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OXIDATIVE CATALYTIC DESULPHURIZATION OF NAPHTHA IN A TRICKLE BED REACTOR

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Abstract

Continuous oxidation by oxygen gas of 2-propyl mercaptan and n-butyl mercaptan present in naphtha are implanted in a trickle bed using a locally prepared catalyst. Incipient Wetness Impregnation method is used to load cobalt on activated carbon (2% Co/AC). Characterization tests, Scanning Electron Microscopy, X-ray diffraction, CO_2-Temperature Programmed Desorption, Temperature Programmed Reduction, and BET surface area showed that the prepared catalyst has an efficient catalyst characteristics. Also, they indicates that Incipient Wetness Impregnation method is good for impregnating cobalt on activated carbon. A catalyst evaluation has been done in a fixed bed reactor and the operating conditions of mercaptans oxidation process varies within a range for each parameter: temperature range (20ºC to 80ºC), liquid hour space velocity range (2.5 hr^{-1} to 10 hr^{-1}), initial concentration of 2-propylmercaptan range (75 ppm to 300 ppm), and initial concentration of n-butyl mercaptan range (100 ppm to 400 ppm). Oxygen pressure is kept constant at 2 bar gauge pressure while the oxygen / mercaptans molar stoichiometric ratio was 10.

The results showed the rate of oxidation reaction is proportional with temperature and inversely proportional with liquid hourly space velocity under the condition of the present study. The initial mercaptans concentrations have a limited effect on conversion. In addition, it is found that 2-propyl mercaptan is more reactive toward oxidation reaction than butyl mercaptan. Besides that, the results showed that the oxidation process did not have a remarkable effect on physical properties of treated naphtha (ASTM distillation, Density, viscosity, Reid vapour pressure, Aniline points, and research octane number) and decreasing occurred in octane rating.

Keywords: Oxidative desulfurization; trickle bed reactor; cobalt; activated carbon.

1. Introduction

Assignment of the oil refining industry is producing environmentally friendly fuels with lower sulfur content [1]. Hydrodesulphurization (HDS) is widely used to treat fuels for their sulfur content. In the HDS process, hydrogen is used to remove sulfur compounds. To obtain lower sulfur contents in fuels by HDS processes, sever conditions of temperature and pressure, large equipments of reactors and catalyst with high activity are required. As a result, this process demands the advanced design of the reactor and stripping columns; however some of sulfur compounds, namely dibenzothiophenes having alkyl substituent on their 4th and/or 6th positions need harsh process conditions including extremely high temperature and high pressure which considerably push the cost of desulfurization plants up [2]. Despite extensive researches into desulfurization by the refineries and the petrochemical industries over the last forty years, few viable alternatives to hydrodesulfurization have been developed like oxidative, extractive, pervaporation, adsorptive, bio, alkylation, catalytic distillation, and precipitation desulfurization but most of them are cost effective on commercial scale. The lack of progress is likely due to a combination of many factors including the effectiveness of HDS, the cost associated with installing new processes, and resistance to change in the established community of refineries [3].

Among the above HDS process, oxidative desulfurization (ODS) has much attention as an alternative process for desulfurization because of its two primary advantages about the HDS process. The greatest advantage of ODS is its capability to carry out in the liquid phase under low temperature (30-70ºC) and low pressure (atm.) condition [4]. Oxidation chemistry represents an alternative route to gasoline and diesel desulfurization with respect to HDS chemistry. Oxidative desulfurization is based on the concept of organic sulfur compounds oxidation under mild operating conditions using various types of catalysts and oxidants, the oxidized organic sulfur compounds become highly polar and enhance the subsequent extraction or adsorption. The catalysts and oxidants used in ODS must be very selective for organic sulfur compounds to prevent the oxidation of olefins or aromatic compounds present in the fuel feed. Oxidation of these compounds reduces the octane rating and increase the loss of feed material by extracting (or adsorption) oxidized hydrocarbon compounds [5-6]. The benefits of ODS process are as following lists:

- Easy deletion of sulfur species that were resistant against the hydrodesulphurization.
- Availability of air in refineries.
- Reduction the sulfur in fuels to new level of ultra low sulfur.
- Good proportion with small and middle refineries.
- Have potential for ultimate desulfurization.
- Fuel oil desulfurization to low amount [7].

The present study aims to prepare a catalyst (activated carbon supported cobalt) and examine its activity in sweetening of naphtha. Mercaptans has been used as a sulfur model compound in a trickle bed reactor with oxygen gas as an oxidant.

2. Experimental

Table 1 shows all variables and conditions that will be taken into consideration during this study. In all experiments, a pressure of 2 bar and oxygen/mercaptans molar stoichiometric ratio is maintained at 10.

Table 1. Variables and conditions of present study

Parameter	Variables number	Values
Catalyst	1	CAT-C
Temperature	4	293K, 313K, 333K, 353K
Initial mercaptans concentration	3	(RSH-C3=300 ppm, RSH-C4=400 ppm) (RSH-C3=150 ppm, RSH-C4=200 ppm) (RSH-C3=75 ppm, RSH-C4=100 ppm)
Liquid hourly space velocity	4	2.5 hr^{-1}, 3.33 hr^{-1}, 5 hr^{-1}, 10 hr^{-1}

2.1. Materials and chemicals

2.1.1. Feedstock

Hydrotreated naphtha (2-propyl mercaptan concentration 8 ppm, n-butyl mercaptan concentration 16 ppm, and total sulfur content 117 ppm) is used in this study as a feedstock, that is obtained from North Refineries Company/Salah Al-Deen 2 Refinery. The physical properties and ASTM distillation of feedstock are shown in Table 2 and Table 3 respectively. All specifications are tested in North Refineries Company laboratories.

