Kinetics of Acidity Removal of Naphthenic Acid Model Compound Using Sub-Critical Methanol

by

Anuar Bin Abdullah

15350

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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Approved by,

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BANDAR SERI ISKANDAR, PERAK

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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.

ANUAR BIN ABDULLAH

ABSTRACT

This paper studies on the reaction kinetics of naphthenic acids model compounds upon reacting with subcritical methanol. Naphthenic acids are the primary contributor to the total acid number of the oil and it can be expressed in terms of total acid number (TAN). Crude oil containing these acids which are corrosive can cause many problems such as equipment failures, high maintenance cost, reduces product quality and environmental disposal problems. The model compounds of naphthenic acid; 2,6 – naphthalene dicarboxylic acid ($C_{12}H_8O_4$) was tested with subcritical methanol under temperature range from 180℃ to 220℃ with a temperature interval of 20℃ in an autoclave reactor. The reaction time for the mixture was from 0 min to 60 min. This experiment reveals that the highest TAN reduction was achieved at 220℃ and 60 minutes where the reduction was about 48.80%. The TAN reduction followed second order kinetics; with Arrhenius parameters of activation energy 7.472 kcal/mol and a pre-exponential factor of 0.877 fraction^{-1}s^{-1}.The result show that methanol is capable to reduce TAN in sub-critical condition with absence of catalyst.

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TABLE OF CONTENTS

LIST OF ABBREVIATION

AEO	Acid-extractable Organics
ASTM	American Society for Testing and Materials
FYP I	Final Year Project I
FYP II	Final Year Project II
GC-FID	Gas Chromatography – Flame Ionization Detector
KOH	Sodium Hydroxide Solution
MgO	Magnesium Oxide
NAs	Naphthenic Acids
NH_3-EG	Ammonia Solution in Ethylene Glycol
OSPW	Oil Sand Process-affected Water
SCW	Super-critical Water
SEDEX	Science, Engineering and Design Exhibition
STIRF	Short Term Internal Research Fund
TAN	Total Acid Number
WPP	Water Partial Pressure

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Naphthenic acids (NAs) are constituents in crude oil usually present at 0–3%. They are complex and composed predominantly of alkyl-substituted cycloaliphatic carboxylic and acyclic (paraffinic) acids (James et al., 2014). Traditionally NAs have been classified as a family of compounds with the formula $C_nH_{2n+z}O_2$, where z is zero or a negative even number, representing the deficiency in hydrogen atoms when the compound undergoes cyclization or unsaturation (Ralph et al., 2013). Completely soluble in organic solvents and oil, NAs are considered water insoluble, with solubility under 50 mg/L (Lisa et al., 2014).

NAs are weak acids, with dissociation constants on the order of 10^5 to 10^6 (Julie et al., 2015). Like most weak acids, NAs form metal salts, such as sodium naphthenate (Lisa et al., 2014). NAs exhibit properties of surfactants due to the hydrophilic carboxyl functional group and the hydrophobic alicyclic end, and specific densities are less than 1 (Lisa et al., 2014).

Research began on oil sands NAs in the 1980s (James et al., 2014) observing simultaneous reduction in NAs, actually known as acid-extractable organics (AEO), and toxicity with oil sand process-affected water (OSPW) treatment. Strong evidence now exists to suggest NAs cause a toxic response. Determining the total NA concentration insufficient in describing toxic effects because molecular structure and composition of the NAs mixture need to be understood and identified (Kindzierski et al., 2012). Higher proportions of lower molecular weight compounds in a NA mixture correlate with high molecular weight NAs, not just increasing carbon number, are likely to be contributing to differences in measured toxicity (Kindzierski et al., 2012).

Naphthenic Acids (NAs) are a group of recalcitrant and hydrophobic compounds comprising a variety of structures. All NAs contain a conserved carboxylic acid group followed by a hydrocarbon chain. Attached to this hydrophobic chain there may be between one and four hydrogenated ring systems. With such diversity within this chemical class, the biodegradation of NAs is difficult to define due to the likelihood of biodegradation pathways interacting with very specific topological structures, NAs classification criteria are continually debated in the scientific community. Thus one pathway likely does not degrade all NAs, and NA research has yet to define any NA degrading pathways (Whitby, 2010)

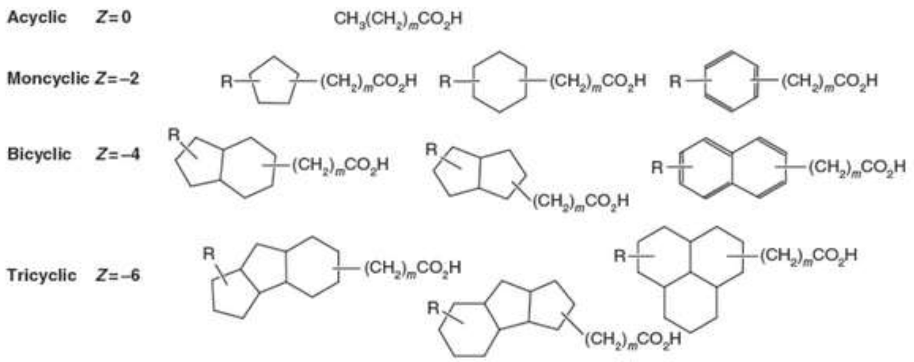

Figure 1.1 Structure of naphthenic acids (NAs) (Whitby, 2010)

NAs are the primary contributor to the total acid number of the oil and it can be expressed in terms of total acid number (TAN) (Mandal et al., 2013). The amount of potassium hydroxide in milligrams that is needed to neutralize the acids in one gram of NA by titration is the measurement of acidity which is Total Acid Number (TAN) (Anderson et al., 2015). When the TAN of the crude oil exceeds 1 mg KOH/g, common materials cannot resist corrosion by petroleum oil and corrosion can occur at any time refineries is to find the right method to remove or reduce the acidic substances from petroleum (Wang et al., 2014).

1.2 Problem Statement

The extraction and treatment of crude oil with high total acid number becoming a vital process as the conventional oil reserves are declining. Crude oil containing these NAs which are corrosive can cause many problems such as equipment failures, high maintenance cost, more frequent turnaround, reduce product quality and environmental disposal problems (Mandal et al., 2012). As a consequence, crude oils with a relatively high TAN have a significantly lower market value (Ralph et al., 2013). Hence, these NAs removal is regarded as a pressing issue.

There are many existing ways to remove NAs. Table below show the current methods for TAN reduction in crude oil.

