Study on Stability of Asphaltenes in Thai Crude Oil

Ekapop Tongton

A Thesis Submitted in Partial Fulfillment of the Requirements for the
Degree of Master of Engineering in Chemical Engineering
Prince of Songkla University
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This is to certify that the work here submitted is the result of the candidate’s own investigations. Due acknowledgment has been made of any assistance received.

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I hereby certify that this work has not been accepted in substance for any degree, and is not being currently submitted in candidature for any degree.

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ชื่อวิทยานิพนธ์ ศึกษาเสถียรภาพของแอสฟัลทีนในน้ำมันดิบในประเทศไทย

ผู้เขียน นาย เอกภพ ทองตัน

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บทคัดย่อ

แอสฟัลทีน (Asphaltenes) เป็นองค์ประกอบหนึ่งของน้ำมันดิบ ซึ่งมักก่อปัญหาสำคัญในอุตสาหกรรมปิโตรเลียม หนึ่งในปัญหานั้นคือการตกตะกอนของแอสฟัลทีน ในประเทศไทยปัญหาการตกตะกอนของแอสฟัลทีนมักพบในกระบวนการขนส่งน้ำมันดิบ เนื่องมากจากการเปลี่ยนแปลงของอุณหภูมิ ความดัน และองค์ประกอบของน้ำมันดิบ ซึ่งส่งผลต่อเสถียรภาพของแอสฟัลทีนในน้ำมันดิบ ทำให้แอสฟัลทีนเกิดการตกตะกอนและก่อให้เกิดปัญหาการอุดตันภายในท่อ ดังนั้นงานวิจัยนี้ได้ทำการศึกษาหาโครงสร้างหรือตัวแปรที่เป็นสิ่งบ่งบอกถึงโครงสร้างของแอสฟัลทีน เพื่อใช้เป็นข้อมูลพื้นฐานในการศึกษาเสถียรภาพของแอสฟัลทีน โดยได้ทำการสกัดและหาปริมาณของแอสฟัลทีนโดยใช้วิธีการกรองแยกและการหมุนเหวี่ยงในน้ำมันดิบแหล่ง L1 และได้ทำการหาปริมาณของแอสฟัลทีนและเรซินในน้ำมันดิบแหล่ง L1 L2 และ L3 นอกจากนี้ได้ทำการศึกษาผลของการใช้ตัวทำละลายเฮกเซนและเฮปเทนต่อปริมาณการตกตะกอนของแอสฟัลทีน สำหรับการสกัดเรซินใช้วิธีการ ASTM D2007 ซึ่งอาศัยแรงโน้มถ่วงในการชะสารละลาย ซึ่งเป็นกระบวนการที่ใช้ระยะเวลานาน ดังนั้นจึงประยุกต์ใช้ปั๊มสุญญากาศในการช่วยในการชะสารละลาย โดยในงานวิจัยนี้ ได้หาปริมาณของเรซินในน้ำมันดิบ L1 โดยใช้ 2 เทคนิคข้างต้นด้วยเช่นกันนี้ แอสฟัลทีนและเรซินที่สกัดได้ถูกวิเคราะห์โดยใช้เทคนิค NMR และ FTIR เพื่อบ่งบอกถึงโครงสร้างเบื้องต้นของแอสฟัลทีนและเรซิน

ผลการทดลองพบว่า ปริมาณแอสฟัลทีนในน้ำมันดิบเมื่อใช้การกรองแยกจะมีปริมาณสูงกว่าแอสฟัลทีนที่ใช้การหมุนเหวี่ยงในการแยก เนื่องจากวิธีการกรองแยกมีสารปนเปื้อนคือ wax ติดมากับแอสฟัลทีนที่ได้รับจากการสกัด โดยปริมาณของแอสฟัลทีนในน้ำมันดิบแหล่ง L1 L2 และ L3 เท่ากับ 1.67 1.36 และ 0.82 เปอร์เซ็นต์โดยน้ำหนัก ตามลำดับ ปริมาณแอสฟัลทีนที่ใช้เฮกเซนและเฮปเทนในการสกัดเท่ากับ 1.69 และ 1.67 เปอร์เซ็นต์โดยน้ำหนัก ตามลำดับ และมีปริมาณเรซินในน้ำมันดิบแหล่ง L1 L2 และ L3 เท่ากับ 14.57 18.89 และ 13.27 เปอร์เซ็นต์โดย

น้ำหนัก ตามลำดับ ในการสกัดเรซินโดยใช้วิธีการสุญญากาศ จะได้ปริมาณสูงกว่าวิธีการ ASTM D2007 เนื่องจากแรงในวิธีการของสุญญากาศสูงกว่าวิธีการ ASTM D2007 ส่งผลให้องค์ประกอบอื่นปนเปื้อนมากับปริมาณเรซินที่สกัดได้โดยเฉพาะกลุ่มอะโรมาติกซึ่งเป็นองค์ประกอบหนึ่งในน้ำมันดิบเช่นกัน

นอกจากนี้ยังได้ทำการศึกษาผลของอุณหภูมิต่อเสถียรภาพของแอสฟัลทีน เนื่องจากเป็นหนึ่งในปัจจัยที่ทำให้แอสฟัลทีนเกิดการตกตะกอน จากการศึกษาพบว่า เมื่ออุณหภูมิสูงขึ้น ส่งผลให้เสถียรภาพของแอสฟัลทีนในน้ำมันดิบมากขึ้น เนื่องจากแอสฟัลทีนสามารถกระจายตัวในน้ำมันดิบได้ดีขึ้น ณ อุณหภูมิสูง สำหรับการศึกษาทางด้านผลของสัดส่วนระหว่างปริมาณแอสฟัลทีนต่อเรซิน ซึ่งเป็นการศึกษาทางด้านขององค์ประกอบภายในน้ำมันดิบพบว่า เมื่อสัดส่วนระหว่างแอสฟัลทีนต่อเรซินสูงขึ้น ส่งผลให้เสถียรภาพของแอสฟัลทีนในน้ำมันดิบลดลง เนื่องจากในการเพิ่มสัดส่วนระหว่างแอสฟัลทีนต่อเรซินที่มากขึ้น นั้นมาจากการเพิ่มปริมาณของแอสฟัลทีนที่มากขึ้น แต่ปริมาณเรซินซึ่งเป็นตัวที่ช่วยในการรักษาเสถียรภาพของแอสฟัลทีนมีปริมาณเท่าเดิม จึงส่งผลให้เสถียรภาพของแอสฟัลทีนลดลง ซึ่งทั้งสองการทดลองทั้งในการศึกษาผลของอุณหภูมิ และสัดส่วนระหว่างปริมาณแอสฟัลทีนต่อเรซิน จะใช้คุณสมบัติทางกายภาพในที่นี้ คือ ความหนาแน่นและความหนืดของน้ำมันดิบ เป็นตัวบ่งบอกถึงเสถียรภาพของแอสฟัลทีนในน้ำมันดิบ

Thesis Title Study on Stability of Asphaltenes in Thai Crude Oil

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Major Program Chemical Engineering

Academic Year 2015

ABSTRACT

The precipitation of asphaltenes from crude oils can lead to serious challenges during oil production and processing due to the change of pressure, temperature and crude oil composition casing the stability of asphaltenes in crude oil. This work was to study of structure or parameters indicating the structure of asphaltenes in order to use the data base to prevent their precipitation and this may help us to understand its function as the stability of asphaltenes. The structural characteristic of asphaltenes from L1 crude oil sources was separated into fractions by using two different procedures; ASTM D2007 and vacuum procedures. Moreover, two light alkanes, including n-hexane (n-C_6) and n-heptane (n-C_7) were also used to precipitate asphaltenes. The asphaltenes and resins contents of L1, L2, and L3 crude oil sources were also determined. Normally, resins extraction by following ASTM procedure is a time consuming process due to the elution process carried out under gravity force. Therefore, the force of vacuum was applied as the alternative ways. So, these two techniques were used to determine the resins contents of L1. Moreover, Proton Nuclear Magnetic Resonance (^{1}H NMR), Carbon Nuclear Magnetic Resonance (^{13}C NMR), and Fourier Transform Infrared (FTIR) spectroscopy techniques were used to characterize the elementary molecular of asphaltenes and resins.

The results showed that the use of filtration technique caused the higher asphaltenes contents due to wax contamination in that fraction. Moreover, the asphaltenes contents in L1, L2, and L3 were 1.67, 1.36, and 0.82 %wt, respectively. The asphaltenes contents precipitated by n-hexane and n-heptane were 1.69 %wt and 1.67 %wt. Also, the resins contents in L1, L2, and L3 were 14.57, 18.89, and 13.27 %wt, respectively. In addition, the use of vacuum technique caused the higher resins contents due to aromatics contamination in that fraction. The primary structural parameter of the asphaltenes of Thai crude oil was revealed for the first time.

The effect of temperature on the stability of asphaltenes was also investigated. It was demonstrated that at higher temperatures, the stability of asphaltenes was higher due to better distribution of asphaltenes in crude oil. Moreover, the stability of asphaltenes depended on the ratios of asphaltenes to resins (A/R ratios) in the crude oil. It was found that the stability of asphaltenes in crude oil decreased when A/R ratios increased due to the precipitation of destabilized asphaltenes. Due to the increase of asphaltenes to resins ratio, the more amounts of asphaltenes must be added in the sample, but the amount of resins playing a role to increase the stability was constant. Moreover, the density and viscosity difference from a change in temperatures and A/R ratios were used to investigate the key parameter in the aggregation of asphaltenes and control the stability of asphaltenes.

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Ekapop Tongton

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CHARPTER 1

INTRODUCTION

1.1 Asphaltenes precipitation

Crude oils are complex hydrocarbon components which have considerable variation in the color, gravity, odor, sulfur content, and viscosity. Oils produced in different regions of the world have compositional characteristics depending on source rock type, and maturity. Asphaltenes are the heaviest and most complex fraction of crude oil. Asphaltenes in different crude oil sources might have different content and structure.[1]

Asphaltenes are one of crude oil component causing a major problem in the petroleum industry known as asphaltenes precipitation. This precipitation problem can occur in the process of drilling (upstream), transportation (midstream), and refining (downstream). Asphaltenes may precipitate in different places along the production processes, for instance, formation of asphaltenes inside of pumps, tubing, wellheads, safety valves, flowlines, and surface facilities as represented in Figure 1.1.[2]

Figure 1.1 Asphaltenes precipitation problem[2]

The precipitation of asphaltenes predominantly depends on their stability in crude oil.[3] The changes of temperature, pressure, and compositions during oil production can induce asphaltenes destabilization. Therefore, asphaltenes tend to precipitate into clusters causing precipitation problem in various processes leading to the decrease of capacity and productivity. Thus, the economics including costs of operation and maintenance is higher than normal.[1, 4]

1.2 Research motivation

Mostly crude oil in Thailand is light crude oil, the asphaltenes content itself is not as high as compared to those of heavy crude oil. Light crude oil with small amount of asphaltenes is more prone to cause problems than heavy oil because heavy crude oil contains many of intermediate components, resins, that are good asphaltenes solvents whereas the light crude oil may consist mainly of paraffinic materials, which are poor soluble for asphaltenes.[5, 6] Moreover, the mixing of different crude oil sources can induce asphaltenes precipitation and deposition due to the change of crude oil composition.[7]

The stability of asphaltenes in Thai crude oil has never been discussed. Additionally, the study of asphaltenes molecular structure is the key to prevent their precipitation and can help understanding its function as the stability of asphaltenes.[8, 9] In order to prevent the asphaltenes precipitation problems as stated above, to know and to understand the structure of asphaltenes in difference crude oil sources, might help preventing asphaltenes precipitation problem.

1.3 Research objectives

In this study, not only the asphaltenes and resins contents as well as asphaltenes structures, but also the asphaltenes precipitation and resins separation methods were investigated. The standard ASTM and the modified ASTM methods were applied in order to quantity and qualify the obtained asphaltenes and resins. The effect of solvent types on the precipitated asphaltenes contents as well as their structures was also studied. In addition, the effect of the temperature and the ratios of asphaltenes to resins on the stability of asphaltenes were also discussed. The objectives of the present study are as follows:

1.3.1 Asphaltenes contents and their structures

1.3.1.1 Studies of the separation methods on asphaltenes contents and their structures.

This work studied the asphaltenes contents and their structures in L1 crude oil. The experiments were conducted by using two different asphaltenes precipitation methods; which are filtration and centrifugation. The precipitated asphaltenes were analyzed their functional groups by using Fourier Transform Infrared (FTIR) spectroscopy technique. Moreover, Proton Nuclear Magnetic Resonance (^{1}H NMR), Carbon Nuclear Magnetic Resonance (^{13}C NMR) were used to determine some structural parameters in the precipitated asphaltenes.

1.3.1.2 Studies of the asphaltenes contents and their structures in three different crude oil sources.

This work studied the asphaltenes contents and their structure in L1, L2, and L3 crude oils. The experiments were conducted according to ASTM D2007 method. The precipitated asphaltenes form three different crude oil sources were analyzed for their functional groups and some structural parameters by using Fourier Transform Infrared (FTIR) spectroscopy and Nuclear Magnetic Resonance (NMR) techniques, respectively.

1.3.1.3 Studies of the effect of solvent types on the asphaltenes precipitation and their structures

This work studied solvent types used to induce asphaltenes precipitation in L1 crude oil. The experiments were conducted by using two different types of solvent, which are n-hexane and n-heptane. The precipitated asphaltenes from two different solvent types were analyzed for their functional groups and some structural parameters by using FTIR and NMR techniques, respectively.

1.3.2 Resins contents and their structures

1.3.2.1 Studies of the separation methods on resins contents and their structures.

This work studied the resins contents and their structure in L1 crude oil. The experiments were conducted by using liquid adsorption chromatography with two different procedures. Resins were separated according to ASTM D2007, the adsorption was carried out under gravity force, and another experiment was done under vacuum pressure. The separated resins were analyzed for their functional groups and some structural parameters by using FTIR and NMR techniques, respectively.

1.3.2.2 Studies of the resins contents in three different crude oil sources

This work studied the resins contents in L1, L2, and L3 crude oils. The experiments were conducted according to ASTM D2007 method.

1.3.3 Asphaltenes stability

1.3.3.1 Studies of effect of operating parameters on asphaltenes stability.

This work was focused on investigating the effect of operating temperatures and the ratios of asphaltenes to resins on asphaltenes stability of L1, L2, and L3 crude oils. The experiments were conducted by measuring density and viscosity deviations of L1, L2, and L3 crude oils due to the variation of temperatures and the ratios of asphaltenes to resins. Experiments were conducted under typical conditions in crude oil transportation process in which on the temperature range of 40°C to 70°C. The ratios of asphaltenes to resins were varied in order to imitate the difference in asphaltenes and resins contents in crude oil.

CHARPTER 2

THEORIES AND LITERATURE REVIEWS

Asphaltenes and resins background were reviewed in this chapter. The first two sections provided some information for asphaltenes and resins in crude oil. The saturates, aromatics, resins, and asphaltenes analysis (SARA analysis) and asphaltenes precipitation mechanism were discussed in the third and fourth sections, respectively. Asphaltenes characterization was reviewed in the last section.

2.1 Asphaltenes

Asphaltenes firstly defined by Boussingault in 1837 as the distillation residue of bitumen are insoluble in alcohol and soluble in turpentine.[10] Asphaltenes are the heaviest and the most complex fraction of crude oil. They are more defined in term of solubility class than structural molecule class. They are soluble in aromatic solvents such as toluene and benzene, but are insoluble in light n-alkane such as n-pentane (n-C_5), n-hexane (n-C_6), and n-heptane (n-C_7).[1, 4]

In general, the structure of asphaltenes consists of aromatic rings, long aliphatic chains, and alicyclic. Each component can be substituted by heteroatoms such as oxygen, nitrogen, and sulfur as well as trace metals, nickel and vanadium. Moreover, the composition and structure of asphaltenes are widely different depending on the origin of crude oil sources. Therefore, the amount of aromatics, alkane, alkyl chains, and heteroatom are altered.[11-13]

The structure of asphaltenes is consistent with the Yen model-stacking asphaltenes fused-ring system which was suggested more than 40 years ago as shown in Figure 2.1.[12, 13]

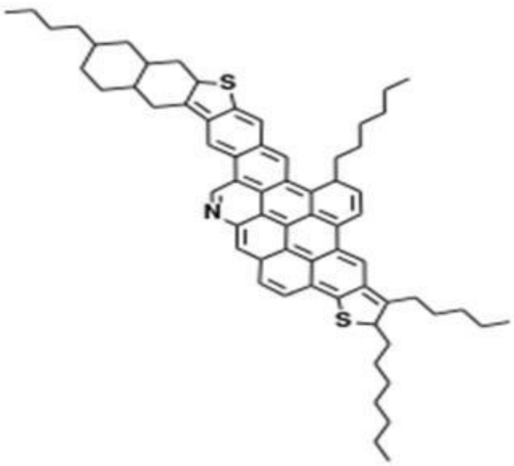


Figure 2.1 Structure of asphaltenes by Yen model[12, 13]

2.2 Resins

Resins, which are separated by using SARA analysis are defined as the composition of crude oil recovered by liquid adsorption chromatography after elution of oils by nonpolar solvents.[14] The Figure 2.2 shows the structures of resins having a similar structure as asphaltenes, but they have a lower content of hydroxyl groups, aromatics, alkane, alkyl, and heteroatoms causing the molecular weight less than asphaltenes.[8]

The role of resins on asphaltenes stability was investigated by Nellensteyn in 1930. He proposed a hypothetical model where resins adsorb on asphaltenes and provide a steric stabilizing layer. The resins in oil prevent the precipitation of asphaltenes by increasing the stability of asphaltenes and decreasing the size and amount of precipitated asphaltenes. They play a role as surfactants in stabilizing colloidal particles of asphaltenes in oil are shown in Figure 2.3.[8, 15] When a solvent, light n-alkane, is added to oil, resins are dissolved in the liquid, leaving active areas of asphaltenes particles, which allow the aggregation of the same and, consequently, asphaltenes precipitation.[8] So the stability of asphaltenes in oil also depends on the ratio of resins to asphaltenes in the oil.[9]

Figure 2.2 The structure of resins[16]

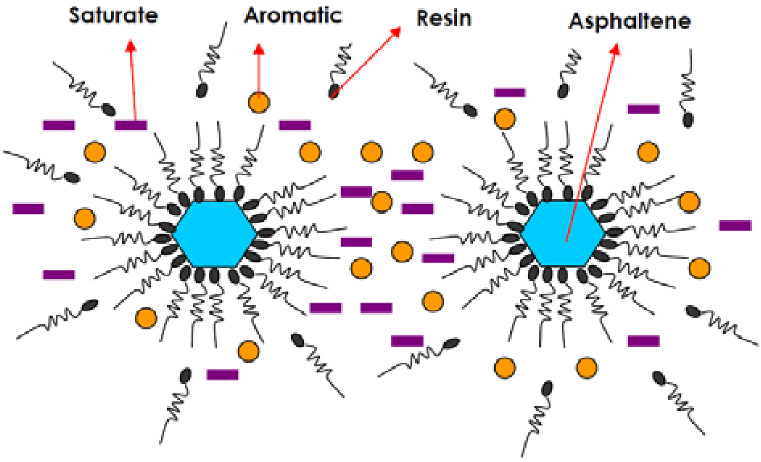


Figure 2.3 The mechanism of resins interacted with asphaltenes[15]

2.3 Saturates, aromatics, resins, and asphaltenes analysis (SARA analysis)

SARA analysis is the method of separating crude oil into saturates, aromatics, resins, and asphaltenes fractions as represented in Figure 2.4. In SARA fractionation, asphaltenes are separated from the other hydrocarbon components by adding n-alkane such as n-heptane or n-propane. The remaining components which are called maltenes are then further fractionated by passing the mixture through a liquid adsorption chromatography column. Each component is removed from the column by flushing with various solvents. Saturates are the molecule containing the maximum number of hydrogen atoms without no double or triple bonds between the carbon and hydrogen atoms. Aromatics normally consist of one or more rings of six carbon atoms and six hydrogen atoms such as benzene (C_6H_6).[17]

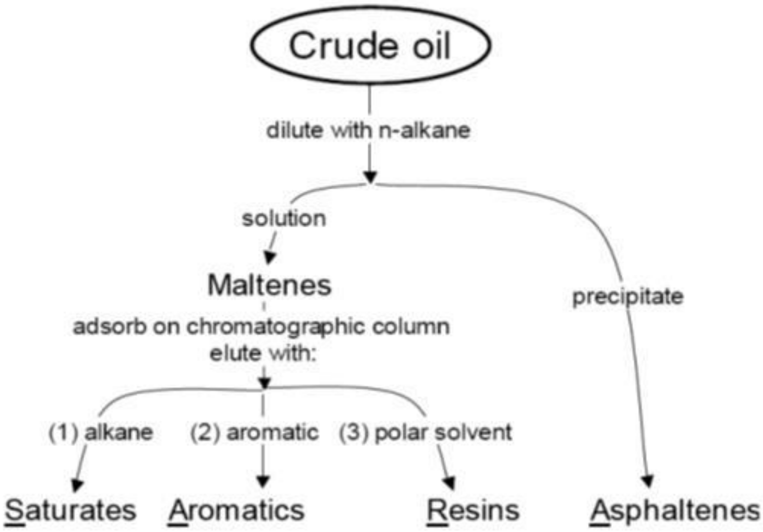
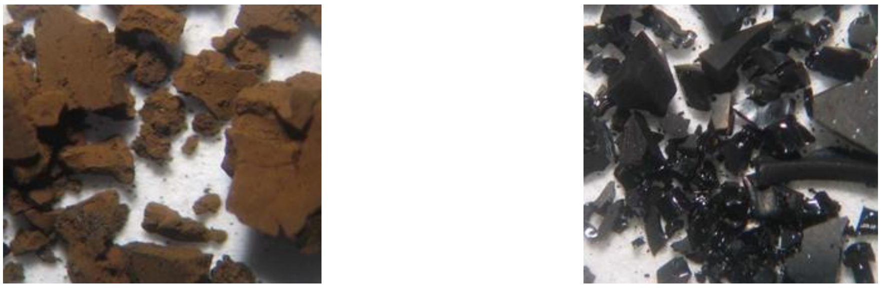


Figure 2.4 SARA analysis[17]

The different types of solvent (n-alkane) used can cause the different appearance of asphaltenes obtained in color and texture. Asphaltenes separated with lower molecular weight alkanes (e.g., propane) would be sticky and more liquid-like as represented in Figure 2.5.[17]



(a) (b)

Figure 2.5 Examples of the appearance of asphaltenes separated from Mars-P crude oil with an excess of (a) n-pentane (n-C_5) and (b) n-heptane (n-C_7)[17]

2.4 The mechanism of precipitated asphaltenes

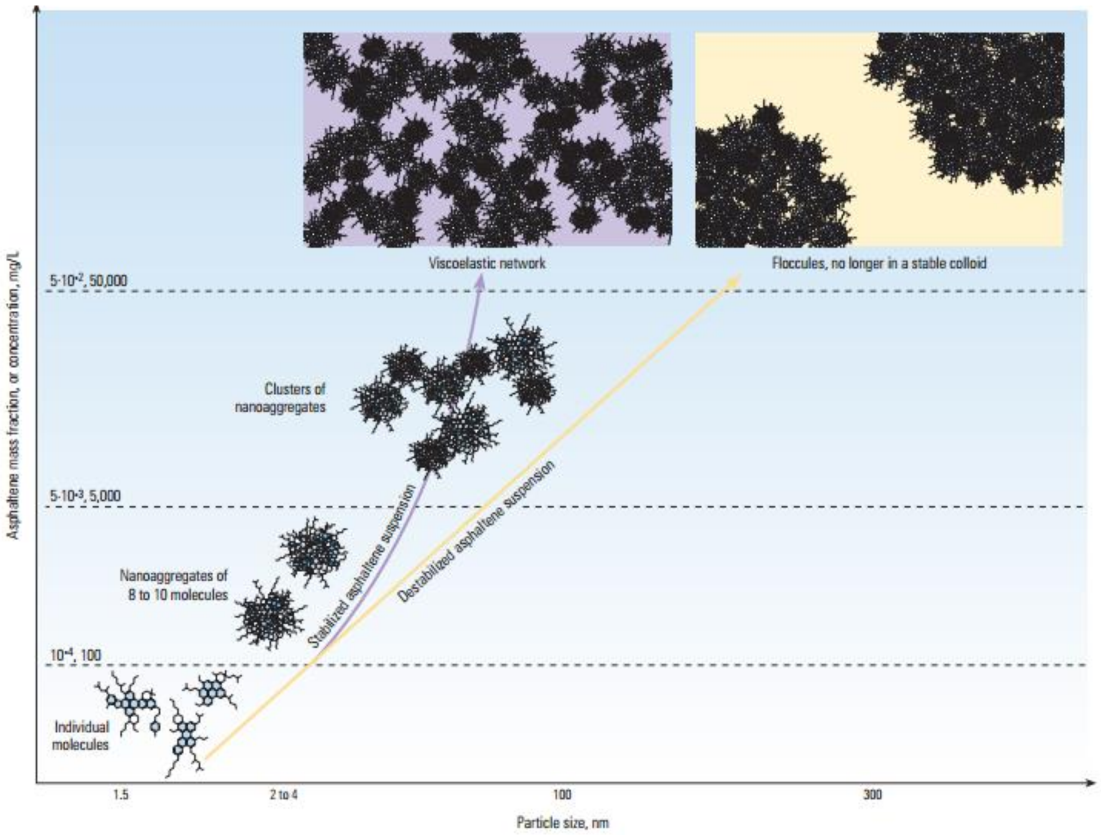


Figure 2.6 The mechanism of precipitated asphaltenes in crude oil and toluene[18]

Figure 2.6 shows the precipitation properties of asphaltenes depending on the types of used solvent; crude oil (purple) or toluene (yellow). When the concentrations or mass fraction of asphaltenes are lower than 100 mg/L or 10^{-4} mass fraction, individual molecules can be seen especially at low concentrations. When concentration increases, the molecules will stick together. As concentration increases to 100 mg/L, or 10^{-4} mass fraction, the molecules is quite near-spherical molecules due to aggregation of eight to ten molecules of asphaltenes. In this area is called nanoaggregates of asphaltenes. Once the concentration are higher than 5,000 mg/L, or mass fraction of $5x10^{-3}$, nanoaggregates becomes the clusters. Alkane chains of adjacent clusters may interact. These clusters may remain in stable colloidal suspension until concentration reaches a mass fraction of 10^{-2}. Therefore, the stability can be reduced at higher concentrations in crude oil causing the asphaltenes clusters precipitation.[18]

2.5 Asphaltenes characterization

Over the past few decades, many literatures have been discussed on the structure of asphaltenes using numerous techniques including ^{1}H NMR and ^{13}C NMR, FTIR, Electron Spin Resonance (ESR), Mass Spectroscopy, X-ray, Vapor Pressure Osmometry (VPO), Electron Microscopy, and Gel Permeation Chromatography (GPC). The use of each technique depends on the objectives of the researches and principles of that technique.[19]

NMR is one of the techniques that is widely used to characterize, especially the ^{1}H NMR and ^{13}C NMR spectroscopy, providing relevant information about the series of structural parameters. The significant data obtained from NMR spectroscopy such as H_{α}, H_{β}, H_{γ}, aliphatic carbon (C_{al}), and aromatic carbon (C_{ar}) are used to calculate the structural parameters, like aromaticity (f_a) and n_{carbon}.[20-22] Moreover, FTIR spectroscopy is also used to characterize the functional groups of asphaltenes such as aromatics, aliphatic including alkane and alkene, and hydroxyl groups.[20, 23-25]

CHARPTER 3
METHODOLOGY

3.1 Chemicals, materials and equipment

Thai crude oil samples in three different sources, L1, L2, and L3, supplied from Petroleum Authority of Thailand (PTT) were used to study in this work. Three crude oil samples were measured some crude oil physical properties. Ambient density measurement (DMA 4500 M) was used to determine the density of crude oils. The viscosity of crude oils was measured by using Electromagnetic viscometer (EV 1000). Liquid Analyzer Gas Chromatography (7890A) was used to characterize crude oil composition in term of amount of each compound in crude oils. Moreover, the cold fingers (CF15200) was used to determine the wax content in crude oil.

The asphaltenes of crude oil samples were induced to precipitate by adding two different light alkane solvents, n-hexane and n-heptane (Ajax Finechem Pty Ltd, Netherlands). After asphaltenes precipitation was occurred, the precipitated asphaltenes were separated from crude oils by using two methods, filtration and centrifugation techniques. Filtration technique consists of suction flask, filter paper (8 μm), borosilicate filtering funnel, and vacuum pump. While the centrifugation technique consists of centrifuge (Equipment & Chemical Co., Ltd, Bangkok) and centrifuge tube. The obtained asphaltenes were redissolved in toluene (Labscan Asia CO Ltd, Thailand) in order to remove the contaminated fraction. Moreover, resins were separated by adsorption on clay (Ashapura volcaly Co., Ltd, Thailand) and were flushed by mixture of toluene and acetone (Labscan Asia CO Ltd, Thailand). Clay was packed into designed column according to ASTM D2007.

3.2 Methodology

3.2.1 SARA analysis

3.2.1.1 Asphaltenes separation

(1) Filtration technique

Asphaltenes were induced to precipitate from crude oil sample (W_{oil}) by weighing 10 g of crude oil and then n-heptane was added 450 ml during stirring the mixture at room temperature to ensure homogeneity. The mixture sample was rinsed through filter paper (8 µm) connected with a 125 mm of borosilicate filtering funnel and a vacuum pump. Asphaltenes were precipitated on the filter paper, which were washed with n-heptane until the washing was colorless. The obtained fractions were resoluble in toluene to separate the contaminated fraction. Dissolved asphaltenes were recovered by toluene evaporation.[17]

(2) Centrifugation technique

(2.1) n-C_7 asphaltenes

A centrifugation based separation technique was developed to quantify the amount of asphaltenes. The centrifuge was set to 4000 rpm, corresponding to a relative centrifugation force (RCF) of 2469. In these experiments, 270 ml of n-heptane was mixed with 7 g of crude oil sample (W_{oil}). The mixture was stirred by magnetic stirrer to ensure homogeneity. Then, each sample was centrifuged at 4000 rpm for 10 min, causing the asphaltenes particles aggregated and precipitated at the bottom of the centrifuge tube. The liquid is decanted to separate it from the asphaltenes particles, which form a compact cake in the bottom of the tube. The asphaltenes were then washed several times with heptane to remove the minor quantity of contamination adhering to the asphaltenes particles until the solution becomes colorless. Toluene was added in each tube to separate the contaminated fraction. Dissolved asphaltenes were recovered by toluene evaporation.[4, 26]

(2.2) n-C_6 asphaltenes

Asphaltenes were separated from crude oil sample (W_{oil}) with the same procedure as n-C_7 asphaltenes but the solvent was changed from of n-heptane to n-hexane.[4, 26]

3.2.1.2 Asphaltenes contents

After toluene evaporation, the obtained asphaltenes ($W_{asphaltenes}$) were weighted. Then asphaltenes contents were calculated, as the following equation.[17]

$$Asphaltenes\ contents\ (\%wt) = \frac{W_{asphaltenes}}{W_{oil}} x100 \qquad (3.1)$$

3.2.1.3 Resins separation

There are two different maltenes, filtration and centrifugation maltenes due to the asphaltenes separation methods. Each maltenes fraction was further separated into saturates, aromatics, and resins by using liquid adsorption chromatography with two different procedures, ASTM D2007 and applied vacuum procedure.

