The Application of K/Al₂O₃ with Ethanolic 2-Metylimidazole for the Extraction of Naphthenic Acid from Crude Oil

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The world's economy is largely dependent on fossil fuels such as petroleum crude oil. Crude oil processing in the oil refinery can cause serious corrosion problems associated with the presence of naphthenic acids (NAs) which reduce the quality of the oil. The presence of these acidic compounds leads to an increase in the Total Acid Number (TAN) value and a decrease in the oil price which can affect the oil industry. The aim of this study was to overcome corrosion problems by reducing the TAN to less than 1.0 mg KOH/g using ethanolic 2-methylimidazole with the aid of a K/Al₂O₃ catalyst. Petronas Penapisan Melaka crude oil with an original TAN value of 4.38 mg KOH/g was used as feedstock in this study. The parameters investigated were reaction time, reaction temperature, catalyst loading and catalyst calcination temperature. The alumina supported catalyst was synthesized through Incipient Wetness Impregnation (IWI) methods and characterized using X-ray Diffraction Spectroscopy (XRD) and Scanning Electron Microscopy (SEM). The TAN of crude oil was successfully lowered to 0.74 mg KOH/g using a K/Al₂O₃ catalyst at a calcination temperature of 1000ºC. Increasing the calcination temperature from 700 to 1000ºC further reduced the TAN value of crude oil.

Key words: Catalysts; crude oil; naphthenic acid; total acid number

The production of petroleum crude oil is increasing every year due to high demand from the oil industry. Crude oil contains large quantities of naphthenic acids (NAs) that consist of an unspecific mixture of several cyclohexyl and cyclopentyl carboxylic acids [1], which are a major cause of serious corrosion problems in oil processing equipment, transportation pipelines, storage tanks and refinery equipment which can lead to high maintenance costs [2]. Besides NAs, there are also aromatic acids, fatty acids, inorganic acids, mercaptans and phenols present in crude oil [3]. The general chemical formula for NAs is $R(CH_2)_nCOOH$ [4] where R is one or more cyclopentane rings and n is typically greater than 12. The corrosive properties of these compounds can also reduce the quality and price of the petroleum crude oil [5].

Previous studies have shown that the acidity of crude oil is usually described by the Total Acid Number (TAN), which is defined as the amount of potassium hydroxide (KOH) in milligrams used to neutralize one gram of oil [6]. ASTM D664 was used to test the acid number of petroleum products using a semi-micro colour titration [7]. If the TAN of crude oil is greater than 0.5 mg KOH/g it is classified as acidic, whereas crude oil with a TAN higher than 1 mg KOH/g is considered highly acidic and likely to cause corrosion problems during processing [8].

Generally, there are numerous methods used to remove and reduce the NAs from acidic crude oil, such as caustic washing, dilution [9], catalytic decarboxylation [10], solvent extraction or catalytic esterification [10]. However, most of these methods have their own disadvantages and lead to high maintenance costs [5]. Dilution is a method where high TAN crude oil is blended with low TAN crude oil, which may reduce the content of NAs to an acceptable value, but the acidic compounds remain and the commercial value of low TAN is reduced [11]. The caustic washing method is commonly used because it can successfully reduce the TAN in crude oil, but this technique produces an emulsion which is very difficult to treat [2,12]. The catalytic decarboxylation method operates at high temperatures up to 700ºC and consumes more energy, which is not

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cost-effective [13]. As for solvent extraction, this requires a large amount of solvent and a lot of energy for solvent recovery.

As described above, it is very important to adopt a simple, cost-effective and environmentally-friendly process for reducing the TAN of acidic crude oil on an industrial level [14]. In this study, an effective method was developed for TAN reduction of highly acidic crude oil with a TAN value of 4.38 mg KOH/g. An extraction technique was used to remove NAs from acidic crude oil by using 2-methylimidazole in ethanol as a NA extractor with the aid of a K/Al$_2$O$_3$ catalyst to speed up the reaction. There are many advantages to the catalytic extraction technique, e.g. it requires only a small amount of chemical reagent for the removal of NAs, the process will not generate any emulsion, it operates at a low temperature of 35ºC and is a cost-effective method to remove the acids in crude oil. The main objective of this study was to investigate the effects of 2-methylimidazole in ethanol solution on the Total Acid Number of petroleum crude oil samples and to characterize the physicochemical properties of the K/Al$_2$O$_3$ catalyst.

