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Membrane recovery of hydrogen from gaseous mixtures of biogenic and technogenic origin

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ABSTRACT

The development of energy effective processes, intensification of chemical and petroleum refining industries, solution of environmental tasks are related with hydrogen. Introductory parts of review are focused on particularity of H_2 generation from biomass (microbiological routes and pyrolysis) and introducing with main industrial hydrogen-containing gaseous mixtures as technogenic sources. Membrane gas separation processes as lower energy consuming ones for H_2 recovery from gaseous sources which are as rule multicomponent gas mixtures are considered in this paper including: (1) estimation of unknown gas permeance of commercial and lab-scale polymeric membranes for such components as CO_2, CO, N_2, CH_4, H_2S and calculation of standard membrane processes for H_2 recovery from multicomponent mixtures; (2) modeling of hydrogen recovery from H_2/CO_2 mixtures by gas–liquid membrane contactors with non-porous polymeric membranes; (3) theoretical and experimental results of hydrogen recovery from gaseous mixtures of technogenic and biogenic origin by combined membrane/PSA systems. It is shown that H_2 recovery can be successfully realized as combination of standard membrane method (H_2 preconcentrating) and PSA (H_2 conditioning). Improving of whole process requires the development of highly selective membranes.

Introduction

Nowadays, the dominating role of hydrocarbon resources in the modern fuel-and-power sector structure is considered by experts as a potential threat of energetic and economical safety of countries. That is why the development and implementation of alternative energy resources is of great importance.

The development of energy effective processes, intensification of chemical and petroleum refining industries, solution of environmental tasks is related with hydrogen. Hydrogen is the key element in many processes of organic synthesis. In petroleum refining (hydrocracking, hydrorefining) up to 37% of obtained H_2 is utilized for the purpose of quality improvement of hydrocarbon fuels with enhanced calorific value and reduced quantity of harmful impurities [1–2]. Hydrogen is widely used (up to 2%) in powder metallurgy, metalworking, production of glass and synthetic diamonds. Hydrogen is applied as a rocket fuel, the combination of liquid hydrogen with liquid oxygen provides maximal energy per weight unit (120.6 MJ/kg(H_2)). In last decades vehicles with H_2 powered

internal combustion engines were developed. Hydrogen−oxygen steam generators for electricity production during peak periods were developed as well. Other perspective areas of hydrogen utilization are production of fats and oils, oxoproducts, synthetic fuels and semiconductors [4−6]. At the same time up to 40% of H_2 is losing in waste streams or burned in technological processes in installations for heat production that is irrational. At present time the most part of H_2 (58−80%) is produced by steam conversion of methane. It is important to note that only 62% of hydrogen is produced as target product, the rest 38% is by-product of other productions.

