



Recycling and Reuse of Organo-sulfur Compounds from Barrels of Natural Gas Contaminated with Mercaptan Odorant

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ABSTRACT

Natural gas is odorized by trace amounts of mercaptans and organic sulfides to be recognized by individuals, in case of gas leakage. These materials may pollute the environment particularly in injection station at local gas plants. Therefore, removal of sulfur compounds from the remaining odorant in barrels is essential. To remove the residual portion of mercaptans and alkylsulfide mixtures different methods were utilized which among them extraction-distillation procedure was implemented in the current study as it is environmentally safe and is a low cost process. Different solvents such as Methyl Ethyl Ketone (MEK), Ethyl acetate, Dichloromethane (DCM), Toluene and Kerosene were attempted for the efficient extraction which among them kerosene was the most desired and the best solvent. Results showed that the implemented method was highly efficient for the removal of odorants in which the regenerated mercaptan from the contaminated barrels could be reused in injection step as well as the original odorant. The GC and ¹H NMR analyses confirmed that the recovered organo-sulfur compounds, mainly composed of tertiary butyl mercaptan, was desired for re-injection into natural gas stream as suitable odorant.

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1. INTRODUCTION

Natural gas is an odorless and colorless flammable fuel. There are many reports that gas leakage in household have caused irreparable fire damage; therefore, to control these incidents, odorization of gas is necessary. Natural gas odorization means addition of an odorant to gas to ensure characteristic odor of natural gas so that the odor becomes distinctive and unpleasant to the consumer. This way, the presence of gas in air in concentrations below the lower explosive limit (LEL) is readily detectable. After addition of any odorant to the gas, physical and chemical properties (except the smell) of natural gas should not change. Generally speaking, in the process of natural gas delivering for both public and industrial uses, odorization provides safety for those who use it. Historically, first gas odorization was carried out in Germany in 1880's by Von Quaglio who used ethyl

mercaptan for detecting gas leakages of blue water gas [1]. However, the real beginning of widespread odorization started in US in 1930's as a consequence of the New London's disaster [2-5].

As high quality natural gas replaced manufactured gas, the need for odorization of this gas increased. Modern gas odorants can be divided into two basic groups. The "classic" sulfur-based odorants which are further subdivided to alkyl mercaptans, alkyl sulfides and cyclic sulfides. The new types of sulfur-free odorants based on acrylates which are being introduced to the market in recent years and have their special potential especially in environmental issues due to their zero sulfur dioxide emissions after gas combustion.

The sulfur compounds which either naturally present or are added intentionally as odorants for leakage detection, include sulfides, mercaptans, disulfides and thiophenes. Typical sulfur odorants are

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tetrahydrothiophene (THT), tertiary butyl mercaptan (TBM), ethyl mercaptan (EM), and dimethyl sulfide (DMS). These sulfur compounds are strong poisons for reformer and fuel cell catalysts. Table 1 summarized the physical properties of sulfur compounds which are commonly used as odorants in natural gas for domestic use [6]. In this table, it was aimed to introduce the potential organo sulfur and to demonstrate odorants with desired physical properties such as high vapor pressure, low flash points and low boiling points which are used in the gas separation process. In our study selection of these solvents was based on their commercial availability and economic factors; our selection of solvent for removal of organo sulfur was based on process simplicity, commercial availability, solvent stability and cost effectiveness.

In general, sulfur compounds should be removed to the lowest possible level prior to fuel processor and fuel cell use. Fuel desulfurization is typically carried out using the following competing technologies: adsorption, selective catalytic oxidation (SCO), hydrodesulfurization (HDS) and extraction [7–10].

In any natural gas plant, about 1 to 5 liters of mercaptans are remained in a 100 liters barrel of gas odorant. At these gas station, a large amount of non-evacuating mercaptans is remained in the barrel that gradually vaporize and thus pollute the air in gas-pressure control station. Therefore, the purpose of the present work is to introduce a facile and clean way to remove and recycle mercaptan residual and contaminants from the mercaptan barrels which is being utilized for odorization of natural gas. According to our knowledge, extraction is

not only one of the oldest and cheapest methods, but also known as a rapid process for the removal of hydrogen sulfide and mercaptans. Furthermore, all the materials which are used in this method can be recovered under vacuum distillation or reduced pressure. Therefore, extraction-evaporation process is environmentally safe and is an economical solution for the removal and reuse of the residual mercaptan from the contaminated mercaptan barrels.

