Hydrogen Production Catalytic Systems for Fuel Elements with Simultaneous Carbon Dioxide Removal from the Reaction Medium

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Abstract

Main catalytic processes and types of fuel for the production of hydrogen for low-temperature fuel elements with simultaneous carbon dioxide removal from the reaction medium are described. Types of adsorption reactors used for absorption and catalytic conversion (ACC) with pressure or temperature swinging, as well as reactors with membrane separation of hydrogen are considered. Descriptions are presented for novel regenerative membrane systems such as adsorbent-membrane reactor and space life support systems. Prospects for the use of ACC in hydrogen power engineering are evaluated.

Key words: hydrogen, adsorption process with pressure and/or temperature swinging, absorption and catalytic conversion, fuel processor, reactor, fuel element, catalyst, adsorbent, patents, reviews

Contents

INTRODUCTION

Catalytic hydrogen production from hydrogen-containing sources, such as water, natural gas, oil and coal, is promising from the point of producing electrical energy with the help of fuel elements [1, 2]. Hydrogen, as opposed to oil or natural gas, cannot serve as an energy source, since there are no hydrogen deposits or basins on the Earth. This substance could represent an energy carrier, *i. e.* a substance convenient for transportation and use by substance wherein the energy is temporarily stored. At a room temperature and atmospheric pressure, the specific density of hydrogen is low (0.089 kg/m^3). At the same time, the energy per mass unit (120 MJ/kg) inherent in hydrogen is higher as compared to all known kinds of organic fuel. The conversion of hydrogen into electric power on the spot allows one to avoid the energy loss inherent in electrical energy wiring. The combustion of hydrogen is not accompanied by hazardous methane or carbonic gas emissions. It should be noted that hydrogen used for proton-exchange membrane fuel elements (PEMFE) should have a high purity level ($C_{CO} \leq 10$ ppm). This fact is, to all appearance, caused by poisoning of platinum electrocatalysts of hydrogen anodic oxidation the anode occurring within the range of PEMFE operating temperatures values from 25 to 90 °C.

Two basic methods for obtaining hydrogen are known. They consist in water electrolysis and natural gas conversion. Obtaining hydrogen *via* water electrolysis is rather expensive process; today by this method is employed to obtain only 4 % of hydrogen all over the world. Obtaining hydrogen *via* a chemical method is rather economic (for example, natural gas oxidation into synthesis gas): the costs in this case are twice less as compared to those inherent in water electrolysis. In our work, the basic attention is given to the production of hydrogen from hydrocarbon fuel employing the processes of adsorption with pressure swinging (PSA, pressure swing adsorption) or temperature swinging (TSA, thermal swing adsorption) within a fuel processor (FP). The mentioned technology is very flexible with respect to the separation and purification of gas mixtures [3]. Nowadays several hundred thousand installations are under operation all over the world, from very small ($\approx$0.354 ncm^3/h, for oxygen obtaining from air for the medical purposes) up to very large (2.83 $\cdot$ 10^6 nm^3/h, for producing hydrogen of 99.999 % purity basing on methane steam conversion and effluent gases from oil refining factories). The concept of PSA for gas separation is rather simple. Certain components from a gas mixture flow are selectively adsorbed at a rather high pressure onto a micro/mesoporous solid adsorbent, whereas the flow itself is at the same time purified. Adsorbed components are further desorbed from the adsorbent via reducing the value of partial pressure inside the reactor, and then the adsorbent could be used repeatedly. The desorption of gases usually does not require any heat to supply.

There are some interesting modifications of PSA: a) fast cyclic PSA (the cycling amounting to several seconds); b) high-temperature cyclic PSA (for extracting CO_2 from hot and wet gases); c) adsorption with vacuum swinging; d) improved sorption reaction processes (ACC), *etc.*

The absorption-catalytic conversion represents a hybrid technology wherein the reaction controlled by equilibrium proceeds in the presence of a sorbent removing undesirable products from the reaction zone. According to Le Chatelier's principle, the yield and the rate of target product formation increase in the sys-

tem under consideration. Further, the sorbent is recycled periodically *via* PSA principle via purging a purifying gas. The production of hydrogen according to the ACC technology is considered the most promising [4, 5]. With the help of a methane steam conversion (MSC) catalyst and a selective chemisorbent for CO_2 extraction within the same reactor, it is possible to obtain hydrogen for a fuel element from natural gas purified from sulphur. The mentioned process was known as early as 1868 [6]. Later, patents have been obtained for carrying out ACC in a reactor with a static bed of catalyst (1933) [7] and with a fluidized-bed catalyst (1963) [8]. Nevertheless, the concept of ACC has not obtained the further development because of low prices for energy and difficulties connected with the processing of a solid sorbent in great amounts. However, nowadays the interest with respect to ACC sharply increases resulting from the increase in the prices for energy and owing to the global warming caused by growing the emissions of hotbed gas CO_2 [9−19]. The extraction and storage of CO_2 from fuel gases and other gases is advantageous for carrying out such catalytic processes as dry methane conversion, carbon gasification (for example, the regeneration of a catalyst *via* decarbonising), and other novel oxidizing processes described in the literature.

The purpose of the present work consists in reviewing the state-of-the-art of absorption and catalytic processes for hydrogen production in adsorption reactors as well as the prospects of using them in hydrogen power engineering. In opinion of prominent scientists, the introduction of hydrogen energy and power engineering should become the state program aimed at the prevention of the future energy crisis and a global climate change [20].

