University of Alberta

Thermal cracking of asphaltene by addition of hydrogen donor solvent

by

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Abstract

Better definition of asphaltene structure is needed to develop new technology for upgrading, and to understand various bitumen properties. Analysis of asphaltene structure is hampered by aggregation of molecules at a length scale of 5 to 10 nm. At 300°C, the addition of aromatic solvents can partly, but not completely suppress aggregation of asphaltenes. This study will investigate a new method, thermal cracking combined with presoaking of a mixture of asphaltene and hydrogen donor solvent to suppress the aggregation and to maximize yield of cracked fragments.

Asphaltene thermal cracking was carried out in micro batch reactor at 430°C by fluidized sand bath for 1 hour. Compared with non-solvent addition in thermal cracking, mixing of tetralin and tetrahydroquinoline with asphaltene greatly reduced the coke yield from 38% to 2%. To further enhance the solvent's hydrogen transfer ability and the disaggregation of asphaltene, a presoaking stage at 200°C was performed prior to thermal cracking. In addition, parallel tests between tetralin and tetrahydroquinoline were conducted at different time periods ranging from 30 minutes up to 3 hours. Effects of nitrogen and oxygen reaction environment were also studied for the presoaking case to check for their effects. Compared with the case of direct solvent addition during thermal cracking, presoaking of either tetralin or tetrahydroquinoline with asphaltene did not show any significant reduction in coke yield for different presoaking periods, gas environment, or cooling interval.

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Chapter 1 Introduction

The depletion of conventional crude oil has led to a shift towards heavy oil and bitumen to meet the ever-increasing global energy demand. Natural bitumen deposits are reported in many countries, but extremely large quantities are found in Alberta, Canada. As one of the largest supplies of bitumen, the oil sands reserve from Canada is playing a significant role in filling the gap of world demands. Based on current technology and prices, bitumen reserves in Canada are estimated at 176.8 billion barrels (28.11×109 m^3), accounting for over 70.8% of global bitumen reserves. Bitumen from oil sands is upgraded to produce synthetic oil comparable to the conventional light sweet crude or to produce pipelineable liquids with little or no diluent.

Asphaltenes are the heaviest portion of petroleum, existing in all of the heavy oil and bitumen resources and most of conventional oil. Compared with about 1% fraction in a light density crude oil, the concentration of asphaltenes in bitumen can be as much as 20%. As a solubility fraction that is soluble in toluene and insoluble in heptane, the asphaltene fraction contains the most complex constituents extracted from the parent oil. Consequently, a number of functional groups contained in asphaltene can form associative interactions and lead to problematic aggregations, leading to detrimental problems for bitumen processing and transportation.

Thermal cracking is the main process to upgrade bitumen by converting high boiling point hydrocarbons to produce light gases and distillable liquids which have more valuable by breaking bonds of large molecules. It is also efficient in rejecting the minerals and solids into coke phase. Coke as the most undesirable side product from oil processing, defined as a carbonaceous material that is insoluble in aromatic solvent such as toluene or benzene. A number of researchers have studied and found that asphaltene are the fraction most responsible for coke formation in bitumen processing.

In the field of petroleum residue conversion, the benefit of hydrogen donors in controlling coking reactions has been demonstrated by Carlson [1]. Tetralin and 9, 10-tetrahydrophenanthrene are the characteristic hydrogen donors that react readily with olefins, thereby eliminating a pathway for coke formation and polymerization and suppressing the yield of coke. In coal liquefaction processes, the hydrogen donor reactions are also considered as an important mechanism to increase the amount of coal conversion and produce upgrading of coal liquids to more valuable products.

However, there are few investigations on the effect of adding hydrogen donor solvents into asphaltene thermal cracking. The purpose of this study is to confirm that addition of hydrogen donor solvents would bring less coke yield for asphaltene thermal cracking reactions, and that a presoaking stage would further disaggregate asphaltene and suppress coke yield. The presoaking period, as environment and the interval cooling after presoaking were also tested in this study as the main three

variables to influence on the presoaking effect.

1.1 Objectives

Two kinds of hydrogen donor solvents, tetralin and 1,2,3,4-tetrahydroquinoline were added into thermal cracking reactions to find out if they can lead to less coke yield.

- To determine the effect of the hydrogen donor solvent addition into thermal cracking on the yield of coke
- To study if solvent presoaking stage in prior to thermal cracking can bring a better disaggregation effect on the coke yield compared with solvent addition thermal cracking. Different variables influencing on presoaking disaggregation effect are investigated such as presoaking period, interval cooling and presoakingenvironment.

Chapter 2 Literature Review

Asphaltenes, which are the heaviest portion and most complex constituents of petroleum fractions, exist in all of the heavy oil and bitumen. A number of functional groups contained in asphaltene can form associative interactions and lead to problematic aggregations, bringing detrimental problems to bitumen processing and transportation. Asphaltenes aggregation is likely a contributor to the coke formation during thermal processes. Different methods to disaggregate asphaltene have received some attention, as described below.

Hydrogen donor solvents have been long recognized for lowering the coke yield in thermal cracking reaction by donating hydrogen to reacting liquid components [1,2]. However, few studies have been done to determine if hydrogen donors are able to provide disaggregation effect for asphaltenes. The literature will be reviewed to define several characteristics of asphaltenes, especially the aggregation properties. Properties of thermal cracking, coke formation and hydrogen donor solvents are also included in this chapter. Finally, the hypothesis of this study was proposed based on all the literature reviewed.

2.1 Asphaltene and characterization

Saturates, aromatics, resins and asphaltenes are fractioned from bitumen which is considered as an extremely heavy crude oil that contains a large number of hydrocarbon components. These four fractionations are defined by SARA method showed in Figure 2-1 [3]. Instead of being defined by molecular structure, asphaltene is defined by a solubility character which is soluble in toluene but precipitates in n-alkanes [3]. By this classification, asphaltene contains the most polar and highest molecular weight components, recognized as the most complex constituents extracted from parent oil. Dilution of Alberta bitumen in n-pentane or n-heptane gives a 10-20% of brown/black solid precipitate as asphaltene. Asphaltene also tend to precipitate out of petroleum mixtures during blending of incompatible crude oils.

Bitumen
n-heptane or
n-pentane

Asphaltenes
(precipitate)

De-asphalted
bitumen (Maltenes)

Saturates Aromatics Resins
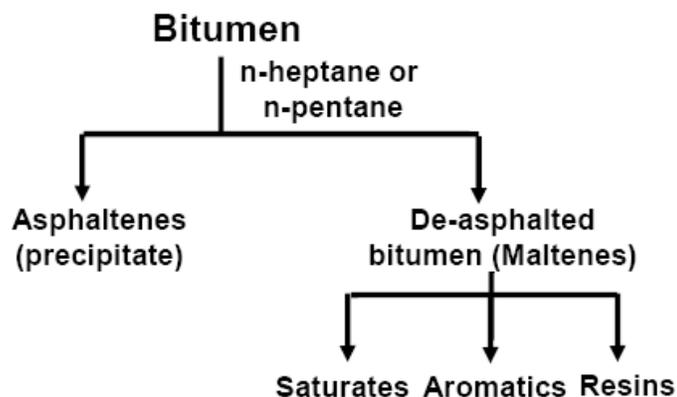
Figure 2-1 SARA fractionation.

In addition, the amount and composition of asphaltene precipitated from bitumen mixed with alkane solvents depend not only on the solvent type and solvent/oil ratio, but also depends on the time and temperature of precipitation condition. In general, the higher rate of solvent/oil ratio, the higher rate of asphaltene precipitated out from oil. At same solvent/oil ratio, lighter alkane can precipitate more asphaltene than heavier alkane (for alkanes lighter than C10). Wang et al. found that maximum amount of precipitated asphaltenes were obtained as the volume ratio of n-heptane to heavy oil reaches 30:1 to 40:1[4]. At higher temperature, asphaltene will tend to remain in solution and the amount of precipitation will be lower.

From the different amount of asphaltene precipitation introduced, the identification of asphaltenes as a solubility class rather than by their chemical characterization has caused ambiguity. For the chemical composition, asphaltenes are a mixture of hydrocarbons containing heteroatoms (N, S, O, Ni, V, etc.). Table 2-1 lists the elemental composition of Athabasca bitumen and the corresponding asphaltene precipitated [5].

Table 2-1 Elemental composition of Bitumen and Asphaltene precipitated from n-heptane

Element	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	H/c
Bitumen, wt%	83.1	10.6	0.4	4.8	1.1	1.53
Asphaltene, wt%	80.8	7.8	1.2	8.8	1.4	1.15

Asphaltenes contain the heaviest components of bitumen and have a much lower H/C ratio than the rest of the oil. The content of heteroatoms in asphaltene is also much higher than bitumen, which are electron deficient and make asphaltenes more polar. Transition metals such as V and Ni are also contained as 0.1-0.2wt % in asphaltene [6].

2.1.1 Asphaltene aggregation

Since asphaltenes contain a number of functional groups, the precipitation of asphaltene from oil can lead to a mixture which can form associative interactions due to both insolubility and the flocculation of colloidal aggregates [7]. Various analytical observations are used to observe the feature of self-associate, including small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), vapor phase osmometry (VPO), ultracentrifugation and etc. A variety of sizes of aggregates ranging from dimers to colloidal particles are found in different solution conditions. Therefore the measurement gives different mean size of asphaltene. The consensus suggests that aggregates in the size range of 5-15 nm dominate when asphaltene are dispersed in toluene [8,9].

Asphaltene likely associate in solutions through a combination of intermolecular interactions, including π-π stacking, hydrogen bonding and acid-base interactions, resulting in more or less extended aggregates. The aggregation depends on solvent, concentration and temperature. By adding more n-heptane into toluene

solvent, asphaltene aggregate size will become larger [10], which means that good solvents will reduce aggregates size. Asphaltene aggregate size has been shown to reduce as the temperature is raised [11]. At high temperature of 300°C, molecular aggregation of asphaltene was still detected [11] suggesting that aggregates may be remarkably stable in heavy oil and significant in production process.

Another important property of aggregation is that the precipitation of asphaltene can result in the entrapment of material which is soluble in n-alkanes. Since the amount of occlusion resolves in n-alkanes, dissolution and reprecipitation will give less and less recovery of asphaltene solids with each cycle. Strause et al [12] observed a cumulative mass loss of 22% from each step of six successive cycles of dissolution and reprecipitation with n-pentane.