Table 2. Physical properties of feedstock (naphtha)

Specification	Naphtha before ODS	Specification	Naphtha before ODS
RVP, psig (312K)	9.8	Boiling range (K)	317-435
Viscosity, cst (298K)	1.32	AP (K)	333
Density, gm/cm3	0.677	RON	67
°API	52.5		

Table 3. ASTM distillation test of feedstock naphtha

Naphtha Before ODS (K)	Distillate volume	Naphtha Before ODS (K)	Distillate volume
317	Initial	390	60 %
327	5 %	403	70 %
339	10 %	414	80 %
346	20 %	421	90 %
352	30 %	435	Final
363	40 %	98 %	Distillate %
375	50 %	2 %	loss

2.1.2. Mercaptans

Two types of mercaptans are used as model sulfur compounds for oxidative desulfurization. They are added to the feedstock with specified concentrations. Table 4 show their specifications.

Table 4. Mercaptans specification

Mercaptans	CAS number	Purity, %	Manufactures	Production date
2-propyl	75-33-2	Minimum 99	BDH chemical Ltd	1989
n-butyl	109-79-5	Minimum 99	BDH chemical Ltd	1989

2.1.3. Oxygen

Oxygen gas is used as oxidant agent; it is obtained from Tikrit Hospital as O_2 cylinder with purity of minimum 97%.

2.1.4. Catalyst

The chemicals and materials used for the preparation of activated carbon supported cobalt were $CoCl_2$ (Sigma, 99% purity), activated carbon (Carlo Erba) and deionized water (North Refineries Company).

2.1.4.1. Catalyst preparation

The catalyst, cobalt over activated carbon catalyst (2% Co / AC), is prepared by incipient wetness impregnation method (IWI). The activated carbon 100 g (sieved in 40-60 mesh) is dried in two steps. Firstly, dried overnight in the oven at 383K then dried in the oven for 4 hours at 453K. The cobalt chloride 2.1 g is added to 11.5cm^3 of deionized water and stirred for at room temperature one hour. The solution is then filtered in a filter paper to separate the precipitates. Activated carbon is evacuated in a flask using vacuum pump to remove gases out of support pores, then cobalt chloride solution is added to activated carbon at 15-20 drop per minute with continuous stirring. The temperature is kept constant at 373K using of water bath. The impregnated activated carbon is washed several times with deionized water to get rid of chloride ions and then dried overnight in the oven at 383K to reduce water content. The dried catalyst is calcinated for 4 hours in the oven at 453K to deposit the active metal over the support, and to acquire the new physical and chemical properties. The prepared catalyst is named as CAT C.

2.1.4.2. Catalyst Characterization

Characterization tests are implanted to specify the chemical and physical properties of CAT C.

2.1.4.2.1. X-ray diffraction

X-ray diffraction (XRD) is a versatile and powerful non-destructive technique for characterizing crystalline materials. D8 Advance X-ray Diffractometer manufactured by Bruker AXS (Germany) and setup in (Nano Technology Center/Malaya University/Malaysia). Data collection and manipulation is under automatically control of EVA software. XRD was operated under 40 kV and 40 mA and the scan was from 10° to 80° in a 2θ-angle with a scan speed of 0.04° per second.

2.1.4.2.2. Scanning Electron Microscopy

Microscopy images of the catalyst surface are obtained using an high resolution FEI Quanta 200F field emission scanning electron microscope (FESEM) manufactured in USA which setup in (Nano Technology Center/ Malaya University/ Malaysia). A small amount of catalyst powder (1 gm) fixed to the sample holder A layer (about 5 nm) of palladium was placed on the surface of the sample After placing the prepared sample into the testing chamber which is protected with nitrogen gas.20 kV- 30 kV voltage was applied to generate the desired SEM images.

2.1.4.2.3. CO_2-Temperature Programmed Desorption

Temperature programmed desorption (TPD) was used to analyze the main properties of the prepared catalyst with carbon dioxide as the absorbate molecule. CO_2-Temperature programmed desorption (CO_2-TPD) experiments were carried out in a system supplied by Ohkura Riken Co. Ltd., (model TP-200) in Nano Technology Center/Malaya University/Malaysia.

Catalyst sample of 0.5 mg is weighed and placed in a quartz tube (8 mm O.D.). Then catalyst sample pre-treated by raising temperature to 673°K for 1 hr by flowing helium at rate of 20 cm^3/min, then cooled to room temperature. The TPD plot was obtained by increasing temperature at rate of 10°K/min from room temperature to 1273K and then retained at this temperature for 15 minutes usingCO_2 gas. CO_2 concentration is determined with a thermal conductivity detector (TCD). The temperature of the catalyst and the TCD current response is monitored and recorded continuously on a personal computer (NEC Model PC9821-Xe10).

