CORRELATION FOR PREDICTING ASPHALTENE DEPOSITION

by

Rofizan Bin Armi

16729

Dissertation submitted to the in partial fulfilment of

the requirements for the

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Universiti Teknologi PETRONAS

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CERTIFICATE OF APPROVAL

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May 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(ROFIZAN BIN ARMI)

ABSTRACT

Flow assurance is a key area for effective production management. It is closely related to solid deposit problems. The solid comes from fluid hydrocarbon solids which include wax, hydrate, and asphaltenes. Asphaltene deposition is one of major problems that ruin production of hydrocarbon and it can deposit anywhere from the reservoir till the surface. Consequently, it is imperative that there should be an approach of minimizing the deposition of asphaltene in production flow lines.

There are several screening criteria that can be considered to determine the asphaltene deposition. This paper will conduct a study on refractive index (RI) and colloidal instability index (CII), which are the ways to measure the deposition of asphaltene by measuring its stability through SARA fraction. This will be done by developing new correlations for refractive index and colloidal instability index (CII) in terms of the density of the crude oil. Generally, this study is more to data analysis and any experiment will not be conducted. The data that used for developing the new correlation is taken from a research by previous UTP student that conducted SARA analysis experiment. Once the new correlations have been developed, refractive index (RI) and CII will be measured and compared with RI and CII obtained from the previous literature.

Results show that the RI and CII values from the new correlation gave almost the same result with the experimental and literature data. Besides, ΔRI acquired from new correlation are compared with ΔRI obtained from experimental and previous literature. The results compared favourably well with experimental values giving the correlation coefficient (R^2) of 0.999.

Hence, it can be said that the new correlation are applicable to measure RI and CII to calculate ΔRI without conducting any SARA analysis experiment since the density value is the only parameter that need to be measured.

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CHAPTER ONE

INTRODUCTION

1.1 Background of Study

In oil and gas industry, to bring the fluid from formation to surface is not simple as people expected. There are many problems that can occur throughout the process for example at the formation, inside tubing and surface pipeline. There are many parameters that need to be considered such as pressure, temperature, flow pattern, and composition of fluid. Shirdel et al.'s (2012) state that flow assurance problems during the transportation and production of fluids may occur because of solid deposit. The production facilities in the stream lines may face significant problem and maybe can lead to serious damage or failure if this solid deposition happen. Petroleum fluid or crude oil can be separated into two, which are hydrocarbon and non-hydrocarbon but non-hydrocarbon only contribute a small fraction of the mixture. Commonly, non-hydrocarbon can be occurred as oxygen, nitrogen and sulphur. While for hydrocarbon, it mainly can be divided into four groups which are saturate, aromatic, resin and asphaltene.

Crude oil is primarily the combination of hydrocarbon and natural compounds of sulphur, nitrogen, and oxygen. Additionally, crude oil contains metallic components including iron, vanadium, and nickel. Hammami & Ratulowski (2007) points out that hydrocarbon substance range from 50% in heavy asphaltic oil or as high as 97% in lighter paraffinic oil. Heavy natural components are scattered among the crude oil and different component and compositional changes cause deposition at both surface and subsurface facilities. Resin, asphaltene and wax are example of heavy organic components.

In the oil field, asphaltene are renowned for clogging surface facilities, flow lines, and subsurface formation. Asphaltenes are known as the "cholesterol" of unrefined petroleum. They hasten, hold fast to surfaces and, in the most pessimistic scenarios, cause immoderate channel blockages. Moreover they modify the wetting attributes of mineral surfaces inside of the reservoir, upsetting oil recuperation productivity.

Deposition of asphaltene is one of the endless troubles that happen in the industry that may give major operational obstacles. Plus, this possibly can affect safety hazards as well as production efficiency. According to Nafice et al. (2012), flow assurance issue such as increment of pressure drop, production rate depletion, plugging of well and pipeline, decrease in permeability as well as wettability inversion may occur because of asphaltene deposition in stream lines, well string or reservoir. Chamkalani (2012) mentioned that big numbers of parameters influencing precipitation as well as asphaltene fluffy nature.

Figure 1.1: Deposition of asphaltene in tubing

Figure 1.2: Asphaltene deposition cause pipe blockage

Despite a lot of study has been conducted to solve this problem, there are still drawbacks in understanding the mechanism (Andersen and Speight, 1999). There are several characteristics need to be considered to know asphaltene stability in crude oil. These include the composition of the surrounding fluid, temperature and pressure. Asphaltene dissolvability is exceptionally subject to the crude composition. For pressure and temperature, asphaltene is less reliant on pressure while barely reliant on temperature. Therefore, this paper focuses on the study of refractive index (RI) and colloidal instability index (CII) in which both RI and CII are used as an indicator for asphaltene stability in order to improve current available researches.

Nearly all of oil and gas companies nowadays face further challenging for both environment and ultra-environment in the exploration, development and production phases. Besides, productions of fluid in these regions are under great pressure and temperature and regularly cause organic solids deposition such as hydrates, asphaltenes and waxes. If that happen, it would bring negative impact on the production and in the end the project economy. In this manner, it is subsequently basic to join the capability of the asphaltene affidavit at the configuration stage itself and having a sound forecast of asphaltene framework.

1.2 Problem Statement

Further study on the stability of asphaltene is crucial in developing further understanding of asphaltene deposition. According to Fan et al. (2002), the stability of asphaltenes in a crude oil are corresponding to the proportions of each of saturates, aromatics, resins and asphaltenes or can be expressed as SARA fractions in that fluid. The effects of pressure and temperature on the solubility of asphaltene are not significant, the crude oil composition which has a considerable effect on asphaltene deposition. Fan et al. (2002) stated that, there are several factors that are need to be considered. Firstly, asphaltene steadiness can be evaluated by and anticipated from RI estimation at the onset of asphaltene precipitation, PRI. Secondly, the more narrow asphaltenes distributions are less balance than broader ones. Lastly, the resins provide stability by widening asphaltene properties range.

Thus, to predict asphaltene deposition, the refractive index must be known. In addition, expectations of the onset asphaltene flocculation dictated by fluid-phase laboratory studies do not essentially infer that deposition of asphaltene will happen amid flow conditions. According to research by Chamkalani (2012), a new correlation of refractive index has been obtained based on correlation by Fan et al. (2002) which shows the better accuracy. The research demonstrates the negative effect of saturate towards the refractive index.

On the other hand, another screening criteria that need to consider is colloidal instability index (CII). Colloidal instability index can be utilized to identify deposit problems in crude oil systems. The CII can be defined as the proportion of the total of saturates and asphaltenes to the entirely of resins and aromatics:

$$CII = \frac{Asphaltene\ + Saturate}{Resin\ + Aromatics} \quad \dots\ \dots\ \dots \quad (1.1)$$

In this research work, endeavours will be made to develop the correlation for predicting asphaltene deposition that can be simulated with suitable computer software and will then be validated and compared with available literature data or previous research.

1.3 Objectives

The objectives of the present study work are:

- To study the deposition of asphaltene by using several screening criteria which are Refractive Index (RI) and Colloidal Instability Index (CII).
- To develop correlation for predicting asphaltene deposition.
- Evaluate and validate the model with literature and experimental data.

1.4 The Scopes of Study

To attain to the above state objectives, the scopes of this research work are:

- The estimation of ΔRI and colloidal instability index (CII) at 20°C and pressure at ambient (1 atm).
- Measure CII and RI as a function of density (ρ) of the crude oil sample not the thermodynamic model at specific temperature and pressure.
- Data analysis will be done instead of conducting any experiment to obtained data in order to develop correlation.
- Only measure ΔRI and CII as the screening criteria to estimate the stability of asphaltene in the crude oil sample.

1.5 Relevancy and Feasibility of the Project

Nowadays, asphaltene deposition is turning into a standout amongst the most created and most studied topic in the industry. This is because of the way that the impact of deposition of asphaltene has on the fluid production system is extensively huge, thus methods to minimize its accumulation is exceedingly progressing. With the support of current and past study, the result of this project is all that much doable.

CHAPTER 2

LITERATURE REVIEW

2.1 Flow Assurance

The term flow assurance is utilized to determine the impacts of hydrate, asphaltene, and wax and their capability to disturb production because of the deposition in the flow system. Besides, inorganic solids deposition emerging from the liquid phase need to point out since it can genuine a significant problem to flow assurance. Since deep water advancement continue to expand, future oil and gas disclosures progressively would be delivered from remote facilities through multiphase stream lines in deep water environments. Mix of oil, gas, water, and condensate form the multiphase fluids. The fluids can possibly cause numerous issues. The problem that may arise such as deposition of asphaltene, hydrates formation, slugging, and emulsion, deposition of wax as well as erosion and corrosion.

Shirdel et al. (2012) state that asphaltenes are the most muddled among the distinctive steam assurance problem in the hydrocarbon reservoirs. Indeed, the diverse nature of asphaltene as for other components of hydrocarbon is the reason of this refinement. Asphaltene are organic substances with high molecular weight. It can dissolve by using toluene and diesel which are aromatics solvents. Precipitation of asphaltene can occur by the addition of n-pentane or n-heptane (molecular-weight alkenes). Nafice et al. (2012) defines asphaltene as the heaviest portion in crude oil and partly dissolved in petroleum. However, in micelle form, asphaltene is halfway dissolved relying upon the extremity of their oil element and vicinity of different mixes in oil. Regarding flow assurance, numerous researchers have the same opinion that the estimations of flow assurance have driven to recognition in which the samples need to be delegated. Sampling methodology has the objective to bring a sample to the lab that is indistinguishable with the reservoir fluid in terms of composition. Regrettably, during the sampling process a large number of the solids come out of solution just as happen in production systems. Thus, flow assurance problems would occur. Temperature and pressure alteration can result in phase changes that can cause sample alteration.

