Kinetics and Reaction Pathways of Naphthenic Acids Model Compound Reaction with Subcritical Methanol for Total Acid Number Reduction

by

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16847

Dissertation submitted in partial fulfilment of

the requirements for the

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MAY 2015

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CERTIFICATION OF APPROVAL

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Approved by,

……………………………………….
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UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
MAY 2015

CERTIFICATION OF ORIGINALITY

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

(THASVINYA A/P NAGARAJAN)

ABSTRACT

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). This paper studies on the reaction mechanism of naphthenic acids model compound upon reacting with subcritical methanol. It also discusses further on the kinetics and reaction pathways of the model compounds of naphthenic acids after reacting with subcritical methanol. Crude oil containing these acids which are corrosive can cause many problems such as equipment failures, high maintenance cost, reduce product quality and environmental disposal problems. The model compound; cyclopentane carboxylic acid with a molecular structure of $C_6H_{10}O_2$ and $z = -2$ will be tested with subcritical methanol under temperature range from 180℃ to 220℃ with a temperature interval of 20℃ in 25 ml hydrothermal autoclave reactor. The reaction time for the mixture is from 10 min to 30 min with a time interval of 10 min. 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. From this experiment, the highest TAN reduction is achieved at 220℃ and 30 minutes where the reduction is about 17.56%. Upon the reaction, the components present in the sample were identified through GC/MS analysis. Reaction pathways for each sample is identified and there are production of ester, alcohol and alkene. From the results obtained, it is proved that the reaction is first order kinetics and independent with concentration. The value of activation energy obtained through the Arrhenius plot is 59.8966 J/mole-K and the value of pre-exponential factor, A is 260.05 s^{-1}. This shows that subcritical methanol able to lower the reaction activation energy and also increases the speed of reaction. To sum up, it is proven that the subcritical methanol is an effective way to reduce the total acid number in crude oil.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

Naphthenic acids (NAs) are water soluble weak acids (Dalmia, 2013) and are a complex group of alkyl-substituted acyclic, monocyclic and polycyclic carboxylic acids (Vaiopoulou *et al.*, 2015). The general chemical formula of naphthenic acid is $C_nH_{2n+z}O_2$, where n is the carbon number, z is referred to as hydrogen deficiency, is a negative even integer and is the number of hydrogen atoms that are lost as the number of rings in naphthenic acid increases. For a given z homolog, there are more than one isomer exists and the molecular weights differ by 2 mass units (H_2) between z-series and by 14 mass units (CH_2) between n-series. The number of possible naphthenic acids, with the same molecular composition, are 134 with n ranging from 6 to 30 and the number of saturated rings ranging from 0 to 6 (Dalmia, 2013).

Naphthenic acids are the primary contributor to the total acid number of the oil (Wang, Li, *et al*., 2014) and it can be expressed in terms of total acid number (TAN) (Mandal *et al*., 2013). TAN is a measurement of acidity that is determined by the amount of potassium hydroxide in milligrams that is needed to neutralize the acids in one gram of oil (Anderson *et al*., 2015). The formula to calculate the TAN in any substance is as follows:

$$\mathrm{TAN}\left(\frac{\mathrm{mg\ KOH}}{\mathrm{g\ NA}}\right) = \left[\frac{\mathrm{V_{KOH}\ x\ N_{KOH}\ x\ CF}}{\mathrm{W_{NA,0}}}\right] \text{(Mandal \textit{et al}., 2013)} \qquad (1)$$

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 and CF = conversion factor = 56.10mg/mmol. The reduction of acidity of naphthenic acid in a substance can be calculated as follow:

$$\mathrm{TAN\ reduction\ (\%)} = \frac{\mathrm{TAN_0 - TAN_t}}{\mathrm{TAN_0}} \mathrm{x\ 100} \text{ (Mandal \textit{et al}., 2013)} \qquad (2)$$

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

High TAN crude oils demonstrates a high density, high viscosity, high content of residue, high total acid number and a high amount of carbon residue (Wang, Li, *et al.*, 2014). Crude oil containing these acids 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). 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 under this condition. Therefore, the crucial problem that facing by the oil refineries is to find the right method to remove or reduce the acidic substances from petroleum (Wang, Li, *et al.*, 2014).

There are few methods that have been tried to resolve this problem such as solvent extraction, adsorption and hydrogenation but none of the method can completely remove the naphthenic acids (Wang, Li, *et al.*, 2014). At present, the deacidification of crude oils can be achieved by destroying the carboxyl group in the acid via esterification, hydrogenation and thermal decomposition (Wang, Zhong, *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. Naphthenic acids are the main contributor to the total acid number of the crude oil and as the temperature increases during oil refining, they can lead to serious corrosion to the processing equipment. The corrosion in high temperature regions within refinery is normally around the crude and vacuum towers (Johnson *et al.*, 2003). Apart from that, these naphthenic acids may cause emulsification during the refining process which makes it hard to separate water from the oil and reduces the oil yield. Moreover, thermal stability also can be affected due to the presence of these acids (Wang, Li, *et al.*, 2014). As a consequence, crude oils with high TAN content are often marketed at a lower market price (Shukri *et al.*, 2014). Hence, it is essential to reduce or remove the naphthenic acids in the crude oil.

There are many existing ways to remove naphthenic acids. However, the current methods require a large investment in equipment, large amount of solvent, high energy consumption and other weaknesses. From these problems, it can be assumed that there is no any effective method to overcome the high TAN in crude oil. From the research on this area of study, it is found that supercritical methanol able to reduce the total acid number (Mandal *et al*., 2013). Thus, the main interest of this paper is to study the kinetics and reaction pathways for one model compounds of NA decomposition using subcritical methanol.

Apart from that, there is no experiment being conducted with the model compound of naphthenic acids; cyclopentane carboxylic acid with subcritical methanol. By carrying this study, it can be found whether decomposition of NA model compound using subcritical methanol can be an effective technique or not.

1.3 Objectives

The objectives of this project are:

i. To investigate the effect of subcritical methanol on the total acid number (TAN) reduction using model compound of naphthenic acids.
ii. To determine the reaction mechanism of naphthenic acids model compound upon reacting with subcritical methanol.
iii. To study the kinetics and reaction pathways of the model compound of naphthenic acids.

1.4 Scope of Study

In the time duration of 28 weeks, experiment will be conducted to study the kinetics and reaction pathways for the one model compound of naphthenic acids; cyclopentane carboxylic acid ($C_6H_{10}O_2$). The model compound will be tested using subcritical methanol at a temperature range of 180℃ to 220℃ which is below the critical temperature where the compound will be in liquid state. Figure 1.1 shows the general phase diagram of a single simple substance. The critical temperature and pressure of methanol is 239℃ and 78.5 atm (Methanex, 2014). Thus, the experiment will be conducted below the critical temperature and pressure.

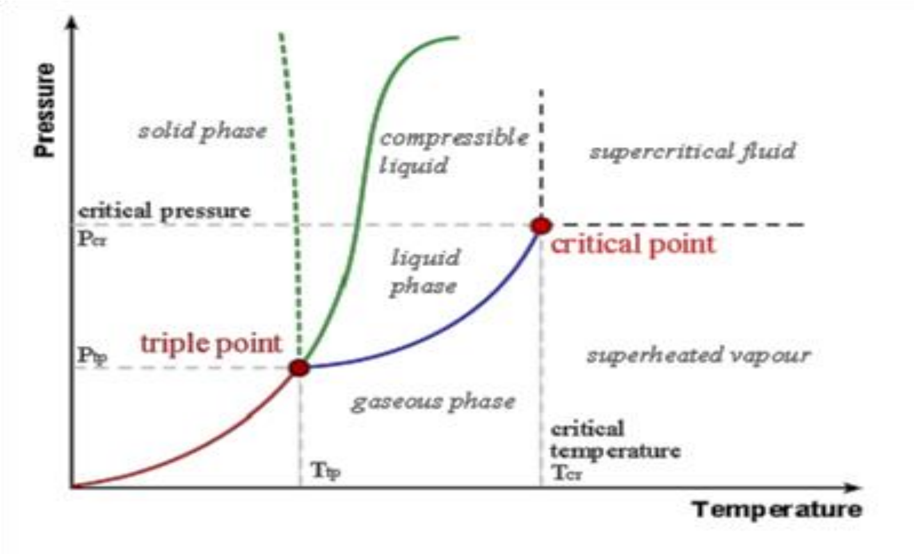


FIGURE 1.1. A general phase diagram (Methanex, 2014)

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 gas chromatography - mass spectrometry (GC/MS) and gas chromatography - flame ionization detector (GC/FID). In total, there will be 18 samples to be tested and analyse.

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 compounds. 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 analysed. 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 analyse 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

There are few physical method which involves separation of the naphthenic acids from the oil for other purposes such as alkali washing, alcohol and ammonia processing, solvent extraction, adsorption, membrane separation and electrostatic separation. The disadvantage of the physical method are it is easy to blend and have a high energy consumption (Wang, Zhong, *et al*., 2014). Apart from the physical methods, there are few efforts had been done to lowered down the naphthenic acid value in crude oil such as by catalytic decarboxylation addition of caustic, blending, neutralization by caustic addition, blending petroleum crude oils with ionic liquid of ethanol, by adding solid acid catalyst and metal oxide catalyst. Hence, these methods have their own weaknesses that created many complications and lead to high maintenance cost (Shohaimi *et al*., 2013).

