

A Comprehensive Review of Classic and Modern Natural Gas Odorants

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ABSTRACT

Flammable Modern Natural Gas besides being colorless, is also odorless. An activity like adding an odorant to gas means odorization. This operation is done to ensure that the gas can be distinguished. In other words, odorization is done to create an unpleasant smell in the air, so that the natural gas, even in small amounts, can be easily identified. Improving safety and increasing the efficiency of utilization of natural gas is a very important subject due to its wide use as one of the main energy sources in industry and home consumers all around the world. So far, various types of compounds identified as "odorant" are increasingly being produced and formulated to be injected into natural gas. This review article describes different aspects of classical and modern natural gas odorants and their odorization process to endorse the introduction of universal sulfur-free odorants for public gas systems. After studying basic chemistry and the history of these compounds, the most important properties of odorants are presented to help recognize the most proper odorant for a specific application and its synthesis methods.

KEYWORDS: *Odorant, Natural Gas, Sulfur, Safety, Odorization, leakage.*

INTRODUCTION

Natural gas is one of the most usable utilities nowadays. Due to Iran's positioning in the Middle East, there is sufficient access to it and this has caused the increasing development of technology and industry for the use of natural gas. The coal gas of yore, most importantly due to sulfur compounds, had a strong odor [1]; provided modern Natural Gas (NG) has approximately no odor or a small odor. Because it is almost quite composed of methane and ethane [2].

Probably the first time miners realized the dangers of odorless combustion gases. In 1880, Julius Quaglio came up with the idea of the odorization of combustible gases. Quaglio participated in different perspectives of water gas, built several gas plants in Austria, Hungary, and Sweden, and also produced coke in Austria, Belgium, and Germany mines [3].

Since the consuming NG is a flammable, colorless, and odorless substance, it is necessary to add a proper additive as an identifier to the main composition of the gas in the final stages of gas distribution, exactly before delivering it to the consumer. Originally safety was the primary purpose of gas odorization; before natural gas overtakes combustible levels in the air, the special odor operates as a warning in the finding of gas. Naturally, odorization is a vital section of the risk management plan for natural gas pipelines [4]. Certain federal pipeline safety regulations, inclusive of the National Fire Protection Association (USA), postulate that combustible gases in pipelines should be traceable by everyone with a normal smell, at one-fifth of the LEL (lower explosion limit). Employing both natural odor of the gas or artificial odorants is possible [5]. nowadays, odorizing as a safety factor of consuming natural gas is an important process requirement and must be done before the gas reaches the consumer. Therefore, identifying and producing new odorizing materials that have better physiological, physiochemical, chemical, and environmental properties is considered one of the novel and practical issues in the energy industry, especially gas. Therefore, appropriate odorants and odorization systems are entire fragments of gas supply system safety [6,7]. In addition to the safety factor, the smell of gas is considered a factor in finding the location of the gas leak and preventing more occurring risks, as well as preventing the wastage of gas due to leakage, and therefore it is very important in the gas industry. Since all aspects of classic and modern odorants are not included in one source, this review article has collected the most important information related to these widely used and essential odorants as a valuable resource for academic and industrial utilization.

ODORANTS & ODORIZATION

A primary interest of any gas transmission company is odorization [6,8]. Since methane which is the main component of natural gas, is colorless and odorless, it is necessary to odorize the gas. It is also true for hydrogen while artificial odorization using an odorant is required to comply with regulations [9]. Major elements in improving and reinforcing a successful odorization plan are adequate monitoring methods, precise injection of the odorant, and perfected record maintenance. For many years, sulfurous agents like THT (Tetrahydrothiophen) or the compound Tert- Butyl Mercaptan (TBM) were used for odorization – despite the negative impact on the environment and industry. The Federal Environment Agency certified “Sulfur dioxide causes damage to humans, animals, and plants in high concentrations. The oxidation products lead to acid rain which endangers sensitive ecosystems such as forests and lakes as well as corroding buildings and materials”. Therefore between 1990 and 2013, the sum of many initiatives led to a clear reduction of sulfur dioxide emissions; Given the growing environmental awareness of society and consumers, there were already requests for a sulfur-free natural gas

odorant in the 80s and 90s. This led scientists of the Engler-Bunte Institute, together with Symrise AG, to develop the sulfur-free natural gas odorant Gasodor® S-free. It was launched on the market in 2001 and is the only DVGW-tested sulfur-free odorant available to date [10].

Over time, this non-sulfur odorant did not completely replace the old odorants and only led to the division of odors into two basic groups: classic and modern. The “Classic” sulfur-containing odorants are subdivided into alkyl sulfides, alkyl mercaptans, and cyclic sulfides. “Modern” odorants, that are based on acrylates, are called sulfur-free odorants [11]. All classic odorants such as Tetrahydrothiophene¹ (C₄H₈S), Dimethyl sulfide² (C₂H₆S), Diethyl sulfide³ (C₄H₁₀S), Methyl ethyl sulfide⁴ (C₃H₈S), Ethyl mercaptan⁵ (C₂H₆S), Sec-butyl mercaptan⁶ (C₃H₈S) and Tert-butyl mercaptan⁷ (C₄H₁₀S) contain sulfur in their chemical composition. As a result of combustion, sulfur becomes sulfur dioxide (SO₂). This pollutant gas showed negative effects directly and indirectly on the environment and human health. The Threshold Limit Value⁸ of SO₂ expressed as a Time-Weighted Average⁹ is 2 ppm; provided, the quantity of odorants added to natural gas, despite being in the order of magnitude of some mg/m³, is not negligible if compared to the TLV of SO₂.

With more details, the minimum concentrations of TBM/IPM/NPM and THT in the distributed Italian gas are respectively equal to 8mg/m³ (TBM/IPM/NPM) and 32mg/m³ (THT), corresponding to 2.3ppm and 8.9ppm. These data show the reasons why, in recent years, the possibility of introducing alternative, sulfur-free odorants, and desulfurization [12,13,14] and, in other words, lightening of fossil fuels is being studied. Since this amount of sulfur is added to natural gas by the odorization process, there is a high demand to identify, synthesize, and introduce sulfur-free odorants that reduce or eliminate pollution from the combustion process of natural gas in urban uses [15].

In addition, these sulfur-free additives are widely used in PEM fuel cells, which are sensitive to small amounts of sulfur, and their catalytic performance is impaired when exposed to sulfur [16]. Figure 1 shows a graph of SO₂ emissions resulting from the combustion of a gas odored by various odorants with different dosages [17].

¹ THT

² DMS

³ DES

⁴ MES

⁵ EM

⁶ SBM

⁷ TBM

⁸ TLV

⁹ TWA

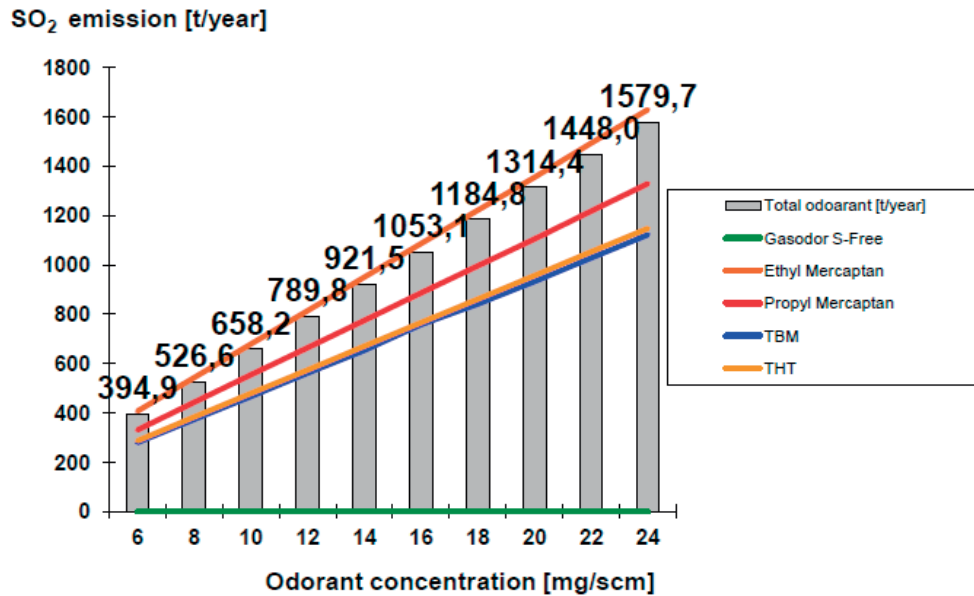


Fig 1. Simulation of SO₂ emission of an odored gas with several odorants, Considering their concentration (Published with permission)

This graph shows that in different concentrations, the highest pollution contribution is related to ethyl mercaptan, and the lowest pollution is related to the sulfur-free odorant that was first produced by German scientists. We have observed in various studies that as a result of the combustion of ethyl mercaptan as a sulfur-based odorant, SO₂ is emitted. Therefore, there was a need for an alternative odorant that does not lead to the production of sulfur dioxide in the facility where the study is carried out [18].

In addition to choosing the proper odorant, the odorization system is of special importance. Choosing a suitable odorizing system is the essential step in the odorization process. Technically, based on the system in which odorants are entered into the gas stream, odorizers are classified into two basic groups as below [2]:

- Chemical vaporization
- Chemical injection

The basis of Vaporization-based systems is the diffusion of odorant into a flowing natural gas stream. Examples of vaporization systems are bypass-type systems and wick odorizers. The significant privilege of these odorizers is their ease of use however they are suitable for stable and low gas flows in general. The injection-type systems work based on direct injection of an odorant into the flowing stream which is stored away from the pipeline. These systems generally cover a wide range of gas flow rates [2].

In the injection method, natural gas odorization is usually done by electronic or pneumatic systems, the difference between which is the way the odorant is injected. In an electrically driven pump, injection is controlled by a mechanical system; while the injection in the pneumatically driven pump system is adjusted by the pressure difference.

Considering the pipelines require odorization, the detectable limits of gas odor, odorants, and odorizing considerations, and monitoring a pipeline system to ensure that the odorization program is meeting the regulatory requirements are the most important aspects of odorization [5]. A desirable odorant should have ideal functional and physical features. These features include preferably being recognizable from odors in daily life and functional

as a warning smell, a low perceptual threshold, slight or no olfactory fatigue, low boiling point, low corrosiveness, and little toxicity. The general properties of an appropriate odorant are listed below in Table 1 [19].

