Sodium Conversion of Asphaltenes

by

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Abstract

Asphaltenes are a solubility class and it is the material in oil that is insoluble in a paraffinic matrix. It is a major contributor to problems in many petroleum operations such as production, transportation, refining, precipitation, crude oil emulsification, and de-emulsification, and high hydrogen consumption during hydroprocessing. Alternative strategies to current industrial practice for the upgrading of asphaltenes are therefore sought out.

Alkali metals can easily give electrons and form donor-acceptor ion pairs. The electron transferred from sodium is delocalized in the aromatic. With the presence of a hydrogen source, hydrogenation of the aromatic system might take place. At the same time, for heteroatoms, there are reports about the bond cleavage and ring-opening reactions by alkali metals, which may help with desulfurization or denitrogenation.

Asphaltenes from the Nexen Long Lake Upgrader was converted with metallic sodium at different temperatures below 250°C to avoid the contribution of thermal reactions. Although Na does not have a significant effect on increasing liquid yield, the aromatic H-content decreased compared to that of the feed asphaltenes. The Na did help with heteroatom removal. The results from the conversion of the asphaltenes suggested Na could react with some oxygen, sulfur and nitrogen groups in asphaltenes, which decreased oxygen, sulfur and nitrogen content. In order to understand the reaction network better, model compounds were investigated with Na as well. It was found that sulfur can be extruded from S-containing heterocycles, but nitrogen and oxygen cannot be extruded from heterocycles. In addition, multinuclear aromatics are hydrogenated by hydrogen transfer.

Keywords: Asphaltenes, Na conversion, desulfurization, hydrogenation

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There are so many unknowns ahead in my life but I believe more good times will come along.

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CHAPTER 1 – Introduction to sodium conversion of asphaltenes

1.1 Background

According to the International Energy Agency, global demand for energy is expected to rise by 35% by 2035 as economies in both developed and emerging countries continue to grow and the standard of living improves in the developing world. It is predicted that the world will need to invest $37 trillion in energy supplies from 2011 to 2035.

One of the world's largest oil deposits is the heavy and extra heavy oil deposits with less than 20° API (933 $kg \cdot m^{-3}$) is in Canada, and another one is in Venezuela [1]. Oil sands are a mixture of sand, water, clay and bitumen. Bitumen is oil that is too heavy or thick to flow or be pumped without being diluted or heated. The largest Canadian oil sands deposit, the Athabasca oil sands is in the McMurray Formation in the city area surrounding the of Fort McMurray, Alberta. It outcrops on the surface about 50 km north of Fort McMurray, where enormous oil sands mines have been established, but is 400 m (1,300 ft) deep southeast of Fort McMurray. Only 3% of the oil sands area containing about 20% of the recoverable oil can be produced by surface mining, so the remaining 80% will have to be produced using *in situ* wells, such as steam assisted gravity drainage (SAGD) etc. The other Canadian deposits are between 350 to 900 m (1,000 to 3,000 ft) deep and will require *in situ* production [1].

The origin of the massive oilsands deposits is that the original source rocks were organic-rich shales in western Alberta that contained organic material that deposited in a marine environment. This organic material formed a polymeric matrix called "kerogen". During mountain building process with high subsurface temperatures, and high pressure, kerogen was converted the in the deeply buried organic-rich shales to light oil and natural gas. Such kerogen deposits are the source of petroleum worldwide. Any fragments of the kerogen that are small enough to dissolve in the lighter oil components emerge to become part of the petroleum or crude oil [2]. This study is concerned with only a subfraction of petroleum, namely, the asphaltenes subfraction.

Asphaltene is defined as solubility class in oil sands. It can dissolve in toluene but not in *n*-pentane (n-C_5) or *n*-heptane (n-C_7) solvents. It has high molecular weight and is a complex mixture of polycyclic aromatic molecules. In general, petroleum asphaltene is characterized by its high heteroatom content which in the case of the Alberta asphaltene is in the range of sulfur 8-9%, oxygen 2-3%, and nitrogen ~1% [2].

There are several challenges when one deals with asphaltenes because of its imprecisely known composition, molecular weight and its tendency to aggregate. Asphaltenes can cause a lot of problem in mining, extraction, upgrading or transportation. A challenge in bitumen chemistry is to understand the structures and properties of asphaltenes (both chemical and physical) and its reactivity.

One bitumen upgrader gasifies asphaltenes in order to provide hydrogen for the primary and secondary upgrading. But other than that, finding reaction pathways that will add value to asphaltenes convert it into maltenes or higher valued products is a big challenge.

1.2 Objectives

The objective of this study was to evaluate the potential benefit of employing sodium metal for the conversion of asphaltenes.

The conversion chemistry is based on the premise that Na is a strong electron donor and that the multinuclear aromatics in asphaltenes will become the electron acceptor. The reaction with sodium forms the Na^+ (aromatic)$^-$ ion pair or (Na)$^{2+}$(aromatic)$^{2-}$ ion pair , which may aid with the extrusion of heteroatoms from heterocyclic aromatics and ring-open aromatics.

The study was specifically limited to temperatures of 250 °C and lower, this temperature range was chosen is to limit the influence of thermal reactions on conversion so only the chemistry of Na was studied in this research thesis. Specific sub-objectives were to determine:

- If sodium reacting with asphaltenes under different temperature helps to gain more liquid yield.
- If sodium helps with desulfurization (e.g.dibenzothiopehene) and denitrogentnation, especially with heteroaromatics.
- If sodium can facilitate C-C bond scission and open multinuclear aromatic ring structures.

1.3 Scope of work

A literature review (Chapter 2) is presented mainly to give the background information of the physical and chemical properties bitumen and asphaltenes including thermal cracking and coking, as well as current heteroatoms removal technologies used in industry (specifically desulfurization). The literature review will also discuss the chemistry of sodium conversion in detail.

The experimental work is presented in three chapters, each dealing with a specific question:

(a) The first experimental chapter (Chapter 3) of this thesis. The liquid yields and heteroatoms extrusion effect of sodium during the conversion of asphaltenes were quantitatively assessed. Triplicate experiments of Na reacted with asphaltenes were performed in the temperature range 250 °C and below. Although liquid yields did not change too much compared to control experiments, elemental analysis data suggested there were some desulfurization and denitrogenation happened during the Na conversion of asphaltenes. NMR data also helped to show some aromatic H transferred and became aliphatic H.

(b) The results obtained in Chapter 3 had to be explained, but asphaltenes are analytically challenging. In the second experimental study (Chapter 4) a few different model molecules. Dibenzothiophene (DBT), carbazole, dibenzofuran, dibenzyl sulfide, diphenyl sulfide, benzyl phenyl sulfide, dibenzylether, diphenyl ether were separately dissolved in tetrahytronaphathalene or 1-methylnaphthlene, and then Na was added under nitrogen environment. The mixtures were heated to 150°C followed by Gas Chromatography-Mass spectrometry (GC-MS) and Gas Chromatography – Flame Ionization Detector (GC-FID) analysis to investigate the chemicals generated in reactions and their concentrations. A highlight from this study was that desulfurized products and partially hydrogenated products from reaction of DBT with Na suggested two pathways of desulfurization analogous to hydrodesulfurization. No denitrogenation or deoxygenation products were found.

(c) Based on the observations in Chapter 4, it appeared as if hydrogenation played a role. In the third experimental study (Chapter 5) various model compounds, dibenzothiophene(DBT), carbazole, dibenzofuran and anthracene were separately reacted with Na under hydrogen atmosphere to study the behavior of hydrogen during Na conversion of asphaltenes. The mixtures were heated to 150°C followed by GC-MS and GC-FID analysis.

References

[1] Dusseault, M.B. Comparing Venezuelan and Canadian heavy oil and tar sands. Petroleum Society's Canadian International Petroleum Conference. **2001,** 2001-61.

[2] Gray, M. R. Upgrading Oilsands Bitumen and Heavy Oil. The university of Alberta Press. Edmonton, **2015.**

CHAPTER 2 – Literature review

2.1 Introduction

In this study there were three different aspects that had to be considered in order to evaluate sodium conversion of asphaltenes. These were the properties of asphaltenes as feed material, current conversion pathways for heteroatom removal and the sodium conversion chemistry of aromatics and heteroaromatics.

2.2 Asphaltenes

The feed material that was employed in this study is asphaltenes. The asphaltenes were obtained from an industrial solvent deasphalting process. This is pointed out, because the industrially produced asphaltenes are not "pure" asphaltenes. Industrial solvent deasphalting does not completely get rid of all the maltenes, compared to laboratory prepared asphaltenes that are precipitated following the ASTM D6560-12 standard method. Industrial asphaltenes appear to be "shining rocks" whereas the labs precipitated asphaltenes are "dull powders".

2.2.1 Asphaltene structure

Asphaltenes have a strong propensity of self-association [1, 2]. Asphaltenes comprises about 18% of Athabasca bitumen and 19% in Cold Lake bitumen. It has a low H/C atomic ratio and a high content of heteroatoms (N, S, and O) and metals (V, Ni, Fe). The elemental composition of *n*-heptane precipitated asphaltenes, abbreviated C_7-asphaltenes, from different crude oils is shown to illustrate the point (Table 2.1.1).

Table 2.1.1 Elemental composition of C_7-Asphaltanes [3]

	Element, weight %					Metal, ppmw	
C_7 Asphaltene	**C**	**H**	**S**	**N**	**O**	**Ni**	**V**
Campana	87.6	8.2	0.5	1.5	2.2	54	81
Heavy Canadian	84.7	7.9	4.5	1.2	1.6	320	697
Lloydminster Wainwright	80.0	8.0	7.9	1.3	2.7	417	1100
Maya	82.3	7.9	6.6	1.2	1.8	724	1468
Mid-Continent U.S.	84.9	8.6	3.8	1.0	1.6	188	309
San Joaquin Valley	84.5	8.3	2.3	2.6	2.3	594	540

Unlike elemental composition that can be determined with little uncertainty, the molecular composition and even average molecular weight of asphaltenes is a point of speculation and debate. Although the set of sub-structures of individual chemical units constituting asphaltenes, such as the number of fused aromatic rings, length of aliphatic chains, and common functional groups is mostly agreed on, an average representation of the asphaltenes molecular structure and weight have been the source of heated discussions [4].

Asphaltenes is defined as a solubility class and may consist of thousands of different compounds. Hence, we need to be cautious when a representative model structure is proposed. There are some common structural motifs. It is found that heteroatoms seem be associated mainly with polynuclear aromatic ring systems, thus attempts have been made to include such associations into average model structures.

The concept of large polynuclear aromatic structures (>10 rings) in petroleum asphaltenes is not consistent with the natural product origins of petroleum, because such structures require extreme temperatures and pressures to form. In addition, heat-resistant polymers which contain aromatic and herocyclic structures like polyquinolines and polyquinoxalines strongly tend to form large condensed systems during pyrolysis and will finally carbonize. Structures that contain smaller polynuclear aromatic hydrocarbons in asphaltenes are more consistent with this behavior when the majority of the nitrogen, oxygen and sulfur species accumulate in the non-volatile residue [5].

2.2.2 Average molecular weight of asphaltenes [6, 7]

The average molecular weight of asphaltenes has often been controversial. Although constituent groups were more or less understood, whether these fundamental units are covalently linked or simply aggregated in solution is a sub issue. Unfortunately this perspective is reinforced when there are practical limitations for measuring asphaltenes molecular weight.

The main limitations in laboratories are: first, there are no standards of asphaltene samples for calibration purpose in different laboratories around the world. In addition, heterogeneity among different asphaltenes creates concerns that results from different laboratories are not identical. As result, the different asphaltenes in various laboratories that are analyzed by different techniques lack standards of comparison.

A few techniques used in different laboratories will be discussed here: One is vapor pressure osmometry (VPO). The primary difficulty with this technique is that VPO require the concentrations of asphaltenes (~1%) to greatly exceed the critical nanoaggregate concentrations of asphaltenes in solution. For instance, in toluene, the nanoaggregate concentrations are on the order of ~100 mg/L. In such case VPO will report the aggregate weights of asphaltenes instead of its actual molecular weight. The aggregate weight is related to both molecular weight and aggregate number. Another difficulty is the extrapolation of VPO results to low concentrations, and this is because asphaltenes in solution will exhibit aggregation at different length scales at different concentrations.

Other than VPO, another technique that is used is gel permeation chromatography (GPC). GPC also has some problems in determining molecular weight of asphaltenes. One problem is that some solvents used in GPC do not dissolve asphaltenes completely, such as N-methyl pyrrolidone (NMP). Another problem is that some GPC column materials are incompatible with toluene, which can totally dissolve asphaltenes. In addition, GPC studies often require higher concentrations of asphaltenes that are not well characterized and may exceed the asphaltenes aggregation concentration.

Another technique to determine asphaltene molecular weight is mass spectrometry. Boduszynski used field ionization mass spectrometry (FIMS) to analyse *n*-heptane asphaltenes and reported a mean asphaltene molecular weight of ~850 g/mol [6]. The difficulty with FIMS analysis is to obtain a gas phase product consisting of large non-volatile components that are subject to potential fragmentation. Laser desorption mass spectroscopy (LDMS) and matrix-assisted laser desorption ionization (MALDI) all experience severe baseline issues when studying asphaltenes. Other studies [7] suggested both laser power and asphaltenes concentration have significant impacts on the mass spectra using laser desorption ionization (including LDMS and MALDI). At low laser power and lower asphaltenes concentration, the molecular weights were around 850 g/mol. With either higher laser power or higher asphaltenes concentration, higher mean molecular weights were obtained.

2.2.3 Asphaltenes aggregation

Asphaltenes can form aggregates that lead to serious problems during oil recovery, transport, and upgrading processes [8]. They may flocculate during the reservoir exploitation because of changes in the thermodynamic (pressure, temperature, composition) or flow conditions. Asphaltene flocculation and deposition can block pore throats in the near well bore zone; the deposition can strongly modify stability properties and relative permeability, and they can also plug tubing and pipelines, settle in transportation tankers or storage tanks and deposit in distillation columns during refinery operation. Furthermore, asphaltenes contribute to catalyst fouling and poisoning [8, 9]. As a result, they cause a decrease of productivity and an increase in the overall operating cost.

Asphaltenes aggregates can be formed in solvents such as toluene, tetrahydrofuran (THF), and pyridine [10] and their stability is dependent upon several factors, including temperature, pressure, and also their concentration. Asphaltenes can form nanoaggregates at very low concentrations around 200 mg/L. If asphaltenes concentrations increase, asphaltenes subsequently go from the monomeric entity to nanoaggregates, followed by further clustering into larger species and flocculate [8].

Gray, et al. [11] pointed out there are strong donor-acceptor interactions that will be absent in petroleum. The large asphaltene molecules will rather have multiple cooperative associations, a combination of acid-base interactions, hydrogen bonding, metal coordination, hydrophobic pockets, and aromatic π-π stacking.

The structure is also representative of the archipelago, or island model representation of asphaltenes structure. Continental structures are reported to be more aggregated and precipitated in toluene, because π-π interactions between the large polynuclear aromatic cores are favored in toluene [9].Associations between molecules are acid-base interactions and hydrogen bonding, metal coordination complex, a hydrophobic pocket, π-π stacking [11].

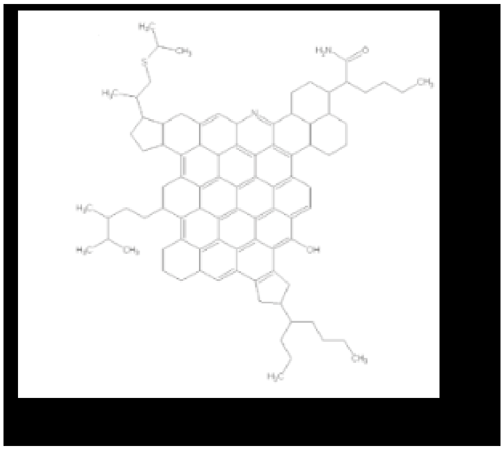


Figure 2.1.1Illustration of a continental model of asphaltenes [9].

2.3 Extrusion of heteroatoms

One of the potential benefits of sodium conversion of asphaltenes that was noted in Chapter 1 was the removal of heteroatoms. In order to better understand heteroatom extrusion chemistry and the challenges involved, an overview is provided of current processes and chemistries for sulfur, nitrogen and oxygen.

2.3.1 Desulfurization

Besides carbon and hydrogen, sulfur is usually the third most abundant element in oilsands derived materials. Crude oils and bitumens vary in sulfur content from less than 0.05 to more than 14%. Most oils contain from 0.1 to 3% sulfur, i.e. less than typically found in oilsands bitumen. Hydrogen sulfide and elemental sulfur dissolved in crude oils often are very minor portion of the total sulfur [12, 13].

The concentration and nature of the sulfur-containing compounds change over the boiling range. The amount of sulfur in a distillation fraction increases with an increase in boiling range shown below as in Table 2.1.2.

Table 2.1.2 Distribution of sulfur compounds of a crude oil

Distillation range (°C)	Sulfur content (%)	Sulfur compound distribution (%)			
		Thiols	Sulfides	Thiophenes	Other[a]
70–180 (naphtha)	0.02	50	50	Trace	–
160–240 (kerosene)	0.2	25	25	35	15
230–350 (distillate)	0.9	15	15	35	35
350–550 (vacuum gas oil)	1.8	5	5	30	60
>550 (vacuum residue)	2.9	Trace	Trace	10	90

Fuel specifications and environmental speculations have become increasingly stringent with respect to sulfur content over the years. The removal of sulfur from oil is consequently one of the central conversion requirements in most refineries and the price (and processing cost) of each barrel of a crude oil is influenced by its sulfur content [15].

Hydrodesulfurization (HDS) is the most commonly used method in the petroleum industry to remove sulfur-containing impurities from crude petroleum feedstocks and fuels. In most cases HDS is performed by co-feeding oil and H_2 to a fixed-bed reactor packed with an appropriate HDS catalyst. The most commonly employed HDS catalyst is $CoMo/Al_2O_3$ and in its sulfided state it comprises of a mixture of MoS_2 and Co_9S_8 and Al_2O_3 as their support. Aside from the $CoMo/Al_2O_3$ catalyst, NiW/Al_2O_3 and $NiMo/Al_2O_3$ catalysts are also used, depending on the nature of the feed. Generally speaking NiMo-catalysts are more hydrogenating, whereas CoMo-catalysts are better at hydrogenolysis [16] and NiW-catalysts are more effective for hydrodenitrogenation. CoMo-catalysts are preferred for the HDS of unsaturated hydrocarbon streams and sometimes more efficient in batch reactors. Whereas NiMo-catalysts are preferred for fractions requiring extreme hydrogenation. It is more efficient for HDS of refractory compounds, such as 4,6-dimethyldibenzothiophene (DMDBT), and for use under the conditions when contact time is limited instead of hydrogen flow [15, 16].

After hydrogen is chemisorbed on the sulfided base metals of the catalyst, it is able to hydrogenate aromatic rings, hydrogenolysis carbon-sulfur bonds [17]. During HDS, the sulfur in the organosulfur compounds is converted to H_2S. Two pathways have been identified for sulfur removal. One is direct catalytic extrusion of the sulfur in a single step. The direct extrusion of sulfur is illustrated using dibenzothiophene as a model compound (Figure 2.1.2). Another is hydrogenation of the aromatic rings, which is then followed by attack on sulfur, which is no longer aromatic, but aliphatic in nature

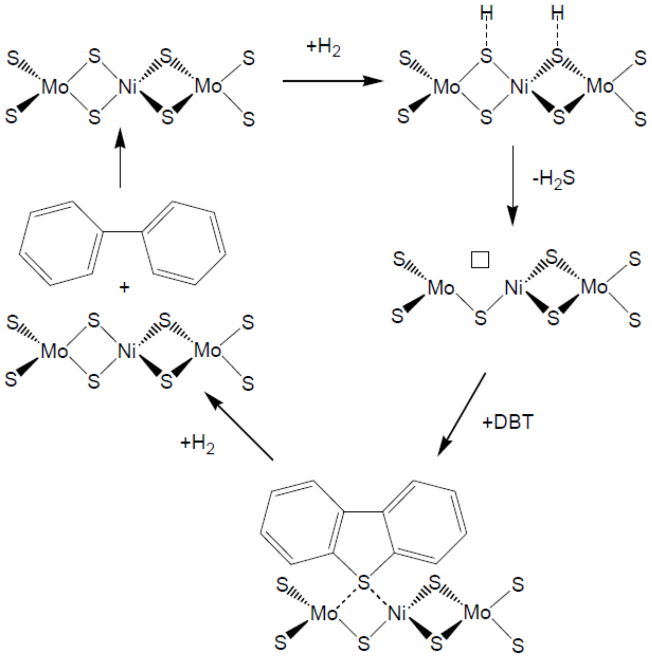


Figure 2.1.2 Mechanism for HDS of dibenzothiophene with Ni-Mo sulfide [17]

are easily oxidized under low temperature and pressure conditions to form the corresponding sulfones as shown in Figure 2.1.3. The oxidant can be hydrogen peroxide/peracid or organic peroxide and no hydrogen is consumed in this reaction. The sulfones are polar compounds so they can in principle be easily extracted. This oxidation chemistry is complementary to hydrotreating, because other sulfur compounds such as disulfides are easy to hydrodesulfurize, but oxidize slowly [18, 19].

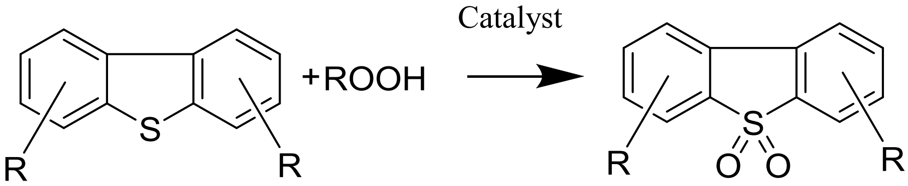


Figure 2.1. 3 Dibenzothiophene Oxidation Chemistry [18]

Reactivity of sulfur compounds for oxidation is increased as the electron density on sulfur atom increases. The reactivities of DBT derivatives are especially influenced by the electron donation of substituted methyl groups, therefore, the reactivity decreases in the order of 4,6-DMDBT > 4-MDBT > DBT, but the reactivities of HDS follow a reversing order. After oxidation, the sulfur compounds are transformed to sulfones [19].

In addition to HDS and ODS, another desulfurization method is alkylation-based desulfurization, including C-alkylation and S-alkylation. This method can only be applied to lighter materials.

For C- Alkylation, it is commercially applied as the Olefinic Alkylation of Thiophenic Sulfur (OATS) process and was designed specifically for upgrading thiophenic compounds rich olefinic gasoline. It exploits the aromaticity of the thiophenic compounds to selectively perform acid-catalyzed aromatic alkylation with olefins (Figure 2.1.4) that causes the molecular mass and boiling point of the alkylated thiophenic compounds to increase, thus enabling their separation by distillation.

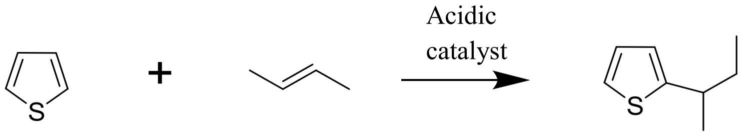


Figure 2.1.4 Alkylation-based desulfurization illustrated by the acid catalyzed [15]

For S-alkylation, thiophenic compounds can be reacted with iodomethane (CH3I) in the presence of silver tetrafluoroborate (Ag-BF4) to produce S-methylatedsulfonium. These alkylated sulfur compounds can precipitate from the oil to be removed. Unlike C-alkylation it does not require separation by distillation that makes separation easier. However, alkylation takes place competitively with aromatic hydrocarbons, restricting its application to oils that are not aromatic-rich. Since bitumen and asphaltenes tend to be aromatic, this technology is not very applicable for desulfurization of them [15].

2.3.2 Denitrogenation

The nitrogen compounds found in petroleum generally are one of two types: heterocycles or non-heterocycles. The latter comprises anilines and aliphatic amines [22].

Generally nitrogen compounds are more difficult than sulfur to remove. In catalytic hydroconversion of vacuum residue, denitrogenation is usually insignificant, and the nitrogen content of the unreacted residue often increases [3]. Industrial HDN is generally carried out over a sulfides CoMo-, NiMo-, or NiW/Al_2O_3 catalysts [22]. As mentioned before, Ni-based catalysts are more active for hydrogenation.

The nitrogen compounds can be easily adsorbed on the catalyst surface, but because the structure of nitrogen heterocycles is more complex than that of sulfur or oxygen heterocycles, especially the presence of two types of nitrogen heterocycle (i.e., pyridinic and pyrrolic), nitrogen compounds show greater variations in adsorptivity and reactivity [22].

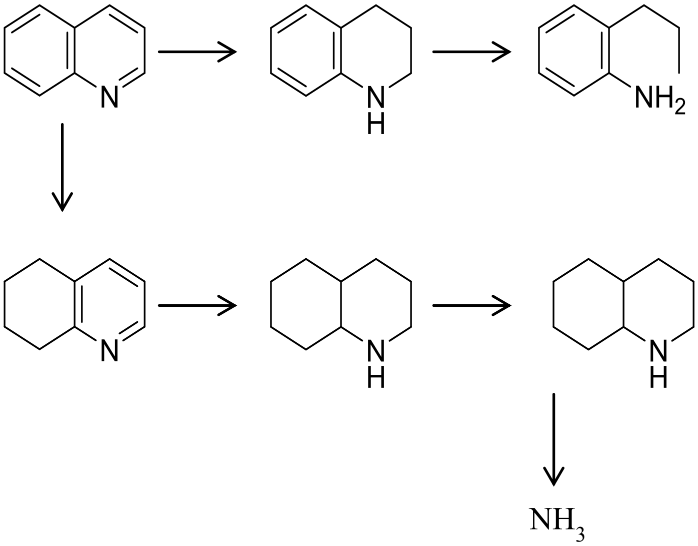


Figure 2.1.5 Reaction pathways for catalytic removal of nitrogen from quinoline [3, 25].

As shown in the Figure 2.1.5 the pathways of denitrogenation of quinoline both require that the nitrogen heterocycle be hydrogenated before N can be removed as NH_3. This is analogous to the second pathway of hydrodesulfurization of dibenzothiophene, which involved hydrogenation of the aromatic ring and then extrution of sulfur.

2.3.3 Deoxygenation

Oxygen groups in petroleum are mainly hydroxyl, carboxyl, carbonyl, and etheric structures. The total oxygen content depends on the feedstock from which the liquids were produced. Most of the oxygen exists in hydroxyl groups in asphaltenes, and carbonyl groups in resins. Esters were identified as the principal contributor of the carboxyl form, while phenolic and alcoholic groups made up the bulk of the hydroxylic oxygen [24, 25].

Instrumental methods capable of determining combined oxygen concentrations are usually less sensitive than techniques for determining sulfur or nitrogen. Oxygen quantification is of the order of 1500 ppm with a relative standard deviation of 5%.

Furimsky [24, 25] reported the HDO of dibenzofuran (DBF) may involve different reactions when the availability of surface-active hydrogen becomes an important factor. As shown in

Figure 2.1.6, route 2 may gain importance compared to route 1. Then, the o-phenyl phenol would be the intermediate present in rather large quantities. The appearance of biphenyl may be attributed either to hydrogenation first then extrusion of O like in route 2 or to direct extrusion of the O atom following route 3. This is similar to desulfurization, but not denitrogenation, which can only take place by what is shown as route 1.

