

RESEARCH ARTICLE

Performance of a novel cobalt phthalocyanine sulfonamide-based catalyst for oxidative desulphurization of gas condensate

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Abstract

Sulphur compounds and mercaptans in gas condensate cause corrosion problems, poison catalysts in catalytic processes, and have adverse environmental impact through SO_x emission upon combustion. Therefore, it is essential to remove sulphur and mercaptan from gas condensate to standard levels. In this study, the oxidative desulphurization (ODS) process in the presence of a cobalt phthalocyanine sulfonamide-based catalyst was investigated. The homogeneous catalyst containing 23 wt.% active material was used and optimum operating conditions of temperature, volume ratio of caustic to gas condensate, caustic concentration, and solvent amount were determined to decrease sulphur content to less than 500 ppm and mercaptan to less than 200 ppm. The catalyst consumption in all experiments was kept constant at a minimum level (0.01 g/400 mL gas condensate). Results showed that this catalyst improved the reaction rate in the lower temperature and lower caustic to feed ratio and lower caustic concentration. The maximum sulphur removal was obtained at 5°C and 4 vol.% of caustic to gas condensate ratio at 16.7 wt.% of caustic concentration. Moreover, this catalyst improved sulphur removal from the gas condensate to about 5% compared to caustic sweetening without catalyst. Sulphur compounds had higher solubility in acetone rather than methanol, and sulphur removal by acetone was 96% while it was 91% for methanol. Finally, the economical and acceptable solvent for sulfoxides removal was methanol with 5% volume fraction.

KEYWORDS

catalyst; demercaptanization; gas condensate, cobalt phthalocyanine sulfonamide; oxidative desulphurization (ODS)

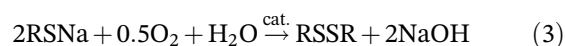
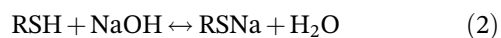
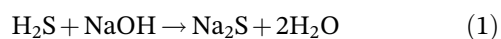
1 | INTRODUCTION

The presence of sulphur compounds in fuel products has a destructive effect on the environment due to conversion to SO_x during fuel combustion.^[1–8] There are different

methods for desulphurization such as hydro desulphurization (HDS),^[9–11] oxidative desulphurization (ODS),^[12,13] adsorption,^[14,15] and bio desulphurization (BDS).^[10,16] In the industrial large scale, HDS is a well established method and hydrogen is reacted with sulphur compounds at high

temperature and pressure (up to 400°C, 100 atm) in the presence of metallic catalyst.^[17,18] This method requires hydrogen production and high operational costs, which require high investment and operating costs.^[19–23] ODS has been noticed in mini refineries that operate at near-atmosphere and intermediate temperature (15–40°C) and demonstrates more sulphur removal compared to HDS. This method does not require expensive hydrogen.^[19,22,24–28] The ODS process includes two stages, that is, a catalytic oxidation reaction, followed by separation of oxidized sulphur products from gas condensate by liquid–liquid extraction.^[22,29] New mechanisms, processes, and inventions for selective ODS have been studied. ODS technology is intended as an alternative to retrofitting HDS units for the production of ultra-low sulphur (ULS) diesel engines or as an alternative to high-pressure HDS equipment. Although refineries have adopted hydrogen treatments for ULS fuels. The approach can optionally serve as an independent unit at the terminal for implementation and handle products that do not meet technical standards if relevant technical problems are resolved. ODS technology still needs additional research and development, especially on catalysts, for more selective oxidation. The commercial process can develop into technical and economic problems.^[30–35] A schematic of the ODS process is shown in Figure 1.

Three reactions occur in the presence of caustic solution (NaOH) and catalyst. In Reaction (1), hydrogen sulphide (H₂S) is separated from hydrocarbons by a diluted caustic solution (NaOH 1–2 wt.%).^[36] Mercaptans in hydrocarbons convert to sodium mercaptides according to Equation (2), and then sodium mercaptide is oxidized to disulphide oil (DSO) in the presence of catalyst according to Equation (3).^[37]



The reaction product DSO is partly miscible with condensate stream and keeps sulphur content at a high level in the hydrocarbon phase.^[38] Therefore, extraction by another solvent is necessary to remove DSO from product and reduce the total sulphur content of the final product. Mercaptane component is used to treat to DSO, and is odourless, non-corrosive, and considerably less harmful for humans and the environment. Some mini-refineries use only the first stage for de-odorization. However, the total sulphur content still is at a high level.

The concentration of caustic solution and the caustic to condensate volume ratio (CCR) defined by Equation (4) are crucial due to economic, environmental, and waste management concerns:

$$\text{CCR}\% = \frac{V_{\text{caustic}}}{V_{\text{condensate}}} \times 100 \quad (4)$$

where V_{caustic} and $V_{\text{condensate}}$ are volume of caustic solution and condensate feedstock, respectively. Selection of a proper catalyst has a key role in the process efficiency and product quality. Also, an economic process requires optimum consumption of chemicals, that is, caustic solution, solvent, and catalyst. Suggesting new catalysts and determining optimum operating conditions for a feedstock with different composition have been subject of research studies.

