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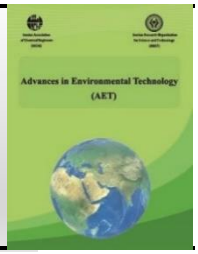


# A green route for wasted sulfur consumption: Kinetic modeling of methyl mercaptan synthesis from refinery $H_2S$ streams over the $K_2Wo_4/Al_2O_3$ catalyst

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**ABSTRACT**

The kinetics of methyl mercaptan production from a reaction between methanol and hydrogen sulfide in the presence of a $K_2Wo_4/Al_2O_3$ catalyst was experimentally studied. Waste streams containing sulfur due to sour gas sweetening in the Nori refinery complex were used instead of pure $H_2S$. This reaction can eliminate the emission of sulfur-containing compounds into the environment and convert them into useful products. The experiments were performed over a fixed-bed reactor at various temperatures and a pressure of 8-10 bars. The values of kinetic parameters estimated by the regression between the kinetic models and the experiments within the ranges have been reported in the literature. The activation energies for methyl mercaptan and dimethyl sulfide were 53.11 and 129.55 (kJ/mol), respectively. ASPEN simulation showed that the molar flow rates of $H_2S$ and methanol (reactants) decreased at the length of the reactor, while this trend for the products (methyl mercaptan, DMS, and $H_2O$) was reversed. The correlation coefficients indicated that the parameters and the model were significant and reasonable for reactor design. The results showed that sulfur-containing waste streams could be used instead of pure $H_2S$ streams. This substitution not only provides a supply for replacing pure $H_2S$ streams but also contains the emission of poisonous sulfur compounds into the environment.

## 1. Introduction

Methyl mercaptan is an important chemical intermediate for the industrial production of methionine that is used as a reactant in the synthesis of dimethyl sulfoxide and dimethyl sulfone. This intermediate also has other applications such as the production of alkane sulfonic acids, plastics, agriculture, and petrochemicals [1,2]. The catalytic reaction between hydrogen sulfide and methanol is one of the most important procedures for methyl mercaptan production. This reaction is facilitated by potassium/tungstate-alkaline oxide supported alumina oxide catalysts at a temperature in the range of 573-773 K and a pressure of 1-25 bars [3-5]. In this process, the methyl mercaptan reaction competes with side reactions such as dimethyl sulfide (DMS), dimethyl ether (DME) and water production. Thus, the determination of optimal values for reaction temperature, pressure, hydrogen sulfide/methanol ration, feed velocity, and the identification of catalyst structure and feed impurities are very crucial [6,7]. Kinetic modeling and the determination of its related parameters are two powerful and critical factors in the successful optimization and modeling of the process and identification of scale up limitations [8]. In other words, achieving an accurate mechanism of reaction is very crucial and cannot be neglected in the optimization process for increasing the efficiency of the desired product. Therefore, the kinetic investigation can be considered as one of the more important goals for researchers in this field to identify the limitations at different scales and seek the appropriate solutions to successfully scale-up. So far, all efforts related to determining the kinetics of the reaction between hydrogen oxide and methanol have been limited to the works reported by Russian scientists and their colleagues [3,9]. They have reported a comprehensive

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mechanism for this reaction and obtained the values of the kinetic parameters. All of these cases are based on reactions performed with laboratory-grade or highly purified materials. In many oil and gas processing plants (such as gas refineries, oil refineries, and some petrochemical plants), the $H_2S$ in acidic gas is converted to solid sulfur through the modified Claus process [10]. In some scenarios, when this conversion is not economically feasible, the acidic gases are sent to the flares and lead to problems such as corrosion of the flare equipment [11], which is also contrary to environmental well-being. This project investigates the possibility of converting the $H_2S$ in refinery streams to methyl mercaptan ($CH_3SH$) through a reaction with methanol in the presence of an industrial catalyst. The $H_2S$ stream was used instead of pure $H_2S$, which was mixed with methanol and introduced to a fixed-bed reactor over the industrial catalyst ($K_2Wo_4/Al_2O_3$) to study its kinetic mechanism. The modeling was performed according to the nonlinear regression method. The innovative aspect of this work is the investigation of the methyl mercaptan kinetic in the presence of hydrocarbons in the feed.

## 2. Material and methods

### *2.1. Materials*

The potassium tungstate and alumina were purchased from Sigma-Aldrich and Sud-Chemie, respectively. The basic properties of sour gas and methanol are presented in Table 1.