2.1.4.2.4. Temperature Programmed Reduction

In the present research, TPR is used to monitor metal support interactions. The reduction of metal oxide $MO_n$by H_2 is described by the following equation:

$$MO_n + nH_2 \rightarrow M + nH_2O$$

Temperature programmed reduction (TPR) experiments are carried out in a system supplied by Ohkura Riken Co. Ltd., (model TP-200) in Nano Technology Center/Malaya University/ Malaysia. 0.5 mg of catalyst sample was weighed and placed in a quartz tube (8 mm O.D.). Then catalyst sample was pre-treated by raising temperature to 673°K for 1 hr by flowing helium at rate of 20 cm^3 / min, then cooled to room temperature. A 30 % H_2 gas mixture is used for reduction in Argon at a flow rate of 30 cm^3/min. Temperature of the reactor is programmed to increase linearly from room temperature to 1273°K at a heating rate of 10°K/min and then retained at this temperature for 15 minutes. The hydrogen concentration is determined with a thermal conductivity detector (TCD). The temperature of the catalyst and the TCD current response is monitored and recorded continuously on a personal computer (NEC Model PC9821-Xe10).

2.1.4.2.4.5. BET surface area

Accurate sorption measurements of a gas on solid surfaces is carried out in Quanta Chrome Autosorb 6B system supplied by Quantachrome Corporation(USA) in Nano Technology Center/ Malaya University/ Malaysia.1 gm of catalyst sample is weighed and placed in a sample cell assembly which is heated to 90°C in 10 min and temperature is maintained for 1 hr then the temperature is raised to 350°C and is maintained for 2 hr. Nitrogen is used as adsorbate source. Physisorption with nitrogen is carried out in an insulated liquid nitrogen bath, at about -196°C. Then, the adsorption and desorption isotherms are obtained automatically using the software of AS-6 for Windows, Version 1.23.

2.1.4.2.4.6. Atomic absorption spectrophotometer

Atomic absorption spectrophotometer (Shimadzu Company, model AA-6200) is used to determine the percentage of active metals on the surfaces of catalyst, which setup in Tikrit University/Chemical engineering department.

2.1.4.2.4.7. Concentration measurements

Mercaptans content in feedstock and product are measured by High Performance Liquid Chromatography (HPLC) DIONEX(UV(JYNKOTYK)/VIS160S) in Tikrit University/Chemical Engineering Department. First, detection of the compounds is performed using UV absorbance; it was found that the wavelength of 2-propyl mercaptan and n-butyl mercaptan was 311 nm and 315 nm respectively. C18 reverse phase column (Philips, 5 μm x 0.4 cm) is used for the measurements. A mixture of (3/2 (v/v)) of methanol (HPLC grade) to water is used as a mobile phase. The mobile phase flow rate is 0.5 ml / min. The wavelength of 2-propyl mercaptan and n-butyl mercaptan is 311 nm and 315 nm respectively. The retention time of reactants (2-propyl mercaptan and n-butyl mercaptan) have been measured and they are equal to 1.7 and 2.3 minutes respectively. Then calibration curve that relates concentration of 2-propyl mercaptan and n-butyl mercaptan to HPLC response are plotted. Comparison between HPLC response recorded by the detector with the calibration curves of n-butyl mercaptan and 2-propyl mercaptan has been made to determine mercaptans concentration.

2.2. Trickle bed reactor system

The oxidation process of mercaptans is carried out continuously in a trickle bed reactor in a co-current mode flowing downward (Figure 1). The fixed bed reactor was made of SS316 alloy into a tubular reactor with dimensions of 77 cm long, 1.6 cm ID, 40 cm bed height. Thus, $D_{reactor} / d_{particle}$ equals to 15.4. The reaction bed is controlled automatically by four sections of 15 cm height steel-jacket heaters. Independent inlet systems for gas and liquid feed allow working at various liquid to gas flow rate ratios.

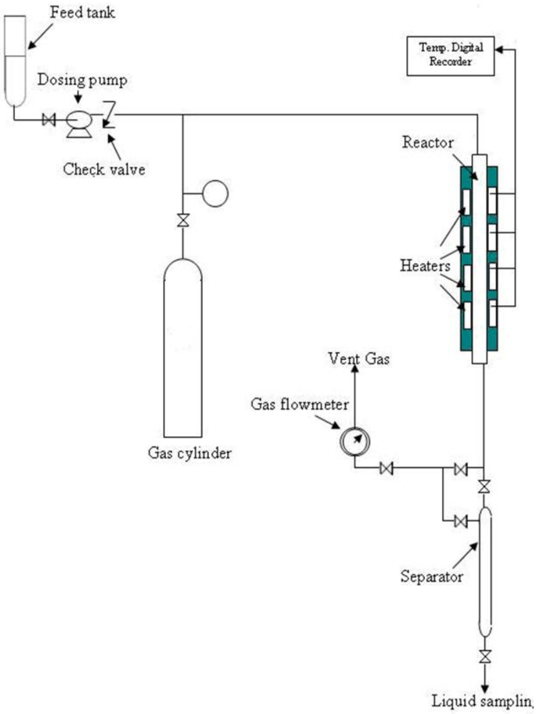

Fig. 1. Schematic representation of the ODS system

Feed tank is used to store the untreated naphtha and it is connected to a dosing pump operating at high pressure with a capacity of 0.0 to 1.65 litter/hr of feedstock up to 20 bar pressure. The oxidant gas, oxygen, is fed by oxygen cylinder at 100 bar that is equipped with a pressure controller to maintain constant operating pressure. The liquid naphtha (mixed with 2-propyl mercaptan and n-butyl mercaptan with specified concentration) and oxygen gas streams are mixed and then fed to the reactor at the required temperature where mercaptans are oxidized to disulfide. There are four exit points on the reactor located at different elevations. The liquid reactants flow rates remains constants all the experimental runs, the variation of liquid hourly space velocity values get by changing catalyst bed length through using the four exit points which equipped with needle valves to control which exit point used to get the required LHSV.