Table 1.1 Available process/methods to reduce TAN in crude oil

No	Current Available Methods	Disadvantages
1.	Blended off high TAN crudes with lower TAN crudes	Costly and non-selective process
2.	Neutralization using polymeric compounds	Involves the use of expensive neutralizing agents which not easily recovered from deacidified products
3.	Extraction separation process	Valuable hydrogen compounds also be removed
4.	Catalytic decarboxylation process	Heavy metals in the crude itself will deposited on catalyst caused the catalyst inefficiency in the respective process

However, the current methods require a large investment in equipment, large amount of solvent, high energy consumption and other weaknesses. All these disadvantages show that almost impossible to remove the NAs from the crudes, but a research by Mandal et al., (2013) found that supercritical methanol able to reduce the TAN through esterification process. Thus, the main interest of this paper is to study the kinetics and reaction pathways for two model compounds of NA decomposition using subcritical methanol instead of supercritical methanol. This is to test either this method can be an effective method or not in TAN reduction.

1.3 Objectives

The objectives of this project are:

i. To investigate the effect of subcritical methanol for reducing TAN of model compounds of NA.
ii. To determine reaction kinetics of TAN reduction from model compounds of NA using subcritical methanol.

1.4 Scope of Study

This paper will focus on the study of kinetics for the model compound of NAs; 2,6 – naphthalene dicarboxylic acid ($C_{12}H_8O_4$) decomposition in experimental basis. The model compound will be tested using subcritical methanol at a temperature range of 180°C to 220°C which is below the critical temperature where the compound will be in liquid state. Below figure shows the general phase diagram of a single simple substance. The critical temperature and pressure of methanol is 239°C and 78.5 atm (Methanex, 2014). Thus, the experiment will be conducted below the critical temperature and pressure, and above the boiling point.

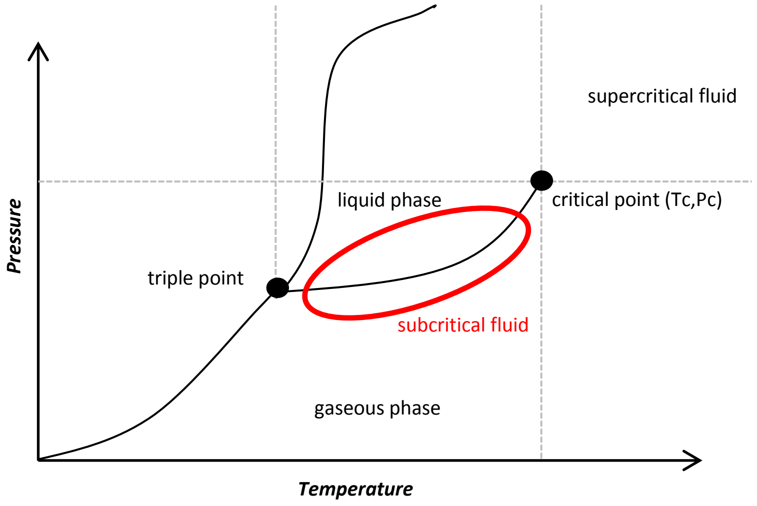

Figure 1.2 A general phase diagram

The experiment will be conducted in a hydrothermal autoclave reactor with Teflon chamber at which the maximum temperature is 230℃ and maximum pressure is 3MPa. The samples will be tested using titration method with sodium hydroxide (KOH) solution and gas chromatography - flame ionization detector (GC-FID). In total, there will be 15 samples to be tested and analyze.

1.5 Relevancy and Feasibility

This project is much relevant to my field of study, Chemical Engineering where it studies on the kinetics and reaction pathways of the model compound. Upon identifying and the quantifying the reaction products using analytical method, an empirical rate of reaction will be developed and the reaction order for model compound can be determined. Moreover, the possible reaction pathways of the model compounds will be analyzed. This may help the study on the reduction of naphthenic acid with the use of methanol. The project duration which is about 28 weeks is plenty enough to conduct the experiment and analyze the results. The given time is well planned in order to achieve the objectives of this project and details of the activities can be seen from the Gantt chart attached in these paper.

CHAPTER 2

LITERATURE REVIEW

2.1 Methods to Reduce TAN in Crude Oil

Crude corrosively problems have been studied since 1950's because of their technical and economic impact on production and refining operations. Crude quality is determined by measurement of some crude properties such as the specific gravity and acid content, which is also a factor in determining the corrosive properties of the crude entering the refinery. Heavy crude have the highest naphthenic acids (NAs) content among all the crude types.

There are many existing ways to remove NAs. Hydrogenation is commonly used for industrial distillates or residual oils, but it requires a large investment in equipment and large amounts of hydrogen. Thus, hydrogenation has not been used for the treatment of crude oils in industry. The combination of alkaline washing and electric treatment is particularly suitable for the deacidification of light distillates. However, this combined process consumes a large amount of alkali that can also cause equipment corrosion and pollution (Wang et al., 2014). Solvent extraction requires a large amount of solvent and high energy consumption because of solvent circulation; thus, no industrial application has been found for solvent extraction. Adsorption separation requires adsorption, desorption and solvent recovery units, which require a large investment in equipment, and isolated naphthenic acids have a lower TAN and price. Due to the influence of other high polar compounds in petroleum, adsorption cannot currently be used for heavy fractions (Wang et al., 2014).

One of the ways to reduce NAs in heavy crude oil is through catalytic neutralization. A series of experiment carried out by Sohaimi et al. which are by utilizing ammonia in ethylene glycol basic solution to perform the catalytic neutralization of the acidic crude oil. The feedstocks used in this study are heavy (crude A) and light (crude B) crude obtained from Petronas Penapisan Melaka, Malaysia and Korean crude (crude C). Ammonia solution in ethylene glycol (NH_3-EG) was prepared to be used as the acid removal agent in the acid base neutralization process. From this study, the results show that 67.4% (3000 mg/L of 4% NH_3-EG) reduction in TAN for crude A and 78.7% (10,000 mg/L of 4% NH_3-EG) reduction for crude C by using the best studied catalyst which is Ca/Al_2O_3 with a calcination temperature of 1100°C. For crude B, there is 71.2% reduction of TAN with 1000 mg/L of 0.4% of NH_3-EG (Sohaimi et al., 2014).

Based on same principle which is by using neutralization method, another study is carried out to reduce the TAN in crude oil by Shukri et al. In this study, instead of using ammonia solution in ethylene glycol, the polyethylene glycol (NH_3–PEG) is used as the acid removal agent with concentrations of 100, 500, and 1000 mg/L. Cerium oxide, zinc oxide and tin oxide based catalysts supported onto alumina prepared with different calcination temperatures and types of dopants are used to aid in the deacidification reaction in this study to reduce the TAN of Korean crude oil. This study gives result of 93.3% TAN reduction for Korean crude oil using $Cu/Ce(10:90)/Al_2O_3$ calcined at 1000°C (Shukri et al., 2015). Compared to previous study, this study gives a higher TAN reduction.

