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Catalytic Reformers with Membrane Separation of Hydrogen

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Abstract

The basic catalytic processes of hydrogen generation, which enclose the efficient use of hydrogen permeable membranes, are discussed. A variety of types of solid membranes are inspected for their suitability for hydrogen extraction from the gas mixture. The constructions of catalytic reformers with an integrated membrane module are given, and advantages of these devices relative to traditional reactors of fuel processor are discussed. The mathematical models of reaction vessels with the membrane release of hydrogen and certain of the simulation results are presented. The prospects for using catalytic reactors with membranes in the hydrogen energetics and transportation facilities are discussed.

Contents

INTRODUCTION

As an energy carrier, hydrogen may have extensive application on condition that the problem of its inexpensive separation from hydrogen-containing sources, like water, natural gas, oil and coal, will be solved [1]. It is well known that hydrogen is not found free in nature, it is always found in the combined state, and yet its advantages as an energy carrier are indisputable. Firstly, hydrogen is unusually energy-intensive carrier: any mode of energy generation with the use of hydrogen (fuel element, ordinary hydrogen heating, hydrogen internal combustion engine) is characterized by a high ratio of energy to mass. Secondly, the use of hydrogen rules out the emission of harmful wastes (CO_2 and methane). Thirdly, the use of hydrogen gives the chance to prevent direct electrification and related sizable loss in energy during its transmission and in storage. However it is necessary to note that the problem of hydrogen production with a high degree of purity ($C_{CO} \leq 10$ ppm), in addition to the extraction of hydrogen for fuel elements with proton exchange membrane, is also in existence.

HYDROGEN PRODUCTION PROCESSES

As of now, natural gas is the dominant source of hydrogen (≥90 %), and yet there are actual prospects for the commercial preparation of hydrogen from water by way of its thermochemical decomposition using heat of the nuclear reactor. Table 1 gives a set of ways of hydrogen production from natural gas.

Methane steam reforming (MSR) is considered as the most developed process that is conducted in two steps: very endothermic

TABLE 1

Basic ways of hydrogen production from natural gas

Process	Reactions	ΔH^{o}_{298}, kJ/mol	Fuel consumption
Methane	$CH_4 + H_2O \Leftrightarrow CO + 3H_2$	206	For technology
steam	$CO + H_2O \Leftrightarrow CO_2 + H_2$	−41	For reaction
reforming (MSR)	$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2$	165	For steam generation
Steam-oxygen	$CH_4 + 0.5H_2O + 0.25O_2 \Leftrightarrow CO + 2.5H_2$	90	For technology
conversion	$CO + H_2O \Leftrightarrow CO_2 + H_2$	−41	For reaction
of methane (SOCM)			For steam generation
			For oxygen separation from air
Partial oxidation	$CH_4 + 0.5O_2 \Leftrightarrow CO + 2H_2$	−36	For technology
of methane (POM)	$CO + H_2O \Leftrightarrow CO_2 + H_2$	−41	For steam generation

reaction of methane with water and CO steam conversion (water-gas process). Methane steam reforming is very endothermic process limited by equilibrium. Theoretical calculations of thermodynamic equilibrium show (Fig. 1) that the high degree of methane conversion (>90 %) is attained at high temperatures (≥850 °C), total pressure 10 atm and relation $H_2O/CH_4 = 3$. The buildup of pressure makes possible increasing the energy efficiency of the process, but the cost of MSR equipment in this situation is essentially increased. In addition, an added use of water-gas process reactor and pressure swing adsorption still further complicates the process and increases its cost.

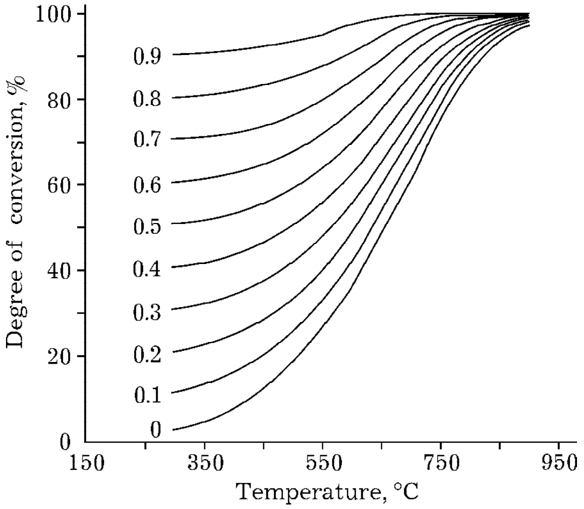

Fig. 1. Action of process temperature and proportion of extracted hydrogen on the degree of methane conversion (process pressure is 10 atm, $H_2O/CH_4 = 3$). Numbers near curves: degree of hydrogen extraction [40].

The high degree of methane conversion can also be obtained at relatively low temperature with a rise in the proportion of the extracted hydrogen (see Fig. 1). These computations were performed through the determination of residual number of hydrogen moles in the equilibrium composition of MSR reaction. When 90 % hydrogen, for one, is extracted from reaction zone, the degree of methane conversion can exceed 94 % at 500 °C. Under thermodynamic equilibrium conditions, without hydrogen extraction, the same result can be attained only at 850 °C. The developed in recent years reactors having selective hydrogen permeable inorganic membranes make it possible to extract hydrogen from the reaction zone during its forming, which leads to considerable lowering the process temperature [2–6].

Methane steam reforming is the well studied process having highly efficient catalysts. The use of one molecule of methane in this process results in four molecules of hydrogen, whereas three molecules of hydrogen are formed on partial oxidation. MSR is seemingly more efficient for hydrogen production, however the little used process of partial oxidation of methane (POM) is more suited with allowance made for energy expenditure on steam generation and maintenance of endothermic reaction (the mixture should be heated). Methane consumption per unit mass of hydrogen formed in POM process is 10 % less [1]. By Brown's calculation [7], an energy criterion cannot be determining in choosing between ways of hydrogen preparation. In other words, energy expenditure per unit mass of hydrogen prepared is much the same no matter how it is prepared. However questions of hydrogen extraction from the gas mixture and its purification remain unsolved. Fuel elements with proton-exchange membranes call for ultrapure hydrogen (99.999 % H_2) that can be obtained from hydrogen-containing mixtures in different ways. One promising way to solve this problem is a membrane technology that makes it possible to extract hydrogen coincidentally with increasing the degree of conversion of the initial reagent and lowering the process temperature.

MEMBRANE TYPES AND TECHNIQUES OF THEIR PRODUCTION

The term “membrane” made its first appearance in 1748 in Nollet’s work devoted to membrane separation of liquids, among them alcohol and water [8]. German physiologist A. Fick has opened in 1855 the diffusion law using parallels between streams of mass and heat as well as has demonstrated that the mass streams are not only proportional to the concentration, but they also are in inverse proportion to the membrane thickness. In 1854 T. Graham, the head of London milt, had expressed a well founded interest in properties of noble metals: in particular, he had found a hydrogen passage through palladium. Graham and Faraday studied gas diffusion laws and membrane methods of gas separation. Graham had made pioneering works on the gas diffusion through ceramic membranes and on measuring diffusion rate of carbon dioxide, hydrogen, oxygen, methane, air, carbon oxide and nitrogen through caoutchouc membranes [9]. Graham’s experimental works had given M. Knudsen the chance to create (1909) a model for penetrability of mesopores [10]. (It is necessary to stress that the molecular diffusion laws are valid for macropores.) Early in the 20th century S. Siwertz had published his own law of hydrogen transfer through palladium membranes of selective penetrability. V. Gryaznov’s remarkable works (1964–1993) wherein membranes based on palladium alloys were first used as catalysts of hydrogenation and dehydrogenation are also worth mentioning [11]. Three types of conjugation were found in hydrogen permeable membranes: 1) energy (heat), 2) thermodynamic (shift of reaction equilibrium), and 3) kinetic (accelerating one reaction at the cost of slowing down other one) [12]. The first two types of conjugation are predominantly realized in catalytic reformers. The heat conjugation, as an example, is used in the compact plate reformer developed in Boreskov Institute of Catalysis, SB RAS, for a fuel processor [13]. The reformer has a structured catalytic block in which MSR is realized at the expense of heat transported through a wall from the zone of exothermic reaction, such as reaction of methane deep oxidation.