**Table 1.** Basic properties of sour gas and methanol used in methyl mercaptan production.

| Property | Value |
|---|---|
| **Sour gas components (mole fraction):** | |
| $H_2S$ | 0.15 |
| $C_3H_8$ | 0.6 |
| $C_4H_{10}$ | 0.25 |
| Feed flow rate (Methanol + Sour gas) (kg/hr) | 0.5-0.32 |
| H2S/Methanol | 1.7 |
| Inlet pressure (bar) | 10 |
| Inlet temperature (K) | 573-673 |
| **Methanol properties:** | |
| Molecular weight (g/mol) | 32 .042 |
| Critical temperature (K) | 786.55 |
| Critical pressure (bar) | 82.2 |
| Critical volume ($cm^3$/mol) | 114 |
| Boiling temperature (K) | 338.11 |

### *2.2. Catalyst preparation*

In this study, alkali and transition metal oxide promoted alumina, especially $K_2WO_4/Al_2O_3$, was chosen as the catalyst due to its appropriate Lewis acid-basic properties. The conversion of methanol rises with an increase in the acid strength of the active sites, while the strong basic site is favorable for the selectivity toward methyl mercaptan [12-13]. The impregnation method was used to prepare the $K_2Wo_4/Al_2O_3$ catalysts, which is used today as an industrial catalyst [4]. The potassium tungstate powder was dissolved in water to make a solution containing 10 wt. % of $K_2Wo_4$. Then, the γ-Alumina was immersed in this solution for 50 min. After filtration, the catalyst was dried at 393 K for 14 h., and this process was repeated two times. Finally, the catalyst was calcined at 723 K for 6h. Table 2 shows the properties of the 10 wt. % $K_2Wo_4/Al_2O_3$ catalyst.

**Table 2**. Properties of the $K_2Wo_4/Al_2O_3$ catalyst used for methyl mercaptan production.

| Parameters | Value |
|---|---|
| Fe content (wt. %) | Lesser than 0.02 |
| Na content (wt. %) | 0.2 ~ 0.6 |
| Alumina content (wt. %) | 99.0 |
| Surface area ($m^2$/g) | 986 |
| Pore volume ($cm^3$/g) | 0.530 |
| Mechanical Strength (MPa) | 3.50 |
| Granule Size (mm) | 2.5-3.5 |

### *2.3. Set-up information*

Figure 1 demonstrates a diagram of a reactor and its elements used for producing methyl mercaptan from sour gas streams as a source of $H_2S$. The reactor was a fixed bed type with a 5.08 cm internal diameter and a height of 27 cm. The amount of catalyst was 550 gr approximately. The procedure of the experiments is as follows. First, the system was purged by injecting nitrogen gas. After a certain period (about 5 minutes), the outlet temperature of the heater located at the reactor inlet was adjusted at 423 K to remove any possible moisture formed on the catalyst surface. After about 10 minutes of the injection, the fluid flow was directed into the reactor through a valve installed to inject sour gas. The inlet gas flow was regulated via FT-100. The overall pressure of the system was also adjusted using a PV-100 valve. In this case, the reactor temperature was raised to about 653 K using two temperature loops installed in the system, namely TC-100 and TC-101. The pressure was also raised to near 10 bar. Next, by turning on the methanol injection pump, the required methanol injection flow rate was adjusted based on the inlet gas flow rate (according to the composition of the inlet gas percentage). The injection conditions must be such that the molar ratio of $H_2S$ and methanol be equal. After reaching an equilibrium state

(after about half an hour), the reactor exhaust gas was analyzed via two methods: $H_2S$ Tube Test and sampling bomb. In the initial tests, due to the high concentration, the $H_2S$ Tube was used. When the percentage of $H_2S$ in products became lower than the detection limit of the $H_2S$ indicator Tube, the sampling was performed along with dilution with nitrogen for injecting to a gas chromatographic devise.