As mentioned earlier, many types of catalyst had been used in order to study the effectiveness in TAN reduction in crude oil. Another example, one study did by Zhang et al. using magnesium oxide (MgO), a type of metal oxide as the catalyst. This study determines the effectiveness in catalyzing decarboxylation reactions based on the formation of CO_2 and the conversion of acid. This MgO has multiple role in this reaction, beside has the ability to adsorb acidic compounds via acid–base neutralization and it can also promote reactions such as decarboxylation and hydrocarbon cracking at the increased temperature (Zhang et al., 2006). During the reaction, RC=OOH IR adsorption is monitored as a semi-quantitative estimate of the effectiveness of the catalyst. By utilizing magnesium oxide as catalyst in this catalytic decarboxylation study, it gives a result of 64.5% TAN reduction.

On the other hand, a study that involving supercritical water (SCW) to assist in NAs reduction had been carried out by Mandal et al. the ability of SCW to reduce TAN is explored at temperatures from 400 to 490°C and water partial pressures (WPPs) from 0 to 45 MPa (As shown in the figure 2.1 above). At temperature of 490°C, WPPs of 45 MPa and reaction time of 90 minutes, this study revealed the TAN reduction of 83% (Mandal et al., 2012). The TAN removal in this research followed the first order kinetics, with Arrhenius parameters of activation energy 66 ± 4 kJ/mol and a pre-exponential factor $(1.4 \pm 0.2) \times 10^5\ s^{-1}$. There also solid deposition in this study, but it is drastically reduced at WPP of 45 MPa. Overall outcome from this study suggest that SCW is capable to reduce TAN in NAs without consuming any catalyst.

Furthermore, the last technique that will be included is the esterification method. Esterification can be done both with catalyst and without catalyst. For catalytic esterification, a study did by Wang et al. utilizing the methanol as alcohol and $SnO\text{-}Al_2O_3$ as the catalyst. The experimental results demonstrated that a high reaction temperature and a low space velocity promote esterification. For a continuous fixed-bed reactor, the optimum reaction conditions are determined to be a methanol to oil ratio of 2 wt. %, a reaction temperature of 300 °C and a space velocity of 2.5 h^{-1}. The total acid number of the crude oil is reduced from 2.8 mg KOH/g NA to a value below 0.5 mg KOH/g NA (Wang et al., 2014). This study presents a higher conversion and reaction rate at lower reaction temperatures and with less methanol consumption.

Last but not least, another esterification study carried out by Mandal et al. but this study is without the use of catalyst. In this study, same alcohol used which is methanol but the experiment performed at supercritical condition. The ability of supercritical methanol to reduce the TAN is explored at temperature range 300 to 350°C (as shown in the figure 2.2 above). From this study, the outcome presents that TAN reduction is 99.77% at reaction temperature of 350°C, methanol partial pressure of 10 MPa and reaction time of 60 minutes (Mandal et al., 2013). This reaction shows that TAN reduction follow first order kinetics, with Arrhenius parameters of activation energy 5.78 kcal/mol and a pre-exponential factor of 1.56 s^{-1}. From this study, it can be conclude that TAN reduction is very efficient through esterification method with no use of catalyst. The summary of the literature review which compares the methods to reduce the TAN is attached in the **Appendix I**.

2.2 Peng-Robinson Equation

The amount of methanol loaded into the reactor was moderated to control methanol partial pressure at constant temperature and reactor volume. The well-known Peng-Robinson equation of state will be used to compute the amount of methanol by fixing the temperature and methanol partial pressure. The Peng-Robinson equation is as follows (Wolfram Alpha, 2015):

$$P = \frac{RT}{V-b} - \frac{a\,(T)}{V^2 + 2bV - b^2} \tag{1}$$

The values of a and b can be calculated from a different formula using critical temperature and pressure. Hence, the volume of methanol can be calculated with the value of pressure, a, b and constant, R.

CHAPTER 3

METHODOLOGY

3.1 Materials and Equipment

The model compounds; 2,6 – naphthalene dicarboxylic acid ($C_{12}H_8O_4$) used for the experiment will be purchased from Avantis Laboratory Supply and used as received without further treatment. Methanol, toluene, 2-propanol, n,n–dimethylacetamide, potassium hydroxide (KOH) and phenolphthalein are some other chemical needed in this experiment.

All the experiments will be carried out in an autoclave reactor (as shown in figure 3.1 below) which is available in University Technology PETRONAS (UTP) and it could sustain a maximum temperature of 230℃ and maximum pressure of 3 MPa. Pipette, burette and clamp also needed for titration. GC-FID used later to analyze the results quantitatively.

Figure 3.1 Hydrothermal autoclave reactor with Teflon chamber

3.2 Experimental Procedures

The composition of the model compound and the subcritical methanol will be 1:26 ratio. The amount of methanol loaded into the reactor was moderated to control methanol partial pressure at constant temperature and reactor volume. The well-known Peng-Robinson equation of state will be used to compute the amount of methanol by fixing the temperature and methanol partial pressure. For the all the samples the composition will be fixed while the temperature and reaction time will be the manipulative parameters.

For the mixture of 2,6 – naphthalene dicarboxylic acid and subcritical methanol, the samples will be reacted under 180°C to 220°C with a temperature interval of 20°C. The reaction time tested for the mixture is from 0 minutes to 60 minutes with a time interval of 10 minutes. After a specific reaction time, the reactor will be removed and cooled in an ice bath. The reactor will be opened and the sample needs be separated for both titration and analytical testing. The overall experimental procedure can be concluded as Figure 3.2 below.