There exist several types of inorganic hydrogen permeable membranes: close-grained membranes based on oxides and metals, porous (monolithic, microporous) ones and composite membranes with a support from ceramics, carbon, polymer, glass, stainless steel. The last type of membranes is said to be asymmetric, since these membranes involve porous support and thin layer of selective penetrability from palladium or zeolite.

The selectivity, penetrability, and useful life are fundamentals of the membrane. Three general types of membranes are distinguished: microporous (pores of size <2 nm), mesoporous (2–50 nm), and macroporous (>50 nm). Compared to conventional hydrogen permeable membranes: mesoporous ceramic (low selectivity), microporous ceramic (low penetrability), and close-grained ceramic (low penetrability), the membranes based on palladium, owing to high hydrogen penetrability and infinite selectivity with respect to hydrogen, are particularly advantageous for the use in catalytic membrane reactors of steam reforming and other processes involving hydrogen preparation [14–24].

The most significant works on the steam reforming, including water gas conversion, are associated in recent years with Pd membrane reactors [2–6, 25–33]. The first information about a reactor with Pd membrane in the form of a disk 100 μm thick made its appearance in the work [2]. In spite of high temperature of the process (700, 800 °C), a hydrogen penetrability was low in consequence of great thickness of the membrane. Authors [23, 24] used the method of chemical metallization in their works and made several thin Pd membranes

(10–26 μm) on the basis of a glass porous support. The degree of methane conversion in the new membrane reactor reached 88 % at lower temperature (500 °C), however the problems of mechanical strength, thermal stability, high-temperature welding and membrane unit design depending on the ceramic support remained unsolved. Authors [4] used a porous steel disk or a tube as supports and made Pd and Pd–Ag composite membranes [4], which enabled them to obtain 63 % conversion at 500 °C and 47 h operating life of the membrane. Authors [25] were also able to make a membrane reactor using thin (20–25 μm) Pd membranes on porous steel tubes and to obtain 45 % methane conversion at 500 °C, 15 % more than in traditional MSR reactor [25]. A somewhat lower degree of methane conversion in this case, as compared with results of the works [23, 24], is conditioned by the lower penetrability of the support. Kikuchi has used in addition a novel method of creating Pd membranes through chemical vapour deposition (CVD) [6]. This method permits making hydrogen permeable membranes not only from palladium, resulting in its wide use in Japan [34–36]. CVD method is used for creating membranes on porous supports in two versions: in the former case a substrate feeds onto one side of porous support, whereas the other side is in vacuum to avoid forming cracks or pinholes. In the latter case, so-called counterdiffusion CVD, a substrate feeds onto either side of the support. α-Al_2O_3 having pores of size 100 nm that is used as a support is coated with γ-Al_2O_3, resulting in decrease of pore size to 4 nm. Thereupon this support is enclosed in an oven to be saturated with tetramethyl orthosilicate of 0.98 mol/m^3 concentration at 45 °C, and then oxygen or ozone are introduced with the speed of flow 200 mL/min at 600 °C. In this manner the silicon dioxide membranes with the factor of separation H_2/N_2 ~ 1000 were prepared. They worked stably during 21 h at 500 °C and steam pressure of 0.76 atm.

Bimodal catalytic membrane that has a microporous topmost layer of silicon dioxide possessing selective hydrogen permeability and located on the support of bimodal structure was prepared by introducing γ-Al_2O_3 into microfiltration membrane from α-Al_2O_3 and following immersion in the solution of nickel nitrate [37]. The hydrogen permeability of Ni-doped silicon dioxide membrane comprised $1 \cdot 10^{-5}\,m^3/(m^2 \cdot s \cdot kPa)$, while the factor of separation H_2/N_2 was equal to 680. When steam methane ratio of 3 : 1, membrane temperature of 500 °C, a pressure in reaction zone of 1 atm, whereas 0.2 atm in permeability zone, the degree of methane conversion reached 70 % against 44 % for equilibrium conversion. Mesoporous membranes were also prepared by a sol-gel technology through the introduction of metal salts ($RuCl_3$, $Pd(NH_3)_4Cl_2$, $RhCl_3$, and H_2PtCl_6) in boehmite sol into a porous aluminium oxide support [38]. These metal dispersed aluminium oxide membranes were used in conducting low-temperature MSR (300–500 °C) and provided a high degree of methane conversion (>85 %) at 500°C with the factor of separation

$\alpha = (H_2/N_2)_P / (H_2/N_2)_R \approx 6$

where P and R are zones of permeability and reforming, respectively. Microporous ceramic membranes (nanocomposite silicon dioxide membranes) being developed to date likewise show the excellent high-temperature hydrogen permeability [39].

It is well known that repeated saturation of palladium membranes with hydrogen followed by its extraction leads to their degradation. Doping Ag, Ni, Rh, Ru makes it possible to add strength of membranes, whereas doping Ni, Ag, Cu, and Au improves their hydrogen permeability. For example, the most coefficient of H_2 permeability is noted for 23 % Ag fraction by weight, which results from a rise in solubility of hydrogen in the membrane and a reduction in the rate of its diffusion in the body with increase in Ag content of the alloy. It is significant that Ag addition is favourable to the transformation of β-PdH phase, which is rich in hydrogen and unstable at more than 300 °C, into α-PdH phase that is stable at higher temperatures. Attempts to use Pd/Ag membranes 50 μm thick prepared by cold rolling were found to be effective in combination with a reaction gas of blowing through a permeability zone. If hydrogen reacted with oxygen or carbon monoxide in permeability zone, the degree of methane conversion in reforming zone reached 70 % at 450 °C [27]. However this kinetic conjugation is of doubtful value because it is necessary to obtain pure rather than bonded hydrogen. Of interest is also realizing apparatus with heat self-providing that is realized in the case of burning a part of penetrated hydrogen and using this heat for MSR process.

The most efficient method of increasing selective permeability of Pd membranes and realizing high degree of methane conversion at 500–600 °C, which is directly proportional to the proportion of the extracted hydrogen, is found to be the advent of ultra-fine membranes (~10 μm) [40–43]. The fine flawless Pd membrane 6 μm thick on the microporous steel tube (MPST) was made through using multidimensional plating mechanism [40]. The reduced flow of hydrogen at 500 °C and pressure difference across the membrane of 1 atm comprised 0.260 mol/($m^2 \cdot s$). At a temperature of 550 °C, a pressure of 5 atm, a volume speed of raw material feeding of 800 $cm^3/(g_{cat} \cdot h)$, steam to methane ratio of 3, and reduced flow of blowing through of 500 cm^3/min the degree of methane conversion and the degree of hydrogen extraction account for 96.6 and 90.4 %, respectively. When employing Pd/CeO_2/MPST fine membrane of 13 μm thick prepared by the refined method of chemical deposition, the reduced flow of hydrogen comprised 0.275 mol/($m^2 \cdot s$) at 550 °C and a pressure of 2 atm, whereas the degree of methane conversion was over 97 % with a stable work of composite membrane during 300 h [41]. The fine (4 μm) Pd–Ag asymmetric composite membrane was prepared on the commercial porous steel tube by the combined method of chemical deposition and electroplating. The degree of conversion as much as 80.72 % has been gained in the membrane reactor for MSR at 500 °C and 5 atm. The membrane has shown a high stability in 11 thermocycles and 20 variable gas cycles. The composite $Pd{-}Pd/\gamma\text{-}Al_2O_3/\alpha\text{-}Al_2O_3$ membrane (a layer 2–3 μm thick of Pd, 3–4 μm of $Pd/\gamma\text{-}Al_2O_3$, and 200 μm of uncovered fibre from Al_2O_3) showed at 400 °C the hydrogen permeability of air tight Pd layer on the order of 8.8 $m^3/(m^2 \cdot h \cdot atm^{0.5})$ and 170–200 $m^3/(m^2 \cdot h \cdot atm)$ for $\alpha\text{-}Al_2O_3$ support, that is, the support resistance comes to only ~5 % of the total one [44]. The hydrogen permeability of the membrane at 430 °C remained practically unchanged during 660 h.

