Conversion of Carbonyl Sulfide Using a Low-Temperature Discharge Approach

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Abstract

Carbonyl sulfide (COS) are usually yielded from the petrifaction industry or steel-making plants. In this study, a low-temperature radio-frequency (RF) plasma approach was used to destruct COS for removing sulfur. The results showed that at an inlet O2/COS molar ratio of 3, the removal efficiency of COS reached 98.4% at 20 W and 4000 N/m², with the major product being SO2 with small amounts of sulfur deposition. The removal efficiency of COS was lower in the H2-containing condition than in the O2-containing one. However, when H2 was added into the COS/N2 mixtures, the products, including major elemental sulfur with CS2 as a minor product, were easily collected and recovered.

Keywords: Carbonyl sulfide; RF plasma; Destruction; Acid rain; Sulfur.

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INTRODUCTION

Carbonyl sulfide (COS) is an odourless, tasteless and colourless polar gas molecule with a boiling point of -50.2°C, which is relatively different from other sulfur-containing impurities of hydrocarbon feedstocks (Adewuyi and Carmichael, 1987). The major emission sources of COS are the conversion of fossil fuels, steel-making plants, and waste landfills. In addition, during the high temperature stage of the Claus process, the formation of COS results from hydrocarbons being present in the flue gas according to the following reactions.

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{S} &= \text{COS} + \text{H}_2\text{O} \quad (1) \\
\text{CH}_4 + \text{SO}_2 &= \text{COS} + \text{H}_2\text{O} + \text{H}_2 \quad (2)
\end{align*}
\]

However, COS that is emitted into the atmospheric environment will not only contribute to the formation of SO₂ and promote photochemical reactions, but will also have an effect on the climate (Lelieveld and Heintzenberg, 1992).

The tail gas from Claus Plants is usually incinerated and COS and CS₂ are converted to the harmful SO₂. CaO is then used as an absorbent to produce CaSO₄ (Borgwardt et al., 1987), though it is not economically viable. An alternative method of reducing the levels of COS involves hydrogenation, which takes advantage of the hydrogen present in the Claus process via reaction (3) by using a Co-Mo-Al₂O₃ type catalyst (Tong et al., 1992; Rhodes, et al., 2000).

\[
\text{COS} + 4\text{H}_2 = \text{H}_2\text{S} + \text{CH}_4 + \text{H}_2\text{O} \quad (3)
\]

In addition, the removal of COS can be carried out using SO₂ to oxidize COS to carbon dioxide and elemental sulfur (SO₂ + 2COS = 2CO₂ + S) (Rhodes et al., 2000). Recently, among the catalytic methods, COS hydrolysis has been recognized as the promising process due to the mild reaction conditions and higher conversion via the reaction (4) (Zhang et al., 2004).

\[
\text{COS} + \text{H}_2\text{O} = \text{H}_2\text{S} + \text{CO}_2 \quad (4)
\]

Odorous and toxic H₂S formed from reactions (3) and (4) need to be further removed using the Claus reaction (2H₂S + SO₂ = 3S + 2H₂O) to produce elemental sulfur (Clark et al., 2001). However, some problems that are caused by the catalytic methods, such as the reduction of catalytic activity, the poison of catalysts, and product selectivities, can be further improved.

So far, the discharge process used to recover sulfur from a high concentration of COS has not been studied. A 13.56 MHz radio frequency (RF) source is commonly used in industry for generating energetic electrons (1-10 eV) to drive electron impact dissociation and penning
dissociation processes. Therefore, conventional reactions that need to be achieved at higher activation energy can now be done at a relatively low gas temperature. The RF plasma approach has been successfully applied to recover elemental sulfur from SO₂ and CS₂ (Tsai et al., 2002; 2004).

Therefore, the objective of this study is to preliminarily demonstrate the RF discharge approach with a dry, low-temperature, non-catalytic, single removal process to convert COS yielding elemental sulfur and CS₂ that can be easily recovered. Moreover, this discharge approach did not yield the major product as H₂S to avoid the requirement of the sequential Claus reaction which is converted H₂S into elemental sulfur.

EXPERIMENTAL SECTION

The experimental setup (Fig. 1) applied here is similar to that used in previous investigations on the destruction of hazardous air pollutants (Tsai et al., 2004; Wang et al., 2005). A laboratory scale reactor that was wrapped by two external copper electrodes coupled to a 13.56 MHz RF generator (Fritz Huttinger Elektronik GmbH, PFG 600) with a matching network (Matchbox PFM) was used. The cylindrical glass reactor (length of 15 cm and inner diameter of 4.2 cm) was mounted vertically. An interval of about 0.6 cm-width with 1.73-slope between the two electrodes (5.5 cm-high) of copper material was set up in order to obtain an optimal matching network for the investigation. Also, to avoid their participating in the plasma-chemical reactions, the electrodes were arranged on the outside of reactor so as to create a capacitor that enables capacitive coupling power into the discharge zone.

