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Mathematical simulation of WGS membrane reactor for gas from coal gasification

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ABSTRACT

Mathematical model of a membrane reactor for the water-gas-shift (WGS) reaction and results of simulation studies are presented. The physicochemical phenomena and brief description of the model are given. Due to the fact that membranes for CO_2 separation exhibit poor selectivity at the elevated temperature range (indispensable for the desired activity of WGS catalysts), the simulations were carried out only for H_2 selective membranes, containing Pd or its alloys. Comparison of the conventional two-stage WGS reactor with the membrane reactor revealed that operating temperature range of the catalyst used in the membrane reactor unit has to be much wider than that in conventional industrial reactors with separate high- and low temperature catalyst stages and with cooling in between. Thus, the research of new catalysts should accompany development of the membrane reactor technology. Simulations discussed in the present paper were focused on processing the gas derived from the coal gasification plant. Some results of mathematical simulations are presented. They reveal that under some conditions the membrane reactor technology can be promising for the hydrogen production from the coal-derived gas.

1. Introduction

For coal dependent countries coal gasification is a chance not only for environmentally friendly processing of their natural resources. It also allows more energy efficient utilisation of coal. Extensive studies on clean coal technologies are being carried out recently in Poland. A new approach to the coal gasification technologies is seriously taken into account in these studies as a source of gaseous energy carrier as well as a source of syngas for chemical industry. One of the options of processing of the coal-derived gas is its further hydrogen enrichment by Water-Gas-Shift (WGS) reaction:

$$H_2O + CO \leftrightarrow CO_2 + H_2, \quad \Delta H^o_{298} = -41\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

WGS is exothermic, reversible and especially in higher temperatures strongly equilibrium limited reaction. Removal of one of the products (i.e. H_2 or CO_2) from the reaction zone circumvents the equilibrium limitations of the reaction. Thus, it can significantly enhance its conversion ratio, so that numerous studies appeared recently on membrane reactors with the reaction (1) accompanied by the simultaneous separation of one of its products, H_2 or CO_2, alternatively.

Profitability of the membrane reactor application for processing of coal-derived gas is not obvious, however. Therefore, a comprehensive analysis should be done to estimate future parameters of this solution. It was decided to perform preliminary analysis based on mathematical simulations of the process. The mathematical model used in the simulations should embrace the most interesting variants of the process. On the other hand the model cannot include too many details, since at this stage of research a lot of detailed data, especially constructional, are unknown.

The relevant literature concerning membrane reactors (MR) models is abundant; thus we shall mention here some chosen examples only. MR models are being described in the literature with various level of complexity. Mostly they are steady-state, one-dimensional in space models e.g. [1–8], but two-dimensional including axial and radial gradients are also being defined [9,10]. Recently unsteady-state (dynamic) models are also presented: e.g. for the reverse-flow MR syngas production [11–13]. An interesting very flexible software tool (a model library) for MR dynamic simulations is presented in [14]. Majority of papers cited here describe tube and shell reactor configuration with reaction zone either in tube or in the shell, but a case of fluidized MR for ultrapure hydrogen production is also analysed in [15,16]. Some models assume isothermal MR operation [1,3,4,7] while the other include heat or enthalpy balances, allowing to simulate non-isothermal or adiabatic operation, what is much more suitable for exothermal WGS reaction. Studies [1,3–6,10] directly concern WGS reaction. Simulations presented in [3–5] were carried out for kinetic data of Cu–Zn low temperature catalyst, while in [6,10] for high temperature Fe–Cr catalyst. Kinetic data based on own investigation of the authors or were taken from the literature. When the reaction rate equations were determined in the kinetic regime authors usually apply effectiveness factor, using the Thiele modulus method.