The deposition of a fine continuous layer of metal on to porous supports presents severe difficulties, however we can circumvent these difficulties by plating fine layers of metal on to the continuous layer of polymeric film [11]. The highly permeable and yet low selectivity by hydrogen polymers (polyethylene, polypropylene *etc.*) are common for metal-containing polymeric compositions. The composite anisotropic metallized membrane from polydiphenylene phthalide, which is composed of several layers of different porosity and covered with a layer of palladium ~1 μm thick, shows a hydrogen production rate of 13.8 $m^3/(m^2 \cdot h)$ at 200 °C and pressure drop of 10 atm. Since MSR process temperature is more than 400 °C, authors [11] have made ternary Pd–In–Y/Rb composite membranes on metal oxides. A 2-μm thick membrane from palladium alloy showed a hydrogen production rate of 10.0 $m^3/(m^2 \cdot h)$ at 400 °C and pressure drop of 2 atm and stood 450 thermal cycles without the loss in selectivity in the process.

The scale investigations with the aim of development and application of membrane separators of hydrogen in onboard fuel processors are carried out in Russian Federal Nuclear Centre–All-Russian Research Institute of Experimental Physics (RFNC–VNIIEF) and Karpov Research Institute of Physical Chemistry. These Institutes with the participation of Institute of Microelectronics Technology and High Purity Materials, RAS, have developed ultrafine palladium composite membranes with porous metallic support and palladium film ≤5 μm thick of high thermal stability on the basis of binary palladium alloys B-1 and B-2 [45]. Palladium alloy B-1 contains silver, gold, platinum, ruthenium, aluminium, and it is effective at working temperatures of 500–600 °C. An alloy B-2 (palladium, silver, indium, and yttrium) is free of deficient precious metals, whereas its permeability is 15–30 % higher than that of B-1 alloy. This alloy is operable up to 600 °C, and yet it is particularly advantageous between 300 and 500 °C. B-1 and B-2 alloys are of high strength, resistance to hydrogen, and very high permeability that is 1.3–3 times higher than it is in the best foreign samples. On 1000-hour trials of tubes from B-1 alloy at working temperature of 600 °C no changes in their tightness and productivity in operation with mixtures of hydrogen and CO_2 (up to 50 %), CO (up to 10 %), CH_4 (up to 10 %), and H_2O (up to 23 %) have been revealed.

In RFNC–VNIIEF the projects of onboard fuel processors using natural gas and petrol and having two membrane separators have been realized. The first is a diffusion separator placed in fuel reformer and having tube or plane membranes 30–100 μm thick, which are stable to heat at 600–650° C. The second separator is placed at the rear of catalytic membrane reformer (CMR) and has composition ultrafine membranes ≤1–3 μm thick for hydrogen extraction of degree 99.999 % from hydrogen-containing mixture coming from CMR. Stand trials of laboratory CMR specimens have shown a great promise for introducing these membrane devices in processors of transportation facilities with fuel cells.

The central problems of preparation of high-quality fine membranes <15 μm thick are surface irregularities and coarse porosity of the support. A comparison of kinetics of MSR and water gas conversion with kinetics of hydrogen permeability has shown that H_2 transfer through membrane (resistance to H_2 diffusion through metal) is the rate-determining factor of MSR process. From cited works it follows that a sufficiently high efficiency in hydrogen separation makes it possible to gain a nearly complete conversion of methane (Table 2). The experimental data show that even with some difficulties the possibility exists of increasing hydrogen permeability and stability of fine composite membranes at a time. As this takes place, the degree of methane conversion in MSR is more than 96 % owing to rise in hydrogen permeability.

CATALYTIC MEMBRANE REFORMERS

According to IUPAC terminology, a membrane reactor is defined as the apparatus that combines in one block the process of separation with the use of membrane and chemical

TABLE 2

Hydrogen separation effectiveness of palladium membranes

Membrane	Method of production	Thickness, μm	Temperature, °C	Pressure difference, atm	Hydrogen flow, mol/(m^2·s)	Separation factor H_2/N_2	Degree of CH_4 conversion, %	Ref.
Pd/MPSS	EP/O	10	480	1	0.089	1000	abs.	[46]
Pd/MPSS	EP	19–20	500	1.01	0.015–0.030	≤5000	abs.	[47]
Pd/MPSS	EP	5	400	1	0.155	100–200	abs.	[48]
Pd/PG	EP	13	500	2.02	0.189	∞	88	[23]
Pd/Al_2O_3	EP	7–15	400	1	0.086–0.134	100–1000	abs.	[48]
Pd/APC	EP	3–4	430	1	0.136	1000	abs.	[44]
Pd/Al_2O_3	CVD	0.5–1.0	350–450	1	0.050–0.100	100–1000	abs.	[49]
Pd–Ag/PG	EP	21.6	400	2.02	0.067	∞	88	[23]
Pd–Ag/MPSS	EP	15	500	2.02	0.103	∞ (H_2/Ar)	abs.	[50]
Pd–Cu/Al_2O_3	EP/O	3.5	350	1	0.056	≥7000	abs.	[51]
Pd–Cu/Al_2O_3	EP/O	1.5	350	1	0.499	93	abs.	[51]
Pd–Ag	CR	50	500	1	0.01	∞	70	[27]
Pd/MPSS	MP/EP	6	500	1	0.260	∞ (H_2/Ar, He)	96.9	[41]
Pd/MPSS	MP/EP	6	550	1	0.300	∞ (H_2/Ar, He)	96.9	[41]
Pd–Ag/MPSS	IEP	4	500	1	0.280	∞	80.2	[43]
Pd–CeO_2/MPSS	CEP/EP	13	500	2	0.275	∞	97	[42]

Notes. 1. MPSS – microporous stainless steel; PG – porous glass; APC – aluminium porous cloth; EP – electroless plating (chemical metallization); O – method of osmotic pressure; CVD – chemical vapour deposition; CR – cold rolling; MP/EP – multidimensional plating/chemical metallization; IEP – improved method of chemical metallization; CEP/EP – combined method of electrolysis and chemical metallization. 2. abs. – absent.

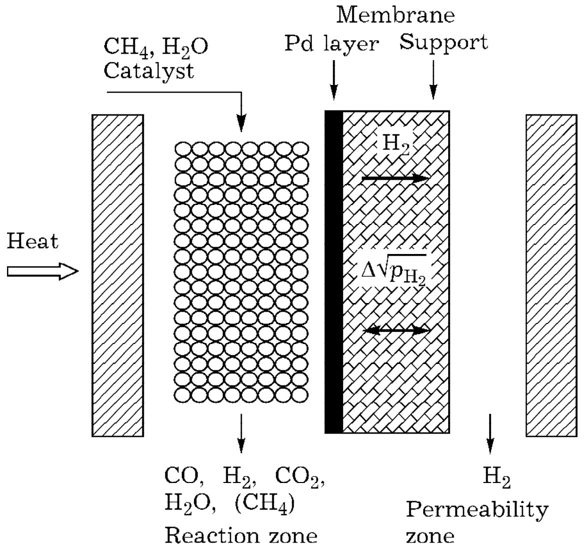

Fig. 2. Principle of operation of catalytic membrane reformer. Hydrogen is uninterruptedly extracted from reaction zone through the membrane. Hydrogen stream through the membrane is proportional to the difference in square roots of hydrogen partial pressures to inlet and outlet of the membrane.

reaction. Catalytic membrane reformer is the membrane reactor in which the catalytic function of membrane is kept to a minimum; that is to say, the number of reactions on the membrane is negligibly small as compared with that of reactions in the poured catalyst layer over the membrane. The target product (hydrogen) is led *in situ* through the membrane to the permeability zone (Fig. 2) and used, say, in a fuel element (FE).