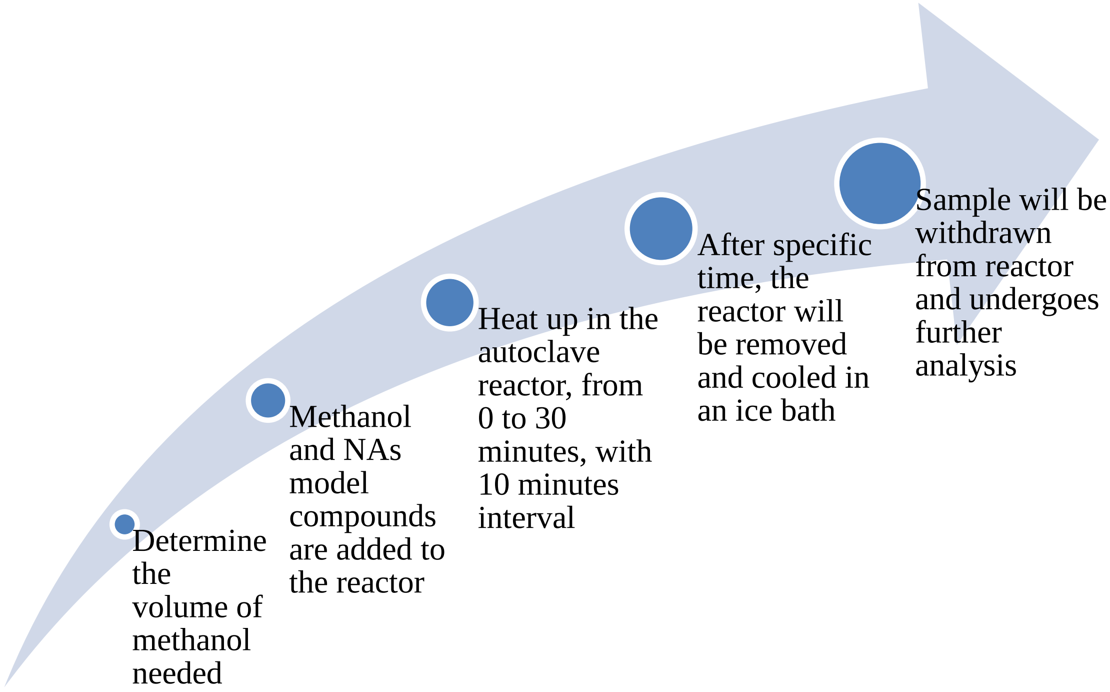

Figure 3.2 Experimental procedures for this project

3.3 Sample Testing

3.3.1 ASTM D 974 – Titration Method

Mahajan et al. showed that the ASTM D 974 method has a good accuracy compared to ASTM D 664 method; thus, the D 974 method is utilized in this project, but phenolphthalein is used as indicator instead of p-naphtholbenzein. Once the sample is collected from the autoclave rector, it will be titrated with 0.05 M potassium hydroxide (KOH) to estimate the TAN by using the equation (2). Then, it will be further calculated the TAN reduction by utilizing the equation (3).

The formula to calculate the TAN in any substance is as follows (Mandal et al., 2013):

$$TAN\left(\frac{mg\ KOH}{g\ NA}\right) = \left[\frac{V_{KOH} \times N_{KOH} \times CF}{W_{NA,0}}\right] \tag{2}$$

Where:
V_{KOH} = volume of KOH in mL,
N_{KOH} = concentration of KOH in mmol/mL,
$W_{NA,0}$ = weight of loaded NA in g
CF = conversion factor = 56.10mg/mmol.

The reduction of acidity of naphthenic acid in a substance can be calculated as follow (Mandal et al., 2013):

$$\text{TAN reduction (\%)} = \frac{\text{TAN}_0 - \text{TAN}_\text{t}}{\text{TAN}_0} \times 100 \tag{3}$$

Where:
TAN_0 = initial TAN in loaded NA
TAN_t = TAN at reaction time

3.3.2 Quantitative Analysis

A part from titration methods, a portion of the sample collected from the autoclave reactor will be analyzed for quantitative analysis utilizing the following methods:

- Gas chromatography – flame ionization detector (GC-FID)
  This method will be used to quantify the composition of the reaction mixture (quantitative analysis). The GC-FID used is from Shimadzu GC-2010 which available in UTP.

For GC-FID analysis, the columns and temperature programs used are as follow:

Table 3.1 Temperature program for GC-FID

No	Parameter	Value
1.	Type of Column	SGE BP-1
2.	Carrier Gas	Helium
3.	Injection Mode	Split
4.	Split Ratio	50
5.	Injection Temperature	300°C
6.	Oven Initial Temperature	50°C

Upon identifying and the quantifying the reaction products using analytical method, an empirical rate of reaction will be developed and the reaction order for the NA model compounds will be determined.

3.4 Gantt Chart and Key Milestone

Table 3.2 Gantt chart and key milestone of this project for FYP I

ACTIVITIES	FINAL YEAR PROJECT I													
	WEEKS													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Introductory Lecture with The Coordinator	■													
Selection of Project Title		■												
First Meeting with Supervisor		■												
Literature Review			■	■	■	■	■							
Selection of Model Compound				■	■									
Selection of Methodology						■	■							
Prepare and Submission of Extended Proposal							■ ✺							
Preparation of Proposal Defense								■	■					
Proposal Defense									■ ✺					
Experimental Work Commences										■	■	■	■	■
Preparation of Interim Draft Report											■	■		
Submission of Interim Draft Report												■ ✺		
Completion and Submission of Interim Report													■ ✺	

✺ = Key milestone of the project

Table 3.3 Gantt chart and key milestone of this project for FYP II

ACTIVITIES	FINAL YEAR PROJECT II													
	WEEKS													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sample Testing			▨	▨	▨	▨	▨							
Preparation and Submission of Progress Report							▨ ✳							
Analyzing the results							▨	▨	▨					
Pre-SEDEX										▨ ✳				
Preparation and Submission of Draft Final Report											▨			
Completion and Submission of Project Dissertation (Soft Bound)												▨ ✳		
Preparation and Submission of Technical Paper												▨ ✳		
Preparation for Viva													▨ ✳	
Completion and Submission of Project Dissertation (Hard Bound)														▨ ✳

✳ = Key milestone of the project

CHAPTER 4

RESULT AND DISCUSSION

4.1 Initial Total Acid Number (TAN_0) Calculation

Before reacting the mixture of naphthenic acid model compound and methanol in the furnace, first the initial TAN number (TAN_0) need to be make known. This TAN_0 is required in order to calculate the TAN reduction later. To calculate the initial TAN, the same procedure is applied. But, instead of reacting the 2,6 – naphthalene dicarboxylic acid with methanol, just the 2,6 – naphthalene dicarboxylic acid mixed with solvent (toluene and 2-propanol with 1:1 ratio) be titrated against 0.05 M KOH solution.

Table 4.1 Initial Total Acid Number (TAN_0) calculation

No	Parameter	Reading 1	Reading 2	Reading 3
1.	Amount of $C_{12}H_80_4$ (g)	0.51	0.50	0.50
2.	Amount of Solvent (ml)	15.00	15.00	15.00
3.	Volume of KOH (ml)	4.65	4.60	4.70
4.	Average volume of KOH (ml)	4.65		
5.	**Initial TAN_0 (mg KOH/g NA)**	**26.09**		

In order to obtain the as accurate as possible result of initial TAN, the titration being conducted for three times and the average result is calculated. Three different volume of KOH obtained through the three separated experiments, the average result of volume of KOH is considered to calculate the initial TAN. The initial TAN calculated is 26.09 mg KOH/g NA and used throughout this project.

4.2 Total Acid Number (TAN) Reduction

As mention earlier, samples of mixture of 2,6 – naphthalene dicarboxylic acid and methanol have been prepared, reacted and analyzed. First part of the analysis is to determine the TAN number reduction in the naphthenic acid model compound samples. To calculate the TAN number, the formula (2) and (3) as mentioned in Chapter 3 had been used. The value of initial TAN used is 26.09 mg KOH/g NA as calculated in section 4.1 earlier.