MATERIALS AND METHODS

Materials and feedstock

The feedstock used in this study was obtained from Petronas Penapisan Melaka, Malaysia and had an original TAN value of 4.38 mg KOH/g. A 40 mL mixture of 2-propanol, toluene and distilled water with a ratio of 49.50:50.00:0.50 was used as the titration solvent to dilute the crude oil sample. A solution of 2-methylimidazole mixed with ethanol was used as a deacidifying agent. Potassium hydroxide and barium hydroxide were utilized as the titrant. A 1% (w/v) phenolphthalein solution was used as an indicator in the catalytic extraction process. A 10% solution of 2-methylimidazole in 90% ethanol was prepared and stirred for about 10 minutes before being stored in a bottle. The solution was then ready to be blended with the crude oil sample.

Preparation of catalyst

Potassium was used as the catalyst of interest, supported on alumina beads. The catalyst was synthesized by the aqueous Incipient Wet Impregnation (IWI) method. Firstly, 3.88 g of KNO$_3$ was weighed in a beaker and dissolved in a small amount of distilled water while stirring. In another beaker, 5 g of alumina (Al$_2$O$_3$) beads were weighed and soaked with 10 ml of distilled water. To homogenize the mixture, the support was immersed in the catalyst solution for 24 hours and stirred at ambient temperature. After that, the support material was transferred onto an evaporating dish with a piece of filter paper. The solution was aged in an oven at 80-90ºC for 24 hours to remove water and allow a coating of metal to form on the surface of the supported catalyst. Next, the catalyst was calcined in a furnace at a temperature of 700ºC for 5 hours with a ramp rate of 5ºC/min to eliminate all metal precursors and excess water or impurities. These procedures were repeated using different calcination temperatures of 900ºC and 1000ºC [5].

Catalyst characterization

The potential catalyst was analyzed by applying several techniques to study its physical and chemical properties. The information obtained was useful to understand the relationship between the catalyst's properties and its performance in the extraction reaction [13]. The characterization techniques used in this study were Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) analysis and X-ray Diffraction Spectroscopy (XRD).

Extraction process

A mixture of crude oil and 2-methylimidazole in ethanol with a mass ratio of 0.4:0.6 was stirred with a magnetic stirrer in a beaker. 10 % 2-methylimidazole (w/w) in ethanol and K/Al$_2$O$_3$ catalyst were added to the crude oil in the beaker. The mixture was stirred for 15 minutes at 27, 30 and 35ºC. After 15 minutes, the mixture was put into a centrifuge tube and centrifuged at 4000 rpm for 15 minutes to separate the chemical reagents with acidic compounds from the crude oil. The 2-methylimidazole solution was the top phase in the centrifuge tube and the deacidified crude oil was the bottom phase [15].

Total Acid Number (TAN) determination

0.2 g of the deacidified crude oil sample was measured and placed in a titration beaker. The sample was then diluted with 40 mL of titration solvent, which consisted of a mixture of toluene, 2-propanol and distilled water in a ratio of 50.00:49.50:0.50. The petroleum crude oil sample was titrated with potassium hydroxide and barium hydroxide solution (0.01 mol/L) according to ASTM D664. The original TAN value for the crude oil sample (TAN = 4.38 mg KOH/g) was determined by the semi-micro colour indicator titration method. 0.1 mL phenolphthalein solution was used as an indicator, and the solution was titrated until a stable red colour was observed. The titration technique was performed on the crude oil sample before and after the catalytic extraction reaction. To express the result, the TAN of the sample was calculated in milligrams of potassium hydroxide per gram of sample (mg KOH/g) using Equation 1,

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

where, 56.1 is the molecular mass of KOH (g/mol), c is the concentration of the standard volumetric

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potassium hydroxide solution (mol/L), V_{KOH} is the volume of titrant required for the determination (mL), V_B is the volume of titrant required for the blank test (mL), and m is the mass of the test portion (g).

RESULTS AND DISCUSSION

X-ray Diffraction Spectroscopy (XRD)

