



# Modelling and optimization of a moving-bed adsorptive reactor for the reverse water-gas shift reaction

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## ABSTRACT

In this work, a novel variant of the reverse water-gas shift reaction is proposed as a promising route to valorize CO<sub>2</sub> as syngas. The reactor concept used is that of an adsorptive moving-bed in order to permit low-temperature operation with high conversions and to improve upon the fixed-bed adsorptive concept previously investigated. The reactor has been modelled for several configurations and subsequently optimized. The results show that an increase up to an order of magnitude in the space-time-yield (STY) is possible by using the moving-bed configuration in comparison to fixed-bed operation. Finally, a bi-objective optimization is carried out to identify the trade-off between operating at higher STY and higher adsorbent loadings.

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## 1. Introduction

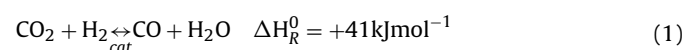
Carbon dioxide concentration in the atmosphere has been steadily increasing over the past few decades. Concerns about the resultant climate change, led to the adoption of the Paris Agreement after the COP21 meeting ([UNFCCC Conference of the Parties \(COP\), 2015](#)). The main proposed goal is to minimize CO<sub>2</sub> emissions in order to keep the mean global temperature increase below 2 °C. To accomplish this objective, it is clear that drastic reductions must be achieved in all CO<sub>2</sub>-emitting industries. Since CO<sub>2</sub> has become to be regarded as an unwanted by-product, alternative CO<sub>2</sub>-free technologies have started to emerge. Nonetheless, when CO<sub>2</sub> generation is unavoidable, it is crucial to address what needs to be done with the CO<sub>2</sub> produced. Alternatives such as Carbon Capture and Storage (CCS) have been proposed as solution. However, the feasibility of CCS, as well as its public acceptance, still represent major hurdles for its adoption on a large-scale. The main challenges for CCS are still: (i) reduction of costs, (ii) understanding of long term risk factors and (iii) quantification and understanding of reservoir options ([Muradov, 2017](#); [Muradov and Veziroğlu, 2008](#)).

Should CO<sub>2</sub> be used as a chemical feedstock, it has been estimated that a 10% recycle of the total emissions would be accomplished and therefore, the net amount of CO<sub>2</sub> produced would be reduced correspondingly ([Aresta, 2010](#)). Carbon Capture and

Utilization (CCU) is the term used to describe this approach. In addition, some authors have mentioned the possibility of joint sequestration and utilization (CCUS) as another viable alternative ([Hasan et al., 2015](#)).

The main issue with utilizing CO<sub>2</sub> is that it is a chemically inert molecule and its activation for use as feedstock is a non-trivial process. A recent review by Klankermayer ([Klankermayer et al., 2016](#)) elucidates the various transformations for CO<sub>2</sub> and classifies them according to the reduction level and the bond-forming processes. From an application point of view, it divides them into high-volume and high-value products.

For the sake of reducing emissions it is clear that high-volume products are of interest. These include methanol, formaldehyde and formic acid derivatives. These products can not only be used as base chemicals, but they also have potential as energy carriers or storage systems. The common denominator in these products is the need for hydrogen in the reactions involved. At the core of these reaction networks, the reverse water-gas shift (rWGS) reaction is encountered:



This reaction can be used to activate CO<sub>2</sub> using hydrogen obtained, for instance, from electrolysis using renewable energy, or, in the worst-case scenario, using 'CO<sub>2</sub>-low' hydrogen, such as that obtained from the pyrolysis of methane, or through electrolysis using a mix of electricity sources. The more reactive product CO can be mixed with excess hydrogen in any given ratio to obtain syngas, which is perhaps one of the most versatile chemical

