).

3.6 Analytical Instruments

The produced oil and gas, as well as deposited coke after heavy oil and bio-oil upgrading reaction, were analysed using the following instruments.

3.6.1 *Density and API Gravity Measurement*

An Anton Paar DMA 35 digital density meter was used to measure the density of each post-reaction sample, the instrument is made up of a glass tube, temperature node and digital display. The measurement is underpinned by an oscillating U-tube model, which draws the liquid up through the tubing from applying pressure to the button and the results are displayed on the digital display as shown in Figure 3.7. Before each recording, calibration was implemented using acetone, both to validate the measurement and to ensure the tubing is free from debris, which read 0.7900 g/ml at 20 ºC. The measurements were performed twice per sample and averaged.

The American Petroleum Institute (API) gravity index, used to determine the grade of heavy oil was then configured using equations 3.6 and 3.7:

Figure 3.7 Photograph of Anton Paar digital density and API gravity meter

$$API\ Gravity\ (^{o}) = \frac{141.5}{SG} - 131.5 \tag{3.6}$$

$$API\ Gravity\ Difference\ (^{o}) = API\ Feed\ oil - API\ \ upgraded\ oil \tag{3.7}$$

where SG is specific gravity (kg/m^3).

3.6.2 *Viscosity Measurement*

A rheometer (Bohlin R6 5103) was utilised to measure viscosities of heavy oil and bio-oil feedstock and upgraded oil samples. A 30 mm parallel moving plate with a 50 µm gap and 1°/60mm cone plate with 3 µm gap was used for heavy oil and bio-oil viscosity measurement respectively. The measurement was performed on the basis of shear stress against shear rate. The increasing shear rate ranging from 0.5 to 500s^{-1} did not affect the oil viscosity, which indicates the Newtonian fluid behaviour of both heavy oil and bio-oil analysed samples. Subsequently, the viscometry of all samples were measured at a shear rate of 100 s^{-1}. Each sample measurement was performed twice to record an average at a temperature of 25 ºC.

3.6.3 *True Boiling Point (TBP) Distribution of Heavy Oil*

Gas Chromatograph (GC) manufactured by An Agilent 6850N (Germany) was calibrated in accordance with the ASTM- D2887 method to characterise and provide an overall TBP distribution range of the feed heavy oil produced upgraded oil and its distillates. This equipment rapidly derives the boiling point distributions of a series of oil fractions via SIMDIS software algorithm from a chromatogram recorded using a J&W 10 m length, µm film thickness and 530 µm inner diameter capillary.

The dilution solvent for each sample was carbon disulphide (CS_2), selected due to its high oil miscibility and low boiling point, where a 1:10 volume ratio of solvent to oil provided a GC syringe with one µl samples. The GC was initially calibrated with a standard mixture of hydrocarbons ranging from C_5 – C_{40} before a sample was introduced. Details of the operating conditions for the GC are provided below:

- Eluent gas flowrate: Helium at 10 ml/min
- Makeup gas flowrate: Nitrogen at 32.3 ml/min
- Hydrogen flow rate: 40 ml/min
- Air-gas flow rate: 450 ml/min
- Flame ionisation detector (FID) temperature: 260 ºC
- Oven temperature (maximum): 280 ºC
- Column temperature gradient: 20 ºC/min

The chromatographic column analyses each sample by dividing hydrocarbon molecules based on their boiling points, which are allocated based on space-time in the column. The results are calculated and presented on the Chemstation software programme (Agilent Technologies Inc.), where the data was collected and analysed to determine the level of oil upgrading. The products of thermal and catalytic cracking during heavy oil upgrading can be expressed by equation 3.8.

$$Heavy\ fractions\ (343\ ^{\mathrm{O}}\mathrm{C}\ +) \rightarrow distillable\ (<\ 343\ ^{\mathrm{O}}\mathrm{C}) +\ \mathrm{gas} +\ coke \qquad (3.8)$$

The final results are presented according to the following oil fractions; Light naphtha with an initial boiling point to 177 °C; middle distillate between 177 °C to 343 °C; and gas oil from 343 °C to 525 °C (Gray, 1994).

3.6.4 *Qualitative and Quantitative Analytical Methods of Bio-Oil*

Selected samples were sent to 'The Centre for Chemical and Materials Analysis' at the Chemistry Department of the University of Birmingham for qualitative and quantitative analysis of low molecular weight compounds of feed and upgraded bio-oil. The GC-MS analysis was carried out using Agilent GC/MS, model 6890N GC/5973 MS and fluoranthene were used as internal standard (I.S) of the measurements. The instrument was equipped with a Zebron ZB-5 ms column (60 m x 0.32 mm i.d., 0.25µm film thickness) coupled with Flame Ionisation Detector (FID) (Figure 3.8). In the FID system, organic constituents carried by helium gas through a retention column and partially burnt by air and hydrogen. FID then can detect the produced ionic sub-compounds and present the results signals at different retention times corresponding to individual components and proportional to the number of compounds.

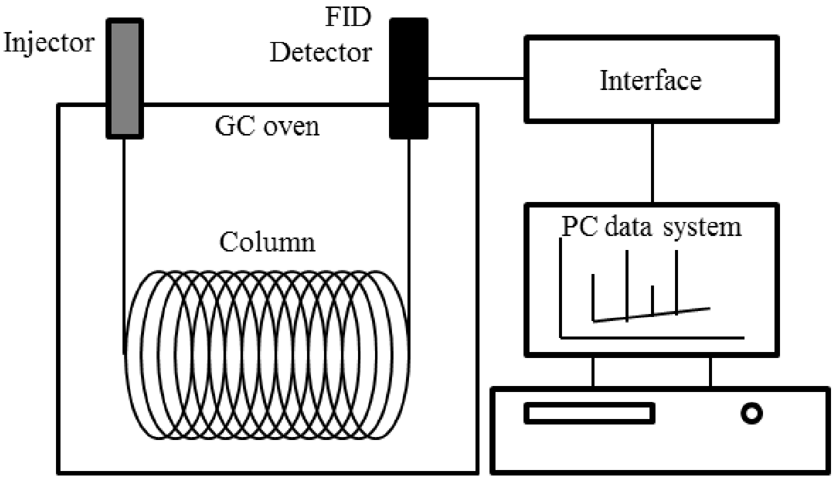


Figure 3.8 Schematic of the GC/FID system.

For each injection 2μl solutions of 2 wt%, bio-oil in acetone was prepared. The oven temperature was maintained at 50 °C for 6 min and heated to 320 °C at the rate of 5°C/min which then held for 5 min. The constant column head pressure was 17.49 psi. The injector was at 230 °C and the FID detector at 300 °C.

3.6.5 *Elemental Analysis*

The nitrogen, hydrogen, carbon and sulfur contents of heavy oil and bio-oil were determined using an elemental analyser (CE Instruments EA 1110). A high-temperature furnace combusts the accurately weighed sample to form CO_2, H_2O, SO_2 and NO gases by passing the combusted product through a particular oxidation reagent. Furthermore, the gases are passed through a copper column to reduce oxides and remove any excess oxygen. A thermal conductivity detector then precisely detected these combustion products. For the bio-oil samples, the higher heating value (HHV) was calculated using Sheng and Aze- vedo's (2016) formula (3.9). The oxygen content was calculated by difference and the DOD, an essential parameter of the bio-oil upgrading reaction, was calculated using the equation 3.10:

$$HHV\ (MJ\ kg^{-1}) = 0.3491 \times C\% + 1.1783 \times H\% + 0.1005 \times S\% - 0.1034 \times O\% - 0.0151 \times N\% \qquad (3.9)$$

$$DoD\ (\%) = \frac{MO(bio-oil) - MO(sample)}{MO(bio-oil)} \times 100\% \qquad (3.10)$$

where MO is the oxygen/carbon molar ratios of feed bio-oil and upgraded oil

3.6.6 *Thermogravimetric Analysis (TGA)*

A thermogravimetric analyser (TGA) was used to analyse the heavy oil deposits and determine the amount of coke. This study used a Netzsch-Geratebau GmbH, TG 209 F1 Iris. For thermally stable species, there will be negligible mass change over a specific temperature range, corresponding to a small slope in the TG trace. On the other hand, some materials degrade with increasing temperature and show a mass loss. Therefore TGA is an instrumental technique to determine the number and quantity of materials such as coke which degrade at relatively high temperature. Approximately 20 mg of recovered carbonaceous deposit and spent catalyst was placed on a platinum crucible above a microbalance. The temperature within the micro-furnace is configured between 25 – 900 ºC, heating at 20 ºC/min, where an isothermal reaction occurs for 20 mins at 900 ºC. The reaction ensures the complete vaporisation of volatile materials embedded within a spent catalyst at an air flow rate of 50 ml/min. Specialist software (Proteus) was used to record changes in sample weight per cent, with weight loss measured by the TGA microbalance. Figure 3.9 illustrates the vacuum-tight thermo-microbalance which uses principles of electromagnetic power compensation for its measurements.

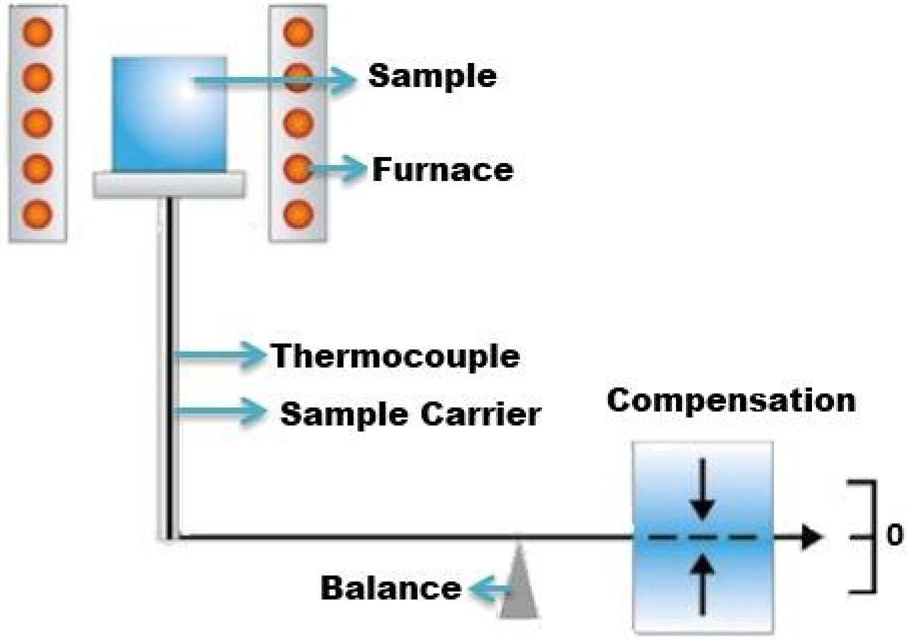


Figure 3.9 The simplified Schematic of the thermo-microbalance of the TGA

3.6.7 *Refinery Gas Analyser (RGA)*

An Agilent, model 7890A RGA-GC was used to measure the compositions of gas produced during the upgrading of heavy oil and bio-oil in accordance with method ASTM D1945-03, the molecules recognized within the analysis were H_2, H_2S, CO, CO_2, and hydrocarbons $C_1 – C_5$. The RGA include three channels, with one FID and two thermal conductivity detectors (TCD). The hydrocarbon constituents were distinguished by an FID channel column HP- PLOT Al_2O_3S capable of separating C_1 to nC_5, which includes isomers, underpinned by a calibration sequence. The column operates H_2 at 45ml/min, N_2 at 25ml/min, air flow at 400ml/min and reference flow at 45ml/min. Components heavier than nC_5 are backflushed through the pre-column. One of the TCD detects gases like H_2 and helium in the gas stream, while the other TCD which carried by helium gas determines gases such as O_2, N_2, CO_2, CO and H_2S. The first TCD channel operates He flow at 2 ml/min and a reference flow at 45 ml/min, whereas the second TCD channel operates N_2 at 2 ml/min and a reference flow at 45 ml/min. The column dimension of the oven is 27 m x 320 µm x 8 µm at a temperature of 200 ^oC. The calibration mix gases are listed in Table 3.7.

Table 3.7 RGA gas composition calibration

Gas	Amount (vol. %)	Gas	Amount (vol.%)
Hydrogen	1	**Methane**	1
Ethane	1	**Propane**	1
Carbon dioxide	3	**Propene**	1
i-butane	1	**n-butane**	1
Trans-2-butene	1	**1-butene**	1
Cis-2-butene	1	**i-pentane**	1
n-pentane	1	**Carbon monoxide**	4
Nitrogen	1	**Hydrogen sulphide**	0.0005

3.7 Asphaltene Measurement

Asphaltene content of each sample of heavy oil was measured using vacuum filtration using a 4.5 cm diameter and 6 μm pore Whatman filter paper under method ASTM-D2007-80. A known amount of each oil sample was mixed with saturated straight-chain alkanes, such as an n-heptane solvent to precipitate an asphaltene division, in the ratio of 1 g oil to 30 g solvent. The asphaltenes were then filtered and washed with n-heptane until all oil residue are removed from the filter and colourless liquid was observed. The asphaltene was placed in the fume cupboard for a day to be dried and weighed. The asphaltene content was calculated using the following equation 3.11:

$$Asphaltene\ (wt\%) = \frac{m_{asphaltene}}{m_{Feed\ oil}} \times 100\% \qquad (3.11)$$

where $m_{asphaltene}$ is the mass of dried, precipitated asphaltene.

4 *Effects of Catalyst on Heavy Oil CAPRI Upgrading*

4.1 Introduction

The performance of catalysts to improve downhole upgrading in the Toe-to-Heel Air Injection (THAI) process is limited because of extensive coking which leads to deactivation. The aim of this chapter is to report an experimental investigation into the reaction variables and effect of different catalyst and supports upon the upgrading of heavy oil under conditions designed to replicate in-situ upgrading in the CAPRI process. The feed oil to the process is the THAI oil which has undergone partial upgrading in-situ. Therefore the experiments reported are designed to indicate the additional upgrading achieved in the CAPRI process. This additional improvement may reduce the requirement for processing in surface upgraders at the refinery and lead to a product which can be more easily pumped without the addition of diluents. One of the main limitations of the performance of the catalyst is its deactivation due to coking arising from the cracking of heavy oil. Despite the additional upgrading achieved with the CAPRI process, the accumulation of coke and metals deposits on the catalyst and pore sites, resulting from cracking of the heavy oil, have a detrimental effect on the catalyst activity, life span, and process. An alternative contacting pattern between the oil and different nanoparticulate catalysts was investigated in this study. Furthermore, the product distribution of the upgrading reaction can be improved by introducing a suitable source of hydrogen which may increase the rate of hydroconversion rather than cracking reactions. In order to mitigate the above-mentioned challenges and increase upgraded oil yield whilst suppressing coke formation, the effect of cyclohexane as hydrogen-donor solvent was studied.

Effectiveness of Pd catalyst in the hydrogenation of heavy oil has been investigated and compared to carbon-supported Ru and unsupported iron oxide. The effectiveness of Pd metal on different supports was then investigated to find the effect of different support in comparison with lab-produced Bio Pd. There are several important characteristics which are used to determine the degree of heavy oil upgrading. Determination of quality of produced oil is achieved through means of quantifying the degree of API gravity and change in viscosity of upgraded oil, coke content, the heavy fractions conversion and impurities such as coke and asphaltene content. Investigations in this section include studies on the effect of temperature and reaction time on thermal cracking in Section 4.2, in order to provide a base-case for comparison with the catalytic upgrading experiments. The effect of catalyst type on CAPRI upgrading presented in Section 4.3, gas media and hydrogen donor solvent (H+) in Section 4.4 to 4.5 palladium catalyst support and bio-Pd metal loading in Sections 4.6 to 4.7.

4.2 Thermal Cracking Effect

In this section, the extent of non-catalytic thermal cracking upgrading using 100 ml batch reactor is reported. The MOZ of the heavy oil reservoir having the range of average temperature as 300-500 °C. Therefore, the investigation was carried out at the following ranges; temperature 350 – 450 °C, reaction time 0 – 120 min, with 20 bar initial nitrogen pressure.

4.2.1 *Effect of Temperature*

The API gravity changes, viscosity alteration and coke deposition of the produced oil samples are presented as a function of reaction temperature in Table 4.1.

The results shown in Table 4.1 indicate an average increase ranging from 0.9 to 7.3° API compared to the original feed oil as temperature increases from 350 to 425 °C. In line with the same trend of improvement of oil quality, it is clear that there is a major reduction in the viscosity of the produced oil after upgrading in comparison with the feed oil, with higher viscosity reduction noticed at 450 °C. As the reaction temperature increased, the viscosity decreased from 0.34 Pa.s at 350 °C to 0.023 Pa.s at 425 °C.

Table 4.1 Effect of thermal upgrading on API gravity, viscosity, coke and Asphaltene yield of heavy oil

Using stirred batch reactor under 20 bar nitrogen medium at 30 min (feedstock: 13 °API and 0.49Pa.s).

Reaction temperature (°C)	API ° gravity (25°C)	Viscosity Pa.s (25°C)	Coke (wt.%)	Asphaltene (wt.%)
350	13.9 ± 0.2	0.342	4.5	11.95 ±0.9
400	17.1 ± 0.18	0.152	9.9	11.33 ±0.3
425	20.1 ± 0.18	0.023	10.8	11.49 ±0.8
450	20.3 ± 0.21	0.025	15.9	11.22 ±0.3

The results in Table 4.1 shows clearly how thermal cracking was promoted when temperature increases which is attributed to the enhancement of thermal cracking reactions leading to breakdown of larger molecules into smaller fragments. This is because of the known effect that increase in temperature enhances the rate of free radical chain reaction mechanism, the results reported here providing a base-case for the extent of thermal cracking for comparison with the catalytic cracking results reported later in this chapter. Examples of the free radical cracking reactions are given below (Hart et al., 2014; Weitkamp, 2012):

1. **Initiation reaction**, in which some of the heavy oil molecules split into two free radicals, formed from C-C and C-heteroatom bond cleavage:

   $CH_3CH_3 \rightarrow 2CH_3^{\bullet}$ (4.1)

2. **Hydrogen-abstraction** where a free radical detaches a hydrogen atom from another C-H bond:

   $CH_3^{\bullet} + CH_3CH_3 \rightarrow CH_4 + CH_3CH_2^{\bullet}$ (4.2)

3. **Radical decomposition** in which a free radical splits into an alkene and an H radical:

   $CH_3CH_2^{\bullet} \rightarrow CH_2 = CH_2 + H^{\bullet}$ (4.3)

4. **Radical addition** where a larger free radical is formed by the addition of hydrogen to the alkene:

$$CH_3CH_2^{\bullet} + CH_2 = CH_2 \rightarrow CH_3CH_2CH_2CH_2^{\bullet} \qquad (4.4)$$

5. **Condensation and polymerization** which is the recombination reaction of two free radicals to form a larger molecule

$$CH_3^{\bullet} + CH_3CH_2^{\bullet} \rightarrow CH_3CH_2CH_3 \qquad (4.5)$$

In these reactions hydrogen, methyl, and ethyl are the smallest and more stable free radicals which could form saturated hydrocarbons in the presence of hydrogen from other radical or C-heteroatom bonds. This breakage causes the production of hydrocarbons with lower molecular weight and from higher molecular weight fraction. The portion of the feed oil converted to coke was determined from TGA (Thermogravimetric Analysis) of the deposited oil left in the reactor. Table 4.1 displays the amount of coke formed during the reaction which indicates the higher temperature favours the production of more coke. On the other hand at reaction above 400 ^{o}C formation of coke increases significantly. This is due to the domination of the condensation and polymerization reaction (eq. 4.5) which occurs in the absence of catalysts. Some studies findings on thermal cracking effects in the literature for fixed bed and batch reactors were in line with these results (Kressmann, et al., 1998; Almarshed, 2015). This provides a base-case for the extent of thermal cracking for comparison with the catalytic cracking.

4.2.2 *Effect of Time*

Thermal upgrading for a sustained period exposes compounds to prolonged cracking reaction with high temperatures and pressures, reducing viscosity and facilitating a high API, compared to oil with zero reaction time. From Table 4.2 it is shown the average increase of 3.7, 7.1 and 8.9° API In comparison with the original feed oil, also the clear reduction of viscosity from 0.175 Pa.s after heating up time to 1.94×10^{-3} when the reaction was continued for 2 hours is demonstrated. However, 2 hours of reaction time causes a significant increase in the production of coke to 13.99 w.t% compared with 10.8 % after only 30 minutes.

Table 4.2 Effect of reaction time on API gravity, viscosity, coke and Asphaltene yield of heavy oil
Using stirred batch reactor under 20 bar nitrogen medium at 425 ºC (feedstock: 13 ºAPI and 0.49Pa.s)

Reaction Time (min)	API º gravity (25ºC)	Viscosity Pa.s (25ºC)	Asphaltene wt.%	Coke wt.%	Remainder oil wt.%
0	20.07 ±0.1	0.175	12.37 ±0.8	6.5	NA
30	20.1 ± 0.18	0.023	11.49±0.8	10.8	10.8
120	21.92 ±0.1	1.94×10^{-3}	2.80 ±0.8	13.99	12.41

This investigation considered a light oil as being defined by the criterion API >20º, ensuring commercial pumping feasibility through a pipeline without additional diluent (Santos et al., 2014). Literature provides a thermal upgrading viscosity value (N_2 atmosphere for 30 mins) of 1.40×10^{-2} Pa.s, used as a baseline minimum in this study (Hart et al., 2015). Hart et al. (2014, 2015) also found thermally upgrading heavy oil (N_2 atmosphere for 30 mins) produced 7.95 ±0.4 wt.% coke, considered a benchmark for this study. The remainder fractions of oil are defined as undesirable oil within arduous residue i.e. bitumen and inherent oil in coke, which is difficult to extract.

From these results, it can be inferred that asphaltene was converted to coke rapidly after the maximum asphaltene peak and the kinetics from asphaltene to coke varies greatly with the fraction of asphaltene. Also, as the temperature rises, the maximum amount of asphaltene is almost the same, but the rate of conversion from asphaltene to coke was accelerated with the shorter reaction time to reach the maximum asphaltene. It implies that reaction temperature is a major factor in the kinetics of upgrading of crude oil. These results are compatible with previous studies that upgrading of crude oil in SCW is consistent with a free radical mechanism in which hydrocarbon radicals are generated by C-C cleavage of aliphatic chain. Since the activation energy of C-C cleavage is closely related to the reaction temperature, temperature affects the overall kinetics of upgrading reaction of crude oil. Coke precursors such as poly-aromatics, olefins, radicals of resins and asphaltenes macromolecules become adsorbed on the catalyst active sites and eventually form large sediments via polymerisation and condensation reactions called protocoke. These are commonly called soft coke and subsequently form hard coke through dehydrogenation reactions and can then be turned to CH_4 through gasification as illustrated in Figure 4.1. (Liu, et al., 2003)

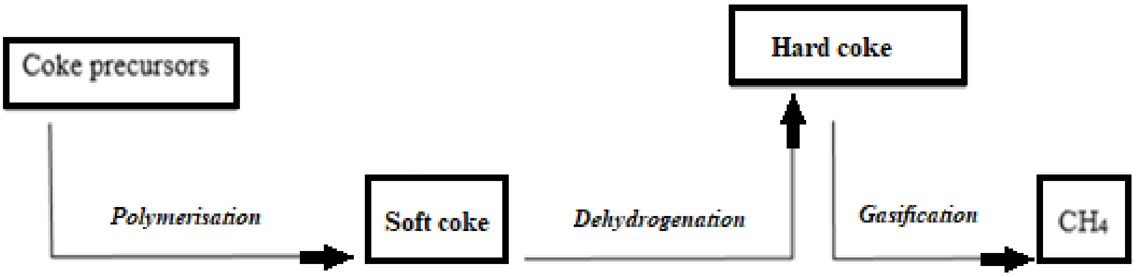


Figure 4.1 Mechanism of coke formation in upgrading reaction

Coke deposition was dominant in 120 mins thermal reaction, which provides an explanation for inhibited asphaltene content of produced oil, by which asphaltene converts to coke compounds with high temperature (Trejo et al., 2004). From Table 4.2 asphaltene content was repressed dramatically at 120 mins thermal reaction, in line with trends envisaging asphaltene cracking as proportional to the heavy oil upgrading rate (Trejo et al., 2004).

4.3 CAPRI Process

Over the past few years, nanoparticles have demonstrated physical (and catalytic) properties that are distinct from those of bulk material. The high surface to volume ratio as well as low mass transfer resistance may make the ultradispersed catalysts more resistant to deactivation compared to pelleted catalysts (Hart et al., 2014). This section investigates the effect of different catalyst metals, support and particle forms upon upgrading of heavy oil by means of catalytic cracking. Varieties of dispersed catalysts were used in a series of experiments in order to investigate the impact of catalyst upon the yield of liquid, gas, and coke deposited was studied. The upgraded oil viscosity, API gravity, and true boiling point (TBP) distribution are compared.

4.3.1 *Effect of Catalyst Type as a function of time*

This section is based on examining the effectiveness and activity of different types of dispersed catalyst for in situ heavy oil upgrading. The performance of supported precious metal catalyst such as ruthenium-based on a carbon support and palladium-based on alumina support catalyst was compared with unsupported iron oxide (Fe_2O_3) catalyst. Noble metal catalysts including Pd (Palladium) and Ru (Ruthenium) based catalysts are known for their performance in hydrogenation and suppressing coke formation. They have been used widely in the hydrotreatment of bio-oils which are naturally low in sulfur (Zhai et al, 2014; Capunitan et al., 2014). The use of virgin noble metals for heavy oil upgrading is relatively very expensive leading to uneconomic viability. However, recently there is increasing interest in the recovery of such metals group like palladium from secondary sources (Murray 2010). On the other hand, since hematite (α-Fe2O3) is one of the most abundant iron oxide minerals, compared to HDT catalysts Fe_2O_3 NPs are relatively much more cost-effective than the rest of catalysts (Khalil et al., 2015). Additionally, they are nontoxic and the preparation of them are relatively simple and, if found useful in catalytic upgrading, would represent a cost-effective alternative. The investigation was conducted in terms of physical properties (i.e., API gravity, viscosity and asphaltenes), product distribution (i.e., light oil, remainder oil, gas and coke), True Boiling Point (TBP) distribution (i.e., naphtha, middle distillate and residue) and product quality (i.e., sulphur and H/C). These tests were conducted at a different reaction time of 30 and 120 min in order to investigate the deactivation of these catalysts over time.

4.3.2 *Effect of Catalyst on Physical Properties*

In industry sulfides of Co, Ni and Mo supported catalysts are commonly used for petroleum and residue upgrading hydroprocessing. Hart (2013) and Leyva (2007) have previously investigated the performance of these catalysts. More expensive metallic catalysts such as palladium, platinum, and ruthenium are also used for the production of higher quality products such as jet fuel, however, use of these catalysts is limited by their higher cost. In Table 4.3, the upgrading trend of the produced oil in terms of change in API gravity is presented using carbon-supported Ruthenium (Ru/C) 5%, Aluminum Oxide supported Palladium (Pd/Al_2O_3) 5% and unsupported Fe_2O_3 was investigated to determine the highest performing catalyst. The API gravity was characteristically higher for tests with 120 min reaction times compared with 30 min, on all the catalysts as discussed above. In particular, the Ru/C catalyst provided a 9.97 and 12.63 ° API at 30 and 120 min reaction time respectively which are considerably higher than Pd/Al_2O_3 and Fe_2O_3 at the same reaction time. It is noticeable that the Ru/C was used at longer (120 min) reaction time, the improvement of 2.66 º API was achieved compared to only 1.02 and 1.19 º API when Pd/Al_2O_3 and Fe_2O_3 were used.

Table 4.3 Effect of catalyst type at different reaction time on heavy oil upgraing
The effect of reactions on API gravity, viscosity, asphaltene and coke yield of heavy oil using stirred batch reactor at a reaction temperature of 425oC under 20 bar nitrogen medium (feedstock: 13 oAPI, 0.49Pa.s and 12.44 wt% asphaltene).

Reaction Time (min)	Thermal	Ru/C	Pd/Al_2O_3	Fe_2O_3
		API gravity of upgraded oil (°)		
30	20.1 ± 0.18	23.27 ± 0.24	21.7 ± 0.91	20.62 ± 0.66
120	21.92 ±0.1	25.93 ± 0.76	22.7 ± 0.86	21.81 ± 0.71
		Absolute viscosity (Pa.s)		
30	0.023	5.24×10^{-3}	6.36×10^{-3}	0.011
120	2.80 ±0.8	6.80×10^{-3}	1.33×10^{-3}	1.5×10^{-3}
		Asphaltene (wt.%)		
30	11.49±0.8	6.68 ± 0.8	6.01 ± 0.6	10.3 ± 0.6
120	2.80 ±0.8	1.20 ± 1.2	5.84 ± 0.3	4.20 ± 0.8
		Coke (wt.%)		
30	10.8 ± 0.2	6.10 ± 0.3	6.54 ± 0.21	7.82 ± 0.8
120	13.99 ± 0.23	12.64 ± 0.42	11.14 ± 0.2	11.82 ± 1.4

The catalysts performance over longer reaction time suggest Pd/Al_2O_3 and Fe_2O_3 catalysts deactivate at a faster rate than that of Ru/C, limiting their efficacy in heavy oil upgrading due to their group metal's differing crystalline structure. Ru, with a complex hexagonal close-packed (hcp) structure, compared to Pd's soft face-centered cubic (fcc) structure, gives a substantial hardening effect, enhancing its erosive wear resistance against carbonaceous deposition (Rakhtsaum, 2013). Moreover, the high amount of sulfur content in heavy oil may cause significant deactivation of palladium, this is because of the formation of strong metal-S bonds and chemisorption of sulfur onto catalyst and reaction with the catalyst active sites, which limits the accessibility of the reactant (Grove et al., 2003). An analogous trend was noticed in the 30 min reactions, albeit less pronounced due to the lack of time for facilitating Pd/Al_2O_3 deactivation. Results for viscosity provide a concurrent trend with API, which demonstrated Ru/C having a greater effect on reducing the heavy oil viscosity.

The performance of Fe-based (Fe_2O_3) was similar to that of Ni-based and Mo-based counterparts previously investigated by Marafi (2008) in terms of API gravity and viscosity. Fe_2O_3 catalyst increased the feed oil API by 7.32 °. Despite the lack of cracking functionality of the unsupported Fe_2O_3 particles (Chuan Wua et al., 2010), it showed identical activity to Pd/Al2O3 in terms of API and viscosity improvement at 120 min reaction. Therefore, the effectiveness of unsupported dispersed Fe_2O_3 as an attractive option for the THAI process when availability and cost are considered. Asphaltenes are the heaviest component of heavy crude oil (Bartholomew, 2001). Their aggregation and deposition can cause many operational problems; they are associated with heavy metals such as Ni and V and heteroatoms like sulfur and nitrogen, which makes them the main cause of catalyst deactivation during the oil upgrading reaction. They reduce the rate of hydrogenation and cause the formation of deposits in the reactor and equipment. During the reaction, the catalyst surface could be blocked because of precipitation of this molecule which denies access of another molecule to the active site of the catalysts. Asphaltene weight percentages are predictably higher in each 30 min reaction compared to the 120 min reactions, underpinned by reduced coke formation in respective samples, proportionally influencing viscosity and API readings. Such parameters are directly influenced by their respective macromolecular weight constituents, i.e. asphaltene content (Bartholomew, 2001). Fe_2O_3 display a difference in asphaltene content of +4.29 wt.% and +3.62 wt.% over Pd/Al_2O_3 and Ru/C respectively suggesting limited coke formation in these catalysts. On the contrary, Ru/C (120 mins) yields a dramatically lower asphaltene content, and disproportionately lower than Pd/Al_2O_3 (120 mins). This again highlights a longer Ru/C catalytic activity profile over Pd/Al_2O_3. Ruthenium enhances the oxidation of the aromatic asphaltene core reaction with the selective conversion of asphaltenes into a carboxylic acid (Peng et al., 1990). Ruthenium- based catalysts have been used for the degradation of asphaltene in the petroleum industry since 1985 (Strausz et al., 1999; Peng et al., 1999). This metal group has the ability to enhance the selective oxidation of aromatic carbons to carbon dioxide in high yields without affecting the carbon in the aliphatic compound (Peng et al., 1999). Asphaltenes have a distribution of molecular weight in the range of 400 to 1500 g/mol and their presence directly affects the viscosity of the upgraded oil (Badre et al., 2006). This indicates the predominant role of asphaltenes in the high viscosity displayed by Fe_2O_3 based on the direct relationship evidenced by the asphaltene content and oil viscosity. A study by Argillier et al., (2002) confirms this relationship. It also suggests a similarity in behaviour between asphaltene content in oil and polymer solution where beyond critical concentration the behaviour resembled that of semi-dilute polymer solutions. (Lilian Padula et al., 2016)

4.3.3 *Effect of Catalyst on Product Yield*

The comparison of the mass balance of the catalytic cracking reaction at 30 min and 120 min against thermal cracking is presented in Table 4.4. Obtaining a high liquid yield product is desired in the upgrading reaction. Generally, the liquid yield can be improved by minimizing the formation of hydrocarbon gases as well as suppressing coke formation. From Table 4.4 the yield of liquid oil obtained with Ru/C nanoparticles supported on carbon was 71.35 with Ru/C and 52.85 wt.%, with Pd supported on alumina 56.15 and 41.95 wt.%, and unsupported Fe_2O_3 68.32 and 50.2 wt.%, at 30 and 120 min reaction time respectively. It is clear that a longer reaction time reduces liquid yield significantly and increases gas yield as well as coke wt.%. This shows that at longer reaction time catalysts become either deactivated or target undesired reaction, associated with higher gas formation. It was found by Wilson (1975) that the metals (e.g., Ni and V) deposited on the catalyst significantly contribute to coke formation, hydrogen subtraction, and excessive yield of gases in the outlet-gas stream at the expense of light oil. Results show Ru/C as more effective in facilitating upgraded light oil with a 15.2 – 10.9 wt. % increase over Pd/Al_2O_3 at 30 and 120 min reaction time respectively, reiterated by API and viscosity readings aforementioned. Pd/Al_2O_3 retains a dramatic amount more remainder oil than other catalysts increasing the probability of Pd/Al_2O_3 deactivating before another catalyst at 30 min and becoming obsolete within the reaction. Remainder oil refers to the oil which has been trapped, not able to flow freely, under the heavy residue and/or coke deposits. The trapped oil, therefore, is more available on the catalyst active surface and after partial deactivation and poisoning of Pd/Al_2O_3 an undesired reaction such as gasification could potentially be targeted In the longer reaction time (120min) the remainder oil decreases significantly from 29.3 wt.% to 18.01 wt.%. However, the remainder oil yield always showed a slight increase with a similar rate to the coke yield in the case of thermal and rest of catalysts reactions. The Feed oil contains 3.61 wt.% sulfur (Table 4.7), Bartholomew et al. (1982) argues sulfur adsorbs very strongly on metal such as Pd and prevents or modifies the further adsorption of reactant molecules, its presence on a catalyst surface usually effects the substantial or complete loss of activity in many important reactions, particularly in hydrogenation reactions. Where the reaction network leads to two or more products, adsorbed sulfur can markedly affect the selectivity by reducing the rate of one of the reactions more than the other.