(1) ASTM D2007 procedure (gravity force)

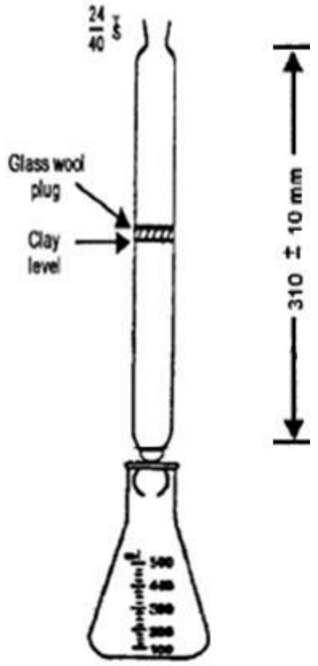


Figure 3.1 Clay adsorption column[17]

Figure 3.1 showed the clay adsorption column. It was prepared by placing 100 g of clay adsorbent in the column. A piece of 25 mm thickness of glass wool was used over the top surface of the clay in the column to prevent agitation of the clay while charging the eluent solvents. It was important that the adsorbents in column be packed to a constant level. A minimum of ten taps with a soft rubber hammer at different points up and down and 25 taps on top of column should be employed to achieve constant level. A suitable rubber hammer may be assembled by fastening two No. 7 or 8 rubbers. Resins were separated from deasphalt oil or maltenes, which was separated asphaltenes out of crude oil. Maltenes were weighed 5 g of sample and then n-heptane was diluted with 25 ml of n-heptane solvent and mix well to ensure a uniform solution. The sample should not display precipitate or flocculate at this point. If a precipitate was present asphaltenes may be removed by the procedure of asphaltenes separation. 25 ml of n-heptane was added to the clay to activate its adsorption. The diluted maltenes were rinsed though column after that approximately 500 ml of n-heptane was rinsed slowly to the column and maintain a head level above the clay beds to wash the saturates portion of the sample from the adsorbents. The first obtained fraction was saturates and solvent recovered by n-heptane evaporation. After n-heptane effluent has essentially drained from the column, charge a 50 to 50 volume mixture of n-heptane and toluene. Collected 1560 ml of the mixed heptane and toluene rinsed to column and maintain a head level. The obtained fractions were recovered by n-heptane and toluene evaporation so that the remained fraction was aromatics with some remaining saturates. Finally, the remained component on the clay were resins and other polar fractions. They were flushed by 50 to 50 volume mixture of toluene and acetone added continually into the column until the effluent liquid was practically colorless. Then, the obtained fractions from column were brought in the separatory funnel. Then, 10 g of anhydrous calcium chloride were added to that fraction in the separatory funnel and shake for about 30 s. Allowed the mixture to settle for at least 10 min. Then, the anhydrous calcium chloride was taken by filter paper. Moreover, the water contamination, which was bottom the separatory funnel due to the highest density, was effluent. Finally the mixed toluene and acetone were evaporated by using evaporator to obtain the fraction of resins.[17]

(2) Vacuum procedure

Normally, resins extraction by following ASTM procedure is a time consuming process. It is due to the elution process carried out under gravity force. Therefore, the force of vacuum was applied to be the alternative ways due to less time than general procedure. Resins were separated from maltenes sample with the same solvent as ASTM D 2007 procedure but the vacuum force was applied. This procedure used vacuum pump for resins separation.

3.2.1.4 Resins contents

The obtained resins (W_{resins}) were weighted, then were calculated the resins contents, as the Eq.3.2

$$Resins\ contents\ (\%wt) = \frac{W_{resins}}{W_{asphaltenes} + W_{maltenes}} x100 \qquad (3.2)$$

3.2.2 Determination of asphaltenes and resins structures in Thai crude oils

3.2.2.1 Nuclear Magnetic Resonance (NMR) (Varian, Germany)

(1) ^{1}H NMR Spectroscopy generated the distribution of H atoms in the aliphatic and aromatic regions of the asphaltenes. Liquid-state proton or ^{1}H NMR spectra operated at 500 MHz. Chemical shifts were reported (in parts per million, ppm), which were relative to the appropriate reference signals. ^{1}H NMR spectra were recorded in deuterated chloroform ($CDCl_3$) with a pulse width of 3 microsecond, a recycle delay of 2 seconds, a spectral width of 16 ppm, a tube diameter of 5 mm, and at least 128 scans.

(2) ^{13}C NMR studies were performed in 5 mm tubes at 298 K at 125 MHz using deuterated chloroform ($CDCl_3$) as the solvent (100 mg of asphaltenes in 0.5 ml of $CDCl_3$). The pulse program was set to inverse gated decoupling with a flip angel 30°. At least 8,000 scans were collected and averaged for each asphaltenes to enhance the accuracy.

3.2.2.2 FTIR Spectroscopy (Bruker, Germany)

FTIR was used to characterize the asphaltenes functional groups. Infrared spectra were recorded on a FTIR spectrometer in the transmittance mode over the wavenumber region of 4000-400 cm^{-1}. Asphaltenes samples were prepared by mixing the materials with spectroscopic-grade potassium bromide (KBr) to obtain a 1 (%wt/%wt) asphaltenes/KBr.

3.2.3 Asphaltenes stability

3.2.3.1 Effect of temperatures on the stability of asphaltenes in crude oil.

The cylinder with a 3.5 cm diameter and 24 cm height containing about 100 ml of crude oil was immersed in a water bath with temperature controller as shown in Figure 3.2. The temperature of the crude oil was kept at 40°C for 3 hours. Then, the crude oil was sampled at three different specific heights of cylinder. The sampling points; A, B, and C are the location of the top, middle, and bottom section of cylinder used to contain crude oil samples, respectively. The obtained crude oil was measured density and viscosity by Ambient Density Measurement (DMA 4500 M) and Electromagnetic Viscometer (EV1000), respectively. The procedures were the same as described in temperature at 40°C, but the temperature of crude oil was changed from 40 to 50, 60, and 70°C, respectively.

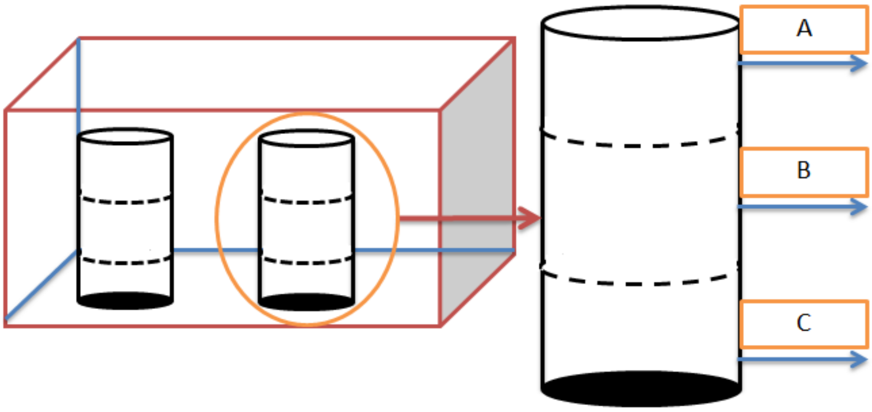


Figure 3.2 Experimental set up for studying the effect of temperature on asphaltenes stability

3.2.3.2 Effect of the ratios of asphaltenes to resins on the stability of asphaltenes in crude oil

Reconstitution of each crude oil sample was prepared with dispersion of asphaltenes and resins in the range of ratios of asphaltenes to resins, 0.042-0.154. These ratios were calculated and varied based on asphaltenes and resins original contents, shown in Appendix D. The asphaltenes were mixed with toluene before resoluble back because they are not resoluble directly in crude oil. In contrast, resins can be soluble in crude oil so they were added directly in their crude oil. The procedure is quite similar to the effect of temperatures on the stability of asphaltenes, but the temperature of each crude oil sources was fixed at 40°C.

CHARPTER 4
RESULTS AND DISSCUSTION

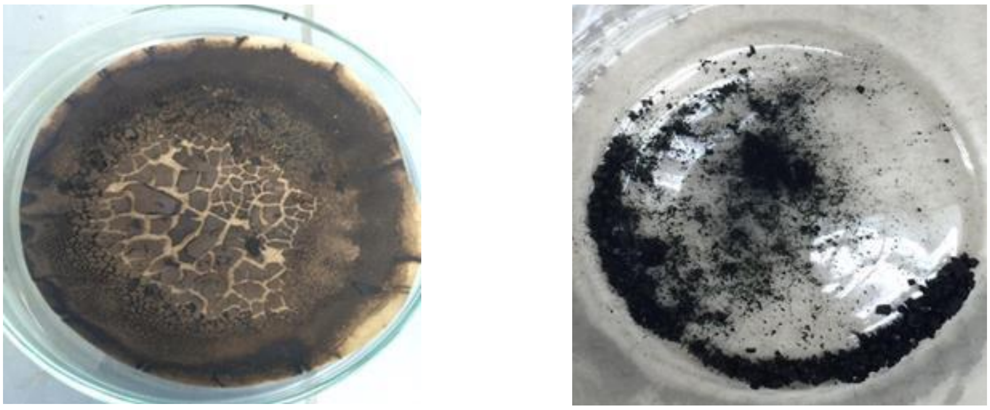
4.1 Asphaltenes contents

4.1.1 Effect of asphaltenes separation methods on asphaltenes contents

The asphaltenes contents of L1 precipitated by filtration and centrifugation techniques were 9.81 and 1.67 %wt, respectively shown in Table 4.1. Obviously, the use of filtration technique caused the higher asphaltenes contents due to the increase of the amount of wax contamination in that fraction. The use of filtration technique had a low pressure causing the temperature reduction during filtration. It was the most common cause of wax deposition because the decrease of temperature causing the wax solubility in crude oil declined.[27] Although the use of filtration technique was a conventional technique, it was not suitable for crude oil consisted of higher wax contents, which is 23.76 %wt at 30°C in L1 crude oil.

Table 4.1 The asphaltenes contents of L1 using the different separation technique with n-C_7

The procedures of separation	Asphaltenes contents (%wt)
Filtration	9.81
Centrifugation	1.67



(a) (b)

Figure 4.1 The obtained asphaltenes separated by (a) filtration technique and (b) centrifugation technique

In addition, the appearance of obtained asphaltenes were shown in Figure 4.1. It was found that the obtained asphaltenes by filtration technique was more blown and stingier solid than asphaltenes that were separated by centrifugation technique due to higher wax contamination of filtration technique. Normally, the asphaltenes samples obtained from both techniques were taken into an oven at 105°C. This condition caused the sample obtained from filtration technique melted on the filter paper. Generally, the asphaltenes were not melted at that temperature so that the obtained asphaltenes by filtration technique was not pure asphaltenes. There are some wax contaminated within these asphaltenes.

4.1.2 The asphaltenes contents of three different crude oil sources

The asphaltenes contents in each crude oil source are shown in Table 4.2. The asphaltenes contents of L1, L2, and L3 precipitated by n-heptane were 1.67, 1.36, and 0.82 %wt, respectively. Apparently, the asphaltenes content of L1 crude oil source is the highest following by L2 and L3. However, there were other parameters that can affect to the amount of asphaltenes precipitations such as solvent-to-crude oil ratio, mixing time, and temperature. These parameters must be fixed to avoid the deviation.[20]

Table 4.2 The asphaltenes contents in each crude oil source using n-heptane as solvents

Crude oil sources	Asphaltenes contents in crude oil (%wt)
L1	1.67
L2	1.36
L3	0.82

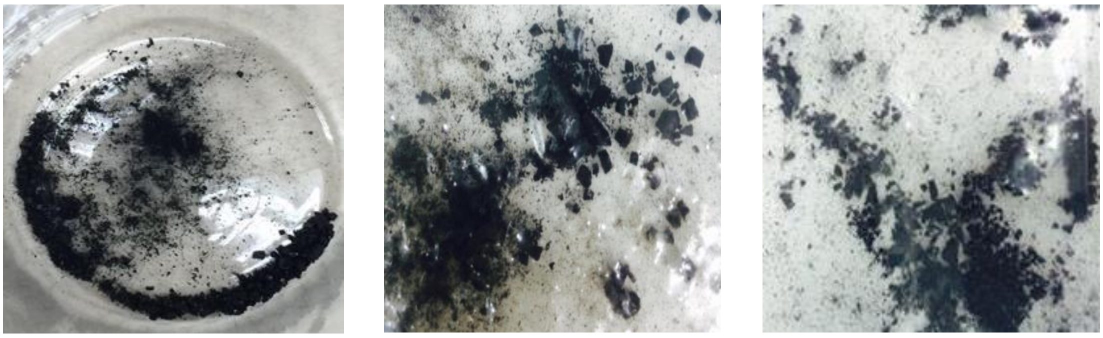

(a) (b) (c)

Figure 4.2 Asphaltenes of (a) L1, (b) L2, and (c) L3 crude oil sources

According to Figure 4.2, the appearance of obtained asphaltenes was black solid for all samples.

4.1.3 Effect of solvent types on the asphaltenes precipitation

The asphaltenes contents in each source are shown in Table 4.3. For example, the asphaltenes contents of L1 precipitated by n-hexane and n-heptane were 1.69 %wt and 1.67 %wt, respectively. Apparently, the use of low soluble carbon-number alkane solvents caused the higher precipitated asphaltenes contents due to the increase in the amount of resins contamination in that fraction.[20-22] The polarity of light n-alkanes affected the amount of separated asphaltenes. The higher polarity of solvents used, the higher asphaltenes precipitation obtained in the solvents.[20-22]

Table 4.3 The asphaltenes contents in L1 crude oil source using the different solvents

Crude oil sources	Asphaltenes contents in crude oil (%wt)	
	Separated by n-hexane	Separated by n-heptane
L1	1.69	1.67

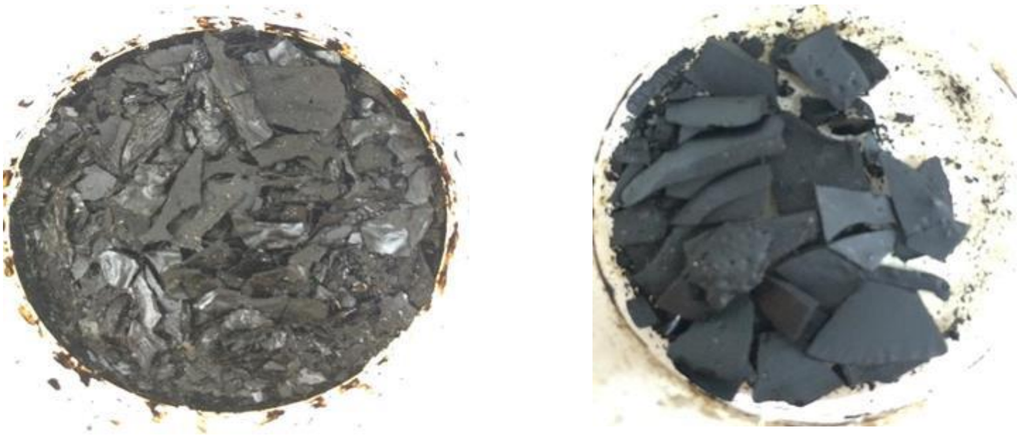

(a) (b)

Figure 4.3 The difference of asphaltenes separated by (a) n-hexane and (b) n-heptane

Moreover, the difference of n-alkane solvents used to separate asphaltenes was caused not only the amount of asphaltenes[1, 4], but also the change of physical properties such as color and texture. Figure 4.3 shows the appearance of the obtained asphaltenes using n-hexane solvent were more black and stingier solid than asphaltenes that were separated by n-heptane solvent.[28]

4.2 Resins contents

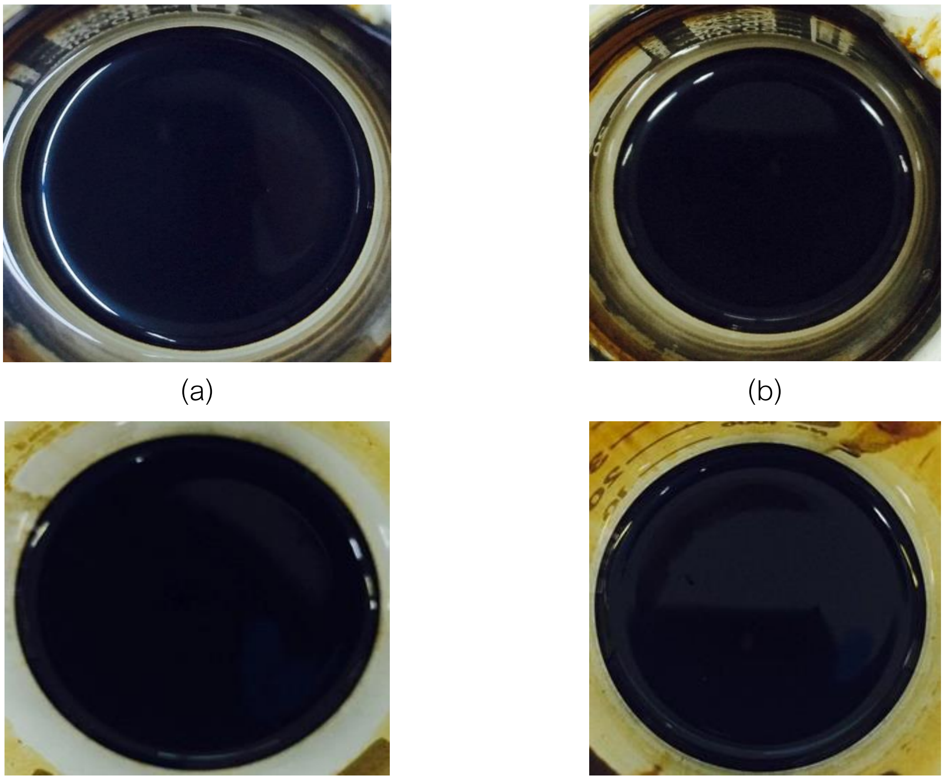
4.2.1 Effect of resins separation methods on resins contents

After asphaltenes were separated from crude oil, the rest from the extraction is called maltenes. The maltenes or deasphalt oil, composes of resins, saturates, and aromatics. Resins were separated from that obtained maltenes by using 2 different techniques, filtration and centrifugation techniques. Normally, extraction of resins from deasphalt oil must follow ASTM procedure which is a time-consuming process. Thus, vacuum pressure supplied by a vacuum pump was applied to enhance the elution process.

The resins contents are shown in Table 4.4. It was found that maltenes obtained from filtration technique, the resins contents separated by ASTM and vacuum procedures were 14.80 %wt and 16.86 %wt, respectively. Maltenes obtained from centrifugation technique, resins contents separated by ASTM and vacuum procedures were 14.57 %wt and 17.12 %wt, respectively. Clearly, the resins contents used the vacuum procedure were higher than ASTM procedure. The use of vacuum procedure for resins separation caused the higher other contamination, especially aromatics that molecule are similar to obtained resins. Moreover, force from vacuum pump, was higher than gravity force (ASTM procedure). This caused the resins contents obtained from vacuum procedure were higher than that.

Table 4.4 Resins contents in L1 source separated by n-heptane that use the different separation techniques

Resin contents (%wt)	Maltenes obtained from filtration technique		Maltenes obtained from centrifugation technique	
	resins separated by ASTM procedure (a)	resins separated by vacuum procedure (b)	resins separated by ASTM procedure (c)	resins separated by vacuum procedure (d)
L1	14.80	16.86	14.57	17.12



(a) (b)

(c) (d)

Figure 4.4 The difference of resins separated by different methods as shown in table 4.4

Additionally, Figure 4.4 showed that the texture was black and gummy liquid as same as all sample.

4.2.2 The resins contents in three different crude oil sources

Resins were separated from that obtained maltenes by using centrifugation technique. The resins contents of L1, L2, and L3 separated by n-heptane were 14.57, 18.89, and 13.27 %wt are shown in Table 4.5, respectively. Obviously, the resins content of L2 crude oil source had the highest content following by L1 and L3, respectively.

Table 4.5 The resins contents in each crude oil sources

Crude oil sources	Resins contents (%wt)
L1	14.57
L2	18.89
L3	13.27

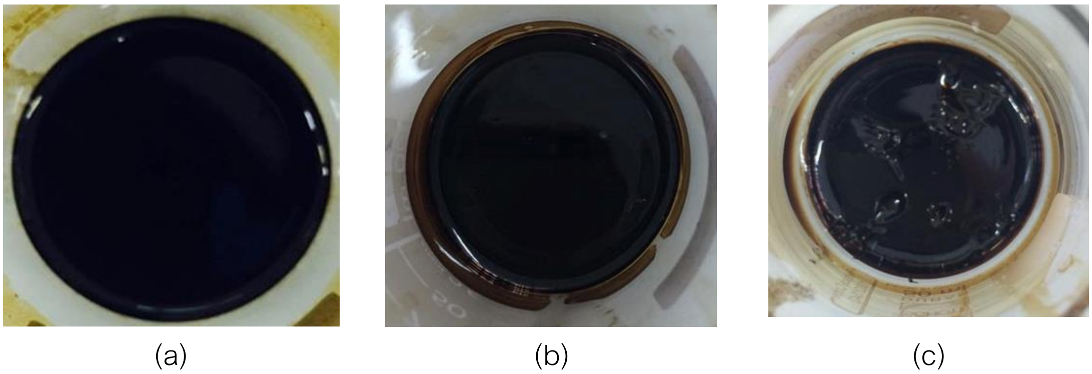

(a) (b) (c)

Figure 4.5 Resins of (a) L1, (b) L2, and (c) L3 crude oil sources

Moreover, Figure 4.5 shows the appearance of L1, L2, and L3-resins separated by n-heptane solvent were black and sticky liquid as same as all samples.

4.3 Asphaltenes structures

4.3.1 Effect of asphaltenes separation methods on asphaltenes structures

4.3.1.1 NMR spectra

^{1}H NMR and ^{13}C NMR spectroscopy were used to characterize the asphaltenes structure. The amount of hydrogen and carbon atoms including the structural parameters can be determined from these techniques. These data were used to predict the structure of asphaltenes for better understanding.[20-22]

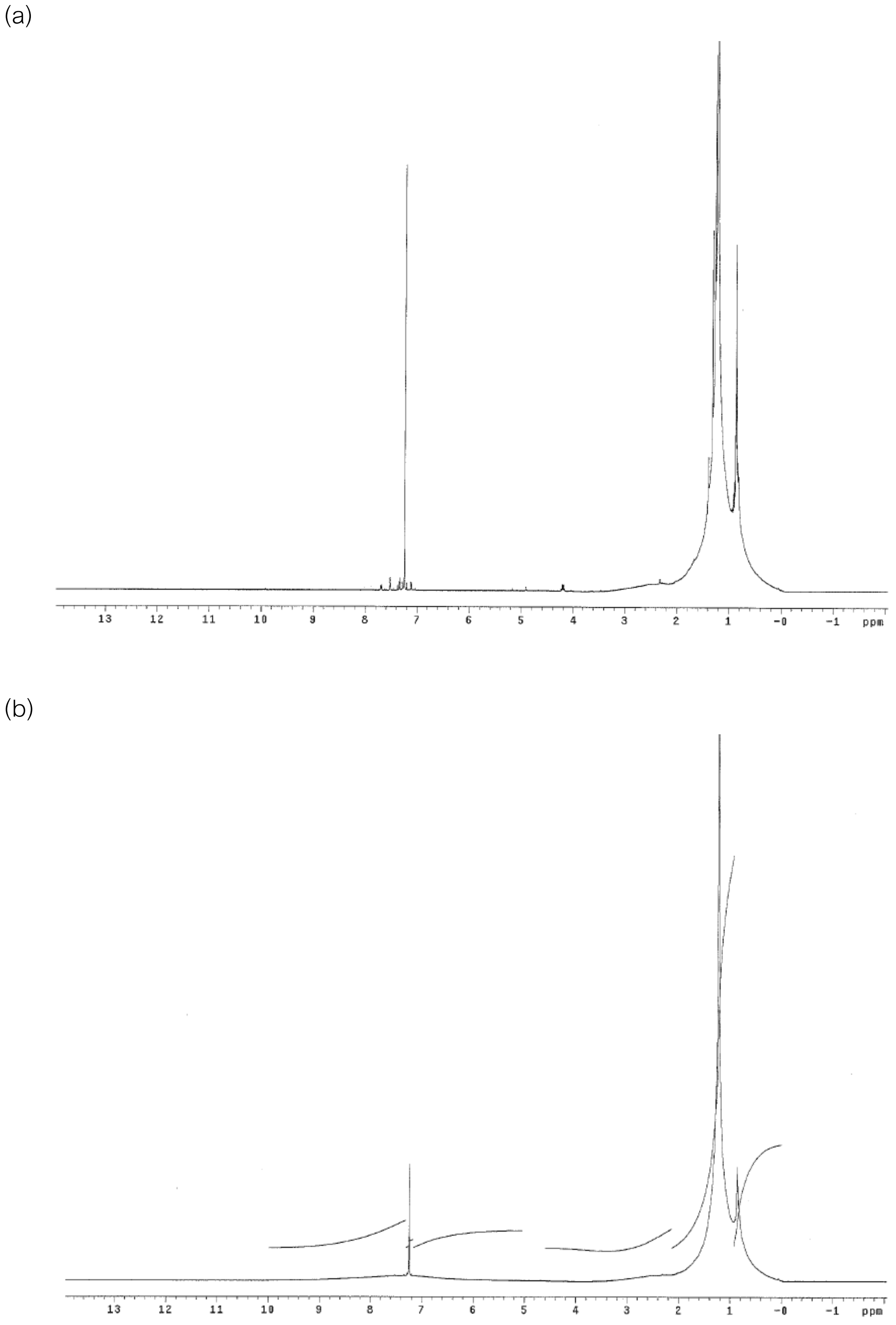
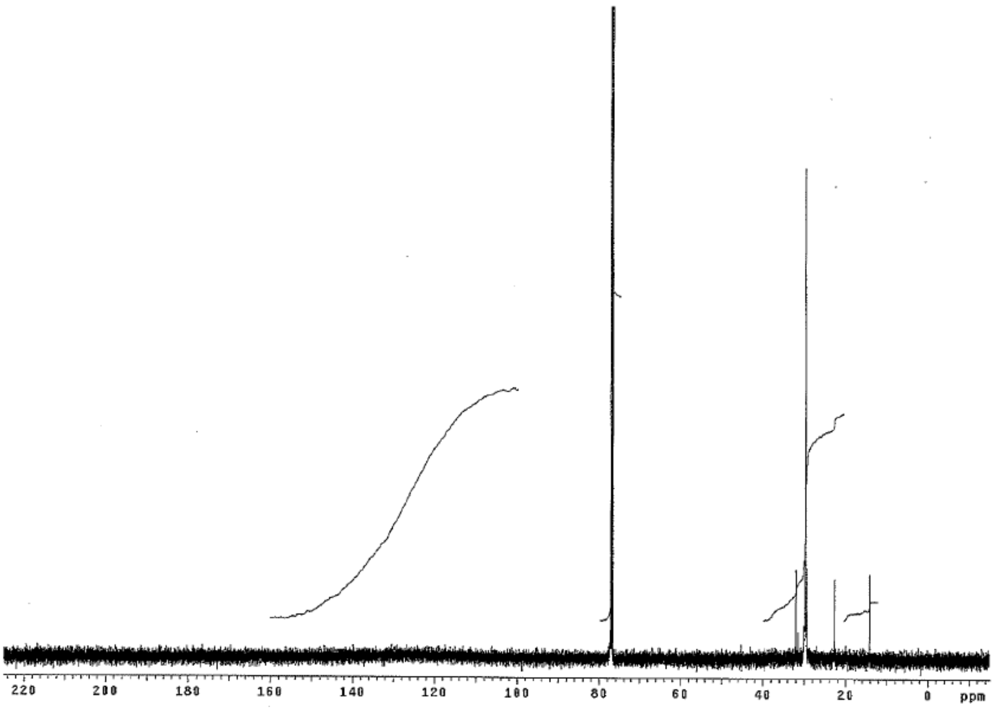


Figure 4.6 The ^{1}H NMR spectrums of asphaltenes separation by (a) filtration technique and (b) centrifugation technique

(a)



(b)

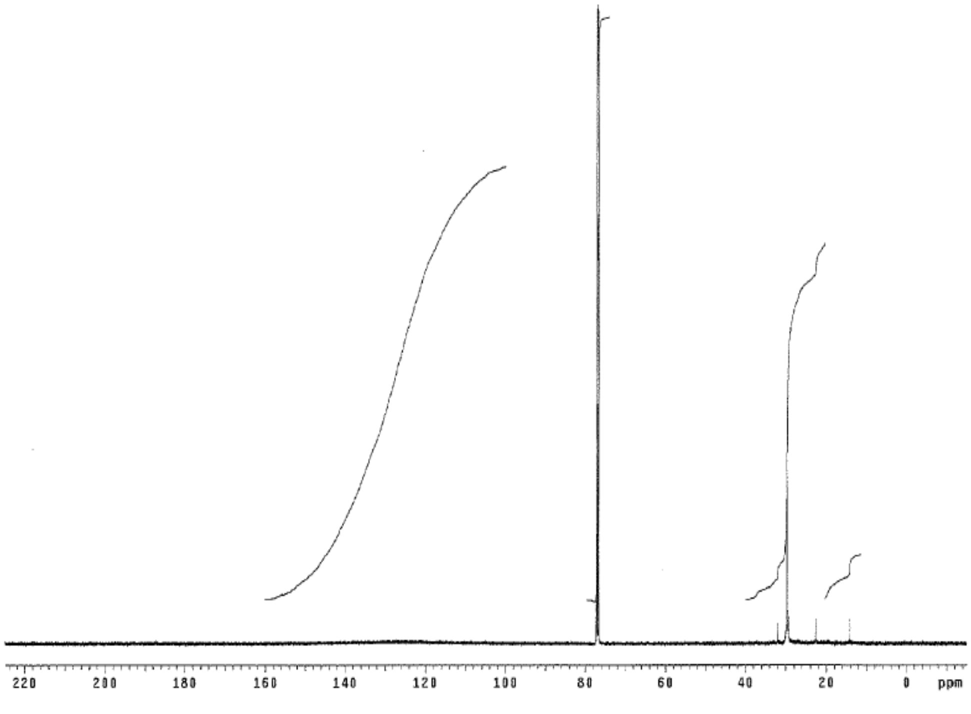


Figure 4.7 The ^{13}C NMR spectrums of asphaltenes separation by (a) filtration technique and (b) centrifugation technique

^{1}H NMR spectrums of asphaltenes separation by filtration and centrifugation techniques are shown in Figure 4.6. Aliphatic proton region is divided into three regions which are α-hydrogen band refers to the α-hydrogen to aromatic ring (2.05-4.5 ppm region), the β-hydrogen band refers to the β-hydrogen to aromatic ring (1.1-2.05 ppm region), and γ-hydrogen band refers to the γ-hydrogen to aromatic ring (0.4-1.1 ppm region).[20-22] These three regions are integrated to obtain % hydrogen (α, β, and γ), respectively.

