Gasification and oxidation of thiophene in supercritical water fluids

A A Vostrikov, S A Psarov, D Yu Dubov, M Ya Sokol, A V Shishkin and O N Fedyaeva

Kutateladze Institute of Thermophysics SB RAS,
1 Lavrentyev Avenue, Novosibirsk, 630090, Russia
E-mail: vostrikov@itp.nsc.ru

Abstract. The paper deals with the gasification of thiophene in supercritical water (SCW) at a molar ratio of $\text{H}_2\text{O}:\text{C}_4\text{H}_4\text{S} = 1:0.107$, a temperature of $873−1023$ K, a pressure of $30$ MPa, and a holding time of $150−600$ s in a batch reactor. The gases of $\text{CO}_2$, $\text{CO}$, $\text{H}_2$, $\text{CH}_4$, and $\text{H}_2\text{S}$ were detected in the composition of SCW gasification products. The maximum degree of thiophene gasification (>99.9%) was achieved at $1023$ K and $600$ s. The conversion of thiophene in SCW is described by a pseudo-first-order macro kinetic equation. It was revealed that the oxidation of thiophene in $\text{H}_2\text{O}/\text{O}_2$ mixture at uniform heating of the reactor ($1$ K∙min$^{-1}$) begins at $T \approx 400$ K. The lack of $\text{O}_2$ results in the formation of soot. It is shown that the formation of sulfuric acid during the oxidation of thiophene in the $\text{H}_2\text{O}/\text{O}_2$ mixture causes corrosion of stainless steel.

1. Introduction

Quality analysis of the produced crude oil [1] shows the global trend in the increased density of produced oil and the content of sulfur in it. The high concentration of S-containing compounds in the oil causes corrosion of the pipelines [2,3]. The combustion of fossil fuels leads to the emission of $\text{SO}_2$ into the atmosphere. Studies show [1,4–8] that one method to remove sulfur or sulfur compounds out of fossil fuels can be their conversion in supercritical water (SCW: $T > 647$ K, $P > 22.1$ MPa). According to [9–11], the combustion of fuels in dense water vapor or SCW increases the energy efficiency and environmental safety of heat and electricity production.

Thiophene is one of the most thermally stable S-containing organic compounds. The degree of desulfurization (the proportion of sulfur atoms converted into $\text{H}_2\text{S}$) of thiophene in SCW ($673$ K, $23.5$ MPa, reaction time $31$ min, autoclave with a mixer) does not exceed $5\%$ [12]. When studying [13] desulfurization of thiophene in SCW ($673$ K, exposure time $10-60$ min, autoclave made of Hastelloy C-276 alloy) in the presence of $\text{NaOH}$ ($1–5$ mol·dm$^{-3}$) and iron powder (300 mesh, $0–0.1$ mol), it was revealed that at the maximum values of the exposure time and the concentration of additives, complete desulfurization of thiophene was achieved. The authors [13] assumed that in the presence of $\text{NaOH}$, thiophene desulfurization occurs by an ionic mechanism, while in the absence of iron powder, it is catalyzed by the reactor walls.

From the above, it follows that the conversion of thiophene in SCW was studied at $T \leq 673$ K. The oxidation of thiophene was studied only at $T < 353$ K in organic solvents in the presence of catalysts [14,15]. The purpose of the present work is to investigate the SCW gasification of thiophene, and its oxidation in the $\text{H}_2\text{O}/\text{O}_2$ mixture at $T \leq 1023$ K and $P \leq 30$ MPa.
2. Experimental procedures

The experimental setup used for studying SCW gasification is described in [16]. Batch tube reactor 1 (10 cm³ in volume) was installed vertically in the thermostat 2 (figure 1). The reactor, high-pressure vessel for SCW preparation 3, collector 4, receiver 5, and their connecting fittings are made of AISI 321H steel. As shown by studies [3,5,6,8], when operating with S-containing substances, the reactor wall was subjected to sulfidation. Therefore, before the experiment, the reactor wall was passivated four times for 60 min in a mixture of H₂O/C₄H₄S = 1/0.214 mol mol⁻¹ at 1023 K. The temperature of the reactor wall was controlled by chromel-alumel thermocouples 6, the pressure in the reactor was measured by a membrane strain sensor 7. Before the experiment, all working volumes were pumped out using a forepump 8.

