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Effect of O_2 enrichment on acid gas oxidation and formation of COS and CS_2 in a rich diffusion flame

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HIGHLIGHTS

- Oxidation of acid gas in a non-premixed flame was studied under oxygen enriched condition.
- Reactivity of CO_2 was significantly promoted in an O_2 enhanced flame.
- COS could be initially formed in the flame inner core by reaction involving CO_2 and sulfur species.
- Formation of COS and CS_2 is promoted under O_2 enriched combustion.

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ABSTRACT

O_2 enriched combustion is applied to a non-premixed acid gas (AG) flame, in which AG and air are injected separately into a vertical reactor via a coaxial burner at atmosphere pressure. Equilibrium predictions of AG oxidation were performed using Aspen Plus and lab-scale experiments with particular focus on formation of COS and CS_2 were undertaken under different combustion conditions. The effects of equivalence ratio ($\Phi = 0.8$, 1.0 and 3.0) and initial O_2 concentration (OC) in air (21, 30 and 50 vol%) have been studied and the flame is interpreted by analyzing the axial temperature and species concentration distributions along the reactor.

AG diffusion flame could be divided into three zones, namely AG decomposition, oxidation and complex reaction zones, among which decomposition zone is tightly associated with formation of COS and CS_2. It is shown that Φ generally determines the flame temperature and controls the H_2S oxidation degree and production rate of H_2 and CO. Reactivity of CO_2 primarily expressed via $CO_2 + H = CO + OH$ during the fuel rich flame. COS is primarily produced in the flame inner core via reactions jointing CO_2 and sulfur species, consequently its formation shows a low sensitivity to Φ in the air-supplied flame. O_2 enrichment basically contributes to higher flame temperature, accelerated H_2S oxidation and advanced CO production. Also an increasing tendency for H_2S to decompose into H_2 and S_2 can be observed. And this factor directly triggers the formation of COS and CS_2 via increasing the presence of CO and sulfur species. COS is formed within extended channels involving the primary production by reaction of $SH + CO_2$ and the secondary by reactions between CO and sulfur species. The CS_2 formation is more complex, mainly comprises of reactions involving CS intermediate and evidently it is enhanced under O_2 enriched combustion.

1. Introduction

Hydrogen sulfide can be widely spotted in raw natural gas. Also it is a significant by-product during various fossil fuel processing industries covering gas sweetening, gasification of coal or biomass and any other desulfuration facilities [1,2]. Generally the industrial AG, which is mainly composed of H_2S and CO_2, can be treated by the modified Claus process to recover H_2S into valuable elemental sulfur. This process consists of two sections, a highly exothermal thermal part in which a portion of H_2S is oxidized into SO_2, and a catalytic reaction part wherein SO_2 reacts with the unburned H_2S to produce elementary sulfur over catalyst bed [1–3]. The principal reactions of the Claus process can be written as follows:

$$H_2\,S + 1.5O_2 \rightarrow SO_2 + H_2O \tag{R1}$$

$$2H_2\,S + SO_2 \rightarrow 1.5S_2 + 2H_2O \tag{R2}$$

Partial oxidation of H_2S (R1), as the fundamental and the most complicated step for the Claus process, has been intensively studied

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Nomenclature

Abbreviations

TCD	thermal conductivity detector
FID	flame ionization detector
FPD	flame photometric detector
AG	acid gas
OC	oxygen concentration, vol.%

Latin symbols

R	reaction
V_{air}	volume flow rate of the air, L/min
V_{H2S}	volume flow rate of H_2S, L/min
V_{N2}	volume flow rate of N_2, L/min
m_{fuel}	mass flow rate of the fuel, kg/min
m_{air}	mass flow rate of the air, kg/min
E_{Φ}	uncertainty of the equivalence ratio, %
E_{OC}	uncertainty of the oxygen concentration, %
E_c	theoretical recycled heat, kJ/h
D	dimensionless axial distance
C_i	conversion rate of species i, %
S_i	product selectivity of species i, %
LHV_i	lower heating value of species i on mole basis, kJ/mol
C_P	specific heat capacity on mole basis, J/(K-mol)

Greek symbols

Φ	equivalence ratio
η_C	heat recycling efficiency of cooling unit, %
η	energy efficiency, %
δV	flow rate controlling resolution, L/min

subscripts

act	actual condition
sto	stoichiometric condition
max	maximum value

during the past decades [4–9]. The structure of H_2S/air diffusion flame under the Claus condition ($\Phi = 3$) can be separated into three zones according to Bernez-Cambot et al. [10]. Motivated by the oxidation heat, H_2S decomposition occurred at the nozzle vicinity and caused initial H_2 and sulfur productions at the first zone. The mixing and combustion was involved in the second zone wherein major oxidation heat was released and SO_2 and H_2O were intensively formed. The third zone incorporated oxidation of H_2 and the Claus reaction (R2). However, the formed H_2 within the H_2S flame inclines to be maintained according to several references about the H_2S-air/O_2 rich flame in traditional diffusion manner [11–13]. And for an industrial Claus furnace whose feed contains significant fraction of CO_2, the reactivity of CO_2 can be stimulated by presence of reductive radicals, and probably gives rise to the formation of unwanted by-products such as COS and CS_2 [14–18]. And this process is anticipated to be enhanced under O_2 enrichment combustion condition.