Table 4.6 The structural parameters of L1-asphaltenes separated by filtration and centrifugation technique

Molecular Parameters	Asphaltenes separation by filtration technique	Asphaltenes separation by centrifugation technique
% of aromatic carbons	50.5	51.9
% of saturated carbons	49.5	48.1
f_a (aromatic carbon fraction)	0.505	0.519
% aromatic hydrogens	6.3	6.2
% hydrogen (α)	4.4	3.3
% hydrogen (β)	71	72.1
% hydrogen (γ)	18.2	18.5
% of saturated hydrogens	93.7	93.8
C/H ratios	1.5	1.1
$n_{carbon} = [H_\alpha + (H_\beta + H_\gamma)]/H_\alpha$	28.8	21.1
aromatic hydrogens/saturated hydrogens	0.067	0.066

The structural parameters of asphaltenes obtained by ^{1}H NMR and ^{13}C NMR were shown in Table 4.6. The n_{carbon} parameters obtained from ^{1}H NMR spectrums were 28.8 and 21.1 for asphaltenes precipitated by using filtration and centrifugation techniques, respectively as shown in Table 4.6. Therefore, n_{carbon}, can be determined by $[H_\alpha + (H_\beta + H_\gamma)]/H_\alpha$. The remaining impurities in the unfractionated asphaltenes that could influence these values, i.e., a lower ‘n’ value correlated to fractionated asphaltenes.[20-22] The use of filtration technique caused the higher asphaltenes contents due to the increase of the amount of wax contamination in that fraction. Therefore, n_{carbon} values of asphaltenes precipitation by filtration technique were higher than asphaltenes precipitation by centrifugation technique.

Moreover, the ^{13}C NMR spectrums of the filtration and centrifugation asphaltenes obtained in this work are shown in Figure 4.7. The aromaticity parameter (f_a) obtained from ^{13}C NMR spectrums can be determined from two different integration domains in that spectrums. It was calculated by $C_{ar}/(C_{ar} + C_{al})$, where C_{al} refers to aliphatic carbons (10-70 ppm region) and C_{ar} refers to aromatic carbon (100-160 ppm region). It indicates a degree of aromatic condensation and levels of hydrogen deficiency.[20-22] The f_a values were 0.505 and 0.519 for asphaltenes precipitation by filtration and centrifugation techniques, respectively. The f_a value of asphaltenes precipitation by filtration technique was lower than asphaltenes precipitation by centrifugation technique. Due to temperature drops during filtration, wax can be occurred. Normally, wax is the aliphatic hydrocarbon so that C_{al} value was higher. Therefore, f_a determined from $C_{ar}/(C_{ar} + C_{al})$ was declined.

4.3.1.2 FTIR spectra

The primary structural parameters of asphaltenes precipitation by filtration and centrifugation techniques obtained from FTIR spectrums are shown in Figure 4.8 and Figure 4.9, respectively. Some key functional groups in both of obtained asphaltenes molecules such as the hydrocarbons groups (aliphatic, aromatics and alicyclic), phenol, and heteroatom are presented.

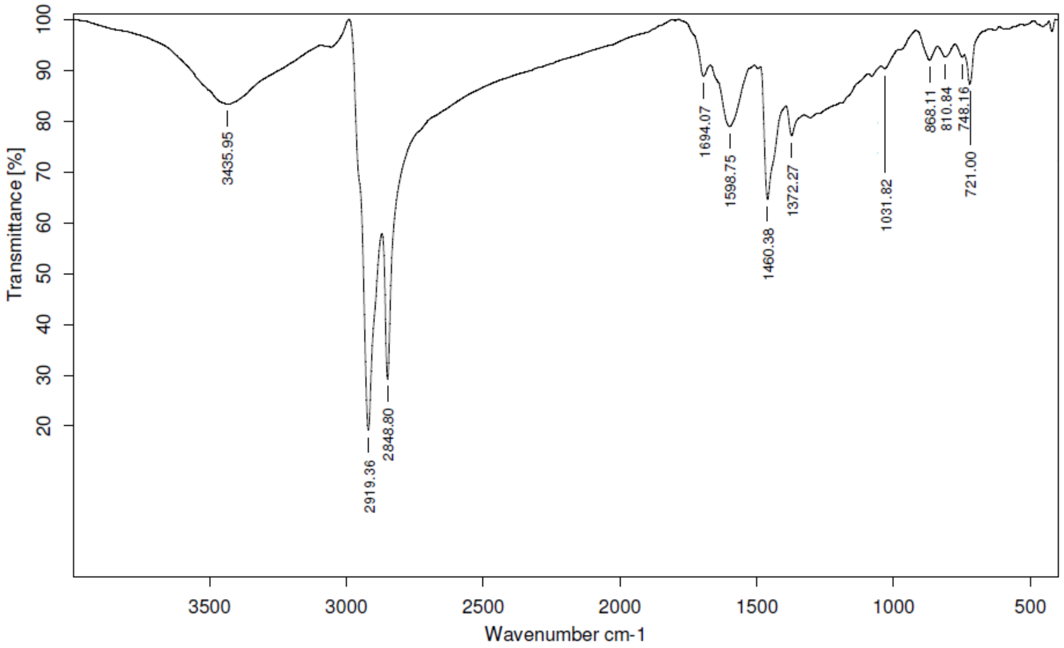


Figure 4.8 The FTIR spectrum of asphaltenes separation by filtration technique

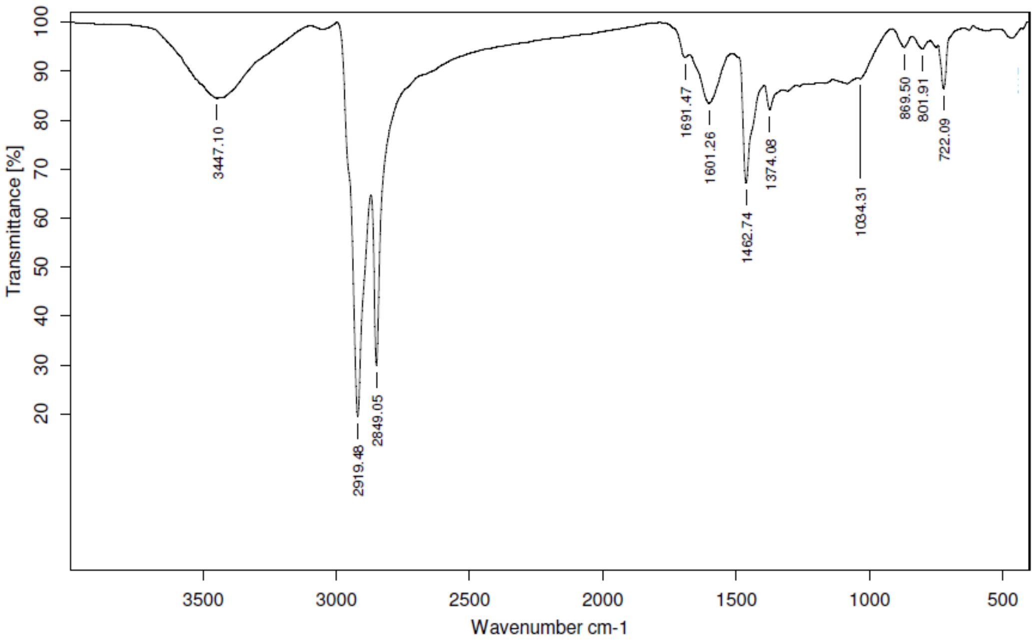


Figure 4.9 The FTIR spectrum of asphaltenes separation by centrifugation technique

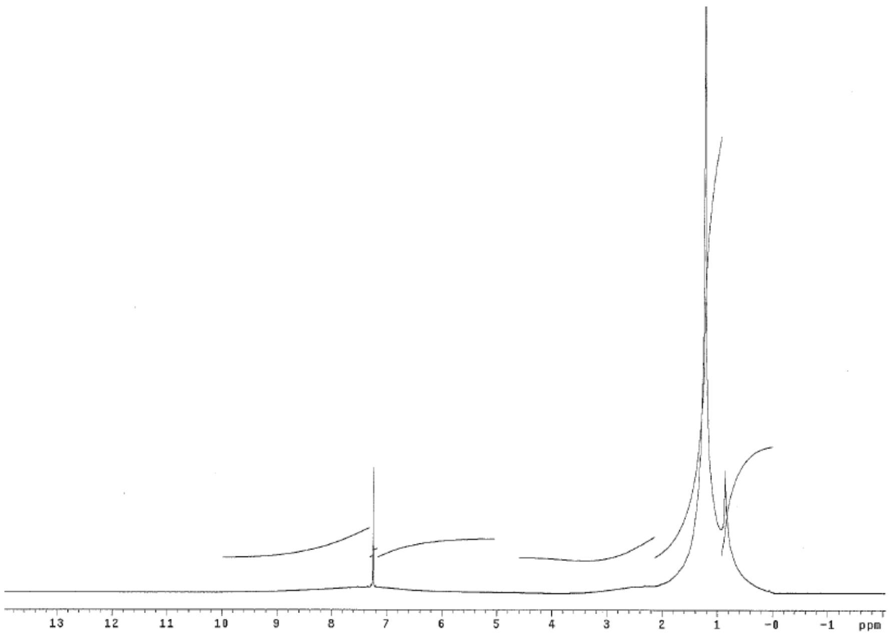
Figure 4.8 and Figure 4.9 show that the absorption band in the region of 3200-3450 cm^{-1} indicates O-H stretching (i.e., 3435.95 and 3433.26 cm^{-1} for obtained asphaltenes from filtration and centrifugation techniques, respectively). The band approximately 2920 and 2850 cm^{-1} shows the CH_3 and CH_2 alkane, respectively. Also, the band at 1700 cm^{-1} represents the carboxylic acids. Aromatic ring is represented the band at 1600 cm^{-1}. The spectrum at 1458 cm^{-1} corresponds the CH_2 bending of aliphatic and naphthenic rings. Additionally, the band at 1383 cm^{-1} shows all CH_3 bending including aliphatic and naphthenic rings. The next band, which appears at ~1032 cm^{-1} is attributed to the sulfoxide groups ($C_2S{=}O$) or ester linkages. Para-disub benzene (C-H) and monosubstituted benzene (C-H) have the band at 800–860 cm^{-1} and 700–750 cm^{-1}. The results do not depend on the used techniques.[20, 23-25]

4.3.2 The structural parameters of three different crude oil sources

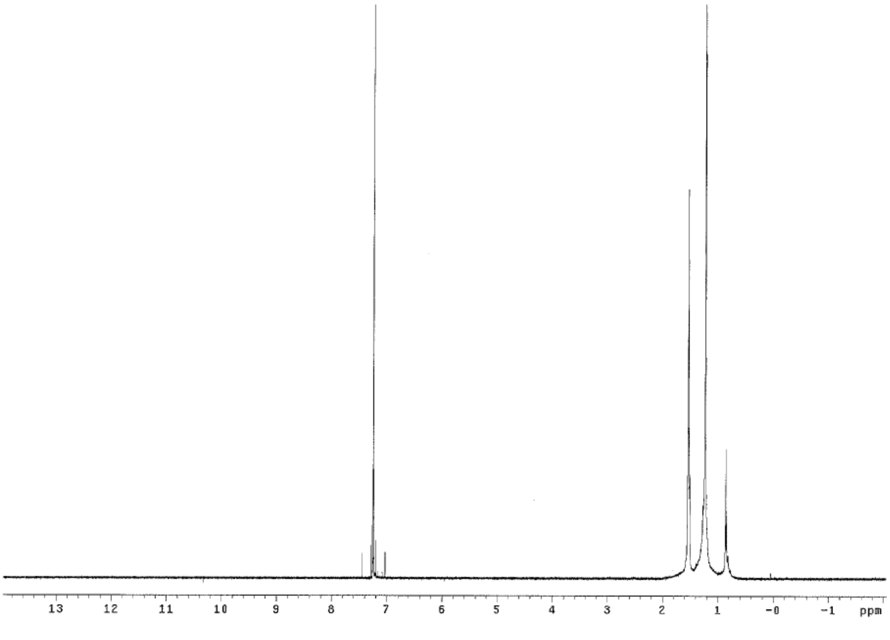
4.3.2.1 NMR spectra

^{1}H NMR and ^{13}C NMR spectrums of asphaltenes of L1, L2, and L3 crude oil sources were shown as Figure 4.10 and 4.11, respectively.

(a)



(b)



(c)

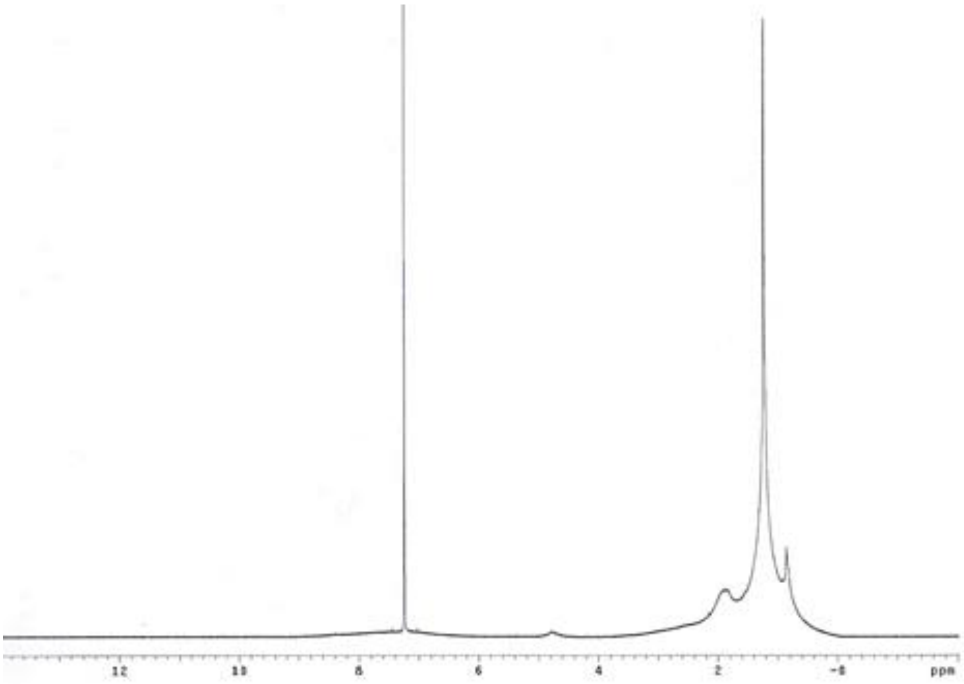
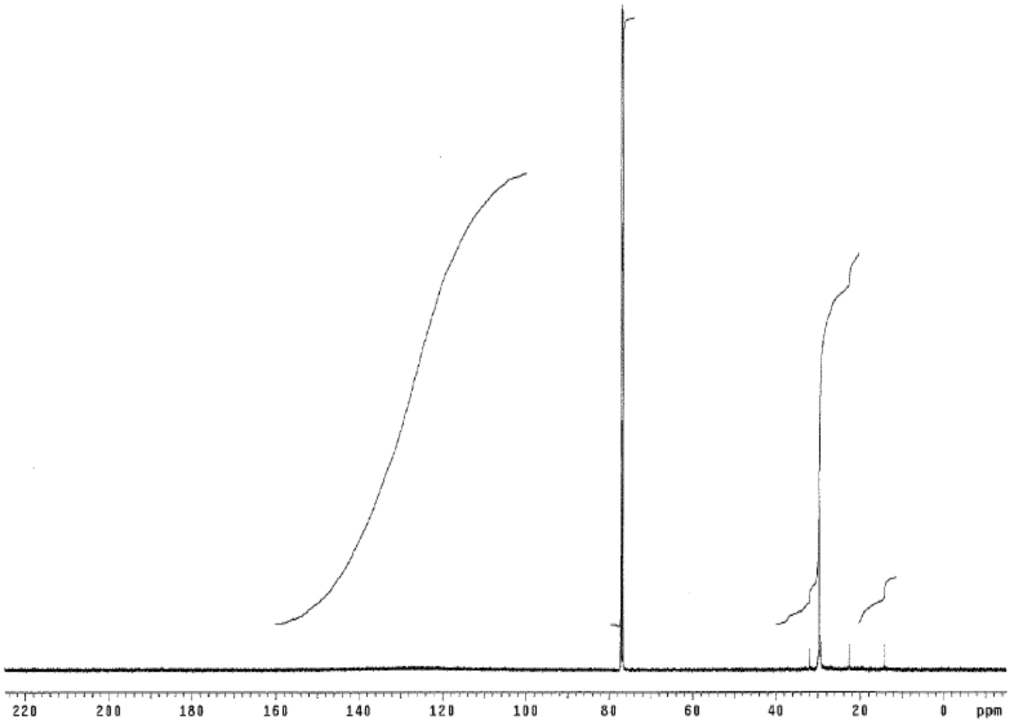


Figure 4.10 ^{1}H NMR spectrums of asphaltenes separation by n-heptane of (a) L1, (b) L2, and (c) L3

(a)



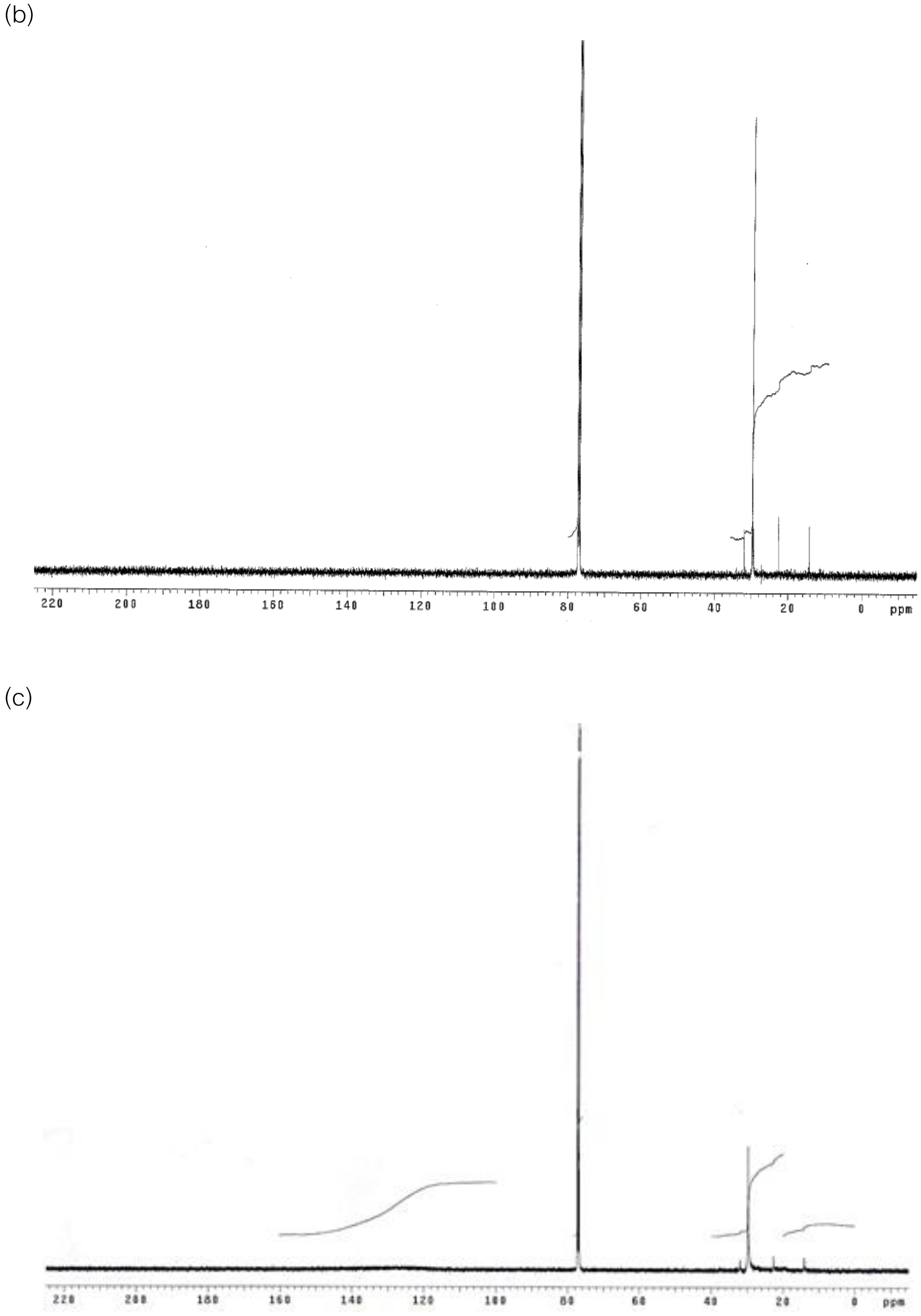


Figure 4.11 ^{13}C NMR spectrums of asphaltenes separation by n-heptane of (a) L1, (b) L2, and (c) L3

Table 4.7 The structural parameters of asphaltenes separated by n-heptane as solvents of L1, L2, and L3 crude oil sources

Molecular Parameters	L1-asphaltenes	L2-asphaltenes	L3-asphaltenes
% of aromatic carbons	51.9	17.3	36.4
% of saturated carbons	48.1	82.7	63.6
f_a (aromatic carbon fraction)	0.519	0.173	0.364
% aromatic hydrogens	6.2	17.6	9.3
% hydrogen (α)	3.3	4.5	4.8
% hydrogen (β)	72.1	69.6	71.5
% hydrogen (γ)	18.5	8.3	14.5
% of saturated hydrogens	93.8	82.4	90.7
C/H ratios	1.1	0.2	0.67
$n_{carbon} = [H_\alpha + (H_\beta + H_\gamma)]/H_\alpha$	21.1	18.4	19.02
aromatic hydrogens/saturated hydrogens	0.066	0.214	0.102

The n_{carbon} parameters obtained from that spectrums were 21.1, 18.4, and 19.02 for asphaltenes precipitation by n-C_7 of L1, L2, and L3, respectively shown as Table 4.7. The n_{carbon} values of L1-asphaltenes had the highest values following by L3, and L2, respectively. The origin of crude oil sources and the process of asphaltenes separation can reflect to n_{carbon} value.[20, 22]

The aromaticity parameter (f_a) values were 0.519, 0.173, and 0.364 for asphaltenes precipitation by n-C_7 of L1, L2, and L3 as shown in Table 4.7, respectively. The f_a value of L1-asphaltenes was the highest value following L3 and L2, respectively. This data represented the molecular structure of L1-asphaltenes, which mainly consisted of the aromatics more than the other sources.[20, 22]

4.3.2.2 FTIR spectra

The FTIR spectrums of L1, L2, and L3 asphaltenes are shown in Figure 4.12-4.14, respectively.

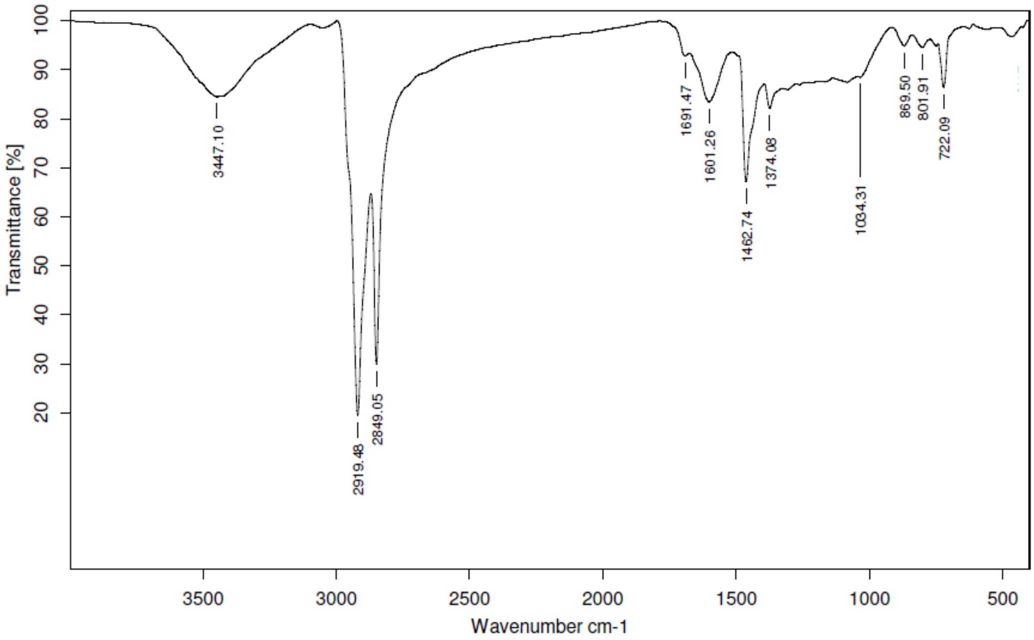


Figure 4.12 FTIR spectrum of L1-asphaltenes

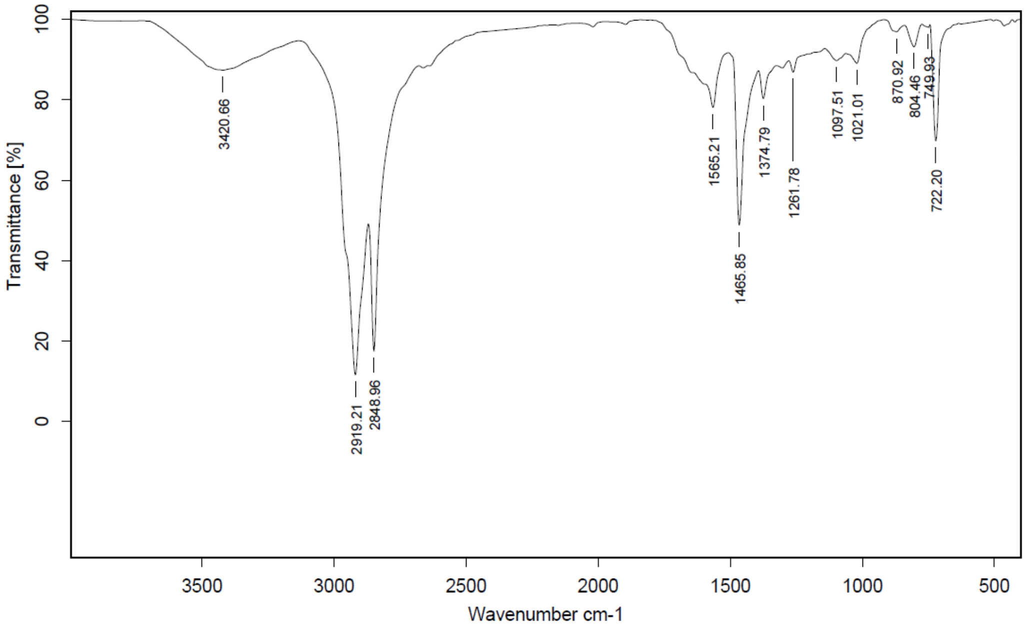


Figure 4.13 FTIR spectrum of L2-asphaltenes

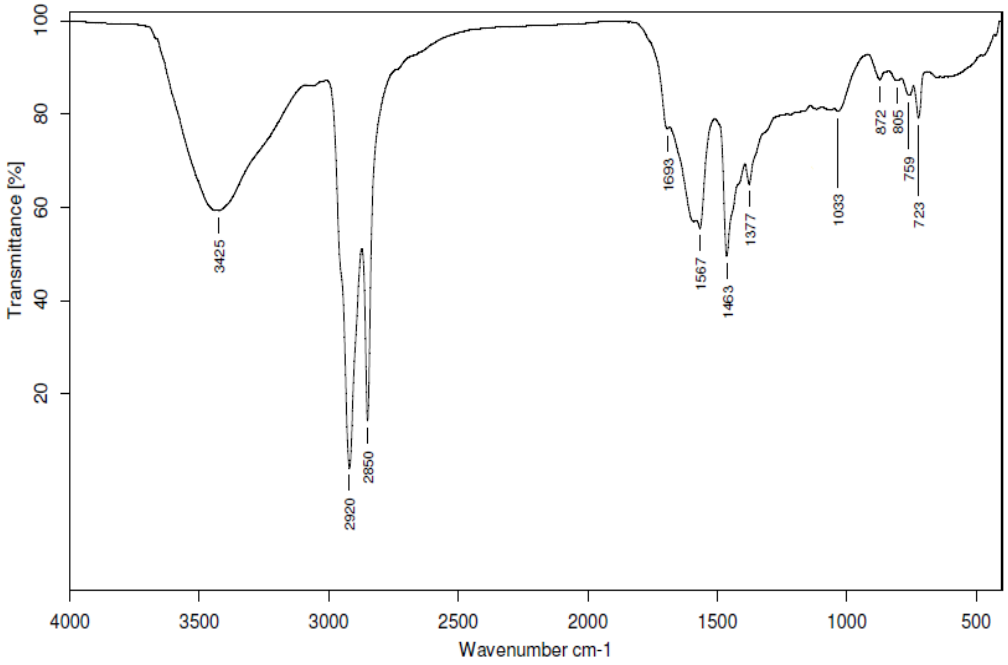


Figure 4.14 FTIR spectrum of L3-asphaltenes

The functional groups of asphaltenes in three crude oil sources indicate O-H stretching, hydrocarbon including aliphatic and aromatic ring, the sulfoxide groups ($C_2S=O$) or ester linkages, Para-disub benzene (C-H), and monosubstituted benzene (C-H), respectively. The results do not depend on the crude oil sources.[20, 23-25]

4.3.3 Effect of solvents types on asphaltenes structures

4.3.3.1 NMR spectra

^1H NMR and ^{13}C NMR spectrums of asphaltenes separation by n-C_6 and n-C_7 asphaltenes are shown as Figure 4.15 and 4.16, respectively.