Asphaltene aggregation has made the characterization of asphaltene difficult since the system might contain both monomers and aggregates. The controversy over asphaltene molecular weight is an obvious example to show the problem brought by aggregates.

2.1.2 Asphaltene flocculation

At extreme low concentration (below 10^{-4} mass fraction) in toluene, asphaltene are dispersed like solution [13]. However, when the concentration reaches above 10^{-4} mass fraction, asphaltene molecules stay together to form nanoaggregates. At higher concentration in toluene, the interactions between nanoaggregates lead to flocculation to form larger clusters and then precipitate out of toluene. In crude oil, the asphaltene

aggregates transition is less easy to show by the current experimental methods. Studies have shown that pressure, temperature and compositions are the factors to effect on asphaltene flocculation and forming deposits. Aromaticity of the solvents can affect asphaltene precipitation most diectly. Reducing temperature and depressurization of crude oil can also induce precipitation. In certain types of crude oil, asphaltene remains in the solution and not precipitate out. Because of precipitation, serious problems such as pipeline plugging and equipment fouling are found during production.

The presences of surfactants also affect the aggregation of asphaltene. They are amphipathic molecules that include both distinct hydrophobic and hydrophilic regions. These molecules can be formed and isolated from an asphaltene micelle. Nature surfactants in crude oil were shown to be able to stabilize asphaltenes [14]. Resins are also believed to be able to solvate asphaltene, reduce the aggregate size and stabilize asphaltene in solvents[15]. Unfortunately, most of the surfactants of interest are thermally unstable, therefore, they can not be extended to use under high-temperature upgrading conditions.

2.2 Thermal cracking and coke formation

2.2.1Thermal cracking and coking processes

Commercial upgrading usually consists of two steps primary and secondary

upgrading. Primary upgrading may include processes such as vacuum distillation, coking, visbreaking and hydroconversion to remove heavy fractions along with some of the heteroatoms and heavy metals. The product from primary upgrading is then further processed in the secondary upgrading to produce synthetic oil by hydrotreating and hydrocracking to remove impurities such as sulfur and nitrogen. Among all the current primary upgraders, coking is the most appealing choice since it can handle the high solid and water content in mined bitumen due to lack of catalyst.

Bitumen and heavy oil needs to be processed in upgraders to convert into high quality synthetic oil and pipelineable liquid. The general objectives of upgrading processes are easily defined as to convert high-molecular weight residue components into distillates, improve the H/C ratio of the distillate products and remove the heteroatoms down to acceptable levels. To obtain these goals, bitumen and heavy oil are required to undergo a number of different processes of thermal and catalytic reactions. The choice of upgrading technology depends on the properties of feed material and the targeted products.

Thermal reactions in the primary upgrading processes are noncatalytic and start to give cracking of organic mixtures at significant rates when they are heated to temperature over 410°C. Thermal treatment of residues ranges from mild treatment for reduction of viscosity to severe treatment for obtaining complete olefins and light ends[16]. The severity of the thermal treatment process is the combination of reaction time and temperature to achieve a given conversion. For example, if no side reactions occur, the very long time thermal conversion under low temperature will equal to

short time conversion under high temperature. Table 2-2 summarized the severity and conversion characteristics of thermal processes [16]. The mild- severity and high-severity processes are frequently used for processing bitumen and heavy oil. Steam cracking is used to convert gases and light distillate to olefins in the vapor phase with extremely short residence times and high temperature.

Table 2-2 Severity and conversion characteristics of thermal processes

Severity	Process	Time, s	Temperature, $^{\circ}$C	Conversion
Mild	Visbreaking	90	425-500	Low
High	Delayed coking	(Semi batch)	435-480	High
	Hydroconversion	3600	420-440	Med-high
	Fluid coking	25	510-540	High
Extreme	Steam cracking	<0.5	>800	High

Among bitumen thermal conversion processes, coking is a major technology since it is efficient to convert heavy hydrocarbons into distillate products and reject the mineral and solids to the coke phase. However, the efficiency comes at the cost of forming coke, which is a carbonaceous solid. The term coke is used to describe any toluene-insoluble solids that may form from oil processing. In coking processes, coke formation is part of the design, targeting an increase the H/C ratio in the liquid products. Other than coking processes, coke is formed as a separate phase, which is

not desirable in the hydroconversion and hydrotreating processes.

2.2.2 Coke yields and Properties

From coking processes, the yield of coke tends to be proportional to the carbon residue content (Measured as CCR or MCR) of the feed. Coke forming tendency is an important parameter for upgrading. It is measured by pyrolyzing a sample of the heavy oil under controlled conditions in absence of oxygen. Coke forming tendency is calculated as the amount of solids formed after the pyrolysis as a fraction of the initial sample weight. Conradson Carbon Residue (CCR), Rambsbottom Carbon Residue (RCR), and Micro Carbon Residue (MCR) are used as the main methods to measure coke forming tendency.

The data of Table 2-3 illustrates how the yield of coke from delayed and fluid coking varies with CCR content of the feed[16].

Table 2-3 Coke yield from delayed and fluid coking varying with CCR feed content

Carbon Residue Wt%	^{O}API	Coke yield weight%	
		Delayed coker	Fluid coker
1		0	
5	26	8.5	3
10	16	18	11.5
15	10	27.5	17
20	6	35.5	23
25	3.5	42	29
30	2		34.5
40	-2.5		46

The formation of large quantity of coke is a severe drawback unless the coke can be put into use. Applications of coke into carbon or graphite products require coke to be low in mineral matter and sulfur content. However, because of the high sulfur and ash content, coke formed from heavy oil and bitumen is hard to use.

2.2.3 Coke formation

Coke can be defined as carbonaceous solid that is formed during thermal reaction of carbon-rich materials. Wiehe (1992) proposed a phase diagram for coke formation behavior based on hydrogen content and molecular weight. He observed that data for different solubility fractions tend to cluster into distinct zones on a plot of molecular weight versus hydrogen content (Figure 2-2).
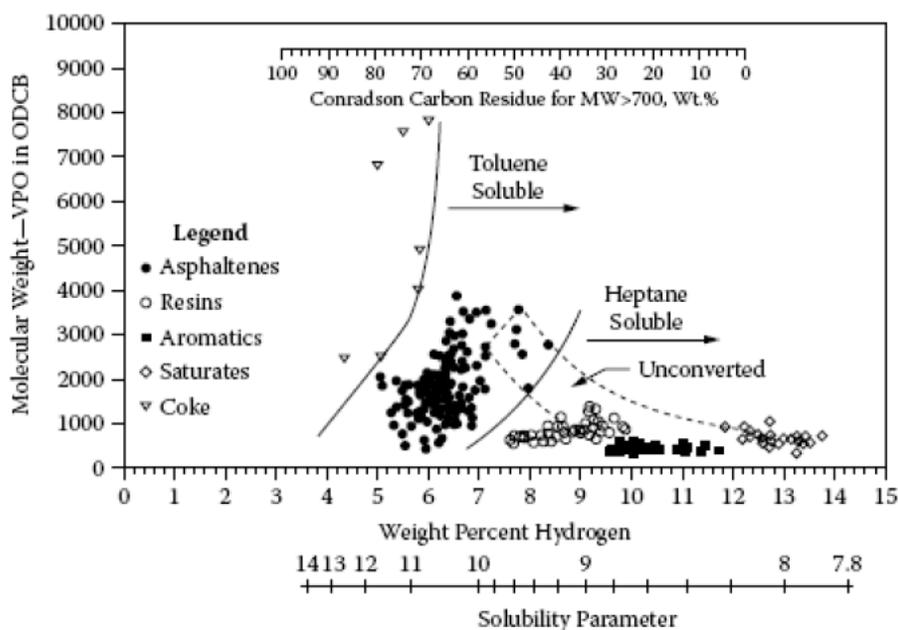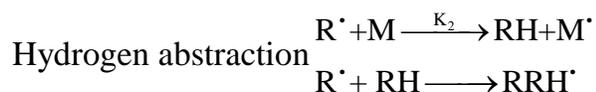

Figure 2-2 The solvent-residue phase diagram of eight different residues and their thermal reaction prouducts displays each of the five classes in unique arrears[16]

The free-radical chain reactions have been demonstrated for alkanes, alkyl

aromatics, and cyclic saturated compounds in both vapor phase and liquid phase. The simplest form is illustrated in the following. Thermal cracking starts from initiation step, where the carbon-carbon bond scission occurs to form free radicals. Then, in propagation step, free radicals react by abstracting a hydrogen atom from hydrocarbon or undergoing further β-scission cracking to produce a new free radical and a stable product. Cracking usually occurs at bonds β to the carbon atom that carries the unpaired electron. Usually, the free radicals are active and energetic. When two free radicals collide, they will release energy for stabilization and that is termination step in the end. The following is an example of chain reactions for n-alkane, described as the simplest form [17].

- Initiation: $M \xrightarrow{k_1} 2R^{\bullet}$

- Propagation:

$$\text{Hydrogen abstraction} \begin{array}{l} R^{\bullet} + M \xrightarrow{K_2} RH + M^{\bullet} \\ R^{\bullet} + RH \xrightarrow{\quad} RRH^{\bullet} \end{array}$$

$$\beta\text{-scission } M^{\bullet} \xrightarrow{k_3} R^{\bullet} + A$$

- Termination: $\text{Radical} + \text{Radical} \xrightarrow{\quad} \text{Products}$
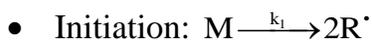
Where M and M• are the parent alkane and parent radicals, respectively, R• and RH are lower alkyl radicals and the corresponding alkanes, respectively, and A represents olefins.

The initiation step to form the radicals can require high activation energy, but once the radicals are formed, then they can propagate through many scission and hydrogen abstraction steps before terminating, leading the chain reaction to be

energetically feasible. Consequently, the overall activation energy for cracking reactions observed is lower than the minimum energy required to break a stable chemical bond.

If the alkyl radical cannot be capped immediately to terminate the reaction or to collide with another alkyl compound, the addition reactions such as polymerization or polycondensation may occur. The addition reactions can be proceeded to from compounds with higher molecular weight leading to coke.

