Plug-flow reactor study of the partial oxidation of methane and natural gas at ultra-rich conditions

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Abstract

The homogenous partial oxidation of fuel-rich CH_4/O_2, $CH_4/C_2H_6/C_3H_8/O_2$ as well as $CH_4/C_2H_6/C_3H_8/H_2/O_2$ mixtures is investigated in a plug-flow reactor at intermediate temperatures ($473 \leq T \leq 973$ K) and a pressure of 6 bar. Experiments are carried out at equivalence ratios (Φ) of 2, 10 and 20. Product species are analyzed by time-of-flight molecular-beam mass spectrometry. The experimental results are further compared with simulations, using a reaction mechanism from the literature. It was found that under the investigated conditions, the onset temperature for CH_4 oxidation is above 773 K. In case of the neat CH_4 mixtures and equivalence ratios of 10 and 20, even at the highest investigated temperature CH_4 conversion is very low ranging from 3 % to nearly 0 %. Due to the higher reactive species content in the natural gas (NG) mixtures, conversion of CH_4 can be raised to 13 % and 10 % with respect to these equivalence ratios. But, the reaction onset temperature is not influenced by the presence of these species. After the oxidation takes place, useful chemicals like synthesis gas (H_2/CO), C_2H_4, C_2H_6 or CH_3OH are formed. Whereas synthesis gas and C_2H_4 are preferentially formed at higher temperatures, CH_3OH formation is limited to the temperature range between 773 and 973 K. Caused by the increased CH_4 conversion in the case of the NG mixtures, much higher yields of all products can be reached at higher Φ. Comparing experiments with simulations it can be noticed that the reactivity of the mixtures is slightly overestimated by the model, shown by higher CH_4 conversion as well as higher product yields. In summary, the addition of small amounts of C_2H_6 or C_3H_8 into CH_4/O_2 mixtures is a good way to initiate CH_4 conversion even at very high Φ. However, the addition of H_2 does not alter the product spectrum.

Introduction

Homogenous partial oxidation in internal combustion engines could be an exergetically viable alternative to normal combustion because it involves the production of useful chemicals while providing work and heat at the same time. The fuel used could be CH_4 as a major component of NG or NG itself, since it will continue to play a major role in the energy sector in the near future and will also be sufficiently available. In addition, the growth of renewable energies requires an expansion of the power grid and new options for storing fluctuating electricity from renewable sources. Here, power-to-gas, i.e. the conversion of renewable electricity

into hydrogen (H_2) and the direct seasonal storage capacity and distribution in existing natural gas infrastructure, can make an important contribution to the transformation of the energy system. To investigate the impact of H_2 addition into NG during these reactions, fuel-rich diluted CH_4/O_2 as well as $CH_4/C_2H_6/C_3H_8$ and $CH_4/C_2H_6/C_3H_8/H_2$ mixtures are investigated at different temperatures in a plug-flow reactor. Product species are analyzed by time-of-flight molecular-beam mass spectrometry. The data are compared to model results with the intention to validate the used reaction mechanism for the uncommon reaction conditions.

Experimental setup

The investigated flow conditions are shown in table 1. A low volume flow of 280 sccm (standard conditions: 273.15 K, 1 atm) is used to ensure compliance with a plug-flow assumption and the high dilution is used to avoid or reduce temperature changes due to exothermal reactions. Details of the experimental setup can be found in [1, 2].

Table 1. Flow conditions

CH_4	O_2	C_2H_6	C_3H_8	H_2	Ar	Φ
[Mol%]						[-]
5.00	5.00	-	-	-	90	2
4.32	5.20	0.43	0.048	-	90	2
4.27	5.16	0.43	0.047	0.095	90	2
8.33	1.67	-	-	-	90	10
7.40	1.78	0.74	0.082	-	90	10
7.27	1.76	0.73	0.081	0.162	90	10
9.09	0.91	-	-	-	90	20
8.12	0.98	0.81	0.090	-	90	20
7.97	0.96	0.80	0.089	0.177	90	20