Table 4.2 TAN reduction at different temperatures (°C) and reaction times (t)

Time (min)	Temp (°C)	180	200	220
5	Amount of MeOH (ml)	15	13	11
	Amount of $C_{12}H_80_4$ (g)	0.57	0.50	0.42
	Volume of KOH (ml)	4.80	4.1	3.35
	TAN (mg KOH/g NA)	23.62	23.00	22.37
	TAN reduction (%)	**9.46**	**11.08**	**14.25**
10	Amount of MeOH (ml)	15	13	11
	Amount of $C_{12}H_80_4$ (g)	0.57	0.50	0.42
	Volume of KOH (ml)	4.45	3.75	3.00
	TAN (mg KOH/g NA)	21.90	21.04	20.04
	TAN reduction (%)	**16.06**	**19.37**	**23.21**
20	Amount of MeOH (ml)	15	13	11
	Amount of $C_{12}H_80_4$ (g)	0.57	0.51	0.42
	Volume of KOH (ml)	4.00	3.30	2.50
	TAN (mg KOH/g NA)	19.68	18.15	16.70
	TAN reduction (%)	**24.55**	**30.42**	**36.00**
30	Amount of MeOH (ml)	15	13	11
	Amount of $C_{12}H_80_4$ (g)	0.57	0.50	0.42
	Volume of KOH (ml)	3.80	3.10	2.20
	TAN (mg KOH/g NA)	18.70	17.39	16.70
	TAN reduction (%)	**28.32**	**35.48**	**43.68**
60	Amount of MeOH (ml)	15	13	11
	Amount of $C_{12}H_80_4$ (g)	0.57	0.50	0.42
	Volume of KOH (ml)	3.70	2.80	2.00
	TAN (mg KOH/g NA)	18.20	15.71	13.36
	TAN reduction (%)	**30.21**	**39.79**	**48.80**

Table 4.2 show the amount of methanol used, amount of model compounds of NAs used and volume of KOH used for titration with respect to the reaction temperature and reaction time. From the obtained TAN value and TAN reduction percentage, it is further analyze in form of the graph method to show the trend (Figure 4.1).

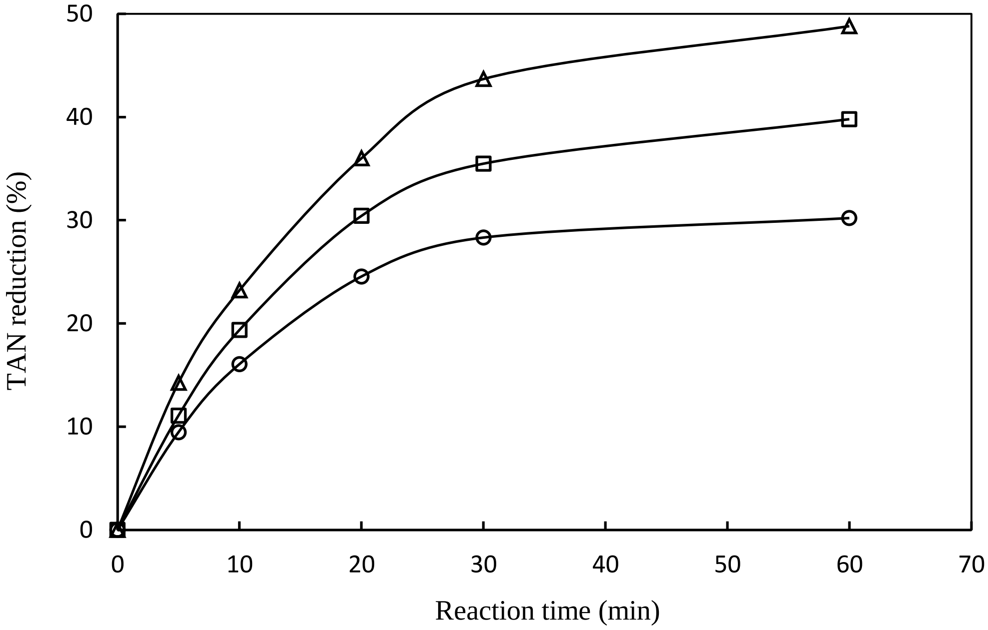

Figure 4.1 TAN reductions at different temperatures and different reaction times (symbols: ○=180°C; □=200°C; Δ=220°C)

In this project, the two manipulated variables are temperature and reaction time. Result can be interpreted in term of temperature, reaction time and overall results. In term of temperature, it is clearly show in the figure 4.1 above that as the temperature increases, the TAN reduction also increases. For each respective reaction time, the higher temperature reaction scheme gives a higher TAN reduction. Theoretically, as the temperature increases, the molecule of methanol and 2,6 – naphthalene dicarboxylic acid move rigorously resulted in more successful collisions and more reaction occurs. Compared to other temperature, at 220°C it gives the highest TAN reduction.

In term of reaction time, the figure 4.1 shows that the higher reaction time gives a higher TAN reduction. Theoretically, as the reaction conducted in longer time, more successful reaction tends to occurs as the system has more time to react. Between 5, 10, 20, 30 and 60 minutes reaction system, the 60 minutes system give the highest TAN reduction. As of the table 4.2 and figure 4.1, the reaction at highest temperature (220°C) and longest reaction time (60 minutes) gives the highest TAN reduction which is 48.80 %. This can be concluded that the TAN reduction is proportional to temperature and reaction time.

4.3 Reaction Kinetics

A reaction kinetics study is required for the reactor design. The reaction order for TAN removal was examined by conducting a series of experiments at temperature of 180, 200 and 220°C under a constant pressure of 1 atm. According to Blauch (2014), the second order reaction is where straight lines obtained from the plots of 1/conc. versus reaction times. In this project, the concentration was defined in term of percentage which obtained from the TAN reduction percentage. Instead of 1/conc. on y-axis, 1/1-x will be used which also indicating the concentration for the model compounds of NAs. Thus, for this project, the plots of 1/1-x versus reaction time were constructed as shown in the figure 4.2 below.

Table 4.3 Parameters of reaction kinetic plot

Time (min)	Temp = 180°C		Temp = 200°C		Temp = 220°C	
	1-x	1/1-x	1-x	1/1-x	1-x	1/1-x
0	1.00	1.0000	1.00	1.0000	1.00	1.0000
5	0.91	1.1045	0.89	1.1246	0.86	1.1662
10	0.84	1.1913	0.81	1.2402	0.77	1.3023
20	0.75	1.3254	0.70	1.4372	0.64	1.5625
30	0.72	1.3951	0.65	1.5499	0.56	1.7756
60	0.70	1.4329	0.60	1.6609	0.51	1.9531

Table 4.3 gives the parameters needed to construct the reaction kinetic plots which are 1/1-x and reaction time. Since mentioned before that the concentration in this project will be in term of percentage, 1/1-x instead of 1/conc. will be used.

