ACID REMOVAL FROM SALINE MEDIA

by

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Dissertation submitted in partial fulfilment of the requirements for the Bachelor of Engineering (Hons) (Petroleum)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the Petroleum Engineering Department Universiti Teknologi PETRONAS in partial fulfillment of the requirement for the BACHELOR OF ENGINEERING (Hons) (PETROLEUM)

Approved by,

(DR RASHIDAH MOHD PILUS)

UNIVERSITI TEKNOLOGI PETRONAS TRONOH, PERAK MAY 2014

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.

MUHAMMAD IMADUDDIN BIN NORDIN

ABSTRACT

Naphthenic acid (NA) is also known as organic acid within the crude. The presence of NA is a major concern in oil and gas industry due to its ability to cause corrosion. The corrosion cause by NA can damage the production and refinery equipment as well as transportation and storage facilities in oil and gas industry. The concentration of acid in the crude can be determined by the value of Total Acid Number (TAN).

In this project, the author used crude oil provided by PETRONAS for experiments. The author will study on the rate of acid extraction using Ionic Liquid (IL). Ionic liquids refer to salt exist in a liquid state over a wide range of temperature. In this project, the author used two different based IL to extract acid in the crude oil sample. Other than that, the author used different sea water volume to study its effect. The project started by doing some research on journal and research paper which related to the topic investigated. In order to obtain result and confirmation regarding the hypothesis or theory made a lot if lab work and experiment are done. There are (3) three main processes involve in this project; Reaction, Extraction and Settling (R: E: S) process. The experiments are done under various parameters to study the effect of varying the parameters on extraction efficiency. Under these parameters set-up and chemicals used, the author will study the rate of acid removal from saline media.

The results of this project show that ionic liquid can be used to extract organic acid from the crude oil. The extraction efficiency is ranging from 50% - 80%. Other than that, increase in salinity's concentration show decrease in TAN of crude oil. The acid extraction is proven to be more efficient under specific parameters; solvent as the solvent, time taken for R: E: S process is 30:60:60 and 800 rpm. Based on the gas chromatography result, the amount of hexanoic acid extracted is more than dodecanoic acid.

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NOMENCLATURE

SHORT FORM	STANDS FOR
IL	Ionic Liquid
TAN	Total Acid Number
NA	Naphthenic Acid
R: E: S	Reaction: Extraction: Settling
GC	Gas Chromatography

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND STUDY

Corrosion is a major problem faced by oil and gas industry as crude oil contains organic acid. Crude oil from part of the world such as Europe, Russia, UAE and others contain high amount of acid, namely naphthenic acid (NA). Naphthenic acid refer to organic acid that rich with saturated ring structures and contain one or more carboxylic acid group. NA has the empirical formula of $R[CH_2]_n$ COOH, where *R* represents a cyclohexane ring. Figure 1 shows molecular structures of naphthenic acid. High amount of NA could cause corrosion in operations equipment such as pipelines, oil refineries, storage tank, separator and others. Thus, extraction of acid from crude oil is necessary to minimize equipment's damage or malfunction. Several methods such as washing with caustic solution, addition of corrosive inhibitors and blending with sweet oil have been developed to solve this problem. Unfortunately, these methods do not work efficiently. Recently, there are studies and research on extraction of NA from crude oil using Ionic Liquids (IL). This method proves to be an eco-friendly process due to its non-volatile, non-flammable and thermally stable properties. In this project, the author is going to study the use of IL under the various condition to extract organic acid, naphthenic acid.



FIGURE 1: Molecular Structures of Naphthenic Acid.

1.2 PROBLEM STATEMENT

Corrosion can cause damage to the plant and equipment due to the high amount of acid, namely naphthenic acid (NA). This has become a major concern in the oil and gas industry. As a result, oil and gas companies spent billions of dollars for maintenance and repair cost. A lot of studies have been done to search for the best method that is efficient, eco-friendly and economically feasible. Methods such as washing with caustic solution, addition of corrosive inhibitors and blending with sweet oil have proven insufficient for large scale process. In this project, the author used ionic liquid to study the extraction the acid from the crude oil.