One of the method to reduce naphthenic acids in crude oil is catalytic decomposition. According to a study on the catalytic reaction towards reduction of naphthenic acids by (Wang, Zhong, *et al*., 2014), it is stated that the deacidification method by calcium oxide or magnesium oxide catalysts is effective at low temperatures but these catalysts do not improve the catalytic reaction efficiency due to their small surface area and pores. The study was conducted using Mg–Al hydrotalcite/c-Al_2O_3 catalyst which is composed of Mg–Al hydro-talcite and c-Al_2O_3, is a type of layered metal oxide material that possesses a large pore diameter and a large surface area. According to Figure 2.1, it is found that the acid removal of the crude oil increased as the reaction temperature increased and with higher concentration of catalyst. When the catalyst/oil ratio is 0.20(wt), the acid removal is much higher than that of 0.1(wt). From the study, the acid removal is more than 80% for the testing crude oil and the appropriate temperature is from 300℃ to 320℃. Besides, catalytic processes can only be conducted with mild reaction conditions (Mandal *et al.*, 2013).

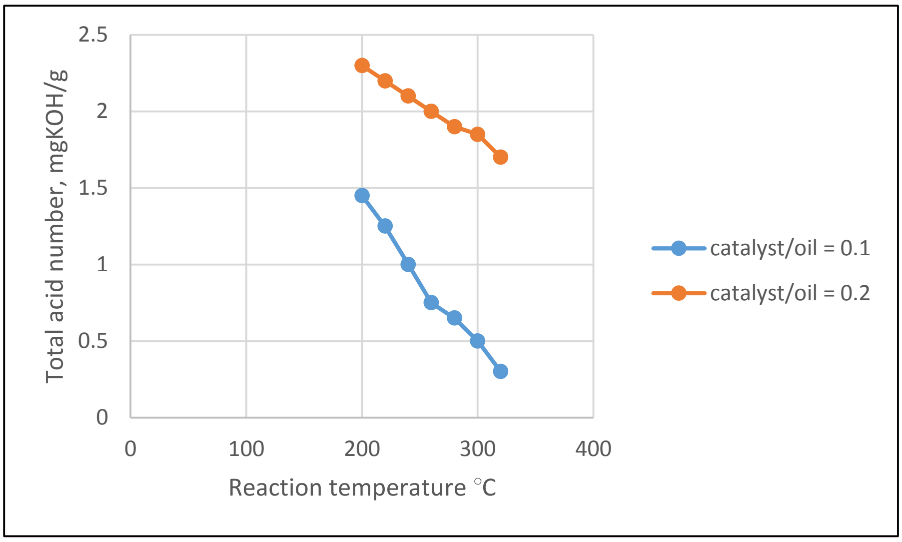


FIGURE 2.1. Effect of reaction temperature (Wang, Zhong, *et al.*, 2014)

Another study was conducted to determine the kinetics of esterification naphthenic acids in Colombian heavy crude oil of high acidity in the absence of a catalyst (Becerra *et al.*, 2012). The tests were conducted at 150, 200 and 250ºC and the reaction time varied between 0 - 600 minutes. The reactor was loaded with 1200 mL of heavy crude and Merck anhydrous methanol at a molar rate of 20:1 alcohol per mol of carboxylic group. A catalyst was not used during this kinetic study. Figure 2.2 shows the conversion results obtained from the esterification reaction of the naphthenic acids. The increase in acid reduction percentage with the increase of temperature indicates that the esterification reaction is endothermic. From the study, the corrosion tests demonstrated a decline of 90.90% in the corrosion rate of carbon steel per ASTM 106 Gr.B, after esterification treatment.

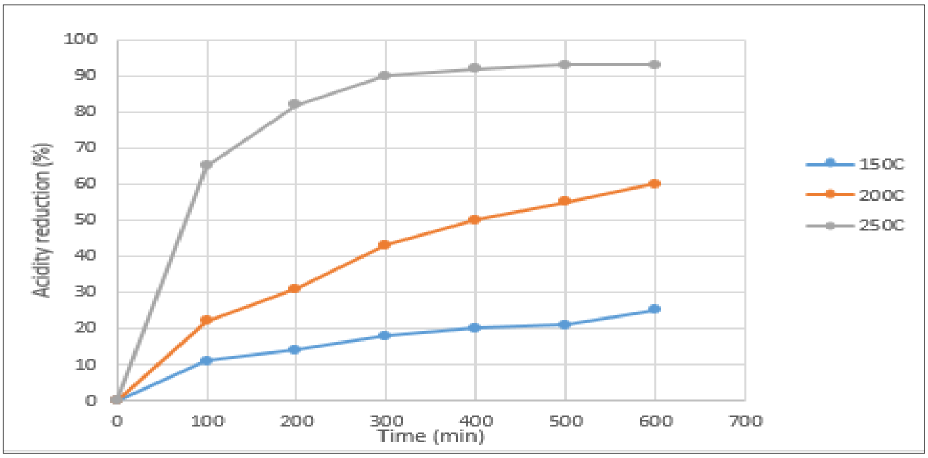


FIGURE 2.2. The effect of temperature on the acidity reduction (Becerra, Jun 2012)

Apart from that, there is another study on the effect of supercritical methanol in reducing total acid number in NAs. The ability of SC-MeOH to reduce TAN was explored at temperatures from 300 to 350°C and methanol partial pressure (MPP) of 10 MPa. Figure 2.3 clearly shows that TAN removal was 99.77% at a temperature of 350°C, MPP of 10 MPa and reaction time of 60 min. The TAN removal followed first order kinetics, with Arrhenius parameters of activation energy 5.78 kcal/ mol and a pre-exponential factor 1.56 s^{-1}. These results suggest that SC-MeOH is capable of reducing TAN from NA with no use of catalyst or additives (Mandal *et al*., 2013).

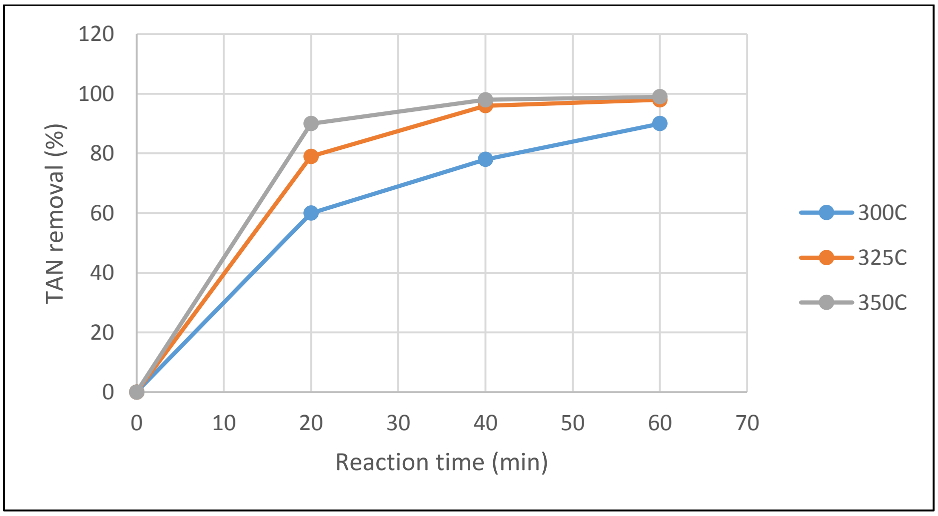


FIGURE 2.3. Variation of TAN as a function of reaction time and temperature at a concentration of 0.068 g/mL (Mandal, 2013)

Followed by with the previous study, methanol was used to remove naphthenic acids but in the aid of catalytic esterification. SnO–Al_2O_3 was used as the catalyst for the esterification of naphthenic acid in crude oil with methanol in a fixed-bed catalytic reactor. The experimental results demonstrated that a high reaction temperature and a low space velocity promote esterification. Apart from considering the reaction temperature, the space velocity was one of the parameter in this experiment. For a continuous fixed-bed reactor, the optimum reaction conditions were 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 was reduced from 2.8 mgKOH/g to a value below 0.5 mgKOH/g which is about 82.14%. The results for this study is clearly shown on the following graph where high temperature is able to reduce the total acid number drastically (Wang *et al.,* 2014)

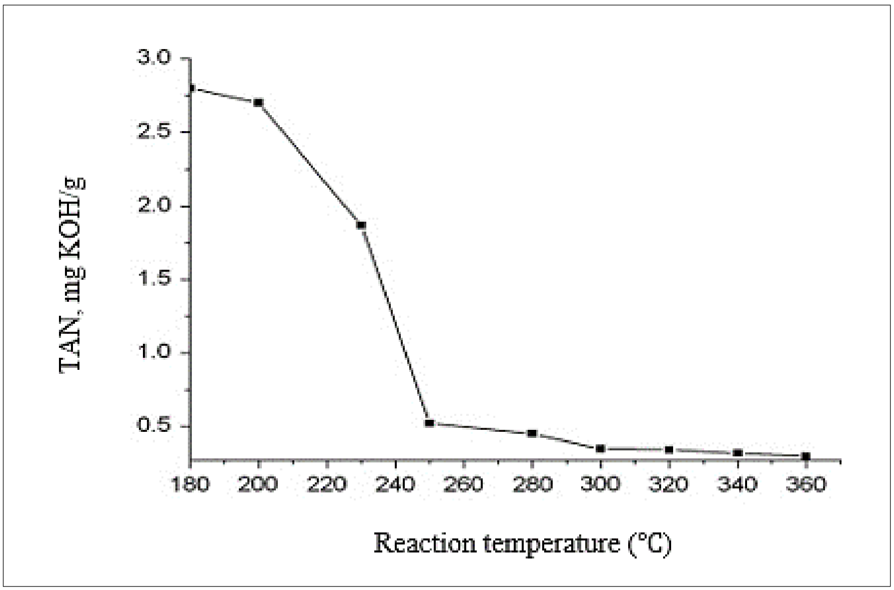


FIGURE 2.4. The effect of temperature on the total acid number (Wang *et al,* 2014)

As the findings from the above studies, it is confirmed that methanol has the ability to reduce the total acid number in naphthenic acids at high temperature which is about 350℃. But, reaction with high temperature and usage of catalyst will lead to high operation cost. Thus, for this research, one model compound of naphthenic acids will be reacted with methanol under temperature range of 180℃ to 220℃ in order to identify the reaction mechanism of the compounds. The summary of the literature review which compares the methods to reduce the TAN is attached in the appendix I.

