

EXTRACTION OF NAPHTHENIC ACIDS FROM ACIDIC PETROLEUM CRUDE OIL UTILIZING 2-METHYLIMIDAZOLE WITH THE AID OF Ca/Al₂O₃ AND Ce/Al₂O₃ CATALYSTS

*Norshahidatul Akmar Shohaimi¹, Wan Azelee Wan Abu Bakar², Nurasmah Mohd Shukri², Amier Khairan Shaidi¹

¹Faculty of Applied Science
Universiti Teknologi MARA, Kampus Jengka,
Bandar Tun Razak, Pahang Malaysia

²Department of Chemistry, Faculty of Science,
Universiti Teknologi Malaysia, UTM
Johor Bahru, Johor, Malaysia

*Corresponding author's email: akmarshohaimi@pahang.uitm.edu.my

Submission date: 30 Sept 2018

Accepted date: 30 Dec 2018

Published date: 30 Jan 2019

Abstract

Naphthenic acids (NAs) is one of the major sources of corrosion in oil pipelines and distillation units in crude oil refineries. Removing NA compounds from crude oils is regarded as one of the most crucial processes in heavy oil upgrading. Catalytic deacidification method had been developed in order to reduce the total acid number values in crude oil. Crude oil from Petronas Penapisan Melaka had been chosen to be studied with original total acid number (TAN) of 2.43 mg KOH/g. The parameters used were different catalyst calcination temperatures, catalyst loading, reagent concentration, reaction times and reaction temperature. Acid removal agent of 2-methylimidazole in ethanol and monometallic calcium and cerium doped with alumina were used as a catalyst. The results showed that with the aid of catalyst, the TAN can be reduced to lower than 1 mg KOH/g. Catalyst of Ca/Al₂O₃ calcined at 900°C gave a better reduction than Ce/Al₂O₃ with 83.54% of TAN reduction (2.43 to 0.4) for Ca/Al₂O₃ catalyst and 71.19% (2.43 to 0.7) for Ce/Al₂O₃ catalyst. The best catalyst underwent several characterization methods such as X-Ray Diffraction Spectroscopy (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetry Analysis (TGA-DTA) for its physicochemical properties. It can be concluded that catalytic deacidification method was effective in extracting NAs from the crude oil thus lowered the TAN value to less than 1 mg KOH/g.

Keywords: Naphthenic acids; Crude oil; Catalysts

1.0 INTRODUCTION / BACKGROUND OF THE STUDY

Crude oil is an intricate blend of natural mixes predominately made out of hydrocarbons and frequently contains a lot of different compounds, for example, natural and inorganic sulphur species, chloride and nitrogen, followed by metals and Naphthenic Acids (NAs). Acidic unrefined petroleum are raw petroleum that contain considerable measures of NAs or different kind of acids. They are likewise called high-TAN crudes after the most widely recognized measure of corrosiveness, the Total Acid Number (TAN) (Zhang

et al., 2006). TAN is known as the number milligrams of KOH required to neutralize the acidity in 1 g of oil. Although its correlation with corrosive behavior is still controversial, it is a commonly accepted criterion for the oil acidity. Based on this measurement, highly acidic crude oils are with a TAN number greater than 0.5 mg KOH/g (Wang et al., 2014).

The high level of NAs content in the crude oils is one of the main causes of corrosion in oil pipelines and refining units in oil refineries (Bota et al., 2010). NA corrosion is a non-fluid consumption process created by naphthenic acids. NA corrosion becomes an issue for crude oil refineries in preparing crudes containing elevated amounts of NAs. The kind of hardware in refining units that can be damaged by NA corrosion are crude feedstock warmers, furnaces, transfer lines and many more (Shalaby, 2005). This will cost the administration more cash to fix the broken equipment because of the NA corrosion.

