University of Calgary

PRISM Repository **https://prism.ucalgary.ca**

The Vault Open Theses and Dissertations

2016

Catalytic Bitumen Partial Upgrading using Methane

Luan, Yingqi

Luan, Y. (2016). Catalytic Bitumen Partial Upgrading using Methane (Master's thesis, University of Calgary, Calgary, Canada). Retrieved from https://prism.ucalgary.ca. doi:10.11575/PRISM/25224 http://hdl.handle.net/11023/3289

Downloaded from PRISM Repository, University of Calgary

UNIVERSITY OF CALGARY

Catalytic Bitumen Partial Upgrading using Methane

by

Yingqi Luan

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF ENGINEERING

GRADUATE PROGRAM IN CHEMICAL AND PETROLEUM ENGINEERING

CALGARY, ALBERTA

September, 2016

© Yingqi Luan 2016

Abstract

It is highly desired to partially upgrade viscous heavy oil, to be transportable by pipeline. Conventionally, this is achieved by expensive catalytic hydrogenation under a hydrogen pressure of 15–20 MPa. In this thesis, it is reported that by using zinc and silver cation-modified HZSM-5 as the catalyst, methane can be activated at a relatively low temperature of 380 °C and a pressure of 5 MPa to efficiently upgrade heavy oil. The product is a partially upgraded crude oil which is more desirable for pipeline transportation and downstream refining. Before the evaluation of different catalysts, the reaction conditions optimization and better support identification is carried out. The catalyst with the best upgrading performance among all developed candidates comparison was 1 wt% Ag–10 wt% Zn/HZSM-5. This study opens a door for upgrading heavy oil with natural gas.

Acknowledgements

Firstly, I would like to express my sincere gratitude and thanks to my supervisor, Dr. Hua Song, for selecting me to undertake this project. His guidance and support were invaluable during the course of this work. Words cannot express my gratitude for my supervisor who was also a moral support to me at demanding situations.

I would like to thank Dr. Zhangxing (John) Chen and Dr. Harvey W Yarranton for their valuable suggestions and informative discussions.

I gratefully acknowledge the Department of Chemical and Petroleum Engineering at the University of Calgary. I would also like to thank all the members of our green catalyst research group.

Table of Contents

Abstract 1
Acknowledgements 2
List of figure 5
List of table 7
Chapter One: Introduction 1
1.1 Synopsis 1
1.2 Background 2
1.3 Objectives 4
1.4 Thesis Structure 5
Chapter Two: Literature Review 7
2.1 Bitumen and Heavy Oil Chemistry 7
2.2 Upgrading 9
2.3 Catalyst Chemistry 14
2.3.1 Zeolite 14
2.3.2 ZSM-5 15
2.3.3 ZrO_2 17
Chapter Three: Experimental Methods 18
3.1 Bitumen Upgrading Autoclave 18
3.2 Feedstock And Chemicals 20
3.3Catalyst Synthesis 20
3.4 Oil Sample Characterizations 21
3.4.1 Water Content Measurement 21
3.4.2 Total Acid Number Measurement 22
3.4.3 Density Measurement 23
3.4.4 Gasoline And Diesel Composition Measurement 23
3.4.5 Oil Stability And Compatibility Measurement 24
3.4.6 Viscosity Measurement 25
3.4.7 Elemental Composition Analysis 26

3.4.8 Coke Yield Analysis 26
3.4.9 Asphaltene Content Measurement 27
3.4.10 GC-MS Measurement 27
Chapter Four: Reaction Condition Optimization 28
4.1 Reaction Conditions Optimization 28
4.2.1 Feed Weight And Agitation Rate 28
4.2.2 Choosing Reaction Time 30
4.2.3 Choosing Reaction Temperature 32
4.2.4 Choosing Reaction Pressure 34
4.3 Conclusion 36
Chapter Five: Bitumen Partial Upgrading Performance of Ag-Zn/ZSM-5 37
5.1 Results And Discussion 37
5.2 Conclusions 43
Chapter Six: Catalyst Formulation Optimization for Performance Enhancement 44
6.1 Effect of Support 44
6.1.1 HZSM-5 44
6.1.2 Zeolite Y 50
6.1.3 Sulfated ZrO_2 54
6.1.4 Zeolite A 55
6.2 Catalyst Optimization Upon Active Metal Loading 56
6.3 Conclusions 60
Chapter Seven: Conclusions and future work 62
7.1 Conclusions 62
7.2 Future Work 63
References 65

List of figure

Figure 2- 1. The hydrogen/carbon molar ratio of various fossil fuels (cited from NETL website)..... 11

Figure 2- 2. The Pentasil Unit of ZSM-5 15

Figure 3- 1. Apparatus Outside 18

Figure 3- 2. Lid of reactor..... 18

Figure 3- 3. Wetness impregnation 21

Figure 3- 4. House-made distillation system for gasoline and diesel content measurement 24

Figure 3- 5. Reference spot definition and visualization for oil sample compatibility and stability measurement 25

Figure 4- 1. Magnetic stirring condition determination procedure 29

Figure 4- 2. Temperature profile collected during bitumen partial upgrading over 1%Ag/ZSM-5..... 33

Figure 4- 3. Product-oil collected over 1% Ag/ZSM-5 catalyst after bitumen upgrading at 1.0 MPa for 150 min 34

Figure 4- 4. The effect of methane pressure on viscosity reduction of the product oil collected after bitumen upgrading at 380 ^{o}C for 150 min 35

Figure 5- 1. Stability test of (a) bitumen and oil products collected under (b) N_2, (c) CH_4, (d) CH_4 with ZSM-5, (e) CH_4 with catalyst Ag-Zn/ZSM-5, and (f) H_2 with catalyst Ag-Zn/ZSM-5..... 39

Figure 6- 1. Viscosity and coke yield of the product oil collected over HZSM-5 with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 ^{o}C for 150 min 46

Figure 6- 2. Stability test of (a) bitumen and oil products obtained using HZSM-5 with SiO_2/Al_2O_3 molar ratios of (b) 23:1, (c) 30:1, (d) 50:1, (e) 80:1 and (f) 280:1 as the catalyst 47

Figure 6- 3. Viscosity and coke yield of the oil products obtained using 1 %Ag/HZSM-5 with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 ^oC for 150 min 49

Figure 6- 4. Stability test of oil products obtained using 1%Ag/HZSM-5 with SiO_2/Al_2O_3 molar ratios of (b) 23:1, (c) 30:1, (d) 50:1, another 80:1 and (f) 280:1 as the catalyst 49

Figure 6- 5. Viscosity and coke yield of the product oil obtained using HY with variable SiO_2/Al_2O_3 molar ratios 51

Figure 6- 6. Stability test of oil products obtained using HY with SiO_2/Al_2O_3 molar ratios of (a) 5.2:1, (b) 30:1, (d) 60:1 and (d) 80:1 as the catalyst under methane environment at 5.0 MPa and 380 ^oC for 150 min 52

Figure 6- 7. Viscosity and coke yield of the product oil obtained using 1%Ag/HY with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 ^oC for 150 min 53

Figure 6- 8. Stability test of oil products obtained using 1%Ag/HY with SiO_2/Al_2O_3 molar ratios of (a) 5.2:1, (b) 30:1, (d) 60:1 and (d) 80:1 as the catalyst under methane environment at 5.0 MPa and 380 ^oC for 150 min 54

Figure 6- 9. Stability and compatibility of oil products using (a) S-ZrO_2 and (b) 1 %Ag/S-ZrO_2 under methane environment at 5.0 MPa and 380 ^oC for 150 min 55

Figure 6- 10. Stability and compatibility of oil products using Zeolite A under methane 56

Figure 6- 11. Viscosity and coke yield of the product oil obtained using metal modified HZSM-5 (30:1) under methane environment at 5.0 MPa and 380 ^oC for 150 min 57

Figure 6- 12. Stability test of oil products obtained using HZSM-5 (30:1) modified by 1%Ag-1%Ga as the catalyst under methane environment at 5.0 MPa and 380 ^oC for 150 min 58

Figure 6- 13. (a) Gasoline and (b) diesel fractions of the product oil collected over 1%Ag-1%Ga/ZSM-5 under methane environment at 5.0 MPa and 380 ^oC for 150 min..... 60

List of table

Table 2- 1. Bitumen Fraction 8

Table 3- 1. Required sample weight corresponding to different expected acid numbers ... 22

Table 3- 2. Reference spot description for oil sample compatibility and stability measurement 25

Table 4- 1. The upgrading performances with various reaction time collected over 31

Table 4- 2. The upgrading performances collected over 1 %Ag/ZSM-5 under methane at 1.0 MPa and various reaction temperatures for 150 min 32

Table 4- 3. The upgrading performances collected over Ag/ZSM-5 under methane at various pressures and 380 ^{o}C for 150 min 35

Table 5- 1. Performance of bitumen upgrading under various environments at 5.0 MPa and 380 ^{o}C for 150 min 38

Table 5- 2. Gasoline and diesel fractions of the oil samples collected before and after bitumen upgrading under various environments at 5.0 MPa and 380 ^{o}C for 150 min 40

Table 5- 3. Properties of the oil samples collected before and after bitumen upgrading under various environments at 5.0 MPa and 380 ^{o}C for 150 min 42

Table 5- 4. Elemental analysis of oil samples collected before and after bitumen upgrading under various environments at 5.0 MPa and 380 ^{o}C for 150 min 43

Table 6- 1. Viscosity and coke yield of the product oil collected over HZSM-5 with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 ^{o}C for 150 min 46

Table 6- 2. Viscosity and coke yield of the oil products obtained using 1 %Ag/HZSM-5 with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 ^{o}C for 150 min 48

Table 6- 3. Viscosity and coke yield of the oil products obtained using HY with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 ^{o}C for 150 min 51

Table 6- 4. Viscosity and coke yield of the product oil obtained using 1%Ag/HY with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 ^oC for 150 min..... 53

Table 6- 5.Viscosity and coke yield of oil products collected over S-ZrO_2 and 1%Ag/S-$ZrO_2$54

Table 6- 6. Viscosity and coke yield of oil products using Zeolite A 55

Table 6- 7. Performance of bitumen partial upgrading using metal modified HZSM-5 catalysts under methane environment at 5.0 MPa and 380 ^oC for 150 min..... 57

Table 6- 8. Gasoline and diesel fractions of the oil sample collected from various runs conducted at 5.0 MPa and 380 ^oC for 150 min..... 59

Chapter One: Introduction

1.1 Synopsis

Hydrocracking is conventionally employed as a process to upgrade heavy crude oil for reducing its viscosity, increasing its H/C ratio, and removing associated impurities. This process is costly and energy inefficient because hydrogen must be generated from a separate unit through natural gas steam reforming and high operation pressure. This research aims to effectively upgrade heavy crude oil including extra heavy oil and bitumen extracted from oil sands to synthetic crude oil with acceptable specifications (i.e. API of 30 ~ 34^{o} and sulfur content of 0.1 ~ 0.2%) and increased productivity at much lower pressure (<3 MPa) by directly using natural gas as the reducing agent. With the right catalyst, methane as the main component of natural gas can be activated to crack and saturate the long carbon chains into crude oil using a synergetic effect occurring between methane and co-existing higher hydrocarbons and remove heteroatoms contained in the heavy crude oil, while itself being converted to produce extra synthetic crude oil. This concept has been indirectly validated through experimental data collected from low rank coal and biomass methane upgrading (He, 2014, He, 2016, Xiao, 2016) and syngas liquefaction performed at near atmospheric pressure. The successful achievement of the research objectives will lead to significant cost and greenhouse gas (GHG) emission reductions of the heavy crude oil upgrading process and make it more economically attractive and environmentally friendly. Moreover, the outcomes obtained from this research will create a novel way of methane activation and liquefaction, leading to the breakthrough in the field of catalysis and its application in clean energy conversion.

1.2 Background

Unlike conventional petroleum deposit, neither heavy oil, nor bitumen extracted from oil sands such as the ones abundant in Canada can be directly sent to existing refineries as feedstock for fuels and lubricants production due to its high viscosity, low hydrogen to carbon ratio, and high impurities content (Speight, 2014). Therefore, such heavy crude oil needs to be efficiently upgraded to meet the standards set by the refineries. Different ways have been attempted to decrease the viscosity of bitumen, including ultrasonic treatment, the addition of microorganisms, the application of a magnetic field and the use of viscosity breaking additive. However, the most effective method involve reacting the oil either thermally or with hydrogen addition. Thermal cracking is suitable for some reduction but risks coke formation. Traditionally, hydrogen thermal cracking is widely employed to break down the long carbon chain of the high molecular weight residues, saturate the formed small molecules, and remove the impurities such as sulfur, nitrogen, and metal out from the upgraded crude oil. However, the involvement of such expensive hydrogen resource which is not naturally available results in the significant cost increase of this upgrading step (Furimsky, 2007). It is thus critical to find out an alternative hydrogen source which is readily available and abundant in nature for prominent upgrading cost reduction, making the whole process more economically attractive.

Currently over 50% of the world's hydrogen production relies on natural gas as the feedstock through steam reforming process (Idriss, 2004). If natural gas can be directly used as the reducing agent instead of using hydrogen, the steam reforming process can be completely eliminated, leading to the upgrading process cost reduction. Furthermore, compared to the traditional hydrogenation process, such novel process can produce extra synthetic crude oil originating from the introduction of natural gas molecules into the carbon chain of raw heavy crude oil, making the upgrading process even more economically favorable.

Natural gas, including shale gas, is another abundant natural resource present in Canada. Due to its chemical inertness and low energy density, natural gas is currently dominantly used for heating residential area and not valuable for transportation or chemical production applications. Therefore, natural gas is sold a lower price than gasoline. Intensive studies have been carried out over the past sixty years by many researchers regarding natural gas utilization for upgrading and a breakthrough has not yet been reported. Hence, developing a technology which can effectively convert natural gas into valuable chemicals will definitely attract the attentions from both industry and academia. The project aims to develop a catalyst system and associated process which can efficiently convert natural gas into crude oil during the heavy crude oil upgrading process. At the same time, the heavy hydrocarbon residue will be sufficiently broken down, rearranged, and saturated into light crude oil under the facilitation of the introduced natural gas.

However, owing to the high bond energy of the C-H in methane, the activation of methane molecules in the presence of catalysts will be the most crucial step for the utilization of methane in this process. Among all the catalysts for methane activation, the ZSM-5 based catalysts have been the most intensively investigated especially for nonoxidation activation due to its high specific surface, adjustable acidity, and structure selectivity (Miao, 2004). Coupled with other active metals (Choudhary, 1997) such as Ga, Ag, Zn, and so on (Baba, 2012), the effect of ZSM-5 based catalysts on conversion of methane to higher hydrocarbons have been investigated and proven (Ding, 2008). According to the researches carried out by Choudhary, *et al.*, the methane conversion with Ga/HZSM-5 catalyst was significantly improved in the presence of higher hydrocarbon reactants, particularly unsaturated hydrocarbons at much lower temperature region (400 ~ 600 ^{o}C) and atmospheric pressure. Based on these results, a novel idea on bitumen upgrading using methane as hydrogen donor has been proposed and investigated in this study. The

bitumen first undergoes thermal cracking to generate unsaturated hydrocarbons. Simultaneously, the charging methane will be activated with the assistance of unsaturated hydrocarbons in the presence of zeolite based catalysts modified by the transition metals as active phase. Then the generated H and CH_x species from methane activation can be further utilized for hydrotreating and carbon chain rearrangement reaction. In this way, the bitumen can be upgraded into lower hydrocarbons as well as generation of extra synthetic crude oil originating from the methane incorporation.

1.3 Objectives

Although similar ideas have been proposed and tested previously, the relatively poor catalytic performance significantly limits its potential commercialization, which might be the reason why there are no further research and development activities being reported in the literature in recently years. A breakthrough in the catalyst design and fabrication must be made before academic and industrial attention can be attracted to the proposed technique. The objective of this thesis is in order to develop the required catalyst for effectively catalyzing methanotreating process. An integrative approach (i.e. iterative with feedback) was adopted in this project. Starting from catalyst preparation, a series of catalyst candidates were synthesized according to the relevant literature and the previous research outcomes from our research group. A supported catalyst was employed for this study, which is very different from the organometallic catalysts used in previous studies (Ovalles et al., 1998). A zeolite type support such as ZSM-5 was formulated bu adjusting the Si:Al ratio and surface modification of phosphorus, alkali or alkali earth, and rare earth metals provided moderate acidity and sufficient oxygen storage capacity (OSC). The target was to catalytically crack down the long carbon chains and complicated polycyclic molecular structure contained in the heavy crude oil while effectively preventing excessive cracking and coke formation. Mo, Ga, Zn, Co, Ag, In, or their combinations was tested as the starting point as the

active metal loaded on the aforementioned support for methane activation. The prepared catalysts were then be fed into a batch reactor pre-filled with heavy crude oil and natural gas and operated under an optimized reaction conditions to evaluate their catalytic performances in sequence. Once all the reaction data were collected and compared, the fresh and spent samples (i.e. catalyst and crude oil) were selectively submitted to determine the physical and chemical properties of the samples, which is beneficial for the reaction mechanism investigation. Based on the interpreted reaction and characterization results, new catalysts with modified formulation and morphology were synthesized and ready for next cycle evaluations. Finally, the most promising catalyst was subjected to a long term stability test using a continuous fixed bed reactor system through which catalyst deactivation mechanism can be explored.

1.4 Thesis Structure

In the first chapter, the upgrading of heavy oil using natural gas as the reducing agent in hydrocracking with the right catalyst and background of heavy oil upgrading was introduced. The research objective to develop a catalyst for effectively catalyzing the methanotreating process was propoeesd

In the second chapter, in bitumen chemistry, bitumen upgrading and catalyst chemistry are reviewed.

In the third chapter, the experimental apparatus and reaction procedure of the heavy oil upgrading and product-oil analysis are discussed.

In the fourth chapter, several factors including temperature, pressure, reaction time, bitumen loading, and agitation rate, are considered. The reaction conditions are optimized based on the catalytic performance on the viscosity reduction and coke yield as well as the stability and compatibility of the oil products.

In the fifth chapter, 1 wt.%Ag-10 wt.%Zn/ZSM-5 catalyst was synthesized using the wet impregnation method and evaluated for triggering the bitumen partial upgrading reaction under a methane environment .The formed crude synthetic oil was extensively analyzed for its quality control in terms of viscosity, acidity, density, water content, gasoline and diesel content, asphaltene content, average molecular weight, stability, and elemental composition.