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Nomenclature

ATR autothermal reforming
b_i exponent for partial pressure of component i in formula (8)
CG coal gasification
C_{pt}, C_{ps} specific heat of fluid in tube and shell, respectively, J mol^{-1} K^{-1}
DFE distance from equilibrium given by formula (11)
DFE_{in}, DFE_{out} distance from equilibrium at the inlet and outlet of the reaction zone (tube)
E_{cat} activation energy for catalyst in Eq. (10), J mol^{-1}
E_{perm} permeation activation energy, J mol^{-1}
F_{ti}, F_{si} molar flow rate of component i in tube and in shell respectively, mol s^{-1}
$F^{out}_{t,\mathrm{H_2}}$, $F^{out}_{s,\mathrm{H_2}}$ molar flow rate of hydrogen on the outlet from tube or shell, respectively, mol s^{-1}
GHSV gas hourly space velocity, h^{-1}
HTC high temperature catalyst
LTC low temperature catalyst
h_{t-s}, h_{suur} tube to shell and shell to surroundings heat transfer coefficients, respectively, W m^{-2} K^{-1}
ΔH heat of reaction, J mol^{-1}
INS Instytut Nawozow Sztucznych (Fertilizers Research Institute)
J_i molar flux of component i through membrane, mol s^{-1} m^{-2}
$k(T)$ reaction rate constant, mole s^{-1} kg^{-1} Pa$^{-(b_1+b_2-b_3-b_4)}$
k_0 pre-exponential factor in Eq. (10), mole s^{-1} kg^{-1} Pa$^{-(b_1+b_2-b_3-b_4)}$
K_p equilibrium constant
L reactor length, m
m exponent: $m=1$ for counter-current; $m=2$ for co-current reactor
MR membrane reactor
n exponent in Eq. (6)
p_{mi} permeability coefficient of component i, mol m^{-1} s^{-1} Pa^{-n}
$p_{mi,0}$ pre-exponential factor in Eq. (7), mol m^{-1} s^{-1} Pa^{-n}
P_{ti}, P_{si} partial pressure of component i in tube and in shell, respectively, Pa
Q_p term given by Eq. (9)
R gas constant, J mol^{-1} K^{-1}
R_1, R_2, R_3 inner and outer radius of tube and inner radius of shell, respectively, m
r_{CO} rate of reaction (1), mole s^{-1} kg^{-1}
$r_{\mathrm{CO_{max}}}$ maximum value of the reaction rate in the reaction zone (tube), mole s^{-1} kg
$R_{\mathrm{H_2}}$ hydrogen recovery factor given by formula (12)
S/C steam to carbon ratio
T_t, T_s, T_{surr} tube, shell and surroundings temperature, K or °C
T temperature, K
T_{in}, T_{out} temperature at the inlet and outlet of the reaction zone (tube), K or °C
TZC-3/1 commercial Polish high temperature catalyst
TMC-3/1 commercial Polish low temperature catalyst
ΔT total temperature increase in the reaction zone (tube), K
V_{Gin} inlet feed gas flowrate to the reactor, dm^3 (STP) s^{-1}
V_{sin} inlet steam flowrate to the reactor, dm^3 (STP) s^{-1}
V_{sweep} inlet sweep gas flowrate, dm^3 (STP) s^{-1}
X carbon monoxide final conversion
z axial coordinate, m
δ membrane thickness, m
ρ_{B1} bulk density of catalyst in tube, kg m^{-3}

A very simple model presented in [1] assumes that WGS reaction kinetics is faster than the hydrogen permeation flux rates (porous membrane is assumed) allowing the feed (retentate) side to be in dynamic equilibrium, therefore in consequence problem of kinetic may be entirely omitted. Simulation results presented in cited studies concerning WGS reaction mostly assumes Pd or Pd alloys composite membranes. Authors from US Department of Energy (US DOE) [1] analysed for WGS reactor inorganic porous membrane, but due to poor hydrogen selectivity such a solution occurred to be not especially advantageous. Thus in more recent study e.g. [17], US DOE decided to develop an inorganic composite palladium-based MR module. Therefore at present palladium containing membranes have to be considered as a standard for the discussed problem. In that case, permeation flux through the membrane is the most often calculated using Sievert's law.

In model simulations authors used to apply very different pressures in the reaction zone from 0.1 to 3 MPa (1–30 bar), while conventional industrial WGS reactors operates with pressures as high 7 MPa (70 bar). Obviously, due to membrane resistance pressure in the retentate side may not be too high, but pressures above 2 MPa should be considered for MR in this case, however.

Gas from numerous coal gasification plants is usually very rich in CO (approximately 35–60 vol% depending on the technology) but with lower H_2 content (30–40 vol%). In the reviewed literature only in one case [5] input gas with high CO content (50% CO/50% H_2O but without H_2) was analysed. These initial conditions in connection with nearly adiabatic regime of MR may have important consequences for catalyst operation parameters. Therefore, in spite of abundant literature this case of MR deserves for further careful analysis. Especially, that gasification is often considered as a part of clean technologies (e.g. for IGCC cycle cf. [18]).

It seems that as a base for an own model building, formulation and notation published in [8] could be very convenient and useful.

The present study is an attempt to fill the gap caused by a lack of the appropriate knowledge about the operation, parameters, and applicability of MR technology used for the hydrogen production from the gas with high CO content, especially from the coal-derived syngas. Thus, the objective of the paper is to show the preliminary results of the simulation of the WGS-MR applied for the coal-derived gas processing. These results allowed for conclusions, which may be important for further research and development of MRs in such an application. The paper also describes the basic and necessary elements of the model used in the simulations. A short outline of the numerical implementation of the model is also given.

2. A brief description of the mathematical model

2.1. General assumptions and physicochemical phenomena included in the model

The model was developed for the "tube in tube" configuration. The reaction zone is packed with the catalyst inside the inner tube; this tube is made of membrane material separating product of reaction (1) to the outer tube (shell). To the shell side an inert sweep gas can be introduced either in co-current or in counter-current configuration with respect to the direction of flow in the tube. The physicochemical phenomena included in the model are schematically shown in Fig. 1.

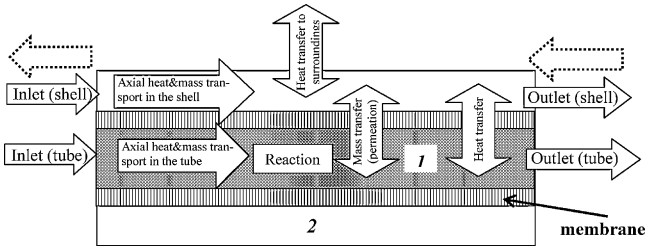

Fig. 1. Graphic outline of phenomena included in the mathematical model of the membrane reactor (1, tube side; 2, shell side).

