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CO_2 Reduction to CO Using a Microwave Heated Catalyst

Thorsten Kayser, Andreas M. Melcher, Guido Link, and John Jelonnek

Institute for Pulsed Power and Microwave Technology, Karlsruhe Institute of Technology, Germany

Abstract – The project CO_2RRECT (CO_2-**R**eaction using **R**egenerative **E**nergies and **C**atalytic **T**echnologies) is about the reduction of CO_2 to CO as a precursor for chemical industry using mostly regenerative energy. [1] The corresponding chemical reactions, either RWGS (reverse water gas shift) or CO_2 reforming are endothermic. Hence energy in the form of heat has to be supplied continuously. In this work, heating is done by microwaves at a frequency of 2.45 GHz. The advantage of this approach is that microwaves penetrate into the catalyst support, getting the heat directly to the location where the reaction takes place, while with conventional heating the heat has to be supplied from the outside, reaching the location of the reaction only by heat conduction and thereby limiting the flow capacity.

Introduction

In this paper a bench-scale microwave applicator is described. It consists of a quartz tube inside a waveguide with the catalyst embedded inside. A gas consisting of the reactants flows through the tube with a temperature above 800 °C while the catalyst support is heated by the microwave. A resonant approach is used for a high efficiency. The electromagnetic and thermal response of the applicator are simulated using COMSOL Multiphysics with the RF and Heat Transfer module considering the mutual coupling between the electromagnetic and thermal field.

The reverse water gas shift reaction [2] is well known in chemical sciences as a method for producing water from carbon dioxide and hydrogen, with carbon monoxide as a side product. In the presence of a suitable catalyst, the reaction takes place according to

$$\mathrm{CO_2} + \mathrm{H_2} \longrightarrow \mathrm{CO} + \mathrm{H_2O}, \quad \Delta H \approx 38\,\mathrm{kJ\,mol^{-1}}\ . \tag{1}$$

A suitable catalyst works in a temperature range above 800 °C. To achieve these temperatures and to supply the necessary energy, required for the RWGS according to equation (1), within the volume of the catalyst bed by conventional heating is difficult, since the heat is transferred from the reactor walls into the reactor volume by conduction, convection, and radiation [3]. So cooling of the reactor volume by the RWGS reaction may dominate the heating and therefore limits the flow capacity of the reactor. Application of microwave heating may help to overcome these limits since microwaves allow for direct heating of the reactor volume, where the energy is needed to activate the endothermic RWGS reaction. In addition to that, a molecular interaction of the educts with the electromagnetic field as an additional driving force for the reaction hast been reported [4].

Modeling of Microwave Heating

The RWGS reaction is an endothermic reaction, meaning that heat from the surrounding space is required to excite and preserve the reaction. Here, microwave radiation is used as a heating source, so Maxwell's equations must be solved for the electromagnetic field distribution in the microwave cavity.

Then the absorbed power per unit volume is given by

$$Q_\mathrm{W} = \frac{1}{2}\omega\varepsilon_0\varepsilon_\mathrm{r}''|\hat{\mathbf{E}}|^2\ . \tag{2}$$

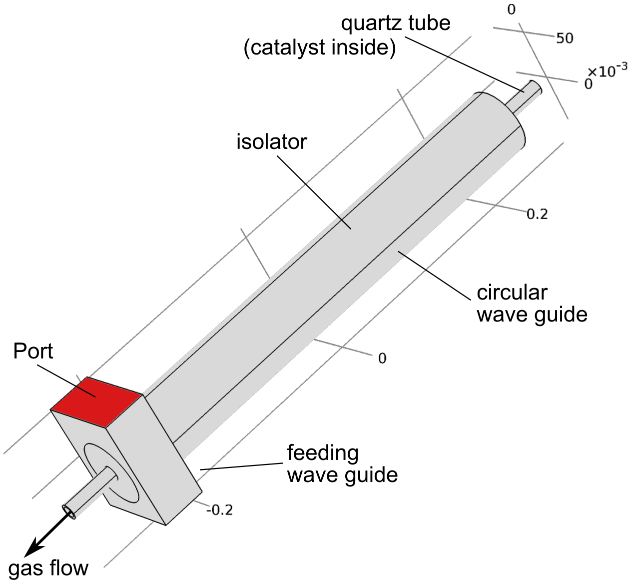


Fig. 1: Model of the applicator with feeding waveguide at the bottom.

The temperature distribution inside the wave guide and the catalyst is given by the well-known heat equation, where it is assumed that the gas flow is inactive, i. e. no convection terms in the heat equation will appear:

$$\rho c_\mathrm{p} \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + Q_\mathrm{W} \ , \tag{3}$$

where ρ is the mass density, c_p is the specific heat capacity, and k is the thermal conductivity.