An efficient demercaptanization (DMC) process has been developed for selective purification of light crude oil and gas condensate. The main principle of the process is the selective oxidation of the liquid phase C1–C3, mercaptan with atmospheric oxygen to disulphide in the presence of IVKAZ or UVKO catalysts in alkaline aqueous solution at high pressure (4–16 MPa). Methyl and ethyl mercaptan content were reduced about 98% in crude oil after the treatment with minimum catalyst consumption (0.05 g catalyst/ton; 50 g caustic soda/ton).^[33,39,40]

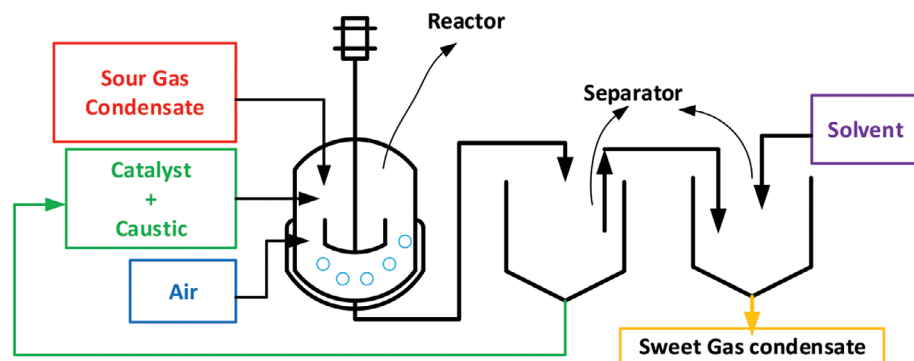


FIGURE 1 Schematic of the oxidative desulphurization (ODS) process.

Mohammadbeigi and Tajerian^[36] investigated demercaptanization of gasoline, kerosene, and gas oil using cobalt phthalocyanine catalyst. They found that the optimum temperature for demercaptanization of kerosene and gas oil was 70–80°C and 50°C for gasoline. The optimum time was 15–20 min for kerosene, 15 min for gasoline, and 15–50 min for gas oil.

Gavrilov et al.^[41] investigated non-extractive oxidative demercaptanization of fuel oil in the presence of copper complex catalysts. Also, they optimized the process by changing the air to fuel oil ratio, catalyst concentration, time of reaction, and temperature. Liu et al.^[42] studied the Merox liquid–liquid sweetening process for liquefied petroleum gas (LPG). Their results showed that caustic concentration is effective on the catalyst dispersion and conversion of mercaptans to mercaptides. They proposed caustic concentration for ODS of LPG is in the range of 2.75 to 4.25 mol/dm³. Afshar et al.^[43] considered Sulfurex liquid–liquid extraction of mercaptans from propane and butane and used LCPS 30 as a catalyst. They obtained the optimum caustic concentration of 14–14.2 wt.%, temperature of 36–37°C for propane cut and 34–35°C for butane cut, and caustic to propane volume ratio of 0.06 and caustic to butane volume ratio of 0.106.

Afshar et al.^[44] studied the ability of a sulfonated cobalt phthalocyanine for LPG sweetening via the Sulfurex process. In this work, the optimum conditions including temperature, caustic concentration, and air injection rate for caustic regeneration were obtained. Results showed that the optimum temperature was 40–41°C at caustic concentration of 14.2 wt.% and excess air of 160–170%. Beshkoofeh et al.^[45] prepared a novel mesoporous catalyst 5%Ni10%Mo/ γ -Al₂O₃ for catalytic ODS of light oils with 13,000 ppm sulphur content. The final product contained total sulphur of 623 ppm after reaction in 120 min at 30°C and 1 mL H₂O₂ as an oxidant for 1 L light oil. The use of H₂O₂ as an oxidant instead of air and acetic acid as a catalyst is also reported in the literature.^[6,46–48]

Some studies focus on the kinetics of catalytic ODS. For example, Motahari et al.^[49] determined reaction kinetics of catalytic oxidation of light mercaptans of LPG in the Merox process. They conducted experiments at the temperature range of 38 to 50°C, optimum catalyst concentration of 200 wt. ppm, and optimum initial caustic concentration of 4.25 gmol/L. They proposed first-order reaction rate equation and determined the parameters of Arrhenius equation.

Sun et al.^[50] combined molecular dynamics simulation preselection and extraction experiments and compared eight solvents for extracting oxidized sulphur from LPG. The results proved that isopropanol (IPA) is the best solvent with maximum sulphur removal and easy

recycling. The sequence of assisted removal efficiency was IPA > ethanol > acetone > monoethanolamine (MEA) > methanol > ethylene glycol. They made cobalt polyphthalocyanine as a catalyst for desulphurization of fuels. They proposed two commercial processes for manufacturing of the catalyst, compared them, and concluded that utilization of dimethylsulfoxide as a solvent is more effective than urea.^[31]

Sano et al.^[51] developed a photo catalyst graphitic (g-C₃N₄) with silver metal which improved the adsorption capacity and the photocatalytic degradation of sulphurous compounds. They found that the silver metal on g-C₃N₄ has higher activity than that on TiO₂ for the adsorption of methyl mercaptan. The Ag metal on graphite increased the photocatalytic degradation of methyl mercaptan to dimethyl disulphide. Cadours et al.^[32] modified activated carbon with some metals for methyl mercaptan removal by the sol–gel method. They compared characterization of the manufactured catalysts via different standard tests and the results showed that metal impregnation on the activated carbon highly increased the methyl mercaptan removal capacity. They sort the catalyst based on catalytic activity reduction in the following sequence: CueAC > NieAC > AleAC > FeeAC > ZneAC.^[27]

Duarte et al.^[52] utilized ultrasonic energy to increase the sulphur removal from diesel oil and oil products in a relatively mild conditions and without metal catalysts. In this method, which was named ultrasound-assisted oxidative desulphurization (UAOD), hydrogen peroxide, acetic acid, and methanol were used. Results showed that the UAOD method in mild operating conditions (atmospheric pressure and maximum temperature of 90°C) compared to conventional HDS process has high efficiency. The utilization of ultrasonic energy in the ODS process can decrease hydrogen peroxide, acetic acid, and methanol consumption and reaction time.^[52]