CATALYTIC PROCESSES FOR HYDROGEN OBTAINING AND CONVERSION REACTORS

Types of fuel

For the production of hydrogen in the fuel processor, various types of fuel can be used: a mixture of either hydrocarbons or their derivatives, or properly oil fuel which could be in general described by the formula $C_nH_mO_z$. The

general conversion scheme for transforming such fuels into hydrogen represents a combination of five basic reactions: steam conversion, catalytic partial oxidation, CO steam conversion, and selective CO oxidation and methanation reactions. The latter reaction is undesirable, since the hydrogen obtained *via* the other reactions is consumed therein. At the same time this reaction is necessary for decreasing CO concentration down to a level plausible in PEMFE operation, as well as for CO_2 removal from the atmosphere of a space vehicle cabin. The reactions indicated could simultaneously be carried out when heavy hydrocarbons are completely reformed into lower alkanes and CO. The rest the lower alkanes including CH_4 can be further converted into synthesis gas or simply oxidized to obtain energy, whereas CO can be converted into CO_2 according to the reaction of water gas steam conversion, to provide obtaining an additional amount of hydrogen. The expression for the gross reaction (fuel a H_2) looks as it follows:

$$C_nH_mO_z + y(O_2 + 3.76N_2) + 2(n - y - z/2)H_2O$$
$$\rightarrow nCO_2 + 2(n - y - z/2 + m/4)H2 + 3.76yN_2 \quad (1)$$

Here n, m, z are the number of carbon, hydrogen, oxygen atoms in $C_nH_mO_z$, respectively; y is oxygen/fuel ratio.

It should be noted that the maximum of efficiency in hydrogen production almost does not depend on the mode of fuel conversion (steam conversion, partial oxidation, autothermal mode) being attained in the thermoneutral point [21]. Hence, a fuel processor should operate either under thermoneutral, or under slightly exothermic conditions, *i. e.* the heat efficiency of reaction (1) $\Delta H \leq 0$.

Each type of fuel exhibits unique physical and chemical properties. The analysis of data from Table 1 [22] demonstrates that the complete conversion of fuel into hydrogen and CO_2 requires for different oxygen amount depending on the kind of fuel, whereas the maxima of energy efficiency values differ from each other for different fuels, though they have been obtained in the ideal autothermal process ($\Delta H = 0$). (The energetic thermal efficiency of reforming represents a ratio between the amount of hydrogen obtained and the amount of the consumed fuel, multiplied by the lowest combustion heat values for hydrogen and fuel, respectively.) Oxygen-containing substances (alcohols, aldehydes, ketones, *etc.*) represent a usual kind of fuel for hydrogen production. Among all the alcohols, methanol is the most attractive as fuel owing to not only moderate conditions of conversion and the best energy efficiency, but also the possibility of obtaining it from renewed sources [23−27]. The

TABLE 1

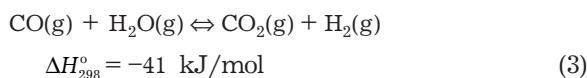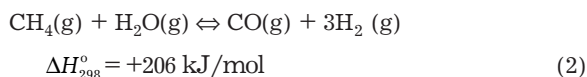Types of fuel and the greatest possible power efficiency of their reforming [22]

Fuel	$C_nH_mO_z$	Calculated thermoneutral O_2/fuel ratio values (x_o) and theoretical power efficiency values						
		n	m	z	ΔH_f, kcal/(g · mol)	$m/2n$	x_o	Efficiency, %
Methanol	CH_3OH	1	4	1	−57.1	2	0.230	96.3
Methane	CH_4	1	4	0	−17.9	2	0.443	93.9
Acetic acid	$C_2H_4O_2$	2	4	2	−116.4	1	0.475	94.1
Ethane	C_2H_6	2	6	0	−20.2	1.5	0.771	92.4
Ethylene	C_2H_4	2	6	2	−108.6	1.5	0. 418	95.2
Ethanol	C_2H_6O	2	6	1	−66.2	1.5	0. 608	93.7
Pentene	C_5H_{10}	5	10	0	−5.0	1	1.595	90.5
Pentane	C_5H_{12}	5	12	0	−35.0	1.2	1.814	91.5
Cyclohexane	C_6H_{12}	6	12	0	−37.3	1	2.143	90.7
Benzene	C_6H_6	6	6	0	−11.7	0.5	1.784	88.2
Toluene	C_7H_8	7	8	0	−2.9	0.57	2.161	88.6
Isooctane	C_8H_{18}	8	18	0	−62.0	1.13	2.947	91.2

catalytic production of hydrogen from methanol for mobile, stationary and portable energy producing units basing on fuel elements was considered in detail by the authors of review [28]. Another alcohol − ethanol − is commonly used as a main additive for gasoline due to its high octane number and low toxicity [29−32]. Recently an interest has been arisen with respect to hydrogen production from phenol [33].

Natural gas [34] and liquefied oil-well gas [35], as well as their substitutes (methane and propane [36]) are considered the most attractive fuel for production of hydrogen due to their huge resources and high conversion efficiency. Nowadays obtain 90 % of hydrogen is produced all over the world from natural gas. Besides, there is a widely developed gas distribution infrastructure formed for today. As well as the gases mentioned above, gasoline is also attractive for the production of hydrogen having an extensive infrastructure, too. However, since 2004 the USA have stopped all studies within the framework of the topic "obtaining hydrogen from gasoline" [28]. Other kinds of fuel, including diesel fuel, bioethanol, biodiesel fuel, alcohol from sugar, are also considered as promising sources for obtaining hydrogen. Using them, hydrogen/synthesis gas is traditionally obtained *via* high-temperature gasification/pyrolysis of biomass with the subsequent catalytic reforming of gas-liquid products. Obtaining hydrogen from coal *via* coal gasification to produce CH_4 and the subsequent employing the ACC technology has been developed in the USA by the authors of ZEC (Zero Emission Carbon) project [37]. About a half of hydrogen produced is used for the stage of gasification, and the rest one is supplied to TE for the generation of electrical energy. According to data presented in [38], the efficiency of coal conversion into electricity amounts to about 70 %. Research work in the mentioned field is under proceeding in England [39] and Japan [40].