O_2 enrichment (or O_2 enhanced) combustion, in which combustion occurs in an oxygen-enriched atmosphere, is seen as one of the most promising technology dealing with CO_2 capture, thermal efficiency improvement and pollutants emissions reduction, etc. [19]. This technology has been applied to the Claus process primarily for furnace temperature increase and contaminants destruction, e.g., mercaptans, benzene, toluene and xylene [20]. These hydrocarbons are deemed to be negative for the performance of catalysts by causing carbon deposition, pore blocking and poisoning in catalyst bed [21]. ZareNezhad et al. evaluated the temperature increasing effect of oxygen enriched air on the H_2S-air flame by equilibrium calculation [22]. It was shown that each 10% increase in equivalent OC would induce a flame temperature increase of 25–50 K. This enables a Claus furnace to process extremely lean AG under specific cases. Meanwhile chemical reactions in a flame will be definitely influenced by the substantially increased temperature, concentrated reactants and different heat transfer environment.

Experimental studies on H_2S doped flame under O_2 enriched condition have been performed in laboratory scale facilities [23,24]. Selim et al. has investigated the role of CO_2 on the H_2S oxidation adopting pure O_2 as oxidant in a vertical combustion reactor. They found the addition of CO_2 into a H_2S-O_2 flame, though slightly decreased the temperature of combustion area, could increase downstream temperature [9]. They concluded the effect of CO_2 on flame temperature was caused by its oxidizing medium role of CO_2 in the reaction pool, probably via R3 shown as follows.

$$CO_2 + H \leftrightarrow CO + OH \tag{R3}$$

This reaction is deemed to represent CO_2 reactivity during combustion, which has been highlighted in many previous studies regarding oxy-fuel combustion [25–28]. Glarborg et al. investigated the influence of high concentration of CO_2 in oxy-fuel combustion of methane with tube furnace experiment and kinetic simulation [25]. CO_2 would compete with O_2 for atomic H and gave rise to CO production via R3, which could be expected to occur strongly at near-burner region for a non-premixed flame. Lee et al. summarized that the direct chemical impacts of CO_2 for combustion were its breakdown by third-body collision and thermal dissociation, and enriched CO_2 made the radiative heat loss essentially important in the flame [29]. Watanabe et al. observed the promotion role of CO_2 during CH_4-O_2 oxidation since CO_2 reactivity reduced the H/OH ratio by converting H into OH [28]. In general, reactivity of CO_2 cannot be neglected during combustion, especially in an O_2 enriched flame.

Much of the previous interest of CO_2 furnace chemistry has evidently stated the relationship between CO_2 and COS and CS_2 [30]. Karan et al. discussed COS formation pathways from homogeneous gas-phase reactions in H_2S-CO_2 and H_2S-CO systems [30]. They concluded that CO, and not CO_2, was the direct source of COS formation dominantly via $CO + H_2S \leftrightarrow COS + H_2$ and $CO + 0.5S_2 \leftrightarrow COS$. This viewpoint was supported by the mechanism study on CO and COS formation in the Claus furnace from Clark et al. [17]. Abián et al. conducted extensive studies about the oxidation of COS and CS_2 and emphasized the role of CS radical in the generation CS_2, chiefly via reacting with sulfur species such as S, S_2 or SH [15]. COS and CS_2, which are dominantly formed in the Claus furnace, often cause the activity degradation of catalyst and contribute to 30–50% sulfur pollutants in the exhaust gas [31]. Thus investigating the formation of COS and CS_2 during AG combustion is of fundamental importance in increasing sulfur recovery and reducing sulfur oxides emission. However, all of the mentioned studies examined formation of COS and CS_2 under plug flow and isothermal conditions, which were quite different from the practical reaction condition in the Claus furnace wherein AG was normally oxidized via the non-premixed flame. To fill this gap, we aim to study the non-premixed AG flame and examine the function of major reactants, H_2S and CO_2 in producing pollutants, COS and CS_2 under O_2 enriched condition.

One of the motivations for the current study is the obvious advantage of applying O_2 enrichment combustion technology to sulfur recovery plants in increasing energy efficiency and processing capacity. However, it remains unclear the transformation from CO_2 into COS and CS_2 during a non-premixed AG flame, though the high reactivity of CO_2