In the sixth chapter, the effect of the support including ZSM5, zeolite Y, ZrO_2, and zeolite A with various porous structures and surface acidities are first evaluated, followed by the contribution examination of active metals including Ag, Zn, and Ga in terms of the viscosity, coke formation tendency, and stability and compatibility of the partially upgraded product oil.

In the seventh chapter, the conclusions of the research are listed and future work is discussed.

.

Chapter Two: Literature Review

2.1 Bitumen and Heavy Oil Chemistry

Bitumen and heavy oil are viscous crude oil consisting of hydrocarbons and their derivatives. They are black or brown in colour and possesses waterproofing and adhesive properties. (Speight, 2007). By definition, heavy oils have a density between 0.93 and 1.0 g/cm^3 and bitumens have a density greater than 1.0 g/cm^3 (reference Unitar or Murray Gray book).

The main elemental species of bitumen are carbon (C) and hydrogen (H), followed by sulfur (S), nitrogen (N) and oxygen (O). The element compositions of bitumen from different regions vary over a relatively narrow range and the average composition is 85 wt% carbon, 13 wt% hydrogen, and a combined heteroatom (S+N+O) content of 2 wt% (Hunt, 1996). The heteroatoms are found mainly in the heaviest fraction of the oil; that is, in the residue and particularly in the asphaltenes.

Bitumen consists of millions of chemical species (REF McKenna and Rodgers etc) which can be characterized into chemical families or distillation cuts. One frequently used characterization method is SARA (saturates, aromatics, resins, and asphaltenes) analysis. In this method, the asphaltenes are precipitated from the oil and therefore are a solubility class. A generally accepted definition of asphaltenes is that they are the components that can be dissolved in toluene, but not in heptane or pentane. The other fractions are separated by liquid chromatography and therefore are adsorption classes. The saturates consist of paraffinic and naphthenic components. The aromatics, resins, and asphaltenes are a continuum of aromatic species of increasing molecular weight, density, aromaticity, polarity, and heteroatom content (Speight, 2014).

Bitumen can also be characterized into boiling point cuts. Since bitumen compounds have different boiling points, when bitumen is heated up to different temperatures, it will separate into different fractions.

Table 2- 1. Bitumen Fraction

Fraction	Temperature (°C)	Carbon Number
Oil Gas	<35	C1-C4
Gasoline	35-190	C5-C10
Kerosene	190-260	C11-C13
Diesel	260-320	C14-C18
Heavy Gas	320-360	C19-C25
Lubricant	360-530	C26-C40
Residue	>530	>C40

The bitumen compounds in different boiling cuts are very different. In oil refining, the carbon number ranges and the distillation temperature ranges belonging to different fractions are shown in Table 2-1. In general, the light and low boiling point fractions are mainly composed of paraffins and naphthenes with low carbon numbers and molecular weights. Middle distillate are mainly composed of paraffins and naphthenes with middle molecular weight and higher carbon numbers. It also contains a certain number of aromatic, naphthenic aromatics and a small amount of sulfur, nitrogen, oxygen compounds. Heavy fractions are mainly composed of naphthenic, aromatic and naphthenic aromatic hydrocarbons with high carbon number and large molecular weights, along with sulfur, nitrogen and oxygen containing compounds. Since asphaltenes are the heaviest and

least volatile fraction of the oil, they are the main component of vaccum residua (Eric Y. Sheu, 1995). Asphaltenes are the also most challenging fraction to refine.

2.2 Upgrading

Several methods for bitumen refining are using by people, including atmospheric distillation and vacuum distillation, catalytic cracking, catalytic reforming, hydrocracking, and delayed coking (Mohan S,2006). Atmospheric and vacuum distillation are physical processes where raw materials are separated into fractions, each with a different boiling point range. These fractions are sent for subsequent processing, and; therefore, atmospheric and vacuum distillation are known as crude oil primary processing.

Hydrocracking is a reactive process in the presence of high pressure hydrogen and suitable catalysts. The heavy molecules in the feedstock are converted into lighter ones, such as gasoline, kerosene, diesel oil and lubricating oil. Hydrogen is added to reduce coke formation and remove the sulfur and nitrogen atoms.

The carbon to hydrogen atomic ratio in heavy oils is often higher than that of light oils including gasoline and diesel. There are two main reaction pathways through which heavy oil upgrading occur. In the first pathway, carbon is rejected as coke to produce light oil of low carbon-to-hydrogen ratio. The other route is via hydrogen addition to favour the yield of liquid product while suppressing coke formation (Speight, 2004). The objectives of these processes are to produce more valuable light crude oil that meets refinery specifications and has minimized heavy metals and sulphur content.

The first reaction approach is often realized by thermal cracking, which removes the sided chains, break the long carbon chains into shorter ones, lower the molecular weight and reduce the viscosity. The free radical mechanism for the thermal cracking process was established decades ago (Greensfelder, 1949). A molecule becomes a free radical by losing a hydrogen atom upon

collision at high temperatures leaving an unpaired electron. Unless they are rapidly stabilized, free radicals can combine to form large molecules and eventually coke.

Coke formation is suppressed in the presence of a hydrogen donating liquid, which acts as the radical scavenger (Greensfelder, 1949). Therefore, a hydrogen donor can be introduced to the reaction matrix during the thermal-catalytic upgrading of heavy oil to form low molecular weight light oil without severe coke formation.

As shown in Figure 2-1, heavy crude oil and oil sands (asphalt and tar sand) have a broad hydrogen-to-carbon (H/C) ratio distribution ranging from 1.2 to 1.7. In order to produce a light crude oil with an H/C ratio centering at 1.9, a hydrogen source must be introduced into the framework of the less saturated hydrocarbon residue. As indicated in Figure 1-1, methane, which is the main component of natural gas, has the highest H/C ratio among all the naturally available carbon materials, which should theoretically provide sufficient hydrogen to upgrade heavy oil and oil sands as hydrogen gas does during hydrotreating process. Moreover, the co-introduced carbon atom from methane molecule will be added to the broken small carbon chain to achieve extra synthetic crude oil, as exemplified in the following simplified chemical reactions 1 and 2.

$$C_{38}H_{56}+18CH_4 \xrightarrow{\text{catalyst}} 7C_8H_{18}+H_2 \qquad \text{(1: methanotreating)}$$

$$C_{38}H_{56}+14.75H_2 \xrightarrow{\text{catalyst}} 4.75C_8H_{18} \qquad \text{(2: hydrotreating)}$$

$C_{38}H_{56}$ (Strausz) is a generalized chemical formula representing the major composition of the heavy oil/bitumen discovered from Alberta without considering the co-existing trace elements such as sulfur, nitrogen, oxygen, and metals present in their organic forms. C_8H_{18} stands for the simplified gasoline product composition. As can be clearly observed when these two reactions are

compared, using methane as upgrading reagent significantly improves the quantity of the final oil product while producing hydrogen as a valuable byproduct. Methane participation in the synthetic crude oil molecule building reaction has been demonstrated during a similar bio crude oil upgrading process where methane was used as hydrogen source to upgrade the crude oil obtained from biomass pyrolysis (Fernando, 2011) and during a coal pyrolysis process where the tar yield was improved in the presence of methane stream (Jin, 2013).

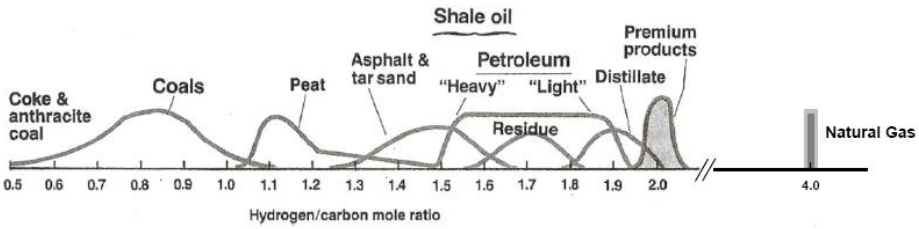


Figure 2- 1. The hydrogen/carbon molar ratio of various fossil fuels (cited from NETL website)

In order to make the aforementioned methanotreating reactions taking place at the similar or even less severe conditions (e.g. less operation pressure) like those used during hydrotreating process (temperature of 380 ~ 480 ^{o}C and pressure of 14 ~ 20 MPa), a specially tailored catalyst system is required. Compared to hydrogen, methane has much more stable molecular structure (tetrahedron), resulting in its inert chemical and physical properties. Therefore, the developed catalyst must activate the methane first to make it as active as hydrogen for participating into the heavy oil upgrading process.

The methane activation is triggered by the first C-H bond cleavage in its tetrahedral structure. Such bond breakage requires an activation energy as high as 104 kcal/mol. However, once the first C-H bond is broken, the formed methyl radical is very active and the remaining C-H bonds cleavage will happen automatically in a chain reaction if there is no termination group to end it.

The desired catalyst should be able to effectively lower the energy barrier allowing the methane activation to occur at less severe reaction conditions.

Although oxidative methane conversion is more favored from the viewpoint of thermodynamics than nonoxidative methane activation (Alvarez-Galvan, 2011, Guo, 2014, Wang, 1993, Wang, 1997, Borry, 1999), the addition of oxidant is detrimental for heavy crude oil upgrading and therefore not applicable for the proposed process (Sahebdelfar, 2012). Many researchers have dedicated themselves to the field of methane activation under nonoxidative condition over the past more than thirty years and many catalyst systems have been reported (Guczi, 1997, Lunsford, 1995, Hutchings, 1989, Xu, 1999, Xu, 2003, Lee, 1988, Amenomiya, 1990, Kolyagin, 2008, Xu, 2003, Weckhuysen, 1998), among which zeolite supported molybdenum catalyst demonstrates the most promising activity toward methane conversion to higher hydrocarbons (Choudhary, 2003). Nonetheless, less than 10 % methane conversion is observed with the catalyst Mo/H-ZSM5 when the temperature is higher than 700^{o}C and the major products are aromatics (Cui, 2011). Obviously, this category of catalyst cannot meet the requirements raised from the methanotreating process. Nevertheless, the pioneering work of Choudhary *et al.* (1997) followed by Baba, 2002, Anunziata, 2011, Anunziata, 2003, Baba, 2003, Anunziata, 2005, Wang, 1997 demonstrated that methane conversion will be significantly improved in the presence of higher hydrocarbon reactants (Ha, 2013), particularly unsaturated hydrocarbons at a much lower temperature region (400 ~ 600 ^{o}C) and atmospheric pressure and which sets the ground for this technology (Baba, 2006, Baba, 2007).

Based on these observations, the co-existing heavy oil which is a mixture of unsaturated long chain hydrocarbons and complicated polycyclic molecular structures (Gray, 2015) should help the activation of methane and its following conversion after its initial cracking into smaller molecules

containing shorter carbon chain aided by the co-existing cracking catalyst. The activated methane molecule will form CH_x and H_{4-x} species (Choudhary, 2005). Hydrogen species will then be used for cracking down the long and unsaturated carbon chain of the heavy crude oil molecules while removing sulphur, nitrogen, and metal out from the crude oil under the facilitation of the developed catalyst. At the same time, the cracked long chain heavy oil molecules should be able to react with the produced CH_x moiety to form more synthetic crude oil (Zhang, 2011). Therefore, a synergistic effect between heavy oil and natural gas is expected to take place during a methanotreating process when a suitable catalyst is added. This synergy has been observed experimentally (Ovalles, 1998, Ovalles, 2003). Ovalles studied the use of an dispersed iron catalyst, derived from $Fe_3(CO)_{12}$, and found that the upgrading reaction reduced the viscosity from 500 to 1.3 Pa s, reduced the sulfur content by 14%, and converted 41% of the >500 °C fraction in the upgraded product with respect to the original crude.

In addition, the moisture originally present in the heavy crude oil or created from the deoxygenation of heavy crude oil or even intentionally added from outside will make the methane activation even easier based on the observations reported in the literature where steam was injected together with methane for heavy crude oil in-situ down hole upgrading (Kuppe, 2008, Ovelles, 2003), which might be attributed to the formed OH species from water cracking (Ovelles, 1995). Furthermore, the conventional hydrotreating process is usually performed at elevated pressure (>1000 psi) and the aforementioned literature work is carried out at atmospheric pressure. According to Le Chatelier's principle, higher operation pressure will benefit the methane conversion during methanotreating process due to the liquid formation. Therefore, it can be expected that even better performance can be achieved when methanotreating process is operated at the similar reaction conditions or even less severe conditions (e.g. pressure < 3 MPa) like the

ones used in hydrotreating. In addition to conventional natural gas, shale gas can be directly employed into the methanotreating process without pre-purification a very energy intensive process. Instead of exerting any negative effect, the co-existing high contents of C2 (~10%) and C3 products (~5%) will not only facilitate the methane conversion, but also contribute to the production of extra synthetic crude oil.

2.3 Catalyst Chemistry

2.3.1 Zeolite

Zeolites, also known as molecular sieves, are a group of crystalline solid with open 3D framework structures made of silicon, aluminum and oxygen (John, 2001). These atoms form $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral, which are linked with each other by sharing all the oxygen atoms at the corners to form regular intra-crystalline cages, cavities and channels, resulting in infinite structures (Richard, 1995). A rich variety of morphologies are generated by varying the assembling manner of these platforms. At present, there are 231 unique zeolite frameworks found, but only over 40 naturally zeolite frameworks are under extensive research (Mohamed, 2015). The structure is neutral when it is consisted of pure silicon and oxygen tetrahedral. When some $[SiO_4]^{4-}$ tetrahedra are replaced by $[AlO_4]^{5-}$ tetrahedral, however, cations are required to balance the extra negative charge. Cations or small molecules may reside in channels and cavities inside of the framework (Richard, 1995). Many zeolites are extensively used in many parts of the world in industry and medicine, which is closely related to their unique morphologies that allow certain molecules to enter the pores and channels, where catalytic sites are located (Wei, 2015).

Zeolites have been used to do the separations and purifications in industry since the middle 50s. They are now used in a variety of applications because of their unique porous properties (Geological Survey, 2008), such as petrochemical cracking, water softening and purification,

separation and removal of gases and solvents, agriculture, animal husbandry and construction. They are also widely used as catalyst support material due to their porous structure as well as the presence of Brönsted acid sites along with Lewis acid sites (Jacques, 1979).

2.3.2 ZSM-5

ZSM-5 (MFI-type zeolite) was first synthesised by Mobile Oil Company in the 1960s, which contained cationic organic amine. The structure of ZSM-5 is formed by linking the pentasil units through oxygen atoms. Each pentasil unit is made of eight five-membered rings (Čejka, 2005). With regards to the structure of the rings, Al or Si atoms are located in the center of the tetrahedra and O atoms are assumed to be bonded between the vertices (Figure2-2) (Čejka, 2005). These pentasil units then form the chains of 10-ring holes like corrugated plate. The crystal phase of ZSM-5 would change with the temperature. The structure is orthorhombic at high temperatures such as higher than 350K, which transfer to monoclinic when the temperature cool down between 300 and 350K. (Hay, 1985)

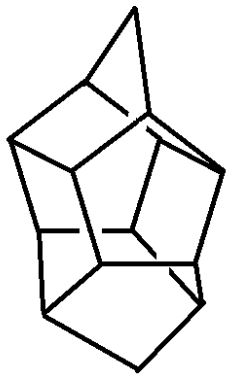


Figure 2- 2. The Pentasil Unit of ZSM-5

Like other zeolites, the Brönsted acidity is proportional to the aluminum content in ZSM-5 framework. When the Al^{3+} replaces the Si^{4+} in a $[SiO_4]^{4-}$ tetrahedron, in order to get the extra negative charge balanced, a cation such as H^+ will be involved. H^+ would form –OH groups on the

bridging oxygen sits, resulting in Brönsted acid sites and enhanced acidity of the framework. (Guisnet, 1984)

Due to its unique chemical composition, crystal structure and physical and chemical properties, ZSM-5 shows excellent catalytic performance in many organic catalytic reactions. ZSM-5 has widely used in industry (Rahimi, 2011, Mohammadaparast, 2015) and it is becoming a promising new petrochemical support for its catalytic performance on methane activation. Most of the catalyst systems that catalyze the methane conversion over non-oxide environment, which is similar to the condition of petroleum processes, are based on ZSM-5 catalysts. Therefore, ZSM-5 is employed as the support material to prepare catalysts and catalyze the heavy oil upgrading under methane environment in this work. Besides ZSM-5, another two technologically important zeolite systems are Zeolites A (LTA-type) and Zeolite Y (FAU-type) due to their extensive application in petroleum cracking and water softening (Hayashi, 2007).

In the early 1950's Zeolites Y was recognized by Union Carbide Laboratories scientists, which have superior stability characteristics majorly due to its higher Si/Al molar ratio of 1.5 to 3 (Steen, 2004). In addition to its improved stability compared to other zeolites, the unique composition and structure and the good catalytic performance associated with these features make zeolite Y based catalysts widely utilized in many important applications such as hydrocarbons conversion since 1959, when the first commercial introduction was established (Michel, 2002). Zeolite Y has been employed among the most import zeolite catalysts in petroleum industry, particularly in fluid catalytic cracking (FCC) process, primarily for the greatest gasoline yield at the highest octane with the greatest degree of catalytic stability (Thomas, 2000), as well as accelerated production of paraffins and aromatics (Vermeiren, 2009). The larger pore size of Zeolite Y (11.24 Å) compared to that of ZSM-5 (6.36 Å) might give rise to improved catalytic performance, since the molecules

of the heavy oil feedstock are larger than conventional petroleum molecules and thus have higher chance to get diffused into larger pores for cracking and structural rearrangement.

Another type of zeolite with a large pore size is Zeolite A. It displays a large pore size of ~11.05 Å and high thermal resistance capability (up to 700 ^{o}C), thus being chosen as a support candidate for triggering bitumen partial upgrading. The first several types of Zeolite A are nearly "saturated" in aluminium in the framework composition with a molar ratio of Si/Al ≈ 1. (Shcherban, 2014) It is considered as the zeolite system with highest possible aluminum content (Kunkeler, 2001). As a consequence, it contains the largest number of cation exchange sites for balancing the framework aluminum, and thus the highest cation content and exchange capacity. When these cation sites are occupied by H^{+}, these sites are converted to Brösted acid sites. Such strong acidity might facilitate the cracking of heavy oil molecules and their further conversion.