Conversion processes and variants of purifying hydrogen

The basic reactions of obtaining H_2 from natural gas represent methane steam conversion (MSC) and the subsequent reaction of carbon monoxide steam conversion (CMSC):

$$CH_4(g) + H_2O(g) \Leftrightarrow CO(g) + 3H_2\ (g)$$
$$\Delta H^o_{298} = +206\ kJ/mol \tag{2}$$
$$CO(g) + H_2O(g) \Leftrightarrow CO_2(g) + H_2(g)$$
$$\Delta H^o_{298} = -41\ kJ/mol \tag{3}$$

Both reactions are restricted by equilibria, therefore to obtain any complete conversion of CH_4 and CO within a separate reactor under normal conditions is impossible. However, when CO_2 is extracted from the gas phase at the moment of its formation the restriction by equilibrium disappears, and almost complete methane conversion could be attained. The reaction of CO_2 extraction could be written as

$$CO_2(g) + S(s) \rightarrow S \cdot CO_2(s) \tag{4}$$
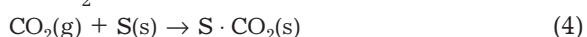
The total reaction could be expressed in the following form:

$$CH_4(g) + 2H_2O(g) + S(s) \rightarrow 4H_2(g)$$
$$+ S \cdot CO_2(s) \tag{5}$$
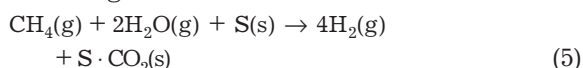
One can see that the sorbent can react with CO_2 with the formation of solid carbonate or with the adsorption onto the surface of a sorbent either in physical or chemical fashion. The main attention of researchers has been given to the sorbents based on calcium and hydrotalcites promoted with potassium. Other sorbents based on mixed lithium and sodium metal oxides were investigated less intensively. A detailed consideration of sorbents and conversion catalysts will be presented in the following publications.

The production of hydrogen with the use of the traditional methane steam conversion process and simultaneous CO_2 extraction has begun almost 30 years ago [41, 42]. In this review we are discussing standard and membrane-based processes of obtaining H_2, as well as some restrictions with respect to ACC; those could be eliminated or, at least, reduced. Flow diagrams for the standard methane steam conversion in traditional and membrane-based FP with three methods of H_2 purification are presented in Fig. 1. The natural gas purified from sulphur is mixed up with water vapour at a ratio $H_2O/C = 2.5−5$ to be fed then into a reformer, where according to reaction (2) H_2 and CO are formed. The traditional conversion represents a highly endothermic process, thus in order to reach a necessary temperature value for the process (800−900 °C), a significant amount of additional energy is required. It was established, that a high pressure of 1.5−2.0 MPa
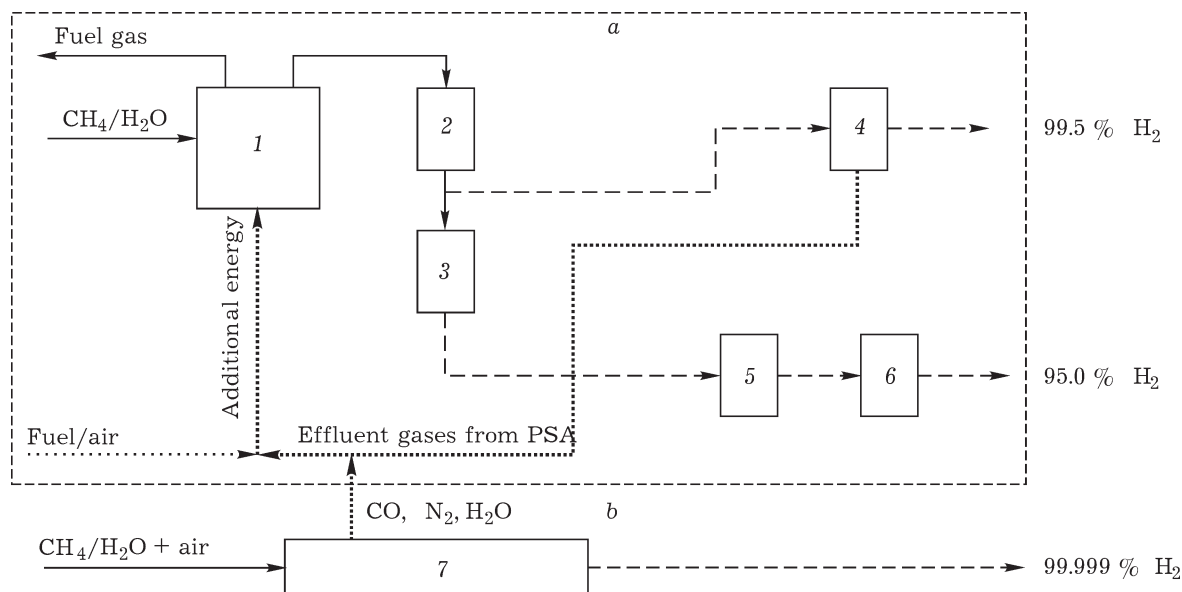
Fig. 1. Block scheme of traditional (*a*) and membrane (*b*) fuel processors for hydrogen production of with three purifying methods: *1* − reformer, *2* − HTR CMSC, *3* − LTR CMSC, *4* − PSA reactor, *5* − scrubber, *6* − methanator or PROX, *7* − membrane reformer.

when carrying out the process is economic despite of a negative influence of pressure upon the conversion of CH_4. The reaction is carried out on nickel catalyst inside pipes in the furnace, where additional energy is generated resulting from the combustion of effluent gases after purifying either hydrogen, or an additional part of natural gas. Reaction (3) is carried out within the two reactors of CO steam conversion: a high-temperature reactor (HTR CMSC) at 35−400 °C and a low-temperature reactor (LTR CMSC) at about 200 °C. For HTR CMSC iron-chromium catalyst is used, whereas for LTR CMSC involves copper-zinc catalyst. Typical gas composition after processing in second CMSC reactor is as it follows (dry, vol. %): H_2 76, CO_2 17, CH_4 4, CO 3 [43]. A catalytic membrane reformer or membrane fuel processor substitute the traditional multi-fuel processor by a single unit wherein both reaction and separation occur simultaneously [44−46].

The existing methods of purifying depend on the assignment of the product − hydrogen. In the case of wet purification, CO_2 is extracted by monoethanolamine (MEA) solution. When the obtained hydrogen-containing gas in a great amount contains CO poisoning the catalysts of the reactor or a fuel element, then either methanation (reverse conversion reaction) or selective oxidation (preferential oxidation, PROX)

are required for decreasing the CO level. The PROX represents a catalytic process whose realizing consists in adding a small amount of O_2 in the presence of H_2 to selectively oxidized CO. The final products of purifying consist of 95 % of H_2 and CO traces.