Important features of the current setup are summarized below. The flow reactor consists of an inert quartz tube with an inner diameter of 6 mm. It is surrounded by a stainless-steel tube for safety reasons. To prevent catalytic reactions with stainless-steel the gap between the quartz and the stainless-steel tube is sealed with teflon tape at both ends. The reactor is heated by a temperature regulated heating tape. A homogeneous temperature profile with deviations below $\Delta T = \pm 5$ K, and an isothermal reaction zone of 45 cm at an overall reactor length of 65 cm is confirmed prior to the experiments with similar gas flows as a function of the set temperature of the heating tape. Gas flows are metered by calibrated mass flow controllers. The reactor pressure is regulated manually with a heated needle valve at the reactor outlet. The reactor is coupled to a time-of-flight mass spectrometer (ToF-MS) for

online measurements. In a differentially pumped three-stage extraction, a gas sample is extracted from the reactor at 6 bar and directed into the ToF-MS with a mass resolution of m/Δm=2500 at a pressure of 10^{-7} mbar. The gases are ionized by electron impact at 18 eV kinetic energy to avoid excessive fragmentation. Uncertainties in the mole fractions of detected species have been calculated by means of the gaussian error propagation law, taking all main error sources into account and are estimated to be around 10 %.

Modeling
In order to validate reaction mechanisms for the atypical reaction conditions of polygeneration processes, the experimental results are compared with simulations. A plug-flow reactor model is used with a fixed temperature profile and constrained pressure for simulations in the Chemical Workbench Ver. 4.1 [3]. The reaction mechanism of Burke et al. [4] is used for the simulations, as it is based on a mechanism, which has been widely validated for several fuels.

Results and discussion
The following figures show the CH_4 conversion as well as yields of CO, H_2 and C_2H_4 as a function of temperature and equivalence ratio. The yields are calculated by dividing the amount of C atoms in the product i by the initial amount of C atoms in the mixture. Symbols represent experimental data and lines simulations. The different mixtures are marked by different colors. From figure 2 it is obvious that the conversion of CH_4 starts around 773 K for all mixtures. If Φ is increased from 2 to 20 the conversion of CH_4 decreases rapidly from 50 % to nearly 0 %. Also at Φ = 10 the conversion is very low (< 4 %).
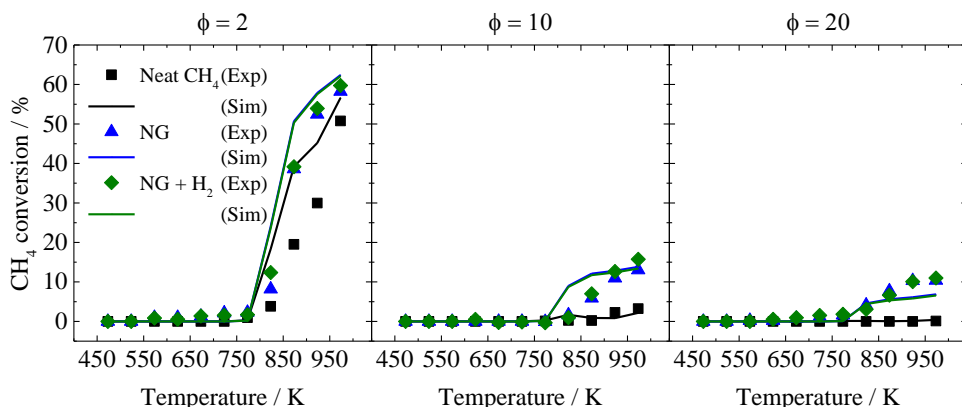

Figure 2. CH_4 conversion as a function of temperature for all investigated mixtures (Symbols: experiment, lines: simulations, NG: natural gas)

In the NG mixtures, much more CH_4 is converted, as more radicals are formed at temperatures above 773 K, mainly from C_2H_6 oxidation. The initiation reaction is