Table 1: General attributes of an appropriate odorant

<i>Item</i>	<i>Properties</i>
1	<i>Low perceptual threshold (<1ppb) (Vol/Vol)</i>
	<i>The odorant perceptual threshold is the least concentration of an odorant in the air that a normal person can easily smell at a location. This amount is different for various levels, but in any case, natural gas should be odorized enough that everyone with an ordinary sense of smelling can easily recognize it when the amount of gas released in the air reaches the lowest point of the ignition limit.</i>
2	<i>Corrosivity and toxicity of combustion products</i>
	<i>Combustion products of odorants must not be toxic, corrosive, or harmful to those materials exposed to them.</i>
3	<i>Proper freezing point</i>
	<i>The odorant should not be frozen at the temperature and pressure of the pipeline.</i>
4	<i>Proper boiling point</i>
	<i>The boiling point should be such that the odorant evaporates easily inside the pipeline without condensation.</i>
5	<i>Specific and recognizable smell</i>
	<i>Odorants should have a specific and recognizable smell that does not mix easily with other smells in the environment and any person with an average sense of smell and normal physiological conditions should be able to recognize the smell. This smell should play a role as a warning.</i>
6	<i>Non-toxicity</i>
	<i>The odorant should not have any side effects when injected into the gas network. Also, contact with this substance in liquid form should not cause poisoning.</i>
7	<i>Adequate permeability and absorption resistance in the soil</i>
	<i>The absorption of these materials in the soil should be so low that in case of gas leakage from the underground pipeline, the gas released will be odorized enough. In other words, odorants should not enter into a chemical reaction with gas or materials used in gas supply systems or soil.</i>
8	<i>Insolubility in water</i>
	<i>The maximum dissolving rate of odorant in water is equal to 2.5 parts per 100 parts by weight. In general, all odorants have very low solubility in water.</i>
9	<i>Proper vapor pressure</i>
	<i>In gas distribution systems where chemical vaporization devices are used, the vapor pressure parameter of the odorant composition is one of the most important features. To minimize the temperature changes that lead to the change in the vapor pressure of the odorant in this type of device, the storage tank of the odor is often placed underground. Odorants with the highest vapor pressure and the lowest threshold are good odorizers.</i>
10	<i>Cloud point</i>
	<i>Odorants should be completely dry to have a low cloud point.</i>
11	<i>Low flash point</i>
	<i>The flash point is a characteristic of the flammability of the odorant, which is important in the transportation and storage of the odor. Most odorants have a higher ignition point than Gasoline and lower than Kerosene; Therefore, for caution in transporting and moving them, it can be done in the same way as Gasoline. Determining the flash point of odorants is done by the TCC method [20].</i>
12	<i>Cost and ease of preparation</i>

	<i>The odorant should be cheap and available, and adding it to the gas should be economical.</i>
13	<i>No effect on the structure of natural gas</i>
	<i>Adding the odorant to the gas should not change the structure and it should not lead to any physical and chemical changes in the fuel [17].</i>
14	<i>Low polymerization rate</i>
15	<i>Low corrosion rate</i>
16	<i>Good solubility in natural gas</i>

As a result, precise injection of odorant, appropriate control methods, and entire record keeping are very serious criteria in the development and sustainability of an efficient odorization process.

CLASSIC ODORANTS

Sulfur odorants known as classic odorants have been used universally since the 1960s. Certain organic sulfur compounds are used for odorization because of their inherent penetrating smell; But during the combustion of fuel, they produce sulfur dioxide causing environmental pollution and many problems that require the use of these compounds to be limited. In addition, a desulfurization system needs to be installed to prevent poisoning of the catalyst by sulfur while using fuel gases in fuel cells due to the presence of sulfur odorants [21]. Among the most popular ones THT, EM, and TMB are listed in Table 2 and their high sulfur content is evident [17].

Table 2: Sulfur content in three of the most widely used classic odorants

<i>Component</i>	<i>Structural formula</i>	<i>Sulfur content in %</i>
<i>Tetrahydrothiophen (THT)</i>	$ \begin{array}{c} \text{H}_2\text{C} - \text{CH}_2 \\ \quad \quad \\ \text{H}_2\text{C} - \text{S} - \text{CH}_2 \end{array} $	36.37
<i>Ethyl mercaptan (EM)</i>	$ \begin{array}{c} \text{H}_2 \\ \\ \text{H}_3\text{C} - \text{C} - \text{SH} \end{array} $	51.61
<i>Tert-butyl mercaptan (TBM)</i>	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C} - \text{C} - \text{CH}_3 \\ \\ \text{SH} \end{array} $	35.55

The above-mentioned compounds are the most widely used sulfur-based odorants, But these compounds include a wider range. A more complete list of common odorization reagents that are often used in combination is summarized in Table 3 [5].

Table 3: Sulfur-containing substances for odorization

<i>Material</i>	<i>Details</i>
<i>Ethyl mercaptan – A mixture of ethyl-, propyl-, and butyl-mercaptans- Methyl ethyl disulfide - Dimethyl disulfide- Diethyl disulfide</i>	<i>Synthesis through the Ziegler-Natta process</i>
<i>Ethyl propyl sulfide - Diethyl sulfide</i>	<i>Up to C30 are synthesized by Ziegler-Natta catalyst</i>
<i>Cyclohexylmercaptan</i>	<i>molecular weight < 15,000 isotacticity ≤ 75%</i>
<i>Dimethyl sulfide</i>	<i>polymer soluble in oil</i>
<i>Tetrahydrothiophene – Thiophenemercaptans with extra pyridine and picoline</i>	<i>Decrease friction in the flow of a hydrocarbon fluid by a factor of 5 at concentrations as low as 1-25 ppm</i>
<i>A combination of ethyl-, propyl-, butyl-, and amyl-mercaptan</i>	<i>---</i>
<i>4-methyl-4-mercapto-2- pentanone and 2-Methoxy-3-isobutyl pyrazine</i>	<i>Polyampholytes</i>

Some repulsive blends consist of compounds like 3-methyl-1-butanethiol, trans-2-butene-1-thiol, and ethyl mercaptan are the desirable compounds used as an odorant in natural gas for leak detection. The popularity of these compounds is because of their exceptionally low odor threshold. In addition, tert-butylmercaptan is prevalent as a single-component odorant. tert-butyl mercaptan is famous for its great oxidation resistance and fine soil penetration. The high freezing point of tert-butylmercaptan is its disadvantage which offers to use it as a part of an odorizing mixture. On the other hand, isopropylmercaptan has proper oxidation resistance and a strong odor. To lower the freezing point of the mentioned compound, isopropyl mercaptan is usually mixed with tert-butyl mercaptan to form a desirable blend [22].

Alkyl sulfides do not have as strong odor as the mercaptans but are resistant to oxidation. So, they are called stand-alone odorants which are added predominantly to degrade the mercaptans' freezing point. The following three categories are the most common classes of blended odorants [22]:

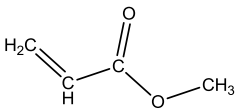
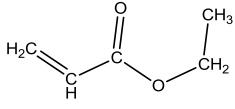
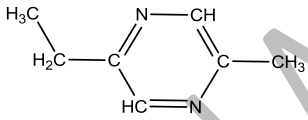
- Mixtures of Mercaptans
- Mixtures containing mercaptan and alkyl sulfide
- Mixtures containing Tetrahydrothiophene and mercaptans

MODERN ODORANTS

Ruhrgas AG developed the idea of a sulfur-free odorant utilization for public gas distribution in early 1995. Haarmann & Reimer, which is currently called Symrise AG, was a manufacturer of fragrances in Holzminden, Germany. The recipe for the sulfur-free odorant called Gasodor S-Free, was developed first with the efforts of the manufacturer. The DVGW Research Center at Engler-Bunte-Institut of Universität Karlsruhe (TH), Gas Technology Consulting Section (DVGW/TBG), performed all the essential steps to enter the first commercial sulfur-free natural gas odorant in the market, in both coordinating and executing aspects [23]. Finally, these efforts led to more than 40 gas distributors in Austria, Germany, and Switzerland having modified their odorization system from mercaptans to a novel sulfur-free odorant, since 2001. The major motivations for introducing sulfur-free odorization are innovating environmentally friendly natural gas besides the probability of using the gas directly without or with less extensive pretreatment in sulfur-sensitive applications [24]. Eventually, this research

led to the production of a sulfur-free odorant whose chemical composition included methyl acrylate, ethyl acrylate, and a stabilizer called methyl ethyl pyrazine with a percentage composition according to Table 4. This odorant was registered under the trade name Gasodor S-free. It was submitted to testing according to DIN EN ISO 13734 [19].

Table 4: Gasodor S-Free Chemical Composition

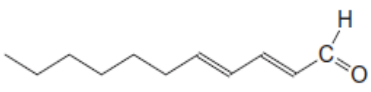
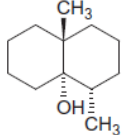
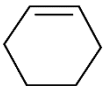
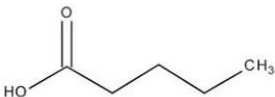
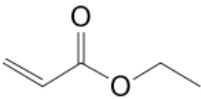
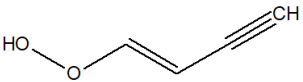
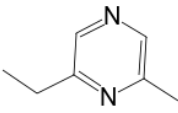
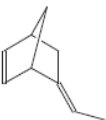


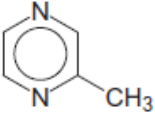
<i>Item</i>	<i>Component</i>	<i>Structural formula</i>	<i>Mass participation %</i>
1	<i>Methyl acrylate</i>		37.4
2	<i>Ethyl acrylate</i>		60
3	<i>Methyl-ethyl-pyrazines</i>		2.5

As mentioned before, these modern odorants are generally from the family of acrylates. In 2014, the first reference gas mixtures of sulfur-free natural gas odorants that are traceable to the International System of Units (SI) were produced and their compositions were validated. These mixtures, which consist of ethyl acrylate and methyl acrylate at amount fractions between 1.1 and 2.1 $\mu\text{mol/mol}$, can be employed to underpin measurements of non-sulfur odorants, which are increasingly being used for odorizing natural gas in gas networks; because they have less harmful properties than traditional sulfur-based odorants. The component 2-ethyl-3-methylpyrazine is used as a stabilizer in non-sulfur odorants [25].

Some research has been done on preparing sulfur-free gas odorants with different compositions. These compounds include such substances: as vinyl or alkyl ethers, alkyl acrylates, cyclohexene, n-valeric acid, ethyl acrylate as well as norbornene derivatives [26]. Although each of these odorants has certain drawbacks. For instance, odorants based on acrylic ester have shown instability from a chemical standpoint. The content of ethylidene norbornene or cyclohexene must be greater than that of mercaptans [21]. Besides, odorants containing nitrogen may motivate the Reinforced formation of nitrogen oxide compounds. These oxides react with sunlight to form ozone. NO_x are known as a toxic compounds.