2. EXPERIMENTAL

2. 1. Materials

All solvents were purchased from Merck (Darmstadt, Germany) and used without purification. Odorant was provided by gas organization of Mazandaran province in Iran. Triethyl amine was provided by Sigma-Aldrich (USA). Other chemical reagents were of analytical grade or higher purity.

2. 2. Determination of the Boiling Point of Mercaptan via Micro Method

At first one side of capillary tube was blocked on the flame. About 1 to 1.5 mL of mercaptane was poured in a small test tube. The capillary tube with closed end was placed upward into the test tube. The test tube wherein a thermometer was placed, was immersed in a paraffin bath. The above system was heated slowly. As the temperature of liquid approached to its boiling point, a few bubbles could be observed flowing out of the end of the capillary tube. When a steady stream of bubbles is

TABLE 1. The properties of sulfur compounds utilized as odorants

Sulfur compounds	Formula	Boiling point (b.p °C)	Density (g/cm³)	Flash point (°C)	Vapor pressure (mmHg)
Methyl mercaptan	MeSH	6.98	0.87	-17.8	1520 at 26.1 °C
Ethyl mercaptan	EtSH	36	0.84	26.6	837.8 at 38.7 °C
Dimethyl sulfide	Me ₂ S	37.5	0.845	-17.8	775.7 at 38 °C
Isopropyl mercaptan	(Me) ₂ CHSH	51-55	0.814	-34.4	455.1 at 37.8 °C
Tert-butyl mercaptan	(Me) ₃ CSH	62-67	0.79-0.82	-26.1	305.1 at 38 °C
<i>n</i> -Propyl mercaptans	<i>n</i> -C ₃ H ₇ SH	67-73	0.84	20.5	263.7 at 37.8 °C
Methyl ethyl sulfide	MeSEt	66.6	0.837	-15	272 at 38.7 °C
Sec-butyl mercaptan	MeCH(SH)Et	73-84	0.829	-23.3	142.2 at 38 °C
Isobutyl mercaptan	(Me) ₂ CHCH ₂ SH	85-95	0.836	-9.4	124 at 37.8 °C
Diethyl sulfide	Et ₂ S	92-93	0.837	-9.0	50.3 at 20 °C
<i>n</i> -Butyl mercaptan	<i>n</i> -C ₄ H ₉ SH	97.2-101.7	0.84	1.67	82.7 at 38 °C
Tetrahydrothiophene	C ₄ H ₈ S	115-124.4	1.0	13	41.4 at 38 °C
<i>n</i> -Pentyl mercaptan	<i>n</i> -C ₅ H ₁₁ SH	104-130	0.84	18.3	27.4 at 37.7 °C

observed, the heater was turned off and the content of the test tube was allowed to cool down to ambient temperature. As the content of the test tube cooled down, changes in the capillary tube were carefully monitored. When the liquid began to flow up into the capillary tube, the temperature of the liquid was recorded as its boiling point temperature [11].

2.3. Solubility of Mercaptan Sample solubility was studied in various organic solvents to select the best solvent for extraction step. For this purpose, 1 mL of mercaptan was added to 5 mL of organic solvents, the solubility was measured and the results are summarized in Table 2.

2.4. Extractive Distillation The extraction process was carried out on contaminated barrels which contained residual sulfur compounds bearing water. The water was collected inside the barrels during the storage in rainy and humid environment. Different solvents were used for the extraction process. In this way, 5 mL of organic solvent, 1 mL of mercaptan and 5 mL of water were thoroughly mixed. In order to investigate the ability of organic solvents to remove mercaptan odorant from water, the aqueous phase was separated and analyzed by gas chromatography-mass spectrometry (GC-MS).

Also, the effect of alkaline condition on the extraction efficiency was studied. Triethylamine was used as a base. A 1% triethylamine solution was prepared for this experiment and the aqueous solution was added to the solvents which were used for extraction. A 45 mL of organic solvent with 1% triethylamine was prepared. The solution was poured in the mercaptan container in three steps (each time 15 mL). At each stage, the container was washed well with the solvent and the amount of smell of the container was examined.

