



# Ceramic counterflow reactor for autothermal dry reforming at high temperatures



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## ARTICLE INFO

### Article history:

Received 25 November 2015

Received in revised form 31 January 2016

Accepted 2 February 2016

Available online 29 March 2016

### Keywords:

Dry reforming of methane

Autothermal reactor model

Catalytic reforming

Ceramic materials

## ABSTRACT

Dry reforming (DRM) is a very promising route for producing carbon rich syngas from key future feed stocks of chemical industry: CO<sub>2</sub> and methane. Partial combustion of methane with pure oxygen, preferably produced via water electrolysis, can be used to compensate for the required heat of reaction in autothermal operation of DRM. Therefore, a novel reactor concept is presented. The multitubular reactor consists of an inert section to perform efficient heat integration and a catalytically coated reaction section where temperatures far above 1000 °C are realized by means of ceramic materials, a suitable catalyst, and simultaneous combustion. A prototype laboratory scale reactor, equilibrium models, and a detailed kinetic model are used to measure the reactor performance in laboratory and in industrial scale. A stable operation is predicted in large scale reactors since constantly high reaction temperatures around 1000 °C can prevent harmful coke formation. Besides, the high temperatures enable CO<sub>2</sub> conversions above 60% along the catalyst zone in a reactor which is characterized by a very simple and scalable design.

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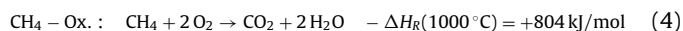
## 1. Introduction

Chemical reactor and catalyst development are mainly driven by emerging new chemical processes. A common trend is the worldwide extended use of renewable energy resources, demanding efficient short and long term energy storage [10]. Energy storage through production of hydrogen and oxygen via water electrolysis is a scalable existing technology [16].

Carbon dioxide, captured e.g. from coal fired power stations, will remain a highly available carbon source. This can be concluded from the predicted increase of CO<sub>2</sub> emissions [17]. Processes for large scale CO<sub>2</sub> separation from power station flue gas exist. Another trend is the growing extraction of natural gas, mainly methane (CH<sub>4</sub>), from so far unused sources, e.g. by fracking technology [9].

Dedicated processes for producing carbon rich syngas from these resources are gaining increasing interest. Synthesis gas, a mixture of hydrogen and carbon monoxide, can be used for producing liquid fuels (Fischer–Tropsch synthesis) or methanol for various value chains of chemical industry [15,21]. Promising routes for the syngas production are given by Eqs. (1)–(3). Apart from the reverse water gas shift reaction (RWGS) or the partial oxidation of methane (POX), dry reforming of methane (DRM) is a reasonable

option. The required energy of this highly endothermic reaction can be provided by simultaneous oxidation of methane (4), enabling an overall autothermal reaction process.



To date, no suitable technology for dry reforming has been scaled to industrial production. Technological improvement in this field strongly depends on new reactor concepts for reaction temperatures well above 1000 °C. Below this temperature limit, severe coke formation occurs in case of DRM without simultaneous combustion [2,3]. Moreover, high temperatures are required for high syngas yield and high carbon monoxide product content. One key to successfully conduct autothermal dry reforming is a suitable reactor concept which allows to exceed this temperature limit in combination with a temperature resistant catalyst.

### 1.1. Requirements and limitations of existing reactor technology

Conventional steam reforming technology is based upon indirect heat transfer from burners through the walls of the reformer tubes. Thermal stability of respective metal reformer tubes limit the reaction temperatures inside the tubes to values below 1000 °C.

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**Notation***Latin letters*

$a_C$	carbon activity (-)
$A_q$	cross sectional surface (m <sup>2</sup> )
$a_V, a_V^*$	specific surface area (m <sup>2</sup> /m <sup>3</sup> )
$c_j$	concentration (mol/cm <sup>3</sup> )
$c_p$	specific heat capacity (kJ/kg/K)
$d$	diameter (mm)
$D_{ax}^G$	mass dispersion coefficient (m <sup>2</sup> /s)
$e$	emissivity of radiation (-)
$E_A/R$	activation temperature (K)
$F_{\zeta\xi}$	view factor between surface $\zeta$ and $\xi$ (-)
$\Delta H_R$	enthalpy of reaction (kJ/mol)
$k$	reaction rate constant (mol/m <sup>2</sup> /s or mol/m <sup>3</sup> /s)
$L$	length (m, mm)
$L_{cat}$	length of catalyst coating (m, mm)
$\dot{m}, \dot{M}$	mass flow (kg/m <sup>2</sup> /s or kg/s)
$MW$	molar mass (kg/mol)
$N$	number of reaction tubes (-)
$p, p_j$	pressure, partial pressure (bar)
$\dot{q}, \dot{Q}$	heat flow (kW/m <sup>2</sup> or kW)
$r, r_V$	specific reaction rate (mol/m <sup>2</sup> /s or mol/m <sup>3</sup> /s)
$T$	temperature (°C, K)
$w$	mass fraction (kg/kg)
$X$	conversion (%)
$y$	volume fraction (m <sup>3</sup> /m <sup>3</sup> )
$z$	axial reactor coordinate (m, mm)

