

Demercaptanization of Distillate (DMD)

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Abstract

Sulfur compounds and mercaptans in hydrocarbon and petroleum cuts lead to environmental pollution and corrosion problems in pipelines and storage tanks. So it is necessary to decrease sulfur and mercaptans concentrations in hydrocarbon cuts to international standard levels in petroleum industries. For this purpose, DMD process has been developed as a demercaptanization process providing the possibility of demercaptanization of different hydrocarbon cuts even crude oil as a feed. In this article, experimental results of different oil feeds sweetening have been presented by using DMD process. Also the optimum conditions of this reaction have been determined by examination of effective factors. The results of this research show that DMD process has the high capability of decreasing of mercaptans and sulfur compounds in hydrocarbon cuts up to environmental standards.

Key words: Demercaptanization, sweetening, DMD process

Introduction

Sulfur compounds are undesirable group of impurities in oil cuts, which must be decreased to the international levels by using proper methods.

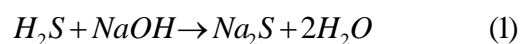
This operation is called, "sweetening process".

Sulfur in hydrocarbon cuts has different forms such as element sulfur (S) (H₂S), COS, CS₂, RSH (mercaptans), thiophene, and other sulfur compounds.

These impurities are oxidized after combustion and cause environmental pollutions. Mercaptans with low molecular weights are volatile, toxic, corrosive and odourless that lead to some problems in storage and transportation of oil cuts. There are different desulfurization and demercaptanization process, however some of them are not applicable any more because of

different environmental & operation problems [1-3].

In recent years, DMD process has been developed as a proper sweetening method. In this process, Hydrogen sulfide (H₂S) is separated from hydrocarbon cut by a diluted Hydroxide solution (1-2 wt%). following this equation (1):



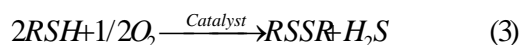
Light mercaptans (C₁-C₃) are separated by using caustic solution of about 8-10 %wt and IVKAZ catalyst, through the equation (2):



Heavy hydrocarbons like heavy naphtha containing (C₄⁺) are converted to disulfide

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by oxidization in the presence of UVKO catalyst. According to equation (3):



Based on the feed types, different DMD processes have been developed for dividing sulfur components[4,5].

Experimental method:

In this experimental research, demercaptanization of different feeds (Kerosene, gasoline, gasoil) has been preceded through two processes, continue and batch, to determine the effective factors and optimum conditions of the process. In this study, the amount of mercaptan is the independent variable that the effect of different parameters to reach the permissible limit of mercaptan has been examined studied.

Comparison of parameters has been done based on available standards. (UOP 163). Materials and feeds used in this study have been given in table 1.

Table 1 Specifications of consumed materials

Type	Company	Specifications
Kerosene	Shiraz refinery	Primary mercaptan 1110 ppm
Gasoline	Tehran refinery	Primary mercaptan 2400 ppm
Gasoil	Shiraz refinery	Primary mercaptan 1160 ppm
Sodium Hydroxide	Merck	99.99% purity
Catalyst	VNIUS	UVKO-2

Laboratory demercaptanization set up for batch operation has been show in fig (1). As shown, demercaptanization process is done in a glass reactor (D=3cm, H=35cm), where heterogen catalyst (UVKO-2) has been installed in a fixed bed and the required air enters from the bottom of the reactor. A heating coil is used to heat the reactor. After the definite time sample is taken from the

system and the amount of residual mercaptans is determined.

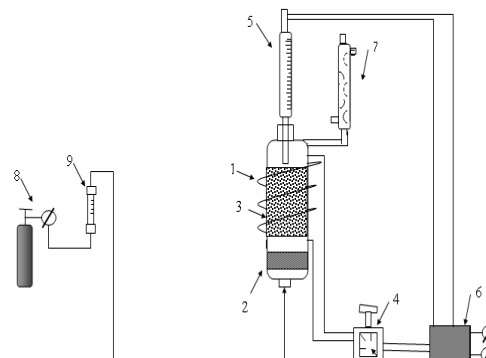


Fig 1 Laboratory set up for a batch demercaptanization process

1. Element 2. Distributor, 3. Catalyst 4. Transformer 5. Thermocouple & Controller 6. Contactor 7. Condensor 8. Air 9. Flow meter

Continuous process for demercaptanization of different feed has been shown in fig 2. Feed with a determined flow rate enters to the bottom of the reactor. The reactor has been filled by a fixed bed catalyst.