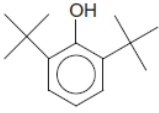
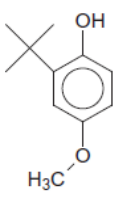
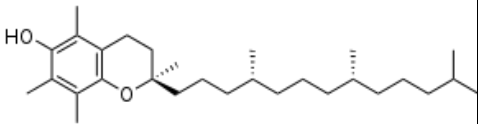
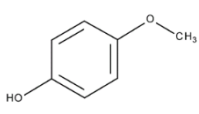
Geosmin which means earth smell, is a preferable compound among the alcohol proper to form an odorant. The human nose is fully sensitive to geosmin odor. It is a natural organic compound generated by microorganisms. Geosmin's scientific name is 2,6-dimethylbicyclo[4.4.0]decan-1-ol. Moreover, trans-2-trans-4-decadienal has a small perceptual threshold then it is not easily identifiable [21]. Some Sulfur-free odorants are listed below in Table 5.

Table 5: Sulfur-Free odorants

<i>Structural formula</i>	<i>Component</i>
	<i>Trans-2-trans-Decadienal</i>
	<i>Geosmin</i>
	<i>Cyclohexene</i>
	<i>n-Valeric acid</i>
	<i>Ethyl acrylate</i>
	<i>1-Methoxy-buten-3-yne</i>
	<i>Methyl ethyl pyrazine</i>
	<i>5-Ethylidene-2-norbornene</i>
	<i>Pyridine</i>
	<i>2-Nonenenitrile</i>
	<i>2-Methylpyrazine</i>

An example of proper sulfur-free odorants is pyrazines and acrylates blends. Some antioxidants like Ionol and butyl hydroxy anisole that are based on hydroquinone monomethyl ether, tert-butyl hydroxytoluene, and α -tocopherol usually added to the odorizing compositions to prevent undesired oxidation. The list of natural gas antioxidants is shown in Table 6.

Table 6: Antioxidants

<i>Structural formula</i>	<i>Component</i>
	<i>Tert-Butylhydroxytoluene</i>
	<i>Butylhydroxyanisole</i>
	<i>α-Tocopherol</i>
	<i>hydroquinone monomethyl ether</i>

sulfur-free odorants or reduced sulfur-content odorants that are available in global markets are commercially called Gasodor S-Free and Spotleak Z. They are generally ethyl acrylate and methyl acrylate blend or a mixture of ethyl acrylate and tetrahydrothiophene, respectively. Sulfur-free odorants which smell more like garlic, could be smelled easily by the normal sense of smell. Hence, the normal sense of smell can not correlate this type of odor with the typical smell of combustible natural gas. This is because consumers are used to the smell of mercaptan as the smell of gas. For this reason, some countries have changed their main odorant of the gas industry to sulfur-free odorants. Of course, successful results have also been reported, but some others returned to the traditional sulfurous odorants [27].

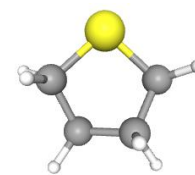
EMPIRICAL & THEORETICAL MODELING

In general, there is no preference between using sulfurous and non-sulfur-free odorants. Each of these odorants has its characteristics that justify its use in certain situations. In the following, while reviewing the types of odor compounds, we will examine the most important properties of odorants in detail. In each section, the three-dimensional structure of the substance and the table of its physical and chemical properties are displayed.

TYPES OF ODORANTS AND THEIR MAIN FEATURES

Tetrahydrothiophene (THT)

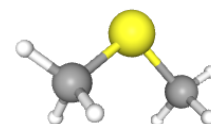
THT is the only member of the cyclic sulfides family used in the odorization of gas. This is the prototype of “stand-alone” odorants. THT is yet used in mixtures along with e.g. TBM due to low permeability in soil. THT is the most resistant to pipeline oxidation. Because of its small odor impact, it is hard to over-odorize with this substance. THT causes a slight skin irritation and has a mild narcotic efficacy.



Odorant	odor	Solubility in water	NEPA Ratings	Structural form	Sulfur content	Flash point	Freezing point	Boiling point	Specific gravity	CAS reg. number	Molecular weight
Tetrahydrothiophene (THT) C_4H_8S	Stench	insoluble			36.37 Wt. %	-7°C	-96°C	115-124°C	1.000	110-01-1	88.172

Dimethyl sulfide (DMS)


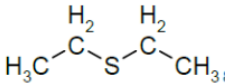
Good oxidation stability and soil permeability are the main features of DMS. Dimethyl sulfide and TBM are mostly used in mixtures together, but due to the relatively high vapor pressure of blends containing DMS, it is not fully suited to vaporization-type odorizers. Higher concentrations of DMS cause nausea. It is a “garlic-stinking” composite that first stimulates and then frustrates the nervous system.



Odorant	odor	Solubility in water	NEPA Ratings	Structural form	Sulfur content	Flash point	Freezing point	g point	gravity	number	w weight
Dimethyl sulfide (DMS) C_2H_6S	Unpleasant Cabbage-like	22 mg/ml			51.61 Wt. %	-38°C	-98°C	37°C	0.800	75-18-3	62.135

Diethyl sulfide (DES)

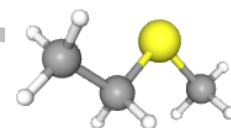
A small odor threshold and good oxidation stability are the main features of DES. The limiting factor for using DES in odorant blends is its high boiling point.


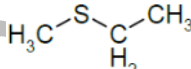
Odorant	odor	Solubility in	NEPA Ratings	Structural form	Sulfur content	Flash point	Freezing point	Boiling point	Specific gravity	CAS reg. number	Molecular
<i>Diethyl sulfide (DES)</i> $C_4H_{10}S$	Garlic-like	3.13 mg/ml			35.55 Wt.%	-9°C	-100°C	90°C	0.837	352-93-2	90.188

Methyl ethyl sulfide (MES)

MES is famous for its great oxidation stability in pipelines and an equal vapor pressure to TBM.

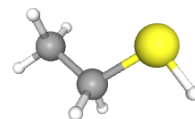
That's why mixtures of TBM/MES are adequate for both odorizers including vaporization and injection type. Methyl ethyl sulfide has similar features to NPM from a toxicological standpoint.


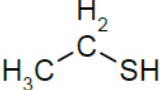


Odorant	odor	Solubility in	NEPA Ratings	Structural form	Sulfur content	Flash point	Freezing point	Boiling point	Specific gravity	CAS reg. number	Molecular
<i>Methyl ethyl sulfide (MES)</i> C_3H_8S	Cabbage-like	insoluble			42.10 Wt.%	-15°C	-106°C	65-67°C	0.842	624-89-5	76.162

Ethyl mercaptan (EM)

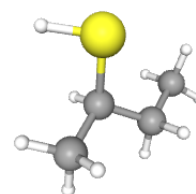
This colorless liquid with a distinct odor is an alkane-thiol in which an ethane molecule has been replaced by its thiol group. This compound is added to the gas to create a smell similar to rotten spicy vegetables.


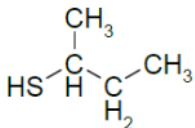


Odorant	odor	Solubility in	NEPA Ratings	Structural form	Sulfur content	Flash point	Freezing point	Boiling point	Specific gravity	CAS reg. number	Molecular
<i>Ethyl mercaptan (EM)</i> C_2H_6S	Leek-like	15.60 mg/ml			51.61 Wt.%	-48°C	-148 - 121°C	34-37°C	0.839	75-08-1	62.135

Sec-butyl mercaptan (SBM)

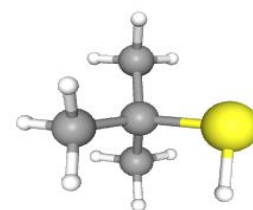
SBM is rarely used in odorant blends. It emanates as an impurity in Tert-butyl mercaptan production or as a by-product. pleasant oxidation stability is one of the characteristics of this branched chain mercaptan. SBM has an almost high boiling point.


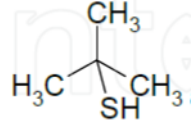


Odorant	odor	Solubility in water	NFPA Ratings	Structural form	Sulfur content	Flash point	Freezing point	Boiling point	Specific gravity	CAS reg. number	Molecular weight
<i>Sec-butyl mercaptan (SBM)</i> $C_4H_{10}S$	Obnoxious	1.32×10^{-3} mg/L			35.55Wt %.	-23°C	-165°C	84-85°C	0.829	513-53-1	90.188

Tert-butyl mercaptan (TBM)

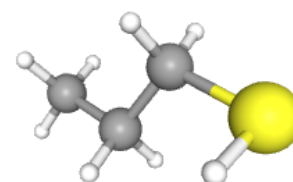
The reasons that make TBM the most used ingredient of gas odorants are normal “gassy odor”, low odor threshold, high oxidation resistance (highest among mercaptans), and good soil penetration. On the other hand, TBM has an important weakness, which is its high freezing point. This feature prevents TBM from being used as an independent odorant. Therefore, TBM should be used in combination with other odorants.


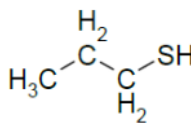


Odorant	odor	Solubility in water	NFPA Ratings	Structural form	Sulfur content	Flash point	Freezing point	Boiling point	Specific gravity	CAS reg. number	Molecular weight
<i>Tert-butyl mercaptan (TBM)</i> $C_4H_{10}S$	Strong offensive	2.0×10^{-3} mg/L			35.55Wt %.	-29°C >	1°C	64°C	0.800	75-66-1	90.188

N-Propyl mercaptan (NPM)

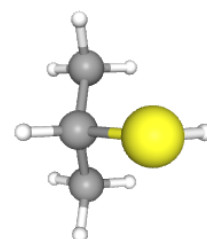
A strong odor besides a low freezing point are the main features of N-Propyl mercaptan. Because of its small oxidation stability, NPM is not used in high concentrations (typically 3-6%). NPM shows a depressive effect on the central nervous system from a toxicological standpoint.


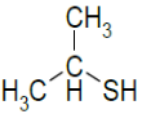


Odorant	odor	Solubility in water	NFPA Ratings	Structural form	Sulfur content	Flash point	Freezing point	Boiling point	Specific gravity	CAS reg. number	Molecular weight
<i>N</i> -Propyl mercaptan (NPM) C_3H_8S	Cabbage-like	1.90X10 ⁺³ mg/L			42.10Wt %	-21 °C	-113 °C	67-68 °C	0.841	107-03-9	76.162

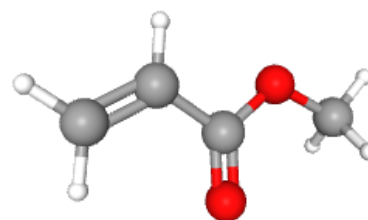
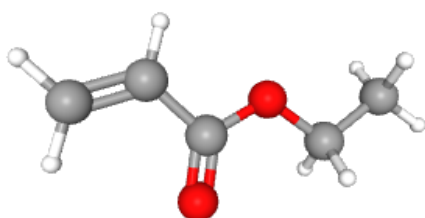
Isopropyl mercaptan (IPM)

IPM, which is known for its strong “gassy odor” and low freezing point, has second place in oxidation resistance among the mercaptans family. To decrease the freezing point, IPM is customarily used in blends along with TBM. Isopropyl mercaptan can be used as a stand-alone odorant in some cases. IPM and NPM have analogous toxicological effects.