2.2 Identification of Model Compound in Naphthenic Acid

The model compound of naphthenic acids were chosen based on the general structures of NAs which have different number of rings according to the number of z. Figure 2.5 shows the general structure of naphthenic acids. The model structures help to identify the accurate model compound of naphthenic acids.

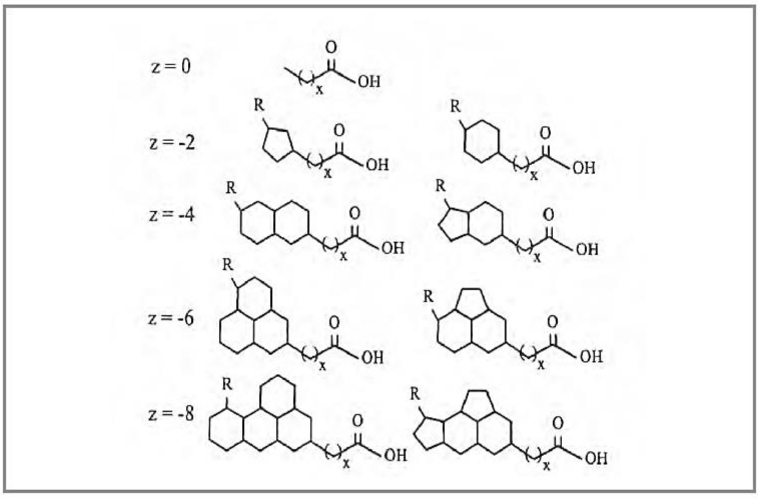


FIGURE 2.5. General structure of naphthenic acids (Dalmia, 2013)

The number of carbon was determined based on Figure 2.6 which shows the retention time of naphthenic acids as a function of n and z in the standard mixture of naphthenic acids (Dalmia, 2013).

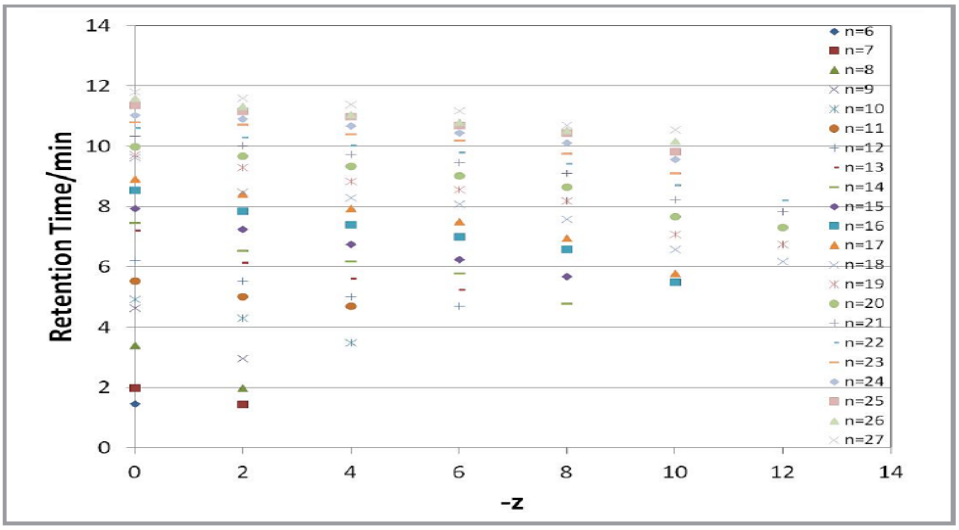


FIGURE 2.6. Retention time of naphthenic acids as a function of n and z (Dalmia, 2013)

The model compound chosen for this project based on the above figure is cyclopentane carboxylic acid ($C_6H_{10}O_2$). Figure 2.7 illustrates the molecular structure and molecular formula of the model compound. Cyclopentane carboxylic acid has one pentyl group with one carboxyl group where z= -2 and n= 6.

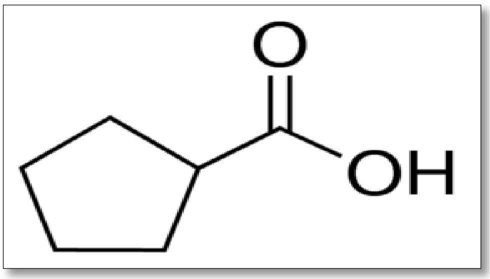


FIGURE 2.7. Molecular structure of cyclopentane carboxylic acid - $C_6H_{10}O_2$ (Sigma Aldrich)

Apart from identifying the model compound from the general structure of NAs, it is also determined by analysing pure naphthenic acid using gas chromatography- mass spectrometry (GC/MS). From the results of GC/MS, cyclopentane carboxylic acid is one of the component in naphthenic acid with a retention time of 6.360 and area percentage of 6.27. It is one of the highest amount of components present in naphthenic acid.

2.3 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:

$$P = \frac{RT}{V-b} - \frac{a\,(T)}{V^2+2bV-b^2} \qquad (3)$$

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 Sample Preparation

3.1.1 Materials

The essential chemical in this experiment is the model compound; cyclopentane carboxylic acid ($C_6H_{10}O_2$). It is a light yellow coloured liquid with a pungent smell. The model compound and other chemicals needed for the experiment were purchased from Avantis Laboratory Supply and used as received without further treatment. Table 3.1 shows the chemicals used in this project.

TABLE 3.1. List of chemicals used for the experiment

NO	CHEMICALS
1	Cyclopentane carboxylic acid
2	Methanol
3	Naphthenic acid
4	Toluene
5	2-Propanol
6	Potassium hydroxide
7	Phenolphthalein

Total of 18 experiments were carried out in a 25ml hydrothermal autoclave reactor with Teflon chamber which was purchased from China. The reactor has stainless steel structure, durable and gas tight. Apart from that, it could sustain a maximum temperature of 230℃ and maximum pressure of 3MPa. Supercritical methanol will need a reactor which can sustain a maximum temperature of 350℃ and this will cause high cost for the project. Hence, the experiments will be proceed with subcritical methanol with a temperature range of 180℃ to 220℃. Figure 3.1 shows the 25 ml Teflon chamber with stainless steel autoclave reactor.

FIGURE 3.1. Hydrothermal autoclave reactor with Teflon chamber

3.1.2 Experimental Procedures

For the all the samples, the composition was fixed while the temperature and reaction time are the manipulative parameters. The concentration of the model compound with the subcritical methanol is 0.08 g/ml. The volume of methanol was calculated using Peng-Robinson equation by fixing the volume of the reactor, temperature and pressure. The pressure was assumed to be low since pressure is not applied in this experiment. For the mixture of cyclopentane carboxylic acid and subcritical methanol at the concentration of 0.08g/ml, the reaction temperature is 180℃ to 220℃ with a temperature interval of 20℃. The reaction time for each mixture is from 5 minutes to 30 minutes. After a specific reaction time, the reactor was removed and certain amount of sample was collected for analytical purposes. The remaining liquid was washed by the solvent; toluene and 2-propanol with a ratio of 1:1. The solution was titrated using phenolphthalein as an indicator in order to determine the total acid number (TAN). The same procedure was repeated for the mentioned temperatures and reaction time. The overall experimental procedures can be concluded as in Figure 3.2.

