

Kinetics and reaction pathways of total acid number reduction of cyclopentane carboxylic acid using subcritical methanol

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Cyclopentane carboxylic acid (CPCA) is a model compound of Naphthenic acids (NAs). This objective of this paper is to discover total acid number (TAN) reduction kinetics and pathways of the reaction between CAPA and subcritical methanol (SubC-MeOH). The experiments were carried out in an autoclave reactor at temperatures of 180–220°C, a methanol partial pressure (MPP) of 3 MPa, reaction times of 0–30 min and CPCA initial gas phase concentrations of 0.016–0.04 g/mL. TAN content of the samples were analyzed using ASTM D 974 techniques. The reaction products were identified and quantified with the help of GC/MS and GC-FID respectively. Experimental results reveal that TAN removal kinetics followed first order kinetics with an activation energy of 13.97 kcal/mol and a pre-exponential factor of 174.21 s⁻¹. Subcritical methanol is able to reduce TAN of CPCA decomposing CPCA into new compounds such as cyclopentane, formaldehyde, methyl acetate and 3-pentanol.

Keywords: cyclopentane carboxylic acid, subcritical methanol, total acid number, naphthenic acid, activation energy.

INTRODUCTION

Naphthenic acids (NAs) present in heavy oil (API gravity between 10 and 20)¹ are the primary contributor to the acidity of heavy oil². Acidity of petroleum oils is expressed in terms of total acid number (TAN), the amount of potassium hydroxide in milligrams that is needed to neutralize the acids present in one gram of oil³. NAs are complex mixtures of alkyl-substituted acyclic and cycloaliphatic carboxylic acids found in hydrocarbon deposits (petroleum, oil sands bitumen, and crude oils)^{4–6}. They are thought to have originated from aerobic microbial degradation of petroleum hydrocarbon⁴. They are described by the general chemical formulae, C_nH_{2n+z}O₂, where n indicates the carbon number and z is zero or a negative, even integer that specifies the hydrogen deficiency resulting from ring formation. The absolute value of z divided by 2 gives the number of rings present in the compounds. The rings can be fused or bridged. Figure 1 shows examples of typical structures of NAs which have a different number of rings⁵. Cyclopentane carboxylic acid (CPCA) is a model compound of NAs whose z value is -2.

The corrosive NAs can cause many problems such as equipment failures, high maintenance cost, more frequent turnaround, reduce product quality and environmental

disposal problems⁷. Research results revealed that corrosion happens at TAN level of 1.5 mg KOH/g and above⁸. Apart from that, these NAs may cause emulsification during the refining process making the separation process more complex. As a consequence, crude oils with high TAN content are often marketed at a lower market price⁹. Therefore, the crucial problem that facing by the oil refineries is to find the right method to remove or reduce the acidic substances from petroleum¹⁰.

There are two ways to increase the value of acidic crude oil such as prevention method and reduction method. The prevention method includes blending, upgrading material and use of metal protective inhibitors. In prevention methods, NA still remains in crude oil which will affect the quality of oil in the earlier stages. So, research is more concentrated on the reduction method. Research results on TAN reduction methods and their disadvantages are summarized in Table 1. Recently, researches are concentrated on reducing acidity of NAs using green processes. Ionic liquids (ILs) and supercritical fluid (SCF) based technologies are widely used in different fields as an environmentally benign process. IL based technology implies high cost. Methanol is simpler form of alcohol having bubble point, T_{bp} = 64.6°C and P_{bp} = 0.1 MPa, and critical point, T_c = 239.45°C and P_c = 8.10 MPa. Methanol below its critical point and above its bubble point is considered as subcritical methanol (SubC-MeOH). Methanol above its critical point is known as supercritical methanol (SC-MeOH). In fact, TAN value of NAs need to reduce at temperature less than distillation temperature of crude oil and low pressure for reducing corrosion in production, storage, and transportation of heavy oil. SubC-MeOH can be the best option for acidity reduction at low cost.

