

개질기 혼합영역에서 탄화수소 연료의 반응 특성에 대한 연구

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Kinetic Study on the Mixing Region of a Hydrocarbon Reformer

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ABSTRACT

Complete mixture preparation of reactants prior to catalytic reforming is an enormously important step for successful operation of a fuel reformer. Incomplete mixing between fuel and reforming agents such as air and steam can cause temperature overshoot and deposit formation which can lead the failure of operation. For that purpose it is required to apply computational models describing coupled kinetics and transport phenomena in the mixing region, which are computationally expensive. Therefore, it is advantageous to analyze the gas-phase reaction kinetics prior to application of the coupled model. This study suggests one of the important design constraints, the required residence time in the mixing chamber to avoid substantial gas-phase reactions which can lead serious deposit formation on the downstream catalyst. The reactivity of various gaseous and liquid fuels were compared, then liquid fuels are far more reactive than gaseous fuels. n-Octane was used as a surrogate among the various hydrocarbons, which is one of the traditional liquid fuel surrogates. The conversion was slightly effected by reactants composition described by O/C and S/C. Finally, threshold residence times in the mixing region of a hydrocarbon reformer were studied and the mixing chamber is required to be designed to make complete mixture of reactants by tens of milliseconds at the temperature lower than 400°C.

KEY WORDS : Reforming(개질), Hydrocarbon(탄화수소), Mixing(혼합), Reaction kinetics(반응동역학), Modeling(모델링)

Nomenclature

τ : residence time, ms

$\tau_{5\%}$: residence time for 5% conversion, ms

τ_t : threshold residence time for C₂H₄ mole fraction to reach 0.001

ATR: autothermal reforming

O/C : oxygen to carbon ratio

S/C : steam to carbon ratio

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1. Introduction

Liquid hydrocarbon fuels provide high energy densities for mobile power generation facilities such as solid-oxide fuel cells in auxiliary power units. However there are numerous challenges in developing compact high-performance reformers. Complete mixture preparation of fuel and reforming agents such as air and steam is certainly one important challenge. Incomplete mixing with air can cause unacceptable temperature overshoots in the catalyst due to over-oxidation. Pyrolysis chemistry in the mixing region upstream of the reforming catalyst can lead to deleterious deposit formation. For example, ethylene is a known deposit precursor and even low levels will cause catalyst fouling. An important design objective is to achieve sufficiently complete mixing in times that are short compared to gas-phase reaction times. For that purpose it is required to develop and apply computational models describing coupled kinetics and transport in the mixing region to assist the design and development of gas-phase mixing chambers upstream of the reforming catalyst. A 3D computational fluid dynamics (CFD) model was developed in the previous study¹⁾. The model is computationally expensive, especially with gas-phase reaction kinetics. Therefore, it is required to study the gas-phase reaction kinetics prior to the coupled model. The purpose of this study is to suggest guidelines for the mixing chamber design from the kinetic study in the mixing region of hydrocarbon reformer.

2. Kinetic model descriptions

Two kinds of mechanisms were applied in the study. Dean's group from Colorado School of Mines (CSM) has developed the kinetic mechanism describing propane oxidation which consists of 369

species and 3649 reactions. The mechanism used was based on the earlier work^{2,3)} from the group with additional updates^{4,5)}. The mechanism was validated against n-hexane pyrolysis⁶⁾ and propane oxidation experiments¹⁾. Lawrence Livermore National Laboratory (LLNL) provides various kinds of hydrocarbon oxidation mechanisms and a mechanism was chosen for this study, which presents both n-octane and n-hexadecane oxidation⁷⁾. The LLNL model consists of 2115 species and 8157 reactions and was developed to describe pyrolysis and oxidation of large alkanes. It includes both high- and low-temperature oxidation chemistry and was validated against extensive database.

The calculations were done with the plug-flow reactor model of the CHEMKIN-PRO software from Reaction Design and it is assumed that the reactor is adiabatic.

3. Results and discussion

3.1 Gas-phase reactivity

To investigate the gas-phase reactivity of gaseous and liquid fuels in the mixing region, two and eight surrogates for CSM and LLNL mechanisms were considered respectively: ethane and propane for both and n-butane, n-hexane, n-octane, n-decane, n-dodecane, and n-hexadecane for LLNL mechanism only. Table 1 shows the initial conditions used. Air was used as an oxygen source. The previous study suggested that the mixing of steam, air and fuel should be complete and the mixture would need to enter the catalyst bed within ~50 ms if the components enter the mixing region at a temperature of 500°C⁶⁾. Therefore, it is investigated the conversion at the residence time of 100 ms.