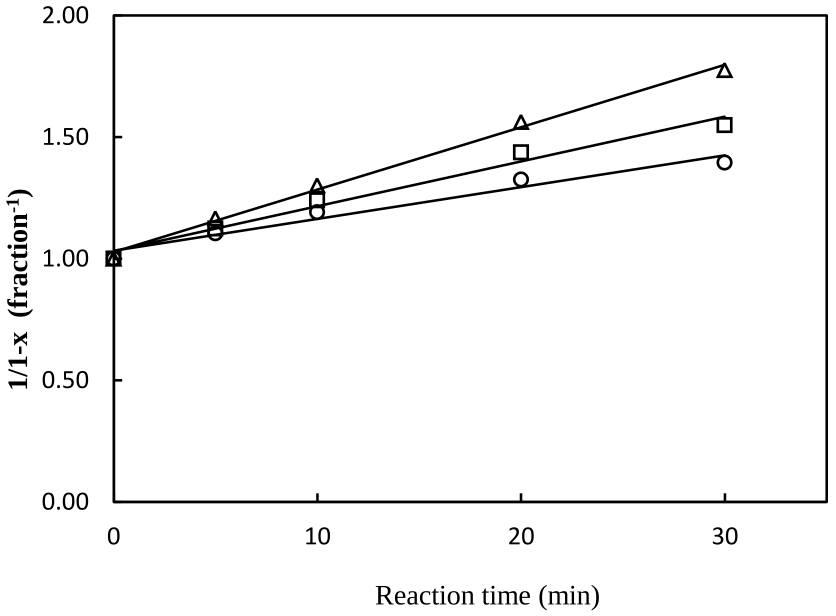

Figure 4.2 Plots of 1/1-x versus reaction time with respect to different temperature (symbols: ○=180°C; □=200°C; Δ=220°C)

A series of straight lines obtained with the least squares method pass almost exactly through line x = 1 on the y-axis, indicating second order kinetics. To verify the second order kinetics of TAN reduction of 2,6 – naphthalene dicarboxylic acid, only the results from 0 to 30 minutes had been used. This is because at this range of time, it's the ideal and accurate time to determine the kinetic of a chemical reaction. The ratio of 2,6 – naphthalene dicarboxylic acid to methanol used have been fixed in this experiment which is 1:26. Based on figure 4.2, this directly indicates that the rate constant is almost independent of NAs concentration and only depends on temperature.

Table 4.4 Rate constant (k) obtained from figure 4.2

Temperature (^{0}C)	Temperature (K)	1000/T (K^{-1})	k Value	ln k
180	453	2.207505519	0.0131	-4.33514
200	473	2.114164905	0.0184	-3.99540
220	493	2.028397566	0.0257	-3.66126

From the figure 4.2, the gradient of each straight line indicate the rate constant *k*, at different temperature. The gradient obtained then tabulated in the table 4.4 above. It is later used to construct the Arrhenius plot (as shown in the figure 4.3 below).

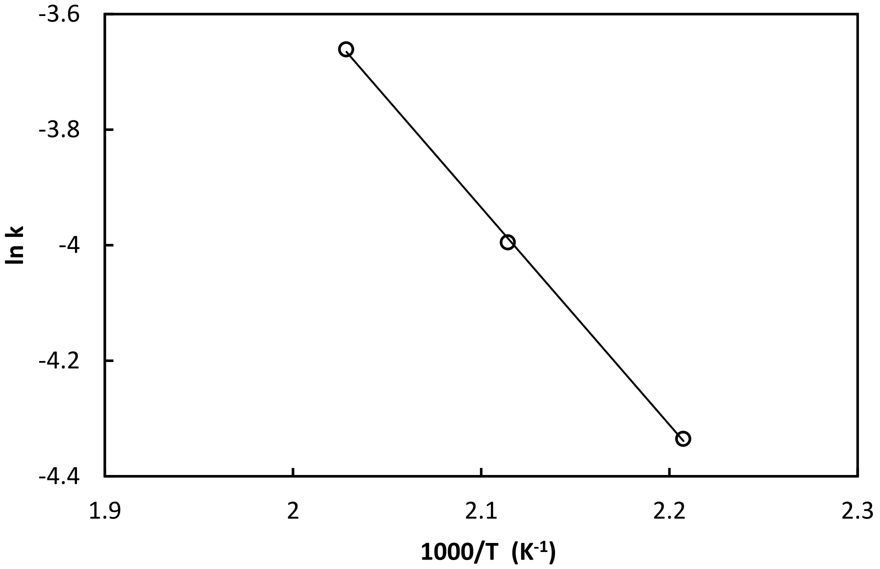

Figure 4.3 Arrhenius plot

Figure 4.3 shows the Arrhenius type dependency of model compounds of NAs removal rates on temperature. From the obtained gradient and y-axis intercept, the Arrhenius pre-exponential factor, *A* and the activation energy for this experiment can be obtained. The calculation is as follow:

$$k = A\, e^{-\frac{E_a}{RT}}$$

$$ln\, k = ln\, A - \frac{E_a}{RT}$$

$$ln\,k \;=\; -\,\frac{E_a}{1000R}\frac{1000}{T} +\; ln\,A$$

From the graph, $\text{y} \;=\; \text{mx} + \text{c}$

Given $\text{R} \;=\; 1.987\;\; \text{cal/mol.K}$

$$m \;=\; -\,\frac{E_a}{1000R} \;=\; -3.7606$$

$$E_a \;= 3.7606(1000R) = \;\; 3.7606(1000)(1.987)$$

$$E_a \;=\; 7472.31 \;\; \text{cal/mol} \quad\; \approx \quad 7.472\,\text{kcal mol}^{-1}$$

$$c \;=\; ln\,A \;=\; 3.9628$$

$$A \;=\; e^{3.9628} \;=\; \frac{52.6}{\text{fraction. min}} \;\times\; \frac{1\text{ min}}{60\text{ s}} \;=\; 0.877\;\; \text{fraction}^{-1}\text{s}^{-1}$$

Thus,

$$k \;=\;\; 0.877\, e^{-\frac{7472.31}{RT}} \;\; \text{fraction}^{-1}\text{s}^{-1}$$

The activation energy and pre-exponential factor discovered on the basis of Arrhenius equation were 7.472 kcal/mol and 0.877 fraction^{-1}.s^{-1} respectively. The sub-critical methanol acts as reaction media and also reactant during the reaction with 2,6 – naphthalene dicarboxylic acid. The reactions which can be considered at high temperature help to accelerate the esterification reaction because the methanol become non-polar and has enhanced its contact with 2,6 – naphthalene dicarboxylic acid at the sub-critical condition. The reaction in sub-critical condition which at quite high temperature help to lower the activation energy and allow for occurring spontaneous reaction. This is based on Arrhenius theory that reaction at high temperature and pressure, it is sufficient to reduce the energy barrier and allow the reaction to undergo spontaneously. Thus, in this experiment, the use of methanol in sub-critical condition is clearly able to reduce the activation energy and help to speed up the reaction.