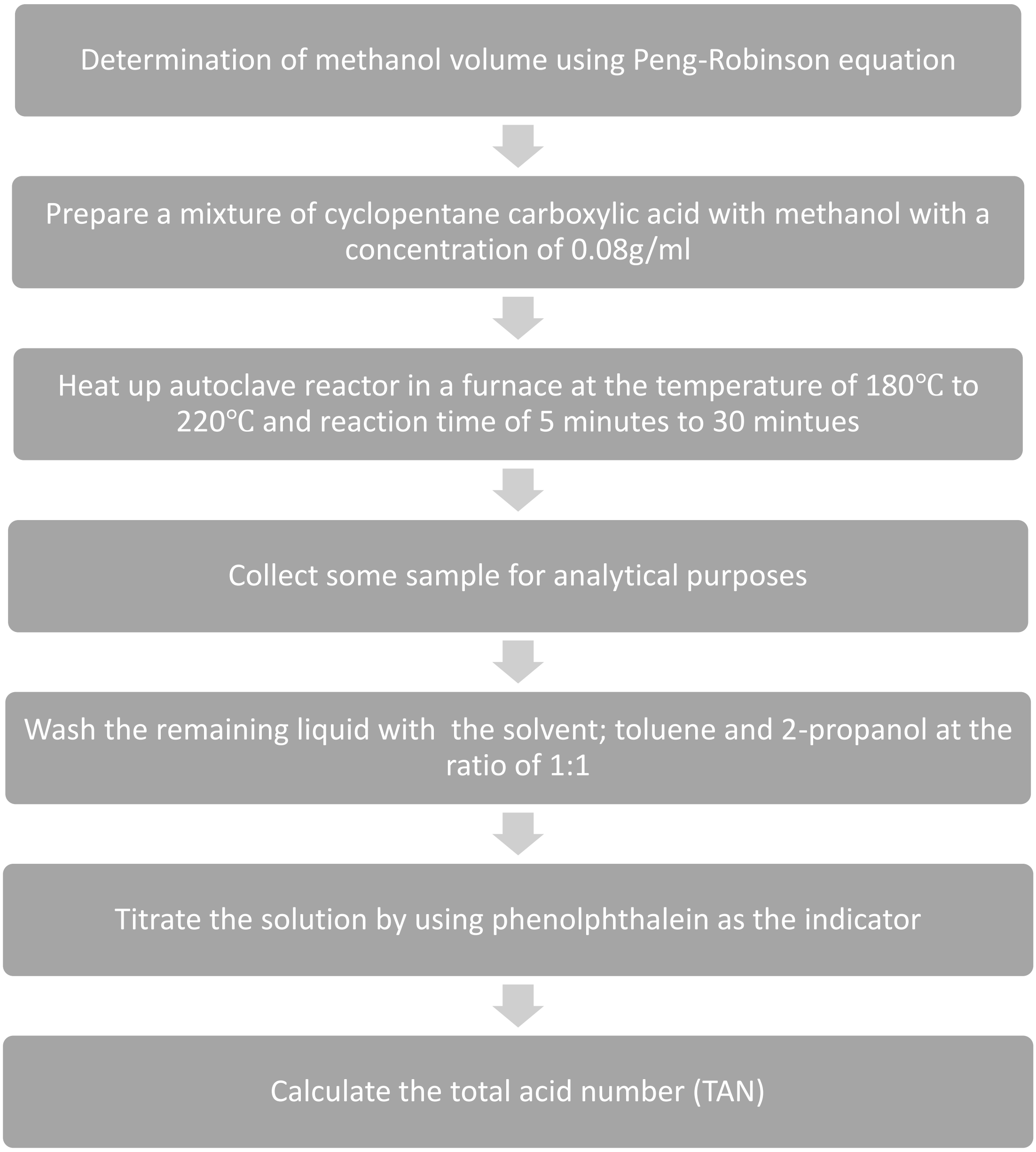


FIGURE 3.2. Experimental procedures of the project

3.2 Sample Testing

All the samples will be analysed using two methods.

i. Gas chromatography – mass spectrometry (GC/MS)
   This method will be used to identify the decomposed components in the reaction mixture. The samples will be tested after acetone is added to it which acts as the reference.
ii. Gas chromatography – flame ionization detector (GC/FID)
   This method will be used to determine the composition of the reaction mixture.

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

3.3 Gantt Chart and Key Milestone

Table 3.2 illustrates the flow of this project for the duration of 28 weeks. Moreover, it also states the key milestones to be achieved for the project.

TABLE 3.2. Gantt chart and key milestone of the project

ACTIVITIES	WEEKS																											
	FINAL YEAR PROJECT 1														FINAL YEAR PROJECT 2													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	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						🟦	🟦																					
Preparation and Submission of Extended proposal								🟦 ◊																				
Preparation of Proposal Defense									🟦	🟦																		
Proposal Defense										◊																		
Experimental Work Commences										🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦										
Preparation of Interim Draft Report												🟦																
Completion and Submission of Interim Report													🟦 ◊															
Sample Testing																	🟦	🟦	🟦	🟦	🟦							

Preparation and Submission of Progress Report																				◊								
Analysing 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

RESULTS & DISCUSSION

4.1 TAN Reduction

Total acid number (TAN) was calculated for all the 18 samples with the formula mentioned in Chapter 1. It was calculated upon each reaction in order to measure the acidity of the sample. Sample which has less TAN means it will cause less corrosion compared to the sample with high TAN. Table 4.1 presents the methanol volume, model compound volume, potassium hydroxide volume and TAN for the 18 samples.

TABLE 4.1. Total acid number (TAN) for the 18 samples

	180 C		**200 C**		**220 C**	
5 min	MeOH (ml)	15	MeOH (ml)	13	MeOH (ml)	11
	$C_6H_{10}O_2$ (ml)	1.2069	$C_6H_{10}O_2$ (ml)	1.0442	$C_6H_{10}O_2$ (ml)	0.88
	KOH (ml)	232	KOH (ml)	202	KOH (ml)	169
	TAN	539.2	**TAN**	542.626	**TAN**	538.688
10 min	MeOH (ml)	15	MeOH (ml)	13	MeOH (ml)	11
	$C_6H_{10}O_2$ (ml)	1.2034	$C_6H_{10}O_2$ (ml)	1.0433	$C_6H_{10}O_2$ (ml)	0.8812
	KOH (ml)	230	KOH (ml)	198	KOH (ml)	164
	TAN	536.106	**TAN**	532.34	**TAN**	522.038
15 min	MeOH (ml)	15	MeOH (ml)	13	MeOH (ml)	11
	$C_6H_{10}O_2$ (ml)	1.2078	$C_6H_{10}O_2$ (ml)	1.035	$C_6H_{10}O_2$ (ml)	0.8802

	KOH (ml)	229	KOH (ml)	192	KOH (ml)	159
	TAN	531.831	**TAN**	520.348	**TAN**	506.697
20 min	MeOH (ml)	15	MeOH (ml)	13	MeOH (ml)	11
	$C_6H_{10}O_2$ (ml)	1.2048	$C_6H_{10}O_2$ (ml)	1.0411	$C_6H_{10}O_2$ (ml)	0.8808
	KOH (ml)	227	KOH (ml)	188	KOH (ml)	154
	TAN	528.499	**TAN**	506.522	**TAN**	490.429
25 min	MeOH (ml)	15	MeOH (ml)	13	MeOH (ml)	11
	$C_6H_{10}O_2$ (ml)	1.213	$C_6H_{10}O_2$ (ml)	1.042	$C_6H_{10}O_2$ (ml)	0.8866
	KOH (ml)	226	KOH (ml)	184	KOH (ml)	149
	TAN	522.613	**TAN**	495.317	**TAN**	471.402
30 min	MeOH (ml)	15	MeOH (ml)	13	MeOH (ml)	11
	$C_6H_{10}O_2$ (ml)	1.2002	$C_6H_{10}O_2$ (ml)	1.0418	$C_6H_{10}O_2$ (ml)	0.8834
	KOH (ml)	220	KOH (ml)	180	KOH (ml)	144
	TAN	514.164	**TAN**	484.642	**TAN**	457.233

Upon calculating the total acid number (TAN) for the 18 samples, TAN reduction was calculated for each sample in order to determine the percentage of acid number reduction after the reaction. It was calculated by substituting the original TAN with TAN after reaction and divided by original TAN. Table 4.2 shows the TAN reduction for each sample after the reaction with subcritical methanol.

TABLE 4.2. TAN reduction for all 18 samples

Reaction time	**TAN Reduction (%)**		
	180 ℃	**200** ℃	**220** ℃
5 min	1.15	1.62	2.87
10 min	1.72	3.49	5.875
15 min	2.50	5.66	8.64
20 min	3.11	8.17	11.57
25 min	4.19	10.2	15.00
30 min	5.74	12.14	17.56

Figure 4.1 depicts the TAN reduction for all 18 samples in term of temperature and reaction time.