The process of adsorption with pressure swinging is efficient in obtaining the hydrogen with ultrahigh purity level; it is in detail described in [3, 42]. In this case a low-temperature CMSC reactor is not used. Composite fixed bed layers containing molecular sieves, silica gel or activated coal are used in PSA providing the continuity of the process with a constant structure of hydrogen-containing and effluent gases. Employing modern PSA reactors one succeeds in attaining the concentration of $H_2 > 99.9$ % with the extraction of H_2 up to 90 %, in this case the concentration of CO usually amounts to ~100 ppm. In order to use such gas for PEMFE, either methanation or PROX is required.

The membrane purifying method allows one to obtain super-pure hydrogen with 99.999 % purity level, as well as to extract CO_2 continuously during entire process. The hydrogen obtained can be used for PEMFE, since the concentration of CO therein does not exceed ~10 ppm. All the three methods of H_2 purification possess specific disadvantages. So, when the methanation or PROX are used the loss of

hydrogen is inevitable; the cost of MEA purification is high due to the requirements for steam in a desorber; PSA units are rather complicated, and the loss of H_2 therein can amount to more than 10 %. A wide application of metal membranes is restrained by their cost, permeability with respect to hydrogen and service life [45, 46]. Ceramic oxygen permeable membranes are under intensive development.

Typical units of a fuel processor with ACC

ACC units in the structure of a fuel processor for PEMFE differ insignificantly in design from the traditional reactors used for methane steam conversion. Their feature consists in the fact that there is CO_2 sorbent in ACC reactor together with the catalyst of methane conversion. Owing to the cyclicity of the ACC process, at the least two identical devices are usually applied: one being in the operation mode, whereas the second is in the mode of sorbent regeneration. Instead of two units, catalytic adsorption reactors could be made in one case with two columns of pipes with the mixture of MSC catalyst and CO_2 chemisorbent (Fig. 2) [47−49]. A novel thermosorption type of reformer proposed by the authors [48, 49] for obtaining hydrogen in the course of steam conversion at the temperature of ~500 °C is designed for using hydrotalcite as a chemisorbent for CO_2. The cyclic process consists of two stages. At the sorption reaction stage, a H_2O and CH_4 mixture is fed at a pressure of 0.15−0.20 MPa and the temperature amounting to ~490 °C into a reactor with the fixed bed layer consisting of a mixture of RCM catalyst and CO_2 chemisorbent. The reactor is heated up at a temperature of ~590 °C and is filled by steam at the pressure and temperature inherent in the reaction. Hydrogen-containing gas (CO < 20 ppm) is output from the reactor at the mentioned pressure. At a stage of thermal regeneration the pressure the a reactor is reduced down to atmospheric value, layer purification by superheated steam is carried out (~590 °C) in a countercurrent flow with the subsequent increase in pressure up to the value required for the reaction, at the same time CO_2 gas is output from the reactor.
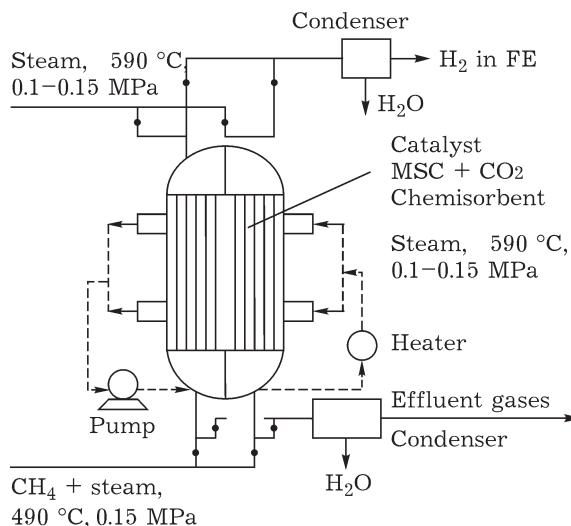

Fig. 2. Scheme of ACC adsorption reactor with temperature swinging [49].

The reactor with a circulating fluidized-bed layer (a transport reactor) represents an ideal system for carrying the regenerated and spent sorbent between the reactor of obtaining H_2 and the reactor of regeneration, for adding fresh sorbent and extracting spent sorbent, as well as for the removal of a part of sorbent for reactivation. Pilot installation with such a type of reactor has been created in the 1970ths in Russia [50, 51]. Fuel was supplied continuously, the adsorbent permanently circulated between a reactor and a regenerator, which allowed single-stage obtaining hydrogen with the purity level higher than 96 %. For fluidized bed reactors, one should use materials with a high mechanical strength with respect to abrasion.

Methane steam conversion (MSC-ACC) in a reactor with fluidized layer with industrial Ni catalyst (Haldor−Topsøe) and dolomite as CO_2 sorbent was carried out using a laboratory-scale reactor [52]. Hydrogen product (98 %, dry mass) has been obtained at 600 °C, atmospheric pressure, at the steam/carbon ratio equal to 3, and at the catalyst/calcinated dolomite ratio equal to 2.5 g/L per 1 g. For the experiments, one reactor was used operated in a periodic mode. The calcination of the layer was carried out at atmospheric pressure, temperature amounting to 850 °C with the use of N_2 gas for purging. At the regeneration stage, the catalyst before feeding with CH_4 and H_2O was reduced in the flow of H_2. A similar laboratory-scale reactor of 1 m

in height with a circulating layer consisted of two fluidized bed reactors connected by a transport pipe (rizer) and loop stoppers, is demonstrated in [53]. The scheme of the reactor provided a continuous circulation of powder without undesirable mixing the gases between the reformer and the regenerator. The internal diameter of both reactors amounted to 5 cm. Dolomite with the separation efficiency about 65 % also was used as CO_2 sorbent. Fresh sorbent and catalyst could be added into the reactor after a certain time. Studies with the same reactor were carried out) by the authors of [54] who investigated the influence of $Ca(OH)_2$ formed upon the composition of gas formed. The scheme proposed for an industrial process based on such a reactor is presented in Fig. 3 [4]. Mathematical models describing the stages of conversion and regeneration in conjugated reactors with fluidized are presented in [5, 55].