![Figure 1. Schematic diagram of the experimental setup: 1 – reactor; 2 – thermostat; 3 – high-pressure vessel for SCW preparation; 4 – collector for the products with a nitrogen trap; 5 – receiver of mass spectrometer; 6 – thermocouples; 7 – membrane strain sensor; 8 – forepump; 9 – valve for introducing SCW into the reactor; 10 – thiophene input system; 11 – product discharge valve; 12 – vacuum gauge; 13 – vessel with liquid nitrogen.](image)

A system with a pneumatic multiplier 10 (figure 1) was used to quickly inject thiophene into the reactor. Thiophene was filled into the injection system in a certain amount at room temperature using a syringe. After achieving a pressure of 30 MPa in the reactor at a given temperature, thiophene was injected into the reactor. After the specified time lag, the valve 9 was closed, and the products from the reactor were discharged into the collector 4 through the valve 11. The composition of the gas mixture was determined using the MS 7303 mass spectrometer by the method [17]. The solid residue was analyzed using a D8 Advance X-ray diffractometer.

The temperature and initial amounts of reagents are shown in table 1. In all experiments, the mass ratio of C₄H₄S/H₂O = 0.5 (molar ratio 0.107) that provided an excess of H₂O even at complete gasification of thiophene during the reaction

\[
\text{C}_4\text{H}_4\text{S}^{(g)} + 8\text{H}_2\text{O} \rightarrow 4\text{CO}_2 + 9\text{H}_2 + \text{H}_2\text{S}, \quad \Delta H_{298}^{\circ} = +125 \text{ kJ mol}^{-1}.
\]  

Here and below, the values of \( \Delta H_{298}^{\circ} \) were calculated based on the reference data [18]. The holding time \( t_r \) in the experiments at each temperature was 150, 300, and 600 s. A total of 12 experiments were conducted.

| \( T \) (K) | \( n_{\text{H}(2)\text{O},0} \) (mmol) | \( n_{\text{C}\text{H}(4)\text{S},0} \) (mmol) | \( \alpha(600 \text{ s}) \) (%) |
|---|---|---|---|
| 873 | 48.5 | 5.2 | 19.1 |
| 933 | 43.3 | 4.6 | 66.3 |
| 983 | 40.1 | 4.3 | 97.2 |
| 1023 | 37.9 | 4.1 | >99.9 |
The oxidation of thiophene in the H2O/O2 mixture was performed using an experimental setup [19] with a tube reactor 65.7 cm² in volume, as the main element. The reactor heating was controlled using a thermal programmer and a chromel-alumel thermocouple Tout mounted on the outer wall of the reactor. The temperature of the reaction mixture Tin was measured by a Pt-Rh/Pt thermocouple inserted into the center of the reaction volume. The pressure of the reaction mixture was measured by a membrane strain sensor. Time dependences of temperature and pressure were recorded with a frequency of 10 Hz.

Reagents (thiophene, water, and oxygen) were filled into the reactor at T = 303 K. Stoichiometric and enriched mixtures (fuel equivalence ratio φ = 1.0 and 1.3) were used in the experiments according to the following reaction

\[ \text{C}_4\text{H}_8\text{S}^{(g)} + 6.5\text{O}_2 \rightarrow 4\text{CO}_2 + \text{H}_2\text{O} + \text{H}_2\text{SO}_4^{(g)}, \quad \Delta H_{298} = -2276 \text{ kJ mol}^{-1}. \]  

(2)

The molar ratio of C4H8S/H2O was 1/5. The reactor was heated at a rate of 1 K min⁻¹ to 873 K. After cooling the reactor, volatile oxidation products were analyzed using a mass spectrometer.