Current world hydrogen consumption in chemical, petrochemical and petroleum refining industry is around 45 Mt/year. The prediction of hydrogen consumption and structure of market in XXI century foresees increasing of hydrogen consumption in 16−20 times to the year 2100 and 80% of this increasing is related to hydrogen utilization as energy carrier. In accordance to estimation [2] if hydrogen content in waste stream is higher than 50% the price of H_2 recovered by membrane, adsorption or cryogenic method is 1.5−2 times lower than price of H_2 obtained by steam conversion of natural gas. Therefore perspective sources of hydrogen can be such waste gas mixtures as blow-down gases of ammonia and methanol production, gases of catalytic reforming processes, cracking, dehydrogenation, operating of coke ovens and installations of olefins, acetylene, butadiene production as well as biohydrogen produced by bacteria and biosyngas produced by pyrolysis of solid biomass waste and wood. As a result the consideration of available hydrogen sources of technogenic and biogenic origin which are as a rule multicomponent gas mixtures with considerable amount of hydrogen seems to be of great importance. Depending on the composition of hydrogen-containing gas mixture the optimal technology for hydrogen recovery can be membrane separation (standard or hybrid membrane systems) since such processes not need energy consumption for phase transitions. This paper represents results of critical analysis of published and own data on application and potential of membrane technologies for hydrogen recovery as from biomass treatment products (renewable sources) as from exhaust gas mixtures of technogenic origin. Introductory parts of review are focused on particularity of H_2 generation from biomass (microbiological routes and pyrolysis) and introducing with main industrial hydrogen-containing gaseous mixtures as technogenic sources. Membrane gas separation processes for H_2 recovery from gaseous sources are considered in this paper. Gas separation properties of membrane polymers, commercially available polymeric membranes and the results of the developed theoretical estimation of permeance in relation to the set of gas components needed are considered as well. Additionally, paper provides some experimental gas permeability data obtained previously and non-published by authors. Critical aspects considered in the paper include: (1) estimation of unknown gas permeance of commercial and lab-scale polymeric membranes for such components as CO_2, CO, N_2, CH_4, H_2S and calculation of standard membrane processes for H_2 recovery from multicomponent mixtures; (2) modeling of hydrogen recovery from H_2/CO_2 mixtures by gas−liquid membrane contactors with non-porous polymeric membranes; (3) theoretical and experimental results of hydrogen recovery from gaseous mixtures of technogenic and biogenic origin by combined membrane/PSA systems. It is shown that H_2 recovery can be successfully realized as combination of standard membrane method (H_2 preconcentrating) and PSA (H_2 conditioning). Improving of the whole process requires the development of high selective membranes. In whole the formulated problems of H_2 recovery demand multidisciplinary interaction of specialists in the field of biomass treatment, chemistry and petroleum refining, membrane technology and engineering, and energy producers as well.

Hydrogen from biomass: microbiological routes and pyrolysis processes

Microbiological routes

Hydrogen can be obtained from water by electrolysis, thermolysis or biologically assisted photolysis (bacteria and algae), from biomass by means of reforming (steam, partial oxidation, autotherma and plasma), pyrolysis or steam gasification (pyrolysis in the presence of added H_2O) [7−10]. The ability to produce hydrogen is inherent to phototrophic microorganisms (green and purple bacteria, cyanobacteria and algae) and many representatives of chemotrophic microorganisms. Cellulose is a complex natural polymer synthesized annually in a great amount by plant biomass of the planet. *Clostridium cellobioparum*, *Selenomonas ruminantium*, *Ruminococcus flavefaciens* and many others anaerobic bacteria are able decompose the cellulose with the formation of hydrogen [11−15].

A lot of the studies are devoted to microbial decomposition of organic materials into hydrogen. They consider different simple sugars, polysaccharides, food wastes and wastewater as a raw material for hydrogen production [16−23]. The process of hydrogen production from lignocellulose considerably complicates technology [23−28] since decomposition of complex polymers requires a specialized enzyme system and additional time spent on hydrolysis of the insoluble polymer. As a cellulose-containing substrate most commonly using paper [29−31], straw [23,32], sawdust [33,34].

The hydrolysis time is the bottleneck of the whole process of producing hydrogen from cellulose containing biomass. This stage can be accelerated by pretreatment of biomass with physical (grinding or heating) or chemical (acid, alkaline and enzymatic hydrolysis) methods to provide availability for microorganisms. Availability of amorphous cellulose to bacterial enzyme complexes after pretreatments increases significantly [35]. The various options for the biomass pretreatment which are most common currently applied described elsewhere [25,36,37]. For instance, the hydrolyzate of miscanthus used as a substrate for cellulolytic microorganism *Caldicellulosirupter saccharolyticus* and *Thermotoga neapolitana* raised the hydrogen yield to 74% and 85% of theoretically possible one (4 mol of H_2 per 1 mol of glucose or 498 ml H_2 per 1 g of glucose), respectively [28]. Thus the pretreatment of cellulose containing materials can significantly increase the efficiency of the hydrogen production that in turn will contribute to further development of the industrial technology [38].

Table 1 – Hydrogen-containing gas mixtures of biogenic origin.