Laboratory-scale and pilot adsorption reactors are used for testing methane steam conversion and usually represent devices of tubular type. Such a reactor in the form of pipe made of stainless steel with internal diameter 12.5 mm and 220 mm long was loaded with an industrial Ni-catalyst (United Catalyst Inc.) containing 25−35 % Ni, 25−35 % NiO, 5−15 % MgO, 15−25 % sodium silicate, and with a CO_2 adsorbent, such as hydrotalcite promoted with potassium [10]. Studies were performed concerning transient modes in the reactor. From the increment in the conversion level of methane due to shifting the equilibrium caused by CO_2 adsorption, mass transfer restrictions were de-

termined concerning the kinetics of adsorption as well as the role of pressure was revealed. A similar reactor for cyclic MSC-ACC testing was made of 40 stainless steel pipes with the internal diameter equal to 25.4 mm and the length of 6100 mm [12]. The average molar fraction of H_2 in the hydrogen-containing gas obtained amounted to ≥87.0 % (dry mass), whereas the concentration of CO_2 and CO did not exceed 130 and 30 ppm, respectively. The steady-state mode of reactor operation was reached after 30 cycles. In order to estimate the reaction and adsorption kinetics under isothermal conditions, a reactor with a variable length of adsorption and reaction zones [56] was used. By the example of two reactions (H_2S extraction from natural gas and crude oil, as well as HCN synthesis from synthesis gas made of raw material) it has been demonstrated that the adsorption and reaction stages proceed with an almost identical reaction rate. A novel hybrid system of adsorbent-membrane reactor (Hybrid Adsorbent-Membrane Reactor, HAMR) for producing hydrogen unites together the reaction of obtaining hydrogen, the membrane separation of H_2 and CO_2 with the adsorption of produced CO_2 in the reaction zone and/or in the zone of permeability [57]. The HAMR system is of potential interest from the standpoint of obtaining pure hydrogen for various mobile and stationary energy-producing units on the base of PEMFE; it has been preliminary investigated in the hybrid membrane reactor with integrated together processes such as reaction, water evaporation through a membrane and its ad-
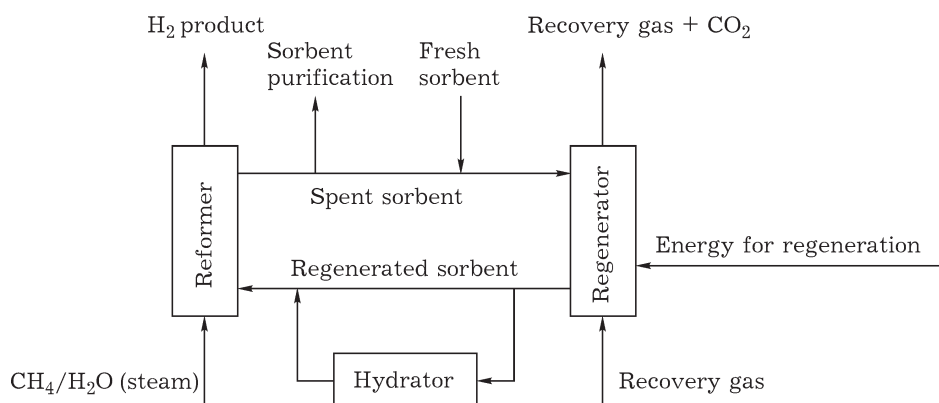

Fig. 3. Probable scheme of an industrial ACC reactor with a circulating fluidized layer and hydrator for maintaining the activity of a sorbent [4].

sorption behind the membrane [58]. The membrane reactor with evaporation was equipped with hydrophilic polymeric membranes selectively permeable for water (polyesterimide, polyimide, as well as microporous zeolite membranes). Water represents an undesirable byproduct (for example, in the reactions of etherification), then water removal promotes an increase in selectivity and the yield of the main product. Combining the separation and adsorption reactions within one apparatus represents a new type of the processes named "reactive separation". Alongside with membrane reactors with fixed bed catalyst (MR) [45, 59−64] and absorption reactors (AR) [9−12, 65−70], HAMR possess the following advantages as compared to traditional reactors of steam methane conversion. They are: 1) increased methane conversion level and hydrogen yield due to shifting the equilibrium of MSC reaction towards products; 2) realizing MSC under softer operational conditions (for example, at lower temperature, pressure, reduced steam consumption); 3) lowered requirements for purifying hydrogen (in the case of MR) or for removing an undesirable product such as CO_2 (in the case of AR).

A schematic diagram of HAMR is demonstrated in Fig. 4. One can see that the catalyst and adsorbent are located on the external side of the membrane with an additional adsorbent located inside the membrane volume. There are various configurations of HAMR: 1) the catalyst is loaded on the reaction side, whereas the adsorbent is loaded into the zone of permeability; 2) the catalyst and adsorbent are loaded on the reaction side with no adsorbent and catalyst in the zone of permeability. In the first variant, the membrane separates the catalyst from the adsorbent, which allows recycling the adsorbent continuously, immediately during the process. This configuration demonstrates the advantage HAMR with respect to AR, where many layers are required for maintaining the continuity of the process while one of them is recycled.