1.3 OBJECTIVES AND SCOPE OF STUDY

The objectives of this project are:

- a) To extract naphthenic acid from crude oil sample using Ionic Liquid (IL).
- b) To study the efficiency of different ionic liquids $(Il_{10}\&Cl_{10})$ on acid extraction.
- c) To study the effect of salinity toward acid extraction in crude oil samples.
- d) To study the effect of varying the parameters (RPM, R: E: S time, type of solvent) on extraction efficiency.
- e) To study the amount of acid extracted using gas chromatography.

The scopes of study of this project are:

- a) Limited to only crude sample with organic acid content.
- b) Limited to only determination percentage of acid reduction.
- c) Limited to only amount of organic acid determination using Gas Chromatography.

1.4 RELEVANCY AND FEASIBILITY OF THE PROJECT

The presence of naphthenic acid in crude oil caused corrosion problem. This solution is not yet discovered as previous methods are found inefficient for larger scale of operations. Thus, more researches need to be done in order to mitigate this problem. For the past few years, previous studies and researches shown that ionic liquids can be used effectively to extract acid. Under the title "Acid Removal from Salinity", the author really thinks that this research can bring benefit to the oil and gas industry. Furthermore, with further research and experiments done by the author, this project can further enhanced the effectiveness of ionic liquids as a solvent to extract organic acid in crude oil. Thus, a larger scale can be done in order to mitigate the corrosion problem.

The time allocated to do this project was 8-months starting from January 2014 to September 2014. The time given was used to do research and experiments in order to obtained results. The author constructs a Gantt chart to keep track on the task in this project. With the supervision of Dr. Rashidah Md. Pilus as the author's supervisor and her resources, the project is completed within the time frame.

CHAPTER 2: LITERATURE REVIEW

2.1 CRITICAL ANALYSIS OF LITERATURE

In the oil and gas industry, the presence of organic acid such as naphthenic acid could cause corrosion to the operating temperature of 200°C and above. The presence of naphthenic acid in crude oil leads to multiple problem which ultimately causing the equipment's failures in petroleum industry, which lead to high maintenances cost. Naphthenic acid (NA) is a term used in petroleum industry to refer to a collection of carboxylic acid [3]. Naphthenic acid are predominantly found in immature heavy crude oil due to the fact that they come from the biodegradation in petroleum hydrocarbon reservoir [5]. Naphthenic acid is characterized by a carboxylic acid functional group attached to a hydrocarbon molecule, and have a generalized chemical formula of $R(CH_2)_2COOH$ where *R* is a cyclopentane ring and *n* is typically greater than 12 [2].

The amount of acid in a crude oil can be determined using ASTM 664 method. The amounts of acid refer to the total acid number (TAN). Total Acid Number (TAN) defined as the number of milligrams of potassium hydroxide (KOH) required neutralizing the acidity of 1g oil [2]. The crude oil is considered acidic if the total acid number (TAN) exceeds 0.5 mg of KOH/g by titration [1].

Naphthenic acid extraction from crude oil is a priority in minimizing corrosion in the processing equipment especially in oil refineries and pipelines. Aside from the corrosive effect, NA also lead to formation of stable emulsions by forming metallic naphthenates that reduces interfacial tension and affecting the process that involve phase separation stages [6]. Moreover, presence of naphthenic acid in crude oil could cause the deactivation of catalyst and foaming in desalter [1]. All these problems lead to high cost maintenance and downtime. The presence of acid in crude oil will reduce the quality of the crude oil produced and as a result will cause the market price for the crude oil to decrease. Thus, extraction of acid such as naphthenic acid must be done in order to mitigate these problems in future.

Many studies have been done to mitigate this corrosion problem due to the presence of naphthenic acid in crude oil. The common industry practices to overcome the problems consist of blending with sweet crude or washing with caustic solution to lower the acid level, addition of corrosion inhibitors and utilization of expensive corrosion resistant construction material for the processing unit [3]. The previous methods used include dilution or caustic washing methods to reduce the TAN number of heavy crude oil [2]. But these methods proved to be unsatisfactory due to its expensive cost, unsuitability to bulk conditions and due to the production of heavy crude oil continue to increase in amount. Thus, many research and experiments are carried out to address the setback of the methods mentioned above. Based on the research and experiment done by Zhang etc. all (2006), it is found that the extraction of naphthenic acid could be done through catalytic decarboxylation on Magnesium Oxide. The study was done under unsuitable operating condition which used temperature of 150°C -250°C. As a result, the study is not reliable as the result is not obvious.