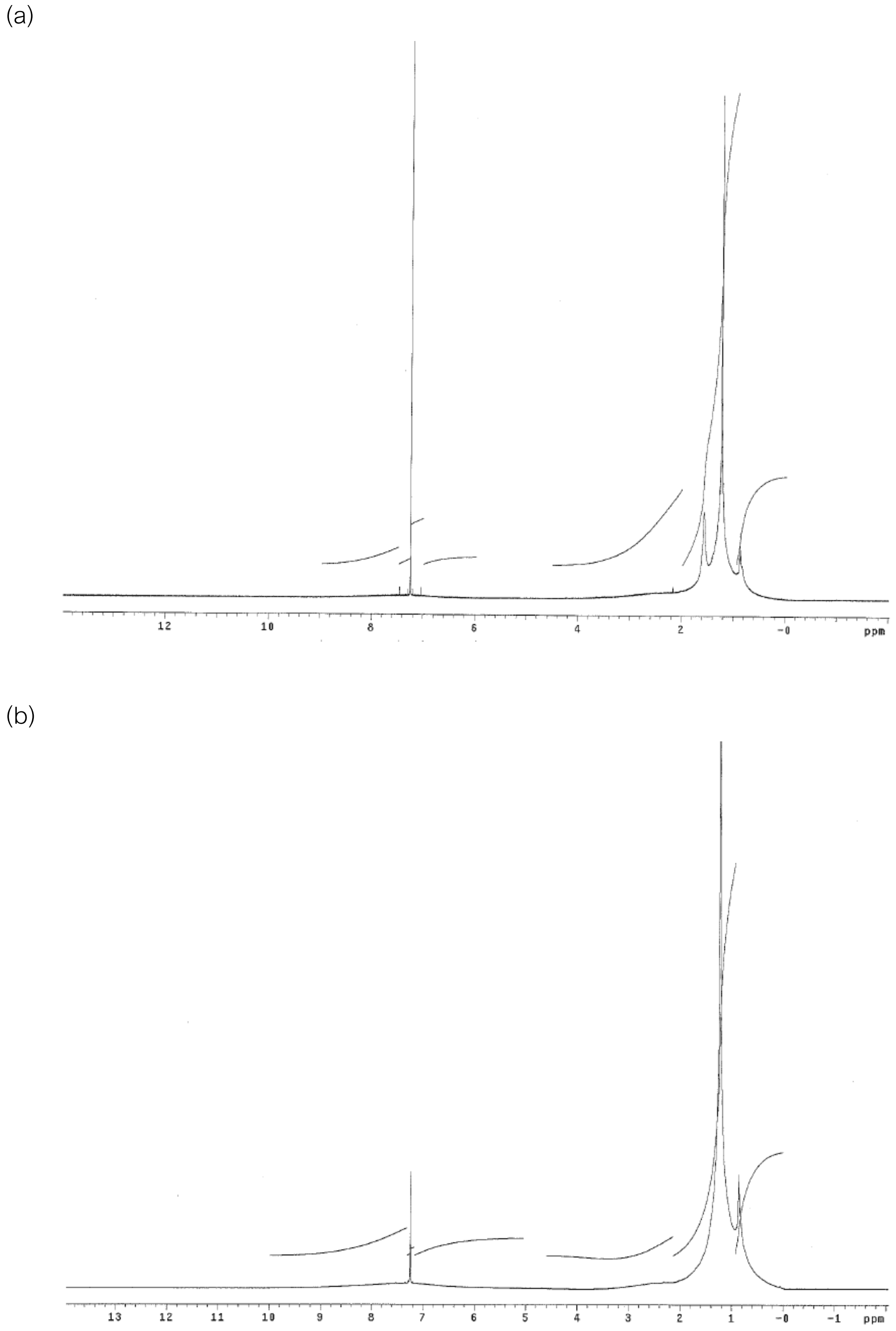
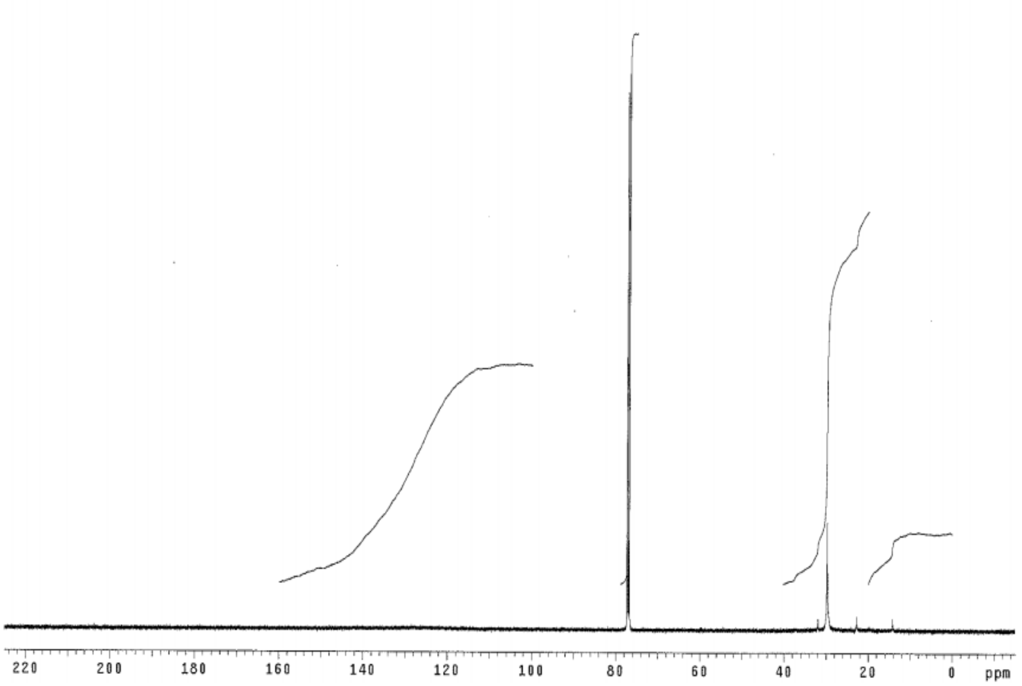


Figure 4.15 ^{1}H NMR spectrums of asphaltenes separation by (a) n-hexane and (b) n-heptane

(a)



(b)

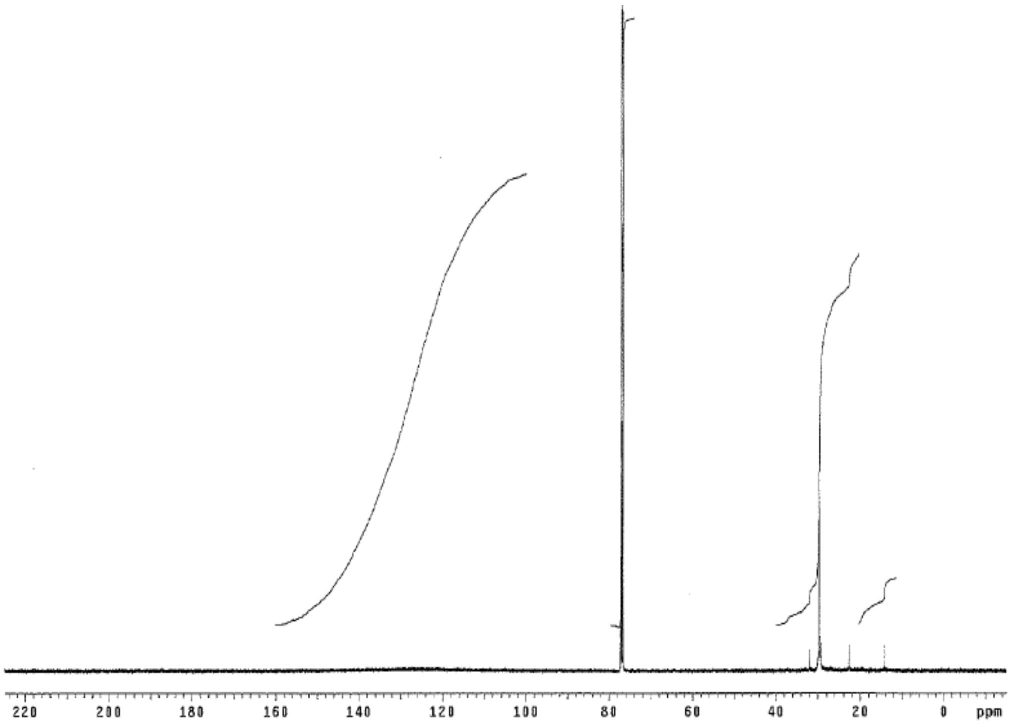


Figure 4.16 ^{13}C NMR spectrums of asphaltenes separation by (a) n-hexane and (b) n-heptane

Table 4.8 The structural parameters of asphaltenes separated by n-hexane and n-heptane as solvents

Molecular Parameters	n-C_6 asphaltenes	n-C_7 asphaltenes
% of aromatic carbons	33.9	51.9
% of saturated carbons	66.1	48.1
f_a (aromatic carbon fraction)	0.339	0.519
% aromatic hydrogens	10.59	6.2
% hydrogen (α)	3.53	3.3
% hydrogen (β)	72.3	72.1
% hydrogen (γ)	13.6	18.5
% of saturated hydrogens	89.41	93.8
C/H ratios	0.57	1.1
$n_{carbon} = [H_\alpha + (H_\beta + H_\gamma)]/H_\alpha$	25.3	21.1
aromatic hydrogens/saturated hydrogens	0.118	0.066

According to Table 4.8, the n_{carbon} parameters obtained from ^1H NMR spectrums were 25.3 and 21.1 for asphaltenes precipitation by using n-C_6 and n-C_7, respectively. The lighter n-alkanes were used to separate the asphaltenes, the more resins contamination is occurred. Therefore, n_{carbon} values of asphaltenes precipitation by n-hexane are higher than those precipitations by n-heptane.[20-22]

The aromaticity parameter (f_a) values were 0.645 and 0.173 for asphaltenes precipitation by n-C_6 and n-C_7, respectively. The f_a value of n-C_6 asphaltenes was lower than the n-C_7 asphaltenes. The separation efficiency of aromatics from crude oil sample using n-heptane was more than the use of n-hexane as solvent for separation. The previous study showed that the use of n-C_7 as solvent to precipitate asphaltenes has a higher values of f_a.[20, 22]

4.3.3.2 FTIR spectra

Figure 4.17 and 4.18 show the FTIR spectrums of n-C_6 and n-C_7 asphaltenes, respectively

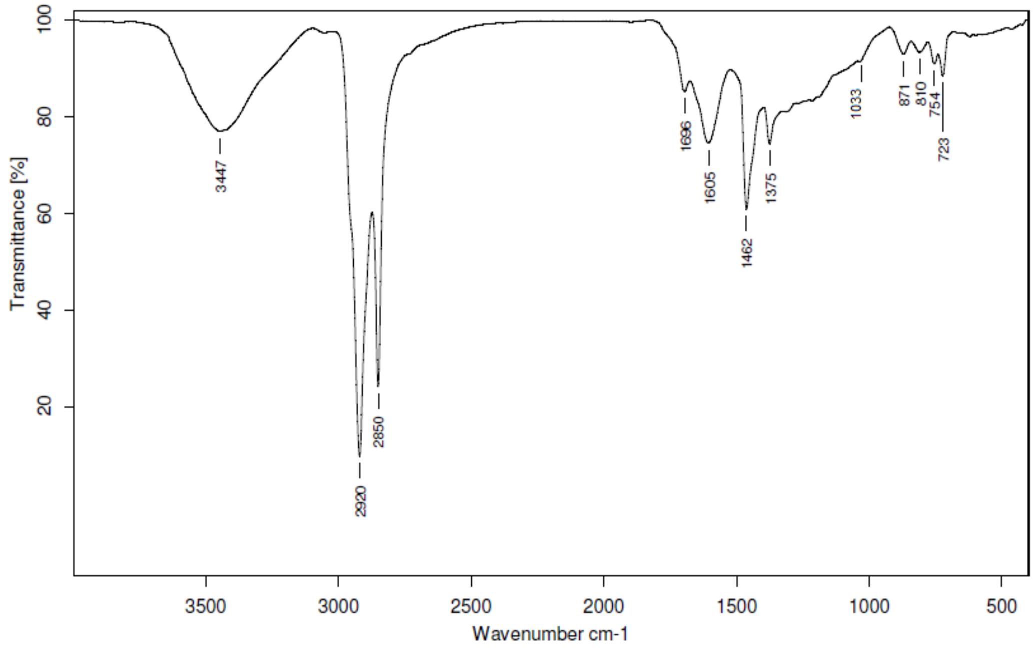


Figure 4.17 FTIR spectrum of n-C_6 asphaltenes

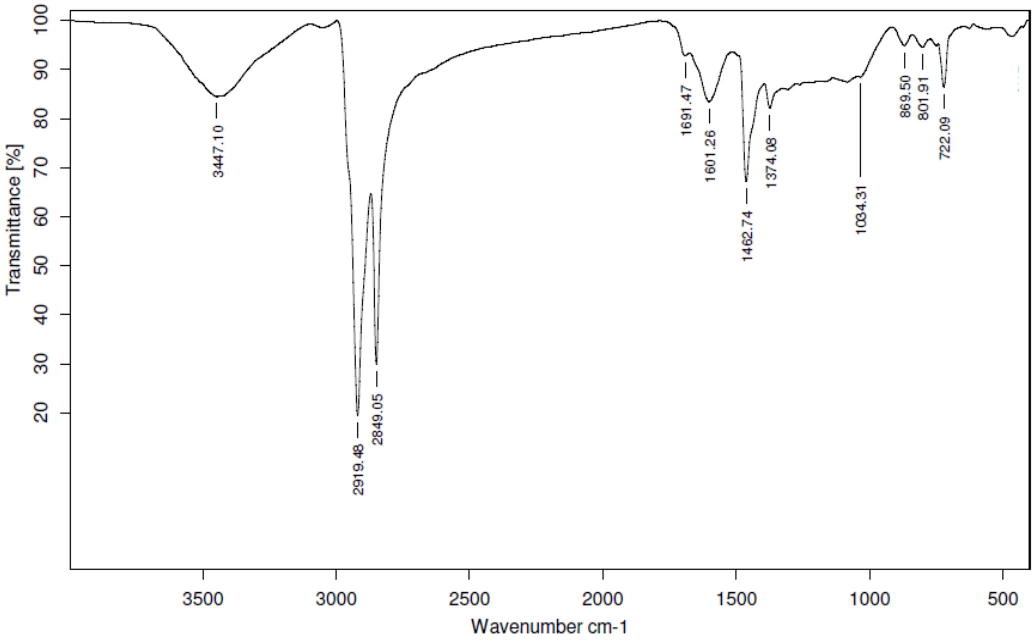


Figure 4.18 FTIR spectrum of n-C_7 asphaltenes

The obtained results of FTIR spectrum from both solvents; n-C_6 and n-C_7 show the similar functional group of asphaltenes precipitation.[20, 23-25] The use of FTIR technique to determine asphaltenes structure indicates only the primary structural parameter. Therefore, NMR needs to be used in this study for a better understanding of the structural parameter.

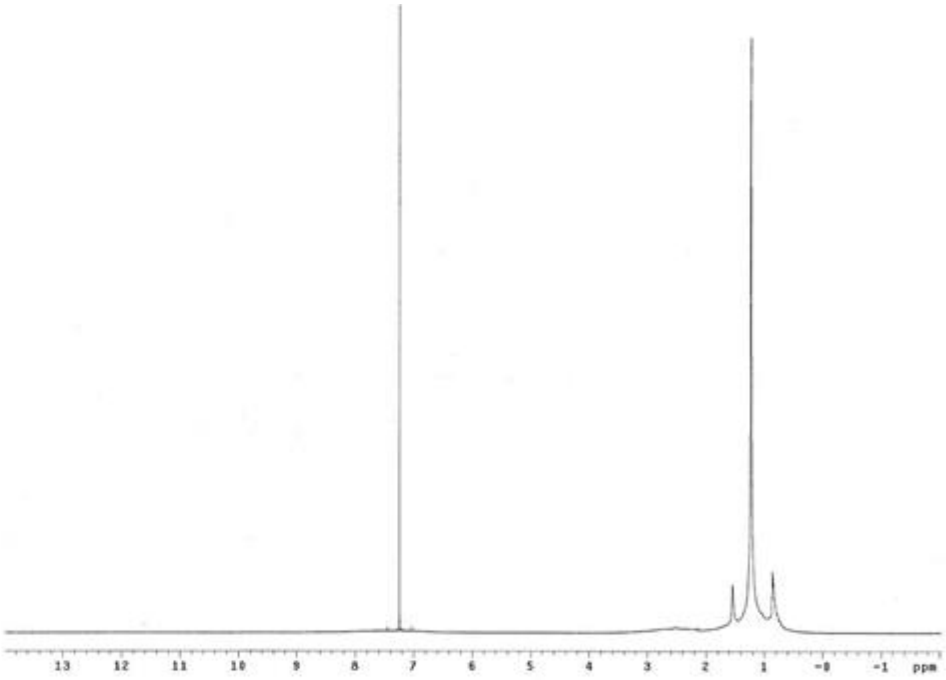
4.4 Resins structures

4.4.1 Effect of resins separation methods on resins structures

4.4.1.1 NMR spectra

^1H NMR spectrums results of ASTM resins and vacuum resins obtained from both maltenes are shown in Figure 4.19 and 4.21, respectively. Moreover, Figure 4.20 and 4.22 show the ^{13}C NMR spectrums of ASTM resins and vacuum resins obtained from both maltenes, respectively.

(a)



(b)

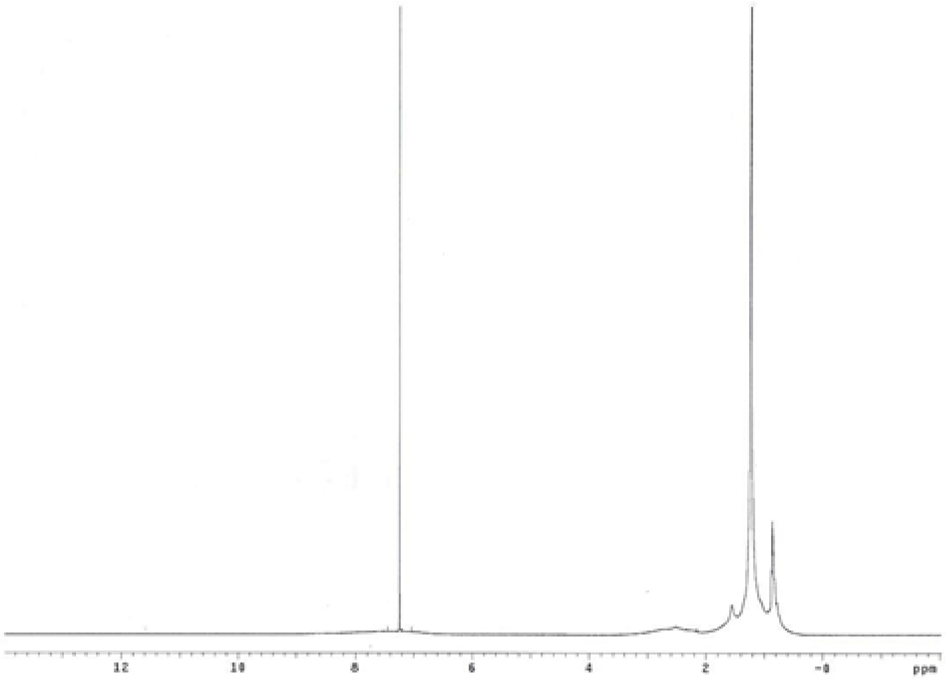
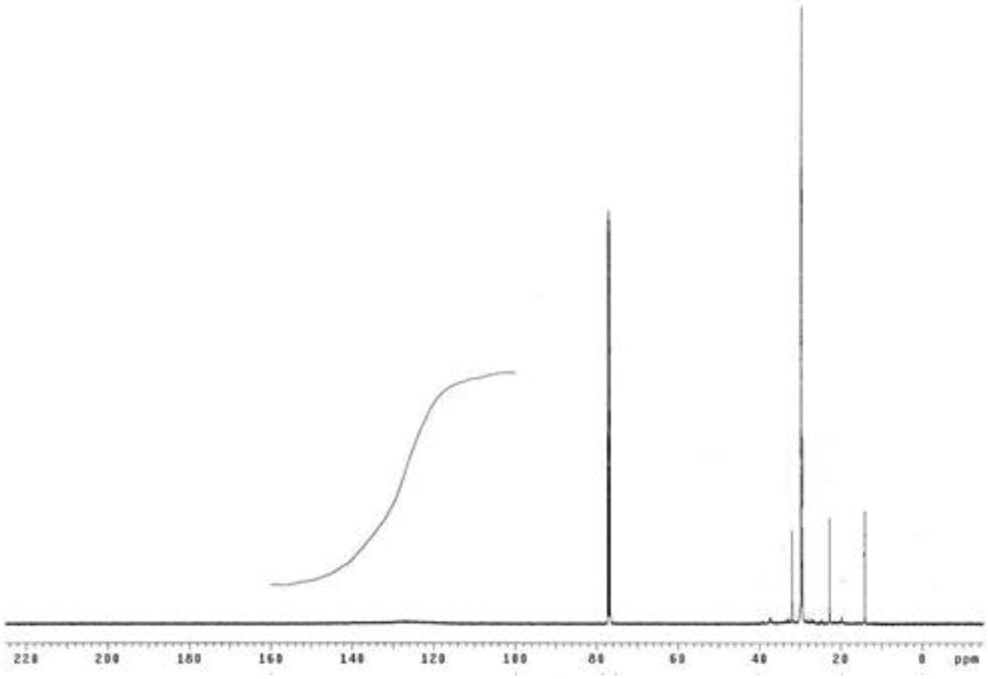


Figure 4.19 ^{1}H NMR spectrums of (a) resins (filtration, ASTM) and (b) resins (filtration, vacuum)

(a)



(b)

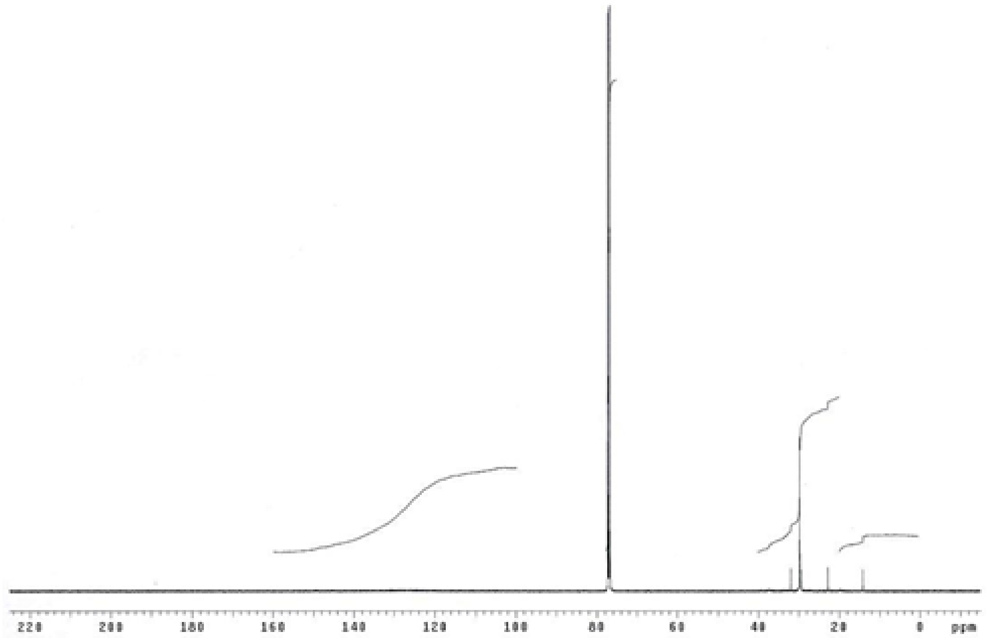
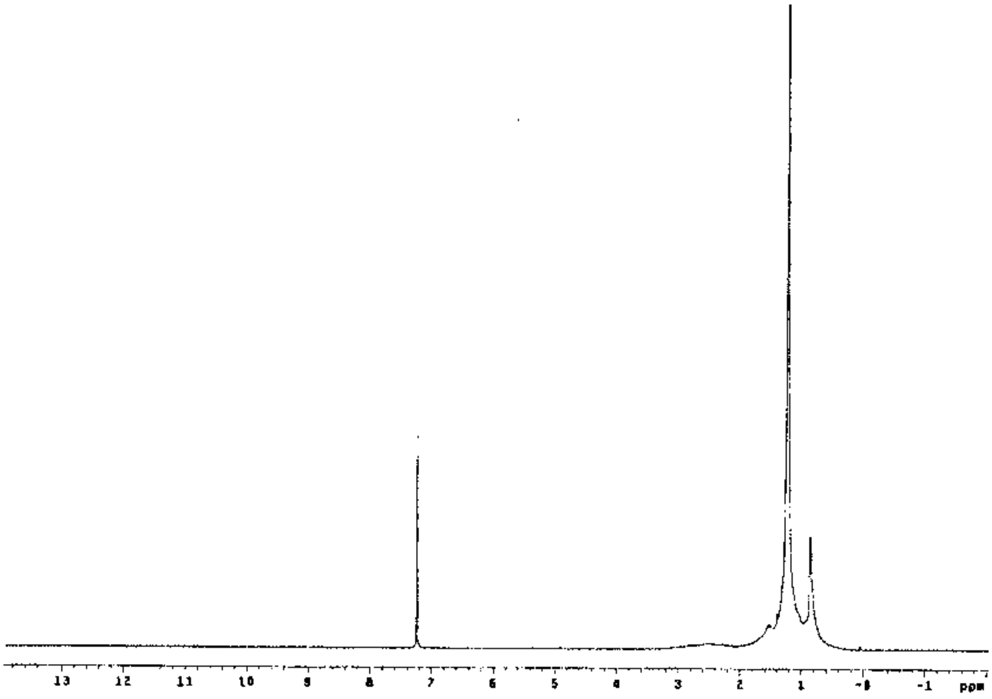


Figure 4.20 ^{13}C NMR spectrums of (a) resins (filtration, ASTM) and (b) resins (filtration, vacuum)

(c)



(d)

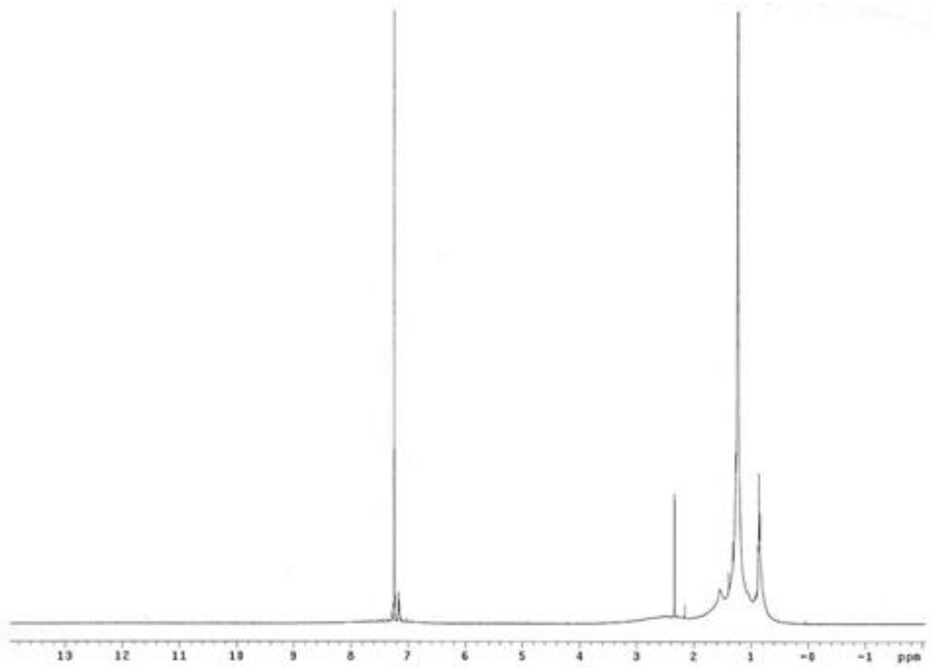
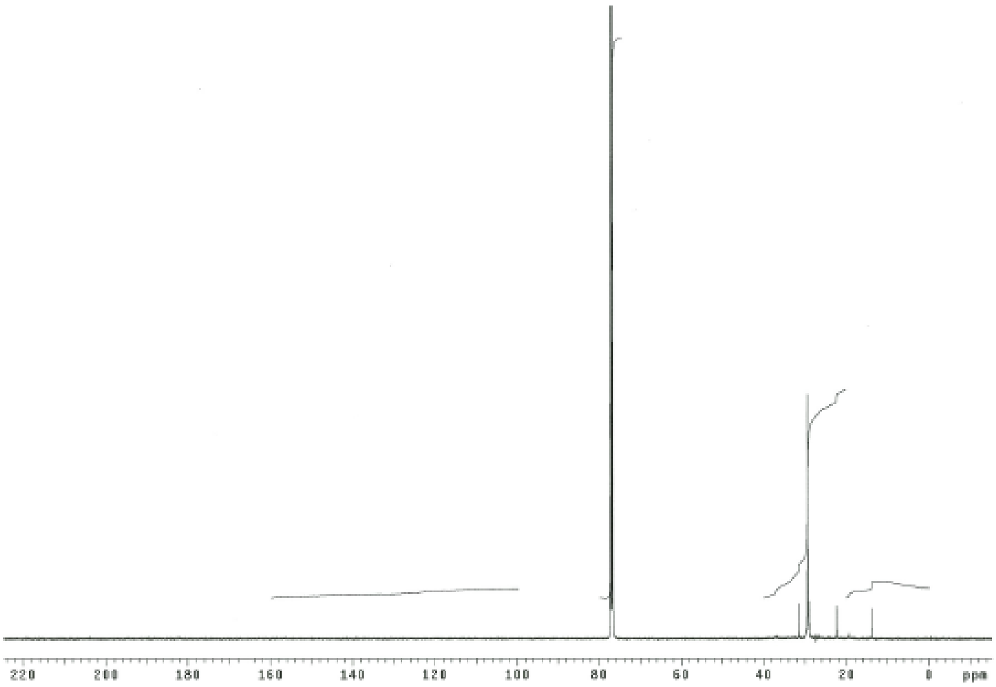


Figure 4.21 ^{1}H NMR spectrums of (c) resins (centrifugation, ASTM) and (d) resins (centrifugation, vacuum)

(c)



(d)

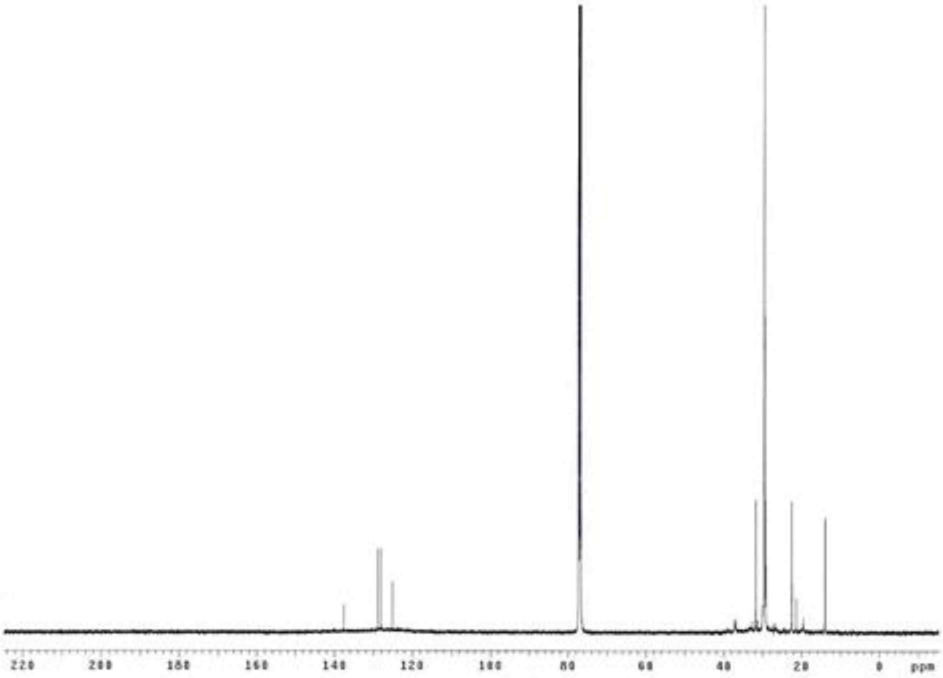


Figure 4.22 ^{13}C NMR spectrums of (c) resins (centrifugation, ASTM) and (d) resins (centrifugation, vacuum)

Table 4.9 The resins structural parameter in L1 source separated by n-heptane that use the different separation techniques

Molecular Parameters	Maltenes obtained from filtration technique		Maltenes obtained from centrifugation technique	
	resins separated by ASTM procedure (a)	resins separated by vacuum procedure (b)	resins separated by ASTM procedure (c)	resins separated by vacuum procedure (d)
% of aromatic carbons	26.7	32.9	24.4	29.1
% of saturated carbons	73.3	67.1	75.6	70.9
f_a (aromatic carbon fraction)	0.267	0.329	0.244	0.291
% aromatic hydrogens	8.8	9.0	5.0	6.9
% hydrogen (α)	9.0	7.0	9.8	6.2
% hydrogen (β)	66.6	68.5	70.2	69.6
% hydrogen (γ)	15.6	15.4	15.0	17.3
% of saturated hydrogens	91.2	91.0	95.0	93.1
$n_{carbon} = [H_\alpha + (H_\beta + H_\gamma)]/H_\alpha$	10.1	12.9	9.7	15.0
aromatic hydrogens/saturated hydrogens	0.096	0.099	0.052	0.074

Table 4.9 shows the resins structural parameter in L1 source separated by n-heptane that use the different separation techniques. Maltenes obtained from filtration technique for asphaltenes separation, the n_{carbon} parameters of resins separated by ASTM and vacuum procedures were 10.1 and 12.9, respectively. Maltenes obtained from centrifugation technique for asphaltenes separation, the n_{carbon} parameters of resins separated by ASTM and vacuum procedures were 9.7 and 15, respectively. The use of vacuum technique caused the higher resins contents due to the increase of the contamination, especially aromatic in that fraction.[20, 22] Therefore, n_{carbon} values of resins

separated with vacuum technique were higher than resins precipitated with ASTM technique. Maltenes obtained from filtration technique for asphaltenes separation, The f_a values of resins separated by ASTM and vacuum procedures were 0.267 and 0.329, respectively.