2.3 Hydrogen donor solvents

A wide variety of solvents can function as hydrogen donor solvents as they have the ability to dehydrogenate and donate the resulting hydrogen to hydrogen-deficient reacting species [18]. The standard compound of this type is 1,2,3,4-tetrahydronaphthalene, or tetralin. Tetralin is able to donate 4 moles of hydrogen atoms to other species and produce a stable naphthalene molecuele.
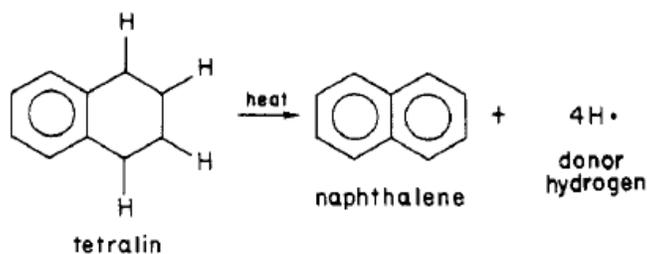

Figure 2-3 Tetralin donating hydrogen figure

Hydrogen donors have been recognized to be extremely important to control coking reactions. By reacting very actively with olefins, hydrogen donors are able to eliminate the pathway for polymerization and coke formation, therefore suppressing coking reactions. Gray et al.[17] reacted n-hexadecane and tetralin together and observed yield of olefins were highly suppressed with products of series of alkyl-tetralins. The rate of cracking of n-hexadecane in tetralin was half the rate observed for the pure compound. Both observations were consistent with the formation of benzylic type tetralyl radicals by the abstraction of α-hydrogen from tetralin, thereby the yield of coke was suppressed.

In coal liquefaction process, the method of hydrogen addition from both donor solvents and gaseous hydrogen is employed to prevent charring and increase upgraded liquid fuel products. However, in gaseous hydrogen addition process, the operation pressure is much higher thus hydrogen donor solvents are more advantageous.

Curtis et al. [19] evaluated the hydrogen transfer efficiency in coal liquefaction between three species of hydrogen-rich donors as cyclic olefins, hydraromatics and cycloalkanes. They found out that for 30 min thermal reaction condition at 380 ^{o}C, the amount of hydrogen release from an equivalent weight of donors was in the order of cyclic olefins>hydroaromatics>cycloalkane.

Wiehe et al [20] found that 1,2,3,4-tetrahydroquinoline (THQ) is a super reactive hydrogen donor in the conversion of resid fractions. From his hydrogen donating mechanism, THQ can highly reduce the thermal reaction rate by reducing the free-

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radical concentration so that the thermal cracking rate was reduced and less coke was formed. This mechanism of hydrogen donating from donors proposed by Wiehe was developed from phase separation mechanism of coke formation [21]. Free radicals were formed during thermal cracking reactions by breaking bonds between aromatic cores and the pendent groups of asphaltenes. Hydrogen donors can terminate the free radicals when the asphaltenes are dispersed in the oil phase. With loss of pendent groups, aromatic cores from asphaltene become less soluble and undergo a phase separation, leading to less donor hydrogen that can be abstracted by the free radicals. As a result, the asphaltene free radicals end up to form insoluble coke.

Based on the observations from Gray, Curtis and Wiehe, hydrogen donors are very efficient to transfer hydrogen in both oil and coal thermal reactions. Following their progress, in this study, hydrogen donors were added into asphaltene thermal cracking stage at 430 ^{o}C to test the hydrogen transfer ability. It was expected that hydrogen addition in thermal cracking can largely reduce coke yield.

2.3.1 Effect of Presoaking

Miura et al. [22] pretreated coal with tetralin at 100-250°C under 1 MPa in nitrogen environment and then the swollen coal was flash pyrolyzed. They reported drastic increase of volatile matter and tar yield for both Taiheiyo Coal (TC) and Morwell Coal (MW). To find out the best pretreatment temperature, TC and MW coals were pretreated in a temperature range from 25°C to 350°C. The maximum total

volatile matter and tar yield were obtained in the temperature range of 100-250°C. When the pretreatment of coal was performed at 25°C, no swelling was found and the micropore volume of coal was same as the raw coal, leading to the same yield of the total volatile and tar after pyrolysis.

Miura et al. concluded that the significant result was brought by tetralin through a physical effect of enlargement of coal micropores, as well as a chemical effect of hydrogen transfer. To summarize, Miura et al. succeeded by employing pretreating coal with tetralin at a mild condition. Their idea lies in accomplishing intimate contact between solvent and coal particles, so that the coal particles were swollen and the solvent was able to retain in coal micropores.

Following the success of coal pretreatment with hydrogen donors from Miura et al., the presoaking stage was considered in this study to disaggregate asphaltenes, which was performed prior to asphaltene thermal cracking stage. For the presoaking temperature, a temperature was chosen at 200°C based on the fact that Miura observed the maximum tar and volatile yield at 100-250°C. Longer presoaking period would be expected to bring better disaggregation effect of asphaltene and lead to less coke yield from thermal cracking reaction stage.

The second factor of interest is the gas environment for presoaking. Lee et al. reported that several chemical reactions occur in the presence of oxygen during heating of heavy oil [23]. The formation of the oxygenated compounds became part of the coke product and tetrahydrofuran solubles, which enabled a potential trend of producing more coke yield than it from less oxygen presence in heavy oil. In addition

to the oxygen content, low-temperature oxidation (LTO) effect was compared with and without the presence of water. They found that the destructive effect of LTO was reduced, but also the less tetrahydrofuran solubles and coke were formed. Based on these results, different presoaking environment of oxygen amount may be a factor to test.

The cooling interval between the stages of presoaking and thermal cracking is also a variable could affect the coke yield, since it is possible that the temperature drop of the mixture of asphaltene and donor solvent in cooling interval can reduce the presoaking stage effect. So, different periods of cooling interval were gained in this study.

2.4 Hypothesis

Ground on the literature introduced above, two hypothesizes were proposed in this study：

1. Addition of hydrogen donor solvents into asphaltene thermal cracking reactions will reduce coke yield compared with pure asphaltene reaction.

2. Presoaking of asphaltene with donor solvents prior to thermal cracking can further reduce coke yield compared with none presoaking stage. Three factors such as the presoaking period, environment and the cooling interval could influence the presoaking effect.

Chapter 3 Experimental Studies

3.1 Experimental material

The experimental materials used in this study are asphaltene and two kinds of hydrogen donor solvents. The detail information will be introduced as follows.

3.1.1 Asphaltene

The main feed for this study is industrial asphaltene, precipitated by pentene from Athabasca bitumen from the steam-assisted gravity drainage production. This material has low concentration of mineral solids. The heptane-insoluble content in industrial asphaltene is about 50% and the detail compositions are showed in the table below [24].

Table 3-1 Industrial Asphaltene compositions

Feed name	Heptane-insoluble content (wt%)	Toluene-insoluble content (ppm)	V Content (ppm)	Ni Content (ppm)
Industrial Asphaltene	50	<0.05	580	230

3.1.2 Hydrogen donor solvents

To reduce coke yield and optimize the liquid product, the donor solvents 1,2,3,4-Tetrahydronaphthalene and 1,2,3,4-Tetrahydroquinoline were used. These solvents have the ability to donate hydrogen to asphaltene during thermal reactions. The properties of these two compounds are listed in the Table 3-2. Both of these solvents were provided from Sigma-Aldrich Co. LLC.

Table 3-2 Hydrogen donor solvents characteristics

Donor solvent name	Structure	Boiling Point ℃	Solubility Parameter (δ, Mpa$^{1/2}$)	Purity
1,2,3,4-Tetrahydroydronaphthalene		206-208	18.6	99%
1,2,3,4-Tetrahydroquinoline		249	19.9	98%
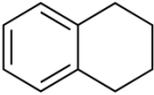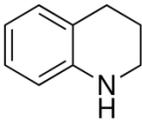
3.2 Experimental Equipment

Several micro batch reactors with same design were used in this study to

carry out reactions. The schematic of the micro reactor is introduced in figure 3-1. The volume of the micro reactor is 10 mL and it was chosen because the mixture of asphaltene and solvent donor with shaking steel balls occupy about 2.5 mL in volume and they could be appropriately located at the 1/4 position of reactor in the bottom. This stainless steel micro batch reactor consists of a 19.05 mm (3/4") outer-diameter (OD) stainless steel tube, 76 mm (3") in length, which was joined with a Swagelok reducing union at the top and a Swagelok cap at the bottom.

The 1.6 mm OD (1/16") stainless reactor neck has a length of 17.1cm (6 ¼"). The lower end was joined to the reducing union, and the upper end was joined with a Swagelok severe service union bonnet needle valve. This valve was located at the top of rector neck to allow for operation at severe temperature and pressure condition up to 600 °C and 20 MPa. A connector was connected to the needle valve to perform nitrogen purging step while hooking up with nitrogen cylinder. In the middle of the bracket holder, there is a round hole located used to attach the reactor to the rod and immerse in into a sand bath.