A new class of solvent, namely ionic liquids has recently shown promising application for reducing the acid content in crude oil [3]. Ionic liquids refer to salt in the liquid state and exist over a wide range of temperature. IL are typically nonvolatile, nonflammable and thermally stable and have been used to ensure green chemical process [1]. Figure 2 shows a common ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) used in the oil and gas industry. It was observed that ionic liquid were suitable for the separation of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons [7]. The acid removal rate using ionic liquid such as 1-*n*-butyl-3-methyl Imidazolium with different anions are proven to achieve as high as 99% [3].



FIGURE 2: Common Ionic Liquid (1-butyl-3-methylimidazolium hexafluorophosphate) used in Oil and Gas Industry.

In oil and gas industry, pipeline is the common medium of transportation used to transfer the crude oil from one location to another. Since the crude oil contains acid, it may damage the pipeline in the long term. This has been a major problem faced by oil and gas industry. The pipeline corrosion is a more difficult phenomenon that happens due to the instantaneous actions of some rhetorical behavior of the crude oil [9]. There are many types of corrosion occurred in oil and gas industry such as sweet & sour corrosion, galvanic corrosion, erosion corrosion and stress corrosion cracking in the oil and gas industry [10]. The corrosion could happen in the refinery system such as furnaces tubes, transfer line, tower packing, pump interval, valves and fittings [8]. The naphthenic acid corrosion mechanisms are as follow:

$$Fe + 2RCOOH = Fe(RCOO)_2 + H_2$$
(1)
$$Fe + H_2S = FeS + H_2$$
(2)

$$Fe(RCOO)_2 + H_2S = FeS + 2RCOOH$$
(3)

Equations 1 show the reactions involves in corrosion process. Iron naphthenate (corrosion) produced is soluble in oil. Equations 2 indicate the attack of sulphur on the pipeline wall. As a result, an iron sulfide is produced and it is insoluble. This iron sulfide can inhibit the naphthenic acid corrosion as it can provide protective layer (at low temperature) inside the pipeline wall. This reaction is also known as sour corrosion. Equation 3 state that the soluble iron naphthenate will react with the hydrogen sulfide to regenerate NA and produce iron sulfide. Hence, increase the content of NA and iron sulfide will cause blockage in the pipeline.

CHAPTER 3: METHODOLOGY

3.1 RESEARCH METHODOLOGY

The author has used analytical and experimental method in order to execute and finish the project. Through these methods, the objectives of this project are achieved. Gantt charts are used to track project schedules. Gantt chart is useful in showing activities (tasks or events) displayed against time. Appendix 1 and 2 shows Gantt chart prepared by the author during the 8-months of project implementation.

In order to understand the project, researches were done on the important key points of the project. The author used past journals, research paper, reference books and seek consultation from related lectures to gain knowledge and collect information. The scopes of research are limited to ionic liquid, total acid number, salinity and rate of acid extraction. In this project, two different based ionic liquid will be used to study the rate of acid extraction in crude samples. For example, Il_{10} is an imadazolium based while Cl_{10} is an ammonium based. Different based ionic liquids will have different efficiency toward acid extraction. The amount of ionic liquids used are determined based on the total acid number, thus various calculation are required. Analytical method is used to analysis liquid chromatography's result. Based on the result obtained, the amount of acid extracted can be known. Other than that, which acid extracted most can be determined. From the result, the efficiency of the acid extraction can be calculated. The information obtained through analytical method is important before implementing the experiments.

