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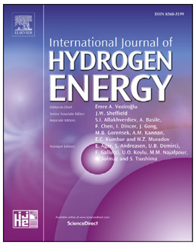

# CFD study of heat and mass transfer in ethanol steam reforming in a catalytic membrane reactor☆

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ABSTRACT

This work shows the analysis of ethanol steam reforming process within a catalytic membrane reactor. A 2-D non-isothermal CFD model was developed using Comsol Multiphysics, based on previous experimentally validated isothermal model. A comprehensive heat and mass transfer study was carried out utilizing the model. Operating conditions such as liquid hourly space velocity (LHSV) (3.77–37.7 $h^{-1}$), temperature (673–823 K), reaction side pressure (4–10 bar) and permeate side sweep gas flow pattern were discussed. A temperature gradient along the reactor was observed from the model and a “cold spot” was seen at the reactor entrance area, which is unfavorable for the highly endothermic ethanol steam reforming process. By changing the sweep gas pattern to counter-current, the “cold spot” appears to be smaller with a reduced temperature drop. By studying the individual reaction rates, reverse methane steam reforming (methanation) was observed, caused by the low temperature in the “cold spot”. Optimal operating conditions were found to be under LHSV = 37.7 $h^{-1}$ and counter-current sweep gas conditions.

## Introduction

Conventional steam reforming processes with fossil fuels for hydrogen production play a major part in the hydrogen industry as of today. Ethanol steam reforming (ESR) is studied since bio-ethanol is considered a carbon neutral hydrogen source compared to methane from natural gas, it has low toxicity and easy storage and high energetic density [1]. ESR is endothermic, and requires high temperatures with effective heat management [2]. Conventional packed bed reactors do not present many degrees of freedom for the reactor design engineer. Particle diameter is one, but this is usually constrained by the opposing requirements of good intraparticle diffusion and bed pressure drop. For this reason interest has developed in alternative configurations such as fluidized beds, micro-channels or monoliths, and catalytic membrane reactors.

Structured catalysts, in the form of monoliths, have some advantages over fixed beds. They prevent channeling of flow, have lower pressure drop, and upscaling is easy [3]. Reaction efficiency, in terms of ethanol conversion, hydrogen production and heat consumption is a concern, and attempts to improve it by changing channel geometry in a microreactor have recently been made [4]. One approach to heat management has been to

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couple endothermic ethanol reforming to exothermic ethanol combustion in a parallel plates reactor [5].

Catalytic membrane reactors (CMR) are attracting more interest due to their benefit of high reactant conversion and hydrogen yield [6,7]. As the hydrogen production and separation are conducted in the same unit, the depletion of hydrogen from the reaction area causes a change in composition, allowing achieving higher conversions. Consequently, more hydrogen is generated compared to the traditional packed bed reactor (PBR); this process is known as process intensification. Many aspects like spatial velocity, ethanol to steam ratio and sweep gas have been studied in order to fully understand the performance of CMR and also to achieve a better reactor performance [8,9]. For example, for the membrane reactors with sweep gas on the permeate side, increasing sweep gas flow rate has a positive influence on the reactor performance; increasing membrane permeance can enhance the hydrogen production as well [10]. Hydrogen partial pressure, the driving force for hydrogen permeation through palladium membranes, has been found to have a positive influence on hydrogen recovery and yield [9,11]. In steam reforming processes, another often-studied parameter is the reacting temperature, as the process is usually highly endothermic, and both reaction rate and equilibrium benefit from high temperatures. In addition, for membrane reactors, the heat supply to the reaction zone also has to compensate for the energy loss from the enthalpy that the hydrogen carries away while permeating through the membrane [12]. Some studies have been done to reduce the required heat supply for both packed bed reactor [13] and membrane reactor [14] by proposing a “heat-integrated” or “autothermal” reactor. The concept is to couple endothermic and exothermic reactions in the same unit to form a “homogenous reactor”. For traditional reactors, two conjugate reactions are placed in parallel and separated by a wall [15–17], while for membrane reactors, it is often accomplished by integrating two conjugated reactions on each side of the membrane [18].