2.3.3 ZrO_2

Along with zeolites, ZrO_2 is also used as the catalyst's support to explore the catalytic performance in heavy oil upgrading under methane environment. The structure of ZrO_2 belongs to the cubic crystal system. Its space group is Fm3m with crystalline structure of fluorite with a lattice constant value of the cubic phase a = 5.139 Å (Stefanovich, 1994). The surface acidity of ZrO_2 is enhanced by sulfate treatment. The obtained sulfated ZrO_2 (S-ZrO_2) has been widely used as a catalyst support material in the literature (Liu, 2012, Joo, 2013, Khan, 2013) due to its high surface acidity which might benefit the heavy crude oil cracking that is an important step in the methanotreating process. Therefore, it is also employed as a support material in this work for bitumen partial upgrading evaluation as the acidic support for active metal loading.

Chapter Three: Experimental Methods

3.1 Bitumen Upgrading Autoclave

The reaction were carried out in a 500 mL Parr 4575 HP/HT bench top autoclave reactor with 5000 psi (345 bar) and 500 °C rating, Figure 3-1. The reactor is appeared with a Model No. A1120HC. With an ø10mm X 30mm stir. A heating mantel was used to heat up the reactor under magnetic agitation to disperse the feedstock. The autoclave inside the heating mantel was connected to an inlet pipe and an exhaust duct. An inserted thermometer was used to test the temperature and the pressure gage on autoclave was used to check the pressure, Figure 3-2.

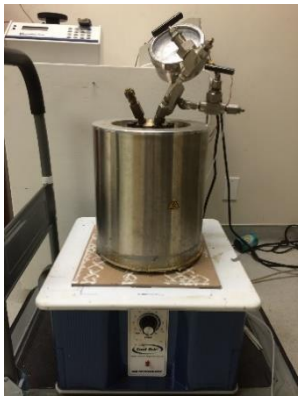


Figure 3- 1. Apparatus Outside

Figure 3- 2. Lid of reactor

The detailed experimental procedure is described blew. The reactions were carried out under high pressures, which were often above 50 bar. Therefore a leak test of the apparatus is crucial for reliable results as well as safety. The leak test was carried out by monitoring the pressure drop within the reactor upon the introduction of high pressure gas, for instance, 50 bar N_2. After passing the leak test, fifty grams of bitumen with 0.5 g catalyst was loaded into a 500 mL Parr reactor that could tolerate high temperature up to 500 ^{o} C and high pressure up to 250 bar. It was pressurized with the feed gas methane, hydrogen or nitrogen to 50 bar, after the air inside the reactor was purged out. A heating mantle was used to heat up the reactor and kept the temperature first at under magnetic agitation to disperse the catalyst well into the bitumen feedstock. The autoclave was then heated up to 380 °C (i.e. reaction temperature). It takes about 35-40 mins to heat the autoclave from 130 to 380 °C. And it takes about 15 mins from 300 to 380 °C. It may have some reaction between 300 to 380 °C. But since the heating time from 300 to 380 °C are all around 15mins in every run, so it assumes that all the reactions have the same effect in the 15mins. And then kept at the reaction temperature for 150 min. When the upgrading reaction was to be terminated, the autoclave body was plunged into a cold water bath which lowered the temperature below 300°C less than 2 min. The bitumen model compounds were also upgraded in a similar manner.

The reaction experimental procedure is as follows:

- Add specified mass of bitumen and catalyst sample into the reactor bomb
- Purge air inside the reactor with nitrogen
- Pressurize the reactor to 50 bar at 21 °C with the reactive gas (methane or hydrogen)
- Raise temperature from 25 to 130 °C, using a heating mantle and then maintain at 130 °C for 30 mins under magnetic agitation

- Heat up to 380 °C in 60 minutes and kept at the reaction temperature for 150 mins
- Plunge autoclave body into a cold water bath at 15 °C
- Test the viscosity of the product-oil in a Viscolead One Series L viscometer at temperature of 25 °C as described later
- The product oil sample was kept in a sealed sample vial in the fridge for future analysis

3.2 Feedstock And Chemicals

A Canadian bitumen was acquired from Syncrude Canada Ltd and used as received without further treatment. Toluene with a purity of > 99.5 wt.% (provided by VWR International) was used to isolate any possible toluene-insoluble solids in bitumen and its upgraded product (i.e. possibly coke and catalyst). Heptane (anhydrous, 99%, Sigma-Aldrich) was exclusively employed to determine asphaltenes content of various oil samples.

3.3Catalyst Synthesis

The ammonium ZSM-5 zeolite with Si/Al = 23 and specific surface area of 425 $m^2 \bullet g^{-1}$ was purchased from Alfa Aesar and calcined at 600 ^oC for 5 h in air to attain the H-type ZSM-5 for further use. The 1 wt.% Ag–10 wt.% Zn/HZSM-5 was prepared by wetness impregnation procedure (shown in Figure 4-1) of HZSM-5 with $AgNO_3$ (99.9+%, Alfa Aesar) and zinc nitrate hexahydrate ($Zn(NO_3)_2 \bullet 6H_2O$, 99%, Alfa Aesar) aqueous solutions in a sequential order, dried in the oven at 92 ^oC overnight, followed by being fired at 600 ^oC for 3 h in ambient air. The resultant catalyst was stored for use.

A typical wetness impregnation procedure is

1. 0.125 g $AgNO_3$ and 3.852 g $Zn(NO_3)_2 \bullet 6H_2O$ are weighed and dissolved in 8.26 g deionized water.
2. 8 g ZSM-5 is in put in a Petri dish and made flat and uniform.

3. The aqueous solution is doped on ZSM-5, while making sure drops are uniform
4. Mix the drops with ZSM-5
5. ZSM-5 is dried at 88 ^{o}C oven before repeating the above steps until all the solution is doped on ZSM-5.

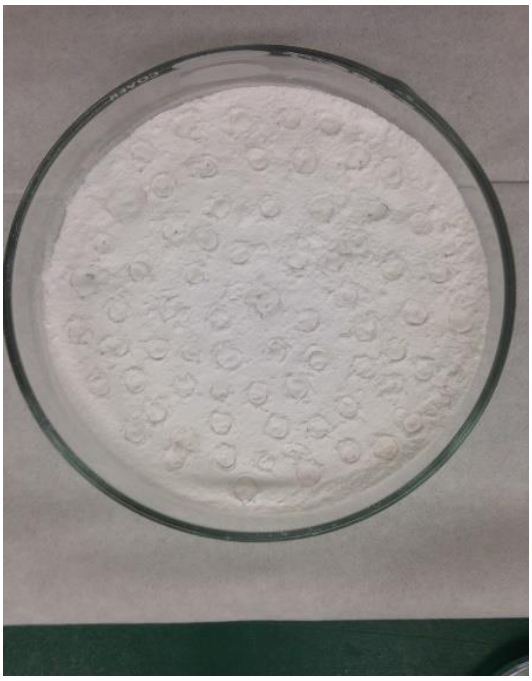


Figure 3- 3. Wetness impregnation

3.4 Oil Sample Characterizations

3.4.1 Water Content Measurement

The water content of liquid sample produced from each run was determined using Karl Fischer titration (Metrohm 870 Titrino Plus) through averaging the results collected from at least three independent measurements. The repeatability of water content measurement is±0.002~0.003 wt.%.

The main compartment of the titration cell contains the anode solution plus analyse. The anode solution consists of an alcohol (ROH), a base (B), SO_2 and I_2. The titration cell also consists

of a smaller compartment with a cathode immersed in the anode solution of the main compartment. The two compartments are separated by an ion-permeable membrane. The Pt anode generates I_2 when current is provided through the electric circuit. The net reaction is oxidation of SO_2 by I_2. One mole of I_2 is consumed for each mole of H_2O. In other words, 2 moles of electrons are consumed per mole of water.

Oil sample with weight of m_1 is dissolved in toluene to make a solution of total weight equal to m_3 with mass concentration of oil controlled between 50%-70%. The resulting solution is injected into the 870 Titrino Plus apparatus using a syringe for water content measurement. After applying correction using Equation 3-1, the water content of the oil sample is obtained as follows.

$$Water\ content\ in\ oil\ sample\ (wt.\%) = water\ content\ of\ solution \times \frac{m_1}{m_3} \qquad (3\text{-}1)$$

3.4.2 Total Acid Number Measurement

The total acid number (TAN) of liquid sample produced from each run was measured using a Metrohm 848 Titrino Plus through averaging the results collected from at least three independent measurements. The TAN is determined for a KOH titration according to Table 3-1, depending on the expected acid number, different oil sample weight is required for accurate TAN value measurement. The oil sample was dissolved in 80 mL titration solvent. After complete dissolution, the acid value was measured. The repeatability of the total acid number measurement is ±0.02~0.04 mg KOH/g.

Table 3- 1. Required sample weight corresponding to different expected acid numbers

Expected acid number mg KOH / g sample	Sample weight	Weighing accuracy
0.05 ... 0.9	10 ± 2 g	100 mg
1 ... 4.9	5 ± 0.5 g	20 mg
5 ... 19	1 ± 0.1 g	5 mg
20 ... 99	0.25 ± 0.02 g	1 mg
100 ... 250	0.1 ± 0.01 g	0.5 mg

3.4.3 Density Measurement

A gas displacement density analyzer (AccuPyc II 1340) manufactured by Micromeritics was employed to measure the density of liquid sample at 15.6 ^{o}C. The measurement temperature is accurately controlled through a PolyScience® LS 51 compact recirculating chiller fabricated by Cole-Palmer.The AccuPyc II 1340 determined the density by measuring the pressure change of helium within the pycnometer. This pycnometer consists of a control module and an analysis module. Thus, the operational status of the pycnometer can be continually monitored in a status window that is displayed via a computer screen. The repeatability of density measurement is ±0.002~0.003 g/cm^3.

3.4.4 Gasoline And Diesel Composition Measurement

The gasoline and diesel fraction distillation was performed by using a home-made batch distillation apparatus as shown in Figure 3-4. The volume of flask is 100 ml and size is 14/20. The sample was distilled at a temperature of 350 ^{o}C for atmospheric distillation and at a temperature of 217 ^{o}C when vacuum was applied at -860 mbar. The repeatability of gasoline and diesel composition measurement is ±0.1~0.2%.

The procedure is as follows:

1. Clean and dry the flasks as well as other glassware. The weight values of the flasks used to hold and collect oil are recorded. The weight of oil sample is determined by the weight difference of the flask holding it.
2. Set up the instruments as Figure3-4.
3. Ramp up temperature to 350 ^{o}C in a controlled manner. The distillated oil is collected in the flask on the right hand side of Figure 3-4. Hold the temperature until no more oil drops getting into the flask.

4. Cool down the system to room temperature. Change another flask for oil collection.
5. Set the vacuum degree -860 mbar and ramp to 217 ^{o}C in a controlled manner. Hold the temperature until no more oil drops getting into the flask.
6. Cool down the temperature after all the diesel collected.
7. Weigh the flasks used to collect oil samples and calculated the gasoline and diesel yield.

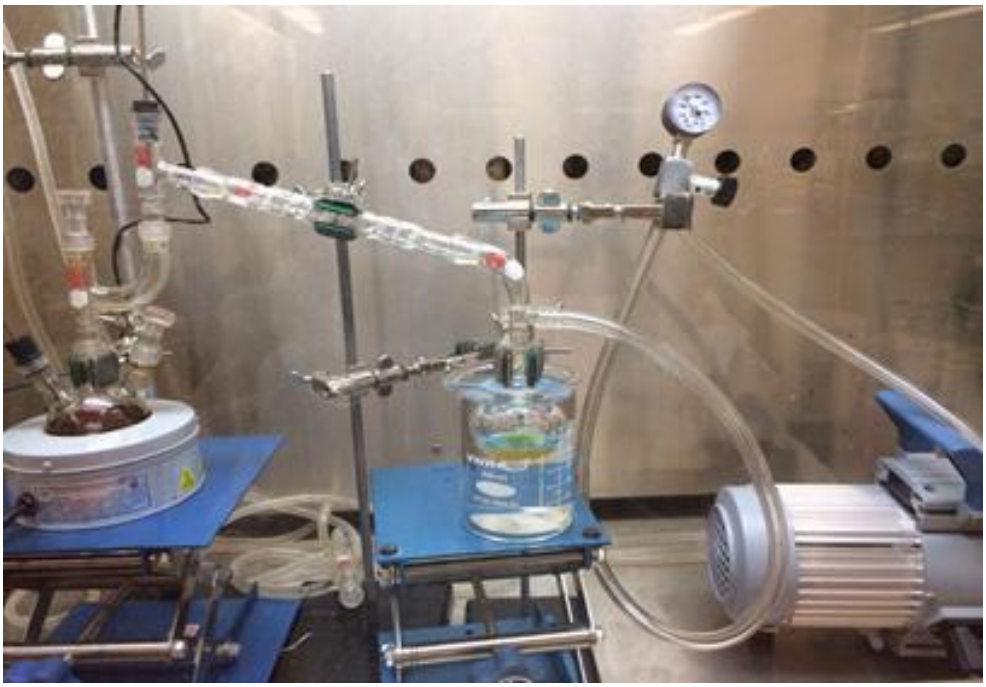


Figure 3- 4. House-made distillation system for gasoline and diesel content measurement

3.4.5 Oil Stability And Compatibility Measurement

The compatibility and stability feature of the collected oil samples was analyzed by engaging a TriboAmix® spot tester designed by TRIBOMAR GmbH and following a testing procedure defined in ASTM D4740. When sample is heated, if it is not uniform, lighter compounds will spread faster compare to heavier, then in the middle of the paper will leave a dark circle which is the heavy compounds. Table 3-2 and Figure 3-5 gave the reference spot definition and visualization for oil sample compatibility and stability measurement. The repeatability of Oil stability and compatibility measurement is 0. It is determined by naked eyes. I do not think there

is “repeatability” You may phrase like: The oil stability and compatibility is determined by running the test multiple times to ensure the results are repeatable.

Table 3- 2. Reference spot description for oil sample compatibility and stability measurement

Reference Spot No.	Characterizing Features
1	Homogeneous spot (no inner ring)
2	Faint or poorly defined inner ring
3	Well-defined inner ring, only slightly darker than the background
4	Well-defined inner ring, thicker than the ring in reference spot Mo.3 and somewhat darker than the background
5	Very dark solid or nearly solid area in the center. The central area is much darker than the background

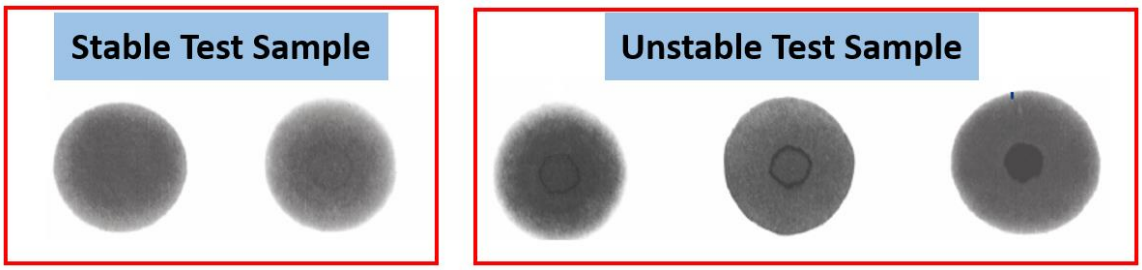


Figure 3- 5. Reference spot definition and visualization for oil sample compatibility and stability measurement

3.4.6 Viscosity Measurement

The viscosity of oil sample was determined by employing a Viscolead One Series L viscometer fabricated by Fungilab at temperature of 25 ^{o}C controlled through an incorporated hot water circulating batch. The viscometer is the viscometer. The calibration is done as follows:

Calibration of reference spindle: The spindles are coaxial spindles. By calibrating these spindles, it is changing the calibration of all the viscometer's spindles.

Calibration of the rest of the spindle: The calibration of any spindle, which is different from the reference spindle, will only modify the values of that individual spindle. The rest of the equipment's spindles will not be affected by this calibration.

The repeatability of viscosity measurement is estimated by carrying out the measurement multiple time. The values are listed in the tables along with the average results.

The procedure is as follows:

1. After product-oil is collected in beaker, the product-oil is added to viscometer.
2. Keep the temperature at 25 ^{o}C
3. The minimum value is the viscosity of oil sample

The repeatability of viscosity measurement is ±10%.

3.4.7 Elemental Composition Analysis

The CHNS analysis was carried out using Elemental Analyzer (Perkin Elmer 2400 Series).

The repeatability of Elemental composition analysis measurement is ±0.1~0.5% wt.%..

3.4.8 Coke Yield Analysis

The coke yield was obtained by first dissolving oil product in toluene. The resulting solution was then filtered and the collected filter paper was put into Soxhlet extractor for extraction until the toluene solvent in extractor was colorless. The collected filter paper was then dried in an oven for 2 hrs at 100 ^{o}C and weighed for coke amount determination. The final coke yield can be determined through Equation 3-2.

$$Coke\ Yield\ (\%) = \frac{\Delta m_{filter\ paper}}{m_{oil}} \times 100\% - spent\ catalyst\ content - solid\ content\ of\ bitumen \quad (3\text{-}2)$$

The repeatability of coke yield measurement is ±0.02~0.09%.

3.4.9 Asphaltene Content Measurement

The asphaltene contents of various oil samples were determined according to ASTM standard D 6560-00. Briefly, small amount of the sample was mixed with heptane and the mixture was heated under reflux. The resultant precipitated asphaltenes, waxy substances, and inorganic material were collected on a filter paper. The waxy substances were then removed by washing with hot heptane in an extractor. After removal of the waxy substances, the asphaltenes were separated from the inorganic material by dissolution in hot toluene. The obtained extraction solvent underwent evaporation and the received asphaltenes were finally weighed for calculating asphaltenes percentage.The repeatability of asphaltene content measurement is ±0.2~0.3%.

3.4.10 GC-MS Measurement

The composition of the product oil was determined by the pre-calibrated Gas Chromatography-Mass Spectrometer (GC-MS: PerkinElmer GC Claus 680 and MS Clarus SQ 8T) equipped with a Paraffins-Olefins-Naphthenes-Aromatics (PONA) column (Agilent HP-PONA). The oven temperature of the GC was programmed to hold at 35 oC for 15 min, ramp to 70 oC at 1.5 oC/min, rise to 150oC at 3 oC/min and hold for 30 min, then ramp to 250 oC at 3 oC/min and hold for 2 min.

Chapter Four: Reaction Condition Optimization

The first step in the upgrading reaction is the activation of the carbon-hydrogen bond in methane, which means breaking the carbon-hydrogen bond to create a free radical. To break the bond, a tailored catalyst must be developed. To screen of the proposed catalysts for better catalytic performance, the influence of several factors, including temperature, pressure, reaction time, bitumen loading, and agitation rate are considered. These factors not only affect the catalytic effect on viscosity reduction of the crude oil and quality of the upgraded oil, but also have a significant influence on the industrial application feasibility of the developed methanotreating process, such as the safety issue, the environmental impact and the economic benefit. Therefore it is necessary to optimize the reaction conditions. The reaction conditions are optimized based on the catalytic performance on the viscosity reduction and coke yield as well as the stability and compatibility of the oil products.