S.S. Severe-Service Union-Bonnet

Needle Valve

1/8" x 1/16" S.S. Swagelok

Tube Fitting, Reducing Union

Reactor neck

3/4" x 1/16" S.S. Swagelok

Reactor top

Tube Fitting, Reducing Union

3/4"S.S. Swagelok Tubing

Reactor bottom

316 S.S. Swagelok Cap for 3/4"tubing

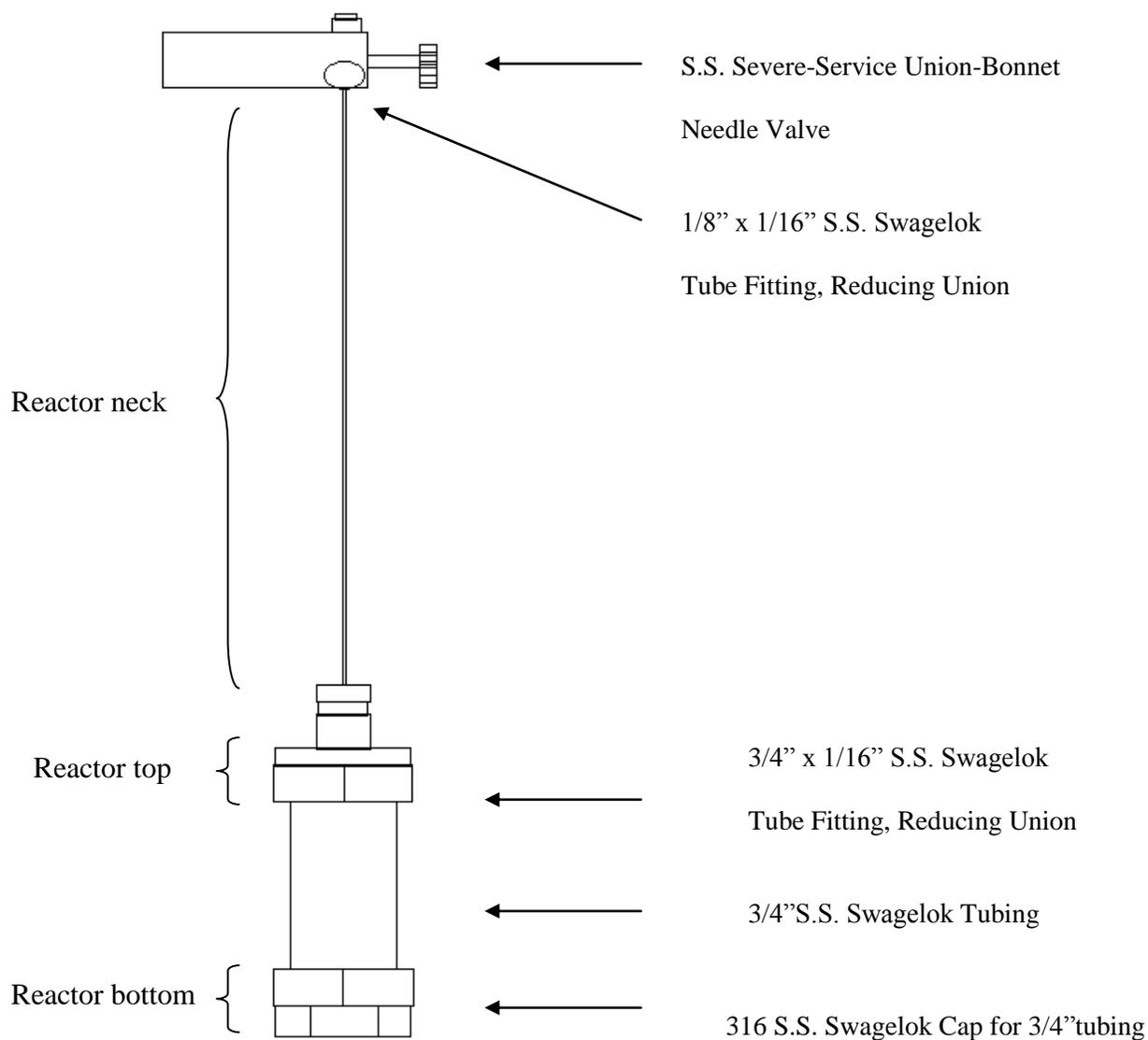**Figure 3-1 Schematic of the micro batch reactor**

Two sand baths (Tecam Fluidized Sand Bath Model No. SBS−4.) were used in this study and they are exactly same in designing and operations. The Figure 3-2 showed below is Sand Bath A for thermal cracking at 430 ℃. While sand bath B was used for presoaking asphaltene with solvent mixtures for one hour at 200℃. The basic design of sand bath is introduced as follows.

As we can see from Figure 3-2, each sand bath was filled up with silica sand as heat transfer media. Sand was fluidized by the airflow to keep the temperature uniform in the entire bath. The rate of air flow not only affects how sand gets fluidized, but also controls the heat transfer rate between sand and micro reactor. For both bath A and B, Gilmont D1703 rotameters were used to regulate the air flow, 40% and 60% were kept constant for bath A and B to keep the temperature file of micro reactor was same through all the experiment were done. A thermocouple (ALL Temperature Sensors) was placed in the middle point along the sand bath to measure the temperature. A temperature controller (OMRON E5CK), receiving signals from thermocouple, maintained the temperature of sand bath at the selected temperature value required.

The bracket of Micro batch reactor was attached to a rod, whose upper body was placed on to the rotating cam powered by the motor. Before inserting micro batch reactor into sand bath, the parallel branch from the rod should be inserted into the guide, as a way to keep the reactor in the middle of sand bath and close to the thermocouple. The motor was then turned on afterwards, moving the reactor a distance of 3cm up and down for the reactor at a frequency of 3 Hz, so that mixing can be provided within the reactor.

Cam

Motor

Guide

Rod
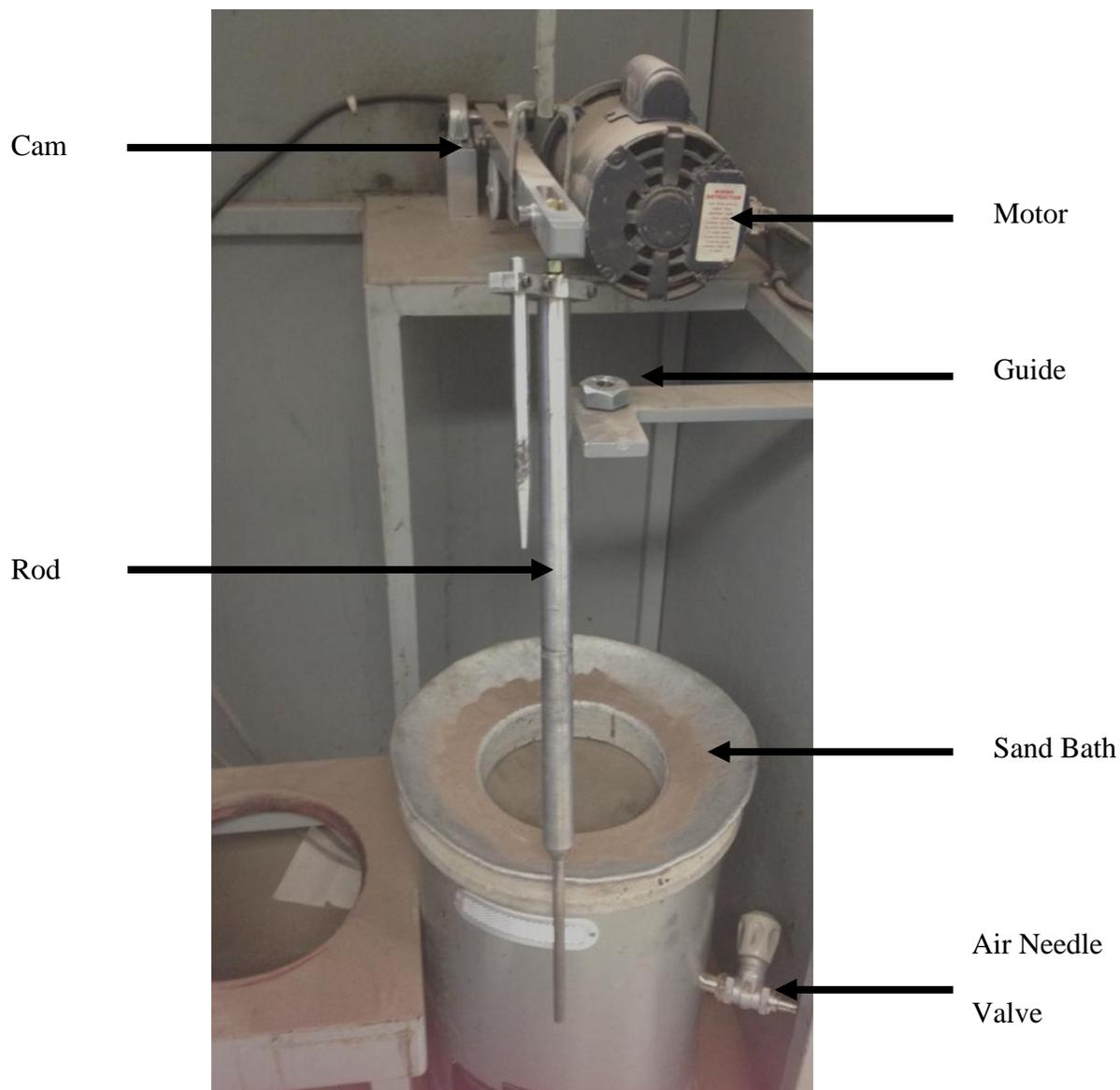
Sand Bath

Air Needle
Valve

Figure 3-2 Image of the sand bath with supporting equipment

An ultrasonic bath (Model 150HT Aquasonic Bath from VWR Scientific) was used in this study to provide an ultrasonic environment for the mixture of asphaltene and donor solvent. This bath has a capacity of 5.7L and provides the frequency 60Hz.

3.3 Experimental methods

3.3.1 Reactor Feed

For the asphaltene thermal cracking reaction, only industrial asphaltene was added into microreactor as feed. For the rest of experiments, industrial asphaltene and one kind of hydrogen donor solvents (Tetralin or Tetrahydroquinoline) were added as feed.

3.3.2 Reactor Loading

Depending on different conditions of each experiment, some samples were loaded into the micro batch reactor inside the glove box to eliminate the effects of oxygen and water loaded in the regular room condition.

The sample loading procedures at regular room condition were as follows. The micro batch reactor together with the cap were placed on the scale and then loaded with 1g of asphaltene, 5 stainless balls, 3g of hydrogen donor solvent (tetralin or tetrahydroquinoline) in sequence. The small stainless balls were used to promote mixing of the asphaltene and solvent mixture during the presoaking and thermal cracking stages.

For the samples loaded inside the glove box, the micro batch reactor with the

bracket and the feed together were transferred into the glove box (UNIlab work station from MBraun Incorporated). The glove box provided an argon atmosphere to avoid oxidation of the hydrogen solvent during reactions. All procedure for loading inside glove box were same as the regular loading at room condition, except the performer need to wear gloves to reach samples inside the glove box. After loading feed by sequence, the reactor should be closed by hand all together with cap, reactor neck and the bracket hold valve to maintain an argon environment inside the reactor. Then transfer the whole reactor out from glove box by the transferring rules employed above.

High purity argon was circulated inside the glove box to maintain an anaerobic environment. Water and oxygen content was constantly kept below 0.1ppm. Two sealed chambers, one large and one small, were located at the right hand side of glove box to allow users to transfer sample into and out from the glove box. The procedures for transferring sample into glove box were as follows:

- Open the chamber door outside and load sample on the tray inside the chamber, then close the chamber door

- Purge the chamber by opening the vacuum valve all the way to the end, when the pressure gauge read less than -25 in. Hg, start to refill the chamber with argon from glove box by turning back the vacuum valve.

- Same purging procedures should be performed 3 times.

- Because of sharing common argon atmosphere, the chamber should be at the same pressure with glove box and then open the chamber door inside to transfer sample into the glove box from chamber

The procedure to transfer sample out of glove box is the same as described above, except the chamber door inside should be opened first to load the sample on the tray, then open the outer chamber door afterwards.

