The Treatment of Acidic Petroleum Crude Oil Assisted by Ca/Al₂O₃ Catalyst

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Crude oil processing in a petroleum refinery is important due to the increasing demand for petroleum by-products. The presence of Naphthenic Acids (NAs) in crude oil is of great concern to the petroleum industry as they can cause corrosion problems in the oil refinery process. In this study, the NA extraction reaction was conducted using 2-methylimidazole in ethanol assisted by a heterogeneous catalyst to speed up the reaction. Calcium nitrate $Ca(NO_3)_2$ loaded at a concentration of 10% on an aluminium oxide (Al_2O_3) support was prepared by the Incipient Wetness Impregnation (IWI) method. The feedstock, obtained from Petronas Penapisan Melaka, had an original Total Acid Number (TAN) value of 4.38 mg KOH/g. The operating conditions used in this catalytic extraction reaction included a reagent to oil ratio of 0.5:0.5, catalyst loading at 5, 10, 15 and 20 wt%, a reaction temperature of 35 °C, reaction time of 15 minutes and catalyst calcination temperatures of 700, 900 and 1000 °C. The TAN value of crude oil was successfully lowered to 0.48 mg KOH/g using a Ca/Al₂O₃ catalyst at a calcination temperature of 1000 °C. The catalyst was extensively investigated using TGA-DTA. Results revealed that a calcination temperature above 700 °C was suitable as all impurities in the metal precursor had been removed. SEM micrographs showed an inhomogeneous distribution of various particle sizes, confirming Ca was present on the prepared catalyst. EDX results confirmed the presence of 6.69 % Ca. It can be concluded that the catalytic extraction reaction method with the aid of Ca/Al₂O₃ was efficient in removing the NAs from acidic crude oil and lowering the TAN value to less than 0.5 mg KOH/g.

Key words: Crude Oil; extraction; heterogeneous catalyst; naphthenic acids

Petroleum crude oil consists of hydrocarbons and other organic compounds found in geological formations beneath the earth's surface. The high naphthenic acid (NA) content in crude oil is the major cause of corrosion in oil pipelines, reducing its quality and market price. [1,2]. NAs cause the formation of highly stable oil-water emulsions and have a harmful effect on the environment [3]. The Total Acid Number (TAN) refers to the number of NAs found in crude oil and is measured by the ASTM D664 method. The TAN represents milligrams of KOH per gram, referring to the liquid needed to neutralize 1 g of acid in the oil sample [4,5]. Several ways of dealing with this difficult problem have already been suggested, such as treatment using ionic liquid [6], liquid-liquid extraction [7], catalytic esterification [8], catalytic decarboxylation [9] and caustic washing [10]. However, these methods have their disadvantages; they are not entirely efficient at reducing the NA content in crude oil and lead to high maintenance costs [11]. It is crucial to adopt a simple, high efficiency, environmentally-friendly method that uses little solvent, operates at a lower reaction temperature, and is cost-effective in reducing the TAN of acidic crude oil at an industrial level. In the catalytic extraction reaction, a basic chemical solution of 2-methylimidazole in ethanol was used with calcium as a catalyst supported on alumina to remove the NAs. The catalytic extraction reaction effectively reduced the TAN to less than 1 mg KOH/g as set by Petronas. Catalytic extraction offers many advantages: it uses a recyclable catalyst, is a cost-effective operational

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method and solves the pipeline's corrosion problem. Hence, this study's objective was to analyze the effects of 2-methylimidazole in ethanol in the presence of Ca/Al_2O_3 to enhance the catalytic extraction reaction to remove organic acids and to characterize the physicochemical properties of the Ca/Al_2O_3 catalyst.

EXPERIMENTAL

Materials and Feedstock

In this work, distilled water, 2-propanol and toluene were used as titration solvents to dilute the crude oil sample. The indicator used in TAN determination was phenolphthalein solution, 1% (w/v) in ethanol. Potassium hydroxide pellets and barium hydroxide were used as titrants. The feedstock used in this research was crude oil obtained from Petronas Penapisan Melaka, Malaysia, which had an original TAN value of 4.38 mg KOH/g. The aluminium oxide beads support (Al_2O_3, < 5 nm) and 2-methylimidazole were obtained from Sigma-Aldrich. Calcium nitrate was obtained from Merck.