Akopyan et al.^[53] investigated ammonia solution as a caustic for light mercaptans (methyl, ethyl, and propyl mercaptans) removal from hydrocarbons mixtures. The results showed that aqueous ammonia could be utilized for light hydrocarbon demercaptanization. The complete extraction of mercaptans occurred for a hydrocarbon, when the process started at the temperature range 40–50°C and then was raised to 60°C gradually, in order to decompose of ammonium mercaptides salts. The advantage of this method is that there is no oxidative catalytic regeneration step and there are no highly toxic wastes. The regeneration of a spent aqueous ammonia is easy; it includes heating (boiling), which leads to a hydrolytic decomposition of ammonium sulphides and mercaptides to release their constituent gases: hydrogen sulphide, mercaptans, and ammonia.^[47] Ammonia is

recycled into the process as regenerated caustic ammonia.^[27,51,53] A catalyst based on the tetrabutylammonium salt of phosphotungstic acid, TBA3PW12O40 (PW12), which is capsulated in the chromium terephthalate metal-organic framework MIL-101, was synthesized. The experiments were carried out at 50°C and H₂O₂ was utilized as oxidant. Results show that sulphur removal reached 100% for oil containing 500 ppm benzothiophene within 1 h, and it reached 100% within 3 h when oil includes 1-benzothiophene. This catalyst could be reused three times in the ODS process with a slight decrease in the catalytic performance.^[31,54] A composite including a NH₄⁺ doped H₄PMo₁₁VO₄₀ as catalyst was made for ODS process of fuel oils. They used 0.1 g (NH₄)₃HPMo₁₁VO₄₀ as catalyst, reaction time was 2 h, reaction temperature was 120°C, and the oxidant was air. In this condition, the conversion of dibenzothiophene reached to 100% and this catalyst could be recycled more than five times with neglect activity reduction.^[55]

In this study, catalytic ODS of sour gas condensate is studied using a cobalt phthalocyanine sulfonamide-based homogeneous liquid phase catalyst. A two-step oxidation and extraction process were designed and conducted at atmospheric pressure in a dual wall reactor (isothermal condition) to find optimum conditions with minimum catalyst consumption. The operating conditions were temperature, CCR, and caustic solution concentration in the catalytic oxidative process. Moreover, type of solvent and volume fraction of solvent were the variables in the extraction step. The optimum conditions were obtained with a target of sulphur content reduction to less than 500 ppm and mercaptane content less than 200 ppm. Also, catalytic oxidation process was investigated in a wide temperature range down to less than 20°C for the first time in this work to show the effectiveness of this catalyst at lower temperatures. Moreover, the catalytic ODS of gas condensate with the used catalyst was investigated for the first time. The minimum catalyst consumption is the main goal of this study compared to other works (Figure 2).

2 | MATERIALS AND METHODS

2.1 | Materials

All chemicals utilized in this study including NaOH, CH₃COONa × 3H₂O, glacial acetic acid, Ag(NO)₃, methanol, ethanol, acetone, and isopropyl alcohol, were supplied by Merck Co. Gas condensate was obtained from an South Pars Gas Complex (SPGC) located in Assaluyeh on the northern Persian Gulf coast. The specifications of gas condensate are summarized in Table 1. Also, cobalt phthalocyanine sulfonamide-based catalyst solution was provided from Artin Azma Mehr Company. The catalyst solution contains 23 wt.% of cobalt phthalocyanine sulfonamide. Other technical specifications of the catalyst are presented in Table 2, and chemical compositions are shown in Table 2.

2.2 | Experimental setup

The experimental set-up includes a double-walled glass, batch continuous stirred tank reactor (CSTR) equipped with an impeller mixer, a thermo circulator (LAUDA company) for temperature control of the reactor, and an air pump for injection of air into the reactor. Water with a constant temperature was circulating in the inner wall to control temperature in all catalytic oxidation reaction experiments. An air pump was used for aeration inside the reactor and improvement of oxidation reactions. Figure 3 shows the reactor of experimental setup.

2.3 | Experimental procedures

2.3.1 | First step: The catalytic oxidation process

In the first step, sulphur compounds react with oxygen in the presence of cobalt phthalocyanine sulfonamide-based

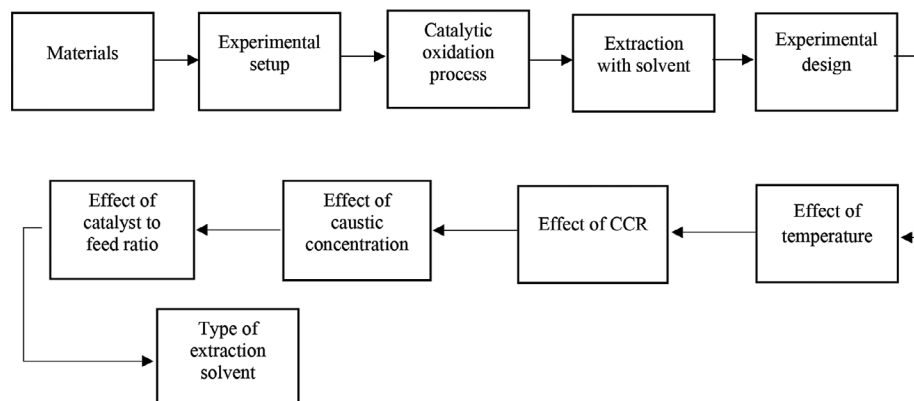


FIGURE 2 General sketch of the article. CCR, condensate volume ratio.

TABLE 1 Specification of gas condensate.

Typical test	Units	Test method	Results
Density @ 15°C	g/cm ³	ASTM D-1298	0.7234
Colour	—	ASTM D-156	> + 30.0
Mercaptan	Ppm	ASTM D-3227	160.34
Sulphur	wt. %	ASTM D-4294	0.0392
Flash point	°C	ASTM D-92	Free
Cooper strip test (3 h@50°C)	—	ASTM D-130	1a
Distillation	—	—	—
Initial boiling point (IBP)	°C	ASTM D-86	48
5%	°C	ASTM D-86	64
10%	°C	ASTM D-86	69
15%	°C	ASTM D-86	74
20%	°C	ASTM D-86	79
30%	°C	ASTM D-86	88
40%	°C	ASTM D-86	97
50%	°C	ASTM D-86	107
60%	°C	ASTM D-86	118
70%	°C	ASTM D-86	130
80%	°C	ASTM D-86	142
85%	°C	ASTM D-86	157
90%	°C	ASTM D-86	174
95%	°C	ASTM D-86	202
Dry point	°C	ASTM D-86	222
Residue	vol. %	ASTM D-86	1.5
Loss	vol. %	ASTM D-86	1.5
Recycle	vol. %	ASTM D-86	97

TABLE 2 Technical data and chemical composition of cobalt phthalocyanine sulfonamide-based catalyst.