4.1 Reaction Conditions Optimization

In order to maximize the role played by the catalysts during the experiments, it is necessary to find suitable reaction conditions. And then all the catalysts will be tried in the same reaction conditions to rule out other factors that may have effect on the quality of the upgraded oil, which may mislead the evaluation of the bitumen partial upgrading capability of catalysts.

4.2.1 Feed Weight And Agitation Rate

Among steps for condition optimization, the first one is choosing the bitumen feed weight for all experiments. Since agitation of the upgrading reaction is through magnetic stirring, the amount of bitumen feed cannot exceed certain amount to make sure the stirrer work well when the reaction is going on. Since the bitumen is very viscous, if the weight of the bitumen is too large, the stir bar will struck inside the reactor and not work at all. Besides this upper limit, the weight of bitumen

cannot be too small. The bottom of the inserted thermometer inside the reactor must merge inside the bitumen, otherwise it will not show the real temperature of the bitumen during the reaction. By taking these two factors into consideration, variable amounts of bitumen were tested in the reaction to determine if the bottom of the thermometer merged inside bitumen and whether the stirrer worked well. When 30 grams bitumen was used, it was noticed that after the reaction the bottom of the thermometer was very clear when the cover of the reactor was removed, indicating that the thermometer did not merge inside the bitumen when the upgrading reaction was proceeding. When 80 grams bitumen was used, the working status of the spinning bar was tested by restarting the magnetic stirrer. It was noticed that the reactor temperature suddenly rose up, indicating that the stirrer was not functioning well inside the reactor during the reaction. However, when bitumen sample weight was lowered to 50 grams, those problems including stirrer malfunction and inaccurate reaction temperature control did not happen again. It may be because 80 grams bitumen was too much for the magnetic stirrer. The stir bar was stuck inside the reactor. So finally a bitumen weight of 50 grams was chosen as the sample weight for all the experiments.

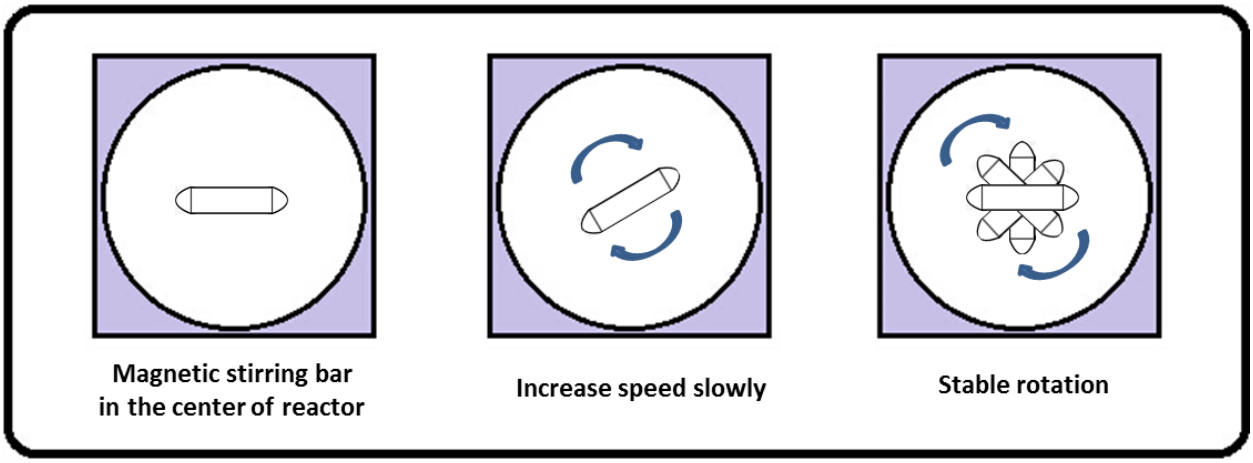


Figure 4- 1. Magnetic stirring condition determination procedure

Another important factor affecting the reaction is the location and the spinning rate of the spinning bar. The reaction speed and the central point of stir bar were determined by following the

steps as illustrated in Figure 3-2. The reactor was placed on the magnetic stirrer and then opened to see if the stir bar was in the middle of the reactor. The position of the reactor then slowly changed until the central point was found where smooth rotation of the charged stir bar is observed. After that, through employing deionized (DI) water as testing liquid, the reaction speed was found by slowly increasing it until stable stir bar rotation was achieved. Finally the optimized agitation rate is controlled at level 4 (approximately equivalent to 240 rpm) according to the setting displayed on the engaged large volume magnetic stirrer manufactured by SP Scienceware (Bel-Art F37028-0001 Cool Stir). Despite the viscosity of DI water is around 1 mPa•s, which is lower than that of bitumen at 380 ^{o}C (estimated to be about 4Pa•s), it is employed as the fluid for the test due to its availability and low cost, as well as the safety concern compared with other organic compounds.

4.2.2 Choosing Reaction Time

The next set of reaction conditions to be evaluated includes reaction time, reaction temperature and reaction pressure. The effects of these parameters on partial upgrading performance were evaluated in terms of viscosity, coke yield, and stability of the product oil as well as process safety.

A catalyst named HP-90, whose composition is 1% Ag loaded on ZSM-5 with a silica-alumina ratio of 23:1, was used for all the experiments in order to find the best reaction conditions for the following catalyst screening. The reaction temperature was kept the same as 380°C and under a reaction pressure of 10 bar. CH_4 was used as gas phase for all the experiments. A series of experiments with reaction time of 60 mins, 90 min, 150 mins, and 180 mins were carried out. After experiments were done, the viscosity and coke yield of the collected product oils were measured. The results are displayed in Table 4-1.

Table 4- 1. The upgrading performances with various reaction time collected over 1 %Ag/ZSM-5 under methane at 1.0 MPa and 380 °C

Reaction Time (min)	Viscosity (cP)	Coke yield (wt.%)
60	1780	0.33
90	5240	0.46
150	2900	0.51
180	950	3.49

* Uncertainties of viscosity and coke yield is 10% and 0.05.

Table 4-1 shows that as reaction time increases, the viscosity of product-oil decreases. However, when reaction time is increased to 180 min, although viscosity is very low (i.e., 954 cP), an extremely high coke yield of 3.49 wt.% is observed. Under the combined consideration of viscosity and coke yield, 150 mins is determined to be the optimized reaction time for future investigation, which would allow enough space for catalyst further optimization with acceptable viscosity (<330 cP) and coke yield (<1 wt.%) for meeting pipeline transportation specifications. The results from 60 mins, 90 mins and 180 mins runs are further discussed. When reaction time is 60 mins, the viscosity of the product-oil is 17830 cP which is too high to allow any further analysis conducted over this upgraded oil. Therefore, 60 mins is not chosen as reaction time. When the reaction time is extended to 90 mins, the product-oil viscosity is significantly reduced to 5236 cP while the coke yield is just slightly increased from 0.33 wt.% up to 0.46 wt.%. When the reaction duration is further lengthened to 180 mins, the promising low viscosity is unfortunately accompanied with unacceptably high coke yield.

4.2.3 Choosing Reaction Temperature

Various upgrading experiments were further run at 350 °C, 380 °C and 390 °C to evaluate the temperature effect and identify the optimized one while keeping reaction duration for 150 mins and methane pressure at 10 bar over HP-90 catalyst. After experiments were completed, the viscosity and coke yield of product-oils were measured. The results are demonstrated in Table 4-2 and Figure 4-2.

Table 4- 2. The upgrading performances collected over 1 %Ag/ZSM-5 under methane at 1.0 MPa and various reaction temperatures for 150 min

Reaction Temperature (ºC)	Viscosity (cP)	Coke yield (wt.%)
350	3100	0.09
380	2500	0.33
390	Not available due to temperature fluctuation	

* Uncertainties of viscosity and coke yield is 10% and 0.05.

From Figure 4-2, it is displayed that when temperature of 390 °C is set as the reaction temperature, the temperature goes up and down all the time and cannot be stable, particularly at the initial 80 mins. As the temperature is always changing, the experiments cannot be controlled at the designated reaction conditions.

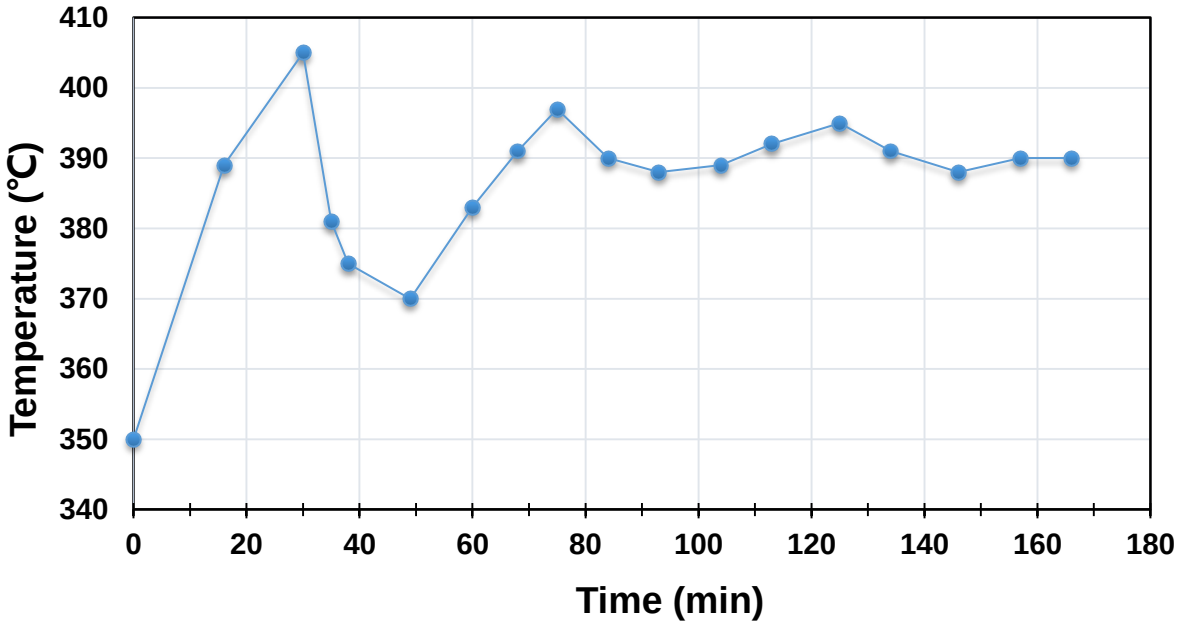


Figure 4- 2. Temperature profile collected during bitumen partial upgrading over 1%Ag/ZSM-5

In addition, it is also observed that lots of solids are generated in the product-oil, indicating severe coke formation, which may be because of the notable temperature fluctuation. As shown in Figure 4-2, reaction temperature can jump up to as high as close to 410℃. It is well known in oil upgrading field that high temperature has a greater tendency for coke formation. The viscosity of the partially upgraded oil cannot be measured accurately due to its high heterogeneity. As shown in Figure 4-2, part of the product-oil is very viscous and settled to the reactor bottom while the top portion has very low viscosity judged from its excellent flowability. Therefore, the analysis cannot be done accurately for 390℃ run. So 390 °C is not chosen as the reaction temperature due to its poor temperature control.

Figure 4- 3. Product-oil collected over 1% Ag/ZSM-5 catalyst after bitumen upgrading at 1.0 MPa for 150 min

When the reaction temperature is 350 °C, the product-oil viscosity is 3145 cP and coke yield is 0.09 wt.%. When the reaction temperature is 380°C, the product-oil viscosity is 2947 cP and coke yield is 0.33 wt.%. Comparing the results under reaction temperature 350 °C and 380 °C, a better viscosity result is obtained at 380 °C and also the coke yield is acceptable. So finally 380 °C is chosen as the reaction temperature.

4.2.4 Choosing Reaction Pressure

Various upgrading experiments were further run at methane pressure of 10 bar, 16 bar, 30 bar and 50 bar to evaluate the pressure effect and identify the optimized one while keeping reaction duration for 150 mins and temperature at 380 ^{o}C over HP-90 catalyst. After experiments were

completed, the viscosity and coke yield of product-oils were measured. The results are demonstrated in Table 4-3 and Figure 4-4.

Table 4- 3. The upgrading performances collected over Ag/ZSM-5 under methane at various pressures and 380 ºC for 150 min

Methane Pressure (MPa)	Viscosity (cP)	Coke yield (wt.%)
1.0	2900	0.51
1.6	1525	0.63
3.0	1405	0.57
5.0	1289	1.03

* Uncertainties of viscosity and coke yield is 10% and 0.05.

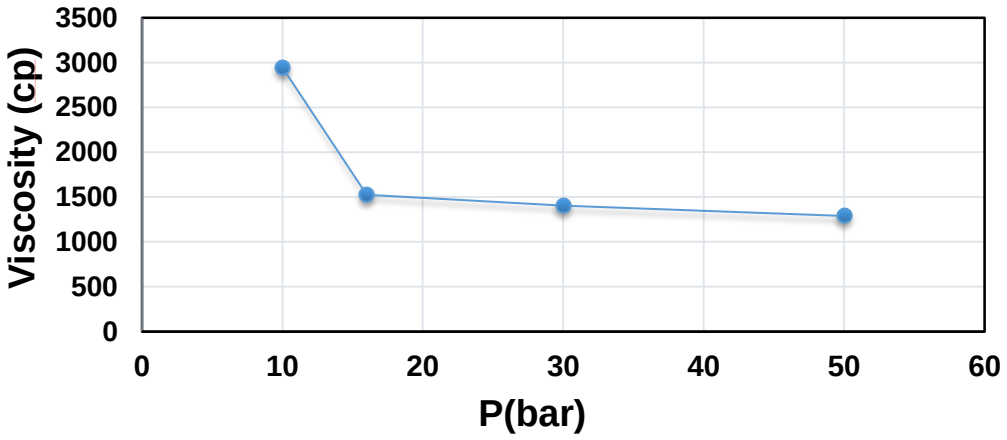


Figure 4- 4. The effect of methane pressure on viscosity reduction of the product oil collected after bitumen upgrading at 380 ºC for 150 min

As clearly shown in Table 4-3 and Figure 4-4, the viscosity of the collected product oil gradually decreased as the methane pressure increased. It is interesting to note that the product oil's viscosity is reduced almost in half when pressure is first increased from 10 bar to 16 bar. However, further pressure increase does not witness such notable viscosity reduction as evidenced in Figure 4-4. For instance, the viscosity is only reduced by 15% when pressure is significantly

escalated from 16 bar to 50 bar. A plausible explanation to this phenomenon is that when the methane pressure gets higher, more methane molecules could be dissolved by bitumen. However, the number available catalytic active sites is not large enough to catalyze the methanotreating process. Therefore, the enhanced viscosity reduction due to lifted methane pressure is not as significant as the low pressure region. Moreover, such high pressure operation also results in the increased rate of coke formation which is almost doubled once the reactor is further pressurized from 30 bar to 50 bar. More importantly, increased operation pressure will be penalized by the significantly increased capital and operation cost for pressure tolerant container and pipeline fabrication and operation, not mentioning the safety concern from high pressure operation. Therefore, methane pressure would be kept at 50 bar without further escalation under a combined consideration of upgrading performance and process economics and safety.

4.3 Conclusion

According to the previous analysis, it can be confidently concluded that the optimal experimental conditions for further study are: the pressure is 5.0 MPa, the weight oil added into the reactor is 50 g, the agitation rate is controlled at level 4 (approximately equivalent to 240 rpm), the reaction temperature is controlled at 380 ^{o}C and the reaction time is 150 mins. These optimized parameters can definitely grant more opportunity to identify better catalyst to facilitate bitumen upgrading for achieving oil product with relatively lower viscosity and acceptable coke yield of oil.

Chapter Five: Bitumen Partial Upgrading Performance of Ag-Zn/ZSM-5

In this study, 1 wt.%Ag-10 wt.%Zn/ZSM-5 catalyst was synthesized using the impregnation method and evaluated for triggering bitumen partial upgrading reaction under methane environment at the reaction conditions as identified in the Chapter 3. The formed crude synthetic oil was extensively analyzed for its quality control in terms of viscosity, acidity, density, water content, gasoline and diesel content, asphaltene content, average molecular weight, stability, and elemental composition.

5.1 Results And Discussion

As demonstrated in Tables 5-1 to 5-4, a synergetic effect (reaction) between methane and bitumen is clearly witnessed during upgrading process when Ag-Zn/ZSM-5 catalyst is charged, which means added, leading to the production of partially upgraded oil with lowest viscosity, highest gasoline and diesel contents, lowest density, lowest acidity, lowest asphaltene content, and lowest molecular weight as well as the highest liquid yield and acceptable coke formation, compared to a series of control runs, indicating the most efficient carbon chain breakage and rearrangement if catalytic methanotreating process is engaged. With an initial methane pressure of 5.0 MPa activated by catalyst Ag-Zn/ZSM-5, bitumen's viscosity is remarkably reduced from a very high value of 848,080 cP to as low as 414 cP under the methane environment, which is comparable with its H_2 counterpart and approaching the oil pipeline transportation requirement set by the governments of Canada and USA (Tsaprailis, 2014). More importantly, it is noteworthy that this efficient reduction of viscosity is accompanied by highest liquid yield and acceptable coke formation in the upgrading when both Ag-Zn/ZSM-5 and methane of 5.0 MPa were used (Table 5-1). Higher liquid yield is observed whenever methane is present, which is especially true when

Ag-Zn/ZSM-5 catalyst is charged, implying the incorporation of methane molecules into the upgraded oil product. Coke particles of over 1 wt% present in the upgraded heavy oil may create sediment with time, which will probably cause clogging to endanger pipeline transportation. Therefore, at low-temperature (380 ºC) and low-pressure yet relatively concentrated methane gas (5 MPa) can be effectively activated by Ag-Zn/ZSM-5 to upgrade viscous heavy oil for boosting flowability with fairly good stability, making pipeline transportation feasible of this unconventional petroleum resource.

Table 5- 1. Performance of bitumen upgrading under various environments at 5.0 MPa and 380 ºC for 150 min

Trial	Atmosphere	Coke yield (wt.%)	Liquid yield (wt.%)	Viscosity (cP at 25 ºC)
Bitumen (no reaction)	---	---	---	848000
Bitumen (no catalyst)	N_2	0.60	94.5	1700
Bitumen (no catalyst)	CH_4	0.55	96.5	1600
HZSM-5	CH_4	0.80	93.8	1400
Ag-Zn/ZSM-5	N_2	0.86	92.9	1300
Ag-Zn/ZSM-5	CH_4	0.75	97.8	410
Ag-Zn/ZSM-5	H_2	0.62	93.1	280

* Uncertainties of viscosity and coke yield is 10% and 0.05.