Maltenes obtained from centrifugation technique for asphaltenes separation f_a values of resins separated by ASTM and vacuum procedures were 0.244 and 0.291, respectively. The aromaticity values of resins separated with vacuum procedure was higher than those of resins separated with ASTM procedure.[20, 22] The use of vacuum procedure for resins separation caused the higher other contamination, especially aromatics. Vacuum procedure, force obtained from vacuum pump, was higher than gravity force (ASTM procedure) leading to higher aromatics carbon fraction.

4.4.1.2 FTIR spectra

Figure 4.23-4.26 show the FTIR spectrums of resin, which were obtained from both techniques including filtration and centrifugation techniques separated by ASTM and vacuum procedures.

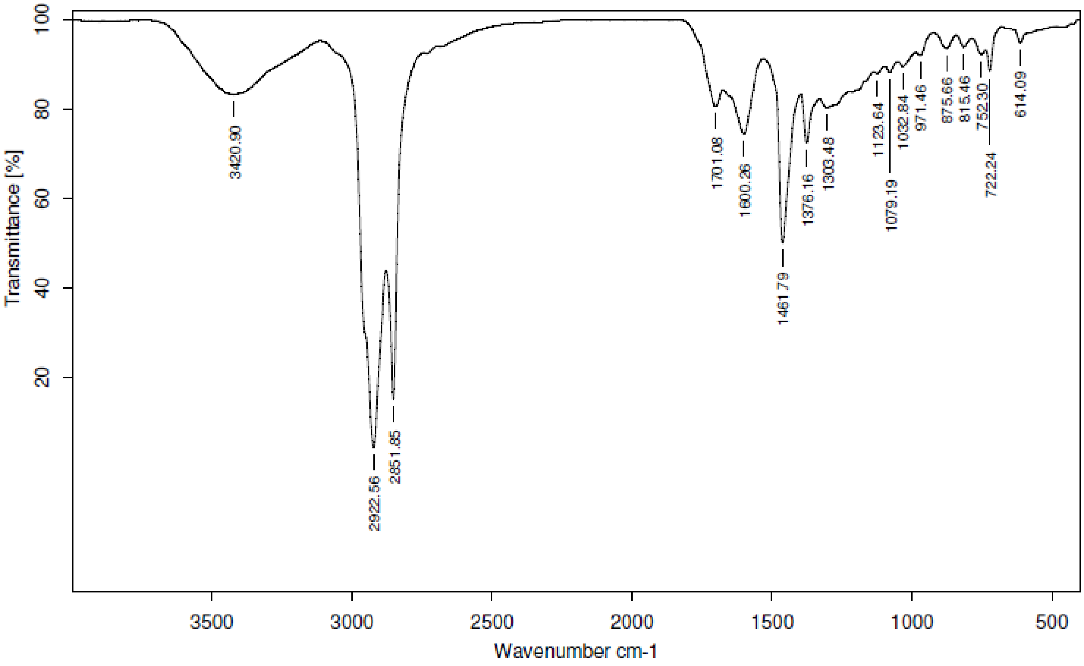


Figure 4.23 FTIR spectrum of resins (a) separated by ASTM procedure

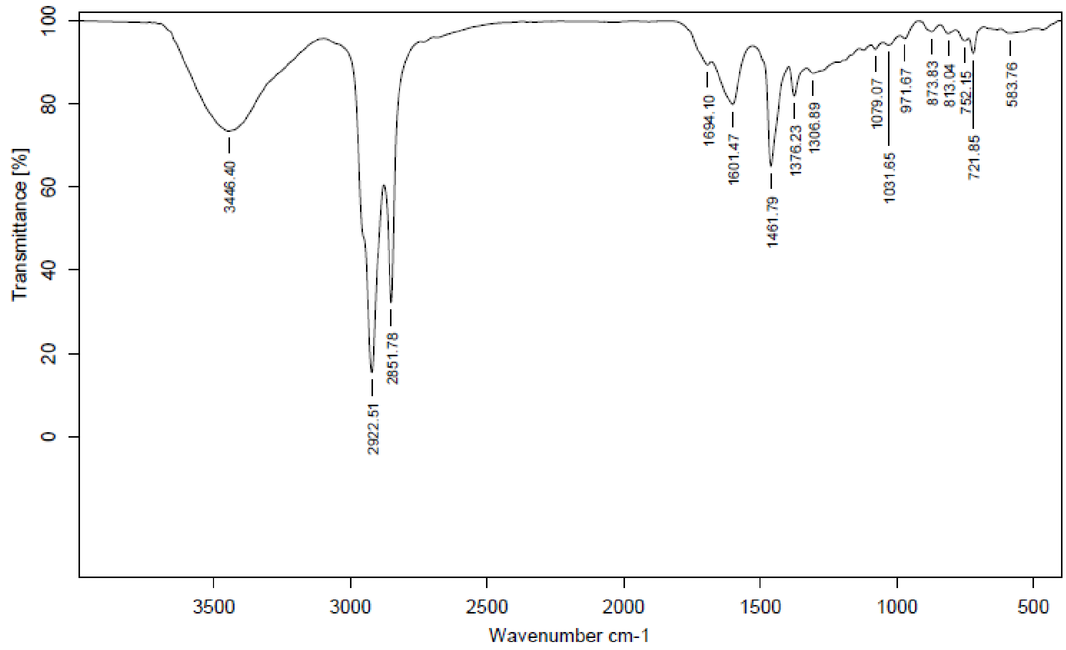


Figure 4.24 FTIR spectrum of resins (b) separated by vacuum procedure

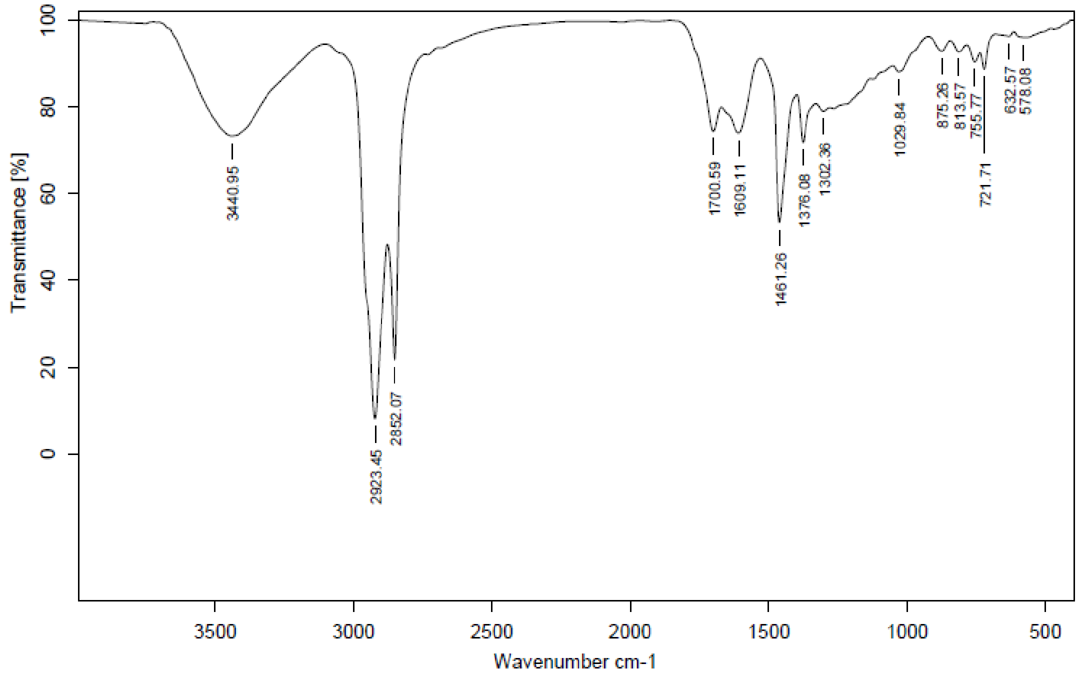


Figure 4.25 FTIR spectrum of resins (c) separated by ASTM procedure

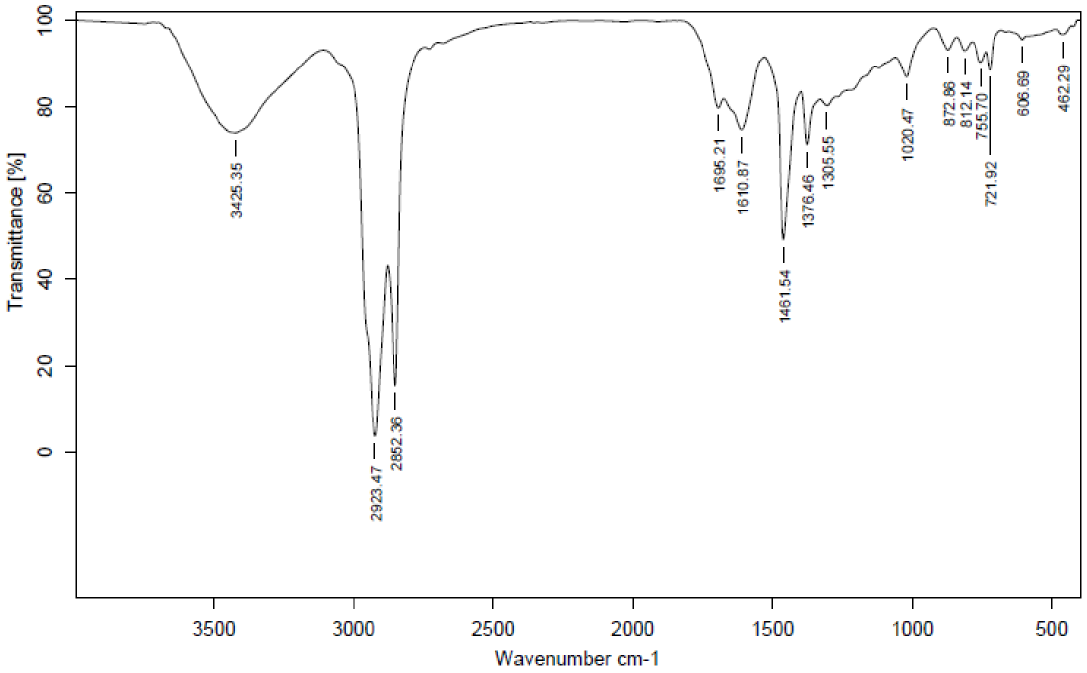


Figure 4.26 FTIR spectrum of resins (d) separated by vacuum procedure

The functional groups of resins in both technique indicate O-H stretching, hydrocarbon including aliphatic and aromatic ring, the sulfoxide groups ($C_2S=O$) or ester linkages, Para-disub benzene (C-H), and monosubstituted benzene (C-H), respectively.[20, 23-25] The results of FTIR spectrums can be concluded that the effect of procedures including ASTM and vacuum used to separate resins did not affect to the functional groups of resins. FTIR techniques can indicate only the qualitative data, which was not different. So NMR technique must be used in this study for better understanding the structural parameter.

4.5 Study on effect of temperatures on asphaltenes stability

In this part, the effect of temperature on the stability of asphaltenes in crude oil has been discussed. Upstream, midstream, and downstream processes involve temperature variations which can cause the precipitation of asphaltenes leading to deposition and fouling problems during the production, transportation and processing of crude oils.[1, 4] In Thailand, the precipitation of asphaltenes problems always occur in transportation of process–piping system so that, in this study the range of simulated temperature will be 40, 50, 60, and 70°C.

However, L2 could not be measured the physical properties at 40°C due to wax problem. Then effect of temperature on asphaltenes stability in L2 crude oil can be studied at 50°C and higher.

Three light crude oil samples with different physical properties including density, viscosity, and composition were tested the effect of temperature on stability of asphaltenes at four different temperatures (40-70°C). The physical properties such as density and viscosity were used as indicators of the stability of asphaltenes.[3, 29] The measured densities and sampling points of each crude oil source at four different temperatures are showed in Figure 4.27, 4.29 and 4.31. Also, the measured viscosities versus sampling points of each crude oil source at four different temperatures are showed in Figure 4.28, 4.30 and 4.32. Moreover, the kinematic viscosity obtained from the combination of density and viscosity in order to better understanding of system are shown in 4.33-4.35. The sampling points; A, B, and C are the location of the top, middle, and bottom section of cylinder used to contain crude oil samples, respectively.

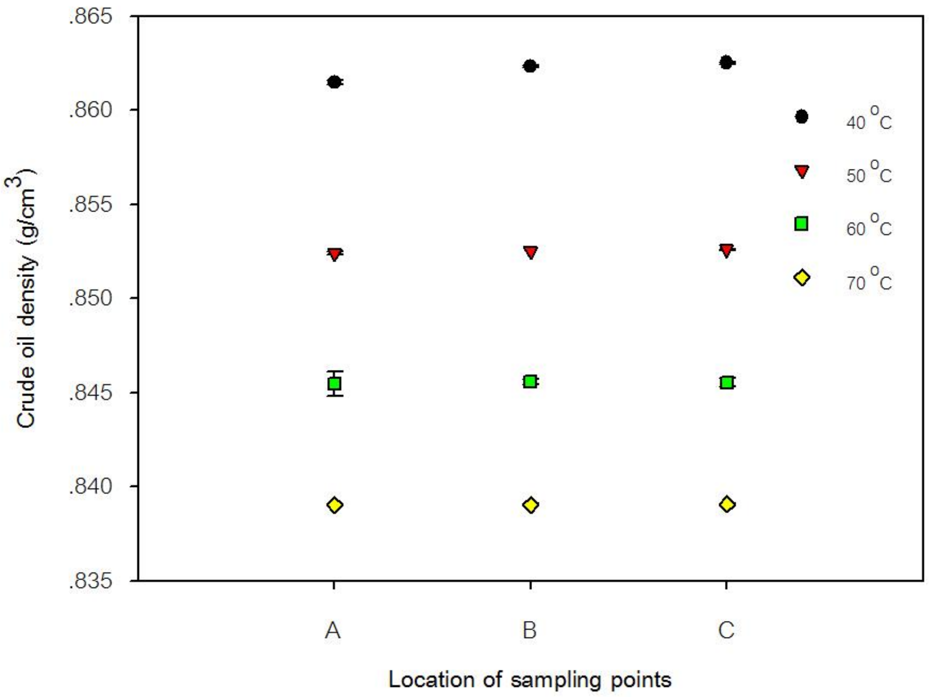


Figure 4.27 Crude oil densities and location of sampling points at different temperatures of L1

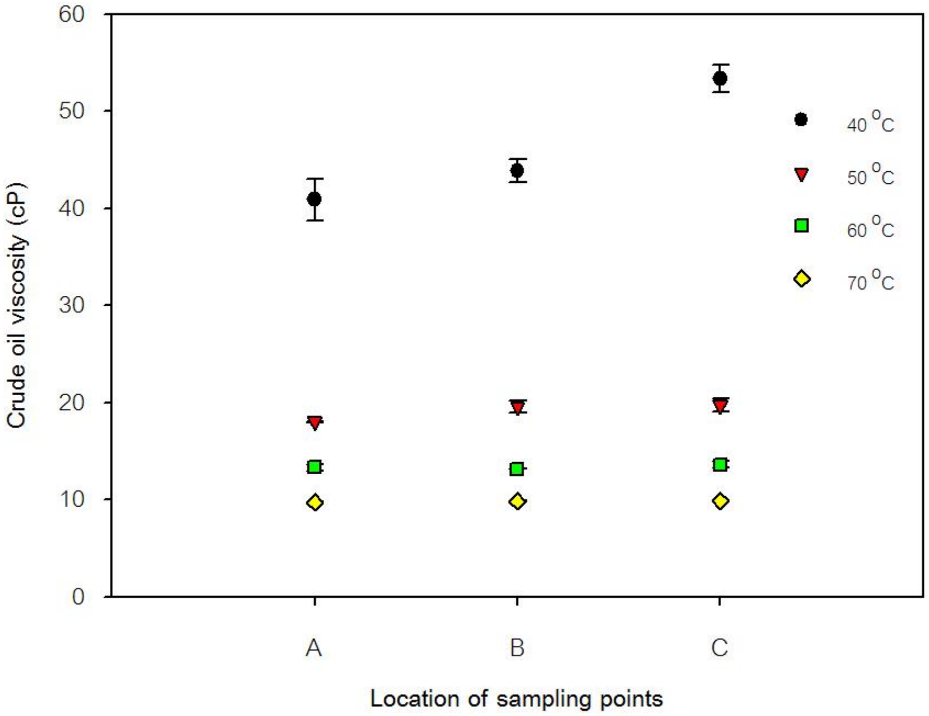


Figure 4.28 Crude oil viscosities and location of sampling points at different temperatures of L1

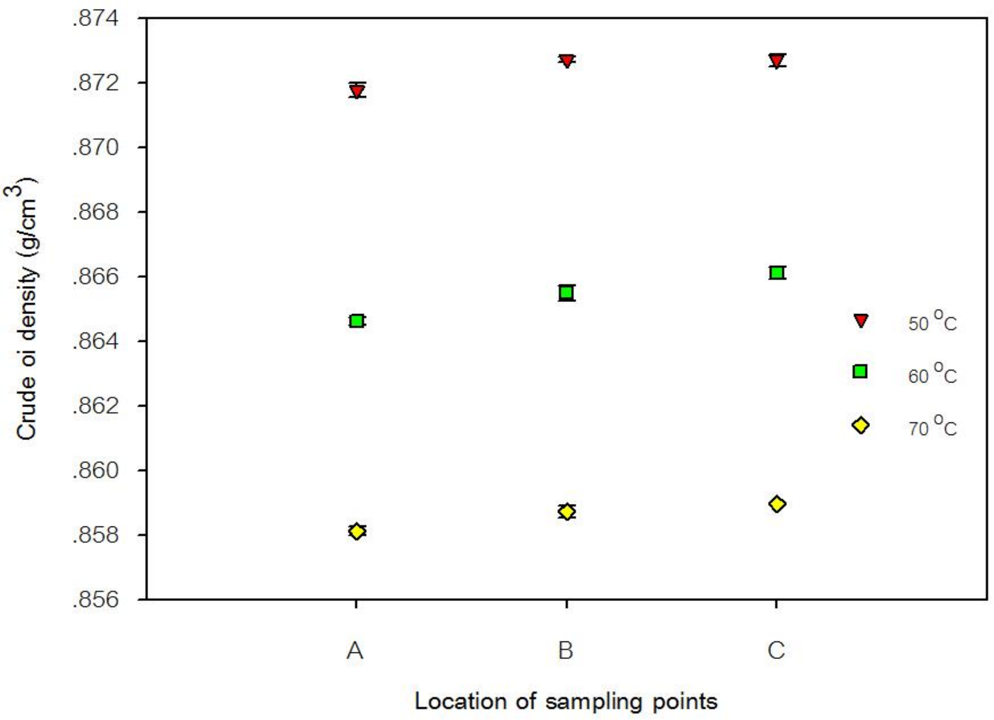


Figure 4.29 Crude oil densities and location of sampling points at different temperatures of L2

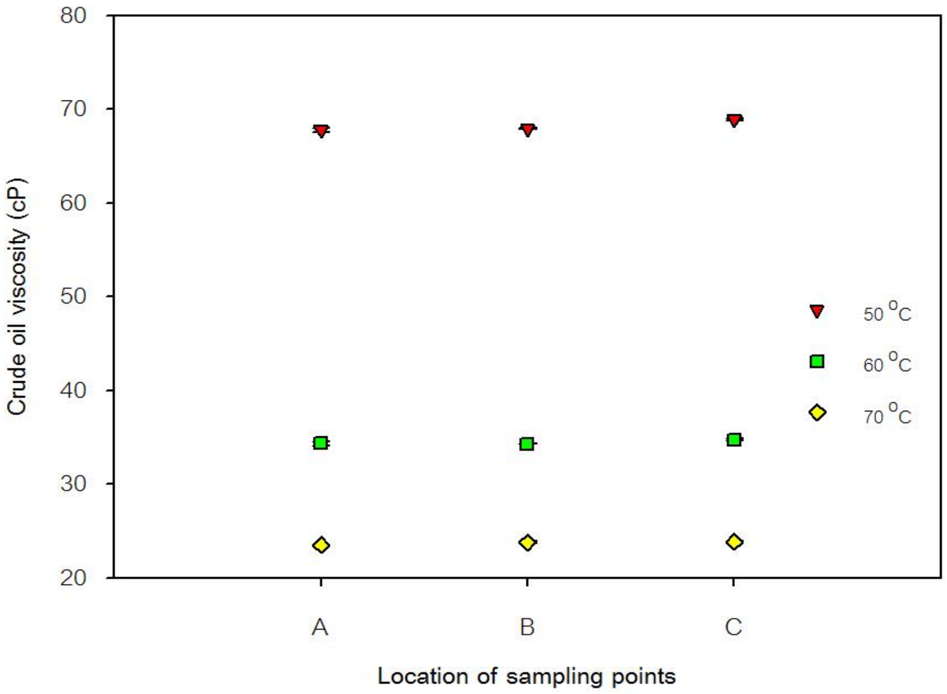


Figure 4.30 Crude oil viscosities and location of sampling points at different temperatures of L2

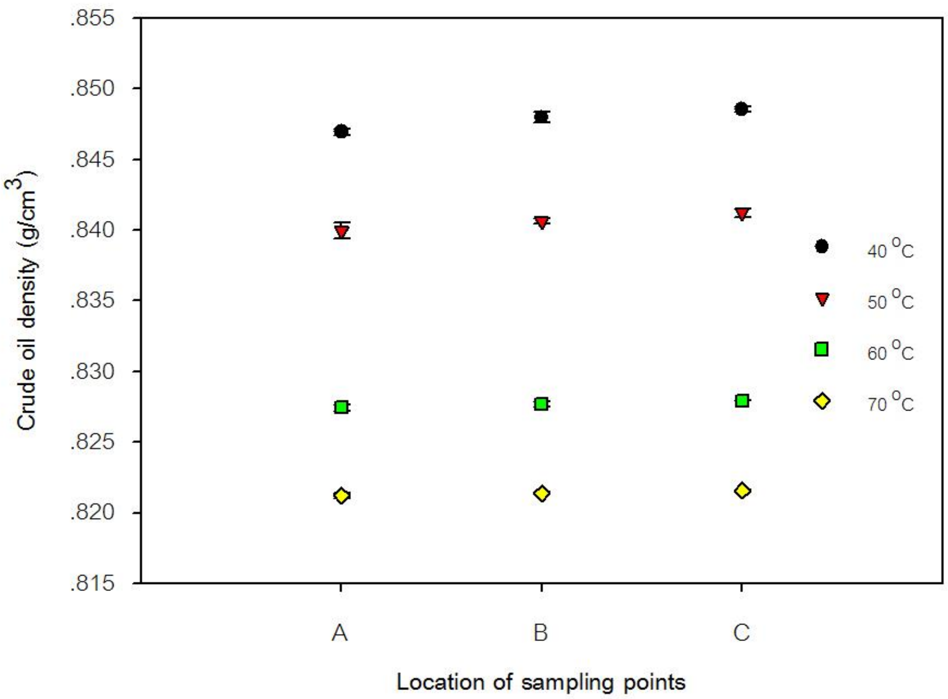


Figure 4.31 Crude oil densities and location of sampling points at different temperatures of L3

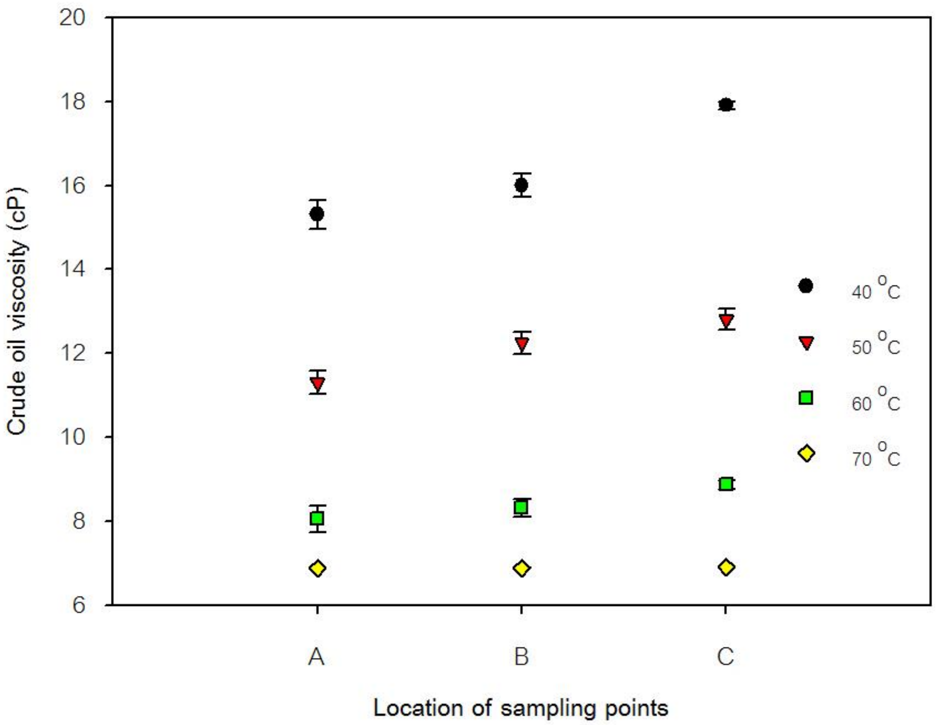


Figure 4.32 Crude oil viscosities and location of sampling points at different temperatures of L3