By this means the membrane in CMR is functioning predominantly as a separator, and yet its permeability is highly susceptible to the action of products of methane-water conversion. This point is discussed in detail in [11]. It has been found that the presence of methane, carbon monoxide and carbon dioxide over a wide range of partial pressures at 700–900 °C does not reduce hydrogen transfer, whereas a steam slightly adds hydrogen permeability of the membrane from Pd-based alloy bearing 6 mass % Ru. The filtration function of the membrane may be reduced in consequence of carbon black formation in accordance with the reaction $CO + H_2 \Leftrightarrow H_2O + C$, however this is not possible except in the case of violating the MSR technology (for example, in the case of overheating a reaction zone). Carbon deposit on membranes also does not take place on condition that $H_2O/CH_4 > 2.5$. According to [45], the presence of methane and carbon dioxide over a wide interval of temperatures has little or no effect on hydrogen permeability of palladium membranes.

Catalytic membrane reformers are used not only in MSR processes, but also in POM processes [52, 53], in reactors of water gas conversion [54] and preferential oxidation of carbon monoxide [55]. However there is for the moment little evidence for the operation of these membrane reactors. Their design and principle of operation are close to those of CMR for MSR, whereas the distinction lies only in

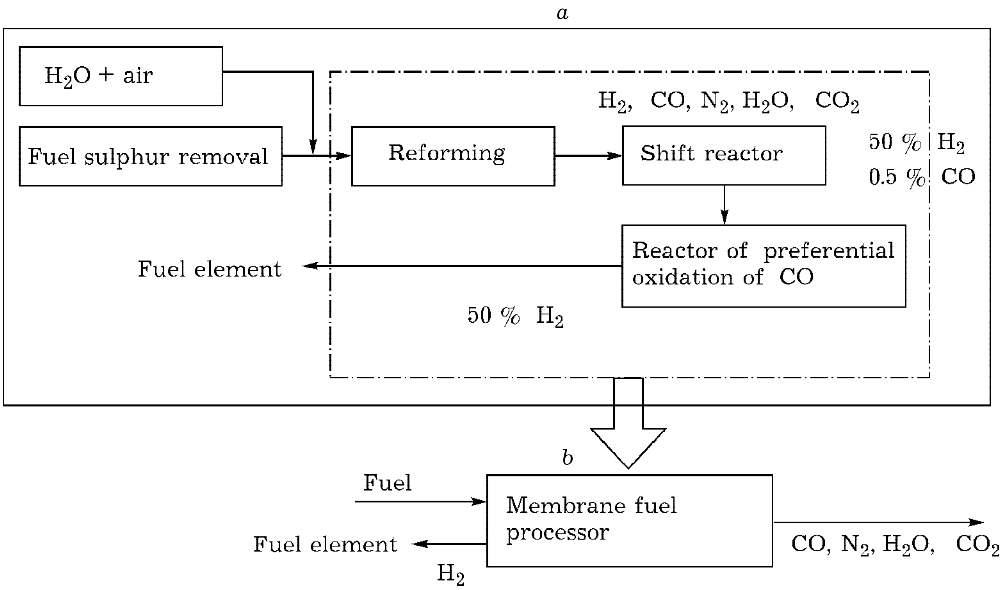

Fig. 3. Block diagrams of traditional (*a*) and membrane (*b*) fuel processors of hydrogen production for fuel element.

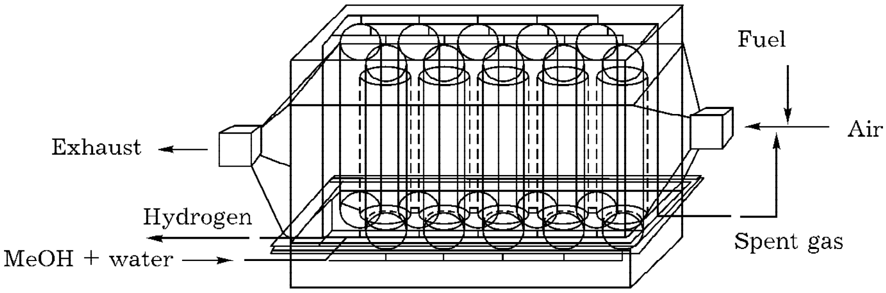

Fig. 4. Diagram of 30-kW_e methanol fuel processor with 10 modules of 3-kW_e each [57].

catalysts of gas mixture reforming and membrane types. In the membrane reactor for POM, for one, multilayer Pd membranes on TiO_2 support were used [52, 53] with Pd layer 10–21 μm thick. In the reactor of CO preferential oxidation the membranes from zirconium oxide stabilized with yttrium oxide were used.

As of now, catalytic membrane reformers, which produce hydrogen from various carbon-bearing fuels: methane, methanol, ethanol, benzene, and others, by steam or autothermal (steam-oxygen conversion) reforming, are accepted as the most developed and close to realization. Much attention is given to the use of Pd membrane reactors in generation of ultrapure hydrogen [56–68]. Catalytic membrane reformer (membrane fuel processor) takes the place of a traditional multi-apparatus fuel processor in the form of one block wherein both reaction and separation are at work (Fig. 3) [56]. Owing to its compactness, CMR is very attractive for designers of electric transportation facilities operating on hydrogen fuel.

At the moment CMRs with a broad spectrum of productivity (from 1 to 10^4 cm^3 H_2/h and over) are used for commercial and research purposes. As to design features, CMRs as diffusion apparatus may be arbitrarily classified under two chief groups: the tubular and tabular. The first present the banks of thin-walled seamless or seam tubes loaded with internal or external gauge pressure of gas mixture. The application of capillary tubes is particularly appropriate for high-pressure CMR. The tabular diffusion units are characterized by a wide variety of design and process implementation and made, as a rule, from foil on porous or ribbed support. The foil is corrugated for the action of stresses caused by the difference between coefficients of linear expansion of foil and support materials to be reduced. However units of this sort hold their shape only to moderate pressures (10–20 atm). The cost of tabular diffusion units is smaller than tubular ones by a factor of 2–3.

Let us consider CMR specimens developed in modern times. Catalytic membrane reformer of 30 kW_e electric capacity that has been created [57] for transportation facilities (Fig. 4) shows the following properties: module volume 3.9 L, mass without flanges 5.7 kg, hydrogen productivity 2.3 m^3/h. The module diagram is shown in Fig. 5. A membrane means for hydrogen extraction from reformate was integrated into steam reactor. As a result of testing Pd–Cu and Pd–Ag alloys and V–Ni–Cr alloy coated with palladium, Pd–Cu foil 25 μm thick was used for membrane preparation. It was determined that the specific hydrogen flow increases with increasing temperature and pressure to the membrane: at 300 °C and hydrogen partial pressure of 4.14 atm this flow was 30 cm^3/(min · cm^2). The presence of CO in the reformate tends to reduce a hydrogen flow by approximately 25 %, since an irreversible adsorp-

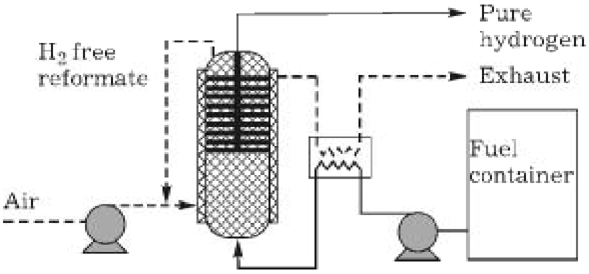

Fig. 5. Diagram of 3-kW_e module of methanol reforming for pure hydrogen production [57]. The bottom half of reformer is packed with Pt catalyst on metal gauze, whereas membrane Pd–Cu tubes are placed in the upper half.