*Greek letters*

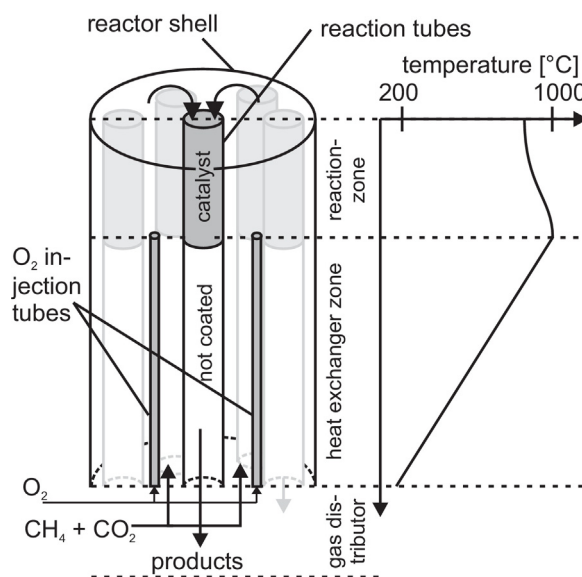
$\alpha$	heat transfer coefficient (W/m <sup>2</sup> /K)
$\beta$	mass transfer coefficient (m/s)
$\eta$	equilibrium constant (-)
$\eta_{he}$	heat exchanger efficiency (%)
$\lambda$	heat conductivity (W/m/K)
$\lambda_{ax}$	heat dispersion coefficient (W/m/K)
$\nu$	stoichiometric coefficient (-)
$\rho$	density (kg/m <sup>3</sup> )
$\sigma$	Stefan–Boltzmann constant (W/m <sup>2</sup> /K <sup>4</sup> )
$\sigma_j$	switch term (-)

*Superscripts*

$a$	outer
$ex$	external, to environment
$G$	gas phase
$i$	inner
$j$	jacket
$P$	products
$R$	reactants
$S$	surface gas phase
$W$	tube wall

*Subscripts*

$i$	reaction index
$in$	inlet
$j$	component index
$out$	outlet



**Fig. 1.** Schematic sketch and expected temperature profile of autothermal counterflow reactor.

recovered at much lower temperatures due to lack of sufficiently temperature stable heat exchanger materials [4].

To avoid Boudouard reaction and methane dissociation, the main reasons for coke formation, temperatures above 1000 °C and a suitable, temperature-stable catalyst as well as catalyst support are necessary for DRM [2]. Presently existing reactor materials for high temperature reactions are based on expensive metallic alloys whose stability is limited to 1000 °C and which are highly susceptible for irreversible metal dusting corrosion in CO-rich gas atmospheres [6].

A suitable reactor material for the high temperature range of dry reforming should therefore be able to withstand temperatures well above 1000 °C at pressures up to 25 bars and have sufficient heat conductivity for a heat-integrated reactor design. Recent substantial improvements in the availability of ceramic materials for high temperature applications show that they can be interesting candidates for this application. This is the base of the present study.

## 1.2. The ceramic counterflow reactor

To test the feasibility of a heat-integrated ceramic reactor for dry reforming, an autothermal counterflow reactor concept has been developed. Fig. 1 shows a schematic picture and a simplified temperature profile inside the reactor. The main features of this concept are the ceramic reaction tubes, which are located inside a ceramic reactor shell. A high temperature insulation outside the reactor shell is used to minimize external heat losses. This insulation can be extended by a pressure-retaining jacket to enable high-pressure operation.

The inner reaction tubes are coated at their top ends both inside and outside with a suitable reforming catalyst. This can be easily done by dip coating the tubes into a catalyst slurry. In Fig. 1 the catalyst section is denoted as reaction zone whereas the uncoated part is called heat exchanger zone. Excessive thermo-mechanical stress on the reaction tubes is avoided because the tubes are only fixed in the gas distributor and can expand freely into the reaction zone.

The DRM reactants (CH<sub>4</sub> and CO<sub>2</sub>) are fed via a gas distributor into the reactor shell space. To avoid back ignition, oxygen, necessary for partial combustion of methane, is added through additional feed tubes, connected with the gas distributor and

Heat of the hot product stream is only used for steam production at lower temperatures. More efficient heat supply is achieved in autothermal reformers by simultaneous methane combustion without spatial separation of combustion and reforming reaction. But the high heat content of the effluent can again only be partially

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