Phenols were observed in the product from fixed-bed catalytic hydrotreating, which explained the increase of product acidity relative to that of the feed. Phenols are the only acidic species which can survive such hydrotreating conditions and the ortho-substituted phenols were found to be especially stable. The dehydroxylation of phenols may then be an important step in the overall HDO.

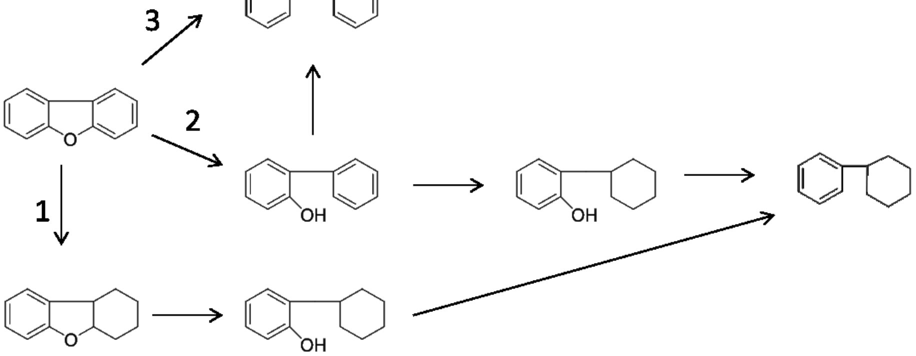


Figure 2.1.6 Mechanism of HDO of dibenzofuran (DBF) [24]

2.4 Sodium reaction with asphaltenes

The reaction of sodium with aromatic compounds is driven by the electropositive nature of sodium. Sodium is well known to very easily give out an electron, and asphaltenes contain a significant concentration of polyaromatics. If the polyaromatics in asphaltenes receive an electron from sodium, an electron donor-acceptor (EDA) ion pair is formed. A single electron donation to form the $Na^+(aromatic)^-$ ion pair and two electron donations form the $(Na^+)_2$ $(aromatic)^{2-}$ ion pair. The electrons can be delocalized in the aromatic, but as a result, the aromatics are more reactive. If hydrogen or a hydrogen source is present in the same system, the donor-acceptor ion pairs can obtain hydrogen from the system and in this way the aromatics are hydrogenated.

Other than hydrogenation of aromatic rings, heteroatom removal from heterocyclic compounds is also of great interest in the upgrading of asphaltenes. If heteroatoms could be eliminated from heterocycles, it would facilitate asphaltenes to maltenes conversion. The research hypothesis was that conversion of asphaltenes with sodium would lead to heteroatom removal and ring-opening of heterocyclic compounds to convert asphaltenes into maltenes. Some evidence to this effect was reported [26].

Because thiophenic compounds are the least reactive organosulfur compounds in fossil fuels, these compounds were also mainly studied as a partial representative for asphaltenes in this paper.

Methods using metallic sodium or sodium hydride with the presence or absence of hydrogen for the removal of sulfur from petroleum distillates with have been reported in the literature [21, 27, 28, 29, 30]. The Birch reduction is the best known form of this reaction and is the “hydrogenation” that takes place with an alkali metal in liquid ammonia with an alcohol as cosolvent. The alcohol provides proton that is transferred and a sodium alkoxide is formed as a side-product.

Little is known about desulfurization of model compounds with alkali metals, except Gilman and others showed that DBT can be desulfurized by treatment with metallic lithium in refluxing dioxane, and the partial hydrodesulfurization of DBT with NaRb and hydrogen at 250°C reported by Friedman and coworkers [21].

Heinz, et al. [21] did some experimental research on the sodium conversion of dibenzotiophene. They used a solution of DBT in decahydronaphthalene to react with sodium at 350°C with and without hydrogen. After the reaction was carried on for a few hours, biphenyl was found, as well as a polymer product. They also proposed a reaction pathway (Figure 2.8).

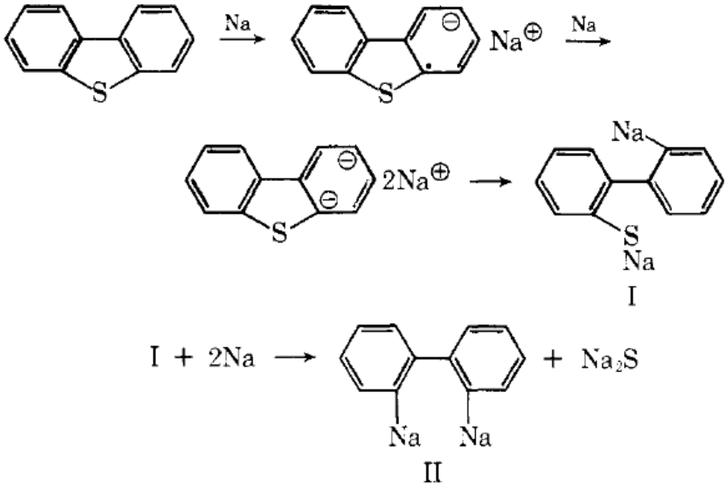


Figure 2.1.7 Mechanism of DBT reacted with Na in decalin under 350°C [21]

They also pointed out that the intermediate adduct, species II in Figure 2.1.7, can receive hydrogen from decahydronaphthalene to produce biphenyl and sodium or sodium hydride, or polymerize [21].

In 2001, Exxon mobile had a patent to use Na for desulfurization of petroleum at above 250 °C, and Na_2S were produced, but under hydrogen atmosphere, NaHS was produced. The Na efficiency was between 60% - 80%. If NaHS was intended to be removed in a two phase liquid-liquid separation, the temperature needs to be above 350°C [31].Another company gave an report claiming an increase of liquid yield and desulfurization as well denitrogenation by Na reacting with bitumen at the temperature of 375 °C. Later on they used electrolysis to recover Na [32].

References

[1] Boduszynski, M. M. Asphaltenes in petroleum asphalt: Composition and formation, Chemistry of Asphaltenes. *Am. Chem. Soc., Div. Pet. Chem., Prepr.* **1979**, *24* (4). CONF-790917.

[2] Miller, J. T.; Fisher, R. B.; Thiyagarajan, P.; Winans, R. E.; Hunt, J. E. Subfractionation and characterization of Mayan asphaltene. *Energy Fuels,* **1998**, 12, 1290–1298.

[3] Gray, M. R. *Upgrading Oilsands Bitumen and Heavy Oil*; University of Alberta Press. Edmonton, 2015.

[4] Yen, T. F. *Pan-Pacific Synfuels Conference*, Japanese Petroleum Institute. Tokyo, **1982**, 11, 547-557.

[5] Sagedghi, M. A.; Chilingarian, G. V.; Yen, T. F. X-ray diffraction of asphaltens. *Energy Sources*, **1986**, 8, 99-123.

[6] Rodgers, R. P.; Marshall, A. G. Petroleomics: Advanced characterization of petroleum derived materials by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). *Asphaltenes, Heavy Oils, and Petroleomics*. Springer Science & Business Media, 2006, 63-93.

[7] Mullins, O. C.; Eric Y. S.; Ahmed H.; Alan G. M. *Asphaltenes, heavy oils, and petroleomics.* Springer Science & Business Media, 2007.

[8] Castillo J.; Hung J.; Goncalves S.; Reyes A. Study of Asphaltenes Aggregation Process in Crude Oils Using Confocal Microscopy. *Energy Fuels*, **2004**, 18, 698-703.

[9] Durand, E.; Clemancrey, M.; Lancelin, J. M.; Verstraete, J.; Espinat, D.; Quoineaud, A.A. Effect of Chemical Composition on Asphaltenes Aggregation. *Energy Fuels*, **2010**, 24, 1051–1062.

[10] Trejo, F.; Ancheyta, J.; Morgan, T. J.; Herod, A. A.; Kandiyoti, R. Characterization of Asphaltenes from Hydrotreated Products by SEC, LDMS, MALDI, NMR, and XRD. *Energy Fuels* **2007**, 21, 2121–2128.

[11] Gray, M. R.; Tykwinski, R. R.; Stryker, J. M.; Tan, X. Supramolecular Assembly Model for Aggregation of Petroleum Asphaltenes. *Energy Fuels,* **2011**, 25, 3125–3134.

[12] Wilson. L. O. Sulfur in heavy oils, oil sands and oil shales. *Argonne National Lab.* [online] https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/22_3_MONTREAL_06-77_0086.pdf

[13] Rall, H. T.; Thompson, C. J.; Coleman, H. J. ; Hopkins, R. L. Sulfur Compounds in Crude Oil. *Washington D.C. UNT Digital Library* [Online] **2015** http://digital.library.unt.edu/ark:/67531/metadc12804/.

[14] Heinrich, G; Kasztelaan, S; Hydrotreating. In *Petroleum Refining*; Leprince, P., Ed.; *Institut Francais du Petrole Publications: Paris,* 2001, 3, 533–573.

[15] Javadli, R.; De Klerk, A. Desulfurization of heavy oil. *Appl. Petrochem. Res.* **2012,** *1,* 3-19.

[16] Topsoe, H.; Clausen, B. S.; Massoth, F. E. *Hydrotreating Catalysis – Science and Technology* , Ed. Anderson, J.R and Boudart, M.; Springer Verlag Berlin, **1996**.

[17] Toshiaki, K.; Atsushi, I.; Weihua, Q. *Hydrodesulphurization and Hydrodenitrogenation: Chemistry and Engineering*, Kodasha:Tokyo**, 1999**.

[18] Gatan, R.; Bargger, P.; Gembicki, V. Oxidative desulfurization: A new technology for ULSD**.** *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem*., **2004**, 49(2): 577-579.

[19] Shujiro, O.; Takeshi, N.; Noriko, T.; Weihua, Q.; Atsushi, I.; Tamotsu, I.; Toshiaki, K. Oxidative Desulfurization of Light Gas Oil and Vacuum Gas Oil by Oxidation and Solvent Extraction. *Energy Fuels*, **2000**, 14: 1232-1239.

[20] Zhao, H. Catalytic Hydrogenation and Hydrodesulfurization of Model Compounds. Ph.D. Thesis, Virginia Polytechnic Institute and State University March 2009.

[21] Heinz, W. S.; Charles, L. D. D.; Raymond, E. M.; Sidney, F. Reaction of Sodium with Dibenzothiophene. A Method for Desulfurization of Residua. *Ind. Eng. Chem.. Process Des. Dev.,* **1974**, 13(4), 433-436.

[22] Ho, T. C. Hydrodenitrogenation catalysts. *Catal. Rev. Sci. Eng.,* **1988,** 30, 117-160.

[23] Satterfield, C. N.; Yang, S. H., Catalytic Hydrodenitrogenation of Quinoline in a Trickle-Bed Reactor - Comparison with Vapor-Phase Reaction. *Ind. Eng. Chem.Proc. Des. Dev.*, **1984**, 23, (1), 11-19.

[24] Furimsky, E. Chemistry of catalytic hydrodeoxygenation. *Catal. Rev. Sci. Eng.* **1983,** 25, 421-458.

[25] Furimsky, E. Catalytic deoxygenation of heavy gas oil. *Fuel,* **1978,** 57, 494-496.

[26] Gordon, J. H. Post Retort, pre hydro-treat upgrading of shale oil. Final report, DOE Award DE-FE0000408, 2013.

[27] Wallace, T. J.; Heimlich, B. N. The decomposition of dibenzothiophene dioxide and related compounds in the presence of molten alkali. *Tetrahedron* **1968**, 24, 1311-1322.

[28] Lyssy, T. M. Reaction of metallic sodium with naphthalene. Dihydronaphthalenecarboxylic acids–1, 4 and –1, 2 and related compounds. *J. Org. Chem.* **1962**, 27, 5-13.

[29] Walker, J. F.; Scott, N. D. Sodium naphthalene. II. Preparation and properties of

dihydronaphthalene dicarboxylic acids. *J. Am. Chem. Soc.* **1938**, 60, 951-955.

[30] Scott, N. D.; Walker, J. F.; Hansley, V. L. Sodium naphthalene. I. A new method for the preparation of addion compounds of alkali metals and polycyclic aromatic compounds. *J. Am. Chem. Soc.* **1936**, 58, 2442-2444.

[31] Brons, G.; Myers, D. R.; Bearden, R. J.; MacLeod, B. J. Process for desulfurization of petroleum feeds utilizing sodium metal. U.S. Patent 6,210,564 B1, April 3, 2001.

[32] Gordon, H. J. Post retort, Pre Hydro-treat Upgrading of Shale Oil. *Ceramatec Inc.* [online] **2015** https://www.netl.doe.gov/file%20library/research/oil-gas/enhanced%20oil%20recovery/fe0000408-final-report.pdf

CHAPTER 3 – Sodium conversion of Asphaltene

Abstract

The reaction of industrial asphaltenes from the Nexen Energy LLC Long Lake upgrader and Na was studied under mild temperature (below 250 °C) to investigate if Na has any effects related to hydrogenation, increase of liquid yield and extrusion of heteroatoms. The temperature threshold was set at 250 °C to limit the potential contribution of cracking and hydrogen disproportionation that becomes prevalent at higher temperatures. In a typical experiment an asphaltenes and Na mixture was added into a micro-batch reactor and heated to different temperatures under the same initial pressure in an inert atmosphere. Various analyses were performed on the products. Sodium did not have a significant influence on liquid yield, but it extruded sulfur and nitrogen.

Keywords: Liquid yield, analysis, Na conversion, asphaltene upgrading

3.1 Introduction

Desulfurization of petroleum distillates with metallic sodium with or without the presence of hydrogen have been reported in the literatures [1, 2, 3, 4]. There has been some published work on catalyzed hydrodesulfurization of model compounds using alkali metals. Gilman and his coworkers [5] reported that DBT could be desulfurized by metallic lithium in refluxing dioxane. The partial hydrodesulfurization of DBT with NaRb and hydrogen at 250°C was reported by Friedman and coworkers [1]. Here the focus will be on sodium.

Na and aromatics are involved as electron donor-acceptor (EDA) ion pairs in the mechanism of Na conversion of aromatics [6]. Na is a strong electron donor and the aromatics are electron acceptors in this reaction. This was discussed in Chapter 2. Once the Na^+ $(aromatic)^-$ ion pair or the $(Na^+)_2(aromatic)^{2-}$ ion pair is formed, it may facilitate bond cleavage. Of specific interest are the ability to aid with the extrusion of heteroatoms from heterocyclic aromatics and to ring-open aromatics.

In this chapter the ability of Na to upgrade asphaltenes was investigated in the temperature range 250 °C and below. This temperature range was selected for mainly two reasons: (a) In an industrial application it would not require the use of a fired heater (furnace) for preheating the feed. (b) The temperature is low enough so that the chemistry of Na can be observed with little contribution of thermal cracking. So, thermal cracking will not contribute to liquid yields or heteroatoms extrusion, and we can observe only the effects of sodium.

3.2 Experimental

3.2.1 Materials

The experiments were performed with asphaltenes, which was supplied by Nexen Energy LLC from their solvent deasphalting unit at the Long Lake upgrader facility in Alberta, Canada. Characterization of the industrial asphaltenes is provided with product characterization data in the Results and Discussion section.

Sodium sticks were purchased from Alfa Aesar (99%, in mineral oil).

3.2.2 Equipment and procedure

All experiments were performed in micro batch reactors and done in triplicate. The setup was constructed using Swagelok 316 stainless steel tubing and fittings with dimensions showing in Figure 3.1.1. The reactor was heated in a fluidized sand bath. The temperature inside the reactor was monitored with a K-type, 1/16 inch diameter, 36 inch length, 316 stainless steel internal thermocouple. The temperature was indirectly controlled by adjusting the temperature of the heated fluidized sand bath (Omega Fluidized Bath FSB).

For each experiment the reactor was filled with 3-4 g asphaltene, and then Na was cut in mineral oil exposed to air and added into the reactor with asphaltene to obtain a Na to asphaltene mass ratio 4, i.e. very large excess. All materials were weighed on a Mettler Toledo New Classic MF ML3002E, maximum mass limit 3200 g, 0.01 g precision, and the exact mass was recorded.

Then reactors were leak tested with nitrogen at absolute pressure of 4.1MPa. For the reactions the reactors were purged and pressurized with nitrogen to an initial pressure of 3.5MPa. The reactors were weighed before and after adding N_2, and then the mass of N_2 gas added was obtained.

The sand bath is heated to the appropriate temperature for the experiment, and after it reached desired temperature, all three reactors for experiments in triplicate were put in to sand bath at same time. Each run lasted for 1 hour from the time that the required temperature was reached; the heat-up time was about five minutes. After experiments finished, reactors were cooled down overnight, while still pressurized, to prevent coking.

It was observed that after taking reactors out of sand bath, some sand would stick to the outside reactor walls. The reactors were cleared of sand, before releasing gas and each reactor was weighed before and after being depressurized. The light gases produced during the reaction and that were released on depressurization, were collected in a gas bag and afterwards analyzed by gas chromatography. At no time was the smell of H_2S or NH_3 detected. The mass of gaseous products produced by the reaction was calculated from the mass differential before and after releasing the gas and subtracting the N_2 mass.

All products were removed from the reactor by washing with pentane. Pentane was also used for deasphalting at the same time. The remaining unconverted sodium was deactivated by reaction with isopropanol, methanol and water sequentially. The mixture was then vacuum filtered using a Millipore™ membrane filters of 0.22 µm pore size and 47 mm diameter to separate the liquid and solids. The solids were dried and weighed. The liquid was a two-phase mixture containing an organic and an aqueous phase. The aqueous NaOH solution was separated from the maltene solution in a separating funnel. The maltene solution and NaOH solution were individually dried on a heating plate at 45 °C and 110 °C respectively. After NaOH solution was dried, it became a light yellow and white colored mixed powder.

All control experiments were performed in same way except no Na was added into the reactors. The setup of the reactors is shown in Figure 3.1.1.

Figure 3.1.1 reactors set-ups and dimensions for asphaltenes reaction with Na

These reactors were anticipated with mass transfer problem.

3.3 Analyses

Gas chromatography. The gaseous products were analyzed using an Agilent 7890A gas chromatograph equipped with both flame ionization and thermal conductivity detectors. A Hay Sep R column, 2.44 × 0.003 m (8 ft × ⅛ inch) was employed. The carrier gas used for analysis was helium with a constant flow of 25 mL/min. The injector temperature was set at 200 °C. The temperature program used started at 70 °C for 7 minutes, then ramping at 10 °C/min to 250 °C and holding for 2 minutes, followed by ramping at 30 °C/min to 300 °C and holding for 8 minutes.

Proton nuclear magnetic resonance spectrometry. The ^{1}H Nuclear Magnetic Resonance (NMR) spectra were obtained by a Nanalysis 60 MHz NMReady-60 spectrometer. The instrument was pre-calibrated with D-chloroform. For analysis products were dissolved in 0.5ml of D-chloroform to achieve a concentration of 0.2g/ml. The diluted samples were placed in 5 mm NMR tubes and analysed using the following parameters: spectral width 12 ppm; number of scans per sample: 32; 4000 points were recorded per scan.

Scanning electron microscope. Scanning Electron Microscope (SEM) analysis was only performed by an employee from Scanning Electron Microscope Laboratory in Earth Sciences Building at University of Alberta.

Analysis details:

- Zeiss EVO MA 15 LaB6 filament scanning electron microscope
- Backscattered images are taken using a Si diode detector
- EDS acquired with a peltier-cooled 10 mm2 Bruker Quantax 200 Silicon drift detector with 123 eV resolution
- Secondary electron images are obtained using an Everhart-Thornley detector
- Working distances and accelerating voltages used to obtain images are listed at the bottom of each image
- Specimen coated with gold are coated using a Nanotech SEMPrep 2 DC sputter coater
- Carbon coated samples are coated with a Leica EMSCDE005

Fourier transform infrared (FTIR) spectroscopy. Infrared analyses were performed with an ABB MB3000 with Pike MIRacle attenuated total reflection attachment. The parameters for analysis in this thesis are tabulated below (Table 3.1):

Table 3.1.1 Parameters for FTIR analysis

Resolution	4 cm^{-1}
Scans	120
Measurement	1
Initial Delay	1s
Acquisition Mode	Transmittance
Wavenumber (cm^{-1})	400-4000
Detector gain	81

Elemental analysis (CHNS analysis). CHNS analysis was only done by the Analytical and Instrumentation Laboratory of the Department of Chemistry located in room E5-43 of the Gunning/Lemieux Chemistry Centre at University of Alberta. CHNS analyses were performed on a thermo Scientific Flash 2000 CHNS and Oxygen combustion analyzer. The data was collected and analyzed using the Thermo Eager Xperience software. The carrier gas sweeps the combustion products onto the chromatographic column (Porapak QS, 4 mm ID, 2 m long), where the gases were separated. Analytical Conditions: tube temperature is 1060°C, oven temperature is 65°C, Carrier gas Helium flowrate is 130 ml/min, and sample delay time is 12 s.

For calibration, the standards were accurately weighed directly into tin cups using a Mettler Toledo UMT2 microgram balance, which is readable to 0.1 microgram. The standards span the range from ~0.5 to ~3 mg. The measured values for these standards should produce results that are within ±0.3% of the theoretical values. If the calibration check result is not within ±0.3%, the instrument was recalibrated.

Thermogravimetric analysis (TGA). TGA used in this research project is TGA/DSC 1 STAR^{e} System from Mettler Toledo company with maximum 5g capacity and 0.1µg readability. Each time before sample runs, the TGA should be temperature calibrated. The atmosphere for analysis was nitrogen with a constant flow of 45 mL/min. The temperature program used started at 26 °C, then ramping at 10 °C/min to 100 °C and holding for 5 minutes, followed by ramping at 10 °C/min to 600 °C. After all experiments were completed, the stored data files were then analyzed using TGA Analysis Software. Asphaltenes samples for each TGA run was about 5 mg.

3.4 Calculations

Material balance. Mass balance is calculated as shown:

$$\text{Mass balance} = \frac{\text{Mass of products}}{\text{Mass of reactants}} \qquad \text{Equation 3.1}$$

Mass of products include the mass of gases, liquids and solids. The mass of reactants are the mass of Na and asphaltene feed, but in control experiments, the mass of reactants is just the mass of asphaltene feed.

Liquid yield. Liquid yield is calculated:

$$\text{Liquid yield} = \frac{\text{Mass of Maltenes}}{\text{Mass of Asphaltene added}} \qquad \text{Equation 3.2}$$

Statistical hypothesis testing. To determine whether differences between experimental values were statistically meaningful differences, statistical hypothesis testing was performed. The Student t-test was performed with 95% confidence. The procedure can be explained as follows.

When comparing means of two populations given finite data, the t-test is used. As with all the other distributions employed in data analysis and statistical inference, tables of tail area probabilities $P(X \leq x)$ are available for various degrees of freedom values.

If Z be is a standard normal random variable, (i.e. $Z \sim N(0, 1)$); and Y is a random variable independent of Z and a $\chi2(\nu)$ distribution. Then the random variable defined as the following ratio:

$$X = \frac{Z}{\sqrt{Y/\nu}} \qquad \text{Equation 3.3}$$

is a Student's t random variable $t(\nu)$. It can be shown that its probability density function (pdf) is:

$$f(x) = \frac{\Gamma[\frac{1}{2}(\nu+1)]}{\sqrt{(\nu\pi}\Gamma(\nu/2)} \frac{1}{(1+\frac{x^2}{\nu})^{(\nu+1)/2}} \qquad \text{Equation 3.4}$$

When the population standard deviation, σ, is unknown, the sample standard deviation, s, will have to be substituted for it. For small sample sizes, when s is substituted for σ, the appropriate test statistic becomes:

$$t = \frac{\bar{X} - \mu_0}{s/\sqrt{n}} \qquad \text{Equation 3.5}$$

that is known to possess a Student's t-distribution, with $\nu = n-1$ degrees of freedom [7].

3.5 Results

3.5.1 Thermal conversion of asphaltenes

It was postulated that there would be little or no measurable contribution to liquid yield due to the thermal conversion of asphaltenes at temperatures below 250 °C. This was verified by performing TGA on the asphaltenes feed under inert atmosphere. The mass loss versus temperature curve is shown in Figure 3.2.1.

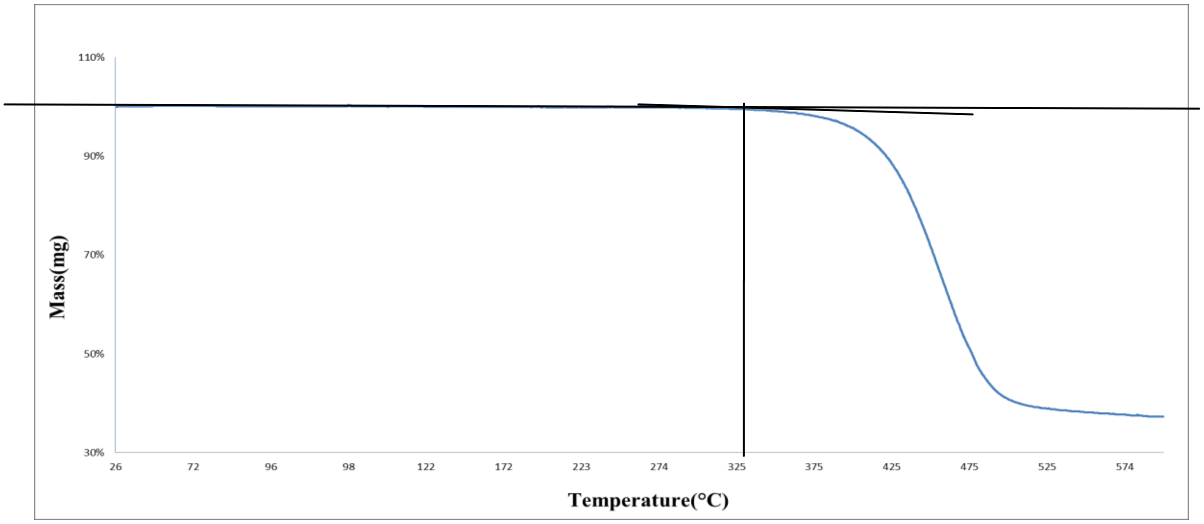


Figure 3.2.1 TGA of industrial asphaltene under inert atmosphere

As shown in the TGA data (Figure 3.2), thermal cracking of asphaltenes stared at about 326°C and the final mass is 36 wt%. This value is also the microcarbon residue (MCR) value of the asphaltenes feed. It therefore appears that thermal cracking would not contribute meaningfully to any change in liquid yield during conversion below 250 °C.

3.5.2 Material balances of reactions in the presence of Na

Triplicate runs for reactions of the industrial asphaltene feed with Na were performed at temperatures of 60 °C, 100 °C, 150 °C, 200 °C and 250 °C. The material balances and yields of solids, liquids and gases are calculated and tabulated in Table 3.2.1.

In this thesis, the solid mass recovered after each experiment is the *n*-pentane precipitated mass of asphaltenes after reaction. The liquid mass refers to the maltenes that can dissolve in *n*-pentane after the reaction, but that was insoluble in water. The gas mass is the mass of gaseous products released after compensating for N_2, as explained in the experimental section.