Table 4.4 Effect of catalyst type at different reaction time on product yield using stirred batch reactor at a reaction temperature of 425oC under 20 bar nitrogen medium

Reaction Time (min)	Thermal	Ru/C	Pd/Al_2O_3	Fe_2O_3
		Gas Yield (wt.%)		
30	12.3 ± 0.86	12.6 ± 0.74	15.3 ± 0.44	11.75 ± 1.2
120	17.9 ± 0.3	20.15 ± 0.24	28.9 ± 0.21	25.6 ± 0.62
		Liquid Yield (wt.%)		
30	66.1 ± 0.21	71.35 ± 0.32	56.15 ± 0.81	68.32 ± 0.66
120	55.3 ± 0.76	52.85 ± 0.67	41.95 ± 0.42	50.2 ± 0.24
		Remainder oil (wt.%)		
30	10.8 ± 0.24	9.95 ± 0.56	22.01 ± 0.71	13.2 ± 0.6
120	12.4 ± 0.43	14.36 ± 1.2	18.01 ± 0.24	13.8 ± 0.33
		Coke (wt.%)		
30	10.8 ± 0.2	6.1 ± 0.3	6.54 ± 0.21	7.82 ± 0.81
120	13.99 ± 0.23	12.64 ± 0.42	11.14 ± 0.24	10.82 ± 1.4

Although remainder oil could potentially contribute to light oil production, this fraction cannot be easily obtained. The ultrafine dispersed catalysts generally are encapsulated with residual oil, asphaltenes, deposited metals such as vanadium and nickel, and coke after the upgrading reactions. Therefore, TGA and DTG (Differential Thermogravimetric) were used to determine the amount of actual coke formed during the reaction by burning off the remainder oil from deposited materials inside the reactor shown in Figure 4.1. From the DTG curve, it is clear that the deposits formed under the reaction with Pd/Al_2O_3 experienced significant mass loss between 400 to 600 ^oC. This verifies the encapsulation and trapping of liquid oil in between deposits that formed during the reaction. It is clear at the temperature about 610 ^oC the asphaltenes are completely burned off. This observation is in line with the findings of Barman et al. (1997). These authors found that asphaltenes from crude oil start to decompose between the temperature of 400 ^{o}C - 620 ^{o}C, which is in line with the signal range demonstrated in the DTG curve shown in Figure 4.2. In this measurement, the deposit above 620 ^{o}C are defined as coke and the high temperature of 900 ^{o}C at the end of the heating period ensures that all carbon products are completely burnt off since higher energy is required to burn-off coke than asphaltenes.

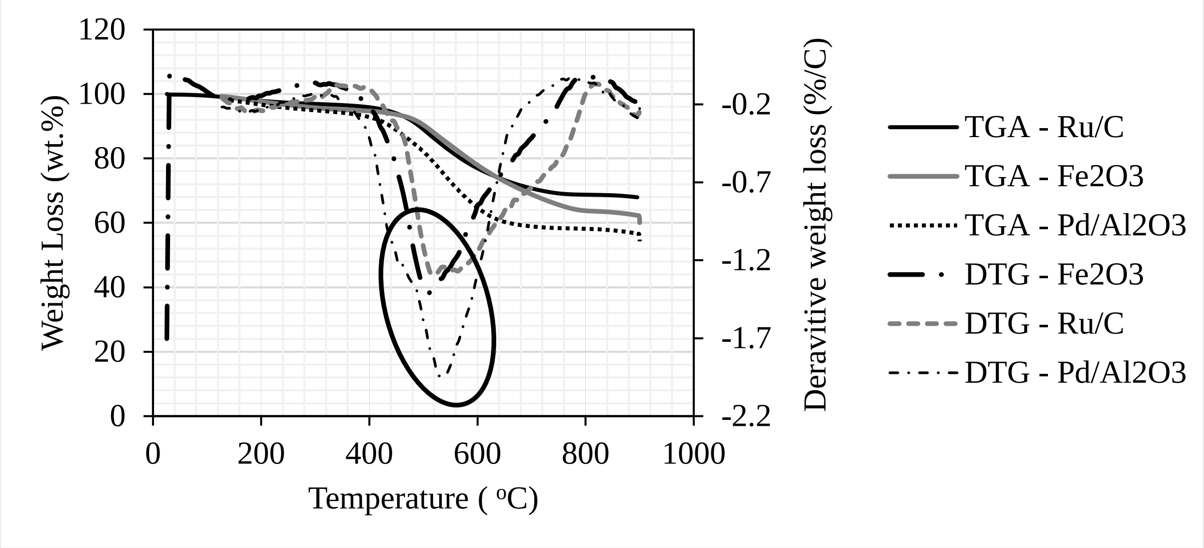


Figure 4.2 TGA and DTG of the deposited coke and residue of upgraded heavy oil
Obtained from the stirred batch reactor using Ru/C, Pd/Al_2O_3 and Fe_2O_3 at a reaction temperature of 425^{o}C under 20 bar nitrogen medium at 30 min.

It has been shown in Table 4.4 that unsupported Fe_2O_3 catalysts give a similar trend of upgrading to Ru/C according to mass balance distribution under the same experimental conditions. Reaction with Fe_2O_3 reduced the coke content by 2.98 and 3.17 wt.% compared to thermal cracking for 30 and 120 min reactions respectively. In addition, in comparison to thermal upgrading, an increase in the liquid amount at 68.3 wt.% and a decrease of gas yield at 11.75 wt.% for 30 min was observed. Fe_2O_3 also produced the lowest coke yield comparing to rest of the catalysts at longer reaction time which may indicate its higher resistance against deactivation.

4.3.4 *Effect of Catalyst on Product Oil True Boiling Point (TBP) Distribution*

According to the ASTM D-2887 standard, the True Boiling Point (TBP) distribution is another characterisation method to evaluate the quality of the upgraded oil. It involves a simulated version of refinery distillation performed using an Agilent 6890 GC equipped with a SIMDIS column, which records the elution of the chromatogram peaks which are then converted to boiling ranges using a software package. Results of TBP of the sample oil after catalytic upgrading as well as thermally cracked and feed oil is shown in figure 4.3. It illustrates the three fractions of distillate into naphtha (IBP - 200 °C), middle distillate (200–343 °C) and residue(> 343 °C).

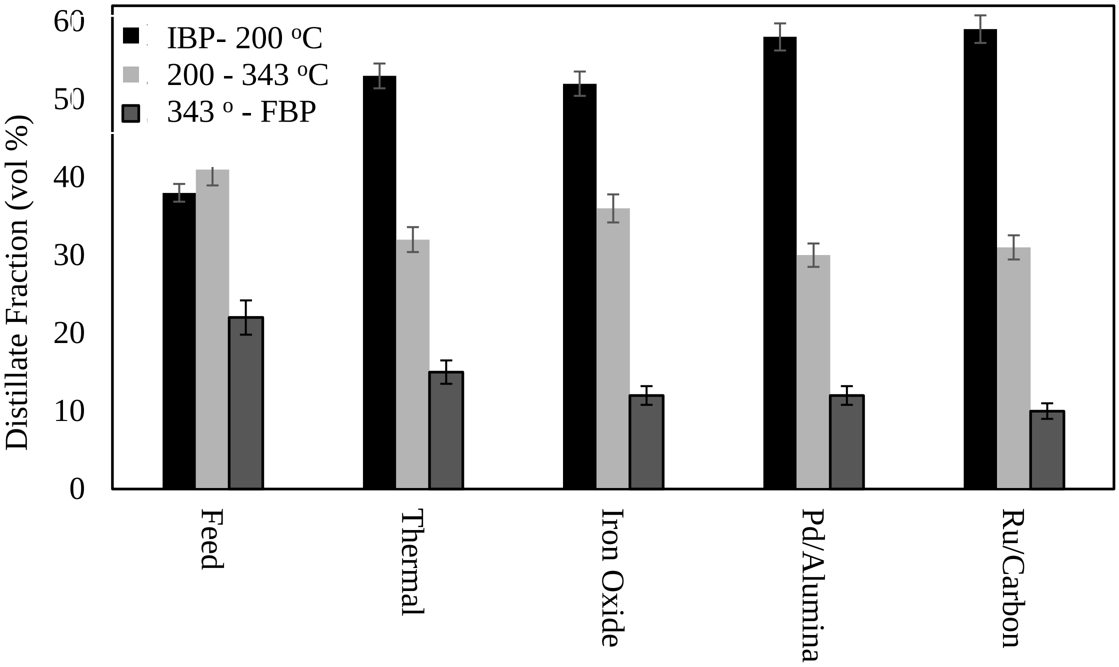


Figure 4.3 Boiling-point fractions for feedstock and produced oil
From Feed oil, thermal, Pd/Al_2O_3, Fe_2O_3 and Ru/C at a temperature of 425 °C, the pressure of 20 bar N_2 at 30 min reaction. IBP (Initial Boiling Point), FBP (Final Boiling Point)

Relative to the feedstock, the conversion of high-boiling species into low-boiling fractions led to boiling point shift to the left of the feed oil TBP blocks due to the following reactions:

- cracking of C-C bonds in the heavy oil
- cracking of C-S and C-N (i.e., C-hetero-atoms bonds) and
- metals removal

Gray (1994) has also pointed out that the reduction of the heteroatoms content of the produced oil could contribute to its low-boiling range more than the original heavy oil. The higher fraction of light hydrocarbon components in the catalytically and thermally upgraded oils relative to the feed oil is the main cause of the improvement in API gravity and lower viscosity achieved. From figure 4.3 it is clear that the feed oil has a relatively smallest fraction of fuel fraction (IBP < 343 °C) relative to the other thermal and catalytic upgraded oil. This is because of the conversion of some of the middle fractions (200-343 °C) and the heavy fractions (> 343 °C) in the feedstock to low-boiling fractions (Initial Boiling Point (IBP)-200 °C) during the upgrading. The increase in naphtha, as well as middle distillates, yield and decrease in the residue fraction (Final Boiling Point (FBP) > 343 °C) is in the order of thermal cracking, Fe_2O_3, Pd/Al_2O_3 and Ru/C.

While the residue fraction (BP > 343 °C) decreased from 22 vol.% in the feedstock and 15 vol.% in thermal upgrading to 12 vol.%, for the upgraded oil by Fe_2O_3 and Pd/Al_2O_3 and 10 vol.% for Ru/C, the gasoline fractions respectively increased from 35 vol.% (feedstock) and 53 vol.% (thermal) to 58 vol.% (Pd/Al_2O_3) and 59 vol.% (Ru/C). In the case of Fe_2O_3 more middle distillates (4 vol.%) and slightly less (1 vol.%), low boiling fraction was produced compared to the non-catalytic reaction. This is because the unsupported Fe_2O_3 are not bifunctional in nature; they do not promote cracking of C-C and C-heteroatom bonds because they lack acid sites, unlike alumina which possesses acid sites that support cracking. The absence of acid sites in the NPs also explains the observed moderate improvement in API gravity and viscosity, as the reaction is driven by thermal cracking (Ovallesa et al., 2003). On the other hand, Pd/Al_2O_3 and Ru/C showed noticeable performance in terms of conversion of middle distillates to light fractions. They have increased the yield of the light fraction by 23 vol.% (Pd/Al_2O_3) and 24 vol.%(Ru/C) which is 6 vol.% and 7 vol.% higher than reaction using iron oxide respectively. This confirms the better performance of Ru/C in terms of improving the oil quality because of its ability to convert both residue fraction as well as middle distillates. The results in this part are also consistent with the results of API gravity and viscosity of upgraded oils shown in Table 4.3.

4.3.5 *Effect of Catalyst on Produced Gas Composition*

Refinery Gas Analyser (RGA) by gas chromatograph was used to determine the quantitative composition of the produced gas in selected reactions and presented in Table 4.5 for thermal cracking and different ultradispersed catalytic upgrading. It is clear that under thermal upgrading and Pd/Al_2O_3 catalytic upgrading, a higher concentration of hydrocarbon gases was produced in relative to catalytic upgrading by ultradispersed Ru/C and Fe_2O_3 catalysts, which is consistent with a high gas yield of product mass balance shown in Table 4.4.

Table 4.5 Produced gas composition for reactions under different catalysts
at temperature of 425 °C, the pressure of 20 bar N_2 at 30 min reaction.

Gas Composition	**$n(C_1-C_5)$ (Vol.%)**	**iC_4-C_5 (Vol.%)**	**Olefin (C_2-C_4) (Vol.%)**	**CO_2 (Vol.%)**	**CO (Vol.%)**	**H_2 (Vol.%)**	**H_2S (Vol.%)**
Thermal	13.87	0.59	0.64	0.18	0.12	1.43	0.0008
Fe_2O_3	10.25	0.88	0.91	0.24	0.11	1.58	0.001
Pd/Al_2O_3	14.19	1.01	0.84	0.45	0.17	1.09	0.0013
Ru/C	11.41	1.42	0.69	0.38	0.12	0.87	0.0021

This is also in line with the observation of Sawarkar et al (2007). The significant differences in the gas composition are the isomers iC_4–C_5 and olefins (C_2–C_4) were produced more with catalytic upgrading than thermal reaction. This provides further evidence of catalytic reactions, rather than just a physical effect of the catalysts upon coke deposition. Furthermore, the presence of hydrogen in the gas composition could promote hydrogenation and hydrocracking reactions. The hydrogen originates from two reaction routes: firstly through hydrogen subtraction from the excited saturated hydrocarbon to form an unsaturated hydrocarbon molecule as illustrated by Equation 4.12.

$$2RH \text{ saturated} \rightarrow 2R \text{ unsaturated} + H_2 \qquad (4.12)$$

$$RH \rightarrow R\bullet + H\bullet \qquad (4.13)$$

$$RH + H\bullet \rightarrow R\bullet + H_2 \qquad (4.14)$$

where R is a hydrocarbon molecule

Secondly, the C–H bond cleavage produces hydrocarbon radicals and active hydrogen. The active hydrogen on collision with another molecule abstracts hydrogen to form a hydrogen molecule, as illustrated by Equations 4.13 and 4.14 (Alfi et al., 2013). In this way the macromolecule structure continues to grow further while the free radical sites at the formed coke surface are revived by continuous hydrogen abstraction (Reyniers, et al., 1994; Wang et al., 2007). The free radicals formed, unsaturated molecules and aromatics are common coke precursors. They promote coke formation by terminating reactions with coke macro-radicals. Alternatively, the active hydrogen can react with other hydrocarbon radicals to form a stable molecule via hydrogen-transfer reactions. Reactions 4.12 to 4.14 could have been inhibited by the addition of hydrogen donor giving rise to less hydrogen in the produced gas. The hydrogen concentration of the produced gas composition decreased by 0.34 vol% in the presence of

Pd/Al_2O_3 and 0.56 vol% in the presence of Ru/C. The spent hydrogen shows these catalysts may have contributed in promoting hydrogenation reaction which explains the higher produced oil quality in the presence of these catalysts. Also, it suggests these catalysts have promoted the hydrogenation of cracked active hydrocarbon fragments and coke precursors to form small chain hydrocarbons which was not achieved under thermal cracking counterpart where a high coke yield was observed. Moreover, the extent of sulfur removal leading to the release of hydrogen sulfide in the presence of catalysts is significantly higher than the thermal cracking counterpart. Additionally, some of the sulfur was removed for the sulfidation of the metallic catalysts component during the reaction as well as coke deposition. Dunleavy et al (2006) argue that sulfur and sulfur-containing species (e.g. H_2S, RSH, RSSR) have poisoning effects when adsorbed onto the metal surface of heterogeneous metal catalysts. With respect to palladium the effects of strong adsorbates such as sulfur have been reported by Lischka et al (2003) in the palladium–hydrogen system with respect to the adsorbate interactions and atomic arrangements on the faces of the palladium metal surface ((21 0), (11 0) and (111)). This further explains the results of the fast deactivation of Pd/Al_2O_3 during the reaction.

4.3.6 *Effect of Catalyst on Elemental Composition*

The results of the micro-elemental analysis of the feed oil compared with samples obtained from thermal, Fe_2O_3, Pd/Al_2O_3 and Ru/C dispersed micro-particulates are presented in Table 4.6. Two main routes of the upgrading of heavy oil are carbon-rejection and/or hydrogen-addition. It can be seen that the H/C atomic ratio increased after thermal and catalytic upgrading relative to the feed oil. However, thermally upgraded oil sample showed the highest carbon-rejection of 6.74 wt.% and the lowest hydrogen content of 9.66 wt.%. Among the catalyst, Pd/Al_2O_3 gave the highest carbon rejection of 3.41 wt.% which is in correlation with the mass balance presented in Table 4.4. Notably, the presented value for carbon-rejection of catalytic upgrading is approximately half that of thermal upgrading. As a consequence, the incorporation of catalyst improved the H/C ratio and suppressed carbon-rejection. Moreover, thermal cracking, Fe_2O_3, Pd/Al_2O_3 and Ru/C reduced the produced oil sulfur content by 18, 20, 31 and 34 wt.% respectively. Some of the sulfur content of the feed oil is removed during the reaction in gaseous form as H_2S, which was confirmed by the relatively higher concentration of H_2S produced gas detected and demonstrated in Table 4.6. This confirms the HDS reaction was promoted in the presence of catalysts, especially when Ru/C was used.

Moreover, an asphaltene compound contains sulfur and nitrogen elements which are presented in benzothiophene and pyrrole respectively (Ancheyta et al., 2002). It can be seen from Table 4.3 that the amount of asphaltenes content of the produced oil in the presence each catalyst are in line with sulfur and nitrogen content amount demonstrated in Table 4.6. This suggests that the sulfur content of produced oil was associated with its asphaltene molecules.

Table 4.6 Micro elemental analysis of feed oil, thermal, and different dispersed catalysts samples

Upgrading at a temperature of 425 °C, pressure of 20 bar N_2 at 30 min reaction

Samples	C (%)	H (%)	S (%)	N (%)	H/C (%)	Carbon rejection (%)
Feedstock	89.92	9.87	3.61	0.62	0.110	
Thermal	83.86	9.66	2.93	0.52	0.115	6.74
Fe_2O_3	87.21	11.09	2.91	0.49	0.127	3.01
Pd/Al_2O_3	86.85	11.52	2.48	0.47	0.133	3.41
Ru/C	87.14	11.83	2.35	0.45	0.136	3.09

4.4 Effect of Cyclohexane and Hydrogen Gas on Catalysts Performance

An alternative pathway for the upgrading of heavy oils can be achieved through Hydrogen-addition, resulting in lower viscosity, higher API gravity, less coke formation and higher liquid yield in comparison with the carbon-rejection route (Liu, et al., 2003). This is due to the ability of the hydrogen source to terminate the part of the active chain and limit the additional free radical reactions which potentially cause larger molecules formation.

The temperature of the combustion zone in the THAI-CAPRI process is between 400–700 °C, therefore steam can be generated through both reservoir water and water formed from combustion reactions. The active hydrogen is formed in the process via Water Gas Shift (WGS) reaction and aquathermolysis. However, the amount of in-situ generated hydrogen won't be enough and therefore additional hydrogen is required to terminate all the active chains in order to limit the addition of free radicals reactions occur during C-C cracking reactions (Muraza, et, al., 2015). Knowing WGS reaction won't be active enough at the temperatures of ~ 400 °C, therefore, additional hydrogen from an external source could potentially inhibit the compound regression of the reacted heavy oil to form larger molecules. However, the addition of hydrogen gas to the reaction media and injecting it into an oil reservoir from an external source can be potentially dangerous and challenging. Hence, in-situ hydrogen can be generated by a suitable hydrogen donor additive introduced into the oil reservoir. The use of polycyclic naphthenic-aromatic or naphthenic compounds that can be reversibly hydrogenated-dehydrogenated in the reacting mixture such as tetralin, decalin, and cyclohexane have been extensively recognized in the literature (Alemán-Vázquez, et al., 2012). Moreover, Cyclohexane is widely used as a donor solvent for industrial applications such as nylon and the dehydrogenation process of cyclohexane has been extensively studied for hydrogen storage and supply (Biniwale et. al., 2005, Charles et. Al., 1986). This part of the chapter investigates the effects of the presence of cyclohexane upon heavy oil upgrading using Ru/C, Pd/Al_2O_3 and

Fe_2O_3. The performance of catalysts in the presence of cyclohexane was investigated in terms of physical properties (i.e., API gravity, viscosity and asphaltenes), product distribution (i.e., light oil, remainder oil, gas and coke), True Boiling Point (TBP) distribution (i.e., naphtha, middle distillate and residue) and product quality (i.e., sulphur and H/C) and evaluated against that achieved with heavy oil reaction under hydrogen with catalysts. The produced oil and cyclohexane formed a homogeneous mixture making it difficult to separate compound. Therefore separation of cyclohexane from the produced upgraded oil will affect the composition of the upgraded oil. This could cause evaporation of hydrocarbons with a lower or similar range of boiling point to cyclohexane (80.7 at 1atm). Therefore, the API° gravity and viscosity reported here are those of the mixture of upgraded oil and cyclohexane.

4.4.1 *Effect of Cyclohexane to Oil Ratio*

Table 4.7 shows the API, viscosity, liquid yield and gas yield of the produced upgraded oil at different cyclohexane to oil mass ratios (C/O) at 425 °C reaction temperature, 20 bar initial N_2 pressure and 30 min reaction time. Notably, the obtained API gravity and viscosity of the cyclohexane and heavy oil mixtures remained within a narrow range as the C/O ratio increases from 0.03 to 0.24. The results were also very similar to thermal upgrading without the presence of cyclohexane. The API gravity and viscosity results of 0.03 and 0.006 C/O ratio compared to the test without cyclohexane confirmed that cyclohexane in low quantities did not contribute in enhancing the physical qualities of the produced oil. However, since cyclohexane has a lower density (0.78 g/cm^3) as compared to the produced oil (0.98 g/cm^3) the improvement of 0.5 ^{o}API in 0.026 C/O ratio produced oil might be attributed to the relative amount of cyclohexane in the mixture. The presence of cyclohexane in higher quantities has enhanced the degree of API gravity as well as the viscosity reduction of the produced oil. However, this does not mean larger quantities of cyclohexane contributes to cracking of C-C bonds. Whose breakage leads to a molecular weight reduction of large molecules resulting in reduced viscosity and increased

API gravity observed in produced upgraded oils (Ovalles et al., 1998). The effect of C/O ratios upon product yields of 0.03 to 0.12 (g/g) from the mass balance given in Table 4.7 shows a slight increase of the liquid yield in the presence of cyclohexane compared to thermal upgrading without the solvent addition. On the other hand, the gas yield was roughly the same. Resultantly, as C/O ratios vary from 0.03 to 0.12 (g/g), the liquid yields did not show further improvement. The respective liquid and gas yields were roughly 79 wt.% and on average of 13 wt.% for 0.03 to 0.11 C/O ratios relative to 76 wt.% and 12 wt.% for thermal upgrading without the solvent.

Table 4.7 Effect of C/O ratio on API gravity, viscosity, liquid yield and gas yield of heavy oil
Uusing stirred batch reactor at 425 oC under 20 bar nitrogen medium (feedstock: 13 oAPI, 0.49Pa.s).

Cyclohexane to Oil ratio (g/g)	**API ° gravity (25°C)**	**Viscosity Pa.s (25°C)**	**Liquid yield wt.%**	**Gas yield wt.%**
0	20.1 ±0.11	0.023	76.91 ±0.8	12.3 ±0.36
0.03	20.0 ±0.21	0.025	79.51 ±0.6	12.6 ±0.27
0.06	20.2 ±0.14	0.021	79.52 ±0.2	12.4 ±0.42
0.12	20.4 ±0.18	0.018	78.49 ±0.3	14.1 ±0.58
0.24	20.8 ±0.12	0.012	69.01 ±0.6	23.3 ±0.36

Meanwhile, in the case of 0.24 C/O ratio, the liquid yield was reduced to 69 wt.%, and the gas yield increased significantly to 23 wt.% which probably related to the dehydrogenation of cyclohexane and dissociation of its benzene ring into methane molecules (Al-Saleh et al., 2003). Figure 4.4 shows the coke yield and asphaltene content of the produced upgraded oil at different C/O ratios. It shows that the presence of cyclohexane reduces the coke yield drastically, however, the rate of reduction of the coke yield becomes less as the C/O ratio increased beyond 0.03. At 0.03, 0.06 and 0.12 C/O ratio (g/g) the coke yield dropped to 7.9, 7.4 and 6.8 wt.% relative to 10.8 wt.% without the presence of the solvent respectively.

Conversely, at 0.24 C/O ratio the coke yield increased by 0.3 wt % compared to its lowest value at 0.12 C/O ratio.

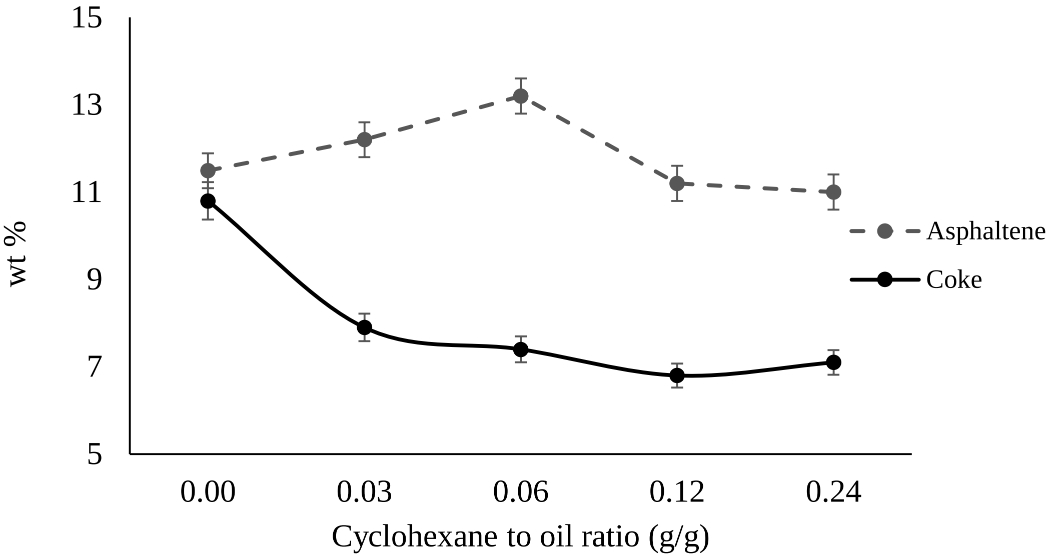


Figure 4.4 Coke yield and asphaltene content after upgrading of heavy oil at different C/O ratio At reaction temperature of 425°C under 20 bar initial pressure of $_{N2}$ at 30 min (feedstock: 12.44 wt% asphaltene)

Moreover, the asphaltene content of the produced oil gradually increased at lower quantities of C/O ratios (0.03 and 0.06 g/g) to 12.2 and 13.2 wt% relative to 11.5 wt.% for thermal upgrading respectively. However, the asphaltene content of the produced oil decreased when higher quantities of cyclohexane were used (0.12 and 0.26 g/g) to 11.2 for 0.12 C/O ratio (g/g) and 11 wt.% for 0.24 C/O ratio (g/g). These results are in agreement with the literature where a similar trend has been reported (Rahmani et al., 2002; Johannes et al., 2012; Alemán-Vázquez et al., 2012).

The cleavage of C-C bonds is believed to proceed by a free radical chain mechanism with cyclohexane hydrogen donor, continually supplying active hydrogen to moderate coke precursors while reducing the asphaltene content (Hongfu et al., 2002). The asphaltene side chains start cracking at high reaction temperature leading to the formation of poly-aromatic core radicals. As a result asphaltene core radical is formed which leads to the precipitation of the asphaltene core, a known coke precursor. The aggregation of asphaltene forms a new phase (coke precursor) which has the poor ability for hydrogen transfer. In the absence of hydrogen supply, an addition reaction between the precipitated asphaltene core radicals occurs and the aggregate becomes more dominant, which results in the formation of a carbonaceous solid product termed coke (Wiehe, 1993). The presence of donor solvent such as cyclohexane would improve the dissolution of the coke precursor in the oil mixture, and donate hydrogen to the asphaltene core (Vernon, 1980). As a result, phase separation can be avoided as the asphaltene core remains in solution, as asphaltene is known to be soluble in aromatic solvents such as tetralin and benzene. This would explain the reason for the low coke yields observed with the addition of cyclohexane. The presence of cyclohexane in higher quantities might have enhanced hydrogen supply for the further cracking mechanism of (more) stabilised intermediates into lighter end hydrocarbons (Rajesh et al., 2005). Therefore significantly higher gas yield of 23.3 wt.% and lower liquid yield of 69 wt.% was obtained from the mass balance (Table 4.7). Meanwhile, an increase in coke content suggested that the higher ratio might have also augmented the level of cyclohexane isomerisation (Biniwale et al., 2005) implying that not all cyclohexane underwent dehydrogenation process.

4.4.2 *Effect of Cyclohexane on Mass Balance*

Table 4.8 shows the effect of hydrogen gas and cyclohexane used as a hydrogen source in comparison with nitrogen media on heavy oil upgrading in the presence of Ru/C, Pd/Al_2O_3 and Fe_2O_3 NPs in terms of product distribution. It can be observed that the product distribution after upgrading of heavy oil in the presence of catalysts under hydrogen showed lower coke formation, where the coke yield decreased by 0.4wt.% for Ru/C, 1.09wt.% for Pd/Al_2O_3 and 0.57wt.% for Fe_2O_3 relative to the control experiments with the same catalysts under N_2. The results showed a better performance of cyclohexane in coke suppression, where the coke yield further decreased by 1.47wt.% for Ru/C, 0.38wt.% for Pd/Al_2O_3 and 0.61wt.% for Fe_2O_3 compared to similar reactions under hydrogen environment. The ability of hydrogen in the suppression of coke formation is mainly because of carbon-to-carbon bonds split as capping of free radical coke precursors formed leads to decrease the weight of molecular compounds in comparison with the original feed oil molecules (Benito at al, 1996; Alamo et al., 2017). The superiority of cyclohexane compared to H_2 in reducing the coke yield could be attributed to the dissolution of the coke precursor in the oil mixture by the aromatic solvent (benzene) as well as H_2 donation to the asphaltene core (Rahmani er al, 2002). Moreover, from Table 4.8 it is clear that in the case of Pd/Al_2O_3 and Fe_2O_3 the liquid yield increased by 1.09wt.% for Pd/Al_2O_3 and 0.57wt.% for Fe_2O_3 as the remainder oil and produced gas amount decreased with hydrogen addition relative to control experiment under N_2. On the other hand, when cyclohexane was used, a significant increase in liquid yield was observed only in the presence of Ru/C (8.31wt.%) and Fe_2O_3 (5.16wt.%). Even though the effect of cyclohexane in reducing the remainder oil and gas yield was similar to the H_2 gas, cyclohexane showed a better impact in achieving of higher liquid yield and less gas yield in the presence of Ru/C compared to Pd/Al_2O_3.

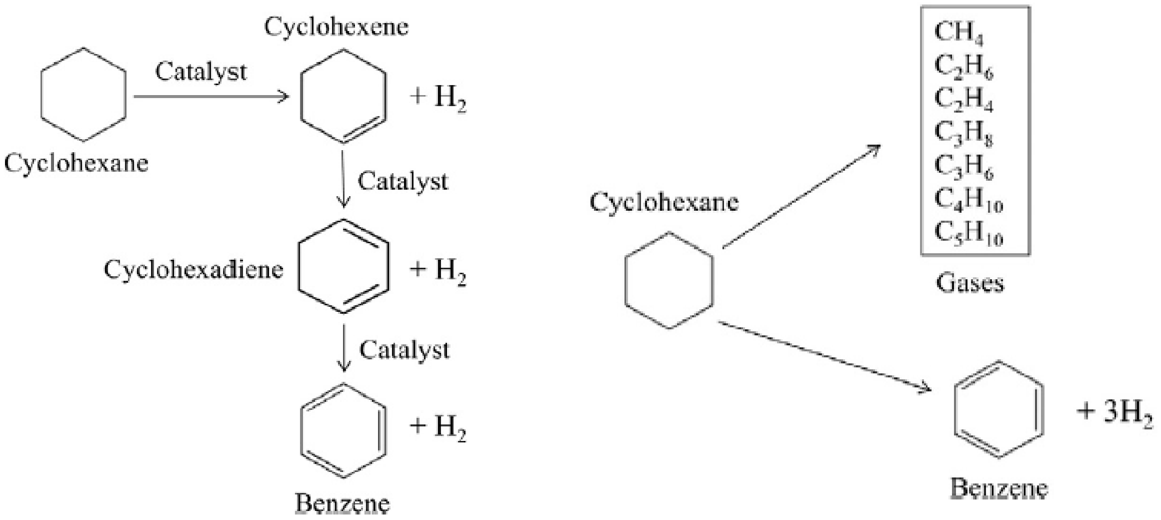


Figure 4.5 Dehydrogenation of CH reaction scheme
(Kou et al., 2013; Slagtern et al., 2010)

The initial step towards the liberation of hydrogen from cyclohexane on the catalyst starts with the adsorption of the cyclohexane molecule followed by dehydrogenation to cyclohexene, cyclohexadiene and benzene at high temperature, as illustrated in Figure 4.5.

Dehydrogenation of cyclohexane to benzene is endothermic, favouring high temperatures such as exposed to during these reactions. (Biniwale et al., 2005). Consequently, the cyclohexane can undergo selective ring-opening to methane, ethane, propane, and butane and their isomers at the reaction temperature (425 °C) range, as has been reported in the literature (Shi et al., 2012). The two parallel reactions occurring are simplified by the reaction scheme shown in Figure 4.4 including cracking of cyclohexane to light hydrocarbons and dehydrogenation to benzene. Slagtern et al. (2010) observed that the produced alkane gases from C_1–C_4 are products of secondary reaction whilst the olefins C_2–C_4 are products of the primary reaction of the cyclohexane ring opening. These reactions are the reason for lower gas yields observed upon the use of cyclohexane relative to that without cyclohexane which is catalytic upgrading under nitrogen and hydrogen environment.