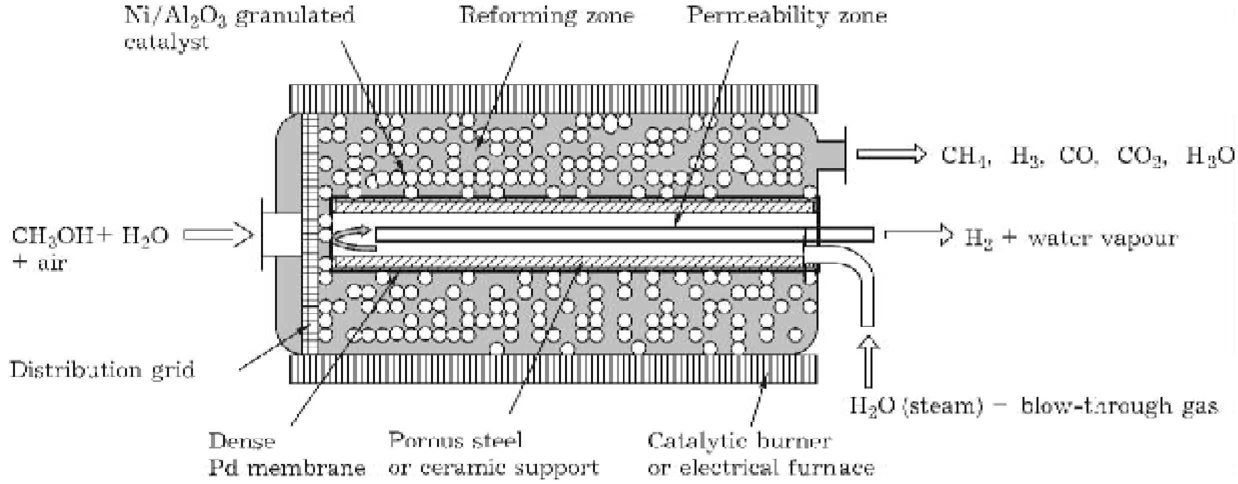

Fig. 6. Diagram of membrane reformer of steam conversion of methanol with countercurrent of blow-through gas [58].

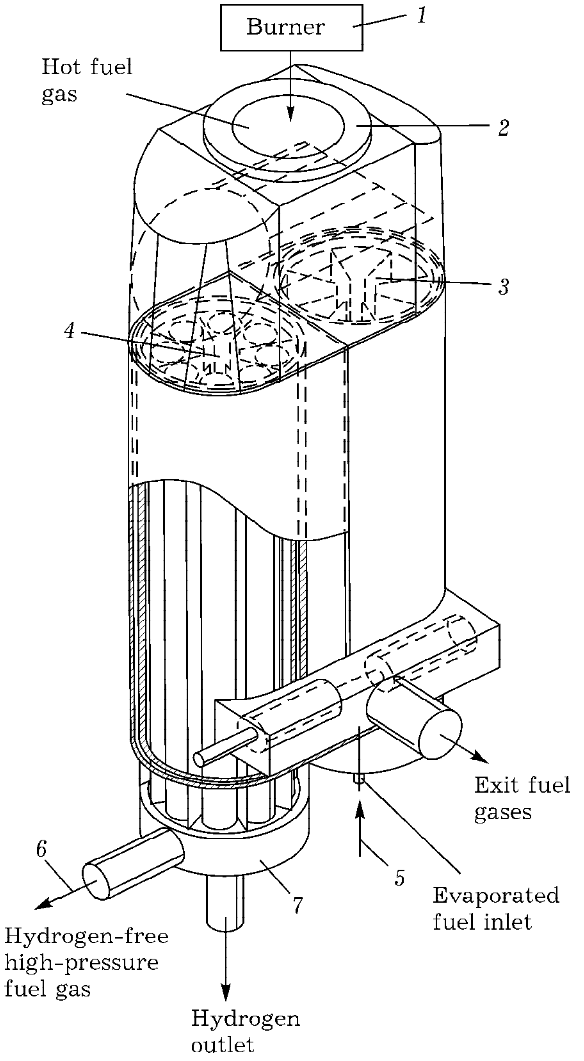

Fig. 7. Methanol compact fuel processor based on steam reforming with membrane separation of hydrogen [59].

tion of CO blocks the centres of hydrogen adsorption (dissociation). CuO/ZnO/Al$_2$O$_3$, CuO/ZnO/TiO$_2$, and CuO/Cr$_2$O$_3$/TiO$_2$ were tested as catalysts of reforming. Hydrogen bearing residual gas was directed into the zone of catalytic combustion surrounding modules (see Fig. 4). Heat released in the process was used for methanol steam reforming. The system that was in the starting position was heated by burning methanol that was injected with the help of a sprayer into the zone of combustion and set on fire. When temperature was near 45 °C, the catalytic burning was started. Platinum on aluminium oxide supported on steel net played the role of burning catalyst. Within 5 min after the start, the outlet temperature of the flow from a jacket was ~350 °C, and after 1 min the hydrogen production began in the module that was heated up to 100 °C. Temperature of heating flow was as great as 500 °C after 12 min of heating, and the reformate temperature at the module outlet was between 300 and 320 °C by the early 20th minute; in this case each of the modules showed the maximum productivity per hydrogen (2.3 m^3/h of 99.9999 % pure and CO content <1 ppm). The fuel processor had the following specific characteristics: power density of the processor – 1 kW/L (0.84 kW/kg), total volume – 40 L, mass – 50 kg. The degree of methanol conversion was equal to 95 %, the proportion of the extracted hydrogen by metallic membrane – 75 %. The rest (25 %) was catalytically oxidized. The total thermal efficiency of the system comprised 89%. The changeover interval (response time) from full load to restart after processor short stopping ran ~2 min.

Comparative analysis of steam and autothermal reforming (ATR) of methanol has shown [58] that for producing 50 kW_e (by electric capacity) the volume of autothermal CMR is 13 L less as compared with one of traditional apparatus of tubular type. However a system of flows in CMR of ATR is somewhat more complicated, and there is in addition a small decline in efficiency of a processor–fuel element system. The diagram of autothermal CMR applied in [58] is presented in Fig. 6. For heat supply of steam CMR the heat of fuel catalytic oxidation, unutilised hydrogen of anodic exhaust of fuel element included, was used. The total efficiency of CMR–FE system made up ~84 %.

A compact multifuel converter for transportation facilities with an integral hydrogen separator was proposed in [59] (Fig. 7). The fuel processor is made in the form of U-shaped tube. From a burner *1*, hot gases flow from above into the reactor through a flange *2* and heat the catalytic zone of cylindrical reactor *3* and also the cylindrical membrane reactor *4*. The evaporated fuel and water are conducted to the right cylinder filled with a catalyst through the branch pipe *5*. Upon reaction of reforming, the gas mixture is directed to the membrane block *4* through U-shaped passage. Low hydrogen reformate is removed through the branch pipe *6*. Hydrogen is extracted from a reformate by a membrane and removed through the collector *7*. The membrane compact fuel processor (Fig. 8) has three concentric zones: *1* – for passage of fuel gas, *2* – for hydrogen (hydrogen collector), and an inner zone *3* for auxiliary gases heating a processor. The membrane filter *4* allows hydrogen separation from reformate and its supply to fuel element through the branch pipe *5*. The over-all dimensions of the membrane processor are the following: diameter 5 cm, length 50 cm, area ~0.4 m^2. The model of catalytic membrane reformer for MSR with a heat integration (fast heating of reformer is effected by the catalytic oxidation of an alcohol or hydrocarbons and after reformate) is advanced in [60].