3.3.3 Reactor sealing and purging with nitrogen

After loading with the sample, the hand tightened reactor was gently loosened to apply the sealent (NeverSeez from Industrial Supply Group, LLC) to the threading of the reactor top. This sealent ensures that reactor could be easily opened after high temperature reactions. For further tightening, the reactor was then held in a bench vice and tightened with a wrench.
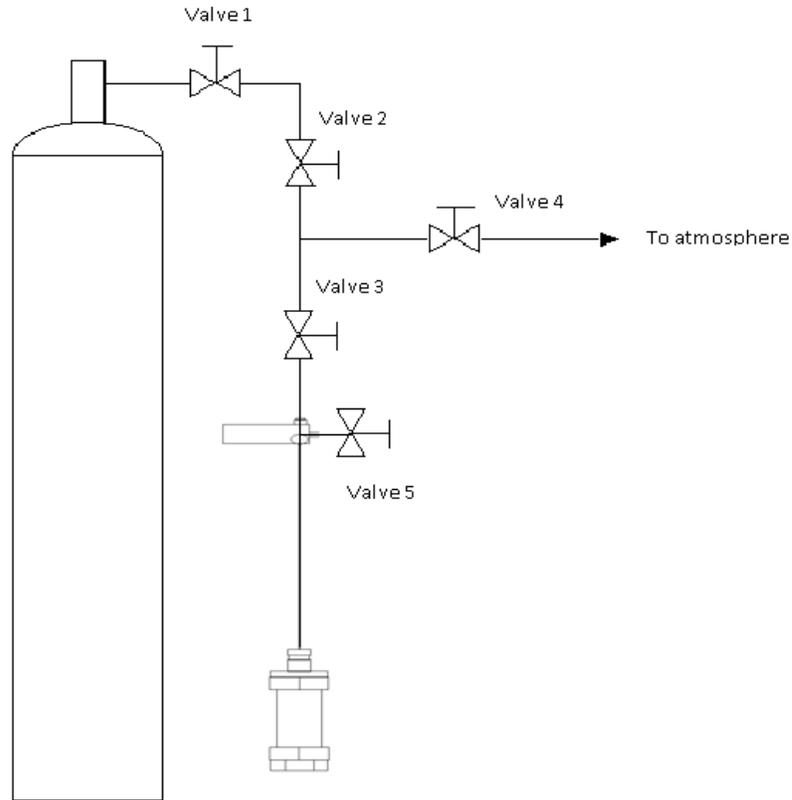
Figure 3-3 Schematic of the nitrogen cylinder connection

The fully closed reactor was connected to a nitrogen cylinder for a leak check at 1379 kPa. After all leaks were removed, a purging step at 551.6 kPa was performed. The following steps were used for the leak check and purging steps, using connections to the nitrogen cylinder (Figure 3-3).

- Open the valves 1, 2, 3 and 5, while keeping valve 4 closed, to let the nitrogen flows through the line.
- Apply the leak detection liquid from the valve 2 along the tube line all the way to the reactor including every fitting area. Wait for at least 2 min to check if there are any bubbles. Usually the air bubble could be found around the

reactor fittings, and that means the reactor should be taken off, retightened and connected to the cylinder to recheck leaks.

- Repeat the leak check step until the leak is eliminated. Then start to purge the reactor with nitrogen at pressure 80 Psi by adjusting the valve 1. Keep the valve 2 and 3 open, while valve 4 closed, and let nitrogen flows into reactor for 2 min.
- Close valve 2 and open valve 4 to purge the gas mixture in reactor and then close valve 4 and open valve 2 to refill the reactor with nitrogen lasting for 2 min. This step should be repeated for at least 3 times.
- Close the valve5 on the reactor first, and then disconnect the reactor.

3.3.4 Ultrasonic mixing

Before either reaction, 30 min of ultrasonic treatment of the micro reactor were used to disperse asphaltenes. The micro batch reactor was inserted into the aquasonic bath filled with 15cm depth of water at room temperature. The sonication would further dissolve the asphaltene in donor solvent and let the mixture become more uniform.

3.3.5 Reaction

In this study, three stages are included in the reaction sequence. The first and last stages are presoaking and thermal cracking individually. Both of them were

carried out in the sand bath with continuous heating. The second stage between presoaking and thermal cracking is the cooling interval.

The presoaking stage was carried out in a 200^oC fluidized sand bath with different time periods and reaction environments. Tests with different time periods varying from 0 to 180min were performed at this stage. Three reaction environments, varies from air and water to a pure argon environment were also used in this presoaking stage. All of these factors were tested as a way to find out if presoaking stage could be effective to disaggregate asphaltene thermal cracking.

Interval cooling was performed after presoaking stage by simply taking out micro batch reactor from sand bath to atmosphere environment. The interval cooling period varies from 0 to 2 hour, as a way to find out if the temperature drop between presoaking and thermal cracking could be a factor to influence on the asphaltene disaggregation effect.

The thermal cracking stage was carried out in the sand bath at 430^oC for 1 hour. Since same amount of coke yield was expected from thermal cracking stage, the time length of thermal cracking was always kept at 1 hour.

3.3.6 Product Recovery and Analysis

After each reaction, the products including gas, liquid and coke were inside the micro reactor. Since coke yield is the most direct way to show if any factors could influence asphaltene disaggregation, coke was the only product collected in

this study.

Most of coke was mixed with liquid product and the rest of it stayed on the inside bottom wall of micro reactor. Gas product was released to atmosphere (inside a fume hood) through a tube connected with microreactor. The entire liquid product was poured into vacuum filtration equipment to remove the coke from the liquid product. With the help of brushing, solvent toluene was repeatedly added into the microreactor to wash off coke. Washed off coke and toluene from micro reactor was also poured into the filtration funnel to remove coke. After repeating the brushing the inside wall of microreactor several times, and filtering coke from toluene, almost all coke was collected by the above method. The filter paper, with a thin coke cake on top, was then removed from filtration equipment and left in fume hood over night to dry. The weight of coke was weighted and coke yield was then calculated.
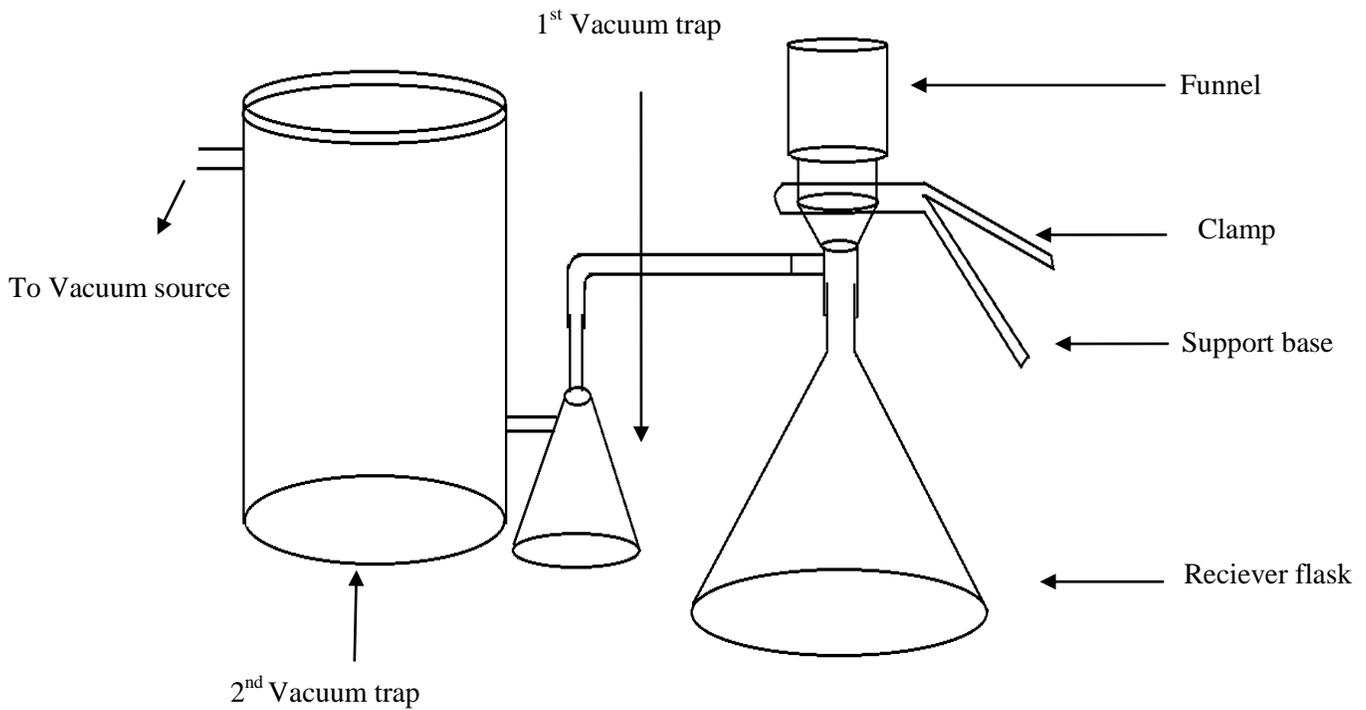
Figure 3-4Schematic of filtration equipment

The schematic of filtration device is introduced in Figure 3-4. Standard All-glass 47mm Filter Funnel Assemblies were manufactured from Millipore, including 300ml volume funnel, support base with a 40/35 female joint and 1000ml receiver flask. The support base provides a 9.6cm^2 effective filtration area on the top flat surface and has aside-arm to connect the vacuum trap. GVWP Filter paper of 0.22um pore size manufactured from Millipore was used to filter coke from other liquid product. The filter paper was put in between of the top surface of support base and the bottom of funnel. An aluminum clamp was applied at the joint of funnel and support base to stabilize the connection. The female joint of support base

was connected to the male joint of receiver flask. Both of the joints have frosting structure to ensure the sealing. Two vacuum traps in series, were connected from the side-arm of the support based to collect filtration solvent. The outlet of second vacuum trap was connected to a vacuum source to provide vacuum power for the whole filtration.

Chapter 4 Discussion and Conclusion

4.1 Validation of Experimental Method

To validate the experimental methods, the microreactor heating profiles during the thermal cracking and presoaking stages and the temperature profile during the cooling interval were obtained.

The measurement procedure was carried out by inserting a thermocouple inside the micro reactor. The thermocouple went through a modified "1/4× 1/16" cap union installed at the bottom part of reactor, to approximately half way along the reactor body. Then the microreactor was loaded with nitrogen pressurized at 552 kPa (80 Psi), with no feed present. To record signals, the thermocouple was linked to a device equipped with analysis software. For all the profiles, the thermocouple setup was the same.

