# **Ionic Liquid Application in Extraction of Acids**

By

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13751

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the requirements for the

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(Petroleum Engineering)

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Universiti Teknologi PETRONAS Bandar Seri Iskandar 31750 Tronoh Perak Darul Ridzuan

#### CERTIFICATION OF APPROVAL

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

Approved by,

(Dr. Rashidah Bt. Mohd Pilus)

UNIVERSITI TEKNOLOGI PETRONAS TRONOH, PERAK MAY 2014

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(Muhammad Syazwann Bin Mohamad Zain)

## ABSTRACT

Technically, naphthenic acid have been known as one of the dynamics that are causing corrosion in petroleum industries. Naphthenic acid is the organic acid inside the crude oil which exist naturally from the aliphatic and cyclic structure inside the source rock. Nowadays,the current method of removing naphthenic acid from crude oil areinefficient because they pollute the environment and have high operating cost. This project will be focussing on the extraction of naphthenic acid from crude oil using ionic liquids through neutralisation process. Ionic liquids have been proven to extract naphthenic acid from crude oil succesfully. Basically, this project will be focusing more on the effect of different parameters on the extraction of naphthenic acidprocess using ionic liquids. The type of acid extracted from the experiment are identified for further studies on the structure because different acid structure inside the crude oil may have different effect on corrosion. This paper discussed the results of the extraction of naphthenic acid which includes the optimum parameters of the experiment.

## ACKNOWLEDGEMENT

Alhamdulillah, Praise be to Allah SWT, the Almighty and may Allah's peace and blessing be upon His servant and messenger Muhammad SAW and upon his family and Companions. Thanks to Allah whom with His willing giving me the opportunity to complete the final year project report.

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# CHAPTER 1 PROJECT BACKGROUND

#### 2.1 BACKGROUND STUDY

Corrosion in petroleum industry has been identified to be caused by the naturally occurring acid inside crude oil or commonly known as naphthenic acid. Naphthenic acids are a collection of carboxylic acids including acyclic and aromatic acids present in the crude oil. It is the main cause of corrosion in oil and gas industry and has been very synonym in this field from long time ago. The presence of naphthenic acid in upstream process has somehow contributes to pipeline corrosion as well as the formation of stable emulsion that slows the rate of separation in the separator. Many efforts have been done in order to mitigate the corrosion problem by extracting the acids but somehow certain technique used nowadays creates other problem such as pollution and also very costly. Nowadays, researchers have found a new technology to remove the content of naphthenic acid inside crude oil which is greener and efficient. The process of removing the acids is by using ionic liquids, which application in chemical processes, and petroleum industry is relatively new. This study will be conducted using different type of ionic liquid and tested with different parameters in order to observe the extraction reaction of naphthenic acid.

#### **1.2 PROBLEM STATEMENT**

The presence of naphthenic acid in crude oil contributes to corrosion problem in both upstream and downstream process. Corrosion is a major problem in oil and gas industry. Therefore effort in mitigating the corrosion needs to be initiated from the upstream process down to the transportation and processing facilities as it has caused losses due to maintenance, replacement and downtime. Other problems arise from high content of naphthenic acid includes the low price and quality of crude oil thus reducing the revenue in oil production.

Although a lot of methods have been used widely in removing naphthenic acid from crude oil, many of them pollute the environment and result in high operating cost. The common technology that is used to remove naphthenic acid is through soda washing. Others include hydrorefining, adsorption, and the use of ammonia. The soda wash refining method badly pollutes the environment and waste oil while the cost for hydrorefining is uneconomical. Overall, the current technology of removing naphthenic acid from crude oil is applicable but not efficient for both processes.

#### **1.3 OBJECTIVES**

- i) To extract naphthenic acid from crude oil using ionic liquids.
- To compare the effectiveness of different ionic liquid in extracting the naphthenic acids
- iii) To study the effectiveness of naphthenic acid extraction from crude oil under different parameters e.g. reaction time & temperature.
- iv) To identify the structure of acid extracted from the separation process.

#### **1.4 RELEVANCY OF THE PROJECT**

The relevancy of the project can be determined by judging on how the project is beneficial if it is conducted. The study on acid removal from pipeline media will give benefits in term of finding new technique and technology to remove naphthenic acid that causes corrosion in petroleum industry. Using ionic liquids as a medium of naphthenic acid extraction can increase the efficiency of acid removal from crude oil. Besides that, from this project we can also improve the current technologies that have been implemented which pollutes the environment and have high operating cost. With this project, we can practice a greener technology of extracting the naphthenic acid.

For the author, the project can benefit him in the terms of understanding the corrosion problem, the upstream process and mitigation of the problem. As a Petroleum Engineering student, it is also important to understand the problems that arise from the crude oil itself besides learning how to extract them from the mother earth and boost production. From this project, the author can correlate corrosion in the upstream part and crude oil and gain exposure to techniques applied in mitigating the problems. This project is relevant to the oil and gas engineering fields.