The distillation process was performed to remove mercaptan from the organic phase mixture completely. In this way, 45 mL of organic solvent, which was utilized for the removal of the odorants from contaminated container, was discharged in distillation apparatus.

TABLE 2. The solubility of mercaptan in different organic solvents

Organic solvent	Boiling point (°C)	Mercaptan and solvent mixture (solubility)
Methyl Ethyl Ketone (MEK)	80	One phase
Ethyl acetate	78	One phase after some time
Dichloromethane (DCM)	40	One phase
Toluene	110	One phase after some time
Kerosene	204	One phase

GC-MS analysis was performed on a GC-Mass model 5973 series of mass selective detector, GC 6890 Agilent Mass spectra were obtained with a Massens POEKROMETER CH-7A VARIN MAT BREMEN.

3. RESULTS AND DISCUSSION

3.1. Solubility Test The solubility of sample was examined in various organic solvents with a boiling point higher and lower than the boiling point of the mixture of commercial sulfur odorant mixture to choose the best solvent for efficient separation in the extraction and distillation processes. In fact, we have conducted the solubility test (Table 2) to find the most desired solvent for the real sample odorants. As it is known, solubility and miscibility are both used to evaluate the ability of one substance to dissolve in another substance. The solubility or miscibility of the solute is dependent on the type of solutes and solvents. The term miscibility refers to the ability of a liquid solute to dissolve in a liquid solvent. Solubility is a more general term, but it is more often used to mean the ability of a solid solute to dissolve in a liquid solvent. Miscible liquids generally mix without limit, that means, they are soluble in all amounts.

3.2. Extraction Process for the Removal of Natural Gas Odorants The extraction process was used to investigate the ability of various organic solvents for the removal of odorants. For this purpose, a mixture of mercaptan and water was prepared, as mentioned in experimental section. After two phases were formed, in order to investigate the efficiency of organic solvents for separation of mercaptan from sample, the aqueous phase was separated and the amount of odorants was quantitatively analyzed by GC. The results showed that among the solvents which were used, ethyl acetate and kerosene were the most effective solvents and completely reduced the odor level of mercaptans (Figure 1).

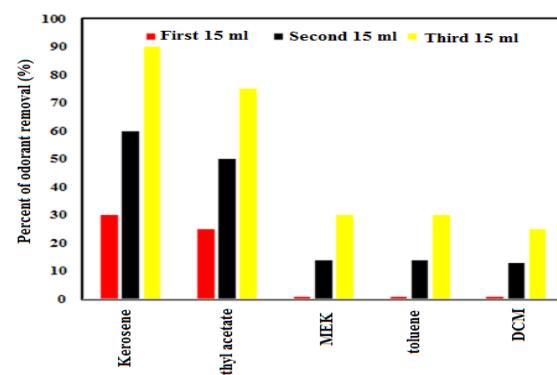


Figure 1. Comparing the ability of various solvents for the removal of odorant

In order to further investigate the influence of higher amounts of solvents and mercaptans, at first 15 mL of various solvents such as ethyl acetate or kerosene, 3 mL of mercaptan and 15 mL of water were well mixed. After mixing and shaking, the sulfur adducts were extracted. The removal of odorant was investigated by extraction in three sequential stages and the combined extracts were analyzed by GC. The results showed that there was not any significant amount of odorant materials remained in the extracted samples when kerosene used as solvent (Figure 2).

In the next step, the ability of solvent for the removal of the odorant compounds from the container which was contaminated with mercaptan without any aqueous phase was studied. This process was performed in three steps as mentioned above and in each step, 15 mL of organic solvent was added to the contaminated container and washed well with additional solvent. When the ethyl acetate/ kerosene solvent was used, in the first stage the odor significantly decreased. After adding the second 15 mL of organic solvent, the amount of odor was reduced to a much lower level, and in the final step after addition of the third 15 mL portion, the container just represented odor free, without odorant smell; the only dominant smell was the smell of solvent. The reproducibility of the extraction process was also tested which was consistent with the similar results.

