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# Experimental and numerical study of applicability of porous combustors for HCl synthesis

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## Abstract

Porous combustors have been studied intensively concerning the combustion of natural gas. The advantages of combustion in porous inert media, such as low emissions, high power turndown ratio of typically 10:1 and compactness, can also be used for different chemical gas phase reactions, e.g. the HCl synthesis from $H_2$ and $Cl_2$. The advantages of porous reactors result from the heat transport properties of the porous medium, i.e. emissivity and conductivity. Heat transport mechanisms and chemical reactions were implemented in a numerical code in order to investigate the $H_2/Cl_2$ system. Important parameters of the reaction, e.g. the laminar flame speed and the adiabatic flame temperature, are higher for the $H_2/Cl_2$ reaction compared to the $CH_4$/air combustion. By studying the influence of $H_2O$ and HCl as inert components it was shown by numerical investigations that the maximum temperature could be decreased to a level, which makes the usage of a porous reactor feasible. A porous reactor for laboratory use was tested with $O_2/CH_4/N_2$ combustion, which delivers even higher adiabatic temperatures and flame speeds than the $H_2/Cl_2$ reaction. Finally, experiments with $H_2/Cl_2$/HCl reaction were carried out and first results are presented. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Porous combustors; Natural gas; HCl synthesis

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## 1. Introduction

Most combustion techniques for gaseous fuels are characterised by free flame structures, where the combustion takes place within a thin reaction layer. The reason for the thin combustion zone bases on the poor heat transport properties of the gas mixture, which make high temperature gradients necessary for heat transfer against the flow direction.

Inserting solid porous material into the combustion region improves the overall heat transport resulting in extended reaction layers and higher burning rates due to gas preheating. The principal heat transport mechanisms in a porous burner are shown in Fig. 1.

The porous burner is split into two zones: region A, where the reactions are quenched due to the small pore size and region C, where reactions and the main heat release take place. The main reactions stabilize between these both regions [1]. This so called quenching principle of stabilization enables very high turndown ratios. The same principles apply for different gas phase reactions, and especially the HCl synthesis from $H_2$ and $Cl_2$ is investigated. For this application, two main parameters of the reaction show a big difference compared with the $CH_4$/air combustion, where usually 1400°C at an excess air ratio of 1.3, are reached at a maximum temperature. The stoichiometric

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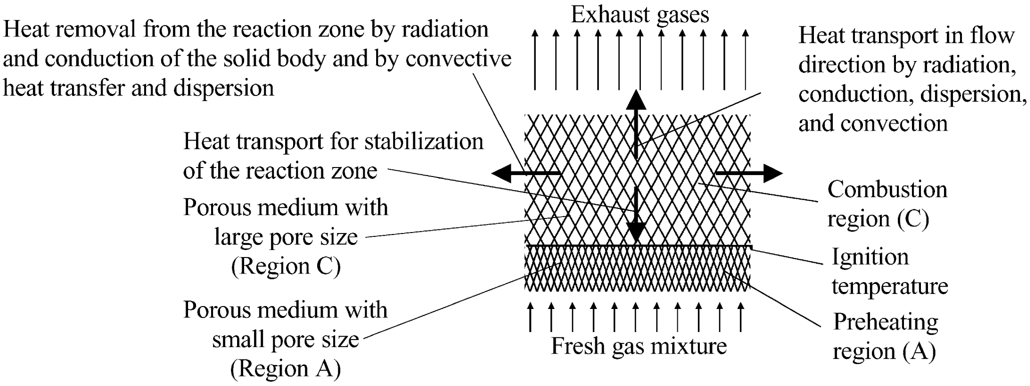

Fig. 1. Heat transport mechanisms in a porous burner.

adiabatic temperature of an $H_2/Cl_2$ flame is with 2400°C significantly higher than the one of the stoichiometric $CH_4$/air combustion with 2000°C. The maximum temperature and the chemical resistance of the solid material are limiting parameters of the porous burner. Additionally, the laminar flame speed of the stoichiometric $H_2/Cl_2$ system is with 2.2 m/s, five times higher than the one of the $CH_4$/air system (Gmelins Handbook [2]). This parameter plays an important role for the stabilization process of the reaction within the porous medium. Furthermore, the stabilization process is even more complex for the $H_2/Cl_2$ reaction, because it can be ignited by UV-radiation, which is also emitted by the combustion itself, which means that ignition might occur far from the hot main reaction region. Therefore, additional measures can become necessary for the stabilization of the $H_2/Cl_2$ combustion process. The great differences of the flame speed and the adiabatic temperature result from the high content of the inert gas ($N_2$) in the $CH_4$/air system, which lowers the adiabatic reaction temperature due to its heat capacity and decreases the flame speed due to lower concentrations of the reactive components. Therefore, $Cl_2/H_2$ combustion with similar properties can only be achieved, if an inert component is added to the $Cl_2/H_2$ mixture. In the following, the results of the numerical study, which aimed on the determination of the influence of inert components are described.