Consequently, the difference of liquid yield results of each catalyst in the presence of cyclohexane could be attributed to the ability of the catalysts in dehydrogenation or hydrogenolysis (C-C bond cleavage) of cyclohexane. It has been determined by previous research that when cyclohexane is used with Pd/SiO_2, Ir/SiO_2 and Ni/SiO_2 catalysts, hydrogenolysis is preferred over hydrogenation (Niccolai et al., 2000; Blakely et al., 1975). Haro (1976) has also shown the presence of Pd does not play a role in the dehydrogenation of cyclohexane. Biniwale (2005) argues that, when the catalysts are supported on active carbon, hydrogenation is selectively preferred. It is proposed from research findings that carbon-supported ruthenium has a positive effect and drives cyclohexane selectivity towards dehydrogenation, rather than hydrogenolysis which is likely to occur under Pd.

4.4.3 *Effect of Cyclohexane on API Gravity, Viscosity and Asphaltene content of Produced Oil*

Table 4.8 also shows the API gravity, viscosity and the asphaltene content of the feed and upgraded oil samples. It is clear that under hydrogen gas reaction media in the presence of Ru/C and Pd/Al_2O_3 the API gravity increased to its highest value achieved: 23.35° and 23.14°. Also, the viscosity decreased to its lowest value of 4.9×10^{-3} and 5×10^{-3} respectively. This improvement in oil quality is more noticeable in the presence of Pd/Al_2O_3 and hydrogen, where the API gravity of produced oil sharply increased by 1.75° and its viscosity decreased by 21% compared to the nitrogen gas media. Conversely, the results obtained in the presence of Ru/C catalyst and hydrogen gas media showed only a slight increase of API gravity (0.38°) and decrease of viscosity (4%) compared when Ru/C was used under nitrogen gas media. This shows that the hydrogen could have inhibited the extent of Pd/Al_2O_3 catalyst deactivation experienced in nitrogen reaction media. It also confirms the fast deactivation of Pd/Al_2O_3 under nitrogen atmosphere can be limited by the addition of hydrogen gas. Furthermore, under hydrogen atmosphere hydrocracking and hydrogenation reactions are favoured. The function of the Pd/Al_2O_3 catalyst is to promote those reactions which lead to smaller molecular weight products, as the alumina promotes cracking of macromolecules whilst the Pd metals transfer active hydrogen to the cracked fragments to form a smaller stable molecule following the carbonium ion mechanism.

Ru/C under hydrogen atmosphere showed similar upgrading results to cyclohexane when this was used as the hydrogen donor solvent. The API gravity was only 0.12° lower and the viscosity 3.5 % higher under hydrogen gas media. However, cyclohexane did not show a similar effect on the performance of the Pd/Al_2O_3 catalyst under a hydrogen atmosphere. Even though cyclohexane in the presence of Pd/Al_2O_3 improved the liquid yield and prohibited coke formation as previously discussed, it did not improve the produced oil quality, unlike hydrogen atmosphere. In fact, it showed a negative impact on the quality of the produced oil in terms of API gravity and viscosity. Further research (Feng et al., 2010; Ali et al., 1999; Maeda et al., 1987) has previously focused on dehydrogenation of cyclohexane on alumina-supported monometallic catalysts such as Rh/Pt/Ir/Re/U on Al_2O_3. These findings indicate that the activity of Rh/ Al_2O_3 catalyst reduces through hydrogenolysis of cyclohexane to propane at temperatures above 425°C, which is the reaction temperature in these experiments (Ali et al., 1999). It is theorized that hydrogenolysis occurs because of the high d-bond character of metals such as Rh and Pd which have respective percentages of 50% and 46% and share the same face-centred cubic lattice structure (Addy et al., 1957). Hence it is proposed that Pd/Al_2O_3 as used in this research undergoes a similar mechanism to Rh/ Al_2O_3, explaining the reduced effectiveness of cyclohexane with Pd compared to Ru/C experiments with hydrogen gas atmospheres. It is suggested that this mechanism are most likely the main cause of upgrading benefits of cyclohexane associated with Ru/C. Furthermore, cyclohexane selectivity appears favorable towards active carbon supports in Ru/C, driving its dehydrogenation pathway as opposed to its hydrogenolysis pathway to propane, prevalent in d bond rich metals (Pd/Al_2O_3) (Biniwale et al., 2005), where cyclohexane was reported as less effective at curbing coke formation (Ali et al., 1999; Hedge, 2016).

Unlike these catalysts (Ru/C and Pd/Al_2O_3) the experiment results in the presence of Fe_2O_3 with cyclohexane and hydrogen atmosphere and cyclohexane produced lower quality oil in terms of API gravity, viscosity and asphaltene content. It is reported in the literature (Hongfu et al., 2002; Gray, 1994; De Bernieres, 1979) that unsupported catalysts such as Fe_2O_3 are not bifunctional in nature; they do not promote cracking of C-C and C-heteroatom bonds in contrast to zeolites and alumina which possess acid sites that support cracking. Hence, the viscosity reduction and API gravity improvement are mainly controlled by thermal cracking, and the presence of Fe_2O_3 with different hydrogen sources would not contribute to cracking. A slight decrease of 0.03° API was observed when Fe_2O_3 was used under a hydrogen atmosphere. However, hydrogen gas is known to contribute towards hydrogenation reactions of free radicals (Watanabe et al., 2010; Loser et al., 1989) which helped to stabilize asphaltene in the reaction medium and would explain the decrease of API gravity as well as the increased viscosity compared to nitrogen atmosphere (Gawel et al., 2005; Dealy, 1979). This is consistent with the higher asphaltene content of the produced oil after upgrading under a hydrogen atmosphere (1.12 wt.%) or cyclohexane (0.9 wt.%) compared to nitrogen atmosphere in the presence of Fe_2O_3. The results confirmed that the hydrogen sources does not promote C-C bond cracking which is mainly controlled by reaction temperature, but may influence the reaction pathways (Panariti et al., 2000).

From Table 4.6 it can be seen that the asphaltene content of the upgraded oil samples in hydrogen atmosphere after catalytic upgrading in the presence of Ru/C and Pd/Al_2O_3 were significantly lower than the upgraded oil samples under nitrogen atmosphere. The asphaltene content of the upgraded oil decreased from 6.68 wt.% (Ru/C under N_2) to 4.96 wt.% (Ru/C under H_2) and 6.01 wt.% (Pd/Al_2O_3 under N_2) to 4.05 wt.% (Pd/Al_2O_3 under H_2) suggests better conversion of asphaltenes into valuable liquid products because of the presence of hydrogen whilst suppressing coke formation. The lower asphaltene content of produced oil in the presence of cyclohexane with the use of hydrogen medium, compared to Ru/C upgrading reaction using nitrogen medium, indicates better hydrogen transfer from cyclohexane solvent assisted by the Ru/C catalyst during upgrading under hydrogen medium. On the other hand, the changes in the properties of the produced oils relative to the catalytic counterpart were small, the results, however, show a narrow trend and effect of cyclohexane on API gravity, viscosity, asphaltene, the yield of upgraded oil and inhibiting coke formation. The reduction in asphaltene content improved the API gravity and viscosity of the upgraded oil.

4.4.4 *Effect on Elemental Composition*

Table 4.8 shows the sulfur content and H/C ratio of the upgraded oil under nitrogen, hydrogen and cyclohexane in the presence of Ru/C, Pd/Al_2O_3 and Fe_2O_3. It is clear that under hydrogen atmosphere the H/C atomic ratio increased from the feed oil value of 0.11 to 0.138 (Ru/C), 0.137 (Pd/Al_2O_3) and 0.126 (Fe_2O_3). The carbon content, as well as the H/C atomic ratio of produced oil under hydrogen medium in the presence of Ru/C and Pd/Al2O3, was relatively higher than the nitrogen atmosphere. This shows that the upgrading of heavy oil under nitrogen atmosphere is majorly carbon-rejection with limited hydrogen-transfer. Moreover, the results of the H/C ratio indicate upgrading reactions in a hydrogen atmosphere in the presence of metal such as Pd and Ru, significantly enhancing hydrogenation reactions. The high portion of the carbon element in the feed oil is associated with poly-aromatic species such as resins and asphaltenes. However, since noble metal catalysts enhance the hydrocracking and hydrogenation activities under a hydrogen atmosphere, components with a high proportion of carbon such as olefins and aromatics are readily hydrogenated. This explains the improvement of elemental hydrogen in the produced oil which was achieved upon the use of hydrogen atmosphere and cyclohexane addition.

The high level of heteroatom such as sulfur poses challenges to downstream processes. Hence, these impurities need to be removed through upgrading to be suitable as refinery feedstock. From Table 4.8, the sulfur content of the produced oil by catalyst NPs under nitrogen was 2.35 wt.% (Ru/C), 2.48 wt.% (Pd/Al_2O_3) and 2.63 wt.% (Fe_2O_3) whilst when cyclohexane was used as hydrogen donor, the extent of sulfur reduction achieved was 7 % (Ru/C), 4 % (Pd/Al_2O_3) and 5 % (Fe_2O_3). However, when hydrogen gas was used as reaction gas medium, sulfur removal was 14 % (Ru/C), 14.9 % (Pd/Al_2O_3) and 6.8 % (Fe_2O_3), which is significantly higher than the values obtained using nitrogen. The further desulfurisation experienced under hydrogen atmosphere can be attributed to hydrodesulfurization (HDS) reactions in the presence of catalysts NPs particles and hydrogen. The reaction pathways through which sulfur can be removed from the different structures in the heavy oil during the upgrading process is illustrated in Figure 4.6. The thiophenes can either undergo hydrogenolysis and/or hydrogenation to nonaromatic sulfide prior to being subjected to cracking and HDS to give H_2S

Which will be discussed in section 4.4.5 (Gray et al., 1995).

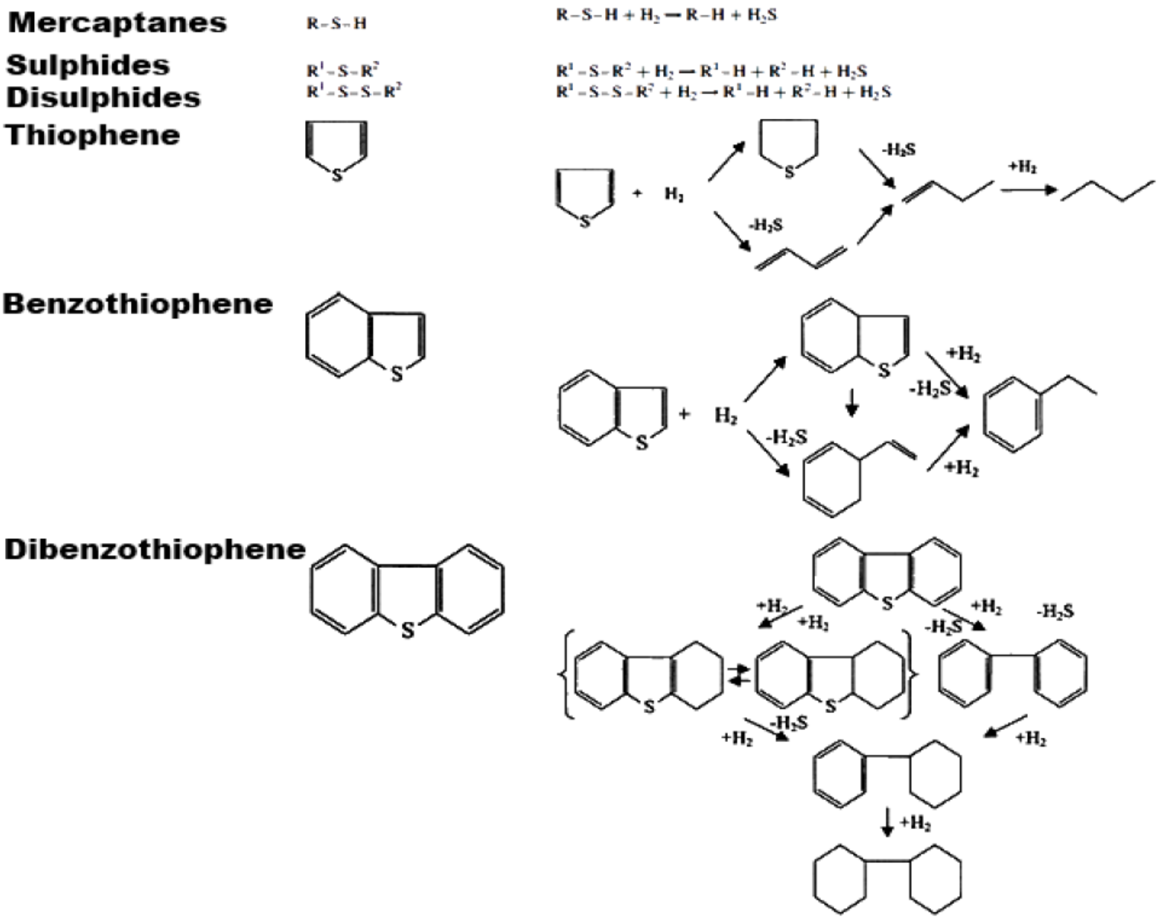


Figure 4.6 Typical organosulphur compounds
(where; R1 and R2 are alkyl hydrocarbon) found in heavy oil and their reaction pathway during upgrading reactions (Babich and Moulijn, 2003)

Table 4.8 Effect of different catalyst in the presence of cyclohexane versus hydrogen media on heavy oil upgrading
Using stirred batch reactor at 425 ºC under 20 bar nitrogen medium (Feedstock: API 13 °, Viscosity 0.49 Pa.s, C5-aphaltene 12.4 wt%, 0.68 wt% (IBP-200 °C), 38 wt% (200-350 °C), 41 wt% (350 °C+), 22 wt%, sulphur 3.61 wt%, Carbon 89.92 wt.%, H/C ratio 0.11)

Catalyst	Product distribution (wt %)					Physical properties		Product qualit		
	Coke	Liquid	Rmn.O	Gas	Asph	API °gravity 25 °C	Viscosity (Pa.s) 25 °C	Sulphur	Carbon	H/C Ratio
(Ru/C) N_2	6.12	71.35	9.95	12.6	6.68	22.97	5.2×10^{-3}	2.35	87.14	0.136
(Ru/C) H_2	5.72	70.64	9.8	13.84	4.96	23.35	4.9×10^{-3}	2.02	87.38	0.138
(Ru/C) $N_{2+}C_6H_{12}$	4.25	79.48	8.20	9.07	4.48	23.23	5.1×10^{-3}	2.19	87.45	0.137
(Pd/Al_2O_3) N_2	6.54	56.15	22.01	15.32	6.01	21.39	6.4×10^{-3}	2.48	86.85	0.133
(Pd/Al_2O_3) H_2	5.45	74.22	10.76	9.58	4.05	23.14	5.0×10^{-3}	2.11	87.02	0.137
(Pd/Al_2O_3) $N_{2+}C_6H_{12}$	5.07	73.69	10.5	10.75	7.35	21.72	8.9×10^{-3}	2.38	87.34	0.133
(Fe_2O_3) N_2	7.82	68.32	13.23	11.75	10.3	20.32	11×10^{-3}	2.63	87.21	0.127
(Fe_2O_3) H_2	7.25	71.12	10.43	11.18	11.42	20.29	14×10^{-3}	2.45	87.32	0.126
(Fe_2O_3) $N_{2+}C_6H_{12}$	6.64	73.48	9.21	12.85	11.21	20.56	14×10^{-3}	2.49	87.48	0.124

4.4.5 *Effect on Produced Gas Composition*

Results in Table 4.9 show the quantitative composition of the produced gas during the experiments for ultradispersed Ru/C catalytic upgrading under nitrogen and hydrogen atmosphere as well as in the presence of cyclohexane solvent under nitrogen atmosphere. 0.65 and 1.11 vol.% of olefin were produced when upgrading was carried out with and without cyclohexane respectively under nitrogen atmosphere. It is argued that the use of hydrogen decreases the amounts of ethene, propene, trans-2-butene, and cis-2-butene decreased upon the use of hydrogen as reaction media and cyclohexane as a solvent compared to the use of nitrogen gas, which makes an overall 0.59 vol.% and 0.46 vol.% decrease of olefin gases respectively. This shows that hydrogen is involved in the reaction and the addition of hydrogen promotes hydrogenation of olefins to paraffins, which was further confirmed by a corresponding increase in the amount of paraffins compared to nitrogen atmosphere in the outlet gas. The Ru/C is responsible for the hydrogenation function which helps to moderate free radicals and coke precursors produced from cracking of heavy oil and subsequently lowers coke yields for Ru/C catalytic upgrading. In the presence of hydrogen both hydrocracking and hydrogenation occur concurrently. This is in conformity with the results reported by Kim et al. (1998) who measured hydrogen consumption in the presence of an HDN catalyst which may also explain the relatively higher upgrading in the presence of hydrogen and cyclohexane in terms of API gravity upgrading and viscosity reduction.

Consequently, the extent of sulphur removal resulting in the release of hydrogen sulphide in the presence of cyclohexane and under hydrogen atmosphere is 1.2 and 1.6 times more than experienced under nitrogen atmosphere respectively. Hence, the level of hydrodesulphurisation (HDS) function of the Ru/C catalyst is greatly enhanced in the presence of hydrogen and cyclohexane. This indicates that the generated active hydrogen from catalytic decomposition of cyclohexane can be partly consumed by hydrodesulphurisation, resulting in additional H_2S in the released gas.

Table 4.9 Produced gas composition for Ru/C
In the presence of cyclohexane versus hydrogen and nitrogen media; uusing stirred batch reactor temperature 425°C, pressure 20bar

Gas Composition	n(C_1-C_5) (Vol.%)	iC_4-C_5 (Vol.%)	Olefin (C_2-C_4) (Vol.%)	CO_2 (Vol.%)	CO (Vol.%)	H_2 (Vol.%)	H_2S (Vol.%)
Thermal	13.37	0.59	0.54	0.21	0.01	1.43	0.0006
(Ru/C) N_2	10.25	0.88	1.11	0.24	0.01	1.58	0.003
(Ru/C) H_2	12.29	1.16	0.52	0.11	0.21	73.64	0.0048
(Ru/C) N_2+C_6H_{12}	11.61	1.02	0.65	0.13	2.37	18.63	0.0036

4.5 Effect of Bio-Palladium Catalyst versus Pd/C and Pd/Al_2O_3 Catalyst

Palladium nanoparticles are known to have a significant catalytic activity especially in hydrogenation reactions (Zhang et al., 2015). Palladium has a face-centered cubic (fcc) structure which is able to adsorb hydrogen. Hydrogen, therefore, fills the palladium metal at the molecular level to form palladium hydride (Flanagan et al., 1991). The remarkable capacity of palladium for adsorption of hydrogen makes this precious metal a highly suitable and efficient catalyst with industrial significance. The effect of Pd/Al_2O_3 upon upgrading of heavy oil in comparison to other metal/inorganic catalysts was discussed earlier in this chapter. The result showed an improvement of the quality of the produced oil, even though the catalyst becomes deactivated early in the reaction due to the relatively high sulfur content of heavy oil. It was reported that the sulfur tolerance of such catalysts can be increased by improving the metal dispersion (Gonzales et al., 2010). Therefore with an effective catalyst support, crystallite size and geometry of active metal deposited on the support could potentially promote catalyst performance by maintaining the stabilisation of the active metal, even though some may not take part in the reaction. However, the use of Pd metal for the heavy oil upgrading would be prohibitively expensive leading to uneconomic viability. There is increasing interest and technology to recover palladium group metals from secondary or waste sources such as urban road dust (Murray et al., 2010). Upon heating, some components of the biomass support may be modified between temperatures of 200 and 700 ^oC, although the catalytic activity of the Pd nanoparticles remains intact (Zhu, 2014). At 425^oC experimental condition, the bacterial biomass would have been destroyed releasing the Pd NPs into the reaction medium. This chapter illustrates the comparison between commercial Pd/Al_2O_3, Pd/C and Pd catalyst supported on *E.coli* bacteria which was prepared in the lab for the upgrading of heavy oil. Consequently, the effect of palladium loading onto the biomass has also been compared in terms of produced oil physical property, quality, and product yield.

4.5.1 *Effect of Pd Support on Elemental Composition*

Table 4.10 presents the effect of thermal cracking, bacterial biomass only and Pd nanoparticles supported on bacterial biomass, carbon and alumina upon heavy oil upgrading in the in terms of product distribution, physical properties (API, viscosity, and TBP) and product quality (Asphaltene, Sulfur and Hydrogen). The test result of the E.coli biomass is presented for comparison purposes to thermal upgrading. The result indicates biomass alone does not play a major role in terms of improving the produced oil quality however it slightly increases the liquid yield by 1.8 wt.% and marginally reduces coke formation by 0.96 wt.% which might be because of the adsorption of hydrocarbon molecules by E.coli cells. Moreover, the small reduction of asphaltene content of produced oil could potentially be because of the presence of fine particles which may result in aggregation at nucleation sites of heavy molecules such as asphaltene (Berna et al., 2006). omparing the API gravity of the oil produced by thermal upgrading to the produced oil with 5 wt.% Pd upon different supports reactions under the same experimental conditions, it was found that API increased by 7.7^o (Pd/biomass), 7.8^o (Pd/C) and 8.4^o (Pd/Alumina), respectively. An improvement of additional 0.8^o API was observed for alumina supported Pd compared with the biomass or carbon supports. Although the performance of bio Pd catalyst in terms of the API gravity against non-catalytic thermal cracking is small, the viscosity that was reduced to 0.023 Pa.s after thermal upgrading, further reduced to 0.0061 Pa s (bio Pd), 0.0062 mPa s (Pd/C), and 0.0064 mPa s (Pd/Alumina), respectively, after catalytic upgrading with Pd NPs on different supports. The produced oil when carbon-supported Pd including the bio Pd (to be considered as carbon at a high temperature of the reaction) was used as a catalyst showed slightly better performance in terms of the viscosity reduction. This may be due to the adsorption affinity of carbon for the larger molecules because of its large surface area and high surface activity (Hart et al., 2013). This also explains the slight improvement in the produced oil quality in terms of the asphaltene content, where 6 and 3.5 % of asphaltene content were removed in the produced oil using bio Pd/C and bio Pd respectively, compare to Pd upon alumina support. The coke yield of the reaction with 5 wt.% of Pd nanoparticles supported on alumina was 6.54 wt.%, *E. coli* support 5.21 wt.% and with carbon support 5.31 wt.%. The higher coke yield of alumina supported catalyst is attributed to the higher API gravity improvement of the produced oil compared to other carbon supported catalysts. Acidic supports such as alumina enhance the cracking function of the Pd catalyst because of its acidic sites (Leyva at el., 2007). Moreover, the produced oil with acidic alumina supported Pd catalyst shows high carbon rejection of 3.41 wt.% compared to 3.05 and 3.09 wt.% of neutral, supported bio Pd and Pd/C respectively. Hydrocracking and hydrogenation reactions are considered more significant than carbon rejection for coke formation occurring during the reaction (Greaves et al., 2004). The liquid yield can be improved by minimizing the formation of hydrocarbon gases as well as suppressing coke formation. Pd/Alumina has strong acid sites support to enhance the breakage of C–C and C-heteroatom bonds, hence the extent of carbon rejection during the upgrading reactions and therefore more production of gas and coke (Klerk et al., 2014). Carbon and biomass supported Pd catalyst produced similarly 10.2 and 10.92 wt.% of remainder oil respectively, unlike Alumina supported Pd with 29 wt.% remainder oil, i.e. ~ 3 times better The DTG curve from Figure 4.7 clearly shows Pd/Al_2O_3 deposits extensive mass loss compared to Pd/C and Pd/*E.coli*. As discussed earlier the major difference in the 5 wt.% Pd catalysts is the support material. Therefore the significant amount of trapped oil and residue in the deposited material could be attributed to alumina support of Pd.

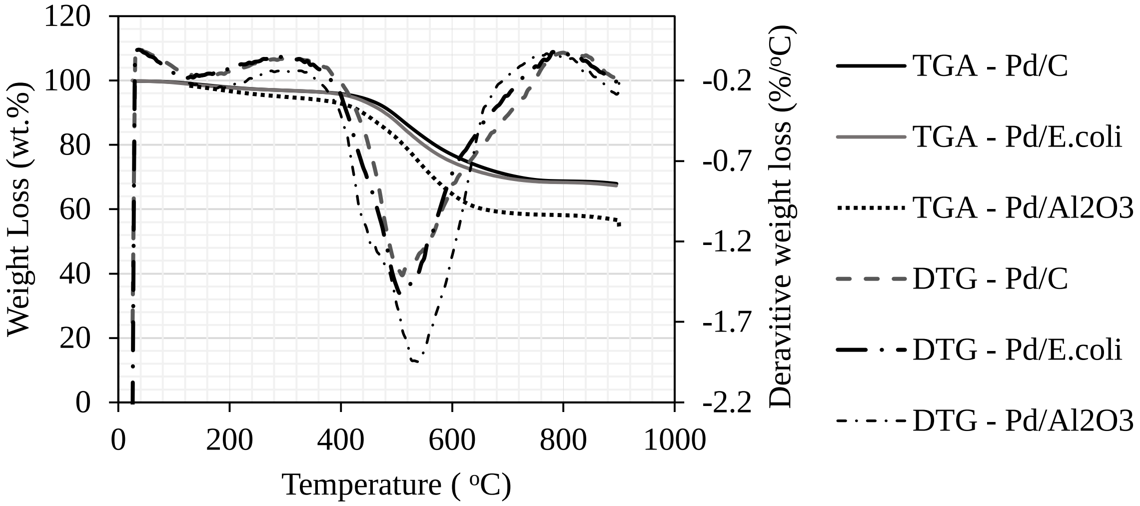


Figure 4.7 TGA and DTG of the deposited coke and residue of upgraded heavy oil
Obtained from the stirred batch reactor using Pd/E.coli, Ru/C, and Pd/Al_2O_3 and Fe_2O_3at a reaction temperature of 425°C under 20 bar nitrogen medium at 30 min.

Table 4.10 Effect of Pd catalyst on different support on heavy oil upgrading

Using stirred batch reactor at 425 ºC under 20 bar nitrogen medium (Feedstock: API 13 °, Viscosity 0.49 Pa.s, C5-asphaltene 12.4 wt%, 0.68 wt% (IBP-200 °C), 38 wt% (200-350 °C), 41 wt% (350 °C+), 22 wt% sulphur , 3.61 wt%)

	Product distribution (wt%)					SIMDIS Boiling point distribution of produced liquid(wt %)			Physical properties		Product quality (wt %)	
Catalyst	Coke	Liquid	Rmn.O	Gas	Asph	(IBP-200 °C)	(200-350 °C)	(350°C+)	API gravity 25 °C	Viscosity (Pa.s) 25 °C	Sulphur	Carbon rejection
Thermal	10.8	66.1	10.8	12.3	11.49	53	32	15	20.1	0.023	2.83	6.74
E. coli alone	9.84	67.91	9.7	11.55	11.45	53	33	14	20.0	0.021	2.83	6.73
Pd/C	5.31	71.61	10.2	12.88	5.65	58	30	10	20.8	6.2×10^{-3}	2.44	3.09
Pd/*E.coli*	5.21	73.18	10.92	10.69	5.81	58	30	10	20.7	6.1×10^{-3}	2.45	3.05
Pd/Al_2O_3	6.54	56.15	29.31	15.3	6.01	58	30	12	21.4	6.4×10^{-3}	2.48	3.41

4.5.2 *Effect of Cell Metal Loading*

An early review in part 4.5.1 showed that palladium catalysts on *E.coli* support have similar selectivity and activity towards hydrocracking compared with carbon support. To further investigate the relationship between metal loading and activity, bio-catalysts with different Pd loadings were manufactured with a total of 3, 5 and 20 wt. % of palladium of overall catalyst mass. The metals were dissolved in a solution containing *E. coli* which were then reduced using hydrogen. More details of the catalyst production were discussed in Method and Materials section.

Table 4.11 Effect of Pd loading of bio Pd catalyst on API gravity and coke yield of heavy oil
Using stirred batch reactor at t at 425 ºC under 20 bar nitrogen medium at 30 min. (feedstock: 13 ºAPI).

Bio Catalyst	**API º gravity (25ºC)**	**Coke (wt.%)**
Bio Pd (3 wt.%)	21.1 ± 0.18	4.72
Bio Pd (5 wt.%)	20.7 ± 0.12	5.21
Bio Pd (20 wt.%)	19.3 ± 0.21	7.12
Pd/C (5 wt.%)	20.8± 0.24	5.31

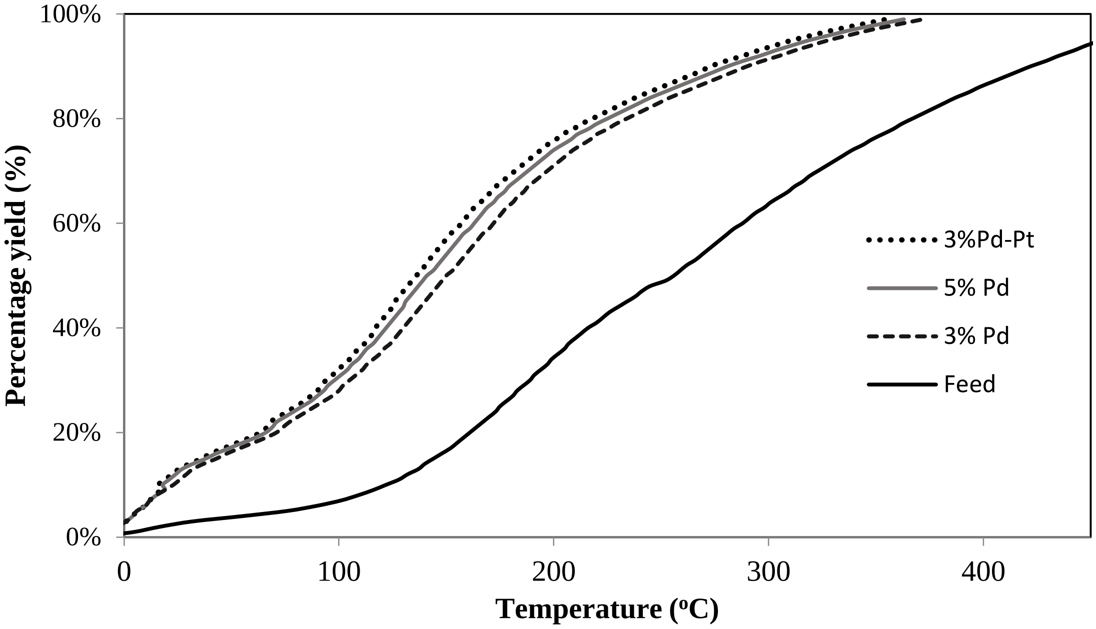


Figure 4.8 TBP distribution curves of feedstock and produced oil
Using 3 wt.% Pd-Pt, 5 wt.Pd and 3 wt.% Pd bio-catalysts stirred batch reactor at 425 °C under 20 bar nitrogen medium

Table 4.11 and Figure 4.8 show the quality of produced oil after catalytic cracking reaction using bio-Pd with 3, 5 and 20 wt.% palladium loading, which caused an improvement in produced oil quality by increasing the API value to 8.1, 7.7 and 6.3 °API respectively. The results clearly show higher catalytic activity in the case of a lower concentration of Pd loaded upon the biomass. Figure 4.8 presents the TBP distribution curves of the produced oil to the left of the boiling temperature axis with reference to the feedstock curve. This means that high boiling (or high molecular weight) components in the feedstock have been converted into lighter ones. The increase in conversion with decreasing of Pd metal loading was responsible for the shift of the TBP curve in Figure 4.5. This is because, at higher loading of Pd, larger metal clusters (Figure 4.6) were formed and limited the dispersion of active metals on the *E.coli* cells which could potentially cause a disruption of accessible active sites on the surface of the catalyst. However, it is possible that in the case of lower loading of Pd (less than 3 %), the eruption of metal particles through the outer surface of the cell surface and wall could potentially be restricted, providing less available active sites for upgrading reaction. The morphologies of the fresh particles of bio Pd catalysts were studied and shown in Figure 4.9 using SEM (scanning electron microscope) analysis. It is observed that the ensembles of bacteria are overlapping each other while showing the individual bacteria with well-maintained original rod-shapes. In general, the SEM analysis of the cells can hardly distinguish the presence of the metal depositions on the bacteria. With the detection of backscattered electrons, the presence of well-dispersed metal NPs is clearly evidenced by the bright dots which correspond to metallic deposits. The dots present the variation of the size of deposited metal particles in BSE (back-scattered electrons) images which proves the particle growth with the increase of Pd loading as compared to the formation of additional metal-loaded sites.

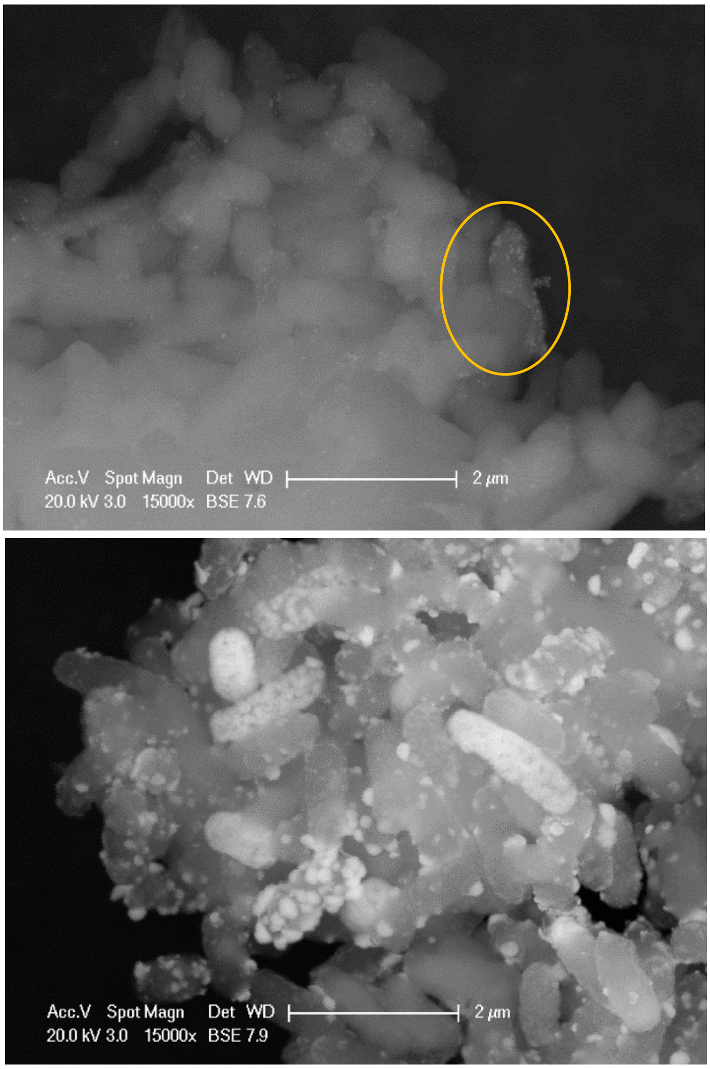


Figure 4.9 BSE images of bio-catalyst powders of a) 3wt%Pd/E. coli; b) 20wt%Pd/E. coli

The particle distribution of 20 wt.% bio Pd Figure 4.9 b) loading cell tended to be one very large metal cluster accompanied by very few scattered small particles. In contrast, the 3 wt% bio Pd in Figure 4.5 a) shows relatively evenly located metal particles with significantly smaller sizes. Additionally Table 4.11 shows less coke formation in the case of lower Pd (3%Pd<5%Pd<20%Pd) metal loading on the bacteria support. Since the surface of the dispersed catalyst is where the upgrading takes place, it is very likely that coke deposit forms also on the surface where the active sites are. When coke forms, these active sites are encapsulated by residual oil, asphaltenes, and deposited metals. Therefore as there are more active metals on the surface area of the catalyst more coke will be expected to form around them. This could be clearly seen in the comparison case of 3% Pd (4.7% wt. coke) versus 20 % Pd (7.1% wt.% coke) loading. On the other hand formation of slightly more coke in the case of 5%Pd (5.2% wt. % coke) corresponds to the higher upgrading of oil in terms of API which is in the same trend with an increase of the amount of coke rejected during the reaction (Hart et al., 2015).