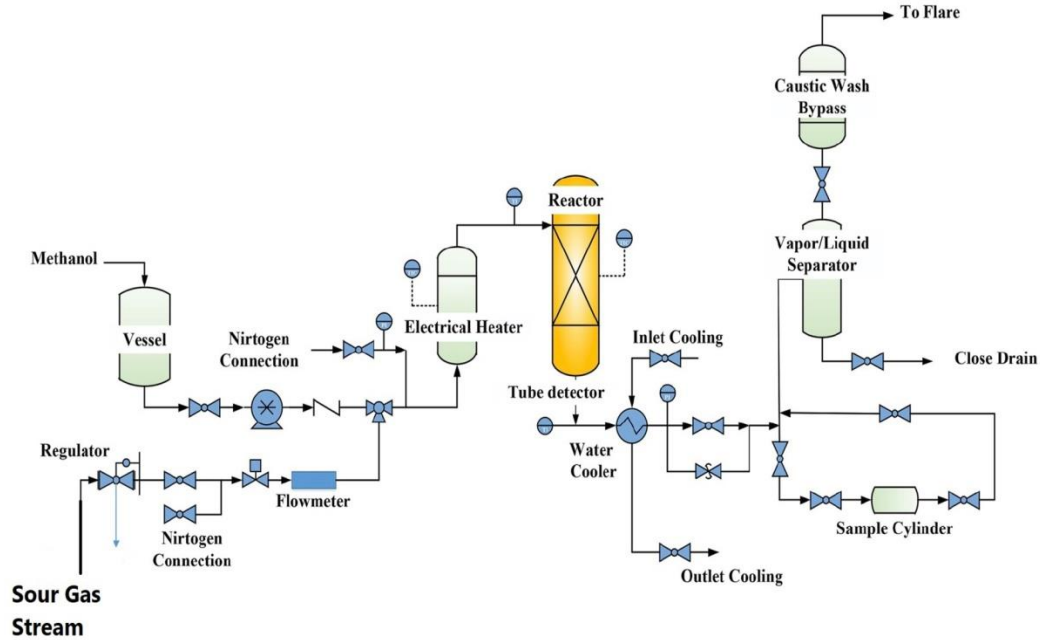


**Fig. 1.** Diagram of the used reactor for methyl mercaptan production from sour gas streams.

*2.4. Kinetic experiments*

The experiments were carried out with a mixture of $CH_3OH$ and $H_2S$ stream in a temperature range of 300-370 K, pressure range of 8-10 bar and WHSV range of 0.66 $h^{-1}$. To avoid the effect of deactivation, fresh catalysts were loaded in each experiment series. The particles were packed to achieve a more uniform bed temperature; the catalyst was loaded in the middle of the reactor and reduced for 3 hours at 673 K and atmospheric. After the catalyst treatment, the process conditions were slowly moved to interest points.

The molar flow rate of each of the components in the feed is calculated as follows:

$$F_i^0 = v_0\, C_i = \frac{v_0\, P_i}{RT} \tag{1}$$

To calculate the consumption rate of each elements, the equation of the differential reactor is used, and consequently, the equation of the plug reactor changed as follows:

$$\frac{W_{cat}}{F_i^0} = \int_{Xi.out}^{Xi,in} \frac{dXi}{-Ri} = \frac{1}{(Ri)_{Ave}} \int_{Xi.out}^{Xi,in} dXi = \frac{Xi,out - Xi,in}{(Ri)_{Ave}} \tag{2}$$

$$(-Ri)_{Ave} = \frac{F_i^{\,0}\,(Xi,out - Xi,in)}{W_{cat}} = \frac{Fi,in - Fi,out}{W_{cat}} \tag{3}$$

$$\frac{W_{cat}}{F_i^0} = \frac{Xi}{-Ri} \tag{4}$$

Hence:

$$-Ri = \frac{F_i^0 Xi}{W_{cat}} \tag{5}$$

Generally, experimental data for the kinetic modeling was collected at various temperatures and is shown in Table 3. After reaching a steady-state, the conversion of $H_2S$ was calculated. In order to investigate the reaction kinetics, the mentioned values were set for conversions to convert the second equation into the third one (dXi → ΔXi). Considering a 2% catalyst deactivation, the catalysts were replaced every 24 hours; after each replacement, the first set of data was considered as the base and subsequently measured again to avoid possible errors like speed changing.