Four outlet streams flow from the reactor to a heat exchanger then to gas-liquid separator in order to separate excess oxygen from the treated naphtha that withdrawn from four sample points.

3. Results and discussion

3.1. Catalyst characterization

The activity of a catalyst depends on its physical and chemical properties. This involves identification of various properties such as surface area, pore structure, metal dispersion, crystal structure, microscopy imaging and element distribution. Characterization results of the prepared catalyst are presented in this section. Table 5 shows techniques used in characterizations and their objectives.

Table 5. Catalysts tests and their objectives

Test	Purpose
SEM	Dispersion of active metals on support surfaces
XRD	Identify the crystalline structure
BET	Measure of surface are , pore volume , pore size distribution
CO2-TPD	Identify basic site on catalyst surface
TPR	Monitor metal support interactions

3.1.1. Scanning Electron Microscopy

Figures 2 and 3 show the elemental mapping obtained by SEM for CAT-C; it shows good surface distribution of cobalt over activated carbon surface, cobalt is represented by white regions and activated carbon represented by dark regions. These results ensure that Incipient Wetness Impregnation method (IWI) is an efficient method to prepare these types of catalysts with good active metal distribution.

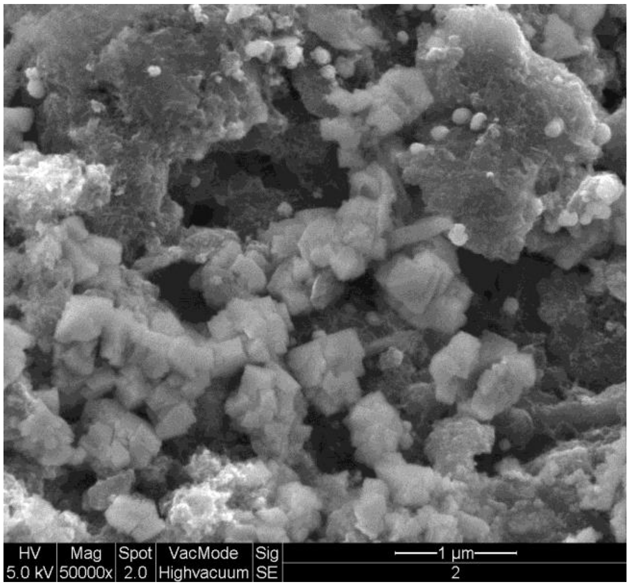

Figure 2. SEM images of activated carbon supported cobalt (CAT-C, 1µm)

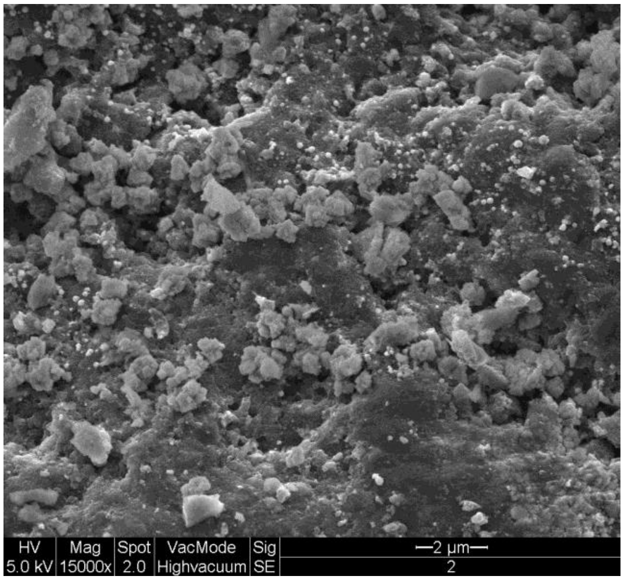

Figure 3. SEM images of activated carbon supported cobalt (CAT-C, 2µm)

3.1.2. X-ray diffraction

The XRD profiles of prepared CAT-C is shown in Figure 4. The characteristic diffraction peaks of copper (CAT-C) are marked in red color. The diffraction profiles exhibited peaks at 2θ for cobalt peaks around 56, 63, and 79. The characteristic peaks of cobalt indicates that cobalt has been loaded on activated carbon successfully. The addition of cobalt does not influence the crystallinity of activated carbon which is in agreement with the findings of Cruceanu *et al.* [8]. Several peaks appear with cobalt, this fact attributes to the reduction of cobalt [9-10].