Preparation of Catalyst

For the preparation of catalysts, calcium nitrate $Ca(NO_3)_2$ was used as a catalyst precursor and supported alumina beads (Al_2O_3) were prepared by the aqueous Incipient Wetness Impregnation (IWI) method [12]. In this study, the metal precursor chosen was calcium nitrate due to its high catalytic performance. 6.14 g of Ca salt was weighed and dissolved in a small amount of distilled water while stirring. In another beaker, 5 g of alumina beads were weighed and soaked with 10 mL of distilled water. The precursor solution was added dropwise into a beaker containing alumina beads that had already been placed in distilled water and stirred continuously at room temperature for 24 hours. The prepared catalyst was then dried in an oven at 80 - 90 ºC for 24 hours to remove water and allow a coating of metal to form on the surface of the supported catalyst. This was followed by calcination in the furnace at 700, 900, and 1000 °C for 5 hours using a heating rate of 5 °/min to eliminate all the metal precursors and impurities [13].

Catalyst Characterization

The catalyst was examined by Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDX). A TESCAN VEGA3 instrument from Novatiq Scientific Singapore was used to view the surface morphology of the potential catalyst, which was combined with EDX to obtain information on the elemental composition at an energy of 15.0 kV. Fourier Transform Infrared Spectroscopy (FTIR) was

utilized to determine the functional groups present in the sample. The universal Attenuated Total Reflectance (ATR) technique was employed to identify the compound in the catalyst samples. Thermal Gravimetry Analysis-Differential Thermal Analysis (TGA-DTA) with a Perkin Elmer Pyris 1 TGA simultaneous thermal analyser was used to confirm the percentage of weight loss from the sample catalyst.

Non-catalytic Reaction

The efficiency of the reagent as an acid removal agent to lower the TAN value of crude oil was measured at various reaction times (10, 15, 20 and 25 minutes) and various reaction temperatures (27, 30, 35, 40, and 45 °C. In this reaction, the crude oil was treated with 2-methylimidazole in ethanol with a mass ratio of 0.5: 0.5 (5 mL crude oil and 5 mL reagent). The mixture was stirred for 10 minutes at 27 °C. Then, the mixture was placed in a centrifuge tube and centrifuged at 4000 rpm for 15 minutes. After centrifuging, the deacidified crude oil was measured by potentiometric titration according to ASTM D664. The reaction was continued with the catalyst because the TAN value obtained was still higher than 1.0 mg KOH/g.
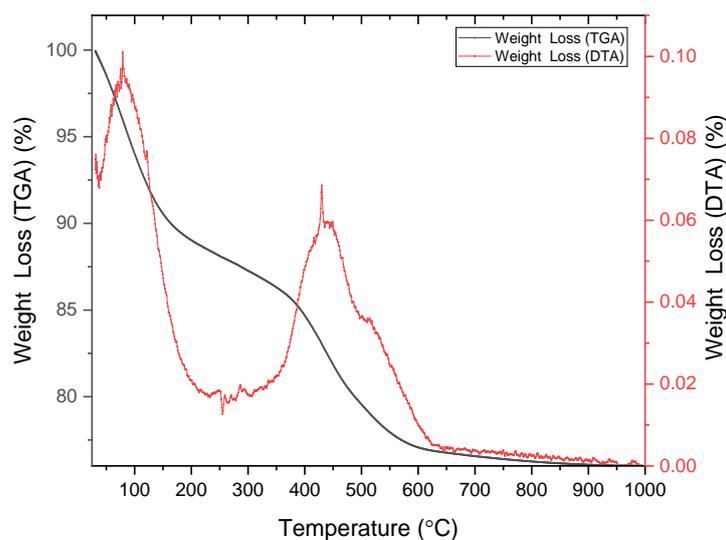
Catalytic Extraction Process