There are numerous methods to reduce or remove the acidity of crude oils for example, adsorption, solvent extraction (Colati et al., 2013), esterification (Li et al., 2013), catalytic decarboxylation (Ding et al., 2009), and thermal decomposition. Soda wash technique is considered as the most sparing and productive strategy for treating the corrosive streams from refinery but this method will produce an emulsion which problematic to treat. The purpose of this study is to find the low cost method in reducing the TAN of crude oil and at the same time producing high quality of crude oil. In this study, 2-methylimidazole in ethanol is used as an acid removal agent with the aids of two different catalysts which are Ca/Al₂O₃ and Ce/Al₂O₃.

2.0 METHODOLOGY

2.1 Material and Feedstock

The feedstock that was used in this study is heavy crude oil that had been obtained from Petronas Penapisan Melaka with TAN of 2.43 mg KOH/g. The 40 mL mixture of 2-propanol, toluene and distilled water with ratio of (40.5:50:0.5) were used as a titration solvent. Ethanol also was used as extraction solvent. Phenolphthalein solution, 1% (w/v) in ethanol was used as the indicator in the deacidification process. As titrants, potassium hydroxide pellets and barium hydroxide were used.

2.2 Catalyst Preparation

Monometallic calcium and cerium catalysts were studied and calcined at different calcination temperatures of 800°C, 900°C and 1000°C. The catalysts have been prepared using aqueous Incipient Wet Impregnation (IWI) method. Each of 5 g metal salts of the catalysts used was weight in a beaker and dissolved in 5 mL of distilled water. Then, the solution was mixed together and stirred continuously by magnetic bar for 30 minutes at room temperature to homogenize the mixture (Shohaimi et al., 2013).

In this preparation of catalysts, support material of Al₂O₃ was used with diameter of 4 to 5 mm. The support was then dipped into the catalysts solution for 1 hour and transferred onto evaporating dish containing glass wool on it. At 80-90°C and for 24 hours, the catalysts then was aging inside an oven to eliminate excess water and permit high-quality coating of the metal on the surface of the supported catalysts. Then, at 800°C for 5 hours using a ramp rate of 5°C/min, it then was followed by calcination in the furnace to remove excess of water or impurities and also all the metal precursor. Same procedure was repeated for the other calcination temperature of the catalysts (Shohaimi et al., 2013). Potential catalysts were characterized by X-Ray Diffraction Spectroscopy (XRD) and Thermal Gravimetry Analysis (TGA) to study its physicochemical properties.

2.3 Deacidification Process

A total of 10% (w/w) of 2-methylimidazole derivative solutions were mixed together with 90% of ethanol, 0.4% of selected catalyst and PETRONAS Penapisan Melaka crude oil. A 2 neck round bottom flask equipped with a magnetic stirrer was used to pour the mixture solution and thermometer used to control the reaction at constant temperature. Parafin oil was used to ease maintaining the constant temperature that were 27°C, 40°C and 60°C.

At a constant temperature, the mixture was stirred during the extraction process (Shukri et al., 2015). Next, the mixture was put into a centrifuge bottle and was centrifuge with speed of 50 x 106 rpm for 20 minutes to remove the acidic components from crude oil sample. Reagent with 2-methylimidazole liquids will be at the top of the centrifuge tube and the deacidified crude oil will be at the bottom (Sun & Shi, 2015). Several parameter studied were concentration of reagent used, catalyst calcination temperatures, catalyst loading, reaction times and reaction temperature.

3.4 Total Acid Number (TAN) Determination

A 0.2 g crude oil after treatment with 2-methylimidazole were measured and placed in a titration beaker. A 40 mL mixture of titration solvent with ratio of (40.5 2-propanol : 50 Toluene : 0.5 distilled water) was then poured into the titration beaker that contained the crude oil sample. Semi-micro colour indicator titration method was used to determine the TAN value. Phenolphthalein solution, 0.1 mL was used as an indicator where the end-point for the titration method was observed by the stable red colour. Potassium hydroxide solution (0.01 mol/L) with barium hydroxide was used as titrant. This titration method was done in the fume hood with the aids of nitrogen gas that was placed in the top of beaker to eliminate any impurities present. The TAN of the sample will be calculate in milligrams of potassium hydroxide per gram of sample (mg KOH/g) and express by using this equation:

$$TAN = \frac{56.1 \times c \times (V_{KOH} - V_B)}{m}$$

Where:

- 56.1 = Molecular mass of KOH (g/mol).
- c = Concentration in moles per liter of standard volumetric potassium hydroxide solution.
- V_{KOH} = Volume of titrant for each test (milliliters).
- V_B = Volume for blank test (milliliters).
- m = mass (grams) of crude oil sample.