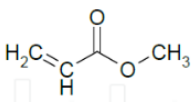



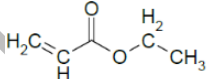
Odorant	odor	Solubility in water	NFPA Ratings	Structural form	Sulfur content	Flash point	Freezing point	Boiling point	Specific gravity	CAS reg. number	Molecular weight
Isopropyl mercaptan (IPM) C_3H_8S	Strong skunk	4.84X10 ⁺³ mg/L			42.10Wt %	-34 °C	-113 °C	53 °C	0.814	75-33-2	76.162

Ethyl acrylate (EA) & Methyl acrylate (MA)



The main components of the sulfur-free odorant are MA and EA (together with Methylethyl Pyrazine). They have small odor thresholds and proper soil permeability (which is somewhat less in dry soil). In special circumstances, if hydrocarbon condensate happens in the pipeline, it can particularly be “washed out” from the gas flow.

Odorant	odor	Solubility in water	NFPA Ratings	Structural form	Sulfur content	Flash point	Freezing point	Boiling point	Specific gravity	CAS reg. number	Molecular weight
Methyl acrylate (MA) $C_4H_6O_2$	Acrid	4.94X10 ⁻⁴ mg/L			0 Wt. %	-3 °C	-75 °C	78-81 °C	0.953-0.957	96-33-3	86.089

Odorant	odor	Solubility in water	NFPA Ratings	Structural form	Sulfur content	Flash point	Freezing point	Boiling point	Specific gravity	CAS reg. number	Molecular weight
Ethyl acrylate (EA) $C_5H_8O_2$	Acrid penetrating odor	15 mg/ml			0 Wt. %	8.3 °C	-72 °C	99-100 °C	0.900	140-88-5	100.115

PROS & CONS OF USING ODORANTS

Odorized gas has significant capabilities compared to odorless natural gas, the most important of which are safety, the possibility of gas leakage detection, and economic efficiency. In other words, adding odorants to gas should provide a suitable level of safety for the consumer and make it possible to achieve these three goals. Of course, it should be considered that consumer safety is the most important factor. Since natural gas does not have a specific smell, it cannot be detected by people. Therefore, if there is a gas leak in the surroundings, no one will notice the presence of the gas and its consequences. So, the presence of an odorant in the gas makes the gas identifiable to the consumers, and if a gas leak occurs, people move away from the area.

Ensuring the safety of gas consumers

The most important feature of odorized gas is that any normal person who is in the vicinity of this fuel can be aware of its presence in the surroundings. In other words, providing warning levels before gas leaks reach explosive levels is one of the main goals [28]. If an odor leak occurs at the injection site, the surrounding people will assume that a gas leak has occurred, and the areas will be evacuated and business will be cut off. If such events are repeated over time, people living in that area will lose their olfactory sensitivity to the smell of natural gas and will not be able to detect gas leaks. If such problems become common, people in the surrounding area

will become desensitized to the odor of a potential gas leak. It means that the goal of using odorants has been questioned.

Leak detection

If the odorless gas is flowing in the pipeline, it is not possible to detect its leakage by unequipped people, and if the amount of gas is wasted, there will be significant risks. Leaks in pipelines can be detected using a test fluid. The test fluid, a mixture of dimethyl sulfide in a solvent, is injected into a pipeline. The test fluid escapes through the leak, and the odorant is released from the closed segment.

Energy saving

Natural gas is one of the most consumed daily energies of today's human beings, and its supply and delivery to the consumer imposes exorbitant costs on governments. Therefore, it is necessary to prevent the wastage of this laborious and expensive energy source as much as possible. If odorless natural gas leaks, it is difficult to know about the leakage, and a significant amount of gas is released, which in addition to its dangerous consequences, leads to gas wastage; But adding an odorizing agent to the gas makes the location of the gas leak quickly detectable and corrected. As a result, there is an odorizing agent that prevents more wastage of gas and its economic losses.

Influence on fuel cells

Hydrogen odorization, from different aspects, has become a challenging issue with the advent of hydrogen fuel cells [29]. Conventional odorants might have had adverse effects on the performance of fuel cells. Commercial odorants used to detect gas leaks poison the catalysts used in hydrogen fuel cells, particularly for proton exchange membrane fuel cells. A mixture of nitrogen compounds with acrylic acid was chosen as a sulfur-free odorizer for this odorization [30]. Hence, for hydrogen generation in fuel cells, the natural gas or other petroleum gases used to produce hydrogen must be sulfur-free. Otherwise, a desulfurization step should be performed, which adds additional costs to the hydrogen production in the reforming process. Sulfur-containing compounds cause the toxicity of the catalysts based on noble metals exerted in fuel cells. This is why fuel cells are not sulfur-resistant. Therefore, it is necessary to use materials such as zinc oxide to remove sulfur compounds like mercaptans from gas flow. However, sulfur elimination from some specific materials such as thiophene is not as easy as other compounds by zinc oxide. Then, a specific hydrodesulfurization process, using hydrogen gas, may be required to remove sulfur.

Further complexity of hydrogen fuel comes from the nature of hydrogen flame propagation. The flames spread more easily upwards than downwards when gases burn in the air. It occurs due to the natural upward convection of hot burnt gases. The upward and downward propagating combustion limits for methane, propane, and petroleum gases, are approximately the same. Nevertheless, the amount of odorant needed for leak detection in hydrogen could be greater than 2.5 times that needed for methane or propane; because they vary by a factor of 2.5. The greater amount of odorant needed to detect the smell of hydrogen complicates the sulfur poisoning obstacles for hydrogen gas used in fuel cells [30].

Odor-fading

One of the most specific obstacles to odorization is Odor Fading. The gas may be sufficiently odorized at the source, but if it no longer has the desired impact and odor intensity by the time it reaches the customer, the fugitive gas may go undetected and lead to a serious fire or explosion hazard [22]. For instance, the presence of rust and air in a pipeline may be a catalyst for the oxidation of mercaptans. This results in products that do not smell at all.

There may be three reasons for fading:

1. Oxidation that causes the formation of disulfides due to the interaction of oxygen and iron oxide.
2. Absorption or adsorption of the odorant on the surface of a plastic pipe Due to the presence of new pipe materials.
3. Low-quality gas may cause odor covering or reaction of odorant elements with contaminations in the gas stream. Odorizing dry gas is easier and does not cause the odor to fade. The presence of condensed liquids in the pipeline can cause the absorption of odor constituents. Odor masking may also occur for odors caused by any contaminants in the gas.

Odor-fading of LPG stored in carbon steel containers can occur due to the catalytic effects of the containers. Deactivation of the corresponding steel surfaces can be done through treating the surface with a deactivating agent before exposing the walls to the odorized LPG to delay odor-fading [31]. Mercaptobenzothiazole, benzotriazole, benzothiazyl disulfide, tolyl triazole, or a combination of these compounds are examples of these agents [32]. It is also suggested to develop a mathematical model and the right software to predict the fading of odors [33]. For example, recently, in 2021, research was conducted on the causes of odor-fading in the natural gas distribution network in Iran [34]. In this research, different affecting parameters on odor fading of natural gas were investigated by an experimental apparatus comprised of a new 10-inch steel pipe which is generally used in gas distribution networks. The chemical reaction of odorant with available iron oxide on the surface, physical adsorption of odorant in the porous surface of the iron oxide, odorant settling down, and presence of rust in the pipeline were tracked at high-pressure experiments. According to the obtained results, it was shown that, while the effect of mercaptan settling down is negligible, the chemical reaction of the mercaptan with iron oxide (or rust) available on the inner surface of the pipe and/or with the solid particles within the gas stream mainly contain iron oxides, plays the most important role on the odor fading of natural gas. Moreover, although the porous inner surface of new pipes would result in the adsorption of some mercaptan molecules on the surface of the pipe, the share of physical adsorption against chemical adsorption (i.e. chemical reaction) is small.

Environmental problems & and the solutions

The most obvious environmental consequence of using sulfur-base odorants for natural gas odorization is the production of sulfur dioxide gas, which became the origin of the formation of non-sulfur odorants to reduce or eliminate the detrimental effects of natural gas combustion.

Another bad effect of sulfur odorizers is related to injected gas in tanks. If natural gas for storage in natural reservoirs is odorized with sulfur compounds, a possible environmental impact can result. The most amount of the odorant is lost in the formation. If the loss happens in a reservoir adjacent to an aquifer, it could contaminate the water and lead to environmental problems. Water is also often injected into the reservoir when gas is drawn off. In some cases, water with a heavy characteristic odor has been reported. To control this issue a stripping column has been introduced [35].

Decontamination of contaminated groundwater can also be done using iron [36]. This technique was suggested for the in situ remediation of ethyl mercaptan-contaminated groundwater. Instead of irreversible surface adsorption, researchers suggest chemical reactions with iron. Extraction is also a practical method for removing gas odorants. This process is similar to what happens in the usual glycol dehydration and desulfurization process [37,38]. The recommended cleaning process removes tetrahydrothiophene, which is a progressive technique of oxidation based on water treatment using UV radiation in the presence of hydrogen peroxide [39].

Since odorant leakage occurs abundantly in different concentrations, many oxidation reactions occur for the oxidation of mercaptans to remove the smell. The most common method is the Merorx process. In this process, through a catalytic reaction, mercaptans in the presence of iron oxide and a trivial amount of oxygen, are converted into disulfides. In other words, the Merox process proceeds based on the performance of an iron-based catalyst [40] in an alkaline media to increase the oxidation of mercaptans to disulfides. Merox process units are based on catalytic oxidation of the mercaptans and contain two steps of caustic soda redox and extraction as follows [41]:

Extraction step:



Redox step:



The general reaction in the presence of a catalyst:



Corrosion and the Solutions

Sulfur-containing compounds (SCCs) are commonly the most abundant heteroatom-containing components in petroleum. SCCs can be classified into six basic classes according to their functional groups:

- Hydrogen sulfide
- Elemental sulfur
- Mercaptans (thiols)
- Sulfides (acyclic and cyclic)
- Polysulfides (disulfides, trisulfides, etc.)
- Thiophenes

The first four types are reactive and corrosive. The volatile SCCs are easily recognized by their smell of pungent rotten-egg odor. They can be converted into toxic H₂S upon burial (thermal stress) or heat. The pungent mercaptans are usually oxidized into disulfides through the Merox process before transportation to meet specifications because they are also highly corrosive to pipelines, tankers, and storage tanks [42]. tert-butylmercaptan and its blends are very harmful but they are among the low-corrosive odorants [5]. One of the possible sinks for odorants is the adsorption of pipeline dust and incrustations, besides the absorption in natural gas condensate. Pipeline dust which is largely composed of metal oxides, is a heterogeneous corrosion yield of the gas pipelines [24]. The sulfur content in gas increases the corrosiveness potential of the sent medium [5]. Because water can cause possible subsequent equipment corrosion, there should be no water in the composition of odorants [24].