Fig. 1 illustrates the effect of temperature on the conversion of gaseous and liquid fuels pre-

Table 1 Summary of initial conditions for the gas-phase reactivity of gaseous and liquid fuels

Surrogate	Mole fraction			
	Surrogate	O ₂	N ₂	H ₂ O
Ethane	0.087	0.139	0.515	0.260
Propane	0.059	0.143	0.531	0.267
n-Butane	0.045	0.145	0.539	0.271
n-Hexane	0.031	0.147	0.547	0.276
n-Octane	0.023	0.148	0.551	0.278
n-Decane	0.019	0.149	0.554	0.279
n-Dodecane	0.016	0.149	0.555	0.280
n-Hexadecane	0.012	0.150	0.557	0.281

dicted by using LLNL mechanism. Essentially, liquid fuels are more reactive than gaseous fuels. Liquid fuels decompose from the temperature of 350°C which is 200°C less than the decomposition temperature of gaseous fuels. With increasing temperature the conversions of liquid fuels are rapidly increased from 350°C to 400°C, then slightly decreased by 450°C. This conversion is associated with the production of substantial amounts of ethylene⁽⁶⁾. Note that n-butane, one of gaseous surrogate fuels

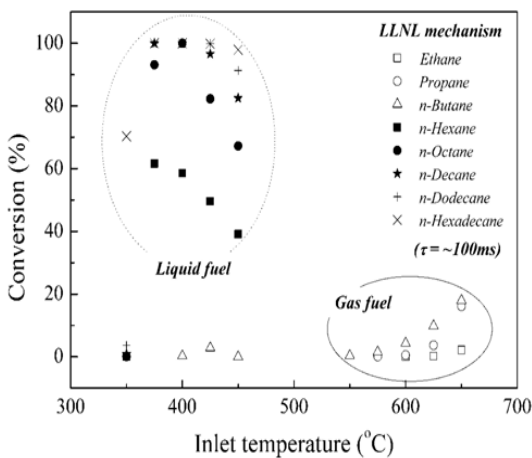


Fig. 1 Predicted conversion of gas and liquid fuels for ATR case (cf. Table 1) at the residence time of 100 ms predicted by using LLNL mechanism

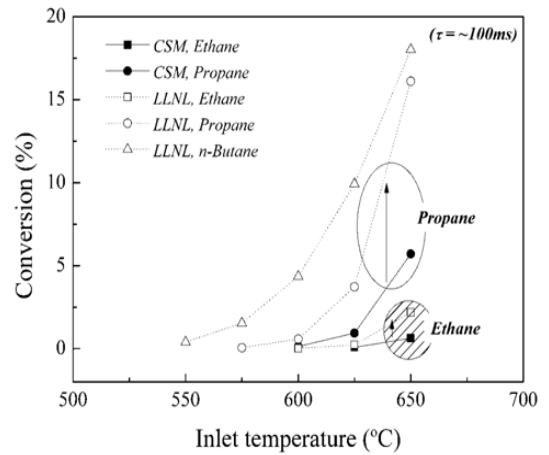


Fig. 2 The conversion of gaseous fuels for ATR case (cf. Table 1) at the residence time of 100 ms predicted by using CSM and LLNL mechanisms

shows a small amount of conversion between 400 and 450°C though there is no conversion between 450 and 550°C. This behavior is indicative of the Negative Temperature Coefficient (NTC) behavior often observed in the ignition of hydrocarbon fuels⁽⁸⁾. Fig. 2 describes the reactivity of gaseous fuels predicted by using both CSM and LLNL mechanisms. The results show that LLNL mechanism predicts gaseous fuels more reactive than CSM mechanism which is more reliable in low-temperature oxidation⁽¹⁾, the reaction being occurred in the mixing region of hydrocarbon reformer. LLNL mechanism somewhat over-predict the conversion of hydrocarbon surrogate though it includes both high- and low-temperature pathways of alkane oxidation.