Parameter	Norm according to TU	Actual
Appearance	Solution of dark-blue to blue-green colour	Solution of dark-blue colour
Reaction rate constant of mercaptide oxidation, $k \cdot 10^4, s^{-1}$, at least	35	Corresponds
Mass fraction of sulphur acids of cobalt phthalocyanine, %, at least	40	Corresponds
Mass fraction of insoluble impurities, %, at least	2	Corresponds
Components		Mass fraction, %
Dichlorosulphonic acid of cobalt Phthalocyanine Or Dibromdisulphonic acid of cobalt Phthalocyanine		15–25
Tri(2-hydroxyethyl)amine		4.7–13.3
Alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)		0.45–8
Water		To 100

catalyst and oxidized sulphur compounds were produced. In each experimental run, the thermocirculator was set on a specific temperature and 400 mL of gas condensate

with total sulphur of 0.32 wt.% was introduced into the glass reactor. Then, chemicals including NaOH and catalyst were mixed with the gas condensate. After that, air

was injected to the reactor by an air pump and this point was considered as the start point of the experimental records. The mixtures were mixed at a constant temperature in a range of 5 to 35°C for 90 min at the mixing rate of 550 rpm. At the end of reaction, two liquid phases with different densities formed as shown in Figure 4 and were separated in a separating funnel. The upper phase was gas condensate and the lower phase was catalyst and caustic solution. After separation of catalyst and caustic mixture, the reacted condensate was contacted with a solvent in the liquid-liquid extraction step to separate remaining sulphur compounds. All tests were carried out at atmospheric pressure.

2.3.2 | Second step: Extraction with solvent

The second step involves separation of oxidized, highly polar sulphur compounds from reacted condensate through liquid-liquid extraction by a polar solvent such as methanol, ethanol, or acetone. 50 mL of the reacted gas condensate was poured into a decanter and 25 mL of solvent was added to the decanter and shaken severely for 5 min, then settled for 10 min to observe two distinct phases. The upper phase was solvent containing oxidized sulphur compounds and the lower phase was the sweet gas condensate, which was separated and tested for remaining sulphur content by energy dispersive X-ray fluorescence (SPECTROSCAN SE, Russia) according to ASTM D4294. Moreover, hydrogen sulphide and mercaptans in liquid hydrocarbons were measured with potentiometric titrimetric method (716 DMS Titrino, Metrohm Ltd.) based on ASTM PA19428. All experiments were repeated

three times and mean values were reported as well as standard deviation.

The most important limitations of this study are:

- The inability to control the intensity of the air flow;



FIGURE 4 Two-phase liquid after the catalytic oxidation process.

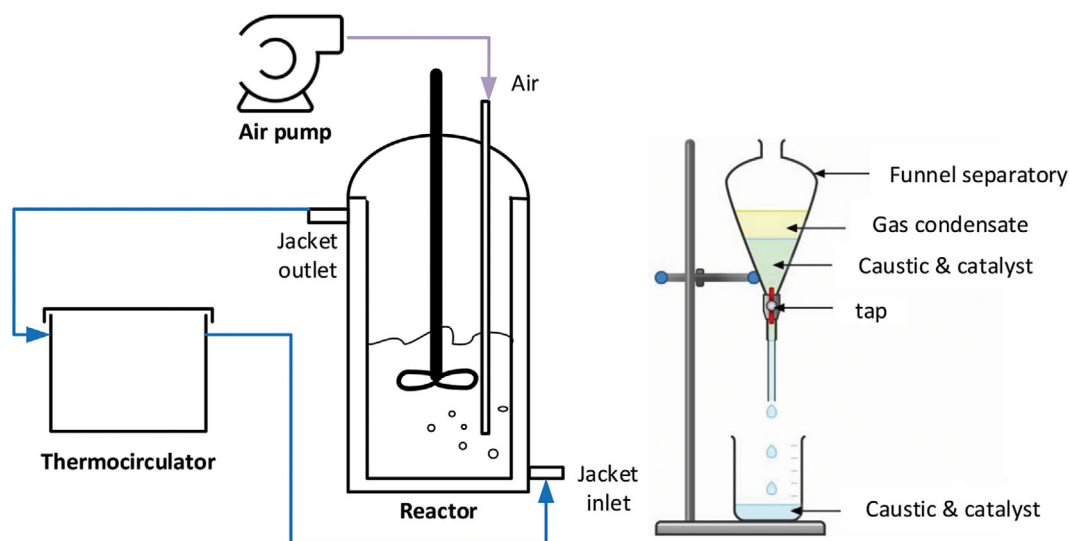


FIGURE 3 The experimental setup.

- The impossibility of wearing the reactor head completely, which would lead to the evaporation of a small amount of condensate;
- The expensiveness of the materials needed to test the amount of mercaptan and the need for large amounts of it;
- The sensitivity of the mercaptan titrator.

2.4 | Experimental design

There are seven variables in these experiments, as presented in Table 3. Based on the experimental design, a total of 26 experiments were conducted with the details shown in Table 2. The crucial parameters were temperature, CCR, NaOH concentration, amount of catalyst,

TABLE 3 Experimental design.