The aim of this technical paper is to explore the capability of SubC-MeOH for reducing acidity of CPCA, a model compound of NAs. In addition, TAN removal kinetics and reaction pathways are also explored at temperatures of 180–220°C, methanol partial pressure (MPP)

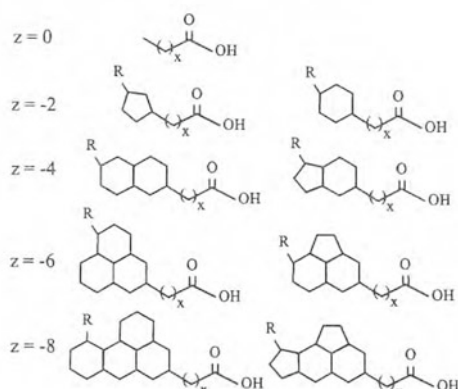


Figure 1. General structure of NAs

Table 1. Summary of techniques employed in TAN reduction of crude oil

Technique employed	Raw materials	Operating condition	TAN removal [%]	Disadvantages	References
Catalytic destruction	Hydrocarbon oils	T: 300–475°C Catalyst: calcium carbonate containing about 1% lithium carbonate	Not mentioned	Catalytic process is not suitable for treating heavy oil	Rudolf ¹¹ , 1941
Catalytic decarboxylation	Texaco crude oil and Acid mixture (CPCA, cyclohexane carboxylic acid (CHCA), benzoic acid (BA), pentyl-cyclopentane carboxylic acid, heptyl-benzoic acid)	Texaco crude oil: T: 300°C, t = 4 h Catalyst: NA-Cat-7 Acid mixture: T: 200°C, t = 4 h Catalyst: NiSiO ₂ , NA-Cat-1, NA-Cat-3, NA-Cat-4	Texaco crude oil: 78.80 Acid mixture: CPCA conversion: NiSiO ₂ : 21.50, NA-Cat-1: 25.50, NA-Cat-3: 70.80, NA-Cat-4: 86.50	Catalytic process is not suitable for treating heavy oil	Zhang et al. ¹² , 2005
Solvent extraction	Second vacuum fraction (SVF, a vacuum gas oil pumped from the second position in the vacuum distillation tower of petroleum)	T: 60–90°C Additive: an ammonia solution of ethylene glycol	85	Efficiency of the process is not high and additives are required	Wang et al. ¹³ , 2006
Thermal cracking and catalytic decarboxylation	Bitumen-derived HVGO	T: 360°C Catalyst: CaO	100	Catalytic process is not suitable for treating heavy oil	Ding et al. ¹⁴ , 2009
Catalytic decarboxylation	Model acid solution includes five different acids such as CPCA, CHCA, Cyclohexane propionic acid (CHPA), BA and Trans-4-pentyl cyclohexane carboxylic acid (TP-CHCA).	T: 400–800°C, t: 10 h Catalyst: alkali earth metal oxides were used in this study, CM–MeO, C–MeO, and CP–MeO (Me = Mg, Ca, Sr, Ba).	Close to 100	Catalytic process is not suitable for treating heavy oil	Oh et al. ¹⁵ , 2011
Esterification	Naphthenic acids from Colombian heavy crude oil	T: 150–200°C, t = 600 min	90.90	Processing time is long	Quiroga-Becerra et al. ¹⁶ , 2012
Supercritical water	Naphthenic acids	T: 400–490°C, P: 0–45 MPa, t = 0–90 min	83	High temperatures support corrosion and require more investment in the equipment	Mandal et al. ⁷ , 2012
Supercritical methanol	Naphthenic acids	T: 300–350°C, P: 10 MPa, t = 0–60 min	96.87	High temperatures support corrosion and require more investment in the equipment	Mandal et al. ³ , 2013
Ionic liquid (IL) based extraction	Doba crude oil	T: 25–90°C t: 20 min IL: tetraalkylammonium and tetraalkylphosphonium amino acid based ILs	94.97	IL is costly and separation of IL is also difficult.	Anderson et al. ¹⁷ , 2013
Esterification	Crude oil	T: 300°C, Space velocity: 2.5 h ⁻¹ , Catalyst: SnO–Al ₂ O ₃	82.14	Catalytic process is not suitable for treating heavy oil	Wang et al. ² , 2014
Catalytic decomposition	China crude oil	T: 330°C Catalyst: Mg–Al hydrotalcite/γ-Al ₂ O ₃	80	Catalytic process is not suitable for treating heavy oil	Wang et al. ¹⁰ , 2014
Catalytic decomposition	Korean crude oil	T: 35–40°C Catalyst: Cu/Ce (10:90)/Al ₂ O ₃ Reagent: 4% ammonia solution in polyethylene glycol	93.3	Catalytic process is not suitable for treating heavy oil	Shukri et al. ⁹ , 2015
Catalytic decarboxylation	High-acidity crude oil	T: 300–350°C, t: 4 h Catalyst: steel slag	43.50	Catalytic process is not suitable for treating heavy oil.	Dias et al. ¹⁸ , 2015
IL based extraction	Naphthenic acids	T: 30°C, t: 1 h IL: N-alkyl imidazolium ionic liquids with highly alkaline phenolate anions IL/oil: 0.01–0.09	100	IL is costly and separation of IL is also difficult	Shah et al. ¹⁹ , 2016