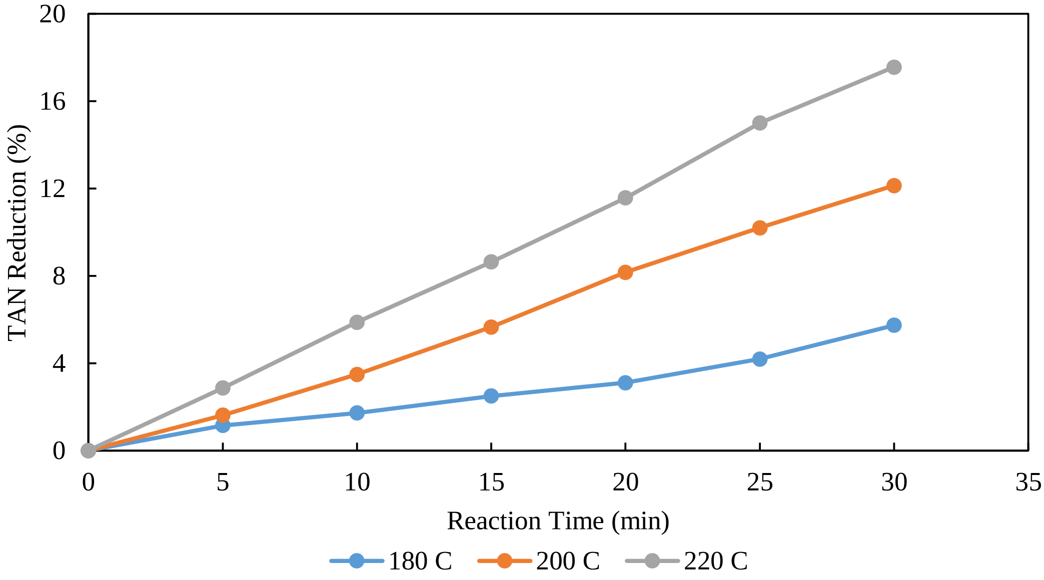


FIGURE 4.1. TAN reduction vs reaction time

The graph explains that total acid number (TAN) reduction increases as the temperature and reaction time increases. As for this experiment, the highest TAN reduction achieved at the temperature of 220℃ and 30 minutes. TAN was able to reduce from 554.6250 to 457.2334 which is about **17.56 %**. This results explains that subcritical methanol is able to reduce the total acid number in crude oil.

4.2 Reaction Pathways of Cyclopentane Carboxylic Acid with Methanol

The 18 samples were analysed using gas chromatography-mass spectrometry (GC/MS) analysis in order to identify the components present in the sample after the reaction. The GC/MS column was a non-polar BPX-5 capillary column. Reaction mechanism for each temperature was identified from the GC/MS results. Below tables show the possible products produced at each reaction temperature and time. Example of GC/MS result is attached in appendix II.

4.2.1 Reaction at 180 ℃

Table 4.3 shows the possible products produced at reaction temperature of 180℃ and reaction time of 5 to 30 minutes.

TABLE 4.3. Possible products for 180℃

Reaction time (min)	**Possible products**	
	Type of reaction	**Name and structure of product**
5	Addition	2- Tridecanone ($C_{13}H_{26}O$)
	Hydrogenation	Formaldehyde (CH_2O)
	Ester	Ethyl ester ($C_6H_{12}O_2$)
10	Addition	2- Tridecanone ($C_{13}H_{26}O$)
	Hydrogenation	Formaldehyde (CH_2O)
	Cyclic breaking	Cyclopentane (C_5H_{10})
15	Hydrogenation	Formaldehyde (CH_2O)
	Cyclic breaking	Acetic acid ($C_2H_4O_2$)
	Cyclic breaking	Propanedioic acid ($C_3H_4O_4$)
20	Hydrogenation	Formaldehyde (CH_2O)
	Addition	2- Tridecanone ($C_{13}H_{26}O$)
	Decarboxylation	Cyclopentane (C_5H_{10})
	Removal of C-O bond	Benzaldehyde (C_7H_6O)
25	Cyclic breaking	Acetic acid ($C_2H_4O_2$)
	Cyclic breaking	Cyclobutanecarboxylic acid ($C_4H_7CO_2H$)
	Cyclic breaking	Cyclopropanecarboxylic acid ($C_3H_5CO_2H$)
30	Ester	Methyl ester ($C_3H_6O_2$)
	Ester	Ethyl ester ($C_6H_{12}O_2$)
	Cyclic breaking	Cyclopentane (C_5H_{10})
	Cyclic breaking	Formaldehyde (CH_2O)

The highest TAN reduction at 180 °C was achieved at reaction time of 30 min which is about 5.74%. Thus, GC/MS results for the reaction temperature of 180 °C at 30 min was analysed and the sample shows the presence of formaldehyde, cyclopentane methyl ester and ethyl ester were observed. This shows molecular structure of the model compound which contains one pentyl and one carboxyl group transformed to be bigger and smaller structures. A significant reaction is the removal of carboxyl group and it was achieved at 10 min. Figure 4.2 indicates the reaction pathways of cyclopentane carboxylic acid at 180 °C for the reaction time of 30 min.

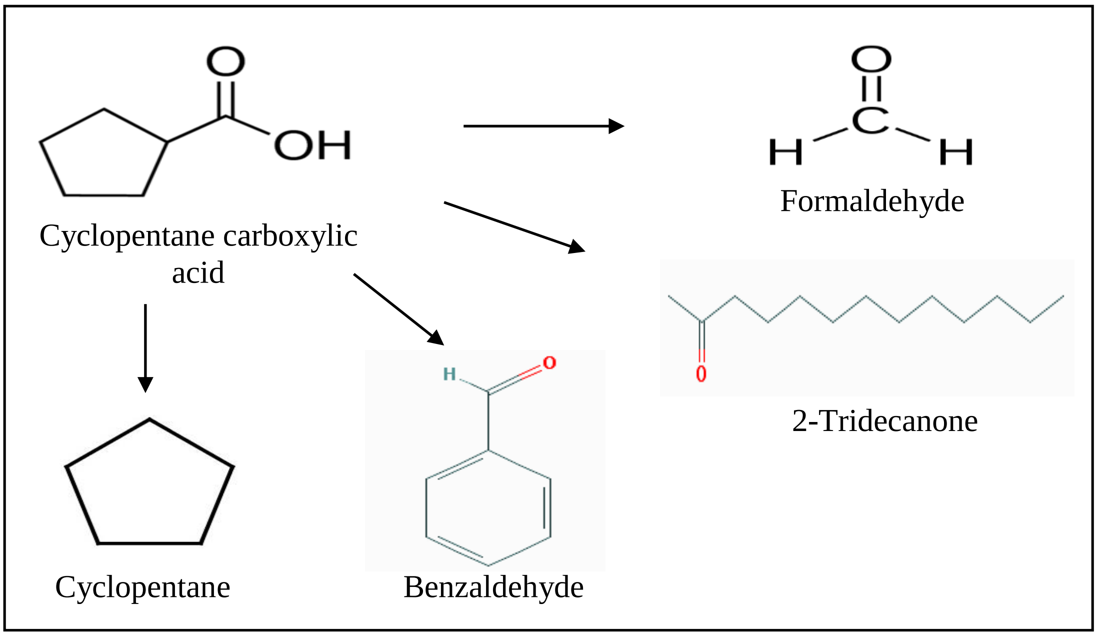


FIGURE 4.2. Reaction pathway at 180 °C for the reaction time of 30 min

4.2.2 Reaction at 200°C

Table 4.4 shows the possible products produced at reaction temperature of 200°C and reaction time of 5 to 30 minutes.

TABLE 4.4. Possible products for 200°C

Reaction time (min)	**Possible products**	
	Type of reaction	**Name and structure of product**
5	Addition	2- Tridecanone ($C_{13}H_{26}O$)
	Hydrogenation	Formaldehyde (CH_2O)
	Cyclic breaking	1,3 - Dioxolane ($C_3H_6O_2$)
	Cyclic breaking	Butenoic acid ($C_4H_8O_2$)

10	Addition	2- Tridecanone ($C_{13}H_{26}O$)
	Cyclic breaking	2,3 - Pentadiene (C_5H_8)
	Cyclic breaking	1,3 - Butadiene (C_4H_6)
15	Ester	Diethyl ester ($C_4H_{10}O$)
	Alcohol	3-Pentanol ($C_5H_{12}O$)
	Cyclic breaking	2-Propenoic acid ($C_3H_4O_2$)
`20	Alcohol	Isopropyl alcohol (C_3H_8O)
	Alkane	Ethane (C_2H_6)
	Acid	Pentanoic acid ($C_5H_{10}O_2$)
	Alcohol	Ethanol (C_2H_6O)
25	Addition	2- Tridecanone ($C_{13}H_{26}O$)
	Hydrogenation	Formaldehyde (CH_2O)
	Acid	Pentanoic acid ($C_5H_{10}O_2$)
30	Addition	2- Tridecanone ($C_{13}H_{26}O$)
	Hydrogenation	Formaldehyde (CH_2O)
	Cyclic breaking	1-Hexen-4-yne (C_6H_8)
	Acid	Octadecanoic acid ($C_{18}H_{36}O_2$)

Reaction for 30 min at 200°C shows the presence of 2- tridecanone, formaldehyde, 1-hexen-4-yne and octadecanoic acid. There are similar products as 180°C, however smaller molecular size compound also being identified. Figure 4.3 indicates the reaction pathways of cyclopentane carboxylic acid at 200 °C for the reaction time of 30 min.