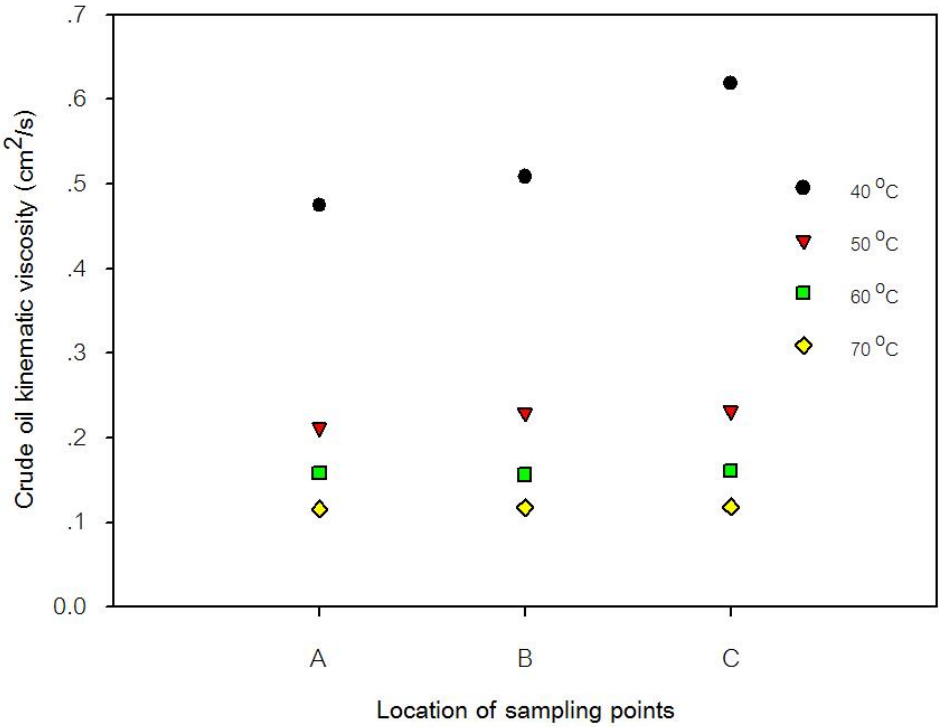


Figure 4.33 Crude oil kinematic viscosities and location of sampling points at different temperatures of L1

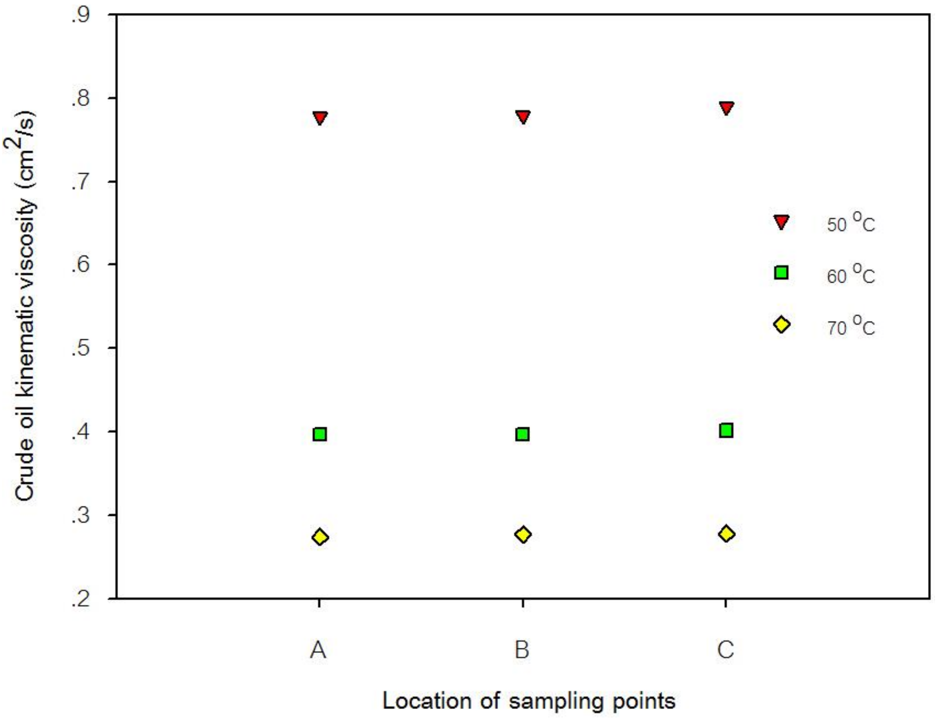


Figure 4.34 Crude oil kinematic viscosities and location of sampling points at different temperatures of L2

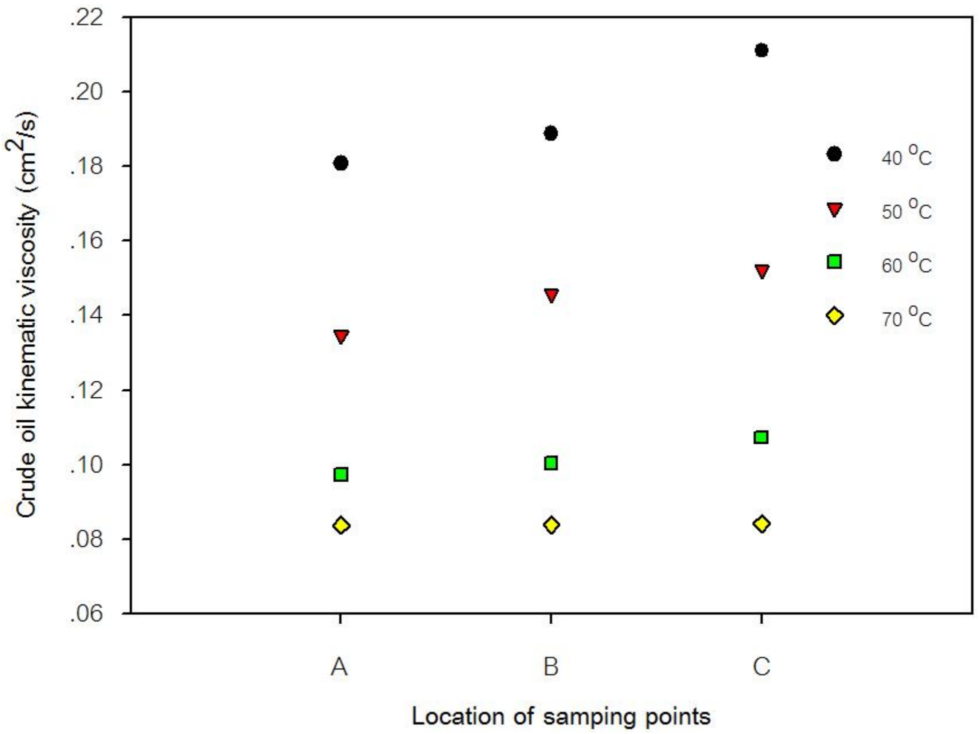


Figure 4.35 Crude oil kinematic viscosities and location of sampling points at different temperatures of L3

The Figure 4.27-4.32 showed that, with an increase in the temperature at the same sampling points, the density and viscosity of each crude oil sample decreased as showed in Figure 4.27-4.32. This is due to the increase of temperature to the crude oil causes the greater kinetic energy and higher inter molecular forces of the crude oil molecules. Therefore, each crude oil unit takes up more space casing more freely to move as the temperature increases causing the decrease of density and viscosity.[30, 31] For example, sample of crude oil L1 at the top section of cylinder, the crude oil density decreased from 0.8615 to 0.8390 g/cm^3 and the crude oil viscosity decreased from to 40.909 to 9.707 cP with an increasing of the temperature from 40 to 70°C. In addition, crude oil density decreased from 0.8625 to 0.8391 g/cm^3 and the crude oil viscosity decreased from 53.369 to 9.924 cP at the bottom section of cylinder.

Moreover, when the points of sampling were changed from the top (A) to bottom (C) section of cylinder at a constant temperature. The densities and viscosities of crude oil increased, particularly at lower temperature (40°C). For example, sample of crude oil L3, the crude oil density increased from 0.8470 to 0.8486 g/cm^3 and the crude oil viscosity increased from to 15.309 to 17.912 cP with the changing of sampling points from the top (A) to bottom (C) section of cylinder at 40°C. However, the crude oil density slightly decreased from 0.8212 to 0.8216 g/cm^3 and the viscosity slightly decreased from 6.886 to 6.920 cP at 70°C. This indicates that the irregular distribution of asphaltenes in cylinder causing the measured densities and viscosities of the bottom section of cylinder are higher than the top section of cylinder, especially at 40°C. [3, 32] The lower temperature of crude oil causes each asphaltenes units are closer together, resulting in the higher aggression of each asphaltenes molecules in crude oil.[3, 32] Therefore, the stability of asphaltenes decreased with the decreasing of temperatures. On the other hand, the stability of asphaltenes increased with increasing of temperatures. Similar trends were reported in the effect of temperature on asphaltenes precipitation by using two types of crude oil and different solvents. The results were founded that the temperature increased from 40°C to 60°C, the asphaltenes solubility increased, was similar for both crude oil samples.[32] Moreover, the dissolution of asphaltenes in toluene at different temperatures were also reported. The results showed the asphaltenes aggregated when the temperature decreased.[33]

Moreover, Figure 4.33-4.35 show that the trend of kinematic viscosity results is more clearly than the density and viscosity results. Normally, the kinematic viscosity was calculated from viscosity and density, which is the combination between that two parameters. Therefore, the use kinematic viscosity indicating the stability of asphaltenes was better than density or viscosity individually.

4.6 Study on effect of ratios of asphaltenes to resins on asphaltenes stability

The crude oil compositions, especially the asphaltenes and resins contents, have been reported that they effect on the stability of asphaltenes, were the most important factors to control stability of asphaltenes. According to the original asphaltenes to resins ratios in L1, L2, and L3 are 0.114, 0.072, and 0.062, respectively.

The effect of ratios of asphaltenes to resins on the stability of asphaltenes was studied by varying ratios of asphaltenes to resins. Asphaltenes were added to the original crude oil source in order to increase asphaltenes to resins ratios.[33]

In order to in reconstitute crude oil composition, asphaltenes and resins must be resoluble back in each original crude oil source with varying amount of them. However, asphaltenes are not soluble directly in crude oil, they are mixed with toluene prior to be resoluble in crude oil. To increase ratios of asphaltenes to resins by adding asphaltenes, while resins are constant, asphaltenes must be mixed with toluene prior to resoluble in each crude oil. The addition of toluene in original crude oil effects on its density and viscosity. Then density and viscosity of original crude oil with that mixed toluene is lower than original crude oil.[33]

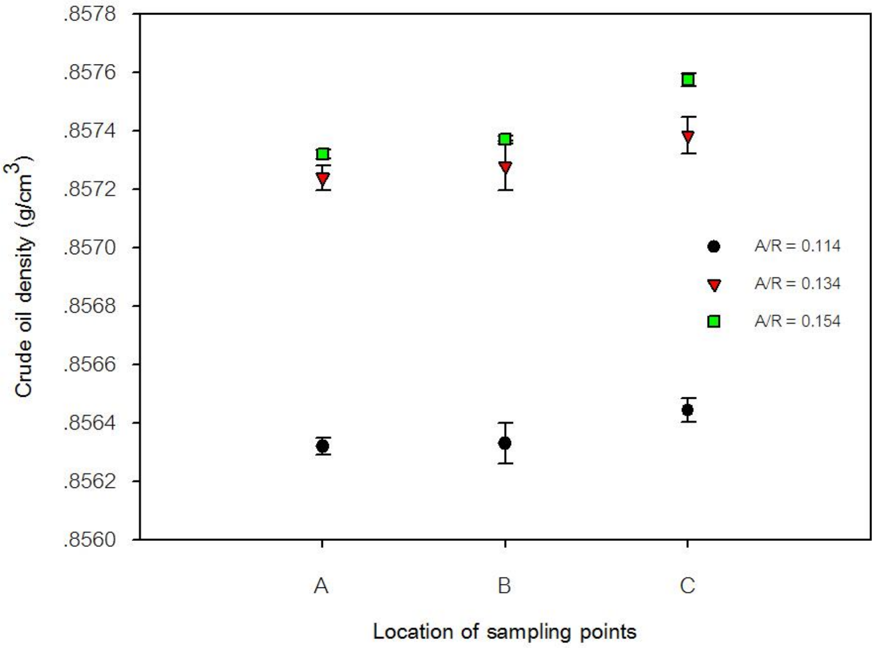


Figure 4.36 Crude oil densities and location of sampling points at different ratios of asphaltenes to resins of L1

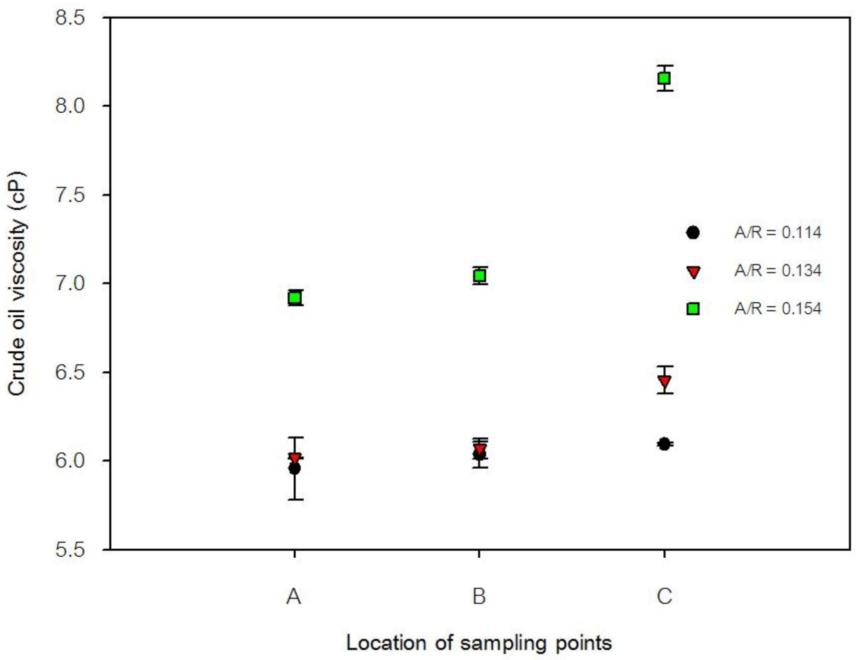


Figure 4.37 Crude oil viscosities and location of sampling points at different ratios of asphaltenes to resins of L1

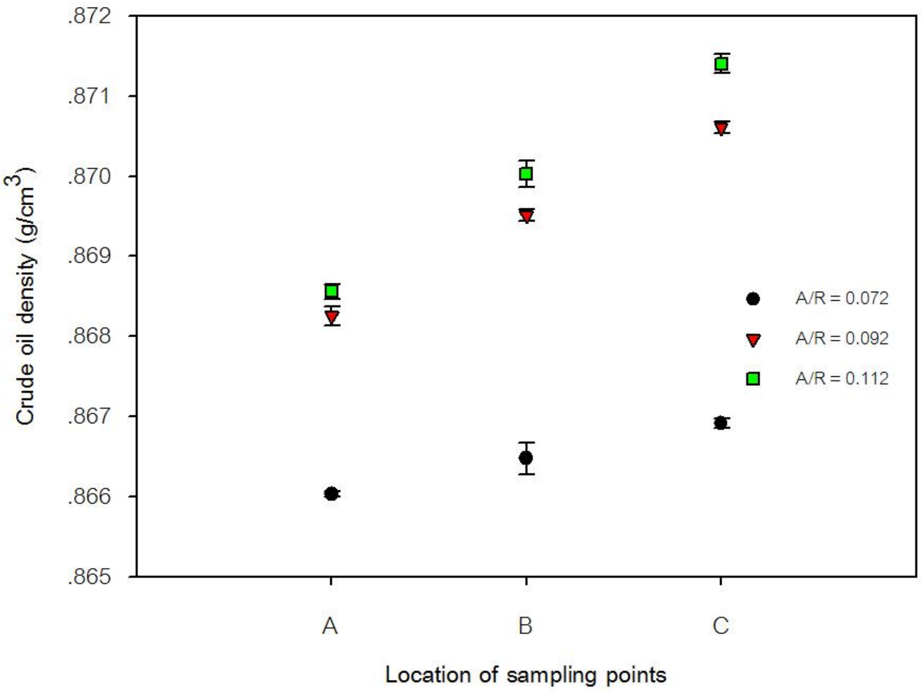


Figure 4.38 Crude oil densities and location of sampling points at different ratios of asphaltenes to resins of L2

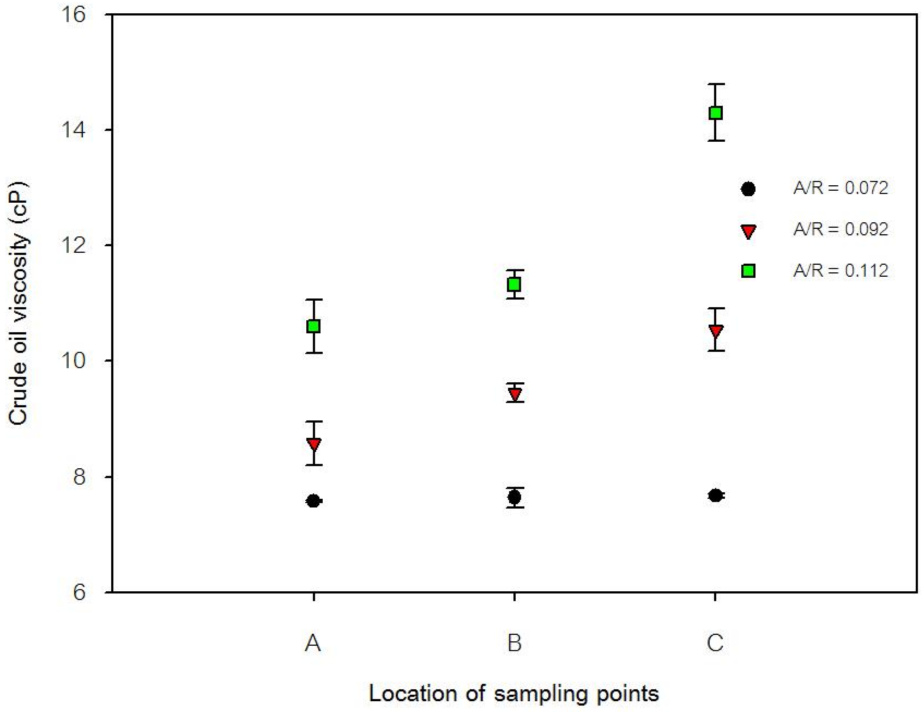


Figure 4.39 Crude oil viscosities and location of sampling points at different ratios of asphaltenes to resins of L2

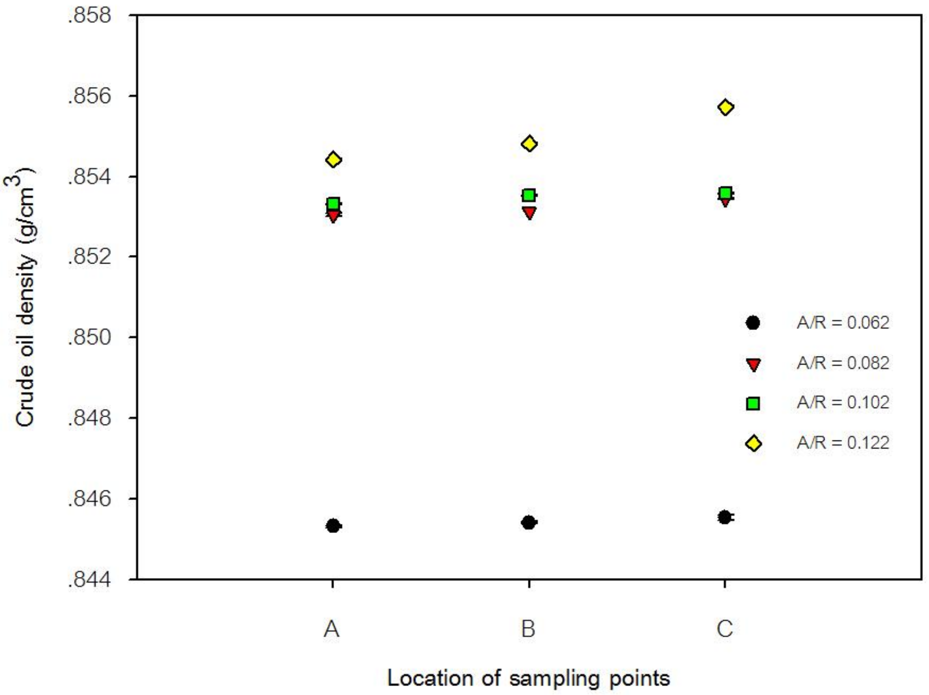


Figure 4.40 Crude oil densities and location of sampling points at different ratios of asphaltenes to resins of L3

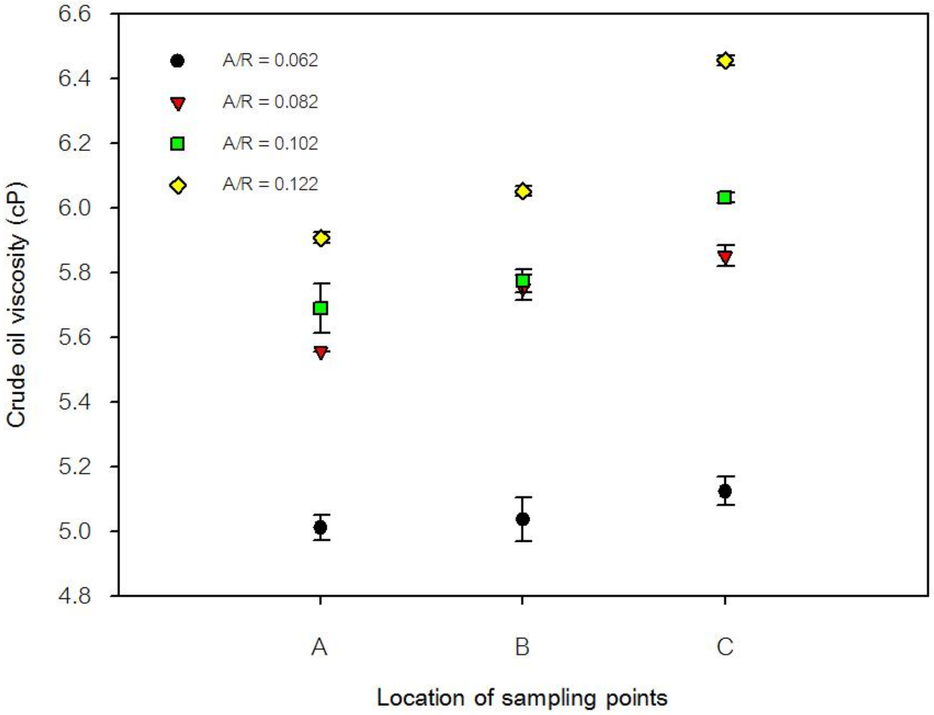


Figure 4.41 Crude oil viscosities and location of sampling points at different ratios of asphaltenes to resins of L3

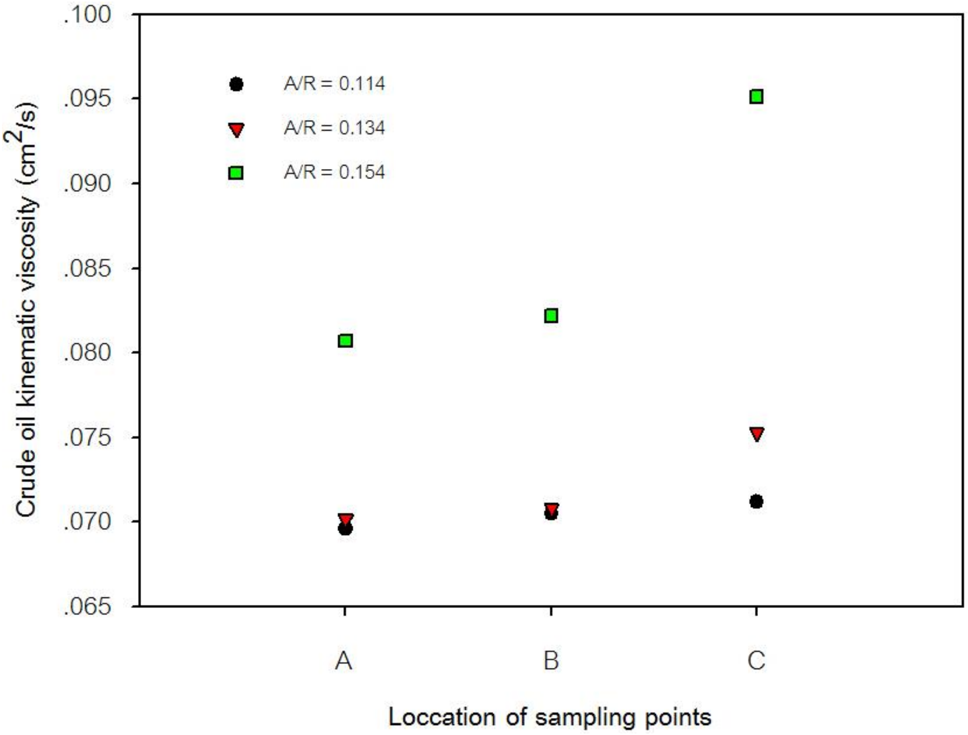


Figure 4.42 Crude oil kinematic viscosities and location of sampling points at different ratios of asphaltenes to resins of L1

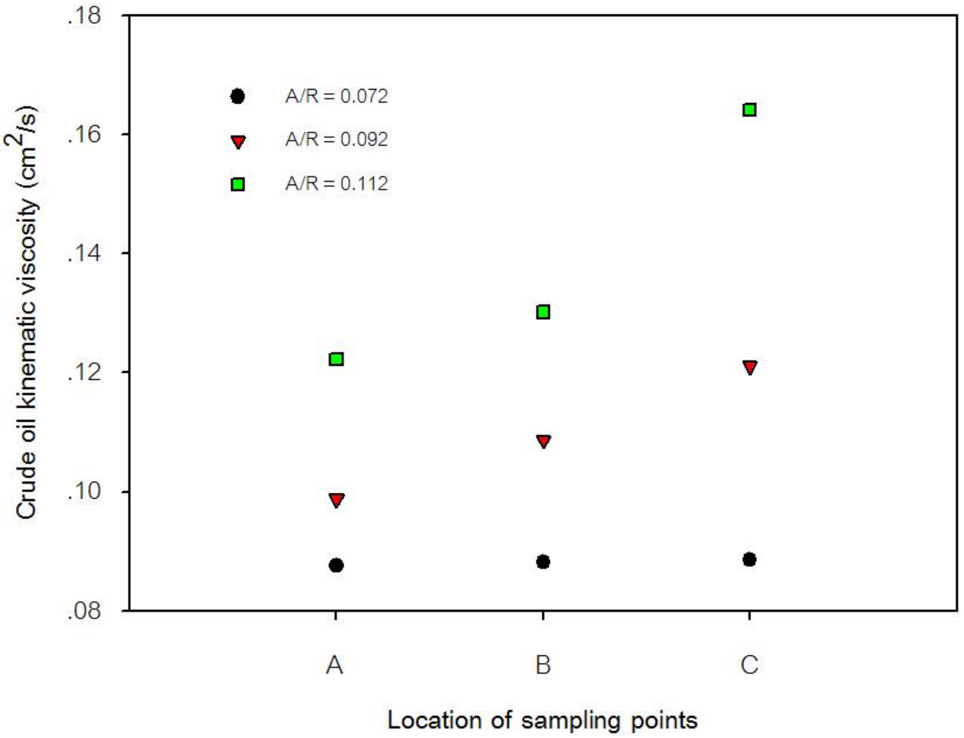


Figure 4.43 Crude oil kinematic viscosities and location of sampling points at different ratios of asphaltenes to resins of L2

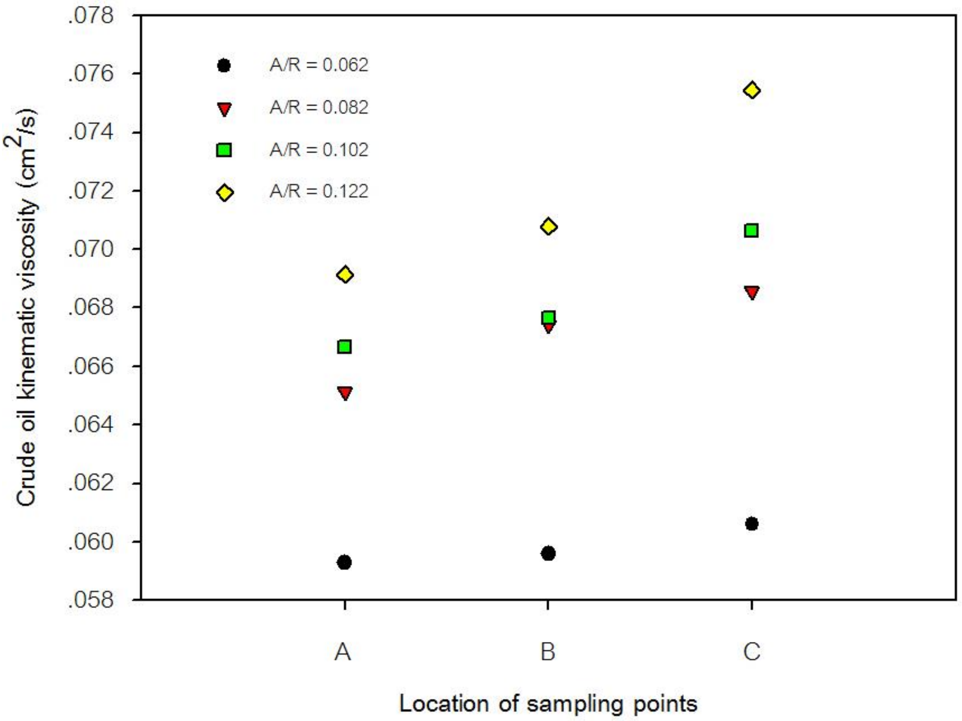


Figure 4.44 Crude oil kinematic viscosities and location of sampling points at different ratios of asphaltenes to resins of L3

The measured densities and viscosities of each crude oil sample versus the points of sampling at different ratios of asphaltenes to resins are shown in Figure 4.36-4.41. This shows that, as the increase of A/R ratios at a constant of point of sampling, the densities and viscosities of each crude oil samples increased, particularly at the lowest points of cylinder. For example, the density increased from 0.8563 to 0.8573 g/cm^3 and the viscosity increased from to 5.959 to 6.921 cP with an increasing of A/R ratios from 0.114 to 0.154 at the top section (A) of cylinder of L1. In addition, the density of crude oil increased from 0.8564 to 0.8576 g/cm^3 and the viscosity of crude oil increased from 6.097 to 8.158 cP at the bottom section (C) of cylinder because the amount of asphaltenes increased as A/R ratios increased.