3.2 The effect of O/C and S/C on the conversion of n-octane

The products from hydrocarbon ATR depend on the operating conditions such as O/C, S/C and temperature⁽⁹⁾. Hence, the gas-phase reactivity needs to be investigated under the various operating conditions. The temperature effect is the most

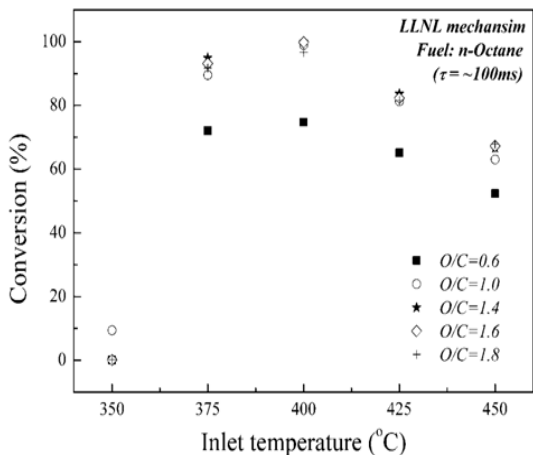


Fig. 3 The O/C effect on the conversion of n-octane for ATR case with S/C of 1.5

dramatic as described in the former section. Fig. 3 and Fig. 4 show the predicted impact of O/C (with the constant S/C of 1.5) and S/C (with the constant O/C of 1.6) on the conversion of n-octane at a fixed residence time of 100 ms. Table 2 presents the initial conditions used. LLNL mechanism was applied. The cases show similar conversions to each other, which have O/C higher than 1.0, the oxygen stoichiometric corresponding to n-octane

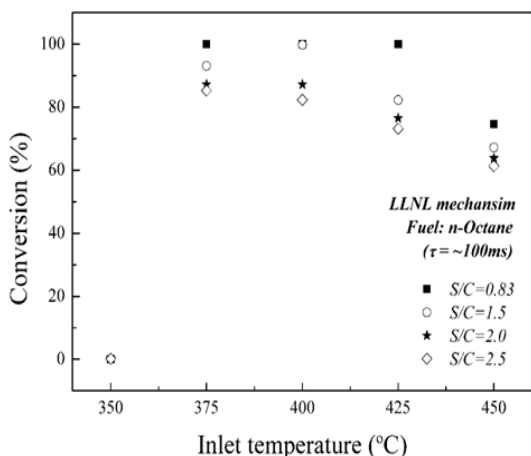


Fig. 4 The S/C effect on the conversion of n-octane for ATR case with O/C of 1.6

Table 2 Summary of initial conditions for O/C and S/C effects on the gas-phase reactivity of n-octane

	O/C	S/C	Mole fraction				Heat production [J/cm ³]
			n-C ₈ H ₁₈	O ₂	N ₂	H ₂ O	
O/C effect	0.6	1.5	0.028	0.135	0.501	0.337	0.142
	1.0		0.020	0.158	0.586	0.236	0.145
	1.4		0.015	0.170	0.633	0.182	0.145
	1.6		0.014	0.174	0.649	0.163	0.146
	1.8		0.012	0.178	0.662	0.148	0.145
S/C effect	1.6	0.83	0.015	0.188	0.700	0.098	0.177
	1.5		0.014	0.174	0.649	0.163	0.147
	2.0		0.013	0.165	0.615	0.207	0.130
	2.5		0.012	0.157	0.585	0.246	0.114

partial oxidation reaction. The conversion is not increased by the abundant oxygen in the given residence time, but the conversion is decreased as S/C is increased as shown in Fig. 4.

3.3 Threshold residence time in the mixing region

The goal of this study is to suggest guidelines for the mixing chamber design from the kinetic study in the mixing region of hydrocarbon reformer. One of the important design constraints is a threshold residence time in the mixing chamber. Intuitively the degree of mixing will be improved with long residence time, but gas-phase reactions will be occurred and ethylene, a known deposit precursors, will be produced. As Kang's study⁶⁾, two parameters are derived from each calculation: the time required for 5% of the fuel to be consumed ($\tau_{5\%}$) and the time required for the ethylene mole fraction to reach 0.001 (τ). The threshold ethylene mole fraction is defined as 0.001, the mole fraction at which it has been observed to begin to form deposits from catalytic reaction in downstream reforming catalyst¹⁰⁾. Fig. 5 and Fig. 6 present $\tau_{5\%}$