A new type of membrane reformer combining steam and oxidizing methane reforming types is reported in [61]. The fast circulating fluidised catalyst bed was used in the reforming zone. The hydrogen separation from a reaction zone was effected by way of filtering through tubes (2941 pieces) 2 m in length, ~1 mm in diameter, Pd membrane 20 μm thick, whereas oxygen of the air penetrated through air-tight perovskite oxygen permeable tubes (15224 pieces) 2 m in length, ~4.9 mm in diameter, membrane ~55 μm thick. Certain of the reformer properties are given: the process temperature is 560 °C, $H_2O/CH_4 = 4$, a reactor of volume 0.015 m^3, pressure in the reactor is 22 atm, hydrogen yield (mol H_2/mol CH_4) is 3.204. The productivity per unit volume of the membrane reactor is 8.2 times that of the traditional commercial tubular reactor with a stationary layer of the catalyst.

The compact methanol steam reactor with an integral hydrogen separator was proposed in [62]. For methanol steam reforming it was also proposed the use of a two-jacket palladium membrane reactor wherein methanol steam reforming and CO conversion are run at a time [63]. Hydrogen is extracted from reformate with the help of a palladium tube. The degree of

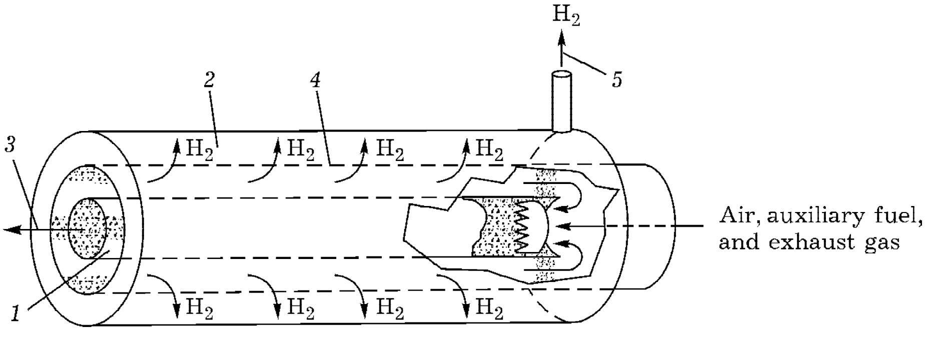

Fig. 8. Compact membrane fuel processor [59].

methanol conversion at 350 °C and operating pressure of 12 atm was 97 %, whereas hydrogen utilization with membrane module reached 74 %. The novel hybrid adsorbent-membrane reactor containing hybrid stationary layer of catalyst with a membrane and being integrated with MSR through porous ceramic membrane with CO_2 – adsorption system was examined in conditions of temperatures and pressures common to varied transportation and stationary applications [64]. The membrane reactor with fluidized bed and two membranes (Pd membrane for H_2 extraction and perovskite membrane for O_2 entering) placed in two sections for reasons of difference in temperature regimes was proposed in [65]. Methane steam reforming with water-gas process (Pd membrane) proceeds in the upper section, whereas the partial oxidation (perovskite membrane) is realized in the lower section. Testing of the reactor in low-temperature MSR was carried out at stoichiometric H_2O/CH_4 relations. Partial oxidation of methanol was studied in membrane reformer with Pd membrane at start temperature of 300 °C [66]. Authors [67] tested membrane reformer with fluidised catalyst by investigating methane steam reforming (reactor is heated through a wall) or partial oxidation of methane (air is injected into a layer of catalyst). Hot catalyst grains circulated from the zone of oxidizing reforming into the zone of steam one in pilot reactor 0.13 m in diameter and 2.3 m in height. The yield of extracted hydrogen (99.999 % pure) comprised 0.96 mol H_2/mol CH_4. Testing of industrially prepared catalytic membrane reactor for MSR was conducted to make an estimate of influences of different reduced flows in reaction and permeability zones [68]. The reformer of this type was demonstrated to have simpler diagram of the process, low temperature, and low fuel consumption with higher degree of methane conversion as compared with a traditional MSR reactor.

The discussed above constructions and specifications of catalytic membrane reformers allow definite conclusions that hydrogen extraction from reformate with the use of membranes is a promising source for transportation facilities and power units. An autothermal reforming is more preferential for handling the problem of heat supply of reforming zone. Membrane modules built into reforming reactors serve both for hydrogen extraction from reaction zone and for oxygen introduction into catalytic layer. Catalytic membrane reformers incorporate the following advantages: high compactness, energy density, lower temperature of the process, and simpler diagram of flows; however their operating resource remains to be moderate. To illustrate, the best membrane samples today are only stable for some hundreds of hours, whereas reforming catalysts can operate in CMR for 1000 h and up. The application of cartridge technology of replacing membrane modules in CMR can be one of the ways for added operating resource of these reformers.

MATHEMATICAL MODELS OF CATALYTIC MEMBRANE REFORMERS

Mathematical models of membrane reactors with catalysts were being developed from the late 1970s [69]. The simulation of the catalytic membrane reformers with methane steam reforming was coming into progress of particular intensity from 1990s owing to Xu and Froment's elaboration of models of true kinetics of methane steam reforming and water gas conversion in the classical tubular reactor with $Ni-Mg/Al_2O_3$ commercial catalyst [70–72]. Mathematical simulation makes it possible to estimate the dependence of the key parameters of MSR process in the catalytic membrane reformer: degree of CH_4 conversion and hydrogen yield – on operational features like rate of raw material injection, steam/methane ratio, membrane thickness, reactor length, temperature, total pressure, hydrogen pressure on each side of the membrane, CMR geometry, permeability to hydrogen, heat distribution, direction of flows in zones (direct flow, counterflow), composition of raw material and blow-through gas, and others [4, 5, 25–28, 30, 52, 53, 56–61, 68, 70, 71, 73–85].

More recently, Xu and Froment's kinetic model [69, 70] has been adapted to membrane reactor [4]. The model is based on Langmuir–Hinshelwood reaction mechanism and includes 13 steps. According to [71], the rates of MSR reactions can be determined by the following expressions:

$$W_1 = \frac{k_1}{p_{H_2}^{2.5}}\left[p_{CH_4}p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_1}\right] / \mathrm{DEN}^2 \qquad (1)$$

$$W_2 = \frac{k_2}{p_{H_2}}\left[p_{CO}p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_2}\right] / \mathrm{DEN}^2 \qquad (2)$$

$$W_3 = \frac{k_3}{p_{H_2}^{3.5}}\left[p_{CH_4}p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_1 K_2}\right] / \mathrm{DEN}^2 \qquad (3)$$

where k_i is the rate constant of i-reaction ($k_i = A_i \exp\left(-\frac{E_i}{RT}\right)$); p_i is partial pressure of i-component; K_i is the equilibrium constant of i-reaction;

$$\mathrm{DEN} = 1 + K_{CO}p_{CO} + K_{H_2}p_{H_2} + K_{CH_4}p_{CH_4} + K_{H_2O}p_{H_2O} / p_{H_2} \qquad (4)$$

where K_j is the adsorption constant of j-component (j = CO, H_2, CH_4, H_2O):

$$K_j = A_j \exp\left(-\frac{\Delta H_j}{RT}\right)$$

A feature of this kinetic model lies in the fact that the equations (1)–(4) are true only when hydrogen is present in initial mixture; otherwise reaction rates become infinite in size. The relation between hydrogen and methane at entry: $p_{H_2}^0 / p_{CH_4} \le 10^{-6}$, has been selected for solving these equations, resulting in well-agreed data of thermodynamic calculations for methane equilibrium conversion [4]. Values for parameters of equations (1)–(4) are presented below:

Preexponential		Energy, J/mol	
A_1, $\mathrm{mol \cdot Pa^{0.5}/(m^3 \cdot s)}$	$2.60 \cdot 10^{20}$	E_1	$2.40 \cdot 10^5$
A_2, $\mathrm{mol/(m^3 \cdot s \cdot Pa)}$	$3.80 \cdot 10^3$	E_2	$6.71 \cdot 10^4$
A_3, $\mathrm{mol \cdot Pa^{0.5}/(m^3 \cdot s)}$	$6.27 \cdot 10^{19}$	E_3	$2.44 \cdot 10^4$
A_{CO}, $\mathrm{Pa^{-1}}$	$8.23 \cdot 10^{-10}$	ΔH_{CO}	$-7.07 \cdot 10^4$
A_{H_2}, $\mathrm{Pa^{-1}}$	$6.12 \cdot 10^{-14}$	ΔH_{H_2}	$-8.29 \cdot 10^4$
A_{CH_4}, $\mathrm{Pa^{-1}}$	$6.65 \cdot 10^{-9}$	ΔH_{CH_4}	$-7.07 \cdot 10^4$
A_{H_2O}	$1.77 \cdot 10^5$	ΔH_{H_2O}	$8.87 \cdot 10^4$

A kinetic model (1)–(4) is principally used for CMR simulation, whereas authors [30] have used kinetics of reforming on commercial catalyst GIAP-3-6N. Until recently, only unidimensional one-temperature models with a longitudinal transfer of heat and material through catalyst layer as well as longitudinal removal of hydrogen into permeability zone or oxygen input into reforming zone were used predominantly for the mathematical description of a reforming zone. Pressure drop across the catalyst layer has become taken into account only a short time previously [78]. A model with only longitudinal transfer of material was used for a permeability zone.

A stationary model of membrane reformer is conventionally described by equations of material balance in the form of reduced flows for each component in reaction zone and for hydrogen in permeability zone, including blow through gas (such as H_2O):

$$\frac{dN_i}{dl} = \rho_c(1-\varepsilon)A_r \sum_{j=1}^{J} \sigma_{i,j} W_j - N_i^{Pd} \frac{\pi\phi}{A_r} \qquad (5)$$

(i = CH_4, H_2, H_2O, CO, CO_2)

$$\frac{dN_i^{Pd}}{dl} = N_{H_2}^{Pd} \frac{\pi\phi}{A_r} \quad (i = H_2O, H_2) \qquad (6)$$

and equation of energy balance

$$\frac{dT}{dl} = \frac{\sum_{j=1}^{J} W_j(-\Delta H_j)\rho_c(1-\varepsilon)A_r + Q}{\sum N_i C_{p\,i}} \qquad (7)$$

where N_i is molar speed of i-component; T is temperature; l is reactor length; ρ_c is catalyst density; ε is layer porosity; A_r is cross-section area between tubes; $\sigma_{i,j}$ is stoichiometric coefficient of i-component in j-reaction; W_j is rate of j-reaction; ϕ is external diameter of membrane; ΔH_j is heat effect of j-reaction; Q is rate of heating along reactor; $C_{p\,i}$ is specific heat capacity of i-component.

The hydrogen flow ($\mathrm{mol/m^2 \cdot s}$) through palladium membrane can be described, by Siwertz's law [74], as

$$N_{H_2}^{Pd} = \frac{Q_0 e^{-E_p/(RT)}}{\delta}\left(P_{H_2\,R}^n - P_{H_2\,P}^n\right) \qquad (8)$$

where Q_0 is preexponential factor; E_p is activation energy of permeability; δ is membrane thickness; P_{H_2} is partial pressure of hydrogen; low indexes R and P designate zones of reforming reactions and permeability respectively; n is exponent of partial pressure of hydrogen ($n > 0.5$ for the dependence of the rate of hydrogen permeability on the influence of surface processes). The transfer of hydrogen through a dense Pd membrane is realized by way of hydrogen adsorption, dissociation, diffusion of hydrogen atoms through a metal lattice, recombination of hydrogen atoms on the side of low pressure, and desorption of molecular hydrogen. In effect the quantity n depends on temperature that determines surface processes and the rate of hydrogen dissolving in palladium. According to [4], for 79 % Pd–21 % Ag membrane 20 μm thick $Q_0 = Q_0\rho = 1.776 \cdot 10^{-3}\rho$ (ρ is molar density of gases in reaction zone, mol/m^3) and E_p = 15.7 kJ/mol. Siwertz's law breaks down for membranes <15 μm thick (n = 0.5), whereas it can be used with $n = 0.5$ for $\delta \geq 15$ μm. The transfer of hydrogen through a porous support is controlled by Poiseuille's flow and Knudsen's diffusion. Comparison analysis of characteristic time of hydrogen transfer through Pd membrane with $\delta = 30$ μm ($\tau \approx 0.72$ s), porous support 8 mm thick ($\tau \approx 0.029$ s), catalyst layer 20 cm long ($\tau \approx 0.05$ s) and of reforming reaction, as such, at $P_R = 1$ atm, T = 500 °C ($\tau \approx 0.000355$ s) has shown that MSR process in catalytic membrane reformer is limited by hydrogen transfer through a dense Pd membrane only. Catalytic membrane reformer with autothermal reforming is completed with perovskite oxygen-permeable membrane for oxygen supply into reforming zone. The mathematical model for reformer of this type is complemented by oxygen flow into reforming zone, which leaves the (10 atm) the scheme contains a single polymeric module followed by Pd separator and Pd membrane reactor. As this takes place, a surface area of Pd membranes, a compression pressure, and hydrogen losses are minimal.

Figures 9–13 show the comparison data on CMR simulation. From these figures we notice that the use of membrane reformers is more effective as compared with traditional tubular reactors (TTR). While the building up of pressure in the reforming zone of TTR adds to hydrogen body, its yield (H_2/CH_4) drops. By contrast, the yield of hydrogen in CMR grows (see Fig. 9). The action of total pressure on the increase in hydrogen yield is confirmed by the results obtained in [30] (see Fig. 10): the degree of methane conversion in TTR reduces with increase in pressure (a consequence of reversibility of reforming reaction), whereas it increases in CMR. The rise of total pressure in the process of autothermal conversion of methane has a similar effect on hydrogen yield (see Fig. 11). Reduction in the partial pressure of hydrogen in permeability zone at the expense of increasing the blowing-through rate, as an example, causes the differential in H_2 pressure across the membrane to increase (see Fig. 12). As this takes place, the flow of outgoing hydrogen increases and the degree of methane conversion increases sharply. For reference, in TTR at 500 °C, 9 atm, and rate of raw material supply of 0.3 h^{-1} the degree of methane conversion does not exceed 20 %, whereas in

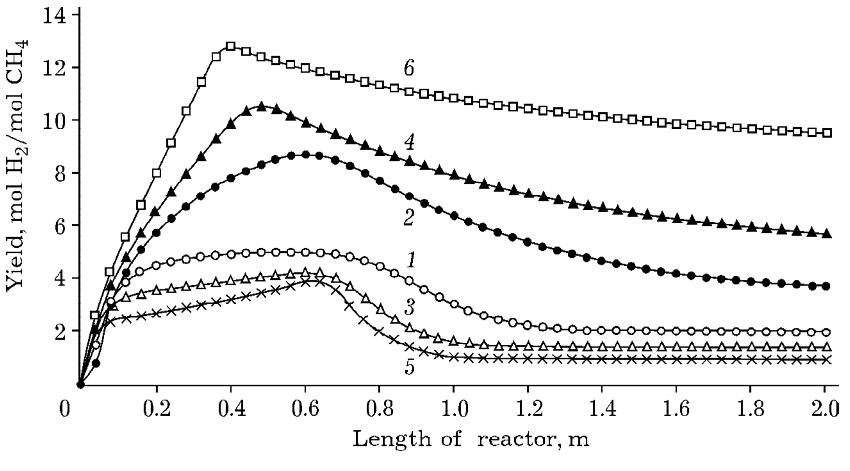

Fig. 9. Action of pressure in reaction zone on hydrogen yield [61]: *1*, *2* – P = 5 atm (*1* – without membranes, *2* – with membranes); *3*, *4* – P = 10 atm (*3* – without membranes, *4* – with membranes); *5*, *6* – P = 20 atm (*5* – without membranes, *6* – with membranes).

model described by equations (5)–(8) fundamentally unaffected.