of 3 MPa, reaction temperatures of 0–30 min and CPCA initial gas phase concentrations of 0.016–0.04 g/mL.

METHODOLOGY

Material used

CPCA (C₆H₁₀O₂) was chosen as a model compound of NAs in this study. It has one cyclopentyl group with one carboxyl group where z = –2 and n = 6. This compound (purity: 99%) was purchased from Sigma-Aldrich and was used without further treatment. It is almost a colorless liquid having molecular weight 114.14 g/mol, boiling point 216°C, and density 1.053 g/mL at a temperature

of 25°C. Other reagents, toluene, 2-propanol, potassium hydroxide, and phenolphthalein were obtained from EMD Corporation and were used without further treatment. The mixture of toluene, and 2-propanol at a ratio of 1:1 was used as solvent for collecting the samples and determining TAN.

Equipment

All experiments were performed in 25 ml autoclave reactor fabricated by Shanghai Yanzheng Experiment Instrument Co., Ltd., China for maximum temperature of 230°C and pressure of 3 MPa (gauge). The reactor is a stainless steel structure, durable and gas-tight. Inner

chamber of the reactor is made from polytetrafluoroethylene (PTFE) to minimize corrosion.

Experimental procedure

Approximately 0.40–1.0 g of CPCA and 0.72–0.87 g (approximately 0.9–1.1 mL) of methanol were charged into the autoclave reactor. The amount of loaded methanol was maintained to control MPP at constant reactor volume and reaction temperature. The well-known Peng-Robinson equation of state was exercised to compute the amount of methanol by fixing the temperature and the MPP. A precise amount of methanol was charged into the reactor for the time of experiments. The reactor was then loaded into a furnace that was preheated to the planned temperature. After a specific reaction time, the reactor was removed from the furnace and kept it in a water bath by allowing sufficient time to cool the reactor at room temperature. Finally, the products were collected in sample bottles by washing the reactor interior at least three times with the solvent.

Analytical procedure

Mandal et al.^{3, 7} disclosed that American Society for Testing Materials (ASTM) D 974 has sufficient accuracy for evaluating TAN value. This method was used in this study for evaluating TAN value. In this process, a mixture of toluene and 2-propanol in 1:1 ratio was used as solvent and phenolphthalein was used as an indicator for detecting end point. A precise amount of recently prepared 0.05 mol/L standard potassium hydroxide solution was utilized as a titrant. The analysis was carried out carefully to achieve low TAN value. The following terms are used in this study:

Titration was conducted to estimate the acidity of NAs. TAN was calculated by identifying the amount of potassium hydroxide needed to neutralize 1 g of CPCA using the following equation:

$$\text{TAN} \left(\frac{\text{mg KOH}}{\text{g CPCA}} \right) = \left[\frac{V_{\text{KOH}} \times N_{\text{KOH}} \times 56.10}{W_{\text{CPCA},0}} \right] \quad (1)$$

where V_{KOH} is volume of KOH in mL, N_{KOH} is the concentration of KOH in mmol/mL, and is the amount of NA in g.