The reagent was prepared with 10% (w/w) 2-methylimidazole and 90% of ethanol. Crude oil and 2-methylimidazole in ethanol with a reagent to oil ratio of 0.5:0.5 (5 ml of reagent and 5 ml of crude oil) were reacted in a beaker with the aid of a magnetic stirrer. Different amounts of Ca/Al_2O_3 catalyst (5, 10, 15 and 20 wt%) were added to the mixture. The mixture was stirred for 15 minutes at 35 °C. After the reaction was complete, the mixture was placed in a centrifuge tube and centrifuged at 4000 rpm for 15 minutes to separate the chemical reagent and acid compounds from the crude oil. The top layer of the centrifuged solution was 2-methylimidazole with acid compounds extracted from the crude oil, while the bottom layer was mainly deacidified crude oil [13].

Total Acid Number (TAN) Determination

The deacidified crude oil was measured and placed in a titration beaker. Then, the sample was diluted with 40 mL of titration solvent (2-propanol, toluene, and distilled water) in a ratio of 49.5:50:0.5 by volume. A semi-micro colour indicator titration method was used, based on the ASTM D664 standard method [14]. The crude oil was titrated with potassium hydroxide (0.01 mol/L) and barium hydroxide solution until a stable red colour was observed. The TAN value of the sample was calculated based on the following equation (1) [15].

$$TAN \text{ (mg KOH/g)} = \frac{56.1 \times c \times (V_{KOH} - V_B)}{m} \quad (1)$$

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Figure 1. TGA-DTA thermogram of Ca/Al$_2$O$_3$ catalyst after ageing in an oven at 80 °C for 24 hours

where 56.1 is the molecular mass of KOH (g/mol), c is the concentration of the standard volumetric potassium hydroxide solution (mol/L), V_{KOH} is the volume of titrant used to reach the equilibrium point (mL), V_B is the volume of titrant required for the blank titration (mL), and m is the sample mass (g).

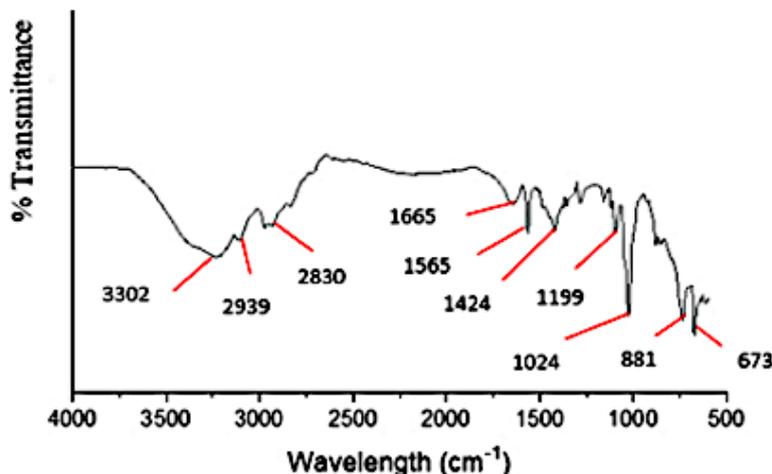## RESULTS AND DISCUSSION

### Thermal Gravimetry Analysis-Differential Thermal Analysis (TGA-DTA)

The Ca/Al$_2$O$_3$ catalyst prepared by the IWI method was analyzed by TGA-DTA after being heated in an oven at 80 - 90 °C for 24 hours. Figure 1 shows that the Ca/Al$_2$O$_3$ catalyst underwent three different thermal decomposition phases. Weight loss at the first stage was 11.50% from 30 - 250 °C due to the loss of surface water and a crystal water molecule. With a weight loss of 12.04% at 250 – 600 °C, the second stage showed the complete removal of water and formation of a pure metal oxide [16], where the loss of H$_2$O occurred from 320 to 420 °C. The third stage continued from 600 to 1000 °C with a weight loss of 76.00% due to the loss of nitrate and surface hydroxyl molecules [17]. The occurrence of water molecules was due to the hygroscopic property of the supported catalyst sample apart from the preparation method used. It can be concluded that the impurities and water were successfully removed by thermal treatment, and heating until 700 °C yielded the pure metal oxide.