Source	Gas composition, vol.%							Reference
	H_2	CH_4	$C_{2}+$	CO	CO_2	N_2	H_2S	
Biohydrogen	1—80	0—2	–	–	6—12	1—80	0—12	[50,54]
Biohydrogen	57—60	–	–	–	39—43	1—5	–	[55]
Biosyngas	25—42	1	–	25—42	10—35	2—5	1	[10]
Biosyngas, model	33	–	–	17	–	50	–	[53]
Solid waste pyrolysis	31—32	25—31	–	20—27	7—13	–	–	[10]
Catalytic pyrolysis of pine tree	49.7—52.8	3.8—5.3	1.1—1.6	33.7—34.5	8.6—8.7	–	–	[56]
Pyrolysis of wet sewage sludge	36.7	14.7	7.1	21.8	13.6	6.3	–	[57]
Pyrolysis of coffee hulls	9.3—40.1	0—11.3	0—2.5	20.6—32.7	17.7—56.6	–	–	[58]
Gasification of Siberian elm	44.3	5.9—7.9	–	17.1	26.8—31.1	–	–	[52]

The maximal amount of hydrogen usually produced by bacteria consuming various sugars and realizing acetate as the main metabolic product. The productivity of hydrogen evolving consortium can be sufficiently high, for example 360 ml of hydrogen per L of cultivation medium an hour (in this case the hydrogen yield was 3.67 mol per 1 mol of sucrose [39,40] demonstrated the hydrogen yield equivalent to 413.4 ml of H_2 per 1 g of glucose (3.32 mol of hydrogen per 1 mol of glucose), that corresponds to 83% of theoretical maximum. The interest of researchers is now focused on hydrogen production by microbial communities [40—46]. The using of microbial consortium has a several advantages compare with the using of pure culture: 1) sterilization of the cultivation medium is not required since the microbial consortium usually quite resistant to external microbial impact; 2) adaptation to wide range of organic compounds occurs faster due to diversity of microbial consortium; 3) wide range of substrate can be used as a substrate for hydrogen production [47]. However cultivation of microbial consortium can be associated with the problem of results reproducibility due to the changes in community composition [44,46,48].

The hydrogen producing consortiums can be created artificially by combining several species of microorganisms. *Clostridium thermocellum* is one of the most common cellulolytic hydrogen producing microorganism [33,49]. In the case of combination of this organism with hydrogen producing *Thermoanaerobacterium thermosaccharolyticum*, the intensity of

cellulose decomposition and hydrogen yield increased significantly (from 0.8 mol of H_2 per mole of glucose for single culture to 1.8 mol H_2 per mole of glucose for microbial association [44]). Approximately the same dependence was demonstrated while combination of *C. thermocellum* with *Clostridium thermopalmarium* [50].

Calculations show that the efficiency of energy conversion contained in the substrate into hydrogen is still not sufficiently high. Therefore it would be inappropriate to develop industrial systems aimed to production of hydrogen only. However, if the process of producing hydrogen will be combined with producing other useful products or recycling process, the creation of such technology would be prospective. In case of hydrogen (biohydrogen) we have deal with gas phase mixtures consisted of H_2 (20—80 % vol.) and CO_2 (80—20% vol.) which need to be separated to recover energy carrier (e.g., investigated in frames of FP6 IP "Non-thermal production of pure hydrogen from biomass" № 019825).

Pyrolises processes

Pyrolysis and steam reforming pyrolysis of biomass have received considerable attention of various research groups for last years. Thermochemical reactions like pyrolysis, combustion and gasification performed at high temperatures using dry lignocellulosic biomass of straw or wood. The technologies consist of transformation of biomass into H_2,

Table 2 – Hydrogen containing gas mixtures of technogenic origin [59—61].