TAN reduction was calculated in order to identify the extent of reduction of acidity in CPCA using the equation shown below:

$$\text{TAN reduction (\%)} = \frac{\text{TAN}_0 - \text{TAN}_t}{\text{TAN}_0} \times 100 \quad (2)$$

where TAN_0 is the initial TAN in loaded CPCA and is the TAN at reaction time, t .

The reaction products were also analysed using gas chromatography-mass spectrometry (GC/MS) method for identifying reaction products. The column, BPX5 non polar and low bleed capillary column, 30 m long by 0.25 mm diameter was used. The samples were diluted by adding methylene chloride before charging the samples in GC/MS analyser at a specified temperature program. In addition, the reaction products were quantified using Gas chromatography – flame ionization detector (GC-FID) using same column and temperature program.

All experiments were carried out triple. The error margin of the achieved data was less than 4% with 95% confident.

RESULTS AND DISCUSSION

TAN reduction

Mandal et al.⁷ discovered that SC-MeOH have capability of reducing approximately 100% TAN of NAs at a temperature of 350°C and a MPP of 10 MPa. But this condition is very high to treat heavy oil for reducing corrosion as a pre-treatment. Quiroga-Becerra et al.¹⁶ discovered that approximately 95% TAN was reduced from NAs obtained from Colombian heavy crude oil at temperature of 250°C, reaction time of 600 min, and a methanol to acid ratio of 20:1. It is no doubt that SubC-MeOH can reduce acidity of NAs. To observe the capability of SubC-MeOH for TAN reduction of CPCA, approximately eighteen experiments were performed at temperatures of 180–220°C, a CPCA gas phase concentration of 0.032 g/mL, and reaction times of 0–30 min. CPCA used in this study had an initial TAN value 545.5 mg KOH/g CPCA. Figure 2 shows that TAN removal of CPCA was increasing with increasing reaction temperature and time at a specific MPP. Approximately 17.56% TAN was removed at a temperature of 220°C, a MPP of 3 MPa, a reaction time of 30 min. SubC-MeOH is a good solvent for CPCA. During reaction, CPCA and methanol was mixed properly with increasing temperature and thus increase the collisions between them to increase the rate of reaction.

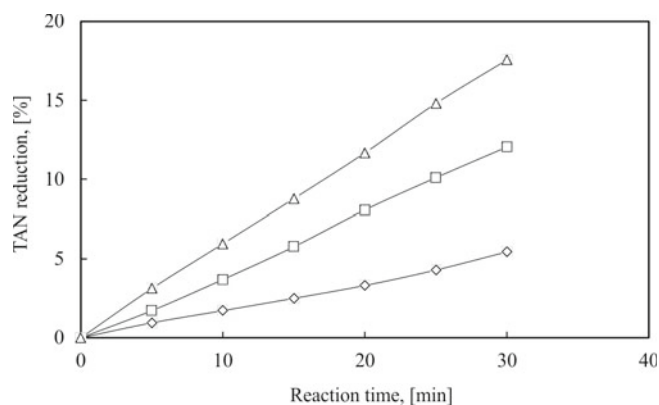


Figure 2. Variation of TAN reduction at a function of temperature and reaction time (Symbol: ◇, at temperature of 180°C; □, at temperature of 200°C; Δ, at temperature of 220°C)

TAN reduction kinetics

Reaction kinetics is very important to design chemical reactor. Mandal et al.³ shows that TAN reduction kinetics of the reaction of NA and SC-MeOH follow first order kinetics. Besides that reaction between some organic acids and fatty alcohol showed first order kinetics with respect to acid²⁰. On the other hand, Wang et al.¹³ proves that reaction kinetics of esterification reaction between NA and methanol with and without SnO catalyst follows second order kinetics. Likewise esterification reaction between oleic acid and methanol under the pressure also shows the second order kinetics²¹. Similarly, the kinetics of the esterification process of NAs in Colombian heavy crude oil using methanol without adding any catalyst