Fourier Transform Infrared Spectroscopy (FTIR)

Figure 2 illustrates the FTIR spectrum of the reagent layer on the Ca/Al$_2$O$_3$ catalyst after extraction. The reagent layer was tested with the optimum parameters, whereby catalyst calcination at 1000 °C efficiently removed the NAs. The catalyst loading was 20 wt% with a reagent to oil ratio of 0.5:0.5 (5 mL of reagent and 5 mL of crude oil). According to Shohaimi et al., [18], the FTIR spectra for Ca/Al$_2$O$_3$ in the reagent layer showed peaks in the range of 1029 to 673 cm^{-1} due to the stretching mode of the metal oxide group. This stretching mode was used as an indicator for the formation of the metal oxide catalyst as all the impurities had been removed by heating at high temperatures. The asymmetric stretching of the O-H group of ethanol molecules was observed at 3302 cm^{-1}. A stretching mode for C-H was also observed at 2939-2830 cm^{-1} which may derive from the NA chain where the carboxylic acid group is usually attached through a CH group [19]. Besides, C-N and C-O stretching bands were present in the reagent layer after extraction at 1424 cm^{-1} and 1024-1199 cm^{-1} due to 2-methylimidazole in ethanol as well as NAs. A C=O peak was observed at 1665-1565 cm^{-1} due to the presence of NAs. The Ca/Al$_2$O$_3$ also generated many peaks after the reaction, signifying the impurities from NAs or reagents bound to the catalyst surface. A catalyst offers a basic surface site for the reagent to react with NAs in the catalytic reaction. As the NAs bind to the catalyst, the catalyst degenerates and its efficiency in lowering the TAN value reduces [18].

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Figure 2. FTIR spectra of the 2-methylimidazole reagent layer on Ca/Al$_2$O$_3$ after extraction

a) 700 ºC   b) 900 ºC   c) 1000 ºC   d) after use at 1000 ºC
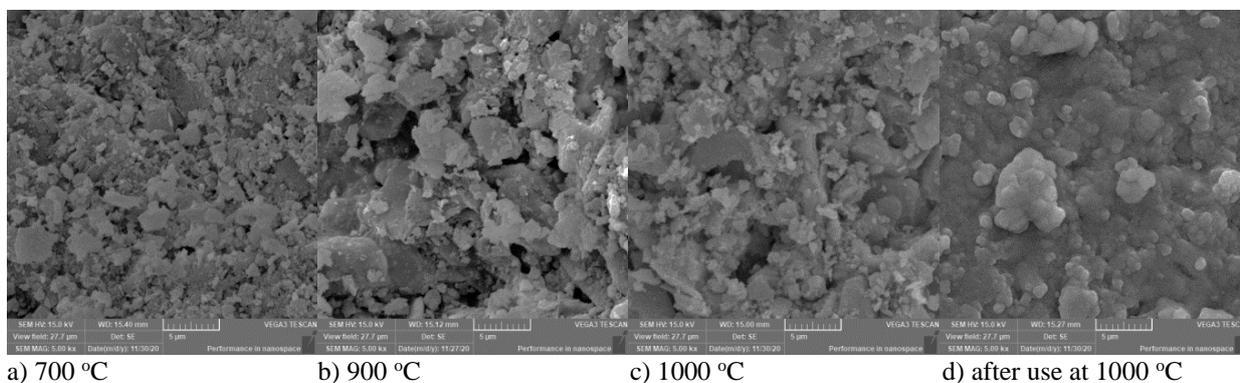
Figure 3. SEM micrographs (5000x magnification) of Ca/Al$_2$O$_3$ at different calcination temperatures a) 700 ºC, b) 900 ºC, c) 1000 ºC and d) after use at 1000 ºC.