4.1.1 Thermal Cracking Heating Profile

The microreactor heating profile under the thermal cracking condition was obtained to validate the repeatability of the microreactor heat-up, as illustrated in Figure 4-1, with the sand bath set temperature at 430°C for 1 hour reaction time.

Figure 4-1 shows the temperature of the microreactor as a function of time starting from 0 min, when the microreactor was inserted into sand bath and agitation was begun. The temperature of microreactor was above 420°C within 292 s, and then the microreactor reached a steady state temperature at 423. 7°C. After 1 hour of reaction was completed, the microreactor was taken out from sand bath to quench in a 20°C water bucket to stop the reaction. The temperature dropped from 423.7°C to 100°C within 88 s.
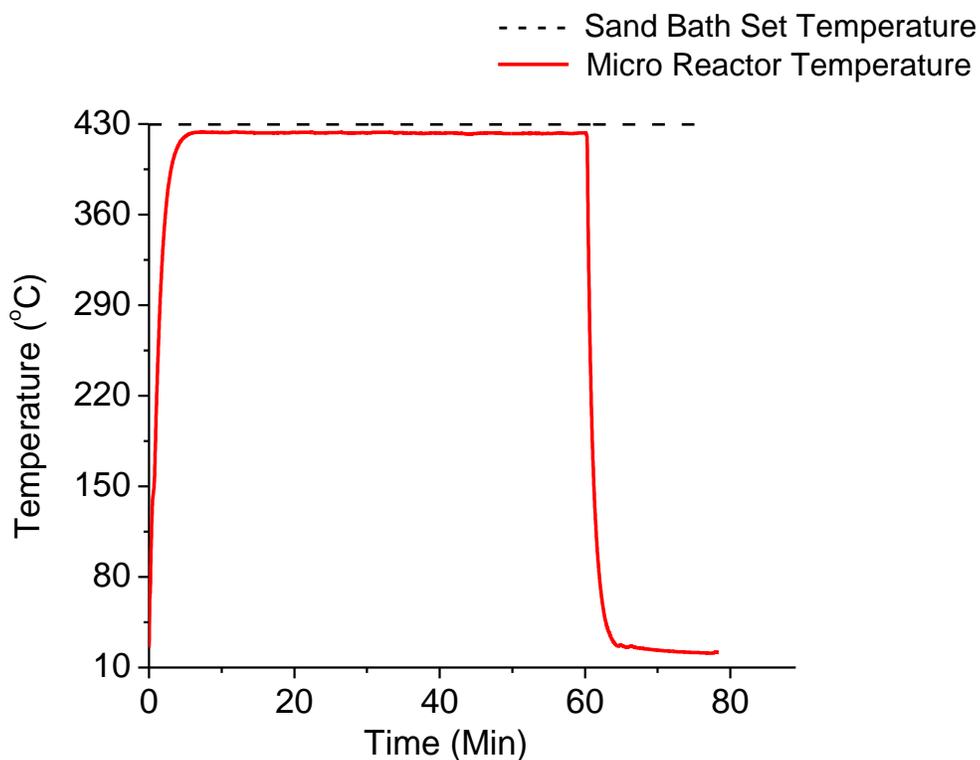
Figure 4-1 Micro reactor temperature profile of 1 hour thermal cracking at 430°C

4.1.2 Presoaking Heating Profile

The microreactor heating profile during the presoaking stage was obtained to validate the heat-up phase as illustrated in Figure 4-2, with the sand bath set temperature at 200°C for a 1 presoaking period. The microreactor was inserted into the 200°C sand bath and the temperature was recorded from 0 min. The temperature of the microreactor reached 180°C within 178 s once the presoaking started. The steady state temperature reached 197.8°C after 288 s. After the 1 hour presoaking stage, the reactor was taken out from sand bath to the room temperature environment to drop the temperature by air cooling.
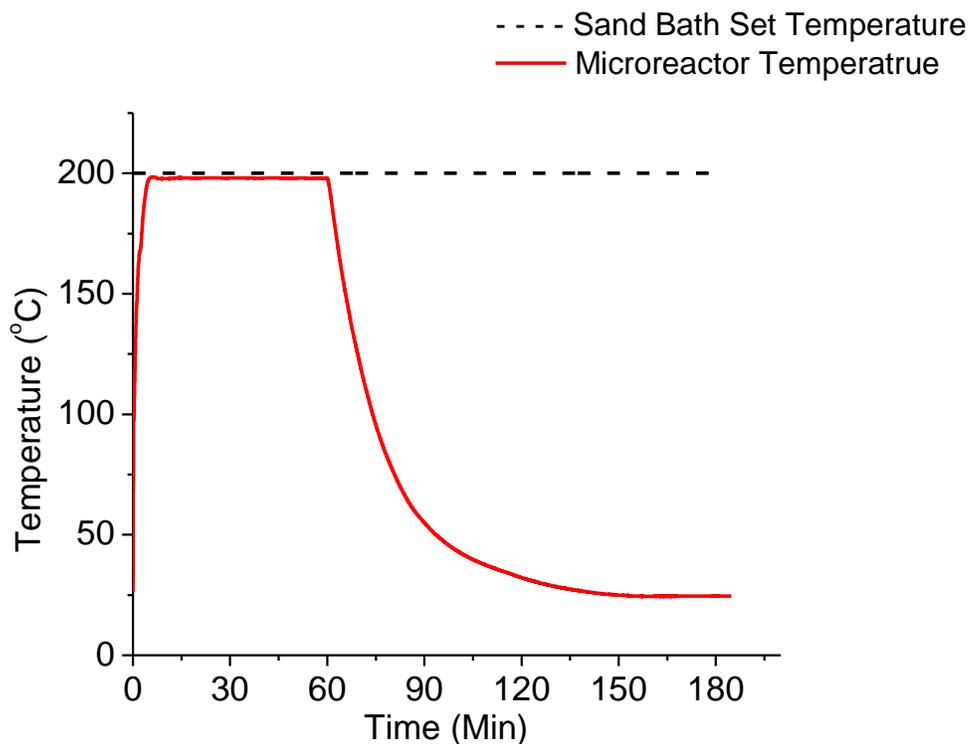
Figure 4-2 Micro reactor temperature profile of 1 presoaking at 200oC

4.1.3 Cooling interval Temperature profile

To test the cooling interval as a factor which could have an influence on the disaggregation effect of hydrogen donors (as introduced in the hypothesis}, after 1 hour of presoaking the microreactor was taken out from sand bath and put in the room temperature environment to cool down. The temperature of microreactor dropped to $25^{o}C$ in 1 hour and 29 min after the cooling started. For the rest of

cooling interval, the microreactor temperature was maintained at room temperature. Cooling interval is a factor to test, which may influence the disaggregation effect on asphaltene thermal cracking.

Different cooling intervals represent the time period to drop the temperature between presoaking and thermal cracking. To create a cooling interval, reactor was put in room temperature air after the presoaking for varying time periods from 0 to 120 min to investigate if different cooling interval will affect the coke yield. A temperature profile of microreactor going through 1 hour presoaking, 2 hour interval cooling and 1 hour thermal cracking by sequence is shown in Figure 4-3. The temperature of the microreactor drops from 200°C to room temperature during the 2 hour cooling interval. For the 1 hour cooling interval, thermal cracking will start at 120min, when the temperature of microreactor drops at 32.3°C, and the rest of temperature profile will be kept same. For the 0 min cooling interval condition, the microreactor was taken out from sand bath A to insert into sand bath B directly after 1 hour presoaking without going through any cooling interval.
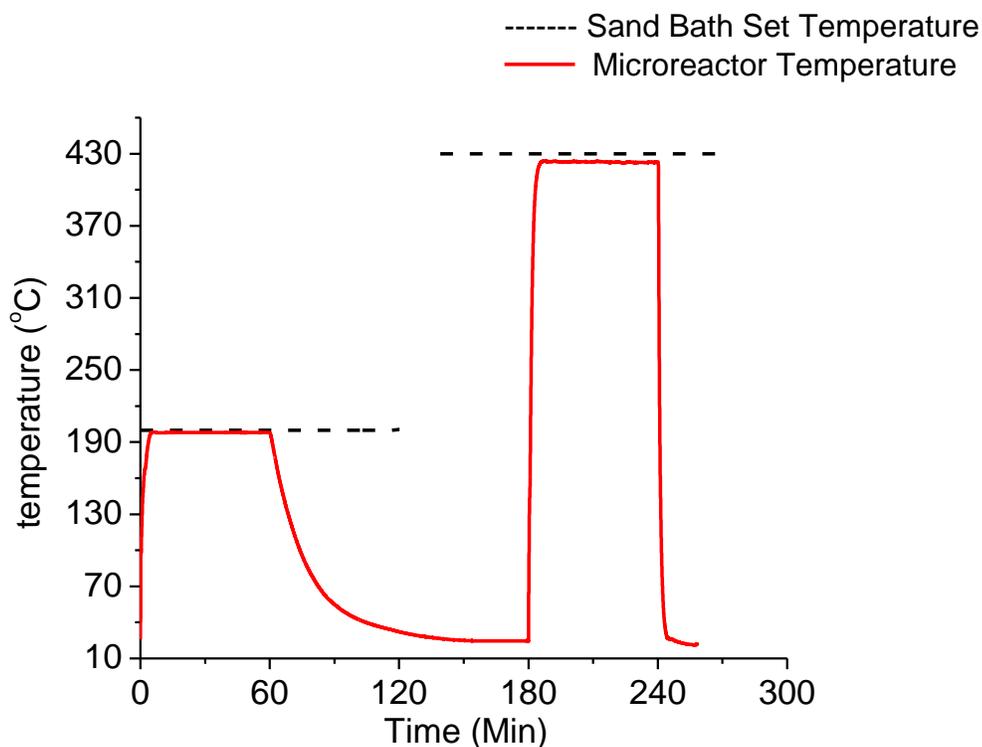
Figure 4-3 Microreactor temperature of presoaking, interval cooling and thermal cracking

4.2 Hydrogen Donor Solvent Addition Effect on Thermal Cracking

Tetralin and tetrahydroquinoline (THQ) hydrogen donor solvents were added into the thermal cracking reactions, as a way to find out if hydrogen transfer can be provided from hydrogen donor solvents.

Firstly, asphaltene thermal cracking was carried out without solvent in the micro batch reactor at a temperature of $430^{o}C$ for 1 hour. 1g of industrial asphaltene was loaded with 5 stainless balls. Before inserting the reactor into sand bath, the regular purging, leak test and 30min sonication steps were performed in sequence as

introduced in Chapter 3.3.5.