Just as it is in the case of an adsorption reactor of methane steam conversion, HAMR requires for coordinating the properties of adsorbent with catalytic system. Two adsorbent types were proposed: layered double hydroxide promoted with potassium (layered double hydroxides, LDH) stably operating at low tem-
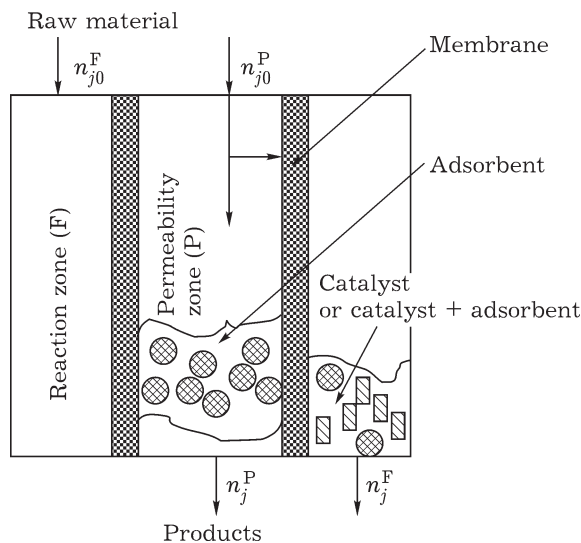

Fig. 4. Scheme adsorbent membrane a reactor [57]. n_{j0}^{P}, n_{j0}^{F}, n_{j}^{P}, n_{j}^{F} − rates of component j in the zone of permeability (P) and the reaction zone (F) at the reactor inlet/outlet.

perature (less than 500 °C) [9, 12, 71], and CaO or industrial dolomite which is used at typical temperature values of steam conversion (650−700 °C) [69]. However, its regeneration requires for higher (>850 °C) temperature [11, 70]. These severe conditions are, to all appearance, caused by a gradual deterioration of adsorbent properties and a potential sintering of the conversion catalyst. Any mismatch between the reaction and regenerative conditions complicates the process to a considerable extent. The regeneration of the adsorbent (CO_2 removal) is carried out using various methods: *via* pressure decrease, temperature rise or purging an inert gas [18].

Nowadays there is a novel type of high strength membranes employed in HAMR based on silicon carbide resistant against high-temperature steam is used. SiC nanoporous defectless membranes have been prepared *via* chemical vapour deposition/chemical vapour infiltration technique using two different precursors such as triisopropylsilane ($(C_3H_7)_3SiH$, or TPS) and 1,3-disilabutane ($CH_3SiH_2CH_2SiH_3$, or DSB) [72]. As against DSB membranes, the TPC membranes are high-temperature resistant and thermostable ones. Another traditional method of impregnation and coating (conventional dip-coating technique) was used for making membranes stable at 450 °C from a ceramic precursor (allylhydropolycarbosilane), and in particular from allyl-substituted hydropolycarbosilane.

These membranes are not susceptible to deactivation resulting from coke and sulphur and thus were used in the reactors for conversion carbon monoxide (water-gas shift reactor) and for methane steam conversion where the membrane is functioning in the presence of high-temperature steam. The permeability with respect to hydrogen amounted up to $(4–6) \cdot 10^{-7}$ mol/(m$^2 \cdot$ s $\cdot$ Pa) being constant during 120 h, the separation factor $H_2/H_2O \approx 2.5$. The permeability with respect nitrogen appeared almost two order of magnitude lower than that for hydrogen ($4.55 \cdot 10^{-9}$ mol/(m$^2 \cdot$ s $\cdot$ Pa)). The concentration of CO in SiC membrane reactor with fluidized bed catalyst in the zone of permeability was not lower than 100 ppm. Hence, in order to use the hydrogen obtained in PEMFE one should take additional measures for decreasing (reduction) the level of CO down to 10 ppm.

The experimental investigation of HAMR has been performed for the reaction of CO steam conversion with the use of layered double hydroxide as a adsorbent for CO_2 and nanoporous H_2 selective carbon membrane as a molecular sieve (carbon molecular sieve, CMS) [23]. The reactor was made of stainless steel, the internal diameter being of 3.175 cm, 25.4 cm long. The length of the CMS membrane amounted to 25.4 cm, the internal and external diameters being of 0.35 and 0.57 cm, respectively. Catalyst (30 g) and/or adsorbent (70 g) were loaded into the annular space between the membrane and the reactor. The reactor was heated by a three-zone furnace. For controlling the temperature, three separate temperature regulators, three thermocouples positioned in three different places of the layer, and a thermocouple sliding along the layer (placed in thermowell) were used. The control of pressure performed using a backpressure regulator. Gas pressure in the zone of permeability was maintained equal to atmospheric value in all the experiments. Gas leaving the reactor passed through a condenser and a moisture separator. Regenerative CO_2 adsorbents and LDH (with the formula $(Mg)_{1-x}(Al)_x (OH)_2(CO_3)_{x/2} \cdot mH_2O$) were tested. The adsorbents were recycled directly *in situ via* purging by nitrogen or by steam. In the course of testing, $CuO/ZnO/Al_2O_3$ Haldor–Topsøe industrial catalyst was used for low-temperature

CMSC reactions was used. For kinetic testing, the catalyst was activated (the process of copper oxide reduction into metal copper) *via* heating at 220 °C in a flow consisting of 50 % N_2, 30 % H_2, 20 % H_2O. The following kinetic model has been obtained:

$$r = 12.06 \exp\left(-19.596/RT\right) \cdot P_{CO} P_{H_2O}^{0.5} (1 - \beta) \quad (6)$$

where r is the reaction rate, mol(g$_{cat} \cdot$ h); $\beta = (1/K_g)(P_{CO_2} P_{H_2} / P_{CO} P_{H_2O})$; K_g is the equilibrium constant for the CMSC reaction; P_j is the partial pressure of component j ($j = 1$ for CO_2, $j = 2$ for H_2, $j = 3$ for CO, $j = 4$ for H_2O, $j = 5$ for N_2).

In order to determine the characteristics of CMS membrane (permeability level and separation factor), several series of experiments were performed with the use of separate gases (CO, CO_2, H_2, Ar, CH_4 and N_2) and a mixture containing CO, CO_2, H_2 and H_2O. The permeability of component j through the membrane was determined according to the empirical mass transfer equation:

$$F_j = U_j (P_j^F - P_j^P) \quad (7)$$

Here F_j is permeability of component j, m^3/(m$^2 \cdot$ h $\cdot$ MPa); P_j^F, P_j^P are partial pressures of component j in the zones F and P, respectively; U_j − membrane permeability.

The separation factor (SF) was determined as the ratio between the hydrogen permeability and the permeability of corresponding gas. It has been obtained, CMS membrane permeability with respect to H_2 is equal 0.13446−0.16847 m^3/(m$^2 \cdot$ h $\cdot$ MPa), whereas the SF for CO amounted to 34.87, for CO_2 this value was equal to 15.75, amounting to 47.86 for N_2.