Experiments are performed in order to obtain the results. In this project, two different based ionic liquids will be tested on crude oil samples. Crude oil samples were prepared by using a real crude oil with the addition of certain amount of sea water volume and known amount of organic acids. In this project, two organic acid are used which are haxanoic acid and lauric acid. Table 2 shows the list of crude oil samples. There will be three (3) main process involved in this experiment which are reaction process, extraction process and settling process (R: E: S). In the reaction process, ionic liquid is added into the crude sample. The addition of ionic liquid will neutralize the acid content in the crude sample. Then, a solvent (methanol or water) is used to extract the IL-NA layer from the crude. This process is known as

extraction process. Lastly, the samples will be left to settle down (settling process). The experiments will be conducted under fixed and manipulating parameters. The fixed parameters refer to parameters that are fixed throughout the execution of the project while the manipulating parameters refer to different parameters applied to the samples for different experiments. Table 1 shows the parameters set up for this project. In this project, two different based IL are used to test on the crude samples which refer to experiment 5 and 7. Experiment 2 and 3 will represent the study of types of solvent to extract the IL-NA layer. Other than that, experiment 7, 8 and 10 shows the effect of time taken to do the process. RPM effect are shown through experiment 4 and 5. After that, samples will be sent for gas chromatography for further analysis. Based on the result obtained, the amount of acid extracted can be known. In this project, the organic acid investigate are hexanoic acid, C_6 and dodecanoic acid, C_{12} .

R: E: S Process Time (min)	Type of Ionic Liquids	Type of Solvents	Rotary per minute (RPM)
30:30:30	Il ₁₀	Water	600
30:30:60	Cl ₁₀	Methanol	800
30:60:60			

TABLE 1: Parameters used in the Experiments

TABLE 2: List of Crude Samples

No.	Crude Sample	Ionic Liquid	R:E:S (min)	Temperature	Solvent	RPM
1.	TAPIS (4G) + Salt water (1g)	Il_{10}	30:60:60	90	Methanol (2.5g)	600
	Salinity (3.5%)					
2.	TAPIS $(4G)$ + Salt water $(1g)$	Il_{10}	30:60:60	90	Methanol (2.5g)	600
	Salinity (5%)					
3.	TAPIS (4G) + Salt water (1g)	Il ₁₀	30:60:60	90	Water (2.5g)	600
	Salinity (3.5%)					
4.	TAPIS (5g)	Il_{10}	30:60:60	90	Methanol (2.5g)	800
5.	TAPIS (5g)	Il_{10}	30:30:60	90	Methanol (2.5g)	600
6.	TAPIS (5g)	<i>Cl</i> ₁₀	30:60:60	90	Methanol (2.5g)	800
7.	TAPIS (5g)	<i>Cl</i> ₁₀	30:30:60	90	Methanol (2.5g)	600
8.	TAPIS (5g)	<i>Cl</i> ₁₀	30:30:30	90	Methanol (2.5g)	600
9.	TAPIS (5g)	<i>Cl</i> ₁₀	30:30:30	90	Methanol (2.5g)	800
10.	TAPIS (5g)	<i>Cl</i> ₁₀	30:60:60	90	Methanol (2.5g)	600

3.2 PROJECT ACTIVITIES



FIGURE 3: Project Activities for FYP I and FYP II

TABLE 3: Project Key Milestones

No	Task/Activities	Due Date
1	Submission of extended proposal of the project	21-Feb-14
2	Submission of proposal defense	11-Mar-14
3	Safety briefing for laboratory	22-Mar-14
4	Discussion on the procedure and flow of the experiment	2-Apr-14
5	Initiation of experiment and collection of data	11-Jun-14
6	Submission of Draft Interim Report	11-Apr-14
7	Submission of Interim Report	17-Apr-14
8	Submission of Progress Report	9-Jul-14
9	Pre-SEDEX Competition	23-Jul-14
10	Submission of Technical Paper & Dissertation (Soft Bound)	13-Aus-14
11	VIVA Presentation	25-Aug-14

CHAPTER 4: RESULT & DISCUSSION

4.1 DATA GATHERING & ANALYSIS

It is important to know the acid number of crude oil samples as it indicates the acidity of the crude oil. The TAN is also used as a reference to determine the amount of ionic liquid used. The TAN can be determined using ASTM 664 method. But TAN can also be calculated theoretically. TAN is defined as the numbers of milligrams of potassium hydroxide (KOH) required neutralizing the acidity of 1g oil. In this project, TAN of 4 mg KOH/g already pre-determined.