4.6 Conclusion

The performance of ultra-fine dispersed catalysts in the catalytic upgrading of heavy oil ‘downhole’ was investigated. Different types of transition metals dispersed catalysts for in situ catalytic upgradings of heavy oil during the THAI heavy oil recovery process were examined in a stirred batch reactor at the following reaction conditions; Pressure 20 bar, temperature 425 ^oC and residence time 30 min under nitrogen atmosphere. It was found that the quality of the produced oil was significantly increased from 13 up to 24 ^{o}API gravity in the presence of a dispersed catalyst in the following order Ru/C > Pd/Alumina > Pd/C Pd/*E.coli* > Fe_2O_3. Though the API gravity increment and viscosity reduction between produced oil by thermal cracking and upgrading with bio Pd was marginal, upgrading with bio Pd shows a benefit in terms of lower yield of coke against thermal and feed oil and also improved quality of produced oil with approximately 32% and 53% reduction in sulfur and asphaltene contents. The use of cyclohexane was evaluated against that of hydrogen gas. The thermal reaction in the presence of cyclohexane under nitrogen atmosphere significantly reduced coke yield by 37%.wt compared with a nitrogen environment alone under the same conditions. Also, the coke decreased by 6–16 wt.% when cyclohexane was used as a hydrogen donor in the presence of catalyst NPs. An estimated 0.012 CH: oil ratio was found to suppress coke formation in a similar manner to upgrading under a hydrogen atmosphere at the same conditions. This makes the solvent a potential alternative for the use of hydrogen in the upgrading process. The results of the simulated distillation, viscosity reduction, asphaltene, sulfur, and metals content after upgrading showed that the alternative Pd/biomass nanoparticles have the potential of achieving a similar level of upgrading as obtainable with typical HDS catalyst particles such as Pd supported on carbon and alumina, respectively. Additionally, less coke formation and slightly higher improvement of produced oil were observed in the case of lower Pd loading of the cell. However, preparation of metal nanoparticles requires a significant experimental procedure. Additionally, the cost of preparing the biomass support using the anaerobic *E.coli* bacteria is relatively high, due to the need for exclusion of oxygen and the complex growth media used but other studies have shown the effective use of ‘second hand’ *E. coli* to make catalytically active bio-Pd (J. Zhu et al 2016 Appl Catal B) . Moreover, the cells can grow aerobically and then harvested and place them under N_2 to get them anaerobic which could potentially reduce the catalysts production cost. Future studies would address these challenges and nominate their suitable alternative. Effective bio Pd can be biorefined from wastes such as road dust and scraps with comparable activity using catalyst from waste leachate to that reported here (A.J. Murray, J.B. Omajali 2016) Focus on improvement in terms of upgrading and reduction of the preparation cost of bio-Pd such as use of aerobic *E. coli* bacteria, grown in simple growth media could potentially decrease the production cost. However, a more detailed cost analysis is required.

5 *Upgrading of Fast Pyrolysis Oil via HDO*

5.1 Introduction

Bio-oil produced from biomass using pyrolysis process has a potential of replacing crude oil (Luo et al., 2015). Pyrolysis bio-oil has several advantages over fossil fuels; the first advantage is that as compared to the fossil fuels they are able to generate fewer emissions, almost they contain no emissions of sulfur and the emissions of NOx are also found to below. The second advantage is that these fuels are sustainable (Huber et al., 2006). However high content of oxygen (35-50%) and water (15-30%) that results in the low calorific value of 17 mJ/kg as compared to the 40 mJ/kg calorific value of fossil fuel (Bridgwater, 2004), prevents the direct use of bio-oil as a fuel of transportation (Castello et al., 2016). Moreover, the stability of bio-oil during transport and storage is undermined by its large molecular weight as well as its high oxygen content. Functional groups containing oxygen such as hydroxyketones, carboxylic-acids, hydroxyaldehydes and sugars are the main cause of self-polymerization and instability of bio-oil (Elliot et al., 2007). Therefore removing oxygen from produced oil as well as reducing its high molecular weight compounds, improves the oil stability, viscosity and heating value (Bridgwater, 2004). There are several processes which could be used for upgrading of fast pyrolysis oil, including; catalytic cracking (Jacobson et al., 2013), emulsification (Ikura et al., 2003) and hydro-de-oxygenation (HDO) (Wildschut et al., 2009). However the focus of this research is on HDO process because of its higher produced oil quality which contains less oxygen and lower viscosity (Wildschut et al., 2009).

The present research aims to examine the effects of process conditions, particularly the reaction temperature, for HDO of fast pyrolysis oil with Pd/C in a batch reactor set up in order to find an optimum condition in terms of the product yield, viscosity and oxygen content with minimum hydrogen uptake. Thus, this chapter compares the product yield, physicochemical features of viscosity, water content, acidity, degree of deoxygenation and hydrogen consumption as well as transformation of light species under a wide range of HDO conditions. Moreover, the same bio Pd catalyst which was also used for heavy oil upgrading (Chapter 4) has been compared to commercial Pd/C in terms of produced oil viscosity and DOD (Degree of Deoxygenation) at different HDO temperature.

The early finding showed the viscosity and degree of coking can increase significantly at high HDO reaction temperature which could increase the transportation cost as well as nozzle plugging. Therefore, the solvents were introduced to reduce the produced oil viscosity and formation of coke (Xingmin et al., 2014). Section 5.5 of this chapter investigates the effects of ethanol (polar) and cyclohexane (non-polar) solvents upon the HDO of bio-oil at different temperatures. The DOD, water content viscosity and acidity of produced oil were studied in this section.

5.2 Effect of Time and Temperature on Product Phase Distribution

The liquid products collected from almost all HDO reactions were in two phases, i.e. an aqueous phase which was observed to be either yellowish or transparent (around 40 wt% of the total weight) and a dark brown organic phase with a higher density than aqueous phase (around 45 wt% of the total weight). Samples from the produced gas (around 10 wt% of the total weight) and used catalysts with trace of coke were also collected at the end of each experiment. Figure 5.1 shows separation of phases after a typical HDO reaction.

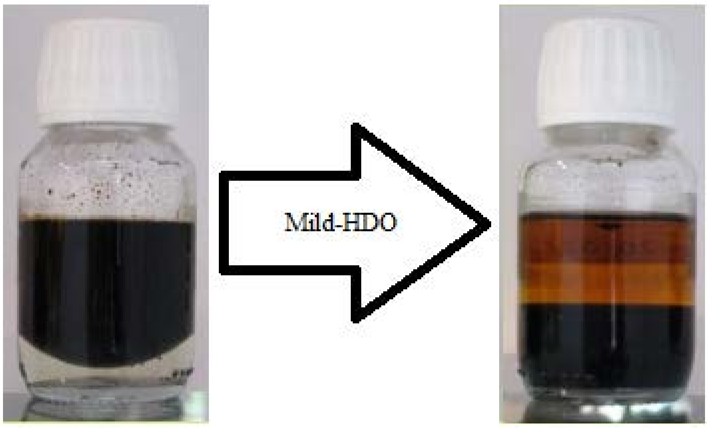


Figure 5.1 Mild hydrodeoxygenation at 230 oC of bio-oil
Using stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium.

However, only single dark-brown liquid (organic phase) was obtained when the HDO reaction was conducted at below 160 ^{o}C. Venderbosch et al., (2010) also reported this phenomenon for the mild-HDO of bio-oil at temperature below 175 ^{o}C and 150 ^{o}C respectively.

Table 5.1 Elemental composition of feed bio oil

Elemental Composition	**Value**
C [wt%]	55 %
O [wt%]	38.5 %
H [wt%]	6.5 %
N [wt%]	0.34 %

During the upgrading of bio-oil, various reactions take place including decarbonylation, decarboxylation, hydrocracking, HDO, hydrogenation and polymerisation routing to coke formation (Mortenson et al., 2011). Through all of these reactions, gases comprised of mainly CO, CO_2 and CH_4 and water (including heavy polymer) were produced (Wildschut et al., 2009). However, the principal reaction is HDO and the overall reaction may be summarized by the stoichiometry of equation 5.1 (Bridgwater, 1996). The equation is derived the original bio-oil elemental composition shown in Table 5.1. However nitrogen was neglected as a trace component.

$CH_{1.4}O_{0.52} + 0.82\ H_2 \rightarrow 1\text{“}CH_2\text{”} + 0.52\ H_2O$ (5.1)

where “CH_2” express an unspecified hydrocarbon product.

Figure 5.2 details the yields of organics, aqueous and gas phase as a function of reaction temperature at 1 and 5 hrs. Figure 5.2 shows aqueous phase after HDO at 160 ^{o}C appears to be very much lower than the other temperatures at the reaction time of 1 hour, which suggests the reaction didn’t get going very much at 160 ^{o}C, 1 hour. It is interesting to see the effect of reaction time on the conversion of phases on reactions operated at lower temperatures between 160-170 ^{o}C. During the first hour of HDO reaction a significant amount organic phase was converted to the aqueous phase and as the reaction time extended up to 5 hrs only 2 wt% additional water formation was observed. On the other hand, the amount of produced aqueous phase at 5 hrs HDO reaction was identical to 1 hrs reaction at 350 ^{o}C and only 2 % higher at 300 ^{o}C, while the cumulative amount of gas produced throughout the reaction time was increased by 27 % for 350 ^{o}C and 21 % for 300 ^{o}C. This means that the time of the reaction highly influenced the phase distribution at high HDO temperature. The results presented in Figure 5.2 that, as the reaction temperature increases, the oxygen compound of the organic phase is converted to either aqueous or gas phase. Therefore the higher HDO temperature will result in a lower yield of organic phase. It is also clear at reactions between 160 to 250 ^{o}C the aqueous phase and gas yield increased with function of reaction temperature at the rate of 0.03% and 0.01% /^{o}C respectively. Thus most of oxygen was rejected in the form of water, and insignificant amount oxygen was rejected as a gas form. However, for reactions at above 250 ^{o}C, the rate of the conversion of organic to aqueous phase was – 0.03% /^{o}C (negative), while the gas yield was + 0.03% /^{o}C which indicate most of the oxygen was rejected in a form of gas.

According to Zacher (2014), the oxygen in the organic phase can be rejected in a form of water, CO and CO_2 through combination of reactions including HDO, decarboxylation and decarbonylation. The results from Figure 5.2 suggests deoxygenation increases with increasing of HDO temperature. However, at reaction higher than 250^{o}C, HDO occurs mainly through, decarboxylation and decarbonylation which indicates at higher reaction temperature oxygen removed through gas formation at the expense of lowered carbon yield.

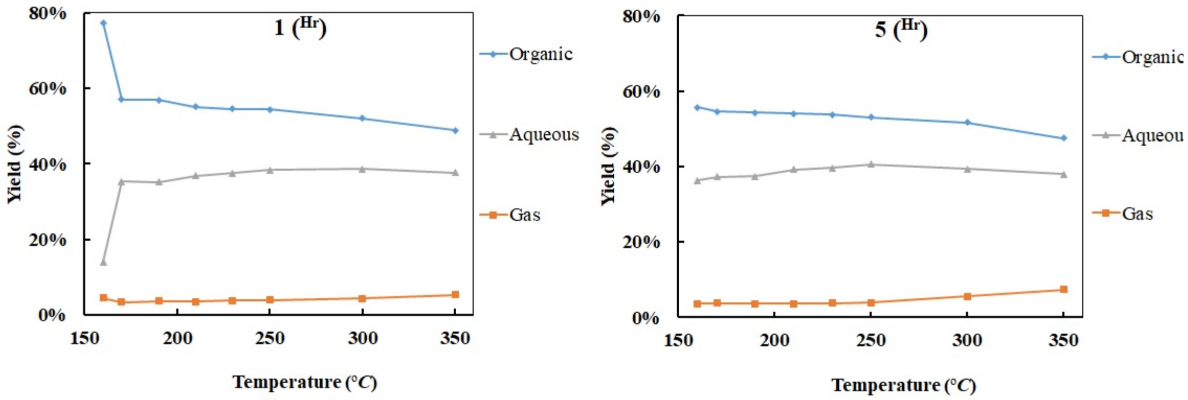


Figure 5.2 Effect of temperature at different reaction time on product yield

Using stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium.

Adjaye et al., (1992) believe lower oxygen rejection into water is desirable because it maintains the bio-oil hydrogen and reduces the consumption of feed H_2 for formation of water. This could also save the available H_2 for hydrocracking reactions as well as in saturating double bonds. On the other hand, Zacher et al., (2014) find this phenomena unattractive because of its negative impact on the yield of the organic phase. Arboast et al., (2013) argues even though the removing oxygen in a form of water is the ideal route, however, it is important to improve the H_2 efficiency in order to balance the cost associated with using H_2. Therefore it is very important to evaluate the different ways (high HDO temperature or lower HDO temperature with longer reaction time) for the extent of deoxygenation (Asmaa et al., 2010).

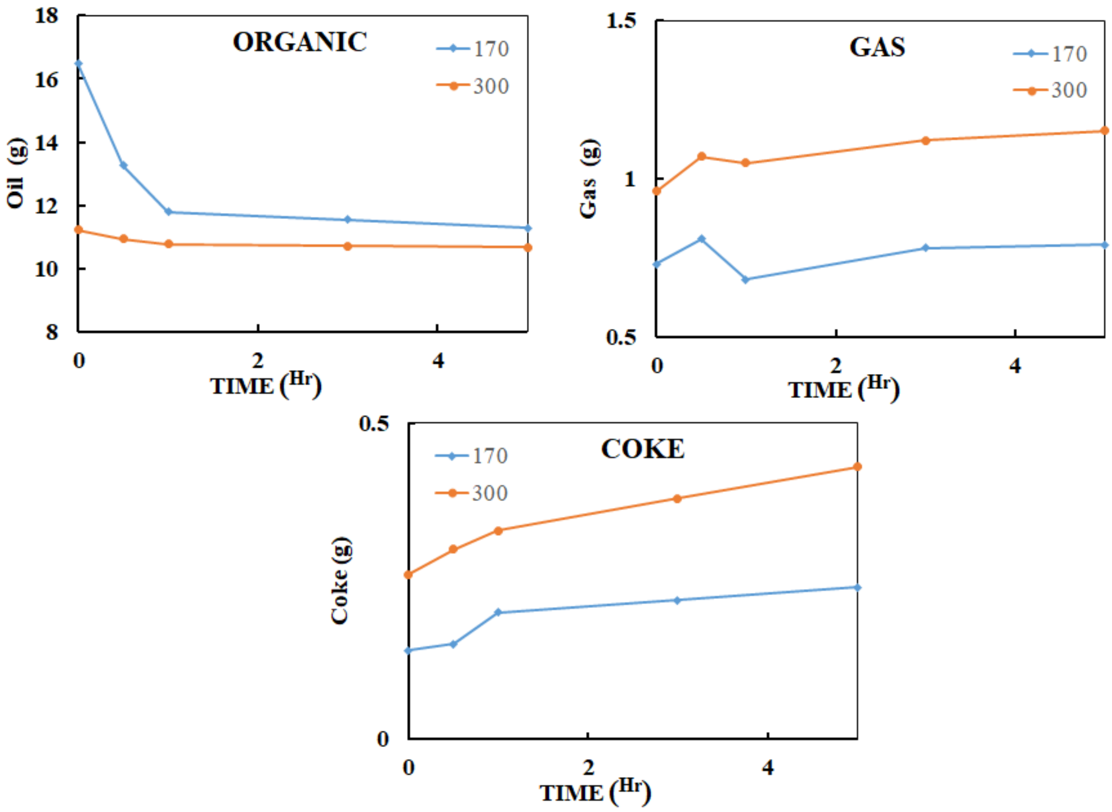


Figure 5.3 Effect of time and temperature on amount of organic, gas and coke
Using stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium

The coke and gas formation for HDO reactions at 170 °C and 300 °C is shown in Figure 5.3. The results indicate that for the HDO reaction at 300 °C the amount of coke is increased with the rate of 0.034 g/h compared to 0.02 g/h for HDO reaction at 170 °C. Moreover, the amount of gas formed during the HDO reaction at 300 °C was almost twice as gas formed in the HDO reaction at 170 °C. The increase of solid and gas yields at the higher temperature over time and the decrease of oil yield is because of the increase in cracking, reforming, polymerization and free-radical reactions rates at high temperatures (Adjaye et al., 1992).

Chantal et al., (1984) suggest increase in HDO reaction temperature, cause the char-forming components of the bio-oil to crack into lighter gaseous and coke. Moreover, at reaction temperature above 300 °C, the coke decomposition could potentially delay the coke build-up on the catalyst, which results in the increase of both the gas and coke yields in the same pattern.

5.3 Effect of Time and Temperature on Produced Oil Quality

5.3.1 *Product Water Content*

The water content of the original bio-oil occurs because of the feedstock moisture as well as the dehydration which takes place during the pyrolysis reaction. This explains the wide range of water content of different bio-oils which depend on the process condition and its original feedstock. The water content of the original bio-oil used in this research is 19 wt.%. The water is miscible with the oligomeric lignin-derived components. This is because of the solubility of water in organic phase is enhanced by polar hydrophilic compounds which are mainly formed by the decomposition of carbohydrates including; alcohols, ketones and low molecular weight acids (Czernik et al., 2004). The high water content of bio-oil, lowers its heating value, flame temperature and reduces its combustion rate. However, it decreases the oil viscosity and leads to a more uniform temperature profile during engine combustion as well as lowering NOx emissions from combustion (Meier et al., 1997).

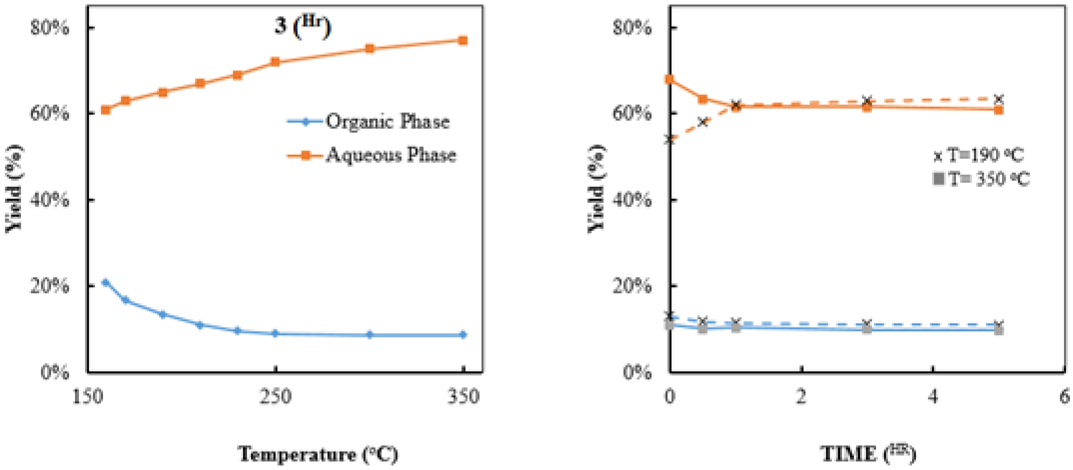


Figure 5.4 Effect of temperature and time on HDO products water content
using stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium.

Figure 5.4 shows that with increasing HDO temperature, the water content of the aqueous phase increased and the organic phase water content decreased. The decrease in the water content of the organic phase was more significant at HDO reaction temperature below 250 °C. This tendency was because of the higher dehydration of the bio-oil which was improved with increased temperature (Adjaye et al., 1992). The reduction of organic phase water content implies that during the HDO reaction hydrophobic/non-polar compounds were formed and forced the produced water to move to the aqueous phase (Gunawan et al., 2013). It is interesting to note that the yield ratio of the organic phase and aqueous phase remained constant, even though there was a significant change in the products water content. This indicates that during the HDO reaction organic compounds were also formed in the aqueous phase and migrate to the organic phase (Li et al., 2013). A similar tendency also can be noticed for the effect of reaction time during HDO at 190 °C and 350 °C. On the other hand, it is interesting to see that during the HDO reaction at 350 °C, the water content in the aqueous phase dropped during in the first hour. This could be potential because of some hydrolysis reactions which may have occurred at higher temperature of 350 °C (Arboast et al., 2013).

5.3.2 *Product Viscosity*

Bio-oil from woody feedstocks tend to be relatively viscous and unstable compared to crude oil (Kim et al., 2009). Storing of bio-oil produced by pyrolysis would result in an increase in its viscosity over time. Bio-oil, especially when it is exposed to air, forms thick glue-like material as it goes through reactions such as polymerization and condensation; (Diebold, 1999; Oasmaa et al., 2004). These reactions are caused by the high amount of volatiles and nonvolatile oxygen-containing compounds mainly water (Oasmaa and Peacocke, 2001). Diebold (1999) suggested that aldehydes leading to the formation of hydrates, as well as unsaturated carbon bond of the bio-oil are prone for formation of larger molecules, especially in presence of acids. Thus, these reactions cause an increase in viscosity and instability

(Agblevor and Besler, 1996). Moreover, relatively higher molecular weight lignin-derived compounds with molecular weight of 700 to 1000 g/mol have considerable effect on bio-oil viscosity. These compounds also have a tendency of reacting with aldehydes (Tang et al., 2014). Thus, bio-oil HDO processes are required to overcome the ageing problem as well as maintaining its viscosity in order to utilize the oil for fuels or chemicals. Figure 5.4 shows the viscosity of upgraded oil after HDO reaction is increased compared to 0.04 Pa.S viscosity of the feed bio-oil. At relatively low HDO temperature between 160 to 190 ^{o}C. The viscosity of upgraded bio-oil increased significantly with the function of temperature and time. At high oxygen contents, the feed oil contains substantial amounts of water, which maintain the bio-oil viscosity relatively low. However, upon the HDO reaction, and consequently the oxygen removal and the phase separation of the bio-oil, the viscosity increases significantly by up to 52 % from the value for the feed bio-oil. The highest viscosity was observed for produced oil of 190 ^{o}C HDO reaction for 1 hr time, where the yield of aqueous phase (Figure 5.1) was 37 wt%. Moreover, it is well known that hydrogenation of aldehydes to alcohol is among the fastest and easiest reaction to take place in HDO of bio-oil. This increases the rate of loss of volatiles compound which contributes to increasing of the viscosity of bio-oil (Baldauf et al., 1994; Jiang and Ellis, 2010).

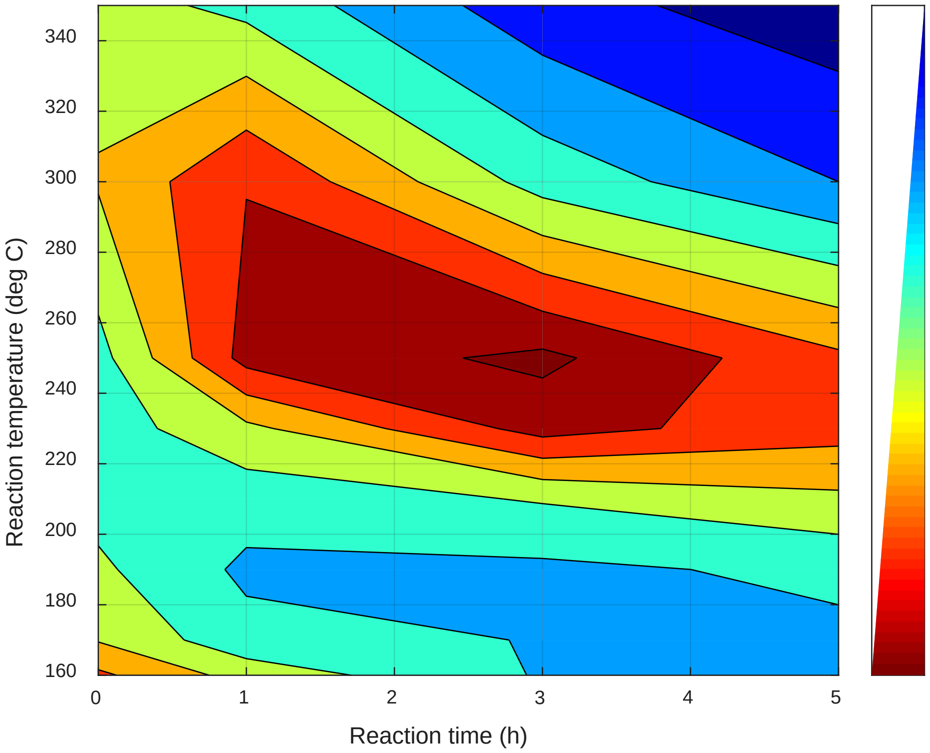


Figure 5.5 Effect of time and temperature on products viscosity
Using stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium (bio-oil viscosity 0.04 Pa.S at 20 ^{o}C)

Figure 5.5 shows the viscosity of the produced oil at 3 h of HDO decreased from 0.061 Pa.S at 190 ^{o}C to a minimum of 0.033 Pa.S at 250 ^{o}C before increasing to a maximum of 0.068 Pa.S at 350 ^{o}C. The significant decrease of the viscosity at a moderate temperature between 190 to 300 ^{o}C is because of hydrocracking and hydrogenation reactions which can occur at higher temperature. According to Oh et al., (2015) at this temperature range of the HDO reaction, levoglucosan which contributes to the bio-oil high viscosity, converted into relatively stable esters such as hexadecanoic acid ethyl ester via hydrogenation, dehydroxylation and ring-opening has shown in Figure 5.6.

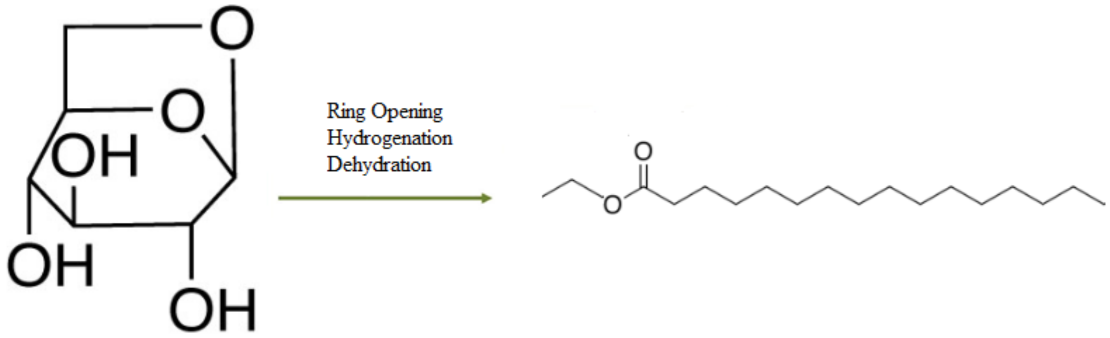


Figure 5.6 Reaction network for the conversion of levoglucosan to hexadecanoic acid ethyl ester.

As the HDO temperature increased from 250 to 350 °C, the produced oil viscosity increased gradually to a maximum value of 0.073 Pa.S at 5 h reaction. The significant increase in viscosity of the produced oil at higher temperature is due to increased polymerization and condensation reactions. Similarly, the increase of the HDO reaction time also caused an increase in the viscosity. More coke is produced at a higher temperature which causes catalyst deactivation in longer HDO reaction time. Therefore polymerization reaction rate increases while the hydrogenation rate decreases as the catalyst lose its performance activity (Sharma et al., 1992). Moreover, at higher temperature HDO, as the reaction continues at longer time the available hydrogen in the reactor decreases significantly (as discussed later). Therefore the rate of hydrogenation reaction decreases proportionally (Wildschut et al., 2009).

5.3.3 *Product Oxygen Content*

Low heating value and high acidity of bio-oil are caused by its high oxygen content, thus deoxygenation is critical in the case of bio-oil upgrading which occurs through HDO (Elliot et al., 2007). The degree of DOD was calculated based on the molar O/C ratio. After the HDO, the O/C ratio of the bio-oil (feed value 0.7) decreased to 0.3– 0.6 due to deoxygenation. The lowest degree of DOD ratio was 7% achieved at the lowest temperature (160 °C) HDO reaction, which steadily increased with an increase in reaction time.

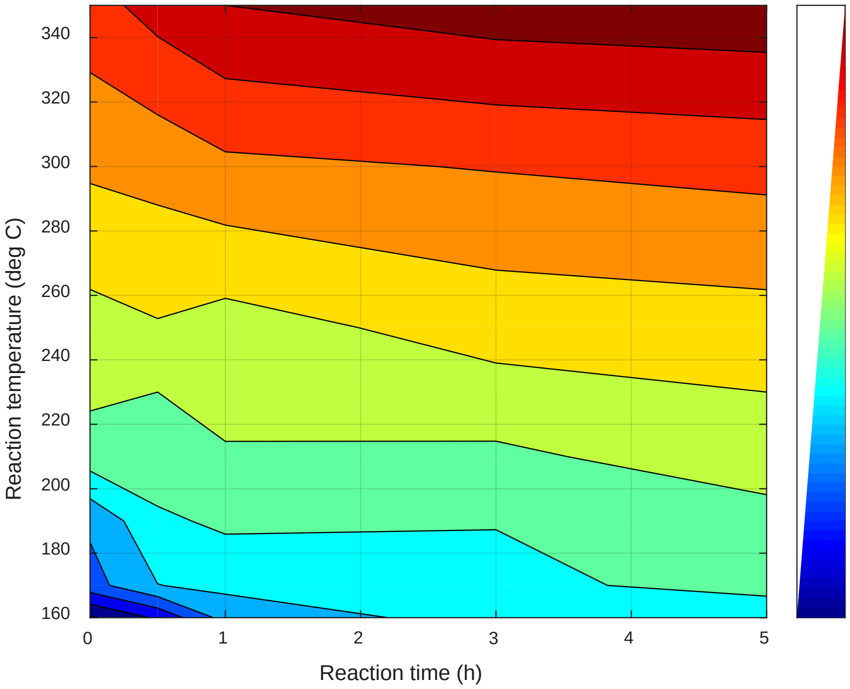


Figure 5.7 Effect of time and temperature on DOD (%)
Using stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium (bio-oil oxygen content 38.5%)

Figure 5.7 shows that most of the deoxygenation occur during the first-hour HDO reaction which is in line with product yield results. Moreover, it is also clear that the DOD of produced oil is significantly dependent on the HDO reaction temperature and to a much lesser extent to reaction time. Thus, the maximum deoxygenation is achieved at higher temperatures and long times. However, as previously discussed operating at high temperature resulted in polymerisation and gasification which increases the viscosity and the coke yield, and decreases the yield of organic phase.

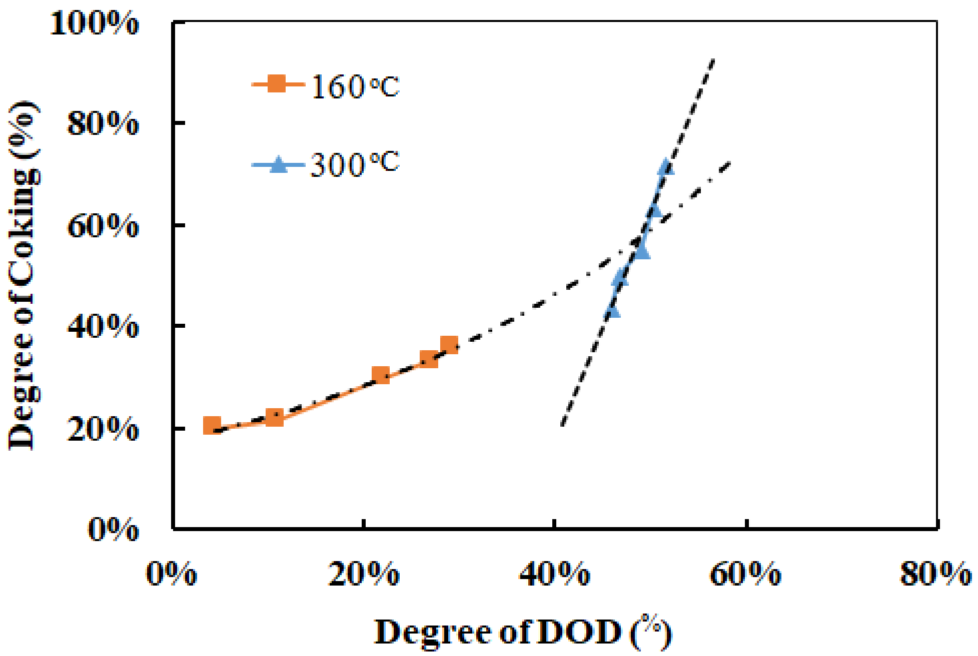


Figure 5.8 Degree of coking (%) as a function of degree of DOD (%)
Using stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium (bio oil oxygen content 38.5%)

The results from Figure 5.8 illustrates how the degree of coking as function of DOD increases significantly at higher HDO temperature compared to lower temperature. The results show DOD reaction at high HDO temperature could cause fast catalyst deactivation as a result of intense coke formation. Furthermore, it illustrates high degree of DOD% is achieved at lower HDO temperature with longer time. It is, therefore, an important aspect to evaluate at which operating condition the oxygen should be removed.