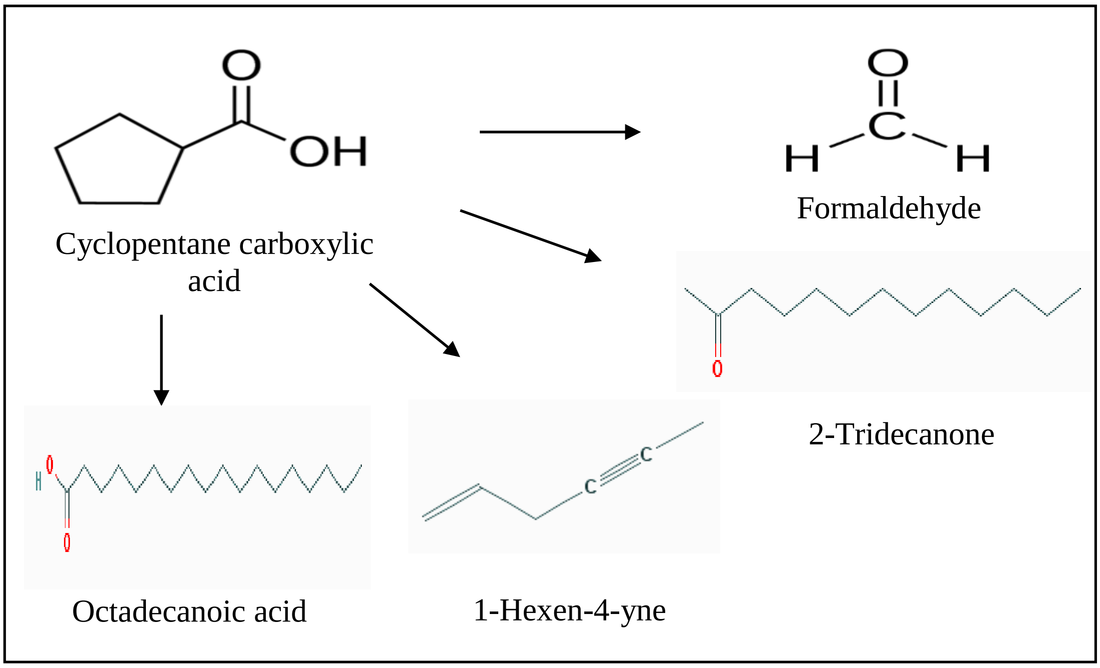


FIGURE 4.3. Reaction pathway at 200 °C for the reaction time of 30 min

4.2.3 Reaction at 220℃

Table 4.5 shows the possible products produced at reaction temperature of 220℃ and reaction time of 5 to 30 minutes.

TABLE 4.5. Possible products of 220℃

Reaction time (min)	**Possible products**	
	Type of reaction	**Name and structure of product**
5	Hydrogenation	Formaldehyde (CH_2O)
	Addition	2- Tridecanone ($C_{13}H_{26}O$)
	Ester	Methyl ester ($C_3H_6O_2$)
	Acid	2-Propenoic acid ($C_3H_4O_2$)
	Cyclic breaking	Butanal (C_4H_8O)
	Acid	Benzoic acid ($C_7H_6O_2$)
10	Hyrogenation	Formaldehyde (CH_2O)
	Addition	2- Tridecanone ($C_{13}H_{26}O$)
	Acid	2-Butenoic acid
	Ester	Bis (2-methylpropyl) ester ($C_{12}H_{22}O_4$)
	Acid	2-Butenoic acid ($C_4H_6O_2$)
15	Hyrogenation	Formaldehyde (CH_2O)
	Alcohol	Ethanol (C_2H_6O)
	Addition	1,5,9-Undecatriene ($C_{11}H_{18}$)
	Acid	Pentanoic acid ($C_5H_{10}O_2$)
20	Hyrogenation	Formaldehyde (CH_2O)
	Acid	Acetic acid ($C_2H_4O_2$)
	Addition	2- Tridecanone ($C_{13}H_{26}O$)
	Cyclic breaking	Cyclopentane (C_5H_{10})
	Ester	Dimethyl ester (C_2H_6O)
25	Hyrogenation	Formaldehyde (CH_2O)
	Ester	Methyl ester ($C_3H_6O_2$)
	Cyclic breaking	Cyclopentane (C_5H_{10})
30	Hydrogenation	Formaldehyde (CH_2O)
	Alcohol	3-Pentanol ($C_5H_{12}O$)
	Ester	Methyl ester ($C_3H_6O_2$)
	Decarboxylation	Cyclopentane (C_5H_{10})

The highest TAN reduction at 200 ℃ was achieved at reaction time of 30 min which is about 17.56%. Thus, GC/MS results for the reaction temperature of 180 ℃ at 30 min was analysed and cyclopentane carboxylic acid has been breaks down into formaldehyde, 3-pentanol, methyl ester and cyclopentane. This indicates the production of alcohol and ester and most importantly the bond breakage of the model compound. It is believed that total acid number managed to reduce after the reaction as the result of bond breakage. Figure 4.4 shows the reaction pathways of cyclopentane carboxylic acid at 200 °C for the reaction time of 30 min.

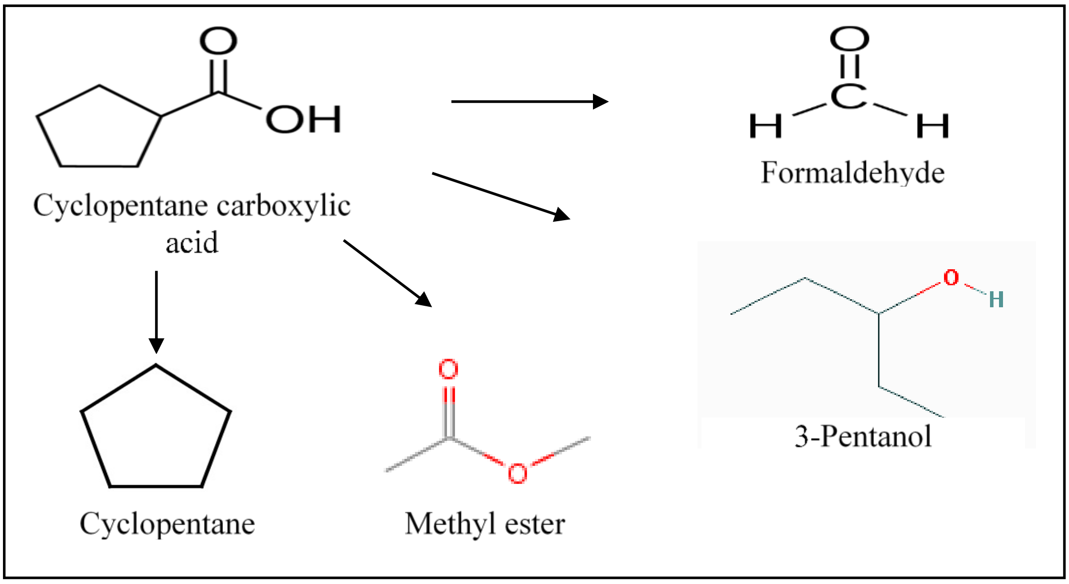


FIGURE 4.4. Reaction pathway at 220 °C for the reaction time of 30 min

4.3 Gas Chromatography-Flame Ionization Detector (GC/FID) Analysis

Apart from GC/MS, the samples were also analysed using GC/FID to identify the concentration of cyclopentane carboxylic acid. 4 standards were prepared with concentration of 0.02g/ml, 0.04g/ml, 0.06g/ml and 0.08g/ml to obtain a calibration curve. Calibration curve helps to identify the concentration of the component with the value of peak area. Figure 4.5 illustrates the calibration curve obtained from the standards prepared. Example of GC/FID result is attached in appendix III.

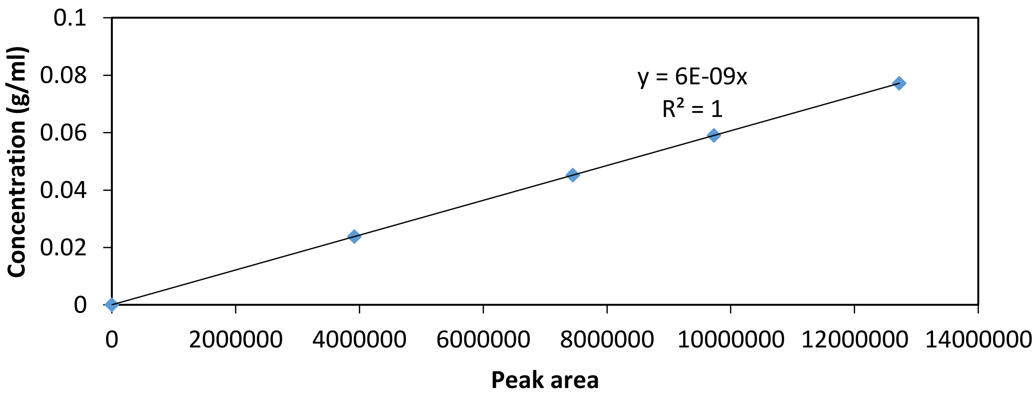


FIGURE 4.5. The calibration curve

The graph produced an equation of $y = 6^{E-9}x$. The concentrations of cyclopentane carboxylic acid for the 3 temperatures were identified through this equation. Table 4.6 shows the concentration of cyclopentane carboxylic acid after the respective reactions.

TABLE 4.6. Concentration of cyclopentane carboxylic acid

Reaction time (min)	**Concentration (g/ml)**		
	180 ℃	**200 ℃**	**220 ℃**
5	0.0805	0.0794	0.0776
10	0.0803	-	-
15	0.0795	0.0779	0.0746
20	0.0782	-	0.0687
25	-	0.0766	-
30	0.0752	0.0741	0.064

Figure 4.6 illustrates on the decrease of concentration as the reaction time and temperature increases.