Secondly, a series of tests of solvent addition in thermal cracking were completed. 3g of solvent either tetralin or THQ were added into 1g industrial asphaltene, maintaining the ratio of solvent to asphaltene at 3:1, with 5 stainless balls loaded as well. Except extra solvent was added into thermal cracking, the rest of steps were exactly same compared with asphaltene thermal cracking.

4.2.1 Coke yields comparison between asphaltene and hydrogen donor solvent addition thermal cracking

After the each reaction, coke was filtered from the filtration equipment, and then the coke yields for both asphaltene and solvent-addition thermal cracking were calculated based on the product and feed data. The equation 4.1 below shows how coke yield was calculated. Coke amount (g) means mass of coke collected on filter paper; asphaltene amount (g) means mass of feed asphaltene were loaded before thermal cracking. The calculations are the same for not only for both conditions in this section, but also same for different presoaking factors in the following sections.

$$\text{Coke yield }\%=\frac{\text{Coke amount }(g)}{\text{Asphaltene amount }(g)} \text{ (Equation 4.1)}$$

Figure 4-4 shows the coke yields from solvent-free asphaltene thermal cracking and solvent addition into thermal cracking (Tetralin and THQ). It is very obvious that both Tetralin and THQ can help to reduce the coke yield from 38% to
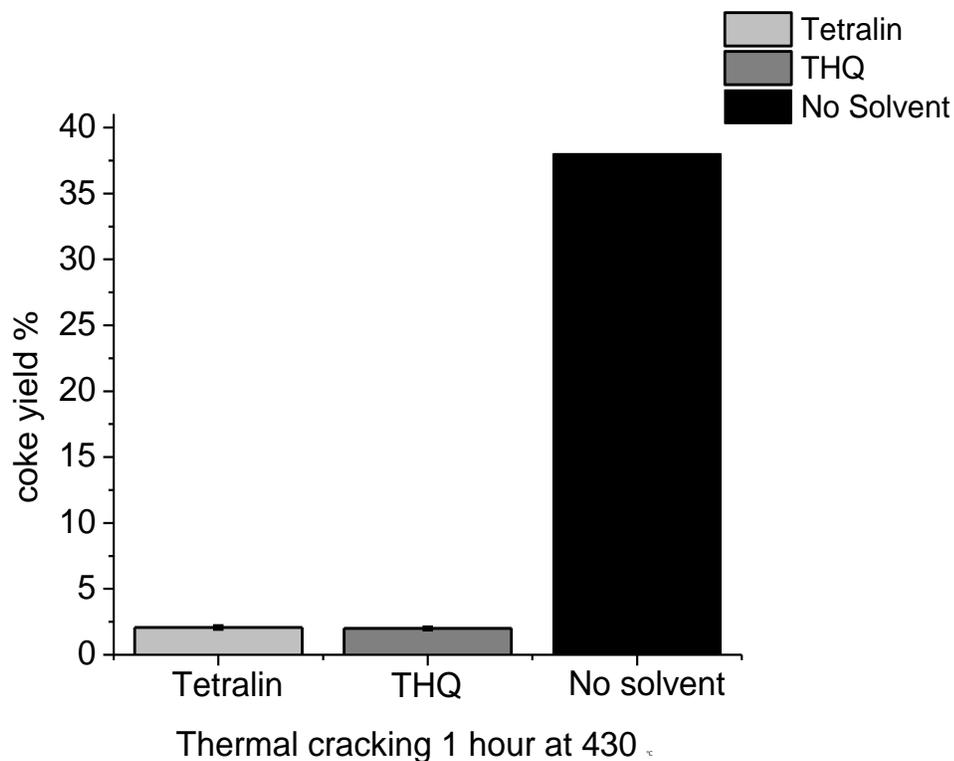
2.07% and 2.00% individually.

Figure 4-4 Coke yield on asphaltene and solvent addition thermal cracking tests (Error bars were calculated from seven repetition tests of tetralin and THQ individually)

By addition of hydrogen donors into thermal cracking, the coke yields were suppressed significantly by the hydrogen donation. This result is consistent with the studies introduced in the Chapter 2, showing that hydrogen donors have the ability to control coking reactions and lower coke yield. Consequently, the first hypothesis of this study, that addition of hydrogen donors into thermal cracking will suppress coke yield, was proved by this result.

4.3 Presoaking Effect on Coke yield

From the above results, hydrogen donor solvents are able to bring a significant suppression of coke formation in thermal cracking. Will presoaking stage further lower coke yield by the disaggregation asphaltenes as the second hypothesis proposed? To find out the answer, the 200°C presoaking stage was created prior to the 1 hour thermal cracking stage, while keeping all the other steps the same. Factors such as presoaking period, presoaking environment and the cooling interval after presoaking are the main three factors that could potentially influence the coke yield, and the following study will investigate each of the factors.

4.3.1 Effect of presoaking period

The different presoaking periods were used to check the effect of this variable. The regular purge steps were performed to make sure the presoaking environment was the same; also, right after the presoaking step was finished, the reactor was removed from the 200°C sand bath A to 430°C sand bath B to start the thermal cracking step, which kept the cooling interval time at 0 min. Presoaking periods from 0 to 180 min were carried out for tetralin, and from 0 to 60 min presoaking for THQ.
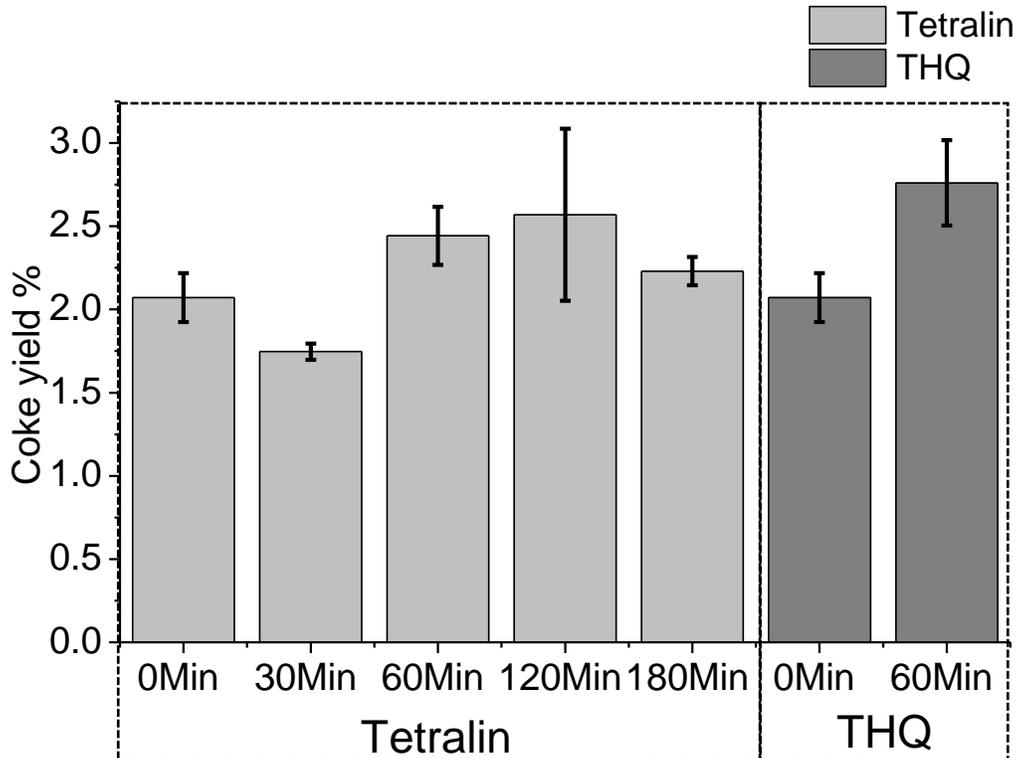
Figure 4-5 Coke yields of different presoaking period (Error bars were calculated from triplicate tests)

Figure 4-5 shows coke yields of Tetralin and THQ added into thermal cracking with different presoaking period. The standard error bar of a series of same presoaking period tests can be found on each coke yield bar, calculated from standard deviation divided by square root of sample size (Equation 4.2).

Figure 4-5 shows coke yields of Tetralin and THQ added into thermal cracking with different presoaking period. The standard error bar of a series of same presoaking period tests can be found on each coke yield bar, calculated from standard deviation divided by square root of sample size (Equation 4.2).

$$SE = \frac{s}{\sqrt{n}}$$ (Equation 4.2)

From figure 4-5, it is easy to observe that the error bars overlap each other in the tetralin tests indicating no significant effect. A students t-test on the THQ tests shows that there is no significant difference between the 60 min presoaking and no presoaking tests. Consequently, for both donor solvents the presoaking period is not a factor to that influences the coke yield from thermal cracking.

As introduced in Chapter 2, Miura's pretreatment of hydrogendonor solvents prior to coal flash pyrolysis work brought a drastic increase of both the total volatile matter and the tar yield [22]. He concluded the result is based on both the physical effect to enlarge the micropores of coal molecules and the chemical effect of hydrogen transfer donated by donor solvents to stabilize the coal fragments. Compared with Miura's result, the presoaking stage of hydrogen donor solvents with different periods did not affect the coke yields in this study. One possible reason for the result stems from the difference of solubility between coal and asphaltene. Asphaltene can totally disperse in both of the donor solvents at room temperature, down to the level of nanoaggregates, while most of coal particles could not dissolve in tetralin. As a solid material, tetralin was able to affect the pore structure and enlarge the coal micropores. The coal micropore size increased with the pretreatment temperature in Miura's study, giving enhanced mass transfer of volatiles out of the solid matrix. For pretreatment at 25°C, the minimum micropore size was the same as from raw coal. The maximum coal micropore size, which was

1.5 times larger than it from raw coal, was obtained at a temperature range for pre-treatment with tetralin at 100-250°C. Accordingly, by employing the pretreatment, the intimate distance between coal and solvents can be achieved so that more amounts of easily reacted hydrogen can be transferred from tetralin to coal.

In contrast to coal, asphaltene can totally disperse in donor solvents down to a length scale of 5-15nm. Scattering studies suggest that the aggregates of asphaltene are partly suppressed at reaction temperatures [8,9]. The lack of effect due to the presoaking could be due to several factors:

1. Rapid kinetics of swelling and disaggregation – If the interactions between the solvent and the asphaltenes are rapid at reaction temperatures, then presoaking would have no effect because the reaction environment for the asphaltene molecules would be the same in both cases.