Figure 1 shows the diffractogram pattern for K/Al_2O_3 catalysts calcined at 700, 900, 1000 and the used catalyst at 1000ºC. The catalysts were amorphous at all calcination temperatures, with a low degree of crystallinity which revealed that the vibrating particles were more random in arrangement and have a short-range order [5]. The catalyst calcined at 700ºC showed a high signal to noise ratio while those calcined at 900 and 1000ºC had low signal to noise ratios. The fresh and used catalysts revealed no significant differences because K/Al_2O_3 catalyst has a small rate of deactivation. With the increase in calcination temperature, the intensity of characteristic lines also increases [14]. Due to their highly amorphous nature, these catalysts have a larger surface area because of their small particle size. Based on the diffractogram patterns, the catalyst calcined at 700ºC showed a predominance of Al_2O_3 in rhombohedral phase at 2θ = 32.20, 37.56, 41.90 and 67.22º. For the catalyst at 900ºC and the used catalyst at 1000ºC, the Al_2O_3 in cubic phase was dominant. K/Al_2O_3 catalyst calcined at 900ºC gave 2θ values of 32.60, 37.35, 41.30, 45.86 and 67.11º. The used catalyst gave the same phase as the one at 900ºC, with Al_2O_3 in cubic phase at 2θ = 32.09, 46.01, 58.50, 66.88 and 68.30º. At the highest calcination temperature of 1000ºC, Al_2O_3 once again overshadowed the catalyst, but a different lattice of

hexagonal phase was formed at 2θ = 15.73, 32.26, 45.73, 58.30º. The sample also exhibited a sharp diffraction peak at 66.86º. The results show that the cubic phase of the Al_2O_3 species probably acts as an active site and speeds up the catalytic reaction process of K/Al_2O_3 catalyst. Besides this, the amorphous structure has made the K_2O phase undetectable. The disappearance of the K_2O peak in the XRD pattern was probably due to the small size of K_2O particles which are below the detection limit of the XRD, and low K loading in the catalyst as shown in the EDX data.

Scanning Electron Microscope (SEM) analysis

SEM micrographs of K/Al_2O_3 catalysts calcined at 700, 900 and 1000ºC and the used catalyst at 1000 ºC are shown in Figure 2 (a), (b), (c) and (d) respectively with 5000x magnification. Figure 2 (a) and (b) show that the catalyst's rough surface morphology was inhomogeneously distributed and highly amorphous, indicating that the active components of the metal oxide are highly dispersed in the alumina support. The smaller particle size of the catalyst leads to a greater dispersion. The catalysts at both calcination temperatures show an aggregation of smaller particles [16] which increase the surface area of the catalyst. The smaller particle size [17] plays an important role to exhibit higher catalytic activity. Figure 2 (c) and (d) illustrate that the catalyst's surface was not well dispersed and densely packed, as it has a mixture of small and larger particle sizes. The result showed that K/Al_2O_3 catalyst calcined at 1000ºC has a larger particle size compared to K/Al_2O_3 catalysts calcined at 700 and 900ºC. The agglomeration of particles when heated at high temperature increases the particle size of the catalyst.
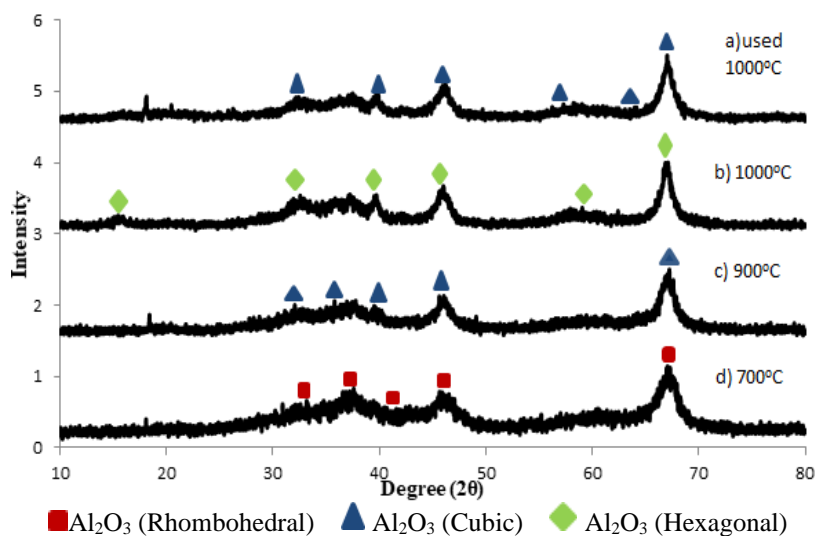

Figure 1. The XRD diffractogram of K/Al_2O_3 catalyst calcined at 700, 900 and1000ºC and the used catalyst at 1000ºC.