3. Results and discussion

After each experiment, the following products were detected: C4H8S, CO2, CO, H2, CH4, H2S, COS, and benzene, the ratio of which depended on the temperature. Figure 2 shows the time dependencies of the yield of these products, calculated using the formula \( x = n_j / n_{C4HS,0} \), where \( n_j \) is the number of moles of the \( j \)-th product. From the comparison of these data with the products of reaction (1), it follows that the gasification of thiophene in all the experiments was incomplete. Close values of H2 and CO2 concentrations (figure 2c and 2d, respectively) indicate that H2 and CO2 are formed mainly through the water gas shift reaction

\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2, \quad \Delta H_{298} = -41.2 \text{ kJ mol}^{-1}. \]  

(3)

According to [20], at \( T \leq 723 \text{ K} \), benzene is oxidized in SCW to form CO2, hydrocarbons, H2, CO, and carbonized residue. The study of benzene combustion in SCW/O2 fluid [21] has shown that the composition of volatile products was dominated by CO2 and H2O. The total proportion of CH4, CO, H2, toluene, and xylene did not exceed 3% mol. From the results [20,21] and the data presented in figure 2, it follows that at \( T < 1023 \text{ K} \), benzene is converted in SCW mainly into CO2, CH4, CO, and H2. Based on this, the conversion of benzene in SCW can be described by the following reaction

\[ \text{C}_6\text{H}_6 + 3\text{H}_2\text{O} \rightarrow 3\text{CO} + 3\text{CH}_4, \quad \Delta H_{298} = +87.2 \text{ kJ mol}^{-1}. \]  

(4)

The high methane content in the products (figure 2e) indicates that under the conditions of the present work, steam reforming was incomplete.

During pyrolysis of thiophene within the temperature range of 1598–2022 K, C2H2, C2H2SH, H2S, CS2, CH4, saturated and unsaturated hydrocarbons C2–C4, and benzene were formed [22]. After the conversion of thiophene in liquid water (573 K, reaction time 28 days, quartz autoclave), CO2, CO, H2, CH4, H2S gases, and C2–C4 hydrocarbons were detected [23]. When converting thiophene in SCW with the addition of 10% H3PO4 (623 K, reaction time 5 days, stainless steel autoclave), tetrahydrothiophene, 2-methyl-tetrahydrothiophene, alkyl derivatives of thiophene, and benzene were detected in the reaction products [24]. A comparison of the product composition and yield shows that both hydrogenation and oxidation of thiophene occurs in SCW, while at \( T > 873 \text{ K} \), high-molecular compounds are gasified through steam reforming and water gas shift reactions.

According to X-ray diffraction analysis, the solid carbonized residue of the thiophene gasification in SCW consisted of \( \approx 80\% \) of amorphous carbon. Metal oxides and sulfides (Fe3O4, Fe1.5S, CuFeS2, CuFe2O4, and Cu2(Fe,Ni)3InS4), included in structural materials, were \( \approx 20\% \).

Taking into account reactions (3) and (4), the thiophene gasification reaction (the formation of a solid carbonized residue is neglected due to its chemical inertia and a small amount) can be written as

\[ \text{C}_4\text{H}_8\text{S} + (a_1 + a_3)\text{H}_2\text{O} \rightarrow a_1\text{CO} + a_2\text{CH}_4 + (1 - a_3)\text{H}_2\text{S} + a_3\text{COS} + a_3\text{C}_6\text{H}_6. \]  

(5)
Figure 2. Time dependences of the product yield obtained during SCW gasification of thiophene: \( a - C_6H_6, b - H_2S, c - H_2, d - CO_2, e - CH_4, f - CO, g - C_6H_6, h - COS; \) symbols are the experimental data: 1 – 873 K, 2 – 933 K, 3 – 983 K, 4 – 1023 K; curves are the quantities calculated taking into account reactions (3)–(5) and equations (6)–(8).

The component material balance condition allows obtaining \( a_3 = \frac{2 - 3(a_1 - a_2)}{5}; \) \( a_4 = \frac{4 - a_1 - a_2 - a_3}{6}. \) Only \( a_1 \) and \( a_2 \) stoichiometric coefficients remain unknown. Since the ratio of COS:H\(_2\)S obtained in experiments is close to the equilibrium and small within the entire temperature range under study, the redistribution of sulfur atoms between COS and H\(_2\)S can be ignored. Based on reactions (3)–(5), the simplest kinetic model of thiophene gasification in the SCW can be composed. Taking into account incomplete gasification of thiophene, the conversion rates of substances in the SCW in reactions (3)–(5) were written as pseudo-first-order equations, while for the temperature dependence of the rate constants, the Arrhenius equation \( k = k_0 \exp\left(-\frac{E_a}{RT}\right) \) was adopted. Here \( k_0 \) is the frequency factor (s\(^{-1}\)), \( E_a \) is the effective activation energy (kJ mol\(^{-1}\)), and \( R \) is the universal gas constant. When solving the system of equations, the sum of squares of relative deviations of the calculated amount of each substance from its experimental value was minimized. As a result, the following equations for the reaction rate constants (3)–(5) were obtained:

\[
k_3 = 10^{1.3\pm0.2}\exp\left(-\frac{79\pm7}{RT}\right),
\]

\[
k_4 = 10^{16.4\pm0.6}\exp\left(-\frac{370\pm20}{RT}\right),
\]

\[
k_5 = 10^{11.4\pm0.8}\exp\left(-\frac{250\pm22}{RT}\right).
\]

The parameter values for the \( k_3 \) constant are consistent with the set of known data on the macro kinetic description of the water gas shift reaction conducted using iron/chromium-oxide catalysts [24].
The constant $k_5$ showed a good correspondence with the constant obtained in [22] when describing the rate of pyrolysis of thiophene by a first-order kinetic equation within the temperature range of 1019–1233 K ($k_0 = 2.2 \cdot 10^{11} \text{s}^{-1}$, $E_a = 270 \pm 10 \text{ kJ mol}^{-1}$).

The time dependences of the amount of each substance detected in the experiments, calculated according to the constants $k_3$–$k_5$, are shown as curves in figure 2. It can be seen that the obtained description of experimental points is satisfactory. For the stoichiometric coefficients of the reaction (5) at $t_r = 600 \text{s}$ and $T = 983$–1023 K ($k_0 = 2.2 \cdot 10^{11} \text{s}^{-1}$, $E_a = 270 \pm 10 \text{ kJ mol}^{-1}$),

The enthalpy of the reaction (5) in this case is equal to $-60.6 \text{ kJ mol}^{-1}$. It follows that the thiophene gasification in the SCW, as well as gasification of naphthalene in the SCW [16], proceeds with the heat release.

Table 1 shows the degree of thiophene gasification $\alpha = (1 - n_{\text{C}_4\text{H}_4\text{S},f})/n_{\text{C}_4\text{H}_4\text{S,0}}$, where $n_{\text{C}_4\text{H}_4\text{S},f}$ is the amount of thiophene detected in the collector (figure 2a) after the experiment at $t_r = 600 \text{s}$ for each temperature, while $n_{\text{C}_4\text{H}_4\text{S,0}}$ is the initial amount of thiophene. A comparison of these values with the conversion degree of thiophene obtained in [12,23] shows that the rate of SCW gasification of thiophene increases sharply at $T > 823 \text{ K}$.

Figure 3 shows the time dependences of the temperature difference between the reaction mixture and the outer wall of the reactor, as well as the pressure of the reaction mixture when thiophene is oxidized in water vapor with a lack of $\text{O}_2$. It can be seen that the oxidation of thiophene in water vapor begins at a lower temperature ($\approx 400 \text{ K}$) compared to the gasification and thermal decomposition (figure 2). The fact that the dependence $\Delta T(t)$ (figure 3a) did not move to the positive range of values $\Delta T$ (figure 3a) indicates that heterogeneous reactions on the reactor wall prevailed during the oxidation of thiophene in water vapor. The decline of the curve $\Delta T(t)$ at $T_{\text{out}} = 550–580 \text{ K}$ may result from endothermic pyrolysis and steam reforming reactions. The type of time dependences of pressure and the rate of pressure change reflects (figure 3b) the thiophene and water evaporation processes (according to [18], thiophene and water should have completely evaporated at 424 and 502 K), as well as changes in the number of species in the gas phase resulted from oxidation and thermolysis.