2.2. Basic balance equations of the model

Generally the model is similar to that published by Kumar et al. [8]. However, the comprehensive model presented there was reduced in the present study by assumption that the reaction occurs on the tube side only. The momentum balance equations were also neglected, since constant values of pressure along axis in the tube and shell were assumed for preliminary studies. The model was extended, however, by adding separate heat balances for the tube and shell side, thus avoiding some simplifying assumption made by Kumar et al. [8] (equal temperatures in the tube and shell, i.e. neglecting the heat exchange between them and assuming negligible heat loss to surroundings).

Basic model equations have a general form:

Tube side molar balances for reactive components i

$$\frac{dF_{t,i}}{dz} \pm \pi R_1^2 \rho_{B1}(r_{CO}) + 2\pi R_1 J_i = 0 \quad (2)$$

Shell side molar balances for components i

$$(-1)^m \frac{dF_{si}}{dz} - 2\pi R_2 J_i = 0 \quad (3)$$

where $m = 2$ for co-current and $m = 1$ for counter-current reactor.
Tube side heat balance equation

$$F_t C_{pt} \frac{dT_t}{dz} = -\left[\pi R_1^2 \rho_{B1} \Delta Hr_{CO} + \pi \frac{R_1 + R_2}{2} h_{t-s}(T_t - T_s)\right] \quad (4)$$

Shell side heat balance equation

$$(-1)^m F_s C_{ps} \frac{dT_s}{dz} = \pi \frac{R_1 + R_2}{2} h_{t-s}(T_t - T_s) - \pi R_3 h_{surr}(T_s - T_{surr}) \quad (5)$$

Balance equations for inert components as well as boundary conditions for co- and counter-current version are rather obvious and will not be presented here.

The model enables us to simulate (for known membrane permeability) either reactor with H_2 or CO_2 selective membranes. However, taking into account that WGS reaction catalysts usually operate in the temperature range from 180 to 500 °C, a membrane used in such a reactor should maintain a fair selectivity of the separated component in this temperature range too. Metallic membranes (usually containing Pd or its alloys) have good selectivity even for elevated temperatures as high as 900 °C. Unfortunately, most of membranes for CO_2 separation reveal rather poor selectivity in high temperatures. Due to this fact and taking into account the purely practical aim of the present study the decision was made to focus the tests on H_2 separation option by using available data for Pd and Pd alloy composite membranes. It was assumed that the following Sievert's type formula describes permeation for these membranes:

$$J_{H_2} = \frac{p_{mH_2}}{\delta}\left[P_{tH_2}^n - P_{sH_2}^n\right] \quad (6)$$

where a permeation coefficient is given by the Arrhenius type formula as a function of temperature:

$$p_{mH_2} = p_{mH_2O} \exp\left(\frac{-E_{perm}}{RT}\right) \quad (7)$$

For simulations in the present study, data for membrane were characterised by a high H_2 permeation through membrane. For other components, i.e. CO_2, CO and H_2O permeation coefficients are assumed zero. The choice of adequate membrane suitable for industrial conditions is to be done during the next part of studies.

Kinetic reaction formula for WGS reaction on various catalysts can easily be modified in the simulation software code. For present simulations kinetic equations for high temperature Fe–Cr–Cu catalyst (commercial symbol TZC 3/1) or alternatively low temperature Cu–Zn catalyst (commercial symbol TMC 3/1) were applied.

For the catalysts the following reaction rate formula was applied:

$$r_{CO} = k(T) \times \frac{P_{tCO}^{b1} P_{tH_2O}^{b2}}{P_{tCO_2}^{b3} P_{tH_2}^{b4}} \times \left(1 - \frac{Q_p}{K_p}\right) \quad (8)$$

where:

$$Q_p = \frac{P_{CO_2} \times P_{H_2}}{P_{CO} \times P_{H_2O}} \quad (9)$$

and

$$k(T) = k_0 \exp\left(\frac{-E_{cat}}{RT_t}\right) \quad (10)$$

Activation energies E_{cat} and partial pressures exponents in Eq. (8) for the catalyst TZC 3/1 can be found in [19], where E_{cat} are different for the temperature range $T_t < 370$ °C and $T_t \geq 370$ °C. Values of the parameters necessary to calculate reaction rate r_{CO} were obtained for the present study by courtesy of the industrial catalyst producer [20], but unfortunately without a permission for publishing these data due to commercial reasons. Kinetic equations used in the simulations and their parameters were determined by investigation of the full size pellets of the catalysts [19,21], thus it was not necessary to introduce effectiveness factor into the model.

2.3. Model implementation

A simulation tool PSE gPROMS ModelBuilder 3.1.3 was used for implementation of the model. A computer program was developed using an equation oriented gPROMS language. The model took advantage of physical properties data bases and numerical procedures (discretization schemes) for differential equations built into the gPROMS package. It allowed overcoming many possible numerical difficulties to get easily the assumed accuracy of the solution.

2.4. Principles of the simulations performed

Initially some tests of the model were carried out to check its numerical stability and reliability of simulation results. Test simulations were made for many various data sets. Good numerical stability of simulations was achieved for pressures in the reaction zone (tube) as high as 3 MPa (for the co-current flow) and as high as 2.5 MPa (for the counter-current flow). It was assumed that a pressure of 2.5 MPa in the reaction zone is practically the highest which can be applied for present palladium membranes, so basically this value was used in majority of simulations for the tube side. Some tests for other pressure values were also carried out, however. The goal of the tests was to confirm that, in the next stage of studies, the model may be used in extensive simulations, which should allow for qualitative and quantitative decisions for further development of this technology in processing of the coal-derived gas.