In order to investigate the effect of base on the extraction process, triethylamine was used to optimize the removal of mercaptan odorant. A 1% triethylamine solution was prepared and added to the kerosene (solvent which was used for the extraction). This mixture was then used for the removal of odorants from container which was contaminated with mercaptan. At first, the mixture of kerosene with 1% triethylamine was prepared. The solution was added to the container in three steps, each time 15 mL. At each stage, the container was washed well with the solvent and the amount of thiols in the container was measured. The reaction is illustrated in Figure 4. As results show in Figure 5, the improvements were not significant when the base was used.

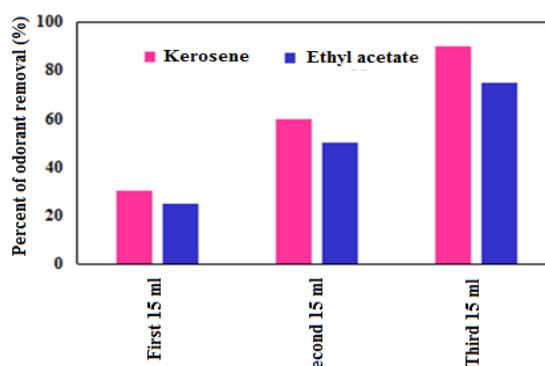


Figure 2. Effect of ethyl acetate and kerosene on the removal of odorant in the presence of water

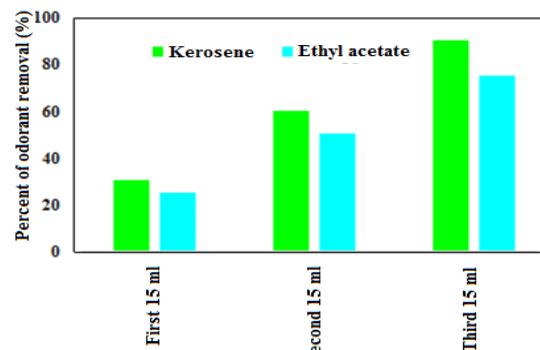


Figure 3. Effect of ethyl acetate and kerosene on the removal of odorant without aqueous phase

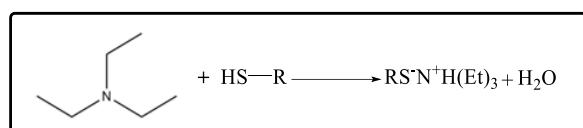


Figure 4. Possible chemical reaction of trimethylamine with mercaptan

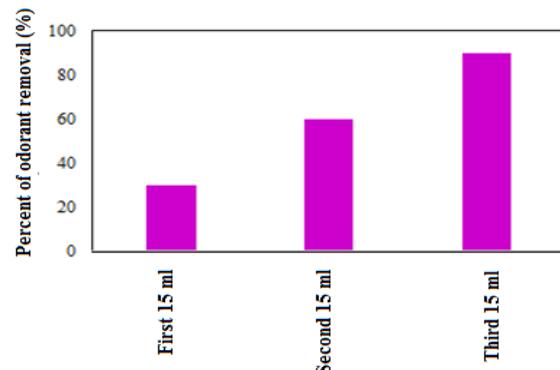


Figure 5. Effect of triethylamine on the removal of odorant

3. 3. Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

For GC analysis, the odorant sample was first vaporized at injection point and then injected into the injection port. Elution was brought about by the flow of N₂ gas as mobile phase.

The commercial odorant sample which was collected from Mazandaran province gas station was analyzed by GC-MS. As shown in Figure 6, most of the components which are commonly used in gas odorants, such as propyl mercaptan, butylmercaptan, methylmercaptan and ethylmercaptan, were identified at retention times between 4 and 6 min. In this figure, our developed technique was reliable; analysis showed that exact separated peaks were identified at specific retention times. Usually, the x-axis of the gas chromatogram shows the retention time which is the time taken for the analytes to pass through the column and reach the mass spectrometer detector. The peaks that are shown

correspond to the time at which each of the components reached the TCD detector.

The contaminated containers were washed by the kerosene as solvent three times (3×15 mL) in the presence and/or absence of aqueous phase. Then the resulting samples were analyzed by GC-MS (Figures 7 and 8). The results showed that in comparison with the pure odorant, in the mass spectrum of the final extracted samples, no peaks were observed at the retention time between 4 to 6 min which are related to the presence of thiol and sulfide materials in odorants. These results indicated efficient extraction of sulfur compounds by kerosene. The peaks at 10 to 18 min were related to the alkanes that existed in the lean solvent oil which was used as solvent.