In the composition of the partial oxidation products of thiophene in water vapor, $\text{CO}_2$, $\text{CO}$, $\text{C}_4\text{H}_4\text{S}$, and a large amount of soot were detected. An increase in the $\text{O}_2$ content in the reaction mixture reduces the yield of soot. In contrast to the SCW gasification of thiophene, in which the main S-containing product is $\text{H}_2\text{S}$, the oxidation of thiophene in the $\text{H}_2\text{O}/\text{O}_2$ mixture is accompanied by the formation of sulfuric acid, which, in turn, causes corrosion of stainless steel.
Conclusion
The gasification of thiophene in SCW was studied at temperatures of 873−1023 K and a pressure of 30 MPa. During the conducted research, CO₂, CO, H₂, CH₄, and H₂S were detected in the gasification products. The solid carbonized residue of SCW gasification of thiophene contains amorphous carbon, as well as metal oxides and sulfides that are part of constructional materials. The SCW gasification of thiophene is described by a pseudo-first-order macro kinetic equation. The maximum SCW gasification degree of thiophene is achieved at 1023 K and a reaction time of 600 s. It was revealed that the oxidation of thiophene in the H₂O/O₂ mixture begins at a lower temperature than gasification and thermal decomposition. The formation of H₂SO₄ as a result of thiophene oxidation leads to the corrosion of stainless steel. From the results obtained, it follows that the combustion of S-containing fuels in the H₂O/O₂ mixture should be carried out with an excess of O₂ and in the presence of additives that neutralize sulfuric acid.

References
[1] Demirbas A, Alidrisi H and Balubaid M A 2015 Petrol. Sci. Technol. 33 93
[2] Meriem-Benziane M, Bou-Said B and Boudouani N 2017 J. Petrol. Sci. Engin. 158 672
[3] Vostrikov A A, Fedyaeva O N, Shishkin A V, and Sokol M Ya 2017 J. Eng. Thermophys. 126 314
[4] Demirbas A 2016 Petrol. Sci. Technol. 34 622
[5] Fedyaeva O N and Vostrikov A A 2016 J. Supercrit. Fluids 111 121
[6] Fedyaeva O N, Antipenko V R and Vostrikov A A 2014 J. Supercrit. Fluids 88 105
[7] Fedyaeva O N and Vostrikov A A 2013 J. Supercrit. Fluids 83 86
[8] Fedyaeva O N, Antipenko V R, Dubov D Yu, Kruglyakova T V and Vostrikov A A 2016 J. Supercrit. Fluids 109 157
[9] Queiroz J P S, Bermejo M D, Mato F, and Cocero M J 2015 J. Supercrit. Fluids 96 103
[10] Yan Q, Hou Y, Luo J, Miao H, and Zhang H Energy Conv. Management 129 122
[11] Chen Z, Zhang X, Li S and Gao L 2017 Energy 134 933
[12] Patwardhan P R, Timko M T, Class C A, Bonomi R E, Kida Y, Hernandez H H, Tester J W, Green W H 2013 Energy & Fuels 27 6108
[13] Yoshida S, Takewaki K, Miwa K, Wakai C, and Nakahara M 2004 Chem. Lett. 33 330
[14] Kong L, Li G and Wang X 2004 Catalysis Letters 92 163
[15] Zhao D S, Zhou E P, Wang J L, Li F T, and Wang N 2008 Petrol. Sci. Technol. 26 1099
[16] Vostrikov A A, Dubov D Yu, and Psarov S A 2001 Rus. Chem. Bul. Int. Ed. 50 1480
[17] Fedyaeva O N, Vostrikov A A, Shishkin A V, Sokol M Y, Fedorova N I and Kashirtsev V A 2012 J. Supercrit. Fluids 62 155
[18] Lemmon E W, McLinden M O and Friend D G 2018 Thermophysical properties of fluid systems in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, ed P J Linstrom and W G Mallard (Gaithersburg MD, 20899: National Institute of Standards and Technology) https://webbook.nist.gov/chemistry/fluid/
[19] Fedyaeva O N, Artamonov D O, and Vostrikov A A 2019 Combust. Flame 210 183
[20] Yong T L-K and Matsumura Y 2013 J. Jap. Petrol. Inst. 56 331
[21] Vostrikov A A and Psarov S A 2004 Tech. Phys. Let. 30 96
[22] Memon H U R, Williams A, and Williams P T 2003 Int. J. Energy Res. 27 225
[23] Clark P D, Hyne J B and Tyrer J D 1984 Fuel 63 125
[24] Smith B R J, Loganathan M, and Shantha M S 2010 Int. J. Chem. React. Eng. 8 Review R4