Scanning Electron Microscopy (SEM) Analysis

Figure 3 shows the SEM micrographs (5000x magnification) of the Ca/Al$_2$O$_3$ catalyst calcined at 700, 900, 1000 ºC and after use as a catalyst at 1000 ºC. The catalyst showed a rough surface morphology with inhomogeneous spherical shapes and a mixture of small and large particle sizes. The smaller particles play an important role in exhibiting higher catalytic activity [20]. As a result, the smaller particles were easily dissolved in the oil, while the larger particles remained. Figures 3(a) and (b) show that the catalysts calcined at 700 and 900 ºC were not well dispersed and had a mixture of small particle sizes with irregular morphology. A catalyst with smaller particles presents a greater outer surface area, so more reactions can occur at the surface [21]. The micrographs clearly illustrate that the Ca/Al$_2$O$_3$ catalyst calcined at 1000 ºC (Figure 3(c)) had a larger average particle size than Ca/Al$_2$O$_3$ catalysts calcined at 700 and 900 ºC. Figure 3(d) shows that the catalyst surface was densely packed, which lowered its surface area, thus decreasing catalytic activity.

Energy Dispersive X-Ray (EDX) Analysis

Table 1 shows the elemental compositions and distribution of the Ca/Al$_2$O$_3$ catalysts at 700, 900, 1000 ºC and after use at 1000 ºC. The catalyst calcined at 700 ºC contained 3.99 wt.% of Ca, while the catalyst calcined at 900 ºC contained 5.33 wt.%. EDX analysis of the Ca/Al$_2$O$_3$ catalyst revealed that the catalyst calcined at 1000 ºC had the highest amount of Ca, at 6.69%. For the metal oxide catalyst in this study, the weight percentage of Al was the highest (49.97 wt.%) at 700 ºC. The amount of support material is more important as the support material plays a role in controlling, homogenizing and stabilizing the metal oxide phase in the catalyst. The result obtained from the elemental analysis showed that elements were inhomogeneously distributed on the surface of the supported catalyst. The composition of Ca in the used catalyst was lower. It has been reported that the accumulation of Al hinders the Ca species, hence decreasing its composition [12]. The Ca loading in the catalyst after reaction dropped drastically to 1.15 wt.%, due to the migration of Ca particles into the

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Table 1. Elemental composition from EDX analysis of Ca/Al$_2$O$_3$ catalysts calcined at 700, 900, 1000 °C and after use at 1000 °C.

Calcination Temperature (°C)	Element	Weight Composition (%)
700	Al	49.97
	Ca	3.99
	O	46.04
900	Al	46.07
	Ca	5.33
	O	48.61
1000	Al	47.97
	Ca	6.69
	O	45.34
1000 (used)	Al	10.94
	Ca	1.15
	O	66.70
	C	21.21

porous area of the alumina support during the reaction [22; 23]. As the calcination temperature increased, the weight composition for O and C also increased. At the same time, the percentage of Al decreased due to the extra oxygen from the high temperature ashing and C from impurities or the crude oil itself. Thus, the SEM and EDX results were in good agreement and confirmed the dispersion of alumina in non-crystalline form due to interaction with the catalyst.

Effect of Reaction Temperature

The crude oil mixture was treated with 2-methylimidazole in ethanol with a mass ratio of 0.5:0.5 (5 mL of crude oil and 5 mL of reagent) at temperatures in the range of 27 – 45 °C to find the best reaction temperature to reduce the TAN with a reaction time of 15 minutes. 2-methylimidazole in ethanol was chosen as the acid removal agent in this study because the crude oil treated with this basic chemical did not produce an emulsion after the treatment process. Figure 4 shows that the TAN removal decreased with increasing reaction temperatures. At 45 °C, the acid removal was equivalent to 36% of the original TAN, from 4.38 mg KOH/g to 2.81 mg KOH/g. Nevertheless, there was only a small reduction in the TAN value. Based on economic factors, the reaction temperature of 35 °C was selected for further analysis since it could reduce the value of TAN to 3.37 mg KOH/g. This temperature was deemed suitable for cost-efficient and environmentally friendly methods as required by most petroleum industries nowadays [24]. According to Shi et al. [7], reaction temperature plays a minor role in the deacidification reaction. As high temperatures trigger the decomposition of oil, temperatures above 35 °C were not investigated because they may affect the reusability of catalysts.