In order to gain a better picture of the stability and compatibility of the oil products collected from various runs reported in Table 5-4, the spot tests over all these oil samples were performed and the results are presented in Figure 5-1. For giving a better interpretation of the oil dispersion images included in Figure 5-1, the reference spot description (Table 3-2 and Figure 3-5) given by ASTM D4740 is also cited. Referring to this definition, it can be easily concluded from Figure 5-1 that the oil product collected after bitumen upgrading under the environment of methane with Ag-Zn/ZSM-5 charged exhibits the best stability and compatibility compare to bitumen and oil

products collected under N_2, CH_4 and CH_4 with ZSM-5, and is approaching that from H_2 run, making it more suitable for pipeline transportation.

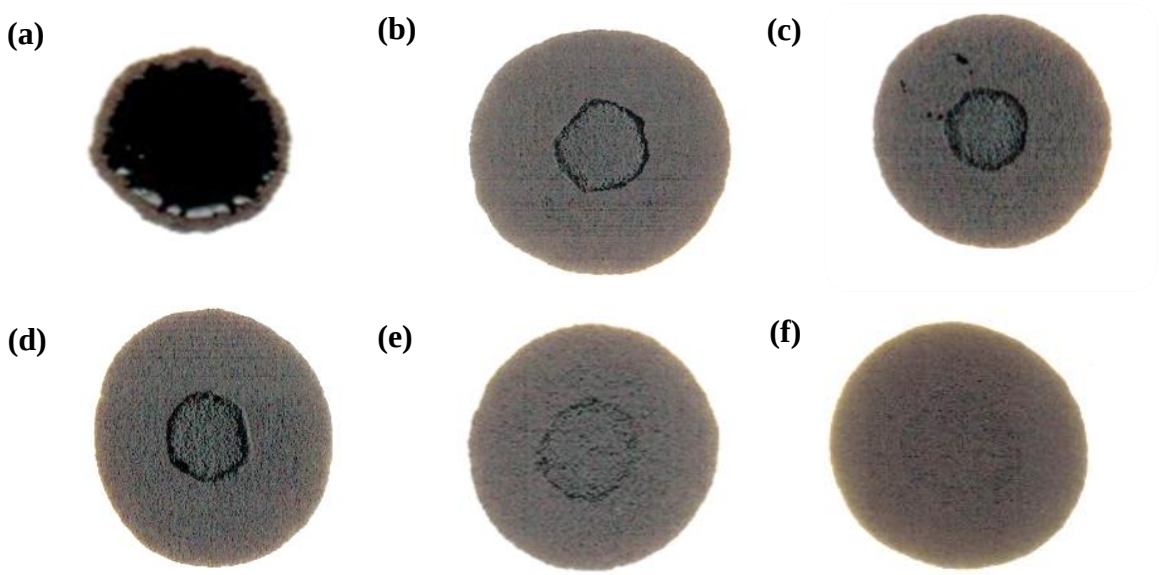


Figure 5- 1. Stability test of (a) bitumen and oil products collected under (b) N_2, (c) CH_4, (d) CH_4 with ZSM-5, (e) CH_4 with catalyst Ag-Zn/ZSM-5, and (f) H_2 with catalyst Ag-Zn/ZSM-5

When Table 5-2 is visited for gasoline and diesel fractions, the gasoline fraction and the total gasoline and diesel fraction from bitumen upgrading with methane in the presence of Ag-Zn/ZSM-5 are the highest among all the oil samples in comparison, which would notably lessen the burden of downstream refining and thus benefit its cost reduction. Furthermore, compared to those collected from all other control runs, the more than double boost of gasoline fraction from catalytic methanotreating process provides us another evidence of the synergetic effect occurring between methane and bitumen during upgrading under the facilitation of suitable catalyst on heavy oil molecules cracking and rearrangement for getting desirable final oil products.

As an important property to reflect the quality of the upgraded oil present in Table 5-1,

densities of all the aforementioned oil products were measured and included into Table 5-3 for comparison. The lowest density is observed for the oil sample collected under the environment of methane with Ag-Zn/ZSM-5 catalyst, the density is equal to 14.7 API and consistent with the viscosity reduction and gasoline and diesel fraction enhancement data present in Table 5-2.

Table 5- 2. Gasoline and diesel fractions of the oil samples collected before and after bitumen upgrading under various environments at 5.0 MPa and 380 °C for 150 min

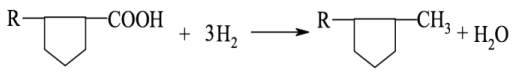
Trial	Atmosphere	Gasoline (wt.%)	Diesel (wt.%)	Total gasoline and diesel (wt.%)
Bitumen (no catalyst)	N_2	0.2	11.9	12.2
Bitumen (no catalyst)	CH_4	6.9	20.8	27.7
Bitumen (no catalyst)	CH_4	6.9	23.7	30.7
HZSM-5	N_2	6.5	25.3	31.7
Ag-Zn/ZSM-5	N_2	6.3	26.6	32.9
Ag-Zn/ZSM-5	CH_4	13.4	23.4	36.8

* Uncertainties of gasoline, diesel and total fraction are 0.1, 0.1 and 0.2, respectively.

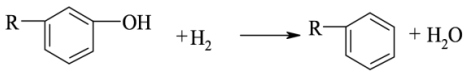
Moreover, the less acidity of the upgraded oil indicated by the reduced TAN value makes it less corrosive to the inner wall of the pipeline, thus extending the lifetime of the pipeline. As evidenced by the data shown in Table 5-3, the oil product acquired from methane run with Ag-Zn/ZSM-5 catalyst demonstrates the lowest acidity (0.026 mg KOH/g), which is more than 100 times smaller than that of the raw bitumen and over 10 times smaller compared to that collected from its N_2 counterpart, clearly indicating the reaction between bitumen and methane when suitable catalyst is engaged.

As listed in Table 5-3, the increased water content is accompanied by the reduced total acid number when upgrading occurs under the environment of methane with the facilitation of the catalyst, which is probably due to the hydrodeoxygenation reactions taking place in the presence

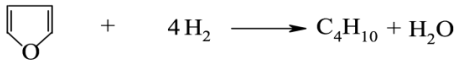
of hydrogen formed from activated methane as exemplified in Reactions 1-3.



(1)



(2)



(3)

The excellent cracking capacity of Ag-Zn/ZSM-5 during bitumen upgrading is further evidenced when the averaged molecular weights of various oil products tabulated in Table 5-3 are compared. The lowest molecular weight (330 g/mol) belongs to the oil product received during bitumen upgrading under methane with Ag-Zn/ZSM-5 catalyst present, which is even lower than that collected from the same run but with bare support charged, implying that Ag and Zn loadings are not only active in methane activation, but also beneficial for the cleavage of long carbon chain.

In order to evaluate the effect of catalytic methanotreating on reduction of asphaltenes, the major contributor of the high viscosity of bitumen and the most difficult component in bitumen to be upgraded, the asphaltene content measurements of various oil products have been performed and the results are also compiled in Table 5-3.The oil product derived from catalytic methane run exhibits the highest asphaltene reduction (44.1%) when the asphaltene content of raw bitumen is referred, further evidencing the positive contribution of the presence of Ag-Zn/ZSM-5 and methane as a combination to bitumen upgrading.

Table 5- 3. Properties of the oil samples collected before and after bitumen upgrading under various environments at 5.0 MPa and 380 °C for 150 min

Oil Sample	Liquid Product Properties			
	Density (g/cm^3)	TAN (mg KOH/g)	Water Content (wt.%)	Asphaltene content (wt.%)
Bitumen (no reaction)	1.028± 0.003	2.59±0.04	0.159± 0.003	22.1±0.3
Bitumen+N_2 (no catalyst)	0.996± 0.002	0.51±0.02	0.147± 0.002	16.8±0.3
Bitumen+ CH_4 (no catalyst)	0.987± 0.003	0.24±0.02	0.162± 0.002	16.1±0.3
Bitumen+CH_4 (HZSM5)	0.976± 0.003	0.26±0.02	0.171± 0.003	14.8±0.2
Bitumen+N_2 (Ag-Zn/ZSM-5)	0.976± 0.002	0.39±0.03	0.158± 0.002	14.4±0.2
Bitumen+CH_4 (Ag-Zn/ZSM-5)	0.967± 0.003	0.03±0.02	0.185± 0.003	12.3±0.2

* Uncertainties of density, TAN, water content and asphaltene content values are 0.001, 0.01, 0.001 and 0.1

In addition, elemental analyses of the oil products collected from various runs have also been conducted and the results are reported in Table 5-4 for determining its saturation degrees in term of H/C atomic ratio and verifying the participation of methane into upgrading process. The highest H/C ratio is observed over the oil sample obtained from catalytic methane run, clearly confirming the involvement of methane and its positive role played on oil quality enhancement. Moreover, the increase of H/C atomic ratio is also accompanied by slight reduction of nitrogen and sulfur contents when referring to the raw bitumen's composition, implying the denitrogenation and desulfurization reactions happening to a small degree during bitumen upgrading.

Table 5- 4. Elemental analysis of oil samples collected before and after bitumen upgrading under various environments at 5.0 MPa and 380 °C for 150 min

Oil Sample	Carbon (wt.%)	Hydrogen (wt.%)	H/C Atomic Ratio	Nitrogen (wt.%)	Sulfur (wt.%)
Bitumen(no reaction)	81.1	10.3	1.52	1.9	6.5
Bitumen+N_2(no catalyst)	81.9	10.4	1.53	1.7	5.6
Bitumen+CH_4(no catalyst)	81.8	10.3	1.51	1.8	5.8
Bitumen+CH_4(HZSM5)	81.9	10.2	1.49	1.8	5.7
Bitumen+N_2(Ag-Zn/ZSM-5)	81.7	10.5	1.54	1.7	5.9
Bitumen+CH_4(Ag-Zn/ZSM-5)	81.3	11.2	1.65	1.7	5.6

* Uncertainties of the weight percentage value is 0.1

5.2 Conclusions

The work reported here demonstrates the feasibility of upgrading of bitumen with cheap methane on zeolite supported catalyst modified with transition metals as active phases at moderate conditions to yield partially upgraded crude oil suitable for pipeline transportation with no or significantly reduced need of diluent addition. With methane introduction during bitumen catalytic thermal cracking, in addition to the increased productivity (97.8 wt.%), the quality of the acquired oil product are also significantly enhanced in terms of flowability (~414 cP), density (0.967 g/cm^3), acidity (0.03 mg kOH/g), saturation degree (H/C=1.65), averaged molecular weight (330 g/mol), distillation fractions (total gasoline and diesel content=36.8 wt.%), and compatibility (spot #2 according to the reference). The performance of this novel process is comparable with the state-of-the-art hydrotreating process but is much more cost effective. The performance variation with feed gases, bitumen thermal cracking and catalysts apparently demonstrated the existence of synergistic effect among them. Moreover, the partially upgraded oil product can be further upgraded for gasoline and diesel productions by modifying the catalysts, which is a promising future work.

Chapter Six: Catalyst Formulation Optimization for Performance Enhancement

The performance of a supported catalyst not only is influenced by the loaded active metals, but also depends on the catalyst support materials. Therefore, it is highly necessary to perform a systematic investigation regarding the effect of catalyst supports and active metals on the performance of bitumen upgrading, respectively. In this study, the effect of support including ZSM-5, zeolite Y, ZrO_2, and zeolite A with various porous structures and surface acidities are first evaluated, followed by the contribution examination of active metals including Ag, Zn, and Ga in terms of the viscosity, coke formation tendency, and stability and compatibility of the partially upgraded product oil. The experimental procedures described in Chapter 3 are followed to obtain the results reported in this chapter. Therefore, no experimental sections are included here unless otherwise stated.

6.1 Effect of Support

6.1.1 HZSM-5

The effect of the acidity of the HZSM-5 on the quality of the product oil is determined by employing HZSM-5 variable SiO2/Al2O3 molar ratios as the catalyst. The viscosities of the product oil and coke yields are displayed in Table 6-1 and Figure 6-1. It is noticed that when HZSM-5 with a SiO2/Al2O3 molar ratio of 30:1 is charged, the viscosity of oil product is greatly reduced from 848,080 cP to 963 cP under CH4 environment, indicating that the most efficient carbon chain and polycyclic structure breakage and rearrangement are achieved under this condition. Besides viscosity, another factor affecting the quality of partial upgraded oil is the coke formation. Coke particles of over 1 wt.% present in the oil may create sediment and cause clogging

that jeopardizes the crude oil transportation through pipelines. It is worth noting that the efficient reduction of viscosity achieved with HZSM-5 (30:1) is accompanied by the acceptable coke formation at 0.73 wt.%. The stability of the product oil are displayed in Figure 6-2. Comparing with the reference spots generated by stable/unstable samples (Table 3-2 and Figure 3-5), the inner rings present in the obtained spots indicates that the stability of the samples is not good. Despite the instability of the product oil, the comparison between the HZSM-5 catalysts shows that the one with a SiO2/Al2O3 molar ratio of 30:1 shows the best capability in carbon chain and polycyclic ring breaking and rearrangement. Within the zeolite framework, the charge-balancing proton (H+) species are in the OH- group of the Si(OH)Al species, which could act as Brönsted centers in the catalytic processes. The Brönsted sites of zeolites are responsible for the cracking of hydrocarbon molecules. They are also considered as the active sites for the isomerization and alkylation reactions. The acidity of the zeolite is closely related to the concentration of the Brönsted sites, which can be tuned by changing the ratio of Al to Si within the framework, i.e., variable SiO_2 to Al_2O_3 molar ratios. Among the ZSM-5 samples with variable SiO_2 to Al_2O_3 molar ratios, the one with a ratio of 30 demonstrates the best catalytic performance, suggesting that the acidity associated with this SiO_2 to Al_2O_3 ratio is the optimized value to achieve the best performance.

Table 6- 1. Viscosity and coke yield of the product oil collected over HZSM-5 with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 °C for 150 min

	Bitumen	No catalyst	HZSM-5 (23:1)	HZSM-5 (30:1)	HZSM-5 (50:1)	HZSM-5 (80:1)	HZSM-5 (280:1)
Viscosity (cP)	85000	1620	1520	960	1400	1200	1460
Coke Yield (%)	-	0.55	0.69	0.73	0.84	1.28	0.89

* Uncertainties of viscosity and coke yield is 10% and 0.05.

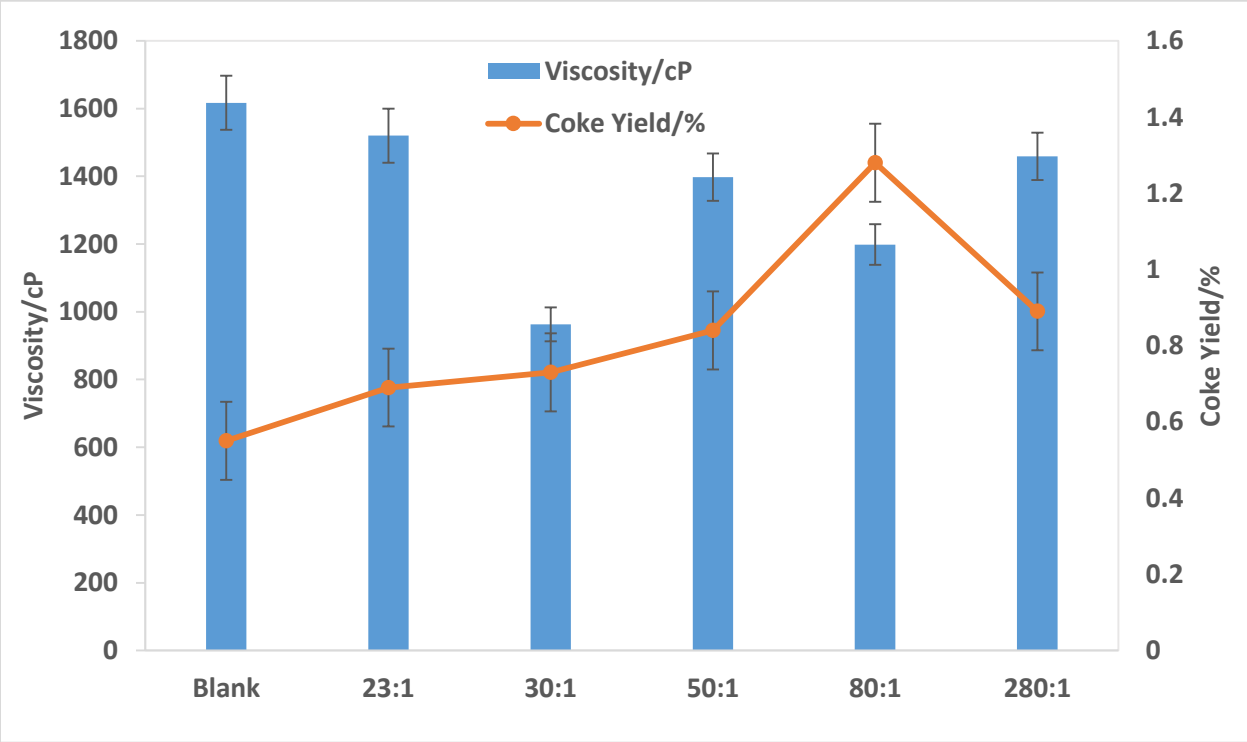


Figure 6- 1. Viscosity and coke yield of the product oil collected over HZSM-5 with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 °C for 150 min

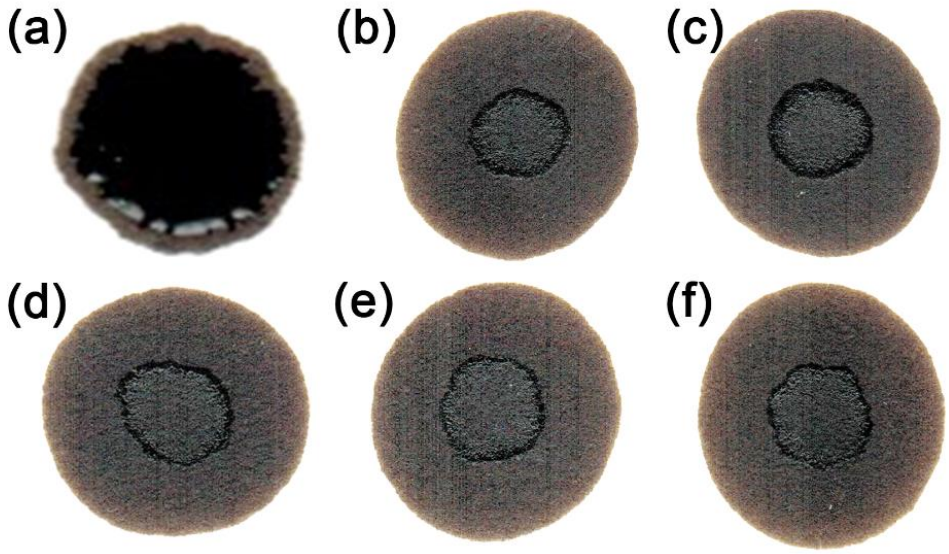


Figure 6- 2. Stability test of (a) bitumen and oil products obtained using HZSM-5 with SiO_2/Al_2O_3 molar ratios of (b) 23:1, (c) 30:1, (d) 50:1, (e) 80:1 and (f) 280:1 as the catalyst

The effect of Si:Al ratio in the ZSM-5 framework on bitumen partial upgrading is further evaluated by doping silver cations to HZSM-5 support. The catalytic performance of these catalysts are evaluated by running reaction at 380 ^{o}C under 5 MPa CH_4 for 150 min. and measuring the viscosity and the coke yield of the product oil. The results are summarised in Table 6-2. When 1 %Ag/HZSM-5 (30:1) is employed as the catalyst and co-fed with methane, a lowest viscosity of 715.3 cP is observed (Figure 6-3). The spot test results illustrate that the stability and compatibility of the oil product collected in the presence of 1%Ag/HZSM-5 (30:1) is the best among all the oil samples. Such a low viscosity accompanied by good stability indicates that the loading of silver not only enhances the carbon chain and polycyclic structure breakage and rearrangement capability of HZSM-5 (30:1), but also improves the uniformity of the oil product. The increased coke yield, which might be a result of the enhanced cracking capability, must be addressed before the catalyst is used in practical application. These results further confirm that the best bitumen partial

upgrading capability of ZSM-5 comes from the one with Si to Al ratio of 30:1 which might be due to its moderate surface acidity.