using TAN
$$4mg \frac{KOH}{g}$$

= for 5 g of oil $\rightarrow 20mg \frac{KOH}{g}$
= 0.02 g KOH $\times \frac{1 \mod KOH}{56.1 g}$
= 0.0004 mol of KOH
= 0.0004 mol of acid

In order to neutralize acid totally, the amount of ionic liquid used must be the equal to the amount of acid. That means the amount of ionic liquid used must be also 0.0004 moles. The amount of ionic liquids can be calculated using the mass of IL, its molecular weight or density. Using these properties, the volume of the IL needed for the reaction to complete can be known.

In this project, crude oil samples are prepared using crude oil with addition of acid. Acid used in the experiments are 0.0003 moles of hexanoic acid and 0.0003 moles of lauric acid. Hexanoic acid is the carboxylic acid with general formula of $C_6H_{12}O_2$ while lauric acid (also known as dodecanoic acid) refers to the saturated fatty acid with a 12-carbon atom chain, C₁₂. Figure shows molecular structure of hexanoic acid and lauric acid. The amounts of acids added into the crude oil samples already pre-determined. The calculations for amount of acids used are as follow:



FIGURE 4: Hexanoic Acid Molecular Structure



FIGURE 5: Lauric Acid Molecular Structure

Amount of Hexanoic acid required: $W = 116.16 \frac{g}{mol} \times 0.0003$ W = 0.035 gAmount of Lauric acid required: $W = 200.32 \frac{g}{mol} \times 0.0003$ W = 0.0601 g

From the calculation stated above, it can be observed that the amount of acids added into the crude oil samples is 0.0006 moles while the amount of ionic liquid used to neutralize the acid is only 0.0004 moles. This is because we do not want all the acid to be neutralized by the ionic liquid as we would like to study the amount of the acid extracted under the gas chromatography. Another important aspect of this project is the solvent recovery. Solvents such as methanol and water are used as one of the manipulating parameters. Solvent is used to extract the IL-NA mixture from the crude oil. In this project, the author able to study the efficiency of both solvent in separating the IL-NA layer from the crude oil layer. The solvent recovery can be calculated as follow:

> Weight of Solvent, $S = W_1 - W_2$ Solvent Recovery (%) = $\frac{S}{W_1} \times 100$ W_1 = weight of IL + NA + Solvent W_2 = weight of IL + Na

4.2 RESULTS & DISCUSSION

Two types of ionic liquid are used in this project, which are CL_{10} and IL_{10} . The result of different ionic liquid application can be seen through Figure 6. In terms of TAN, the author found out that gives CL_{10} better result compared to IL_{10} . The acid extracted using CL_{10} is 70.69% while IL_{10} reduce acid by 54.17%. This may due to the fact that Cl_{10} structure is more compatible with the crude sample compared to IL_{10} , making it react more effectively.



FIGURE 6: Acid Reduction vs. Type of IL

The author able to study the effect of salinity toward acid extraction in crude oil samples using experiment 1 and 2 from table 2. Based on Figure 7, it can be observed that the concentration of salinity have effect on the total acid number and acid reduction. The salt water made up of molecule bonded by ionic. The ionic molecule is able to react with the organic molecule in the crude sample. As a result, total acid number reduces slightly when the author increases the salinity from 3.5% to 5%.



FIGURE 7: Acid Reduction vs. Salinity (%)

Temperature and stirring rate play important roles in determining the efficiency of reaction and extraction process in this project. High temperature will give more energy to the molecules to collide and break-make bonds other molecules. The temperature must be set accordingly as too high temperature will make the phase transition inefficient. In this project, two different stirring rate are used; 600 rpm and 800 rpm. Low stirring rate will make the molecules less interact and collide with each other due to less energy on the molecules. Thus, the efficiency of reaction and extraction process will be less. The result will be different if higher rate of stirring rate is used. Stirring effects are best shown through sample no. 6 and no. 10 or no. 8 and no. 9. Figure 8 show the result based on the stirring effect.