Exhaust gas mixture	Composition of gas mixture, vol.%								
	H_2	CH_4	$C_{2}+$	C_nH_{2n}	CO	CO_2	N_2	Ar	NH_3
Gases of petroleum refineries and petrochemistry									
Flue gas from reforming installations based on platinum catalyst	86.6—92.7	3.2	3—10.2	–	–	–	–	–	–
Butane dehydrogenization	71.6	12.7	1—3	11—13	0.1—0.5	0.1—0.5	–	–	–
Syngas of butadiene-1,3 production	74.6	11.5	–	–	13.9	–	–	–	–
Flue gas from acetylene production	50—63	5—8	–	–	27—30	3—10	1.5—2.0	–	–
Blow-down gases from ammonia production	65—60.5	13—8.5	–	–	–	–	22—20	4.5	2
Blow-down gases from methanol production	63.6—63.8	23.2—23.4	–	–	4.7	6.5—6.6	1.8	–	–
Methane-hydrogen fraction (after pyrolysis gas separation)	47.3	45.0	2.0	2.3	–	–	–	–	–
Gas from catalytic cracking	25.9	35.6	18.7	19.8	–	–	–	–	–
Gases of solid fossil fuels treatment									
Coke gas	50—62	24—28	0.8	2.1	5—8	2—3	3—5	–	–
Water-gas (steam gasification of coal)	47	1	–	–	43	3.7	–	–	–
Lurgi process	36.2	13.1—14.0	–	–	14.4	34.0	1.2	–	–
Generator gas	13	1.7	–	–	24	5.5	55.5	–	–

various useful chemicals or fuel. It took all the best what had been developed for technology of char gasification. The ratio of C and H_2O in the dry and ash-free lignocellulose can be regarded as approximately 50:50 (by weight), however content of the releasing heat approximately 20% greater due to containing of C—H and C—OH bonds. As a rule hydrogen production from biomass is considered as three stages process: (1) pyrolysis of raw biomass to produce the main hydrogen containing gas products, volatile tar, and solid char; (2) cracking and reforming of liquid oil and gases, and (3) char gasification [51]. Pyrolysis uses heat to degrade a feedstock in an oxygen absence condition to a combustible mixture of gases along with liquid oil and char fractions. The yields of end products of pyrolysis and the composition of gas mixtures depend on following parameters: temperature, biomass species, particle size, heating rate, operating pressure and reactor configuration, as well as the type of append catalysts [52]. Depending on mentioned parameters raw biosyngas contains around 10–50 vol.% of H_2, 5–56 vol.% CO_2, and 17–45 vol.% of CO and other impurities such as H_2S, N_2, CH_4 and H_2O (Table 1). CH_4 can be further converted to H_2 and CO by air reforming and CO_2 can be separated using conventional process [53].

Among many types of biomass (Table 1) that can be pirolyzed to produce H_2, lignocellulosic biomass has received attention because it does not require the diversion of feed resources. As an example the wood is composed of cellulose (35–50%), hemicelluloses (20–30%), and lignin (20–30%), as well as inorganic salts and extractives (low-molecular-weight organics). Thus the biomass pyrolysis is in fact the pyrolysis of a mixture of cellulose, hemicellulose, and lignin in the presence of various minor compounds. Lignocellulosic biomass (plant biomass) conversion can be achieved from various resources, including: (1) forestry wastes such as logging wastes, sawmill wood waste, and residues of the trees and shrubs; (2) agricultural residues like animal and crop wastes (e.g. corn stover) and (3) energy crops like corn, sugarcane, grasses and aquatic plants like water hyacinth.

While various research groups have investigated suitable technology and processes for bio-hydrogen and biosyngas production, the issue of the gas treatment for H_2 recovery has not received much attention.

Hydrogen of technogenic origin: main industrial hydrogen-containing gaseous mixtures as sources of hydrogen

As it was mentioned earlier waste gas mixtures of technogenic origin can be additional perspective sources of hydrogen. Some examples of such mixtures are presented in Table 2.

Waste gas streams considered are hydrogen-containing multicomponent gas mixtures which contain significant amount of CO_2 and other impurities that demands application of hydrogen recovery stage for its further utilization. In spite of additional charges for hydrogen recovery this process can be economically profitable. Estimation shows that in case of hydrogen content in waste stream higher than 50% the price of H_2 recovered by existing methods can be 1.5–2 times lower than price of H_2 obtained by steam conversion of natural gas. At the same time many waste streams contain lower than 50%

of H_2 therefore the improvement of H_2 concentrating and recovery methods from industrial waste gas streams is important problem.