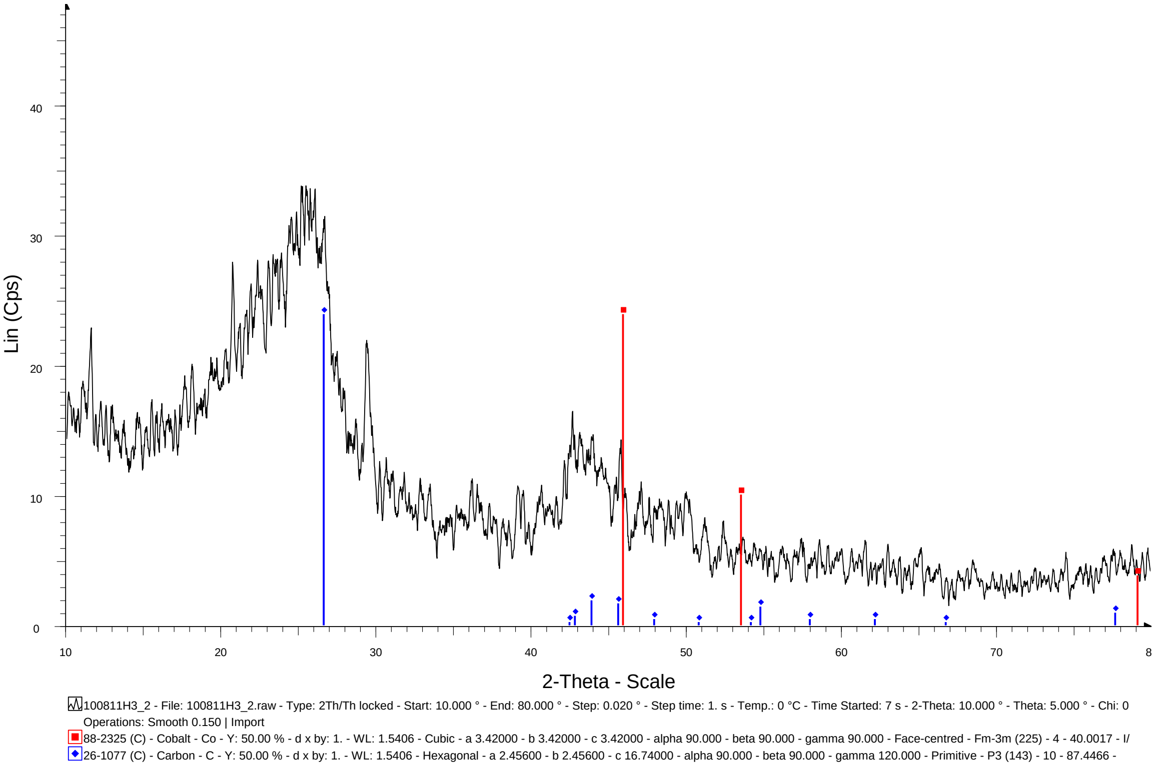

Figure 4. XRD patterns for CAT-C

3.1.3. BET surface area

Measurements of the surface area, pore volume, and average pore diameter of CAT C are shown in Table 6 and Figure 5.

Table 6. Texture characteristics of support and prepared catalyst.

Property	AC	CAT-C
Total surface area, m^2/gm	280.3	141.5
Pore volume, cm^3/gm	0.115	0.06369

It concluded from the results of BET analyses that CAT-C has a lot of shallow mesopores. The surface area, pore volume, and pore size distribution have been reduced after incorporation of cobalt in CAT-C. This is due to partial pore blockage in activated carbon. A similar finding is obtained by Hulea *et al.* [11], Zhou *et al.* [12], and Shah *et al.* [13].

3.1.4. CO_2-temperature programmed desorption (CO_2-TPD) and temperature programmed reduction (TPR)

The principle in temperature-programmed techniques is that the surface is cleaned and then exposed to a gas at a relatively low temperature. When the desired coverage has been reached, the pressure is reduced, the temperature is increased linearly and the flux of desorbing molecule is detected. CO_2- TPD used for investigating the strength of sites basicity over catalyst surfaces by determination of the quantity of gas desorbed from the catalyst submitted to a linear temperature ramp. Figure 6 shows CO_2-TPD plot of CAT-C and reveals that the basicity of these catalysts is affected by type of active metals loaded on activated carbon. The larger peak area and intensity of CAT-C shows that the basic sites are significant.

TPD of CAT-C shows two peaks with relatively weak intensity at 373K and after reaching a temperature of 993K. However, oxidation of mercaptans needs moderate or strong acid base.

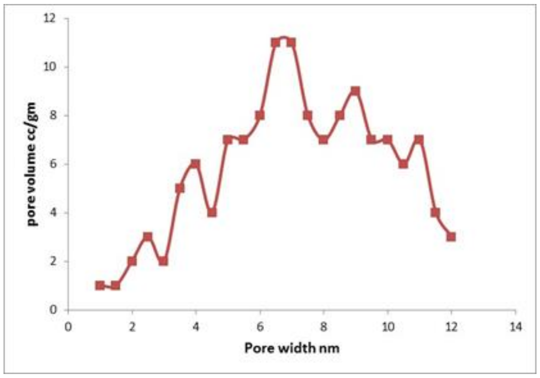

Figure 5. Pore size distribution of CAT-C

Temperature programmed reduction (TPR) has been widely used for the investigation and characterization of metal incorporated and metal supported catalysts. TPR peak area represents the amount of hydrogen consumption and peak temperature which represents the reducibility of the metal oxide or oxides.