Therefore, using nanocatalysts from the family of mesoporous carbon-based catalysts [2,17,43] is recommended to reduce the amount of interaction between substance and gas transfer bed which results in reducing the amount of corrosion, as well as reducing the environmental effects of natural gas consumption and removing sulfur from the composition of this flammable gas, which leads to the release of a significant amount of sulfur dioxide in the environment. These mesoporous carbon-based catalysts such as MCM [44-46], CMK [47], and SBA [48] are ideal for the production of modern odorants by green synthesis methods [49].

The main application of these mesoporous materials, which are divided into silicate and non-silicate [50-55], is in separation and catalytic operations. This classification is based on the type of ingredient of the cavities walls, which are divided into two classes of non-silicate and silicate mesoporous materials that have a carbon skeleton [56]. They are also an appropriate base for metals substitution such as Iron, Cobalt, Nickel, and Copper. Among all, nickel and zinc have shown good reactivity.

In the present work, mesoporous silica nanoparticles (MSNs) with well-ordered hexagonal structures can be synthesized using Sodium Carboxy Methyl Cellulose [57].

MCMs are a group of mesoporous silicate compounds that are generally used as surface adsorbents, ion exchangers, and various catalyst supports [58,59]. For example, (2-Hydroxyethyl)-trimethylammonium hydroxide is used as an organic base for the synthesis of highly ordered MCM. In an easier and more rapid method for the synthesis of highly ordered MCM, the surfactant is dissolved in a mixture of water/ethanol and then the ammonia solution and sodium acetate are added to this solution [45,46].

The CMK-type materials such as CMK-1, CMK-3, and CMK-4 are a part of the ordered mesoporous carbons (OMCs) category which have been prepared by carbonization of template route using ordered mesoporous silica, e.g. SBA and carbon precursors, e. g. sucrose and furfuryl alcohol. Due to the carbonaceous structural properties, large specific surface area, pore volume, regular pore structure, and tunable porosity, they have been employed as adsorbents and catalysts, such as electrocatalysts and supported metal catalysts. For example, Ni-doped SBA-3 mesoporous materials with different nickel percentages were synthesized via the incipient wetness impregnation (IWI) method using hydrated nickel nitrate salt followed by calcination which was utilized as a hard template, and sucrose as the carbon source in the preparation of a novel Ni-doped mesoporous carbon (henceforth denoted as x wt.% Ni/MC, where x represents the nickel loading weight percentage) [60].

Relatively economical and harmless reactants in the concentrated reaction medium, high yield process, simple and accessible medium, and recovery capability are the most important factors that should be considered in the synthesis of the mentioned catalytic compounds.

SYNTHESIS & FABRICATION OF ODORANTS

Classic odorants synthesis

Mercaptans are the most abundant classic odorants that are synthesized by several methods. The experimental analysis for achieving their structural and functional basis for characterization and identification can be carried out by FT-IR and GC-MS analysis [61]. The common methods of synthesizing are as follows [5]:

- Ethyl bromide reaction with hydrogen sulfide according to reaction 4.
$$\text{CH}_3\text{-CH}_2\text{-Br} + \text{H}_2\text{S} \rightarrow \text{CH}_3\text{-CH}_2\text{-SH} + \text{HBr} \quad \text{Reaction 4.}$$
- Hydrogen sulfide reaction with an olefin in the presence of a catalyst according to reaction 5; the reaction of hydrogen sulfide and pure ethylene leads to the production of ethyl mercaptan. In this reaction, no

separation problems happen because the required mercaptan is the only mercaptan product. If the reactants consist of more than one type of olefin like ethylene and propylene, there is a possibility that both propyl mercaptan and ethyl mercaptan will be formed. As a result, the separation step should take place. Mentioned mercaptans cannot be easily separated by extraction, filtration, distillation, and membrane diffusion. However, ethyl mercaptan can be selectively produced using a mixture of fuel gas in the presence of molybdenum and cobalt oxides and particular catalysts [62].



- Sulfides reaction with hydrogen sulfide according to reaction 6.



- Mercaptans and sulfides selective production through alcohols according to reaction 7.

Hydrogen sulfide and the alcohol are reacted in the presence of a catalyst blend, which is of electrophilic substitution type. Various kinds of primary and secondary alcohols can participate in such a reaction. The mercaptan or sulfide produced in this method contains less than 30% unreacted alcohol.



Modern odorants synthesis

As mentioned previously, the basis of modern odorants is light acrylates, generally methyl acrylate and ethyl acrylate, which are ester derivatives of acrylic acid. To prohibit undesired polymerization, 50–500 ppm of an inhibitor is normally added to acrylic acid. The storage tank of this acid must be made of stainless steel, glass, polypropylene, polyethylene, or at least coated with one of these materials because of its relatively high corrosiveness. Moreover, special conditions must be provided for the storage of acrylic acid: Keep away from direct sunlight, store at temperatures 15–30°C, and prevent freezing. Frozen acrylic acid can be melted through an air or water bath up to 30°C. However, to avoid localized heating, it is recommended to stir the acrylic acid while melting. In practice, 80% acrylic acid aqueous solution is mostly used. This aqueous solution has a freezing point between -3 to -5 °C.

Generally, acrylic esters require less inhibitor, between 50–500 ppm, in comparison to acrylic acid. Acids are more corrosive compared to esters, but esters should also be stored in containers made of stainless steel, glass, polypropylene, polyethylene, phenolic resin, or at least coated with one of these materials. Acrylates that should be stored at temperatures of 0–10°C have different grades comprising little or no inhibitor. Methyl and ethyl acrylates can create explosive gas mixtures in air even at room temperature because of their really small flash points. Although oxygen is a good inhibitor, its concentration in large tanks is kept between 6-8 vol% to prohibit the formation of flammable compounds. For the generation of polyacrylates, acrylic esters are generally used particularly. Polyacrylates are used mostly for the production of coatings, textiles, binders for paper, adhesives, leather, and paints.

Methyl acrylate synthesis

Methyl acrylate, which makes up about 30% to 40% of the modern odorant ingredients, is practically synthesized via several different methods as mentioned below [63]:

1- **Industrial method:** The standard industrial reaction for producing methyl acrylate is esterification with methanol under acid catalysis (sulfuric acid, p-toluenesulfonic acid, or acidic ion exchangers). The

transesterification is facilitated because methanol and methyl acrylate form a low boiling azeotrope (boiling point 62–63 °C).

2- **Debromination method:** Methyl acrylate can be prepared by debromination of methyl 2,3-dibromopropanoate with zinc.

3- **Pyrolysis of methyl lactate:** Methyl acrylate is formed in good yield on pyrolysis of methyl lactate in the presence of ethenone (ketene). Methyl lactate is a reproducible green chemical.

4- **Hydrocarboxylation:** The nickel tetracarbonyl-catalyzed hydrocarboxylation of acetylene with carbon monoxide in the presence of methanol also yields methyl acrylate.

5- **Transition metal catalysts:** The reaction of methyl formate with acetylene in the presence of transition metal catalysts also leads to methyl acrylate

6- **Dehydration:** Dehydration of methyl lactate on a zeolite bed.

7- **One-pot synthesis:** The vapor phase oxidation of propane (2-propenal) with oxygen in the presence of methanol leads to the production of methyl acrylate. In general, the oxidation of propene, which produces acrylic acid, happens through a heterogeneous catalytic oxidation process in the vapor phase with air and steam. This reaction leads to the formation of methyl acrylate in the presence of methanol in a single step.

Ethyl acrylate synthesis

The highest composition of non-sulfur odorant ingredients belongs to ethyl acrylate, which accounts for more than 60% of odorant ingredients. This organic compound is the ethyl ester of acrylic acid which is a colorless liquid with a characteristic acrid odor. It is also a volatile component of Beaufort cheese and pineapple (a type of cheese manufactured in a small area of the French Alps). It is synthesized in different ways [59] as follows:

1- Esterification:

Esterification of acrylic acid in the liquid phase is industrially more momentous than the gas phase. Sulfuric and p-toluenesulfonic strong acids are preferable catalysts, but some solid acids like cation-exchange resins are desirable catalysts to enhance the esterification process, due to control the waste disposal problems. In general, in esterification processes where ethanol and methanol are used, cation-exchange resins are favored. But in esterification processes where pentanols and octanols higher alcohols with slower rates of esterification are used, sulfuric acid is a desirable catalyst. Large quantities of sulfuric acid are needed to produce ethyl acrylate via liquid-phase esterification of ethylene and acrylic acid, so this route to the production of ethyl acrylate is not economically feasible [64]. Fisher esterification is a reversible reaction that proceeds so slowly. An acid catalyst is added to increase the rate of the reaction, typically H_2SO_4 while acting as a dehydrating agent too. This homogenous acid catalyst has pollution and corrosion obstacles and separation from the reaction medium is hard, but it is cheap enough for commercial industrial production. To overcome the problems caused by the use of sulfuric acid, ion exchange resin is used as a catalyst. Ion exchange is the reversible interchange of ions between a solid and a liquid in which no permanent change in the structure of a solid. This catalyst is facilitated by recovery and recycling. Its reuse increases the productivity and cost-effectiveness of esterification reactions. Due to easier workup, the chemical industry has a strong preference for ion exchange resin catalysts but these catalysts do not offer the selectivity observed in homogenous catalysts. Limitation of ion exchange resins is the temperature limit which is typically below 120°C but nowadays catalysts like Nafion can go up to about 200°C. The cost of Nafion is high compared to other catalysts. The demand for environmentally friendly processes, with less energy

consumption, and the various types of ion exchange resins give them direct advantages in any competition with homogeneous catalysts [65].