Geometry of membrane reformers used in [4, 5, 25, 26, 56, 58, 61, 76, 78, 82] is tube-in-tube. The inner tube is a palladium membrane supported on the outer surface of the porous steel tube or ceramic support. The intertubular volume fills up with granular catalyst. A special device heats reactor externally. Analysis of literature data shows that model of this type is the most popular. The plane reformer for a determination of the membrane permeability was used in [81] only. The investigation of the systems with integrated membrane modules of three types (polymer ones, Pd separators, and Pd membrane reactors) has been carried out for hydrogen extraction from synthesis gas [82]. Analysis of possible alternatives of the location of membrane modules with the aim of minimizing the surface area of expensive palladium membranes has shown that the scheme of hydrogen extraction using two polymeric membrane modules, Pd separator and two Pd membrane reactors is more preferential at a low pressure of synthesis gas (5 atm). At a high pressure of synthesis gas

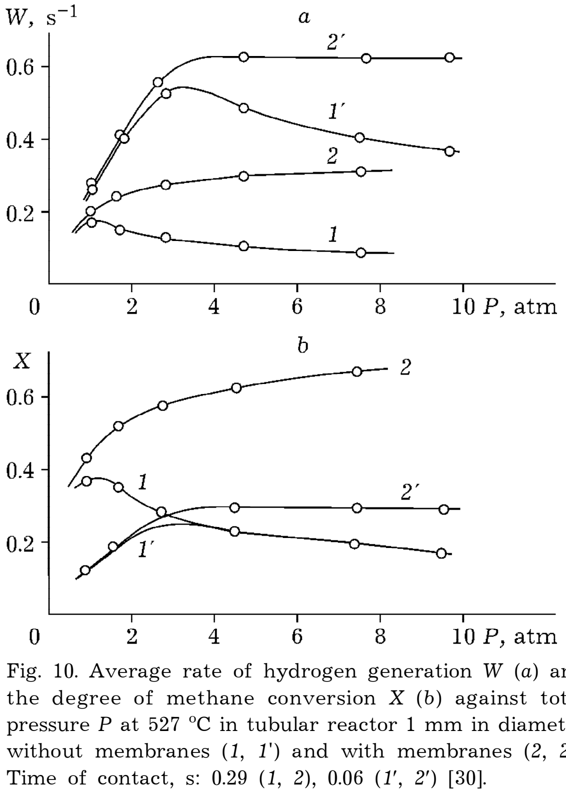

Fig. 10. Average rate of hydrogen generation W (a) and the degree of methane conversion X (b) against total pressure P at 527 °C in tubular reactor 1 mm in diameter without membranes (*1*, *1*′) and with membranes (*2*, *2*′). Time of contact, s: 0.29 (*1*, *2*), 0.06 (*1*′, *2*′) [30].

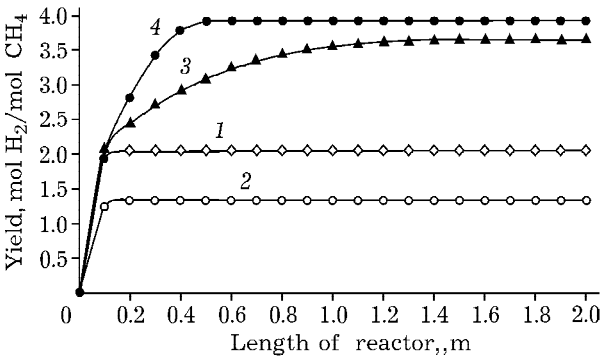

Fig. 11. Yield of hydrogen at different pressures in reforming zone for an isothermal variant (T = 627 °C, H_2O/CH_4 = 3.562 mol/mol, P_{H_2} = 1 atm) [61]: *1*, *3* – P = 506.5 kPa (*1* – without membranes tubes, *3* – with five membranes tubes); *2*, *4* – P = 1519.5 kPa (*2* – without membranes tubes, *4* – with five membranes tubes).

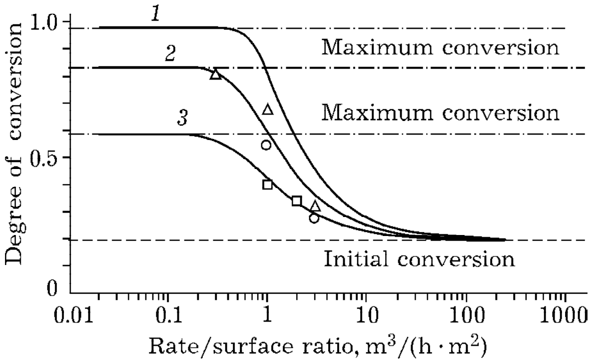

Fig. 12. Action of partial pressure of hydrogen in permeability zone on the degree of methane conversion (500 °C, pressure in reforming zone is 9 atm, the mass rate of mixture supply at entry ≤3 h^{-1}). P_{H_2}, atm: 0.4 (*1*), 0.7 (*2*), 1 (*3*) [26].

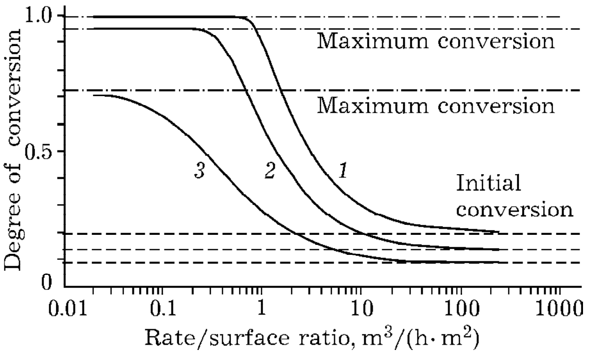

Fig. 13. Action of temperature on the degree of methane conversion at total pressure in reforming zone of 9 atm (partial pressure of hydrogen in permeability zone is 0.3 atm). T, °C: 500 (*1*), 450 (*2*), 400 (*3*) [26].

the membrane reformer at partial pressure of hydrogen in permeability zone of 0.4 atm it is more than 83 %. The advantages of catalytic membrane over traditional tubular reactor are most conspicuous in studies of the action of temperature on the degree of methane conversion (see Fig. 13). With increasing temperature from 400 to 500 °C, as an example, the degree of methane conversion in TTR does not exceed 19 %, whereas in CMR it runs experimentally to 70 %, and analogue computations lead to essentially complete conversion (~100 %).

CONCLUSIONS

Catalytic membrane reformers incorporate the following advantages: high-energy efficiency (≥80 %), small size, good performance, low temperature of reforming process. This equipment produces ultra-pure hydrogen in one step, and the degree of raw material conversion is higher-than-equilibrium. A near complete methane conversion (up to 100 %) can be reached in CMR at ~500 °C. The produced hydrogen is free from CO and suitable for use in low-temperature fuel elements. Hydrogen productivity of reformers with integrated membrane modules of hydrogen separation from reaction mixture and with oxygen introduction into reaction zone is eight times as much as a productivity of traditional tubular reactors.

Widespread introducing CMR is presently retarded owing to a set of reasons: relatively short operating life of membranes, their inadequate stress-strain permanence, and, most importantly, a high cost of palladium that is a basic component. What is more, there is no evidence yet of cost characteristics of membranes and production procedures and techniques for tubular and plate CMR. Nevertheless, advances in development of ultrafine composite membranes on different supports point to the outlook for introducing membrane technology into coming hydrogen energetics.

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