Table 6- 2. Viscosity and coke yield of the oil products obtained using 1 %Ag/HZSM-5 with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 °C for 150 min

	Ag/HZSM-5 (23:1)	**Ag/HZSM-5 (30:1)**	**Ag/HZSM-5 (80:1)**	**Ag/HZSM-5 (80:1)**	**Ag/HZSM-5 (280:1)**
Viscosity (cP)	1270	720	1320	1180	1580
Coke Yield (%)	0.97	1.72	0.70	0.75	0.92

* Uncertainties of viscosity and coke yield is 10% and 0.05.

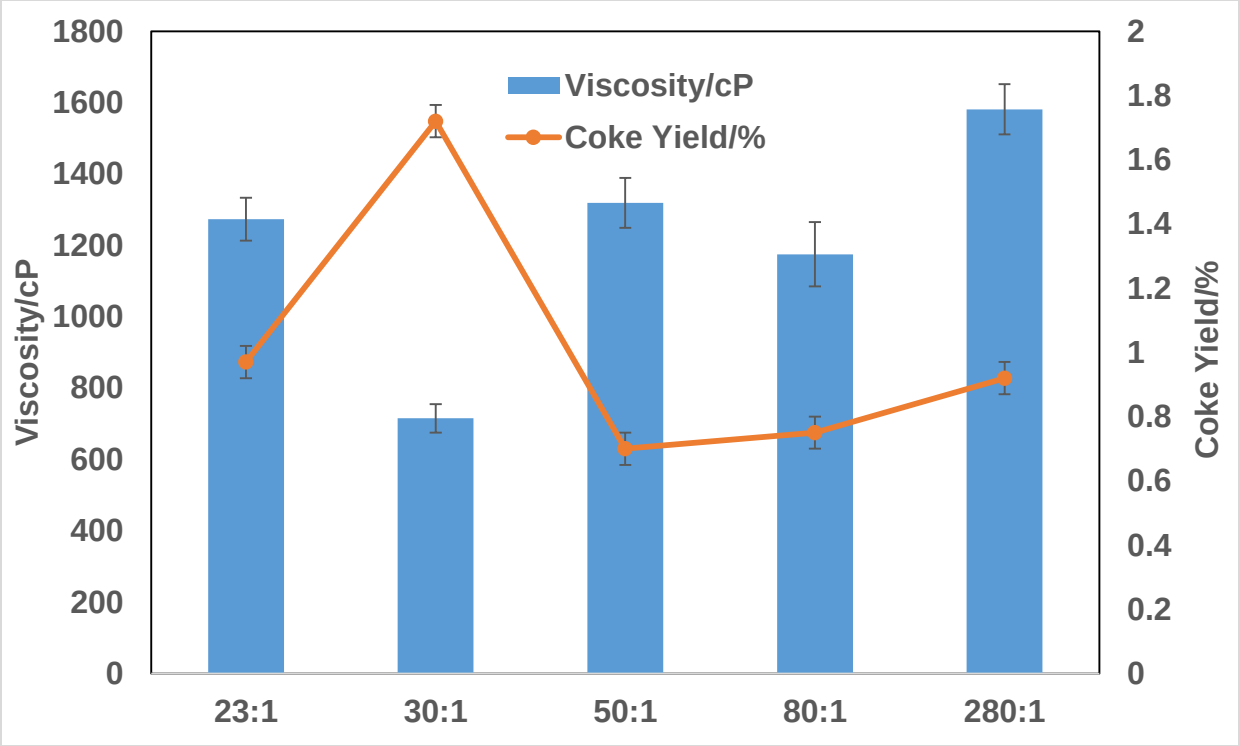


Figure 6- 3. Viscosity and coke yield of the oil products obtained using 1 %Ag/HZSM-5 with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 °C for 150 min

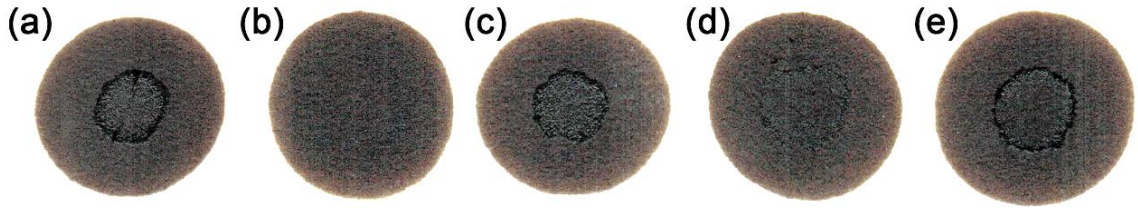


Figure 6- 4. Stability test of oil products obtained using 1%Ag/HZSM-5 with SiO_2/Al_2O_3 molar ratios of (b) 23:1, (c) 30:1, (d) 50:1, another 80:1 and (f) 280:1 as the catalyst

6.1.2 Zeolite Y

Besides ZSM-5, another class of zeolite that is currently widely used in petroleum industry is Zeolite Y. The larger pore size of Zeolite Y (11.24 Å) compared to that of ZSM-5 (6.36 Å) might give rise to improved catalytic performance, since the molecules of the heavy oil feedstock are larger than conventional petroleum molecules and thus have higher chance to get diffused into larger pores for cracking and structural rearrangement. To evaluate the effect due to the support structure as well as the acidity, the catalytic performance of H-type Zeolite Y (HY) with various SiO_2/Al_2O_3 molar ratios are evaluated by running the reactions at 380 ^oC for 150 min. under 5 MPa CH_4 environment. The viscosity and coke yield are shown in Table 6-3. The lowest viscosity is observed when HY (30:1) is charged (Figure 6-5). When the results obtained here are compared to that using HZSM-5 (30:1), however, it is noticed that the coke yield gets slightly increased from 0.73 wt.% to 0.95 wt.%. The stability and compatibility of the oil products obtained using HY are poor according to the images generated through spot test (Figure 6-6).

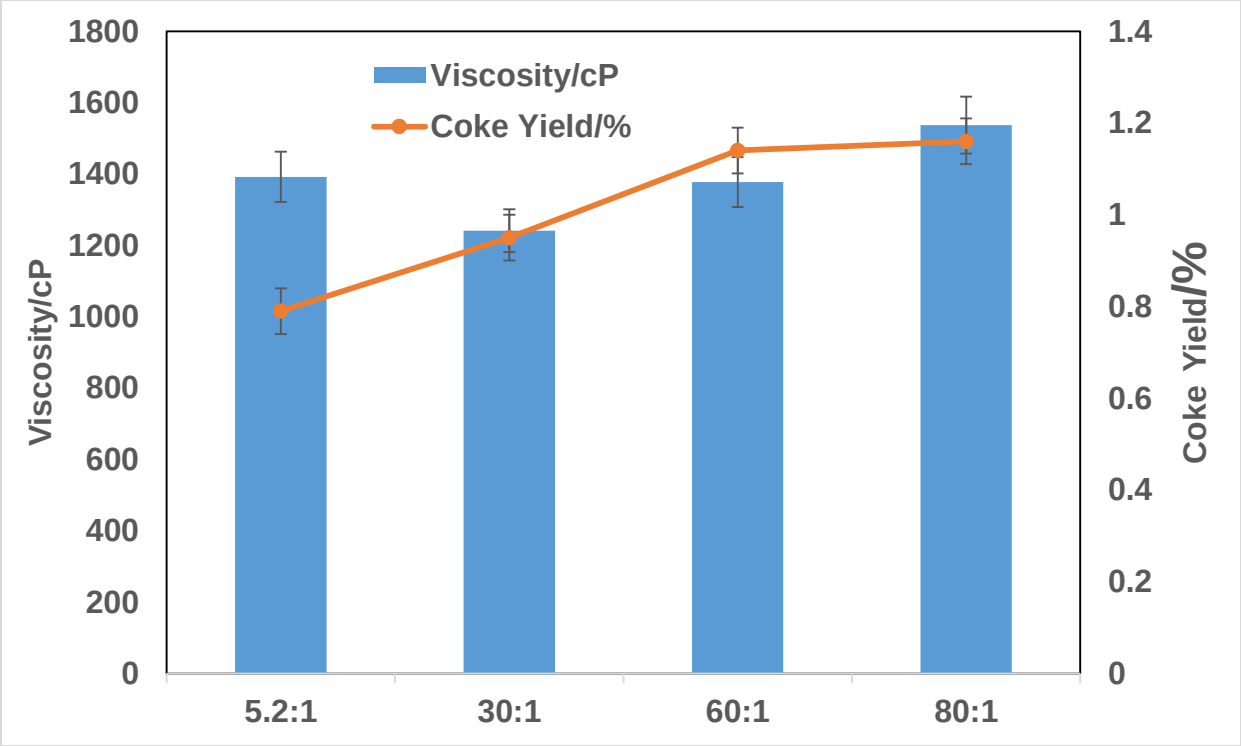


Figure 6- 5. Viscosity and coke yield of the product oil obtained using HY with variable SiO_2/Al_2O_3 molar ratios

Table 6- 3. Viscosity and coke yield of the oil products obtained using HY with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 °C for 150 min

	HY (5.2:1)	HY (30:1)	HY (60:1)	HY (80:1)
Viscosity (cP)	1390	1240	1380	1540
Coke Yield (wt.%)	0.79	0.95	1.14	1.16

* Uncertainties of viscosity and coke yield is 10% and 0.05.

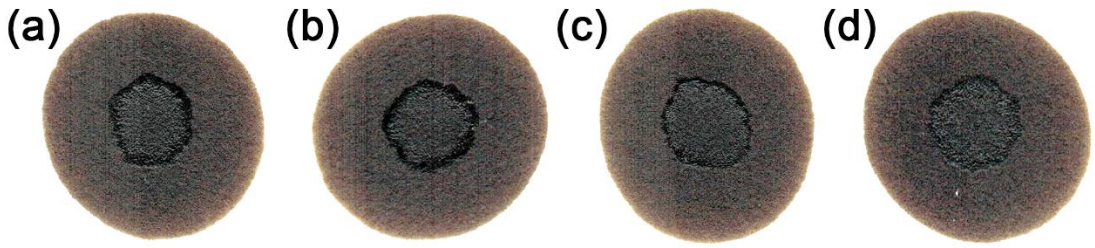


Figure 6- 6. Stability test of oil products obtained using HY with SiO_2/Al_2O_3 molar ratios of (a) 5.2:1, (b) 30:1, (d) 60:1 and (d) 80:1 as the catalyst under methane environment at 5.0 MPa and 380 ^oC for 150 min

Similarly to what has been done for HZSM-5, 1 wt % Ag/HY is prepared by loading silver cations to HY for the further investigation of its Si:Al ratio effect on bitumen partial upgrading. The viscosity and coke yield of the product oil collected over these catalysts are displayed in Table 6-4 and Figure 6-7. Comparing with the results of HY, the viscosity of the liquid product is reduced. When HY (80:1) is used, the viscosity of the oil product is reduced by 442 cP upon the loading of silver cations. These observations demonstrate that the introduction of silver to the catalyst improves the catalytic capability of the catalyst in terms of carbon chain and polycyclic structure breakage and rearrangement. The stability and compatibility of the samples (Figure 6-8), however, were not improved by the loading of Ag species. When the results obtained from Ag/Y are compared to those from Ag/ZSM-5, it is clear that lower viscosity along with better stability and compatibility are observed when Ag/ZSM-5 catalysts, especially that with a SiO_2/Al_2O_3 molar ratio of 30:1, are charged.

Table 6- 4. Viscosity and coke yield of the product oil obtained using 1%Ag/HY with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 °C for 150 min

	1%Ag/HY (5.2:1)	1%Ag/HY (30:1)	1%Ag/HY (60:1)	1%Ag/HY (80:1)
Viscosity (cP)	1350	1200	1130	1100
Coke Yield (wt.%)	0.61	0.89	0.49	1.09

* Uncertainties of viscosity and coke yield is 10% and 0.05.

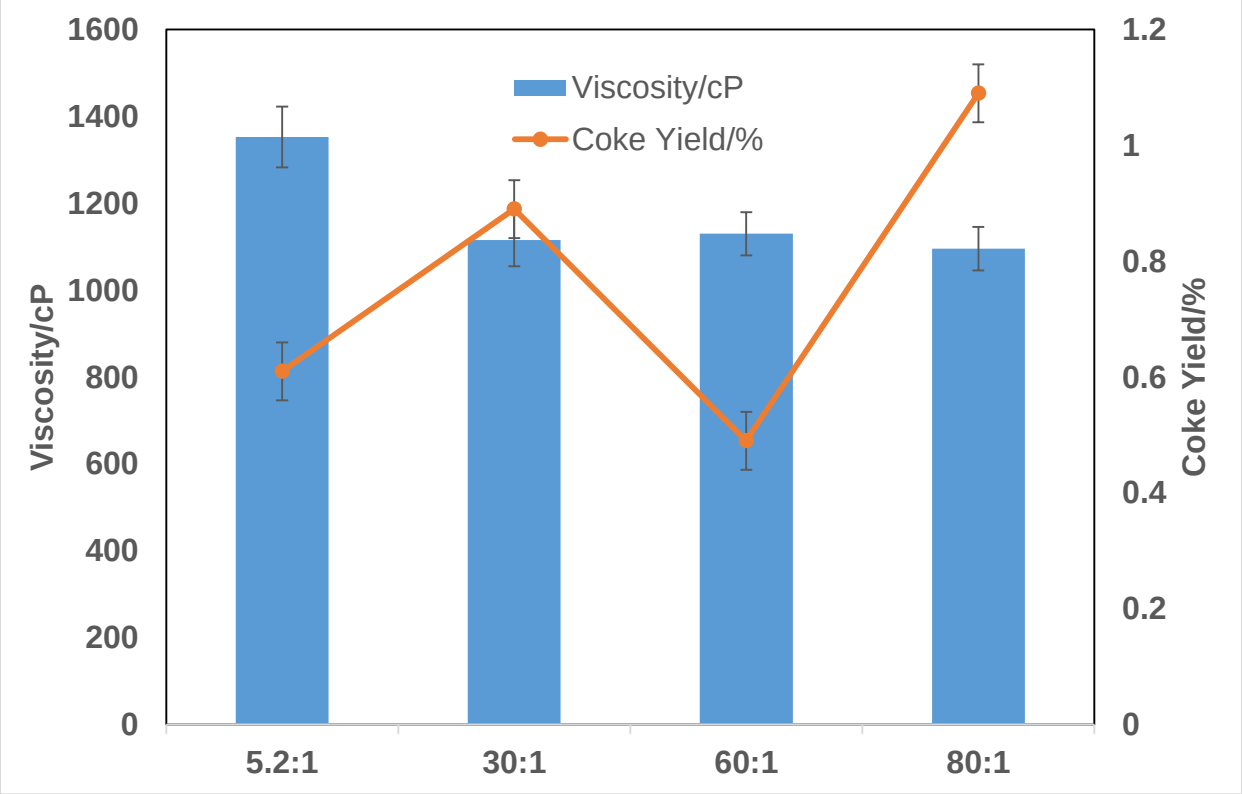


Figure 6- 7. Viscosity and coke yield of the product oil obtained using 1%Ag/HY with variable SiO_2/Al_2O_3 molar ratios under methane environment at 5.0 MPa and 380 °C for 150 min

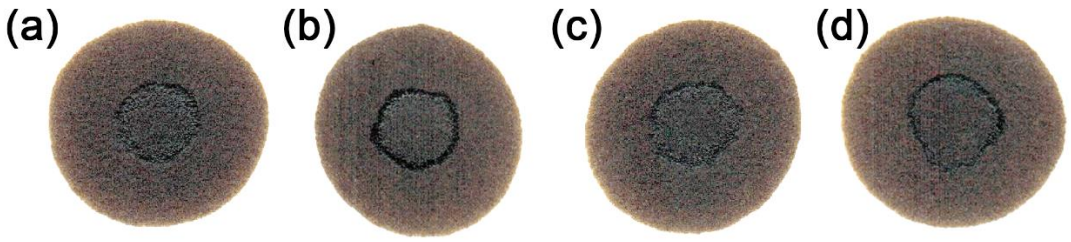


Figure 6- 8. Stability test of oil products obtained using 1%Ag/HY with SiO_2/Al_2O_3 molar ratios of (a) 5.2:1, (b) 30:1, (d) 60:1 and (d) 80:1 as the catalyst under methane environment at 5.0 MPa and 380 °C for 150 min

6.1.3 Sulfated ZrO_2

The Sulfated ZrO_2 (S-ZrO_2) has been numerously reported in the literature with high surface acidity which might facilitate heavy crude oil cracking. Therefore, it has been included in this study for bitumen partial upgrading evaluation as the acidic support for active metal loading. As shown in Table 5-5, S-ZrO_2 is not good support candidate for bitumen upgrading in terms of viscosity reduction, but it is effective in controlling coking yield. Moreover, Ag loading at 1 wt.% onto the S-ZrO_2 support does not facilitate the viscosity reduction but notably enhance the coke formation resistance. The stability and compatibility of the resulting product oil collected over S-ZrO_2 and 1%Ag/S-ZrO_2 are all poor as evidenced in Figure 6-9, thus not deserving further study.