![Experimental apparatus and flowcharts.](image)
When the reaction experiments were in process, an in-line Fourier transform infrared (FTIR) spectrometer (Bio-Rad, Model FTS-7) downstream of the reactor was used for quantifying compounds including COS, SO₂, CS₂, CH₄, C₂H₂, C₂H₄, CO and CO₂. Moreover, the samples were injected into the gas chromatograph (GC, HP 6890, column is G.S.Q, 30 m × 0.53 mm) equipped with a pulsed flame photometric detector (PFPD) to identify sulfur-containing compounds and to check the accuracy of the results.

Comprehensive ranges of experimental conditions, including an inlet H₂/COS molar ratio (RH₂) of 0-4.5, inlet O₂/COS molar ratio (RO₂) of 3, applied power (20-90 W) at room temperature (about 300 K), and an inlet COS molar fraction (COS) of 5% with a total flow rate of 200 mL/min (at STP) were probed for COS conversion. The flow rates of high-purity COS (Merck), H₂ or O₂ with balanced N₂, were regulated by mass flow controllers. The gases were introduced into a gas mixer, and then conducted into the RF plasma reactor to perform the experiments. All tests were done at a lower operating pressure (1333 or 4000 N/m²) in order to generate and keep a discharge with a lower effluent temperature.

**RESULTS AND DISCUSSION**

**Removal efficiency of COS at various inlet H₂/COS molar ratios and operating pressures**

In order to examine the influences of the inlet H₂/COS molar ratios (RH₂) at two levels of operating pressure on the removal efficiency of COS (RECOS), the experiments were carried out at a fixed 30 W. Fig. 2 shows that a higher RECOS can be achieved at a lower RH₂ and a lower pressure. As RH₂ increased from 0 (without H₂) to 4.5 at 30 W, RECOS decreased slightly from 99.8% to 97.7% at a lower pressure (1333 N/m²), whereas the RECOS reduced significantly from 89.2% to 73.4% at a higher pressure (4000 N/m²) (Fig. 2). At a higher operating pressure, electrons move in a shorter mean free path, resulting in lower mean electron energy that gathers a lower reaction rate of nonelastic collisions (Roth, 1995). Thus, less COS molecules were dissociated and a lower RECOS was achieved. However, because a higher pressure is preferred for practical operation in the future, the sequential experiments were carried out at 4000 N/m² to keep the discharge working. In addition, a higher RH₂ value means a higher feeding concentration of hydrogen, which consumes parts of the energetic species in the discharge zone and decreases RECOS.
Fig. 2. The removal efficiencies of COS for various operating pressures and inlet H\textsubscript{2}/COS molar ratios at 30 W.

**Removal efficiency of COS at various additives and applied powers**

Fig. 3 shows RECOS in the RF plasma with no additive, RO\textsubscript{2} = 3, and RH\textsubscript{2} = 0.6 and 3, at an applied power of 20-90 W. For the no additive condition, RECOS increased from 88.0% to 98.0% by elevating power from 20 W to 90 W, indicating that the RF plasma process was adequate for converting pure COS in N\textsubscript{2}. However, when an additive (H\textsubscript{2} or O\textsubscript{2}) was added, different RECOS trends were found. The addition of O\textsubscript{2} resulted in the elevation of RECOS, while adding H\textsubscript{2} reduced RECOS because the oxidation of COS and dissociated fragments is rapid and can prevent the recombination of COS. However, when H\textsubscript{2} molecules were added and attached to the energetic species, the reaction rate of H\textsubscript{2} or H reacting with COS or dissociated compounds was not enough to elevate RECOS, especially at a higher inlet H\textsubscript{2} concentration. When the power was increased from 20 W to 90 W, RECOS increased slightly from 98.4% to 99.8% at RO\textsubscript{2} = 3. This was much higher than the increases for RH\textsubscript{2} = 3, where RECOS rose from 64.3% to 97.0% (Fig. 3). Moreover, at RH\textsubscript{2} = 0.6, RECOS decrease only a little less than in the no H\textsubscript{2} condition.

