



# Chemical kinetics mechanism for oxy-fuel combustion of mixtures of hydrogen sulfide and methane



Dominik Bongartz, Ahmed F. Ghoniem\*

Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

## ARTICLE INFO

### Article history:

Received 14 May 2014

Received in revised form 1 August 2014

Accepted 27 August 2014

Available online 26 September 2014

### Keywords:

Sour gas

Sulfur

Hydrogen sulfide

Methane

Oxy-fuel

Kinetic modeling

## ABSTRACT

Oxy-fuel combustion of sour gas, a mixture of natural gas (essentially methane (CH<sub>4</sub>)), carbon dioxide (CO<sub>2</sub>), and hydrogen sulfide (H<sub>2</sub>S), could enable the utilization of large natural gas resources, especially when combined with enhanced oil recovery. In this work, a detailed chemical reaction mechanism for oxy-fuel combustion of sour gas is presented. To construct the mechanism, a CH<sub>4</sub> sub-mechanism was chosen based on a comparative validation study for oxy-fuel combustion. This mechanism was combined with a mechanism for H<sub>2</sub>S oxidation, and the sulfur sub-mechanism was then optimized to give better agreement with relevant experiments. The optimization targets included predictions for the laminar burning velocity, ignition delay time, and pyrolysis of H<sub>2</sub>S, and H<sub>2</sub>S oxidation in a flow reactor. The rate parameters of 15 sulfur reactions were varied in the optimization within their respective uncertainties. The optimized combined mechanism was validated against a larger set of experimental data over a wide range of conditions for oxidation of H<sub>2</sub>S and interactions between carbon and sulfur species. Improved overall agreement was achieved through the optimization and all important trends were captured in the modeling results. The optimized mechanism can be used to make qualitative and some quantitative predictions on the combustion behavior of sour gas. The remaining discrepancies highlight the current uncertainties in sulfur chemistry and underline the need for more accurate direct determination of several important rate constants as well as more validation data.

© 2014 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

## 1. Introduction

A large fraction of the world wide natural gas resources is currently not usable because it consists of ‘sour’ natural gas, or sour gas [1]. Unlike regular ‘sweet’ natural gas, which is made up mainly of methane (CH<sub>4</sub>) and some other light hydrocarbons, sour gas also contains large amounts of hydrogen sulfide (H<sub>2</sub>S) and carbon dioxide (CO<sub>2</sub>). Depending on the gas field, the volume fractions of these contaminants often vary between zero and 30% each [2]. Both substances are undesirable; H<sub>2</sub>S is toxic and its combustion products (especially sulfur trioxide (SO<sub>3</sub>)) can cause severe corrosion problems, while CO<sub>2</sub> lowers the heating value of the gas. If the concentrations of H<sub>2</sub>S and CO<sub>2</sub> get too high, expensive purification processes are necessary if the natural gas is to be used in a conventional gas fired power plant, which can make the use of the gas uneconomic.

Oxy-fuel combustion may provide a solution to this problem. In oxy-fuel combustion, the fuel is burned in pure oxygen (O<sub>2</sub>) and some diluent (usually either CO<sub>2</sub>, water (H<sub>2</sub>O), or a mixture of these) instead of air. This yields combustion products consisting mainly of CO<sub>2</sub> and H<sub>2</sub>O, which allows for easy separation of CO<sub>2</sub> by condensation of H<sub>2</sub>O and makes oxy-fuel combustion an option for carbon capture and sequestration [3,4]. Since the production of O<sub>2</sub> is energy intensive, oxy-fuel systems are likely to operate close to stoichiometry (equivalence ratio  $\phi \approx 1$ ) to avoid wasting either fuel or energy for air separation. Thus, the combustion temperature is controlled by adjusting the amount of diluent that is added to the combustor.