Construction of a Microwave Heated Catalyst

The computational domain and geometry of the applicator is shown in Fig. 1. The main part consists of a metal cylinder which acts as a waveguide for the microwave field. The diameter of this circular waveguide is chosen in such a way that the cutoff frequency of the desired base mode is below the operating frequency 2.45 GHz and no higher modes will appear. The feed is a standard rectangular WR340 wave guide with a 2.45 GHz magnetron as the microwave source. The catalyst is embedded inside a quartz tube in the center of the outside circular waveguide. The catalyst zone is split into a chemical active part and a “non-active” pre-heating zone. The volume between the outer surface of the quartz tube and the inner surface of the circular waveguide is filled with insulating material (ALTRA® KVS High Temperature Vacuum Formed Board, type KVS184/400, Rath Company, USA). This is necessary to keep the heat inside the cylinder so that high temperatures can be achieved. The quartz tube is filled with pellets of material like Cordierite ($Mg_2Al_4Si_5O_{18}$), alumina (Al_2O_3) or zirconium oxide (ZrO_2) which act as a support for the catalyst. The lower and upper parts remain empty for the inflow and outflow of the reactants and products of the RWGS reaction.

During operation, gas consisting of the reactants flows through the tube passing through the porous media. From the feeding port, the electromagnetic wave propagates along the cylinder while dissipating to heat inside the catalyst support. The non-dissipated part of the wave is reflected at the end of the cylinder, causing a standing wave inside the applicator. This leads to a narrow-band resonant design that is highly efficient.

Some dimensions of the applicator are given in Table 1. The materials are assumed to be piecewise homogeneous materials. The material properties are given in Table 2. These properties are valid at room temperature (20 °C) and assumed to be constant over the considered temperature range as a first approximation.

Table 1: **Dimensions of Applicator.**

Component	Dimension	Value
circular waveguide	length	484 mm
	inner diameter	64 mm
	outer diameter	80 mm
quartz tube	inner diameter	11 mm
	outer diameter	15 mm
catalyst (active)	length	271 mm
preheat zone	length	213 mm

Table 2: **Material Parameters**

Material	ε_r	$\tan\delta$	k in $\frac{\mathrm{W}}{\mathrm{K\,m}}$	ρ	c_p in $\frac{\mathrm{J}}{\mathrm{K\,kg}}$
Cordierite	5	0.05	0.7	2500	1110
quartz glass	3.8	$4{\cdot}10^{-4}$	1.8	2203	900
isolator	1.2	0	0.04	20	900

The dielectric properties of the catalyst supports are given for non-porous media from which the effective values have to be estimated for a relative porosity of about 0.5. In this simulation the support of the catalyst consists of Cordierite.

Simulation

The applicator is simulated and optimized using COMSOL Multiphysics 4.2, a finite element software which is able to compute solutions described by a system of simultaneously coupled partial differential equations representing fully coupled physical problems. In this case, the electromagnetic field and the temperature distribution are mutually coupled. The electric field acts a heat source for the thermal field, which in turn influences the electromagnetic field as the material parameters are usually temperature dependent even if they are assumed constant for now. The geometric parameters were determined such that a good matching is achieved at the design frequency of 2.45 GHz. Therefore, the S_{11} scattering parameter at the waveguide port is calculated by the electromagnetic waves module in the frequency range from 2.3 GHz to 2.6 GHz.

Two different simulations were performed. The first one consists of two steps. At first a boundary mode analysis with a center frequency 2.45 GHz is performed, followed by a frequency domain simulation in the above mentioned frequency range. For both steps the same mesh is used, and is refined by the automatic mesh refinement of COMSOL. The electromagnetic field distribution inside the applicator is also calculated.

In the second simulation, the temperature distribution inside the applicator and catalyst support is calculated using the previously calculated electric field as a heat source. The same mesh as for the electromagnetic simulation is used. The fully coupled electromagnetic-thermal simulation has been done by the microwave heating module. The excitation of the structure occurs at the waveguide port at the operating frequency 2.45 GHz. The input power is 800 W. The total simulated heating time is 70 s. At the present state of the model, no gas flow is considered. An experimental setup of the simulated applicator is in preparation.

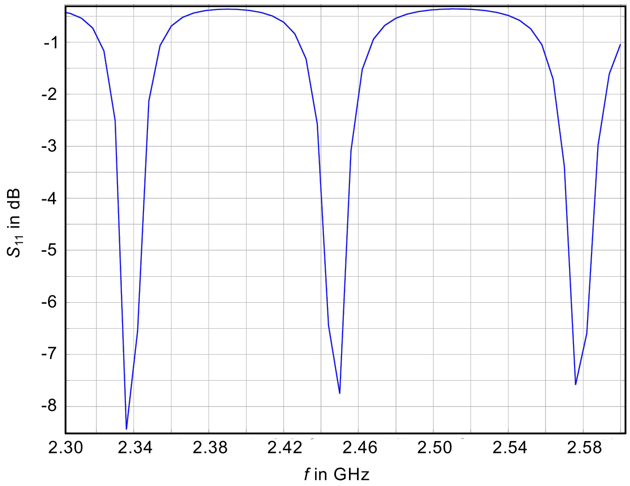


Fig. 2: S_{11} input reflection factor for the Cordierite applicator.