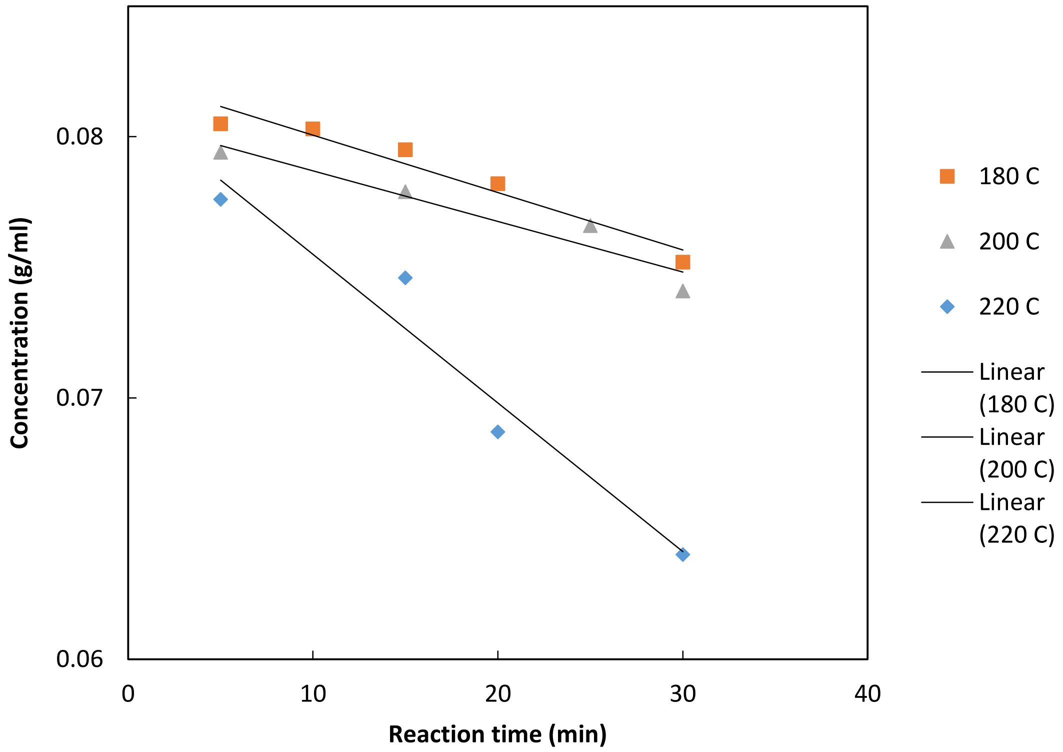


FIGURE 4.6. Concentration vs reaction time

The above graph explains that the concentration of cyclopentane carboxylic acid when the reaction time and temperature increases. Temperature 220 °C and reaction time of 30 min shows the most decrement in the concentration which is from 0.08 g/ml to 0.064 g/ml.

4.4 Total acid number reduction kinetics

Kinetics plot was plotted using the total acid number reduction. This graph is being plotted in order to find the value of kinetics constant, k through the gradient of the graph and to find the order of kinetics. Figure 4.7 shows the kinetics plot plotted using –ln (1-X) against reaction time.

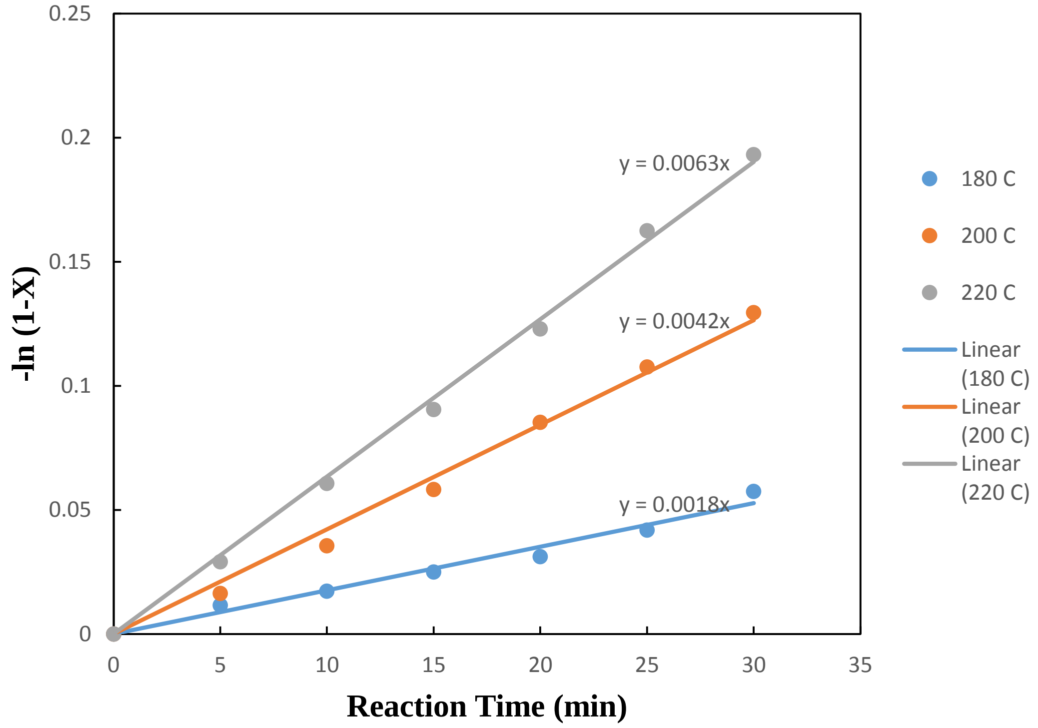


FIGURE 4.7. Kinetics plot

The straight lines which were obtained with the least squares method passed almost exactly through the origin, indicating first order kinetics. This proves that TAN reduction is almost independent of cyclopentane carboxylic acid concentration. The value of kinetics constant obtained from kinetics plot for 180°C, 200°C and 220°C are 0.0018, 0.0042 and 0.0063 respectively. The values of k were used to plot Arrhenius plot.

4.5 Arrhenius plot

Arrhenius plot was constructed to identify the activation energy and pre-exponential factor of the reaction. The equation used to plot Arrhenius plot is as per below:

$$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{4}$$

Activation energy was obtained through the value of gradient and pre-exponential factor was obtained through the intercept of the graph. Figure 4.8 illustrates the Arrhenius plot.

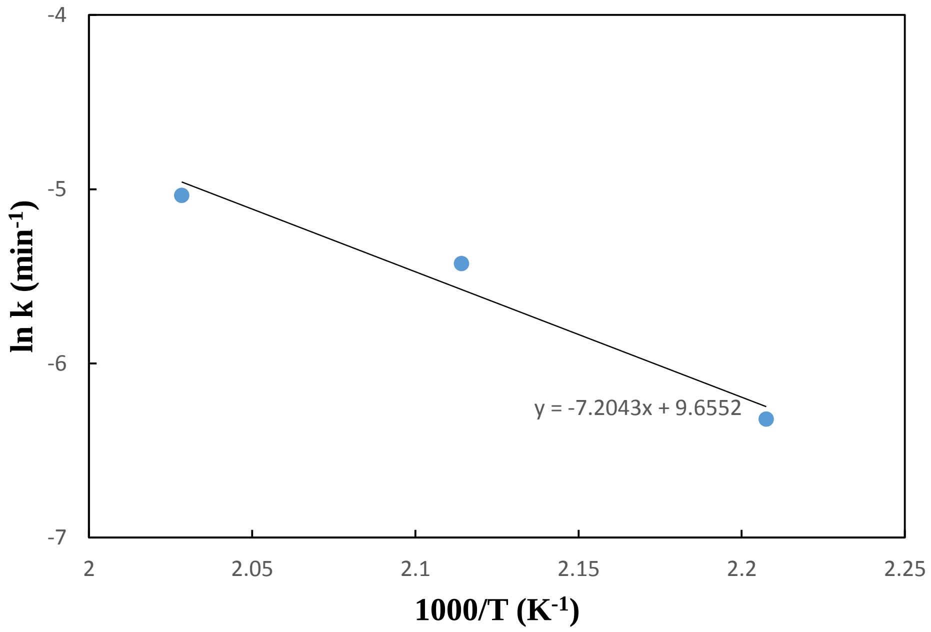


FIGURE 4.8. Arrhenius plot

The value of activation energy obtained through the Arrhenius plot is 59.8966 J/mole-K. Besides that, the value of pre-exponential factor, A is 260.05 s^{-1}. This shows that subcritical methanol able to lower the reaction activation energy and also increases the speed of reaction.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In conclusion, the total acid number for each sample was calculated after the respective reaction. It is observed that the TAN reduces as the temperature and reaction time increases. From this experiment, the highest TAN reduction is achieved at 220℃ and 30 minutes where the reduction is about 17.56%. Upon the reaction, the components present in the sample were identified through GC/MS analysis. Reaction pathways for each sample was identified and there are production of ester, alcohol and alkene. Furthermore, GC/FID results shows that the concentration reduces as the temperature and reaction time increases. From the results obtained, it is proved that the reaction is first order kinetics and independent with concentration. The value of activation energy obtained through the Arrhenius plot is 59.8966 J/mole-K and the value of pre-exponential factor, A is 260.05 s^{-1}. This shows that subcritical methanol able to lower the reaction activation energy and also increases the speed of reaction. To sum up, it is proven that the subcritical methanol is an effective way to reduce the total acid number in crude oil.