2- High-pressure Reppe process:

Ethyl acrylate is also synthesized through acetylene, carbon monoxide, and ethanol by Reppe reaction. The high-pressure reactions catalyzed by heavy metal acetylides, especially copper acetylide, or metal carbonyls are called Reppe Process. This process can be classified into four large classes: vinylization, catalytic ethynylation of aldehydes, reactions with carbon monoxide, and cyclic polymerization. BASF company developed an experiment at approximately 14MPa and 200°C in which nickel bromide–copper(II) bromide acts as a catalyst. However, some drawbacks such as the formation of nickel carbonyl as a hazardous pollutant during the reaction and the expenses of acetylene are worth mentioning. Nickel carbonyl evaporates when exposed to air. It has very acute (short-term) toxicity on aquatic life and also high chronic (long-term) toxicity to aquatic life. Acute and chronic impacts on birds, land animals, or plants have not been determined. Nickel carbonyl is generally considered the most toxic form of nickel and upon inhalation produces both respiratory tract and systemic effects. Individuals poisoned by acute exposure to nickel carbonyl exhibit instantaneous and delayed effects. The recommended airborne exposure limit for Nickel carbonyl is 0.001ppm averaged over a 10-hour work shift. Based on these significant disadvantages, a more economical process which is direct oxidation of propene, had been chosen. In the direct oxidation method, the low cost of propylene is replaced by the high cost of acetylene making it an economical method. On the other hand, the need to use transition metals is one of the other limitations of the Reppe reaction.

3- Industrial production:

Ethyl acrylate can be chemically manufactured using various industrial techniques. The most outstanding procedure is to cause a reaction between ethanol and acrylonitrile in the presence of sulphuric acid as the catalyst. Additionally, manufacturers may also use phenolic-type inhibitors, and polymerization inhibitors, such as hydroquinone or phenothiazine, soluble manganese, or cerium salts to aid its production as well as prevent the involuntary polymerization of monomers. Other compounds used in this reaction are ethanol, carbon monoxide, and acetylene.

4- Hydrolysis of acrylonitrile:

Hydrolysis of acrylonitrile due to the presence of propene and the large amounts of NH_4HSO_4 waste has low efficiency. Hence this method is not economically attractive. That's why Ugine Kuhlmann, Mitsubishi Petrochemical, and Mitsubishi Rayon abandoned this process. Although Asahi Chemical still applies this method.

5- Ketene procedure:

The many steps and toxicity of β -propiolactone are the major drawbacks that caused this method to be banned by Celanese and B. F. Goodrich for a long time. During the ketene procedure, acetone or acetic acid will pyrolyze to the ketene.

6- Thermal depolymerization of polypropiolactone:

polypropiolactone abbreviated PPL is an intermediate for the production of acrylic acid followed by acrylate esters. Thermal depolymerization of polypropiolactone includes the generation of PPL through the carbonylation of ethylene oxide. Polypropiolactone is a high molecular weight biodegradable polymer with attractive mechanical and physical properties that make it suitable for packaging and other thermoplastic applications. This aliphatic polyester is stable, easily transportable, and cost-competitive. PPL can be thermally pyrolyzed to acrylic acid although it is resistant under different conditions. This method overcomes the problems caused by glacial acrylic acid transportation and reduces the complications of acrylic acid or acrylate ester production. The present method encompasses safe and efficient methods for providing highly pure acrylic acid. The inventive techniques include the step of producing polypropiolactone from ethylene oxide at a first location, transporting the polymer to a second location, and pyrolyzing the polypropiolactone to prepare glacial acrylic acid. In certain embodiments, the step of pyrolyzing the polymer is performed constantly in conjunction with a polymerization process to make SAPs. From one perspective, the present procedure provides the ability to use a less expensive feedstock at one site to satisfy broader geographic demand for acrylic acid and its derivatives. For instance, the present contraction can be deployed to utilize the C2 component of shale gas and carbon monoxide to make the polymer polypropiolactone. PPL is a stable substance that can be safely transported and stored for extended periods with no safety concerns or the quality declines attendant with shipping and storing glacial AA. When glacial acrylic acid is needed, methods of the present invention provide it in highly pure type through a step of decomposing the polypropiolactone at the point of AA use. Hence, in certain embodiments, the present procedure enables the achievement of acrylic acid and acrylate esters in a safe and/or less expensive and/or highly flexible fashion.

7- Procedure of ethylene cyanohydrin:

The reaction of ethylene oxide and hydrogen cyanide leads to the formation of ethylene cyanohydrin. Then it can be dehydrated to acrylic acid in the presence of sulfuric acid as a catalyst. Union Carbide and Rohm & Haas used this method in the past but due to the HCN and the NH_4HSO_4 waste challenges, stopped using this method. Cyanide is an extremely toxic matter that will cause death if inhaled, ingested, or absorbed through the skin. The wastes (cyanides produced) should be kept away from all kinds of acids. HCN compounds should be disposed of as hazardous waste. These factors make the work very hard and dangerous. Ammonium bisulfate is toxic by skin absorption, too. Inhalation, ingestion, or skin contact with NH_4HSO_4 waste may cause severe injury or death. Furthermore, touching molten materials may lead to strong eyes and skin burns. That's why the process has been abandoned.

8- Allyl ether partial oxidation:

Production of allyl acrylate via partial oxidation of diallyl ether in acetonitrile solvent can be catalyzed by Li-doped MnO_2 (mesoporous structure). moderate conditions, a recyclable inhomogeneous catalyst, no precious metals, and easy isolation are the characteristics of this reaction. Almost complete conversion of allyl ether with near complete chemo-selectivity towards acrylate ester derivatives can happen on the best occasion. The aerobic oxidation of allyl ethers to corresponding acrylate esters using various cation-doped mesoporous manganese oxide materials takes place in this technique. As mentioned before, The absence of any precious metal, easy isolation of the products, and the use of a reusable heterogeneous catalyst in the absence of acidic or alkaline media make this

process noteworthy for the oxidation of allyl ethers. Determining optimal conditions for this reaction demonstrated these results: Temp. 80 °C, 6 h in an air balloon in the presence of meso-Li-Mn₂O₃ as the catalyst.

Production of lower alkyl acrylates

According to Figure 2, a small amount of alcohol about 10-30% with acrylic acid is poured into the fixed-bed reactor during -step a- at a temperature of 60–80°C. The reactor is filled with a kind of cation-exchange resin. Then the reaction liquid goes to the ester stripper -step b- and unreacted alcohol, desired ester, and water are removed overhead using part of the bottoms from the light-ends column -step e- as reflux. The bottom liquid from the ester stripper -step b- contains unreacted acid and is recycled to the reactor. Part of the recycled liquid is fed into the bottom stripper -step c-, where high-boiling materials, such as inhibitors, impurities, and polymers, are removed to prevent their accumulation in the reaction system [64].

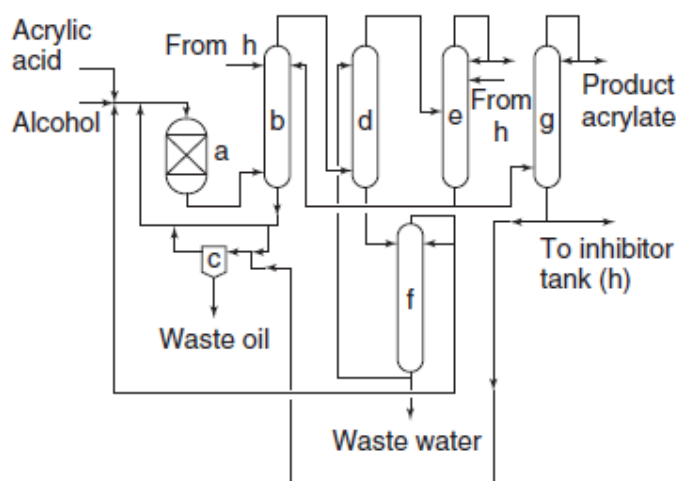


Fig 2. Scheme of lower alkyl acrylates production process (Published with permission)

- a: Esterification reactor
- b: Ester stripper
- c: Bottom stripper
- d: Extraction column
- e: Light-ends cut column
- f: Alcohol-recovery column
- g: Product column

The mixture of ester and alcohol without any amount of acid, distilled from the ester stripper -step b- is fed into the extraction column -step d-, where the alcohol is extracted with water from the top of the column. The raffinate from the top of the column goes into the light-ends cut column -step e-, where light ends such as water, acetate, and alcohol are separated overhead. The extract from the bottom of the extraction column is fed into the alcohol-recovery column -step f-, where the alcohol is recovered for reuse in the reaction. Part of the bottom liquid is reused as extracting water; the rest is taken out as waste, concentrated, and either treated biologically or incinerated. Crude ester from the bottom of the light-ends column is distilled in the product column -step g- to attain very pure acrylate. The bottom liquid from the product column is recycled (via the inhibitor tank) to the ester stripper and light-ends cut column -step e- to be reused as an inhibitor. However, a part of it is sent to the

bottom stripper -step c- to recover ester and separate high-boiling materials such as polymers. Hydroquinone or phenothiazine as polymerization inhibitors are added to each column. The light-ends cut column and the product column are operated at reduced pressure to permit lower distillation temperatures.

This process for making alkyl acrylates is quite economical because only a small excess of alcohol is applied and the inhibitor is reused; this leads to low energy and inhibitor consumption. The yield reaches 95% and 97% based on acrylic acid and alcohol, respectively. The product purity exceeds 99.5 wt%.

RESULTS & DISCUSSION

Considering the topics that were discussed in the theoretical part, the results of the review of odorants can be obtained in response to three basic questions.

1- What are the effective items in the selection of the odorant and their degree of odorizing?

Many important parameters influence the selection of the gas odorizer, But the most important of these include [66]:

- Mixture type and the effect of each component.
- Type and quality of odorized gas: Gas odorizing naturally or artificially / The presence of oxygen or moisture or heavy hydrocarbons in large quantities.
- The nature and capacity of the gas supply system: Nature and type of materials and equipment used / System life / Duration of using the system / Specifications and features of the piping and pipeline.
- Soil condition: Soil moisture / Absorption power by the clay in the main soil.
- The history and plan of odorization: Documents related to the odorization plan / Experiences / Leakages records.

2- How to measure odor detectability in the laboratory?

Recognition and detection thresholds are two of the most important criteria for detecting odor. The minimum concentration of odorant that people can reliably distinguish from fresh air is defined detection threshold. The detection threshold values of conventional odorants based Triangle Odor Bag method are given in Table 7 [67]. It should be noted that due to the differences in measurement conditions, equipment, and parameters affecting several methods, the amount of detection threshold declared for these odorants according to the desired method can be different.