3.0 RESULT AND DISCUSSION

3.1 X-Ray Diffraction Spectroscopy (XRD)

The XRD patterns for Ca/Al₂O₃ catalyst calcined at temperatures of 800°C, 900°C, and 1000°C was shown in Figure 1. The diffractogram pattern illustrates that catalyst calcined at 800°C and 900°C was relatively amorphous, lack of periodicity, have short range order and a high noise to signal ratio as shown by the occurrence of broad peaks that match to Al₂O₃ cubic phase as the proof for the catalyst which occurred at $2\theta = 31.77, 37.52, 45.78$ and 66.94 for 800°C calcination temperature and at $2\theta = 32.0, 37.92, 45.96$ and 67.33 for 900°C calcination temperature.

When the calcination temperature was increased to 1000°C, the diffractogram illustrated calcinations pattern and interestingly two species formed at this temperature resultant to orthorhombic Al₂O₃, and body-centered cubic CaAl₄O₇. The body-centered cubic CaAl₄O₇ species was suspected to be an active site for the catalyst. The intensity of the characteristic lines increased as the calcination temperature increased (Shohaimi et. al., 2014). The phase which was dominated by alumina support was revealed as cubic Al₂O₃ occurred at $2\theta = 26.33, 34.516, 50.69, 61.17, 66.698$. There is also base-centered cubic CaAl₄O₇ species present at $2\theta = 31.008, 32.494, 32.986, 35.419, 36.838$ and 51.834 .

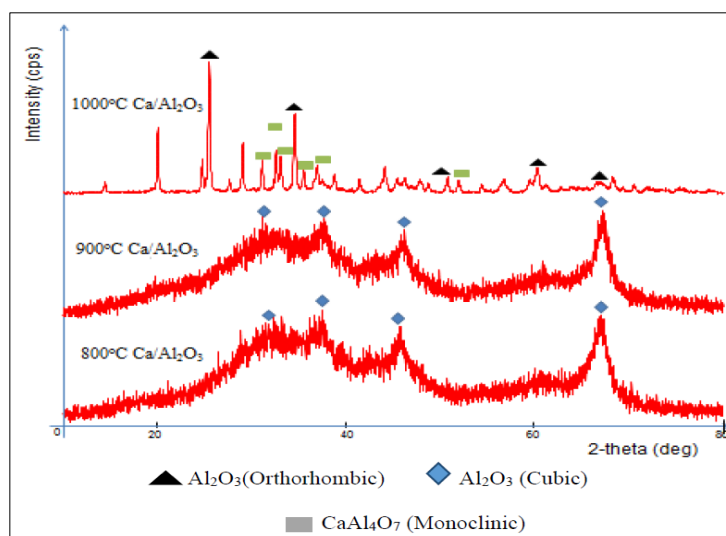


Figure 1 The XRD diffractograms of Ca/Al₂O₃ catalyst calcined at 800°C, 900°C and 1000°C

3.2 Thermal Gravimetry Analysis (TGA)

The thermogram of the tested catalysts shows three stages of mass loss as reveal in Figure 2. Weight loss between 170–440°C was due to loss of crystal water, surface water molecule and complete removal of water while weight loss between the range of 440–570°C which was assigned due formation of pure metal oxide. Lastly, loss of hydroxyl molecules was proven by the weight loss between the ranges of 570–900°C. The occurrence of water molecule was due to the hydroscopic property of the supported catalysts sample apart from the preparation method used.