Table 6- 5.Viscosity and coke yield of oil products collected over S-ZrO_2 and 1%Ag/S-ZrO_2

Catalyst Code	---	ZrO_2	1%Ag/ZrO_2
Atmosphere	CH_4	CH_4	CH_4
P_0 at 25°C, bar	50	50	50
t, min	150	150	150
T, °C	380	380	380
Coking yield/%	0.55	0.04	-0.28
product LS viscosity@25°C, cP	1620	1500	1450

* Uncertainties of viscosity and coke yield is 10% and 0.05.

Figure 6- 9. Stability and compatibility of oil products using (a) S-ZrO_2 and (b) 1 %Ag/S-ZrO_2 under methane environment at 5.0 MPa and 380 ^oC for 150 min

6.1.4 Zeolite A

Inspired by the work using HY with large pore size, zeolite A with large pore size of ~11.4 Å and high thermal resistance capability (up to 700 ^oC) is chosen as the support candidate for triggering bitumen partial upgrading. However, as documented in Table 6-6, it is unfortunately not good support candidate for bitumen upgrading in term of viscosity reduction. The stability and compatibility of the resulting product oil collected over zeolite A is poor as evidenced in Figure 6-10, thus also not deserving further study.

Table 6- 6. Viscosity and coke yield of oil products using Zeolite A

Catalyst Code	---	Zeolite A
Atmosphere	CH_4	CH_4
P_0 at 25°C, bar	50	50
t, min	150	150
T, ^oC	380	380
Coking yield/%	0.55	0.73
product LS viscosity@25°C, cP	1620	1560

* Uncertainties of viscosity and coke yield is 10% and 0.05.

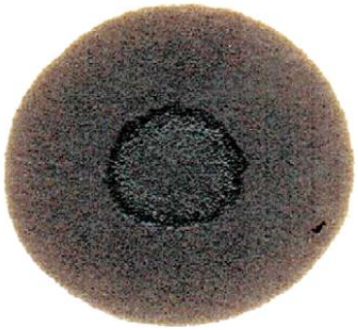


Figure 6- 10. Stability and compatibility of oil products using Zeolite A under methane

6.2 Catalyst Optimization Upon Active Metal Loading

According to the aforementioned studies, HZSM-5 (30:1) and its 1 wt.% Ag loaded on are identified as the best support and catalyst in terms of the highest viscosity reduction and excellent product oil stability and compatibility. However, the viscosity (715 cP) and coke yield (1.72 wt.%) of the product oil collected over Ag/HZSM-5(30:1) is still above the pipeline transportation specifications and thus cannot be accepted. Therefore, the addition of promoter metal species including zinc and gallium are explored to lower the viscosity and coke yield without compromising the stability and compatibility of the product oil. Once 1 % Zn is introduced into the framework of ZSM-5 (30:1) along with 1 %Ag, the viscosity is lowered from 715 cP to 667 cP, while the coke yield is significantly reduced from 1.72 % to 0.62 % as shown in Table 5-7 and Figure 5-11. By adding more Zn, i.e., 10 % Zn, to Ag/HZSM-5, the viscosity and coke yield are reduced to 455 cP and 0.44 %. Upon the addition of gallium, the viscosity is further decreased to 278 cP, which is even lower than the viscosity of the product oil collected over 1 %Ag-10 %Zn/ZSM-5 (23:1) as reported in Chapter 4. Furthermore, this lowest viscosity among all the oil samples in comparison is accompanied with an acceptable coke yield (0.80 wt.%) and excellent stability and compatibility as evidenced in Figure 6-12, making it more applicable for pipeline transportation and downstream refining in petrochemical industries.

Table 6- 7. Performance of bitumen partial upgrading using metal modified HZSM-5 catalysts under methane environment at 5.0 MPa and 380 °C for 150 min

Catalyst	1%Ag-10%Zn/HZSM5 (30:1)	1%Ag-1%Zn/HZSM5 (30:1)	1%Ag-1%Ga/HZSM5 (30:1)
Viscosity (cP)	460	670	280
Coke Yield (wt.%)	0.44	0.62	0.80

* Uncertainties of viscosity and coke yield is 10% and 0.05.

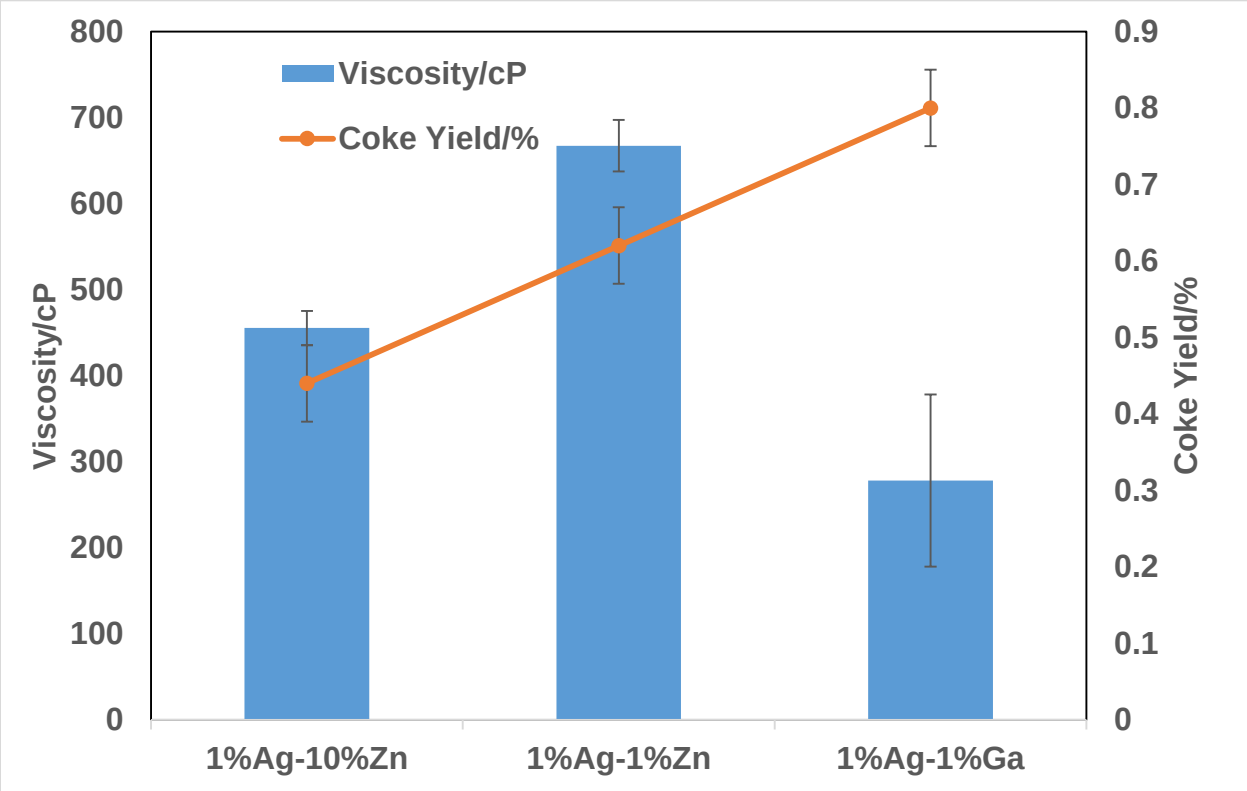


Figure 6- 11. Viscosity and coke yield of the product oil obtained using metal modified HZSM-5 (30:1) under methane environment at 5.0 MPa and 380 °C for 150 min

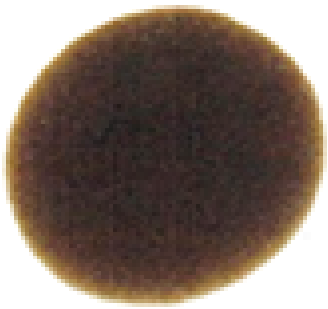


Figure 6- 12. Stability test of oil products obtained using HZSM-5 (30:1) modified by 1%Ag-1%Ga as the catalyst under methane environment at 5.0 MPa and 380 ºC for 150 min

The composition of the oil sample obtained over 1 %Ag-1 %Ga/ZSM-5 (30:1) is further analyzed. The gasoline and diesel fractions are listed in Table 6-8 and compared with those of the bitumen feedstocks, oil samples from control experiments carried out under N_2 and CH_4 environment without catalyst, and the product oil over 1 % Ag-10 % Zn/ZSM-5 (23:1) which have been reported in previous work (Guo, 2016). The presence of 1 % Ag-1 % Ga/ZSM-5 (30:1) under CH_4 environment gives a significant increase in both gasoline and diesel fractions. Compared with the bitumen feedstock, the total gasoline and diesel weight percentage is increased from 12.15 % to 43.51 %. It is worth noting that this value is even higher than that collected over 1 % Ag-10 % Zn/ZSM-5 (23:1) (i.e., 36.77%). The enhanced total gasoline and diesel fraction might be one of the reasons that the viscosity of the product oil is lower compared with the oil obtained over 1 % Ag-10 % Zn/ZSM-5 (23:1). When 1 % Ag-1 % Ga/ZSM-5 (30:1) charged in the reaction, the molecules of the bitumen feedstock are cracked and rearranged under CH_4 environment more efficiently, leading to more gasoline and diesel molecules, which might dilute the product oil matrix and lower the viscosity. It is also worth noting the increased gasoline and diesel fractions

are critical for the application of the partial upgrading process due to the reduced burden for the downstream refining, leading to a notable cost reduction.

Table 6- 8. Gasoline and diesel fractions of the oil sample collected from various runs conducted at 5.0 MPa and 380 °C for 150 min

Trial	**Atmosphere**	**Gasoline (wt%)**	**Diesel (wt%)**	**Total gasoline and diesel (wt%)**
Bitumen	-	0.2	12. 0	12.2
-	N_2	6.9	20.8	27.7
-	CH_4	6.9	23.7	30.7
1%Ag-10%Zn/HZSM-5(23:1)	N_2	6.3	26.6	32.9
1%Ag-10%Zn/HZSM-5(23:1)	CH_4	13.4	23.4	36.8
1%Ag-1%Ga/HZSM-5(30:1)	CH_4	16. 0	27.5	43.5

* Uncertainties of gasoline, diesel and total fraction are 0.1, 0.1 and 0.2, respectively.

The distilled gasoline and diesel fractions are further analyzed by GC-MS as described in the following paragraph for identifying their compositions which are categorized into aromatics, olefins, paraffins, and naphthenes as displayed in Figure 6-13. In addition, the image of the collected gasoline and diesel fractions are also included. The olefin content does represent an issue in the long-term storage and transportation, particularly in the gasoline fraction products. The single step processing cannot meet all the industrial criteria for pipeline transportation. Therefore, the olefin conversion of the cracking distillates is an ongoing work in research group.

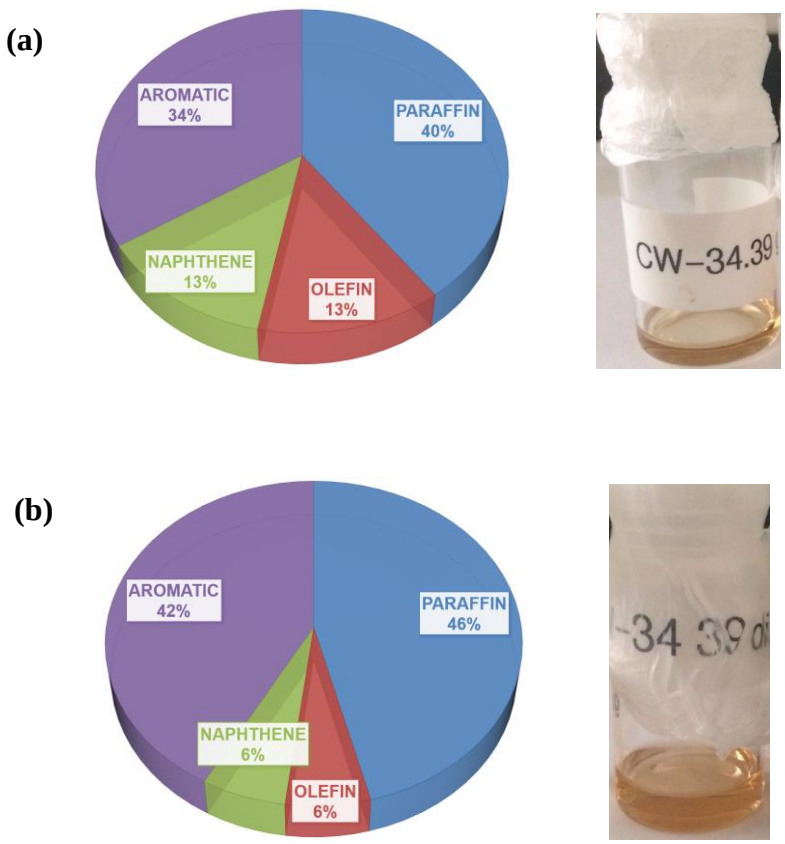


Figure 6- 13. (a) Gasoline and (b) diesel fractions of the product oil collected over 1%Ag-1%Ga/ZSM-5 under methane environment at 5.0 MPa and 380 ºC for 150 min

6.3 Conclusions

The work reported in this study demonstrates the technical feasibility of bitumen partial upgrading performance enhancement by catalyst formulation optimization. Through evaluating the influence of catalyst's support and active metal on product oil's viscosity, coke formation, and stability, the best catalyst candidate is identified as 1 wt.%Ag-1 wt.%Ga/ZSM-5 (Si:Al=30:1) among all the tested catalyst formulations. When this catalyst is charged into the bitumen partial upgrading process, product oil with viscosity of as low as 278 cP, coke yield of 0.8 wt.%, and #1 stability, and gasoline and diesel fraction contents of as high as 43.5 wt.% is successfully achieved, which triggers a strong need as a future work for understanding the involved catalytic reaction

mechanism in order to facilitate catalyst rational design embedded with even better upgrading performance.

Chapter Seven: Conclusions and future work

7.1 Conclusions

From reaction conditions optimization section, the best reaction conditions include sample weight at 50 g, agitation rate at ~240 rpm, reaction duration for 150 min, reaction temperature at 380 ^{o}C, methane pressure at 50 bar.

1 wt% Ag–10 wt% Zn/HZSM-5 was then selected as the catalyst candidate to evaluate the technical feasibility of the bitumen partial upgrading process under methane environment at reaction conditions identified above. According to the experimental results, a synergistic effect between methane and bitumen is clearly witnessed during the upgrading process when the Ag–Zn/ZSM-5 catalyst is used, leading to the production of partially upgraded oil with the lowest viscosity (414 cP), highest gasoline and diesel contents (36.8 wt.%), lowest density (0.967 g/cm^3), lowest acidity (0.03 mg/g KOH), lowest asphaltene content (12.3 wt.%), and lowest molecular weight (330 g/mol) as well as the highest liquid yield (97.8 wt.%) and acceptable coke formation (0.75 wt.%), compared to a series of control runs, indicating the most efficient carbon chain and polycyclic structure breakage and rearrangement if the catalytic methanotreating process is utilized.

Catalyst formulation is further optimized for achieving enhanced bitumen partial upgrading performance through evaluating the contributions from support and active metals. From the catalyst support identification section, the best catalyst support tested was the ZSM-5 with a silica to alumina ratio of 30:1, which can reduce the viscosity of the bitumen to as low as 963 cP. When loaded with 1 %Ag, the best catalyst is still based on ZSM-5 with a silica to alumina ratio of 30:1, which can reduce the viscosity of the bitumen to as low as 715 cP. Moreover, once 1%Ga is introduced into the ZSM-5 framework with Sil:Al of 30:1 along with 1% Ag, better partial upgrading performance is witnessed in terms of further viscosity reduction to 278 cP and enhanced

gasoline and diesel contents at 43.5 wt.% accompanied with acceptable coke formation at 0.8 wt.% and excellent #1 stability & compatibility according to the given reference.

The work reported here demonstrates the feasibility of upgrading of bitumen with cheap methane on a zeolite supported catalyst under moderate conditions to yield partially upgraded crude oil suitable for pipeline transportation with no or significantly reduced need of diluent addition. With methane introduction during bitumen catalytic thermal cracking, in addition to the increased productivity, the quality of the acquired oil product is also significantly enhanced in terms of flowability, density, acidity, saturation degree, averaged molecular weight, distillation fractions, and compatibility. The performance of this novel process is comparable with the state-of-the-art hydrotreatment process but it is much more cost-effective. The performance variation with feed gases, bitumen thermal cracking and catalysts apparently demonstrated the existence of a reaction among them.

7.2 Future Work

Since the need for heavy oil partial upgrading is so demanding for significantly diluent usage minimization, developing a more effective methanotreating catalyst is still an important future work, which can achieve the partially upgraded oil with even better quality and higher quantity. And also more work needs to be done in how to run the reaction in lower temperature and pressure, in order to achieve better process economics and ease process operation.

More sample characterizations, such as XRD, GC-MS, TEM and XPS, will be performed to get a better understanding of the involved catalytic reaction mechanism, beneficial for the rational design of the engaged catalyst. Model compounds will be reasonably selected to represent crude oil for better mechanistic study of the involved upgrading reactions. It is well known that heavy oil is rather complex in molecular composition31 and a heavy oil model compound is frequently employed to trace its upgrading chemistry. In addition, isotopic labelled methane (e.g. CD_4 or

$^{13}CH_4$) will be employed to further evidence the participation of methane in the upgrading reaction and track its reaction pathway.

Long term stability test will be conducted and catalyst deactivation mechanism will be identified for its potential commercialization. And more chemical additives can be evaluated to achieve further viscosity reduction of the partially upgraded oil for meeting pipeline transportation specifications and the burden from downstream refining.

References

Absi-Halabi,M., Stanislaus, A.," Coke formation on catalysts during the hydroprocessing of heavy oils" Appl. Catal., 72,193–215, 1991.