Table 7: Detection thresholds of chemicals [67]

<i>Chemical</i>	<i>Concentration (v/v)</i>
<i>Isopropyl mercaptan - C₃H₈S</i>	<i>6 ppt</i>
<i>Geosmin - C₁₂H₂₂O</i>	<i>6.5 ppt</i>
<i>Ethyl mercaptan - C₂H₆S</i>	<i>8.7 ppt</i>
<i>n-Propyl mercaptan - C₃H₈S</i>	<i>13 ppt</i>
<i>tert-Butylmercaptan - C₄H₁₀S</i>	<i>29ppt</i>
<i>sec-Butylmercaptan - C₄H₁₀S</i>	<i>30 ppt</i>
<i>Diethyl sulfide - C₄H₁₀S</i>	<i>33 ppt</i>
<i>Methyl mercaptan – CH₄S</i>	<i>70 ppt</i>
<i>Ethyl acrylate - C₅H₈O₂</i>	<i>260 ppt</i>
<i>Hydrogen sulfide -H₂ S</i>	<i>410 ppt</i>
<i>Tetrahydrothiophene -C₄H₈S</i>	<i>620 ppt</i>
<i>Dimethyl sulfide -C₂H₆S</i>	<i>3000 ppt</i>
<i>Methyl acrylate -C₄H₆O₂</i>	<i>3500 ppt</i>

To test the measurement scenario, a group of people are exposed to puffs of air in the laboratory. Each session of the experiment covers various tests in which people have to categorize several odorized and odorless puffs of air. The smellers should determine which one of the sampled puffs smells stronger compared to the others even if they are not sure. The accurate recognition possibility of odorized samples in a certain experiment increases according to the concentration of odorant through an s-shaped diagram. For example, methyl mercaptan has an odor recognition threshold of only 0.0021ppm. That's why, it is often mixed with natural gas as a leak indicator. However, nearly one person in 1000 is unable to detect the intense odor of this mercaptan [5].

In some experimental techniques, the smellers present a relatively strong odor as a sample at first, then lower concentrations to distinguish the lowest concentration that smells like the sample. Some techniques are implemented in such a way that people apply tags to a series of puffs to find which sample will receive the minimum concentration tag.

The notions mentioned above have long been understood in the study of human sensation and perception generally, proposing that it seems easy to determine a concentration that is "readily detectable", at least in the lab. However, measured thresholds for a certain composite can change even in controlled laboratory studies [68].

The factor that quantifies the intensity of odors is the Odor Index. Based on Equation 1. this factor (OI) is equal to the vapor pressure of odor versus the odor recognition threshold:

$$OI = \frac{\text{Vapor pressure (ppm)}}{\text{Recognition threshold (ppm)}} \quad \text{Equation 1.}$$

It is clear that the OI is a dimensionless number. Hence, an OI of less than 1 shows negligible vapor pressure of the component that can easily be smelled [5].

3- Which factors can alter the detection of odor in reality?

Panel members actively detect odors with little distraction in the laboratory. Few studies have worked on the influence of attention and other cognitive factors on the recognition of NG odorants, because people usually concentrate on their own activities and do not pay special attention to surroundings. One research found that

subjects who were asked to read a message in the dim light were less likely to notice the smell of natural gas in the lab compared to subjects who were not distracted [69].

One of the serious factors that potentially affect the ability of odor detection is adaptation. It means that it is much harder to detect a certain odor for someone who is constantly or periodically exposed to it than for someone who smells it occasionally. Attention is momentous in the detection of odor. For example, odor adaptation differs from habituation, in which the person no longer notices the smell but can detect if concentrates. In contrast, a person will be unable to smell a certain odor because of olfactory adaptation, unless the person should not be exposed to that smell for a while to smell the odor again. Adaptation can also be problematic when a gradual gas leak occurs indoors. Comparable adaptation is described in some experimental research in the laboratory, in which smellers can not recognize a warning odor even in relatively high concentrations [70].

It is noteworthy that there is pure air in the olfactory laboratories, but in daily life, warning odors of natural gas are one of several odorous substances in the surroundings. Universally, odorous substances are mutually suppressive, which is why any specific odor is less perceptible in a combination of odors [71]. Several reports show that a flow of natural gas consists of usual amounts of odorants based on analytical measurements, has no odor or little odor, or does not create the smell of gas in the air. This issue is still mysterious, though other odorous compounds in the gas or material of the pipeline may affect the odorant odor recognition. Another issue is that sulfurous compounds used in combination with natural gas odorants exist in abundance in daily life and are smelled a lot by people, such as odors from cooking meats and vegetables or odors of decay. In addition to issues caused by adaptation and habituation, recognizing natural gas odor is difficult due to the formation of odor background. Then more research is required to figure out how important such effects might be.

CONCLUSION

Our review shows that the “Classic” sulfurous odorants that are sorted into alkyl sulfides, alkyl mercaptans, and cyclic sulfides irrespective of all the environmental problems they beget, are still welcomed by the gas industry in the world. This popularity is due to the high level of assurance of these materials to ensure the safety of consumers. on the other hand, “Modern” sulfur-free odorants based on acrylates have shown the least environmental problems and negative effects on human and animal health, But exploiting these materials has practical and industrial limitations that have made modern odorants unable to completely replace classic odorants. The results of the studies show that scientists have not succeeded in synthesizing, offering, and commercially producing a desirable odorant that has all the factors required for sufficient effectiveness. It means, that among the available natural gas odorants, it is not possible to choose a combination as the best odorizer. Only based on the environmental, industrial, and commercial requirements, it is possible to prefer some compounds of gas odorants over the rest of them. What is important in this selection is that the chosen material facilitates the safety of gas consumers as much as possible and speeds up the leak detection process. Considering that the harmful effects caused by these materials such as environmental pollution, corrosion, cost imposition, and destruction of equipment and facilities involved in the production, consumption, and transfer processes should be minimized. Therefore, in this theoretical research, the most important existing records and necessary information were collected to conduct research and produce a desirable odorizing material that is optimal from every point of view. In this regard, it is suggested to conduct more studies on the method of synthesis, formulation, effectiveness, adaptability to the environment, economic aspect, and the transfer of knowledge obtained from the laboratory to the industry.

REFERENCES

- [1] Robertson S.T., History of Gas Odorization, GTI Electronic Symposium Proceedings in Odorization (1980).
- [2] Wise P., Rowe S., Dalton P., "[Odorization of Natural Gas: What are the Challenges?](#)", bioRxiv, USA (2021).
- [3] Quaglio J., "[Wassergas als der Brennstoff der Zukunft: Strong's Patent zur Bereitung von Heizgas in Verbindung mit Lowe's Verfahren](#)", J.F. Bergmann, Germany, 1-68 (1880).
- [4] Muhlbauer W.K., "[Pipeline Risk Management Manual: Ideas, Techniques and Resources](#)", Gulf Professional Publishing, Burlington Canada, 3rd ed, 223-242 (2004).
- [5] Fink J., "[Petroleum Engineer's Guide to Oil Field Chemicals and Fluids](#)", Gulf Professional Publishing, USA, 455-471 (2015).
- [6] Henderson DF., [Large Volume Odorization Installation Operation and Maintenance](#), Odorization, USA, 3, 239-249 (1993).
- [7] Toth JM., Natural Gas Odorization and its Techniques, Annual Appalachian Gas Meas Short Course Proceedings, USA, 49, 170-174 (1989).
- [8] Oudman P., Odorization and Odorant Monitoring Practices at Canadian Western Natural Gas Company Limited, Institute of Gas Technology, USA, 3, 389-405 (1993).
- [9] Mouli-Castillo J., Orr G., Thomas J., Hardy N., Crowther M., Stuart Haszeldine R., et al., [Comparative Study of Odorants for Gas Escape Detection of Natural Gas and Hydrogen](#), International Journal of Hydrogen Energy, 46, 14881-14893 (2021).
- [10] Fries KR., "[Consumer Survey on the Olfactory Evaluation of Different Natural Gas Odorants](#)", Symrise AG., Germany, 1, 2-9 (2015).
- [11] Ivanov I., Strmen J., Jones L., [Pre-odorization or Pickling of New Natural Gas Pipe](#), Pipeline & Gas Journal, 236, 11, 48-54 (2009).
- [12] Teymoury M., Samadi-M A., Vahid A., Miranbeigi A., [Adsorptive Desulfurization of Low Sulfur Diesel Fuel using Palladium Containing Mesoporous Silica Synthesized via a Novel In-situ Approach](#), Fuel Processing Technology, 116, 257-264 (2013).
- [13] Vahid A., Mazochi M., Baniyaghoob S., [Deep Desulfurization of Naphtha using CMK Containing Nickel Metal Nanoparticles](#), Farayandno [in persian], 67, 31-41 (2022).
- [14] Rezaei P., Baniyaghoob S., Hosseini Sadr M., [Fe₃O₄@SiO₂@AgO Nanocomposite: Synthesis, Characterization and Investigation of its Photocatalytic Application](#), Journal of Electronic Materials, 48, 3285-3296 (2019).
- [15] Capelli L., Sironi S., Del Rosso R., [Odour Emission Factors: Fundamental Tools for Air Quality Management](#), Chemical Engineering Transactions, 40, 193-198 (2014).
- [16] Borup RL., Kusoglu A., Neyerlin KC., Mukundan R., Ahluwalia RK., Cullen DA., [Recent Developments in Catalyst-related PEM Fuel Cell Durability](#), Current Opinion in Electrochemistry, 21, 192-200 (2020).
- [17] Liszka K., Laciak M., Oliinyk A., [Analysis of New Generation Odorants Applicability in the Polish Natural Gas Distribution Network](#), AGH Drilling, Oil & Gas, 31(1), 59-71 (2014).
- [18] Sisman E., Cankaya S., Kececi E., Teymourfamianasl M., Uyan Ucar Z., Bulut B., et al., [Identifying the Environmental Hotspots of Sulfur-free Odorant for LPG Storage and Filling by Life Cycle Approach](#), Science of the Total Environment, 886, 163816 (2023).