	Temperature (°C)	Caustic concentration (vol.)	CCR	Vol.% methanol
Temperature effect				
1	35	50%	8%	50%
2	25	50%	8%	50%
Solvent amount				
3	5	50%	8%	50%
4	5	50%	8%	50%
5	5	50%	8%	25%
6	5	50%	8%	20%
7	5	50%	8%	5%
CCR effect				
8	35	50%	4%	50%
9	25	50%	4%	50%
10	5	50%	4%	50%
11	5	50%	4%	20%
12	5	50%	4%	5%
Caustic concentration effect				
13	35	16.70%	8%	5%
14	25	16.70%	8%	5%
15	5	16.70%	8%	5%
	Temperature (°C)	Caustic concentration (vol.)	CCR	IVC amount
IVC effect				
16	35	16.70%	8%	0
17	25	16.70%	8%	0
18	5	16.70%	8%	0
	Temperature (°C)	Caustic concentration (vol.)	CCR	Solvent (50%)
Solvent type effect				
19	25	50%	8%	Methanol
20	25	50%	8%	Ethanol
21	25	50%	8%	Acetone
	Temperature (°C)	Caustic concentration (vol.)	CCR	Methanol
Catalyst and caustic recycling				
22	25	16.70%	8%	5%
23	25	16.70%	8%	5%
24	25	16.70%	8%	5%
25	25	16.70%	8%	5%
26	25	16.70%	8%	5%

Abbreviation: CCR, condensate volume ratio.

solvent type and volume, and number of catalyst and caustic recycling.

3 | RESULTS AND DISCUSSION

This section presents the results of all experiments as well as discussion on the effect of operating parameters including temperature, caustic to condensate (CCR), caustic concentration, catalyst to feed ratio, and solvent for extraction.

3.1 | Effect of temperature

Temperature has significant effect on the desulphurization of gas condensate. Figure 5 shows total sulphur (wt.%) and mercaptan content (ppm) in the gas condensate after desulphurization process versus temperature at different CCR values. According to the results, minimum

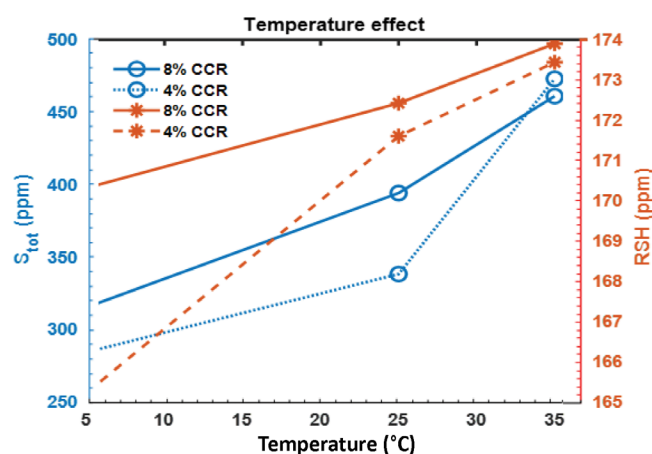


FIGURE 5 Temperature and condensate volume ratio (CCR%) effects on sulphur and mercaptane removal in a catalytic oxidation process. The overall formula of mercaptans is RSH.

residual sulphur and mercaptane is obtained at 5°C and CCR of 4%. Therefore, the sulphur removal process is favoured at a lower temperature as desulphurization reaction constant decreases by decreasing temperature because of exothermic reaction.^[44,56,57] Moreover, the temperature reduction leads to precipitation of sodium sulphide and carbonate salts out of caustic solution and it is separated more easily. In addition, as the catalytic oxidation of gas condensate is performed at atmospheric conditions in the mini refineries, there is a risk of gas condensate evaporation at higher temperature due to its high vapour pressure. Hence, the reactors should be equipped with a coolant jacket or cooling coil to operate more efficiently at low temperature.

3.2 | Effect of CCR

Another point to mention in Figure 5 is the effect of CCR on process performance. The CCR, defined by Equation (4), is an important parameter from reaction, economic, and environmental aspects. An optimum CCR is needed for a sufficient contact of caustic and condensate in the reactor. Lower CCR values result in lower conversion of mercaptans to mercaptides and higher residual sulphur content in the product. On the other side, dissolution of oxygen in the reaction system reduces at higher CCR values. This results in the formation of disulphides in the gas condensate and increases the residual total sulphur in the final product.^[44] As shown in Figure 5, the optimum CCR decreases at lower temperatures. Also, the difference between total sulphur and mercaptane content of final product between 4% and 8% of lower temperature is more than that at high temperature. According to the results, the catalyst has a better performance and the process requires less caustic at lower temperature. The less caustic consumption implies a more economic demercaptanization process. Similar

TABLE 4 The effect of volume ratio of caustic to gas condensate changing in different temperature on desulphurization and demercaptanization process.

S _{tot} of sour GC (ppm)	RSH of sour GC (ppm)	Temperature (°C)	CCR (%)	S _{tot} of sweet GC (ppm)	Sulphur removal (%)	RSH of sweet GC (ppm)	RSH removal (%)
3533	1904.68	35	8%	461	86.95 ± 1.6	173.9	90.86 ± 1.2
3533	1904.68	25	8%	394	88.84 ± 1.1	172.42	90.94 ± 1.1
3533	1904.68	5	8%	315	91.08 ± 1.3	170.31	91 ± 1.1
3533	1904.68	35	4%	473	86.61 ± 1.4	171.6	90.99 ± 1.2
3533	1904.68	25	4%	338	90.43 ± 1.3	173.44	90.89 ± 1.1
3533	1904.68	5	4%	284	91.96 ± 1.4	165.21	91.33 ± 1.05

Note: The overall formula of mercaptans is RSH.

Abbreviations: CCR, condensate volume ratio; GC, gas condensate.

results were obtained by Afshar et al.,^[44] where they suggested an optimum caustic/propane volume ratio of 0.06 and an optimum caustic/butane volume ratio of 0.106 for LPG demercaptanization feed. Therefore, optimal conditions of temperature and volume percent of caustic to gas condensate are 5°C and 4%. A lower CCR would result in lower chemical consumption and less waste production, as both are important for the economic and sustainable process.

