NEUTRALIZATION OF HIGHLY ACIDIC CRUDE OIL UTILIZING 2-METHYLIMIDAZOLE IN POLYETHYLENE GLYCOL SOLUTION

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Abstract

The naphthenic acids (NA) compound occurs naturally in the acidic crude oil and lead to corrosion problem in the oil refinery. Various methods can be used to reduce the NAs concentration in acidic petroleum crude such as catalytic decarboxylation, dilution or caustic washing but all these methods have its own weaknesses. The main objective of this study is to reduce total acid number (TAN) value of crude oil through neutralization process using catalyst and reagents. The parameters studied were catalysts calcination temperature, catalyst loading and reagent concentration. The acid removal agent used was a mixture of 10% 2-methylimidazole in polyethylene glycol (PEG) with reagent concentration of 100, 500, 1000 and 1500 ppm. Calcium was chosen as a base for the catalyst while Cu and Ni were used as a dopant. The potential catalyst was characterized by FTIR and TGA-DTG for its physical and chemical characteristics. Catalyst with calcination temperature of 1000°C, 7 beads of catalyst loading, 500 ppm of 2-methylimidazole in PEG, reaction temperature (35°C) and 5 minutes reaction times showed 97% deduction of TAN value from 3.93 to 0.13 mg KOH/g.

Keyword: Acidic crude oil, Naphthenic acid, Neutralization

Introduction

Naphthenic acid (NA) is a highly viscous liquid with a complex structure containing aromatic, aliphatic, poly and monocyclic carboxylic acids. It can be toxic to the fish and other aquatic life (Jones et al., 2001). Currently, the major problems in the petroleum industry are the corrosive properties of NA, which can lead to serious corrosion of equipment, mainly at high temperature (230-400°C), environmental disposal problem, higher maintenance costs, and the crude oil with low quality was produced. The consequences of the higher doses of NA still remain unknown; however, corrosion will happen if the total acid number (TAN) is more than 0.5 mg KOH/g (Huang et al., 2006; Wang et al., 2006). During the refinery process, if acidic species in the petroleum cannot be disposed, it will affect the quality of the final product, equipment, and environmental pollution.

There are various methods could be used to reduce NA such as catalytic decarboxylation, dilution, hydrogenation, caustic washing, esterification, and neutralization. Unfortunately, all these methods have their own weaknesses. Firstly, dilution is a procedure where a low TAN and high TAN were mixed together as the procedure. However, NA still remains in the crude oil and crude oil with low TAN was reduced (Shohaimi et al., 2015). Another method to decrease TAN in crude oils is by caustic washing, but an emulsion can be formed in wastewater that was hard to handle (Zhang et al., 2006; Shi et al., 2008). Esterification or neutralization can be used to remove NA, but this method has disadvantages after the process because it can be broken easily into salts and weak in nature. In the distillation column on crude oil refinement conditions, the ester can be decomposed into fatty acids (Park et al., 2011).

In this study, the heterogeneous catalyst is used in the neutralization process which it can reduce the high acidic crude oil with a low value of TAN. It will produce a high performance of operating unit which lead to low maintenance cost. When the TAN value is low, it will reduce the corrosion in oil pipelines and distillation units. The oil produced will be in good quality thus increase its market price. The corrosion in productions, storages, and transportations of heavy oil will be reduced when the value of TAN decrease at lower temperature and pressure.

Materials and Methods

Materials and feedstock

The materials were used without further treatment and purchased from QReC^{TM}. The heavy crude oil used as the feedstock in this study was obtained from Petronas Penapisan Melaka Malaysia (PPM) with the original TAN value of 3.93 mg KOH/g. A 2-propanol and toluene will be used as a titration solvent to dilute the crude oil sample. A reagent of 2-methylimidazole was used as acid removal agent and mixed with polyethylene glycol (PEG) with molecular weight 600 g/mol. In deacidification study, phenolphthalein solution in 1% (w/v) of ethanol was used as an indicator. Barium hydroxide and potassium hydroxide pellets were utilized as titrants (Shukri et al., 2017). Aluminium oxide, calcium nitrate, copper (II) nitrate and Nickel nitrate were purchased from Sigma - Aldrich.