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## Nomenclature

### Symbols

A	Area(/m <sup>2</sup> )
b	Parameter for langmuir isotherm(/Pa <sup>-1</sup> )
c	Concentration(/mol m <sup>-3</sup> )
C	Dimensionless concentration(/mol m <sup>-3</sup> )
c <sub>p</sub>	Heat capacity(/J mol <sup>-1</sup> K <sup>-1</sup> )
D	Diameter(/m)
Da	Damköhler number(/-)
K <sub>eq</sub>	Equilibrium constant(/-)
k <sub>G</sub>	Overall mass transfer coefficient(/m s <sup>-1</sup> )
k <sub>LDF</sub>	Mass transfer coefficient for adsorption(/s <sup>-1</sup> )
f <sub>1</sub>	First objective function (molar flux)(/mol m <sup>-2</sup> s <sup>-1</sup> )
f <sub>2</sub>	Second objective function (outlet adsorbent loading)(/mol kg <sup>-1</sup> )
F <sub>p</sub>	Correction term for the rWGS kinetics(/-)
h	heat transfer coefficient(/W m <sup>-2</sup> K <sup>-1</sup> )Heat transfer coefficient(/W m <sup>-2</sup> K <sup>-1</sup> )
ΔH	Change of enthalpy(/J mol <sup>-1</sup> )
L	Length(/m)
N	Number of discretization points/Number of reactor sections(/-)
$\dot{N}$	Mole flux(/mol m <sup>-2</sup> s <sup>-1</sup> )
Nu	Nusselt number(/-)
p	Partial pressure(Pa)
P	Total pressure(/Pa)
Pe	Péclet number(/-)
Pr	Prandtl number(/-)
q	Adsorbent loading(/mol kg <sup>-1</sup> )
Q	Dimensionless adsorbent loading(/-)
r	Reaction rate(/mol m <sup>-3</sup> s <sup>-1</sup> )
R	Ideal gas constant(/J mol <sup>-1</sup> K <sup>-1</sup> )
R	Radius(/m)
Re	Reynold's number(/-)
St	Stanton's number(/-)
t	Time(/s)
T	Temperature(/K)
u	Velocity(/m s <sup>-1</sup> )
U	Dimensionless velocity(/-)
V	Volume(/m <sup>3</sup> )
x	Axial coordinate(/m)
X	Dimensionless axial coordinate(/-)
y	Molar fraction(/-)

### Greek Symbols

γ	Parameter for langmuir isotherm(/-)
δ	Parameter for langmuir isotherm(/-)
ε	Porosity(/-)
ϑ	Vector of decision variables(/mixed)
κ	Parameter describing the change in thermal conductivity(/-)
λ	Thermal conductivity(/J K <sup>-1</sup> m <sup>-1</sup> s <sup>-1</sup> )
ν	Stoichiometric coefficient(/-)
ρ	Density(/kg m <sup>-3</sup> )
τ	Tortuosity(/-)
τ	Mean residence time(/s)
φ	Fraction of either catalyst or adsorbent in the bed(/-)
θ	Dimensionless temperature(/-)
Ψ	Vector containing the variables (temperature, molar fractions, velocity)(/mixed)

### Sub- and Superscripts

0	Initial/standard conditions
ad	Adiabatic

ads	Adsorbent
bed	Referring to the fixed bed
cat	Catalyst
eff	Effective
eq	Equilibrium
G	Gas phase
GS	Between gas to solid
GW	Between gas and wall
inlet/in	At reactor inlet
max	Maximum
mf	Minimum fluidization
outlet	At the reactor outlet
p	Particle
prod	Product
R	Reactor
rxn	Reaction
s	Saturation
S	Solid phase
SG	Between solid and gas
SW	Between solid and wall
T	Total
W	Wall

### Abbreviations

CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CCUS	Carbon capture, utilization and sequestration
COP	Conference of the parties
LDF	Linear driving force
MADS	Mesh adaptive direct search
NOMAD	Nonlinear optimization by mesh adaptive direct search
ODE	Ordinary differential equation
STY	Space-Time-Yield
rWGS	Reverse water-gas shift
VNS	Variable neighborhood search

feedstocks. Syngas can namely be converted into methanol, which can itself be further processed to diverse chemicals or olefins; it can be used in the Fischer-Tropsch synthesis for fuels, amongst many other uses (Baliban et al., 2012).

Industrially, the rWGS reaction has not been used for this purpose and is mostly used to control the C/H ratio in gas mixtures. The main challenge this reaction faces is the unfavorable equilibrium. For reasonable conversions, temperatures above 1073 K are required ( $X_{eq}(1073\text{ K}) = 0.51$ ), and, since the reaction is endothermic, this means that a high temperature heat source must be available. The feasibility of this reaction has thus always been subject to question. As an alternative, low-temperature rWGS suffers from a very unfavorable equilibrium, but at temperatures around 523 K, several downstream heat sources can be exploited to provide the necessary heat of reaction. To circumvent the equilibrium challenge, an adsorptive reactor has been proposed as a solution (Agar, 2005). By adsorbing the water vapor formed, the equilibrium can be shifted to the product side. In addition, the exothermicity of the adsorption provides heat for the reaction of the same order of magnitude as the reaction enthalpy (Simo et al., 2009), thereby minimizing the need for external heat input.

For adsorptive reactors, the conventional reactor concept is that of a fixed-bed, for the rWGS, preliminary studies (Jung et al., 2013) as well as theoretical optimizations (Munera Parra et al., 2017) have been performed to demonstrate its feasibility for the rWGS. Moreover, adsorptive reactors can be found in other applications such

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