Table 1
Basic parameter values used in the simulations.

Quantity	Value
Inner radius of tube R_1	2.0 cm
Outer radius of tube R_2	2.2 cm
Inner radius of shell R_3	2.8 cm
Exponent n in Eq. (6)	0.552
Membrane thickness δ	11.4 μm
Pre-exponential factor in Eq. (7) $p_{mi,0}$	5.29×10^{-8} mol m^{-1} s^{-1} Pa^{-n}
Permeation activation energy E_{perm}	644 J mol^{-1}
Total pressure in reaction side (tube)	2.5 MPa (25 bar)
Total pressure in permeate side (shell)	0.1013 MPa (~1 bar)
WGS catalyst description for which kinetic data were supplied by the catalyst producer:	
LTCatalyst (TMC-3/1) producer's basic data:	
CuO	min 50 wt%
ZnO	min 20 wt%
Al_2O_3	min 10 wt%
Graphite	~2 wt%
Shape: tablets (diameter × height)	4.5 × 3.5 mm
HTCatalyst (TZC-3/1) producer's basic data:	
Fe_2O_3	min 71.5 wt%
Cr_2O_3	min 7.3 wt%
CuO	min 1.25 wt%
Graphite	~2 wt%
Shape: tablets (diameter × height)	6 × 6 mm

Due to the reasons described in Section 3 at present there is a lack of appropriate kinetic data for WGS catalyst able to fulfil demands necessary for the MR. For the present study kinetic data obtained from Polish catalyst producer of industrial high and low temperature catalysts were used. They were Fe–Cr–Cu HTC [19] and Cu–Zn LTC [21] with commercial producer's symbols TZC-3/1 and TMC-3/1, respectively – for details see Fertilizers Research Institute (INS) web page [20]. Since these data are not precisely adequate for the case studied one should consider simulation results obtained as only a rough estimation of the problem. Some conclusions concerning membrane WGS reactor can be obtained, however. As a sweep gas in the shell nitrogen was assumed in simulations.

Basic parameter values used in the simulations are listed in Table 1.

3. Conventional vs. membrane WGS reactors for coal gasification derived gas

3.1. Operating temperature range for catalysts in conventional and membrane WGS reactors

A substantial difference exists in a catalyst operating temperature range between conventional and membrane WGS reactors. Fig. 2 presents schematic representations of a conventional (a) and membrane reactor (b). Conventional plant consists of two-stage WGS process with the high temperature adiabatic reactor at the first stage followed by the cooler and the low temperature adiabatic reactor as the second stage. On the other hand as a membrane WGS reactor the single-stage tube in tube construction is usually proposed, where the tube from the shell side is separated by the selective permeable membrane (see Fig. 2b). Of course, for larger reactors a multi-tubular constructions should be applied. In conventional plants (Fig. 2a) the process between high and low temperature stage is divided by a cooler, decreasing significantly an inlet temperature to the IInd stage. Thus the total temperature increase not exceeding approximately 200 + 100 = 300 °C can be adjusted individually to the range, usually from 300 to 500 °C for conventional high temperature catalyst (HTC) and from 180 to 280 °C for low temperature catalyst (LTC). As a base for further analysis of the MRs some simulations of the conventional two-stage

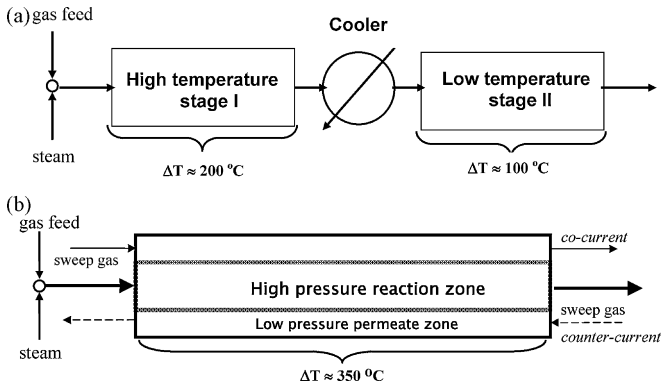

Fig. 2. Schematic representation of a conventional two-stage adiabatic WGS reactor installation (a), and adiabatic membrane reactor (b) with co-current (→) or counter-current (←) sweep gas flow in the permeate zone.

reactors were also done (cf. items 1–4 in Table 3) for comparison. Simulations of conventional reactor stages were substantially calculated using the same model equations as for MR (see equations in Section 2), but assuming permeation coefficients equal to zero for all gas components. These simulations assumed 2 different gas compositions at the inlet to the Ist stage. "Composition CG" means gas components concentrations as the average in the coal-derived gas at the outlet of the SHELL Company or PRENFLO industrial gasification technology (with negligible amount of CH_4 in products), while "composition ATR" – composition usually obtainable from the conventional autothermal methane reforming. Inlet gas composition feeding the IInd stage was assumed alternatively as "composition INS" what means that the components concentrations are assumed as recommended by the Polish catalysts producer [20] for the IInd stage inlet, or as composition calculated for the outlet of the simulated Ist stage reactor with CG coal-derived gas feed. The two-stage conventional reactor, but with composition CG gas feed exhibits overall conversion of 92.4% (calculated from conversions of the 2 stages, cf. items 1 and 4 in Table 3). It could hardly be higher, since the first stage is limited with the temperature limit for the catalyst (<500 °C), while the IInd stage is equilibrium controlled at the outlet. Similar reactor but with composition ATR gas (items 2 and 3 in Table 3) allows to get higher 98.3% final conversion.