Table 3.2.1 Material balances and yields of asphaltene reactions with Na

T (°C)	Time (h)	Asp. (g)	Na (g)	Gas(g)	Solid mass(g)	Liquid mass(g)	NaOH mass(g)	Na mass(g)	Mass balance	Liquid yield	Average liquid yield	Standard deviation
250	1	3.14	0.87	-0.03	2.54	0.53	1.69	0.97	101.8%	16.9%	17.0%	0.13%
250	1	3.17	0.83	-0.05	2.40	0.54	1.83	1.05	100.8%	17.0%		
250	1	3.15	0.80	-0.06	2.50	0.54	1.50	0.86	99.8%	17.1%		
200	1	3.29	0.83	-0.08	2.66	0.65	1.34	0.77	99.0%	19.8%	19.7%	2.2%
200	1	3.43	0.86	-0.03	2.67	0.75	1.47	0.85	99.4%	21.9%		
200	1	3.36	0.86	-0.26	2.70	0.59	1.49	0.86	98.3%	17.6%		
150	1	3.13	0.78	0.04	2.58	0.56	1.35	0.78	100.2%	17.9%	19.8%	1.8%
150	1	3.13	0.79	-0.31	2.56	0.67	1.22	0.70	100.3%	21.4%		
150	1	3.15	0.80	-0.02	2.62	0.63	1.42	0.82	103.0%	20.0%		
100	1	3.27	0.80	-0.07	2.81	0.59	1.40	0.81	103.3%	18.0%	17.2%	1.2%
100	1	3.19	0.79	-0.01	2.81	0.52	1.26	0.73	101.9%	16.3%		
60	1	3.51	0.87	-0.09	3.21	0.41	1.48	0.85	102.1%	11.7%	13.2%	2.1%
60	1	3.19	0.79	-0.12	2.91	0.39	1.10	0.63	98.8%	12.2%		
60	1	3.21	0.81	-0.03	2.93	0.50	1.11	0.64	101.2%	15.6%		

The mass balances (Table 3.2.1) are all between 98% - 103%, which is acceptable. But the average liquid yield ranges from 13.2% to 19.8% with standard deviation lower than 3%, so the liquid yields do not very too much for reaction between 60°C-250°C.

An indication of the 95% confidence interval for discriminating the observed liquid yield (maltenes yield) from the maltenes content in the industrial asphaltene is shown in Figure 3.3.

The solid line shows real experimental liquid yield whereas the dashed lines give the range of liquid yield at 95% confidence level.

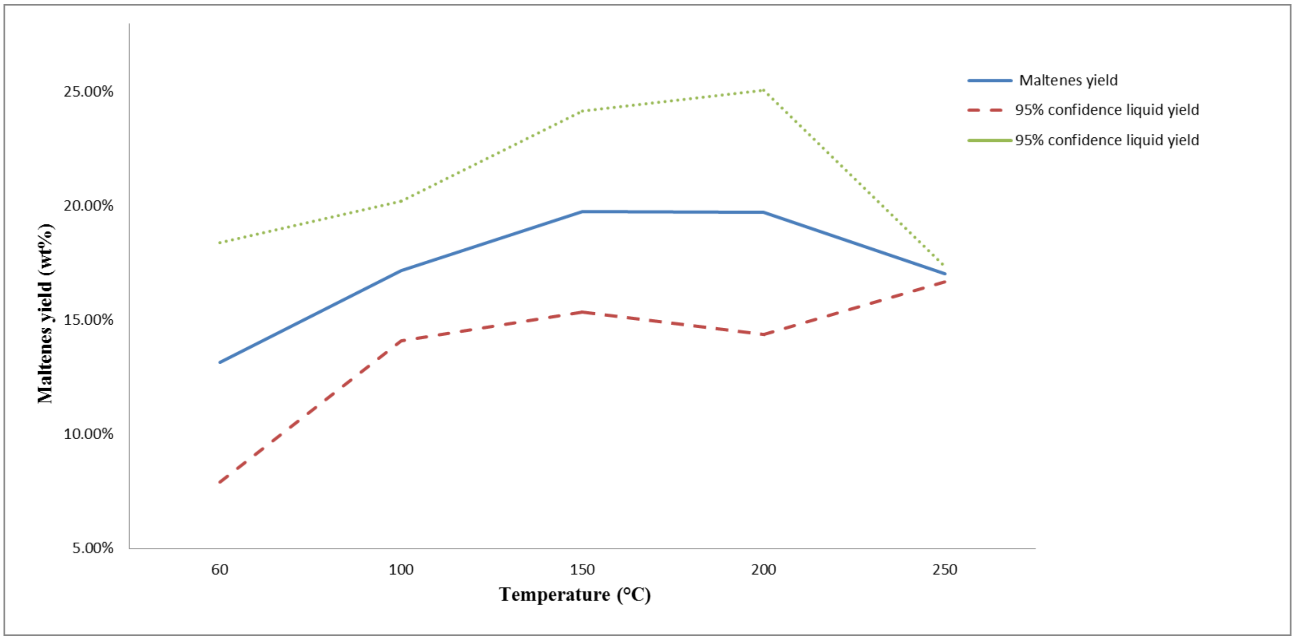


Figure 3.2.2 Liquid yield of asphaltenes react with Na under different temperatures

The maltenes content of the industrial asphaltene was found to be 21 wt% with the standard deviation 0.92%. It appears that if sodium conversion had an effect on the liquid yield, it decreased the liquid yield. This is the opposite of what was anticipated.

It was necessary to confirm that there were not other low temperature reactions, such as addition reactions, that would cause the liquid yield to decrease independently of the reaction with Na. Such reaction would not have been observed by TGA, since the products would be heavier and not volatile, i.e. no mass loss would accompany such reactions. It was therefore decided to perform a series of control experiments.

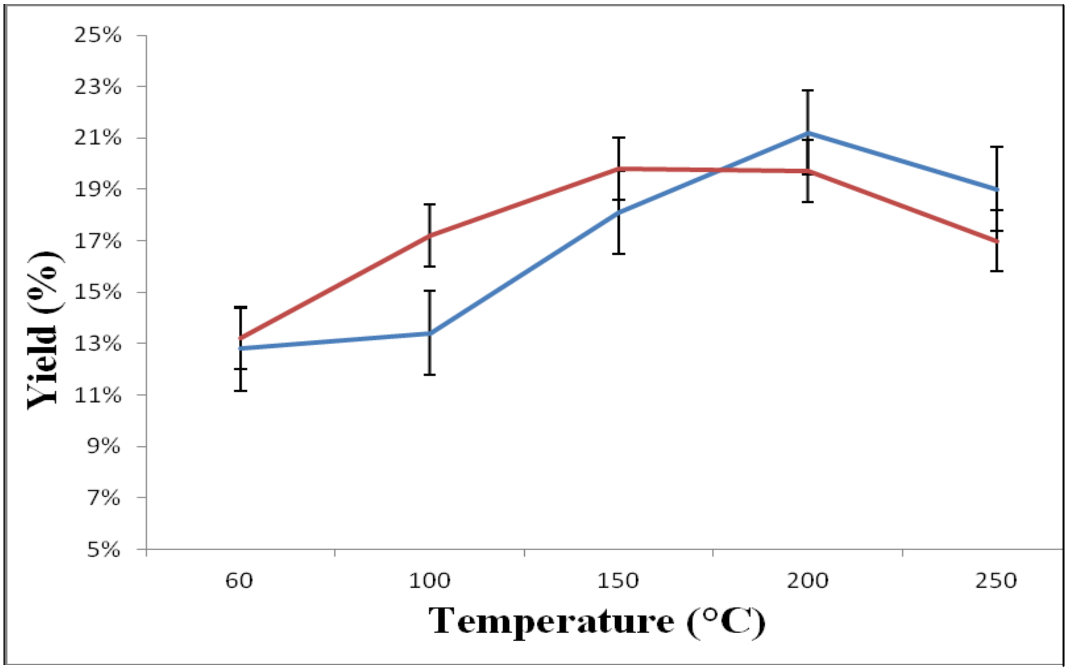
3.5.3 Material balances of reactions in the absence of Na (control experiments)

In order to see if Na was the cause of the change in liquid yield, the control experiments were done with the same procedure and conditions except that no sodium was added into the reactions. The material balances and yield profiles are presented in Table 3.2.2.

Table 3.2.2 Material balances and yields of asphaltene reactions without Na

T (°C)	Time (h)	Asp. (g)	Na (g)	Gas (g)	Solid mass(g)	Liquid Mass(g)	Mass balance	Liquid yield	Average liquid yield	Standard deviation
250	1	3.18	0.00	-0.45	2.5	0.65	99.7%	20.4%	19.0%	2.3%
250	1	3.24	0.00	-0.38	2.75	0.53	101.9%	16.4%		
250	1	3.13	0.00	-0.23	2.49	0.63	100.3%	20.1%		
200	1	3.27	0.00	-0.45	2.41	0.75	97.3%	22.9%	21.2%	1.5%
200	1	3.53	0.00	-0.38	2.88	0.71	102.3%	20.1%		
200	1	3.25	0.00	-0.23	2.52	0.67	98.8%	20.6%		
150	1	3.12	0.00	-0.07	2.4	0.67	99.0%	21.5%	18.1%	3.1%
150	1	3.25	0.00	-0.22	2.46	0.57	93.9%	17.5%		
150	1	3.08	0.00	-0.07	2.51	0.47	97.4%	15.3%		
100	1	3.23	0.00	-0.43	2.86	0.37	100.6%	11.5%	13.4%	1.9%
100	1	3.15	0.00	-0.04	2.62	0.48	99.1%	15.2%		
100	1	3.35	0.00	-0.08	2.91	0.45	100.9%	13.4%		
60	1	3.38	0.00	-0.06	2.95	0.46	101.5%	13.6%	12.8%	1.0%
60	1	3.52	0.00	-0.44	3.09	0.46	101.4%	13.1%		
60	1	3.33	0.00	-0.25	2.92	0.39	100.0%	11.7%		

The liquid yield data of the reaction of industrial asphaltenes in the presence and absence of Na were compared (Figure 3.4). The solid line shows real experimental liquid yield whereas the dashed lines gives the liquid yield of control experiments.



*The blue line is liquid yield after Na conversion of asphaltenes, and the brown line is liquid yield after control experiments.

Figure 3.2.3 Liquid yield of asphaltenes after reaction with Na compared with control experiments.

From Table 3.2.2 and Figure 3.2.3 we can see that numerically the liquid yield of the control experiments spanned a larger range, from 12.8% to 21.2%, than the reactions with Na. When considering the standard deviation, there was no meaningful difference in the liquid yield between the reactions with and without Na. This is not to say that there was no difference, but the decrease in liquid yield appeared to be a consequence of reactions that took place irrespective of whether Na was present or not.

Since it seems that there is a sharp drop in liquid yield for control experiment between 150 °C and 100°C, a series of control experiments were performed with 10°C temperature intervals. The material balances and yield profiles are shown below (Table 3.2.3).

Table 3.2.3 Material balances and yields of asphaltene reactions without Na (second set)

T (°C)	Time (h)	Asp. (g)	Na (g)	Solid mass(g)	Liquid mass(g)	Mass balance	Liquid yield	Average yield	Standard deviation
150	1	3.75	0	2.96	0.47	92.0%	12.5%	14.4%	2.0%
150	1	3.87	0	3.21	0.64	100.0%	16.5%		
150	1	4.00	0	3.32	0.56	97.5%	14.0%		
140	1	3.43	0	2.55	0.76	97.1%	22.2%	19.0%	3.1%
140	1	4.04	0	3.21	0.76	98.8%	18.8%		
140	1	3.87	0	3.22	0.62	99.7%	16.0%		
130	1	3.79	0	2.94	0.78	98.7%	20.6%	14.6%	5.2%
130	1	3.66	0	3.14	0.46	98.9%	12.6%		
130	1	3.90	0	3.46	0.42	100.0%	10.8%		
120	1	3.66	0	3.05	0.65	101.6%	17.8%	14.9%	2.5%
120	1	4.21	0	3.60	0.58	99.8%	13.8%		
120	1	4.01	0	3.42	0.53	99.0%	13.2%		
110	1	4.27	0	3.90	0.22	97.0%	5.2%	7.2%	4.4%
110	1	4.56	0	4.22	0.19	97.2%	4.2%		
110	1	4.18	0	3.56	0.51	97.9%	12.2%		
100	1	3.78	0	3.42	0.38	101.1%	10.1%	10.4%	1.3%
100	1	4.14	0	3.63	0.49	100.0%	11.8%		

100	1	4.18	0	3.82	0.39	101.2%	9.3%		

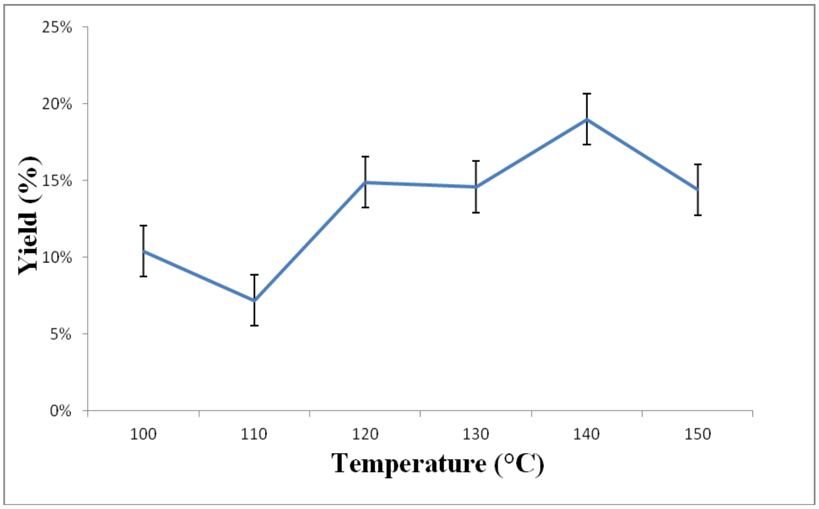


Figure 3.2.4 Liquid yields of control experiments between 100 °C and 150 °C

From the data in Table 3.2.3 and Figure 3.2.4, the liquid yields are not a sharp decrease as thought before but rather a mild change with the temperature change.

3.5.4 Effect of reactions on the aromatic hydrogen content of liquid products

Since Na did not have a significant effect on increasing liquid yield, it was decided to investigate if the reaction of Na and asphaltenes caused a change in the aromatic hydrogen content compared to thermal conversion on its own. The liquid products from the reactions with Na and without Na were analyzed by ^{1}H NMR and the results are listed in Tables 3.2.4 and 3.2.5 respectively. The asphaltenes feed was also characterized in the same way and it had an aromatic hydrogen content of 13.5% with the standard deviation 0.54%.

Table 3.2.4 ^{1}H NMR Characterization of liquid products from reaction with Na

T (°C)	Aromatic H-content (wt %)	Standard Deviation
250	9.0%	0.4%
200	10.6%	0.2%
150	9.4%	1.2%
100	10.0%	0.2%
60	8.6%	0.1%

Table 3.2. 5 ^{1}H NMR Characterization of liquid products from control reactions without Na

T (°C)	Aromatic H-content (wt %)	Standard Deviation
250	5.8%	1.2%
200	6.5%	1.4%
150	7.0%	0.1%
100	12.3%	0.0%
60	11.1%	0.2%

In the temperature range 150 °C to 250 °C it appeared that the liquid products after reaction in the presence of Na had a higher aromatic hydrogen content than the products after reaction without sodium. Again there appeared to be a transition in the reaction taking place between 100

°C and 150 °C, which was confirmed by analyzing the liquid products from the second set of control experiments with 10 °C temperature intervals (Table 3.2.6).

Table 3.2.6 ^{1}H NMR Characterization of liquid products of control experiments without Na performed in the temperature range 100-150 °C

T (°C)	Aromatic-H content (wt %)	Sample standard deviation
100	16.3%	0.5%
110	16.7%	0.0%
120	13.8%	2.1%
130	15.5%	3.5%
140	9.4%	1.0%
150	10.7%	0.8%

According to Table 3.2.6, the aromatic-H content changed as reaction temperature was increased from 100 °C to 150°C. We can see that in this range, aromatic-H transferred to become aliphatic-H at temperatures of 140 °C and higher.

3.5.5 Effect of reactions on the infrared spectra

FTIR analysis was conducted and the two spectra shown below are representative of the feed (Figure 3.2.5) and products (Figure 3.2.6). The other spectra of the liquid products obtained at different temperatures after reaction in the presence of Na had similar peak wavenumbers.

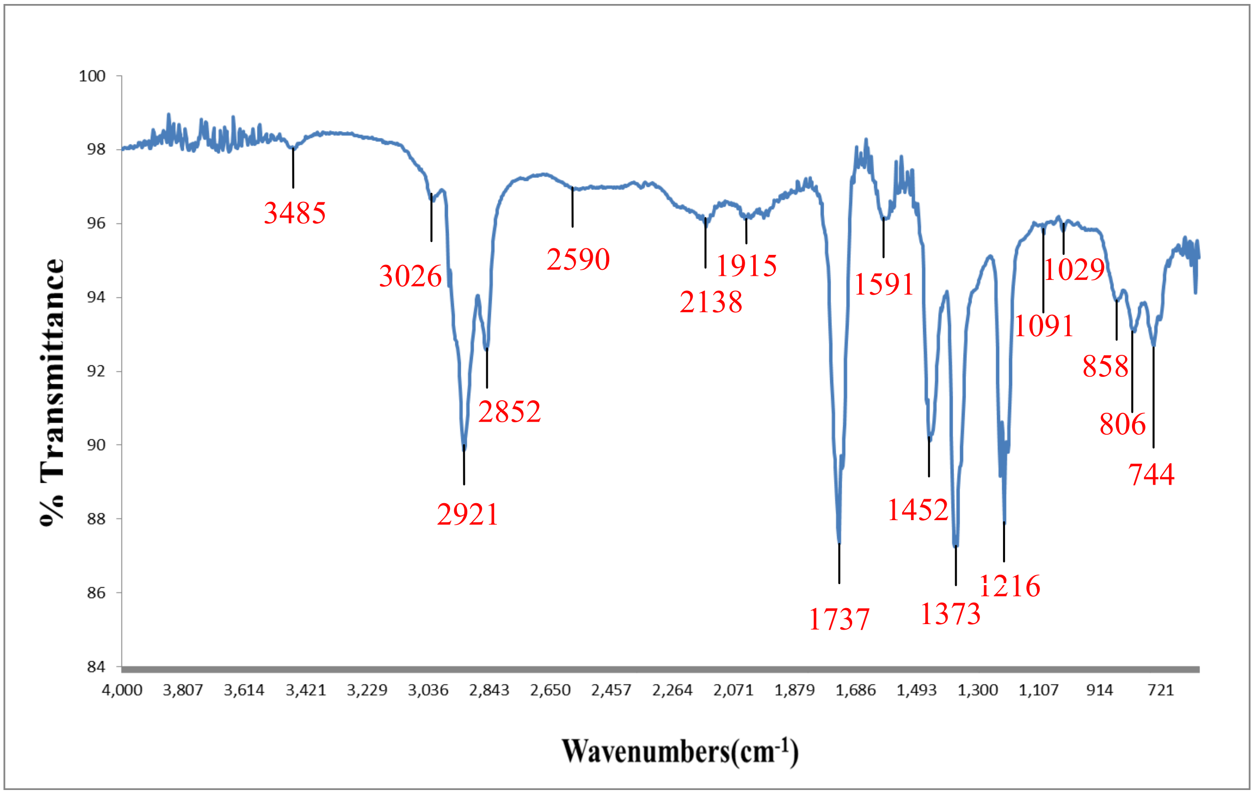


Figure 3.2.5 FTIR spectrum for Nexen asphaltenes feed

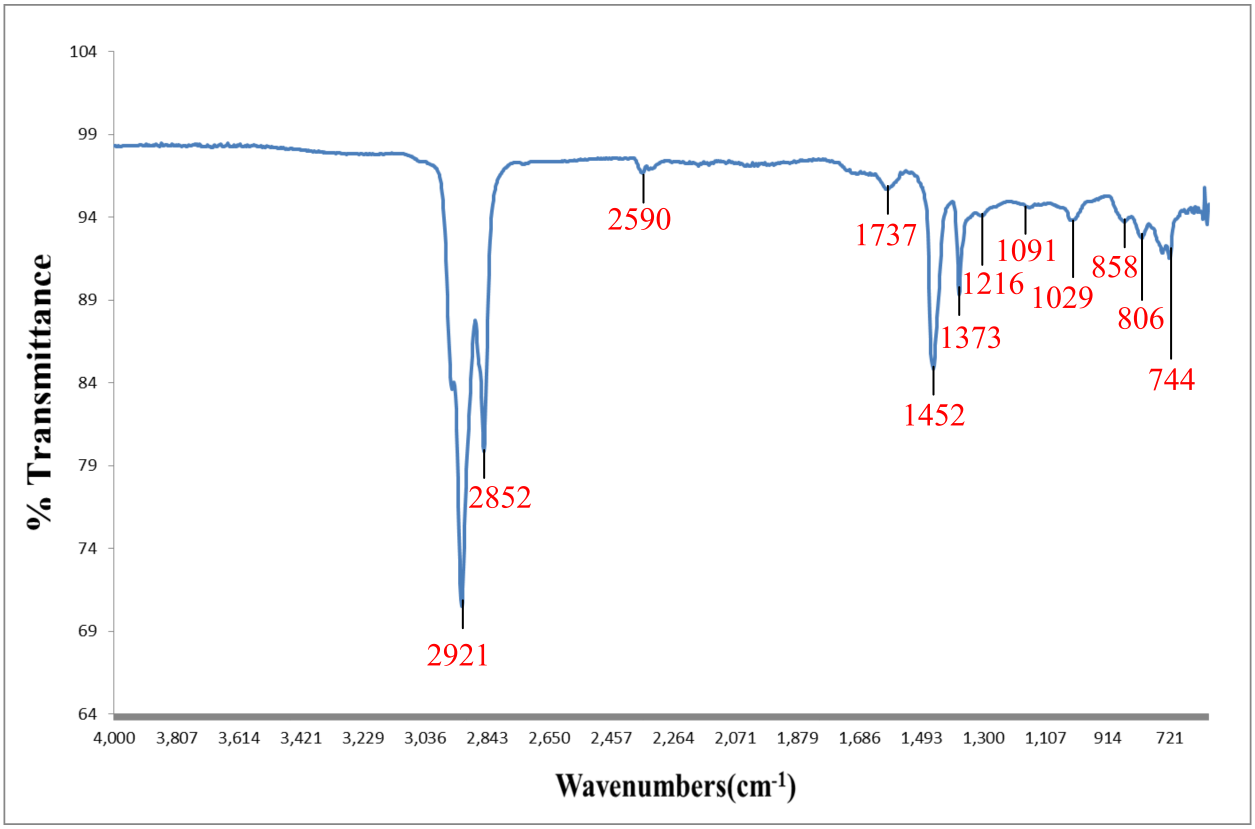


Figure 3.2.6 FTIR spectrum of liquid product after Na conversion reaction at 250 °C

The FTIR spectra in Figures 3.2.6 and 3.2.7 were compared. Absorption at some wavenumbers did not change, but a number of changes were observed and tentatively interpreted (Table 3.2.7).

Table 3.2.7 Comparison of FTIR spectra of raw asphaltenes feed and liquid product after reaction at 250 °C with Na

Same peaks (wavenumbers/cm^{-1})	Possible bonds
2921, 2852	Aliphatic C-H stretching
1452	The C=C ring stretching
Changed peaks (wavenumbers/cm^{-1})	
3485	N-H stretching
3026	Alkenes(C=C)
2590	Sulfur compounds(S-H)
2138	N-H amine salts
1915	Asymmetric C=C stretching
1737	Carbonyl (C=O)
1591	N-H bending
1373	Aliphatic C-H bending
1029, 1091, 1216	C-O stretching
858, 806, 744	C-H Out-of- Plane bending

In the comparison of FTIR spectra between Na conversion maltenes products and raw asphaltenes feed, some sulfur, nitrogen and oxygen groups were less or disappeared after reaction. Peak 2590 cm^{-1} standards for sulfur groups (S-H) and it was less in Na conversion of the maltenes product than in the feed asphaltenes, 2138 cm^{-1}, 3485 and 1591 cm^{-1} stand for N-H bond, e.g. amines, which presented in feed asphaltenes but not in maltenes product after Na conversion. 1737 cm^{-1} peak standards for carbonyls was a lot less amount than in raw feed. 1029

cm^{-1}, 1091 $cm^{-1}$and 1216 cm^{-1} peaks which indicate C-O bonds, e.g. esters, alcohols and phenol, almost disappeared. This suggested that Na reacted with some sulfur, nitrogen and oxygen groups in the asphaltene. In addition, at 858 cm^{-1}, 806 cm^{-1}, and 744 cm^{-1}, the peaks stand for aromatic C-H bending, and they are less in the maltenes from Na conversion, that is, there are more aliphatic hydrogen in maltenes than in asphaltenes which is consistent with NMR results. In order to confirm that the changes were not caused by thermal reactions, but by reaction with Na, the FTIR spectrum of the reaction product (Figure 3.2.6) was also compared to the FTIR spectrum of the control experiment (Figure 3.2.7).

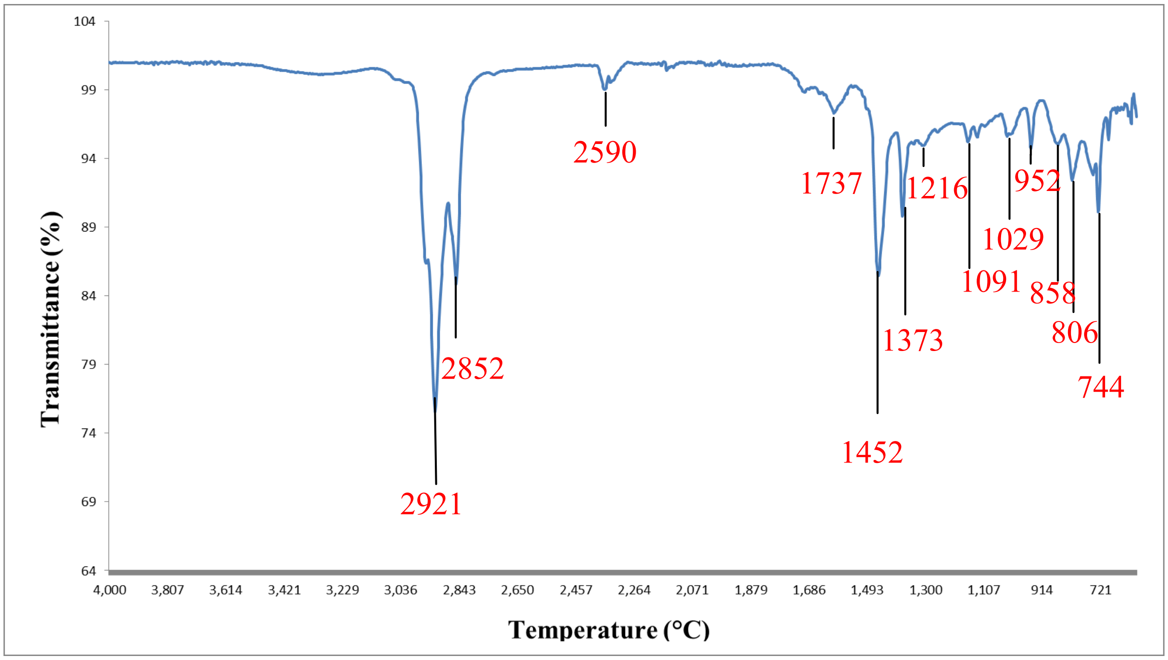


Figure 3.2.7 FTIR spectrum for control experiment at 250 °C without Na

Table 3.2.8 Comparison of FTIR spectra of liquid products after reaction at 250 °C with and without Na

Same peaks (wavenumbers/cm^{-1})	Possible structures
2852,2921	C-H stretching
1452	The C=C ring stretching
1373	Aliphatic C-H bending
Different peaks (wavenumbers/ cm^{-1})	Possible structures
2590	Sulfur compounds (S-H)
1737	Carbonyl (C=O)
1029, 1091, 1216	C-O stretching
952	Cyclic anhydride (C=O stretching)
858, 806,744	C-H Out-of-Plane bending

After compared all the FTIR spectra of reacted samples with control experiments, here are the table listing the same peaks and different peaks (Table 3.2.8).