2. No disaggregation – If the asphaltenes did not disperse, then presoaking would have no impact. From the introduction in Chapter 2, Miura's work of coal pretreatment with tetralin at elevated temperature brought the micropores enlargement [22] which leads to the inspiration of this work that presoaking of asphaltene can give a fairly level of asphaltene disaggregation.

3. Low coke yield – The reaction conditions in this study gave relatively low coke yields of circa 2 wt%. This selection was designed, in order to investigate the ability of presoaking to give essentially coke-free operation. The data of Figure 4-2 show that the repeatability of the experiments was very good, so that changes in

coke yield in range of 1 wt% are significant. Consequently, these experiments

gave enough coke to give statistically significant tests of whether soaking with the

donor solvents was beneficial.

Work on fouling of heat exchangers suggests that kinetics of disaggregation

of asphaltenes may be slow. Wiehe suggests that once asphaltenes are unstable at

room temperature, they will foul heat exchangers even at elevated temperatures [20].

Although the aggregation may decrease as temperature increases, the rapid heating

in a heat exchanger may be more rapid than the rate of dispersion of the asphaltenes.

The critical difference from Weihe's arguments and this study is that unstable

asphaltenes form flocs with sizes over 1 μm, which is orders of magnitude larger

that the nano-aggregates of 5-15 nm that we would expect to be present in the

present study. The much larger particles would be much slower to redisperse in the

liquid medium.

4.3.2 Effect of oxygen in presoaking stage on coke yields

Different presoaking environments were tested by using different amounts of

air maintained inside the reactor during the presoaking step.

Firstly, the regular purge step helped to maintain an intermediate amount of

oxygen and water compared with the other two methods. Under the regular purge

procedure, the reactor was purged by 1379 kPa (200psi) nitrogen at least three times,

so that most of the oxygen and water can be removed during purging. In this case some oxygen would still be dissolved in the solvent liquid.

Secondly, a method of no purge was used as a way to maintain the highest amount of oxygen and water inside the reactor. With no purge step, the reactor was not purged and consequently the gas inside reactor has exactly same composition as atmosphere air, which means the largest oxygen and water amount was contained in microreactor.

Lastly, loading the sample in a glove box helped to create an oxygen and water free environment inside the reactor. The asphaltene and solvent were put inside glove box one day ahead to remove those dissolved oxygen. The sample loading and finger-tight sealing of the reactor were both performed inside the glove box, so that the glove box tests means the least oxygen and water in the reactor environment.
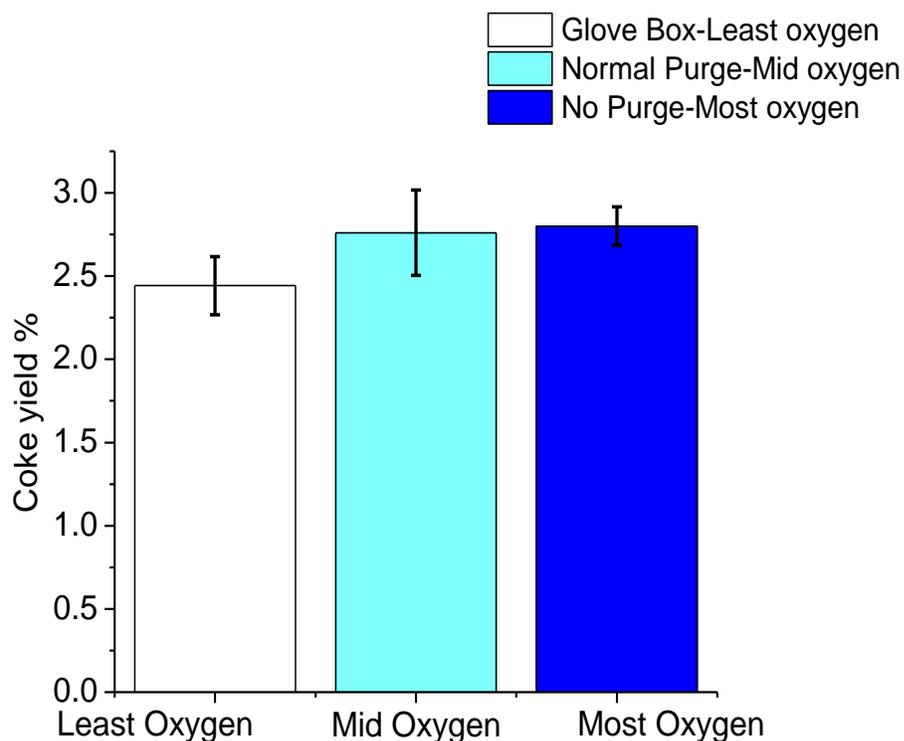
Figure 4-6 Coke yields of different presoaking environment (Error bars were calculated from triplicate tests)

The coke yields of different presoaking environment are shown in figure 4-6. From figure 4-6, the standard error bars overlap each other, showing that different amounts of trace oxygen is not a factor that could influence the coke yield in the presoaking experiments. As introduced in chapter 2, Lee et al. found out the presence of oxygen resulted in more coke and tetrahydrofuran formation [23]. However, in this study, oxygen content over the range tested is not a factor that impacts the coke yield.

4.3.3 Effect of cooling intervals between presoak and thermal cracking

The coke yields of different cooling interval with Tetralin and THQ are shown in Figure 4-7. From the figure, it is obvious to see that coke yields from each donor solvent are very close at 2.5% and leads to the conclusion that cooling interval could not affect the coke yield of thermal cracking. From Figure 4-3, for the 0 hour cooling interval, the thermal cracking starts from $200^{o}C$ right away after presoaking; For 1 hour cooling interval, the temperature of the mixture of the donor solvent and asphaltene dropped to $32.3^{o}C$ before thermal cracking; For 2 hour cooling interval, the temperature of the mixture dropped to room temperature and maintained at $21.5^{o}C$ for over 35 min before the thermal cracking started.
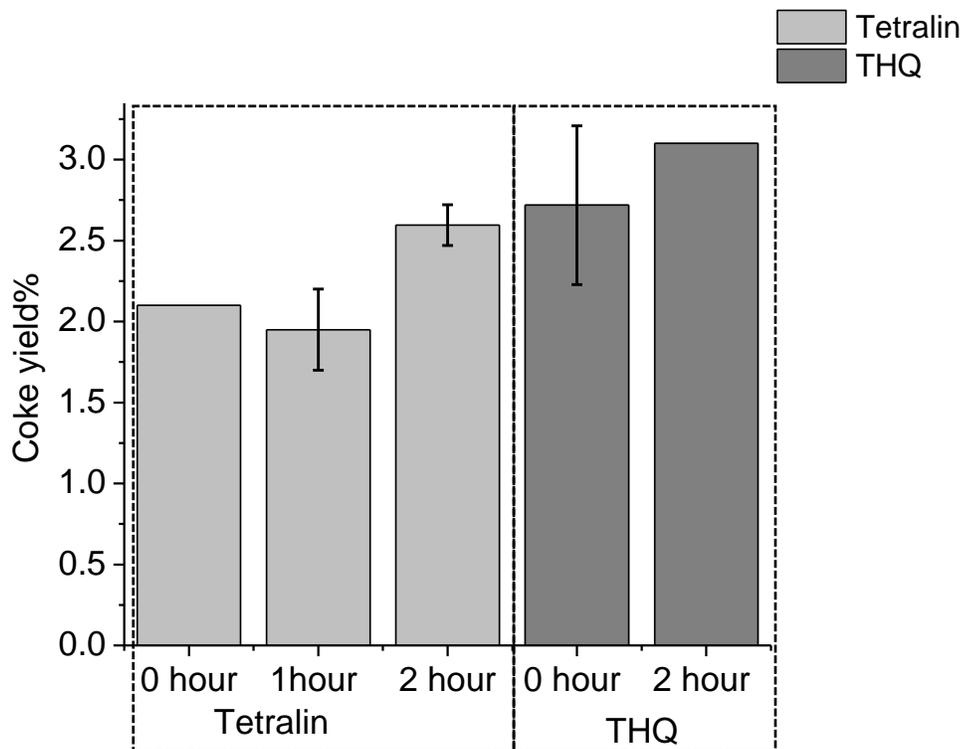
Figure 4-7 Coke yields of different cooling interval between presoaking and thermal cracking (Error bars were calculated from triplicate tests)

In chapter 2, it was expected that a cooling interval after the presoaking stage could lead to the reduction of presoaking affect because of the temperature drop of the mixture. However, different periods of cooling did not affect any of the presoaking results, so that the coke yields from thermal cracking were unaffected.

4.4 Implication

The large coke reduction effect brought by hydrogen donor addition shows

the potential application of hydrogen donor solvents into the field of heavy oil processing. It has long been recognized that hydrogen donor has the extraordinary ability to control coking reactions; however it has never been employed in any of the process from refineries or upgraders so far simply because of the extremely high cost. It only can be used in large scale production when the dose is significantly reduced. Next, the challenges of solvents separation and regeneration come along to overcome.

Based on the hydrogen donor solvent to asphaltene ratio as 3: 1 in this study, a fully mixed liquid phase reaction environment was created so that the coking control could be reached at maximum. Accordingly, it becomes even harder to scale up this ratio of solvent to oil into industry process. So, an economic optimum of resid or heavy oil process employing hydrogen donor solvents is in great request.

Chapter 5 Conclusion

5.1 Conclusions

Two conclusions can be drawn from the results in the above sessions:

1. Addition of hydrogen donor solvents in thermal cracking reactions can significantly reduce coke yield from 38% to 2%.

2. The presoaking stage did not further suppress coke formation varies from different period, environment and interval cooling period.

5.2 Future work

The results from this study can be used as an input to give a more complete picture for the role of hydrogen donor solvents in asphaltene thermal cracking reactions. Some future works are recommended as follows:

More works are needed to analyze the liquid and gas products from thermal cracking reactions, since it is possible that hydrogen donor disaggregation effect does exist. And at the same level of coke yield, the improvement of liquid and gas products qualities could be an evidence for the disaggregation effect.

Naphthalene, which is stable and produced from tetralin by donating 4 moles of hydrogen, has the similar solubility feature compared with tetralin, so that it can be added to thermal cracking reactions as a way to distinguish the abilities of

disaggregation and hydrogenation from hydrogen donors.

For industry application, the ratio of hydrogen donor solvent to asphaltenes and the thermal cracking reaction conditions are two quite important factors to test in experiment scale and pilot plants to ultimate the process.

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