#### **1.4 FEASIBILITY OF THE PROJECT**

This project is feasible and can be done within the time frame because the availability of ionic liquid lab in the university laboratory. All the equipments, apparatus, materials and chemicals can be obtained inside the laboratory. The procedure to conduct the experiment is not too many but requires a complete understanding regarding the topic and also needs accuracy and precision. The project is estimated to be finished around 2-3 months to complete the work to appreciable amount and applicable results.

## 1.6 SCOPES OF STUDY

The scopes of study of this project are:

- i) Setting up the laboratory scale experiment to extract naphthenic acid from crude oil using ionic liquids.
- ii) Analyze the reaction between crude oil and ionic liquids and the efficiency of naphthenic acid removal.
- iii) Study the effectiveness of removing naphthenic acid from crude oil with different parameters.
- iv) Measure the solvent recovery achievable in the extraction process.
- v) Identify the structure of acid extracted from the separation process.

# CHAPTER 2

## LITERATURE REVIEW

#### Introduction

In petroleum industry, one of the main problems affecting the business is corrosion. This problem occurs in both upstream and downstream process and has been proven to affect the integrity of the pipelines that connected both field. One of the contributors to the problem is the naturally occurring acid inside the crude oil or commonly known as naphthenic acid. According to Wang et al. (2014), the primary contributor to the total acid number of the crude oil is naphthenic acid and it causes problem such as corrosion to the equipment inside the plant as the temperature increases during oil refining. This compound also contributes to delays in separation at the upstream level. If we manage to solve this problem from the upstream process, it will be a huge advantage since it will solve separation issues, pipeline corrosion and corrosion of the plant equipments. So the main question here is, what is naphthenic acid and how we can extract this acid from saline media in order to mitigate corrosion problem?

#### Naphthenic Acid

Generally, naphthenic acid is the term used to define all naturally occurring organic acid inside crude oil. It is classified as carboxylic monoacids of the general formula  $R(CH_2)_n$  COOH, where R represents any cycloaliphatic structure and is used to categorize all carboxylic acid inside crude oil including acyclic and aromatic acids (Shi et al.,2008).Basically, this definition of naphthenic acid is accepted in most literature related to the topic. Figure 1 shows the general structure of naphthenic acid. These compounds exist naturally in the crude oil originated from the reservoir itself.

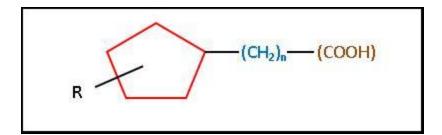


Figure 1 : General Structure of Naphthenic Acid

The amount of naphthenic acid inside the crude oil can be determined by measuring the total acid number (TAN) of the crude oil. According to Hasiah et al. (2012), total content of acid in crude oil or TAN is defined in a milligram of potassium hydroxide (KOH) required to neutralize one gram of oil and is determined according to ASTM 664 method. This statement is also supported by Anderson et al. (2013) and Bota & Nesic (2013). Besides that, Wang et al. (2014) stated that oils with TAN above 0.5 mgKOH/g are classified as acidic oils, whereas oils with a TAN above 1 mgKOH/g are classified as high acidic oils. Kane & Cayard (2002) also reported that high TAN inside crude oils indicates that there are high levels of acid present in the crude oil.

#### Corrosion involving naphthenic acid in pipeline media

Hydrocarbon inside the reservoir at the offshore platform is transferred to the downstream facilities to be processed through pipelines. Crude oil from the reservoir which contains acyclic and aromatic acid structures flow inside pipeline and react with the metal pipe. This process is known as corrosion which can be categorized into two types namely iron corrosion and sulfur corrosion. Figure 2 shows the mechanism of the corrosion (Bota & Nesic , 2013 , Dettman et al. , 2010).

Fe + 2RCOOH	¢	$Fe_2(RCOO^-)_2 + H_2$	(1)
$Fe + H_2S$	₹	$FeS + H_2$	(2)
$Fe_2(RCOO^-)_2 + H_2S$	₹	FeS + 2RCOOH	(3)

Figure 2 : Mechanism of Corrosion

Based on equation (1) we can see that naphthenic acid reacts with iron which is the metal pipelines producing iron naphthanates (oil soluble). Equation (2) describes the interaction of iron with hydrogen sulfide resulting in iron sulfide. Iron sulfide is not soluble in oil and forming a layer of protection at the surface of the metal. However, equation (3) shows that the iron naphthanates reacts with hydrogen sulfide in solution and produce more iron sulfide and more naphthenic acid .These iron sulfides precipitate in solution or crude oil causing blockage. This process will keep repeating and this is actually the mechanism of corrosion inside pipeline that involve naphthenic acid.