TPR reduction patterns of CAT-C is shown in Figure 7. The reductions are performed up to 1273K and the patterns show a complete reduction of the metal species. The reduction peaks of CAT-C starts at 673K to 1173K. The TPR patterns occurs at high that is attributed to a strong interaction between cobalt and activated carbon. Several peaks are shown at different temperatures, this is due to metal distribution on a wide range of micro, meso, and macro-pores. This result agrees with Ramos-Luna and Cedeno-Caero [14] and Ghani *et al.* [10].

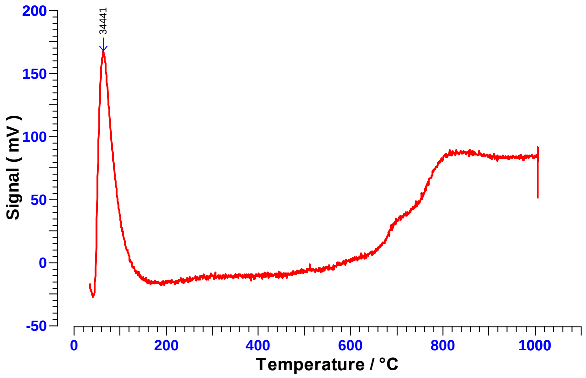

Figure 6. Plot of CO_2-TPD of CAT-C

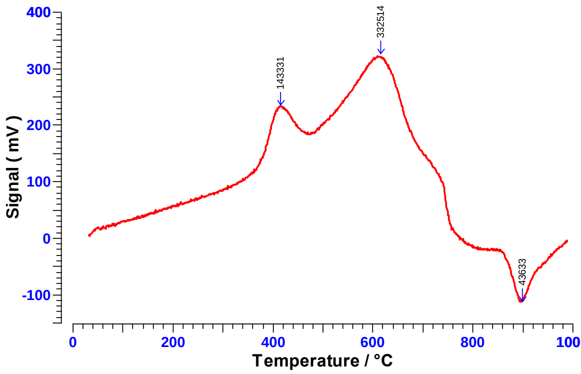

Figure 7. Plot of TPR for CAT-C

3.2. Influence of temperature

The influence of temperature on conversion of mercaptans to disulfide is studied at 293K, 313K, 333K, and 353 K. In the present study, the oxidation of 2-propyl mercaptan and n-butyl mercaptan has been conducted at low temperatures because of the following reasons:

1. High rate of OSCs conversion that has been obtained at low temperature in previous studies [15-16], which is good to save energy while running ODS process;
2. Side reactions may occur at higher temperatures as a result of oxidation of some organic compounds. So unstable fuels form, as well as some reactions products poison the catalyst [17].

It is clearly seen from Figure 8 mercaptans increases as temperature increases is accompanied by an increase of mercaptans conversion and it affected by the following factors:

Activation energy: Activation energy measures the amount of energy that reactants must have before they can overcome barrier between them and the product state. According to Arrhenius equation, the reaction rate constant is a function of reactants temperature (direct proportion) and activation energy (inverse proportion).

$$K = K_o e^{\left(\frac{-E_a}{RT}\right)} \ldots \qquad (1)$$

The increase of temperature will increase the number of molecules having the minimum activation energy required for ODS reaction. Thus, the number of molecules involves in the oxidation reaction increase according to equation1 that is in turn increases the conversion. This result agrees with Xia and Su [15] and Farshi and Rabiei [18], they had proved that temperature influences oxidation reaction in which reaction rate is activation energy dependent.

Effect of physical properties: Temperature rising is proportional to Henry's constant and diffusivity and inversely proportional to viscosity and surface tension. Thus, raising temperature will raise the absorption rate of molecular oxygen in liquid naphtha, diffusing rate of mercaptans and the rate of dissolved oxygen inside CAT-C pores that occupy the active sites when oxidation reaction occurs. As a result, mass transfer limitation between gas-liquid (external gradients), liquid-solid (external catalyst diffusion), and inside catalyst pores (internal catalyst diffusion) decrease as process temperature increases. This result agrees with Leitao and Rodrigues [19] and Paniv *et al.* [17] who showed that temperature increase affect the physical properties of reactant (density, vapor pressure, aniline point, and viscosity) which in turn increases conversion of ODS process.

Changing of reactants phase: Although raising temperature from 313K to 333K changes the phase of 2-propyl mercaptan from liquid to vapor (boiling point 326K), vapor phase is more active in ODS reaction due to its high diffusion rate of molecules inside catalyst pores. However, N-butyl mercaptan phase does not experience phase change during the course of raising temperature from 293K to 353K (n-butyl mercaptan boiling point 373 K). This result agrees with Choi et al. [20] who showed that the diffusivity of OSCs increases if reaction phase changes from liquid to vapor, then the conversion increased. Zhao *et al.* [21] showed that raising temperature leads to a drop in conversion due to decomposition of hydrogen peroxide (oxidant) to water and oxygen.

Side reactions: Conducting of mercaptans oxidation at 293K-353K does not promote formation of gum or catalyze another side reaction to form new oxidized compounds that may poison the catalyst and inhibit the oxidation reactions. This behavior is clearly seen in Figure 8. Liu *et al.* [22] showed that the temperature increase made linear increase in conversion because there were no by-products formed. However, Paniv *et a*l. [17] showed that the increase in mercaptans conversion (in kerosene) was caused by rising temperature in spite of formation of gum and oxidation of heavy hydrocarbon molecules.