follows second order kinetics¹⁶. To discover the reaction order of the reaction between CPCA and SubC-MeOH, a plot of $-\ln(1-X)$ where X denotes fraction of TAN reduction versus reaction time is plotted (Fig. 3). Each set of data give straight line which obtained with the least square method pass almost exactly through the origin indicating first order kinetics with respect to TAN removal. The experiments were conducted by changing the initial concentration of CPCA at a temperature of 220°C and a MPP of 3 MPa, indicating that reaction rate is independent on initial CPCA concentration. The reaction kinetics analysis of this study was tested and evaluated to a maximum of 17.56% TAN removal as kinetics data were more compatible with first order kinetics at this extent²². An Arrhenius type temperature dependency acidity removal rate constant is presented in Figure 4. By exploring this plot the activation energy and pre-exponential factor of the said reaction was discovered and the respective values were 13.97 kcal/mol and 174.21 s⁻¹. Thus the Arrhenius equation can be rewritten as:

$$k_{\text{SubC-MeOH}} = 174.21e^{\frac{-13.97}{RT}} \quad (3)$$

The activation energy for reaction between SC-MeOH and NAs is 5.78 kcal/mol³. Wang et al. in 2006¹³ obtained activation energy of 36.74 kcal/mol and 24.89 kcal/mol for esterification reaction between methanol and NA with 1wt.% SnO catalyst and without catalyst respectively. In addition, the activation energy for the esterification reaction of NAs in Colombian heavy crude oil¹⁶ and methanol at temperatures of 150–250°C is 17.27 kcal/mol. Thus, SubC-MeOH requires higher energy than SC-MeOH, and lower energy than the other methods

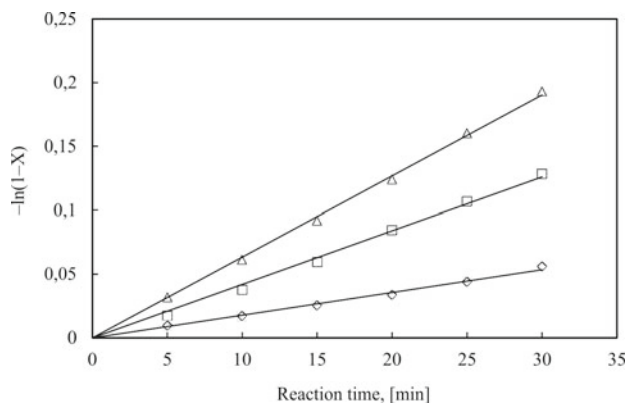


Figure 3. TAN reduction kinetics plot (Symbol: \diamond , at temperature of 180°C; \square , at temperature of 200°C; Δ , at temperature of 220°C)

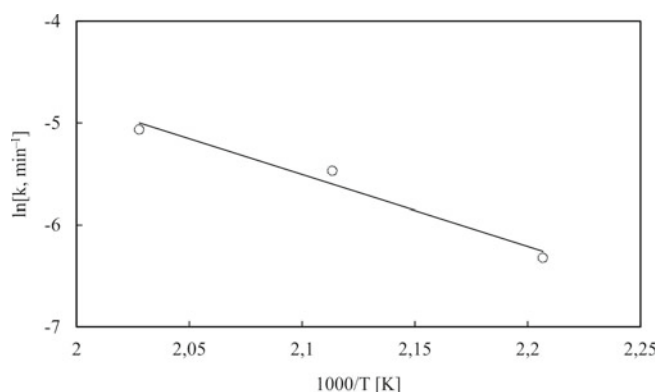


Figure 4. Arrhenius plot

presented by Wang et al. and Quiroga-Becerra et al. The methanol in this reaction is behaved not only as reaction medium but also as reactant.