The type of crude oil also gives impact on the corrosion inside the pipeline media. There are two types of crude oil, sweet crude and sour crude. Sour crude contain high amount of sulphur which reduces the quality of the crude. Sulfidic corrosion are most likely will happen on sour crude but iron corrosion will happens on both sweet and sour crude.

#### Problem contributed by naphthenic acid

"The presence of naphthenic acid in crude oil in greater or lesser amounts lead to multiple problem which are causing equipment failures at petroleum industries, lead to high maintenance costs and more frequent turnarounds, reducing the product quality and causing environmental disposal problem" (Mandal et al., 2011). This statement is supported by Wang et al. (2014) and also Sun & Shi (2012). Naphthenic acid is very synonym with the petroleum oil refineries corrosion since a long time ago. In conjunction with the corrosion problem, according to Wu et al. (2004) the nature of such corrosion phenomenon and its controlling factors are still ambiguous. The reasons could be due to quite complex factors that influence the naphthenic acid corrosion, and the deficiency in experimental installations to effectively stimulate high-temperature and fast-flow conditions.

In addition to the corrosion problem cause by naphthenic acids on oil refinery equipment, besides corrosion, it also affects the sludge wastewater treatment systems. Missiti et al. (2013) in their studies managed to prove that the source of acids in the refinery wastewater is from naphthenic acid inside the crude oil and are impacting the environment.

#### Current technology for removing naphthenic acid

Nowadays, there are many technology that have been used to remove naphthenic acid from crude in order to overcome the corrosion problem that continues rising in petroleum industry. Wang et al. (2014) in his research highlights the methods to remove naphthenic acid which includes hydrogenation, solvent extraction, adsorption, decomposition and esterification. Anderson et al. (2013) also mention about the removal of naphthenic acid which can be achieved by non-destructive method such as solvent extraction, adsorption and esterification. Besides that, they added the non-catalytic destructive methods such as thermal decomposition, catalytic decarboxylation and hydrotreating.

The most common method in the application of removing naphthenic acid in petroleum industry is by soda washing. However, through this method, it has been proven to cause pollution to the environment (Sun & Shi, 2012).Soda washing is not applicable and reliable for removing naphthenic acid as also indicated by other studies. They also added that hydrorefining, ammonia refining, solvent refining and adsorption refining have high operating cost and are uneconomical throughout the implementation. Shi et al. (2008) mentioned that methods by heating, hydrogenation and esterification on the other hand destroy the naphthenic acid which can be used in paints, drying agents, detergents and solvents making industries.

#### **Ionic Liquid**

Ionic liquids are compound that consist of entirely ions and it is a new class of solvent and often exist as fluid at room temperature. According to Moosavi and Daneshvar (2013), ionic liquids have been widely used as solvents for synthesis and catalysis, electrolytes, lubricants and media for the formation and stabilization of nanoparticles. In addition, the physical, chemical and electrochemical properties of ionic liquid are very suitable for many types of application in different industry. Shi et al. (2008) stated that ionic liquids are typically nonvolatile, nonflammable and thermally stable, hence its application is mostly related to being the green chemical process. This statement is supported by Moosavi and Daneshvar (2013) who mentioned that the low volatility of ionic liquids making it a serious alternative for volatile organic compound which contributes towards a clean and "green" chemistry.

Recent studies by Hasiah et al. (2012) managed to prove that ionic liquid can be used to decrease the amount of acid inside crude oil and also remove the suphur compound. Acid reduction inside crude oil means that naphthenic acid is removed and thus mitigating corrosion problem. "Ionic liquids were suitable for the separation of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbon" (Sun & Shi, 2012).

#### Conclusion

In a nutshell, we already understand that the main cause for corrosion in pipeline which is naphthenic acid and sulfidic components. However, the current technologies used to remove this acid from crude oil have their setbacks while implemented. Therefore, this project will be beneficial in introducing a reagent, ionic liquid, which is known as a green solvent and capable of extracting naphthenic acid at the same time.

#### 2.2 CITATION AND CROSS REFERENCING

For this literature review, this project was being referred to several research papers from Fuel journal and also from National Association of Corrosion Engineers (NACE) regarding naphthenic acid and corrosion problem. Besides that, there are also other journals which are related to the ionic liquids. Most of the journal and publication was retrieved from science direct website. The details of the journals, reports and research papers can be read from the reference part of this project paper.

#### 2.3 RELEVANCY AND RECENTNESS OF LITERATURE

This literature review helped to give a greater understanding and knowledge of the project. The critical analysis literatures provided much basic theoretical knowledge of the naphthenic acid, problem contributed by naphthenic acid and also regarding ionic liquids. This has led to gain a bigger perspective to understand the project and its goals. As for the recentness, the literatures collected from various sources varied in terms of their publication. The choosing of sources based on the period of publication and also by the content which related to the project.