For MR (Fig. 2b) the temperature increase in the reaction zone (about 350 °C) is even higher than overall increase in the conventional process. This is due to significant drop of the total flowrate along the tube caused by the permeation of separated component. Simulations of the heat exchange between the reaction zone in the tube and permeate zone in the shell through the membrane revealed that cooling the reaction zone by the cold sweep gas flowing in the shell side is negligible. Thus it could not significantly reduce the temperature increase in the reaction zone. Thus neither present industrial HTCs nor LTCs allow for adequately wide operating temperature range demanded for the membrane WGS reactor. It was observed elsewhere [22] that existing commercial catalysts will not survive such adiabatic temperature increase. Similarly, in

Table 2
H_2/CO ratio for various sources of the syngas processed in WGS reactor.

Technology	Source	H_2/CO ratio
Steam-methane reforming (SMR)	[24]	3–5
Steam-methane reforming combined with oxygen secondary reforming (SMR/O_2R)		2.5–4
Autothermal reforming (ATR)		1.6–2.65
Partial oxidation (POX)		1.6–1.8
Coal gasification (CG)	[25]	0.5–1.15

Table 3
Summary of the main simulations performed.

No	Option	L [m]	V_{sin} (STP) [dm^3/s]	V_{Gin} (STP) [dm^3/s]	V_{sweep} (STP) [dm^3/s]	GHSV [h^{-1}]	S/C [–]	X [–]	T_{in} [°C]	T_{out} [°C]	ΔT [K]	DFE_{in} [–]	DFE_{out} [–]	$r_{CO_{max}}$ [mol/(kg s)]	R_{H_2} [–]
Conventional reactors															
1	Conventional reactor Ist stage with HTC (TZC-3/1) – feed gas composition CG	0.7	0.6	0.7	–	5320	1.39	0.603	300	518	218	0.9998	0.51034	0.0458	
2	Conventional reactor Ist stage with HTC (TZC-3/1) – feed gas composition ATR	1.1	0.6	0.7	–	3386	2.80	0.827	300	454	154	0.9990	0.0128	0.0134	
3	Conventional reactor IInd stage with LTC (TMC-3/1) – feed gas composition INS	0.8	0.364	0.8	–	4168	14.97	0.903	227	250	23	0.9515	5.1E−06	0.0075	
4	Conventional reactor IInd stage with LTC (TMC-3/1) – IInd st. inlet gas composition – after the Ist stage reactor with CG coal-derived gas feed	0.3	0.0001	1.2	–	11460	1.87	0.808	180	317	137	0.9957	6.1E−05	0.0369	
Membrane reactors (counter-current)															
5	MR with HTC (TZC-3/1) with high input temp.	1.2	12.0	8.0	10.0	47746	2.43	0.947	400	658	258	0.9995	0.6321	0.3595	0.963
6	MR with HTC (TZC-3/1) with low input temp.	1.2	12.0	8.0	10.0	47746	2.43	0.053	300	309	9	0.9999	0.9999	0.0195	0.998
7	MR with LTC (TMC-3/1)	0.5	15.0	3.0	1.5	103132	8.12	0.999	180	299	119	0.9999	0.1586	0.3406	0.857
8	MR with LTC (TMC-3/1) (cat. act. × 0.01)	0.25	1.0	0.4	1.0	16042	4.06	0.999	180	407	227	0.9999	0.8282	0.0484	0.999
Single-stage reactor without membrane (comparison)															
9	HTC (TZC-3/1) with high input temp.	1.0	10.0	16.0	–	74484	1.01	0.462	400	586	186	0.9989	0.4576	0.3694	
10	HTC (TZC-3/1) with high input temp.	1.2	12.0	8.0	–	47746	2.43	0.623	400	548	148	0.9995	0.7105	0.1717	
11	LTC (TMC-3/1)	0.5	15.0	3.0	–	103132	8.12	0.984	180	295	115	0.99999	0.6923	0.3406	
12	LTC (TMC-3/1) (cat. act. × 0.01)	3.5	1.0	0.4	–	1145	4.06	0.968	180	372	192	0.99999	0.1197	0.0033	
Membrane reactors (co-current)															
13	MR with HTC (TZC-3/1)	1.0	10.0	16.0	10	74484	1.01	0.683	400	708	308	0.9989	0.0965	0.8741	0.836
14	MR with LTC (TMC-3/1)	0.5	15.0	3.0	1.5	103132	8.12	0.999	180	300	120	0.9999	0.0600	0.3406	0.786
15	MR with LTC (TMC-3/1) cat. act. × 0.01	0.25	1.0	0.4	1.0	16042	4.06	0.978	180	401	221	0.9999	0.9203	0.0393	0.960

Feed gas compositions are given in Table 4. For items from 5 to 15 coal-derived feed gas with composition CG was assumed for simulations