As stated by Shah et al. [25], the heating processes in the petroleum industry are costly, and the difference in extraction efficiency at a higher temperature is not very important; thus, a low temperature reaction is preferable.

Effect of Reaction Time

To investigate the effect of reaction time on the reduction of TAN, various reaction times ranging from 10 to 25 minutes were trialled at a fixed temperature of 35 °C. According to Shi et al., [7], with 20% (w/w) of 2-methylimidazole solution in ethanol, acid removal from crude oil increased with reaction time, and approximately 64% of acid was removed at 30 °C with a reaction time of 10 minutes. The 2-methylimidazole solution in ethanol is an ionic liquid with basic properties while NAs are weak acids. Therefore 2-methylimidazole in ethanol reacted quickly with crude oil to remove the NAs. Figure 5 shows that as the reaction time increased from 10 to 25 minutes, the TAN decreased from 3.41 to 2.42 mg KOH/g, indicating that sufficient time was required for the reagent to decompose in the crude oil mixture, while a longer reaction time would consume more energy. It is possible that the longer the reaction time, the faster the deacidification rate. With a reaction time of 10 minutes, the TAN value was still high at 3.41 mg KOH/g because of the limited time available to remove NAs in the crude oils. With 15 minutes reaction time, the TAN value reduced to 3.37 mg KOH/g. Therefore, 15 minutes was chosen for the catalytic reaction study since longer reaction times consume more energy, leading to higher operating costs. In a study done by Shi et al. [7], the acid removal rate also increased with reaction time, although it increased quite slowly and remained constant for 10 minutes.
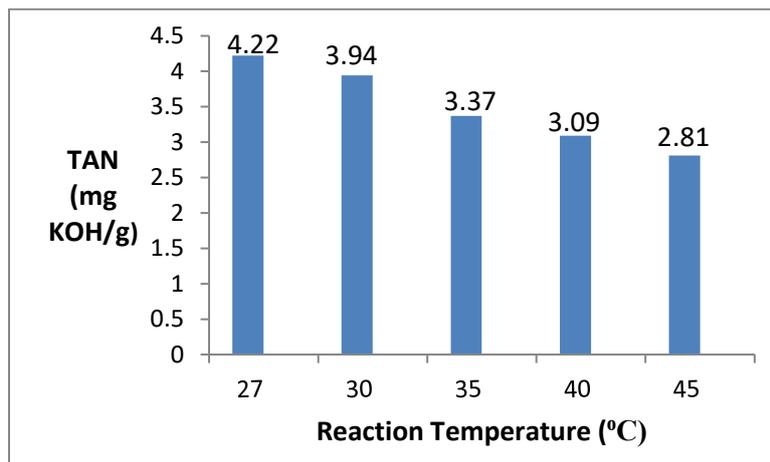
Figure 4. Effect of different reaction temperatures on the TAN value of crude oil for a reaction time of 15 minutes
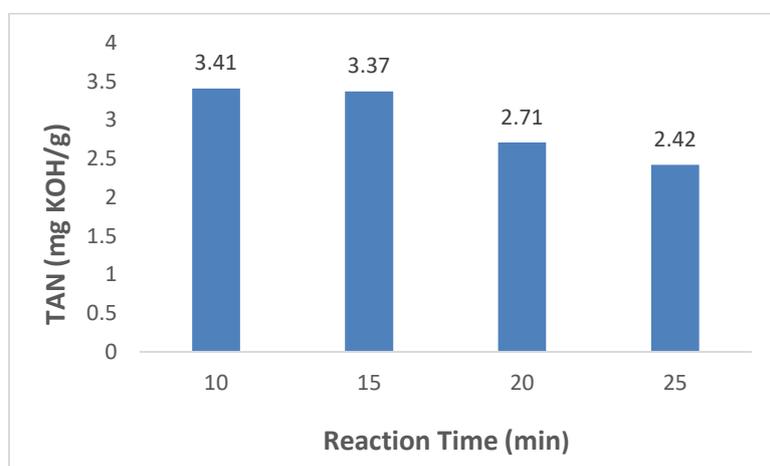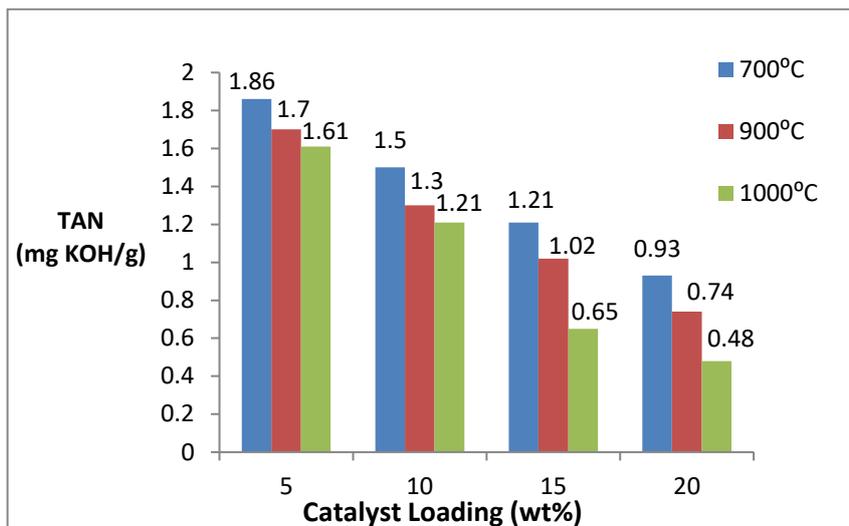