4.4 GC-FID Analysis

As mention earlier, the samples from this experiment also had been analyzed with Gas Chromatography – Flame Ionization Detector (GC-FID). It aimed to identify the concentration in the samples after the reaction between subcritical methanol and the model compounds of NAs itself. Table 4.5 and figure 4.4 show the result of GC-FID analysis.

Table 4.5 Samples concentration obtained from GC-FID analysis

Sample		Area Under Graph	Concentration (g/ml)
Time (min)	Temperature (°C)		
0	180	-	0.0300
10		2243870	0.0231
20		2063458	0.0210
30		1786938	0.0186
0	200	-	0.0300
10		1935348	0.0202
20		1685962	0.0175
30		1426732	0.0153
0	220	-	0.0300
10		1761567	0.0183
20		1562895	0.0159
30		1239663	0.0132

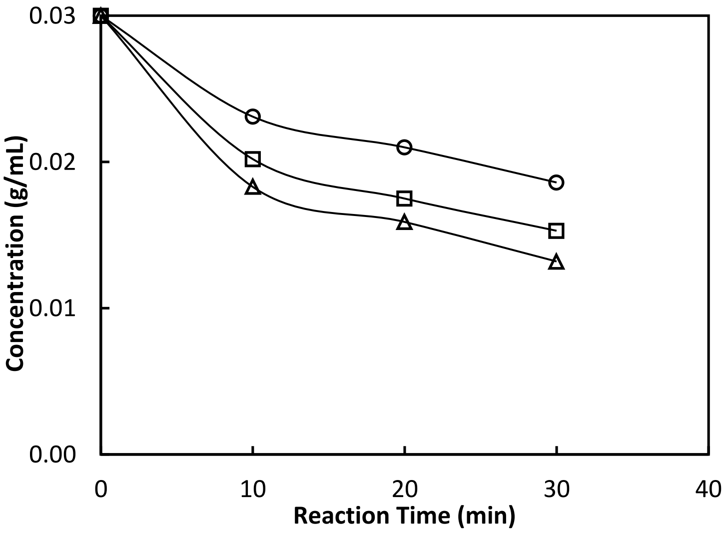

Figure 4.4 GC-FID analysis on TAN reduction of model compounds of NAs (symbols: ○=180°C; □=200°C; Δ=220°C)

This experiment start with concentration of 0.03 g/mL of 2,6 – naphthalene dicarboxylic acid. As move along with the reaction at different time, the concentration of the model compounds of NAs also decreases, this indicate that some molecules of 2,6 – naphthalene dicarboxylic acid have interact with methanol at sub-critical condition to form new components. Each of the samples has been analyzed with GC-FID, the samples graph of GC-FID results can refer to **Appendix II**.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

TAN reduction had been studied to explore the effects of temperature on esterification process between NAs and subcritical methanol in a batch type reactor. For the overall result, the highest TAN reduction 48.80 % which is achieved at temperature of 220°C and 60 minutes reaction time. The TAN reduction followed second order kinetics; with Arrhenius parameters of activation energy 7.472 kcal/mol and a pre-exponential factor of 0.877 fraction^{-1}s^{-1}. To sum up, it is proven that the sub-critical methanol is another alternative way to reduce the total acid number (TAN) in crude oil.

5.2 Recommendation

- ✓ Instead of running experiment at maximum of 60 minutes reaction time, this project can further been tested at longer reaction time up to 90 minutes or 120 minutes to allow more reaction to occur.
- ✓ The further research can be conducted using pure naphthenic acids or other naphthenic acid model compounds to further understand the reaction mechanism of TAN reduction in crude oil.
- ✓ The furnace used for this experiment comes with large heating power, the overshoot temperature when running this experiment is quite high up to 40°C differences from the set temperature before it soak. Thus, lower heating power furnace is recommended for further research of this project.

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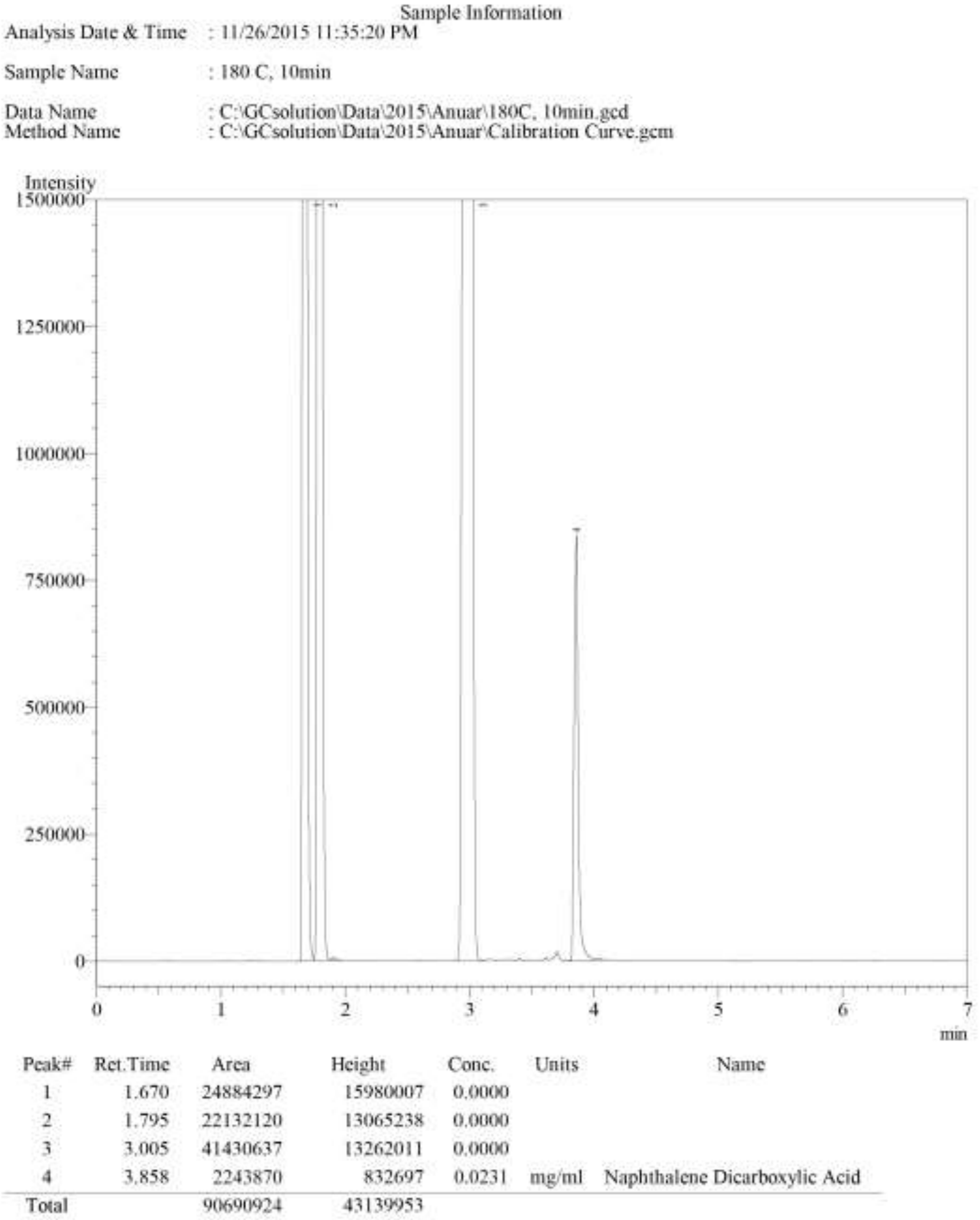
Appendix I: Summary of Literature Review