It is shown in the FTIR spectra and the comparisons of the control experiments and the Na conversion products; the maltenes product from Na conversion has less amount of S-H bond at 2590 cm^{-1}. This indicated Na contributed to sulfur removal more than control experiments. C-O bond at 1029 cm^{-1}, 1091 cm^{-1} and 1216 cm^{-1} was less in Na conversion product, which means Na helped eliminate aliphatic oxygen functional groups. Especially regarding the C=O bond, at 1737 cm^{-1} the peak is less and 952 cm^{-1} the peak totally disappeared in maltenes from Na conversion. Peaks at 858 cm^{-1}, 806 cm^{-1}, and 744 cm^{-1}, are slightly less in the maltenes from Na conversion, that is, there are more aliphatic hydrogen in maltenes products from reactions with Na than without it.

3.3.6 Effect of reactions on the elemental composition

The elemental composition of the asphaltenes feed (Table 3.2.9) and the liquid products from the conversion of the asphaltenes with Na (Table 3.2.10) are presented.

Table 3.2.9 Elemental analysis of the feed material

Composition	Industrial asphaltenes feed material	Laboratory precipitated materials	
		C_5-asphaltenes	maltenes
C (wt%)	80.34	81.61	82.24
Standard deviation	0.12	0.19	0.36
H (wt%)	7.95	7.62	8.95
Standard deviation	0.06	0.05	0.12
N (wt%)	1.11	1.25	0.67
Standard deviation	0.00	0.01	0.03
S (wt%)	7.67	7.68	6.25
Standard deviation	0.10	0.19	0.18

Table 3.2.10 Elemental analysis of liquid products after reaction with Na

T (°C)	wt% Nitrogen	wt% Carbon	wt% Hydrogen	wt% Sulfur
250	0.48	84.17	10.75	3.23
Standard deviation	0.02	0.53	0.16	0.26
200	0.53	83.41	10.13	4.47
Standard deviation	0.04	0.70	0.34	0.45
150	0.55	82.97	10.35	4.65
Standard deviation	0.01	0.30	0.09	0.12
100	0.54	82.47	10.41	4.11
Standard deviation	0.41	0.01	0.67	0.16
60	0.47	83.53	7.22	3.79
Standard deviation	0.27	0.04	0.33	0.18

The liquid products obtained after reaction of the asphaltenes at 100-250°C, but not after reaction at 60°C, had a H/C ratio range from 1.45-1.57, higher than maltenes products from asphaltenes precipitation. The sulfur and nitrogen contents were also lower compared to the maltenes from asphaltenes precipitation.

Maltenes from asphaltenes precipitation without any treatment, it has low H/C ratio, which is 1.31, high sulfur and nitrogen content, which are 6.25% and 0.67% separately. But after Na treatment, H/C ratio becomes 1.46-1.53 except for at 60°C, and sulfur were removed 25-48%, nitrogen 18-30%. So above 100°C sulfur and nitrogen was largely removed. Under 60°C H/C ratios did not change too much and this may due to unmelted Na, which would make conversion more transport limited.

The elemental composition of the liquids from the control experiments was also determined (Table 3.2.11).

Table 3.2.11 Elemental analysis of liquid products from control experiments without Na

T (°C)	wt% Nitrogen	wt% Carbon	wt% Hydrogen	wt% Sulfur
250	1.20	81.41	7.83	8.06
Standard deviation	0.08	0.78	0.27	0.42
200	1.25	81.73	7.81	7.86
Standard deviation	0.015	0.13	0.06	0.04
150	1.01	81.63	8.68	6.93
Standard deviation	0.00	0.27	0.04	0.06
100	1.21	81.75	7.93	7.73
Standard deviation	0.02	0.85	0.09	0.15
60	0.84	81.40	8.87	7.00
Standard deviation	0.04	0.83	0.27	0.36

In Table 3.2.11, the molar H/C ratio is between 1.15-1.31, which is similar to that of the feed asphaltenes (1.19), but lower than the molar H/C ratio of the liquid products from the reaction with Na (Table 3.2. 10), which was between 1.46-1.53 except for reaction at 60°C.

3.5.7 Scanning electron microscopy of solids

SEM analysis was done in order to figure out the composition of the solid samples obtained after deactivation of Na and drying of the aqueous product. The SEM back scattering image is shown in Figure 3.2.8 together with the X-ray fluorescence spectra of the light area numbered one (Figure 3.2.9) and the dark area numbered two (Figure 3.2.10).

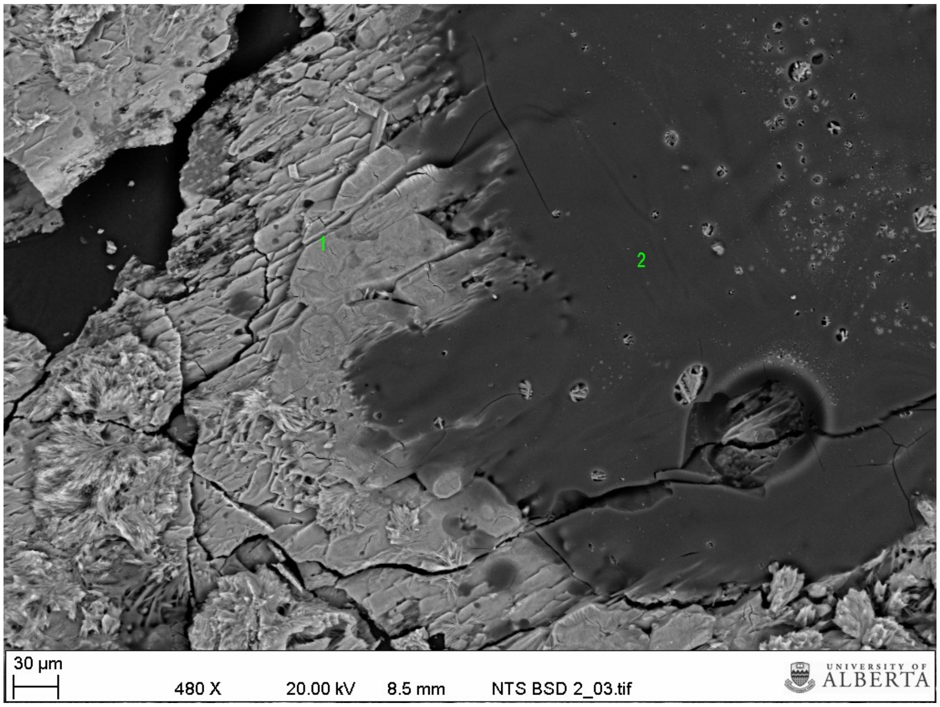


Figure 3.2.8 SEM analysis of solid sample from the aqueous phase after Na deactivation

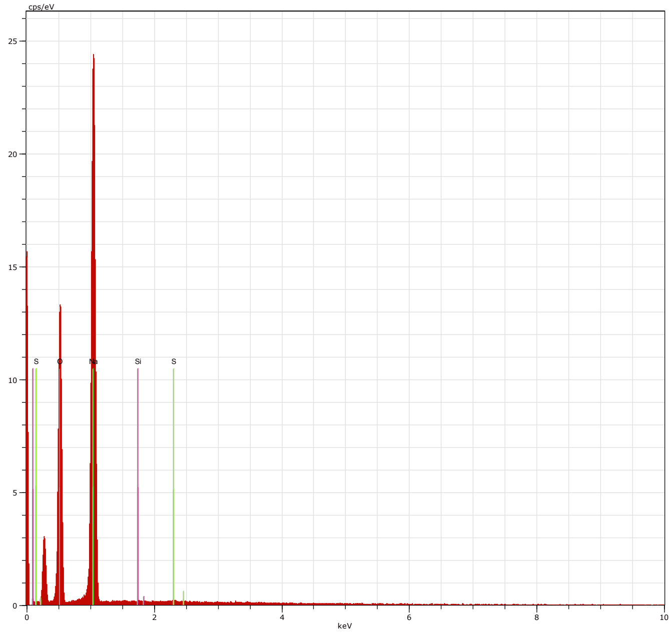


Figure 3.2.9 Elemental composition of area 1 in SEM

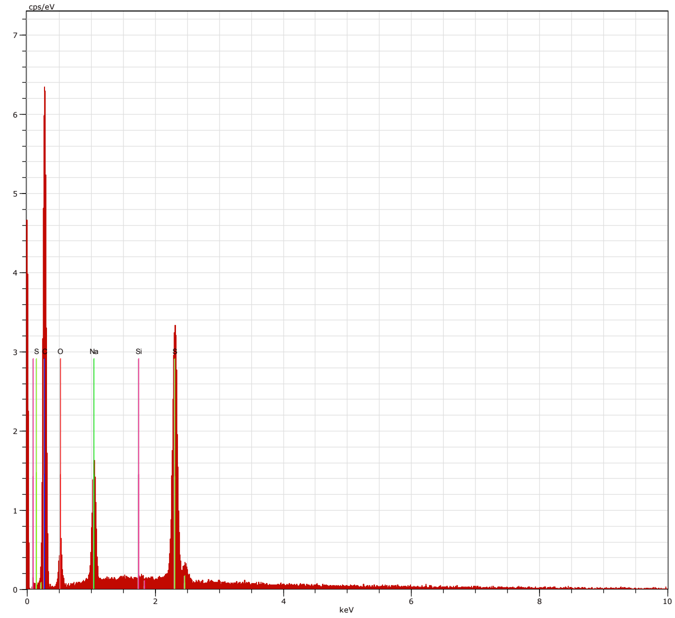


Figure 3.2.10 Elemental composition of area 2 in SEM Figure 3.9

The semi-quantitative analysis presented in Figures 3.2.9 and 3.2.10 can be found in Table 3.2.12.

Table 3.2.12 Elemental composition based on analyses in Figures 3.2.9 and 3.2.10

Detected area in SEM figure	Wt% C	Wt% O	Wt% S	Wt% Na
Area 1	0	43.16	0.28	56.55
Area 2	75.82	11.56	7.58	5.00

Area 1 is NaOH and area 2 is hydrocarbons layer on the surface of NaOH that came out with NaOH during separation of maltenes and NaOH. From the SEM spectrum and elemental composition of both area 1, the C content is 0 which means it is purely inorganic chemicals so even if there is still some sulfur present, the sulfur does not come from hydrocarbons, it is speculated that Na_2S is also present, and the mass ratio of NaOH: Na_2S is 139.

And as to area 2 in the sample, since SEM can only detect a thin layer of surface, the Na may come from NaOH or may stay in the maltenes.

3.5.8 Phases during the reactions

After the reaction of Na and asphaltenes, the reactors were opened. The surface of the product in the reactor was shiny and smooth, which indicated that the Na and asphaltenes on the surface melted. After removing the surface layer, some solids appeared to be unmelted close to the middle and bottom of the reactor.

An analysis by DSC microscope was conducted to see the metling point of asphaltenes with temperature range 25 °C-375 °C. Pictures showing the images of ashphaltenes samples between 28 °C-170 °C were taken.

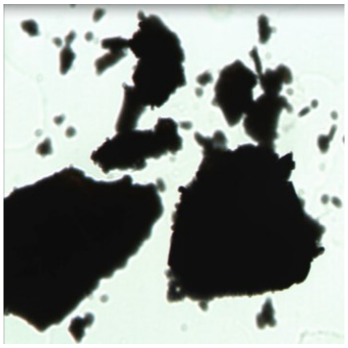


Figure 3.2.11 Image of asphaltenes under 28 °C

Figure 3.2.12 Image of asphaltenes under 80 °C

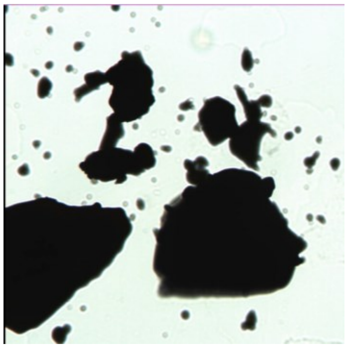


Figure 3.2.13 Image of asphaltenes under 110 ° C

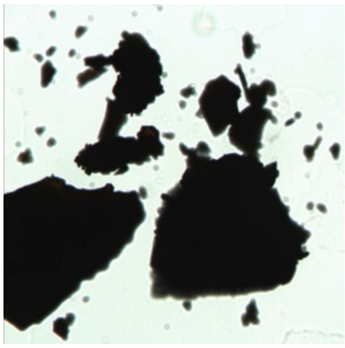


Figure 3.2.14 Image of asphaltenes under 124° C

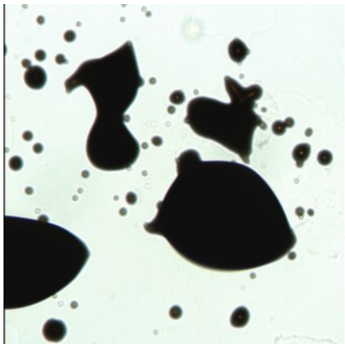


Figure 3.2.15 Image of asphaltenes under 142 ° C

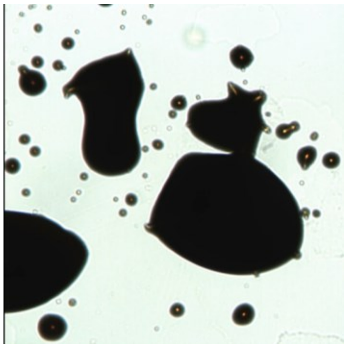


Figure 3.2.16 Image of asphaltenes under 150 ° C

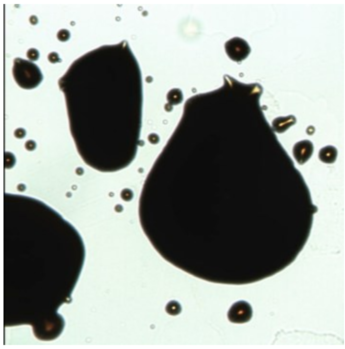


Figure 3.2.17 Image of asphaltenes under 160 ° C

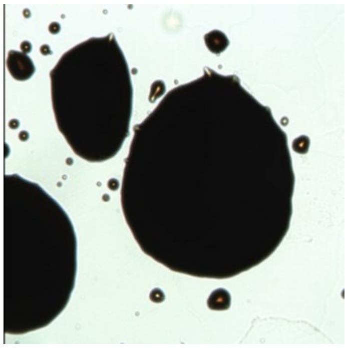


Figure 3.2.18 Image of asphaltenes under 170 ° C

The melting processes observed from Figure 3.2.11 to Figure 3.2.18 suggested that before 110 °C, there was no melting, between 110 °C- 170 °C, the asphaltenes became fluid and melting of the asphaltenes occurred in this temperature range. The experiments of Na conversion of asphaltenes were conducted between 60 °C – 250 °C. The melting point of Na is above 110 °C. Thus, below 110° C the reaction happened was solid-solid phases which can have mass transfer limits. However above 110 °C, the reactions mainly started to have multiple phases with melted and unmelted asphaltenes with melted Na present. Especially between 150 °C – 250 °C, the reactions were mainly liquid-liquid phases.

3.6 Discussion

It is shown that liquid yield of reactions of Asphaltene with Na compared to control experiments under the same temperatures does not change a lot, mainly range between 15-20%. Considering the standard deviation is around 3%, the liquid yield are pretty much the same, which means Na does not have a significant effect on increasing liquid yield. Moreover the liquid yields did not have a sharp decrease as thought before, but rather a mild change within the 100-150°C temperature range. For reactions under 60°C, which is below sodium's melting point, the mass transfer will be very slow between solid Na and solid Asphaltene, then the low liquid yield would be expected.

The aromatic H-content dropped compared to feed Asphaltene. Since the aliphatic H and aromatic H add up to 100%, then the aliphatic H weight percent increased. There was no other hydrogen source present in the batch reactors. It is speculated that some aromatic H became aliphatic H through partial hydrogenation. The hydrogen came from the feed materials by internal transfer of hydrogen. For example, Na may get H from one aliphatic branch or ring and become NaH, and then NaH would attack some aromatic rings and give H to the rings so that the double bond can be saturated and the linked aromatic H became aliphatic H.

Compared to the aromatic H weight percentage in the liquid sample after Na conversion, the aromatic H content is lower in control experiments samples, which means there were some light components separated from asphaltenes and came out as liquid during the conversion with Na.

The NMR analysis was done for control reactions between 150°C and 100°C. Both liquid yields and aromatic-H suggested a mild change with temperature.

From the FT-IR spectra comparisons among the feed asphaltenes, maltenes products after Na conversion of asphaltene and after control experiments, we can see a lot of oxygen bonds, some sulfur bonds and nitrogen bonds that decreased or disappeared in the maltenes products after Na conversion compared to the feed. But compared to the control experiments, Na did help with more heteroatoms removal. This may suggest Na can react with some oxygen, sulfur and nitrogen group in asphaltene, which decreased oxygen, sulfur and nitrogen content.

Elemental analysis was done to confirm with the hypothesis and found out sulfur and nitrogen content in maltenes products did decrease after Na conversion, whereas no very much change after control experiments.

In addition, the hydrogen/ carbon (H/C) ratio is an important property of crude oils. It gives an indication of the value of the oil. Greater the H/C ratio, the higher the value of the oil. H/C ratio closer to 2 is desirable. It is concluded that Na did have some effects on increasing H/C ratio and reducing the percentage of sulfur and nitrogen in maltenes products especially. This may be because Na reacted with heteroatoms in asphaltenes and transferred some hydrogen making some aromatics lighter and causing those molecules to turn into liquid products.

In industrial asphaltenes, there is more than just asphaltnenes, because malteness can also be present due to partial asphaltnene precipitation. In labs, precipitated asphaltene is a powder, whereas the Nexen asphaltenes are shining rocks. In this case, Na may also react with the maltenes and made them lighter with less sulfur or nitrogen, and transfer some H to aromatics.

From the SEM spectrum and elemental composition of both area 1 and 2 in the sample, we can conclude that Na mainly comes out of the system as NaOH (from deactivation of excess Na) and a small amount of hydrocarbon including sulfur also comes out. From elemental analysis, sulfur was reduced after Na conversion of asphaltenes; the removed sulfur may come out with asphaltenes, and Na_2S is a stable compound, so sulfur can also be Na_2S in the product.

We can conclude that sulfur and nitrogen present in liquids, solids and came out with some hydrocarbons with NaOH and Na_2S.

Phase studies were conducted and the results indicated that both Na and asphaltenes could start to melt above 110 ° C, so below this temperature, mass transfer limit will be an issue to the reactions.

References

[1] Sternberg, W. H.; Donne, D. L. C.; Markby, E. R.; Friedman, S. Reaction of Sodium with Dibenzothiophene. A Method for Desulfurization of Residua. *Ind. Eng. Chem. Process Des. Dev*. **1974**, 13(4), 433-436.

[2] Wallace, T. J.; Hofmann, J. E.; Schriesheim.A. Base-catalyzed elimination studies on sulfones, sulfoxides, sulfides, disulfides, and mercaptans in dimethyl sulfoxide. *J. Am. Chem. Soc*. **1963**, 85, 2739-2743.

[3] *Polynuclear aromatic compounds* (Adv. Chem. Ser. 217); Ebert, L. B. Ed.; American

Chemical Society: Washington DC, 1988.

[4] Ignasicak, T.; Kemp-Jones, A.V.; Strausz, O.P. The molecular Structure of Athabasca Asphaltene. Cleavage of the Carbon-Sulfur Bonds by Radical Ion Electron Transfer Reactions. *J. Org. Chem.* **1977**, 42, 312-320.

[5] Gilman, H.; Esmay, D. L. The cleavage of heterocycles with Raney nickel and with lithium. *J. Am. Chem. Soc.* **1953**, 75, 2947-2949.

[6] Tamaru, K. Catalysis by electron donor-acceptor complexes. *Adv. Catal.* **1969**, 20, 327-339.

[7] Babatunde A. O. Random Phenomena: Fundamentals and Engineering Applications of Probability & Statistics. *CRC Press*, Boca Raton **2009**.

[8] Ebert, L. B.; Milliman. G. E.; Mills, D. R.; Scanlon, J. C. Reductive alkylation of aromatic compounds perylene, decacyclene, and dibenzothiophene. *Adv. Chem. Ser.* **1988**, 217, 108-126.

[9] Gilman, H.; Joseph, D. Notes-Lithium Cleavages of some Heterocycles in Tetrahydrofuran. *J. Org. Chem.* **1957**, 22, 851-853.

[10] Wallace, T. J.; Heimlich, B. N. The decomposition of dibenzothiophene dioxide and related compounds in the presence of molten alkali. *Tetrahedron* **1968**, 24, 1311-1322.

[11] Zachariah, A. Low Temperature Pyrolysis and its Application in Bitumen Processing MSc Thesis, University of Alberta Press, Edmonton, August **2014**.

CHAPTER 4 – Sodium conversion of heteroaromatic model compounds

Abstract

In this chapter various heteroaromatic model compounds were reacted with Na to study the way in which Na is able to extrude heteroatoms in asphaltene. A few different model molecules, e.g. dibenzothiophene, carbazole, dibenzofuran, dibenzyl sulfide, diphenyl sulfide, benzyl phenyl sulfide, dibenzylether, and diphenyl ether were mixed with tetrahydronaphathalene. Reactions were conducted under nitrogen environment in the presence of Na. The mixtures were heated to 150°C and the reaction products analyzed to identify the compounds generated during reaction.

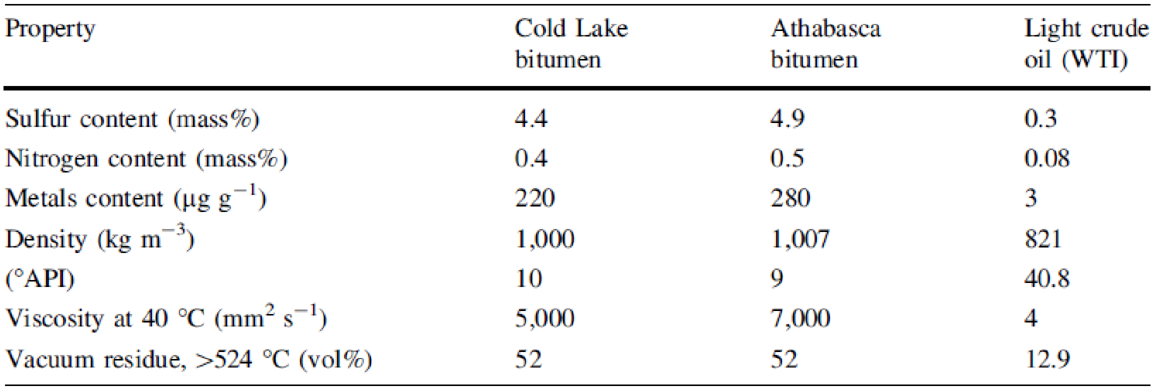
Keywords: model compounds, analysis, Na conversion, extrusion of heteroatoms

4.1 Introduction

Sulfur and nitrogen, along with oxygen, are important organically bound heteroatoms in oilsands bitumen and the asphaltenes derived from the bitumen. Removal of these heteroatoms is desirable. In Chapter 3 it was found that the sulfur and nitrogen content of the liquid products were decreased when reactions were performed with Na.

In conventional bitumen upgrading processes the high concentration of sulfur (Table 4.1.1), and the resulting high concentration of hydrogen sulfide in the effluent from bitumen and heavy oil upgrading, make sulfur the most studied of the heteroatoms. Due to the high sulfur content, metals can form metal sulfides during bitumen upgrading. As a result, the hydrogenating metals of commercial interest for hydrotreating catalysts used with heavy oils and bitumens are the ones that are active in the sulfide form. Many transition metals give some activity for hydrogenation and desulfurization and the most active combinations are molybdenum and tungsten, alloyed with nickel or cobalt [1].

Table 4.1.1 Selected properties of two Canadian oil sands derived bitumens



Property	Cold Lake bitumen	Athabasca bitumen	Light crude oil (WTI)
Sulfur content (mass%)	4.4	4.9	0.3
Nitrogen content (mass%)	0.4	0.5	0.08
Metals content (μg g^{-1})	220	280	3
Density (kg m^{-3})	1,000	1,007	821
(°API)	10	9	40.8
Viscosity at 40 °C (mm^2 s^{-1})	5,000	7,000	4
Vacuum residue, >524 °C (vol%)	52	52	12.9

Often extreme conditions of temperature and pressure are required to obtain significant desulfurization, which also involve high associated cost of hydrogen. Hydrodesulfurization processes are subject to catalyst fouling and poisoning, which adds to the cost. Nevertheless, hydrotreating processes are successfully applied commercially, despite their cost and the drawbacks mentioned [3].

In the present study Na in reaction with asphaltenes would likely form sulfides too, although this was not an aspect that was investigated. Na was not employed as catalyst for hydrotreating, but to produce electron donor-acceptor (EDA) pairs with the multinuclear aromatics and the Na was employed in excess.

What was of interest was heteroatom removal, sulfur in particular, but also nitrogen and oxygen. Of further interest was to identify the compound classes that were amenable to conversion by Na due to its ability to for EDA pairs with multinuclear aromatics. For example, sulfur occurs in different forms (Figure 4.1.1) and removal of sulfur from heterocycles is more difficult than the removal of aliphatic sulfur.

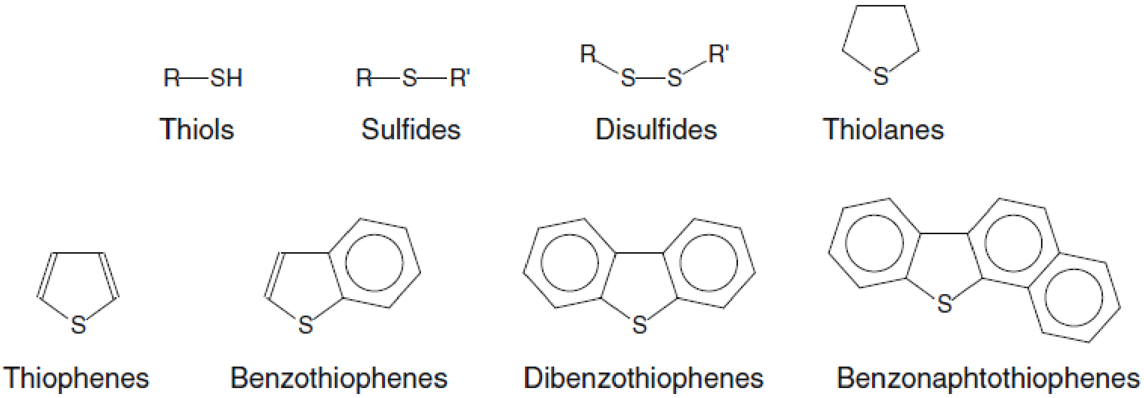


Figure 4.1.1 Important classes of sulfur-containing compounds in crude oil (R = alkyl) [2]

The conversion of selected model compounds with Na at mild temperature and pressure was investigated without added hydrogen.