## 2. Numerical investigation

A numerical study was carried out with the aim of calculating the heat balance of the reactor for the $Cl_2/H_2$ system with the inert components $H_2O$ and HCl, respectively. A parameter study was carried out in order to determine the minimum content of the inert component, which makes the operation of such a reactor possible. The finite volume code Fastest described by Brenner et al. [3] was used for these calculations and a five-step mechanism proposed by Coppersthwaite and Griffiths [4] was implemented for the HCl reaction. The Arrhenius parameters of

Table 1
Arrhenius parameters of the used $H_2/Cl_2$ combustion mechanism [4][a]

| Reaction | $k_0$ | $E_A$ (kJ/mol) | $\Delta H$ (kJ/mol) |
|---|---|---|---|
| $Cl_2 + M \rightarrow 2Cl + M$ | $1 \times 10^{11}$ m$^3$/(s mol) | 182.9 | 245 |
| $Cl + H_2 \rightarrow HCl + Cl$ | $1 \times 10^{6}$ m$^3$/(s mol) | 23.0 | 3 |
| $H + HCl \rightarrow H_2 + Cl$ | $5 \times 10^{6}$ m$^3$/(s mol) | 1.7 | −189 |
| $H + Cl_2 \rightarrow HCl + Cl$ | $8 \times 10^{7}$ m$^3$/(s mol) | 0.6 | −3 |
| $2Cl + M \rightarrow Cl_2 + M$ | $1 \times 10^{5}$ m$^6$/(s mol$^2$) | 0 | −245 |

[a] Rate constant: $k = k_0 \exp(E_A/RT)$, $R = 8.314$ kJ/kmol K, $[T]$ in K.

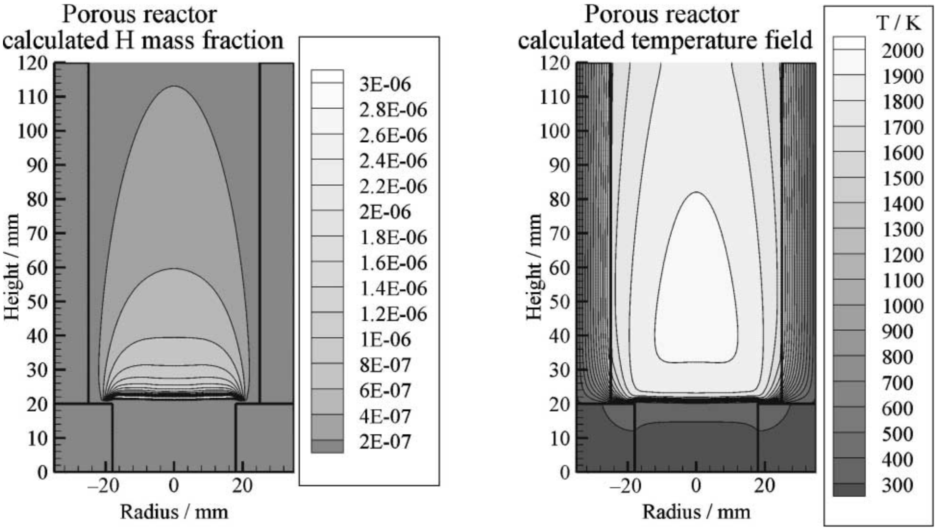

Fig. 2. Calculated H-radical and temperature profile of a porous HCl-reactor, 60% HCl recirculation.

the considered reactions are given in Table 1. Typical results of the numerical calculation are shown in Fig. 2.

It was found that a minimum recirculation of 1.2 mol HCl per mol $Cl_2$, which corresponds to 60% mole fraction of the feed components (60% recirculation), is necessary, which results in a maximum temperature of 1650°C. If 0.95 mol $H_2O$ per mol $Cl_2$ are added, the maximum temperature reaches 1720°C. For the calculations of the $CH_4/O_2/N_2$ combustion a multi-step mechanism proposed by Kazakov and Frenklach [5] was used. With 15% less $N_2$ content compared with a $CH_4$/air system a maximum temperature of 1550°C was reached.