5.4 Effect of Time and Temperature on Product Composition

Fourteen major light organic compounds were identified in the GC/MS analysis and listed in Table 5.2. The total ion chromatograms of feed bio-oil and HDO produced oil are compared in figure 5.9. From Figure 5.9 it is clear that all identified aldehydes in feed oil are removed or converted to alcohol after 1 h of HDO at 300 °C. Moreover, the results suggest the complete disappearance of Hydroxyacetaldehyde, after HDO at low temperatures at 160 °C. This confirms that hydrogenation of aldehydes is the easiest among other functional groups identified in bio-oil. This is in line with findings of Xingmin et al., (2014) which stated all the aldehydes present in bio-oil such as vanillin, butanedial and 4-hydroxy-3,5-dimethoxy-benzaldehyde were not detected in the HDO produced bio-oil. They argue aldehydes present in the bio-oil participate in the condensation reaction with alcohols to form ethers. Increasing the level of ethers as acids and aldehydes decrease will improve the stability of the produced oil (Oasmaa et al., 2004). Moreover, the data shows that about 70 to 85% furfural was converted after 1 to 5 h of HDO at 160 °C, almost all furfural was converted after 1 h Bio-Pd of HDO at temperature higher than 300 °C. As shown in Figure 5.10, the yield of cyclopentanone increased with increasing HDO temperature up to 300 °C, above which the yield slightly decreased. Cyclopentanone can be produced by furfural hydrogenation which explains the increase in its yield. The slight decrease of cyclopentanone yield above 300 °C could be because of its hydrogenation to cyclopentanol and 1-pentanol (Dellanna et al., 2000). However, they were not among the detected compound in the produced oil.

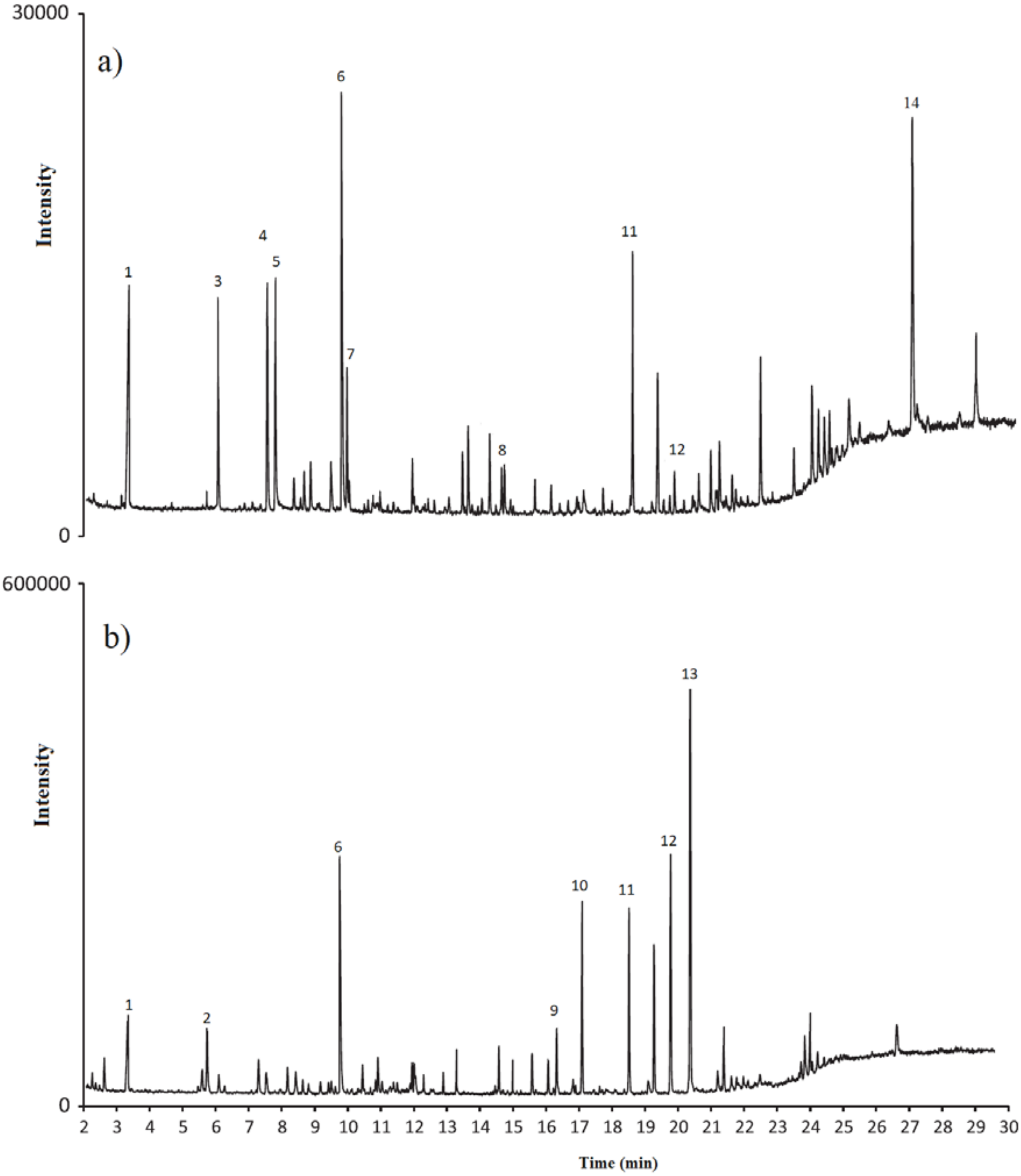


Figure 5.9 GC-MS chromatograms of a) raw bio oil and b) upgraded bio oil organic phase
Using stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium after 1 hr of HDO at 300 °C

Table 5.2 Main Components of bio-oil and upgraded bio-oil using labelled in Figure 5.9

Peak no	Compound	Formula	Retention time (min)
1	Water	H_2O	3.42
2	Cyclopentanone, 2-methyl	$C_6H_{10}O$	5.94
3	Methoxy methanol	$C_2H_6O_2$	6.23
4	Hydroxyacetone	$C_3H_6O_2$	7.53
5	Hydroxyacetaldehyde	$C_2H_4O_2$	7.42
6	Acetic acid	$C_2H_4O_2$	9.42
7	Furfural	$C_5H_4O_2$	9.64
8	Guaiacol	$C_7H_8O_2$	14.57
9	Guaicol, 4-ethyl	$C_9H_{12}O_2$	16.32
10	Guaiacol, 4-propyl	$C_{10}H_{14}O_2$	17.09
11	Syringol	$C_8H_{10}O_3$	18.51
12	4-oxo-pentanoic acid ethyl ester	$C_7H_{12}O_3$	19.77
13	Methyl phenol	C_7H_8O	20.37
14	Levoglucosan	$C_6H_{10}O_5$	26.94

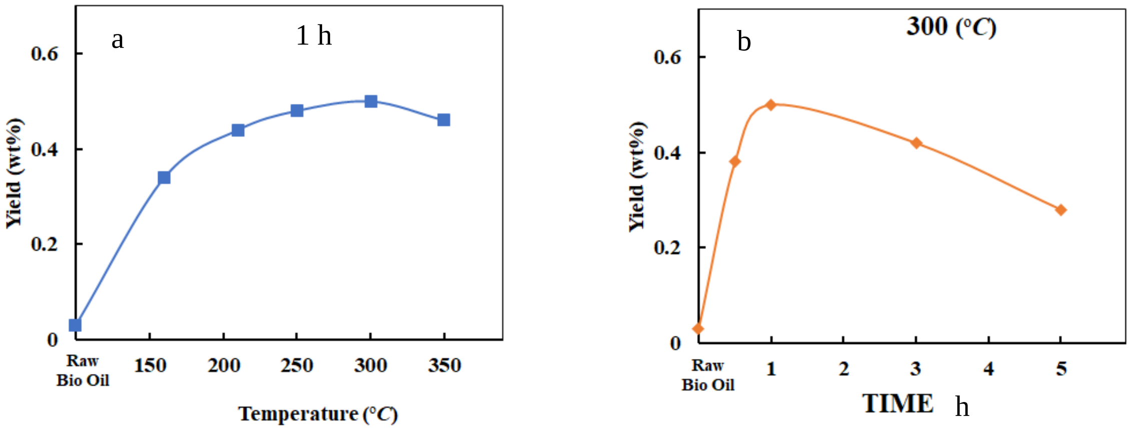


Figure 5.10 Effect of HDO temperature and time on the concentration of cyclopentanone. Uusing stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium.

The yield of cyclopentanone at different HDO time is shown in Figure 5.10 b. The yield reached maxima after about 1 h of HDO at 300 °C and decreased monotonically up to 5 h of HDO reaction.

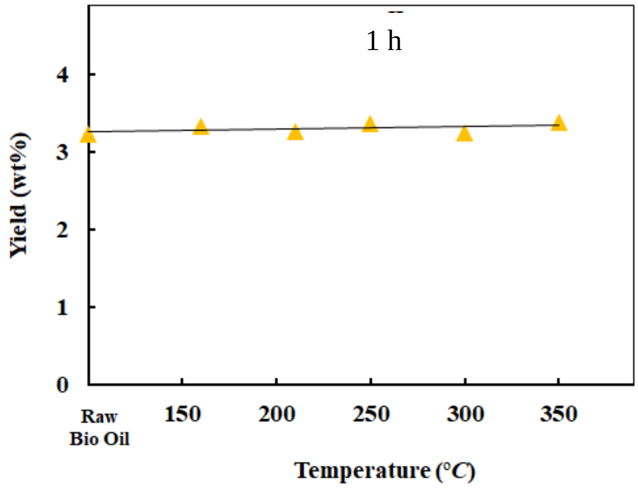


Figure 5.11 Effect of HDO temperature on the concentration of Acetic acid
Using stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium

Carboxylic acid is the major factor in high acidity and instability of bio-oil and acetic acid is the most abundant of which with yield of 3.13 wt.%. The concentration of acetic acid in the feed and produce oil at different HDO temperature is shown in Figure 5.11. The results shows constant yield of this compound at all the HDO temperatures. This is because hydrogenation of carboxylic acids requires more severe conditions such as higher HDO temperature and hydrogen pressure (Elliott, 2007).

The lignin building blocks are monolignols and the bio-oil phenolic compounds are derived from monolignols such as sinapyl alcohol, coniferyl alcohol and p-coumaryl alcohol (Zakzeski et al., 2010). Monolignols availability varies depending on type of biomass feedstock. For example about 90 wt.% of monolignols available in softwood biomass are coniferyl alcohol. On the other hand, hardwood biomass ligin contains approximately 60 wt. % of coniferyl alcohol and 40 wt.% sinapyl alcohol. Thus proportional amount of guaiacol and syringol are present in pyrolysis oil derived from hardwood biomass (Chen et al., 2011).

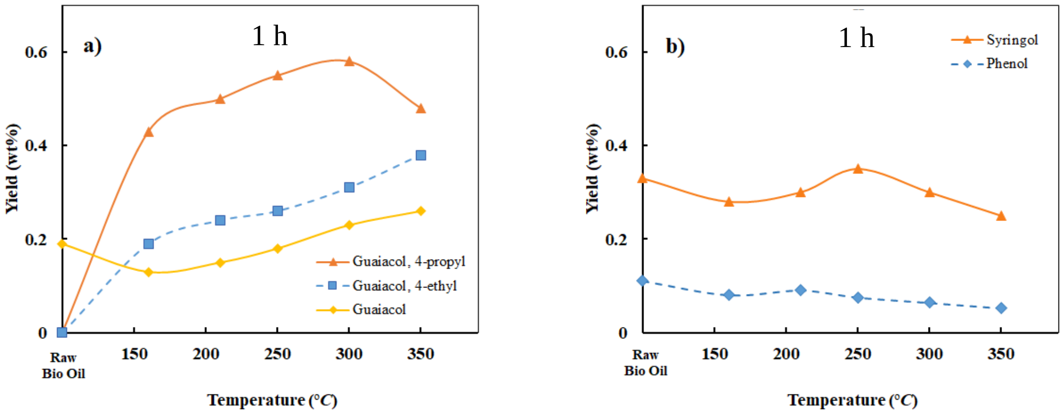


Figure 5.12 Effect of HDO temperature on the concentration of a) Guaiacols b) Syringol and Phenol
Using stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium

The yields of propyl guaiacols, ethyl guaiacols and guaiacols in produced oil at HDO temperature of 160 to 350°C is shown in Figure 5.12 a). The results showed an increase in the concentration of propyl guaiacols and ethyl guaiacols at higher HDO temperature, which indicate the depolymerisation and breakdown of lignin-oligomer at higher temperature and therefore the reduction in viscosity. From Figure 5.12 b) the decrease of yield of phenols with increasing of HDO temperature attributes to its conversion to hydrocarbons i.e alkanes (Kim et al., 2014). On the other hand, in produced oil at 160 °C, the yields of simpler methoxy phenols (guaiacol 5.12 a and syringol 5.12 b) decreased, while at higher HDO temperature the yield of the compounds increased. The increasing yields of guaiacol and syringol are because of the breakdown of lignin-oligomer similar to propyl guaiacols and ethyl guaiacols. On the other hand the decreasing yields of guaiacol and syringol at below 200 °C reaction attributes to their hydrogenation (Li et al., 2011). Moreover, the significant decrease of syringol yield at 300 and 350 °C, is also caused by hydrogenation which suggests higher temperature required for hydrogenation of syringol than guaiacol (Nimmanwudipong et al., 2011).

5.5 Effect of Time and Temperature on Gas Composition

Figure 5.13 shows the composition of the gas phase as a function of the HDO reaction temperature at 1 and 5 h. The gas sample collected at the end of each experiment was mainly hydrogen. Un-reacted hydrogen remained in the system indicates that the reactions were not performed under hydrogen starvation condition. As can be seen from the results in Figure 5.13, the gas phase consists of a mixture of, CO_2 (0.3–4.2 vol.%), CO (0.1–7.8 vol.%) and CH_4 (0.9–5.6 vol.%). The volumetric composition of the produced gas is significantly influenced by the operating conditions such as temperature and the reaction time. Duan et al. (2011) have also identified the temperature as the most effective parameter during HDO of algal bio-oil. The results from Figure 5.13 show the CO_2 and methane concentrations as a function of temperature increased at an about constant rate. Even though the increase of methane as a function of temperature was observed to be much lower than CO_2, at HDO reaction below 250 °C the amount of methane formed was significantly higher than CO_2.

In all of the experiments carried out at different HDO conditions, the volumetric composition of CH_4 increased with reaction time. The results also show higher methanation at higher temperature leading to an increase with reaction time (Lu et al., 2006).

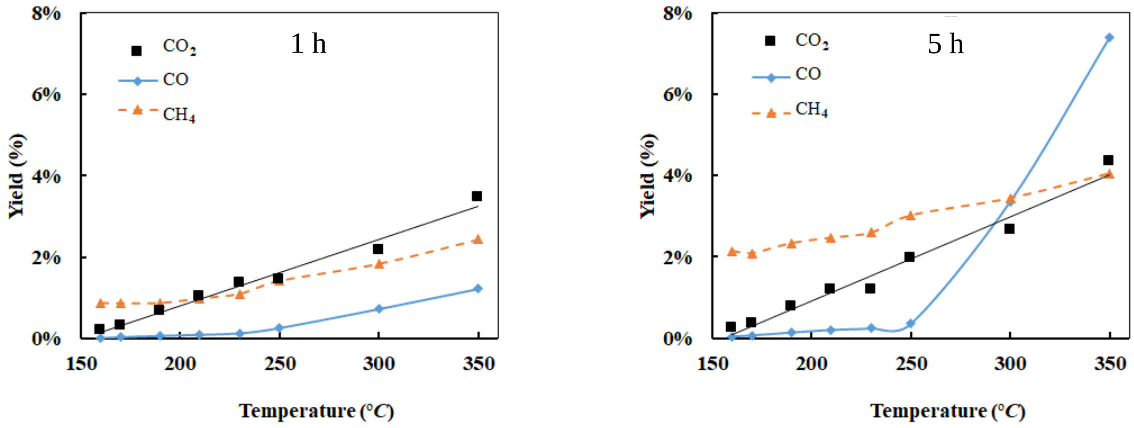


Figure 5.13 Effect of HDO temperature and time on the produced gas composition
Using stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium.

CO and CO_2 are initially formed because of decarbonylation and decarboxylation respectively (Knesevic et al., 2009). The amount of CO increases significantly at HDO temperature above 250 ^oC; This might suggest that, after an initial low production at a lower temperature, further CO is formed by gasification at higher temperature (Kubickova et al., 2005). Moreover, the concentration of CO is also dependent on the reaction time, since the CO gas yield is increased significantly at higher HDO temperature when the holding time increased. The formation of CO which is the fastest steps to gas formation is because of the thermal cracking reaction that occurred at higher HDO temperature which leads to decarbonylation. As the reaction time increased, other reaction such as methanation potentially maintained the amount of CO_2. This is also in line with finding of Wawrzetz et al. (2010). In another study by Yathavan and Agblevor (2013), it is suggested that decarbonylation reaction is the main route for production of CO in HDO and explains its high concentration. Moreover, Fisk et al., (2009) proposed two main routes (reforming and C–O bond cleavage) for conversion of oxygenated compound into gases in the bio-oil upgrading; The oxygen is rejected as CO_2 and hydrogen produced in reforming reaction, while C–O bond cleavage produce water as the co-product. Conversion of lighter oxygenated compounds is likely to occur through reforming pathway, whereas for aromatic compounds oxygen is likely rejected by C–O cleavage. This is because of the stronger C–C bonds of aromatic compounds. Equation 5.2 shows the reforming reaction of bio-oil which is endothermic and Equation 5.3 shows the Water Gas Shift (WGS) moderately exothermic reaction. However, the overall process is endothermic (Remon et al., 2016). As a result, an increase in HDO reaction temperature, increase the equilibrium portion of hydrogen and CO of the produce gas and decrease the concentration of CO_2, because of the exothermic nature of WGS reaction. Additionally, at high-temperature HDO the coke formation increases and therefore the portion of C in the gas decreases. This also explains the increase of the concentration of CO_2 in the gas at higher HDO temperature.

$$_nH_mO_k + (n - k)\, H_2O \rightarrow nCO + (n + m/2 - k)H_2 \tag{5.2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{5.3}$$

5.5.1 *Hydrogen Consumption*

Hydrodeoxygenation reaction requires a large amount of hydrogen to ensure sufficient oxygen removal. Hydrogen consumption during the HDO significantly contributes to the process operational cost (Elliott et al., 2007) and reduction of its use is of prime interest. The calculated hydrogen consumption based on the mass balance at different HDO temperatures as a function degree of deoxygenation is presented in Figure 5.14.

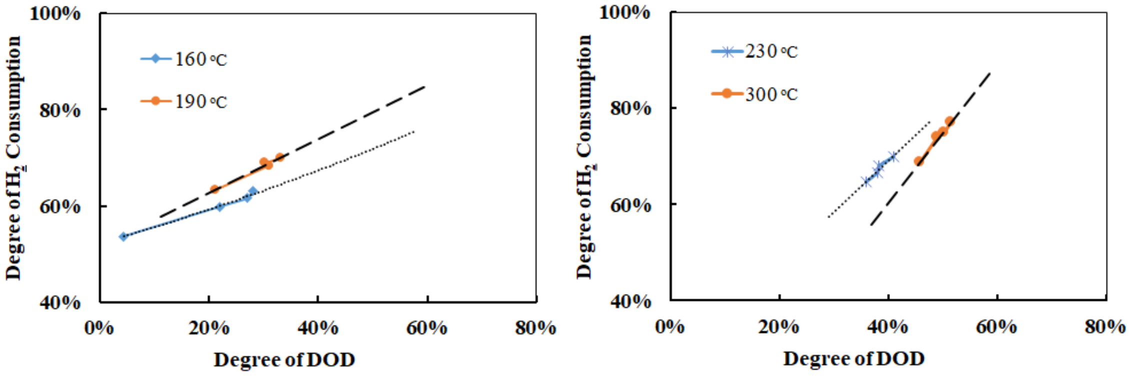


Figure 5.14 Degree of Hydrogen Consumption (%) as a function of degree of DOD (%)
Using stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium.

The results clearly show the effect of degree of DOD on the consumption of hydrogen is dependent on the temperature. Thus, the rate of hydrogen uptake increases significantly when operating the HDO reaction at 160 °C compared to 300 °C. This is in line with the results of produced gas composition, where HDO reaction at 350 °C produced the highest concentration of CO. In this case, oxygen was mostly rejected as carbon via CO_2. Therefore, the rejection of oxygen as CO_2 in the case of HDO at low temperature had preeminence over CO production because two oxygen atoms are removed with one carbon. Hence less carbon was consumed for rejection of oxygen. In addition to that, HDO at high temperature produced more hydrocarbon gases especially methane, which uses high amount of available hydrogen.

According to the observations of Elliott et al. (2007), this is because of the different reactivity of the different types of functional groups in the bio-oil (Grange et al., 1996). He has summarised different functional group's activation energies, the required temperature for the start of reaction (iso-reactivity temperatures) and hydrogen consumption over a Co–MoS_2/Al_2O_3 catalyst. He finds the ketone deoxygenation activation energy to be relatively low, which suggests the deoxygenation of ketones at temperature as low as 190 ^{o}C. On the other hand, molecules such as furans or phenols, which contain more complex bound, have higher activation energy and required significantly higher temperature for deoxygenation reaction. Furimsky et al. (2009) has summarised the different compounds on the basis of their apparent reactivity:

alcohol > ketone > alkylether > carboxylic acid > phenol > alkylfuran > benzofuran > dibenzofuran

This explains the steep increase of hydrogen consumption as a function of DOD at higher HDO temperature. A highly reactive oxygenated compound such as ketone, is converted at low HDO temperature with low hydrogen consumption. But higher temperature requires for hydrogenation of more stable compounds with sterically hindered oxygen and therefore high HDO temperature increases the hydrogen consumption as result of high DOD (Furimsky et al., 2009).

5.6 Effect of Polar and Non-Polar Solvent on Improvement of HDO

The hydrogen-donating hydrocarbons, for example, tetralin, have been usually used as solvents for HDO (Zhang et al., 2015). But, they hardly blend with the bio-oil due to their hydrophobicity and the characteristics of bio-oil are improved only to a few extents. The exceptional properties of the supercritical fluids, for instance gas-like diffusivity and viscosity, faster rates of heat and mass transfer, liquid-like density and dissolving power have drawn increased attention to the supercritical fluid as HDO solvent for bio-oil (Baiker, 1999). For the improved stability of bio-oil through the removal of pyrolytic lignin, the supercritical fluid is found to be effective as per the previous studies (Zhang et al., 2010). Methanol and ethanol are the supercritical solvents that have been used mainly for the upgrading of the bio-oil (Zheng et al., 2012; Dang et al., 2013; Peng et al., 2009). During different processes, the solvents undergo various reactions and can be categorized as polar and non-polar (Huang et al., 2014). As a result, the effects of various types of solvents specifically cyclohexane (nonpolar) and ethanol (polar) upon the bio-oil HDO have been examined in this section. The important factor to be considered is the quality of the oils that have been upgraded as the possible co-feeds for the process of co-refining. Hence, it is preferred to reduce or prevent self-polymerization by the process of upgradation (Mazaheri et al., 2010). In this regard, the comparison of the physical features of acidity, viscosity, the degree of de-oxygenation and water content has been performed.

Table 5.3 Critical Characteristics of Solvents

Solvent	Classification	Molecular Weight (g/mol)	Critical Temperature (℃)	Critical Pressure (bar)	HDO Liquid Yield (%)
Ethanol	Polar	46.07	240.9	61	14.2
Cyclohexane	Non-polar	84.16	278.8	40.73	0

The HDO reaction of bio-oil carried out under the temperature of 280 or 350℃ and pressure of 100 bar of hydrogen for 1 hour. In a ratio of 4:1 oil/solvent (w/w), one of the solvents (cyclohexane and ethanol) was added to each sample of the experiment and the 3 wt.% catalyst corresponding to the bio-oil was also added. The increment in the formation of desired product and heating value and reduction in the yield of coke by increasing the mass ratio of ethanol to bio-oil has been shown by the study of Mazaheri et al (2010). Therefore, it is clear that an important role has been played by the composition of the solvent, type of the solvent and the quantity of solvent that has been used with respect to the bio-oil during the HDO treatment, in the HDO oil quality. However, this section only tries to compare the effect of these solvents. Pd/C used contained 5 wt.% of active metals on active charcoal. The catalyst was added to each sample; each of the solvents was chosen, which existed in the supercritical phase in the mildest running conditions (280 ^{o}C, 100 bar) used in this study (Table 5.3) assuming the critical temperature of solvents won't change when mixed with bio-oil. During the process of HDO, the solvents operated as the co-reactants and the quality of the bio-oil was also affected by them. Hence, the solvents HDO itself was achieved. Table 5.2 describes its features. Four main products coke, two immiscible liquids i.e. organic phase (viscous oil) and aqueous phase (light oil) and gas were obtained after the reaction. After that, by filtration the fraction of the bio-oil that has been stabilized i.e. organic phase, separated from the products and was then analyzed.

5.6.1 *Effects of Solvent on Product Phase Distribution*

Table 5.4 presents the HDO products yields on the basis of the weight of the bio-oil and there has been a significant variation in these yields for different solvents that have been used. Significant composition differences with different temperatures of reaction were shown by the product yields when ethanol was used as an HDO solvent. For ethanol as a solvent, the oil yield in relation to the weight of the bio-oil reduced from 55.3 to 46.8% with the increase in temperature. Whereas, the oil yield increased, from 52.3 to 59.1% and as there was a further increase in the temperature is decreased to 54.6% when cyclohexane was sued as a solvent. It has been indicated by the results that the cyclohexane's HDO ability maximized at a constant temperature of 350 ^oC along with a more minor accelerating effect, decomposition as well as prevention of the formation of coke above the temperature of 280 ^oC. When ethanol (polar solvent) was used, the increase in the reaction temperature from 280 to 350 ^oC, caused steady increment the gas yield from 3.4 to 5.7 wt.%. On the other hand, there was a variation between 5.2 and 5.4% in the gas yield when cyclohexane was used. Hence, it has been determined that further decomposition has been accelerated by the polar solvent i.e. ethanol with an increase in the reaction temperature (Hwang et al., 2014). This can be explained by the polarity reduction and increment in the oil affinity of the water-soluble or polar organic compounds that have been caused by the HDO.

When cyclohexane was used as a solvent, there was the least variation in the yields of the four main products with various reaction temperatures that were used. The range of the gas yield was 5.2 and 5.4% generally, however, the gas yield range for ethanol was 3.4 and 5.7%. This happened due to the hydrodeoxygenation of entire cyclohexane to gas (Table 5.3) however small quantity of hydrodeoxygenated ethanol (~ 15 wt.%) continued in the liquid phase at 280 ^oC. As a result, with the increase in temperature, the formation of Char was prevented homogeneously by the cyclohexane (non-polar solvent). Between the two types of solvents that are used in this experiment, only ethanol can experience hydrogen bonding with the hydroxyl group that is present in the bio-oil. The hydrogen bonding may occur through reduction and hydrogenation of cyclohexane that contends with HDO in the cyclohexane case (Fortman et al., 1991). When ethanol was used in HDO, the portion that is based on the aqueous solvent i.e. the light oil yield was higher as compared to when cyclohexane was used as shown in Table 5.3. The further decomposition of organic compounds into the light oil can be accelerated by the hydrogen bonding between the bio-oil and the solvent (Joshi et al., 2012). The most stable solvent, out of the two solvents that are used in this experiment, with increasing temperature is the non-polar cyclohexane. Whereas, in the prevention of the formation of the coke, the polar ethanol was found to be more effective. The hydrogen bonding between the bio-oil and the solvent may result in the unsteady changes of the product yield that has been obtained from ethanol

Table 5.4 Physiochemical, elemental analysis and mass balance of bio oil and collected organic phase

Using Ethanol and cyclohexane as solvents at 280 and 350 ^{o}C with stirred batch reactor over 5 wt% Pd/C, 0.03 Catalyst/Oil ratio under 100 bar hydrogen medium

	Bio-oil	No solvent	Ethanol		Cyclohexane	
			280 ^{o}C	350 ^{o}C	280 ^{o}C	350 ^{o}C
Water content (wt%)	23.2	11.4	5.2	1.5	12.8	11.1
Viscosity (Pa.S)	0.04	0.056	0.030	0.028	0.037	0.35
TAN (mg KOH/g oil)	221.8	129.7	75.5	73.3	96.3	89.4
Product phase distribution (wt%)						
Organic phase		52.3 (±0.6)	55.3(±1.5)	46.8(±0.4)	59.1(±1.1)	54.6(±0.9)
Aqueous phase		38.8 (±0.9)	39.2(±1.2)	44.8(±1.1)	33.6(±0.9)	37.9(±0.8)
Gas phase		4.8 (±0.03)	3.4(±0.09)	5.7(±0.05)	5.2(±0.06)	5.4(±0.04)
Coke		3.6 (±0.08)	1.9(±0.05)	2.5(±0.08)	2.3(±0.03)	2.1(±0.05)
Elemental analysis (wt%)						
C	55.1	61	63.8	72.2	67.4	69.1
H	6.5	8.8	8.4	8.8	7.8	8.1
O	38.5	22.1	20.4	15.6	19.1	16.8
N	0.34	0.21	0	0	0	0
DOD (%)		48.15	54.24	69.08	59.44	65.20
HHV (MJ/kg)	30.88	33.95	34.28	37.19	34.70	35.40

5.6.2 *Physicochemical Properties of Liquid Products*

During the process of HDO, demoisturization, deoxygenation, hydrocracking, hydrogenation and hydrogenolysis were used to improve the properties of the bio-oil for example, thermal stability, acidity and heating value (Joshi et al., 2012). Whereas in the reaction, the solvent can also perform as a co-reactant (Hwang et al., 2015). However, on the basis of the used HDO solvent, there may be a difference in the improvement of bio-oil. The differences in the physical properties that have been arisen from the utilization of different solvents for example, elemental composition, acidity (TAN , total acid number), chemical composition, water content and viscosity, have been investigated in this study, in order to find the ways in which the quality of the bio-oil has been influenced by the solvent or co-reactant. As has been discussed earlier, after the process of HDO, the bio-oil becomes a phase that is separated into an organic phase (viscous oil) and an aqueous phase (light oil). Therefore, in this study, the properties of both phases are being discussed.

5.6.2.1 Organic Phase Properties

In Table 5.4, quite a few representatives of physicochemical features of produced oils and bio-oils were measured and displayed. The properties of oil were improved by the HDO reaction even when there was no addition of the solvent in the reactants. Whereas the features of acidity and viscosity that can lead to the main engine-related problems cannot be improved by the HDO. The produced oil has reduced acidity from 221.8 to 73.3-96.3, water content from 23.2 to 1.5-11.1 wt.%, viscosity from 0.04 to 0.028-0.037 Pa.S and also improved HV from 30.88 to 34.28 -37.2 mJ/kg as compared to the bio-oil.

When ethanol was used, the water content that is related to the heating value a, reduced from 23.2% in bio-oil to 1.5-5.2 wt% in oil fraction and when cyclohexane was used, it reduced to 11.1-12.8 wt% in bio-oil due to the dehydration or demoisturization of the organic phase. As compared to cyclohexane, the dehydration or demoisturization was carried out more effectively in ethanol but the opposite sequence of these solvents was followed by the consistency of these reactions with the increase in temperature. This was because of the hydrogen bonding between the polar ethanol and hydrogen bonding. When cyclohexane was used as a solvent, the water was not completely separated to the light oil as the non-polar cyclohexane does not experience hydrogen bonding with water which has been demoisturized from the bio-oil and it also does not affect the HDO temperature. A steady increasing trend was shown by the dehydration or demoisturization with the rising temperature. As compared to the TAN of bio-oil that is 221.8 KOH/g oil, the organic phase TAN reduced to 73.3-96.3 mg KOH/g oil. A trend similar to water content was followed by it, as the acids and phenolic hydroxyl groups can experience reactions or hydrogen bonding with polar solvents. In the removal of acids from the bio-oil, lower activity was shown by cyclohexane as compared to ethanol. This is probably because the ethanol reacted with the acids that have been derived from carbohydrates decomposition, and their conversion into the desired compounds, for example, ketones and esters. Nevertheless, the cyclohexane that experienced the process of HDO was converted to the gas phase and therefore it does not react with the compounds present in the bio-oil.

The important point of the reformation of the bio-oil into fuel is the viscosity reduction as during the injection of bio-oil into an engine, many disadvantages have been produced by its high viscosity (Martinez-Palou et al., 2011). The major contributors, especially in the bio-oil viscosity, include the compounds containing nitrogen, aldehydes and sugars, for example, levoglucosan (Oasmaa et al., 2003). Whereas, through dehydration, hydrogenation, decarboxylation and ring-opening, the levoglucosan has been converted into esters by the HDO reaction (Hwang et al., 2015). Hence, for bio-oil, the viscosity lowered from 0.04 Pa.s to 0.028-0.037 Pa.s for the organic phase. In comparison to the bio-oil, over 25% under ethanol and 10 % under cyclohexane of the viscosity has been reduced by all the fractions of the produced oil but the trend of the changing viscosity remains similar along with the other properties.

The calorific value in bio-oil was increased from 30.8 mJ/ kg to 34.3-37.19 mJ/kg in the produced oil. Irrespective of the conditions of the reactions the calorific values of all the organic phases were found to be similar. It was found especially in ethanol that the deoxygenation of the organic compounds was accelerated by certain temperatures. For example, even at a temperature of 280 ^{o}C the deoxygenation was catalysed by ethanol but it was found to be more effective in the acceleration of the process of deoxygenation above the temperature of 350 ^{o}C.

5.6.2.2 Aqueous Phase Properties

A solvent-mixed aqueous phase called the light oil has been obtained after the reaction of HDO. In this reaction, light oil can also be obtained even when there was no solvent utilized but its colour was dark brown in this case like that of the organic phase. The organic compounds in the light oil were found to have compositions that were similar to the compounds of the bio-oil. Contrarily, when a solvent was used in this reaction, the light oil was found to be opaque and has a light yellow colour. It also contained water and some monomers. The representative features of the light oils that have been yielded, for example, acidity and water content have been described in Table 5.5. Acidity and high content of water are the remarkable features of the light oils. The organic phase that have been obtained from the reactions containing ethanol were found to have lower contents of water as compared to the reactions that contained cyclohexane, due to the hydrogen bonding effects that have been discussed earlier. Whereas the light oils water content was also lower when ethanol was used that is 61.5(±2.1) wt.% in comparison to that when cyclohexane was used that is 67.8(±2.6) wt.%. It has been suggested by the results of this experiment that hydrogenolysis and dehydration can be performed simultaneously in the polar atmosphere (Rode et al., 2012). Moreover, when cyclohexane was used, the fact that most of the cyclohexane has been converted into the gas phase has affected the features and yields of the light oil (Table 5.4). The 68.5 wt% water content of light oil that has been obtained without solvent can also provide support to it. There has also been an increase in the acidity (184.5-231.2 mg KOH/g oil) and a similar tendency of water content was also exhibited. The presence of monomeric phenolic compounds or the high content of water resulted in high acidity (Oasmaa et al., 2010).