Application and potential of standard membrane technology for hydrogen recovery from gaseous mixtures

Membrane, adsorption, absorption and cryogenic technologies are applied in industry for the recovery and purification of H_2 [62–68]. Technological zones of optimal installation productivity and target product purity are determined for low energy consumable processes (membrane, short cycle adsorption, ultra short cycle adsorption, Fig. 1). As it can be seen from Fig. 1 membrane processes occupy reasonably broad range: from local membrane equipment (mobile and modular installations) till enough high capacity ones.

Membrane methods take particular place due to the absence of energy consumption for phase transitions. Membrane technologies for hydrogen recovery appeared in the market for the first time in 1980: Separator PRIZM produced by Monsanto for H_2 recovery from blow-down gas of ammonia production. It should be noted that the first gas separating flat-sheet membranes under industrial scale were developed in Russia in 1977 [69]. At present time there are several hundred membrane installations for H_2 recovery in chemical, petrochemical and petroleum refining industrial plants all around the world. The number of companies which produce membrane installations and utilize membrane modules of own or off-site production is quite high. Leading positions are occupied by USA companies: IGS GLOBAL, Air Products, NATCO, CMS, Newpoint Gas, Parker NNI, On Site Gas Systems Inc, Holtec Gas Systems, ProSep Technologies Inc, MTR, PRAXAIR. Big companies from other countries are UBE (Japan), Air Liquide (France), INMATEC, BORSIG Membrane technology (Germany), CAN Gas Systems Company Limited (China). Russia is represented by such companies as GRASIS, KRIOGENMASH, VLADIPOR. Installations for H_2 production of technical purity
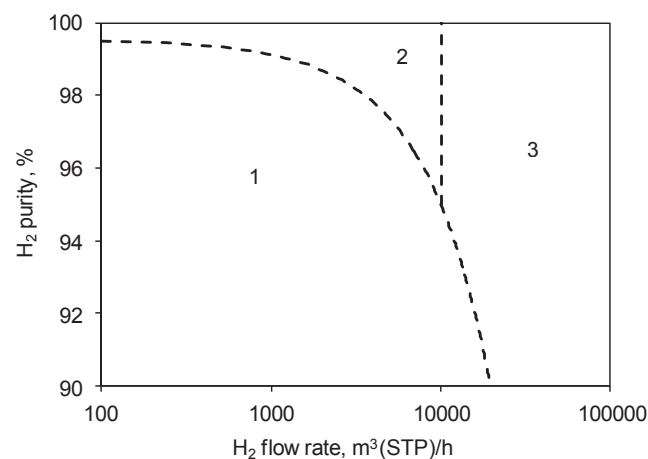

Fig. 1 – **Technological zones of H_2 purification processes: 1 – membranes, 2 – ultra short cycle adsorption, 3 – short cycle adsorption.**

Table 3 − Characteristics of polymers for production of commercially available gas separation membranes.

Polymer	Permeability coefficient, barrer (10^{-10} cm^3(STP)·cm/(cm^2 s cmHg))					Selectivity			Ref.
	CO_2	N_2	CH_4	H_2	CO	H_2/CO_2	H_2/N_2	H_2/CH_4	
Glassy polymers									
Cellulose acetate	10	0.33	0.36	24	−	2.4	72.7	66.7	[6]
Polysulfone	5.6	0.25	0.25	14	−	2.5	56	56	[6]
Polyimide	13	0.6	0.4	50	−	3.9	83.3	125	[6]
Tetrabromopolycarbonate	4.5	0.18	0.12	16[a]	0.16[a]	3.6	88.8	133.3	[74]
Polyvinyltrimethylsilane	190	11	22	200	15[a]	1.1	16.7	9.1	[69]
Rubbery polymers									
Silicon rubber	2700	250	800	550	−	0.20	2.2	0.69	[6]

[a] Estimation of permeability is carried out by method described in Ref. [69].

are produced and supplied by, Air Liquide, UBE, PRAXAIR, UOP and GRASIS. At present time membrane recovery of hydrogen from waste H_2-containing gases is approved and fast developing technology.