2.2 SARA Analysis

Fan et al. (2002) point out that the complexity of reservoir fluid composition analysis can be endless. The quantity of detail gathered ought to be managed by the application for which the information is required. The addition to the assembled analysis of carbon number simply accommodated, a share of stock-tank fluid is constructed. This is for saturate, aromatic, resin and asphaltene or can be summarized as SARA analysis. The purpose of this study plan is to partition oil into its SARA portions. Buriro (2012) expressed that by making the crude oil into SARA analysis, the colloidal instability index can be identified.

Polarizable aromatics consist of one or more aromatics rings. Saturate portion comprises of non-polar material. The material includes cyclic, linear and branched saturated hydrocarbons. The other staying two parts, which are asphaltenes and resins, have polar substituents. The contrast between them is that resins are miscible with pentane or heptane though asphaltenes are insoluble in an abundance of pentane or heptane (Fan et al., 2002).

Based on standard ASTM method, High Pressure Liquid Chromatograph (HPLC) is used to separate crude oil sample into SARA fraction. The crude oil is de-asphalting first to remove asphaltene from the sample. The step includes the saturation of the crude oil with pentane, heptane and hexane which are n-alkanes. The addition of n-alkanes would disturbed the thermodynamic equilibrium colloidal structure of the asphaltene-resin bonding and this would make the asphaltene start to agglomerate together forming precipitants.

Next, n-alkanes would act as mobile phase and then it would be injected into the remaining sample. Saturate starts to elude first and detected by RI detector since saturate have no retention time on the column material. The remaining maltenes is followed by detection of aromatics on UV detector and RI detector which are then collected on the separate vials for weight percent measurement. Finally, a more mobile phase for example Dichloromethane (DCM) is used to elute the remaining resin. Figure 2.1 shows how HPLC works.

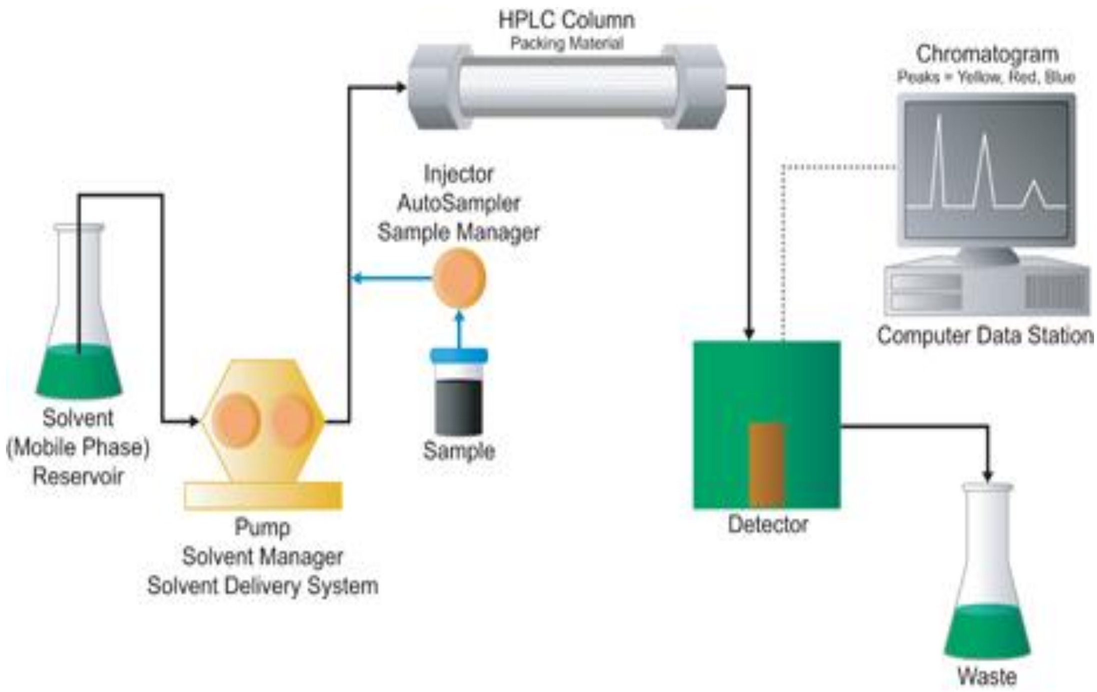


Figure 2.1: HPLC flow diagram system (Extracted from: http://www.waters.com/waters/How-Does-High-Performance-Liquid-Chromatography-Work)

2.3 Fluid compositional characterization

There are increments in aromaticity, oxygen, molecular weight, nitrogen and sulphur compounds in set from oils to resins to asphaltenes. A straightforward approach to differentiate any oil or its portion in terms of aromaticity for asphaltenes and resins for example, is by calculating the H/C. H/C is proportion of hydrogen to carbon atoms. Take C_6H_{14} (n-hexane) for instance, contain 6 carbon atoms and 14 hydrogen atoms with H/C of 2.3 (14/6 = 2.3). While the aromatic benzene C_6H_6 has H/C of 1.0 since it has 6 to 6 fraction of hydrogen to carbon atom. The H/C ratio keep on dropping as the hydrocarbon gets to be more close-packed, with more-condensed aromatic rings having less hydrogen. Most asphaltenes have ratio of hydrogen to carbon atom from 1.0 to 1.3 while ratios for resins ranging from 1.3 to 1.6.

It should be noticed that a delicate balance between the heaviest and the lighter fractions of oil affect the solubility of the asphaltenes. Any unfavourable aggravation in this equalization may impel collection of asphaltene. Asphaltenes are likewise known to aggregate when pressure depletes.

The volume division of the light components inside the crude oil rises when pressure decreases. Thus, this cause solubility parameter increment contrasts between the asphaltene and the crude oil. At bubble-point pressure, the parameter reach maximum. Asphaltene are more solvent below the bubble-point pressure because of evaporation component of crude oil. For temperature, it has less impact on aggregation than pressure and fluid composition. In general, increment in temperature influences the asphaltene aggregation by diminishing the solvating force of the fluids.

Crude oil API Gravity, burial depth, and source also controlled the precipitation of asphaltene. Additionally, the quantity and type of solvent added to the crude oil plays significant part in estimating the amount of asphaltene deposited (Khanifar et al., 2011).

2.4 Phase Behaviour of Asphaltene

In both petroleum and processing industries, asphaltene phase behaviour is very important thing that need to be understand in view of the asphaltene possibility to phase aggregate and phase with alteration in fluid composition, pressure, and temperature. Thus, it is appropriate to recognize and characterize the following terms:

2.4.1 Onset Point

Onset point is described as the composition with minimum measure of flocculent where aggregations of asphaltene particles appear.

2.4.2 Flocculation Onset Point

The term is characterized as the potential of the colloidal particles to clump or flocculate at any condition including changes in composition, temperature, and pressure.

2.4.3 Asphaltene Onset Point

Asphaltene onset pressure is the pressure where asphaltene starts to flocculate. Flocculation is the initial move to asphaltene issues and hence, must be anticipated precisely if want to stay away from asphaltene issues.

2.4.4 Asphaltene Stability

As already discussed, in the oil phase the asphaltene parts are scattered colloids. The resin molecules balanced out the parts which act as defensive bodies for asphaltene particles. The asphaltenes precipitation relies on the stability of the colloidal in this complex system.

2.5 Colloidal Instability Index (CII)

Yen et al. suggested another method to estimate the stability of crude oil by identify the tendency of asphaltene precipitation which is by using colloidal instability index (CII). CII review that asphaltene exists as a colloidal material which is dispersed among the crude oil. Resin molecule surrounded or desorbed asphaltene molecule which are stable thermodynamically. Equation below shows how CII is calculated. The equation taking the ratio of sum of asphaltene and saturate to the sum of resin and aromatic components. If the value of CII is above 0.9, the crude oil is considered unstable which deposition of asphaltene may occur. While if the value of CII is below 0.7, it said that the crude oil is stable. If the CII value is fall within the range 0.7 to 0.9, then the crude oil is moderate stable.

$$CII = \frac{Asphaltene\ + Saturate}{Resin\ + Aromatics}\ \dots\ \dots\ \dots\quad (1.1)$$

2.6 Refractive Index (RI)

Wattana et al. (2003) state that by using refractive index of the crude oil, the presence of asphaltene as well as the stability of crude oil can be easily determined. Refractive index can be defined as the extent to which light refract when passing through an element. Estimation of refractive index can be computed experimentally. In fact, regularly RI is used to relate density and different properties of hydrocarbon dependability (Touba et al., 1997). Refractometer is used to compute RI value. Research by Wand et al. (2000) has shown that the essential qualities of oil or precipitant mixtures are when RI is at the precipitation onset point.

Buckley et al. (1998) showed the relation between refractive index and volume oil fraction. It can be said that refractive index is gradually decrease with the decrease of crude oil volume fraction since the graph showed linear line is plotted. When precipitant for example n-heptane is added into the crude oil, a point would be reached when the asphaltene precipitation would be produced, and because of the non-refractory nature of the asphaltene, the refractive index of the crude oil will gradually decrease upon the addition of the precipitant (Karthighaibalan, 2014). Hence the deviation from linearity that observed can be said as the onset of the asphaltene precipitation.

Refractive index at the onset asphaltene precipitation can be expressed by P_{RI}. Fan et al. (2002) suggested the distinction between RI for oil and RI at the asphaltene precipitation onset can be utilized to measure the stability of asphaltene. It can be defined as:

$$\Delta\, \mathrm{RI} = (\mathrm{RI})_{\mathrm{oil}} - \mathrm{P}_{\mathrm{RI}} \quad \ldots \quad \ldots \quad \ldots \quad (2.1)$$

Based on the research, Fan and his co-workers have come out with the following stability criteria:

- If Δ (RI) > 0.060, the crude oil tend to have stable asphaltenes.
- If Δ (RI) < 0.045, the crude oil tend to have deposit of asphaltene.
- If Δ (RI) < 0.060 and Δ (RI)> 0.045, the crude oil is in the border region.