Overall, from the TGA–DTG analysis, it can be concluded that 32.00% of impurities and water from the materials with total weight loss of 5 g had been removed by thermal treatment and after heating at 800°C, pure metal oxide was obtained. From this investigation, all the nitrate compounds that were originated from metal precursor were removed with calcination temperature of 800°C.

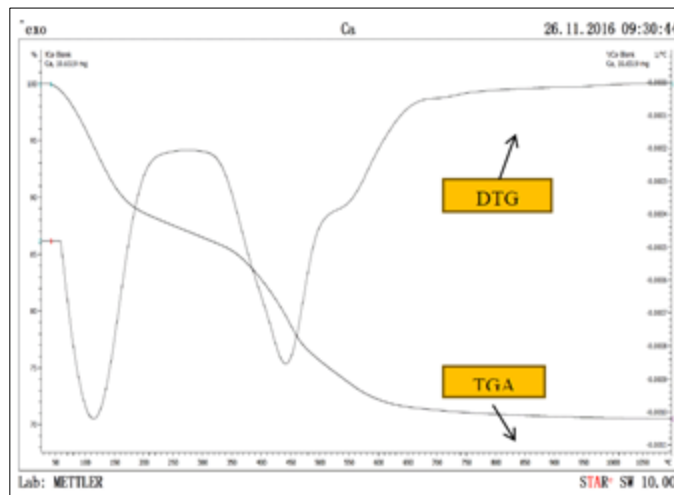


Figure 2 Thermogram of Ca/Al₂O₃ catalyst after aging in an oven for 24h at 80–90°C

3.3 Deacidification Reaction without Catalysts

The original Total Acid Number (TAN) for the untreated crude oil was 2.43 mg KOH/g. The untreated crude oil was test directly without reagent and catalysts using semi–micro color titration method to get the original TAN value. The TAN value of the untreated crude oils will be used as reference to compare with the TAN value of treated crude oil to perceive the effectiveness and efficiency of the reagent and catalyst. Figure 3 shows that various concentration of reagent was used to reduce the value of TAN and also to study the effectiveness of the reagent in reducing the TAN value. The concentration of reagent that was used were 5% to 15% (other remaining percentage was ethanol). From the graph above we can see that the higher the concentration of reagent used, the lower the TAN value obtained. According to Shohaimi et al., (2013), higher value of TAN indicates higher naphthenic acid content presents in the crude oils.

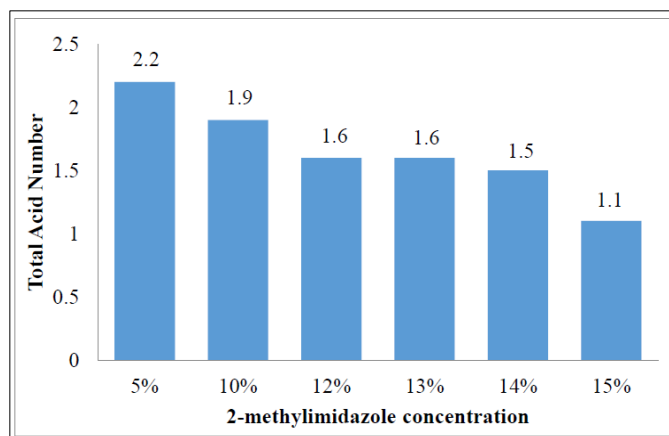


Figure 3 Effect of 2–methylimidazole concentration towards TAN value of PPM crude oils

Results show that the lowest concentration used that was 5% can only reduce the original TAN value from 2.43 mg KOH/g to 2.2 mg KOH/g that was equivalent to 9% total removal efficiency. For highest concentration that was 15% of reagent used, the total removal efficiency was 55% that can reduce the original TAN to 1.1 mg KOH/g but still could not achieve the min TAN required by the industry which should be not more than 1 mg KOH/g. In order to achieve the objective of this study, a catalytic reaction will be conducted to enhance the deacidification process.