**Table 3.** Experimental data and conditions for methyl mercaptan production kinetic modeling.

| No. | Temperature (C) | $P_{H2S}$ | $P_{CH3OH}$ | $r_{CH3SH}$ (mol/h.g) | $r_{DMS}$ (mol/h.g) | $H_2S$ conversion (%) |
|---|---|---|---|---|---|---|
| 1 | 643.15 | 1.7 | 0.7 | 8.4989 | 0.839 | 35.34 |
| 2 | 643.15 | 1.7 | 1.1 | 9.7945 | 1.9303 | 51.94 |
| 3 | 643.15 | 1.7 | 0.7 | 8.505 | 0.836 | 35.35 |
| 4 | 643.15 | 1.7 | 1.1 | 9.6674 | 1.8637 | 52.01 |
| 5 | 573.15 | 1.7 | 1.1 | 9.731 | 1.782 | 61.09 |
| 6 | 573.15 | 1.7 | 0.7 | 8.565 | 0.506 | 38.75 |
| 7 | 573.15 | 1.7 | 0.7 | 8.4692 | 0.5039 | 38.76 |
| 8 | 573.15 | 1.7 | 1.1 | 9.8074 | 1.6938 | 60.96 |
| 9 | 583.15 | 1.8 | 0.9 | 10.1505 | 1.1354 | 48.63 |
| 10 | 593.15 | 1.8 | 0.9 | 10.2415 | 1.098 | 39.81 |
| 11 | 608.15 | 1.8 | 0.9 | 10.1366 | 1.1423 | 45.33 |
| 12 | 608.15 | 1.8 | 0.9 | 10.2366 | 1.1423 | 45.33 |
| 13 | 608.15 | 1.7 | 1.5 | 11.0868 | 4.5503 | 67.66 |
| 14 | 608.15 | 1.8 | 0.6 | 8.8984 | 0.4527 | 33.35 |
| 15 | 608.15 | 1.8 | 0.9 | 10.1262 | 1.1475 | 45.31 |
| 16 | 608.15 | 1.8 | 0.9 | 10.1417 | 1.1398 | 45.34 |
| 17 | 608.15 | 1.8 | 0.9 | 10.1366 | 1.1423 | 45.33 |

## 3. Results and discussion

Heterogeneous systems assume that the surface properties of catalyst particles remain constant. In other words, the particles preserve their shapes and properties during the reaction. Thus, it can be concluded that this process is actually formed from parallel reactions that progress at a certain rate [14]. In kinetic modeling, it is assumed that each catalytic process must pass eight steps including:

1. The reactant molecules are transferred to the vacancy of the catalyst particles by diffusion or through the transport phenomena.
2. The molecules diffuse between fluid elements to the external surface of the catalyst particle. This is the so-called extra particle diffusion.
3. In the case of non-porous particles, the reactants chemically adsorb on the surface, but in porous particles, the active sites are distributed at the inner surface of the particles, and these molecules must penetrate the pores to reach the sites. This process is called intra-particle diffusion. This diffusion phenomenon can also be modeled using the Stephen Maxwell equations for multicomponent diffusion.
4. The adsorbed molecules begin to react and produce the products as adsorbed molecules. This superficial reaction is an intrinsic reaction stage.
5. The product molecules desorbed from the surface.
6. In the porous particles, products begin to penetrate to the outside of the particles.
7. The products enter the liquid phase through extra particle diffusion.
8. The product molecules leave the vicinity of the catalyst particles by transport phenomena and are directed to the reactor outlet.

Yermakova and Mashkina [2] reported that the kinetic mechanism of this reaction could be described according to the Langmuir-Hinshelwood-Hougen-Watson (LHHW) adsorption theory. In this theory, the reactants adsorbed on the catalyst surface and a reaction occurred between the surface adsorbed species. In other words, two molecules adsorbed on the neighboring sites, and the adsorbed molecules underwent a bimolecular reaction. Considering the above-mentioned assumptions and the results reported by Yermakova and Mashkina, methyl mercaptan synthesis can be demonstrated by the following equations:

$$CH_3OH + H_2S \rightarrow CH_3SH + H_2O \quad (6)$$

$$CH_3SH + CH_3OH \rightarrow (CH_3)_2S + H_2O \quad (7)$$

$$2CH_3SH \rightarrow (CH_3)_2S + H_2S \quad (8)$$

$$2CH_3OH + H_2O \rightarrow (CH_3)_2S + 2H_2O \quad (9)$$

$$2CH_3OH \rightarrow (CH_3)_2O + H_2O \quad (10)$$

$$(CH_3)_2O + CH_3OH \leftrightarrow (CH_3)_2SH + CH_3OH \quad (11)$$

$$(CH_3)_2O + H_2S \leftrightarrow (CH_3)_2SH + CH_3OH \quad (12)$$

It should be noted that in industrial reactors used for methyl mercaptan production, in order to increase the selectivity and consequently reduce the production of dimethyl sulfide as a by-product, the ratio of hydrogen sulfide to methanol in the feed is adjusted between 2 to 3. It is important to note that by ignoring the reaction of dimethyl sulfide production, the conversion of hydrogen sulfide is preferred to high percentage amounts, and the desired product of methyl