The separation of gases can be carried out by two types of membranes: porous and non-porous, which have different mass transfer mechanisms [6,70]. More than 500 patents on H_2-selective membranes were published during 2000−2011. More than 50% of patents are devoted to the synthesis of organic (polymeric) membranes, around 25% of patents are devoted to porous inorganic membranes and around 25% of patents are devoted to non-porous inorganic membranes based on palladium and its alloys. Systematic review of patent literature, investigation groups and recommendations for development of certain membranes (polymeric, ceramic, palladium based) for recovery/purification of H_2 is represented in Refs. [4,71,72]. Published data show that high selective membranes for single stage H_2 recovery from gas mixtures containing CO_2, CO, N_2, CH_4 and other components still not exist. Nevertheless in Ref. [73] it is mentioned that industrial membrane module based on palladium alloy (PdInRu) for H_2 purification is already developed. This module has following characteristics: operating temperature 250−800 °C, feed pressure 20 MPa, initial H_2 concentration 30−98%, H_2 concentration in product stream 99.9999% and higher, product stream pressure 0.1−5 MPa, lifetime more than 2 years. It is important to note that specific productivity of palladium alloys is strongly dependent on high temperature and therefore significant energy consumption is necessary to provide high productivity process.

Gas separation by non-porous polymeric membranes

Polymeric membranes are considered as the most advanced development in gas separation processes. The driving force of gas transfer through polymeric non-porous membrane is the difference of chemical potentials of components. Mass transfer though polymeric membrane is a complex process including sorption and dissolution of a substance on one surface, diffusion through the volume of polymer to the second surface and desorption from it.

Table 3 represents characteristics of polymers used for industrial gas separation membranes production.

One can see that for the most of polymers used in industry H_2/CO_2 selectivity varies from 0.2 to 3.9, at the same time polymers with higher selectivity demonstrate lower permeability coefficient. Therefore it is quite difficult to select membrane for hydrogen recovery from multicomponent gas mixture which also contains CO_2. On the other hand these polymeric membranes can be used for preconcentrating of H_2 and its following recovery by other technique.

Commercially available polymers and membrane modules

More than 2000 new polymers for gas separation were synthesized during the last 30 years. Nevertheless only a few polymers which demonstrate acceptable permeability and selectivity are used for industrial production of membranes and membrane modules. For example: polysulfone, polyimide, cellulose acetate, tetrabromopolycarbonate, silicon rubber. The reason of selection of a certain polymer for membrane production is the importance of other criteria except permeability and selectivity. Industrial application of membrane material is determined by such important parameters as ability of formation of thin and mechanically strong film, durability, chemical stability, price, etc. Effective thickness of selective layer of industrial membranes is often in the range of 0.05−0.2 μm. This layer is formed on a porous non-selective support layer. Membranes can have flat or hollow fiber geometry, packing density of membrane module

Table 4 − Selectivity of commercially available polymeric membranes.

Selectivity	Polymer					
	Polyaramide (Medal)	Cellulose acetate (Separex)	Polysulfone (Permea)	Polyimide (Ube)	Tetrabromopolycarbonate (MG)	Silicon rubber
H_2/CO_2		2.4	2.5	3.8	3.5	0.2
H_2/N_2	>200	72−80	56−80	88−200	90	22
H_2/CO	100	30−66	40−56	50−125	100−123	0.69
H_2/CH_4	>200	60−80	80	100-200	120	0.8

Table 5 — Main developers and producers of membranes and membrane systems.

Producer	Process	Polymer	Type of module[a]
Permea (Air Products)	Gas separation	Polysulfone	HF
Medal (Air Liquide)	Air separation	Polyimide, polyamide	HF
IMS (Praxair)	Air separation, recovery of H_2	Polyimide	HF
GENERON (MG)	Air separation, recovery of H_2	Tetrabromopolycarbonate	HF
Separex (UOP)	CO_2/CH_4 separation	Cellulose acetate	SW
Kvaerner	CO_2/CH_4 separation	Cellulose acetate	SW
Cynara (Natco)	CO_2/hydrocarbons separation	Cellulose acetate	HF
Aquilo	Air separation	Polyphenylenoxide	HF
Parker-Hannifin	Air separation, recovery of H_2	Polyamide, polyphenylenoxide	HF
UBE	Vapor/gas separation, air separation	Polyimide	HF
GKSS licensees	Hydrocarbons recovery	Siloxane-containing copolymers	DT
MTR	C_4H_{10}/N_2 separation, hydrocarbons recovery	Polyalkylsiloxane	SW

[a] HF — hollow fiber membrane module, SW — spiral wound membrane module, DT — disk-type membrane module.