3.4 Effect of Ca/Al₂O₃ and Ce/Al₂O₃ Catalyst Loading

This parameter was study to observe the effectiveness and efficiency of using catalyst with reagent on the TAN value. Monometallic catalyst of Ca/Al₂O₃ and Ce/Al₂O₃ was prepared from metal precursor of Ca(NO₃)₂ and Ce(NO₃)₂ due to its higher solubility in water if compared to the other salt such as chloride. Figure 4 shows that 800°C calcination temperature of Ca/Al₂O₃ and Ce/Al₂O₃ catalysts was used as constant variable to determine the ideal catalyst loading's percentage. From the result obtained, it can be seen that the higher the percentage of catalysts loading used, the lower the value of TAN. The catalysts added into the crude oil solution gave a better reduction on the TAN for crude oil of Petronas Penapisan Melaka if compared to the reaction without addition of catalysts. So we can conclude that by using reagent with catalysts, the catalysts help to reduce NA from the crude oils by reaction on the surface of the catalysts which is NA structure binds on surface of the catalysts thus reducing the TAN value (Shohaimi et. al., 2014).

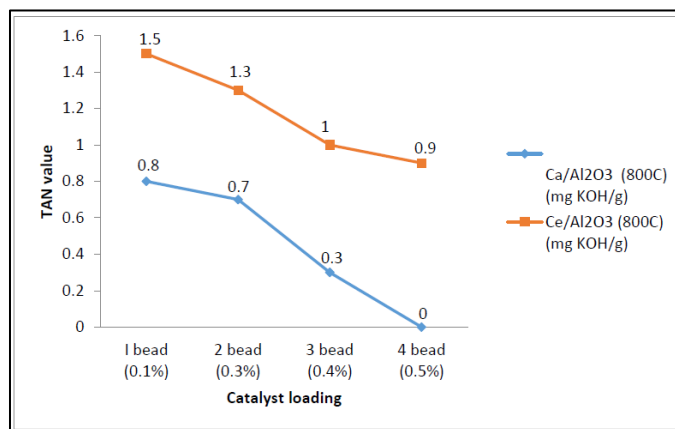


Figure 4 Effect on catalysts loading towards TAN value of PPM crude oil

By using 1 bead (0.1%) of Ca/Al₂O₃, the TAN value obtained was 0.8 mg KOH/g and 4 beads loadings (0.5%) showed the complete removal of NAs compound. For 3 beads loadings (0.4%), the TAN value observed was 0.3 mg KOH/g and we take 2 beads loadings (0.3%) as optimum parameter because it can decrease original TAN = 2.43 to 0.7 mg KOH/g. Even though catalyst loading of 4 beads can decrease to approximately TAN = 0, but in order to reduce the cost of the reaction, lower amount of catalyst loading is more preferable as it also reduced the TAN to less than 1 mg KOH/g as required by the industry.

For 1 bead catalyst loading (0.1%) of Ce/Al₂O₃, the TAN value only decreased to 1.5 mg KOH/g, a little less compared to using no bead at all that was 1.9 mg KOH/g while for 2 beads catalyst loading (0.3%) the TAN value was 1.3 mg KOH/g. For 3 beads catalyst loading (0.4%) and 4 bead catalyst loading (0.5%), the results were 1.0 and 0.9 mg KOH/g respectively. As observed from the data above, the more increasing in catalyst loading used, the more decreasing the TAN value. The comparison between these two catalysts of Ca/Al₂O₃ and Ce/Al₂O₃ reveal that Ca/Al₂O₃ catalyst was more effective in removing the NAs in crude oils as it can decrease the original TAN value to 100% removal using 4 bead (0.5%) catalyst loading, while for Ce/Al₂O₃ catalyst only can decrease original TAN value to 0.9 mg KOH/g. This probably due to the high basicity of Calcium Catalyst compared to Cerium Catalyst.