Previously, an experimental study along with an isothermal computational fluid dynamics (CFD) analysis was conducted by the authors [19] and a large-scale membrane reactor with a membrane surface area of 150 $cm^2$ was utilized in the study. The 2D simulation model provided an accuracy of 91% compared with the experimental data. In this study, the non-isothermal behavior was included into the existing model for the comparison with the previous study. A temperature gradient was observed as expected, and a “cold spot” was shown adjacent to the membrane. The study of reaction rate was introduced and since the process reaches equilibrium very soon after the reactants enter the reactor, different inflow rates and counter-current sweep gas flow were discussed in order to fully use the reactor length and membrane surface area.

## Methodology

### System description

The tubular CMR consisted of a reactor shell containing the membrane tube. The reactor shell had an outer diameter of 0.0286 m and a length of 0.4064 m. Commercial nickel-based catalysts were used in the experiment, a two-screen cage for the catalyst was designed in order to separate the catalyst and the membrane surface. A palladium-gold alloy permeable membrane tube with a surface area of 150 $cm^2$, an outer diameter of 0.5 inch (0.0127 m) and a length of 15 inches (0.381 m) was then placed in the middle of the cage and put inside the reactor shell. The thickness and the structure of the membrane was Pd 6.9 μm/Au 0.2 μm/Pd 6.7 μm/Au 0.1 μm The whole system was then placed into a well-insulated oven with controlled temperature in order to provide an isothermal environment for the reactor. Thermocouples were placed outside of the reactor shell surface, in order to monitor the temperature of the shell. The shell temperature is not necessarily the same as the set oven temperature thus the temperature boundary condition in the simulation was set to be the value from the thermocouples. The geometry was the same as in Castro-Dominguez et al. [20] and Ma et al. [19]. Reactions were carried out on the shell side (retentate side) and hydrogen was depleted by the membrane simultaneously and collected from the tube side (permeate side). A mixture of reactants with a steam to ethanol ratio of 5 was fed into the retentate side with LHSV of 3.77 $h^{-1}$, before entering the system, the reactant flow went through a preheater in order to reach the same temperature as the oven. Helium was used as sweep gas and was introduced into the system with an inflow rate of 65 ml/min. This rate was chosen to be the same as the experimental rate in the previous study, and was not varied in the present work. Before the reaction started, a permeation test and helium leak test was conducted and the hydrogen permeance was shown to be 11 $Nm^3m^{-2}h^{-1}bar^{-0.5}$ and 21 $Nm^3m^{-2}h^{-1}bar^{-0.5}$ at 350 °C and 450 °C respectively, and a helium leak of $7.987 \times 10^{-3}$ kg/$(m^2s\ bar)^{-1}$ was observed [19].

### 2-D simulation methods

Among all the side reactions of ethanol steam reforming with commercial nickel based catalyst, only the following most representative reactions are considered in the simulation [21].

$$\text{ESR} \quad C_2H_5OH \leftrightarrow CH_4 + CO + H_2 \quad \Delta H_1 = 49\ \text{KJmol}^{-1} \tag{1}$$

$$\text{WGS} \quad CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_2 = -41\text{KJ/mol}^{-1} \tag{2}$$

$$\text{MSR} \quad CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H_3 = 205\text{KJ/mol}^{-1} \tag{3}$$

$$\text{MSR} \quad CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H_4 = 165\text{KJ/mol}^{-1} \tag{4}$$

Many studies of the kinetics of ethanol steam reforming using different catalysts were carried out [22] and the kinetics used in our model were presented (Table 1) and validated using data from the existing references [23,24] in the previous publication [19]. Notice that in the previous study, temperature terms in the kinetics were considered as constant (shell temperature) while in the current study temperature was defined as a variable and coupled with heat transfer equations. In addition, hydrogen permeance of the membrane is also a function of temperature, which is included in the current study.

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