Preparation of catalyst

Bimetallic calcium catalyst with nickel and copper acted as dopants were prepared in this study. The based-dopant ratio used was 10 (dopant) to 90 (base). In this study, the calcination temperatures used were 800°C, 900°C and 1000°C. The catalysts were prepared by using an aqueous Incipient Wetness Impregnation (IWI) method (Bakar et al., 2013). Nitrate salt was used as a precursor for calcium (Ca) catalyst. Based on the desired ratio, each of 5 g metal salts which was calcium nitrate $Ca(NO_3)_2$ was weighed in a beaker and the salt was dissolved in the small amount of distilled water (5 mL). The mixture became homogenize when the solutions were mixed together and stirred continuously by the magnetic bar for 30 minutes at room temperature (Shohaimi et al., 2014).

The aluminium oxide (Al_2O_3) was used as support materials with diameter of 3 to 5 mm. Then, the support was dipped into catalyst solution for 1 hour and transferred onto an evaporating dish lined with glass wool. To eliminate moisture content and allowed high-quality coating of the metal on the surface of the supported catalyst, the catalyst was aged inside an oven at 80-90°C for 24 hours (Shohaimi et al., 2015). By using a ramp rate of 5°C/min and followed by calcination in the furnace at 800°C for 5 hours, all the impurities, metal precursor and excess water were removed. The preparations of the potential catalyst were further optimized at a temperature of 900°C and 1000°C (Shohaimi et al., 2015).

Total Acid Number (TAN) determination

A 11.2 g of 2-methylimidazole was mixed in 100 mL polyethylene glycol with a molecular weight of 600 g/mol in a beaker. The mixture was then stirred with low heat until it completely dissolved. The glass-bottle was wrapped with an aluminium foil to prevent any contamination which will probably affect its effectiveness. A 0.2 g of crude oil sample was weighed in 100 mL beaker and diluted with the 40 mL of titration solvent mixture of 2-propanol: toluene: distilled water (49.5:50:0.5) (Shukri et al., 2017). A beaker equipped with a magnetic stirrer was filled with crude oil and 2-methylimidazole solution in PEG (MW:600) by a certain mass ratio. The constant temperature was controlled at 27°C, 35°C, and 40°C and then the mixture solutions were put into a beaker equipped with magnetic stirrer and thermometer (Shukri et al., 2015). Then the mixture of the solution was stirred for 5 minutes until it dissolved along with the catalyst loading of 3 beads.

Semi-micro color indicator titration process was used to determine the TAN value for Melaka crude oil (TAN = 3.93 mg KOH/g). The stable red color was observed at the end of the titration process after the titrant's solution was stirred continuously by the magnetic stirrer. A 3 drops of phenolphthalein solution were utilized as an indicator. The titration technique was studied on PPM crude oils before and after catalytic deacidification steps. The titrants used were barium hydroxide, $Ba(OH)_2$ and potassium hydroxide (KOH) solutions. The same procedure was repeated by using copper and nickel as a dopants with different concentration of reagent used (100, 500, 100, 1500 ppm), different catalyst loading (3, 4, 5, 7 beads), different calcination temperatures (800, 900, 1000°C), different reaction temperature (27, 35, 40°C) at constant reaction times of 5 minutes. The TAN values of the samples were calculated in milligrams of potassium hydroxide per gram of sample (mg KOH/g) by using the following equation:

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

Where,

56.1 = Molecular weight of KOH in g/mol.

c = Concentration in mol/L of the standard volumetric KOH solutions

V_{KOH} = Volume in mL, of titrant required for the determination

V_B = Volume in mL, of titrant required for the blank test

m = Mass in grams, of the test portion

Results and Discussion

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR results for fresh and spent bimetallic catalyst of Cu/Ca and Ni/Ca(10:90)/Al_2O_3 are shown in **Figure 1**. The peaks that assigned for the Cu/Ca and for Ni/Ca catalyst are tabulated in **Table 1**. The results obtained show a group assignment for peaks that exist in Cu/Ca and Ni/Ca(10:90)/Al_2O_3 catalyst at 960.75 - 527.21 cm^{-1} at a calcination temperature of 1000°C before and after neutralization process which due to the stretching mode of metal oxide group. This statement was supported by Shukri et al. (2017) where it stated that the wavelength < 800 cm^{-1} indicated the stretching mode for metal oxide of the catalyst.