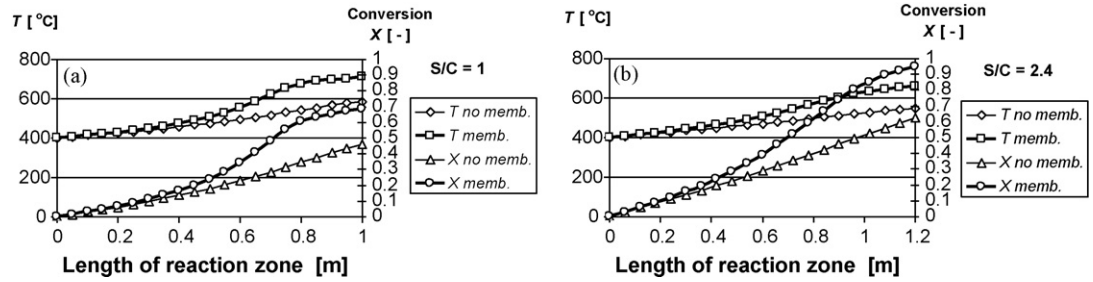

Fig. 3. Temperature and CO conversion profiles along the reaction zone (tube) in the reactor with HTC without membrane separation (no memb.) and with H_2 separation (memb.): (a) in co-current reactor with GHSV = 74,000 h^{-1} and S/C = 1.0 (items 9 and 13 in Table 3) (b) in counter-current reactor with GHSV = 47,700 h^{-1} and S/C = 2.4 (items 5 and 10 in Table 3).

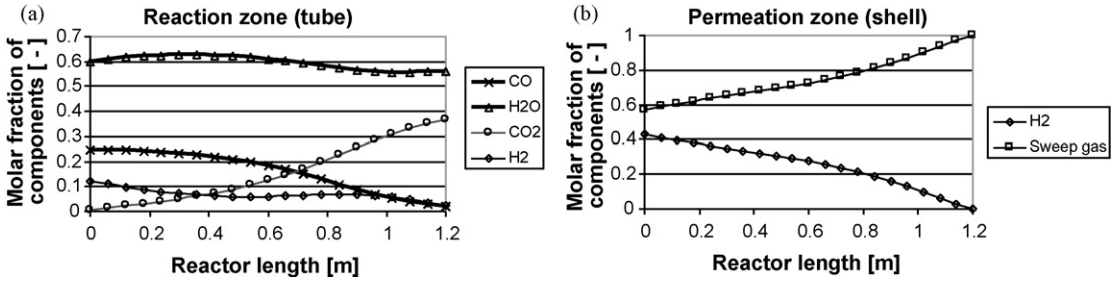

Fig. 4. Molar fraction of major components in the reaction (a) and permeation zone (b) of the counter-current reactor with HTC catalyst with GHSV = 47,000 h^{-1} and S/C = 2.4 (item 5 in Table 3).

DOE Hydrogen Program report [23] as a target for 2015 a catalyst temperature range of 200–600 °C is expected.

3.2. WGS reactor inlet syngas composition, steam to carbon (S/C) ratio and GHSV

The inlet gas processed in conventional WGS reactors is usually derived from hydrocarbons (mainly methane) processing. Composition of the gas feed for WGS reactor from these sources is different from that derived from coal gasification, generally when the ratio H_2/CO is taken into account. Table 2 comprises the range H_2/CO for various syngas production technologies (cf. [24,25]). For coal-derived gas H_2/CO ratio at the inlet to WGS is significantly lower than for the other technologies. Available catalyst kinetic data for conventional WGS technologies usually were determined for gas composition with higher H_2/CO ratio, thus they are not necessarily adequate for coal-derived WGS processing.

Steam to carbon ratio in input gas is an important factor for WGS processing. In a typical hydrogen plant with natural gas feed S/C ratio covers the range 3–5 for HTC and 3.5–5.5 for LTC (see [26]). Too low S/C reduces CO conversion, while too high is economically ineffective due to too high steam loss in the process. It seems that for membrane reactor S/C should not exceed value of 4.0 to be economically and technologically justified. It could be expected (e.g. [23]) that when appropriate catalyst is developed high CO conversion is possible even for S/C value around 2–2.5.

Conventional industrial WGS reactors, both in the high and low temperature stage are charged with rather low GHSV value, which usually does not exceed 4000 h^{-1} cf. [20]. Achmed et al. [27] estimate that the state of art reactors operate in the 2000–5000 h^{-1}. Efforts are being made, however, to investigate new catalysts allowing for much higher space velocity. Various sources (e.g. [27–29]) estimate that modern WGS catalyst should operate with the gas hourly velocity from at least 20,000 to as high values as 70,000 h^{-1}. So for simulations of the membrane reactors GHSV much higher than 5000 h^{-1} can be assumed as a target value.

4. Simulation results

The main simulation results are presented in Table 3. Generally the present simulations were carried out for two types of industrial catalysts: HTC with commercial symbol TZC-3/1 or LTC with symbol TMC-3/1 (for details see: [19–21]). It was assumed, however, that for each simulation case MR was packed with only one of these types of catalysts. Because the WGS reaction is equilibrium controlled a distance from equilibrium DFE, defined as:

$$DFE = 1 - \frac{P_{tH_2} \times P_{tCO_2}}{K_p \times P_{tCO} \times P_{tH_2O}} \quad (11)$$

at the inlet and outlet of the reaction zone was also presented in Table 3.