In the case of sour gas, the problem of the low heating value can therefore be overcome when employing an oxy-fired combustion strategy by recycling less diluent to the combustor. Furthermore, the fact that oxy-fuel systems operate close to stoichiometry might alleviate corrosion issues associated with sulfur-containing combustion products. If the carbon dioxide produced in the oxy-fuel process is used for enhanced oil recovery (EOR), an additional revenue stream can be generated to counteract the higher cost and complexity of the process [5]. However, the use in EOR also gives

\* Corresponding author at: 77 Massachusetts Avenue, Room 3-344, Cambridge, MA 02139, USA. Fax: +1 617 253 5981.

E-mail addresses: [dominikb@mit.edu](mailto:dominikb@mit.edu) (D. Bongartz), [ghoniem@mit.edu](mailto:ghoniem@mit.edu) (A.F. Ghoniem).

rise to different requirements for the combustion products, one important change being that the  $O_2$  content has to be limited to ppm levels [6].

To investigate the potential of this approach, it is necessary to characterize the combustion behavior of sour gas and in particular its chemical kinetics. We therefore need a detailed chemistry model that can capture most of the phenomena that arise from the unusual fuel and combustion environment. Eventually, such a model can also serve as a basis for the development of a reduced mechanism suitable for use in multi-dimensional computational fluid dynamics (CFD) simulations. Specifically, a good model should fulfill the following requirements:

- Capture the effects of  $CO_2$  or  $H_2O$  diluted oxy-fuel conditions on the laminar burning velocity and the ignition delay time of  $CH_4$  over a range of temperatures.
- Predict the formation and consumption of carbon monoxide (CO) and  $O_2$  under oxy-fuel conditions with reasonable accuracy.
- Give accurate predictions for the laminar burning velocity and ignition delay time of  $H_2S$  over a range of temperatures and for different diluents.
- Predict the formation of  $SO_3$  under the conditions of interest.
- Capture possible interactions between carbon and sulfur species and reproduce the correct relative oxidation speed of  $CH_4$  and  $H_2S$ .

The purpose of this paper is to assemble and optimize a detailed chemical reaction mechanism for sour gas combustion that fulfills these requirements. We first present a comparative study of mechanisms for oxy-fuel combustion of  $CH_4$  to identify a suitable  $CH_4$  sub-mechanism. Next, we describe how this  $CH_4$  mechanism was combined with a mechanism for the oxidation of  $H_2S$  and explain our optimization of the sulfur kinetics. Finally, we give a summary of the performance of the combined mechanism against experimental data (including but not limited to the optimization targets) on sulfur oxidation and interactions between  $CH_4$  and  $H_2S$ .

## 2. Mechanism for oxy-fuel combustion of $CH_4$

While there has been a considerable amount of work on modeling combustion of  $CH_4$  in air, so far only few reaction mechanisms have been developed or at least tested specifically for the special conditions that are typical in oxy-fuel combustion (that is combustion close to stoichiometry in the presence of large fractions of  $CO_2$  or  $H_2O$ ). This group of mechanisms includes the GRI-Mech 3.0 [7], the mechanism developed by Glarborg et al. [8–10], and the mechanism developed by Dagaut et al. [11,12]. However, to our knowledge there has been no comprehensive comparative study yet to show how well these mechanisms capture the effects caused by the unusual combustion environment.

In our case, the O–H subset of the mechanism is particularly important since it will also be used by the sulfur part of the mechanism (see Section 3). Therefore, we also included the AramcoMech 1.3 mechanism by Metcalfe et al. [13] in our study, since it is based on a recent O–H model [14] which (unlike the older mechanisms mentioned above) includes the latest advances in this area, such as, for example, the improved rate constant for the reaction  $H + O_2 = OH + O$  [15]. It should be noted that AramcoMech 1.3 does not contain a model for formation of nitrogen oxides ( $NO_x$ ). However this is not expected to be a major problem when dealing with oxy-fuel combustion, since a number of studies have found  $NO_x$  formation to be negligible for realistic  $O_2$  purities [16–18].

Several studies have shown that adding  $CO_2$  to  $CH_4$ -air flames reduces the laminar burning velocity of  $CH_4$  through both thermal

and chemical effects [19–21]. The extent of this reduction is captured correctly by all three tested mechanisms (see Fig. 1). For the mechanism by Dagaut et al., we encountered numerical difficulties for all burning velocity calculations.