- [19] Schmeer F, Reimert R. [Entwicklung Eines Schwefelfreien Odoriermittels: Aktueller Stand. Diskussion](#), Gas-Erdgas, 144(1), 52-58 (2003).
- [20] European Patent EP1529092, [Gas Odorization using Ketones](#) (2007).
- [21] US Patent 7182796, [Odorant for Fuel Gas](#) (2007).
- [22] Usher MJ., [Odor Fade-possible Causes and Remedies](#), Proc., 285, 1-12 (1999).
- [23] German Patent DE10058805A1, [Odorants for Gases](#) (2002).
- [24] Graf F., Kröger K., Reimert R., [Sulfur-free Odorization with Gasodor S-free: A Review of the Accompanying Research and Development Activities](#), Energy & Fuels, 2007, 21(6), 3322-3333 (2007).
- [25] Brown AS., Vanderveen MH., Arrhenius K., Downey L., [Traceable Reference Gas Mixtures for Sulfur-free Natural Gas Odorants](#), Analytical Chemistry, 86(13), 6695-6702 (2014).
- [26] US Patent 7108803, [Gas Odorization Method](#) (2006).
- [27] Wagner T., [Experience Report for the Regional Central Odorization with Sulfur-free Odorants](#), Gas-Erdgas, 146(10), 560-563 (2005).
- [28] Ripley DL., Goetzinger JW., Whisman ML., [Human Response Research Evaluation of Alternate Odorants for LP-gas](#), Gas Processors Association, 129, 1-26 (1990).
- [29] US Patent 5049312, [Test-fluid Composition and Method for Detecting Leaks in Pipelines and Associated Facilities](#) (1991).
- [30] CA Patent 2052242, [Test-fluid Composition and Method for Detecting Leaks in Pipelines and Associated Facilities](#) (1993).
- [31] CA Patent 1274692, [Odor-fading Prevention from Organosulfur-odorized Liquefied Petroleum Gas](#) (1990).
- [32] US Patent 4701303, [Odor-fading Prevention from Organosulfur-odorized Liquefied Petroleum Gas](#) (1987).
- [33] Altpeter Jr, [Research Recommended to Develop Odorant-fade Model, Pipeline & Gas Industry](#), 80(2), 39-40 (1997).
- [34] Esfandiari K., Banihashemi M., Mokhtari A., Soleimani P., [Experimental Investigation of Influencing Parameters on Natural Gas Odor Fading in Gas Distribution Networks](#), Journal of Natural Gas Science and Engineering, 95, 104191 (2021).
- [35] Girod JF., Leclerc JP., Muhr H., Paternotte G., Corriou JP., [Removing a Small Quantity of THT from Gas Storage Groundwater through Air Stripping and Gas-phase Carbon Adsorption](#), Environ. Progr., 15(4), 277-282 (1996).
- [36] Huang F., Lee R., [Degradation of Ethyl Mercaptan in the Presence of Zero-valence Iron](#), Proceedings Volume 4th US DOE Tulsa Univ. et al Petrol. Environ. Conf. (1997).
- [37] EP Patent 0781832, [Process for the Complete Treatment of Natural Gas on a Production Site](#) (1997).
- [38] US Patent 5803953, [Process for Treatment of Natural Gas at a Storage Site](#) (1998).
- [39] Panneman HJ., Pot-Gerritsen RC., Kuiper-Van Loo EM., Pastoor H., Janssen-Van Rosmalen R., [UV-oxidation Process for Water Treatment at Gas Plant Sites](#), 20th Int Gas Union World Gas Conf., 269-285 (1997).
- [40] Jabalameli M., Zamani Y., Baniyaghoob S., Shirazi L., [Study of Iron-Based Catalysts Performance in Fischer-Tropsch Synthesis](#), Catal. Ind., 15, 132-143 (2023).

- [41] Motahari K., Abdollahi-Moghaddam M., Rashidi A., [Mechanism Study and Determination Kinetic of Catalytic Oxidation of Mercaptans in Merox Process](#), South African Journal of Chemical Engineering, 33, 116-124 (2020).
- [42] Yehua H., Yanfen Zh., Chunming X., Chang Samuel H., [Molecular Characterization of Sulfur-containing Compounds in Petroleum](#), Fuel, 221, 144-158 (2018).
- [43] Rahbar-Shamskar K., Aberoomand Azar P., Rashidi A., Baniyaghoob S., Yousefi M., [Synthesis of Micro/Mesoporous Carbon Adsorbents by In-situ Fast Pyrolysis of Reed for Recovering Gasoline Vapor](#), Journal of Cleaner Production, 259, 120832 (2020).
- [44] Samadi-Maybodi A., Vahid A., [\(2-Hydroxyethyl\)-trimethylammonium Hydroxide as an Organic Base for the Synthesis of Highly Ordered MCM-41](#), Solid State Sciences, 13, 271-275 (2011).
- [45] Teymouri M., Samadi-Maybodi A., Vahid A., [A Rapid Method for the Synthesis of Highly Ordered MCM-41](#), Int. Nano Lett. 1(1), 34-37 (2011).
- [46] Samadi-Maybodi A., Teymouri M., Vahid A., Miranbeigi A. [In Situ Incorporation of Nickel Nanoparticles into the Mesopores of MCM-41 by Manipulation of Solvent-solute Interaction and its Activity toward Adsorptive Desulfurization of Gas Oil](#), Journal of Hazardous Materials, 192, 1667-1674 (2011).
- [47] Peng X., Kumar Jain S., Kumar Singh J., Liu A., Jin Q., [Formation Patterns of Water Clusters in CMK-3 and CMK-5 Mesoporous Carbons: A Computational Recognition Study](#), Phys. Chem. Chem. Phys., 20, 17093-17104 (2018).
- [48] Vahid A., Qandalee M., Baniyaghoob S., [H₂S Removal using ZnO/SBA-3: New Synthesis Route and Optimization of Process Parameters](#), Scientia Iranica, 24(6), 3064-3073 (2017).
- [49] Jafari M., Yousefi M., Baniyaghoob S., [Green Synthesis and Characterization of AgCl Nanoparticle using Onopordum Acanthium Extract](#), International Journal of Biolife Sciences, 1(3), 154-158 (2022).
- [50] Samadi-Maybodi A., Vahid A., [Synthesis of Mesoporous Silica Nanoparticles using a Hydrogel](#), International Nano Letters, 3, 1-3 (2013).
- [51] Sarrafi Y., Mehrasbi E., Vahid A., Tajbakhsh M., [Well-Ordered Mesoporous Silica Nanoparticles as a Recoverable Catalyst for One-pot Multicomponent Synthesis of 4H-Chromene Derivatives](#), Chinese Journal of Catalysis, 33, 1486-1494 (2012).
- [52] Rahbar-shamskar K., Rashidi A., Baniyaghoob S., Khodabakhshi S., [In-situ Catalytic Fast Pyrolysis of Reed as a Sustainable Method for Production of Porous Carbon as VOCs Adsorbents](#), Journal of Analytical and Applied Pyrolysis, 164, 105520 (2022).
- [53] Moosa-Zadeh S., Shariati Sh., Yousefi M., Baniyaghoob S., Kefayati H., [Using of Steel Slag and Waste Rusted Iron Shavings for Biosynthesis of Nano Zero-valent Iron Nanoparticles with Magnetite Coating](#), Journal of Applied Research in Chemistry, 15(4), 52-61 (2022).
- [54] Mehrasbi E., Sarrafi Y., Vahid A., Alinezhad H., [Sulfonic Acid-functionalized Mesoporous Silica Nanoparticles \(SAMSNs\): A Recoverable Heterogeneous Acid Catalyst for Green Synthesis of dicoumarols](#), Research on Chemical Intermediates, 41, 4929-4941 (2014).
- [55] Samadi-Maybodi A., Vahid A., [High Yield Synthesis And Characterization Of Well-Ordered Mesoporous Silica Nanoparticles Using Sodium Carboxy Methyl Cellulose](#), Journal of Non-Crystalline Solids, 357, 1827-1830 (2011).

- [56] Zolfaghari M., Abromandazar P., Vahid A., Baniyaghoob S., [Synthesis And Characterization Of Bimodal Mesoporous Silica Nanoparticles For The Removal Of Sulfur From Model Fuel](#), Iranian Physical Chemistry Conference Proceeding, 18, 625-627 (2016).
- [57] Samadi-Maybodi A., Vahid A., Baniyaghoob S., [Study Of The BZ Oscillating System In The Presence Of Silica Nanoparticles Containing Nio Using A New Approach](#), Scientia Iranica, 23(6), 2735-2741 (2016).
- [58] Hazrati N., Abdouss M., Vahid A., Miranbeigi A., Mohammadalizadeh A., [Removal Of H₂S From Crude Oil Via Stripping Followed By Adsorption Using ZnO/MCM-41 And Optimization Of Parameters](#), International Journal of Environmental Science and Technology, 11(4), 997-1006 (2014).
- [59] Rahbar Shamskar K., Rashidi A., Aberoomandazar P., Yousefi M., Baniyaghoob S., [Synthesis Of Graphene By In Situ Catalytic Chemical Vapor Deposition Of Reed As A Carbon Source For VOC Adsorption](#), Environmental Science and Pollution Research, 26(4), 3643-3650 (2019).
- [60] Saffarian-D A., Vahid A., Baniyaghoob S., Saber-Tehrani M., Malek Mohammadi R., [Deep denitrogenation of Model Diesel Fuel using Ni-doped Mesoporous Carbon](#), ChemistrySelect, 6, 1073-1081 (2021).
- [61] Gopinath S., Devan P.K., Pitchandi K., [Production of Pyrolytic Oil from ULDP Plastics using Silica-alumina Catalyst and used as Fuel for DI Diesel Engine](#), The Royal Society of Chemistry, 10, 37266-37279 (2020).
- [62] US Patent 5352838, [Selective Production of Ethyl Mercaptan](#) (1994).
- [63] IARC Working Group, [Re-Evaluation Of Some Organic Chemicals Hydrazine And Hydrogen Peroxide](#), IARC, 71, 1447-1489 (1999).
- [64] Ohara T., Sato T., Shimizu M., etc., [ULMANN'S Encyclopedia Of Industrial Chemistry](#), Wiley-VCH Verlag GmbH & Co., 1, 1-11 (2020).
- [65] Bhaskar Bhandare R., [Ion Exchangers as Catalyst in Esterification Reaction: A Review](#), International Journal of Chemical Engineering Research, 10(2), 105-118 (2018).
- [66] Bernhart M., Driesen E., Kaesler H., Mansfeld G., [Sulfur Free Odorant For Natural Gas](#), International Gas Research Conference, 3, 362-366 (1998).
- [67] Yoshio Y., Nagata E., [Measurement Of Odor Threshold By Triangular Odor Bag Method](#), Environmental Science, 118-127 (2003).
- [68] Devos M., Patte F., Rouault J., Laffort P., van Gemert LJ., ["Standardized Human Olfactory Thresholds"](#), IRL Press at Oxford University Press, 29-45 (1990).
- [69] Whisman ML., Goetzinger JW., Cotton FO., Brinkman DW., [Odorant Evaluation: A Study Of Ethanethiol And Tetrahydrothiophene As Warning Agents In Propane](#), Environmental Science & Technology, 12(12), 1285-1288 (1978).
- [70] Wilby FV., [An Objective Method For Determining An Adequate Level Of Odorization In Natural Gas](#), Institute of Gas Technology, 278-351 (1990).
- [71] Thomas-Danguin T., Sinding C., Romagny S., El Mountassir F., Atanasova B., Le Berre E. et al., [The Perception Of Odor Objects In Everyday Life: A Review On The Processing Of Odor Mixtures](#), Front Psychol., 5, 504-510 (2014).