Table 5.5 Water content and acidity of the collected aqueous phase

	No solvent	Ethanol	Cyclohexane
Water content (wt%)	68.5(±2.4)	61.5(±2.1)	67.8(±2.6)
TAN (mg KOH/g oil)	358.8	184.5	231.2

5.7 Effect of Bio Pd versus Commercial Pd/C

5.7.1 *Bio-Oil Characterisation Effect on DOD*

The performance of the bio-Pd catalyst in the bio-oil upgrading was compared to the commercial Pd supported on activated carbon catalyst at verities of HDO temperature ranges. Table 5.6 presents the yield of product phase distribution of HDO at 190, 250 and 350 °C for both catalysts. Bio-Pd showed a similar performance to Pd/C in terms of maintaining the yield of organic and aqueous phase at all HDO reaction temperature. However for higher temperature HDO the yield of organic phase slightly reduced by ~0.4 wt%.

Using stirred batch reactor over 5 wt% Pd/C and 5 wt% bio-Pd, 0.03 Catalyst/Oil ratio with 3 h reaction time under 100 bar hydrogen medium.

Table 5.6 Product yield distribution of HDO

Using stirred batch reactor over 5 wt% Pd/C and 5 wt% bio-Pd, 0.03 Catalyst/Oil ratio with 3 h reaction time under 100 bar hydrogen medium.

Catalyst	**Pd/C**			**Bio-Pd**		
HDO Temperature	190 °C	250 °C	350 °C	190 °C	250 °C	350 °C
Organic phase	58.6 (±0.8)	56.1 (±0.4)	51.9 (±0.6)	58.7(±1.1)	56.3(±0.3)	51.5(±0.9)
Aqueous phase	35.4 (±0.9)	38.3 (±0.9)	38.1 (±0.1)	35.6(±0.9)	37.9(±0.8)	38.3(±0.8)
Gas phase	4.1 (±0.05)	4.4 (±0.06)	5.7 (±0.5)	3.9(±0.06)	4.6(±0.04)	6.6(±0.04)
Coke	1.3 (±0.02)	1.8 (±0.08)	4.3 (±0.6)	1.2(±0.03)	1.7(±0.05)	3.6(±0.05)

When bio-Pd used during lower temperature HDO reaction of 190 and 250 °C, slightly less coke formation was observed (0.07 and 0.06 wt% respectively). However, for HDO at 350 °C the difference of coke formation was more significant between the catalysts with ~16 wt.% less coke production of bio-Pd compared to commercial Pd/C. Conversely, the gas produced during HDO reaction at high temperature of 350 °C was ~15 wt.% higher than same reaction using Pd/C. This could potentially indicate that the bio-Pd activity is reduced significantly at higher HDO temperature, which caused higher gasification reaction leading to formation of higher gas yield.

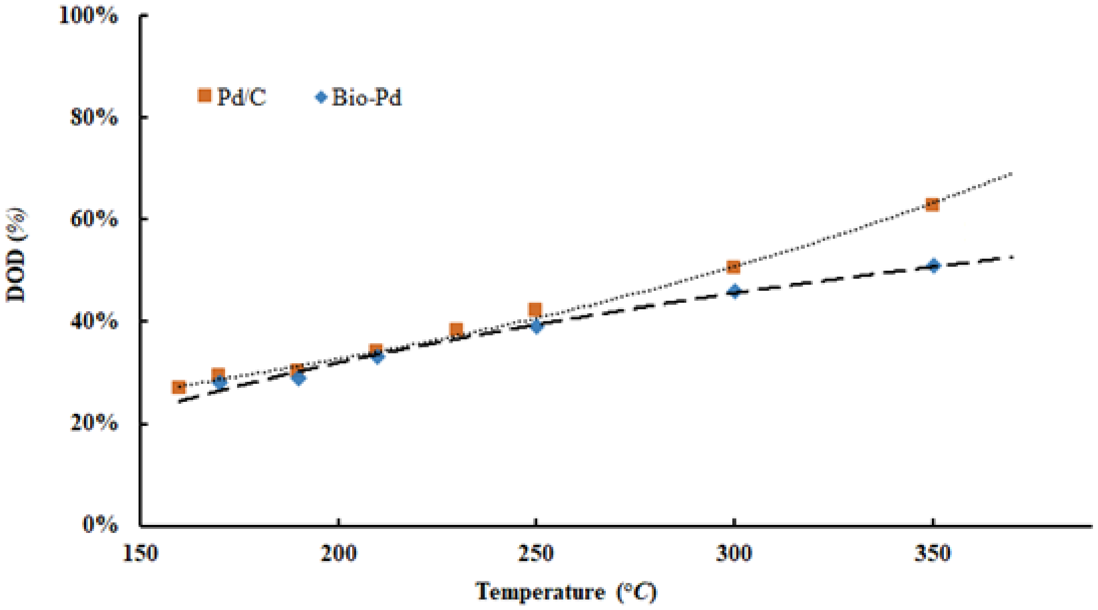


Figure 5.15 Effect of temperature on DOD (%)
Using stirred batch reactor over 5 wt% Pd/C and bio-Pd, 0.03 Catalyst/Oil ratio with 3 h reaction time under 100 bar hydrogen medium (bio oil oxygen content 38.5%)

Figure 5.15 illustrates a comparison of catalysts performance in terms of the DOD of upgraded bio-oil at different HDO temperature. At all of the HDO reaction temperature the commercial Pd/C showed higher ability in deoxygenation of bio-oil. The performance of bio-Pd at lower HDO temperature (170 - 210 °C) was similar to the commercial catalyst, while at higher HDO temperature above 250 °C, bio-Pd performance in removing oxygen was decreased significantly.

The viscosity of upgraded oil presented in Figure 5.16 also shows a better performance of bio-Pd at lower HDO temperature. For lower temperature HDO reaction the viscosity of produced oil is reduced as temperature increased. The lowest viscosity of upgraded oil (0.033 Pa.s for Pd/C and 0.038 Pa.s for bio-Pd) achieved at 250 °C HDO. At higher HDO temperature above 250 °C viscosity of produced oil using both catalysts started to increase due to polymerisation.

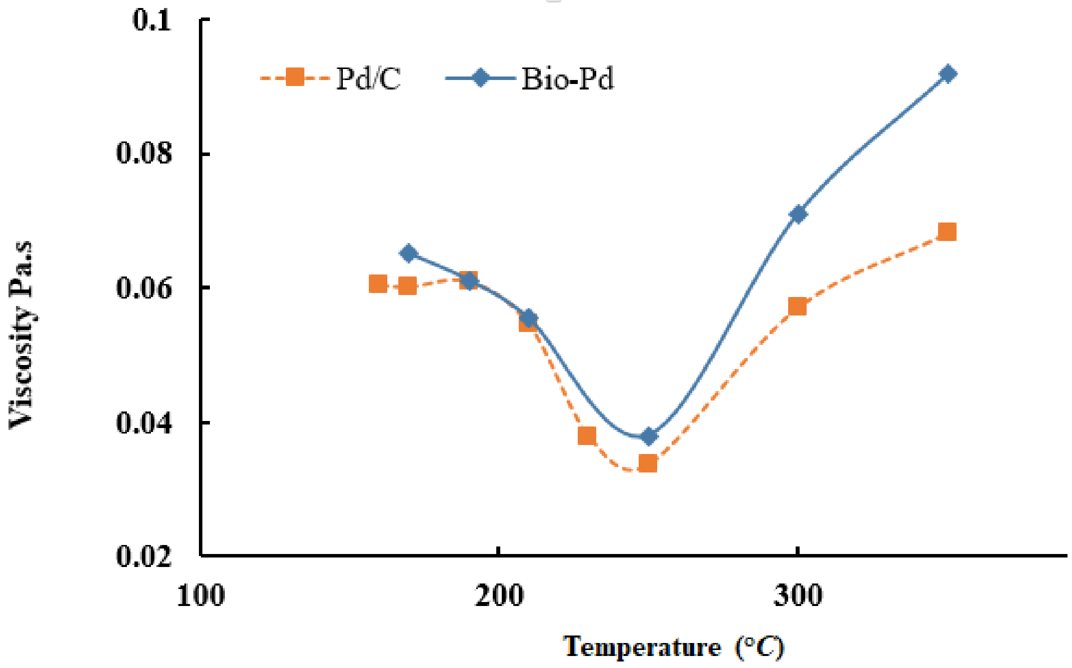


Figure 5.16 Effect of temperature on product oil viscosity
Using stirred batch reactor over 5 wt% Pd/C and bio-Pd, 0.03 Catalyst/Oil ratio with 3 h reaction time under 100 bar hydrogen medium (bio-oil viscosity 0.04 Pa.S at 20 °C)

However, in the case of bio-Pd the increase of viscosity is much more significant compared to the commercial Pd/C. The lower activity of bio-Pd at higher HDO temperature could attribute to nature of its support material which is less stable compared to activated carbon. The biomass support undergoes decomposition at higher temperature and leaves the metals NPs unsupported. This potentially reduces the bio-Pd catalytic activity for HDO of bio-oil at high-temperature. This is also in line with the results of DOD as well as relatively higher gas yield at high HDO temperature. Moreover, the slightly higher viscosity of produced oil using bio-Pd at 170 ºC indicates the hydrogenation reaction occurs at lower temperature in the case of Pd/C.

5.7.2 *Catalyst Characterisation*

Figure 5.17 shows thermogravimetric profile of both catalysts before and after HDO reaction. The maximum weight loss of activated carbon support of commercial Pd/C because of carbon oxidation is 390 ºC, while the observed maximum weight loss of reclaimed Pd/C was at 340 because of the coke formation. The maximum weight loss bacterial biomass support of bio-Pd lost at 245 ºC which is due to its nature of its bacterial support and its decomposition. The decomposition of bio mass is likely to occur through pyrolysis reaction at higher temperature. Moreover, the significantly higher weight loss compare to reclaimed bio-Pd confirms the conversion of biomass support of the catalyst during the HDO reaction. This confirms the weaker support of bio-Pd compares to commercial Pd/C, hence its lower activity at higher HDO reactions.

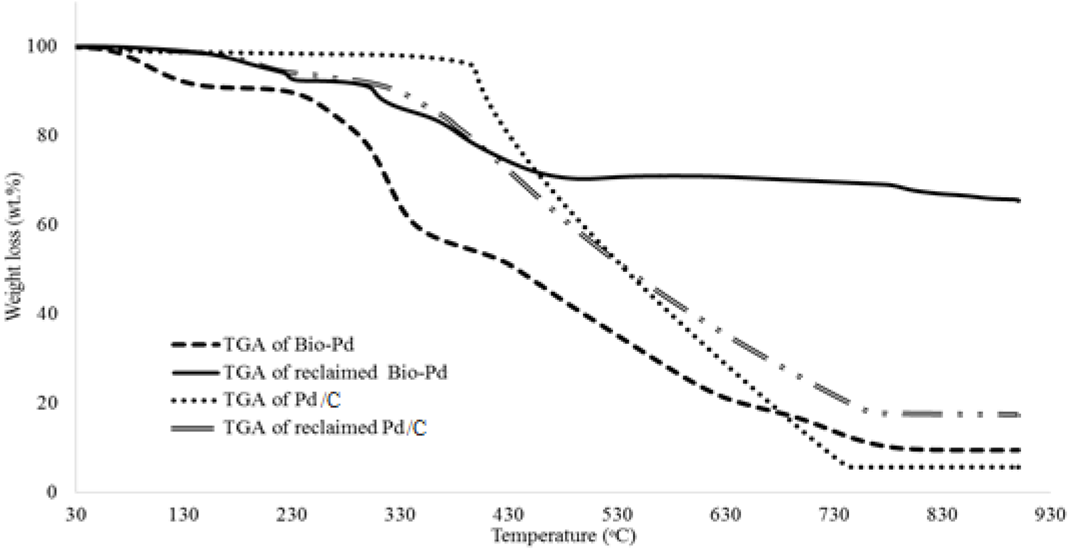


Figure 5.17 TGA of fresh and the deposited coke of bio-Pd and Pd/C

5.8 Conclusion

The effects of process conditions, particularly the reaction time and temperature for HDO of fast pyrolysis oil in the presence of 5 wt.% Pd/C was investigated in a parr batch reactor setup. The produced oil after each experiment were compared in terms of the product yield, viscosity, water content and degree of deoxygenation.

At HDO temperature between 160 to 250^{o}C the aqueous phase and gas yield increased with the function of reaction temperature at the rate of 0.03% and 0.01% per degree respectively. Also most of oxygen was rejected in the form of water, and insignificant amount oxygen was rejected as a gas form. The decrease in the water content of the organic phase was more significant at HDO reaction temperature below 250 ^{o}C. This tendency was because of the higher dehydration of the bio-oil which was improved with increased temperature.

The highest viscosity was observed for produced oil of 190 ^{o}C HDO reaction for 1 hr time, where the yield of the aqueous phase was 37 wt%. The viscosity of the produced oil at 3 h of HDO decreased from 0.061 Pa.S at 190 ^{o}C to a minimum of 0.033 Pa.S at 250 ^{o}C before increasing to a maximum of 0.068 Pa.S at 350 ^{o}C. The significant decrease of the viscosity at moderate temperature between 190 to 300 ^{o}C is because of hydrocracking and hydrogenation reactions which can occur at higher temperature. The viscosity of produced oil increased with increasing of HDO temperature above 250 oC because of polymerisation reaction. More coke is produced at higher temperature which causes catalyst deactivation in longer HDO reaction time. Therefore polymerization reaction rate increases while the hydrogenation rate decreases as the catalyst lose its performance activity.

The GC-MS results confirmed all aldehydes identified in raw bio-oil disappeared from the produced oil after hydrotreatment for 1 h at 300 °C. The yield of cyclopentanone increased with increasing HDO temperature up to 300 °C, above which the yield slightly decreased. Carboxylic acids concentration remained constant as it requires more severe conditions for hydrogenation. The concentration of propyl guaiacols and ethyl guaiacols increased at higher HDO temperature which indicates the depolymerisation and breakdown of lignin-oligomer at higher temperature and therefore the reduction in viscosity.

The gas-phase consists of a mixture of, CO_2 (0.3–4.2 vol.%), CO (0.1–7.8 vol.%) and CH4 (0.9–5.6 vol.%). The amount of CO in the gas production increased significantly at HDO temperature above 250 ^oC; suggesting, after initial low production of CO at lower temperature, further CO is formed by gasification at higher temperature. In all of the experiments carried out at different HDO conditions, the volumetric composition of CH_4 increased with reaction time.

When ethanol was used as a solvent, the oil yield in relation to the weight of the bio-oil reduced from 55.3 to 46.8% with the increase in temperature. Whereas, the oil yield increased, from 52.3 to 59.1% and as there was a further increase in the temperature is decreased to 54.6% when cyclohexane was sued as a solvent. The produced oil has reduced acidity from 221.8 to 73.3-96.3, water content from 23.2 to 1.5-11.1 wt%, viscosity from 0.04 to 0.028-0.037 Pa.S and also improved HV from 30.88 to 34.28 -37.2 MJ/Kg as compared to the bio-oil. When ethanol was used, the water content that is related to the heating value a, reduced from 23.2% in bio-oil to 1.5-5.2 wt% in oil fraction and when cyclohexane was used, it reduced to 11.1-12.8 wt% in bio-oil due to the dehydration or demoisturization of the organic phase. As compared to the TAN of bio-oil that is 221.8 KOH/g oil, the organic phase TAN reduced to 73.3-96.3 mg KOH/g oil. In the removal of acids from the bio-oil, lower activity was shown by cyclohexane as compared to ethanol. In comparison to the bio-oil, over 25% under ethanol and 10 % under cyclohexane of the viscosity has been reduced by all the fractions of the produced oil but the trend of the changing viscosity remains similar along with the other properties.

The lowest viscosity of upgraded oil (0.033 Pa.s for Pd/C and 0.038 Pa.s for bio-Pd) achieved at 250 °C HDO. At higher HDO temperature above 250 °C viscosity of produced oil using both catalysts started to increase due to polymerisation. However, in the case of bio-Pd the increase of viscosity is much more significant compared to the commercial Pd/C.

The performance of bio-Pd in terms of DOD at lower HDO temperature (170 - 210 °C) was similar to the commercial catalyst, while at higher HDO temperature above 250 °C, bio-Pd performance in removing oxygen was decreased significantly. The biomass support undergoes decomposition at a higher temperature and leaves the metals NPs unsupported. This potentially reduces the bio-Pd catalytic activity for HDO of bio at high temperature. The maximum weight loss bacterial biomass support of bio-Pd lost at 245 °C which is due to the nature of its bacterial support and its decomposition.

6 Conclusions and Recommendations

6.1 Conclusions

The main target of this study was to compare the performance of bio-Pd catalyst in comparison to commercial catalyst in two different application heavy oil and bio-oil upgrading. The upgrading of heavy oil was conducted in a stirred batch autoclave reactor of 100 mL capacity at temperature between 350 to 450 ^{o}C under 20 bar nitrogen and hydrogen atmosphere, while the upgrading of bio-oil samples were conducted a stirred batch reactor of 100 mL capacity Parr reactor at temperature between 160 to 350 ^{o}C under 100 bar hydrogen.

The upgraded heavy oil product was evaluated through means of quantifying degree of API gravity and change in viscosity of upgraded oil, coke content, the heavy fractions conversion and impurities such as coke and asphaltene content. While the evaluation of upgraded bio oil product was done by comparing the produced oil after each experiments in terms of the product yield, viscosity, water content and degree of deoxygenation.

6.1.1 *Heavy Oil*

It was found that the quality of the produced oil was significantly increased from 13 up to 24 ^{o}API gravity in the presence of a dispersed catalyst in the following order Ru/C > Pd/Alumina > Pd/C Pd/*E.coli* > Fe_2O_3. The yield of liquid oil obtained with Ru/C nanoparticles supported on carbon was 71.35 wt.% and 52.85 wt.%, with Pd supported on alumina 56.15 and 41.95 wt.%, and unsupported Fe_2O_3 68.32 and 50.2 wt.%, at 30 and 120 min reaction time respectively. The results also showed Ru/C as more effective in facilitating upgraded light oil with a 15.2 – 10.9 wt. % increase over Pd/Al_2O_3 at 30 and 120 min reaction time respectively. While the residue fraction (BP > 343 °C) decreased from 22 vol.% in the feedstock and 15 vol.% in thermal upgrading to 12 vol.%, for the upgraded oil by Fe_2O_3 and Pd/Al_2O_3 and 10 vol.% for Ru/C, the gasoline fractions respectively increased from 35 vol.% (feedstock) and 53 vol.% (thermal) to 58 vol.% (Pd/Al_2O_3) and 59 vol.% (Ru/C). In the case of Fe_2O_3 more middle distillates (4 vol.%) and slightly less (1 vol.%) low boiling fraction was produced compared to the non-catalytic reaction.

The significant differences in gas composition is the isomers iC_4–C_5 and olefins (C_2–C_4) were produced more with catalytic upgrading than thermal reaction. The hydrogen concentration of the produced gas composition decreased by 0.34 vol.% in the presence of Pd/Al_2O_3 and 0.56 vol.% in the presence of Ru/C. The spent hydrogen shows these catalysts may have contributed in promoting hydrogenation reaction which explains the higher produced oil quality in the presence of these catalysts. Among the catalyst Pd/Al_2O_3 gave the highest carbon rejection of 3.41 wt.% which is in correlation with mass balance. Notably, the presented value for carbon-rejection of catalytic upgrading is approximately half that of thermal upgrading. Moreover, thermal cracking, Fe_2O_3, Pd/Al_2O_3 and Ru/C reduced the produced oil sulfur content by 18, 20, 31 and 34 wt.% respectively.

The API gravity increment and viscosity reduction between produced oil by thermal cracking and upgrading with bio Pd was marginal, upgrading with bio Pd shows a benefit in terms of lower yield of coke against thermal and feed oil and also improved quality of produced oil with approximately 32% and 53% reduction in sulfur and asphaltene contents.

The use of cyclohexane was evaluated against that of hydrogen gas. The thermal reaction in the presence of cyclohexane under nitrogen atmosphere significantly reduced coke yield by 37%.wt compared with a nitrogen environment alone under the same conditions. Also, the coke decreased by 6–16 wt.% when cyclohexane was used as a hydrogen donor in the presence of catalyst NPs. An estimated 0.012 CH:oil ratio was found to suppress coke formation in a similar manner to upgrading under hydrogen atmosphere at the same conditions. This makes the solvent a potential alternative for use of hydrogen in the upgrading process. The results of the simulated distillation, viscosity reduction, asphaltene, sulfur, and metals content after upgrading showed that the alternative Pd/biomass nanoparticles have the potential of achieving a similar level of upgrading as obtainable with typical HDS catalyst particles such as Pd supported on carbon and alumina, respectively. Additionally, less coke formation and slightly higher improvement of produced oil were observed in the case of lower Pd loading of the cell. However, preparation of metal nanoparticles requires the significant experimental procedure. Additionally, the cost of preparing the biomass support using the anaerobic *E.coli* bacteria is relatively high, due to the need for exclusion of oxygen and the complex growth media used but other studies have shown the effective use of 'second hand' *E. coli* to make catalytically active bio-Pd (Zhu et al 2016 Appl Catal B) . Moreover, the cells can grow aerobically and then harvested and place them under N_2 to get them anaerobic which could potentially reduce the catalysts production cost. Future studies would address these challenges and nominate their suitable alternative.

6.1.2 *Bio-Oil*

At HDO temperature between 160 to 250 ^{o}C the water and gas yield increased with function of reaction temperature at the rate of 0.03 and 0.01 per degree of Celsius respectively. Also most of oxygen was rejected in the form of water, and insignificant amount oxygen was rejected as a gas form. The decrease of the water content of the organic phase was more significant at HDO reaction temperature below 250 ^{o}C. This tendency was because of the higher dehydration of the bio oil which was improved with increased temperature.

The highest viscosity was observed for produced oil of 190 ^{o}C HDO reaction for 1 hr time, where the yield of aqueous phase was 37 wt%. The viscosity of the produced oil at 3 h of HDO decreased from 0.061 Pa.S at 190 ^{o}C to a minimum of 0.033 Pa.S at 250 ^{o}C before increasing to a maximum of 0.068 Pa.S at 350 ^{o}C. The significant decrease of the viscosity at moderate temperature between 190 to 300 ^{o}C is because of hydrocracking and hydrogenation reactions which can occur at higher temperature. The viscosity of produced oil increased with increasing of HDO temperature above 250 °C because of polymerisation reaction. More coke is produced at higher temperature which causes catalyst deactivation in longer HDO reaction time. Therefore polymerization reaction rate increases while the hydrogenation rate decreases as the catalyst loses its performance activity.

The GC-MS results confirmed all aldehydes identified in raw bio oil disappeared from the produced oil after hydrotreatment for 1 h at 300 °C. The yield of cyclopentanone increased with increasing HDO temperature up to 300 °C, above which the yield slightly decreased. Carboxylic acids concentration remained constant as it requires more severe conditions for hydrogenation. Concentration of propyl guaiacols and ethyl guaiacols increased at higher HDO temperature which indicate the depolymerisation and breakdown of lignin-oligomer at higher temperature and therefore the reduction in viscosity.

The gas phase consists of a mixture of, CO_2 (0.3–4.2 vol.%), CO (0.1–7.8 vol.%) and CH_4 (0.9–5.6 vol.%). The amount of CO in the gas product increased significantly at HDO temperature above 250 °C; suggesting, after an initial low production of CO at lower temperature, further CO is formed by gasification at higher temperature. At high temperature HDO the coke formation increases and therefore the portion of C in the gas decreases. This is also explains the increasing of the concentration of CO_2 in the gas at higher HDO temperature. In all of the experiments carried out at different HDO conditions, the volumetric composition of CH_4 increased with reaction time.

When ethanol was used as a solvent, the oil yield in relation to the weight of the bio-oil reduced from 55.3 to 46.8% with the increase in temperature. Whereas, the oil yield increased, from 52.3 to 59.1 wt.% and as there was a further increase in the temperature is decreased to 54.6 wt.% when cyclohexane was sued as a solvent. The produced oil has reduced acidity from 221.8 to 73.3-96.3, water content from 23.2 to 1.5-11.1 wt.%, viscosity from 0.04 to 0.028-0.037 Pa.S and also improved HV from 30.88 to 34.28 -37.2 MJ/Kg as compared to the bio-oil. When ethanol was used, the water content that is related to the heating value a, reduced from 23.2% in bio-oil to 1.5-5.2 wt% in oil fraction and when cyclohexane was used, it reduced to 11.1-12.8 wt% in bio-oil due to the dehydration or demoisturization of the organic phase. As compared to the TAN of bio-oil that is 221.8 KOH/g oil, the heavy oil TAN reduced to 73.3-96.3 mg KOH/g oil. In the removal of acids from the bio-oil, lower activity was shown by cyclohexane as compared to ethanol. In comparison to the bio-oil, over 25% under ethanol and 10 % under cyclohexane of the viscosity has been reduced by all the fractions of the produced oil but the trend of the changing viscosity remains similar along with the other properties.

The lowest viscosity of upgraded oil (0.033 Pa.s for Pd/C and 0.038 Pa.s for bio-Pd) achieved at 250 °C HDO. At higher HDO temperature above 250 °C viscosity of produced oil using both catalysts started to increase due to polymerisation. However in the case of bio-Pd the increase of viscosity is much more significant compared to the commercial Pd/C.

The performance of bio-Pd in terms of DOD at lower HDO temperature (170 - 210 °C) was similar to the commercial catalyst, while at higher HDO temperature above 250 °C, bio-Pd performance in removing oxygen was decreased significantly. The biomass support undergoes decomposition at a higher temperature and leaves the metals NPs unsupported. This potentially reduces the bio-Pd catalytic activity for HDO of bio at high temperature. The maximum weight loss bacterial biomass support of bio-Pd lost at 245 °C which is due to the nature of its bacterial support and its decomposition.

6.2 Recommendations

- Focus on improvement in terms reduction of the preparation cost of bio-Pd such as the use of aerobic *E. coli* bacteria, grown in simple growth media could potentially decrease the production cost.
- Bio-Pd will be more effective in multiple stage upgrading of heavy oil prior to HDS.
- It is best for bio-Pd to be used in an application with an operating temperature lower than 250 ^oC. Because of the nature of its bacterial support which makes it less stable at higher operating conditions.
- Therefore use of bio-Pd in the second stage bio-oil upgrading can be more effective in terms of hydrogenation of bio-oil. In the second stage hydrogenation reaction is the main target which can be achieved with lower operational temperature.
- FT-IR analysis on raw and upgraded bio-oil can detect and identify the higher molecular mass component of the oil in order to explain the rise of viscosity at higher temperature with more detail.

7 References

Addy, J. & Bond, G. 1957, "Catalysis on metals of group 8. Part 1. Reaction of cyclopropane and of propane with deuterium over a palladium catalyst", *Transactions of the Faraday Society,* vol. 53, pp. 368-376.

Adib, R., Murdock, H., Appavou, F., Brown, A., Epp, B., Leidreiter, A., Lins, C., Murdock, H., Musolino, E. & Petrichenko, K. 2015, "Renewables 2015 global status report", *Paris: REN21 Secretariat,* vol. 83, pp. 84.

Adjaye, J.D., Sharma, R.K. & Bakhshi, N.N. 1992, "Catalytic conversion of wood derived bio-oil to fuels and chemicals" in *Studies in Surface Science and Catalysis* Elsevier, , pp. 301-308.

Agblevor, F. & Besler, S. 1996, "Inorganic compounds in biomass feedstocks. 1. Effect on the quality of fast pyrolysis oils", *Energy & Fuels,* vol. 10, no. 2, pp. 293-298.

Agblevor, F.A., Mante, O., McClung, R. & Oyama, S. 2012, "Co-processing of standard gas oil and biocrude oil to hydrocarbon fuels", *Biomass and Bioenergy,* vol. 45, pp. 130-137.

Albers, P., Pietsch, J. & Parker, S.F. 2001, "Poisoning and deactivation of palladium catalysts", *Journal of molecular catalysis A: Chemical,* vol. 173, no. 1-2, pp. 275-286.

Alemán-Vázquez, L., Cano-Domínguez, J. & García-Gutiérrez, J. 2012, "Effect of tetralin, decalin and naphthalene as hydrogen donors in the upgrading of heavy oils", *Procedia Engineering,* vol. 42, pp. 532-539.

Alfi, M., Barrufet, M.A., Da Silva, P.F. & Moreira, R.G. 2013, "Simultaneous application of heat and electron particles to effectively reduce the viscosity of heavy deasphalted petroleum fluids", *Energy & Fuels,* vol. 27, no. 9, pp. 5116-5127.

Ali, A., Hyder, S. & Nain, A. 1999, "Studies on molecular interactions in binary liquid mixtures by viscosity and ultrasonic velocity measurements at 303.15 K", *Journal of Molecular liquids,* vol. 79, no. 2, pp. 89-99.

Ali, L.I., Ali, A.A., Aboul-Fotouh, S. & Aboul-Gheit, A.K. 1999, "Dehydrogenation of cyclohexane on catalysts containing noble metals and their combinations with platinum on alumina support", *Applied Catalysis A: General,* vol. 177, no. 1, pp. 99-110.

Almao, P.P., Trujillo, G.L., Peluso, E., Galarraga, C., Sosa, C., Algara, C.S., Lopez-Linares, F., Ortega, L.A.C. & Reques, N.G.Z. 2017, *Systems and methods for catalytic steam cracking of non-asphaltene containing heavy hydrocarbons,* .

ALMARSHED, A. 2015, *Laboratory investigation of nanoscale dispersed catalyst for inhibition coke formation and*
upgrading of heavy oil during THAI process, PhD edn, University of Birmingham.

Al-Saleh, M.H., Saadeh, W.H. & Sundararaj, U. 2013, "EMI shielding effectiveness of carbon based nanostructured polymeric materials: a comparative study", *Carbon,* vol. 60, pp. 146-156.

Ancheyta, J., Centeno, G., Trejo, F., Marroquin, G., Garcia, J., Tenorio, E. & Torres, A. 2002, "Extraction and characterization of asphaltenes from different crude oils and solvents", *Energy & Fuels,* vol. 16, no. 5, pp. 1121-1127.

Antal Jr, M.J., Allen, S.G., Schulman, D., Xu, X. & Divilio, R.J. 2000, "Biomass gasification in supercritical water", *Industrial & Engineering Chemistry Research,* vol. 39, no. 11, pp. 4040-4053.

Arbogast, S., Bellman, D., Paynter, J. & Wykowski, J. 2013, "Advanced biofuels from pyrolysis oil… Opportunities for cost reduction", *Fuel Processing Technology,* vol. 106, pp. 518-525.

Arbogast, S., Bellman, D., Paynter, J. & Wykowski, J. 2013, "Advanced biofuels from pyrolysis oil… Opportunities for cost reduction", *Fuel Processing Technology,* vol. 106, pp. 518-525.

Arbogast, S., Bellman, D., Paynter, J. & Wykowski, J. 2012, "Advanced bio-fuels from pyrolysis oil: The impact of economies of scale and use of existing logistic and processing capabilities", *Fuel Processing Technology,* vol. 104, pp. 121-127.

Arbogast, S., Bellman, D., Paynter, J. & Wykowski, J. 2012, "Advanced bio-fuels from pyrolysis oil: The impact of economies of scale and use of existing logistic and processing capabilities", *Fuel Processing Technology,* vol. 104, pp. 121-127.

Argillier, J., Coustet, C. & Henaut, I. 2002, "Heavy oil rheology as a function of asphaltene and resin content and temperature", *SPE International thermal operations and heavy oil symposium and international horizontal well technology conference*Society of Petroleum Engineers,

Atkins, L., Warren, M., Barnes, C., Favela, R. & Higgins, T. 2011, "Heavy crude oil: A global analysis and outlook to, 2030", *Hart energy consulting report,* .

Babich, I. & Moulijn, J. 2003, "Science and technology of novel processes for deep desulfurization of oil refinery streams: a review☆", *Fuel,* vol. 82, no. 6, pp. 607-631.

Badre, S., Goncalves, C.C., Norinaga, K., Gustavson, G. & Mullins, O.C. 2006, "Molecular size and weight of asphaltene and asphaltene solubility fractions from coals, crude oils and bitumen", *Fuel,* vol. 85, no. 1, pp. 1-11.

Baldauf, W., Balfanz, U. & Rupp, M. 1994, "Upgrading of flash pyrolysis oil and utilization in refineries", *Biomass and Bioenergy,* vol. 7, no. 1-6, pp. 237-244.

Barman, B.N., Skarlos, L. & Kushner, D.J. 1997, "Simultaneous determination of oil and coke contents in spent hydroprocessing catalyst by thermogravimetry", *Energy & Fuels,* vol. 11, no. 3, pp. 593-595.

Bartholomew, C.H. 2001, "Mechanisms of catalyst deactivation", *Applied Catalysis A: General,* vol. 212, no. 1-2, pp. 17-60.

Bartholomew, C., Agrawal, P. & Katzer, J. 1982, "Sulfur poisoning of metals" in *Advances in catalysis* Elsevier, , pp. 135-242.

Bassam Fattouh 2018, *Peak oil demand and long-run prices,* BP, Group chief economist, BP.

Bennett, J., Creamer, N., Deplanche, K., Macaskie, L., Shannon, I. & Wood, J. 2010, "Palladium supported on bacterial biomass as a novel heterogeneous catalyst: A comparison of Pd/Al2O3 and bio-Pd in the hydrogenation of 2-pentyne", *Chemical Engineering Science,* vol. 65, no. 1, pp. 282-290.

Bennett, J., Mikheenko, I., Deplanche, K., Shannon, I., Wood, J. & Macaskie, L. 2013, "Nanoparticles of palladium supported on bacterial biomass: New re-usable heterogeneous catalyst with comparable activity to homogeneous colloidal Pd in the Heck reaction", *Applied Catalysis B: Environmental,* vol. 140, pp. 700-707.

Bennett, J.A., Creamer, N.J., Deplanche, K., Macaskie, L.E., Shannon, I.J. & Wood, J. 2010, "Palladium supported on bacterial biomass as a novel heterogeneous catalyst: A comparison of Pd/Al2O3 and bio-Pd in the hydrogenation of 2-pentyne", *Chemical Engineering Science,* vol. 65, no. 1, pp. 282-290.

Bennett, J.A., Mikheenko, I.P., Deplanche, K., Shannon, I.J., Wood, J. & Macaskie, L.E. 2013, "Nanoparticles of palladium supported on bacterial biomass: New re-usable heterogeneous catalyst with comparable activity to homogeneous colloidal Pd in the Heck reaction", *Applied Catalysis B: Environmental,* vol. 140–141, no. 0, pp. 700-707.