4.1. Simulations with HTC

As an example of the results obtained, Fig. 3 presents the tube temperature and CO conversion profiles along the reaction zone, for the case of pressure 2.5 MPa in the tube and 0.1 MPa in the shell. In Fig. 3a, a comparison of the profiles in tube without membrane and for the co-current reactor with the membrane separation is given. A relatively low final conversion for the MR (X = 68.3%) is caused by the relatively low $S/C \approx 1$. Higher S/C ratio (cf. Fig. 3b) is advantageous, providing both lower temperature increase ΔT and significantly higher final CO conversion. Detailed simulation parameters for the examples shown in Fig. 3 are presented in Table 3 (items 9, 13, 5 and 10). On the other hand in both cases

Table 4
Feed gas compositions used in simulations.

Feed gas composition	CO	CO_2	H_2	N_2	Others
	[vol% on dry basis]				
CG	61.6	1.7	30.6	4.8	1.3
ATR	30.6	1.7	61.6	4.8	1.3
INS	3.04	15.27	60.67	20.44	0.58
CG IInd st.	20.69	26.58	48.17	3.59	0.97

shown in Fig. 3 the output temperature is too high for conventional HTC, as it significantly exceeds 500 °C, usually allowed for this type of catalyst. The input temperature of 400 °C for both cases is higher than normally applied for HTC (around 300 °C), but for coal-derived gas composition HTC kinetic data used for the present simulations exhibit too low reaction rate in the temperatures below 400 °C (cf. example shown in Table 3, item 6). Significant gain of using the membrane separation is visible in these cases, since CO conversion is much higher for the case with vs. without membrane separation reactor. As an example, Fig. 4 presents molar fractions of components along the reactor length in the tube and shell of the reactor for the case corresponding to item 5 in Table 3.

4.2. Simulations with LTC

Similar simulations for industrial LTC were also carried out. Kinetic data for the catalyst TMC-3/1, normally used for calculations of the conventional syngas processing were provided by its producer [20]. Kinetic data for this catalyst were determined for the gas composition prevailing at the inlet to IInd stage of the reactor. Such a gas usually contains on dry basis around 3 vol% of CO and considerable amounts (about 60 vol%) of H_2. These data can thus be completely irrelevant to the kinetics corresponding to the coal-derived gas which contains around 60% of CO and 30% of H_2. Thus, for CG technology coal-derived gas composition exhibited reaction rates about 100 times higher than for conventional IInd stage reactor (average gas composition according to data supplied by the producer – named here as "INS gas composition"). Therefore, additionally some simulations with reaction rate calculated by original kinetic equation multiplied by 0.01 were also carried out, as more realistic for practical purposes. For every simulated case a high final conversion (from 97.8% to 99.9%) was obtained. For simulations using original kinetic data for the catalyst (items 7 and 14) in order to get the temperature increase not exceeding the allowed value of $\Delta T_{max} = 120$ K a very high S/C value (above 8) should have been applied. Such a case would not be economically justified due to very high steam loss. Moreover, very high GHSV > 100,000 h^{-1} confirms that very high reaction rates calculated for this catalyst seem to be exaggerated. Simulations performed for much lower GHSV ≈ 16,000 h^{-1} and more realistic $S/C \approx 4$ but with catalyst activity lowered 100 times seem to be more realistic (cf. item. 8 or 15 in Table 3), although $\Delta T = 227$ K is too high than originally allowed for LTCs. Further decrease of the S/C ratio in future will depend on how high temperature increase will be allowed for new types of catalysts designed for MRs.

4.3. Counter- vs. co-current membrane reactor

Advantage of counter- over co-current MR is clearly stressed in [30]. Some other authors also made similar suggestions. Hence, a comparison of these two configurations with the other reactor parameters unchanged seemed to be justified in the present project. Thus, additionally co- and counter-current membrane separations were also compared. Comparison of items 7 and 8 with 14 and 15 in Table 3 shows that final conversion only in one case (item 15) is a bit worse for co-current configuration. Hydrogen recovery factor defined as:

$$R_{H_2} = \frac{F^{out}_{s,H_2}}{F^{out}_{t,H_2} + F^{out}_{s,H_2}} \quad (12)$$

was calculated for every case simulated with membrane separation. These coefficient values make larger difference between the co- and counter-current version. In every case separation is visibly better for counter-current configuration, but the difference is not very large. One should stress, however, that all MR simulations presented in Table 3 were performed for rather high pressure of 2.5 MPa (≈25 bar) in the reaction zone and nearly atmospheric pressure in permeation zone. The results shown in [30] concerned basically the pressure of about 2.1 bar. Simulations in the present study confirm that superiority of counter-current reactor in terms of the separation coefficient (12) can be more visible for lower pressures in the reaction zone.

5. Conclusions

The membrane WGS reactor applied for processing of the coal-derived gas can be applied generally for 2 different industrial purposes;

- hydrogen enrichment of the coal gasification gas to adjust the syngas H_2/CO ratio for demands of an appropriate chemical synthesis (e.g. to Fisher Tropsch, methanol synthesis etc.);
- for pure hydrogen production.

It seems that membrane reactor used for the second case should be more economically attractive due to very high H_2 separation coefficients. Any detailed economic estimation in the present project was not made, however. At present state of art sufficient selectivity of the membrane separation in the temperatures necessary for WGS catalytic reaction makes H_2 more feasible than CO_2 separation. Thus, only this case was studied in the present project. Some drawback of this option is that the hydrogen is recovered on the low-pressure side, so it should be compressed again for transport or possibly as supply for majority of chemical synthesis.