3.5 Effect of Catalyst's Calcination Temperature

Figure 5 displays the optimum catalyst calcination temperature for Ca/Al₂O₃ that is 900°C by using 2 beads (0.3) catalyst loading with TAN of 0.4 mg KOH/g while Ce/Al₂O₃ catalyst shows best TAN reduction up to 0.6 mg KOH/g by using 3 beads (0.4%) of catalyst loading. For Ca/Al₂O₃ catalyst, it shows that the TAN value was increased from 0.4 to 0.5 mg KOH/g when calcination temperature of 900°C increased to 1000°C. This probably due to the low surface area of the catalyst calcined at higher temperature and was proven by XRD diffractogram that the increase in calcination will increase the crystallinity of the catalyst. Increase in crystallinity would also increase the particle size of the potential catalyst thus reducing the surface area of the catalyst. The catalysts were calcined at calcination temperature of 800°C and above because all the impurities in the catalysts precursor have been removed at these temperature. This result was in agreement with TGA result obtained in Figure 2 where pure catalyst obtained after calcined at 800°C.

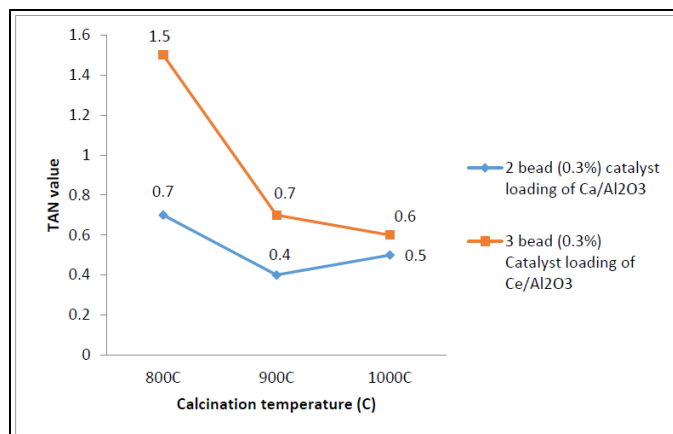


Figure 5 Effect of calcination temperature towards TAN value of PPM crude oil

3.6 Effect of Reaction Time

From Figure 6 below, the ideal reaction time for Ca/Al₂O₃ and Ce/Al₂O₃ catalysts were 10 min as it gave the best result that was 0.4 mg KOH/g and 0.7 mg KOH/g. With 5 minutes reaction time, the TAN value is still higher due to limited time for the reaction to occur to eliminate the NAs in the crude oils for both catalysts. By using 15 minutes reaction times for Ca/Al₂O₃ catalyst, the TAN value was increased to 0.5 mg KOH/g but the value is considered as approximately 0.4 mg KOH/g because if reaction times increase at certain times, the TAN value will remain constant after that.

For Ce/Al₂O₃ catalyst, at 15 minutes reaction times, the TAN value remains the same with 10 minutes reaction times with TAN of 0.7 mg KOH/g. It can be concluded that the optimum reaction time was 10 minutes as the TAN remained constant when the reaction time was increased. As cited by Shi et al., (2008) from their study, he said that it was observed that when the reaction time increased, the acid-removal rate also increased but, acid-removal rate increased very slowly and remained constant 10 minutes.