Bennett, J.A., Mikheenko, I.P., Deplanche, K., Shannon, I.J., Wood, J. & Macaskie, L.E. 2013, *Nanoparticles of palladium supported on bacterial biomass: New re-usable heterogeneous catalyst with comparable activity to homogeneous colloidal Pd in the Heck reaction.*

Benson, S.W. 1978, "Thermochemistry and kinetics of sulfur-containing molecules and radicals", *Chemical reviews,* vol. 78, no. 1, pp. 23-35.

Bernfeld, G., Bird, A., Edwards, R., Köpf, H., Köpf-Maier, P., Raub, C.J., te Riele, W., Simon, F. & Westwood, W. 1985, "Platinum-group metals, alloys and compounds in catalysis" in *Pt Platinum* Springer, , pp. 92-317.

Binazzi, A., Ferrante, P. & Marinaccio, A. 2015, "Occupational exposure and sinonasal cancer: a systematic review and meta-analysis", *BMC cancer,* vol. 15, no. 1, pp. 49.

Biniwale, R.B., Kariya, N., Yamashiro, H. & Ichikawa, M. 2006, "Heat transfer and thermographic analysis of catalyst surface during multiphase phenomena under spray-pulsed conditions for dehydrogenation of cyclohexane over Pt catalysts", *The Journal of Physical Chemistry B,* vol. 110, no. 7, pp. 3189-3196.

Biniwale, R.B., Kariya, N. & Ichikawa, M. 2005, "Dehydrogenation of cyclohexane over Ni based catalysts supported on activated carbon using spray-pulsed reactor and enhancement in activity by addition of a small amount of Pt", *Catalysis letters,* vol. 105, no. 1-2, pp. 83-87.

Biniwale, R.B., Kariya, N. & Ichikawa, M. 2005, "Dehydrogenation of cyclohexane over Ni based catalysts supported on activated carbon using spray-pulsed reactor and enhancement in activity by addition of a small amount of Pt", *Catalysis letters,* vol. 105, no. 1-2, pp. 83-87.

Boucher, M., Chaala, A. & Roy, C. 2000, "Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part I: Properties of bio-oil and its blends with methanol and a pyrolytic aqueous phase", *Biomass and Bioenergy,* vol. 19, no. 5, pp. 337-350.

Boucher, M., Chaala, A. & Roy, C. 2000, "Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part I: Properties of bio-oil and its blends with methanol and a pyrolytic aqueous phase", *Biomass and Bioenergy,* vol. 19, no. 5, pp. 337-350.

Bridgwater, A.V. 2012, "Review of fast pyrolysis of biomass and product upgrading", *Biomass and Bioenergy,* vol. 38, pp. 68-94.

Bridgwater, A.V. 2012, "Upgrading biomass fast pyrolysis liquids", *Environmental Progress & Sustainable Energy,* vol. 31, no. 2, pp. 261-268.

Bridgwater, A.V. 2003, "Renewable fuels and chemicals by thermal processing of biomass", *Chemical Engineering Journal,* vol. 91, no. 2-3, pp. 87-102.

Bridgwater, A.V. & Grassi, G. 2012, *Biomass pyrolysis liquids upgrading and utilization,* Springer Science & Business Media.

Bridgwater, A. 1996, "Production of high grade fuels and chemicals from catalytic pyrolysis of biomass", *Catalysis today,* vol. 29, no. 1-4, pp. 285-295.

Bridgwater, A. 1994, "Catalysis in thermal biomass conversion", *Applied Catalysis A: General,* vol. 116, no. 1-2, pp. 5-47.

Bridgwater, A., Toft, A. & Brammer, J. 2002, "A techno-economic comparison of power production by biomass fast pyrolysis with gasification and combustion", *Renewable and Sustainable Energy Reviews,* vol. 6, no. 3, pp. 181-246.

Briggs, B.D. & Knecht, M.R. 2012, "Nanotechnology meets biology: peptide-based methods for the fabrication of functional materials", *The journal of physical chemistry letters,* vol. 3, no. 3, pp. 405-418.

Bu, Q., Lei, H., Wang, L., Wei, Y., Zhu, L., Liu, Y., Liang, J. & Tang, J. 2013, "Renewable phenols production by catalytic microwave pyrolysis of Douglas fir sawdust pellets with activated carbon catalysts", *Bioresource technology,* vol. 142, pp. 546-552.

Bulushev, D.A. & Ross, J.R. 2011, "Catalysis for conversion of biomass to fuels via pyrolysis and gasification: a review", *Catalysis today,* vol. 171, no. 1, pp. 1-13.

Capunitan, J.A. & Capareda, S.C. 2014, "Hydrotreatment of corn stover bio-oil using noble metal catalysts", *Fuel Processing Technology,* vol. 125, pp. 190-199.

Carcoana, A. 1992, "Applied enhanced oil recovery", .

Carrier, M., Joubert, J., Danje, S., Hugo, T., Görgens, J. & Knoetze, J.H. 2013, "Impact of the lignocellulosic material on fast pyrolysis yields and product quality", *Bioresource technology,* vol. 150, pp. 129-138.

Carrillo, J.A. & Corredor, L.M. 2013, "Upgrading of heavy crude oils: Castilla", *Fuel Processing Technology,* vol. 109, pp. 156-162.

Castanier, L., Baena, C., Holt, R., Brigham, W. & Tavares, C. 1992, "In situ combustion with metallic additives", *SPE Latin America Petroleum Engineering Conference*Society of Petroleum Engineers, .

Castanier, L. & Brigham, W. 2003, "Upgrading of crude oil via in situ combustion", *Journal of petroleum science and engineering,* vol. 39, no. 1-2, pp. 125-136.

Chen, S. & Manos, G. 2004, "Study of coke and coke precursors during catalytic cracking of n-hexane and 1-hexene over ultrastable Y zeolite", *Catalysis letters,* vol. 96, no. 3-4, pp. 195-200.

Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M.B. & Hay, A.G. 2011, "Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution", *Bioresource technology,* vol. 102, no. 19, pp. 8877-8884.

Collard, F. & Blin, J. 2014, "A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin", *Renewable and Sustainable Energy Reviews,* vol. 38, pp. 594-608.

Conaway, L.M. 2000, *System for processing industrial sludges,* .

Connan, J. 1984, "Advances in petroleum geochemistry", .

Creamer, N.J., Mikheenko, I.P., Yong, P., Deplanche, K., Sanyahumbi, D., Wood, J., Pollmann, K., Merroun, M., Selenska-Pobell, S. & Macaskie, L.E. 2007, "Novel supported Pd hydrogenation bionanocatalyst for hybrid homogeneous/heterogeneous catalysis", *Catalysis Today,* vol. 128, no. 1–2, pp. 80-87.

Creamer, N.J., Mikheenko, I.P., Yong, P., Deplanche, K., Sanyahumbi, D., Wood, J., Pollmann, K., Merroun, M., Selenska-Pobell, S. & Macaskie, L.E. 2007, "Novel supported Pd hydrogenation bionanocatalyst for hybrid homogeneous/heterogeneous catalysis", *Catalysis Today,* vol. 128, no. 1–2, pp. 80-87.

Creamer, N.J., Mikheenko, I.P., Yong, P., Deplanche, K., Sanyahumbi, D., Wood, J., Pollmann, K., Merroun, M., Selenska-Pobell, S. & Macaskie, L.E. 2007, *Novel supported Pd hydrogenation bionanocatalyst for hybrid homogeneous/heterogeneous catalysis*.

Creaney, S., Allan, J. & Brooks, J. 1990, "Classic petroleum provinces", .

da Costa Lopes, André M, João, K.G., Rubik, D.F., Bogel-Łukasik, E., Duarte, L.C., Andreaus, J. & Bogel-Łukasik, R. 2013, "Pre-treatment of lignocellulosic biomass using ionic liquids: wheat straw fractionation", *Bioresource technology,* vol. 142, pp. 198-208.

Dang, Q., Luo, Z., Zhang, J., Wang, J., Chen, W. & Yang, Y. 2013, "Experimental study on bio-oil upgrading over Pt/SO42-/ZrO2/SBA-15 catalyst in supercritical ethanol", *Fuel,* vol. 103, pp. 683-692.

De Luca, G., de Philip, P., Dermoun, Z., Rousset, M. & Verméglio, A. 2001, "Reduction of technetium (VII) byDesulfovibrio fructosovorans is mediated by the nickel-iron hydrogenase", *Appl.Environ.Microbiol.,* vol. 67, no. 10, pp. 4583-4587.

Dealy, J.M. 1979, "Rheological properties of oil sand bitumens", *The Canadian Journal of Chemical Engineering,* vol. 57, no. 6, pp. 677-683.

Dell'Anna, M., Gagliardi, M., Mastrorilli, P., Suranna, G. & Nobile, C. 2000, "Hydrogenation reactions catalysed by a supported palladium complex", *Journal of Molecular Catalysis A: Chemical,* vol. 158, no. 2, pp. 515-520.

Demaison, G. 1978, "Tar Sands and Super Giant Oil Fields", *Oil &Gas Journal,* vol. 76, no. 30, pp. 202-205.

Deplanche, K. & Macaskie, L. 2008, "Biorecovery of gold by Escherichia coli and Desulfovibrio desulfuricans", *Biotechnology and bioengineering,* vol. 99, no. 5, pp. 1055-1064.

Deplanche, K. 2009, *New nanocatalysts made by bacteria from metal solutions and recycling of metal waste, .*

Deplanche, K., Caldelari, I., Mikheenko, I.P., Sargent, F. & Macaskie, L.E. 2010, "Involvement of hydrogenases in the formation of highly catalytic Pd (0) nanoparticles by bioreduction of Pd (II) using Escherichia coli mutant strains", *Microbiology,* vol. 156, no. 9, pp. 2630-2640.

Deplanche, K., Murray, A., Mennan, C., Taylor, S. & Macaskie, L. 2011, "Biorecycling of precious metals and rare earth elements", *Nanomaterials,* vol. 2011, pp. 279-314.

Deplanche, K., Bennett, J.A., Mikheenko, I.P., Omajali, J., Wells, A.S., Meadows, R.E., Wood, J. & Macaskie, L.E. 2014, "Catalytic activity of biomass-supported Pd nanoparticles: Influence of the biological component in catalytic efficacy and potential application in 'green' synthesis of fine chemicals and pharmaceuticals", *Applied Catalysis B: Environmental,* vol. 147, no. 0, pp. 651-665.

Deplanche, K., Bennett, J.A., Mikheenko, I.P., Omajali, J., Wells, A.S., Meadows, R.E., Wood, J. & Macaskie, L.E. 2014, *Catalytic activity of biomass-supported Pd nanoparticles: Influence of the biological component in catalytic efficacy and potential application in 'green' synthesis of fine chemicals and pharmaceuticals*.

Difiglio, C. 2014, *Oil, economic growth and strategic petroleum stocks*.

Duan, P. & Savage, P.E. 2011, "Upgrading of crude algal bio-oil in supercritical water", *Bioresource technology,* vol. 102, no. 2, pp. 1899-1906.

Dunleavy, J. 2006, "Sulfur as a catalyst poison", *Platinum Metals Review,* vol. 50, no. 2, pp. 110.

Eberhardt, W. 2002, "Clusters as new materials", *Surface Science,* vol. 500, no. 1, pp. 242-270.

Edwards, J.H., Schluter, K. & Tyler, R.J. 1985, "Upgrading of flash pyrolysis tars to synthetic crude oil: 1. First stage hydrotreatment using a disposable catalyst", *Fuel,* vol. 64, no. 5, pp. 594-599.

Elliott, D.C. 2007, "Historical developments in hydroprocessing bio-oils", *Energy & Fuels,* vol. 21, no. 3, pp. 1792-1815.

Elliott, D.C. & Baker, E. 1984, "Upgrading biomass liquefaction products through hydrodeoxygenation", *Biotechnol. Bioeng. Symp.;(United States)*Battelle Memorial Institute, Richland, WA, .

Elliott, D.C., Biller, P., Ross, A.B., Schmidt, A.J. & Jones, S.B. 2015, "Hydrothermal liquefaction of biomass: developments from batch to continuous process", *Bioresource technology,* vol. 178, pp. 147-156.

Elliott, D.C. & Hart, T.R. 2008, "Catalytic hydroprocessing of chemical models for bio-oil", *Energy & Fuels,* vol. 23, no. 2, pp. 631-637.

Elliott, D.C., Hart, T.R., Neuenschwander, G.G., Rotness, L.J. & Zacher, A.H. 2009, "Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products", *Environmental progress & sustainable energy,* vol. 28, no. 3, pp. 441-449.

Elliott, D.C., Hart, T.R., Neuenschwander, G.G., Rotness, L.J. & Zacher, A.H. 2009, "Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products", *Environmental progress & sustainable energy,* vol. 28, no. 3, pp. 441-449.

Elliott, D.C., Hart, T.R., Neuenschwander, G.G., Rotness, L.J. & Zacher, A.H. 2009, "Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products", *Environmental progress & sustainable energy,* vol. 28, no. 3, pp. 441-449.

Elliott, D.C., Hu, J., Hart, T.R. & Neuenschwander, G.G. 2008, *Palladium catalyzed hydrogenation of bio-oils and organic compounds,* .

Fan, L., Zhang, Y., Liu, S., Zhou, N., Chen, P., Cheng, Y., Addy, M., Lu, Q., Omar, M.M. & Liu, Y. 2017, "Bio-oil from fast pyrolysis of lignin: Effects of process and upgrading parameters", *Bioresource technology,* vol. 241, pp. 1118-1126.

Feng, H., Elam, J., Libera, J., Pellin, M. & Stair, P.C. 2010, "Oxidative dehydrogenation of cyclohexane over alumina-supported vanadium oxide nanoliths", *Journal of Catalysis,* vol. 269, no. 2, pp. 421-431.

Fisk, C.A., Morgan, T., Ji, Y., Crocker, M., Crofcheck, C. & Lewis, S.A. 2009, "Bio-oil upgrading over platinum catalysts using in situ generated hydrogen", *Applied Catalysis A: General,* vol. 358, no. 2, pp. 150-156.

Flanagan, T.B. & Oates, W. 1991, "The palladium-hydrogen system", *Annual Review of Materials Science,* vol. 21, no. 1, pp. 269-304.

Foo, K. & Hameed, B. 2011, "Microwave-assisted preparation of oil palm fiber activated carbon for methylene blue adsorption", *Chemical Engineering Journal,* vol. 166, no. 2, pp. 792-795.

Forzatti, P. & Lietti, L. 1999, "Catalyst deactivation", *Catalysis today,* vol. 52, no. 2-3, pp. 165-181.

Fotadar, U., Zaveloff, P. & Terracio, L. 2005, "Growth of Escherichia coli at elevated temperatures", *Journal of Basic Microbiology: An International Journal on Biochemistry, Physiology, Genetics, Morphology, and Ecology of Microorganisms,* vol. 45, no. 5, pp. 403-404.

Fukuyama, H., Terai, S., Uchida, M., Cano, J.L. & Ancheyta, J. 2004, "Active carbon catalyst for heavy oil upgrading", *Catalysis today,* vol. 98, no. 1-2, pp. 207-215.

Furimsky, E. 2009, "Lowered emissions schemes for upgrading ultra heavy petroleum feeds", *Industrial & Engineering Chemistry Research,* vol. 48, no. 6, pp. 2752-2769.

Furusawa, T. & Tsutsumi, A. 2005, "Comparison of Co/MgO and Ni/MgO catalysts for the steam reforming of naphthalene as a model compound of tar derived from biomass gasification", *Applied Catalysis A: General,* vol. 278, no. 2, pp. 207-212.

Gagnon, J. & Kaliaguine, S. 1988, "Catalytic hydrotreatment of vacuum pyrolysis oils from wood", *Industrial & Engineering Chemistry Research,* vol. 27, no. 10, pp. 1783-1788.

Galarraga, C.E., Scott, C., Loria, H. & Pereira-Almao, P. 2011, "Kinetic models for upgrading athabasca bitumen using unsupported NiWMo catalysts at low severity conditions", *Industrial & Engineering Chemistry Research,* vol. 51, no. 1, pp. 140-146.

Gawel, I., Bociarska, D. & Biskupski, P. 2005, "Effect of asphaltenes on hydroprocessing of heavy oils and residua", *Applied Catalysis A: General,* vol. 295, no. 1, pp. 89-94.

Goldstein, J.I., Newbury, D.E., Echlin, P., Joy, D.C., Fiori, C. & Lifshin, E. 1981, "Electron-Beam-Specimen Interactions" in *Scanning Electron Microscopy and X-ray Microanalysis* Springer, , pp. 53-122.

Gosselin, P., Hrudey, S.E., Naeth, M., Plourde, A., Therrien, R., Van Der Kraak, G. & Xu, Z. 2010, "Environmental and health impacts of Canada's oil sands industry", Royal Society of Canada Ottawa, Ontario, Canada, .

Goudriaan, F. & Peferoen, D. 1990, "Liquid fuels from biomass via a hydrothermal process", *Chemical Engineering Science,* vol. 45, no. 8, pp. 2729-2734.

Gray, M.R., Ayasse, A.R., Chan, E.W. & Veljkovic, M. 1995, "Kinetics of hydrodesulfurization of thiophenic and sulfide sulfur in Athabasca bitumen", *Energy & Fuels,* vol. 9, no. 3, pp. 500-506.

Gray, R.M. 1994, *Upgrading petroleum residues and heavy oils,* CRC press.

Greaves, M., El-Sakr, A., Xia, T., Ayasse, C. & Turta, A. 1999, "Thai-New Air Injection Technology For Heavy Oil Recovery And In Situ Upgrading", *Annual Technical Meeting*Petroleum Society of Canada.

Greaves, M., Dong, L. & Rigby, S. 2012, "Simulation study of the toe-to-heel air injection three-dimensional combustion cell experiment and effects in the mobile oil zone", *Energy & Fuels,* vol. 26, no. 3, pp. 1656-1669.

Greaves, M., Saghr, A., Xia, T., Turtar, A. & Ayasse, C. 2001, "THAI-new air injection technology for heavy oil recovery and in situ upgrading", *Journal of Canadian Petroleum Technology,* vol. 40, no. 03.

Greaves, M., Xia, T.X. & Ayasse, C. 2005, "Underground upgrading of heavy oil using THAI-'toe-to-heel air injection'", *SPE International Thermal Operations and Heavy Oil Symposium*Society of Petroleum Engineers, .

Gunawan, R., Li, X., Lievens, C., Gholizadeh, M., Chaiwat, W., Hu, X., Mourant, D., Bromly, J. & Li, C. 2013, "Upgrading of bio-oil into advanced biofuels and chemicals. Part I. Transformation of GC-detectable light species during the hydrotreatment of bio-oil using Pd/C catalyst", *Fuel,* vol. 111, pp. 709-717.

Guo, L., Bai, J., Li, C., Meng, Q., Liang, H., Sun, W., Li, H. & Liu, H. 2013, "A novel catalyst containing palladium nanoparticles supported on PVP composite nanofiber films: Synthesis, characterization and efficient catalysis", *Applied Surface Science,* vol. 283, no. 0, pp. 107-114.

Haro, J., Gomez, R. & Ferreira, J. 1976, "The role of palladium in dehydrogenation of cyclohexane over Pt□Pd/Al2O3 bimetallic catalysts″, *Journal of Catalysis,* vol. 45, no. 3, pp. 326-331.

Hart, A. 2014, *Advanced Studies of Catalytic Upgrading of Heavy Oils,* PhD edn, University of Birmingham.

Hart, A., Greaves, M. & Wood, J. 2015, "A comparative study of fixed-bed and dispersed catalytic upgrading of heavy crude oil using-CAPRI", *Chemical Engineering Journal,* vol. 282, pp. 213-223.

Hart, A., Leeke, G., Greaves, M. & Wood, J. 2013, "Down-hole catalytic upgrading of heavy oil and bitumen to meet tomorrow's energy needs: the THAI–CAPRI process", *Proceeding of the third North Am Symp Chem React Eng March,* pp. 17.

Hart, A., Shah, A., Leeke, G., Greaves, M. & Wood, J. 2013, "Optimization of the CAPRI process for heavy oil upgrading: effect of hydrogen and guard bed", *Industrial & Engineering Chemistry Research,* vol. 52, no. 44, pp. 15394-15406.

Hart, A., Greaves, M. & Wood, J. "A comparative study of fixed-bed and dispersed catalytic upgrading of heavy crude oil using-CAPRI", *Chemical Engineering Journal,* , no. 0.

Hart, A., Leeke, G., Greaves, M. & Wood, J. 2014, "Down-hole heavy crude oil upgrading by CAPRI: Effect of hydrogen and methane gases upon upgrading and coke formation", *Fuel,* vol. 119, no. 0, pp. 226-235.

Hashemi, R., Nassar, N.N. & Almao, P.P. 2014, "Nanoparticle technology for heavy oil in-situ upgrading and recovery enhancement: Opportunities and challenges", *Applied Energy,* vol. 133, pp. 374-387.

Hashemi, R., Nassar, N.N. & Pereira Almao, P. 2013, "Enhanced heavy oil recovery by in situ prepared ultradispersed multimetallic nanoparticles: A study of hot fluid flooding for Athabasca bitumen recovery", *Energy & Fuels,* vol. 27, no. 4, pp. 2194-2201.

Hashemi, R., Nassar, N.N. & Pereira Almao, P. 2013, "In situ upgrading of Athabasca bitumen using multimetallic ultradispersed nanocatalysts in an oil sands packed-bed column: Part 1. Produced liquid quality enhancement", *Energy & Fuels,* vol. 28, no. 2, pp. 1338-1350.

HIGHLIGHTS, P. 2013, "Platinum alloys: a selective review of the available literature", *Platinum Metals Rev,* vol. 57, no. 3, pp. 202-213.

Hilten, R.N., Bibens, B.P., Kastner, J.R. & Das, K. 2009, "In-line esterification of pyrolysis vapor with ethanol improves bio-oil quality", *Energy & Fuels,* vol. 24, no. 1, pp. 673-682.

Hirsch, R.L. 2005, "The inevitable peaking of world oil production", *Bulletin of the Atlantic Council of the United States,* vol. 16, no. 3, pp. 1-10.

Hongfu, F., Yongjian, L., Liying, Z. & Xiaofei, Z. 2002, "The study on composition changes of heavy oils during steam stimulation processes", *Fuel,* vol. 81, no. 13, pp. 1733-1738.

Hoshyargar, V. & Ashrafizadeh, S.N. 2013, "Optimization of flow parameters of heavy crude oil-in-water emulsions through pipelines", *Industrial & Engineering Chemistry Research,* vol. 52, no. 4, pp. 1600-1611.

Huang, X., Korányi, T.I., Boot, M.D. & Hensen, E.J. 2014, "Catalytic depolymerization of lignin in supercritical ethanol", *ChemSusChem,* vol. 7, no. 8, pp. 2276-2288.

Huber, G.W., Iborra, S. & Corma, A. 2006, "Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering", *Chemical reviews,* vol. 106, no. 9, pp. 4044-4098.

Hunt, J.M. 1995, "Petroleum geochemistry and geology", .

Hwang, H., Oh, S., Choi, I. & Choi, J.W. 2015, "Catalytic effects of magnesium on the characteristics of fast pyrolysis products–Bio-oil, bio-char, and non-condensed pyrolytic gas fractions", *Journal of Analytical and Applied Pyrolysis,* vol. 113, pp. 27-34.

IEA 2018, , *Conclusion of IEA Collective Action*. Available: https://www.iea.org/newsroom/news/2005/december/2005-12-26-.html [2019, .

Ikura, M., Stanciulescu, M. & Hogan, E. 2003, "Emulsification of pyrolysis derived bio-oil in diesel fuel", *Biomass and Bioenergy,* vol. 24, no. 3, pp. 221-232.

Ingledew, W. & Poole, R. 1984, "The respiratory chains of Escherichia coli.", *Microbiological reviews,* vol. 48, no. 3, pp. 222.

Jacobson, K., Maheria, K.C. & Dalai, A.K. 2013, "Bio-oil valorization: a review", *Renewable and Sustainable Energy Reviews,* vol. 23, pp. 91-106.

Jahirul, M., Rasul, M., Chowdhury, A. & Ashwath, N. 2012, "Biofuels production through biomass pyrolysis—a technological review", *Energies,* vol. 5, no. 12, pp. 4952-5001.

Jahirul, M., Rasul, M., Chowdhury, A. & Ashwath, N. 2012, "Biofuels production through biomass pyrolysis—a technological review", *Energies,* vol. 5, no. 12, pp. 4952-5001.

Jiang, X. & Ellis, N. 2010, "Upgrading bio-oil through emulsification with biodiesel: thermal stability", *Energy & Fuels,* vol. 24, no. 4, pp. 2699-2706.

Johannes, I., Tiikma, L., Luik, H., Tamvelius, H. & Krasulina, J. 2012, "Catalytic thermal liquefaction of oil shale in tetralin", *ISRN Chemical Engineering,* vol. 2012.

Jones, S.B., Meyer, P.A., Snowden-Swan, L.J., Padmaperuma, A.B., Tan, E., Dutta, A., Jacobson, J. & Cafferty, K. 2013, *Process design and economics for the conversion of lignocellulosic biomass to hydrocarbon fuels: fast pyrolysis and hydrotreating bio-oil pathway,* .

Jones, S.B., Valkenburt, C., Walton, C.W., Elliott, D.C., Holladay, J.E., Stevens, D.J., Kinchin, C. & Czernik, S. 2009, *Production of gasoline and diesel from biomass via fast pyrolysis, hydrotreating and hydrocracking: a design case,* .

Joshi, N. & Lawal, A. 2012, "Hydrodeoxygenation of pyrolysis oil in a microreactor", *Chemical Engineering Science,* vol. 74, pp. 1-8.

Kabir, G. & Hameed, B. 2017, "Recent progress on catalytic pyrolysis of lignocellulosic biomass to high-grade bio-oil and bio-chemicals", *Renewable and Sustainable Energy Reviews,* vol. 70, pp. 945-967.

Kay, B.D., Peden, C.H. & Goodman, D.W. 1986, "Kinetics of hydrogen absorption by Pd (110)", *Physical Review B,* vol. 34, no. 2, pp. 817.

Khalil, M., Lee, R.L. & Liu, N. 2015, "Hematite nanoparticles in aquathermolysis: A desulfurization study of thiophene", *Fuel,* vol. 145, pp. 214-220.

Kim, H.S., Kim, T.W., Koh, H.L., Lee, S.H. & Min, B.R. 2005, "Complete benzene oxidation over Pt-Pd bimetal catalyst supported on γ-alumina: influence of Pt-Pd ratio on the catalytic activity", *Applied Catalysis A: General,* vol. 280, no. 2, pp. 125-131.

Kim, J., Longstaff, D.C. & Hanson, F.V. 1997, "Upgrading of bitumen-derived heavy oils over a commercial HDN catalyst", *Fuel,* vol. 76, no. 12, pp. 1143-1150.

Kim, Y., Wendt, S., Schwegmann, S., Over, H. & Ertl, G. 1998, "Structural analyses of the pure and cesiated Ru (0001)–(2× 2)-3O phase", *Surface Science,* vol. 418, no. 1, pp. 267-272.

Knezevic, D., van Swaaij, W. & Kersten, S. 2009, "Hydrothermal conversion of biomass. II. Conversion of wood, pyrolysis oil, and glucose in hot compressed water", *Industrial & Engineering Chemistry Research,* vol. 49, no. 1, pp. 104-112.

Koido, K., Watanabe, Y., Ishiyama, T., Nunoura, T. & Dowaki, K. 2017, "Fate of sulphur during simultaneous gasification of lignin-slurry and removal of hydrogen sulphide over calcium aluminate supported nickel oxide catalyst", *Journal of Cleaner Production,* vol. 141, pp. 568-579.

Krejci, K. 1932, "Rule of density of oils", *AAPG Bulletin,* vol. 16, no. 10, pp. 1038-1038.

Kressmann, S., Morel, F., Harlé, V. & Kasztelan, S. 1998, "Recent developments in fixed-bed catalytic residue upgrading", *Catalysis Today,* vol. 43, no. 3-4, pp. 203-215.

Kubičková, I., Snåre, M., Eränen, K., Mäki-Arvela, P. & Murzin, D.Y. 2005, "Hydrocarbons for diesel fuel via decarboxylation of vegetable oils", *Catalysis Today,* vol. 106, no. 1-4, pp. 197-200.

Kubitschek, H. 1990, "Cell volume increase in Escherichia coli after shifts to richer media.", *Journal of Bacteriology,* vol. 172, no. 1, pp. 94-101.

Lampert, J.K., Kazi, M.S. & Farrauto, R.J. 1997, "Palladium catalyst performance for methane emissions abatement from lean burn natural gas vehicles", *Applied Catalysis B: Environmental,* vol. 14, no. 3-4, pp. 211-223.

Lee, J., Kim, K. & Kwon, E.E. 2017, "Biochar as a catalyst", *Renewable and Sustainable Energy Reviews,* vol. 77, pp. 70-79.

Leiby, P.N., Oladosu, G.A., Uria Martinez, R. & Johnson, M. 2019, *2018 Benefits Study of Emergency IEA Oil Stocks: Final CRADA Report,* .

Liangxiang, J. 2005, "Energy first", *Middle East Quarterly,* .

Lischka, M. & Groß, A. 2003, "Hydrogen on palladium: A model system for the interaction of atoms and molecules with metal surfaces", *Recent Developments in Vacuum Science and Technology,* vol. 37, no. 661, pp. 2.

Liu, B., Li, J., Qi, C., Li, X., Mai, T. & Zhang, J. 2017, "Mechanism of asphaltene aggregation induced by supercritical CO 2: insights from molecular dynamics simulation", *RSC Advances,* vol. 7, no. 80, pp. 50786-50793.

Liu, D., Yu, Y. & Wu, H. 2013, "Differences in water-soluble intermediates from slow pyrolysis of amorphous and crystalline cellulose", *Energy & Fuels,* vol. 27, no. 3, pp. 1371-1380.

Lloyd, J.R. 2003, "Microbial reduction of metals and radionuclides", *FEMS microbiology reviews,* vol. 27, no. 2-3, pp. 411-425.

Lloyd, J.R. 2003, "Microbial reduction of metals and radionuclides", *FEMS microbiology reviews,* vol. 27, no. 2-3, pp. 411-425.

Lloyd, J.R., Yong, P. & Macaskie, L.E. 1998, "Enzymatic recovery of elemental palladium by using sulfate-reducing bacteria", *Applied and Environmental Microbiology,* vol. 64, no. 11, pp. 4607-4609.

Lloyd, J.R., Yong, P. & Macaskie, L.E. 1998, "Enzymatic recovery of elemental palladium by using sulfate-reducing bacteria", *Applied and Environmental Microbiology,* vol. 64, no. 11, pp. 4607-4609.

Loser, U., Scherzer, K. & Weber, K. 1989, "KINETIC-DATA ESTIMATION FOR HYDROGEN-TRANSFER REACTIONS, USING THE BOND-STRENGTH-BOND-LENGTH (BSBL) METHOD", *Zeitschrift Fur Physikalische Chemie-Leipzig,* vol. 270, no. 2, pp. 237-245.

Lu, J. & Heyden, A. 2015, "Theoretical investigation of the reaction mechanism of the hydrodeoxygenation of guaiacol over a Ru (0 0 0 1) model surface", *Journal of catalysis,* vol. 321, pp. 39-50.

Lund, V.J., Stammberger, H., Nicolai, P., Castelnuovo, P., Beal, T., Beham, A., Bernal-Sprekelsen, M., Braun, H., Cappabianca, P., Carrau, R., Cavallo, L., Clarici, G., Draf, W., Esposito, F., Fernandez-Miranda, J., Fokkens, W., Gardner, P., Gellner, V., Hellquist, H., Hermann, P., Hosemann, W., Howard, D., Jones, N., Jorissen, M., Kassam, A., Kelly, D., Kurschel-Lackner, S., Leong, S., McLaughlin, N., Maroldi, R., Minovi, A., Mokry, M., Onerci, M., Ong, Y.K., Prevedello, D., Saleh, H., Sehti, D.S., Simmen, D., Snyderman, C., Solares, A., Spittle, M., Stamm, A., Tomazic, P., Trimarchi, M., Unger, F., Wormald, P.J., Zanation, A. & European Rhinologic Society Advisory Board on Endoscopic Techniques in the Management of Nose, Paranasal Sinus and Skull Base Tumours 2010, "European position paper on endoscopic management of tumours of the nose, paranasal sinuses and skull base", *Rhinology.Supplement,* vol. 22, pp. 1-143.

Lv, G. & Wu, S. 2012, "Analytical pyrolysis studies of corn stalk and its three main components by TG-MS and Py-GC/MS", *Journal of Analytical and Applied Pyrolysis,* vol. 97, pp. 11-18.

Mabbett, A.N., Sanyahumbi, D., Yong, P. & Macaskie, L.E. 2006, "Biorecovered precious metals from industrial wastes: single-step conversion of a mixed metal liquid waste to a bioinorganic catalyst with environmental application", *Environmental science & technology,* vol. 40, no. 3, pp. 1015-1021.

Macaskie, L., Creamer, N., Essa, A. & Brown, N. 2007, "A new approach for the recovery of precious metals from solution and from leachates derived from electronic scrap", *Biotechnology and bioengineering,* vol. 96, no. 4, pp. 631-639.

Macaskie, L., Creamer, N., Essa, A. & Brown, N. 2007, "A new approach for the recovery of precious metals from solution and from leachates derived from electronic scrap", *Biotechnology and bioengineering,* vol. 96, no. 4, pp. 631-639.

Macaskie, L., Mikheenko, I., Yong, P., Deplanche, K., Murray, A., Paterson-Beedle, M., Coker, V., Pearce, C., Cutting, R. & Pattrick, R. 2010, "Today's wastes, tomorrow's materials for environmental protection", *Hydrometallurgy,* vol. 104, no. 3-4, pp. 483-487.

Macaskie, L.E., Creamer, N.J., Essa, A.M.M. & Brown, N.L. 2007, "A new approach for the recovery of precious metals from solution and from leachates derived from electronic scrap", *Biotechnology and bioengineering,* vol. 96, no. 4, pp. 631-639.

Maeda, A., Kunimori, K. & Uchijima, T. 1987, "Dehydrogenation of cyclohexane on alumina-supported rhodium catalysts. Effect of oxidation-reduction treatment on the catalytic activity", *Chemistry Letters,* vol. 16, no. 1, pp. 165-166.

Manganaro, J., Chen, B., Adeosun, J., Lakhapatri, S., Favetta, D., Lawal, A., Farrauto, R., Dorazio, L. & Rosse, D. 2011, "Conversion of residual biomass into liquid transportation fuel: an energy analysis", *Energy & Fuels,* vol. 25, no. 6, pp. 2711-2720.