3.3. Influence of liquid hourly space velocity LHSV

The influence of liquid hourly space velocity on conversion of mercaptans oxidation are studied at 2.5 hr^{-1}, 3.33 hr^{-1}, 5 hr-1, and 10 hr^{-1}. In all the experiments implanted in the present study, LHSV has been changed by changing the bed length (or bed volume V) according to equation 2:

$$LHSV = \frac{\upsilon}{V} \ldots\ldots\ldots\ldots \qquad (2)$$

While the naphtha volumetric flow rates (or naphtha velocity) is kept constant to reduce the reactor deviance from the ideal behavior of trickle bed reactor. The variation of naphtha volumetric flow rates (or naphtha velocity) make the reactor experiences a deviation by affecting some of the hydrodynamic characteristics like catalyst wetting, radial and axial dispersion (back mixing), and liquid hold up. These hydrodynamic limitations in result can mask the results and lead to misinterpretations in developing kinetic models [23]. Increasing the liquid hourly space velocity results in shortening of the contact time between reactants and catalyst particles. Thus, the chance for more oxidation reaction to occur has been reduced. This behavior is clearly seen in Figure 9 that agrees with the results of Huanget *et al.* [24], and Napanang and Sooknoi [25].

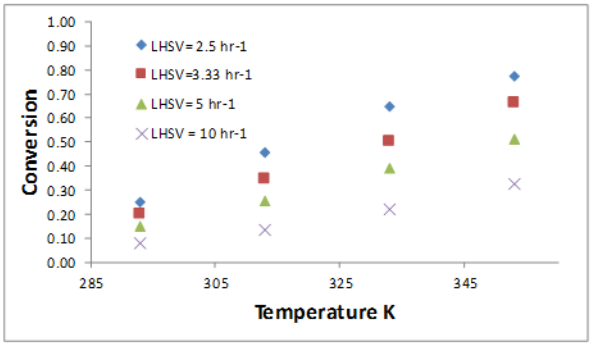

Figure 8. Effect of temperature on conversion of n-butyl mercaptan oxidation. (CAT-C, initial n-butyl mercaptan concentration 100 ppm)

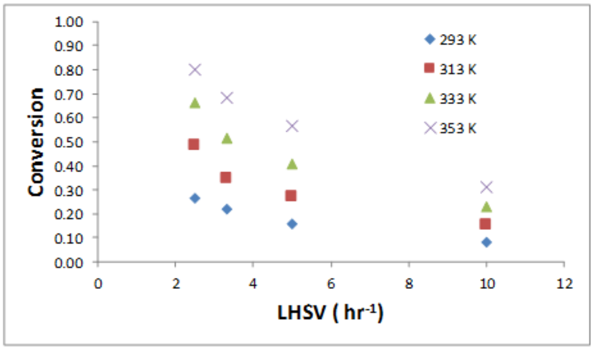

Figure 9. Effect of LHSV on conversion of 2-propyl mercaptan oxidation. (CAT-C, 2-propyl mercaptan concentration 150 ppm)

3.4. Influence of initial concentration of mercaptans and mercaptans reactivity

The influence of initial concentration of 2-propylmercaptan is studied at 75 ppm, 150 ppm, and 300 ppm. The obtained results are shown in Figures 10 and 11, they show the dual activity of cobalt and activated carbon towards adsorption, and oxidation of mercaptans at high and low initial concentration of mercaptans. The results obtained by present study agreed to Wang *et al*. [26] who proved that increase of initial concentration made an increase in conversion. However, it agrees partially with Alcaraz *et al.* [27] who showed that high conversion obtained at high initial concentration but after period of operation the higher conversion obtained at low initial concentration due to irreversible adsorption of oxidized mercaptans on catalyst active site. The results also disagree with Huang et al. [24] and Wang *et al.* [26] who observed high conversion at low initial concentration.

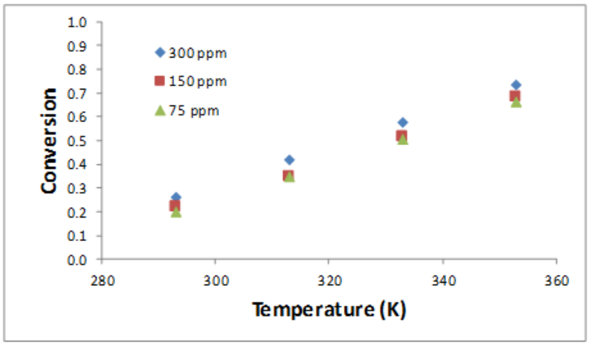

Figure 10. Effect of initial 2-propyl mercaptan concentration on its conversion by oxidation reaction. (CAT-C, LHSV = 3.33 hr^{-1})

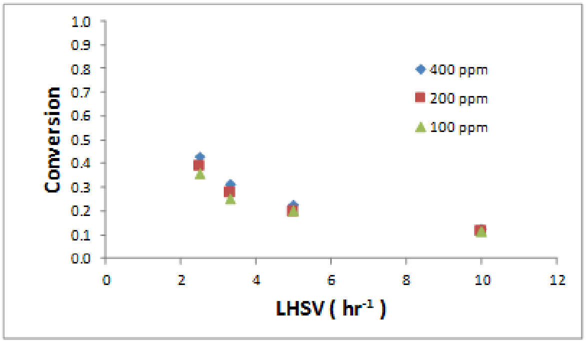

Figure 11. Effect of initial n-butyl mercaptan concentration on its conversion by oxidation reaction. (CAT-C, temperature = 313 °K).