Results of sulphur removal and demercaptanization percent are presented in Table 4. The overall formula of mercaptans is RSH. As observed in this table, increase of caustic to feed percent from 4% to 8% does not have a significant effect on the sulphur and mercaptane removal. Thus, the optimum volume of caustic to gas condensate is 4%.

3.3 | Effect of caustic concentration

The caustic used in the demercaptanization reactions are essential for conversion of mercaptanes to mercaptides

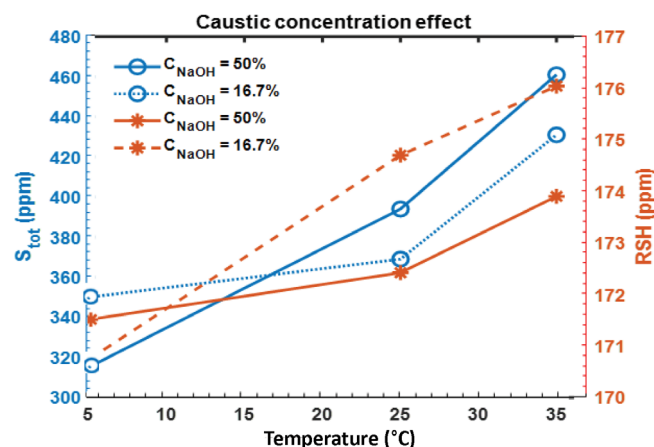


FIGURE 6 The effect of caustic solution in different temperature on sulphur and mercaptane removal (condensate volume ratio [CCR] = 8%). The overall formula of mercaptans is RSH.

and further to disulphides, as mentioned in Reactions (2) and (3). A caustic solution with higher concentration provides better catalyst dispersion and lower mass transfer resistance of mercaptides.^[42] Previous studies suggest different optimum concentrations of caustic solution for demercaptanization process depending on parameters such as condensate feed type, initial sulphur and mercaptane content, desired quality of the final product, and so forth. For example, Afshar et al.^[44] suggested caustic concentration of 14–14.2 wt.% for sweetening of propane and butane. Liu et al.^[42] proposed optimum caustic concentration in range of 2.75 to 4.25 mol/dm³ for LPG sweetening by caustic.

In this study, two caustic concentrations of 16.7 and 50 wt.% were investigated with CCR of 8% at three temperatures of 5, 25, and 35°C. Results shown in Figure 6 indicate that the high concentration of caustic solution (50 wt.%) caused further reduction of sulphur and mercaptane content in the sweet gas condensate at 5°C. On the other hand, a caustic solution with lower concentration (16.7 wt.%) leads to increased sulphur and mercaptane removal at higher temperatures. However, the sulphur and mercaptane removal increase to about 1% at 5°C when caustic concentration of 50 wt.% is utilized. Results of experiments at different temperatures and caustic solution concentrations are shown in Table 5. According to this table, increasing concentration of caustic solution from 16.7 to 50 wt.% provides a slight improvement in sulphur and mercaptane removal to about 1% at 5°C, indicating an insignificant influence on the process performance. Therefore, the lower caustic concentration of 16.7 wt.% is preferred at all temperatures.

The remaining caustic and catalyst make a green, viscous liquid phase which is separated from sweet gas condensate and can be recycled to the new batch of catalytic oxidation reactions. Figure 7 illustrates the potential of recycled caustic solution and catalyst to reuse for sulphur removal. These experiments were performed at 25°C,

TABLE 5 Effect of caustic solution concentration on desulphurization and demercaptanization process.

S_{tot} sour GC (ppm)	RSH of sour GC (ppm)	Temperature (°C)	Caustic concentration (vol.%)	S_{tot} sour GC (ppm)	Sulphur removal (%)	RSH of sweet GC (ppm)	RSH removal (%)
3533	1904.68	35	50%	461	86.95 ± 1.6	173.9	90.86 ± 1.2
3533	1904.68	25	50%	394	88.84 ± 1.1	172.42	90.94 ± 1.1
3533	1904.68	5	50%	315	91.08 ± 1.3	170.31	91 ± 1.1
3533	1904.68	35	16.70%	431	87.80 ± 1.6	176.04	90.72 ± 2.2
3533	1904.68	25	16.70%	369	89.55 ± 1.4	174.7	90.82 ± 2.1
3533	1904.68	5	16.70%	350	90.09 ± 1.7	170.73	91.03 ± 2.2

Note: The overall formula of mercaptans is RSH.

Abbreviation: GC, gas condensate.

CCR of 8%, caustic solution concentration of 16.7 wt.%, reaction time of 90 min, and mixing rate of 550 rpm. As the maximum acceptable S_{tot} in the sweet gas condensate

is 500 ppm, minimum sulphur removal should be 85% for the feedstock of this study; therefore, according to Figure 7, the spent caustic and catalyst can be reused twice and after that fresh caustic and catalyst should be charged in the reactor.

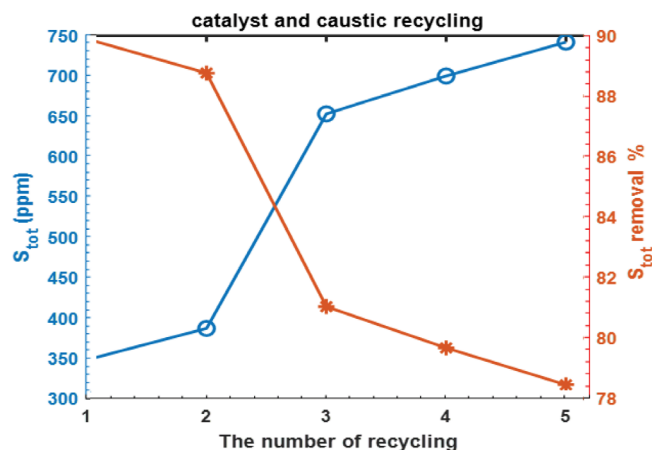


FIGURE 7 The effect of caustic and catalyst recycling ($T = 25^\circ\text{C}$, condensate volume ratio [CCR] = 8%, NaOH concentration = 16.7 wt.%, reaction time = 90 min, mixing rate = 550 rpm).