Marafi, A., Kam, E. & Stanislaus, A. 2008, "A kinetic study on non-catalytic reactions in hydroprocessing Boscan crude oil", *Fuel,* vol. 87, no. 10-11, pp. 2131-2140.

Marafi, M. & Stanislaus, A. 2001, "Influence of catalyst acidity and feedstock quality on hydrotreating catalyst deactivation by coke deposition", *Petroleum Science and Technology,* vol. 19, no. 5-6, pp. 697-710.

Matos, J., Rosales, M., González, G. & De Navarro, C.U. 2010, "Changes on texture and crystalline phase of activated carbon-supported Ni-Ca catalyst during dry methane reforming", *Open Materials Science Journal,* vol. 4, pp. 125-132.

Mawhood, R., Gazis, E., de Jong, S., Hoefnagels, R. & Slade, R. 2016, "Production pathways for renewable jet fuel: a review of commercialization status and future prospects", *Biofuels, Bioproducts and Biorefining,* vol. 10, no. 4, pp. 462-484.

Mazaheri, H., Lee, K.T., Bhatia, S. & Mohamed, A.R. 2010, "Sub/supercritical liquefaction of oil palm fruit press fiber for the production of bio-oil: effect of solvents", *Bioresource technology,* vol. 101, no. 19, pp. 7641-7647.

Mazaheri, H., Lee, K.T., Bhatia, S. & Mohamed, A.R. 2010, "Sub/supercritical liquefaction of oil palm fruit press fiber for the production of bio-oil: effect of solvents", *Bioresource technology,* vol. 101, no. 19, pp. 7641-7647.

Mazaheri, H., Lee, K.T., Bhatia, S. & Mohamed, A.R. 2010, "Subcritical water liquefaction of oil palm fruit press fiber for the production of bio-oil: effect of catalysts", *Bioresource technology,* vol. 101, no. 2, pp. 745-751.

McGrath, T.E., Chan, W.G. & Hajaligol, M.R. 2003, "Low temperature mechanism for the formation of polycyclic aromatic hydrocarbons from the pyrolysis of cellulose", *Journal of Analytical and Applied Pyrolysis,* vol. 66, no. 1-2, pp. 51-70.

Meeyoo, V., Lee, J., Trimm, D. & Cant, N. 1998, "Hydrogen sulphide emission control by combined adsorption and catalytic combustion", *Catalysis today,* vol. 44, no. 1-4, pp. 67-72.

Meyer, R.F. 1987, "Exploration for heavy crude oil and natural bitumen", .

Mikheenko, I.P., Rousset, M., Dementin, S. & Macaskie, L.E. 2008, "Bioaccumulation of palladium by Desulfovibrio fructosivorans wild-type and hydrogenase-deficient strains", *Applied and Environmental Microbiology,* vol. 74, no. 19, pp. 6144-6146.

Mikheenko, I.P., Rousset, M., Dementin, S. & Macaskie, L.E. 2008, "Bioaccumulation of palladium by Desulfovibrio fructosivorans wild-type and hydrogenase-deficient strains", *Applied and Environmental Microbiology,* vol. 74, no. 19, pp. 6144-6146.

Mohammed, I.Y., Abakr, Y.A., Yusup, S., Alaba, P.A., Morris, K.I., Sani, Y.M. & Kazi, F.K. 2017, "Upgrading of Napier grass pyrolytic oil using microporous and hierarchical mesoporous zeolites: Products distribution, composition and reaction pathways", *Journal of Cleaner Production,* vol. 162, pp. 817-829.

Moore, R., Laureshen, C., Belgrave, J., Ursenbach, M. & Mehta, S. 1997, "In-situ combustion in heavy-oil reservoirs: Problems and perspectives", *In Situ,* vol. 21, no. 1, pp. 1-26.

Morley, N. & Eatherley, D. 2008, *Material Security: Ensuring resource availability for the UK economy,* C-Tech Innovation Limited.

Mortensen, P.M., Grunwaldt, J., Jensen, P.A., Knudsen, K. & Jensen, A.D. 2011, "A review of catalytic upgrading of bio-oil to engine fuels", *Applied Catalysis A: General,* vol. 407, no. 1-2, pp. 1-19.

Mortensen, P.M., Grunwaldt, J., Jensen, P.A., Knudsen, K. & Jensen, A.D. 2011, "A review of catalytic upgrading of bio-oil to engine fuels", *Applied Catalysis A: General,* vol. 407, no. 1-2, pp. 1-19.

Mowery, D.L., Graboski, M.S., Ohno, T.R. & McCormick, R.L. 1999, "Deactivation of PdO–Al2O3 oxidation catalyst in lean-burn natural gas engine exhaust: aged catalyst characterization and studies of poisoning by H2O and SO2", *Applied Catalysis B: Environmental,* vol. 21, no. 3, pp. 157-169.

Muraza, O. & Galadima, A. 2015, "Aquathermolysis of heavy oil: A review and perspective on catalyst development", *Fuel,* vol. 157, pp. 219-231.

Muraza, O. & Galadima, A. 2015, "A review on coke management during dry reforming of methane", *International Journal of Energy Research,* vol. 39, no. 9, pp. 1196-1216.

Murray, A. 2012, *Synthesis of Precious Metal Nanoparticles Supported on Bacterial Biomass for Catalytic Applications in Chemical Transformations*, University of Birmingham.

Murray, A., Omajali, J., Del Mastio, Y., Hart, A., Wood, J. & Macaskie, L. 2015, "Potential for conversion of waste platinum group metals in road dust into biocatalysts for cracking heavy oil", *Advanced Materials Research*Trans Tech Publ, , pp. 623.

Murray, A., Omajali, J., Del Mastio, Y., Hart, A., Wood, J. & Macaskie, L. 2015, "Potential for conversion of waste platinum group metals in road dust into biocatalysts for cracking heavy oil", *Advanced Materials Research*Trans Tech Publ, , pp. 623.

Murray, A., Zhu, J., Wood, J. & Macaskie, L. 2017, "A novel biorefinery: biorecovery of precious metals from spent automotive catalyst leachates into new catalysts effective in metal reduction and in the hydrogenation of 2-pentyne", *Minerals Engineering,* vol. 113, pp. 102-108.

Niccolai, G., Locatelli, F., Candy, J., Uzio, D., Didillion, B. & Basset, J. 2000, "Hydrogenolysis of cyclohexane over Ir/silica catalyst: A mechanistic study of carbon-carbon bond cleavage on metal surfaces.", *ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY*AMER CHEMICAL SOC 1155 16TH ST, NW, WASHINGTON, DC 20036 USA, , pp. U866.

Nimmanwudipong, T., Runnebaum, R.C., Block, D.E. & Gates, B.C. 2011, "Catalytic reactions of guaiacol: reaction network and evidence of oxygen removal in reactions with hydrogen", *Catalysis letters,* vol. 141, no. 6, pp. 779-783.

No, S. 2014, "Application of bio-oils from lignocellulosic biomass to transportation, heat and power generation—A review", *Renewable and Sustainable Energy Reviews,* vol. 40, pp. 1108-1125.

Noguera, G., Araujo, S., Hernández, J., Rivas, A., Mendoza, D. & Castellano, O. 2012, "A comparative activity study of a new ultra-dispersed catalyst system for a hydrocracking/hydrotreating technology using vacuum residue oil: Merey/Mesa", *Chemical Engineering Research and Design,* vol. 90, no. 11, pp. 1979-1988.

Oasmaa, A. & Boocock, D.G. 1992, "The catalytic hydrotreatment of peat pyrolysate oils", *The Canadian Journal of Chemical Engineering,* vol. 70, no. 2, pp. 294-300.

Oasmaa, A., Elliott, D.C. & Korhonen, J. 2010, "Acidity of biomass fast pyrolysis bio-oils", *Energy & Fuels,* vol. 24, no. 12, pp. 6548-6554.

Oasmaa, A., Kuoppala, E., Selin, J., Gust, S. & Solantausta, Y. 2004, "Fast pyrolysis of forestry residue and pine. 4. Improvement of the product quality by solvent addition", *Energy & Fuels,* vol. 18, no. 5, pp. 1578-1583.

Oasmaa, A., Kuoppala, E., Selin, J., Gust, S. & Solantausta, Y. 2004, "Fast pyrolysis of forestry residue and pine. 4. Improvement of the product quality by solvent addition", *Energy & Fuels,* vol. 18, no. 5, pp. 1578-1583.

Oasmaa, A. & Peacocke, C. 2001, *A guide to physical property characterisation of biomass-derived fast pyrolysis liquids,* Technical Research Centre of Finland Espoo.

Oasmaa, A., Solantausta, Y., Arpiainen, V., Kuoppala, E. & Sipila, K. 2009, "Fast pyrolysis bio-oils from wood and agricultural residues", *Energy & Fuels,* vol. 24, no. 2, pp. 1380-1388.

Oh, S., Hwang, H., Choi, H.S. & Choi, J.W. 2015, "The effects of noble metal catalysts on the bio-oil quality during the hydrodeoxygenative upgrading process", *Fuel,* vol. 153, pp. 535-543.

Oh, S., Hwang, H., Choi, H.S. & Choi, J.W. 2015, "The effects of noble metal catalysts on the bio-oil quality during the hydrodeoxygenative upgrading process", *Fuel,* vol. 153, pp. 535-543.

Oh, S., Hwang, H., Choi, H.S. & Choi, J.W. 2014, "Investigation of chemical modifications of micro-and macromolecules in bio-oil during hydrodeoxygenation with Pd/C catalyst in supercritical ethanol", *Chemosphere,* vol. 117, pp. 806-814.

Oh, S., Hwang, H., Choi, H.S. & Choi, J.W. 2014, "Investigation of chemical modifications of micro-and macromolecules in bio-oil during hydrodeoxygenation with Pd/C catalyst in supercritical ethanol", *Chemosphere,* vol. 117, pp. 806-814.

Omajali, J.B., Hart, A., Walker, M., Wood, J. & Macaskie, L.E. 2017, "In-situ catalytic upgrading of heavy oil using dispersed bionanoparticles supported on gram-positive and gram-negative bacteria", *Applied Catalysis B: Environmental,* vol. 203, pp. 807-819.

Onwudili, J.A. & Williams, P.T. 2016, "Catalytic conversion of bio-oil in supercritical water: Influence of RuO2/γ-Al2O3 catalysts on gasification efficiencies and bio-methane production", *Applied Catalysis B: Environmental,* vol. 180, pp. 559-568.

OPEC 2019, , ***Monthly Oil Market Report***.
Available: https://www.opec.org/opec_web/en/publications/338.htm [2019, .

Ortiz-Moreno, H., Ramírez, J., Cuevas, R., Marroquín, G. & Ancheyta, J. 2012, "Heavy oil upgrading at moderate pressure using dispersed catalysts: Effects of temperature, pressure and catalytic precursor", *Fuel,* vol. 100, pp. 186-192.

Ortiz-Moreno, H., Ramírez, J., Sanchez-Minero, F., Cuevas, R. & Ancheyta, J. 2014, "Hydrocracking of Maya crude oil in a slurry-phase batch reactor. II. Effect of catalyst load", *Fuel,* vol. 130, pp. 263-272.

Ovalles, C., del Carmen García, M., Lujano, E., Aular, W., Bermúdez, R. & Cotte, E. 1998, "Structure/interfacial activity relationships and thermal stability studies of Cerro Negro crude oil and its acid, basic and neutral fractions", *Fuel,* vol. 77, no. 3, pp. 121-126.

Ovalles, C., Filgueiras, E., Morales, A., Rojas, I., de Jesus, J.C. & Berrios, I. 1998, "Use of a dispersed molybdenum catalyst and mechanistic studies for upgrading extra-heavy crude oil using methane as source of hydrogen", *Energy & Fuels,* vol. 12, no. 2, pp. 379-385.

Ovalles, C., Filgueiras, E., Morales, A., Scott, C.E., Gonzalez-Gimenez, F. & Embaid, B.P. 2003, "Use of a dispersed iron catalyst for upgrading extra-heavy crude oil using methane as source of hydrogen☆", *Fuel,* vol. 82, no. 8, pp. 887-892.

Ovalles, C., Filgueiras, E., Morales, A., Scott, C.E., Gonzalez-Gimenez, F. & Embaid, B.P. 2003, "Use of a dispersed iron catalyst for upgrading extra-heavy crude oil using methane as source of hydrogen☆", *Fuel,* vol. 82, no. 8, pp. 887-892.

Ovalles, C., Rivero, V. & Salazar, A. 2015, "Downhole upgrading of orinoco basin extra-heavy crude oil using hydrogen donors under steam injection conditions. Effect of the presence of iron nanocatalysts", *Catalysts,* vol. 5, no. 1, pp. 286-297.

Ovalles, C., Filgueiras, E., Morales, A., Scott, C.E., Gonzalez-Gimenez, F. & Pierre Embaid, B. 2003, "Use of a dispersed iron catalyst for upgrading extra-heavy crude oil using methane as source of hydrogen☆", *Fuel,* vol. 82, no. 8, pp. 887-892.

Padula, L., Balestrin, Lia Beraldo da Silveira, Rocha, N.d.O., de Carvalho, Carlos Henrique Monteiro, Westfahl Jr, H., Cardoso, M.B., Sabadini, E. & Loh, W. 2016, "Role of asphaltenes and additives on the viscosity and microscopic structure of heavy crude oils", *Energy & Fuels,* vol. 30, no. 5, pp. 3644-3651.

Panariti, N., Del Bianco, A., Del Piero, G. & Marchionna, M. 2000, "Petroleum residue upgrading with dispersed catalysts: Part 1. Catalysts activity and selectivity", *Applied Catalysis A: General,* vol. 204, no. 2, pp. 203-213.

Parker, H.L., Rylott, E.L., Hunt, A.J., Dodson, J.R., Taylor, A.F., Bruce, N.C. & Clark, J.H. 2014, "Supported palladium nanoparticles synthesized by living plants as a catalyst for Suzuki-Miyaura Reactions", *PloS one,* vol. 9, no. 1, pp. e87192.

Parr Instrument 2018, , *PARR REACTOR*. Available: https://www.parrinst.com/products/stirred-reactors/series-4560-100-600-ml-mini-reactors/ [2018, .

Pastorova, I., Botto, R.E., Arisz, P.W. & Boon, J.J. 1994, "Cellulose char structure: a combined analytical Py-GC-MS, FTIR, and NMR study", *Carbohydrate research,* vol. 262, no. 1, pp. 27-47.

Patwardhan, P.R., Dalluge, D.L., Shanks, B.H. & Brown, R.C. 2011, "Distinguishing primary and secondary reactions of cellulose pyrolysis", *Bioresource technology,* vol. 102, no. 8, pp. 5265-5269.

Peng, B., Yuan, X., Zhao, C. & Lercher, J.A. 2012, "Stabilizing catalytic pathways via redundancy: selective reduction of microalgae oil to alkanes", *Journal of the American Chemical Society,* vol. 134, no. 22, pp. 9400-9405.

Peng, P., Morales-Izquierdo, A., Lown, E.M. & Strausz, O.P. 1999, "Chemical structure and biomarker content of Jinghan asphaltenes and kerogens", *Energy & Fuels,* vol. 13, no. 2, pp. 248-265.

Peng, X. & Barteau, M. 1990, "Dehydration of carboxylic acids on the MgO (100) surface", *Catalysis Letters,* vol. 7, no. 5-6, pp. 395-402.

Peng, Y. & Wu, S. 2010, "The structural and thermal characteristics of wheat straw hemicellulose", *Journal of Analytical and Applied Pyrolysis,* vol. 88, no. 2, pp. 134-139.

Rahmani, S., McCaffrey, W. & Gray, M.R. 2002, "Kinetics of solvent interactions with asphaltenes during coke formation", *Energy & Fuels,* vol. 16, no. 1, pp. 148-154.

Rana, M.S., Ancheyta, J., Rayo, P. & Maity, S. 2007, "Heavy oil hydroprocessing over supported NiMo sulfided catalyst: An inhibition effect by added H2S", *Fuel,* vol. 86, no. 9, pp. 1263-1269.

Remón, J., Arauzo, J., García, L., Arcelus-Arrillaga, P., Millan, M., Suelves, I. & Pinilla, J. 2016, "Bio-oil upgrading in supercritical water using Ni-Co catalysts supported on carbon nanofibres", *Fuel Processing Technology,* vol. 154, pp. 178-187.

Remón, J., Arcelus-Arrillaga, P., García, L. & Arauzo, J. 2016, "Production of gaseous and liquid bio-fuels from the upgrading of lignocellulosic bio-oil in sub-and supercritical water: Effect of operating conditions on the process", *Energy Conversion and Management,* vol. 119, pp. 14-36.

Remón, J., Broust, F., Volle, G., García, L. & Arauzo, J. 2015, "Hydrogen production from pine and poplar bio-oils by catalytic steam reforming. Influence of the bio-oil composition on the process", *International Journal of Hydrogen Energy,* vol. 40, no. 16, pp. 5593-5608.

Remón, J., Medrano, J., Bimbela, F., García, L. & Arauzo, J. 2013, "Ni/Al–Mg–O solids modified with Co or Cu for the catalytic steam reforming of bio-oil", *Applied Catalysis B: Environmental,* vol. 132, pp. 433-444.

Reyniers, G.C., Froment, G.F., Kopinke, F. & Zimmermann, G. 1994, "Coke formation in the thermal cracking of hydrocarbons. 4. Modeling of coke formation in naphtha cracking", *Industrial & Engineering Chemistry Research,* vol. 33, no. 11, pp. 2584-2590.

Rhoe, A. 1979, "C. de Blignieres", *Hydrocarbon Processing,* , pp. 131.

Rotaru, A., Jiang, W., Finster, K., Skrydstrup, T. & Meyer, R.L. 2012, "Non-enzymatic palladium recovery on microbial and synthetic surfaces", *Biotechnology and bioengineering,* vol. 109, no. 8, pp. 1889-1897.

Samolada, M., Baldauf, W. & Vasalos, I. 1998, "Production of a bio-gasoline by upgrading biomass flash pyrolysis liquids via hydrogen processing and catalytic cracking", *Fuel,* vol. 77, no. 14, pp. 1667-1675.

Sánchez Berna, A., Moran, V.C., Romero Guzmán, E. & Yacaman, M.J. 2006, "Asphaltene aggregation from vacuum residue and its content of inorganic particles", *Petroleum Science and Technology,* vol. 24, no. 9, pp. 1055-1066.

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", *Proc. 7th UNITAR International Conference on Heavy Oil and Tar Sand, Beijing, China, 27-30 October*, pp. 1189.

Sertić-Bionda, K., Kuzmić, V. & Jednačak, M. 2000, "The influence of process parameters on catalytic cracking LPG fraction yield and composition", *Fuel Processing Technology,* vol. 64, no. 1-3, pp. 107-115.

Shah, A.A., Fishwick, R.P., Leeke, G.A., Wood, J., Rigby, S.P. & Greaves, M. 2011, "Experimental optimization of catalytic process in situ for heavy-oil and bitumen upgrading", *Journal of Canadian Petroleum Technology,* vol. 50, no. 11/12, pp. 33-47.

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 & Environmental Science,* vol. 3, no. 6, pp. 700-714.

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 & Environmental Science,* vol. 3, no. 6, pp. 700-714.

Sharma, R. & Bakhshi, N. 1993, "Upgrading of pyrolytic lignin fraction of fast pyrolysis oil to hydrocarbon fuels over HZSM-5 in a dual reactor system", *Fuel Processing Technology,* vol. 35, no. 3, pp. 201-218.

Shen, D. & Gu, S. 2009, "The mechanism for thermal decomposition of cellulose and its main products", *Bioresource technology,* vol. 100, no. 24, pp. 6496-6504.

Shen, D., Gu, S. & Bridgwater, A.V. 2010, "Study on the pyrolytic behaviour of xylan-based hemicellulose using TG–FTIR and Py–GC–FTIR", *Journal of Analytical and Applied Pyrolysis,* vol. 87, no. 2, pp. 199-206.

Sheu, Y.E., Anthony, R.G. & Soltes, E.J. 1988, "Kinetic studies of upgrading pine pyrolytic oil by hydrotreatment", *Fuel Processing Technology,* vol. 19, no. 1, pp. 31-50.

Sheu, Y.E., Anthony, R.G. & Soltes, E.J. 1988, "Kinetic studies of upgrading pine pyrolytic oil by hydrotreatment", *Fuel Processing Technology,* vol. 19, no. 1, pp. 31-50.

Slagtern, Å., Dahl, I.M., Jens, K.J. & Myrstad, T. 2010, "Cracking of cyclohexane by high Si HZSM-5", *Applied Catalysis A: General,* vol. 375, no. 2, pp. 213-221.

Speight, J.G. 2014, *The chemistry and technology of petroleum,* CRC press.

Speight, J.G. 2009, "**Enhanced Recovery Methods for Heavy Oil and Tar Sands**", , pp. 268.

Stephen, H. 2013, "Unconventional oil and gas resource development", *Journal of Unconventional Oil and Gas Resources,* .

Stevens, P.D., Li, G., Fan, J., Yen, M. & Gao, Y. 2005, "Recycling of homogeneous Pd catalysts using superparamagnetic nanoparticles as novel soluble supports for Suzuki, Heck, and Sonogashira cross-coupling reactions", *Chemical communications,* , no. 35, pp. 4435-4437.

Strausz, O.P., Mojelsky, T.W., Lown, E.M., Kowalewski, I. & Behar, F. 1999, "Structural features of Boscan and Duri asphaltenes", *Energy & Fuels,* vol. 13, no. 2, pp. 228-247.

Stuckey Jr, A.N., Blackwell, N.E. & Del Valle, I.G. 1969, *Process for the preparation of low sulfur fuel oil,* .

Synder, A., Augustyniak, E., Laudanska-Olszewska, I. & Wesolek-Czernik, A. 2004, "Evaluation of blood-flow parameters in extraocular arteries in patients with primary open-angle glaucoma before and after surgical treatment", *Klinika oczna,* vol. 106, no. 1-2 Suppl, pp. 206-208.

Tang, W., Fang, M., Wang, H., Yu, P., Wang, Q. & Luo, Z. 2014, "Mild hydrotreatment of low temperature coal tar distillate: product composition", *Chemical Engineering Journal,* vol. 236, pp. 529-537.

Taylor, S. 2012, *Recovery of platinum group metals from waste sources,* .

Teella, A., Huber, G.W. & Ford, D.M. 2011, "Separation of acetic acid from the aqueous fraction of fast pyrolysis bio-oils using nanofiltration and reverse osmosis membranes", *Journal of Membrane Science,* vol. 378, no. 1-2, pp. 495-502.

Tester, J.W., Anderson, B.J., Batchelor, A., Blackwell, D., DiPippo, R., Drake, E., Garnish, J., Livesay, B., Moore, M. & Nichols, K. 2006, "The future of geothermal energy", *Impact of Enhanced Geothermal Systems (EGS) on the United States in the 21st Century, Massachusetts Institute of Technology, Cambridge, MA,* vol. 372.

Tomishige, K., Asadullah, M. & Kunimori, K. 2004, "Syngas production by biomass gasification using Rh/CeO2/SiO2 catalysts and fluidized bed reactor", *Catalysis Today,* vol. 89, no. 4, pp. 389-403.

Trejo, F., Ancheyta, J., Morgan, T., Herod, A. & Kandiyoti, R. 2007, "Characterization of asphaltenes from hydrotreated products by SEC, LDMS, MALDI, NMR, and XRD", *Energy & Fuels,* vol. 21, no. 4, pp. 2121-2128.

Trejo, F., Ancheyta, J., Morgan, T., Herod, A. & Kandiyoti, R. 2007, "Characterization of asphaltenes from hydrotreated products by SEC, LDMS, MALDI, NMR, and XRD", *Energy & Fuels,* vol. 21, no. 4, pp. 2121-2128.

Trejo, F., Centeno, G. & Ancheyta, J. 2004, "Precipitation, fractionation and characterization of asphaltenes from heavy and light crude oils", *Fuel,* vol. 83, no. 16, pp. 2169-2175.

Trimm, D. 2001, "The regeneration or disposal of deactivated heterogeneous catalysts", *Applied Catalysis A: General,* vol. 212, no. 1-2, pp. 153-160.

Truong-Huu, T., Chizari, K., Janowska, I., Moldovan, M.S., Ersen, O., Nguyen, L.D., Ledoux, M.J., Pham-Huu, C. & Begin, D. 2012, "Few-layer graphene supporting palladium nanoparticles with a fully accessible effective surface for liquid-phase hydrogenation reaction", *Catalysis today,* vol. 189, no. 1, pp. 77-82.

Van Soest, P. 1967, "Development of a comprehensive system of feed analyses and its application to forages", *Journal of animal science,* vol. 26, no. 1, pp. 119-128.

Venderbosch, R.H., Ardiyanti, A.R., Wildschut, J., Oasmaa, A. & Heeres, H. 2010, "Stabilization of biomass-derived pyrolysis oils", *Journal of Chemical Technology & Biotechnology,* vol. 85, no. 5, pp. 674-686.

Venderbosch, R. & Prins, W. 2010, "Fast pyrolysis technology development", *Biofuels, bioproducts and biorefining,* vol. 4, no. 2, pp. 178-208.

Venderbosch, S., Johannes, H., Teerenstra, S., Loosveld, O.J., van Bochove, A., Sinnige, H.A., Creemers, G.M., Tesselaar, M.E., Mol, L. & Punt, C.J. 2011, "Prognostic value of resection of primary tumor in patients with stage IV colorectal cancer: retrospective analysis of two randomized studies and a review of the literature", *Annals of surgical oncology,* vol. 18, no. 12, pp. 3252.

Vernon, L.W. 1980, "Free radical chemistry of coal liquefaction: role of molecular hydrogen", *Fuel,* vol. 59, no. 2, pp. 102-106.

Volkman, J.K., Alexander, R., Kagi, R.I., Rowland, S.J. & Sheppard, P.N. 1984, "Biodegradation of aromatic hydrocarbons in crude oils from the Barrow Sub-basin of Western Australia", *Organic Geochemistry,* vol. 6, pp. 619-632.

Wang, J., Reyniers, M. & Marin, G.B. 2007, "Influence of dimethyl disulfide on coke formation during steam cracking of hydrocarbons", *Industrial & Engineering Chemistry Research,* vol. 46, no. 12, pp. 4134-4148.

Wang, J., Chang, J. & Fan, J. 2010, "Upgrading of bio-oil by catalytic esterification and determination of acid number for evaluating esterification degree", *Energy & Fuels,* vol. 24, no. 5, pp. 3251-3255.

Wang, S., Guo, X., Liang, T., Zhou, Y. & Luo, Z. 2012, "Mechanism research on cellulose pyrolysis by Py-GC/MS and subsequent density functional theory studies", *Bioresource technology,* vol. 104, pp. 722-728.

Wang, Y., Li, X., Mourant, D., Gunawan, R., Zhang, S. & Li, C. 2011, "Formation of aromatic structures during the pyrolysis of bio-oil", *Energy & Fuels,* vol. 26, no. 1, pp. 241-247.

Wang, Y., Yao, J., Li, H., Su, D. & Antonietti, M. 2011, "Highly selective hydrogenation of phenol and derivatives over a Pd@ carbon nitride catalyst in aqueous media", *Journal of the American Chemical Society,* vol. 133, no. 8, pp. 2362-2365.

Watanabe, S. & Arunajatesan, V. 2010, "Influence of acid modification on selective phenol hydrogenation over Pd/activated carbon catalysts", *Topics in Catalysis,* vol. 53, no. 15-18, pp. 1150-1152.

Wawrzetz, A., Peng, B., Hrabar, A., Jentys, A., Lemonidou, A. & Lercher, J. 2010, "Towards understanding the bifunctional hydrodeoxygenation and aqueous phase reforming of glycerol", *Journal of Catalysis,* vol. 269, no. 2, pp. 411-420.

Widyawati, M., Church, T.L., Florin, N.H. & Harris, A.T. 2011, "Hydrogen synthesis from biomass pyrolysis with in situ carbon dioxide capture using calcium oxide", *International Journal of Hydrogen Energy,* vol. 36, no. 8, pp. 4800-4813.

Wiehe, I.A. 1993, "A phase-separation kinetic model for coke formation", *Industrial & Engineering Chemistry Research,* vol. 32, no. 11, pp. 2447-2454.

Wildschut, J., Mahfud, F.H., Venderbosch, R.H. & Heeres, H.J. 2009, "Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts", *Industrial & Engineering Chemistry Research,* vol. 48, no. 23, pp. 10324-10334.

Wilson, G.R. 1975, *Heavy oil demetallization and desulfurization process, .*

Winters, J. & Williams, J. 1969, "Microbiological alteration of crude oil in the reservoir", *American Chemical Society Division of Fuel Chemistry Paper PETR,* vol. 86, pp. E22-E31.

Worasuwannarak, N., Sonobe, T. & Tanthapanichakoon, W. 2007, "Pyrolysis behaviors of rice straw, rice husk, and corncob by TG-MS technique", *Journal of Analytical and Applied Pyrolysis,* vol. 78, no. 2, pp. 265-271.

Xia, T., Greaves, M., Werfilli, W. & Rathbone, R. 2002, "Downhole conversion of Lloydminster heavy oil using THAI-CAPRI process", *SPE International Thermal Operations and Heavy Oil Symposium and International Horizontal Well Technology Conference*Society of Petroleum Engineers, .

Xia, T. & Greaves, M. 2002, "Upgrading Athabasca tar sand using toe-to-heel air injection", *Journal of Canadian Petroleum Technology,* vol. 41, no. 8, pp. 51-57.

Xia, T. & Greaves, M. 2002, "Upgrading Athabasca tar sand using toe-to-heel air injection", *Journal of Canadian Petroleum Technology,* vol. 41, no. 08.

Xifeng, Z., Jilu, Z., Qingxiang, G. & Qingshi, Z. 2005, "Property, Up-grading and Utilization of Bio-oil from Biomass [J]", *Engineering Science,* vol. 9.

Xiong, K., Lu, C., Wang, Z. & Gao, X. 2015, "Kinetic study of catalytic cracking of heavy oil over an in-situ crystallized FCC catalyst", *Fuel,* vol. 142, no. 0, pp. 65-72.

Xiu, S., Rojanala, H., Shahbazi, A., Fini, E. & Wang, L. 2012, "Pyrolysis and combustion characteristics of Bio-oil from swine manure", *Journal of thermal analysis and calorimetry,* vol. 107, no. 2, pp. 823-829.

Xiu, S. & Shahbazi, A. 2012, "Bio-oil production and upgrading research: A review", *Renewable and Sustainable Energy Reviews,* vol. 16, no. 7, pp. 4406-4414.

Xu, X., Zhang, C., Zhai, Y., Liu, Y., Zhang, R. & Tang, X. 2014, "Upgrading of bio-oil using supercritical 1-butanol over a Ru/C heterogeneous catalyst: role of the solvent", *Energy & Fuels,* vol. 28, no. 7, pp. 4611-4621.

Yathavan, B.K. & Agblevor, F. 2013, "Catalytic pyrolysis of pinyon–juniper using red mud and hzsm-5", *Energy & Fuels,* vol. 27, no. 11, pp. 6858-6865.

Yong, P., Rowson, N.A., Farr, J.P.G., Harris, I.R. & Macaskie, L.E. 2002, "Bioaccumulation of palladium by Desulfovibrio desulfuricans", *Journal of Chemical Technology & Biotechnology,* vol. 77, no. 5, pp. 593-601.

Yong, P., Rowson, N.A., Farr, J.P.G., Harris, L.R. & Macaskie, L.E. 2003, "A novel electrobiotechnology for the recovery of precious metals from spent automotive catalysts", *Environmental technology,* vol. 24, no. 3, pp. 289-297.

Yu, H., Huang, Y., Ying, H. & Xiao, C. 2007, "Preparation and characterization of a quaternary ammonium derivative of konjac glucomannan", *Carbohydrate Polymers,* vol. 69, no. 1, pp. 29-40.

Zacher, A.H., Olarte, M.V., Santosa, D.M., Elliott, D.C. & Jones, S.B. 2014, "A review and perspective of recent bio-oil hydrotreating research", *Green Chemistry,* vol. 16, no. 2, pp. 491-515.

Zhai, Y., Zhu, P., Li, S., Zhang, C., Li, Z., Xu, X., Chen, G., Tan, Z., Zhang, R. & Liu, Y. 2014, "Hydrotreatment of bio-oil over Pd-based catalysts", *Journal of Renewable and Sustainable Energy,* vol. 6, no. 4, pp. 043129.

Zhang, C., Yuan, G., Liu, D., Chen, H., Liu, D. & Wang, R. 2003, "An Experimental Study of the Gaseous Pollution Emissions in Petroleum-Coke-Fired Fluidized Beds", *17th international conference on fluidized bed combustion*American Society of Mechanical Engineers, , pp. 267.

Zhang, H., Sarica, C. & Pereyra, E. 2012, "Review of high-viscosity oil multiphase pipe flow", *Energy & Fuels,* vol. 26, no. 7, pp. 3979-3985.

Zhang, Q., Chang, J., Wang, T. & Xu, Y. 2007, "Review of biomass pyrolysis oil properties and upgrading research", *Energy conversion and management,* vol. 48, no. 1, pp. 87-92.

Zhang, Q., Chang, J., Wang, T. & Xu, Y. 2007, "Review of biomass pyrolysis oil properties and upgrading research", *Energy conversion and management,* vol. 48, no. 1, pp. 87-92.

Zhang, X., Wang, T., Ma, L., Zhang, Q. & Jiang, T. 2013, "Hydrotreatment of bio-oil over Ni-based catalyst", *Bioresource technology,* vol. 127, pp. 306-311.

Zhang, D., Chen, L. & Ge, G. 2015, "A green approach for efficient p-nitrophenol hydrogenation catalyzed by a Pd-based nanocatalyst", *Catalysis Communications,* vol. 66, no. 0, pp. 95-99.

Zhu, J. 2014, *Synthesis of Precious Metal Nanoparticles Supported on Bacterial Biomass for Catalytic Applications in Chemical Transformations*, PhD edn, University of Birmingham.

Zhu, J., Wood, J., Deplanche, K., Mikheenko, I. & Macaskie, L.E. 2016, "Selective hydrogenation using palladium bioinorganic catalyst", *Applied Catalysis B: Environmental*, vol. 199, pp. 108-122.

Zhu, J., Wood, J., Deplanche, K., Mikheenko, I. & Macaskie, L.E. 2016, "Selective hydrogenation using palladium bioinorganic catalyst", *Applied Catalysis B: Environmental*, vol. 199, pp. 108-122.

Zhu, J., Wood, J., Deplanche, K., Mikheenko, I. & Macaskie, L.E. 2016, "Selective hydrogenation using palladium bioinorganic catalyst", *Applied Catalysis B: Environmental*, vol. 199, pp. 108-122.