4.2 Experimental

4.2.1 Materials

The model compounds used were dibenzothiophene (98%), carbazole (98%), dibenzofuran (98%), dibenzyl sulfide (99%), diphenyl sulfide (98%), benzyl phenyl sulfide (98%), dibenzyl ether (98%), diphenyl ether (99%) and benzyl phenyl ether (97%), 1-methylnaphthalene (96%), decahydronaphthalene (mixture of *cis* + *trans*, 97%) purchased from Sigma-Aldrich Corporation. Sodium sticks were purchased from Alfa Aesar (99%, in mineral oil). Nitrogen gas (>99.998%) was purchased from Praxair Canada.

4.2.2 Equipment and procedure

For a typical experiment about 2 g of targeted reactant, e.g. dibenzothiophene (DBT), was added to a 250ml flask. Then 25ml of solvent, which mostly was a *trans*- and *cis*-decalin mixture, was added to serve as potential hydrogen source. Lastly about 5.3g of Na was added to the flask. The molar ratio of targeted reactant, Na and solvent was around 1:2.2:16.2.

Then the flask was connected to a nitrogen cylinder. Nitrogen flow was maintained through the flask for 10-15 minutes to get rid of oxygen in the flask before heating. The nitrogen flow was maintained for the whole experiment so that the reaction was conducted in an oxygen-free atmosphere. The reaction mixture was heated on a hot plate to the required temperature. The experiments that were performed are shown in Table 4.2.1.

It took less than 5min to reach the desired temperature. After reached certain temperature, the mixture was kept at the temperature for 22 hours. The mixture was stirred at 500 rpm. At the end of this period the reaction mixture was cooled down and sodium was deactivated using isoproponal, methanol and water using the same procedures as in Chapter 3. After that, the organic liquid product was analyzed. The workflow is shown in Figure 4.2.1.

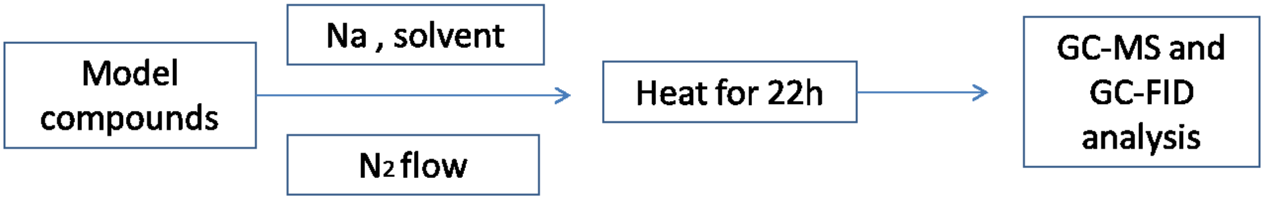


Figure 4.2.1 Workflow of model compounds with Na under N_2

Table 4.2.1 Experiments conducted with different model compounds and Na

Reactant 1*	Reactant 2*	Solvent*	Temperature (°C)
Na	DBT	Decalin	110
Na	DBT	Decalin	130
Na	DBT	Decalin	150
Na	DBT	1-Methylnaphthalene	150
Na	Carbazole	Decalin	150
Na	Dibenzofuran	Decalin	150
Na	Dibenzyl sulfide	Decalin	150
Na	Diphenyl sulfide	Decalin	150
Na	Benzyl phenyl sulfide	Decalin	150
Na	Dibenzyl ether	Decalin	150
Na	Diphenyl ether	Decalin	150
Na	Benzyl phenyl ether	Decalin	150

* Molar ratio of reactant 1: reactant 2: solvent = 2.21:1:6.2

All masses were weighed on a Mettler Toledo New Classic MF ML3002E, with maximum mass limit 3200g, 0.01g precision.

4.2.3 Analyses

The reaction products from the model compounds experiments were identified using an Agilent 78820 GC with 5977E mass spectrometer for GC-MS. The products were quantified by analysis with an Agilent 7890A gas chromatograph with flame ionization detector (GC-FID). The GC-FID was using a DB-5 MS column with 30m × 0.25mm × 0.25μm parameters, and GC-MS was using a HP-5 column that was 30m × 0.25mm × 0.25μm. The temperature program for both GC-

MS and GC-FID started at 90 °C, with a hold of time of 0.5 minutes, after which the temperature was increased by 5°C/min up to 325 °C, and then held for 5 minutes.

Part of the study relied on quantitative data and the peak areas from the GC-FID chromatograms were related to product mass by employing appropriate FID response factors (as discussed in Section 4.2.4).

4.2.4 GC-FID response factors

For quantification an internal standard, tetralin, was chosen. Tetralin (8%) was spiked in a mixture composed with 4% of dibebzothiophene, decalin and biphenyl, which was the standard solution. (Strictly speaking this could have been done for all compounds in this study, but it was not, because only part of the study required quantitative data). After injected into GC-FID, the response factor of the internal standard relative to each compound can be calculated according to the equation:

$$\text{Response Factor} = \frac{A_x \times C_{is}}{A_{is} \times C_x} \qquad \text{(Equation 4.2.1)}$$

Where A_x is the area of the target analyte, C_{is} is the concentration of the internal standard, A_{is} is the area of internal standard on GC-FID chromatogram, C_x is the concentration of the target analyte.

After running the standard solution, response factors of tetralin with respect to each analyte was known.

For analysis, spike the same concentration of internal standard into sample as in the standard solution. Once the GC-FID chromatograms of the samples were collected, the actual concentration of the species could be determined. With tetralin as internal standard the areas of each compound in the chromatograms could be converted to a concentration using the response factors. Here is the list of response factors for reactants and solvents to tetralin (Table 4.2.2).

Table 4.2.2 Response factor for each compound

Compound	Concentration ($\times 10^{-3}$mg/mg solution)	Average response factor	Standard Deviation (%)
DBT	4.62	1.12	2.35
Biphenyl	4.62	0.96	0.80
Decalin	4.62	0.86	0.16
Tetralin	9.24	1.00	

4.2.5 Calculations to evaluate transport limitations

The Na metal employed in the study would melt at reaction temperature to create a separate liquid phase. However, transport could be limiting. In order to determine whether the reaction was mass transfer limited, the calculations that are described were performed.

It was assumed that the reaction rate could be approximated as a pseudo first order reaction. The test reaction of interest was desulfurization of DBT to produce biphenyl. Since the DBT could also be converted to other products, biphenyl was used as basis to calculate the amount of DBT converted to biphenyl based on the concentration of biphenyl from GC-FID analysis by Equation 4.2.2:

$$\Delta W_{DBT} = \frac{W_{biphenyl}}{M_{biphenyl}} \times M_{DBT} \qquad \text{(Equation 4.2.2)}$$

Where ΔW_{DBT} is the mass change of DBT, $W_{biphenyl}$ is the mass of biphenyl produced in the reaction, $M_{biphenyl}$ and M_{DBT} are the molecular mass of biphenyl and DBT respectively.

The first-order reaction kinetic equation for any compound “A” is given by Equation 4.2.3:

$$\frac{-d[A]}{dt} = k[A] \qquad \text{(Equation 4.2.3)}$$

Where the k is first order reaction rate(s^{-1}), [A] is the molar concentration (mole/liter). After integration,

$$\ln[A] = -kt + \ln[A]_0 \qquad \text{(Equation 4.2.4)}$$

Where $[A]_0$ is the initial concentration of the molecule A, which in this case is DBT. [A] is the concentration of DBT after the time of t.

Since no vapor or gas was generated during the reaction, the volume did not measurably change. The mass balance was between 99%-100%, so the mass of DBT can be used to calculate in the first order kinetic equation instead of molar concentration.

The rate constant is given by the Arrhenius equation (Equation 4.2.5):

$$k = Ae^{-Ea/(RT)} \qquad \text{(Equation 4.2.5)}$$

Where k is the reaction rate constant, A is the pre-exponential factor, E_a is the activation energy, and R is the universal gas constant. Taking the natural logarithm,

$$\ln k = \frac{-E_a}{R}\frac{1}{T} + \ln(C) \qquad \text{(Equation 4.2.6)}$$

Accordingly, for a non-transport limited reaction the values of –ln *k* should be inversely proportional to T (K). Once the realationship of –ln *k* and 1/T is plotted, it can be determined whether the reaction was mass transfer limited or not.

4.3 Results

4.3.1 Dibenzothiophene (DBT) conversion with Na using decalin as a solvent

After the reaction of DBT with Na at 110°C, 130°C and 150°C separately for 22 hours, GC-MS analysis was done to investigate what kind of products that were generated. The GC-MS chromatogram for one of the reactions (at 110°C) is shown to illustrate the typical product distribution (Figure 4.3.1).

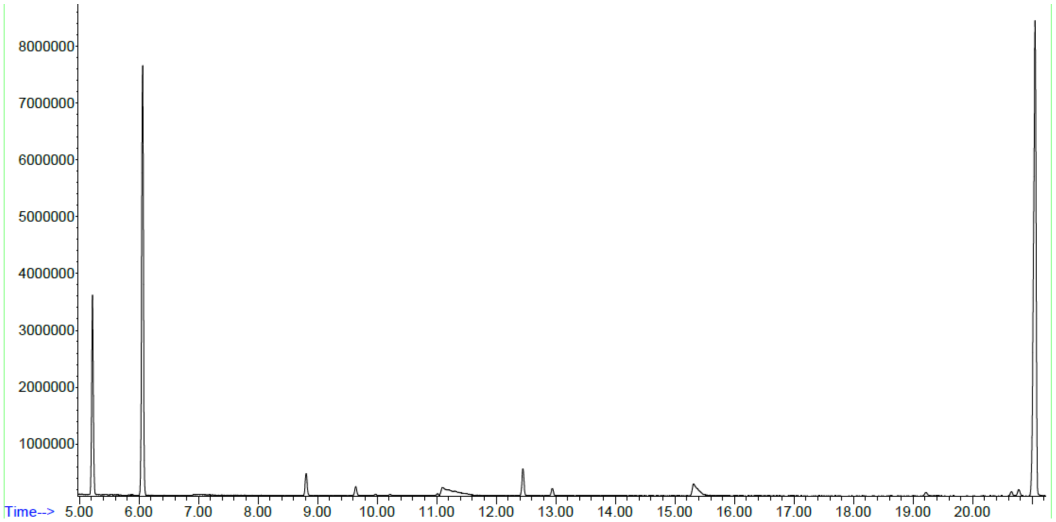
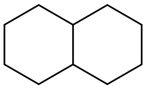
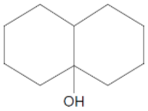
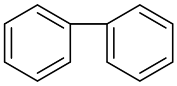
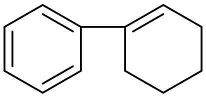
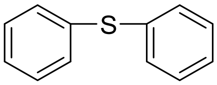
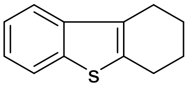
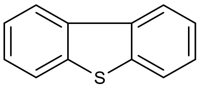


Figure 4.3.1 GC-MS chromatogram for product of the reaction of dibenzothiophene and Na in decalin at 110 °C for 22 h.

The retention time and corresponding structures identified from their electron impact mass spectra are presented below in Table 4.3.1.

Table 4.3.1 Retention time and possible structures in GC-MS chromatogram

Retention Time (min)	Structure	Name	Area percentage (%)
5.22 and 6.15		*trans*- and *cis*-Decalin	12.89 and 30.13
8.83 and 9.64	 isomers	1-hydroxybicyclodecane	1.73 and 0.79
12.44		Biphenyl	2.22
11.16,15.32 and 19.22	Unidentified compounds		0.91, 2.83 and 0.42
12.95		1-phenyl cyclohexene	0.67
20.65		Diphenyl sulfide	0.40
20.78		1,2,3,4- tetrahydrodibenzothiophene	0.66
21.05		Dibenzothiophene	46.33

From the GC-MS chromatogram (Figure 4.3.1), the products at 12.95 min retention time were partially saturated biphenyl. Only one double bond was apparent in one of the 6-membered rings. Such partial saturation was also observed for DBT, with partially saturated DBT found at 20.78 min retention time. These products have one saturated ring connected with sulfur and the other benzene ring, which means that Na results in some hydrogenation. At 12.44 min retention time biphenyl appeared which means that Na attacked the sulfur directly without hydrogenation. The alcohol at 8.83 and 9.64min were the products during deactivation of unreacted Na, and it would appear in products from other Na converted model compounds.

After analyzing the products by GC-FID, the concentration was determined and the conversion of DBT was calculated. Based on these values the rate constant k could be calculated. The conversion of DBT and corresponding values of –ln *k* have been tabulated (Table 4.3.2). The relationship between –ln *k* and 1/T is shown in Figure 4.3.2.

Table 4.3.2 Temperatures and corresponding conversions

Temperature (°C)	DBT Conversion	- ln *k*
150	45.9% ‡	11.77
130	5.1%	14.22
110	4.1%	14.44

* No conversion of the solvent was observed.

‡ The conversion of DBT at 150 °C was an order of magnitude higher than at 130 or 110 °C.

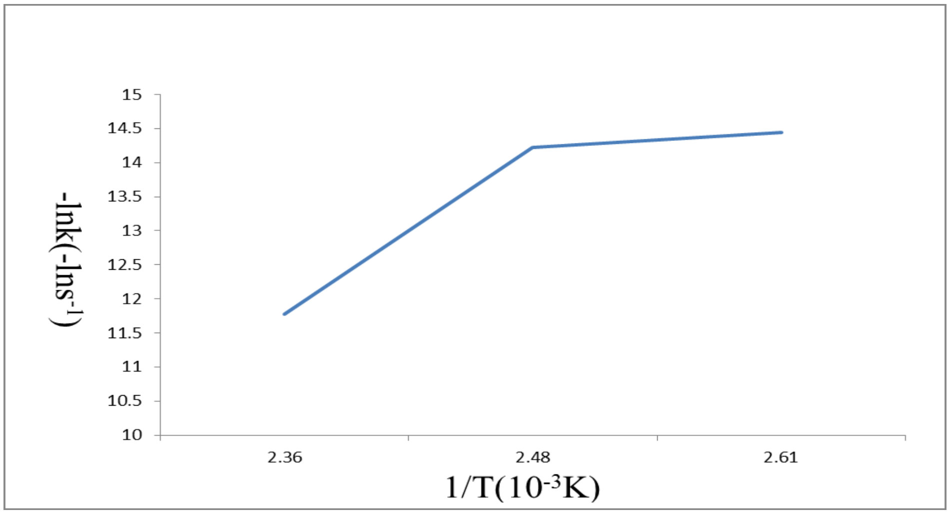


Figure 4.3.2 Relationship of –ln k and 1/T

The –ln k versus 1/T relationship in Figure 4.3.2 is not linear. The conversion at 150°C is the best in all the three temperatures.

4.3.2 Dibenzothiophene (DBT) conversion with Na using 1-methylnphathalene as a solvent

It was of interest to determine whether the solvent assisted conversion in some way. Decalin was a potential source of hydrogen for hydrogen transfer, but no decalin dehydrogenation products were observed (Section 4.3.1). However, the 1-hydroxybicyclodecane was likely formed during the Na deactivation procedure from bicyclodecene. Thus, the solvent was indeed responsible for hydrogen transfer.

1-Methylnaphthalene could interact with Na to form an EDA pair, but it has limited hydrogen transfer capability, beyond a benzylic hydrogen.

The product from the reaction of DBT and Na in 1-methylnaphthalene at 150 °C for 22 h was analyzed. The conversion of DBT to biphenyl was 4.0 %. No other products apart from the solvent and DBT feed were observed. There were some heavier products, potentially methylnaphthalene dimers, in the 30-40 min retention time range.

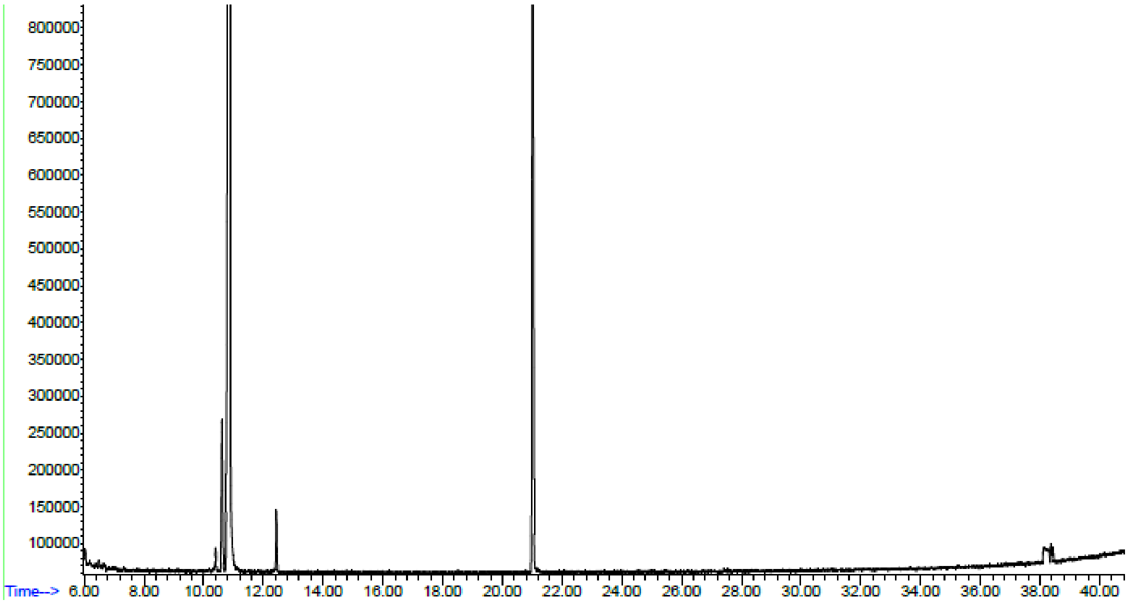
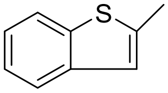
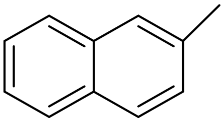
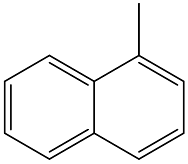
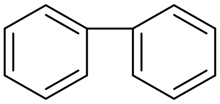
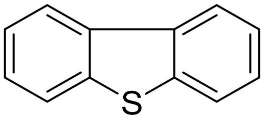


Figure 4.3.3 GC-MS chromatogram for product of the reaction of dibenzothiophene and Na in 1-methylnaphthlene at 150 °C for 22 h

Table 4.3.3 Peaks and molecular structures in GC-MS chromatogram of the product after reaction of DBT and Na in 1-methylnaphthlene

Retention Time (min)	Structure	Name	Area percentage (%)
10.41	 impurity from 1-methylnaphthlene	2-methylbenzothiophene	0.17
10.62		2-methylnaphthlene	0.98
10.83		1-methylnaphthlene	89.03
12.44		Biphenyl	0.34
21.02		DBT	8.92
38.02 and 38.404	Unidentified		0.39 and 0.17

4.3.3 Carbazole conversion with Na using decalin as a solvent

After the reaction of carbazole and Na at 150°C for 22 hours, the products were analyzed. The chromatogram (Figure 4.3.4) and list of compounds that were identified (Table 4.3.4) are reported. In Figure 4.3.4 the peak at 21.50 min is dibenzothiophene due to contamination of wash solvent for GC-MS, so it is not listed in Table 4.3.4. According to the chromatogram, at 22.07 min, we can see one benzene ring in carbazole is partially hydrogenated.

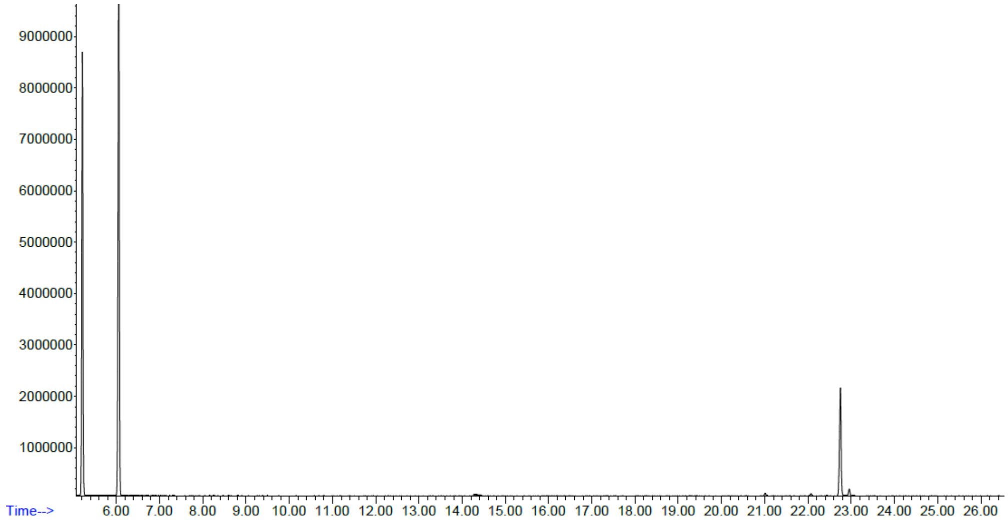
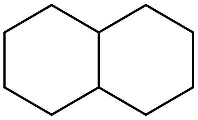
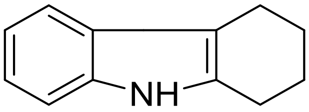
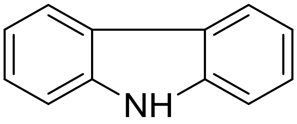


Figure 4.3.4 GC-MS chromatogram for reaction of Carbazole and Na

The peaks and structures of molecules are:

Table 4.3.4 Peaks and molecular structures in GC-MS chromatogram

Retention Time (min)	Structure	Name	Area percentage (%)
5.22 and 6.06		*Trans*- and *Cis*-Decalin	37.04 and 48.87
22.07		2,3,4,9-tetrahydrocarbazole	0.30
22.75		Carbazole	12.96
22.96	Unidentified	Possibly 1,1'-biphenyl-2-amine	0.82

About the peak at 22.96 min, mass spectrum is shown below (Figure 4.3.5):

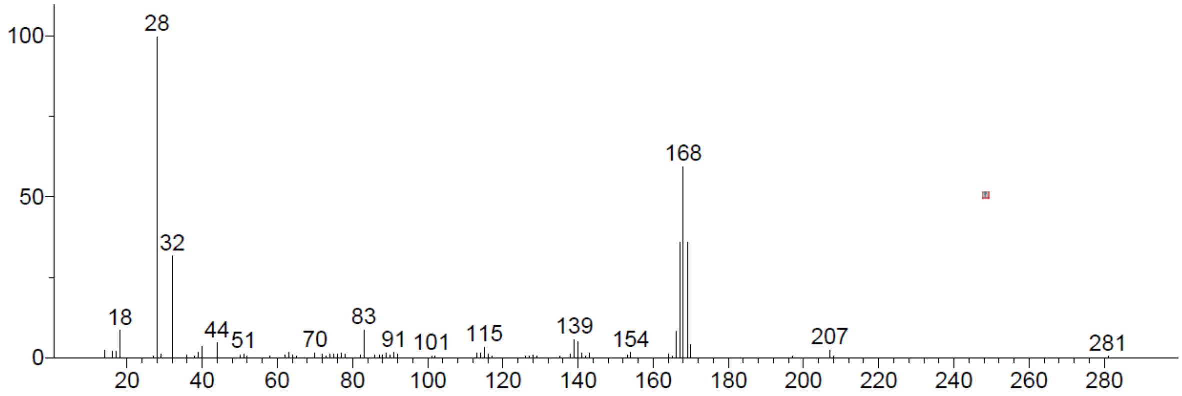
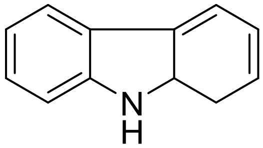
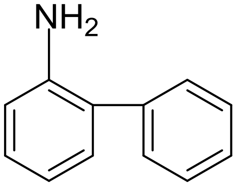


Figure 4.3.5 Mass spectrum for the compound at 22.96 min

Two possible structures were given:

a) 

b) 

In order to know which product is more possible, the FTIR spectrum of the mixture was recorded as provided below (Figure 4.3.6). A primary amine has two peaks at 3500-3400 cm^{-1}, whereas a secondary amine has one peak near 3400 cm^{-1}. As shown in the FTIR spectrum, there is only one absorption at 3450 cm^{-1}, so it is very like to be secondary amine, thus structure a) is more likely to be the compound at 22.96 min.

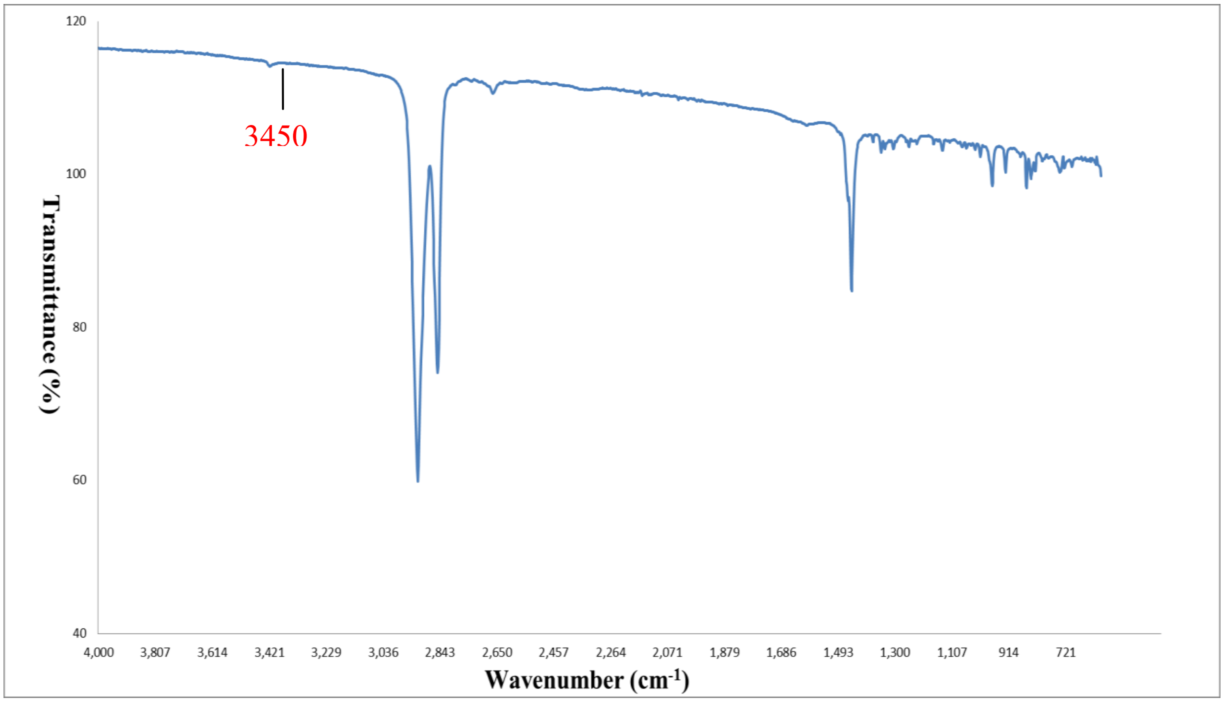


Figure 4.3.6 FTIR spectrum of product from reaction of Na and carbazole that was used to assist with the identification of the unknown product at 22.96 min

4.3.4 Dibenzyl sulfide reacted with Na using decahytronaphathalene as a solvent

The GC-MS chromatogram in Figure 4.3.5 and possible structures in Table 4.3.7 suggested C-C and C-S bond breaking.