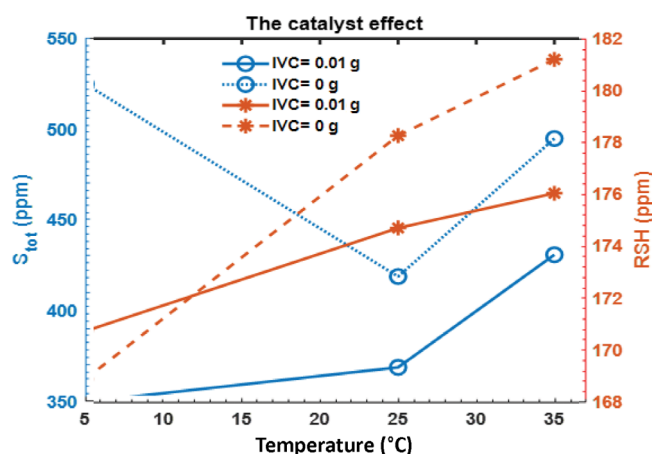


FIGURE 8 Comparison of catalytic oxidation with caustic wash in different temperature (volume ratio caustic to feed = 8% and caustic concentration = 16.7%). The overall formula of mercaptans is RSH. IVC, catalyst to condensate volume ration.

3.4 | Effect of catalyst to feed ratio

In all catalytic oxidation experiments, a minimum amount of 0.01 g (about 0.05 mL) catalyst was used per 400 mL gas condensate, corresponding to catalyst to condensate volume ratio (IVC) of 0.0125%, calculated by Equation (5):

$$\text{IVC}\% = \frac{V_{\text{IVKAZ}}}{V_{\text{condensate}}} \times 100 \quad (5)$$

Experiments were conducted at different IVC values to evaluate the potential of catalyst and find the minimum catalyst consumption for sweetening the gas condensate to get a target total sulphur of lower than 500 ppm and mercaptane content of lower than 200 ppm in the final product. Experiments were conducted at the CCR of 8%, caustic solution concentration of 16.7 wt.%, reaction time of 90 min, and mixing rate of 550 rpm. Results are summarized in Table 5 and shown in Figure 8. The catalyst has a significant effect at the temperature of 5°C , where it could improve the sulphur removal to 90%, while it was 85% without catalyst. At other temperatures, catalyst could improve sulphur and mercaptane removal about 2% rather than sweetening without catalyst (Table 5). However, an important point is that the experiments were performed with the minimum amount of catalyst and the desulphurization percent. Results of desulphurization and demercaptanization are presented in Table 6. The optimum temperature for catalytic oxidation process is 5°C , while it is 25°C for caustic solution sweetening.

TABLE 6 Comparison of catalytic oxidation with caustic wash without catalyst.

IVC (gr)	Temperature ($^\circ\text{C}$)	S_{tot} sour GC (ppm)	RSH of sour GC (ppm)	S_{tot} of sweet condensate (ppm)	Sulphur removal (%)	RSH of sweet GC (ppm)	RSH removal (%)
0	35	3444	1904.68	495	85.62 ± 1.7	182.3	90.42 ± 2.1
0	25	3444	1904.68	419	87.83 ± 1.4	178.26	90.64 ± 1.9
0	5	3533	1904.68	525	85.14 ± 1.35	168.88	91.13 ± 2.4
0.01	35	3533	1904.68	431	87.80 ± 1.6	176.04	90.72 ± 2.2
0.01	25	3533	1904.68	369	89.55 ± 1.4	174.7	90.82 ± 2.1
0.01	5	3533	1904.68	350	90.09 ± 1.7	170.73	91.03 ± 2.2

Abbreviations: GC, gas condensate; IVC, catalyst to condensate volume ration.

3.5 | Type of extraction solvent

The residual oxidized sulphur compounds should be extracted out of the reacted condensate phase through liquid–liquid extraction by a polar solvent. In the present work, acetone, ethanol, and methanol were used for this purpose. Solvents were added at 50% volume ratio to the condensate and the whole system was shaken for 10 min, then settled and the two phases were separated.

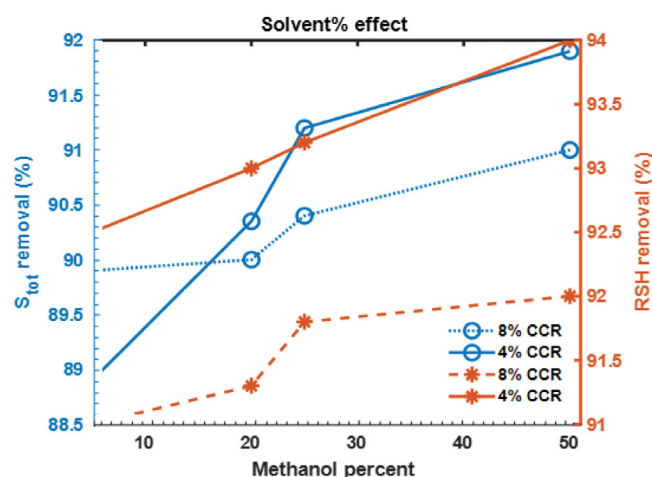


FIGURE 9 The effect of solvent amount in the separation step. The overall formula of mercaptans is RSH. CCR, condensate volume ratio.

The condensate phase was then separated from the bottom of the decanter. All solvents act efficiently and reduce the residual sulphur content by more than 85% so that the treated condensate contains the desired level of sulphur. The best solvent is acetone with maximum sulphur removal of 96%, followed by ethanol and methanol. Also, sulphur removal by ethanol and methanol is more than 85%, and both solvents are acceptable. Methanol is the best solvent with good extraction capacity and relatively low price, which is important from economic point of view, especially at high plant capacities. Moreover, methanol has low latent heat, and can be easily separated from the wastes containing the sulphur components by distillation.