The simulations revealed that any present commercial catalysts are not directly appropriate for the one-stage membrane WGS reactor due to their too narrow temperature range of operation. Future application of this technology will depend on development of new catalysts with a relatively low initial reaction temperature and adequately wide operating temperature range. It seems that the catalyst should withstand operation approximately from 200 to 550 °C. Such a catalyst should allow a very high CO conversion in a single step membrane reactor with relatively low $S/C \approx 2.0$–2.5. On the other hand, simulations performed in the present study suggest that even for a moderately active catalyst GHSV value of the membrane reactor can be much higher than 5000 h^{-1}, which is a norm in conventional industrial reactors.

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References

[1] A.S. Damle, S.K. Gangwal, V.K. Venkataraman, Gas Separation & Purification 8 (1994) 101.
[2] C. Hermann, P. Quicker, R. Dittmeyer, Journal of Membrane Science 136 (1997) 161.
[3] A. Basile, G. Chiappetta, S. Tosti, V. Violante, Separation and Purification Technology 25 (2001) 549.
[4] G. Barbieri, A. Brunetti, T. Granato, P. Bernardo, E. Drioli, Industrial & Engineering Chemistry Research 44 (2005) 7676.
[5] A. Brunetti, A. Caravella, G. Barbieri, E. Drioli, Journal of Membrane Science 306 (2007) 329.
[6] M.E. Adrover, E. López, D.O. Borio, M.N. Pedernera, Chemical Engineering Journal (2009), doi:10.1016/j.cej.2009.04.057.
[7] M.E. Ayturk, N.K. Kazantzis, Y.H. Ma, Energy & Environmental Science 2 (2009) 430.

[8] S. Kumar, P.R. Shah, S. Shankar, S. Kumar, Journal of Chemical Reactor Engineering (Article A5) 4 (2006) 1.
[9] K.A. Hoff, J. Poplsteinova, H.A. Jakobsen, O. Falk-Pedersen, O. Juliussen, H.F. Svendsen, International Journal of Chemical Reactor Engineering 1 (Article A9) (2003) 1.
[10] N.C. Markatos, E. Vogiatzis, K. Koukou, N. Papayannakos, Transaction of IChemE, PartA, Chemical Engineering Research and Design 83 (A10) (2005) 1171.
[11] J. Smit, G.J. Bekink, M. van Sint Annaland, J.A.M. Kuipers, Chemical Engineering Science 62 (2007) 1239.
[12] J. Smit, G.J. Bekink, M. van Sint Annaland, J.A.M. Kuipers, Chemical Engineering Science 62 (2007) 1251.
[13] J. Smit, M. van Sint Annaland, J.A.M. Kuipers, Chemical Engineering Science 60 (2005) 6971.
[14] M. Mangold, M. Ginkel, E.D. Gilles, Computers & Chemical Engineering 28 (2004) 319.
[15] C.S. Patil, Membrane reactor technology for ultrapure hydrogen production (PhD Thesis) Vol. PhD, University of Twente, Enschede, The Netherlands 2005, p. 245.
[16] C.S. Patil, M. Van Sint Annaland, J.A.M. Kuipers, Chemical Engineering Science 62 (2007) 2989.
[17] A.S. Damle, T.P. Dorchak, Journal of Energy and Environment Research 1 (2001) 77.
[18] M.C. Carbo, D. Jansen, W.G. Haije, A.H.M. Verkooijen, Fifth Annual Conference on Carbon Capture and Sequestration, Alexandria VA, U.S.A., 8–11 May, 2006.
[19] A. Gołębiowski, K. Stołecki, Chemik 3 (1998) 72.
[20] Polish catalysts producer's web page, Instytut Nawozów Sztucznych (Fertilizers Research Institute): http://www.ins.pulawy.pl/EN/index.php/content/view/113/114/.
[21] Z. Janecki, Z. Śpiewak, A. Gołębiowski, S. Magdziarz, P. Kowalik, K. Stołecki, P. Baran, Przemysł Chemiczny 82 (2003) 704.
[22] L. Lefferts, Project: Water-Gas-Shift Reaction in a Catalytic Membrane Reactor for Fuel-cell Application, Faculty of Science and Technology – University of Twente 2003–2007.
[23] T.H. Vanderspurt, IV.C.9 Advanced Water-Gas-Shift Membrane Reactor, DOE Hydrogen Program 2005, p. 199.
[24] B.M. Tindall, M.A. Crews, Hydrocarbon Processing (Nov. 1995) 75.
[25] M. Ściążko, H. Zieliński, Termochemiczne przetwórstwo węgla i biomasy, Zabrze, 2003.
[26] Haldor Topsoe A/S Commercial Leaflets – High & Low Temperature Shift Catalysts.
[27] S. Achmed, D. Papadias, L. Miller, D. Applegate, VII.F.5 Fuel Processing R&D, DOE Hydrogen Program, 2005, p. 921.
[28] L. Thompson, IV.C.14 Transition Metal Carbide Water Gas Shift Catalysts, Hydrogen, Fuel Cells, and Infrastructure Technologies, FY 2002 Progress Report.
[29] D.J. Myers, J.F. Krebs, S. Yu, M. Krumpelt, IV.C.13 Water-Gas Shift Catalysis, Hydrogen, Fuel Cells, and Infrastructure Technologies, FY 2002 Progress Report.
[30] W.S.W. Ho, Development of Novel Water-Gas-Shift Membrane Reactor, Hydrogen, Fuel Cells, and Infrastructure Technologies – FY 2002 Progress Report, DOE, 2002, p. 364.