Besides, Fan and his colleagues related the $(\mathrm{RI})_{\mathrm{oil}}$ with SARA fraction as below:

$$\begin{aligned}(\mathrm{RI})_{\mathrm{oil}} = {} & [0.016624 \times (\mathrm{R} + \mathrm{As})] + (0.014982 \times \mathrm{A}) \\ & + (0.014452 \times \mathrm{S}) \quad \ldots \quad \ldots \quad \ldots \quad (2.2)\end{aligned}$$

However, Chamkalani (2012) has developed a new correlation of refractive index which, with additional information to demonstrate the negative effect of saturate. The correlation is more accurate and better precision to determine RI compare with what Fan et al. suggested. The relation develops by Chamkalani can be expressed as:

$$\begin{aligned}(\mathrm{RI})_{\mathrm{oil}} = {} & -0.0008515 \times \mathrm{S} - 0.0002524 \times \mathrm{A} + 0.0016341 \times \mathrm{R} + 0.0013928 \times \mathrm{As} \\ & + 1.524412 \quad \ldots \quad \ldots \quad \ldots \quad (2.3)\end{aligned}$$

The stability of asphaltene also can be shown by the following flow chart:

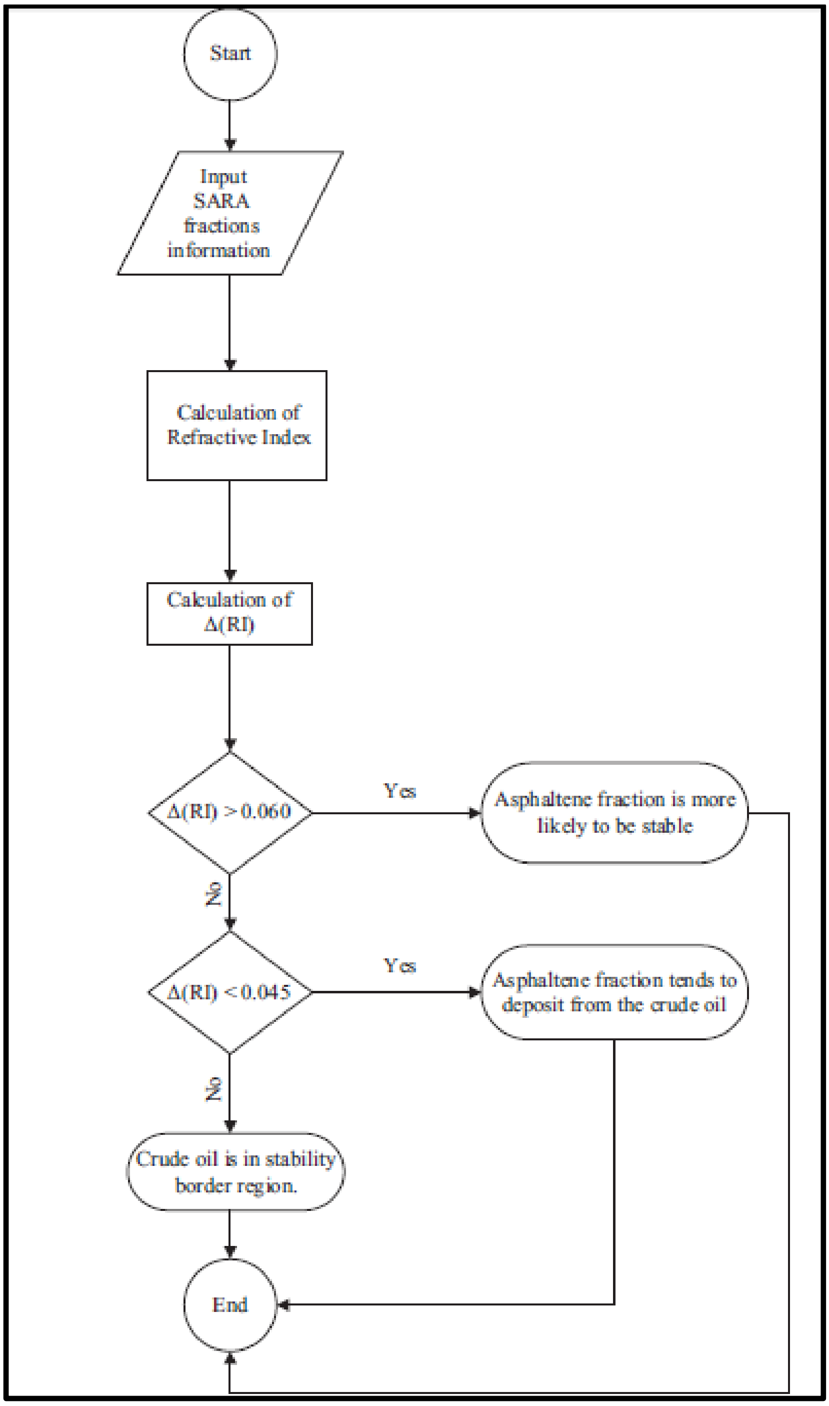


Figure 2.2: Flow chart to determine stability of asphaltene (Chamkalani et al., 2012)

CHAPTER 3

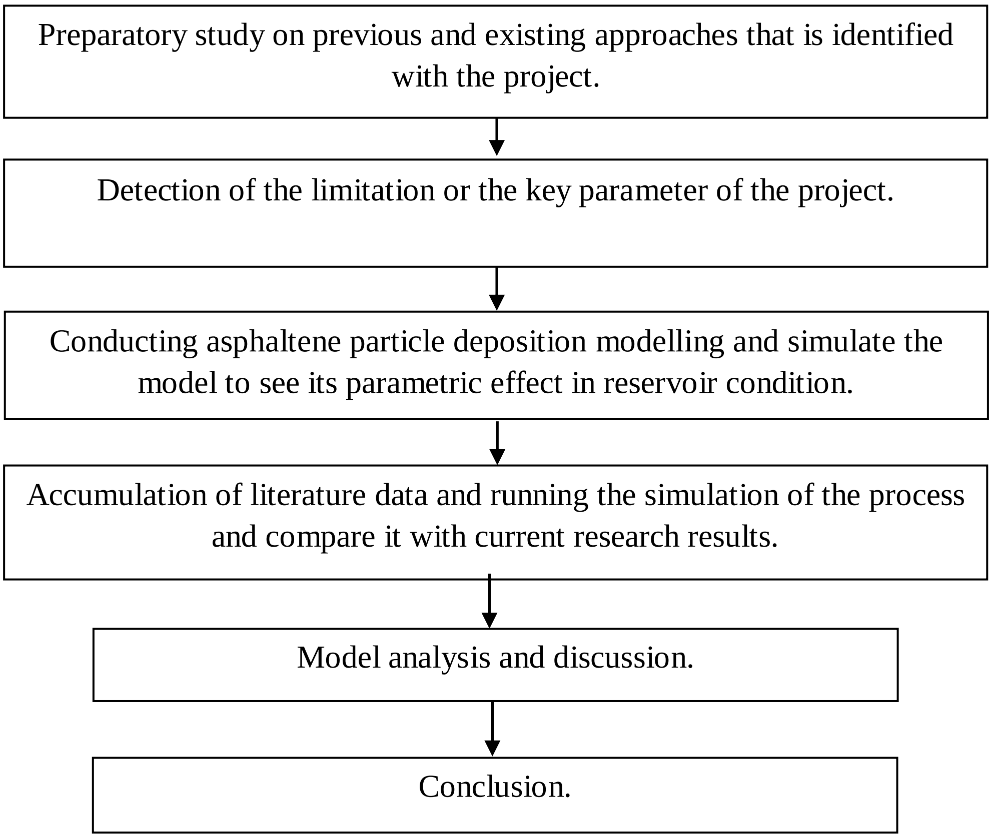
MODEL DEVELOPMENT

3.1 Research Methodology

The approach of this study work mostly will be done by research, literature data collection, literature review and analysis of available data. An experimental and a modelling approach are available for this study. Nevertheless, experiments will not be conducted because of the restricted time that is accessible and also due to the unavailability of such equipment to be used. This study is based on SARA analysis. Since there is no experiment will be conducted, therefore the data are obtained from Karthigaibalan (2014) experimental data. Then various parameters regarding screening on crude oil stability on precipitation of asphaltene is utilized so that identification of asphaltene precipitation tendency can be conducted. Besides, development of correlation based on the proposed parameters can be carried out. For this study, the relationship between density of the crude oil and RI is conducted. To develop the correlation, graph of RI against density would be plotted. Then the trend or regression for that graph is determined. There are several trend-line option that can be choose such as linear, exponential, logarithmic, polynomial, power, and moving average. The trend-line that will be chooses and use depends on the R^2 value. Trend-line that gives R^2 value that is almost one will be chosen. Next, after the trend-line is chosen, an equation that displays that particular graph will be the new correlation.

3.2 Flow of the Project and Project Activities

The flow of the project will be:



3.3 Gantt Chart and Key Milestone

The Gantt chart on the Table 3.1 and Table 3.2 shows the amount of work completed with allocated time in relation to the amount planned for both FYP 1 and FYP 2.

Based on the Gantt chart, the key milestones are:

1) Developing the refractive index (RI) and colloidal instability index (CII) correlation model.
2) Calculating ΔRI and CII from the new correlation.
3) Compare it with present research outcome.
4) Analyze the correlation.
5) Discussion and conclusion.

3.3.1 Timelines for FYP 1

Table 3.1: Gantt chart for FYP 1

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic														
2	Preliminary Research Work														
3	Submission of Extended Proposal														
4	Proposal Defense														
5	Project work continues														
6	Submission of Interim Draft Report														
7	Submission of Interim Report														

Suggested milestone

Process

3.3.2 Timelines for FYP 2

Table 3.2: Gantt chart for FYP 2

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work Continues															
2	Submission of Progress Report															
3	Project Work Continues															
4	Pre-SEDEX															
5	Submission of Draft Final Report															
6	Submission of Dissertation (soft bound)															
7	Submission of Technical Paper															
8	Viva															
9	Submission of Project Dissertation (Hard Bound)															

Suggested milestone

Process

CHAPTER 4

RESULT AND DISCUSSION

The results obtained in this chapter are based on Karthighaibalan (2014) experimental data. Firstly, the value of refractive index obtained from Karthighaibalan's experiment is analysed and compared with refractive index acquired from Fan et al correlation. This followed by the correlation between both screening criteria, which are RI and CII and density. However, from Karthighaibalan (2014) research, the densities of the crude oil samples are not provided. For this study, the density values are gained and calculated by using Chamkalani correlation that relates the density of the crude oil and the SARA fraction.