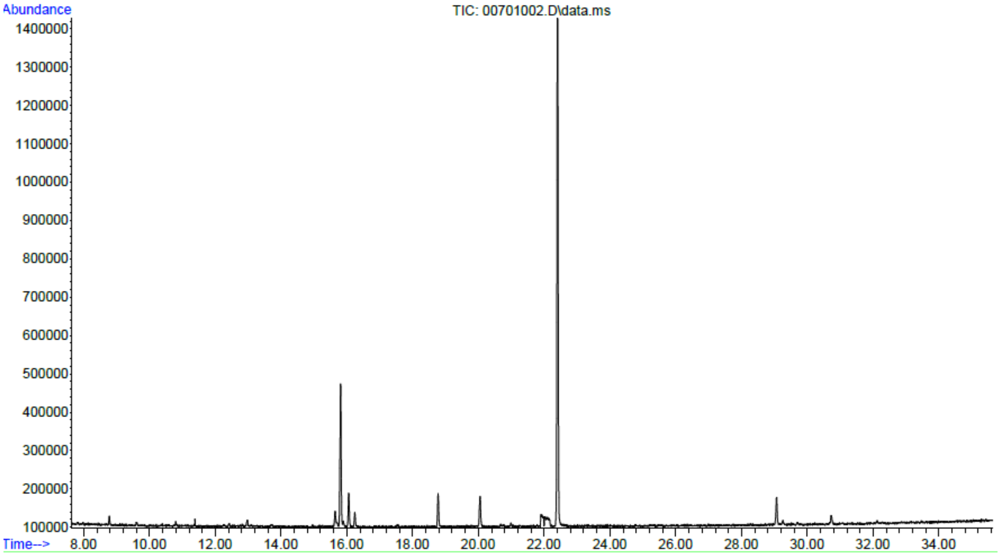
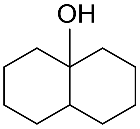
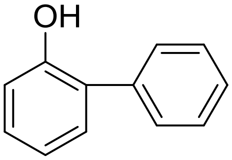
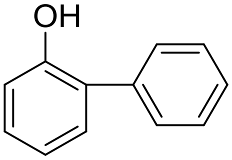
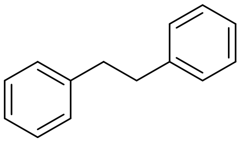
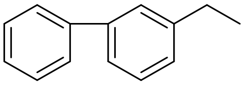
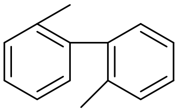
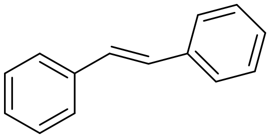
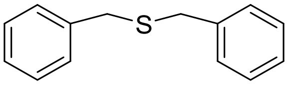


Figure 4.3.7 GC-MS chromatogram of dibenzyl sulfide reacted with Na

Table 4.3.5 Retention time and possible structures of dibenzyl sulfide reacted with Na

Retention Time (min)	Structure	Name	Area percentage (%)
8.78		1-hydroxybicyclodecane	0.90
10.81,11.39, 13.7,21.91 and 22.09	Unidentified		0.81,0.37,0.53,2.58 and 2.51
12.98		1'1'-biphenyl-2-ol isomer	0.78
15.65		1'1'-biphenyl-2-ol isomer	2.55
15.81		Bibenzyl	13.44
16.06		2-ethyl-1,1'-biphenyl	3.43
16.24		2,2'-dimethyl-biphenyl	1.55
18.78$^{(a)}$	Unidentified		3.70
20.05		Stilbene	3.56

22.41		Dibenzyl sulfide	57.98
29.08 and 29.26	Unidentified*		3.18 and 0.73
30.73	Unidentified*		1.40

*unidentified molecule structure may be addition products with high molecular weight.

(a) The structure at 18.78 min and also showed up later on in benzyl phenyl sulfide was a possible structure. The mass spectrum was shown below:

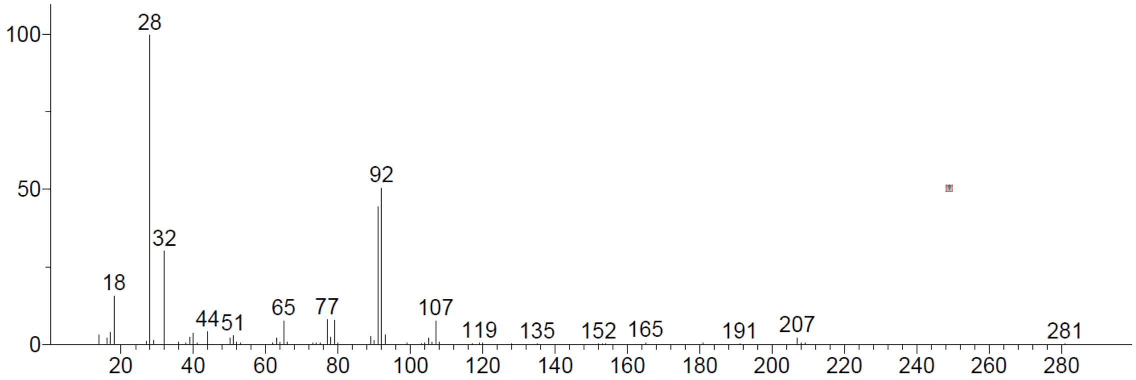


Figure 4.3.8 Mass spectrum for the product at 18.78 min

At 20.05 min there is a double bond where the sulfur used to be, so Na may have eliminated the S from dibenzyl sulfide, followed by radical recombination. But at 16.03 and 16.24 min, there shows the rearranged product that may result from the C-C bond breaking (if the isomers were correctly identified).

4.3.5 Diphenyl sulfide reacted with Na using decahytronaphathalene as a solvent

After the reaction of diphenyl sulfide and Na at 150°C for 22 hours, the products were analyzed. The chromatogram (Figure 4.3.9) and list of compounds that were identified (Table 4.3.6) are shown here.

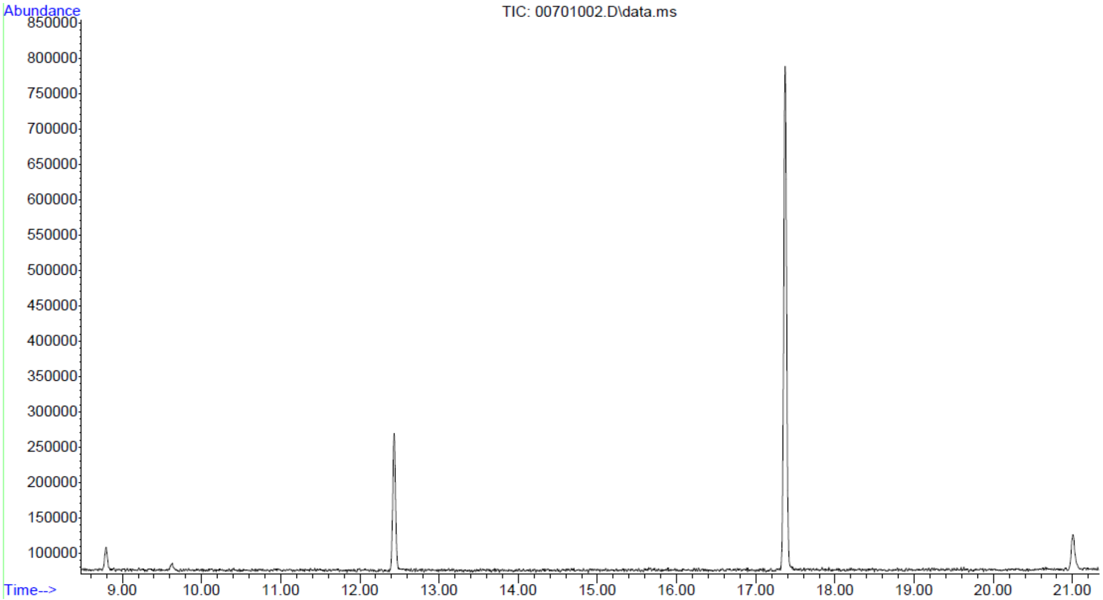
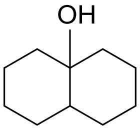
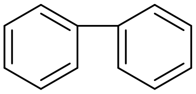
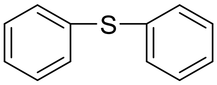
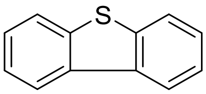


Figure 4.3.9 GC-MS chromatogram of diphenyl sulfide reacted with Na

Table 4.3.6 Retention time and possible structures of diphenyl sulfide reacted with Na

Retention Time (min)	Structure	Name	Area percentage (%)
8.80		1-hydroxybicyclodecane	3.94
9.64	Unidentified		2.14
12.43		Biphenyl	19.11
17.37		diphenyl sulfide	68.39
21.01		DBT	6.42

Na may directly attack the sulfur in diphenyl sulfide and extruded it, thus forming biphenyl at 12.43 min shown in Figure 4.3.9. But different from dibenzyl sulfide, there is also C-C bond formed between the two rings at 21.01 min.

4.3.6 Dibenzyl ether reacts with Na using decahytronaphathalene as a solvent

In Figure 4.3.10 and Table 4.3.7, at 18.78 min was the rectant dibenzyl ether, at 19.95 min was hydrogen added on to the oxygen, and then at 20.05 was a double bond replaced the –OH group. Dibenzyl ether did have oxygen removed after adding hydrogen onto oxygen first.

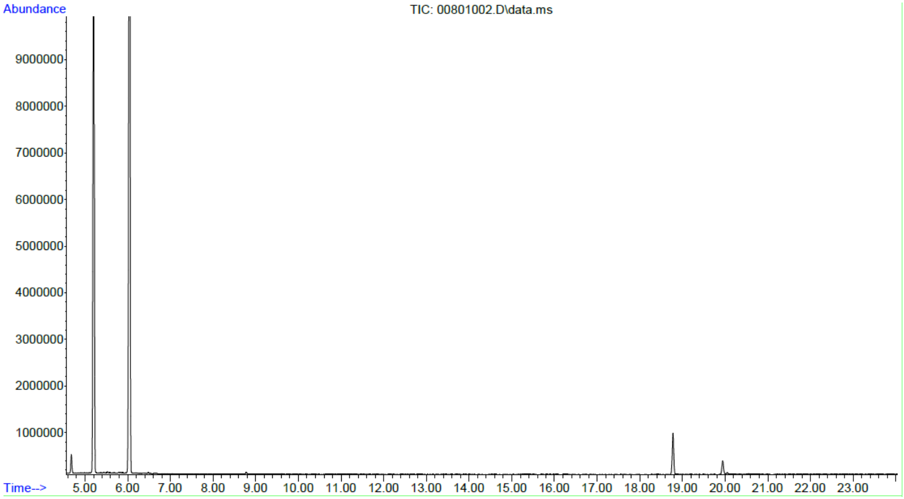
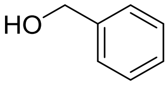
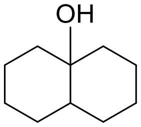
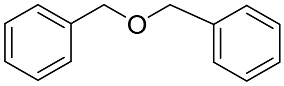
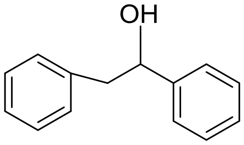
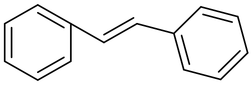


Figure 4.3.10 GC-MS chromatogram of dibenzyl ether reacted with Na

Table 4.3.7 Retention time and possible structures of dibenzyl ether reacted with Na

Retention Time (min)	Structure	Name	Area percentage (%)
4.69		Benzyl alcohol	17.68
8.79		1-hydroxybicyclodecane	2.88
18.78		Dibenzyl ether	55.52
19.95		2-diphenyl ethanol	20.48
20.05		Stilbene	3.43

4.3.7 Diphenyl ether reacts with Na using decahytronaphathalene as a solvent

After the reaction of diphenyl ether and Na at 150°C for 22 hours, the products were analyzed. The chromatogram (Figure 4.3.11) and list of compounds that were identified (Table 4.3.8) are shown here.

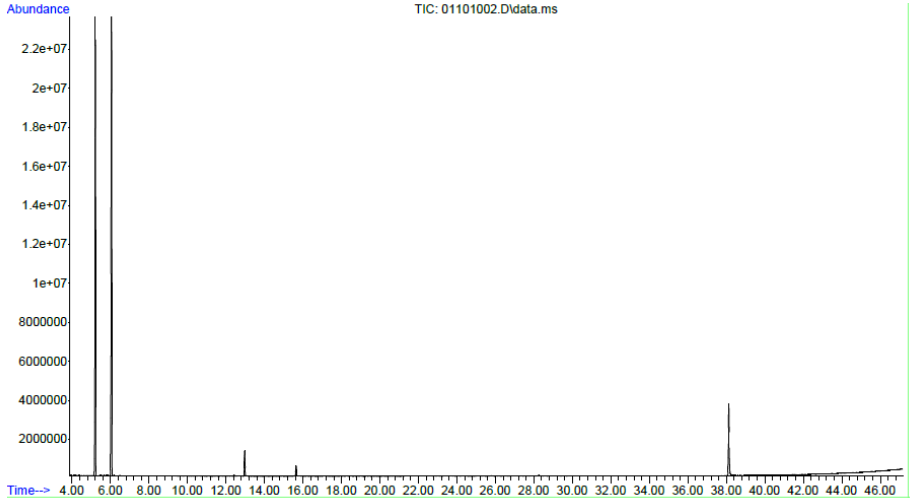
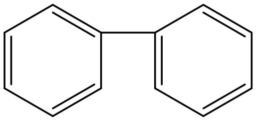
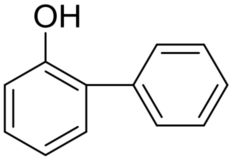
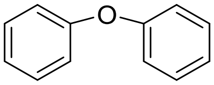
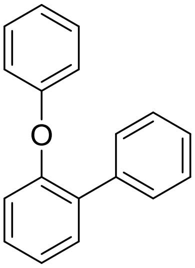
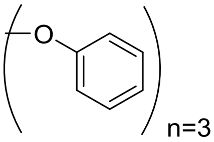
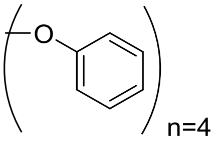


Figure 4.3.11 GC-MS chromatogram of diphenyl ether reacted with Na

Table 4.3.8 Retention time and possible structures of diphenyl ether reacted with Na

Retention Time (min)	Structure	Name	Area percentage (%)
12.41		Biphenyl	1.35
12.97		1’1’-biphenyl-2-ol	19.78
15.69		Diphenyl ether	9.29
25.81		2-biphenyl-phenyl ether	0.68
28.26		Polyphenyl ether	1.33
38.13		Polyphenyl ether	67.57

From the chromatogram in Figure 4.3.11 and Table 4.3.8, we can see at 12.41 min biphenyl was a product, at 25.81 min, 28.26 min and 38.13 min, there are more rings connected together inserted of just two rings in the reactant diphenyl ether.

4.3.8 Benzyl phenyl sulfide reacted with Na using decalin under different reaction time

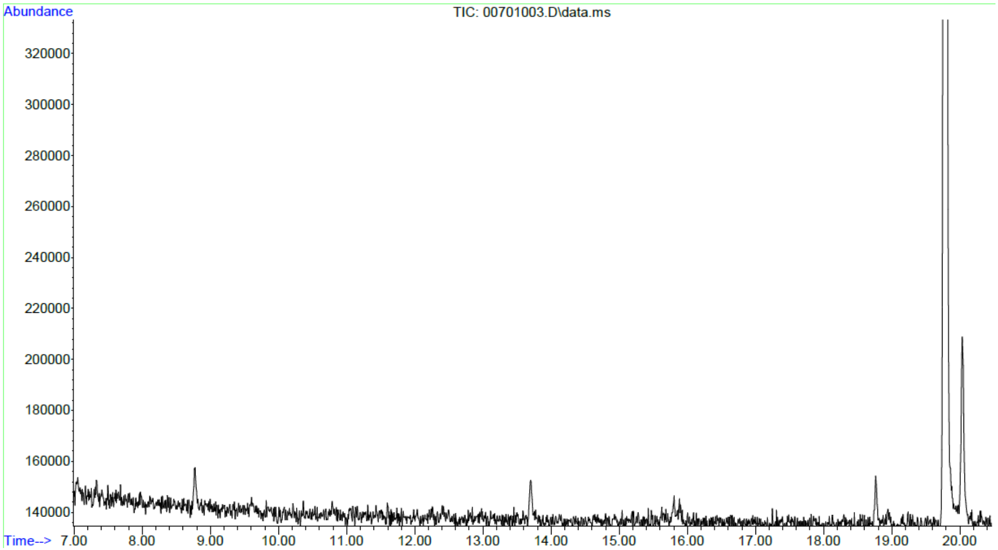
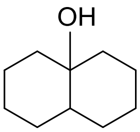
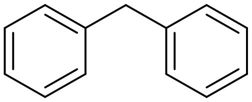
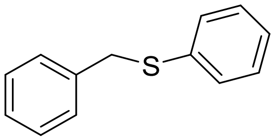
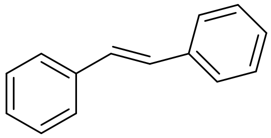


Figure 4.3.12 GC-MS chromatogram of benzyl phenyl sulfide reacted with Na for 1h

Table 4.3.9 Retention time and possible structures of benzyl phenyl sulfide reacted with Na for 1h

Retention Time (min)	Structure	Name	Area percentage (%)
8.78		1-hydroxybicyclodecane	0.93
13.71		Diphenylmethane	1.33
18.77	Unidentified		0.92
19.80		Benzyl phenyl sulfide	92.97
20.06		Stilbene	3.85

After benzyl phenyl sulfide and Na reacted for 1h, there was no biphenyl produced, but there was sulfur extrusion as shown in Figure 4.3.12 at 13.71min. Hydrogenation might happen as well, the chemical structure at 18.77min may have one hydrogenated ring. As to the compound at 20.06min, it may due to the opening of C-C bond on the side chain and two benzyl rings formed a double bond.

The experiment was repeated at longer residence times, 3 h and 6 h respectively, to better study the products formed during the reaction.

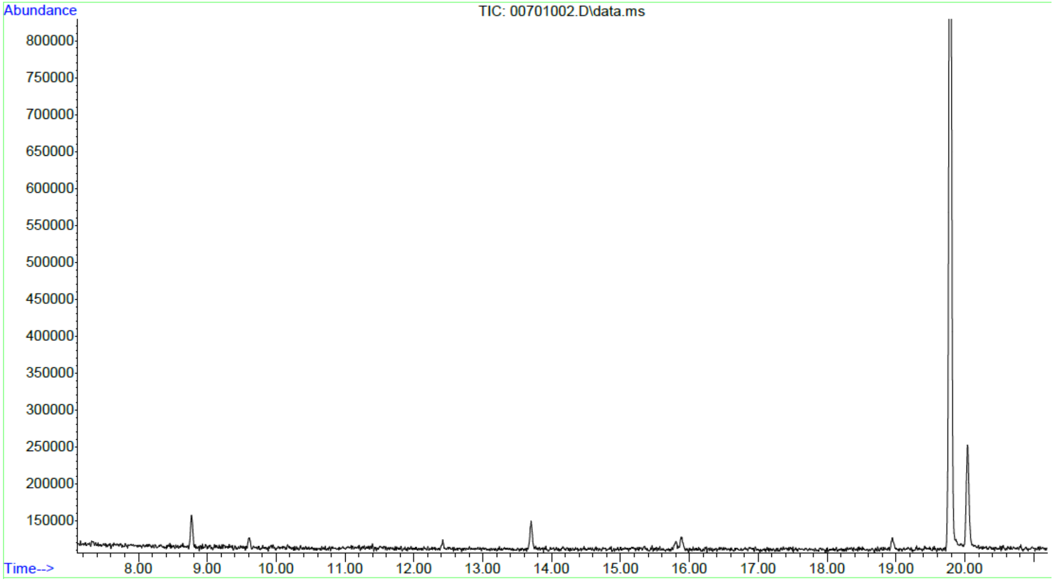
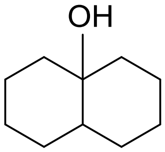
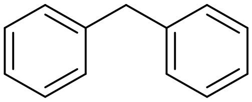
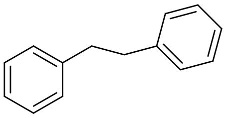
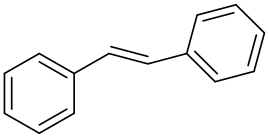
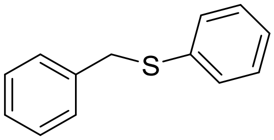
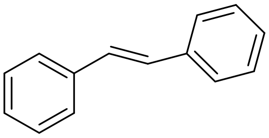


Figure 4.3.13 GC-MS chromatogram of benzyl phenyl sulfide reacted with Na for 3h

Table 4.3.10 Retention time and possible structures of benzyl phenyl sulfide reacted with Na for 3h

Retention Time (min)	Structure	Name	Area percentage (%)
8.75		1-hydroxybicyclodecane	2.85
9.64,12.38 and 18.96	Unidentified		1.04, 0.69 and 1.51
13.70		Diphenylmethane	2.46
15.80		Bibenzyl	0.93
15.88		Stilbene	1.50
19.81		benzyl phenyl sulfide	79.03
20.04	 isomer 2	Stilbene	9.98

Compared to 1h reaction of benzyl phenyl sulfide and Na, 3h reaction has same products. But still no biphenyl produced. The compound at 20.06min, it may due to the opening of C-C bond on the side chain and two benzyl rings formed a double bond. At 15.80 min, the double bond on between two rings is hydrogenated.

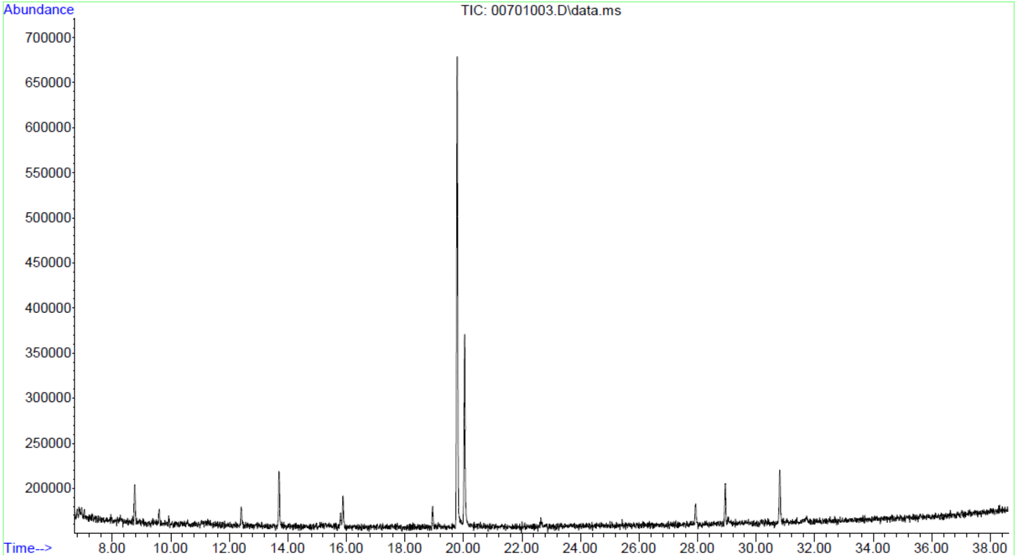
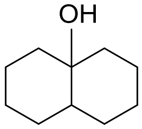
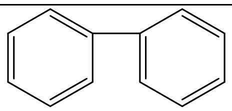
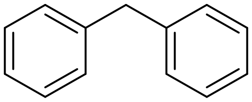
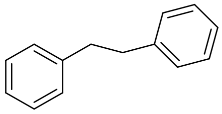
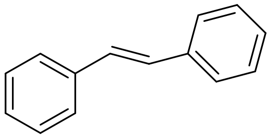
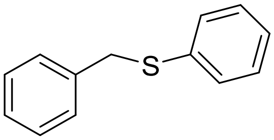
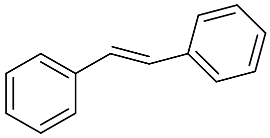
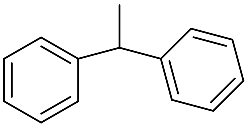
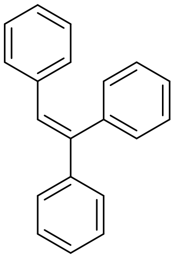
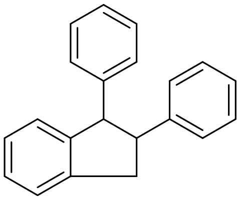


Figure 4.3.14 GC-MS chromatogram of benzyl phenyl sulfide reacted with Na for 6h

Table 4.3.11 Retention time and possible structures of benzyl phenyl sulfide reacted with Na for 6h

Retention Time (min)	Structure	Name	Area percentage (%)
8.78		1-hydroxybicyclodecane	3.45
9.59, 9.64 and 22.64	Unidentified		1.68, 0.32 and 1.54
12.41		Biphenyl	2.12

13.70		Diphenylmethane	6.11
15.80		Bibenzyl	2.01
15.88		Stilbene	3.23
18.95	Unidentified		2.38
19.81		benzyl phenyl sulfide	41.71
20.04	 isomer 2	Stibene	20.55
27.91		1,1-diphenylethane	3.67
28.95		1,1',1"-(1-ethenyl-2-ylidene)*tris*- benzene	4.19
30.81		1,2-diphenylindan	7.04

After increasing the reaction time to 6h, there started to be biphenyl produced which is different from 1 and 3h reaction time. Other than that, according to Figure 4.3.14 and Table 4.3.11, some addition products appeared as well at 27.91 and 30.81min. This suggested longer reaction time may lead to higher percentage of addition reactions. At 15.80 min, the double bond between two rings was hydrogenated.