the reaction of C_2H_6 with O_2 forming an ethyl radical (C_2H_5) and a hydroperoxyl radical (HO_2). HO_2 reacts with CH_4, C_2H_6 and C_3H_8 forming the respective alkyl radical and hydrogen peroxide (H_2O_2), which will finally decompose to two OH radicals. As the most important reaction with respect to CH_4 conversion is the H-abstraction by OH radicals to methyl radicals (CH_3) and water (H_2O) [5], the consumption of CH_4 is enhanced. This is confirmed by global reaction flow analyses for all mixtures at these conditions using the reaction mechanism of Burke et al. [4]. So even at $\Phi = 20$, 10 % CH_4 is converted at temperatures above 873 K. H_2 addition into the NG mixture, however, does not influence the oxidation process. The general trends are predicted well by the model, whereas the CH_4 conversion is slightly overestimated for all mixtures at $\Phi = 2$ and 10 in the temperature range between 773 K and 923 K and underestimated at $\Phi = 20$ at temperatures higher than 873 K. Two of the main products are CO and H_2, both presented in figure 3. In this figure, the CO yield was multiplied by a factor of 4 and 9 for the $\Phi = 10$ and 20 cases, respectively.
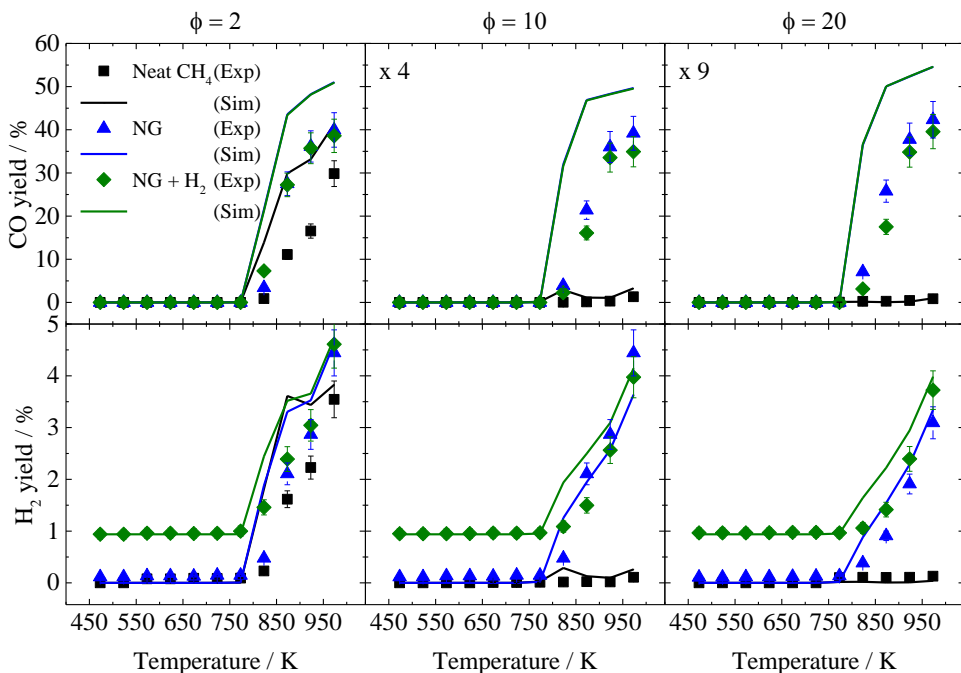

Figure 3. Yields of synthesis gas as a function of temperature (Symbols: experiment, lines: simulations, NG: natural gas)

It can be noted that the formation of CO and H_2 increase with rising temperature and that the highest CO yields can be achieved at $\Phi = 2$. For H_2, yields of 4 – 5 % can be observed at 973 K for all NG mixtures as well as the neat CH_4 mixture at $\Phi = 2$. As less CH_4 is converted at $\Phi = 10$ and 20, compared to $\Phi = 2$, it can be concluded that

the most H_2 is formed out of C_2H_6 and C_3H_8 oxidation, as up to 80 % of these reactants are converted at 973 K. All H_2 containing mixtures show the same behavior as NG mixtures without H_2 with the difference that the H_2 yields start at 1 %, as this is the amount which is in the mixture. At temperatures higher than 773 K, the H_2 yields are similar in both mixtures. Comparing experimental results with simulations it is seen that the model predicts a higher reactivity of all mixtures, since predicted yields are almost always higher than experimental ones.