Figure 5. Effect of different reaction times on the TAN value of crude oil at 35 ºC.

Effect of Catalyst Loading

Adding a catalyst to the reagent during the reaction helped to further reduce the NA content of crude oil. The reaction occurred at the surface of the catalyst with the NAs bound to the catalyst's surface, thus decreasing the TAN value [26]. An alkaline earth metal with Al$_2$O$_3$ beads was chosen because the metals in this group are known for their basicity and high catalytic performance. A catalyst of Ca/Al$_2$O$_3$ with basic characteristics (based on the periodic table) was needed in this study because NAs are acidic pollutants [27]. Al$_2$O$_3$ beads were applied as a support in this research because the catalyst is easy to separate and reuse after the reaction process. The Al$_2$O$_3$ support as a heterogeneous catalyst has advantages because of its unique physical and chemical properties and the size of the beads which have an average diameter of 4-5 mm. The alumina beads are easy to separate at the end of the reaction [13]. Figure 6 shows the effect of different metal catalysts on the reduction TAN at calcination

temperatures of 700, 900, and 1000 ºC.

Based on the results with the Ca/Al$_2$O$_3$ catalyst calcined at 700 ºC, increasing the amount of catalyst slightly enhanced the reduction of TAN. The lowest TAN value obtained was 0.93 mg KOH/g using the 20 wt% catalyst. To further reduce the TAN value, the calcination temperature was increased to 900 ºC. The Ca/Al$_2$O$_3$ catalyst effectively reduced the TAN value from 0.93 to 0.74 mg KOH/g. Upon increasing the calcination temperature to 1000 ºC, the same catalyst successfully decreased the TAN value to 0.48 mg KOH/g, compared with the original TAN value which was 4.38 mg KOH/g. With an increase in the calcination temperature from 700 to 1000 ºC and a reaction temperature of 35 ºC, the TAN value decreased to < 1. Liu et al. [26], stated that a high catalyst loading would increase the number of active sites that come into contact with crude oil, thus reducing the yield of NAs. Thus, the 20 wt% Ca/Al$_2$O$_3$ catalyst calcined at 1000 ºC was chosen as the best catalyst as it was able to reduce the TAN value to < 0.5 mg KOH/g.