4.1 Refractive Index (RI)

Based on experiment conducted by Karthighaibalan, the refractive index of Dulang, Dubai, Miri, and Tapis are measured by using refractometer. The sample is put on the bowl-shape tray at the refractometer and closed the tray. After that the equipment would directly measure the RI of that particular crude oil sample. Figure 4.1 below shows the refractometer equipment. The refractive index of each sample is tabulate in Table 4.1.

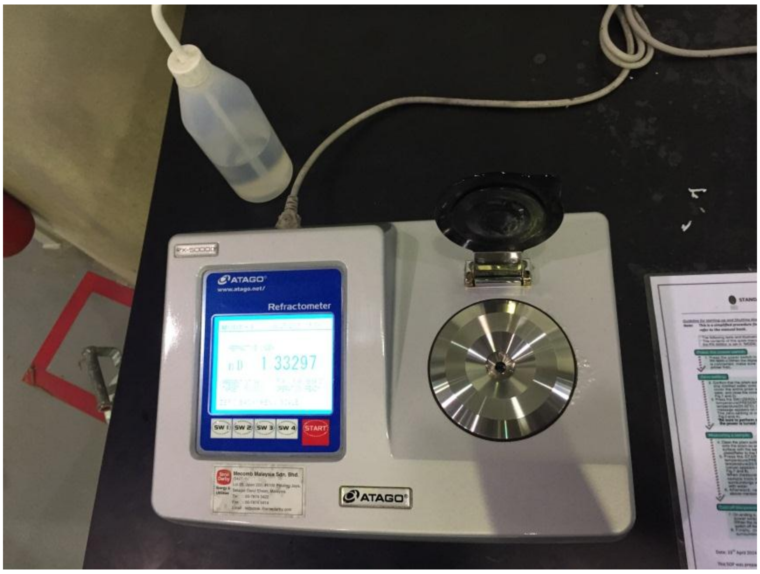


Figure 4.1: Refractometer

Table 4.1: RI data analysis

Crude Oil	Refractive Index (RI)
Tapis	1.46584
Miri	1.48933
Dubai	1.49816
Dulang	1.47594

4.2 Correlation between Refractive Index and SARA Fraction

The SARA fraction for each crude oil sample is achieved by conducting experiment using High Pressure Liquid Chromatograph (HPLC). Table 4.2 shows the SARA fraction for Dulang, Tapis, Dubai, and Miri crude oil based on Karthighaibalan's experimental data.

Table 4.2: SARA fraction

Crude Oil	Saturate (wt %)	Aromatic (wt %)	Resin (wt %)	Asphaltene (wt %)	CII
Tapis	84.82	13.30	1.75	0.13	5.64
Miri	52.08	13.38	34.42	0.12	1.09
Dubai	58.42	20.41	20.83	0.34	1.43
Dulang	85.17	12.39	2.26	0.18	5.83

CII stability criteria as suggested by Yen et al. stated that if CII is more than 0.9 considered unstable and CII less than 0.7 is considered stable. While if the CII value is in between 0.7 and 0.9 is said to be in the border region. Thus, from the data in Table 4.2 it can be assumed that the entire crude oil samples are not stable and asphaltene deposition are tend to occur since all CII values are higher than 0.9.

Figure 4.2 through 4.5 show the relationship between RI and SARA fraction. The RI values taken from the experiment is compared with the RI calculated from Fan et al. correlation by using Karthighaibalan SARA fraction data.

Table 4.3: RI of experiment and calculated at particular saturate fraction

	Saturate (wt %)	RI(Experiment)	RI (Fan et al.)
Tapis	52.08	1.4658	1.4563
Miri	58.42	1.4893	1.5273
Dulang	84.82	1.4759	1.4571
Dubai	85.17	1.4982	1.5020

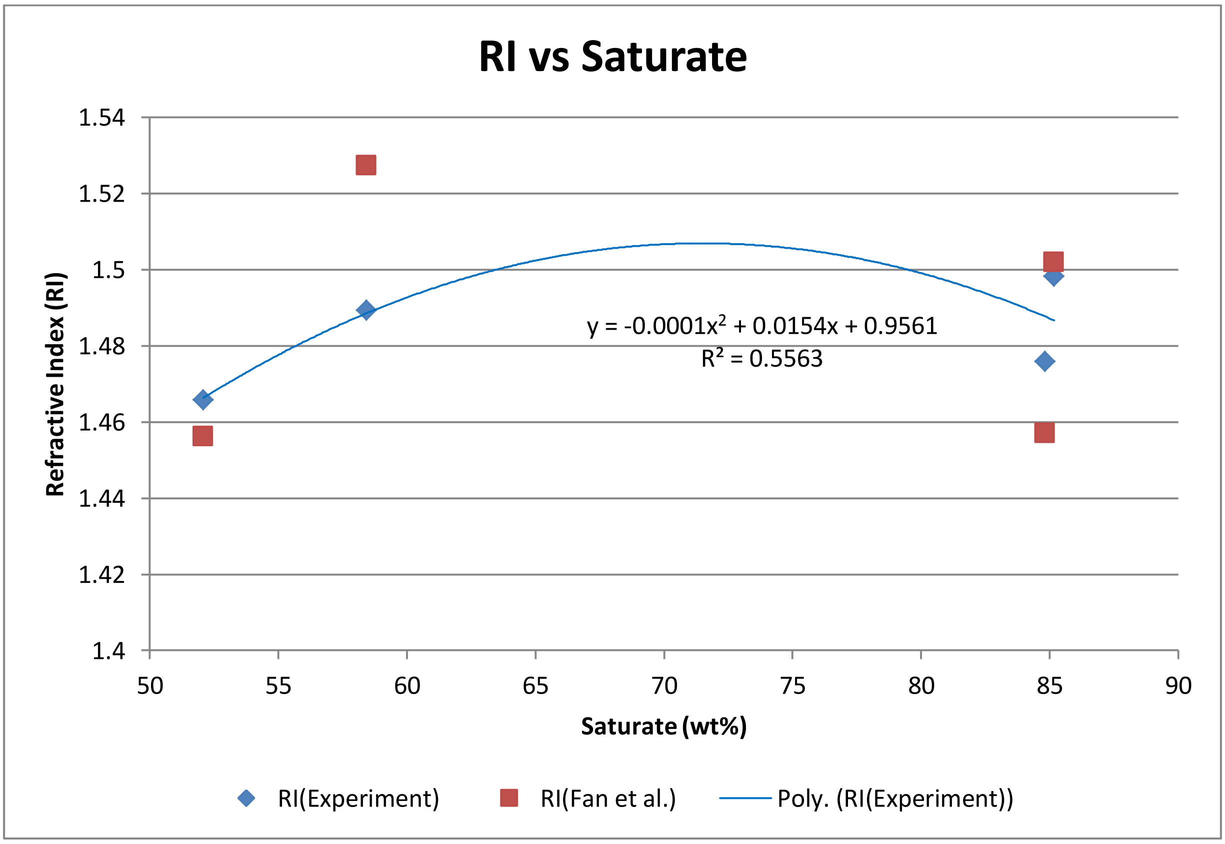


Figure 4.2: Correlation between amounts of saturate fractions and RI of the crude oil

Table 4.4: RI experiment and calculated at particular aromatic fraction

	Aromatic (wt %)	RI(Experiment)	RI (Fan et al.)
Dubai	12.39	1.4982	1.5020
Dulang	13.30	1.4759	1.4571
Tapis	13.38	1.4658	1.4563
Miri	20.41	1.4893	1.5273