# **CHAPTER 3**

# METHODOLOGY

#### **3.1 RESEARCH METHODOLOGY**

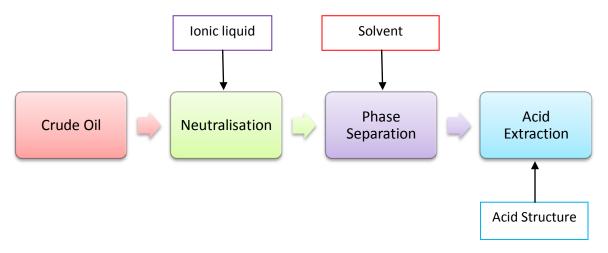


Figure 3 : Process Flow of the Extraction of Naphthenic Acid

Figure 3 shows the process flow for the extraction of naphthenic acid from crude oil. This shows the general process of how the project was done during the project works phase. Basically, the acid is extracted through neutralization and solvent-solvent extraction process. The main important thing in order to analyze the result of the project is the total acid number which will be used to determine the effectiveness of naphthenic acid extraction. In addition, the chromatograph of the sample is also needed to study the acid structure. The detailed procedure is discussed as follows.

## <u>Procedure</u>

- 1) 5g of Crude oil is prepared.
- Acid is added into crude oil based on the calculated amount. Two types of acids which are Hexanoic Acid and Dodecanoic Acid.
- 3) TAN Before of the sample is measured using Autotitrator 70.
- 4) Ionic Liquid is added based on the calculated amount.
- 5) The sample is heated and for the reaction process to take place. (See attachment 1)
- 6) Solvent is added for the extraction and settling process.
- TAN After is measured from the de-acidified oil layer to observe the reduction in TAN. (see attachment 2)
- 8) The solvent layer is **rotavap** to remove the solvent. (see attachment 3)
- 9) Diluted HCL is added into the sample to regenerate the acids.
- 10) The sample (see attachment 4) is tested with Gas Chromatography.
- 11) Step 1 is repeated with different set of parameters.

Parameters:

- i. Type of Crude Oil
- ii. Type of Ionic Liquid
- iii. Reaction, Extraction & Settling (RES) time.
- iv. Temperature

#### \* Acid Calculation

The TAN is set to be 4mg KOH/g For 5g of Oil  $\rightarrow 20 \text{mg} \frac{KOH}{g}$ =0.02g KOH  $\times \frac{1 \text{ mol } KOH}{56.1g}$ = 0.0004 mol KOH = **0.0004 mol NA**  *Notes*: The reason why we put acid inside the crude oil is because we receive both TAPIS & MIRI Crude Oil from PETRONAS Penapisan Melaka (PPMSB) in a treated form. So, there are minimal acids left in the crude oil. In addition, even though we set the TAN to be 4 mg KOH/g, there is still the need to measure TAN before as impurities/components in oil may influence the TAN reading.

#### \* Naphthenic Acid Preparation

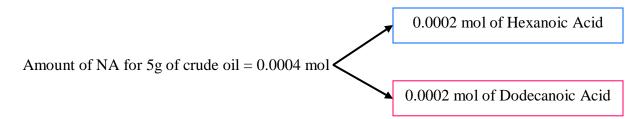
There are two types of NA that are used in this experiment:

1) Hexanoic Acid

Molar Mass	= 116.16 g/mol
Density at 24 °C	$= 0.929 \text{ g/cm}^3$
Melting Point	= -3.4 °C
<b>Boiling Point</b>	= 205.8 °C

2) Dodecanoic Acid (Lauric Acid)

Molar Mass	= 200.32 g/mol
Density at 24 °C	$= 1.007 \text{ g/cm}^3$
Melting Point	= 43.8 °C
<b>Boiling Point</b>	= 297.9 °C



In order to achieve the 4<sup>th</sup> objective of this project which is to study the structure of acid extracted, we need to put excess amount of NA inside the crude oil. This is because, if the ionic liquid managed to extract all acids from crude oil, there are no acid left to determine the type of acid that are most extracted. Hence, for some of the parameters, we will use **0.0003 mol** of each acid.

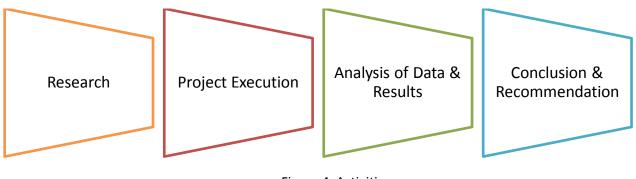
Mass of Acid Required (g) = Mol of Acid (mol) / Molar Mass  $\left(\frac{g}{mol}\right)$ 

#### \* Ionic Liquid Preparation

There are 3 types of ionic liquid that will be used in the study namely IL10, ML10 and CL10. IL10 is the imidazolium-based ionic liquid while ML10 and CL10 are ammonium-based ionic liquid.