Simulation Results

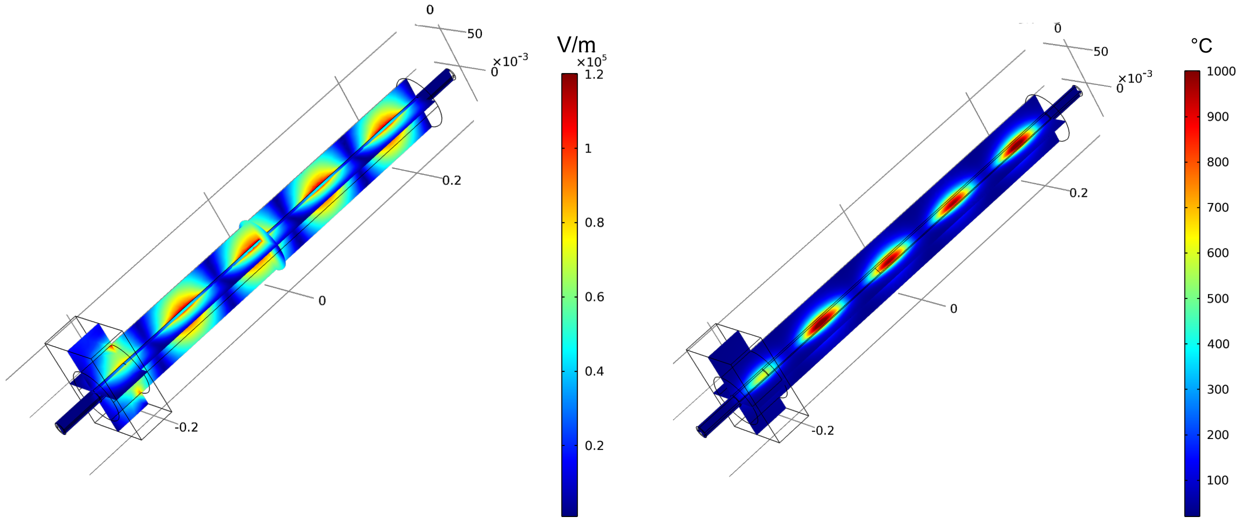
The calculated S_{11} parameter is shown in Fig. 2. One can see several minima at the resonant frequencies. The dimensions are chosen such that one resonance is at 2.45 GHz, i. e. the center of the frequency axis. The matching at this frequency is better than −7.5 dB, which is good enough to get a further enhancement of the matching using a stub tuner. The 3 dB-bandwidth is quite small – only ± 50 MHz due to the high quality factor of the cavity. This is enough for proper operation under the condition of constant material parameters. As these may change, some tunable elements will be provided in the final design which will change the effective electric length of the cylindrical waveguide. The corresponding electric field distribution is shown in Fig. 3a.

One can see four equidistant maxima along the cylinder due to the standing wave inside the cylinder. This corresponds to the resonant design of the applicator. At the resonance frequencies, a whole number of such maxima (half of the wavelength) fit into the longitudinal direction of the cylinder. A higher local electric field strength causes more heating at that location. The positions of these “hot-spots” give a clue about suitable locations for the catalyst. As the material parameters do not change in the present state of the model, the complex amplitude of the electric field, and hence the positions of the maxima, remain constant during the processing.

The electric field acts as a heat source inside the catalyst support according to equation (2) causing the corresponding temperature distribution shown in Fig. 3b. The temperature distribution shows several hot spots which correspond to the maxima of the electric field. In the center of these spots the temperature achieves 1000 °C, which is the desired value, after 70 s of heating time. These spots can serve as preheating zones or active zones if they are covered with the catalyst material. It is expected that the temperature distribution will be more homogeneous once the convection by the gas flow is considered in the model.

Conclusion and Outlook

In this work, basic modeling of microwave heating of a catalyst used for the RWGS reaction consisting of electromagnetic and thermal contributions is introduced. The modeling and simulations are done with the goal of finding a setup which guarantees optimal heating of the catalyst. In future work the model will be extended with contributions coming from fluid dynamics and reaction kinetics. It is also important to notice that the material parameters, especially of the catalyst support, are dependent on the temperature.



(a) electric field distribution

(b) temperature distribution

Fig. 3: Simulated results, field distributions inside the applicator.

The results of high-temperature dielectric measurements will be incorporated into the model. Furthermore, an experimental reactor for the microwave heating of the RWGS reaction will be constructed based on the simulation results.

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