(specific membrane area) being higher in case of hollow fiber membranes. Realization of membrane process at industrial scale usually demands high membrane area therefore membrane modules with hollow fibers are used predominantly (around 75% of cases), membrane modules with flat membranes are used more often in the form of spiral wound (around 15% of cases) than in form of flat-sheets (usually disktype) that is caused as by technical as by economical reasons [6]. Selectivity of some industrial gas separation membranes is presented in Table 4.

It can be seen from Table 4 that H_2/CO_2 selectivity of membranes is quite low. Therefore it is not possible to built one-stage process for hydrogen recovery from multicomponent gas mixtures which contain CO_2. On the other hand polymeric membranes can be very effective for separation of H_2/CO or H_2/N_2 pairs. Main developers and producers of membranes and technological processes are presented in Table 5.

Variety of H_2-containing gas mixtures of biogenic and technogenic origin demands the estimation of membrane properties of polymeric membranes for a set of mixture components. Unfortunately permeability data of many desired components are not available for the most of commercial membranes. Nevertheless it is possible to estimate necessary values using calculation method suggested in Ref. [75]. In present work we used such calculations in order to predict the permeability of membrane for a number of gases. Details of this approach were described earlier in Ref. [69] and recent achievements in Ref. [76].

Calculated values were compared with available and own experimental data and satisfactory agreement was found for all considered membranes. This approach was also validated by comparison of results of calculation with experimental data reported in the literature for great numbers of polymers.

Obtained data (Tables 6 and 7) confirm that recovery of H_2 from multicomponent mixtures containing CO, CO_2, N_2 by membranes is difficult task. Therefore it is necessary to increase polymer selectivity keeping good film-formation properties, high mechanical characteristics and permeability for effective separation of such gas mixtures as H_2/CO_2, He/CO_2 and $He/CO_2/CH_4$. This purpose can be achieved, for example, by fluorination of membrane [77].

On the other side these polymeric membranes can be used for preconcentrating of H_2 and its following recovery by other technique as the above mentioned. Some examples of H_2 separation processes calculation of by membrane modules are shown below.

Calculation of H_2 concentrating from multicomponent mixtures by membrane method

Optimization methods and general approach for membrane module simulation are well known from literature e.g. Refs. [79,80]. These approaches use several models of membrane unit and process, mainly for binary gas mixtures separation. Calculation of multicomponent gas mixture separation was carried out using computer program developed at TIPS RAS

Table 6 — Permeance of commercial and lab-scale gas separation membranes with estimation of values for a set of gases.

Membrane or membrane module	Gas permeance, L(STP)/(m^2 h atm)									
	H_2	He	CO_2	O_2	SO_2	H_2S	N_2	CO	CH_4	C_2H_6
Hollow fiber GENERON® [78]	160[a]	180	45	13.6	10.3[a]	4[a]	1.8	1.6[a]	1.3	0.56[a]
Hollow fiber Air Products® [78]	151	151	104	22.7	47.5[a]	14.3[a]	3.8	6.6	6.3	3.79[a]
Spiral wound Silar®	440	250	2000	400	2570	1195	190	270	545	1644[a]
Flat sheet membrane polyvinyltrimethylsilane [77].	2000	1800	1600	450	1000[a]	350[a]	120	150[a]	220	142[a]
Fluorinated composite polyvinyltrimethylsilane flat sheet membrane [77]	355[a]	342	249	29.6[a]	77.7[a]	23.9[a]	10.6	9.46[a]	6.2	4.81[a]
Matrimid 5218® hollow fiber membrane [77].	214[a]	238.6	70.6	3.76[a]	21.4[a]	2.84[a]	0.258[a]	0.57[a]	1.23	0.21[a]
Fluorinated composite Matrimid 5218® hollow fiber membrane [77].	145[a]	207.9	18.87	0.69[a]	2.99[a]	0.35[a]	0.03[a]	0.07[a]	0.14	0.01[a]

[a] Estimation values.