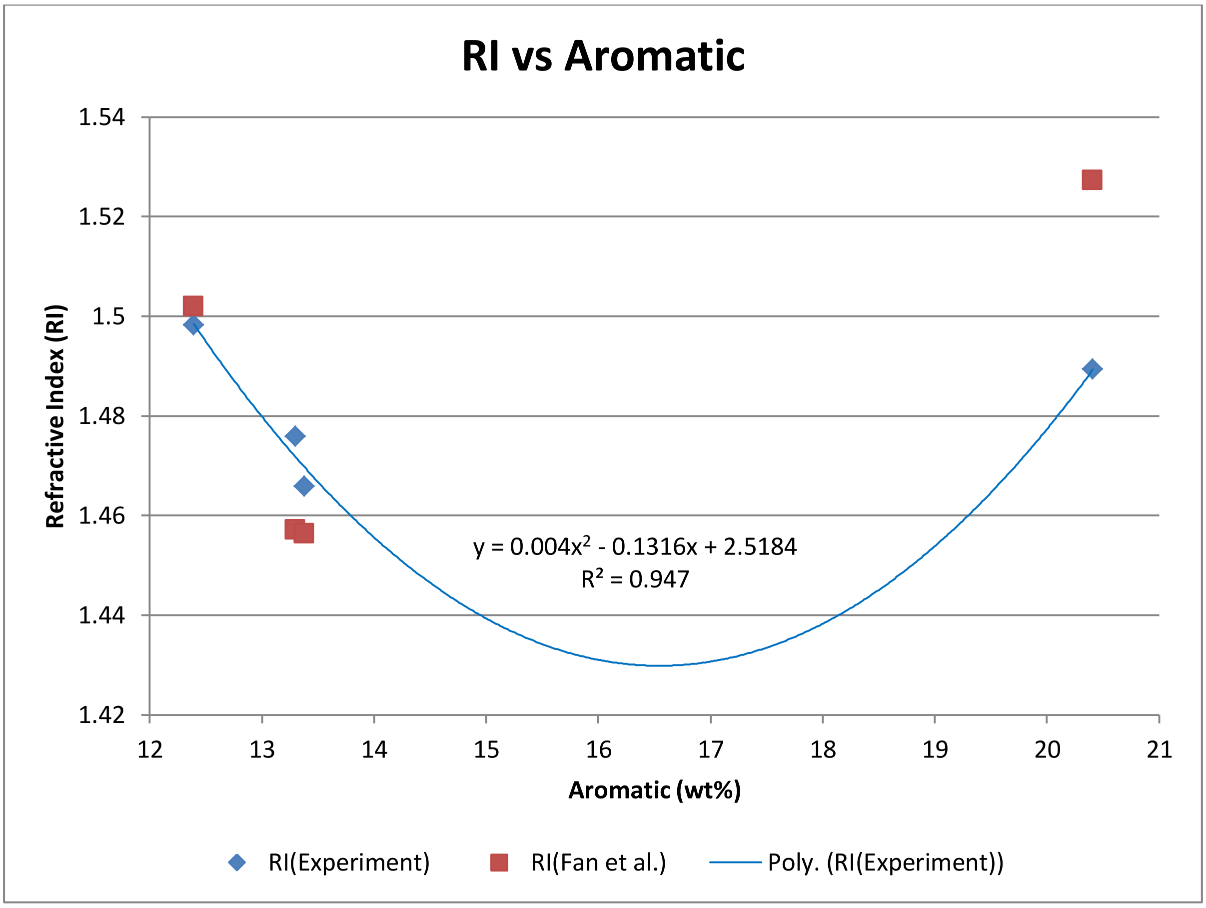


Figure 4.3: Correlation between amounts of aromatic fractions and RI of the crude oil

Table 4.5: RI of experiment and calculated at particular resin fraction

	Resin (wt %)	RI(Experiment)	RI (Fan et al.)
Dulang	1.75	1.4759	1.4571
Dubai	2.26	1.4982	1.5020
Miri	20.83	1.4893	1.5273
Tapis	34.42	1.4658	1.4563

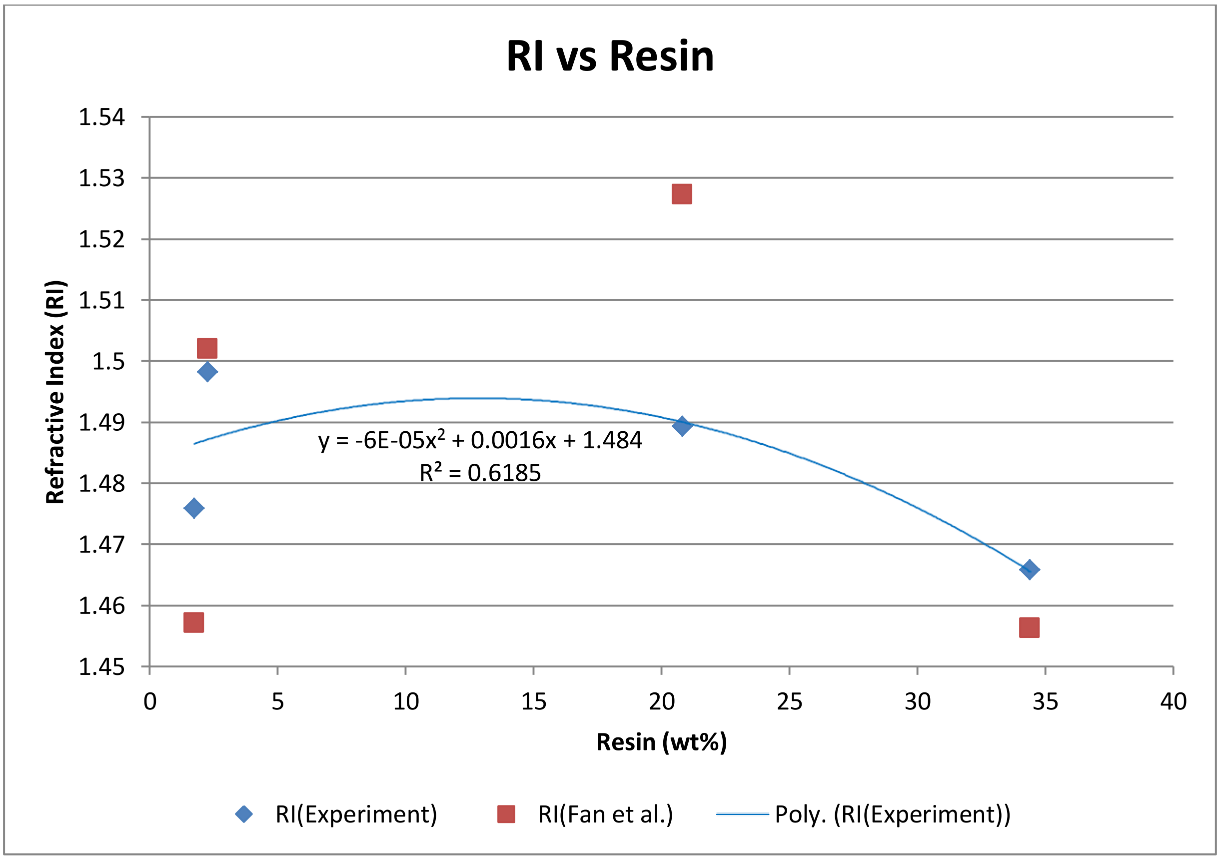


Figure 4.4: Correlation between amounts of resin fractions and RI of the crude oil

Table 4.6: RI of experiment and calculated at particular asphaltene fraction

	Asphaltene (wt %)	RI(Experiment)	RI (Fan et al.)
Tapis	0.12	1.4658	1.4563
Dulang	0.13	1.4759	1.4571
Dubai	0.18	1.4982	1.5020
Miri	0.34	1.4893	1.5273

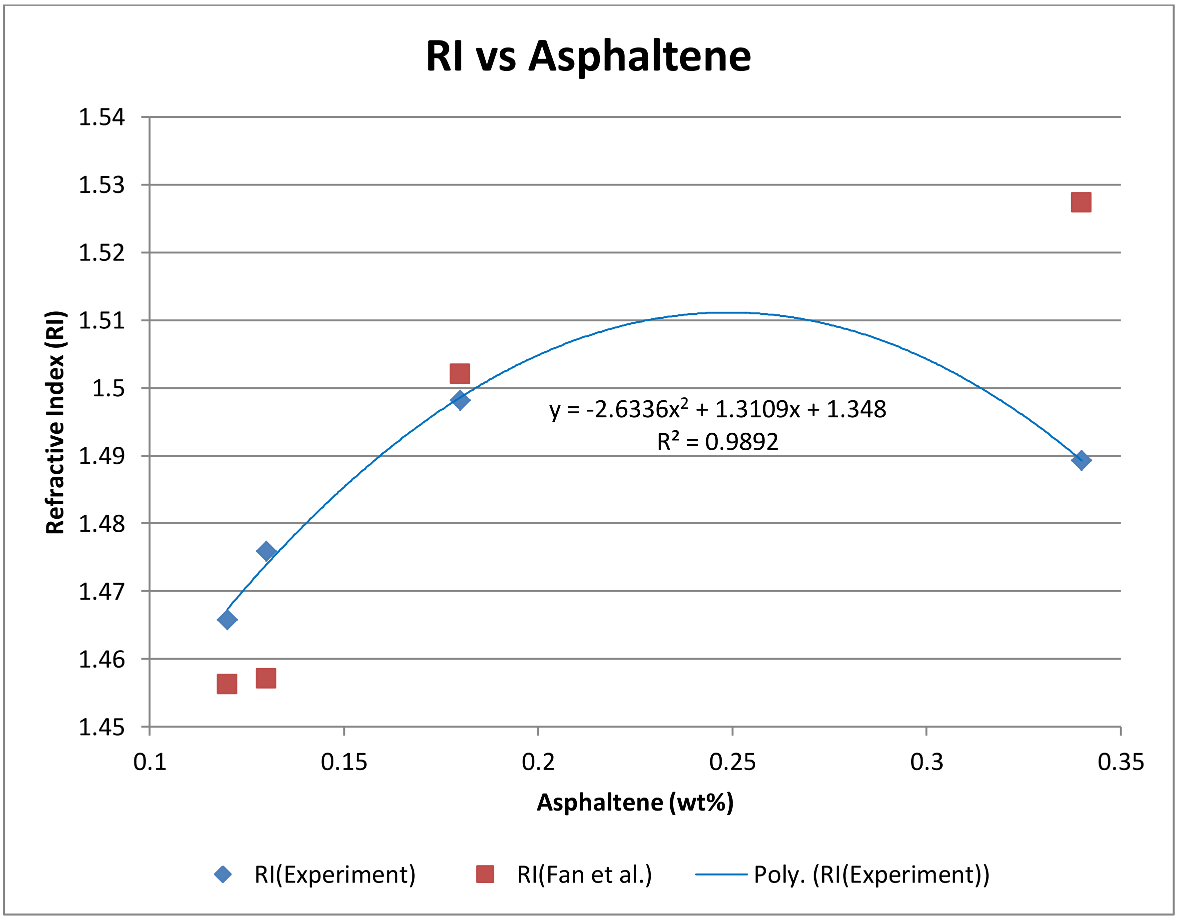


Figure 4.5: Correlation between amounts of asphaltene fractions and RI of the crude oil

Based on Figure 4.2 through Figure 4.5, the plot shows that the RI from experimental data give the same trend-line as RI obtained from Fan et al. correlation with R^2 value almost 1.

4.3 Correlation between Density and Refractive Index

This part show the relation between RI and CII values with density of the crude oil as parameter. Since the density data of Dulang, Tapis, Dubai, and Miri sample are not available, the density value of those samples have to be calculated by using correlation. Based on Chamkalani (2011), density of crude oil can be computed by using correlation below by utilising SARA fraction:

$$\rho = 0.1402635 \times S + 0.1390173 \times A + 0.1655588 \times R^{0.9731603} + 0.1014975 \times AS^{1.121967} - 13.26466 \quad \ldots \quad \ldots \quad \ldots \quad (4.1)$$

where S is saturate, A is aromatic, R is resin, and AS is asphaltene percent. The density of Dulang, Tapis, Miri and Dubai sample are determined and shown in Table 4.7. The relation between RI from experimental data and density is plotted in Figure 4.6 so that a new correlation can develop. From the plot, the following correlation is proposed:

$$RI = 43.599\rho^3 - 124.9\rho^2 + 118.09\rho - 35.331 \quad \ldots \quad \ldots \quad \ldots \quad (4.2)$$

By using the new correlation, a new set of RI is calculated and the results are compared with experimental RI and RI attained from Fan et al. correlation.