1 mol of hydroxide will neutralize 1 mol of acid. So, 0.0004 mol of IL is required for this study. The mass of ionic liquid needed are weighed accordingly to achieve the required amount.

#### **3.2 PROJECT ACTIVITIES**



# Figure 4: Activities

#### 3.2.1 Research

This is the first step of the project activities in order to meet the objective of this project. Research regarding the main subject which is naphthenic acid is done in detailed in order to fully understand the purpose of the project. Besides that, the research on the corrosion mechanism and ionic liquids are also done as it is also related to the project. Previous studies regarding this project were analyzed critically so that a solid result can be produced towards the end of the project. All the research papers are latest and obtained from the trusted and reliable source to ensure that the project is highly accurate.

#### 3.2.2 Project Execution

After all the research has been done, the next part is the execution part. In this part, experiment was conducted to prove the arguments and to achieve all the objectives stated in the early part of the paper. The experiment was conducted using the university facilities and on Tapis & Miri crude oil. The method of extracting the naphthenic acid is describe in the research methodology section and was executed step by step precisely to ensure an accurate results. Based on the method of the project, the results are believed able to achieve the objective of the project.

#### 3.2.3 Analysis of Data and Results

For the part, the results of the project have been analyzed precisely and thoroughly. The results are discussed in the results and discussion part.

#### 3.2.4 Conclusion and Recommendation

This is the last part of the project and will be done after critically analyzed the results. A firm and accurate conclusion have been made and related to the objective of the project. Besides that, recommendations regarding the project have also been suggested for the expansion and for a better result in the future. Conclusion and recommendation are further discussed in the last chapter of this report.

#### 3.3 KEY MILESTONE

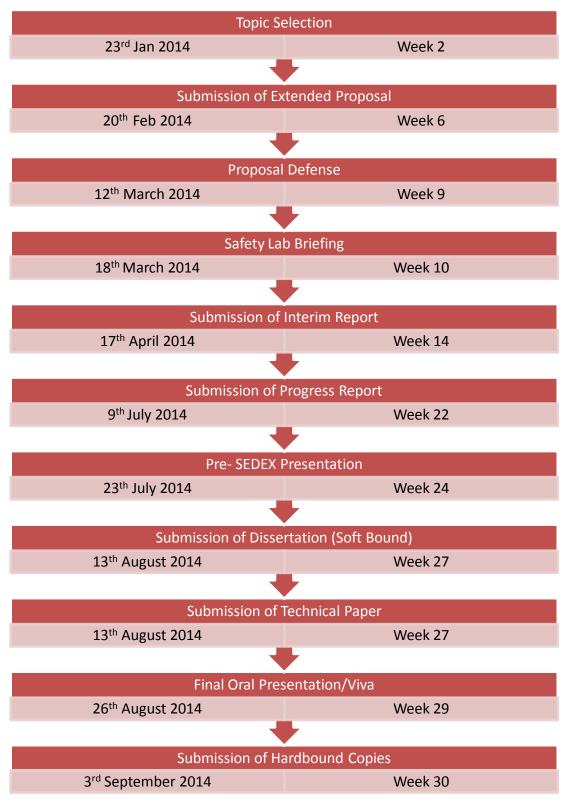


Figure 5: Key Milestone

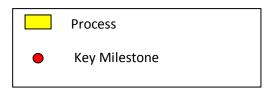
# 3.4 GANTT CHART

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	Preparation for Proposal														
	Defense														
5	Proposal Defense														
6	Safety Lab Briefing										•				
7	Project Work Continues														
8	Submission of Interim														
	Draft Report														
9	Submission of Interim														
	Report														•

# Timeline for FYP I

# Timeline for FYP II

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
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														



# 3.5 MATERIAL & APPARATUS

Chemicals	Amount (g)	Purpose					
Tapis Crude Oil	45	Hydrocarbon source					
Miri Crude Oil	20	Hydrocarbon source					
IL10	3	Ionic Liquid					
ML10	1	Ionic Liquid					
CL10	1	Ionic Liquid					
Hexanoic Acid	2	Short Chain Aliphatic Structure					
Dodecanoic Acid	3	Long Chain Aliphatic Structure					
Dilute Hydrochloric Acid	10	To regenerate naphthenic acid					
Methanol	70	Solvent & Preparing ASTM solvent					
Hexane	30	To extract organic acids					
Toluene	45	Preparing ASTM solvent					
Distilled Water	5	Solvent & Preparing ASTM solvent					
Silicon Oil	150	To ensure even heating					