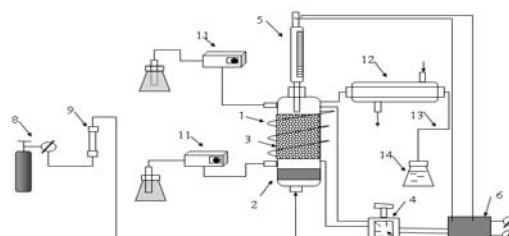


Fig 2 Continuous demercaptanization process

1. Element 2. Distributor 3. Catalyst 4. Transformer 5. Thermocouple & Controller 6. Contactor 7. Hydroxide sodium 8. Air 9. Flowmeter 11. Dosing Pump 12. Condensor 13. Product outlet 8. Demercaptanized product

After sulfur compounds and mercaptans removal, the product leaves the reaction condition from top of the column. Then the amount of residual mercaptan is determined by sampling and testing. Also oxygen injection has been provided for oxidization of heavy mercaptans.

Demercaptanization conditions of hydro-carbon cuts (kerosene, gasoline and gasoil) have been given in table 2.

Table 2 Test conditions of demercaptanization process

Type of hydrocarbon cuts	System							Consideration
	Batch				Continuous			
	Feed (ml)	Air (ml/min)	Temp ($^{\circ}$ C)	Time (min)	Feed flow rate(ml /min)	Air flow rate (ml /min)	Temp ($^{\circ}$ C)	
kerosene	50	0.5	70-80	15-20	3-5	0.2	70	
gasoline	50	0.5	50	15	2.5- 9.5	0.2	40-50	Two stage extractions by NaOH(gasoline /caustic=1.1)
gasoil	50	0.5	70-80	15-50	5	0.2	70	Primary washing by NaOH solution (1% wt)

Results and Conclusion

The results of the experimental studies of two cases of continuous and batch processes have been given in tables 3,4.

Temperature and flow rate of air affect the demercaptanization efficiency. However the optimum conditions of the process were been determined by different tests. As shown in fig 3, increasing of air flow rate up

to 4 ml/min decreases the residual mercaptans in kerosene, which shows the increasing rate of oxidization reaction. However because of the bed cooling and increasing of droplet diameter, which decrease the residence time of feed, the efficiency of the reaction will decrease and the amount of the residual mercaptans will increase.

Table3 Results of kerosene demercaptanization in a batch system

No.	Temperature ($^{\circ}$ C)	Time (min)	Air flow rate (ml/min)	Mercaptan after oxidization
1	80	20	0.5	< 1ppm
2	80	15	0.25	< 1ppm
3	70	15	0.25	7 ppm
4	70	15	0.2	5 ppm

Table 4 Results of kerosene demercaptanization in a continuous process

No	Temperature ($^{\circ}$ C)	Air flow rate (ml/min)	Kerosene flow rate (ml/min)	Mercaptan after oxidization
1	70	3	0.2	6 ppm
2	70	3.4	0.2	5 ppm
3	75	3	0.2	<1 ppm
4	75	3.4	0.2	<1 ppm
5	70	5	0.25	6 ppm
6	70	5	0.23	4 ppm
7	70	5	0.2	2 ppm

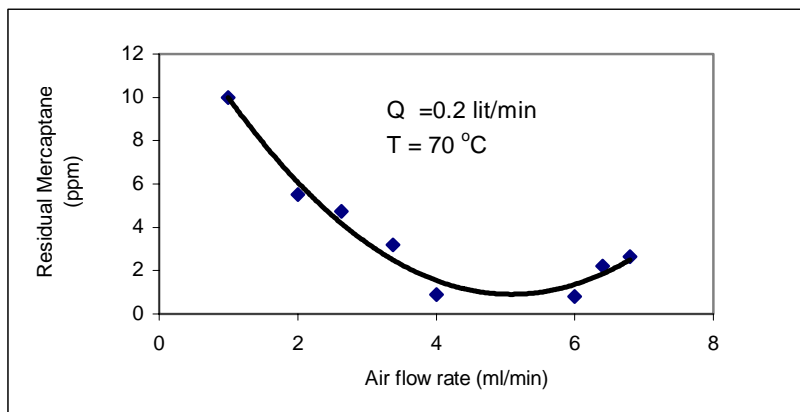


Fig3- Residual Mercaptane in Kerosene Versus Air Flow rate

It must be considered that increasing of air flow rate more than twice the stoichiometry does not have any effect on decreasing of the amount of residual mercaptans. Demercaptanization of gasoline was similar to Kerosene demercaptanization. In this case suitable temperature was about 50°C.