Table 4.7: Density of crude oil sample obtained using Chamkalani correlation

	DENSITY	RI (Experiment)	RI (Fan et al.)
Dulang	0.777	1.4759	1.4571
Dubai	0.785	1.4982	1.5020
Miri	0.976	1.4893	1.5273
Tapis	1.092	1.4658	1.4563

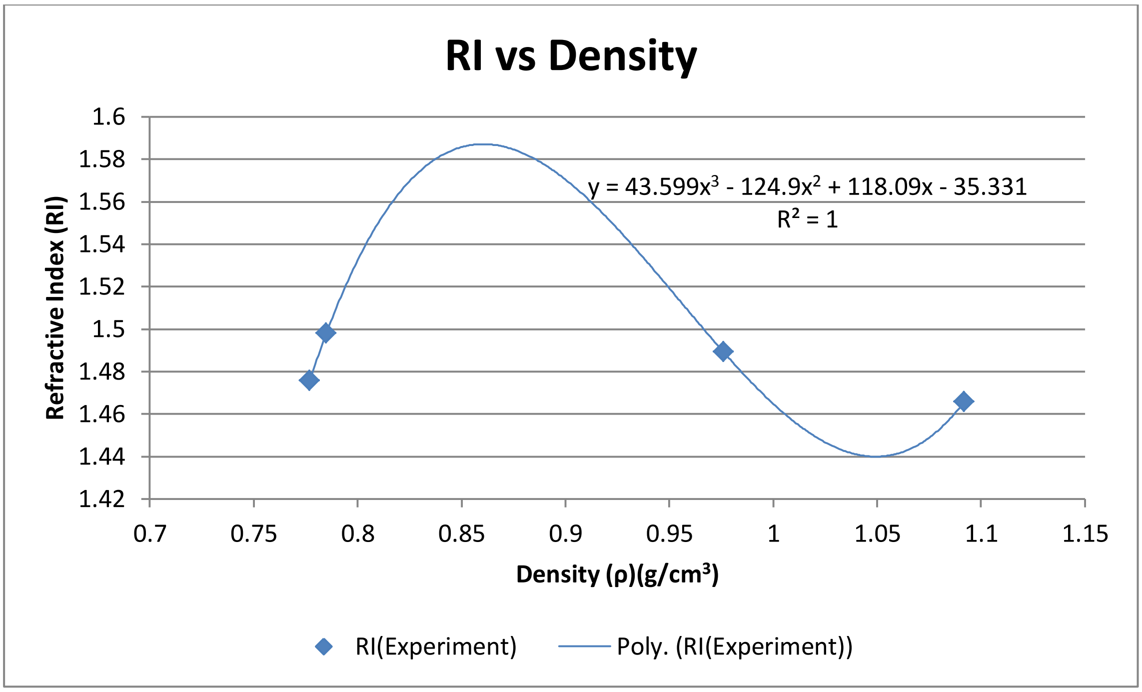


Figure 4.6: Correlation between RI and density

By using the proposed correlation, a new set of density value is calculated. More density value is measured to get a better and more accurate data. Table 4.8 shows the RI of crude oil acquired from the proposed correlation.

Table 4.8: RI obtained from the proposed correlation

Density (ρ)	RI (Proposed)	RI (Fan et al.)
0.700	1.0854	1.0997
0.750	1.3736	1.3804
0.777	1.4714	1.4571
0.785	1.4936	1.5020
0.800	1.5277	1.5444
0.850	1.5805	1.5799
0.900	1.5647	1.5803
0.950	1.5129	1.5218
0.976	1.4827	1.5273
1.000	1.4580	1.4596
1.050	1.4325	1.4475
1.092	1.4579	1.4563
1.150	1.6008	1.6295

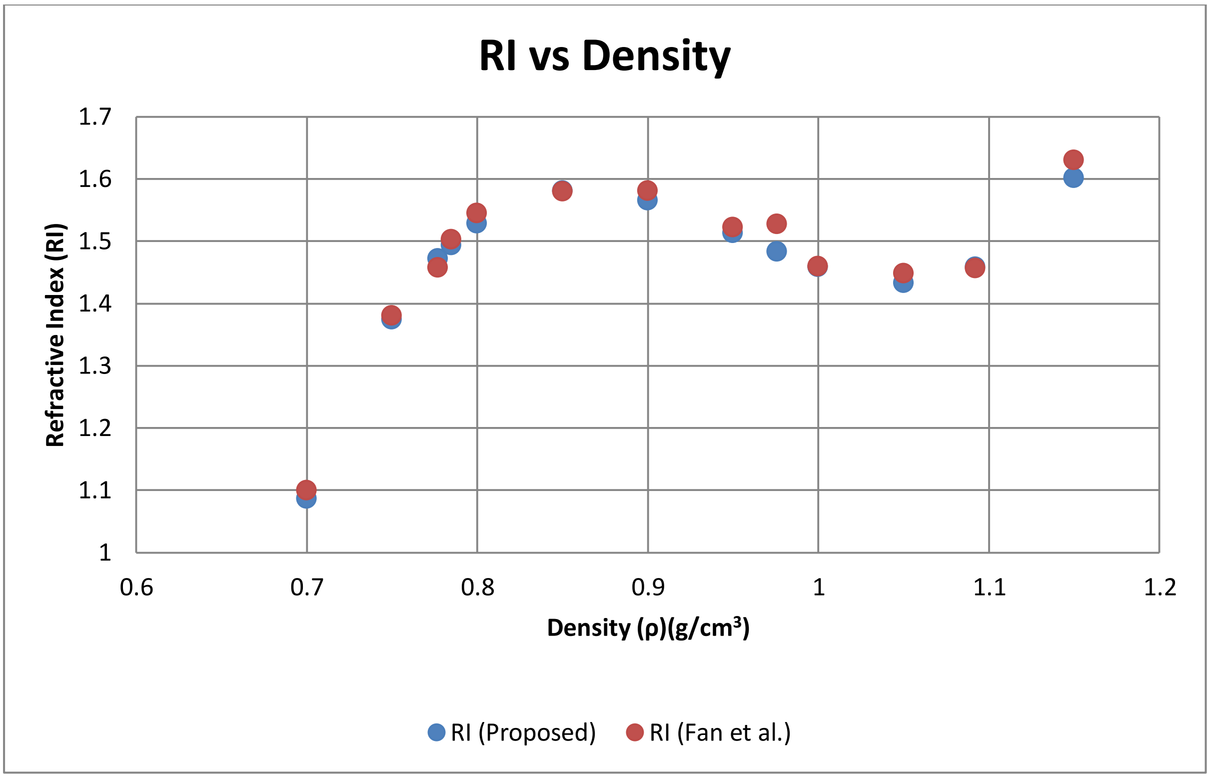


Figure 4.7: Comparison of RI from proposed correlation and Fan et al. (2002)

As shown in Figure 4.7, the RI values calculated from the proposed correlation shows a very good result since the graph follows almost the same with Fan et al. data.

4.4 Correlation between Density and Asphaltene Onset Precipitation (P_{RI})

Since the RI from the new correlation is already obtained, the calculation for the new ΔRI can be made. From the new set of ΔRI, the data then will be compared with the ΔRI that acquired from Fan et al. correlation and ΔRI from experiment to measure its accuracy. As already stated, the ΔRI can be measured by calculating the differences between the refractive index of the crude oil and the refractive index at the onset precipitation, P_{RI}:

$$\Delta\,\mathrm{RI} = (\mathrm{RI})_{\mathrm{oil}} - \mathrm{P}_{\mathrm{RI}} \quad \dots \quad \dots \quad \dots \quad (2.1)$$

The refractive index at the onset precipitation data is obtained from the previous study of Karthighaibalan (2014). Karthighaibalan represented measurement of the P_{RI} by plotting the graph of RI against crude oil volume percent. P_{RI} can be identified from the linear line, where the deviation from the linearity indicates the precipitation of the asphaltene.

A graph of P_{RI} against density is needed to be plotted as to develop the correlation that relates both parameters. Based on Figure 4.8, a new correlation has been developed which is:

$$P_{RI} = -0.306\rho^2 + 0.6536\rho + 1.124 \quad \dots \quad \dots \quad \dots \quad (4.3)$$

From the above correlation, a new set of P_{RI} value is measured. Then, the P_{RI} values is used to measure ΔRI by utilising RI from the new correlation, RI calculated from experimental data and also RI obtained from Fan et al. correlation as presented in Table 4.10 through Table 4.12.