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a) 700ºC   b) 900ºC   c) 1000ºC   d) after used 1000ºC
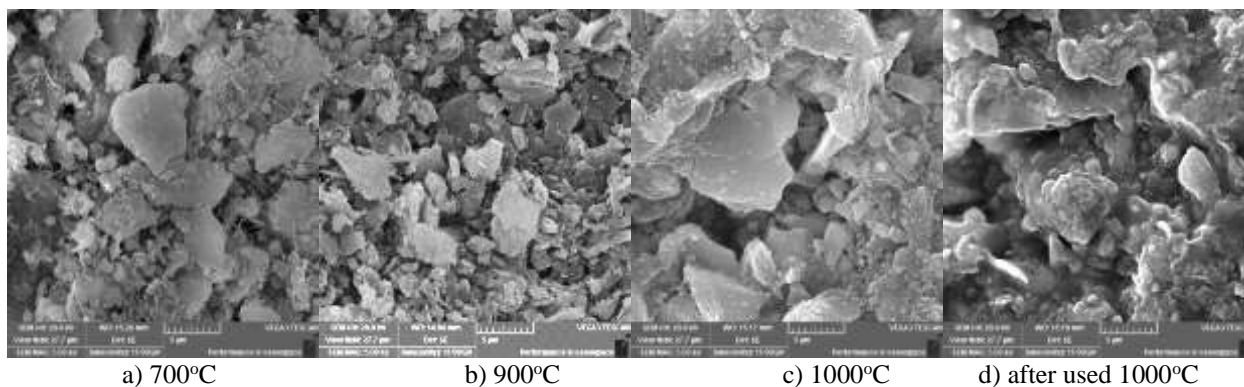
Figure 2. SEM micrographs of K/Al₂O₃ at different calcination temperatures a) 700ºC, b) 900ºC, c) 1000ºC and d) used 1000ºC with 5000x magnification.

Energy Dispersive X-Ray (EDX) analysis

Table 1 shows the elemental composition and distribution of the K/Al$_2$O$_3$ at 700, 900 and 1000ºC and the used catalyst at 1000ºC. The SEM with EDX mapping shows the expected elemental constituents. EDX analysis provides useful information on the percentage of the elements present in the sample, to see how much of the catalyst was coated on the support. EDX analysis shows that K/Al$_2$O$_3$ calcined at 900ºC had the highest K loading (wt.%) at 6.50 wt.%, followed by 700ºC with 5.63 wt.% and 1000ºC with 2.46 wt.%. For the metal oxide catalyst in this study, the weight percentage for Al was the highest at 1000ºC, at 51.36 wt.%. The percentage of K loading dropped to 2.46 wt.% after calcination at 1000ºC which could be due to the metal being diffused into the bulk matrix of the catalyst [18]. As the calcination temperature increased, the wt.% of K decreased probably because of the extra oxygen coming from burning at high temperatures [5]. EDX confirmed the presence of K, O and Al in the potential catalyst. It was observed that on increasing the calcination temperature from 700 to 1000ºC, the elemental composition of K was reduced. This is due to the agglomeration of Al which will hinder the K species, thus reducing its amount. The catalyst after reaction revealed that the K loading dropped drastically to 0.36 wt.% probably due to the migration of K particles into the porous area of the alumina support during the reaction [19,20].

Table 1. Elemental composition from EDX analysis for K/Al$_2$O$_3$ catalyst calcined at 700, 900, 1000 and the used 1000ºC catalyst

Calcination Temperature (ºC)	Element	Weight Composition (%)
700	Al	49.34
	K	5.63
	O	45.03
900	Al	48.79
	K	6.50
	O	44.72
1000	Al	51.36
	K	2.46
	O	46.18
1000(used)	Al	5.91
	K	0.36
	O	69.55
	C	23.47
	S	0.24
	N	0.47

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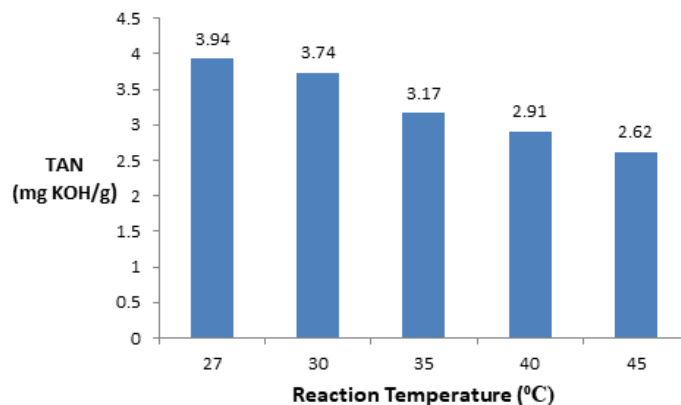Naphthenic Acid from Crude Oil