The authors of [73] have demonstrated that the yield of hydrogen, its extraction level and the conversion of CO in HAMR system is higher, than in an adsorption reactor. The mathematical model of HAMR system developed earlier by the authors of [57], describes well experimental data concerning CMSC.

Considered above devices for the extraction of CO_2 with a simultaneous production of hydrogen nowadays are intensively investigated at a laboratory level. The transition to an industrial scale, to all appearance, could take place already in the near future, since the advantages of adsorption reactors as compared to traditional reactors are rather significant.

REGENERATIVE MEMBRANE LIFE SUPPORT SYSTEMS FOR SPACE

Extracting and recycling CO_2 exhibit large-scale potential applications in the chemical and a power engineering industries, as well as in the space branch [74, 75]. For example, the life support system (LSS, air revitalization system, ARS) should provide the extraction of CO_2 from the atmosphere wherein cosmonauts stay. For short-term flights, CO_2 level could be controlled *via* sorption on metal hydroxides such as LiOH. However, for long-term space applications, continuous regenerative technologies including pressure swing adsorption and membranes are required, which in addition to CO_2 extraction could be used for the regeneration of oxygen, too. One of the problems concerning the application of catalytic reactor technologies for space is presented by the fact that CO_2 concentrations are dilute. The necessity of introducing the stage of preliminary CO_2 concentration complicates the process to a considerable extent. Employing the technology of reactive separation (catalytic and separation stages being joined together *in situ*) with the use of high-temperature membranes provides additional synergism causing the efficiency of both stages to increase. Gas CO_2 is usually not considered to be toxic; its concentration in the terrestrial atmosphere is at a level of $330-350$ ppm. However, a high concentration of CO_2 could cause respiratory problems. The life support system at the International Space Station is maintaining the content of CO_2 at a level of about 2000 ppm, but at a high locomotor activity of cosmonauts, for example in a space environmental suit, this level is equal or lower than 5000 ppm.

One of approaches to the extraction of CO_2 consists in the use of methanation reaction (Sabatier) wherein CO_2 catalytically reacts with hydrogen to produce simultaneously methane and water:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \ \Delta H = -165.4 \text{ kJ/mol} \quad (8)$$

A schematic diagram of LSS is demonstrated in Fig. 5 and includes the system for CO_2 extraction based on the Sabatier reaction. Gas CO_2 taken from cabin is recycled in a subsystem lowering its content, where CO_2 catalytically reacts with H_2. (Hydrogen is generated together with O_2 in an electrolysis system.) Water as the reaction product of the Sabatier reaction enters to a water-separating system to provide *via* electrolysis an additional oxygen supply into a cabin. The Sabatier reaction kinetics was investigated by the authors of [76, 77]. Reaction (8) is exothermic, and the equilibrium conversion of CO_2 is to a considerable extent reduced at the temperature higher than 300 °C. In order to perform the reaction, supported Ni, Ru catalysts [78, 79] were used. The reaction mechanism is presented in [80]. A membrane reactor with permeable membrane based on SiO_2 and industrial 0.5 % Ru/Al_2O_3 catalyst has been earlier investigated by authors [81]. Mixtures H_2/CO_2 within a range $1-5$ were been used fed into the reaction zone at an increased pressure (0.2 MPa) for obtaining a high CO_2 conversion level. An interesting application of a membrane reactor to the extraction of CO_2 with the production of CH_4 and water has been proposed in [82]. The methane formed has been converted on Ni/SiO_2 catalyst into graphite carbon and hydrogen according to the reaction:
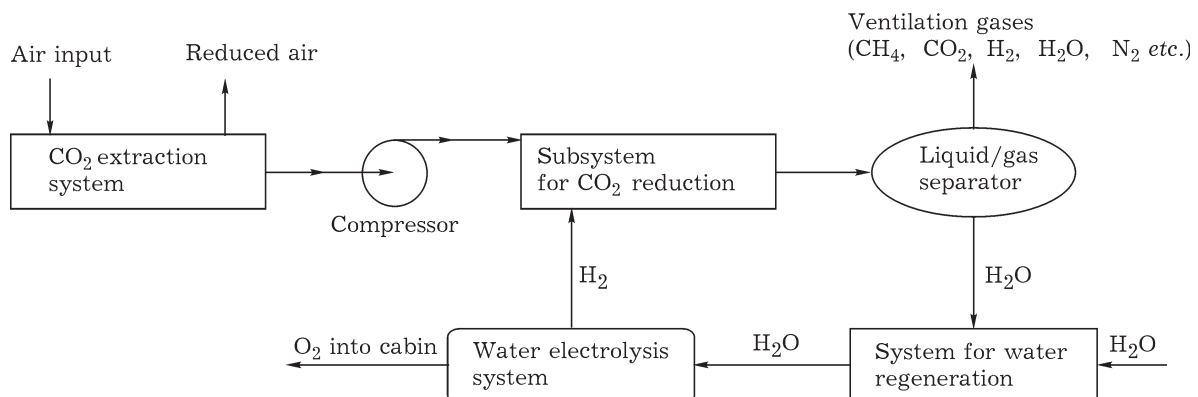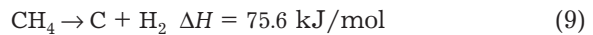
$$CH_4 \rightarrow C + H_2 \ \Delta H = 75.6 \text{ kJ/mol} \quad (9)$$

Fig. 5. Standard life support system with the subsystem for CO_2 reduction [75].

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$$
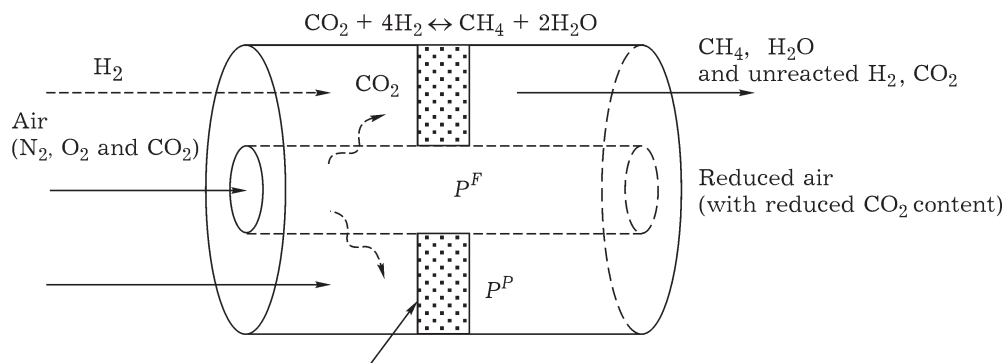
Fig. 6. Scheme of a membrane reactor for an orbital life support system and maintaining the CO_2 level ≤ 2000 ppm [75].