Additionally, with the change of sampling location from the top (A) to the bottom section (C) of cylinder at a constant A/R ratio, the densities and viscosities of crude oil increased, particularly at higher A/R ratio. For example, the density and viscosity of L1 at the top section (A) were 0.8573 g/cm^3 and 6.921 cP, respectively, whereas the density and viscosity at the bottom section (C) were 0.8576 g/cm^3 and 8.158 cP. The irregular distribution of asphaltenes in cylinder might occur during the measurement of densities and viscosities leading to the obtained value of the bottom section was higher than the top section of cylinder.[29, 34, 35] This represented that the stability of asphaltenes in crude oil decreased causing the precipitation.[8, 9, 34-36] Therefore, the stability of asphaltenes in crude oil decreased, especially at high A/R.

Moreover, Figure 4.42-4.44 show that the trend of kinematic viscosity results is related to density and viscosity results, but is more clearly than that. The use kinematic viscosity indicating the stability of asphaltenes was better than density or viscosity.

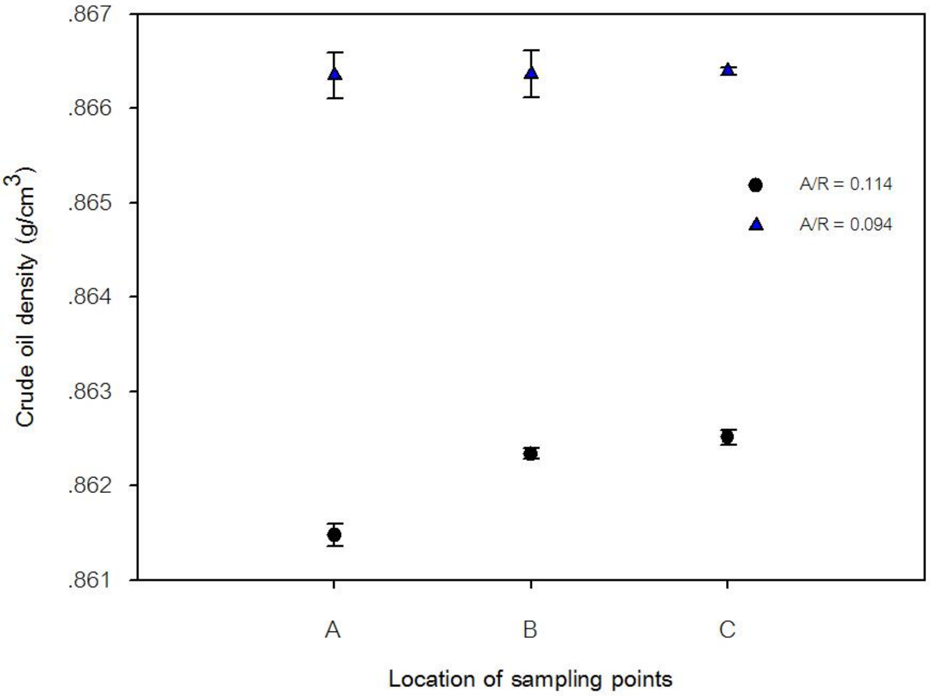


Figure 4.45 Crude oil densities and location of sampling points at different ratios of asphaltenes to resins of L1

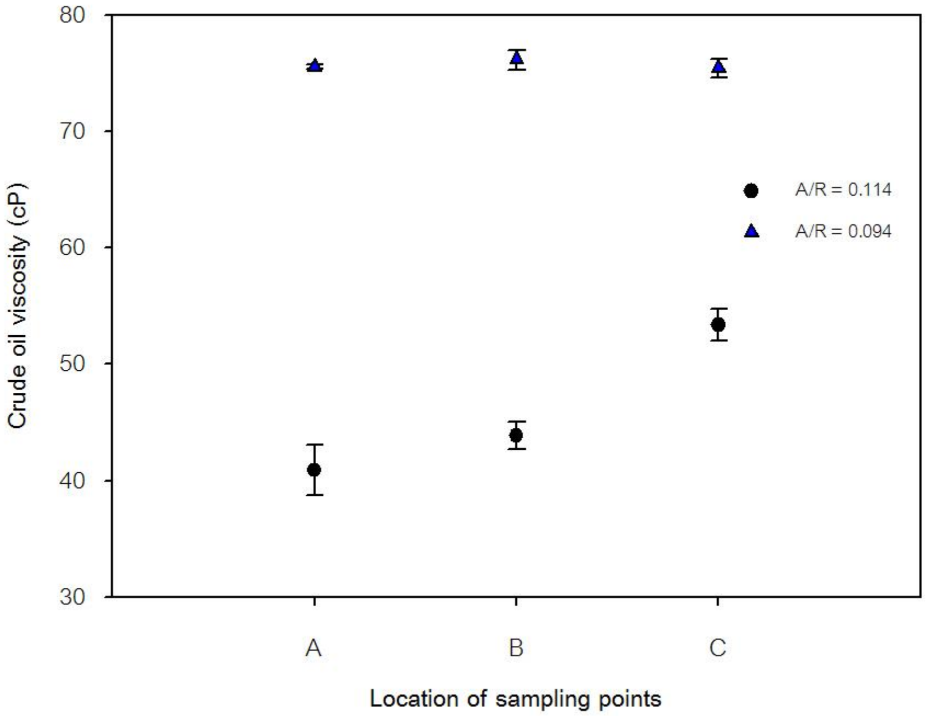


Figure 4.46 Crude oil viscosities and location of sampling points at different ratios of asphaltenes to resins of L1

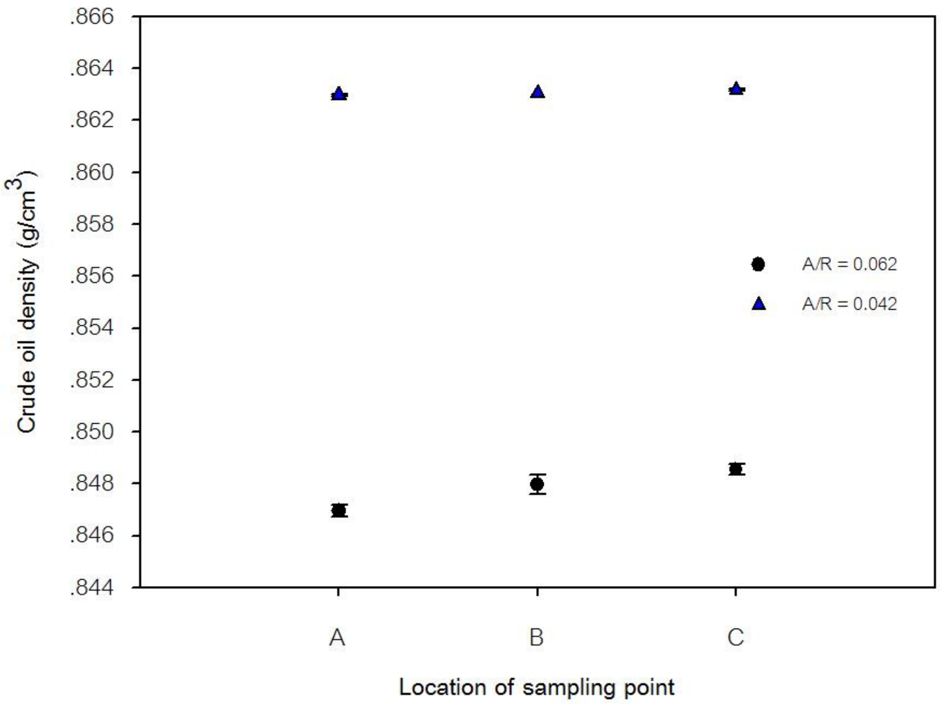


Figure 4.47 Crude oil densities and location of sampling points at different ratios of asphaltenes to resins of L3

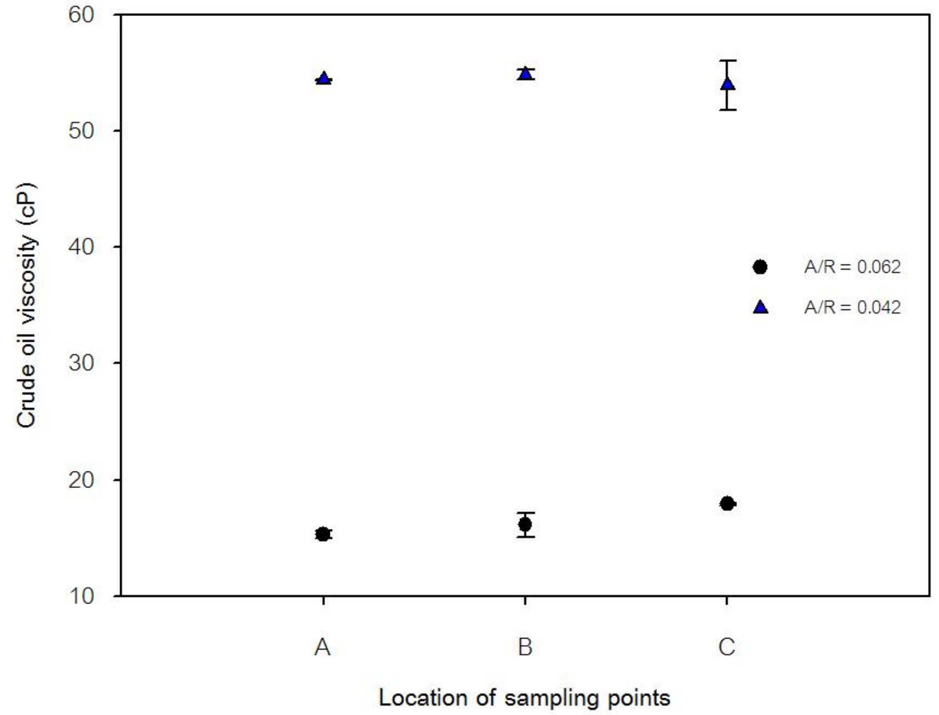


Figure 4.48 Crude oil viscosities and location of sampling points at different ratios of asphaltenes to resins of L3

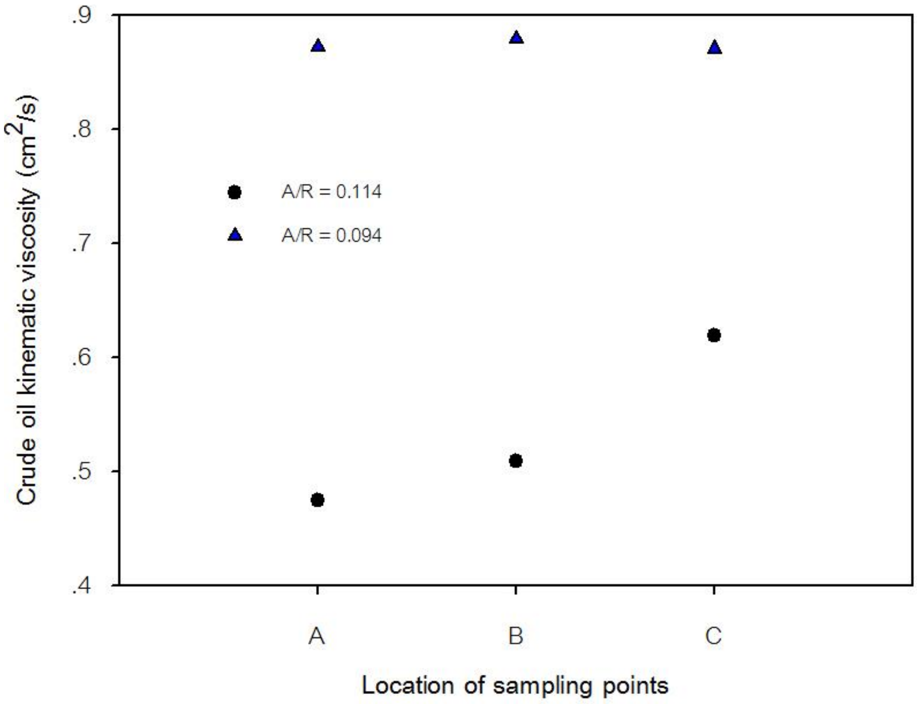


Figure 4.49 Crude oil kinematic viscosities and location of sampling points at different ratios of asphaltenes to resins of L1

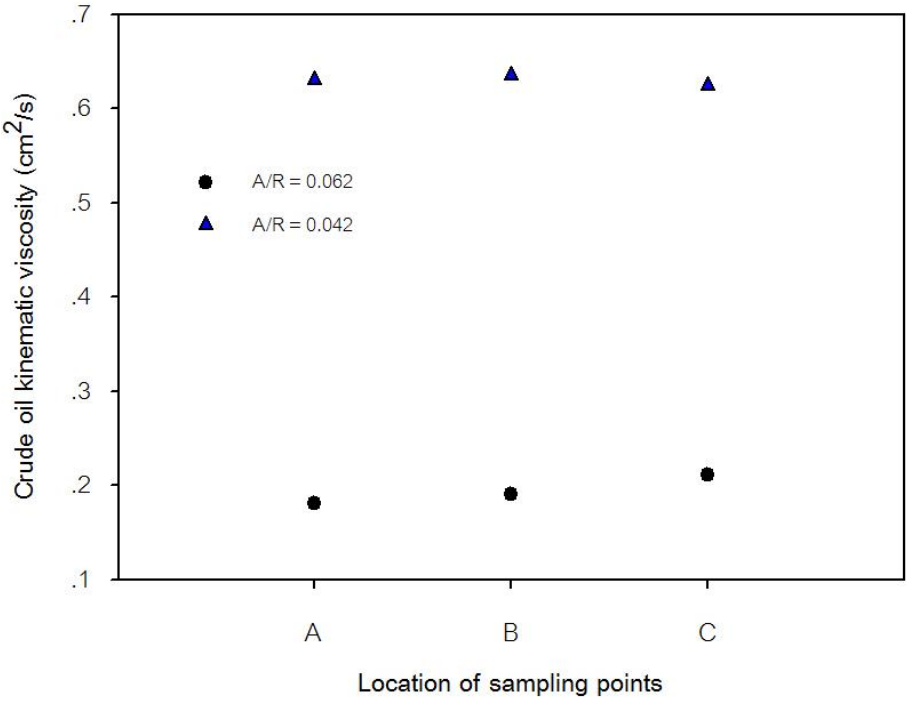


Figure 4.50 Crude oil kinematic viscosities and location of sampling points at different ratios of asphaltenes to resins of L3

On the other hand, to reduce ratios of asphaltenes to resins, resins must be added directly in original crude oil sample. It was found that the measured densities and viscosities of each reconstituted oil sample increased at the constant point of sampling. Because the amount of resins that are added to crude oil having sticky texture. However, resins can increase the stability of asphaltenes due to the measured densities and viscosities of the bottom were similar to the top section of cylinder. This represented that the stability of asphaltenes in crude oil was increased with the addition of resins[8, 9, 34-36][8, 9, 34-36][8, 9, 33-35] as shown in Figure 4.45-4.48.[8, 9, 34-36] The results were quite similar to that. Resins can improve the solubility of asphaltenes because the increase of resins to asphaltenes would greatly reduce the present toluene used to be soluble in asphaltenes.[37] Figure 4.49-4.50 show that the kinematic viscosity results is similar to density and viscosity results, but is more obviously than that. The use kinematic viscosity indicating the stability of asphaltenes was better than density or viscosity discretely.

CHARPTER 5
CONCLUSION AND SUGGESTIONS

5.1 Conclusion

5.1.1 Asphaltenes precipitation

The amount of asphaltenes of L1 precipitated by filtration technique was higher than centrifugation techniques. The use of filtration technique caused the higher asphaltenes contents due to the increase of the amount of wax contamination in that fraction. The use of filtration technique had a high pressure drop causing the temperature reduction during filtration. Therefore, n_{carbon} values of asphaltenes precipitation by filtration technique were more than asphaltenes precipitation by centrifugation technique. In contrast, f_a values of asphaltenes precipitation by filtration technique were lower than that.

The asphaltenes contents of L1, L2, and L3 precipitated by n-heptane were 1.67, 1.36, and 0.82 %wt, respectively. The appearance of obtained asphaltenes of L1, L2, and L3 were black solid as same as all sample. In addition, the amount of precipitated asphaltenes out of L1 by n-hexane was higher compared to that obtained by n-heptane. The asphaltenes precipitated by n-C_6 alkane had the higher amount of the contamination from their unfractionation. Mainly of previous study showed that the use of n-C_7 as solvent precipitated the asphaltenes resulting in the higher values of f_a. The separation efficiency of aromatics from crude oil sample using n-heptane was more than the use of n-hexane as solvent for separation. The functional groups of asphaltenes of Thai crude oil, obtained from FTIR spectrums, consisted of aliphatic, aromatics, alicyclic, phenol, and some heteroatoms. The functional groups of asphaltenes do not depend on asphaltenes separation methods, crude oil sources, and used solvents.

5.1.2 Resins separation

The resins contents used the vacuum procedure were higher than that used ASTM procedure. The use of vacuum technique caused the higher resins contents due to the increase of the contamination, especially aromatic in that fraction. Vacuum procedure, force obtained from vacuum pump, was higher than gravity force (ASTM procedure). This caused the resins contents obtained from vacuum procedure were more than that. In addition, n_{carbon} and f_a values of resins separated with vacuum technique were higher than resins separated with ASTM technique. The use of vacuum procedure for resins separation caused the higher other contamination, especially aromatics. This causes n_{carbon} and f_a of resins separated with vacuum technique were higher than that. Moreover, the resins contents of L1, L2, and L3 separated by n-heptane were 14.82, 18.89, and 13.27 %wt, respectively. Obviously, the resins content of L2 crude oil source had the highest content following by L1 and L3, respectively. Moreover, the appearance of L1, L2, and L3-resins separated by n-heptane solvent were black and sticky liquid. Although the use of different techniques for resins separation, the functional groups of resins separated with vacuum and ASTM techniques are still consist of aliphatic, aromatic, alicyclic, phenol, and some heteroatoms.

5.1.3 Stability of asphaltenes

The temperature of crude oil is one of important parameters controlling the stability of asphaltenes in crude oil. The stability of asphaltenes decreased with the decreasing of temperatures, especially at 40°C. This is because of its lower solubility in crude oil. Consequently the operated temperature, which is not the problems of asphaltenes precipitation in Thai crude oil, should be the range between 50-70°C. Also, the stability of asphaltenes decreased with the increasing ratios of asphaltenes to resins. Due to the increase of A/R ratio by adding asphaltenes into crude oil, while resins contents playing a role to increase the stability are constant. Moreover, the stability of asphaltenes in crude oil was increased with the addition of resins. Resins can improve the solubility of asphaltenes because the increase of resins to asphaltenes would greatly reduce the present toluene used to be soluble in asphaltenes. So the stability of asphaltenes in oil depends on the ratio of asphaltenes to resins.

5.2 Suggestions

5.2.1 The use of NMR including ^{1}H NMR and ^{13}C NMR and FTIR techniques was just the primary structural parameters and functional groups. The other additional techniques such as Liquid Chromatography – Mass Spectrometry (LC-MS), X-Ray Diffraction (XRD) should be used to predict the structure of asphaltenes and resins.

5.2.2 The effect of temperature on stability of asphaltenes, the design of cylinder used to contain the crude oil samples should be more suitable for sampling.

5.2.3 Operating pressure, which is one of significant effect casing the stability of asphaltenes, should be further studied.

5.2.4 The additional studies of other composition in crude oil including saturates and aromatic because they can effect on the stability of asphaltenes.

REFERENCES

1. Abbas, O., et al., PLS regression on spectroscopic data for the prediction of crude oil quality: API gravity and aliphatic/aromatic ratio. Fuel, 2010. 98: p. 5-14.
2. Amin A, R.M., Shepler R, Smedstad E and Ratulowski J, Subsea Development from Pore to Process. Oilfield Review 2005. 17(1): p. 4-17.
3. Maldi Ghanavati, M.-J.S., and Ahmad Ramazani, Effects of Asphaltene Content and Temperature on Viscosity of Iranian Heavy Crude oil:Experimental and Modeling Study. Energy & Fuels, 2013. 27: p. 7217-7232.
4. Tabish Maqbool, A.T.B., and H. Scott Fogler, Revisiting Asphaltenes Precipitation from Crude Oils: A Case of Neglected Kinetic Effects. Energy & Fuels, 2009. 23: p. 3681-3686.
5. Spiecker, P.M., et al., Effects of petroleum resins on asphaltene aggregation and water-in-oil emulsion formation. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2003. 220: p. 9-27.
6. R.B. de Boer, K.L., M.R.P. Eigner, and A.R.D. van Bergen, Screening of Crude Oils for Asphalt Precipitation: Theory, Practice, and the Selection of Inhibitors. Society of Petroleum Engineers, 1995. 10(01): p. 55-61.
7. Ghloum, E.F., M. Al-Qahtani, and A. Al-Rashid, Effect of inhibitors on asphaltene precipitation for Marrat Kuwaiti reservoirs. Journal of Petroleum Science and Engineering. 70: p. 99-106.
8. Speight, J.G., Petroleum Asphaltenes Part 1 Asphaltenes, Resins and the Structure of Petroleum. Oil & Gas Science and Technology, 2004. 59: p. 467-477.
9. F.O.Ebhodaghe, C.I.O.a., Asphaltenes Deposition and Remediation in Crude Oil Production:Solubility technique. Engineering and Appiled Sciences, 2011. 6: p. 258-261.
10. Boussingault, M., Memoire sur la Composition des Bitumes. Annales de Chimie et de Physique, 1937. LXIV: p. 141-151.

11. J. Ancheyta, G.c., F.Trejo, G.Marroquin, J.Garcia, E.tenorio, and A.Torres, Extraction and Characterization of Asphaltenes from Different Crude Oils and Solvents. Energy & Fuels, 2002. 16(5): p. 1121-1127.

12. MR, G., Consistency of Asphaltene Chemical Structures with Pyrolysis and Coking Behavior. Energy & Fuels, 2003. 17: p. 1566-1569.

13. Peng P, F.J., Sheng G,Morales-Izquierde A, Lown EM and Strausz OP, Ruthenium -Ions Catalyzed Oxidation of an immature Asphaltene:Structural Features and Biomarker Distribution. Energy & Fuels, 1999. 13: p. 266-277.

14. Goual, M.S.a.L., Role of Resins on Asphaltene Stability. Energy & Fuels, 2009. 24: p. 2275-2280.

15. Ali F. Alta'ee, O.S.H., Sima Sh. Alian, and Ismail M. Saaid, Experimental Investigation on th Effect of CO2 and WAG Injection on Permeability Reduction Induced by Asphaltene Precipitation in Light Oil. engineering and Technology, 2012. 6: p. 999-1004.

16. Rogel, E., Simulation of Interactions in Asphaltene Aggregates. Energy & Fuels, 2000. 14: p. 566-574.

17. Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay-GelAbsorption Chromatographic Method. AMERICAN SOCIETY.

18. Hammami, K.K., Hammami A, Flannery M and Stankiewicz A, Evaluation of Asphaltene Instability and a Chemical Control During Production of Live Oils. Petroleum Science and Technology, 2003. 21: p. 629-645.

19. Leyva, C., et al., Chemical characterization of asphaltenes from various crude oils. Fuel Processing Technology, 2013. 106: p. 734-738.

20. L. Davarpanah, F.V.a.A.D., Strutural Study of Asphaltenes from Iranian Heavy Crude oil. Oil & Gas Science and Technology, 2013.

21. Seidl, R.C.S.a.P.R., 1H and 13C NMR for determining Average molecular Parameters of Asphaltenes from vacuum Residue distillation. Petroleum Science and Engineering, 2004. 3(3): p. 63-67.

22. Trejo F., C.G., and Ancheyta J. , Precipitation, fractionation and characterization of asphaltenes from heavy and light crude oils. Fuel 2004. 83: p. 2169-2175.

23. I.Hovell, R.R.C.a., Characterization of Functional Groups of Asphaltenes in Vacumm Residues Using Molecular Modeling and FTIR techniques. Petroleum Science and Technology, 2007. 25: p. 41-54.

24. L.M. Petrova, N.A.A., T.R. Foss, and G.V. Romanov, Structural Features of Asphaltene and petroleum Resin Fractions. Petroleum Chemistry, 2011. 51: p. 252-256.

25. Larkin, P., Infrared and Raman Spectroscopy; Principles and Spectral Interpretation: Elsevier Science.

26. Ail Abedini, S.A., Farshid Torabi, Yaser Saki and Navid Dinarvand, Mechanism of the reversibility of asphaltene precipitation in crude oil. Elsevier, 2011. 78: p. 316-320.

27. Allen, T.O.a.R., Production Operations. Oil and Gas Consultants International. Vol. second edition. 1982, Tulsa, Oklahoma.

28. Abdel M.Kharrat, K.I., and Farshid Mostowfi, Asphaltene Content Measurement Using an Optical Spectroscopy Techique. Energy & Fuels, 2013. 27: p. 2452-2457.

29. Peng Luo, Y.G., Effects of asphaltene content on the heavy oil viscosity at different temperatures. Elsevier, 2007. 86: p. 1069-1078.

30. Francis S. Manning, R.E.T., and Richard E. Thompson, Oilfield Processing of Petroleum Crude Oil. 1994.

31. Latil, M., Enhanced Oil Recovery. 1961.

32. Laura Moreno Arciniegas, T.B., Asphaltene precipitation, flocculation and deposition during solvent injection at elevated temperatures for heavy oil recovery. Elsevier, 2014. 124: p. 202-211.

33. Espinat, D.F., D.Barre, L.Frot, and B.Briolant, Effects of temperature and pressure on asphaltenes agglomeration in toluene. A light, X-ray, and neutron scatting investigation. Energy & Fuels, 2004. 18: p. 1234-1249.

34. Goual, M.S.a.L., Role of Resins on Asphaltenes Stability. Energy & Fuels, 2010. 24: p. 2275-2280.

35. P. Matthew Spiecker, K.L.G., Chad B. Trail, Peter K. Kilpatrick, Effects of petroleum resins on asphaltene aggregation and water-in-oil emulsion formation. Elsevier, 2002: p. 9-27.

36. Nor, C.M.S.a.N.M., Relationship Between SARA Fractions and Crude Oil Fouling. Applied Sceinces, 2012. 12(23): p. 2479-2483.

37. J.S., W.J.a.B., Asphaltene-stability in crude oil and aromatic solvents-The influence of oil composition. Energy & Fuels, 2003. 17: p. 1445-1451.

38. Villa, G.D.G.a.M., Reliability Analysis on PVT Correlations. Society of Petroleum Engineers, 1994.

39. Guo-Qing Tang, N.R.M., Influence of brine composition and fines migration on crude oil/brine/rock interactions and oil recovery. Petroleum Science and Engineering, 1999. 24: p. 99-111.