# Table 1 : List of Materials

Apparatus	Amount
Round Bottom Flask	3
Rotavap Flask	2
Beaker	2
Measuring Cylinder	2
Sample Bottle	13
Weighing Balance	1
Magnetic Stirrer with heater	2
Rotavap Machine	1
Autotitrator T70	1
Pipette	2
Disposable Dropper	15

## Table 2 : List of Apparatus

# **CHAPTER 4**

# **RESULTS & DISCUSSION**

## 4.1 DATA GATHERING & ANALYSIS

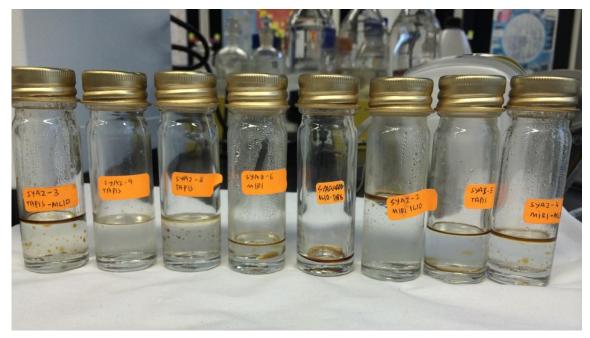


Figure 6 : IL-NA + Dilute HCl

Figure 6 shows the IL-NA + Dilute HCl that has been extracted from the crude oil using methanol as a solvent under different parameters. The TAN After of the deacidified crude is measured using Autotitrator machine.

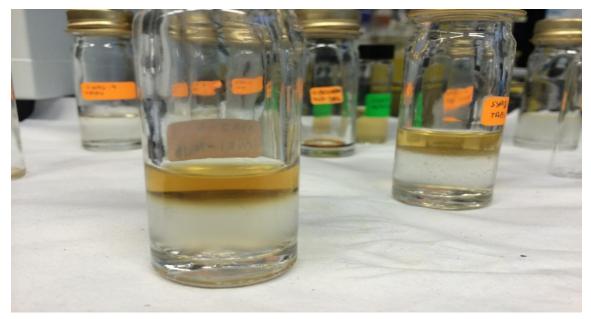
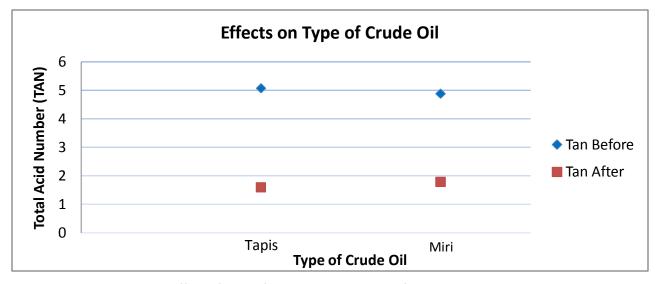


Figure 7 : IL-NA - Dilute HCl + Hexane

The extracted acids were sent for Gas Chromatography analysis to check the chromatograph of each acid.

#### 4.2 **RESULTS & DISCUSSION**



#### 4.2.1 Type of Crude Oil

Figure 8 : The effect of type of crude oil on the rate of naphthenic acid extraction

Figure 8 shows the effect of different type of crude oil on the rate of naphthenic acid extraction. The experiment was conducted using IL10 with fixed variables namely stirring rate, temperature and reaction time. Based on the graph, we can see that the total acid number for both Tapis and Miri are reduced. This proved that by using ionic liquid, we can extract naphthenic acid from crude oil. In addition, the reduction of acid number is not the same for both crude oil. TAN reduction in Tapis is slightly better but comparable to Miri. This could be due to the impurities inside the crude oil or the different compounds hence structures of hydrocarbon in different crude oils. It shows that IL10 perform better in Tapis crude oil.

Notes: The commercialized Total Acid Number (TAN) for crude oil is 0.5mg/KOH. From this experiment, we only want to observe whether ionic liquid can be used to extract naphthenic acid form crude oil. Further research on lowering the TAN until the acceptable number shall be conducted in the future.



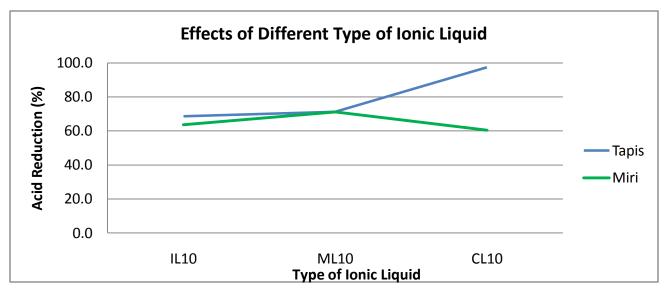


Figure 9 : The effects of different type of ionic liquid on the rate of naphthenic acid extraction

Different type of ionic liquid will gives different results on naphthenic acid extraction because the structure of the ionic liquids is not the same. As being stated in the methodology part, IL10 is imidazolium-based ionic liquid and both ML10 and CL10 are ammonium based.