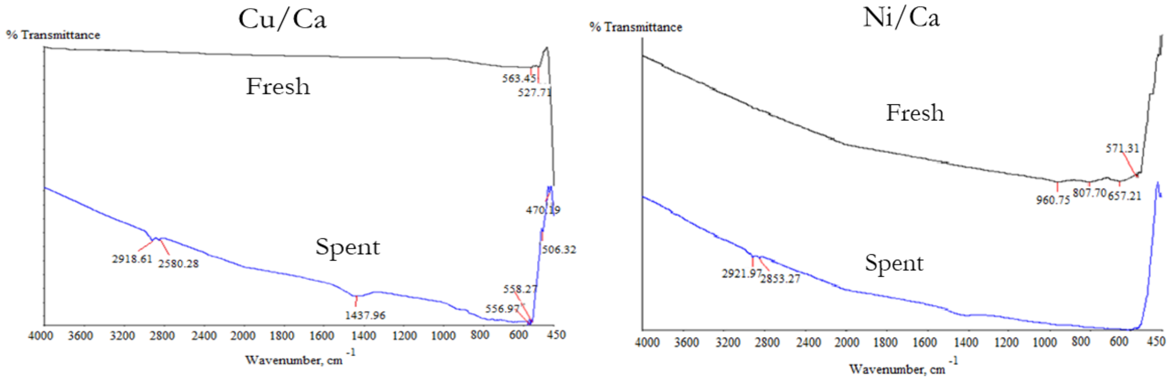

Figure 1 FTIR spectra for fresh and spent of Cu/Ca(10:90)/Al_2O_3 and Ni/Ca(10:90)/Al_2O_3 catalyst at calcination temperature of 1000ºC

According to Shohaimi et al. (2014), it can be concluded that the catalyst before deacidification process that calcined at 1000°C gave complete formation of pure metal oxide and also removed the nitrate precursor that was present in the catalyst samples. This can be seen from the FTIR spectra that were observed from both of bimetallic metal oxide catalyst. The NA was reduced effectively by using both catalysts calcined at 1000°C.

Based on the FTIR spectrum of Cu/Ca, it can be observed that there was intense absorption detected at wavelength of 1437.96 cm^{-1} after reaction due to sp^2 C-H stretching while at a frequency of 2850.28 - 2918.61 cm^{-1} indicated the presence of C-H (sp^3, stretch) stretching. This is probably due to the presence of impurities from alkane and alkene groups of long chain acids which have bound to the catalyst surface. The peaks for Ni/Ca in FTIR spectrum showed similar stretching at 2853.27 - 2921.97 cm^{-1}.

Table 1 FTIR peaks assignment of Cu/Ca and Ni/Ca(10:90)/Al_2O_3 catalyst

Catalyst	Wavenumber (cm^{-1})	Assignment
Fresh Cu/Ca(10:90)/ Al_2O_3	563.45-527.71	Stretching mode of metal=oxygen (M=O)
Spent Cu/Ca(10:90)/ Al_2O_3	2918.61-2850.28 1437.96 566.97–558.27	sp^3 C-H stretching sp^2 C-H stretching Stretching mode of Metal=Oxygen (M=O)
Fresh Ni/Ca(10:90)/ Al_2O_3	960.75-571.31	Stretching mode of Metal=Oxygen (M=O)
Spent Ni/Ca(10:90)/ Al_2O_3	2921.97 2853.27 557.23	sp^3 C-H stretching sp^2 C-H stretching Stretching mode of metal=oxygen (M=O)

In conclusion, the catalyst surface for Cu/Ca and Ni/Ca(10:90)/Al_2O_3 that was observed by FTIR spectrum showed a similar pattern as a fresh catalyst. TAN value for crude oil by using Cu/Ca and Ni/Ca catalysts gave the same reduction where the value was reduced to 0.13 mg KOH/g from initial TAN of 3.93 mg KOH/g.

Thermal Gravimetry Analysis-Differential Thermal Gravimetry (TGA-DTG)

The catalysts were characterized by TGA-DTG analysis to study its thermal stability after aged overnight in an oven at 80°C -90°C. TGA profile exhibited some well-defined section of weight loss accompanied by different slopes of thermogravimetric trace (weight loss rate). The temperature was programmed from 60°C to 1000°C. The thermogram of the Cu/Ca (10:90)/Al_2O_3 catalyst showed four stages of weight loss while for Ni/Ca(10:90)/Al_2O_3 showed 3 stages of weight loss. **Figure 2** shows the thermograms for Cu/Ca(10:90)/Al_2O_3 and Ni/Ca(10:90)/Al_2O_3 catalyst while the detailed of weight loss for each stage is tabulated in **Table 2**.