In addition, RECOS at 20 W was apparently lower than that at 90 W except with the addition of O\textsubscript{2} (Fig. 3), which reveals that a higher discharge power results in a higher removal efficiency. This is because the larger plasma density resulted in the elevation the probabilities of electron impact dissociation or penning dissociation. However, the influence of applied power on RECOS apparently weakens at a power greater than 60 W because RECOS was greater than 95% regardless of what additive was added (Fig. 3).
Comparisons of sulfur-containing products using different additives

Though the addition of O2 improved RECOS, the sulfur-containing product patterns in Table 1 revealed that the major product was harmful SO2 with elemental sulfur (minor) and CS2 (trace amount, the fraction of sulfur atoms that converted from COS to CS2 was less than 0.2%). Because the bond dissociation energy for OS = O (131.8 kcal/mol) is much higher than that for SC = S (102.7 kcal/mol), SO2 is the most dominant S-containing end product in COS/O2/N2 plasmachemical reactions and can be formed via the following reactions:

\[
\begin{align*}
\text{COS} + \text{O} & = \text{SO} + \text{CO} \quad (5) \\
\text{O}_2 + \text{S} & = \text{O} + \text{SO} \quad (6) \\
\text{SO} + ((\text{O}+\text{M}), \text{O}_2, \text{SO}) & = \text{SO}_2 + (\text{M}, \text{O}, \text{S}) \quad (7)
\end{align*}
\]

However, SO2 is still an important air pollutant that causes acid deposition. Hence, adding O2 to remove COS is not the best choice. A better alternative is to convert COS into mainly elemental sulfur and CS2, which are easily recovered through solid and liquid form, respectively. Table 1 showed that COS with/without H2 addition can be removed by yielding elemental sulfur (major, expressed as S1, which was calculated by the mass balance of S atoms) and CS2 as the minor sulfur-containing product with only trace amounts of SO2 (the fraction of sulfur atoms that converted from COS to SO2 was about 0.2-2.96%).
Table 1. Comparison of sulfur-containing products after different additives were added into the COS/N₂ mixtures at an applied power of 20-90 W.

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>COS without additive</th>
<th>Inlet H₂/COS ratio = 3</th>
<th>Inlet O₂/COS ratio = 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Major</strong></td>
<td>Elemental sulfur (87.1%-94.1%)*</td>
<td>Elemental sulfur (77.7%-92.8%)</td>
<td>SO₂ (86.6%-97.4%)</td>
</tr>
<tr>
<td><strong>Minor</strong></td>
<td>CS₂ (2.32%-4.98%)*</td>
<td>CS₂ (3.48%-10.8%)</td>
<td>Elemental sulfur (2.24%-13.3%)</td>
</tr>
<tr>
<td><strong>Trace</strong></td>
<td>SO₂ (1.21%-2.96%)*</td>
<td>SO₂ (0.20%-0.63%)</td>
<td>CS₂ (0.04%-0.19%)</td>
</tr>
</tbody>
</table>

*:in parenthesis means the mass fraction of sulfur atoms converted from COS into elemental sulfur (S₁), CS₂ or SO₂, respectively.

Importantly, no detectable H₂S was found, which is very different from traditional catalytic reactions, such as COS hydrogenation (reaction (3)) and hydrolysis of COS and CS₂ (reaction (4)) that produce H₂S as the major product first, and then remove H₂S via producing elemental sulfur through the Claus reaction. The results indicate that the RF discharge process can directly convert COS into recoverable elemental sulfur or CS₂ with/without H₂ addition. Moreover, no H₂S is yielded because the bond dissociation energy of HS-H (92.0 kcal/mol) and S-H (83.5 kcal/mol) in H₂S was apparently lower than that of SC = S (102.7 kcal/mol) and C = S (170.5 kcal/mol) in CS₂. Hence, CS₂ is more thermodynamic stable than H₂S. In addition, even H₂S was yielded; it would be easily dissociated through reacting with O to form SO as the precursor of product SO₂. These properties favored the existence of CS to the formation of CS₂ other than H₂S in the H₂/COS/N₂ plasma.

However, the difference between H₂ and no H₂ addition conditions is the yield of sulfur-containing products: more elemental sulfur and SO₂ were found in the no H₂ environment (that is, COS plasmalysis), while more CS₂ was detected when H₂ was added. CS₂ can be easily recovery in liquid form when the temperature is lower than the boiling point (46.25°C); hence, CS₂ can be more easily collected than elemental sulfur, making the H₂/COS/N₂ plasma approach a potential solution.
CONCLUSIONS

In this study, high concentration of COS was successfully destructed and converted into other sulfur-containing products by adding H2 or O2, or without an additive, utilizing a low-pressure RF discharge approach. The important finding is that no H2S was detected, which is very different from the traditional catalytic removal process, including COS hydrogenation (\(\text{COS} + 4\text{H}_2 = \text{H}_2\text{S} + \text{CH}_4 + \text{H}_2\text{O}\)) and hydrolysis of COS and CS2 (\(\text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2\)). The discharge approach replaced major product H2S with elemental sulfur that can be easily recovered with or without H2, and can avoid the requirement of the sequential Claus reaction in order to convert H2S into elemental sulfur. However, due to the relatively low pressure, this approach is not currently practical.

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