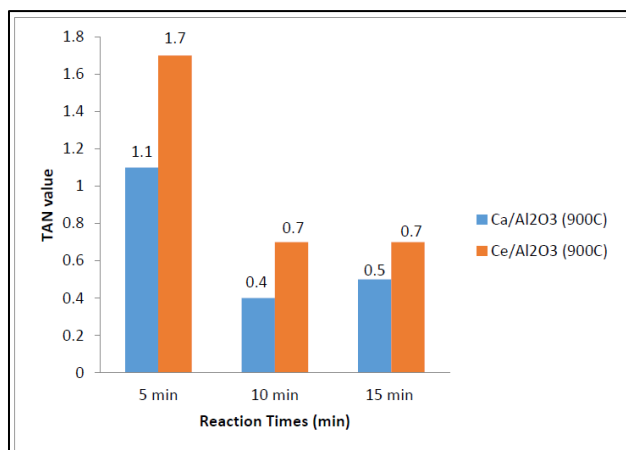


Figure 6 Effect on reaction time towards TAN value of PPM crude oil

3.7 Effect of Reaction Temperature

Figure 7 summarizes that increase in reaction temperature also increases the TAN of crude oil. This is due to higher viscosity when temperature of the reaction is increased thus preventing the deacidification of naphthenic acid to occur. Catalyst of $\text{Ca}/\text{Al}_2\text{O}_3$ gave the lowest TAN value which was 0.4 mg KOH/g at room temperature. Then, the TAN value had increased to 0.9, 1 and lastly to 1.2 mg KOH/g as the temperature of the reaction increased to 40°C, 50°C and 60°C. For $\text{Ce}/\text{Al}_2\text{O}_3$ catalyst, the lowest TAN value achieved was 0.7 mg KOH/g for reaction at room temperature. Then, the TAN value had increased to 1, 1.4 and lastly 1.5 mg KOH/g as the temperature of the reaction increased to 40°C, 50°C and 60°C. Creating a deacidification process with low reaction temperature in order to achieve environmental friendly method with lower energy consumption is required by most petroleum industry nowadays.

As cited by Shi et al., (2008), the temperature has a very small effect and plays a minor role on the acid-removal rate. So it can be concluded that the optimum reaction temperature for both catalysts were at room temperature which gave the best result of TAN value of 0.4 mg KOH/g for $\text{Ca}/\text{Al}_2\text{O}_3$ catalyst and 0.7 mg KOH/g for $\text{Ce}/\text{Al}_2\text{O}_3$ catalyst. Shah et al., (2014) stated that heating process in the industrial scale requires high cost and the different in extraction efficiency at a higher temperature is not very important thus a low temperature is more preferable. Reusability of the catalysts also will be affected if high temperature reaction is used (Sun & Shi, 2012).

4.0 CONCLUSION AND FUTURE WORKS

The research study has proven that deacidification technique had successfully removed acidic compound in acidic Petronas Penapisan Melaka crude oil with the aid of monometallic alkaline earth metal oxides that were $\text{Ca}/\text{Al}_2\text{O}_3$ and $\text{Ce}/\text{Al}_2\text{O}_3$ catalysts. In overall comparison for both catalysts, it can be concluded that the $\text{Ca}/\text{Al}_2\text{O}_3$ catalyst was more effective in removing the NAs presence in crude oils if compared to $\text{Ce}/\text{Al}_2\text{O}_3$ catalyst. The overall reaction condition's result reveals that $\text{Ca}/\text{Al}_2\text{O}_3$ catalyst gave higher percentage of TAN reduction which was 83.5% (TAN = 0.4 mg KOH/g) while $\text{Ce}/\text{Al}_2\text{O}_3$ catalyst only reduced the TAN to 0.7 mg KOH/g with 71.2%.

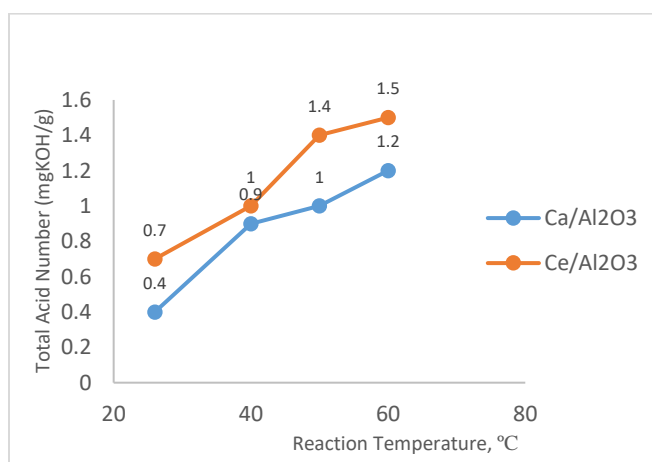


Figure 7 Effect on reaction temperature towards TAN value or PPM crude oil

Acknowledgement

We gratefully acknowledged the financial support by the Research Grant, iRAGS (Vote no.: 600RMI/IRAGS 5/3 (14/2015)) and Faculty of Science, UTM for providing facilities in order to complete this work.