Reaction pathways

CPCA was decomposed into other non-acidic compounds by reacting with methanol at subcritical condition. Figure 5 depicts that concentration of CPCA was decreasing with increasing reaction temperature and time. Initial CPCA concentration was 0.0324 g/mL. This value was decreased to 0.0256 g/mL at a temperature of 220°C, a MPP of 3 MPa, a reaction time of 30 min. Esterification reaction is a well-known process of TAN reduction of crude oil. But at the crude oil refinement temperature some esters can decompose into organic acids and create problems on distillation column and product quality as the structure of the ester will determine its thermal stability. Mandal et al.³ in 2013 have done experiments using NA and SC-MeOH and have identified esters (like, nonanoic acid, methyl ester; decanoic acid, methyl ester and so on), saturated alkylbenzenes (like, heptylbenzene), and alkanes (like, decosane) using GC-MS that were not present in NA samples. Current study revealed that non catalytic SubC-MeOH process reacted with CPCA and produced not only ester but also cyclopentane, formaldehyde and alcohol (Fig. 6). The reaction products were quantified using GC-FID and the results are presented in Table 2. GC/MS and GC-FID analysis results show that the reaction products contains cyclopentane, formaldehyde and 2-tridecanone at temperature of 180°C, reaction time of 15 min. Calvert et al.²³

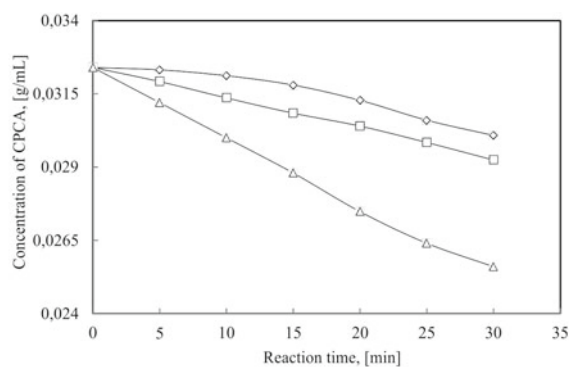


Figure 5. Variation of CPCA concentration at a function of temperature and reaction time (Symbol: \diamond , at temperature of 180°C; \square , at temperature of 200°C; Δ , at temperature of 220°C)

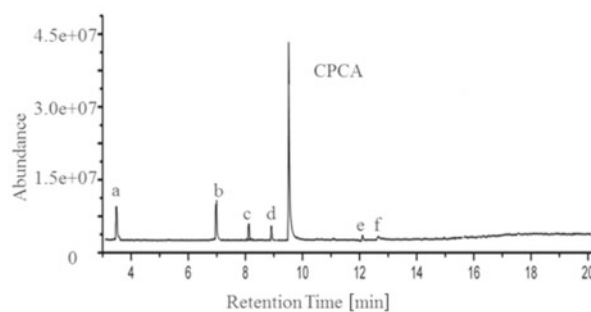
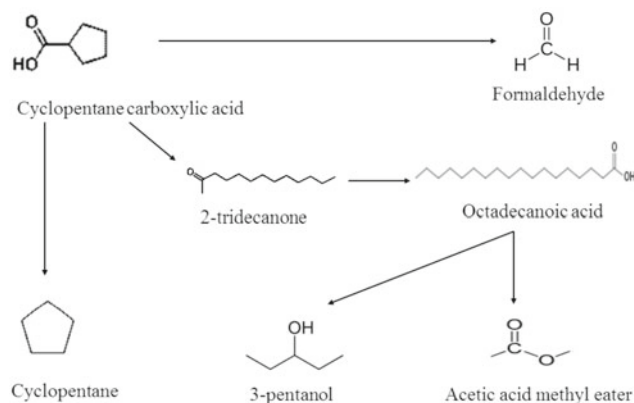


Figure 6. GC-MS chromatogram for CPCA at a temperature of 220°C, MPP of 3 MPa (a. Formaldehyde; b. Cyclopentane; c. Acetic acid methyl ester; d. 3-pentanol; e. 2-tridecanone; f. Octadecanoic acid)