There have been a number of studies on the impact of  $H_2O$  on the burning velocity of  $CH_4$  [22–25]. While all three tested mechanisms can predict the decrease of the burning velocity through  $H_2O$  addition equally well at atmospheric pressure, AramcoMech 1.3 performs better at elevated pressure (see Fig. 2).

Levy et al. [26] measured the ignition delay time of  $CH_4$  in different diluents and found that neither  $CO_2$  nor  $H_2O$  have a significant effect. All four mechanisms considered here agree reasonably well with their measurements in mixtures containing  $CO_2$  (see Fig. 3a) and both  $CO_2$  and  $H_2O$  (see Fig. 3b).

Recently, the influence of  $CO_2$  and  $H_2O$  on CO oxidation has been investigated by several researchers (e.g., [12,27]). Our tests showed that all four mechanisms are able to reproduce the inhibiting effect of large  $CO_2$  concentrations on CO oxidation observed by Abián et al. [27] both for lean and rich conditions (see Fig. 4; only the case with the highest  $CO_2$  content is shown here for better readability). The experimental data is best reproduced by GRI-Mech 3.0. The Glarborg mechanism predicts the onset of CO oxidation to be at slightly lower temperatures than what is observed experimentally.

The enhancing effect of moderate concentrations of  $H_2O$  on CO oxidation in the presence of  $CO_2$  in the same experiment is captured qualitatively by all mechanisms (see Fig. 5; again, only the case with the highest  $H_2O$  content is shown). The inhibiting effect of larger concentrations of  $H_2O$  on CO oxidation at very lean conditions ( $\phi \approx 0.04$ ) observed by Glarborg et al. [28] is also captured by all models (see Fig. 6). In both cases, the Glarborg mechanism again predicts lower temperatures for the onset of CO oxidation.

While previous cases studied the impact of  $CO_2$  and  $H_2O$  on CO oxidation, all mechanisms can at least qualitatively predict the effect of  $CO_2$  on CO concentrations in  $CH_4$  oxidation in the experiment of Glarborg and Bentzen [8] (see Fig. 7). At stoichiometric and fuel-rich conditions, the temperature above which increased CO is observed is best predicted by AramcoMech 1.3 and the Dagaut mechanism.

In summary, AramcoMech 1.3 provides the best overall agreement with the experimental data in the presented relevant validation cases, especially for the burning velocity at elevated pressure and CO formation in  $CH_4$  oxidation. Based on this observation and the fact that it contains the most recent O–H submodel of the mechanisms considered here, we selected it as the basis for our mechanism for sour gas combustion.

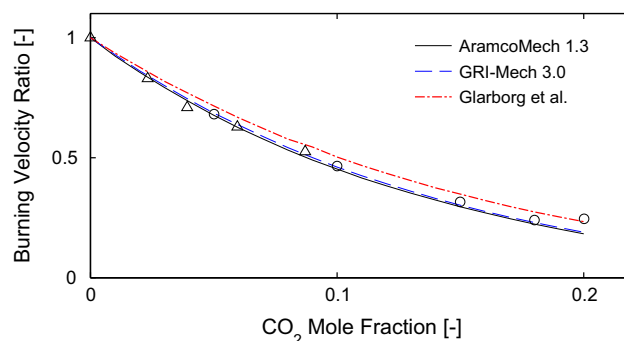


Fig. 1. The modeling results (lines) agree well with the experimental data (symbols) of Halter et al. [20] (○) and Kishore et al. [21] (△) on the reduction of the laminar burning velocity of stoichiometric  $CH_4$ -air flames through  $CO_2$  addition ( $T = 300\text{ K}$ ,  $p = 1\text{ atm}$ ).

Download English Version:

<https://daneshyari.com/en/article/166714>

Download Persian Version:

<https://daneshyari.com/article/166714>

[Daneshyari.com](https://daneshyari.com)