From Figure 9, we can see that all three types of ionic liquids manage to reduce the TAN of the crude oil which indicates that the acid is extracted from the crude oil. This is the main objective of this project. Besides that, the percentage of acid reduction using IL10 and ML10 is quite comparable while CL10 performs better in Tapis compared to others but poorly in Miri Crude Oil. This is maybe because the structure of CL10 is very compatible with Tapis but not with Miri.

However, the study on the properties of CL10 and Tapis should be done thoroughly before we can further conclude on the results. Based on these observations, IL10 is comparable to ML10. CL10 would be a good candidate for extraction of acids from Tapis.



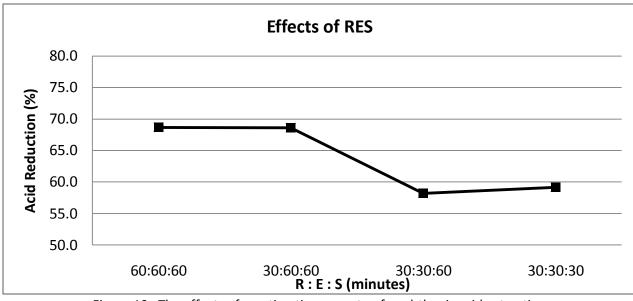


Figure 10 : The effects of reaction time on rate of naphthenic acid extraction

RES refers to the reaction, extraction and settling time of the experiment. The graph in Figure 10 is plotted based on different RES time which are 60:60:60:30:60. : 60, 30:30:60 and 30:30:30 (minutes). The experiments were conducted on Tapis crude oil using IL10 and at the same temperature and stirring rate.

Based on Figure 10, we can observe that the percentage of acid reduction in RES of 60: 60 and 30: 60: 60 are quite the same. However, the acid reduction for 30: 30: 60 and 30: 30: 30 are low compared to the others. From the graph, we can say that 30: 60: 60 are the best RES time because the acid reduction is the same with 60: 60: 60 but it requires less reaction time. This is very good because when we reduce the time, we also save the operating cost. However, reduction in extraction and settling times further proven inefficient in extracting the acids. Hence, 30: 60: 60 is chosen as the optimum RES for the experiment.



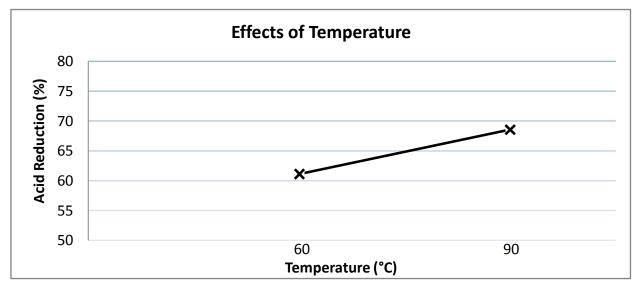


Figure 11 : The effects of temperature on rate of naphthenic acid extraction

Based on the previous study, we already know that 90°C is the optimum temperature for the extraction process. These parameters are conducted to show the effects between 90°C and 60°C temperature. The experiments were conducted on Tapis crude oil using IL10 at the same RES and stirring rate. Based on Figure 11, we can see that the percentage of acid reduction in 90°C is higher compare to 60°C.

#### 4.2.5 Type of Acid Extracted

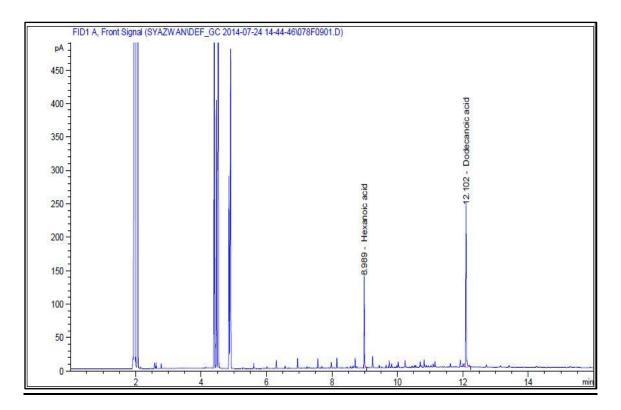


Figure 12 : Gas Chromatography

Figure 12 shows the result from Gas Chromatography regarding the chromatograph of the sample. Based on the overall results, dodecanoic acid is the type of acid that are extracted the most from the experiment.

From previous study which were conducted using benzoic acid, hexanoic acid and dodecanoic acid, IL10 manage to extract benzoic acid the most because of the aromatic structure of inside IL10 makes it more soluble in the hydrocarbons resulting in better mixing and increasing extraction efficiency. However, in this study when only hexanoic acid and dodecanoic acid are present, dodecanoic acid is the most acid extracted. This indicates that, the long aliphatic structures inside the ionic liquid enabling it to extract dodecanoic acid the most which may be due to compatibility and increasing solubility between the long aliphatic moieties of the two.