FIGURE 8: Acid Reduction vs. RPM

In this project, crude sample undergo three processes: R: E: S process. This is best shown through crude sample no. 7, no. 8 and no. 10 or crude sample no. 6 and no. 9. Time taken to do each process is different for each crude sample. Time taken to do the processes plays significant role as it associated with each process. This is because as time goes on, it will increase the efficiency of the process. Figure 9 show the result obtained based on the time taken for each R: E: S process. The results show that 30: 30: 60 gives better extraction compared to 30: 30: 30 and 30: 60: 60. The results obtained may from the expected due to the fact that there error when conducting the experiments.



FIGURE 9: Acid Reduction vs. R: E: S process time

Other than that, solvent are also one of the parameters set for this experiments. Methanol is used as solvent to extract and separate the layer between the crude oil and the ionic liquid-naphthenic acid (IL-NA). This is because methanol consists of short chain molecules making it difficult to dissolve in the hydrocarbon. Other solvent such as water is used to study the efficiency of separation phase between crude oil with IL-NA. The results are shown based on crude sample no. 1 and no. 3 (Figure 10). The amount of solvent used is not really significant as less amount of solvent can give the same result as when using more solvent. Effect of solvent's amount toward acid reduction can be seen in Figure 11.



FIGURE 10: Acid Reduction vs. Solvent Type



FIGURE 11: Acid Reduction vs. Solvent Amount

Figure 12 and 13 show results obtained from gas chromatography. Based on Figure 11 and 12, the author studies the amount of acid extracted using gas chromatography. From the GC, it can be determined which acid is extracted the most. In this project, two types of organic acid are used which are hexanoic acid and dodecanoic acid. Based on the results obtained, it can be observed that hexanoic acid is the most extracted acid compared to dodecanoic acid. Figure 12 refer to the standard fresh sample test on the gas chromatography while Figure 13 shows the result of GC of one of the crude samples.



FIGURE 12: GC's for Standard Fresh Sample



FIGURE 13: GC's Result for Crude Samples

CHAPTER 5: CONCLUSION & RECOMMENDATIONS

Based on the experiments done by the author, it can be concluded that application of ionic liquids are effective in extracting organic acid from crude oil. The efficiency of the acid extraction depend on the parameters set up. Suitable parameters set up will result in higher acid extraction. Other than that, it can be concluded that salinity do have an effect toward the acid extraction. All the objectives set up for this project managed to be achieved. As a conclusion, ionic liquid can be used to extract organic acid namely, naphthenic acid.

Improvement can be made in this project in order to obtained better results. If this project can be used for further research, it is recommend that the project can be apply in a larger scale or in plant in order to further study the efficiency of ionic liquid in extracting acidic crude oil. Previous studies and research only limited in a small scale operation, thus no true validation or confirmation can be done. As a conclusion, the quality of oil is important as quality oil bring profit to the oil and gas company.

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APPENDICES

TABLE 4: FYP I Gantt chart

Activities	Week No/ Date													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Selection of Project Topic														
Preliminary Research Work														
Understanding project title														
 Journal and research paper on Naphthenic Acid, Ionic Liquid, and mechanism of extraction of acid. 														
Familiarize with existing extraction techniques or experiments														
by reading research paper														
Submission of extended proposal														
Proposal Defense														
Researches and project work continues														
 Continue reading research paper 														
 Material safety data sheet (MSDS) 														
Preparation for experiments:														
 Safety briefing 														
 Chemical and apparatus set-up 														
Submission of Draft Interim Report														

Submission of Interim Report													
Collect data													
Validate data (case study)	FYP 2												
Submission of Project Dissertation (Final Report)													

TABLE 5: FYP II Gantt chart

Activities	Week No.														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Project work continues															
Submission of progress report															
Project work continues															
Pre-SEDEX															
Submission of draft Final report															
Submission of Dissertation (soft bound)															
Submission of Technical Paper															
Viva															
Submission of Project Dissertation (hard bound)															



FIGURE 14: Reaction: Extraction: Settling Process



FIGURE 15: IL-NA Layer from the Crude Oil Sample



FIGURE 16: ROTAVAP Process to Evaporate the Solvent Content



FIGURE 17: Final Sample used for Gas Chromatography



FIGURE 18: Sample after ROTAVAP