Residual mercaptans in gasoline after DMD process versus time have been shown in fig 4. As shown, mercaptans in gasoline, by a

catalyst reaction are oxidized after 3 minutes and reach to the permissible limit (5 ppm) .

In continuous process, the suitable temperature for gasoline demercaptanization is about 50°C. But NaOH injection does not affect on the oxidization, even the extra injection of NaOH may cause reverse effect, because of occupation of active sites of catalyst by NaOH. The results of demercaptanization of gasoline sample in the batch process have been given in table 5.

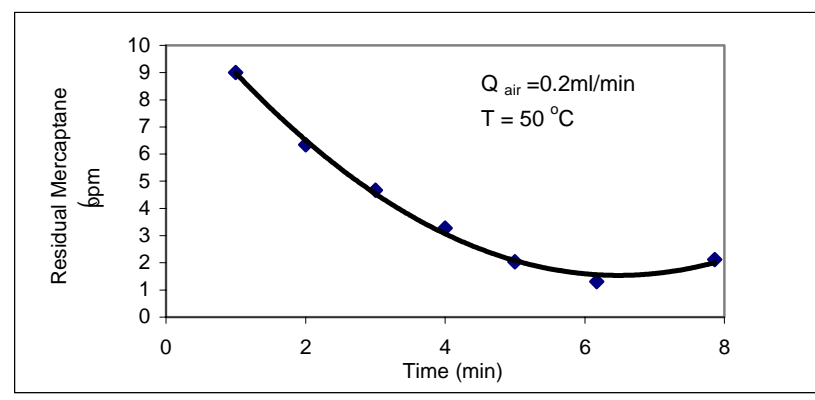


Fig 4 Residual Mercaptane Versus Time

Table 5 Gasoline demercaptanization in a bath system

No.	Temp(°c)	Time (min)	Air flow rate (ml/min)	Mercaptane after oxidization
1	50	1	0.2	9 ppm
2	50	3	0.2	5 ppm
3	50	5	0.2	3 ppm
4	50	6.1	0.2	<1 ppm

As shown in table 6 the optimum conditions of gasoline demercaptanization in the continuous process have been determined by change of the temperature and flow rate of air.

Gas oil demercaptanization process is similar to Kerosene demercaptanization. The results have been given in tables 7,8.

Table (6)- Gasoline demercaptanization in a continuous process

No.	Temperature (°C)	Residence time (min)	Air flow rate (ml/min)	Gasoline flow rate (lit/min)	Mercaptan after oxidization
1	40	4	0.2	0.2	6 ppm
2	40	3	0.25	0.2	6 ppm
3	40	5	0.25	0.2	<1 ppm
4	50	4	0.25	0.2	<1 ppm
5	50	3	0.25	0.2	6 ppm

Table (7)- Gas oil demercaptanization in a batch process

No.	Temperature (°C)	Oxidization time (min)	Air flow rate (lit/min)	Mercaptan after oxidization
1	80	20	0.5	<1ppm
2	80	15	0.25	<1ppm
3	70	15	0.25	7ppm
4	70	15	0.2	5ppm

Table 8 Gas oil demercaptanization in a continuous system

No.	Temperature (°c)	Air flow rate (ml/min)	Gas oil flow rate (lit/min)	Mercaptan after oxidization
1	80	0.5	2.7	15 ppm
2	90	0.5	2.7	8 ppm
3	90	0.25	2.5	5 ppm
4	90	0.25	2.7	7 ppm

At first gas oil sample was washed by diluted sodium hydroxide solution (1% wt) for naphthenic acid removal.

Although increasing the temperature increases the rate of oxidization, it leads to increasing of saturation pressure of feed. So the temperature of the reaction must be

minimized to reach to the minimum pressure.

The catalyst of DMD process has high activity, so decreasing of mercaptans in hydrocarbon cuts to permissible limit (gasoline <5 ppm, gas oil & kerosene < 10 ppm) is possible.

Suggestions:

In the next stage of this study, Research Institute of Petroleum Industry has installed a pilot plant with the capacity of 20 bbl/day and demercaptanization of different feeds has been done successfully through continuous operation. It must be mentioned that this process is installing in Kharg Petrochemical Company.

Considering the localization of this process in Research Institute of Petroleum Industry with the cooperation of VNIIS, technology transfer and DMD unit installation in different refineries and petroleum industries are possible. Even DMD process is an economic process which can be a proper substitution for Merox process.

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