mercaptan is obtained at high levels. However, the parallel converting reaction of methyl mercaptan to dimethyl sulfide actually requires methanol. Hence, this reaction produces dimethyl sulfide as an unwanted product and consumes the methanol, which leads to low conversion of hydrogen sulfide to methyl mercaptan. More injection of methanol to the system shifts the reaction towards DMS production. One of the effective ways to increase methyl mercaptan selectivity is reversing or injecting of DMS into the inlet of the reactor, which causes a decrease in the rate of parallel reactions. This act leads to an increase in selectivity, up to 90% for industrial methyl mercaptan production. The analysis of the products showed that methanethiol is the dominant product, which was synthesized through reaction 5. Reactions 6-8 are responsible for the dimethyl sulfide production. The production of dimethyl ether also progressed by means of reaction 9 and was converted to methanethiol via reaction 10-11. These reactions (10-11) can be performed thermodynamically, but their rates will not be mentioned in the final equation [3]. If the active sites on the surface of the catalyst showed by θ and assuming that methanol occupied an active site by losing a hydrogen, the kinetic equations can be calculated as follows:

$$CH_3OH + [\theta] \overset{K_1, K_{-1}}{\longleftrightarrow} CH_3O_s + H_2O \quad (13)$$

$$H_2S + CH_3O_S \overset{k_2}{\rightarrow} CH_3SH + [\theta] \quad (14)$$

$$CH_3SH + CH_3O_S \overset{k_3}{\rightarrow} (CH_3)_2S + [\theta] \quad (15)$$

$$CH_3OH + CH_3O_S \overset{k_4}{\rightarrow} (CH_3)_2O + [\theta] \quad (16)$$

$$H_2O + [\theta] \overset{K_5, K_{-5}}{\longleftrightarrow} H_2O_s \quad (17)$$

By replacing $k_2 = k_{MT}$, $K_1 = k_1/k_{-1}$ and $K_5 = k_5/k_{-5}$

$$r_{MT} = \frac{k_{MT}\, K_1\, P_{H2S}\, P_{CH3OH}}{P_{H2O} + K_1\, P_{CH3OH} + K_5\, P_{H2O}^2} \quad (18)$$

$$r_{DMS} = \frac{k_{DMS}\, K_1\, P_{H2S}\, P_{CH3OH}}{P_{H2O} + K_1\, P_{CH3OH} + K_5\, P_{H2O}^2} \quad (19)$$

As seen in the above equations, it can be understood that decreasing the partial pressure of $H_2S$ leads to an extreme decrease in the rate reaction of methyl mercaptan synthesis. Adding some water to the feed (and subsequently increasing the water partial pressure) decreases the efficiency of both the production reaction rates of methyl mercaptan and DMS synthesis. The methanol partial pressure increases in the reactor and leads to progress in the efficiency of both the methyl mercaptan and DMS reactions. The nonlinear fitting tab from Matlab software (2014 a) was used to obtain the values of the kinetic parameters in Equations 18-19. The estimated coefficients for the kinetic of methyl mercaptan and DMS reactions from the experimental data (Table 3) fitting are listed in Table 4.

**Table 4.** Kinetic parameters values for methyl mercaptan and DMS reaction.

| Parameter name | Value |
|---|---|
| $k_{MT}$ (mmol/g.h.MPa) | 4.19±0.8 |
| $k_{DMS}$ (mmol/g.h.MPa$^2$) | 0.79±0.8 |
| $K_1$ (1/MPa) | 1412.19±0.8 |
| $K_5$ (1/MPa) | 2136.25±0.8 |
| $R^2$ | 0.965 |
| $R^2$adj | 0.963 |
| Rmsd | 4.07E-06 |
| Variance | 2.706E-10 |

The power law equation was used to investigate the activation energy for both the methyl mercaptan and DMS reactions. The power law model is written as

$$r_i = K(P_{H2S}^0)(P_{CH3OH}^0) \quad (20)$$

By incorporating the Arrhenius law in Equation 20:

$$r_i = k_0 \exp(-\frac{E_i}{RT})(P_{H2S}^0)^n (P_{CH3OH}^0)^m \quad (21)$$

The experimental data were fitted to Equation 15 to obtain the kinetic coefficients. All the related coefficients for the consumption equations of methyl mercaptan and DMS are listed in Table 5.