Table 2. Product distribution at different temperatures

Temperature [°C]	180					
Reaction time [min]	5	10	15	20	25	30
MPP [MPa]	3					
Compounds	Molar yield [%] / Conversion [%]					
Conversion	–	–	2.5	3.31	4.29	5.44
CPCA	–	–	97.5	96.69	95.71	94.56
Cyclopentane	–	–	0.84	1.13	1.5	1.8
Formaldehyde	–	–	0.65	0.82	1.1	1.4
2-tridecanone	–	–	0.68	0.64	0.55	0.42
Octadecanoic acid	–	–	–	0.27	0.18	–
3-pentanol	–	–	–	–	0.25	0.34
Acetic acid methyl ester	–	–	–	–	0.39	0.55
Temperature [°C]	200					
Reaction time [min]	5	10	15	20	25	30
MPP [MPa]	3					
Compounds	Molar yield [%] / Conversion [%]					
Conversion	–	3.69	5.76	7.97	9.99	11.94
CPCA	–	96.31	94.24	92.03	90.01	88.06
Cyclopentane	–	1.14	1.62	2.3	2.9	3.5
Formaldehyde	–	0.73	1.11	1.5	2.1	2.6
2-tridecanone	–	1.18	1.05	0.85	0.68	0.51
Octadecanoic acid	–	–	0.42	0.27	0.18	–
3-pentanol	–	–	0.65	1.1	1.7	2.2
Acetic acid methyl ester	–	–	0.85	1.6	2.1	2.7
Temperature [°C]	220					
Reaction time [min]	5	10	15	20	25	30
MPP [MPa]	3					
Compounds	Molar yield [%] / Conversion [%]					
Conversion	3.22	5.85	8.68	11.57	14.68	17.08
CPCA	96.78	94.15	91.32	88.43	85.32	82.92
Cyclopentane	1.02	2	3	4	4.8	5.5
Formaldehyde	0.75	1.2	1.7	2.5	3.3	4.2
2-tridecanone	0.78	1.25	1.5	1.2	1.01	0.98
Octadecanoic acid	0.5	0.42	0.32	0.3	0.2	0.15
3-pentanol	–	0.4	0.8	1.5	2	2.5
Acetic acid methyl ester	–	0.5	1	1.5	2.5	3.5

revealed that formaldehyde vapor (boiling point -19°C) is relatively stable with respect to thermal decomposition below 400°C . Cyclopentane is also stable below 240°C ²⁴. Table 2 depicts that a new product, octadecanoic acid, was formed at a temperature of 180°C , reaction time of 20 min; a temperature of 200°C , a reaction time of 15 min and a temperature 220°C , reaction time of 5 min indicating that octadecanoic acid was the secondary product. Octadecanoic acid can be formed from 2-tridecanone as the yield of 2-tridecanone was increased first and then decreased. Two new products, 3-pentanol and acetic acid methyl ester, were formed at a temperature of 180°C , a reaction time of 25 min; a temperature of 200°C , a reaction time of 15 min and a temperature of 220°C , a reaction time of 10 min along with cyclopentane and formaldehyde. The yield of octadecanoic acid was decreasing with increasing reaction time and the yields of 3-pentanol and acetic acid methyl ester were increasing with increasing reaction time. This result indicated that 3-pentanol and acetic acid methyl ester were secondary products which can be produced from octadecanoic acid. Carboxylic acid reacts with alcohol under acid catalyst and produce ester through esterification reaction. Based on the above discussion the estimated reaction pathways of the reaction between CPCA and SubC-MeOH is presented in Figure 7.

**Figure 7.** The estimated reaction pathways of the reaction between CPCA and SubC-MeOH

CONCLUSIONS

The capability of SubC-MeOH on TAN reduction of CPCA was explored in this study. TAN reduction was affected by the reaction temperature and treatment time and was increasing with increasing reaction time and temperature. SubC-MeOH reduced approximately 17.56% TAN of CPCA at a temperature of 220°C , a MPP of 3 MPa, a reaction time of 30 min, and a CPCA concentration of 0.032 g/mL. The kinetics of TAN reduction of CPCA using SubC-MeOH without the addition of catalyst at specified reaction conditions was adjusted to a first order rate law with respect to the TAN reduction of CPCA. Esterification reaction, and cyclopentane, formaldehyde and alcohol formation reactions were involved in the reaction mechanisms of TAN

removal under experimental conditions. The calculated activation energy of the reaction is 13.97 kcal/mol. This value is lower than the reaction of methanol with NAs of Colombian crude oil at temperatures of 150–250°C.

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