# **CHAPTER 5**

# **CONCLUSION & RECOMMENDATION**

#### 5.1 CONCLUSION

Ionic Liquid has been proven to be a good solvent for extracting naphthenic acid from crude oil. From this experiment, we can see that all ionic liquids used managed to reduce the TAN of the crude oil.

The commercialized TAN for crude oil is 0.5mg/KOH and further studies on reducing the TAN to this amount needed to be done in the future. As for this experiment, the main objective of extracting naphthenic acid from crude oil by using ionic liquid is achieved. In order to achieve the optimum extraction process, the experiment must be conducted under certain condition or parameters. By using ionic liquids which has been proven as a green solvent, we can minimize the environmental pollution and high operating cost of the current method.

As for the reaction time, the optimum RES for the acid extraction process is 30:60:60 (minutes). The optimum temperature is  $90^{\circ}$ C.

Based on the results from Gas Chromatography, the type of acid extracted in this part of the project is dodecanoic acid which is the long aliphatic structure inside the crude oil.

#### 5.2 **RECOMMENDATION**

For future works and further extension of the project, we need to lower the TAN until 0.5mg/KOH and below. Furthermore, the regeneration of the ionic liquids and solvent used in the extraction process is recorded. By using this approach, we could enhance the economics of the process and optimize the process conditions. In addition, we should conduct the experiment on a larger scale so that we can improve the accuracy of the results. Moreover, this study should be applied to the offshore platform in order to mitigate the corrosion problem from the upstream process. Further research should be done to find the suitable technique to adapt this to the offshore facilities.

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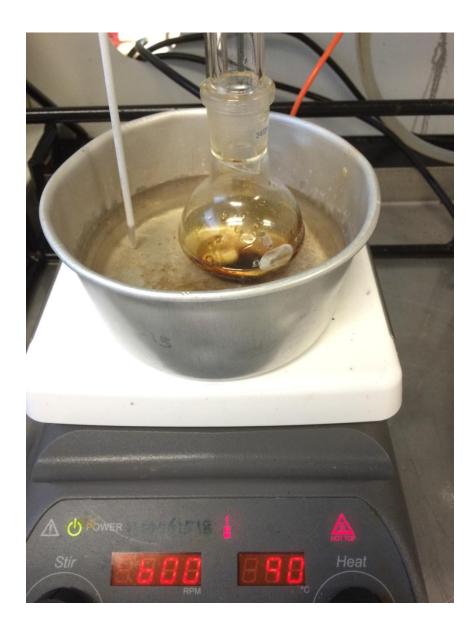
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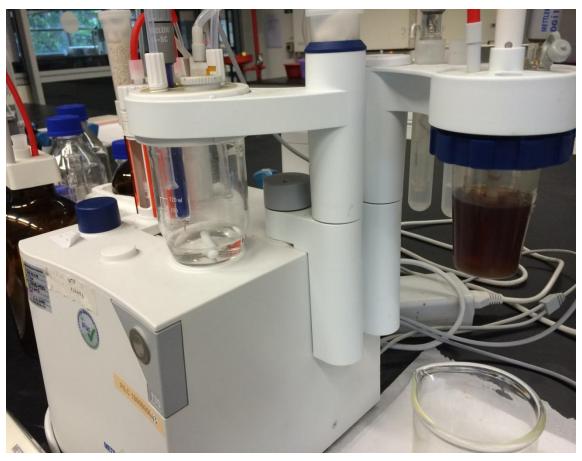
# APPENDICES



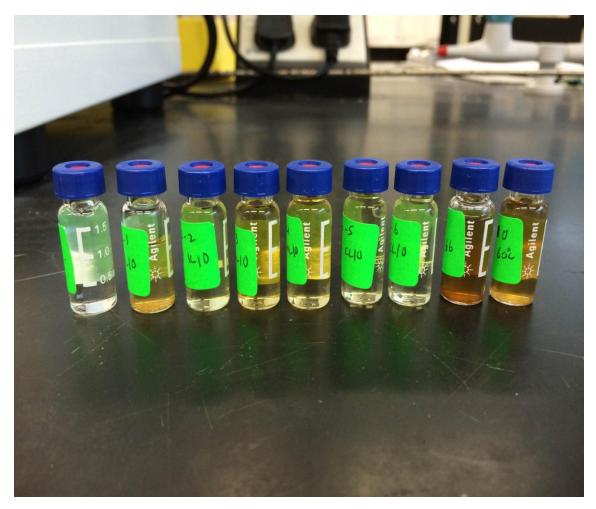
Attachment 1



Attachment 2



Attachment 3



Attachment 4