No	Authors	Year	Operating Condition	Findings	Remarks
1.	Zhang et al.	2006	Catalytic decarboxylation on magnesium oxide (MgO) - Conducted with the in-line flow reactor, catalyst (28–60 mesh) loaded into the tubular reactor, crude oil (additional 2.0 wt.% cyclohexane pentanoic acid - CHPA) was filled in the transfer tank with flow rate was set at 6 ml/h, IR adsorption was monitored as a semi-quantitative estimate of the effectiveness of the catalyst - Temp : 150 - 300°C - Duration : 2 - 6 hours	Result obtained through ASTM standard method D664 (titration) - TAN removal : 64.5% - temp : 300°C - reaction time : 3 hours	- TAN removal low, less than 90% - reaction at high temp, high cost equipment needed - quite long reaction time needed to max TAN removal (only 64.5%) - need to consider the cost of catalyst preparation also
2.	Mandal et al.	2012	TAN reduction using supercritical water (SCW) - a calculated mass of NAs and known amount of water is feed to batch reactor, then placed in oven at desired temp - product then withdrawn from oven and perform titration against prepared solution, a few part of products analyzed using GC-MS and GC-FID - Temp : 400 – 490°C,	Analyzed using ASTM D974 - TAN removal : 83% at temp 490°C, WPP 45MPa, reaction time 90 min - follow 1st order kinetics, Ea = 66 ± 4 KJ/mol A = (1.4 ± 0.2) x 10^5 s^{-1} Tc = 374°C Pc = 22.1 MPa	- TAN removal still less than 90% - reaction at high temp, need high temp equipment and high energy

			- water partial pressures (WPPs) : 0 – 45 MPa - no catalyst/additives		
3.	Mandal et al.	2013	TAN reduction using supercritical methanol (SC-MeOH) - a calculated mass of NAs and known amount of water is feed to batch reactor, then placed in oven at desired temp - product then withdrawn from oven and perform titration against prepared solution, a few part of products analyzed using GC-MS and GC-FID - Temp : 300 – 350°C, - methanol partial pressures (MPP) : 10 MPa - no catalyst/additives	Analyzed using ASTM D974 - TAN removal : 99.77% at temp 350°C, MPP 10MPa, reaction time 60 min - follow 1st order kinetics, Ea = 5.78 kcal/mol A = 1.56 s^{-1} Tc = 239.63°C Pc = 8.08 MPa ρc = 277.49 kg/m^3	- reaction occur at high temp, cost will be main factor due to high temp equipment and high energy needed
4.	Wang et al.	2014	NAs removed by catalytic esterification with methanol ($SnO–Al_2O_3$ as catalyst) - Crude oil and methanol were pre-mixed, then pumped into the fixed bed reactor and heated to the reaction temperature, products were collected to be analyzed - reaction temp : 180 – 360°C - space velocity : 1 – 4 h^{-1} - methanol to oil ratio: 1 – 2 wt%	Result obtained through ASTM standard method D664 (titration) - TAN removal : 82.14% - reaction temp : 300°C - space velocity : 2.5 h^{-1} - methanol to oil ratio of 2 wt%	- TAN removal just roughly 80% - need high temp reaction to obtain max TAN removal - expensive catalyst

5.	Sohaimi et al.	2014	Catalytic neutralization of acidic crude oil utilizing ammonia in ethylene glycol basic solution - normal acid-base neutralization method - types of crude used: Crude A : Heavy crude from PPM Crude B : Light crude from PPM Crude C : Korean crude - ammonia solution in ethylene glycol : 100, 500 and 1000 mg/L - reaction temp : 35 – 40°C - types of catalyst : Mg, Ba and Ca - catalyst calcination temp : 400, 700 and 900°C	Result obtained through ASTM standard method D664 (titration) Crude A: - TAN removal : 67.4% - Catalyst : Ca (900°C cal-temp) Crude B - TAN removal : 71.2% - Catalyst : Ba & Ca (900°C) Crude C - TAN removal : 78.7% - Catalyst : Ba & Ca (900°C)	- TAN removal low, not even exceed 90% - used of costly catalyst - very high calcination temp (catalyst preparation) will cause high equipment cost
6	Shukri	2015	Removal of NAs from high acidity Korean crude oil utilizing catalytic deacidification method - catalyst : CeO, ZnO and SnO based catalysts supported onto alumina - ammonia solution in ethylene glycol : 100, 500 and 1000 mg/L - reaction temp : 35 – 40°C - catalyst calcination temp : 700, 1000 and 1100°C	Result obtained through ASTM standard method D664 (titration) - TAN removal : 93.3% - Catalyst : CeO - calcination temp: 1000°C - reaction temp : 35 – 40°C	- TAN removal low, not even exceed 90% - used of costly catalyst - very high calcination temp (catalyst preparation) will cause high equipment cost

Appendix II: Graph of GC-FID



Sample Information

Analysis Date & Time : 11/26/2015 11:35:20 PM

Sample Name : 180 C, 10min

Data Name : C:\GCsolution\Data\2015\Anuar\180C, 10min.gcd
Method Name : C:\GCsolution\Data\2015\Anuar\Calibration Curve.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	1.670	24884297	15980007	0.0000		
2	1.795	22132120	13065238	0.0000		
3	3.005	41430637	13262011	0.0000		
4	3.858	2243870	832697	0.0231	mg/ml	Naphthalene Dicarboxylic Acid
Total		90690924	43139953			