Figure 12 shows that 2-propylmercaptan is more reactive to oxidation reaction than n-butyl mercaptan. These results attribute to the following properties:

1- 2-propylmercaptan has a lower molecular weight than n-butyl mercaptan. Thus, 2-propyl-mercaptan has electron density larger than n-butyl mercaptan and it is more reactive according to this property.

2- 2-propylmercaptan has a branched structure whereas n-butyl mercaptan has a straight structure. With that, n-butyl mercaptan has a lower steric hindrance than 2-propylmercaptan. Therefore, n-butyl mercaptan is more reactive than 2-propylmercaptan.

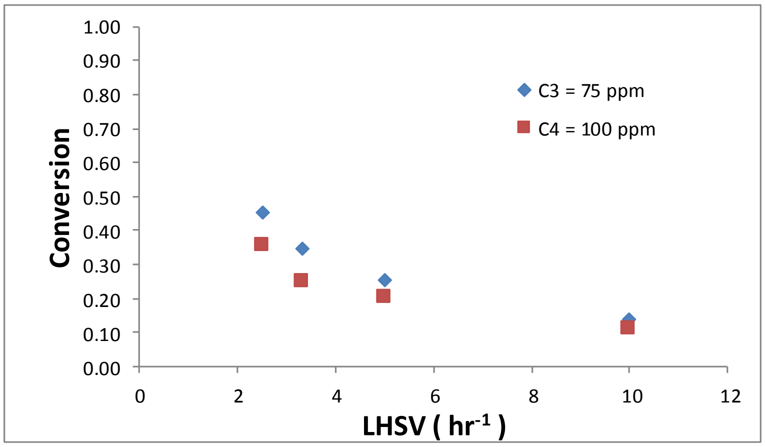

Figure 12. Reactivity of 2-propyl mercaptan and n-butyl mercaptan toward oxidation under the same condition. (CAT-C, temperature: 313 °K)

3.5. The influence of ODS process on physical properties of feedstock

The physical properties and ASTM distillation of feedstock and product at optimum operating condition (temperature 353K, *LHSV*=2.5hr^{-1} ,2-propylmercaptan initial concentration 150 ppm, and n-butyl mercaptan initial concentration 200 ppm) are shown in Tables 7 and 8 respectively.

Table 7. Physical properties of feedstock (naphtha) before oxidation and after oxidation at optimum condition

specification	Naphtha Before ODS	Naphtha after ODS at optimum condition
RVP, psig (312K)	9.8	9.2
Viscosity, cst (298K)	1.32	1.31
Density, gm/cm^3	0.677	0.687
°API	52.5	51.9
Boiling range, (K)	317-435	319- 434
AP, (K)	333	334
RON	67	68

Table 8. ASTM distillation of feedstock (naphtha) before oxidation and after oxidation at optimum condition.

Distillate volume	Naphtha before ODS (K)	Naphtha after ODS at optimum condition (K)	Distillate volume	Naphtha Before ODS (K)	Naphtha after ODS at optimum condition (K)
Initial	317	321	60 %	390	394
5 %	327	335	70 %	403	407
10 %	339	343	80 %	414	417
20 %	346	352	90 %	421	425
30 %	352	363	Final	435	442
40 %	363	372	Distillate %	98 %	97.5 %
50 %	375	385	loss	2%	1.4%

It is obvious that there is no remarkable change in in physical properties and ASTM distillation of feedstock and product at optimum operating conditions. This is attributed to the following reasons:

1. Selectivity of activated carbon supported copper towards organic sulfur compound only, so no side reactions have occurred.

2. Mild operating conditions of oxidation process, which inhibit other oxidation reaction of alkenes and aromatics, presented in hydrotreated naphtha.

These results agree to Liu et al. [22], but disagree to results published by Paniv *et al.* [17] and Boikov et al. [28] because these works were conducted at high temperature which accelerated side reaction and formed by-product.

It is concluded from Tables 7 and 8 that:

- Density, viscosity, and boiling range are approximately the same before and after oxidation reaction because there was no change in the components of hydrotreated naphtha.
- Reid vapor pressure (RVP) decreases slightly because some of the volatile compounds are reacted (2-propylmercaptan) or vaporized (2-propylmercaptan and light hydrocarbons).
- Aniline points (AN) and research octane number (RON) are approximately the same before and after oxidation reaction. This is because the aromatic compounds are not involved in the oxidation reaction. They were not broken or saturated as in hydrodesulfurization process.

Thus, the upgrading of naphtha does not affect its physical properties and has an excellent benefit especially for research octane number (RON) that does not need octane recovery as in hydrodesulfurization process.

4. Conclusions

1. Efficient catalysts have been prepared according to catalyst characterization tests (XRD, SEM, BET, TPD, and TPR).
2. Oxidation of 2-propyl mercaptan and butyl mercaptan present in naphtha (at 317K- 435K) is highly dependent on temperature and liquid hourly space velocity variation at low mercaptans concentrations and under the studied conditions. A slight effect of initial concentration of mercaptans on conversion to disulfides has been noticed.
3. Results showed that 2-propyl mercaptan is more reactive to oxidation reaction than butyl mercaptan.
4. The physical properties of treated naphtha; RVP, API, RON, AP, boiling range, and ASTM distillation changed slightly.

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