Alvarez-Galvan, M.C., Mota, N., Ojeda, M., Rojas, S., Navarro, R.M., Fierro, J.L.G., "Direct methane conversion routes to chemicals and fuels " Catal. Today, 171, 15-23, 2011.

Amenomiya, Y., Birss, V., Goledzinowski, M.," Conversion of methane by oxidative coupling" Catal. Rev.:Sci. Eng., 32, 163–227, 1990.

Anunziata, O., Mercado, G., Pierella, L.B., "Catalytic activation of methane using n-pentane as co-reactant over Zn/H-ZSM-11 zeolite," Catalysis letters, 87 (3-4), 167-171, 2003.

Anunziata, O., Mercado,G., Pierella, L. B. 2nd Mercosur Congress on Chemical Engineering, 2005.

Anunziata, O.A., Cussa, J., Beltramone, A.R., "Simultaneous optimization of methane conversion and aromatic yields by catalytic activation with ethane over Zn-ZSM-11 zeolite: The influence of the Zn-loading factor." Catalysis today, 17 1 (1), 36-42, 2011.

Baba T., Abe, Y., "Metal Cation - Acidic Proton Bifunctional Catalyst for Methane Activation: Conversion of 13CH4 in the Presence of Ethylene over Metal Cations Loaded H-ZSM-5" Appl. Catal., A, 250, 265–270, 2003.

Baba, T., & Sawada, H., "Conversion of methane into higher hydrocarbons in the presence of ethylene over H-ZSM-5 loaded with silver cations. "Physical Chemistry Chemical Physics, 4(15), 3919-3923, 2002.

Baba, T., Inazu, K., “Production of c2+ olefins” Chem.Lett. 35, 142-147, 2006.

Baba, T., Iwase, Y., Inazu, K., Masih, D., Matsumoto, A.,” Catalytic properties of silver-exchanged zeolites for propene production by conversion of methane in the presence of ethene”Microporous Mesoporous Mater., 101, 142–147, 2007.

Baba, T., Sawada, H., “Conversion of methane into higher hydrocarbons in the presence ofethylene over H-ZSM-5 loaded with silver cations”, Phys. Chem. 4, 3919–3923, 2002.

Baerlocher, C., Meier, W. H., Olson, D. H., “Atlas of zeolite framework types, 6th Edition”, 2007.

Bachiller-Baeza, B., Anderson, J. A.,” FTIR and Reaction Studies of Styrene and Toluene over Silica–Zirconia-Supported Heteropoly Acid Catalysts” J. Catal., 212,231–239, 2002.

Belyk, G., Burgart, D., Jablonski, B., Heida, J., Kaiser, T., Bernar R., and Whitelaw, B., “Heavy Oil 101.” Participant Handbook, Canadian Heavy Oil Association, 2013.

Borry, R. W., H. Kim, Y., Huffsmith, A., Reimer, J. A., Iglesia, E.,” Structure and density of Mo and acid sites in Mo-exchanged H-ZSM5 catalysts for nonoxidative methane conversion” J. Phys. Chem. B, 103, 5787–5796, 1999.

Breck, D. W., “Proceedings of the Conference on The Properties and Applications of Zeolites” Soc. Chem md. 18—20, 1979.

Čejka, J., van Bekkum, H., “Zeolites and Ordered Mesoporous Materials: Progress and Prospects.” 157, 2005

Changchang, Liu, Sungchul, Lee, Dong, Su, Zhiteng, Zhang, Lisa, Pfefferle, Gary, Haller. "Synthesis and Characterization of Nanocomposites with Strong Interfacial Interaction: Sulfated ZrO2 Nanoparticles Supported on Multiwalled Carbon Nanotubes." The Journal of Physical Chemistry C 116, no. 41, 21742–52, 2012.

Choudhary, T.V., Aksoylu, E., Goodman, D.W.," Nonoxidative Activation of Methane" Catal. Rev. Sci. Eng., 45, 151-203, 2003.

Choudhary, V. R., Kinage, A. K., & Choudhary, T. V., "Low-temperature nonoxidative activation of methane over H-galloaluminosilicate (MFI) zeolite. "Science, 275(5304), 1286-1288, 1997

.

Choudhary, V.R., Kinage, A.K., Choudhary, T.V., "LOW-TEMPERATURE NONOXIDATIVE ACTIVATION OF METHANE OVER H-GALLOALUMINOSILICATE (MFI) ZEOLITE "Science, 275, 1286-1288, 1997

Choudhary, V.R., Mondal, K.C., Mulla, S.A.R., Chem. Angew. "Significant Influence of Zn on Activation of the C-H Bonds of Small Alkanes by Brønsted Acid Sites of Zeolite." Int. Ed., 44, 4381-4385, 2005.

Cui, Y., Xu, Y., Lu, J., Suzuki, Y., Zhang, Z., "The effect of zeolite particle size on the activity of Mo/HZSM-5 in non-oxidative methane dehydroaromatization" Appl. Catal. A: Gen., 393, 348-358, 2011.

Ding, B., Huang, S., & Wang, W.. "Methane activation over Ag-exchanged ZSM-5 zeolites: A theoretical study. "Applied Surface Science, 254(16), 4944-4948, 2008.

Fernando, S., Anuradh, D., "Deoxygenation of biomass derived oxygenates to hydrocarbons via direct methane", U.S. Patent, US 2011/0313219A1, 2011.

Furimsky, E.” Catalysts for Upgrading Heavy Petroleum Feeds” Stud. Surf. Sci. Catal., 169, 381–387, 2007.

Hydrocarbons: Mechanisms of Reaction. Ind. Eng. Chem. 1949, 41, 2573-2584.

Geological Survey (US) “Zeolites” Minerals Yearbook, Metals and Minerals, Volume I, 2008.

Gray, M., “Upgrading Oilsands, Bitumen, and Heavy Oil”, 2015.

Greensfelder, B. S., Voge, H. H., Good, G. M., “Catalytic and Thermal Cracking of Pure Hydrocarbons: Mechanisms of Reaction.” Ind. Eng. Chem., 41, 2573-2584, 1949.

Guczi, L., Koppány, Zs., arma, K. V., Borkó, L., Kiricsi, I.,” Structure and methane activation, in Progress in Zeolite and Microporous Materials,” Stud. Surf. Sci. Catal. (Eds.: H. Chon, S.-K. Ihm and Y. S. Uh), Elsevier Sci. Publ. Co., Amsterdam, 105, p. 861-868, 1997

Guisnet, Michel., Chen, Yi-Shen., Perot, Guy., “Effect of sodium content on the activiht of ZSM—5 zeolite” Zeolites, Volume 4, Issue 2, 108-109, 1984.

Guo, X., Fang, G., Li, G., Ma, H., Fan, H., Yu, L., Ma, C., Wu, X., Deng, D., Wei, M., Tan, D., Si, R., Zhang, S., Li, J., Sun, L., Tang, Z., Pan X., Bao, X., “Direct, nonoxidative conversion of methane to ethylene, aromatics, and hydrogen.” Science, 344, 616–619, 2014.

Ha, V., Sarioğlan, A., Erdem-Şenatalar, A, Taârit, Y., “An EPR and NMR study on Mo/HZSM-5 catalysts for the aromatization of methane: Investigation of the location of the pentavalent molybdenum” J. Mol. Catal. A: Chem., 378, 279-284, 2013.

Hay, D.G., G. W. West. "Examination of the monoclinic/orthorhombic transition in silicalite using XRD and silicon NMR". J. Catal. 89, 1070–1072, 1985.

Hayashi, Hideki., Furukawa, Hiroyasu., O'Keeffe, Michael., Yagh, Omar. M., “Zeolite A imidazolate frameworks” Journal, 6, 501-506, 2007.

He, P., Song, H., “Catalytic Conversion of Biomass by Natural Gas for Oil Quality Upgrading”, Industrial & Engineering Chemistry Research, 53 (41), 15862-15870, 2014

He, P., Shan, W., Xiao, Y., Song, H., "Performance of Zn/ZSM-5 for In Situ Catalytic Upgrading of Pyrolysis Bio-oil by Methane", Topics in Catalysis, 59(1), 86-93, 2016

Hutchings, G. J., Scurrell, M. S.,” Chemical Society Reviews” Chem. Soc. Rev., 18,251–283, 1989.

Idriss, H., “Ethanol reactions over the surfaces of noble metal/cerium oxide catalysts,” Platinum Metals Review, 48, 105–115, 2004.

Ji Bong, Joo, Austin, Vu, Qiao, Zhang, Michael, Dahl, Minfen, Gu, Francisco, Zaera, Yadong, Yin. “A Sulfated ZrO2 Hollow Nanostructure as an Acid Catalyst in the Dehydration of Fructose to 5-Hydroxymethylfurfural.” ChemSusChem, no. 10, 2001–8, 2013.

Jin, L., Zhou, X., He, X., Hu, H., “Integrated coal pyrolysis with methane aromatization over Mo/HZSM-5 for improving tar yield”, Fuel, 114, 187-190, 2013.

Kr´alik, B., Chang, E. K.,Louie, S. G.,“Structural properties and quasiparticle band structure of zirconia” Phys, 57, 7027,1998.

Kolyagin, Y. G., Ivanova,I. I., Ordomsky, V. V., Gedeon,A., Pirogov, Y. A., “Methane activation over Zn-Modified MFI Zeolite: NMREvidence for Zn-Methyl Surface Species Formation.” J. Phys. Chem. C, 112, 20065–20069, 2008.

Kunkeler, P. J., Downing, R. S., Bekkum, H. v. “Chapter 21 The use of bulky molecules as probes for investigating the contributions of the external and internal pore-wall activities of zeolite catalysts. In Studies in Surface Science and Catalysis.” Elsevier, 137, 987, 2001.

Kuppe, GJ., Rodriguez, H., “Extra Heavy Crude Oil Downhole Upgrading Using Hydrogen Donors Under Cyclic Steam Injection Conditions: Physical and Numerical Simulation Studies” J. Can. Petrol. Technol., 47, 43-51, 2008.

Koh Peck Tian, Abdul Rahman Mohamed, Subhash Bhatia, “Catalytic upgrading of petroleum residual oil by hydrotreating catalysts: a comparison between dispersed and supported catalysts” Fuel, 77, 1221–1227, 1998.

Lee,J. S., Oyama, S. T., “Oxidative coupling of methane to higher hydrocarbons” Catal. Rev.: Sci. Eng., 30,249–280, 1988.

Liu, Changchang., Lee, Sungchul., Su, Dong., Zhang, Zhiteng., Pfefferle, Lisa., Haller, Gary L., “Synthesis and Characterization of Nanocomposites with Strong Interfacial Interaction: Sulfated ZrO2 Nanoparticles Supported on Multiwalled Carbon Nanotubes” *J. Phys. Chem. C*, 116 (41), 21742–21752, 2012.

Lunsford, J. H., Chem, Angew., “The catalytic coupling of methane” Int. Ed. Engl. 34,970–980,1995.

Mech, M., A Comprehensive Guide to the Alberta Oil Sands, 2011.

Miao, S., Wang, Y., Ma, D., Zhu, Q., Zhou, S., Su, L., Tian, D., & Bao, X. Effect of Ag+ Cations on Nonoxidative Activation of Methane to C2-Hydrocarbons. The Journal of Physical Chemistry B, 108(46), 17866-17871, 2004.

Mohammadaparast, Farshid., Halladj, Rouein., Askari, Sima., “The Crystal Size Effect of Nano-Sized ZSM-5 in the Catalytic Performance of Petrochemical Processes: A Review” Chemical Engineering Communications, Volume 202, Issue 4, 2015.

Nazmul Abedin, Khan, Kumar Mishra, Dinesh, Ahmed, Imteaz, Woong Yoon, Ji, Hwang, Jin-Soo, Hwa Jhung, Sung,. “Liquid-Phase Dehydration of Sorbitol to Isosorbide Using Sulfated Zirconia as a Solid Acid Catalyst.” Applied Catalysis A: General, 452, 34–38, 2013.

Nobukawa, T., Yoshida, M., Kameoka, S., Ito, S., Tomishige K., Kunimori, K., “In-situ Observation of Reaction Intermediate in the Selective Catalytic Reduction of N2O with CH4 over Fe ion-exchanged BEA Zeolite Catalyst for the Elucidation of Its Reaction Mechanism using FTIR” J. Phys. Chem. B, 108,4071–4079, 2004.

Ovalles, C., Filgueiras, E., Morales, A., Rojas, I., Jesus, J.C., Berrios, I., “Use of a dispersed molybdenum catalyst and mechanistic studies for upgrading extra-heavy crude oil using methane as source of hydrogen,” Energy & Fuels, 379-385, 1998.

Ovalles, C., Filgueiras, E., Morales, A., Scott, C.E., Gonzalez-Gimenez, F., Embaid,B.P., “Use of a dispersed iron catalyst for upgrading extra-heavy crude oil using methane as source of hydrogen” Fuel, 82, 887-892, 2003.

Ovelles, C., Hamana, A., Rojas, I., Bolívar, R., “Upgrading of extra-heavy crude oil by direct use of methane in the presence of water: Deuterium-labelled experiments and mechanistic consideration”Fuel, 74, 1162-1168, 1995.

Ovelles, C., Valleios, C., Vasquez, T., Rojas, I., Ehrman, U., Benitez, J., Martinez, R., “Downhole upgrading of extra-heavy crude oil using hydrogen donors and methane under steam injection conditions,” Petrol. Sci. Technol., 21, 255-274, 2003.

Qian, K., Rodgers, R., Hendrickson, C., Emmett, M., Marshall, A., “Resolution and Identification of 3000 Nitrogen-Containing Aromatic Compounds from a Single Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrum of Heavy Petroleum Crude Oil,” Energy & Fuels, 2001, 15, 492-498, 2001.

Rakotondradany, F., Fenniri, H., Rahimi, P., Gawrys, K., Kilpatrick, P., Gray, M., “Hexabenzocoronene model compounds for asphaltene fractions: synthesis & characterization,” Energy & fuels 20 (6), 2439-2447, 2006.

Rana, M. S., Sámano, V., Ancheyta , J., Diaz, J. A. I.,” A review of recent advances on process technologies for upgrading of heavy oils and residua” Fuel, 86, 1216–1231, 2007.

Rahimi, Nazi., Karimzadeh, Ramin., “Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: A review” Applied Catalysis: A General, Volume 398, Issues 1–2, 1–17, 2011.

Ribeiro, F. R., Rodrigues, A. E., Rollmann, L. D., Naccache, C.,”Zeolites” Science and Technology, 1984.

Sahebdelfar, S., Ravanchi, M. T., Gharibi, M., Hamidzadeh, M.,” An inherent limitation or performance measure in oxidative coupling of methane?” J. Nat. Gas Chem., 21, 308–313, 2012.

Savage, P. E., Korotney, D. J.,” Pyrolysis Kinetics for LongChain n-Alkylbenzenes: Experimental and Mechanistic Modeling Results,” Ind. Eng. Chem. Res., 29, 499–502, 1990.

Savage,P. E., Klein, M. T., “Asphaltene reaction pathway.2. Pyrolysis of n-pentadecylbenzene.” Ind. Eng. Chem. Res., 26,488–494, 1987.

Shcherban, Nataliya., Barakov, Roman., Yaremov, Pavel., Solomakha, Vladimir., Gryn, Svitlana., Khaynakova, Olena., Ilyin, Vladimir., " Template synthesis, structure, sorption properties and acidity of micro-mesoporous materials obtained from sol-precursor of zeolite BEA" Journal of Porous Materials, Volume 21, Issue 3, 355–363, 2014.

Speight, J G., "New approaches to hydroprocessing." Catalysis Today, 98, 55-60, 2004.

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

Steen, E., Callanan, L.H., Claeys, M., "Recent Advances in the Science and Technology of Zeolites and Related Materials." 2004.

Stefanovich, E. V., Shluger, A., Catlow, C. R., "Theoretical study of the stabilization of cubic-phase ZrO2 by impurities." Phys. Rev. 49, 11560, 1994.

Strausz, O.P., "The Chemistry of the Alberta Oil Sand Bitumen", [Online]

Thomas, F., Degnan, Jr., "Applications of zeolites in petroleum refining" Topics in Catalysis, Volume 13, Issue 4, 349–356, 2000.

Tsaprailis, H.,Properties of Dilbit and Conventional Crude Oils, Alberta Innovates, 2014.

Vermeiren, W., Gilson, J.-P., "Impact of Zeolites on the Petroleum and Petrochemical Industry" Topics in Catalysis, Volume 52, Issue 9, pp 1131–1161, 2009.

Wang, D., Lunsford,J. H., Rosynek, M. P., "Characterization of a Mo/ZSM-5 Catalyst for the Conversion of Methane to Benzene"J. Catal., 169, 347–358,1997.

Wang, L., Tao, L., Xie, M., Xu, G., Huang, J., Xu, Y.," Dehydrogenation and aromatization of methane under non-oxidizing conditions." Catal. Lett., 21, 35–41,1993.

Wang, L., Xu,Y., Tao, L.," Non-oxidative dehydro-oligomerization of methane to higher molecular weight hyerocarbons at low temperatures" Sci. China, Ser. B: Chem., 40, 161–164, 1997.

Wei, Ying. , Parmentier, Tanja E., Jong, Krijn P., Zečević, Jovana., "Tailoring and visualizing the pore architecture of hierarchical zeolites" Inorganic Chemistry and Catalysis, 44, 7234-7261, 2015.

Weckhuysen, B. M., Wang, D., Rosynek, M. P., Lunsford, J. H., "Conversion of methane to benzene over transition metal ion-loaded ZSM-5 zeolites: I. Catalytic characterization" J. Catal., 175, 338–351, 1998.

Xiao, Y., He, P., Cheng, W., Liu, J., Shan, W., Song, H., "Converting Solid Wastes into Liquid Fuel using a Novel Methanolysis Process", Waste Management, 49, 304-310, 2016.

Xu, Y., Lin, L., "Direct conversion of methane under nonoxidative conditions "J. Catal., 216, 386–395, 2003.

Xu, Y., Lin, L.," Direct conversion of methane under nonoxidative conditions" J. Catal., 216, 386-395, 2003.

Xu,Y., Lin, L. "Recent advances in meyjane dehydro-aromatization over transition metal ion-modified zeolite catalysts under non-oxidative conditions" Appl. Catal., A, 188, 53–67, 1999.

Zhang, H., Kong, A., Ding, Y., Dai, C., Shan, Y., "Low-temperature activation of methane over rare earth metals promoted Zn/HZSM-5 zeolite catalysts in the presence of ethylene" J. Nat. Gas Chem, 20, 243-248, 2011