Table 4.9: PRI of each crude oil sample from Karthighaibalan (2014)

	DENSITY	PRI
Dulang	0.777	1.4561
Tapis	0.785	1.439
Miri	0.976	1.4715
Dubai	1.092	1.4725

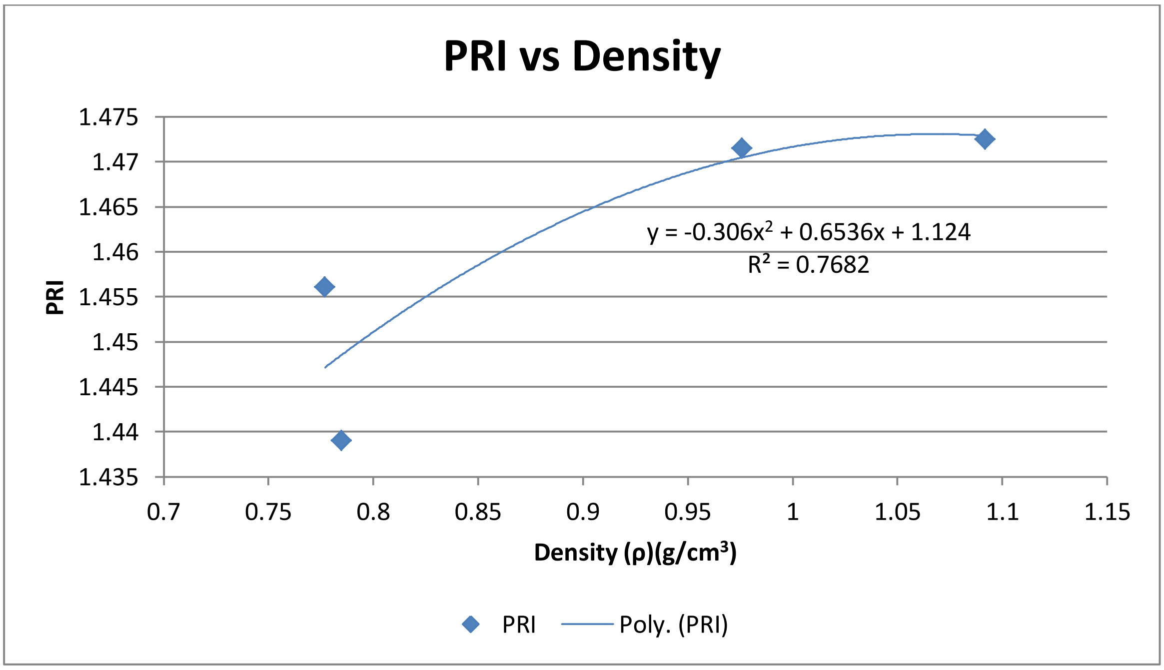


Figure 4.8: Correlation between PRI and density

Table 4.10: ΔRI by utilising RI proposed

Density (ρ)	PRI (proposed)	RI (Proposed)	ΔRI (proposed)
0.700	1.4315	1.0854	-0.3461
0.750	1.4420	1.3735	-0.0684
0.777	1.4471	1.4713	0.0242
0.785	1.4485	1.4935	0.0450
0.800	1.4510	1.5276	0.0766
0.850	1.4584	1.5804	0.1220
0.900	1.4643	1.5646	0.1002
0.950	1.4687	1.5129	0.0441
0.976	1.4704	1.4827	0.0122
1.000	1.4716	1.4580	-0.0136
1.050	1.4729	1.4325	-0.0403
1.092	1.4728	1.4578	-0.0149
1.150	1.4709	1.6008	0.1299

Table 4.11: ΔRI by utilising RI from experimental data

Density (ρ)	PRI (proposed)	RI (Experiment)	ΔRI (Experiment)
0.700	1.4315	1.0886	-0.3429
0.750	1.4420	1.3778	-0.0642
0.777	1.4471	1.4759	0.0287
0.785	1.4485	1.4982	0.0496
0.800	1.4510	1.5324	0.0813
0.850	1.4584	1.5857	0.1272
0.900	1.4643	1.5703	0.1059
0.950	1.4687	1.5187	0.0499
0.976	1.4704	1.4893	0.0188
1.000	1.4716	1.4639	-0.0077
1.050	1.4729	1.4389	-0.0340
1.092	1.4728	1.4658	-0.0070
1.150	1.4709	1.6104	0.1394

Table 4.12: ΔRI by utilising RI from Fan et al. correlation

Density (ρ)	PRI (proposed)	RI (Fan et al.)	ΔRI (Fan et al.)
0.700	1.4315	1.0997	-0.3318
0.750	1.4420	1.3804	-0.0616
0.777	1.4471	1.4571	0.0099
0.785	1.4485	1.5020	0.0534
0.800	1.4510	1.5444	0.0933
0.850	1.4584	1.5799	0.1214
0.900	1.4643	1.5803	0.1159
0.950	1.4687	1.5218	0.0530
0.976	1.4704	1.5273	0.0568
1.000	1.4716	1.4596	-0.0120
1.050	1.4729	1.4475	-0.0254
1.092	1.4728	1.4563	-0.0165
1.150	1.4709	1.6295	0.1585

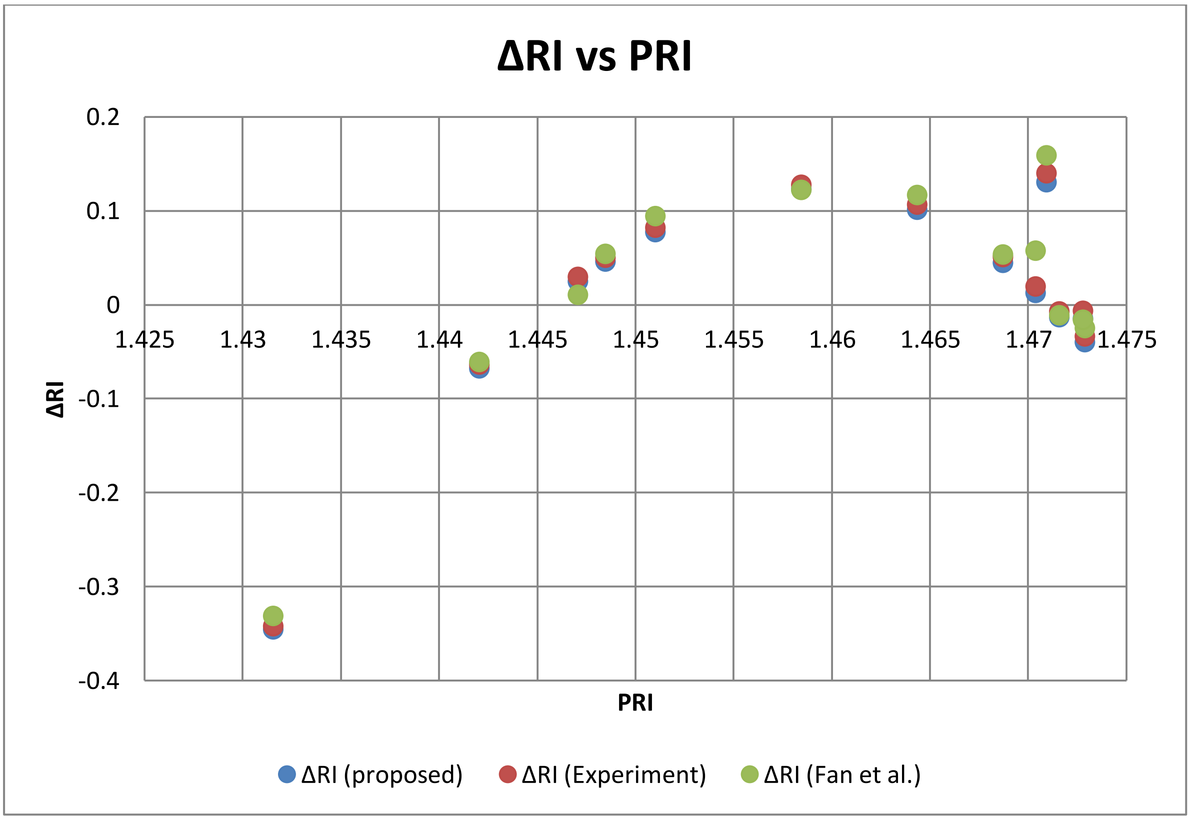


Figure 4.9: Comparison of ΔRI between proposed, experimental, and Fan et al. (2002)

As presented in Figure 4.9, by utilising the proposed P_{RI}, the ΔRI obtained is almost same pattern for the proposed correlation, experimental data, and Fan et al. Hence, it can be said that the proposed correlation are applicable to determine P_{RI} by using density of the crude oil. Finally, the comparison between ΔRI from the proposed, experimental and Fan et al. correlation can be make as shown in Figure 4.10:

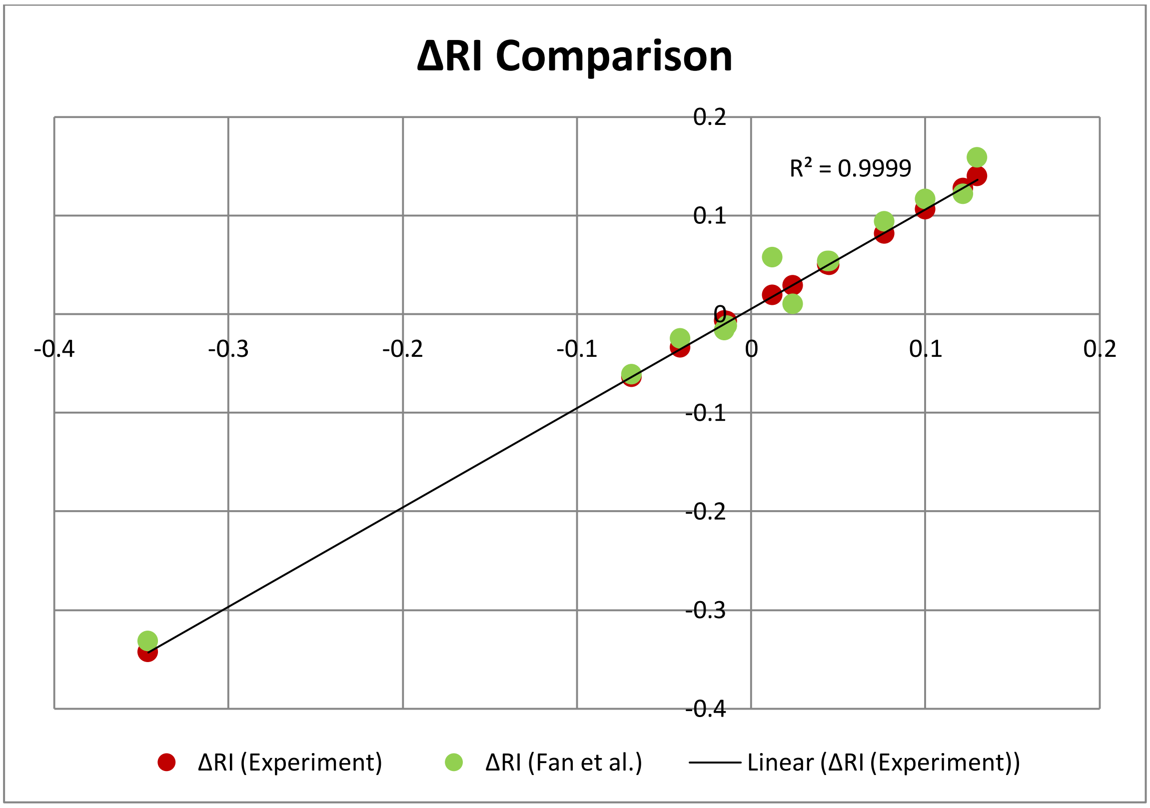


Figure 4.10: ΔRI comparison

As shown in Figure 4.10, the graph gives a satisfactory result as the R^2 value of the plot is almost close to one.