## 3. Experimental results

One potential advantage of the porous burner technology applied to the HCl synthesis is the feasibility of premixing the reactants, which would lead to a decrease in the amount of the required excess $H_2$ for the HCl production. A swirl mixing chamber for laboratory use was designed and tested. Experiments with non-premixed $CH_4$, $O_2$ and $N_2$ were performed in order to determine the mixing of three components in the swirl chamber and in order to evaluate flash back characteristics. Only very small differences of the CO emission characteristic compared with the fully premixed behaviour were detected. The $CH_4/O_2$ system has an even higher flame speed (6 m/s) than the $Cl_2/H_2$ system and also a higher adiabatic temperature of 2800°C (Baukal [6]). The values of the flame speed and the adiabatic temperature can be adjusted by adding $N_2$ as the inert component to the mixture. Experiments were carried out at 2 and 5 kW, which correspond to flow speeds at the inlet of region A of 0.7 and 1.8 m/s, respectively. Flash back occurred at the lowest power setting of 2 kW with the $CH_4/O_2/N_2$system when the $N_2$ fraction was only 86% of the $N_2$ fraction in air, which is shown in Fig. 3. This shows that a high inert content must be fed to the combustor to avoid flash back. At 5 kW a centre temperature of 1550°C was reached, which is the maximum temperature limit of the used ceramic porous medium. Additionally, experiments with $H_2$ and $Cl_2$ with HCl recirculation were performed. In Fig. 4 measured temperature profiles of experiments with 150% HCl recirculation are shown. The temperature in region C reached 960°C. Region A remained cold, which indicates the stabilization of the process between regions A and C. The redox potential, which was measured against Ag–AgCl, indicates a chlorine free

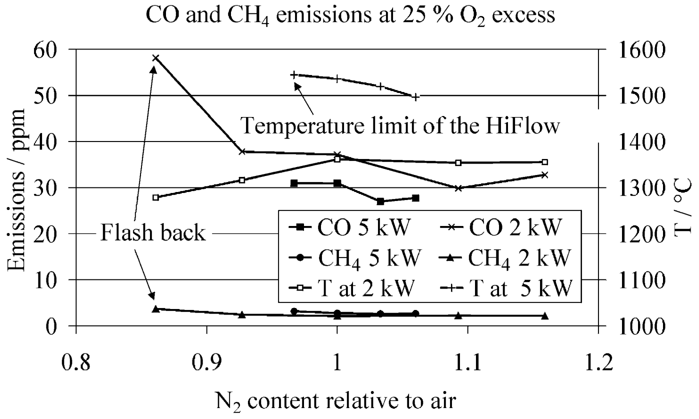

Fig. 3. Emissions and centre temperature of the burner with the $N_2/O_2/CH_4$ system.

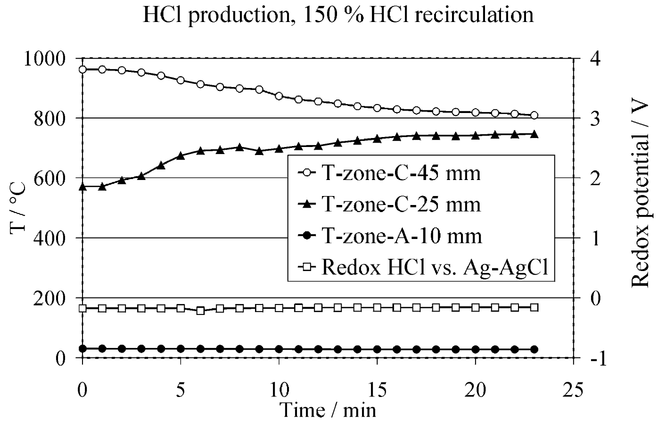

Fig. 4. Reactor temperature and redox potential during 2.9 kg/h HCl production.

produced acid, although significantly lower excess $H_2$ than for state of the art HCl reactors was used.

## 4. Conclusions

The experiments and the numerical results show that porous reactors can be used for gas phase reactions with very high flame speeds and adiabatic temperatures, if an additional inert component is added to the reactants. The amount of the inert component is crucial for both the stability of the reaction and the maximum temperature. It is shown that with a porous reactor using stabilization within the porous matrix, premixing can be used also for very reactive components. Applying the porous burner technology to the HCl synthesis from $H_2$ and $Cl_2$, only very low excess of $H_2$ is required to achieve high quality HCl acid.

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