About 70 % of CO_2 was converted into graphite carbon in this two-stage reactor system.

A life support system on the base of a membrane reactor (MR-based air revitalization system, MARS) has been investigated with respect to an optimum amount of catalyst, membrane area and other parameters [75]. The MARS represents a closed life support system with feedback intended for the control the humidity level, the level of CO_2 and CH_4 in the cabin and maintaining a required amount of oxygen. It is known that one human being consumes usually 850 g O_2 per day breathing out about 1 kg CO_2 per day. In space, oxygen is made with the help of an electrolyser which decomposes water to yield O_2 and H_2. When the adsorption on metal hydroxides is used for the extraction of the exhaled CO_2, as much as ~2.1 t H_2O per year is required for six cosmonauts. Without recycling oxygen via the Sabatier reaction (when produced H_2 and CO_2 are not used), as much as 2.2 ton CO_2 and 233 kg H_2 should be output with ventilation gases into space. The MARS system converts CO_2 and H_2 into water and methane. The secondary conversion of methane (methane decomposition according to reaction (9)) requires for high temperature and a thoroughly developed reactor design, for example, with fluidized bed catalyst. The MARS system under description is not equipped with such a reactor yet, but the studies on obtaining additional hydrogen and carbon within the context of recycling the resources immediately in the course of the process have been already performed [83, 84].

Without taking into account hydrogen recovery according to reaction (9), the optimum conversion of CO_2 is provided according to reaction (8). Every 1 mol of CO_2 exhaled on the average requires for 1.168 mol of O_2 and 2.236 mol of H_2O in order to provide oxygen for breathing in a cabin. A part of H_2O could be recovered according to the Sabatier reaction; in this case the amount of recovered water is determined by amount of hydrogen produced onboard via electrolysis. This provides the conversion level of reaction (8) equal to 58.4 %, which means the preservation of 1.168 mol of H_2O and, correspondingly, 1046 kg of water per year for six cosmonauts. The calculations were performed for an ideal membrane with the CO_2 conversion level amounting to 58.4 % under the conditions of ideal CO_2 transport from a pipe. However, hydrogen supplied into the reaction zone, filled with the catalyst, partially penetrate inside the membrane tube, which results in hydrogen loss. Unreacted hydrogen together with CO_2 and CH_4 is output from the cabin with ventilation gases, though via catalytic oxidation it can be fed back in the form of water. The ratio between H_2 molar velocity within the reaction zone and air velocity in the zone of permeability is defined to be a purge ratio. The air under recirculation in the cabin, taking into account the membrane non-ideality, contains methane (1000 ppm), which prevents the system from explosive conditions in the presence of hydrogen in the cabin.

The main characteristics of the suggested system MARS are presented in Table 2. To all appearance, the membrane has high permeability with respect to H_2, CO_2 and H_2O except for gases CH_4, CO, N_2. The results of the modelling have demonstrated that the higher membrane permeability level, the less should be its area, but the greater amount of the catalyst is

TABLE 2

Key parameters and the range of operation conditions for the MARS system [75]

Parameters	Nominal value	Range
Pressure in the reaction zone (P^F), atm	1.07	–
Pressure in a zone of permeability (P^P), atm	1.00	–
Temperature in reactor (T), ℃	250	–
Flow rate of air (F_0^P), m^3/h	180	–
Permeability for CO_2, $m^3/(m^2 \cdot bar \cdot h)$	1.2	0.8–5.0
Separation factor:		
CO_2/H_2	5.0	–
H_2/CH_4	60.0	–
H_2/H_2O	1.0	–
H_2/N_2	79.4	–
H_2/O_2	84.9	–
Concentration in the zone of permeability, ppm:		
CO_2	5000	3000–5000
CH_4	1000	
H_2O	8000	
H_2O concentration in air, ppm	8000	
Catalyst density (ρ_c), g/m^3	$1.18 \cdot 10^6$	
Membrane length (L), m	1.0	
Internal membrane diameter (D_i), m	0.0035	
External membrane diameter (D_o), m	0.0057	
Area of cross section (A^F), m	0.14	
Layer porosity level	0.515	

required for CO_2 processing. The increase in the CO_2 concentration within a cabin exerts a positive effect since CO_2 in this case could be more readily removed through the membrane. The MARS system considered in the present work has been used for determining the suitability of the reaction separation in the life support system for space applications.

CONCLUSION

Catalytic hydrogen production for fuel elements with simultaneous extraction of carbonic gas from the reaction environment possesses a number of advantages with respect to the traditional scheme of hydrogen obtaining. Employing the ACC technology allows one-stage obtaining hydrogen with purity level ranging within 95.5–99.999 %, in this case the conversion level of initial raw material is higher than the thermodynamically equilibrium value. The thermal efficiency of the ACC process is higher as compared to those for the standard process (79 and 71 %, respectively). Nowadays for the generation of hydrogen mainly natural gas is applied. With the use of CaO chemisorbent, the CH_4 conversion level could be amounted up to 93 % in the case of extracting 85 % of carbon and more than 90 % of hydrogen.

Reactors for obtaining hydrogen *via* the absorption and catalytic conversion differ insignificantly from traditional conversion apparatuses. Schemes for the technology of purifying hydrogen-containing gas from impurities, as well as catalysts for conversion, are well developed, too. The basic problems connected with the use of ACC technology consist in the development of efficient CO_2 sorbents as well as in determining the influence of cyclic conditions upon the activity of catalysts.

Nowadays intensive studies are being performed at the laboratory level of adsorption reactors and processes for obtaining hydrogen therein.

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