The quantitative data obtained from the GC-MS analysis were completely consistent with the qualitative results which confirm the optimized removal of odorant materials such as thiol and sulfide compounds from the gas by using kerosene as the most desired and potential solvent for the extraction of organo-sulfur compounds.

3.4. Nuclear Magnetic Resonance (NMR)

¹H NMR measurements were carried out by a 400 MHz Bruker Avance III NMR Spectrometer using DMSO-d₆ as solvent in the chemical shift (δ) range of 0-10 ppm.

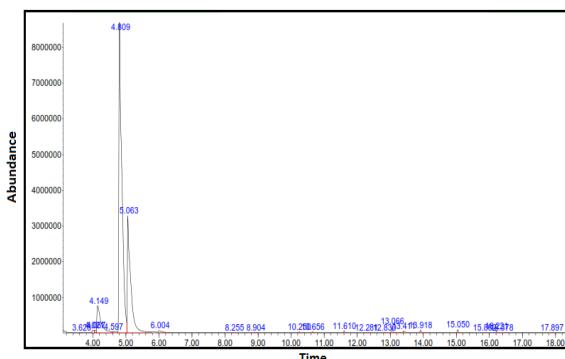


Figure 6. GC-MS analysis of pure odorant sample

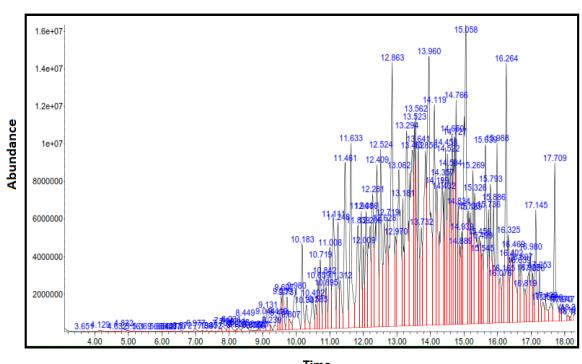


Figure 7. GC-MS analysis of washed containers in the absence of aqueous phase

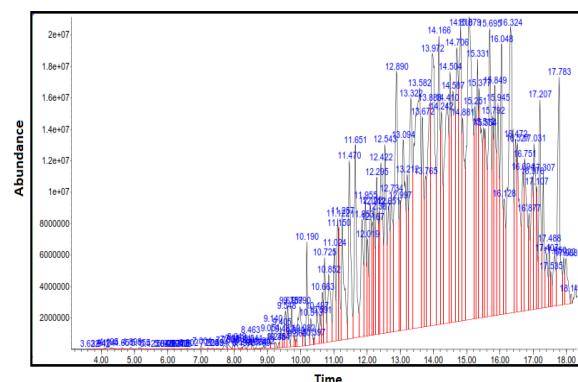


Figure 8. GC-MS analysis of washed containers in the presence of aqueous phase

The proton nuclear magnetic resonance spectra of the pure mercaptan sample and the extracted sample was studied which indicated the efficiency of the extraction-distillation method. According to Figure 9, pure mercaptan sample had protons at chemical shifts of 1.28, 1.45, 1.60, 1.84, 2.12 and 2.53 ppm. Figure 10 shows the NMR spectrum of extracted material. By comparing the NMR spectrum of the extracted samples and gas sample it was found that both of them had index peaks in the same areas. These results lead to claim that an efficient system was designed to recover all the utilized materials. Therefore, the extraction method will be efficient.

As was expected, a large extent of tret-butyl mercaptan is seen due to strong signal appeared at 1.45 ppm. Signal at 2.12 ppm is likely related to the dimethyl sulfide. The triplet depicted at 1.28 ppm and the quarter peaks at 2.53 represent the diethyl sulfide component in odorant sample.