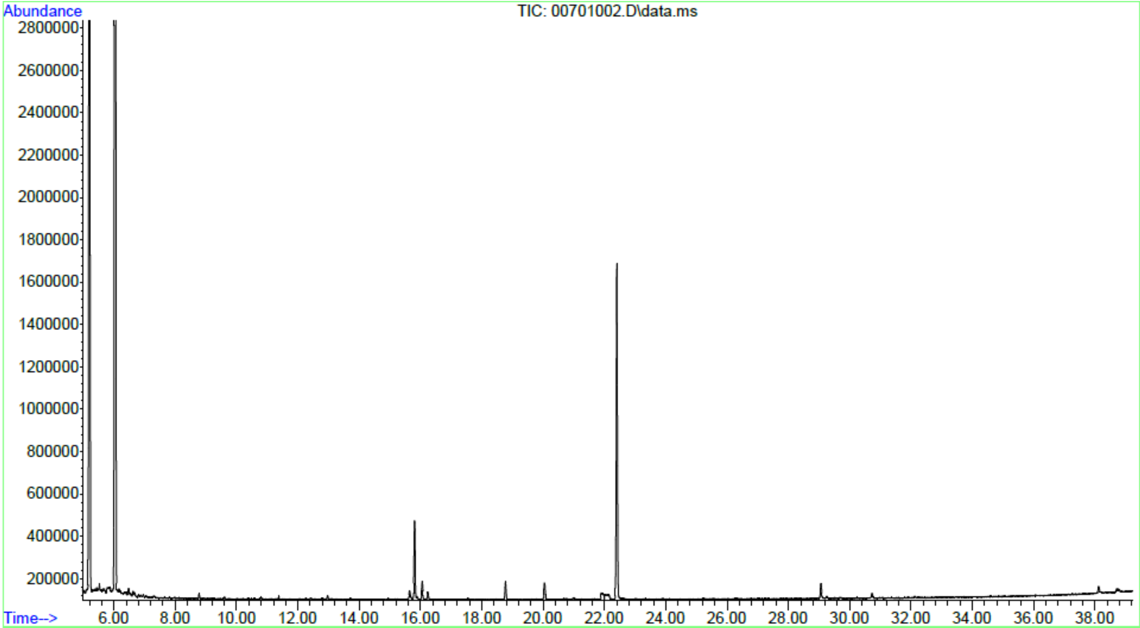
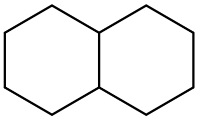
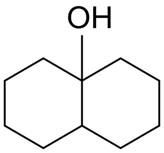
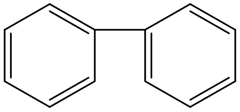
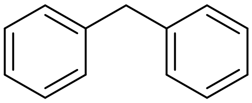
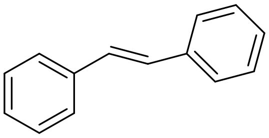
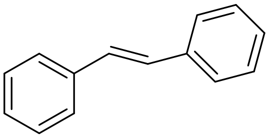
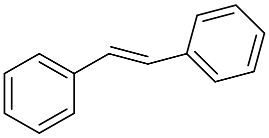
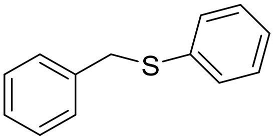
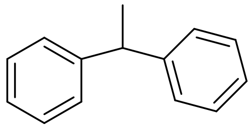
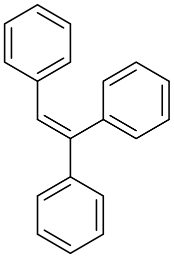
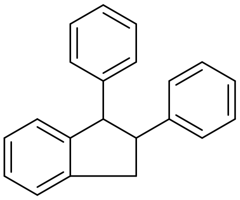


Figure 4.3.15 GC-MS chromatogram of benzyl phenyl sulfide reacted with Na for 22h

Table 4.3.12 Retention time and possible structures of benzyl phenyl sulfide reacted with Na for 22h

Retention Time (min)	Structure	Name	Area percentage (%)
5.22 and 6.06		*Trans*- and *Cis*-Decalin	44.25 48.37

8.78		1-hydroxybicyclodecane	0.07
9.61,10.81, 11.39 and 21.91	Unidentified		0.04, 0.06, 0.03 and 0.21
12.42		Biphenyl	0.05
13.73		Diphenylmethane	0.06
15.82		Stilbene	1.08
15.90	 isomer2	Stilbene	0.07
18.95	Unidentified		
20.08	 isomer3	Stilbene	0.29
22.42		benzyl phenyl sulfide	4.64

27.96		1,1-diphenylethane	0.05
28.95		1,1',1"-(1-ethenyl-2-ylidene)*tris*- benzene	0.26
29.26	Unidentified		0.06
30.81		1,2-diphenylindan	0.11

As expected, more addition reaction products were produced after 22h reaction. In Figure 4.3.15 and Table 4.3.12, we see after 27.96 min, more addition products with two or three rings formed.

4.3.9 Dibenzofuran reacted with Na using decalin as a solvent

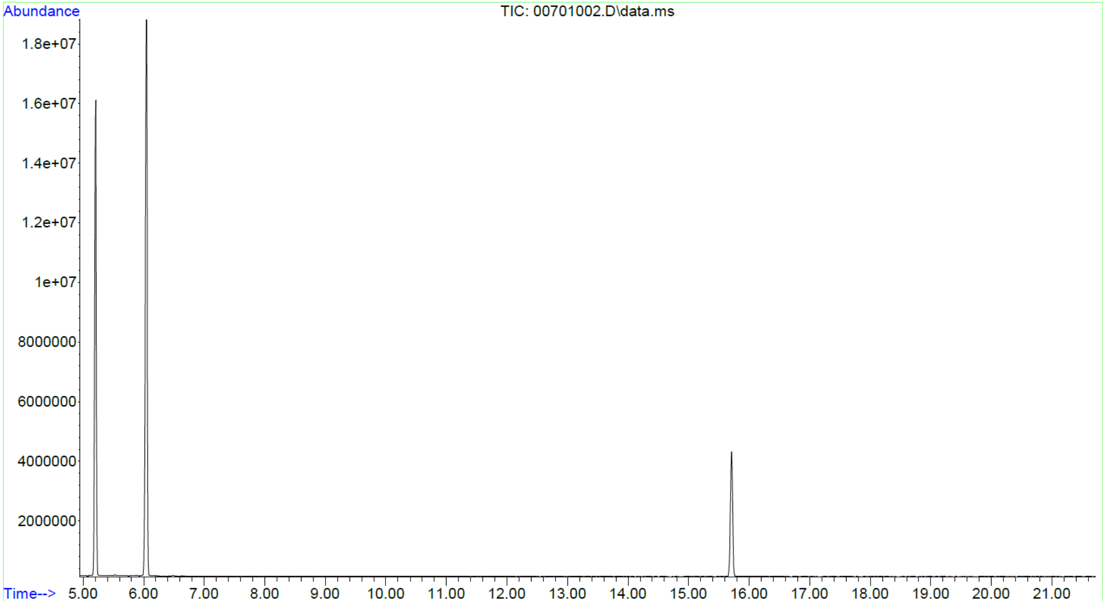


Figure 4.3.16 GC-MS chromatogram for reaction of dibenzofuran and Na

Since oxygen is also a heated topic in heteroatoms extrusion, dibenzofuran is selected to study if Na has an influence on removal of oxygen.

It is the same mole ratio as DBT reacts with Na under the same condition, that is, 150°C for 22 hours. After the reaction, the product was injected into GC-MS to identify the resulted chemical structures.

4.4 Discussions

4.4.1 Dibenzothiophene (DBT) reacted with Na using decahytronaphathalene as a solvent

Based on the different products, we can suspect reaction of dibenzothiophene with Na may consist of two pathways. The proposed pathways are shown here:

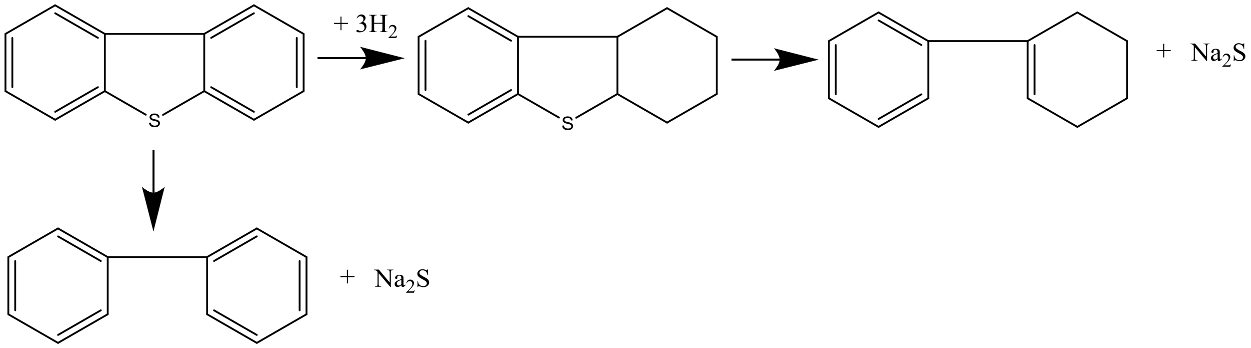


Figure 4.3.17 Possible two pathways of DBT reacting with Na

This is corresponding to how catalysts work for sulfur removal, which is also though two pathways: direct catalytic removal of the sulfur atom in a single step, and hydrogenation of the attached aromatic rings, followed by attack on the sulfur. The mechanism for the interaction of the sulfur compounds, dibenzothiophene, with the catalyst is illustrated in Figure 4.3.15.

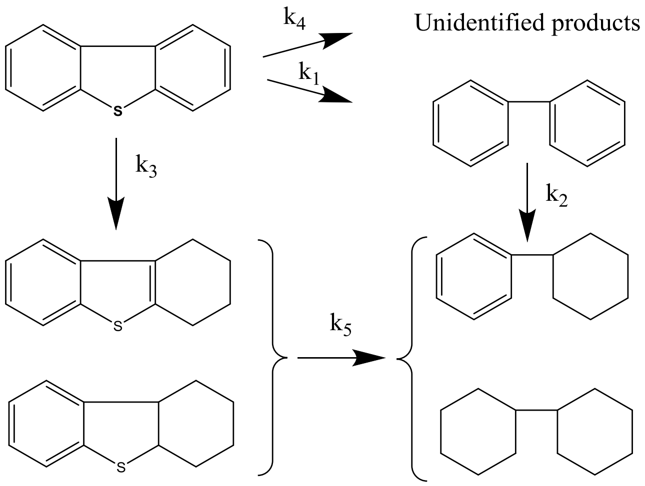


Figure 4.3.18 Hydrogenation of Dibenzothiophene [4, 5]

During heterogeneously catalyzed hydrotreating hydrogen gas can chemisorb on the Ni-Mo sulfide surface for hydrogenation of aromatic rings, hydrogenolysis of carbon-sulfur bonds, or for reaction with surface sulfur. When hydrogen sulfide is released, the left vacancy can strongly adsorb the organic sulfur in compounds such as DBT. Thus the sulfur on the metal-sulfide surface is an integral part of the activity of the catalyst, and accounts for the high selectivity of these catalysts for sulfur compounds [5].

Actually hydrodesulfurization is the most commonly used method in the petroleum industry to reduce the sulfur content of crude oil. In most cases HDS is performed by co-feeding oil and H_2 to a fixed-bed reactor packed with an appropriate HDS catalyst.

As illustrated above, since there are two pathways with catalysts, then it does make sense to have two pathways for Na conversion of asphaltenes.

4.4.2 Carbazole reacted with Na using decalin as a solvent

In order to see if Na also has a similar reaction with heterocyclic nitrogen followed by nitrogen extrusion at mild temperature, cabazole was selected as model compound to react with Na, because it is similar in structure with dibenzothiophene except sulfur is replaced with nitrogen.

No extrusion of nitrogen was seen. The partially hydrogenated benzene ring and nitrogen group does imply two pathways similar to Na conversion of dibenzothiophene.

4.4.3 Dibenzothiophene reacted with Na using 1-methylnphathalene as a solvent

We have known under decahytronaphathalene, DBT will react with Na resulting sulfur removal. In earlier studies, a large amount of research work has been reported on the formation of aromatic hydrocarbon anions and these anions are formed when aromatic hydrocarbons, dissolved in a suitable solvent, are treated with alkali metals. [9, 10, 11] But whether decalin is the only suitable solvent for Na conversion or not needs further comparison with other solvents. From the GC-MS chromatogram, there is biphenyl produced. It is speculated that Na can directly attach dibenzothiophene without reacting with the solvent first.

4.4.4 Dibenzyl sulfide reacted with Na using decahytronaphathalene as a solvent

The GC-MS chromatogram suggested C-C and C-S bond breaking. A double bond was present where the sulfur used to be and sulfur was gone, Na may extrude the S from dibenzyl sulfide, and then hydrogenation can happened with H provided by decalin forming single bond. But at 16.03 and 16.26min rearrangement products were found that may result from the C-C bond breaking.

4.4.5 Diphenyl sulfide reacted with Na using decahytronaphathalene as a solvent

Na may directly attack the sulfur in diphenyl sulfide and extruded it, thus forming biphenyl. But different from dibenzyl sulfide, there is also C-C bond formed between the two rings, which may need to take into consideration during desulfurization because it also formed DBT, Na did not attack the sulfur but instead formed C-C bond, which may increase the amount of Na should be added.

4.4.6 Dibenzyl ether reacts with Na using decahytronaphathalene as a solvent

Dibenzyl ether did have oxygen removed after adding hydrogen onto oxygen first, Na opened the C-O bond, then one hydrogen was added to oxygen, and the C-C bond was formed on the chain, and a –OH. Later on, the –OH came out as a H_2O and formed a double bond.

4.4.7 Diphenyl ether reacts with Na using decahytronaphathalene as a solvent

Diphenyl ether reacted with Na and procuced biphenyl, which means there was deoxygenation that happened. But at the same time, some some addition reactions also happened. This is quite different from dibenzyl ether, which did not have addition reactions observed, which may due to different mechanisms. If Na cut the C-O bond in diphenyl ether, then it is easy to form a stable chain, whereas for dibenzyl ether, if the C-O bond was broken, there is still a $-CH_2$ between benzyl ring and oxygen, then it is not a π system if a chain is formed so the chain will not be as stable.

4.4.8 Benzyl phenyl sulfide reacted with Na using decalin under different reaction time

After benzyl phenyl sulfide and Na reacted for 1h, there was no biphenyl produced, but there was sulfur extrusion from direct sulfur removal. 3h reaction has mostly the same products but still no biphenyl produced, but there is hydrogenation of the double bond between two rings. Only after increasing the reaction time to 6h, there started to be biphenyl produced which is different from 1 and 3h reaction time. Other than that, some addition reactions also happened. This suggested longer reaction time may lead to higher percentage of addition reactions. As a result, more addition reaction products were produced after 22h reaction other than sulfur removal and hydrogenation. Moreover, there are biphenyl produced at 22h, which means the sulfur and two carbons was removed between the two rings.

4.4.9 Dibenzofuran reacted with Na using decalin as a solvent

Different form dibenzothiophene or carbazole, there is not biphenyl produced as indicated in chromatogram. Only decalin and dibenzofuran peaks were shown. Dibenzofuran did not react with Na to remove oxygen in it.

This phenomenon made us think about reactions of DBT and Na again. Difference between DBT and dibenzofuran is the difference of O and S. Oxygen has a higher electron withdraw ability than sulfur so if radicals are present oxygen will attract the radical preventing the hydrogenation, and O^- is very stable with two benzene rings connected so no further deoxygenation happened in the process. That is why chemicals with oxygen are often used as radical traps [12].

4.5 Conclusions

Reactions of Na with dibenzothiophene, carbazole using decalin or 1-methylnaphthalene help us to understand desulfurization process happened in Na conversion of asphaltene. In asphaltene, since there are a lot of aromatics, which may increase difficulties to remove sulfur.

Na can give an electron easily that helps delocalized the aromatics connected with sulfur. Then hydrogen will be easily attached to aromatics by hydrogen transfer, promoting hydrogenation. At the same time, Na can get access to the sulfur directly and extrude the sulfur out of aromatic system.

As to denitrogenation, Na did not have a noticeable influence on nitrogen removal. But carbazlole was partly hydrogenated by Na. No further nitrogen extrusion was observed.

For the solvent selection, 1-methylnaphthalene facilitated with desulfurization as well as decahydronaphthalene.

As to dibenzofuran, the reactions did not work very well. This may due oxygen that has a higher electron withdraw ability than sulfur.

After comparing dibenzyl sulfide and diphenyl sulfide, there were not only desulfurization but also C-C bond that were broken and rearrangements for Na conversion of dibenzyl sulfide, whereas no rearrangement to dipheynyl sulfide but desulfurization and DBT formed during the reaction. For dibenzyl ether, we see the –OH group at one benzne ring in a way that the –OH group came out as H_2O leaving a double bond between two rings. But for diphenyl ether, we did not see an oxygen removal, but more addition reactions happened so that heavier products were formed.

After running reaction of benzyl phenyl sulfide with Na for 1, 3, 6 and 22 hours, disulfurzition appeared quickly at 1h but more C-C bond broken after 6h, more addition reaction occurred. But at the same time of desulfurization, hydrogenation also happened, not only on the aromatic ring, but also the double bond after sulfur is removed in between the two aromatic rings. This may be because addition reaction needs molecules move to each other and form higher aromatic addiction products and this required longer time.

In summary, Na can help with the heteroatoms removal under nitrogen; especially with sulfur it has a good effect. With nitrogen, Na did not show nitrogen removal with carbazole. As to deoxygenation, no effect on removing oxygen in dibenzofuran or diphenyl ether but oxygen was removed from dibenzyl ether as water.

References

[1] Weisser, O.; Landa, S. Sulphide Catalysts :Their Properties and Applications. *Pergamon press*, New York **1973**

[2] Javadli, R.; Arno, d. K. Desulfurization of heavy oil. *Appl. Petrochem. Res.* **2012,** 1:3-

19.

[3] Agarwal, P.; Sharma, D. K. Comparative studies on the biodesulfurization of crude oil with other desulfurization techniques and deep desulfurization through integrated processes. *Energy Fuels* **2010,** 24:518-524.

[4] Sundaram, K. M.; Katzer, J. R.; Bischoff, K. B. Modeling of hydroprocessing reactions. *Chem. Eng. Comm*. **1988,** 71: 53-71.

[5] Gary, M. Upgrading Oilsands Bitumen and Heavy Oil .*U of Alberta Press,* Edmonton **2015.**

[6] Zachariah, A. Low Temperature Pyrolysis and its Application in Bitumen Processing, MSc thesis, *U of Alberta Press,* Edmonton, Agust **2014.**

[7] Adschiri, T.; Shibata, R.; Sato, T; Watanabe, M; Arai, K. Catalytic hydrodesulphurization of dibenzothiophene through partial oxidation and a water-gas shift reaction in supercritical water. *Ind Eng Chem Res* **1998**, 37:2634-2638.

[8] Edward, F. Hydrodenitrogenation of petroleum. *Catalysis Reviews-Science and Engineering* **2005**, 47, (3):297-489.

[9] De Boer, E. Electronic structure of alkali metal adducts of aromatic hydrocarbons. *Adv. Organomet. Chem. 2* **1964**, 115-155.

[10] Sternberg, H. W. ; Delle Donne, C. L. ; Pantages, P. ; Moroni, E. C. ; Markby, R. E. Solubilization of an lvb coal by reductive alkylation. *Fuel* **1971**, 50:432-442.

[11] Gilman, H.; Van Ess, M. W.; Wills, H. B.; Stuckwsch, C. G. The Metalation **of** Phenoxathiin. *J A.Chem.Sci.***1940**, 62:2606-2611.

[12] Donald, L. E. Some comparisons of dibenzofuran and dibenzothiophene types, PHD Thesis*, Iowa State University,* Ames **1951.**

CHAPTER 5 – Sodium conversion of model compounds with hydrogen

Abstract

In this chapter various aliphatic model compounds were reacted with Na under hydrogen atmosphere to study the behavior of hydrogen during Na conversion of asphaltenes. A few different model molecules, dibenzothiophene, carbazole, dibenzofuran and anthracene were chosen for the investigation. After Na was added into the model molecules with decalin, under hydrogen environment, the mixtures were heated to 150°C followed by GC-MS and GC-FID analysis. After qualification, only certain model compounds were hydrogenated or some heteroatoms were removed. Additionally the conversion of each successfully heteroatoms extrusion reaction was calculated and compared within all the chosen molecules.

Keywords: model compounds, hydrogenation, Na conversion, extrusion of heteroatoms

5.1 Introduction

In 1944 Arthur Birch reported that sodium in liquid-ammonia in the presence or absence of available hydrogen from alcohols, shows very different reducing properties and the former combination is capable of reducing a number of methoxyalkylbenzenes and alkylbenzenes [1]. As shown in Figure 5.1, alkali metals can dissolve in liquid ammonia and become powerful reducing agents [2].

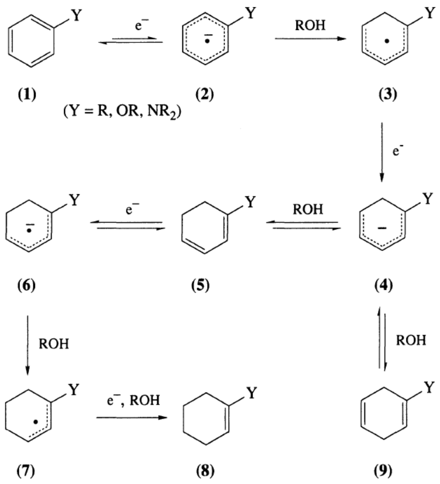


Figure 5.1.1 Alkali metal reduction of aromatics [2]

In Birch reduction, the majority of reductions are performed in presence of proton donors. Alcohols are mostly selected for this purpose in organic synthesis. These donors can protonate the intermediate anion radicals and thus cut down on undesirable side reactions, such as dimerization of the radical anion and polymerization [3].

This made us to think, if instead of using alcohol, we can use other aromatic or cyclic compounds that may also be similar to the environment in oil sands bitumen, for example, 1-methyl naphthalene or decahydronaphthalene (decalin), and H_2 as hydrogen source to compare with the conversion conducted under N_2 atmosphere in Chapter 4.

The desulfurization of residual oil with Na under H_2 was reported [4]. It was found that desulfurization of residual oil at longer reaction times is more effective in the presence of H_2 than in the absence of H_2. This may because that residual oil do not have as much transferable hydrogen in the liquid phase as when decalin is employed as solvent. Hence, the oil itself cannot provide the hydrogen required for hydrogenolysis of adduct II shown in Figure 5.2 as readily as it can be provided by decalin [4].

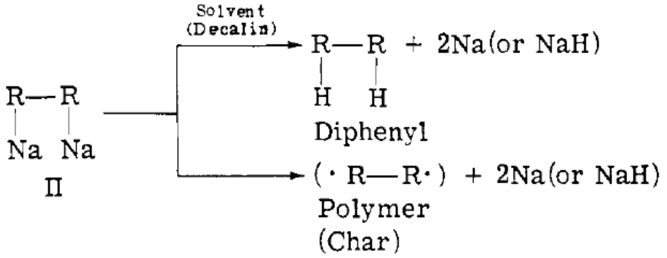


Figure 5.1.2 Mechanism of desulfurization using Na [4]

The earlier hypotheses attribute the hydrogen reduction of unsaturated rings to “nascent” hydrogen that is liberated by the reaction between the alkali metal and the hydrolytic solvent. In general, this hypothesis required that the actual reduction must be carried out by the combination of a hydrolytic solvent and the alkali metal. This is now known not to be the case and in the more recent descriptions of the mechanism the actual reduction is attributed to the alkali metal alone. The primary reduction process is described in terms of the addition of the alkali metal to the aromatic. It is considered that the function of the solvent is merely to replace the metal in the addition compound with hydrogen by a hydrolytic process and that direct reaction between the solvent and the free alkali metal is a side reaction [5]. Irrespective, the solvent still plays a role to satisfy the stoichiometry of the overall reaction.

5.2 Experimental

5.2.1 Materials

The model compounds employed in the investigation were dibenzothiophene (98% purity), carbazole (98% purity), dibenzofuran (98%), and anthracene (98%), which were purchased from Sigma Aldrich. These materials were all tricyclic aromatics and represented the S, N and O containing heterocycles, as well as a hydrocarbon without any heteroatom. Hydrogen gas (>99.95%) and nitrogen gas (>99.998%) were purchased from Praxair Canada. Sodium sticks were purchased from Alfa Aesar (99%, in mineral oil).

5.2.2 Equipment and procedure

All masses were weighed on a Mettler Toledo New Classic MF ML3002E, maximum mass limit 3200g, 0.01g precision.

Initial experiments with the different model compounds were performed mainly to identify the reaction products from reaction with Na at 150°C and 0.86 MPa hydrogen pressure. Subsequent experiments were performed in triplicate to quantify the products that were identified.

Experiments were performed using microbatch reactors. Generally speaking the setup of the reactors were the same as the setup described in Chapter 3 except that the reactors were heated in oil bath and that the oil bath was on a heating plate.

The microbatch reactors were constructed using Swagelok 1/4 inch, 0.035 inch wall 316 stainless steel tubing and fittings. The reactor was heated in an oil bath in a 250 mL flask. The temperature inside the reactor was monitored with a K-type, 1/16" diameter, 36" length, 316SS internal thermocouple, inside a 1/4 inch, 0.035 inch wall stainless steel sleeve and indirectly controlled by adjusting the temperature of the heating plate to heat up oil bath.

For each experiment the reactor was filled with 0.8g-1.0 g model compound. The Na was cut in mineral oil exposed to air and 0.50-0.65 g Na was added into the reactor. Solvent decalin was then added to achieve a molar ratio of the model compound, Na, and decalin of around 1:2.2:16.2. Then reactors were purged and leak tested with nitrogen at a pressure of 3.5MPa. Before the reactions were started, the reactors were purged and pressurized with hydrogen to a pressure of 0.86 MPa. The reactors were weighed before and after adding H_2, and then the weight gas added in was 0.07g-0.09g. This is due to N_2 was not fully eliminated. The oil bath is heated to the appropriate temperature for the experiment, and after it reached desired temperature, the reactors were put in to oil bath at same time. Each run lasted for 22 hours after the required temperature

150°C was reached, which took about 4-5min. After experiments were completed the reactors were cooled down with blowing air.

It is observed that after taking reactors out of oil bath, some oil will stick on to reactor walls. The reactors were cleared of oil, before releasing gas and each reactor was weighed. The reactor was then depressurized. The light gases produced during the reaction and on depressurization were collected in a gas bag, but was too little to obtain reasonable quantification. Each reactor was weighed again. All products were removed from the reactor and the reactor was weighed again to confirm that all products were removed. No smell of H_2S or NH_3 was observed in the gaseous product after reaction.

The experiments with H_2 used the same reactors as in Chapter 3 and the work flow is shown below in Figure 5.2.1.