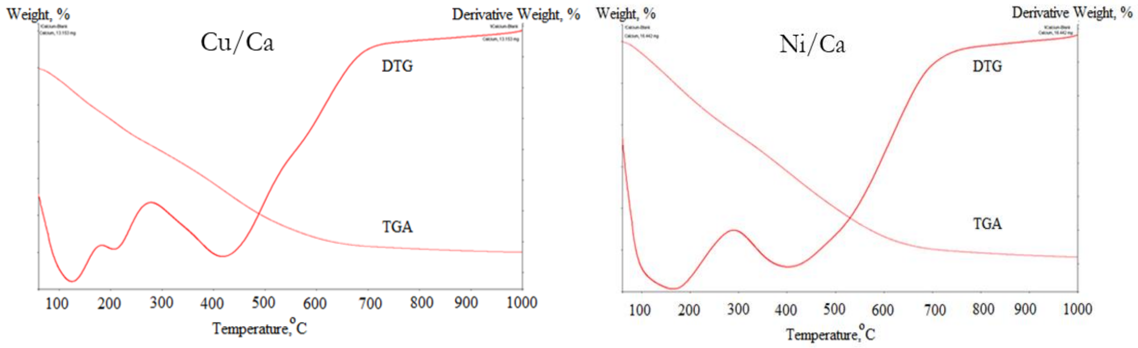

Figure 2 TGA-DTG thermogram of Cu/Ca(10:90)/Al_2O_3 and Ni/Ca(10:90)/Al_2O_3 catalysts after aging in an oven for 24 hours at 60°C

The total weight loss for Cu/Ca was 24.76 % while for Ni/Ca was 25.70 %. These two results showed the complete removal of the impurities on the catalyst around 670°C. Imtiaz et al. (2013) said that impurities were removed from the catalysts even at a lower temperature of 200°C-700°C.

Table 2 TGA analysis result for bimetallic alkaline earth metal oxides catalyst with the uses of Cu and Ni as a dopant

Catalyst	Heating Temperature (℃)	Weight Loss (%)	Description
Cu/Ca(10:90)/ Al_2O_3	60-120	3.07	Loss of crystal water and a surface water molecule.
	120-200	4.36	Complete removal of water
	200-430	9.21	Decomposition of surface hydroxyl and carboxyl groups
	430-1000	8.12	Loss of nitrate compound and surface hydroxyl molecule
Ni/Ca(10:90)/ Al_2O_3	60-150	4.90	Loss of crystal water and a surface water molecule.
	150-400	10.73	Complete removal of water and formation of pure metal oxide
	400-1000	10.07	Loss of nitrate compound and surface hydroxyl molecule.

For Cu/Ca catalyst, the first stage of weight loss ranges between of 60-120°C referred to the loss of crystal water and a surface water molecule. At the temperature of 120-200°C, the weight loss observed could be due to the complete removal of water (Wang et al., 2010). Decomposition of surface hydroxyl and carboxyl groups occurred at 200-430°C. The last stage was at the temperature of 430-1000°C which due to the decomposition of nitrate.

The first stage for Ni/Ca catalyst was at the temperature of 60-150°C revealed the loss of free water molecule and nitrate compound from the supported catalyst. The complete removal of water and formation of pure metal oxide were observed at the temperature of 150-400°C. The nitrate compound and surface hydroxyl molecule were decomposed from the samples in the last stage at the temperature of 400-1000°C (Shohaimi et al., 2014). Heating temperature around 680 to 1000°C of the graphs showed a constant weight loss because at this temperature all the impurities were already removed and the metal oxide was completely formed.

This statement is in agreement with the result shown in the effect of catalyst calcination temperature by using Cu/Ca and Ni/Ca (10:90)/Al_2O_3 catalyst at 1000°C as the calcination temperature below 1000°C is insufficient to eliminate the entire nitrate compounds that were originated from metal precursor (Shohaimi et al., 2014). Therefore, this study proves that by using 1000°C calcination temperature, the TAN value was successfully reduced to 0.13 mg KOH/g where the results can be supported by the complete formation of pure metal oxides when the catalyst was calcined at 1000°C temperature.