Figure 3. Effect of different reaction temperatures towards TAN value at a constant reaction time of 15 minutes

Effect of reaction temperature

To investigate the effects of the reaction temperature on the TAN, the crude oil mixture was added to 2-methylimidazole in ethanol at a mass ratio of 0.4:0.6, at a temperature range of 27-45°C for 15 minutes. Figure 3 shows the TAN removal rate increased with an increase in the reaction temperature, and when the temperature was increased to 45°C, a 40% acid removal rate was achieved from the original TAN of 4.38 mg KOH/g. The TAN was only reduced slightly when a lower reaction temperature of 27 to 35°C was used. Even though the TAN value further decreased when using a 45°C reaction temperature, it still failed to meet the PETRONAS requirement that the TAN value should be less than 1. 35°C was selected as the reaction temperature for further analysis as it was able to reduce the value of TAN to 3.17 mg KOH/g. This reaction temperature was deemed most suitable as it is cost efficient.

Effect of reaction time

The effect of the reaction time was investigated on the reduction of TAN at a fixed reaction temperature of 35°C. Figure 4 shows that as the reaction time increased from 15 to 25 minutes, the TAN further decreased from 3.26 to 2.25 mg KOH/g because more time was required for the decomposition of the reagent in the crude oil. This is because the deacidification rate increases with reaction time. At a reaction time of 10 minutes, the TAN value is higher because of the limited time available for the reaction between the reagent and pollutant to remove NA in the crude oils. With a 15 minute reaction time, the TAN value was reduced to 3.17 mg KOH/g. A 15 minute reaction time was chosen for further studies on the catalytic reaction since using a longer reaction time would increase the likelihood of emulsion problems.
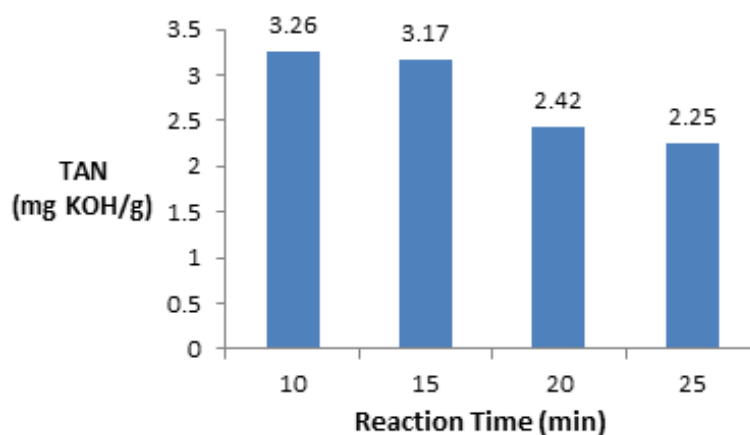

Figure 4. Effect of different reaction times on the TAN values of the crude oils at a constant reaction temperature of 35°C