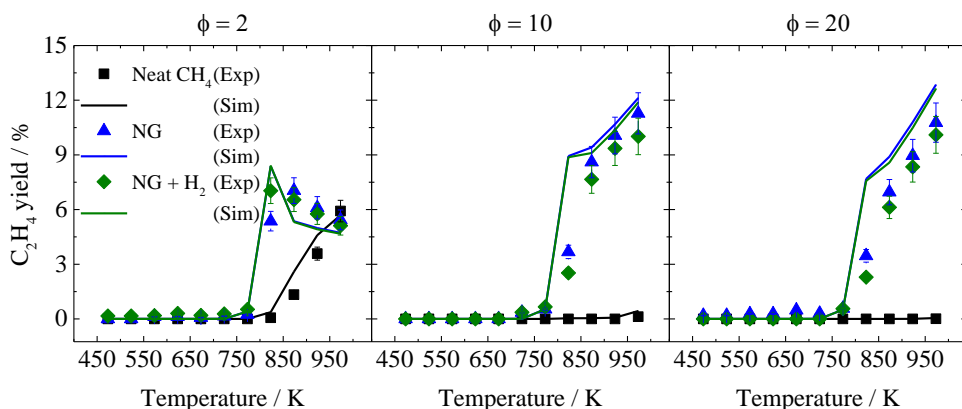C_2H_4 is produced in all NG experiments mainly at high Φ (see figure 4).

Figure 4. Yields of C_2H_4 as a function of temperature (Symbols: experiment, lines: simulations, NG: natural gas)

Regarding the neat CH_4 mixture, C_2H_4 is only formed at $\Phi = 2$ because of the negligible conversion of CH_4 at higher Φ. The maximum yield of C_2H_4 with up to 12 % is observed at the highest investigated temperature (973 K) at both $\Phi = 10$ and 20. But, considering the low CH_4 conversion at these equivalence ratios, it is obvious that C_2H_4 mainly comes from C_2H_6 and C_3H_8 oxidation. At $\Phi = 2$ the maximum yields are about 7 and 6 % for the NG and neat CH_4 mixture, respectively. In case of the NG mixture the maximum can be found at 773 K with slightly decreasing yields at rising temperatures, whereas in the neat CH_4 case a linear increase of the yield can be noticed from 773 K to 973 K. The reason for the higher yields at lower temperatures is that there is a direct route towards C_2H_4 in the reaction network of the NG mixtures. As mentioned before, the initiation reaction regarding NG mixtures yields C_2H_5. This radical reacts with O_2, finally forming C_2H_4 and HO_2. In the neat CH_4 mixture, first of all C_2H_6 is formed by the recombination of two CH_3 radicals. C_2H_5 is then formed by H-abstraction from C_2H_6 by CH_3, OH or HO_2 radicals. Finally, C_2H_4 is formed by the same reaction as in the NG mixture. Therefore, more steps are necessary to produce C_2H_4 out of neat CH_4, which explains the higher yields in the NG experiments. The decrease in the C_2H_4 yields at temperatures above 773 K can be explained by the reaction of C_2H_4 with OH radicals forming an ethenyl radical (C_2H_3) and H_2O. With respect to the reaction flow analysis this reaction becomes

more important at higher temperatures at $\Phi = 2$. Both the trends and the yields are in good agreement to the model predictions

Apart from the shown products, also oxygenated species like methanol (CH_3OH) and formaldehyde (CH_2O) are formed as well as hydrocarbons like C_3H_6 or even C_4- and C_5-species. The maximum CH_3OH yields are found to be around 0.4 % at $\Phi = 2$ and a temperature of 823 K. For C_3H_6, yields of 0.4 % (neat CH_4, $\Phi = 2$) and 1 % (all NG mixtures) can be observed, whereas the maximum shifts towards higher temperatures with rising Φ.

Conclusion

In this study, the homogenous partial oxidation of CH_4 and NG mixtures as well as H_2 doped NG mixtures was investigated in a plug-flow reactor at temperatures between 473 and 973 K and a pressure of 6 bar. It could be observed that the CH_4 conversion can be significantly enhanced if higher reactive species like C_2H_6 and C_3H_8 are present in the mixture. At very high Φ (10 and 20), CH_4 conversion was negligible small in case of the neat CH_4 mixture and was increased to more than 10 % in case of the NG mixtures. As a result of that much higher product yields of synthesis gas, C_2H_4, CH_3OH or C_3H_6, for example, can be obtained with NG at these Φ, compared to neat CH_4. The addition of H_2 into the NG mixture did not alter the product composition in any case. Furthermore, the initiation reactions as well as the reaction pathway towards C_2H_4 have been analyzed by performing global reaction flow analyses with the reaction mechanism of Burke et al. [4]. Simulations, conducted with this mechanism, showed reasonable agreements with the general trends of the yields. Nevertheless, some discrepancies could be observed as well, which corroborate the need for better kinetics models for these uncommon reaction conditions.

References

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