Effect of the reaction temperature

Figure 3 shows that at the reaction temperature of 27°C gave a high TAN value which was 1.78 mg KOH/g and further decreased to 1.31 mg KOH/g at 35°C and lastly decreased to 1.03 mg KOH/g at 40°C. The TAN value for the reaction temperature of 27°C was higher because the deacidification process was too slow at room temperature (27°C) (Zamberi et al., 2016). The catalyst's surface was distracted by the reagent itself and makes the reaction slow and cannot assist the reagent to remove the acids in a period of time (Shukri et al., 2015).

The reaction temperature at 35°C produced TAN value of l.31 mg KOH/g. This experiment needs a low reaction temperature as required by industry to achieve environmental friendly and lower cost production (Zhang et al., 2006). At the reaction temperature of 40°C even though it produced the lowest TAN value which was 1.03 mg KOH/g, higher heating process in the industrial scale lead to higher cost and the difference in extraction efficiency at a higher temperature are not very important so low temperature becomes more preferable (Shah et al., 2014). The reaction temperature of 27°C has produced the highest TAN due to the lower viscosity and makes the deacidification process was slower compared to the reaction temperature of 35°C.

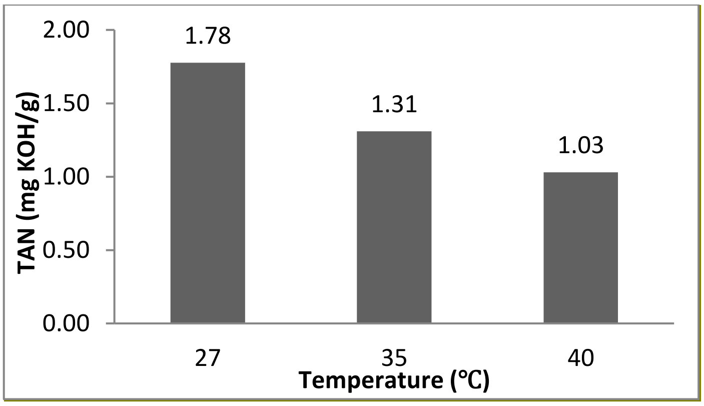

Figure 3 Effect of different reaction temperature towards TAN value. (Constant parameter: reaction time = 5 minutes, concentration of reagent = 500 ppm)

TAN value at the reaction temperature of 40°C was the lowest which was 1.03 mg KOH/g because the viscosity of NA was lower and make the removal of the acid process become much faster. As the temperature increased to 40°C, the conversion of NA required some energy to induce the process (Sun and Shi, 2012). Shohaimi et al. (2014), also explained that the main component in crude oils was vaporized because the favourable temperature for catalytic activity in acid removal process occurs at 35°C to 40°C. Thus, the reaction temperature at 35°C was selected for further investigation on catalyst efficiencies which it produces the low TAN of 1.31 mg KOH/g with (constant parameter: reaction time = 5 minutes, the concentration of reagent = 500 ppm.

Effect of catalyst loading

In this investigation, the $Cu(NO_3)_2$ and $Ni(NO_3)_2$ were acted as dopants for a monometallic of Ca/Al_2O_3. **Figure 4** shows the trend of TAN value with different catalyst loading. The concentration of 2-methylimidazole in PEG used was 500 ppm at the constant reaction temperature of 35°C. These catalysts were tested using different calcination temperatures (800°C, 900°C and 1000°C) and different catalysts loading (3, 4, 5, and 7 beads). As the catalyst added into the PPM crude oils sample, it gave a better reduction on TAN value compared to the reaction without the addition of catalyst.