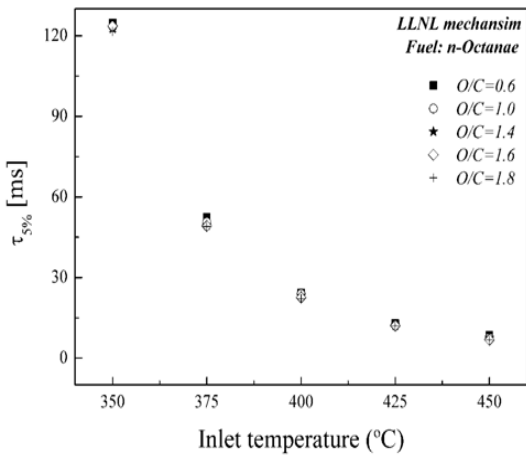


Fig. 5 The O/C effect on $\tau_{5\%}$ for n-octane ATR case with S/C of 1.5

at each temperature with various O/C and S/C and $\tau_{5\%}$ is not affected by composition of reactants. The predictions show that $\tau_{5\%}$ is only changed by inlet temperature and exponentially decreased as the inlet temperature is increased. It can be explained by the exponential increase of reaction rates described by Arrhenius equation. Interestingly $\tau_{5\%}$ and τ_t has linearly proportional to each other and two parameter has actually same value for n-

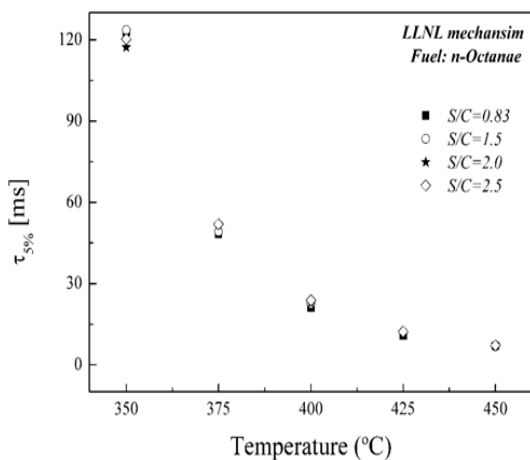


Fig. 6 The S/C effect on $\tau_{5\%}$ for n-octane ATR case with O/C of 1.6

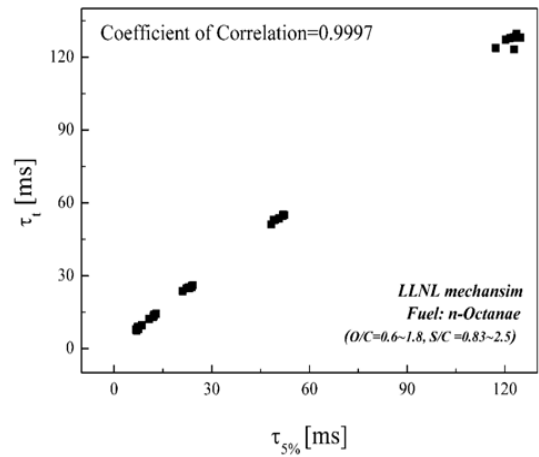


Fig. 7 The relation between the residence time for 5% conversion and the threshold residence time for C_2H_4 mole fraction to reach 0.001

octane as shown in Fig. 7. $\tau_{5\%}$ and τ_t are similar to the residence time at which cool flame reactions are begun to occur¹¹⁾. Therefore, the mixing chamber is required to be designed to make complete mixture by the residence time at which cool flame reactions are begun, ~ 100 ms at $350^\circ C$. At the temperature higher than $400^\circ C$, the threshold resistance times are surprisingly short. The reactants should be mixed at the temperature lower than $400^\circ C$ in tens of milliseconds.

4. Conclusions

It is known that careful attention should be paid to the design of the mixing chamber upstream of an autothermal reformer from the previous studies. For that purpose a prudent approach would be to couple a CFD analysis of the propose mixer design with a detailed kinetic model for the fuel of interest to assess the potential for deposit formation or temperature overshoot. However, the coupled model would be computationally expensive then, it is required to study the gas-phase reaction kinetics

prior to the coupled model. This study suggests one of the important design constraints, the required residence time to avoid significant gas-phase reactions which can derive deposits during catalytic reactions. The reactants should leave the mixing chamber before the residence time at which the cool flame reactions are started.

The required residence time is only affected by the inlet temperature. The gas-phase reactivity of gaseous and liquid fuel are compared and the significant differences are observed. In the previous study¹⁾ the propane was used as the surrogate for liquid fuels and it can be concluded that the relatively low reactivity of propane needs to be compensated for more reasonable predictions. The gas-phase reactivity of n-octane is compared at various O/C and S/C. The effects are relatively small though the higher steam contents somewhat suppresses the conversion.

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