4.5 Correlation between Density and Colloidal Instability Index

The same procedure of determine the correlation between density and RI is applied for this part. Graph of density versus CII is plotted to develop a new correlation to determine density in terms of colloidal instability index. From the analysis, below correlation are developed:

$$CII = -67.123\rho^2 + 140.41\rho - 67.458 \quad \dots \quad \dots \quad \dots \quad (4.4)$$

After a new correlation is determined, a new set of CII is obtained by utilising the new correlation. The new correlation that uses density of crude oil as the parameter is applicable at standard pressure and temperature of 20°C. Finally the CII determined from the proposed correlation, experimental and Fan et al. is compared. The results of analyses are presented in Table 4.13, Figure 4.11 and 4.12.

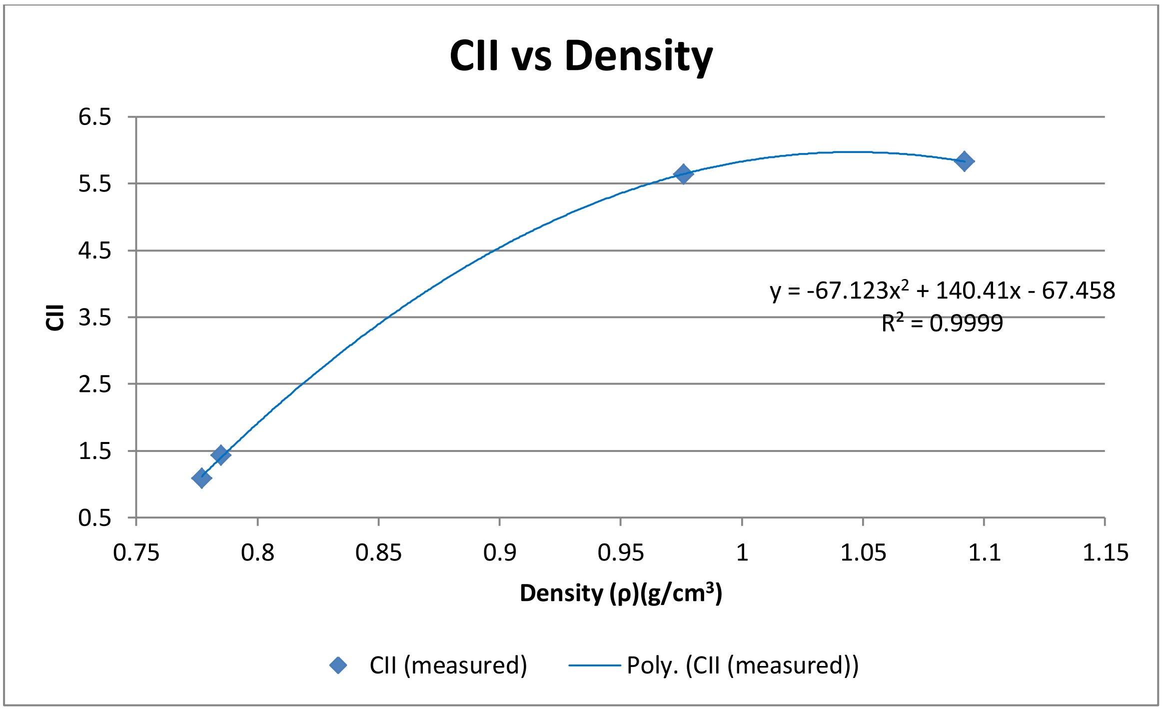


Figure 4.11: Correlation between CII and density

Table 4.13: New set of CII value obtained from proposed correlation

Density	CII (Proposed)
0.750	0.092813
0.777	1.116468
0.785	1.400979
0.800	1.911280
0.850	3.394132
0.900	4.541370
0.950	5.352993
0.976	5.642401
1.000	5.829000
1.050	5.969392
1.092	5.827959
1.150	5.243333

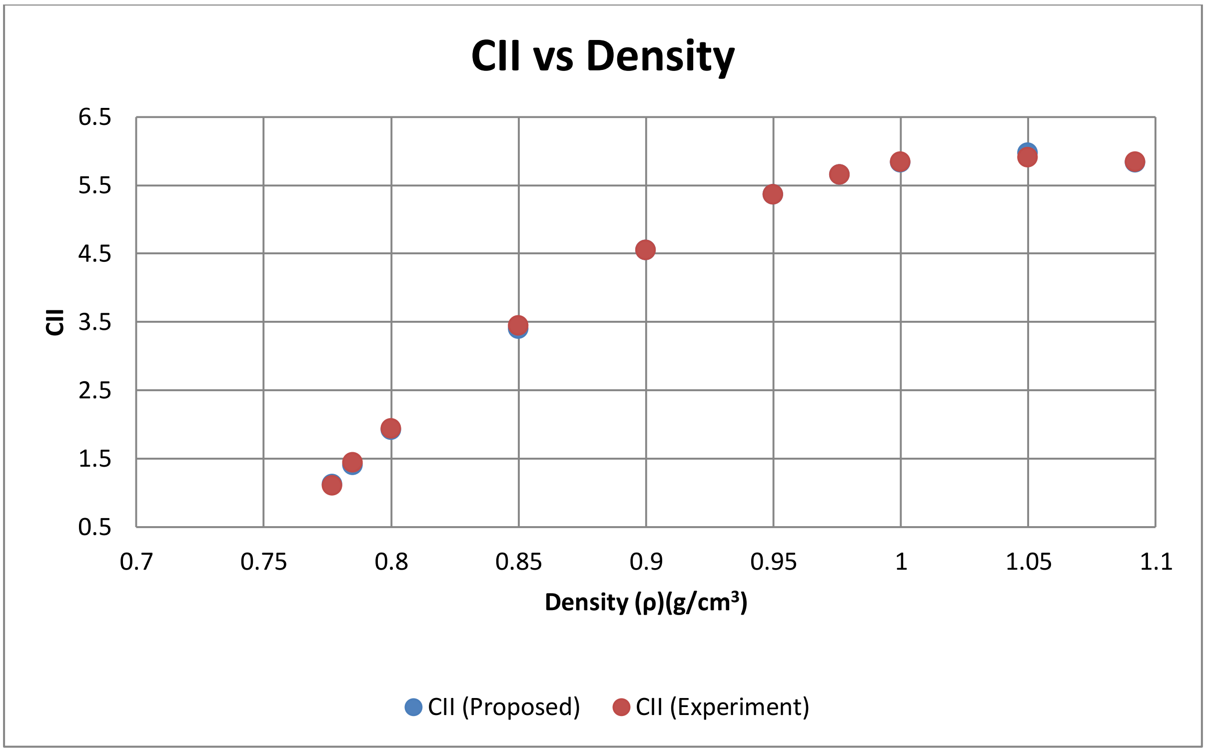


Figure 4.12: Comparison of CII obtained from proposed correlation and from experiment

From Figure 4.12, it is clearly show that the CII obtained from the proposed correlation are nearly the same with the experimental data.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

As a conclusion, up until now the progress of this study still on the right track and followed the objectives of this research which are:

1. To study the deposition of asphaltene by using several screening criteria which are Refractive Index (RI) and Colloidal Instability Index (CII).
2. To develop correlation for predicting asphaltene deposition.
3. Evaluate and validate the model with literature and experimental data.

Based on the RI and CII experimental value, all the crude oil samples shows the tendency to deposit asphaltene. SARA analysis is conducted to estimate the colloidal instability index (CII). The density of the crude oil sample is measured by using correlation from the previous study. The relationship between density and the asphaltene screening criteria such as RI and CII is conducted to see its parametric effect. Two correlations have been developed to predict RI and CII respectively by utilising the density of the crude oil. Correlation of predicting P_{RI} by using density of crude oil also has been developed in order to measure ΔRI. Later ΔRI obtained from the correlation are compared with ΔRI calculated from experimental data and the previous correlation. As an effort for screening asphaltene is done, the obtained relations show satisfactory results and at the same time open new ways to determine RI and CII from density and subsequently diagnosing asphaltene instability for causing problem.

5.2 Recommendations

In order to enhance the project execution and results there a few recommendations that are need to be considered:

1. More crude oil sample should be used to get more accurate and convincing results.
2. Early preparations are need to be done to have enough time for data analysis.
3. Follow the Gantt chart.

To sum up, the background study of asphaltene deposition and an intensive research on previous and literature has been carried out with a specific end goal to emphasize the imperativeness of doing correlation to predict the deposition of asphaltene. This study would significantly benefit the general public since the deposition of fluid hydrocarbon solids including wax, hydrate, and asphaltene to interrupt the production flow system is right now on a high. Numerous looks into are being carried out to decrease the measure of asphaltene deposition and many correlations have developed. For this study, a data analysis methodology will be taken because of the time constraint furthermore the inaccessibility of the supplies to carry out the experiment. With the time table of the venture lined out, ideally this project will be carried out and finished smoothly and on time.

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APPENDIX

Figure A-1: High Pressure Chromatograph (HPLC) Equipment

Figure A-2: Sample inside HPLC

Figure A-3: Refractive Index reading from refractometer