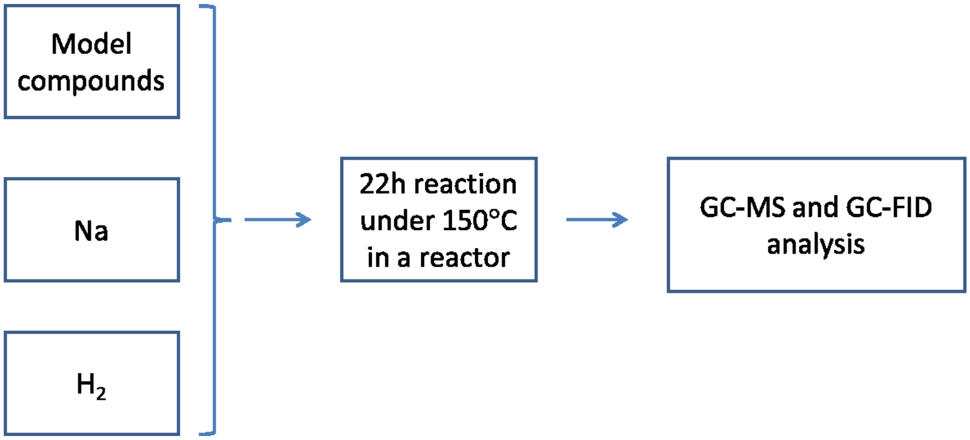


Figure 5.2.1 Experiments work flow for model compounds experiments with H_2

5.2.3 Analyses

The reaction products from the model compounds experiments were identified using an Agilent 7890 GC with 5975C mass selective detector (GC-MS). Quantification was performed using an

Agilent Technologies 7890A gas chromatograph with flame ionization detector (GC-FID). The identification and quantification methods were the same as in Chapter 4.

5.3 Results

5.3.1 Reaction of dibenzothiophene with Na and H_2

The dibenzothiophene and Na in decalin mixture were allowed to react for 22 hours at 150 °C. under H_2 atmosphere. The chromatogram of the product mixture showed only four compounds, *cis*- and *trans*-decalin (solvent), biphenyl at 12.45 min retention time and dibenzothiophene at 21.04 min retention time. The conversion of dibenzothiophene to biphenyl was 1.7 % (Table 5.3.1) and this calculation took the GC-FID response factors into account that were determined in Chapter 4 (Table 4.2.2).

Table 5.3.1 Conversion of DBT with Na under hydrogen

DBT (g)	Na (g)	Conversion	Average conversion
0.81	0.22	1.7%	1.67%
0.80	0.22	1.6%	
0.80	0.22	1.7%	

*No significant conversion of solvent was observed.

During the reactions, the pressure did not have any observed change and the final pressure of reactor before depressurizing was 0.86 MPa. No heavier products were formed. There were some white precipitates formed after cooled down. One concern was that it could have been polymers that formed during free radical reactions.

CHNS analysis was done to analyse the precipitates and results are shown in Table 5.3.2.

Table 5.3.2 Elemental analysis for the precipitate from DBT reacted with Na

Wt% Elements	Wt% C	Wt% N	Wt% H	Wt% S
Run 1	78.49	0.00	4.65	17.13
Run 2	78.46	0.00	4.64	17.09
Run 3	78.38	0.00	4.68	16.99
Run 4	78.08	0.00	4.63	16.94
Average	78.36	0.00	4.65	17.04
Standard deviation	0.18	0.00	0.02	0.09

According to Table 5.3.2, the mole ratio of C: H: S is 12.3:8.7:1.0. The C: H: S molar ratio of dibenzothiophene is 12: 8: 1 and that of biphenyl is 12: 10: 0. It was speculated that this could be dibenzothiophene with a small amount of biphenyl.

The precipitate was analyzed by infrared (Figure 5.3.1) and the spectrum was compared with that if dibenzothiophene and biphenyl.

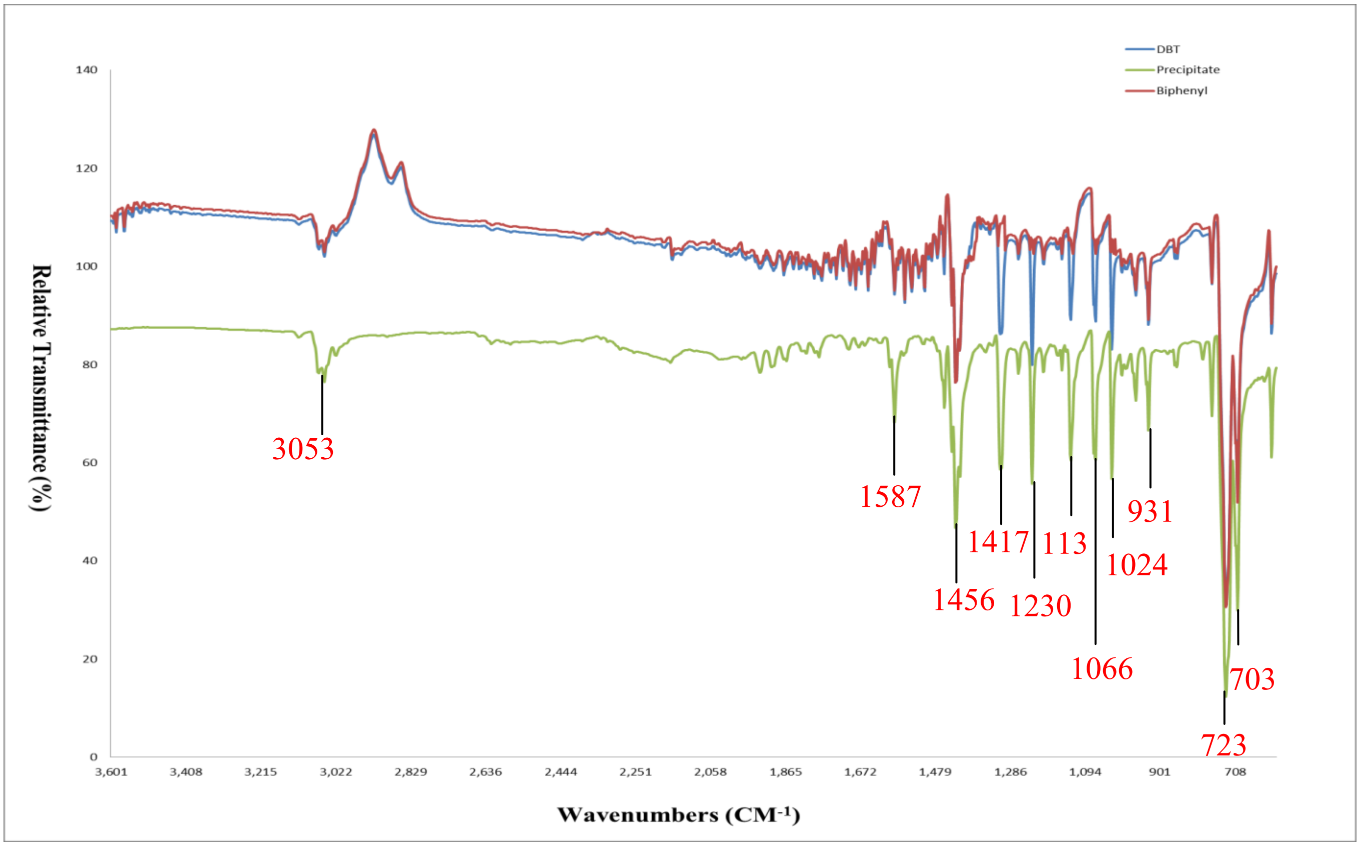


Figure 5.3.1 FT-IR analysis of the precipitate from DBT reacted with Na

a) Aromatic C-H stretch, 3053 cm^{-1}. b) C = C ring stretch, 1587, 1456, 1417 cm^{-1}. c) In-plane C-H bending, 1230, 1130 cm^{-1}. d) Out-of-plane C-H bending, 723,703 cm^{-1}.

5.3.2 Reaction of carbazole with Na and H_2

Carbazole and Na reacted for 22 hours under hydrogen atmosphere. No hydrogenation of cabazole was observed. During the reactions, the pressure did not have any observed change and the final pressure of reactor before depressurizing was 0.86 MPa. No other significant phenomena change observed in the products.

5.3.3 Reaction of dibenzofuran with Na and H_2

Dibenzofuran and Na reacted for 22 hours under hydrogen atmosphere. Even with the presence of hydrogen (H_2) as additional hydrogen source, no deoxygenation happened. This is the same case with reactions under nitrogen, which proved Na does not assist with deoxygenation of oxygen containing heterocycles.

5.3.4 Reaction of anthracene with Na under hydrogen and nitrogen

Anthracene and Na reacted for 22 hours under hydrogen atmosphere. The chromatogram from GC-MS analysis is shown in Figure 5.3.2. The area percentages of the different compounds that were identified are listed in Table 5.3.3.

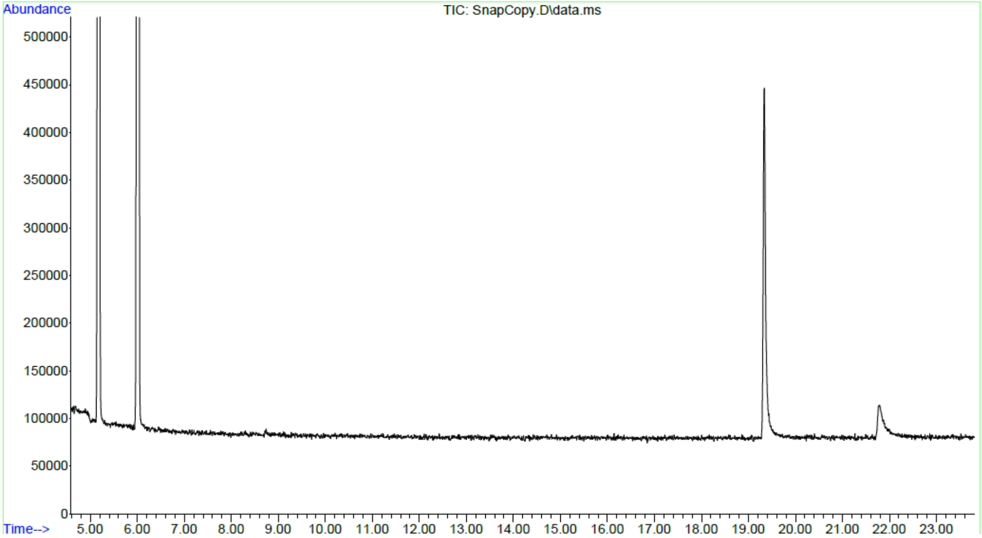
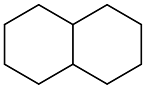
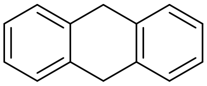
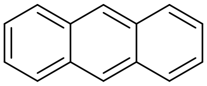


Figure 5.3.2 GS-MS chromatogram for anthracene reacted with Na under H_2 atmosphere

Table 5.3.3 Retention time and structure table for anthracene reacted with Na under hydrogen

Retention Time(min)	Structure	Name	Area percentage (%)
5.18 and 6.02		*trans*- and *cis*-Decalin	47.46 50.27
19.34		9,10-Dihydro-anthracene	1.91
21.79		Anthracene	0.36

In Table 5.3.3, at 21.79 min it is the unconverted reactant anthracene, but at 19.34 min is 9,10-dihydro-anthracene. The middle ring of anthracene was hydrogenated but the other two rings were not. The conversion of anthracene was 84 %. The results are consistent with the reaction chemistry of Na and multinuclear aromatics explained in Chapter 2.

The same reaction was repeated under N_2, to confirm that most of the observed hydrogenation was due to H_2 and not due to the solvent, because not solvent dehydrogenation was observed. The chromatogram is shown in Figure 5.3.3.

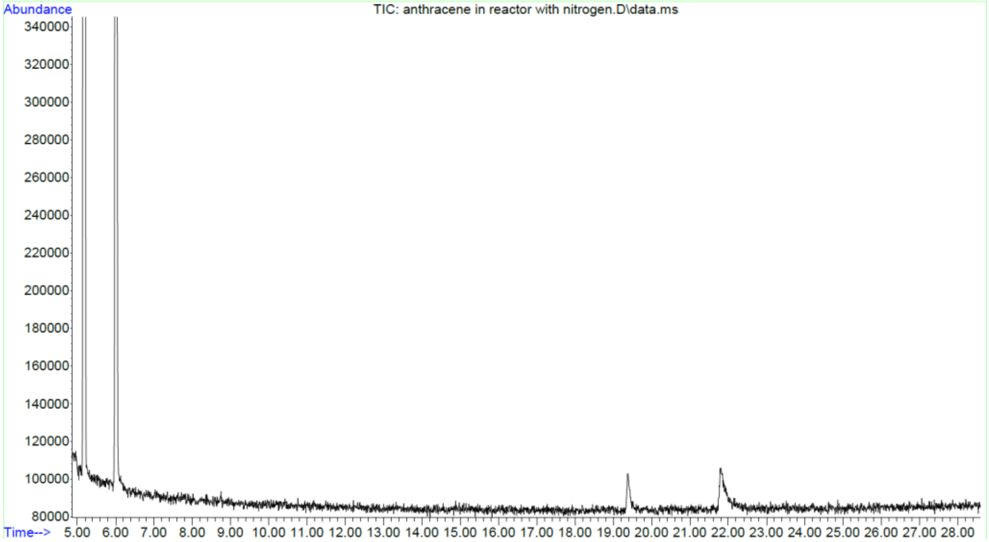
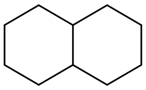
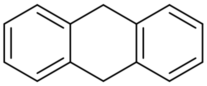
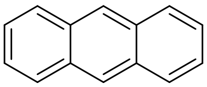


Figure 5.3.3 GS-MS chromatograph for anthracene reacted with Na under nitrogen atmosphere

Table 5.3.4 Retention time and structure table for anthracene reacted with Na under nitrogen

Retention Time (min)	Structure	Name	Area percentage (%)
5.18 and 6.02		*trans*- and *cis*-Decalin	47.12 and 52.25
19.34		9,10-Dihydro-anthracene	0.19
21.81		Anthracene	0.44

In Table 5.3.4, similar to the reaction of anthracene under hydrogen, at 21.81 min it is the reactant anthracene and at 19.34 min 9, 10-dihydro-anthracene. The conversion of anthracene to 9,10-dihydro-anthracene was 30 %.

5.4 Discussion

Dibenzothiophene could react with Na under nitrogen with decalin as a solvent, which has been discussed in Chapter 4 already.

Here we can see biphenyl produced during the reaction of DBT with Na under hydrogen as well. In Chapter 3 dibenzothiophene can also be desulfurized under nitrogen with good conversion. In the industry one of the main desulfurization way is hydrodesulfization as talked about in Chapter 2. Hydrodesulfurization requires H_2 and a proper HDS catalyst, which can also help with hydrogenation of aromatic rings.

In this chapter we saw not only dibenzothiophene were desulfurized, but the anthracene which was used to represent the multinuclear aromatics was hydrogenated. It is known asphaltenes are very aromatic rich, if we can hydrogenate the rings, then it will be easier to remove the sulfur too as it can become aliphatic sulfur. In addition, hydrogenation of the rings also will help with the C-C bond opening, thus lighter products can be produced and less coking will be produced as result.

Carbazole and dibenzofuran was unreactive at the reaction conditions investigated. No heteratom extrusion by Na was observed. Under hydrogen, no hydrogenation was observed either. This was somewhat surprizing, because this was unlike the reactions under nitrogen, where the solvent contributed to hydrogen transfer and partial hydrogenation compounds were detected in the product.

Anthracene had the middle ring hydrogenated and it counted for a high yield based on the GC-MS chromatograph.

References

[1] Birch, A. J. Reduction by dissolving metals. Part I. *J. Chem. Soc*. **1944**, 430.

[2] Mander, L. N. Partial Reduction of Aromatic Rings by Dissolving Metals and by Other Methods. *Comp. Org. Syn.* **1991**, 8, 489–521.

[3] Hudlicky, M. *Reductions in Organic Chemistry*; Ellis Horwood Ltd.: Chichester **1984.**

[4] Sternberg, H. W.; Donne, C. L. D.; Markby, R. E.; Friedman, S. Reaction of Sodium with Dibenzothipphene. A Method for Desulfurization of Residua. *Ind. Eng. Chem. Process. Des. Dev.* **1974**, *13* (4), 433-436.

[5] Wooster, C. B.; Godfrey, K. L. Mechanism of the Reduction of Unsaturated Compounds with Alkali Metals and Water. *J. Am. Chem. Soc.* **1937**, *59* (3), 596-597.

CHAPTER 6 – Conclusion

The conversion of asphaltenes with Na was investigated as an applied study. Although Na does not have a significant effect on increasing liquid yield, the aromatic H-content decreased compared to that of the feed asphaltenes. The Na did help with heteroatom removal. The results from the conversion of the asphaltenes suggested Na could react with some oxygen, sulfur and nitrogen groups in asphaltenes, which decreased oxygen, sulfur and nitrogen content.

It was of interest to know whether the observed decrease in heteroatom content of the asphaltenes was due to removal of aliphatic or aromatic heteroatoms. In order to learn more about the heteroatom removal, reactions of Na with some model molecules using decalin and 1-methylnaphthalene as potential hydrogen transfer agents were performed.

For desulfurization, Na can give an electron easily that helps delocalized the aromatics connected with sulfur. Then hydrogen will be transferred to the aromatics promoting hydrogenation. At the same time, Na is molecularly small so that it can get access to the sulfur directly and some sulfur was removed by direct extrusion out of aromatic system.

As to denitrogenation, Na did not have a notable influence of nitrogen removal in the case of carbazlole. The same was true for deoxygenation of heterocycles. Dibenzofuran was not converted.

For the solvent selection, 1-methylnaphthalene and decahydronaphthalene both facilitated aromatic hydrogenation and desulfurization. Desulfurization can happen either under nitrogen or hydrogen atmosphere.

Recommendations for future work

The following is recommended for future work:

More model compound reactions with Na need to be performed to understand asphaltenes conversion.

The operating range of temperature, hydrogen partial pressure and asphaltenes to Na can be performed. These experiments of Na and asphaltenes will help to find the optimum conditions for Na conversion.

Bibliography

[1] Dusseault, M.B. Comparing Venezuelan and Canadian heavy oil and tar sands. Petroleum Society's Canadian International Petroleum Conference. **2001,** 2001-61.

[2] Gray, M. R. Upgrading Oilsands Bitumen and Heavy Oil. The university of Alberta Press. Edmonton, **2015.**

[3] Boduszynski, M. M. Asphaltenes in petroleum asphalt: Composition and formation, Chemistry of Asphaltenes. *Am. Chem. Soc., Div. Pet. Chem., Prepr.* **1979**, *24* (4). CONF-790917.

[4] Miller, J. T.; Fisher, R. B.; Thiyagarajan, P.; Winans, R. E.; Hunt, J. E. Subfractionation and characterization of Mayan asphaltene. *Energy Fuels,* **1998**, 12, 1290–1298.

[5] Yen, T. F. *Pan-Pacific Synfuels Conference*, Japanese Petroleum Institute. Tokyo, **1982**, 11, 547-557.

[6] Sagedghi, M. A.; Chilingarian, G. V.; Yen, T. F. X-ray diffraction of asphaltens. *Energy Sources*, **1986**, 8, 99-123.

[7] Rodgers, R. P.; Marshall, A. G. Petroleomics: Advanced characterization of petroleum derived materials by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). *Asphaltenes, Heavy Oils, and Petroleomics*. Springer Science & Business Media, 2006, 63-93.

[8] Mullins, O. C.; Eric Y. S.; Ahmed H.; Alan G. M. *Asphaltenes, heavy oils, and petroleomics.* Springer Science & Business Media, 2007.

[9] Castillo J.; Hung J.; Goncalves S.; Reyes A. Study of Asphaltenes Aggregation Process in Crude Oils Using Confocal Microscopy. *Energy Fuels*, **2004**, 18, 698-703.

[10] Durand, E.; Clemancrey, M.; Lancelin, J. M.; Verstraete, J.; Espinat, D.; Quoineaud, A.A. Effect of Chemical Composition on Asphaltenes Aggregation. *Energy Fuels*, **2010**, 24, 1051–1062.

[11] Trejo, F.; Ancheyta, J.; Morgan, T. J.; Herod, A. A.; Kandiyoti, R. Characterization of Asphaltenes from Hydrotreated Products by SEC, LDMS, MALDI, NMR, and XRD. *Energy Fuels* **2007**, 21, 2121–2128.

[12] Gray, M. R.; Tykwinski, R. R.; Stryker, J. M.; Tan, X. Supramolecular Assembly Model for Aggregation of Petroleum Asphaltenes. *Energy Fuels,* **2011**, 25, 3125–3134.

[13] Wilson. L. O. Sulfur in heavy oils, oil sands and oil shales. *Argonne National Lab.* [online] https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/22_3_MONTREAL_06-77_0086.pdf

[14] Rall, H. T.; Thompson, C. J.; Coleman, H. J. ; Hopkins, R. L. Sulfur Compounds in Crude Oil. *Washington D.C. UNT Digital Library* [Online] **2015** http://digital.library.unt.edu/ark:/67531/metadc12804/.

[15] Heinrich, G; Kasztelaan, S; Hydrotreating. In *Petroleum Refining*; Leprince, P., Ed.; *Institut Francais du Petrole Publications: Paris,* 2001, 3, 533–573.

[16] Javadli, R.; De Klerk, A. Desulfurization of heavy oil. *Appl. Petrochem. Res.* **2012,** *1,* 3-19.

[17] Topsoe, H.; Clausen, B. S.; Massoth, F. E. *Hydrotreating Catalysis – Science and Technology* , Ed. Anderson, J.R and Boudart, M.; Springer Verlag Berlin, **1996**.

[18] Toshiaki, K.; Atsushi, I.; Weihua, Q. *Hydrodesulphurization and Hydrodenitrogenation: Chemistry and Engineering*, Kodasha:Tokyo**, 1999**.

[19] Gatan, R.; Bargger, P.; Gembicki, V. Oxidative desulfurization: A new technology for ULSD**.** *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem*., **2004**, 49(2): 577-579.

[20] Shujiro, O.; Takeshi, N.; Noriko, T.; Weihua, Q.; Atsushi, I.; Tamotsu, I.; Toshiaki, K. Oxidative Desulfurization of Light Gas Oil and Vacuum Gas Oil by Oxidation and Solvent Extraction. *Energy Fuels*, **2000**, 14: 1232-1239.

[21] Zhao, H. Catalytic Hydrogenation and Hydrodesulfurization of Model Compounds. Ph.D. Thesis, Virginia Polytechnic Institute and State University March 2009.

[22] Heinz, W. S.; Charles, L. D. D.; Raymond, E. M.; Sidney, F. Reaction of Sodium with Dibenzothiophene. A Method for Desulfurization of Residua. *Ind. Eng. Chem.. Process Des. Dev.,* **1974**, 13(4), 433-436.

[23] Ho, T. C. Hydrodenitrogenation catalysts. *Catal. Rev. Sci. Eng.,* **1988,** 30, 117-160.

[24] Satterfield, C. N.; Yang, S. H., Catalytic Hydrodenitrogenation of Quinoline in a Trickle-Bed Reactor - Comparison with Vapor-Phase Reaction. *Ind. Eng. Chem.Proc. Des. Dev*., **1984**, 23, (1), 11-19.

[25] Furimsky, E. Chemistry of catalytic hydrodeoxygenation. *Catal. Rev. Sci. Eng.* **1983,** 25, 421-458.

[26] Furimsky, E. Catalytic deoxygenation of heavy gas oil. *Fuel,* **1978,** 57, 494-496.

[27] Gordon, J. H. Post Retort, pre hydro-treat upgrading of shale oil. Final report, DOE Award DE-FE0000408, 2013.

[28] Wallace, T. J.; Heimlich, B. N. The decomposition of dibenzothiophene dioxide and related compounds in the presence of molten alkali. *Tetrahedron* **1968**, 24, 1311-1322.

[29] Lyssy, T. M. Reaction of metallic sodium with naphthalene. Dihydronaphthalenecarboxylic acids–1, 4 and –1, 2 and related compounds. *J. Org.*

Chem. **1962**, 27, 5-13.

[30] Walker, J. F.; Scott, N. D. Sodium naphthalene. II. Preparation and properties of dihydronaphthalene dicarboxylic acids. *J. Am. Chem. Soc.* **1938**, 60, 951-955.

[31] Scott, N. D.; Walker, J. F.; Hansley, V. L. Sodium naphthalene. I. A new method for the preparation of addion compounds of alkali metals and polycyclic aromatic compounds. *J. Am. Chem. Soc.* **1936**, 58, 2442-2444.

[32] Brons, G.; Myers, D. R.; Bearden, R. J.; MacLeod, B. J. Process for desulfurization of petroleum feeds utilizing sodium metal. U.S. Patent 6,210,564 B1, April 3, 2001.

[33] Gordon, H. J. Post retort, Pre Hydro-treat Upgrading of Shale Oil. *Ceramatec Inc.* [online] **2015** https://www.netl.doe.gov/file%20library/research/oil-gas/enhanced%20oil %20recovery/fe0000408-final-report.pdf

[34] Wallace, T. J.; Hofmann, J. E.; Schriesheim.A. Base-catalyzed elimination studies on sulfones, sulfoxides, sulfides, disulfides, and mercaptans in dimethyl sulfoxide. *J. Am. Chem. Soc*. **1963**, 85, 2739-2743.

[35] *Polynuclear aromatic compounds* (Adv. Chem. Ser. 217); Ebert, L. B. Ed.; American Chemical Society: Washington DC, 1988.

[36] Ignasicak, T.; Kemp-Jones, A.V.; Strausz, O.P. The molecular Structure of Athabasca Asphaltene. Cleavage of the Carbon-Sulfur Bonds by Radical Ion Electron Transfer Reactions. *J. Org. Chem.* **1977**, 42, 312-320.

[37] Gilman, H.; Esmay, D. L. The cleavage of heterocycles with Raney nickel and with lithium. *J. Am. Chem. Soc.* **1953**, 75, 2947-2949.

[38] Tamaru, K. Catalysis by electron donor-acceptor complexes. *Adv. Catal.* **1969**, 20, 327-339.

[39] Babatunde A. O. Random Phenomena: Fundamentals and Engineering Applications of Probability & Statistics. *CRC Press*, Boca Raton **2009**.

[40] Ebert, L. B.; Milliman. G. E.; Mills, D. R.; Scanlon, J. C. Reductive alkylation of aromatic compounds perylene, decacyclene, and dibenzothiophene. *Adv. Chem. Ser.* **1988**, 217, 108-126.

[41] Gilman, H.; Joseph, D. Notes-Lithium Cleavages of some Heterocycles in Tetrahydrofuran. *J. Org. Chem.* **1957**, 22, 851-853.

[42] Zachariah, A. Low Temperature Pyrolysis and its Application in Bitumen Processing MSc Thesis, University of Alberta Press, Edmonton, August **2014**.

[43] Birch, A. J. Reduction by dissolving metals. Part I. *J. Chem. Soc*. **1944**, 430.

[44] Mander, L. N. Partial Reduction of Aromatic Rings by Dissolving Metals and by Other Methods. *Comp. Org. Syn.* **1991**, 8, 489–521.

[45] Hudlicky, M. *Reductions in Organic Chemistry*; Ellis Horwood Ltd.: Chichester **1984.**

[46] Sternberg, H. W.; Donne, C. L. D.; Markby, R. E.; Friedman, S. Reaction of Sodium with Dibenzothipphene. A Method for Desulfurization of Residua. *Ind. Eng. Chem. Process. Des. Dev.* **1974**, *13* (4), 433-436.

[47] Wooster, C. B.; Godfrey, K. L. Mechanism of the Reduction of Unsaturated Compounds with Alkali Metals and Water. *J. Am. Chem. Soc.* **1937**, *59* (3), 596-597.