5.2 Recommendations

As for recommendation for this project, the experiment should conduct with higher temperature than 220℃ and reaction time more than 30 min since TAN reduction increases as the temperature and reaction time increases. Since the reaction is first order kinetics, it is preferred to make the concentration as the manipulative variable. This project was conducted with concentration of 0.08 g/ml, so higher concentration is better. Last but not least, pressure can be applied to determine the effect of pressure on the total acid number reduction.

REFERENCES

[1] Anderson, K., Atkins, M. P., Goodrich, P., Hardacre, C., Hussain, A. S., Pilus, R., & [1Rooney, D. W. (2015). Naphthenic acid extraction and speciation from Doba crude oil using carbonate-based ionic liquids. *Fuel, 146*, 60-68.

[2] Becerra, H. Q., Miranda, C. M., Cataño, D. L., López, M. H., & Sánchez, M. G. (Jun 2012). A KINETIC STUDY OF ESTERIFICATION OF NAPHTHENIC ACIDS FROM A COLOMBIAN HEAVY CRUDE OIL. *4*(5), 12.

[3] Dalmia, A. (2013). Analysis of Naphthenic Acids in Filtered Oil Sands Process Water (OSPW) using LC/TOF with No Sample Preparation. *Liquid Chromatography/Mass Spectrometry*.

[4] Mandal, P. C., Wahyudiono, Sasaki, M., & Goto, M. (2012). Reduction of total acid number (TAN) of naphthenic acid (NA) using supercritical water for reducing corrosion problems of oil refineries. *Fuel, 94*(0), 620-623.

[5] Mandal, P. C., Wahyudiono, Sasaki, M., & Goto, M. (2013). Non-catalytic reduction of total acid number (TAN) of naphthenic acids (NAs) using supercritical methanol. *Fuel Processing Technology, 106*(0), 641-644.

[6] Shohaimi, N. A. M., Bakar, W. A. W. A., Jaafar, J., & Shukri, N. M. (2013). Treatment of Acidic Petroleum Crude Oil Utilizing Catalytic Neutralization Technique of Magnesium Oxide Catalyst. *1*(3), 5.

[7] Shukri, N. M., Bakar, W. A. W. A., Jaafar, J., & Majid, Z. A. Removal of naphthenic acids from high acidity Korean crude oil utilizing catalytic deacidification method. *Journal of Industrial and Engineering Chemistry*(0).

[8] Vaiopoulou, E., Misiti, T. M., & Pavlostathis, S. G. (2015). Removal and toxicity reduction of naphthenic acids by ozonation and combined ozonation-aerobic biodegradation. *Bioresour Technol, 179*, 339-347.

[9] Wang, Y.-z., Li, J.-y., Sun, X.-y., Duan, H.-l., Song, C.-m., Zhang, M.-m., & Liu, Y.-p. (2014). Removal of naphthenic acids from crude oils by fixed-bed catalytic esterification. *Fuel, 116*(0), 723-728.

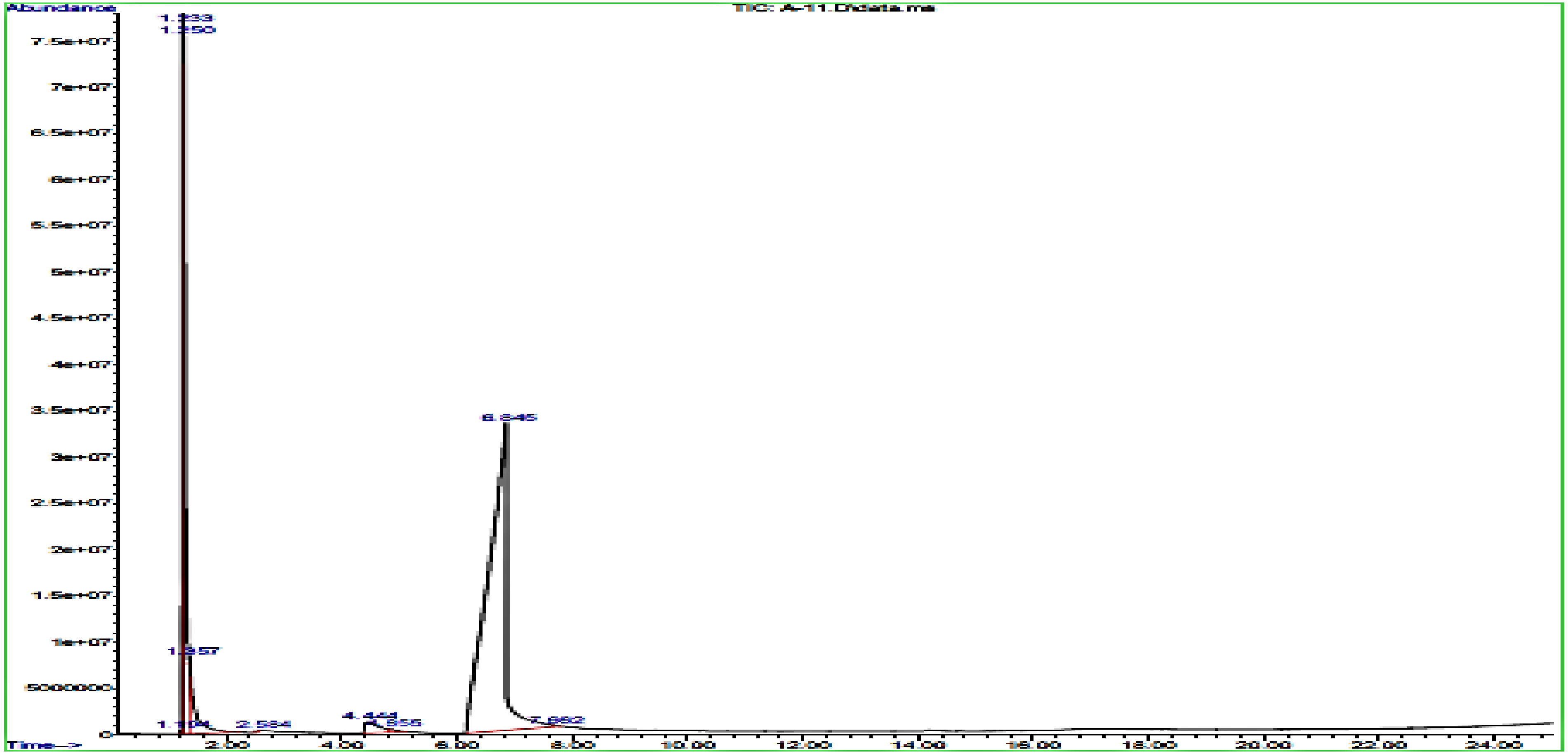
[10] Wang, Y.-z., Zhong, D.-l., Duan, H.-l., Song, C.-m., Han, X.-t., & Ma, X.-r. (2014). Removal of naphthenic acids from crude oils by catalytic decomposition using Mg–Al hydrotalcite/γ-Al2O3 as a catalyst. *Fuel, 134*, 499-504.

APPENDIX I: Literature Review

Author (Year)	Method Used	Chemical Used	Catalytic/ Non-Catalytic Reaction	Operating Temperature	Operating Pressure	Reaction Time	Efficiency	Disadvantages
Mandal, Wahyudiono, Sasaki, & Goto, (2013)	Esterification	Supercritical methanol	Non-catalytic reaction	350 °C	10 MPa	60 min	TAN removal: 96.87%	High temperature
Becerra et al., (2012)	Esterification	Methanol	Non-catalytic reaction	150 - 200°C	-	600 min	TAN removal: 90.90%	Duration of the process
Wang, Li, et al., (2014)	Esterification	Methanol	Catalytic reaction (SnO–Al2O3)	300 °C	-	Space velocity 2.5 h-1	TAN removal: 82.14%	Usage of catalyst
Li, Zhu, Liu & Wu (2013)	Esterification	-	Catalytic reaction (Mg–Al hydrotalcite)	-	-	-	TAN removal > 80%	Usage of catalyst
Mandal, Wahyudiono, Sasaki, & Goto, (2012)	Pyrolysis	Supercritical water	Non-catalytic reaction	490 °C	45 MPa	90 min	TAN removal: 83%	High temperature

Shukri et al., (2015)	Catalytic decomposition	4% ammonia solution in polyethylene glycol (NH_3–PEG)	Catalytic reaction (Cu/Ce (10:90)/Al2O3)	1000 °C	-	-	TAN removal: 93.3%	Very high temperature & usage of catalyst
Zhen et al., (2014)	Catalytic decomposition	-	Catalytic reaction (Mg–Al hydrotalcite/c-Al2O3)	320 °C	1.013 x 10^5 Pa	60 min	TAN removal > 81.5%	Usage of catalyst
Shohaimi, Bakar & Shukri (2013)	Neutralization	Ammonia solution in ethylene glycol (1000 mg/L)	Catalytic reaction (Cu/Mg (10:90)/Al2O3)	1000 °C	-	-	TAN removal: 84.8%	Very high temperature
Dias et al., (2014)	Thermal degradation	-	Non-catalytic reaction	350 °C	-	6 h	TAN removal: 80%	**Proves that 350 °C is suitable temperature
Anderson et al., (2015)	Neutralization	Carbonate-based ionic liquids	Non-catalytic reaction	-	-	-	TAN <0.3 mgKOH g-1	-

APPENDIX II: GC/MS Result



APPENDIX III: GC/FID Result