The amount of methanol used for extraction should be kept at a minimum level to control the remaining oxygen level in the treated condensate. The catalytic oxidation processes were performed at 25°C with caustic concentration of 50% and mixing rate of 550 rpm for 90 min. The results are presented in Figure 9. There is no significant difference between 5% or 50% methanol as a solvent. Therefore, it is recommend that 5% methanol be added to the solution in the separation step.

Table 7 shows comparison of different ODS processes. There are three types of ODS processes: catalytic process with caustic, catalytic process with acid solution, and non-catalytic process. Results show that the catalytic

TABLE 7 Comparison of different disulphide oil (DSO) process.

Feed	Sulphur content ppm	Catalyst	Catalyst amount	Time (min)	Temperature (°C)	Caustic	Air/H ₂ O ₂ oxidant	Caustic or acid amount	Sulphur removal%	Mercaptane removal%	Ref.
Gas condensate	3533	IVKAZ	0.01 g	60	35	NaOH	Air	16.2%	87.80	90.72	
Gas condensate	3533	IVKAZ	0.01 g	60	25	NaOH	Air	16.2%	89.55	90.82	
Gas condensate	3533	IVKAZ	0.01 g	60	5	NaOH	Air	16.2%	90.09	91.03	
Diesel fraction	280	-		60	20	Ammonia	Air	25%	-	43	2 new
Diesel fraction	280	-		60	20	NaOH	Air	25%	-	76	2 new
Butane-butene	1500	cobalt phthalocyanine		-	-	NaOH	Air	-	99.8	-	4 new
Normal Pentane-iso pentane	620	cobalt phthalocyanine		-	-	NaOH	Air	-	99.6	-	4 new
Naphtha	2500	Cobalt phthalocyanine		-	-	NaOH	Air	-	99.8	-	4 new
Butane	285	Acetic acid (UAOD treatment method)	-	9	90	-	H ₂ O ₂		64.8	-	10 new
Fuel oil	-	Acetic acid	8 g	60	50	-	H ₂ O ₂	15 g	98.17	-	30
Fuel oil	-	Formic acid	8 g	60	50	-	H ₂ O ₂	15 g	97.85	-	30
Kerosene	-	Acetic acid	70.65 mL	60	25	-	H ₂ O ₂	103.3 mL	28	-	6
Kerosene	-	Acetic acid	70.65 mL	60	40	-	H ₂ O ₂	103.3 mL	47	-	6
Kerosene	-	Acetic acid	70.65 mL	60	60	-	H ₂ O ₂	103.3 mL	59	-	6
Liquefied petroleum gas (LPG)	1300	Co ²⁺	0.51 kmol/h	240	50	NaOH	Air	15.2%	1.3	38.4	33
Light cycle oil	13,000	5%Ni10%Mo/γ-Al ₂ O ₃	1 g	120	30	-	H ₂ O ₂	1 mL	95.2	-	29
LPG	-	LCPS 30	-	720	37	NaOH	Air	14.2 wt. %	-	88	27

process with caustic solution is more efficient and has the highest sulphur removal. Cobalt phthalocyanine sulfonamide-based catalysts have a high ability to sulphur removal even at a low dosage. Table 7 shows the comparison with other studies and validation of the present study.

4 | SUMMARY AND CONCLUSIONS

In this work, the sulphur of gas condensate with about 3500 wt. ppm sulphur content reduced to the less than 500 ppm via ODS method using cobalt phthalocyanine sulfonamide-based catalyst. It was found that this process could decrease mercaptane content to less than 200 wt. ppm. The amount of catalyst is an important parameter in the process and minimum amount of catalyst was used in this study (about 0.01 g per 400 mL gas condensate). The process was conducted in a glass batch reactor which had a jacket for temperature control and a mixer with mixing rate of 550 rpm was utilized for mixing the solution of gas condensate and chemicals. Also, optimum CCR values were obtained at different temperature to maximize sulphur and mercaptane removal. Moreover, process temperature was a crucial factor, which was examined in a range from 5 to 35°C. Results showed:

- Optimum values of temperature, caustic concentration, and CCR were 5°C, 16.7%, and 4%, respectively.
- Maximum total sulphur and mercaptane removal was about 91% with less than 500 and 200 ppm, respectively.
- Methanol was introduced as an acceptable and economic solvent and the optimum amount was 5 vol.% of gas condensates.
- Sulphur compounds had higher solubility in acetone rather than methanol, and sulphur removal by acetone was about 96% while it was 91% for methanol; however, acetone is more expensive than methanol.

AUTHOR CONTRIBUTIONS

Azadeh Mirvakili: Writing – review and editing; conceptualization; investigation; funding acquisition; writing – original draft; methodology; validation; visualization; software; formal analysis; project administration; data curation; supervision; resources. **Ahmad Baghzar:** Writing – review and editing; visualization; validation; methodology; project administration; investigation; funding acquisition; conceptualization; writing – original draft. **Milad Hooshyar:** Conceptualization; investigation; funding acquisition; writing – original draft; methodology; validation; visualization; writing – review and editing; project

administration; resources; supervision; data curation. **Kimia Zahabi:** Data curation; supervision; resources; project administration; formal analysis; validation; writing – review and editing; writing – original draft; funding acquisition; investigation; conceptualization. **Reza Azin:** Writing – review and editing; visualization; validation; project administration; formal analysis; software; methodology; investigation; writing – original draft; funding acquisition; conceptualization; data curation; supervision; resources. **Yousef Kazemzadeh:** Writing – review and editing; validation; visualization; project administration; resources; data curation; funding acquisition; investigation; writing – original draft; conceptualization.

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DATA AVAILABILITY STATEMENT

All data generated or analyzed during this study are included in this published article.

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