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Investigation of gas-phase reactions in the mixing region for hydrocarbon autothermal reforming applications

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ABSTRACT

Mixture preparation technology plays a critical role in ensuring reformate quality during autothermal reforming of liquid fuels. Incomplete mixing can cause temperature over-shoots and deposit formation within the catalyst bed. However, the time available for mixing is limited by unwanted gas-phase reactions that produce deposit precursors. We perform an analysis of the gas-phase reactions in the mixing region using a well-tested alkane oxidation mechanism taken from the literature. One particularly interesting prediction is that the time for significant reaction to occur does not monotonically decrease as the temperature increases. This is due to the negative temperature coefficient (NTC) kinetics. By mixing within the NTC temperature window, it should be possible to provide substantially more time for mixing. Similarly, one can expand the mixing time by suitable choices of mixture composition. These results provide important guidance criteria for the optimization of a mixer design to avoid undesirable reactions.

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1. Introduction

There are numerous challenges in developing compact, high-performance liquid fuel reformers for mobile power applications, such as solid-oxide fuel cells in auxiliary power units. Achieving complete mixing of liquid fuels and reforming agents (e.g., steam, CO_2 and air) is certainly one important challenge that strongly affects reformate quality. One design objective is to achieve sufficiently complete mixing in times that are short compared to the timescale at which gas-phase reactions occur. Mixing and reaction rates are highly coupled to both fluid dynamics and heat transfer in the mixing region, and thus it is necessary to develop and apply computational models that assist in the design and development of gas-phase mixing chambers upstream of the reforming catalyst. A three-dimensional computational fluid dynamics model was developed in a previous study [1], but it is computationally expensive and limited in the number of species that can be considered. Therefore, it is advantageous to analyze the gas-phase reaction kinetics separately prior to the application of a coupled kinetics-transport model.

There are restrictions to the operating temperature in the mixing region. Commonly used liquid fuels are mixtures of various hydrocarbons having a broad range of boiling points. The lighter components boil below 200 °C, while the heavier components may have boiling points as high as ~350 °C [2]. There would be ample time to mix reactants without the occurrence of any gas-phase reactions provided the temperature could be kept very low. However, the requirement for the fuels to fully vaporize means that the temperature in the mixing region has to be above ~350 °C. Under these conditions there is the potential for unwanted gas-phase chemistry.

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The purpose of this study is to explore the impact of temperature, residence time, and mixture composition on the gas-phase kinetics for representative alkane fuels. This is an extension of an earlier effort [3]; however, a broader range of alkanes is considered and much of the analysis focuses on lower temperatures than in the earlier work. The lower temperature analysis, in particular, reveals new features of the kinetics that can dramatically impact mixer performance.

Mixture preparation prior to reforming or combustion has been investigated by many researchers. Premixing technologies can be divided into two types based on the method of liquid fuel evaporation. Wei et al. suggested fully vaporizing the liquid fuel with an external heating element prior to blending it with air in a static mixer [4]. They argued that isolated evaporation is a more effective way of avoiding self-ignition than an integrated mixing method. Superheated steam is employed as the atomizing gas in a two-phase nozzle, and its presence in the high-temperature zone of the vaporizer suppresses the formation of carbon deposits. The liquid fuel can be vaporized either by electrical energy or heating gas, such as steam, but the use of a heating gas is preferable [2]. However, isolated evaporation requires an additional mixing process outside of the vaporizer, which is necessary to prevent deposit formation or hot spots.

The other method used is direct evaporation of liquid fuel into hot air. Usually, atomized liquid fuel is introduced into the hot oxidizing mixture via injection. Oxidation reactions are initiated by the pre-heated air, which brings a modest amount of heat to the mixture and causes its temperature to increase, initiating the reaction. The exothermic oxidation reactions further increase the temperature. This heat generation is initially largely offset by the energy required for fuel evaporation. As the temperature continues to increase, there is the possibility that the overall reaction rate will begin to decrease as the mixture enters the negative temperature coefficient (NTC) region [5-8], thereby suppressing further reaction. Hartmann et al. [9], Matos Da Silva et al. [10], Founti and co-workers [11-13], Lindström et al. [14] and Al-Hamamre et al. [15] used this approach to completely vaporize liquid fuels, and they suggested designs and/or operating windows for vaporizers. Some of them used recirculation zones in the vaporizer [9,13,14] to increase the homogeneity of the reactant mixture. Direct evaporation is always preferred in terms of simplicity, but there is a significant risk of ignition during mixing.

There have been several studies related to mixture preparation, but these studies are only marginally different from the two basic types of vaporizers described above and can be categorized as one of the aforementioned vaporizing schemes. Most studies were associated with computational fluid dynamics and rarely included reaction kinetics. Founti and co-workers [11-13] provide the only study that considers reaction kinetics in the mixing region. They applied the reduced version of a Lawrence Livermore National Laboratory (LLNL) mechanism that is also used in this work. However, they only considered the effect of heat release from gas-phase reactions on the temperature field in the mixer and did not consider any detailed analysis of the reaction kinetics.

The present work simulates reaction kinetics in the mixing region of a hydrocarbon reformer. An isolated study of the chemical kinetics can provide essential information with respect to the temperature and residence time window necessary for mixing reactants. A specific focus of this analysis is the rate of production of ethylene since the ethylene yield strongly affects deposit formation on the catalyst downstream of the mixing region [16]. We also vary the oxygen/carbon and steam/carbon ratios to begin to address the impact of incomplete mixing.

2. Oxidation of hydrocarbons in the low-temperature region

Detailed kinetic models are available to describe the ignition behavior of a wide range of hydrocarbon fuels with good accuracy [17-19]. The reactivity of peroxy radicals (RO_2) dominates the chemistry in the low and intermediate ranges of temperature, as shown in Fig. 1 [20]. RO_2 is formed by O_2 addition to alkyl radicals (R) following H abstraction from the primary fuel. Besides re-dissociation, RO_2 can isomerize to hydroperoxyalkyl radicals (QOOH) or undergo a concerted elimination reaction to form an olefin and HO_2. There are several pathways for reactions of QOOH, including a chain branching reaction initiated by addition of another O_2 molecule. This chain branching step is recognized as a key reaction
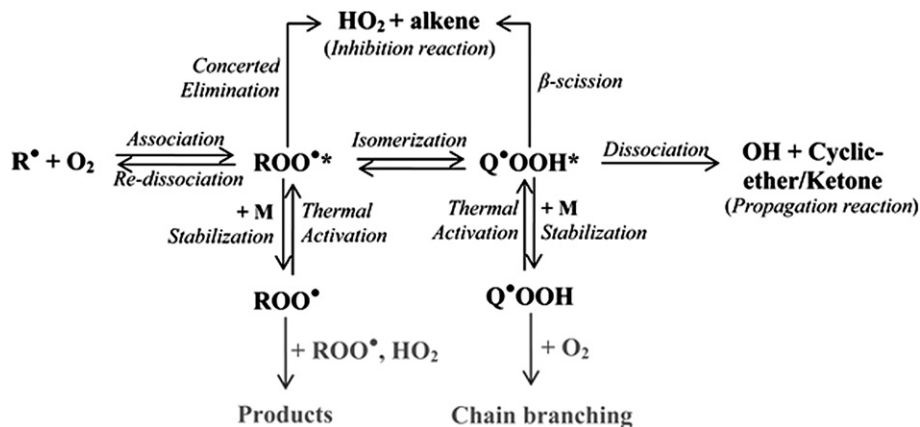

Fig. 1 — Overall reaction path diagram for hydrocarbon oxidation at low temperatures [20].