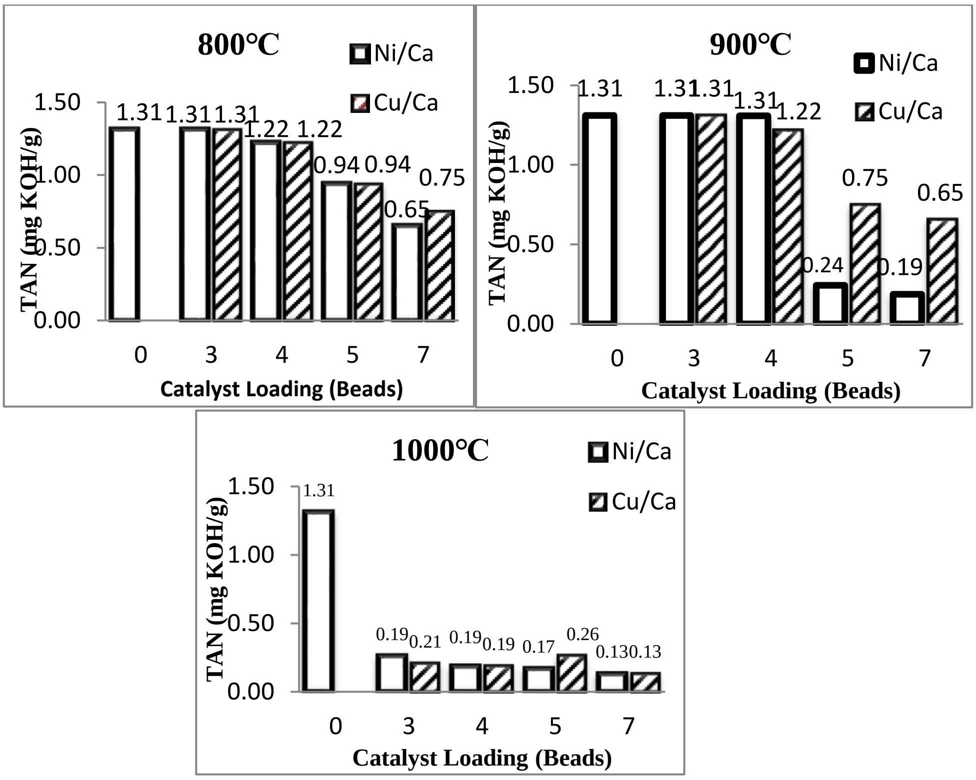

Figure 4 Effect of different catalyst loading towards TAN value. (Constant parameter: reaction time = 5 minutes, concentration of reagent = 500 ppm, reaction temperature= 35°C)

The trend of catalysts loading at a calcination temperature of 800°C was decreasing for both types of catalyst. It could be seen that 7 beads of catalyst successfully reduce the TAN value which produced a good result of TAN value. The 3 beads of catalyst loading slightly reduced the TAN value to 1.50 mg KOH/g for both catalysts at the calcination temperature of 800°C. At catalyst calcination temperature of 900°C, it showed that the reduction of TAN value by using 7 beads of catalyst loading which were 0.65 mg KOH/g (Cu/Ca) (10:90)/Al_2O_3 and 0.19 mg KOH/g (Ni/Ca) (10:90)/Al_2O_3 while 3 beads of catalyst loading gave TAN value 1.31 mg KOH/g (Cu/Ca) (10:90)/Al_2O_3 and 1.59 mg KOH/g (Ni/Ca) (10:90)/Al_2O_3. As observed from the results, an increase in the catalyst loading, will further decrease the TAN value, thus the catalytic reaction becomes faster and efficient. This is due to the addition of basic dopant will lead to the formation of basic catalyst as it was superior to eliminate the naphthenic acid as NA is a weak acid (Shukri et al., 2015).

At a calcination temperature of 1000°C, the trends of TAN value for Ni/Ca were decreasing as the amount of catalyst loading increased while for Cu/Ca the TAN value decrease and increase at 5 beads and become decrease back when adding more catalyst loadings to 7 beads. The best catalyst loading was by using 7 which it reduces the TAN value to 0.13 mg KOH/g for both Cu and Ni beads because the surface area of active site was increased due to the increasing of the catalytic activity by the metal Cu/Ca and Ni/Ca while 3 beads of catalyst loading was not good enough in reducing the TAN value. The cleavage of C-C bond occurs due to the presence of Cu, thus reducing the TAN value (Shukri et al., 2015). It can be concluded that 7 beads of Cu/Ca and Ni/Ca catalysts loading were the best catalyst which it reduced the high TAN value as the acid removal rate increased efficiently.

Conclusion

In this study, the catalytic deacidification method successfully reduced the TAN value of crude oil by meeting the PETRONAS requirement for TAN value which must be less than 1 mg KOH/g to prevent corrosion problem. The TAN value of PPM crude oil was decreased from the initial value of 3.93 mg KOH/g to 0.13 mg KOH/g for both catalysts used which were Cu/Ca and Ni/Ca catalysts with alumina as a support material. The optimum parameter used was 500 ppm of 2-methylimidazole in PEG for reagent concentration, a catalyst calcination temperature of 1000°C, 7 beads of catalysts loading, the reaction temperature of 35°C and at a constant reaction time of 5 minutes.

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Conflict of interests

Authors hereby declares that there is no conflict of interests with any organization or financial body for supporting this research.

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