References

- Bota, M.G., Qu, D. and Nesic, S. (2010). Naphthenic Acid Corrosion Of Mild Steel In The Presence Of Sulfide Scales Formed In Crude Oil Fractions At High Temperature. *Corrosion and Multiphase Technology*, 115-127.
- Colati, K. A., Dalmaschio, G. P., Castro, E. V., Gomes, A. O., Vaz, B. G., and Romão, W. (2013). Monitoring the liquid/liquid extraction of naphthenic acids in brazilian crude oil using electrospray ionization FT-ICR mass spectrometry (ESI FT-ICR MS). *Fuel*, 108, 647-655.
- Ding, L., P. Rahimi, R, Hawkins, S. Bhatt, and Y. Shi (2009). Naphthenic acid removal from heavy oils on alkaline earth-metal oxides and ZnO catalysts. *Applied Catalysis a General*, 121-130.
- Li, X., Zhu, J., Liu, Q., and Wu, B. (2013). The removal of naphthenic acids from dewaxed VGO via esterification catalyzed by Mg–Al hydrotalcite. *Fuel Processing Technology*, 111, 68-77.
- Shah, S. N., Chellappan, L. K., Gonfa, G., Mutalib, M. I., Pilus, R. B., & Bustam, M. A. (2015). Extraction of naphthenic acid from highly acidic oil using phenolate based ionic liquids. *Chemical Engineering Journal*, 284, 122- 144.
- Shalaby, H.M., (2005). Refining of Kuwait’s heavy crude oil: materials challenges. Workshop on Corrosion and Protection of Metals. Kuwait Institute for Science Research, Kuwait.
- Shi, L.J., Shen BX, & Wang GQ. (2008). Removal of naphthenic acids from Beijing crude oil by forming ionic liquids. *Energy and Fuels*, 511-532.
- Shohaimi, N. A. Bakar, W. A., Shukri, N. M., & Jaafar, J. (2013). Treatment of Acidic Petroleum Crude Oil Utilizing Catalytic Neutralization Technique of Magnesium Oxide Catalyst. *Modern Chemistry & Applications Mod ChemAppl*, 01(02).
- Shohaimi, N. A., Bakar, W. A., & Jaafar, J. (2014). Catalytic Neutralization Method for Naphthenic Acid Removal in Crude Oil by Alumina Supported Ca and Ba Catalysts. *Petroleum Science and Technology*, 32(19), 2365 - 2375.
- Shukri, N. M., Jaafar, J., Bakar, W. A., & Majid, Z. A. (2015). Optimization of basic catalyst with ammoniated polyethylene glycol for the removal of naphthenic acid from petroleum crude oil by Box–Behnken design. *Clean Techn Environ Policy Clean Technologies and Environmental Policy*, 17(8), 2387-2400.
- Sun, Y., & Shi, L. (2012). Basic ionic liquids with imidazole anion: New reagents to remove naphthenic acids from crude oil with high total acid number. *Fuel*, 99, 83-87.

Wang, Y., Li, J., Sun, X., Duan, H., Song, C., Zhang, M., & Liu, Y. (2014). Removal of naphthenic acids from crude oils by fixed-bed catalytic esterification. *Fuel*, *116*, 781-792.

Zhang, A., Ma, Q., Wang, K., Liu, X., Shuler, P., & Tang, Y. (2006). Naphthenic acid removal from crude oil through catalytic decarboxylation on magnesium oxide. *Applied Catalysis A: General*, *303(1)*, 771-796.