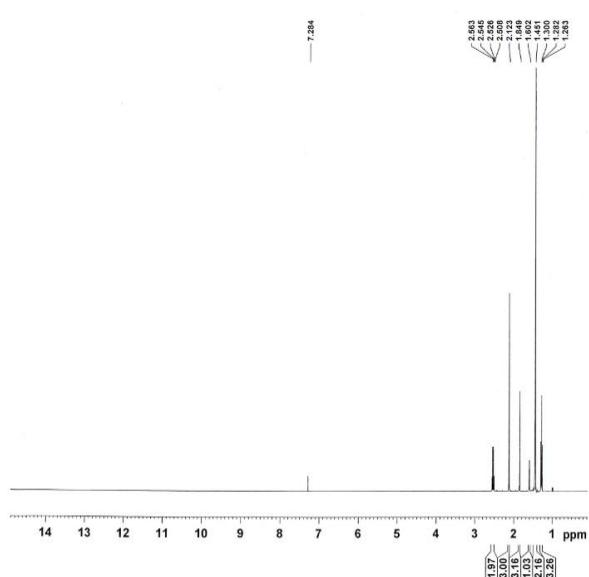


Figure 9. ^1H NMR spectrum of pure mercaptan sample

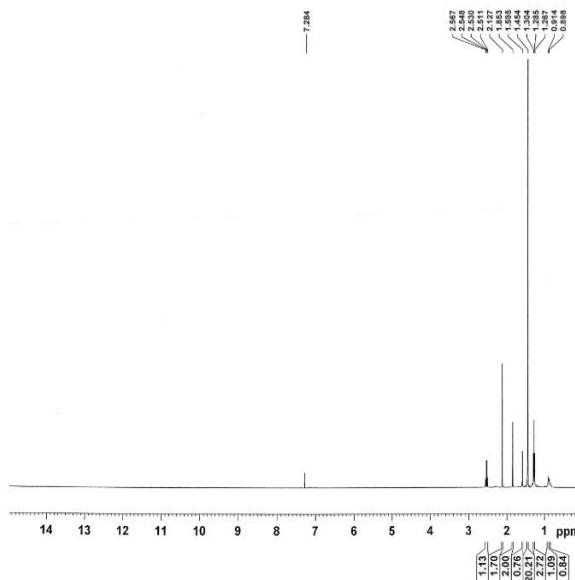


Figure 10. ^1H NMR spectrum of material after extraction

4. CONCLUSION

Natural gas is colorless and odorless which can be dangerous upon leakage. Therefore, by adding sulfur compounds, it is odorized to easily be detected in the event of leakage. To remove these sulfur odorants from containers which are contaminated with these compound, the extraction process was utilized which is fast and economically feasible. The best choice of solvents for extraction was kerosene and ethyl acetate. The organic solvents and extracted mercaptan can be easily recovered under vacuum distillation. According to the results, by using this convenient method the odorant container can be deodorized and the recycled mercaptan mixture could be reused in gas-odorizing injection step in local gas plant.

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Recycling and Reuse of Organo-sulfur Compounds from Barrels of Natural Gas Contaminated with Mercaptan Odorant

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گاز طبیعی با مقادیر جزئی مرکاپتان‌ها و ترکیبات سولفوری آلی بودار می‌شود تا در صورت نشتنی قابل تشخیص باشد. این ترکیبات می‌توانند موجب آلوگی محیط زیست به خصوص در جایگاه توزیق در نیروگاه گاز شوند. بنابراین، حذف بقاوی‌ای ترکیبات سولفوری از بشکوهای آلوده ضروری است. برای حذف بقاوی‌ای مرکاپتان‌ها و مخلوط آنکلی سولفید از روش‌های مختلفی استفاده شده است که از میان آن‌ها فرایند استخراج-تقطیر به دلیل سازگاری با محیط زیست و کم هزینه بودن در مطالعه حاضر مورد استفاده قرار گرفت. حلال‌های مختلفی از قبیل متیل اتیل کتون، اتیل استات، دی‌کلورومنان، تولوئن و کروسن برای استخراج مورد استفاده قرار گرفته‌اند که از بین آن‌ها کروسن مطلوب‌ترین حلال بود. نتایج نشان داد که روش به کار گرفته شده برای حذف ترکیبات سولفوری بسیار موثر است و مرکاپتان بازیافت شده قابلیت استفاده مجدد در مرحله توزیق را دارد. نتایج آنالیز GC و NMR تایید کرد که ترکیبات سولفوری آلی بازیابی شده عموماً حاوی ترت بوتیل مرکاپتان بوده که برای توزیق مجلد به جریان گاز مناسب است.

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