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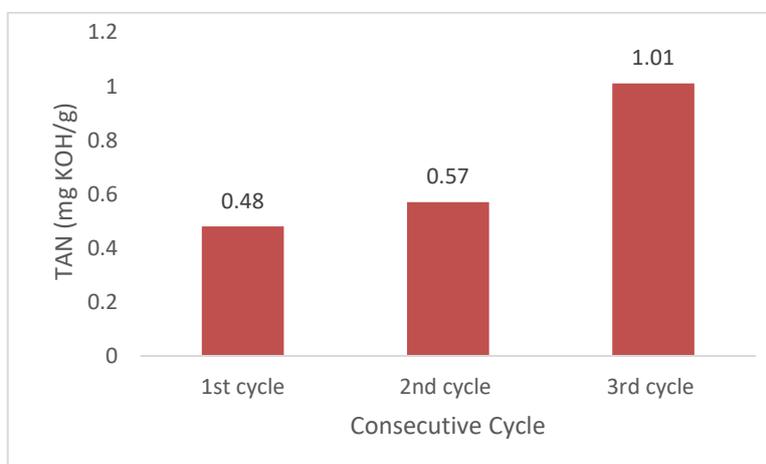The Treatment of Acidic Petroleum Crude
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Figure 6. Effect of different Ca/Al₂O₃ catalyst loadings (5, 10, 15 and 20 wt.%) on the TAN value of crude oil with calcination temperatures of 700 ℃, 900 ℃, and 1000 ℃ at a reaction temperature of 35 ℃ and reaction time of 15 min

The results confirmed that the presence of the catalyst was highly effective in reducing the TAN of highly acidic crude oil.

Effect of Reusability Testing

The reusability of the catalyst was tested by using the same catalyst until it was fully deactivated. In the current study, the reusability of the catalyst was investigated using optimum conditions based on a reaction temperature of 35 ℃ and reaction time of 15 minutes. In this reaction, 20 wt% Ca/Al₂O₃ was added to the optimized reagent to oil ratio of 0.5:0.5 to reduce the TAN value to < 1.0 mg KOH/g. The study was performed on crude oil to investigate the ability and performances of the Ca/Al₂O₃ catalyst in reducing the acid number of crude oil after three cycles using the same catalyst. After one complete extraction reaction,

the Ca/Al₂O₃ catalyst was washed with 2-propanol to remove impurities and adsorbed NAs. Then, the catalyst was dried in an oven for 1 hour at 80 ℃ before being reused for a second reaction. The next cycle for the catalytic extraction reaction was the same as the first. The results of the reusability test for the Ca/Al₂O₃ catalyst are illustrated in Figure 7. The Ca/Al₂O₃ catalyst that was calcined at 1000 ℃ had a higher reusability when the TAN value after two consecutive runs was < 1 mg KOH/g. When the catalyst was used for the 3rd cycle, the TAN value increased from 0.48 to 1.01 mg KOH/g. The TAN value increase after the second cycle was due to the deactivation of the catalyst and the formation of impurities from the accumulation of particles resulting from the reaction of the chemical reagent with crude oil [28]. According to Wang et al. [29], as the catalyst started to deactivate (spent catalyst), the value of TAN increased as the

Figure 7. Reusability test on the potential catalyst Ca/Al₂O₃ calcined at 1000 ℃

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reaction of the catalyst slightly decreased. However, even though the TAN value increased, the second catalytic cycle could still be used because the TAN value was still < 1 mg KOH/g, and thus beneficial for industrial production [30,31]

CONCLUSION

Catalytic extraction is very effective in deacidifying high TAN crude oil samples. This study successfully achieved the objective of finding the optimum conditions to achieve a TAN value below 0.5 mg KOH/g, a requirement of the conventional refinery industry to prevent the most common impurities present in the crude oil. The use of a Ca/Al$_2$O$_3$ catalyst with a reagent was found to reduce the TAN value of crude oil from its original value of 4.38 to 0.48 mg KOH/g. Even better, this catalyst was able to achieve this TAN value with a low reaction temperature (35 °C) and short reaction time (15 min).

ACKNOWLEDGEMENT

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