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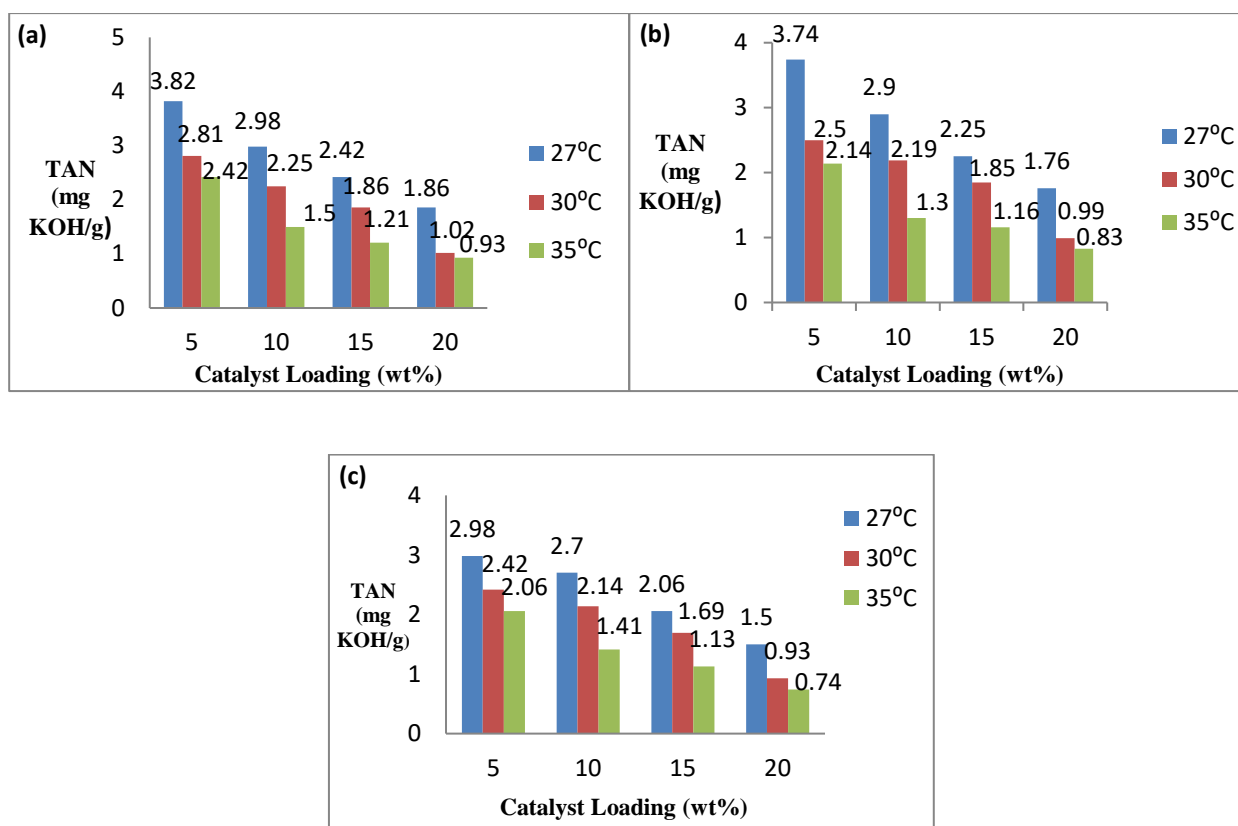Naphthenic Acid from Crude Oil

Figure 5. Effects of different percentages of catalyst loading (5, 10, 15 and 20 wt.%) at different calcination temperatures of (a) 700ºC (b) 900ºC and (c) 1000ºC on the TAN value for crude oil (reaction temperature: 27-35ºC, reaction time: 15 minutes, mass ratio of crude oil and reagent 0.4:0.6)

Effect of catalyst loading

Catalyst loading refers to the amount of catalyst added to the crude oil and chemical reagent during the extraction reaction to enhance the catalytic activity. There were four different catalyst loadings used in the reaction, which are 5, 10, 15 and 20 wt%, at a chosen reaction time of 15 minutes and at reaction temperatures of 25, 30 and 35ºC as shown in Figure 5. The addition of a catalyst with a higher calcination temperature further decreased the TAN of crude oil. This means that addition of the catalyst during the reaction helps to further reduce the NAs in crude oil where the reaction occurs at the surface of the catalyst with NAs bound to the catalysts' surface, thus reducing the TAN value [14]. K/Al$_2$O$_3$ calcined at 1000ºC, at a loading of 20 wt% was the most effective catalyst in lowering the acid number of the crude oil at 35ºC, where it was able to reduce the TAN value to less than 1.0 mg KOH/g. A 0.74 mg KOH/g was obtained from the original TAN of 4.38 mg KOH/g with 83.11% reduction. At 700ºC calcination temparature, the TAN could be reduced up to 0.93 mg KOH/g while at 900ºC, a reduction of 81% was recorded. With an increase in the calcination temperature from 700 to 1000ºC and reaction temperature from 27 to 35ºC, the TAN value was reduced to < 1. Thus, K/Al$_2$O$_3$ calcined at 1000ºC was chosen as the best catalyst in this study.

CONCLUSION

In conclusion, catalytic extraction was proven to be an effective technique in the removal of NAs in crude oil samples. Products of this reaction were found to meet the PETRONAS requirement for the TAN value which must be less than 1 mg KOH/g to prevent corrosion problems from occurring. In this study, we propose an eco-friendly and cost-effective method for TAN reduction in acidic crude oil. K/Al$_2$O$_3$ catalyst was shown to successfully reduce the original TAN from 4.38 to 0.74 mg KOH/g with an optimum calcination temperature of 1000ºC, reaction temperature of 35ºC and catalyst loading of 20 wt%, using 2-methylimidazole in ethanol as the chemical reagent. The XRD diffractograms revealed that the catalyst was highly amorphous, with the presence of Al$_2$O$_3$ dominating the K/Al$_2$O$_3$ catalyst phase, while SEM images showed that the surface morphology was inhomogeneous with a mixture of smaller and larger particles.

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