**Table 5.** Coefficients for consumption equations of methyl mercaptan and DMS (power law).

| Variable | Values | |
|---|---|---|
| | $CH_3SH$ | DMS |
| $k_0$ | 2.93 | 3.69 |
| Ea | 53.11 | 129.55 |
| n | 0.69 | 1.74 |
| m | 2.73 | 0.33 |
| $R^2$ | 0.987 | 0.989 |
| $R^2$adj | 0.984 | 0.987 |
| Rmsd | 0.025 | 0.019 |
| Variance | 0.014 | 0.008 |

In Table 5, it can be observed that the $k_0$ value for the DMS reaction is a little greater, and its activation energy is extremely higher than the $CH_3SH$ reaction. These show that the conditions are more suitable for methyl mercaptan production as the dominant product. The results demonstrated that the formation of methyl mercaptan was 0.69-order and 2.73-order with respect to $H_2S$ and methanol, respectively, which indicated that the feed ratio ($H_2S/CH_3OH$) was a crucial parameter in obtaining methyl mercaptan from $H_2S$ streams. By introducing the obtained data to the ASPEN software, a variation in the molar flow rates for each of the components were simulated at the

length of the reactor. As seen in Figure 2, the molar flow rates of $H_2S$ and methanol (reactants) decreased at the length of the reactor, while this trend for the products (methyl mercaptan, DMS, and $H_2O$) was reversed. It should also be noted that the reactions were fast at the inlet of the reactor, which was due to the high concentration of reactants. Consequently, changes occurred with a large slope, but approaching the end of the reactor, this slope became close to zero.

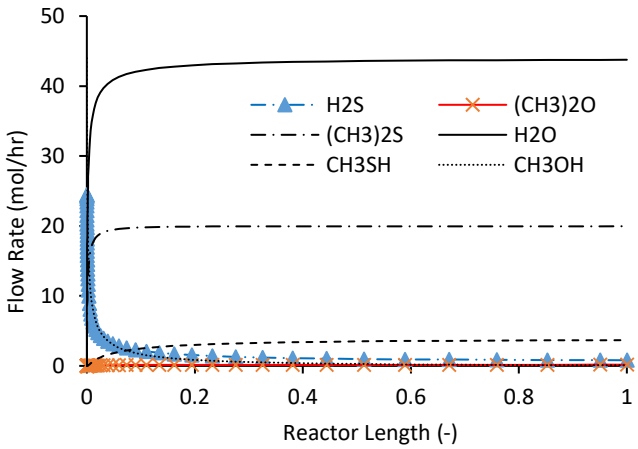


**Fig. 2.** Variation in molar flow rates for each components at length of reactor for methyl mercaptan production process.

## 4. Conclusions

One of the environmental problems in gas refineries and oil companies is the production of waste streams of sulfur that are either burned or enter the atmosphere directly. One way to prevent it is to introduce sulfur-containing streams into the production cycle of valuable products such as methyl mercaptan as a reactant. Sulfur streams can be mixed with a certain ratio of methanol or ethanol and introduced into substrates containing tungstate catalysts to produce this product. This project investigated the reaction kinetics of methyl mercaptan production using a stream containing hydrogen sulfide due to the sweetening of sour gas in the Nori refinery complex to find the limitations of its industrial production. The required data were obtained at various temperatures and a pressure of 10 bars and fitted to related equations using the nonlinear regression method. The rate equations describe the rates of formation of methyl mercaptan as the main product and DMS as the by-product. The main results are listed below.

1- A fixed-bed flow reactor was successfully constructed for the production of methyl mercaptan from the refinery $H_2S$ streams and methanol.
2- A model based on LHHW and power law equations was developed to describe the kinetics of this reaction. The data were successfully fitted with correlation coefficients of more than 0.98.
3- The results demonstrated that the formation of methyl mercaptan was 0.69-order and 2.73-order for $H_2S$ and methanol, respectively.
4- The activation energies for the main product (methyl mercaptan) and by-product (DMS) were 53.11 and 129.55 (kJ/mol), respectively.
5- Adding water to the feed caused a decrease in the rate of both reactions, namely methyl mercaptan and DMS synthesis.
6- Adding more methanol into the reactor resulted in the progress in the efficiency of both the methyl mercaptan and DMS reactions.
7- The results showed that the wasted sulfur-containing streams could be used instead of pure $H_2S$ streams. This substitution not only provides a resource but also curbs the emission of poisonous sulfur compounds into the environment.

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