APPENDIX A

PROPERTIES OF DIFFERENT CRUDE OIL SOURCES

A1. Analysis each crude oil composition of each oil by using the liquid analyzer gas chromatography

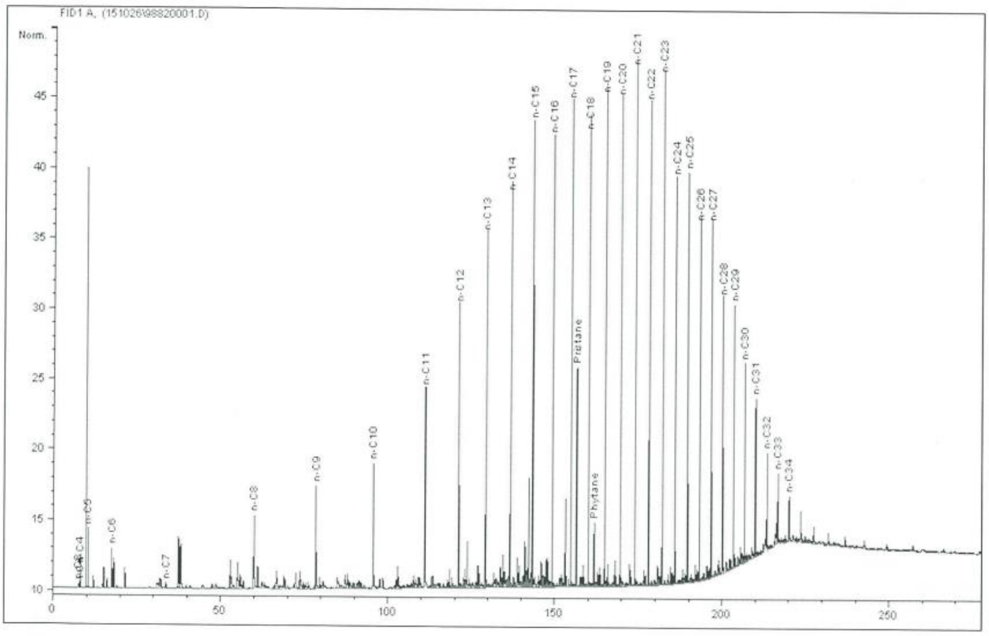


Figure A1.1 GC spectrum of L1 crude oil source

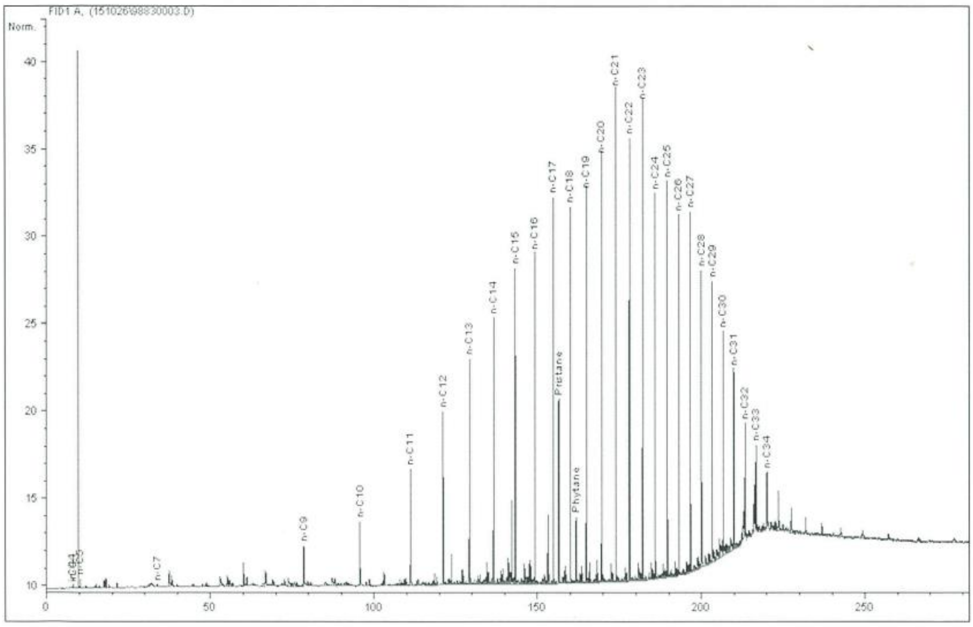


Figure A1.2 GC spectrum of L2 crude oil source

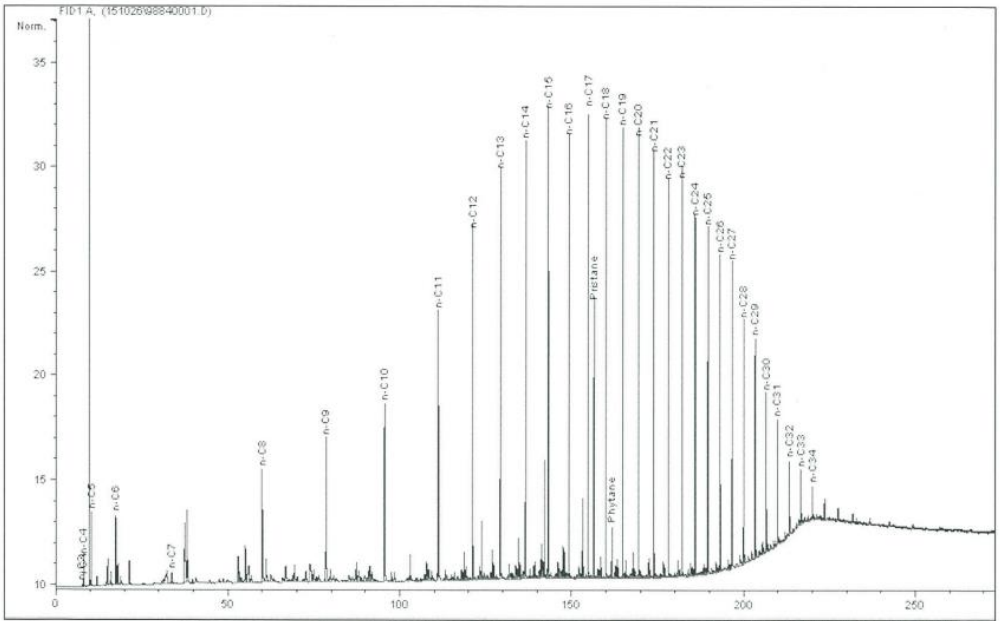


Figure A1.3 GC spectrum of L3 crude oil source

Table A1.1 Compositional analysis of L1 crude oil source

Carbon number	%wt	Carbon number	%wt
C_1	0.00	Phytanes	0.47
C_2	0.00	C_{19}	3.66
C_3	0.01	C_{20}	3.82
C_4	0.06	C_{21}	3.96
C_5	0.26	C_{22}	3.46
C_6	0.88	C_{23}	3.59
C_7	1.53	C_{24}	3.07
C_8	5.36	C_{25}	3.04
C_9	4.12	C_{26}	2.98
C_{10}	3.54	C_{27}	2.95
C_{11}	3.87	C_{28}	2.48
C_{12}	3.55	C_{29}	2.53
C_{13}	4.37	C_{30}	2.59
C_{14}	5.16	C_{31}	2.32
C_{15}	6.34	C_{32}	1.42
C_{16}	4.58	C_{33}	1.37
C_{17}	4.19	C_{34}	0.87
Pristanes	1.64	C_{35+}	2.60
C_{18}	3.36	Total	100

Table A1.2 Compositional analysis of L2 crude oil source

Carbon number	%wt	Carbon number	%wt
C_1	0.00	Phytanes	0.61
C_2	0.00	C_{19}	3.54
C_3	0.00	C_{20}	4.00
C_4	0.01	C_{21}	4.30
C_5	0.04	C_{22}	3.80
C_6	0.12	C_{23}	4.05
C_7	0.67	C_{24}	3.58
C_8	1.87	C_{25}	3.64
C_9	3.15	C_{26}	3.55
C_{10}	2.48	C_{27}	3.70
C_{11}	2.56	C_{28}	3.32
C_{12}	2.29	C_{29}	3.62
C_{13}	3.54	C_{30}	4.10
C_{14}	4.10	C_{31}	3.65
C_{15}	5.20	C_{32}	2.65
C_{16}	4.03	C_{33}	2.49
C_{17}	4.20	C_{34}	1.28
Pristanes	1.64	C_{35+}	4.84
C_{18}	3.38	Total	100

Table A1.3 Compositional analysis of L3 crude oil source

Carbon number	%wt	Carbon number	%wt
C_1	0.00	Phytanes	0.42
C_2	0.00	C_{19}	3.54
C_3	0.00	C_{20}	3.65
C_4	0.09	C_{21}	3.54
C_5	0.33	C_{22}	3.13
C_6	1.36	C_{23}	2.97
C_7	1.84	C_{24}	2.94
C_8	7.21	C_{25}	2.84
C_9	5.25	C_{26}	2.73
C_{10}	4.83	C_{27}	2.67
C_{11}	4.38	C_{28}	2.21
C_{12}	3.91	C_{29}	2.26
C_{13}	5.16	C_{30}	1.94
C_{14}	4.97	C_{31}	1.65
C_{15}	5.12	C_{32}	1.09
C_{16}	4.12	C_{33}	0.88
C_{17}	4.35	C_{34}	0.72
Pristanes	2.09	C_{35+}	2.16
C_{18}	3.65	Total	100

The compositional analysis results of three crude oil samples including L1, L2, and L3 obtained from PTT, Thailand are respectively shown in Table A1.1-1.3. The results showed that all crude oil samples there are light components of all crude oil samples because C_4 was found in all crude oil samples. Obviously, almost all of crude oil samples mainly consist of C_8-C_{18}, but L2 mainly consist of C_{15}-C_{30}. Moreover, L2 crude oil is the highest fraction of heavy components with C_{35+} = 4.84 %wt following L1 and L3, respectively.

A2. Analysis the crude oil physical properties such as density and viscosity at different temperatures (40, 50, 60, and 70°C).

Table A1.4 Densities and viscosities of crude oil sources L1, L2, and L3 as different temperatures

Temp (°C)	L1		L2		L3	
	Density (g/cm^3)	Viscosity (cP)	Density (g/cm^3)	Viscosity (cP)	Density (g/cm^3)	Viscosity (cP)
40	0.8618	41.914	wax	wax	0.8474	15.728
50	0.8549	18.945	0.8722	67.817	0.8403	11.787
60	0.8455	13.144	0.8650	34.322	0.8275	8.188
70	0.8390	9.735	0.8583	23.497	0.8213	6.880

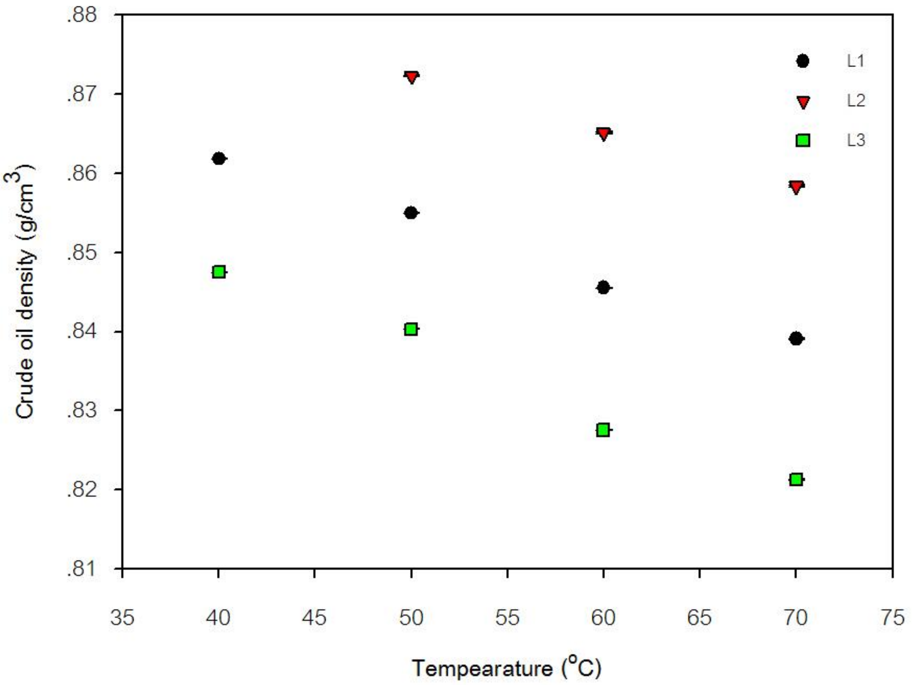


Figure A1.4 The effect of temperature on density of the different crude oil sources L1, L2, and L3

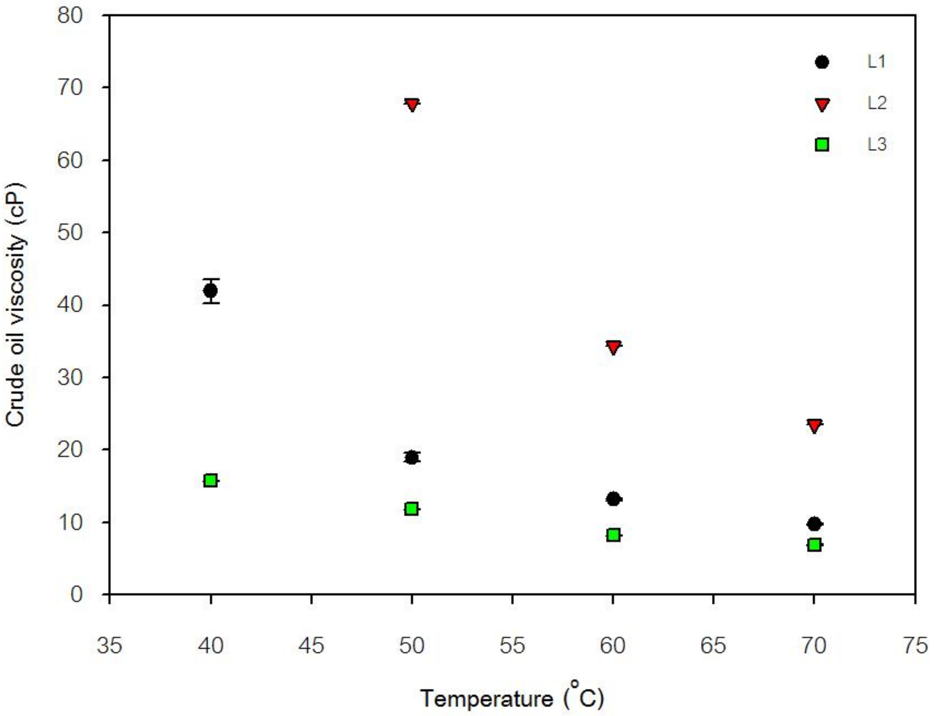


Figure A1.5 The effect of temperature on viscosity of the different crude oil sources L1, L2, and L3

The densities and viscosities of each crude oil source were measured at 40, 50, 60, and 70°C as show in Table A1.4. The densities of each crude oil source L1, L2, and L3 at 50°C were 0.8549, 0.8722, and 0.8403 g/cm^3, respectively. Therefore, API gravity calculated from Eq. A1 and Eq. A2 of each crude oil source were 32°, 28.8°, and 34.8°, respectively. It is due to the API gravity of these crude oil samples, they represented that they are light crude oils.[38] The results showed that L2 was the heaviest crude oil due to its show the lowest API value and was similar as the compositional analysis results from GC spectra.

$$SG_{\text{crudeoil}} = \frac{\rho_{\text{crudeoil}}}{\rho_{\text{water}}} \tag{A1}$$

$$API(^{o}) = \frac{141.5}{SG} - 131.5 \tag{A2}$$

Figure A1.4 shows that, the density of the each crude oil source decreased rapidly as the temperature increased.[39] This is due to the increase in temperature to the crude oil causing the greater kinetic energy and the higher vibrations of the crude oil molecules. Therefore, each crude oil unit takes up more space as the temperature increases causing the decrease of density.[30] Moreover, the effect of temperature on viscosity of each crude oil source is demonstrated in Figure A1.5. The viscosity of the each crude oil source decreased dramatically when the temperature increased.[3, 39] According to the increase in temperature because of added energy effectively causes the molecules of the liquid required energy to overcome inter molecular forces. Therefore, the molecules move further apart causing the decreases in the viscosity.[31]

A3. Analysis the wax content at different temperatures (30, 40, 50, 60, and 70°C).

Table A1.5 Wax content of crude oil sources L1, L2, and L3 as different temperatures

Temp (°C)	Wax content (%wt)		
	L1	L2	L3
30	23.77	46.79	15.42
40	3.06	15.47	1.10
50	0.45	0.66	0.45
60	0.29	0.32	0.18
70	0.25	0.28	0.25

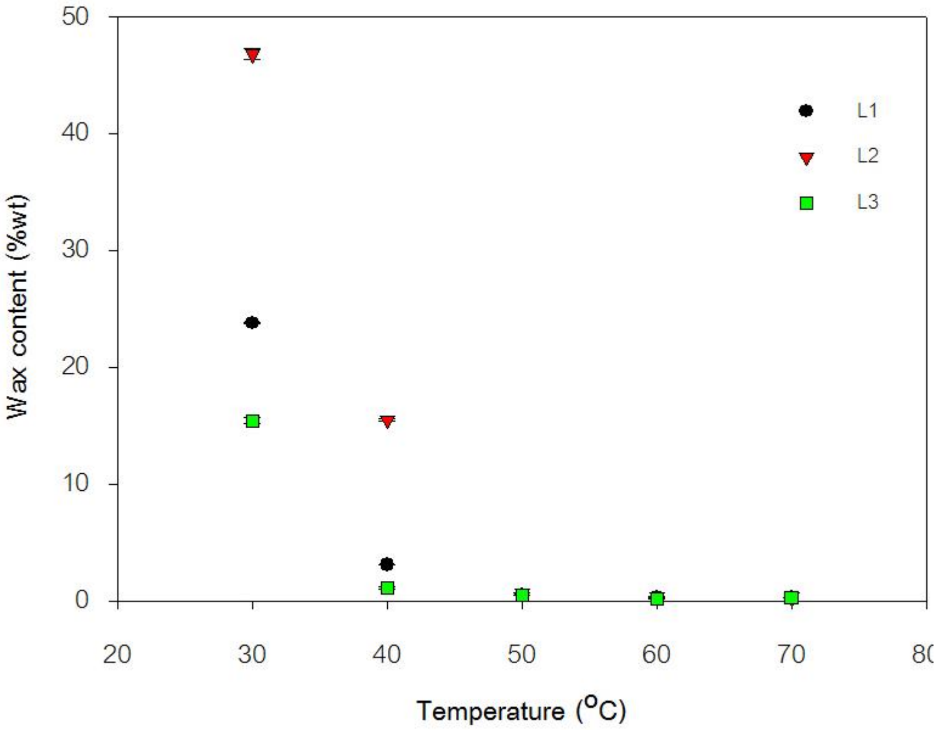


Figure A1.6 The effect of temperature on density of the different crude oil sources L1, L2, and L3

The wax contents of each crude oil source were measured at 30, 40, 50, 60, and 70°C as show in Table A1.5. The wax contents at 30°C were 23.77, 46.79, and 15.42 %wt in L1, L2, and L3, respectively. Apparently, not only the density, viscosity, and C_{35+} of L2 crude oil were the highest value, but also the wax content. Moreover, Figure A1.6 shows that, the wax content of the each crude oil source decreased rapidly as the temperature increased. This is due to the increase in temperature to the crude oil causing the wax solubility in crude oil increased.[27] Therefore, the low wax contents at higher temperature.

APPENDIX B

THE DATA AND DETERMINATION OF STRUCTURAL PARAMETERS

B1. The data of chemical region for determination of structural parameters

Table B1.1 Chemical shift regions of various types of protons[20, 22]

Regions	Chemical shift range (ppm)	Type of protons
Aromatic	6–9	Total aromatic proton
	6–7.2	Mono-aromatics proton
	7.2–7.6	Di-aromatic molecules
	7.2–8.0 or >8.0	Poly-aromatics molecules
Aliphatic	2.05–4.5	H-α to aromatic ring
	1.1–2.05	H-β to aromatic ring in paraffinic CH and CH_2
	0.4–1.1	H-γ to aromatic ring/terminal CH_3
	1.3	CH_2 in long alkyl chains
	0.5–4.5	Total aliphatic proton
	0.9	CH_3 in long alkyl chains
	2.1	CH_2 in aromatic rings
	2.6	CH_3 in aromatic rings

Table B1.2 Chemical shift regions of various types of carbons[20, 22]

Chemical shift range (ppm)	Type of carbon atoms
202-220	Ketone carbonyl
182-170	Acid carboxyl
175-165	Ester or amide carboxyl
100-160	Aromatic carbon
149.2-158	Aromatic carbons attached to heteroatoms
137.2-149.2	Substituted carbons bonded to some alkyl groups (not include methyl and methylene bridge between aromatic rings)
100-128.5	Quaternary aromatic carbons without triple-bridged aromatic carbons
128.5-160	Tertiary aromatic and triple-bridged aromatic carbons
132.5-137.2	Substituted carbons bonded to methyl group or to cycloparaffinic alpha-CH_2
132.5	Naphthalene derivatives and methylated derivatives
129.2-132.5	Bridgehead aromatic carbons
115.0-129.2	Protonated aromatic carbon
5-10.0	Total Aliphatic carbon
25-60	Naphthenic carbon
29.1-31.5	Carbons in alkyl chains ($n > 6$)
27.6-28.6	Carbons in branching position of a terminal iso-propyl group
17.6-20.4	Carbons in CH_3 branches
13.7-15.5	Carbons in terminal position of n-alkyl chains ($n > 6$)
0-20.5	Total carbon in CH_3 groups

Table B1.3 Infrared absorption frequency range of FTIR spectrum[20, 25]

Bonds	Frequency range (cm^{-1})	Functional groups
C–H	3000-2850	Alkanes (stretch)
	2900-2700	Aldehyde
	1450 and 1375	– CH_3 (bend)
	1465	– CH_2 (bend)
	800–860	para-disub benzene
	700–750	monosubstituted benzene
=C–H	3100-3000	Alkenes (stretch)
	3150-3050	Aromatics (stretch)
	1700-1000	Alkenes (bend)
C=C	1680-1600	Alkenes
	1600-1400	Aromatics
C=O	1750-1730	Ester
	1740-1720	Aldehyde
	1725-1700	Carboxylic acids
	1700-1640	Amide
C–O	1300-1000	Alcohols, esters, carboxylic acids
O–H	3650-3200	Alcohols, phenols
	3300-2500	Carboxylic acids
$C_2S=O$	1032	sulfoxide

B2. The determination of structural parameters from NMR spectra

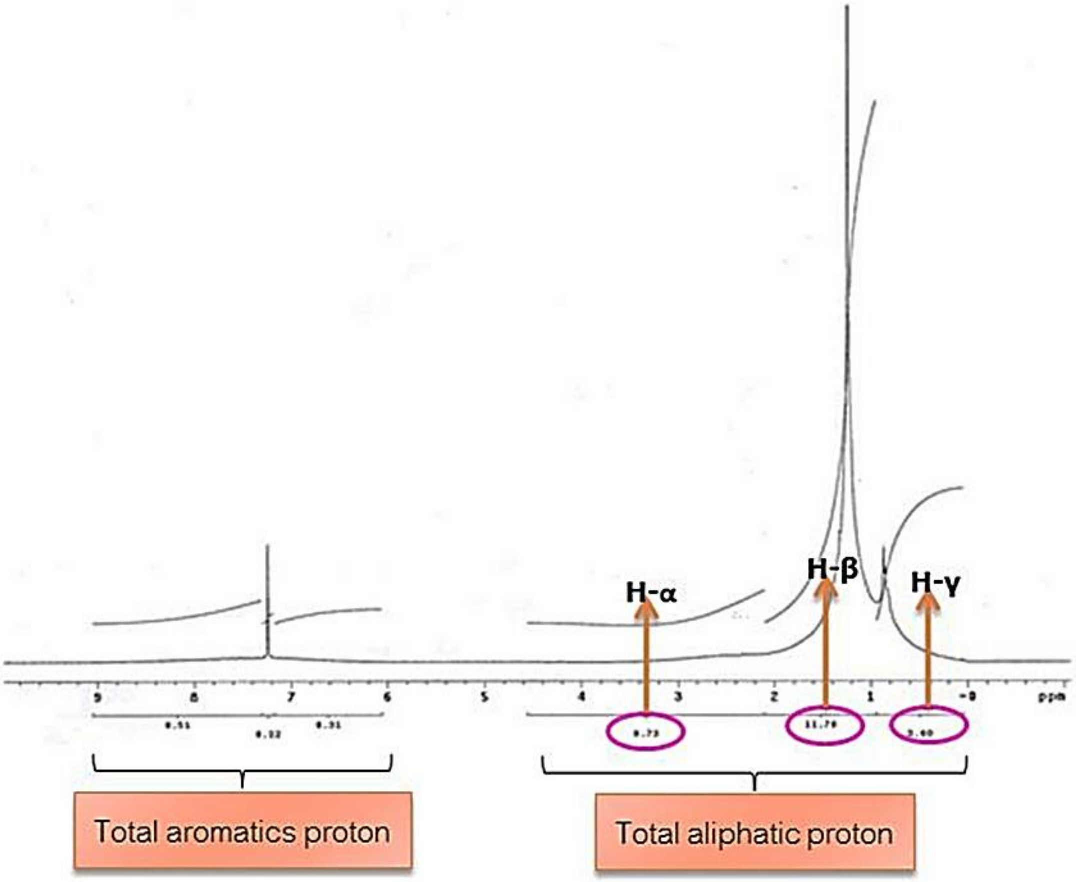


Figure B1.1 ^{1}H NMR spectrum of asphaltenes separation by centrifugation technique

Table B1.4 The determination of structural parameter of asphaltenes separation by centrifugation technique and characterization by ^{1}H NMR technique

	chemical shift range (ppm)	Quality	%wt
Mono-aromatics molecules	6-7.2	0.31 (from ^{1}H NMR spectrum)	$\frac{0.31}{16.47}\times100=1.88$
Di-aromatics molecules	7.2-7.6	0.22 (from ^{1}H NMR spectrum)	$\frac{0.22}{16.47}\times100=1.34$
Poly-aromatics molecules	7.2-8.0 or >8.0	0.51 (from ^{1}H NMR spectrum)	$\frac{0.51}{16.47}\times100=3.10$
Aromatic region	6-9.0	0.31+0.22+0.51 = 1.04	$\frac{1.04}{16.47}\times100=6.31$
H-α to aromatic ring	2.05-4.5	0.73 (from ^{1}H NMR spectrum)	$\frac{0.73}{16.47}\times100=4.43$
H-β to aromatic ring in paraffinic CH and CH_2	1.1-2.05	11.7 (from ^{1}H NMR spectrum)	$\frac{11.7}{16.47}\times100=71.04$
H-γ to aromatic ring/terminal CH_3	0.4-1.1	3 (from ^{1}H NMR spectrum)	$\frac{3}{16.47}\times100=18.21$
Aliphatic region	0.5-4.5	3+11.7+0.73 = 15.43	$\frac{15.43}{16.47}\times100=93.69$
Total = Aromatic hydrogen region + Aliphatic hydrogen region		1.04+15.43 = 16.47	6.31+93.69 = 100
$n_{carbon} = [H_\alpha + (H_\beta + H_\gamma)]/H_\alpha$		$\frac{0.73+(11.7+3)}{0.73}=21.14$	
Aromatic/Aliphatic		$\frac{1.04}{15.43}=0.0674$	

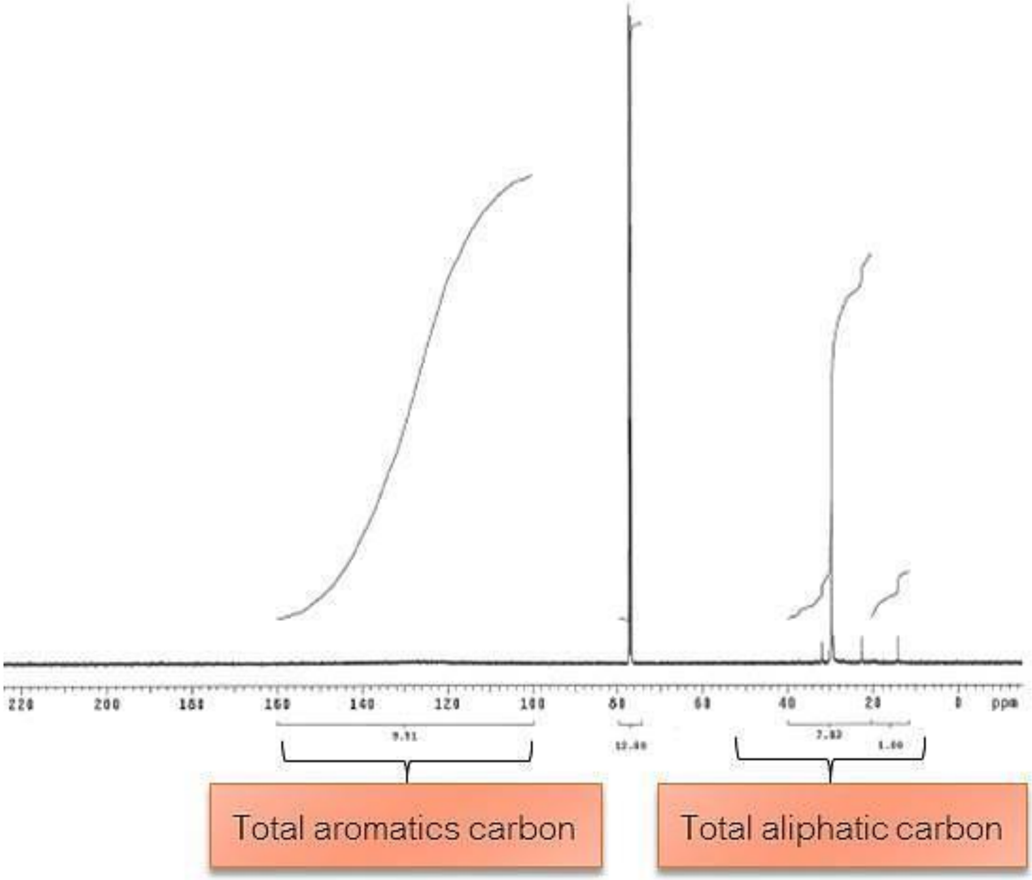


Figure B1.2 ^{13}C NMR spectrum of asphaltenes separation by centrifugation techniques

Table B1.5 The determination of structural parameter of asphaltenes separation by centrifugation technique and characterization by ^{13}C NMR technique

	chemical shift range (ppm)	Quality	%wt
Aromatic carbon	100-160	9.51 (from ^{13}C NMR spectrum)	$\frac{9.51}{18.34}\times100=51.85$
Aliphatic region	10 -70	1+7.83 = 8.83 (from ^{13}C NMR spectrum)	$\frac{8.83}{18.34}\times100=48.15$
Total = Aromatic carbon + Aliphatic carbon		9.51+8.83 = 18.34	
f_a (aromatic carbon fraction) $=C_{ar}/(C_{ar}+C_{al})$		$\frac{9.51}{18.34}=0.5185$	

$$\frac{C}{H} ratio = \frac{\text{Total carbon}}{\text{Total hydrogen}} = \frac{18.34}{16.37} = 1.113$$

APPENDIX C

THE DETERMINATION OF KINENATIC VISCOSITY

The kinematic viscosity is the ratio of viscosity to density. This represents can be calculated by dividing the absolute viscosity of a fluid with the fluid mass density as following equation.

$$\upsilon = \frac{\mu}{\rho} \tag{C1}$$

Where, υ is crude oil kinematic viscosity (cm^2/s)
μ is crude oil viscosity (g/cm s)
ρ is crude oil density (g/cm^3)

Table C1.1 Crude oil densities and location of sampling points at different temperatures of L1

Temp (°C)	The density of different location sampling points (g/cm^3)		
	A	B	C
40	0.8615	0.8623	0.8625
50	0.8524	0.8525	0.8526
60	0.8455	0.8456	0.8456
70	0.8390	0.8391	0.8391

Table C1.2 Crude oil viscosities and location of sampling points at different temperatures of L1

Temp (°C)	The viscosity of different location sampling points (g/cm s)		
	A	B	C
40	0.409	0.439	0.534
50	0.181	0.196	0.197
60	0.134	0.132	0.136
70	0.097	0.099	0.099

Table C1.3 Crude oil kinematic viscosities and location of sampling points at different temperatures of L1

Temp (°C)	The viscosity of different location sampling points (cm^2/s)		
	A	B	C
40	0.4749	0.5089	0.6188
50	0.2118	0.2297	0.2316
60	0.1579	0.1562	0.1610
70	0.1157	0.1175	0.1183

APPENDIX D
THE DETERMINATION OF A/R RATIO

The amount of asphaltenes-to-resins ratios of L1, L2, and L3 were 0.114, 0.072, and 0.062, respectively, which was calculated by Eq.C1

$$\frac{A}{R}\ Ratios = \frac{W_{asphaltenes}}{W_{resins}} \tag{D1}$$

Table D1.1 The determination of ratios of asphaltenes to resins

Sources	Asphaltenes contents (%wt)	Resins contents (%wt)	A/R ratios
L1	1.67	14.57	$\frac{1.67}{14.57}=0.114$
L2	1.36	18.89	$\frac{1.36}{18.89}=0.072$
L3	0.82	13.27	$\frac{0.82}{13.27}=0.062$

APPENDIX E

CONFERENCE PROCEEDINGS

VITAE

Name	Mr. Ekapop Tongton
Student ID	5610120107

Educational Attainment

Degree	Name of Institution	Year of Graduation
Bachelor of Engineering (Chemical Engineering),	Prince of Songkla University	2013

Scholarship and Awards during Enrollment

Scholarship, Graduate School, Prince of Songkla University

Outstanding Poster Presentation Award at the 5th International Conference on Thai Institute of Chemical Engineering and Applied Chemistry Conference 2015, held on November 8-10, 2015, at Pattaya, Thailand.

List of Publication and Proceeding

E. Tongton, N. Pitipuech, S. Khaisri, C. Tongurai, D. Jearsiripongkul, and K. Phalakornkul, "Determination of Asphaltenes Content and Their Structures of L1 Crude Oil," in the *5th International Conference on Thai Institute of Chemical Engineering and Applied Chemistry Conference*, Pattaya, Thailand, 2015, pp. O-114.

E. Tongton, N. Pitipuech, S. Khaisri, C. Tongurai, D. Jearsiripongkul, and K. Phalakornkul, "The Effect of Solvent Types on the Asphaltenes Precipitation and Their Structures of L2-Crude Oil," in the *5th International Conference on Thai Institute of Chemical Engineering and Applied Chemistry Conference*, Pattaya, Thailand, 2015, pp. P-49.