Table 7 — Selectivity of commercial and lab-scale gas separation membranes with estimation values for a set of gases [6,69,74,75].

| Membrane or membrane module	Ideal selectivity							
	H_2/CO_2	H_2/N_2	H_2/CH_4	H_2/CO	He/CO_2	He/N_2	He/CH_4	He/CO
Hollow fibers GENERON®	3.6	88.9	123	100	4.0	100	139	113
Hollow fibers Air Products®	1.5	39.7	24.0	22.9	1.5	39.7	24.0	22.9
Spiral wound, Silar®	0.2	2.3	0.8	1.6	0.1	1.3	0.5	0.9
Flat sheet membrane polyvinyltrimethylsilane (PVTMS) [77].	1.3	16.7	9.1	13.3	1.1	15.0	8.2	12.0
Fluorinated composite polyvinyltrimethylsilane flat sheet membrane (PVTMS-F2) [77].	1.4	33.5	57.3	37.5	1.4	32.3	55.2	36.2
Matrimid 5218® hollow fibers membrane [77].	3.0	829	174	372	3.4	925	194	414
Fluorinated composite Matrimid 5218® hollow fibers membrane (Matrimid 5218® -F2) [77].	7.7	4830	1035	2070	11.0	6930	1485	2970

[81]. Calculations were carried out for biosyngas separation as an example. Concentrating of hydrogen up to 70% guarantees the following effective application of other separation techniques (e.g., PSA). The program allows calculating of gas separation parameters under following flow condition in membrane module: counter-current, co-current, cross-flow, complete mixing. Based on initial conditions of calculated system such as feed and permeate pressure, flow, membrane surface, and membrane separating properties, the concentration of gases in permeate and retentate were obtained depending on stage-cut ($0 < \theta < 1$) which equals to the ratio of " permeate flux to retentate flux". The corresponding properties of membranes for calculation are given in Tables 6 and 7 The choice of model for comparative calculations was done experimentally by using industrial hollow fiber membrane module GENERON® and laboratory scale disk-type module with PVTMS membranes. $He/H_2/CO_2/N_2$ and $He/CO_2/O_2$ mixtures were used in comparative experiments. The best agreement between calculation and experimental data was found for counter-current flow for the case of hollow fiber module and cross-flow for the case of disk-type membrane module.

In order to show how the polymeric membrane affects the separation characteristics several membranes were chosen for calculations. Results of membrane separation of wet sewage sludge pyrolysis gas (obtained from urban waste water and treatment plants) (36.7% H_2, 13.6% CO_2, 14.7% CH_4, 6.3% N_2, 21.8% CO, 7.1% C_2H_6, 0.8% O_2) and pyrolysis of pine tree (49.7% H_2, 8.7% CO_2, 5.5% CH_4, 34.5% CO, 1.6% C_2H_6) and biosyngas (42% H_2, 24% CO, 30% CO_2, 1% CH_4, 2% N_2, 1% H_2S) are represented in Figs. 2 and 3 and Tables 8 and 9. The following operating conditions were considered: feed flow 0.1—60 m^3(STP)/h, pressure drop 10/1 atm, membrane area 10 m^2. Figs. 2 and 3 demonstrate the concentration of H_2 in permeate and retentate of respective membrane module with variation of stage-cut (abbreviation of membranes can be found in Table 7).

The results show that for the same separation performance, the membranes based on high selective polyimide polymer, especially fluorinated Matrimid 5218®, allow to recover more than 95% of hydrogen at its concentration in permeate more than 90% vol. from both considered gas mixtures by application of single membrane separation stage. All considered membranes allow increasing of hydrogen concentration from 36 to 49 up to 70% vol. that is enough for the

subsequent effective purification by PSA method. It should be noted that membranes based on tetrabromopolycarbonate, polysulfone and polyimide provide recovery degree in the range of 92—97%. Tables 8 and 9 show obtained gas compositions after membrane separation with the mentioned characteristics.

a)

b)
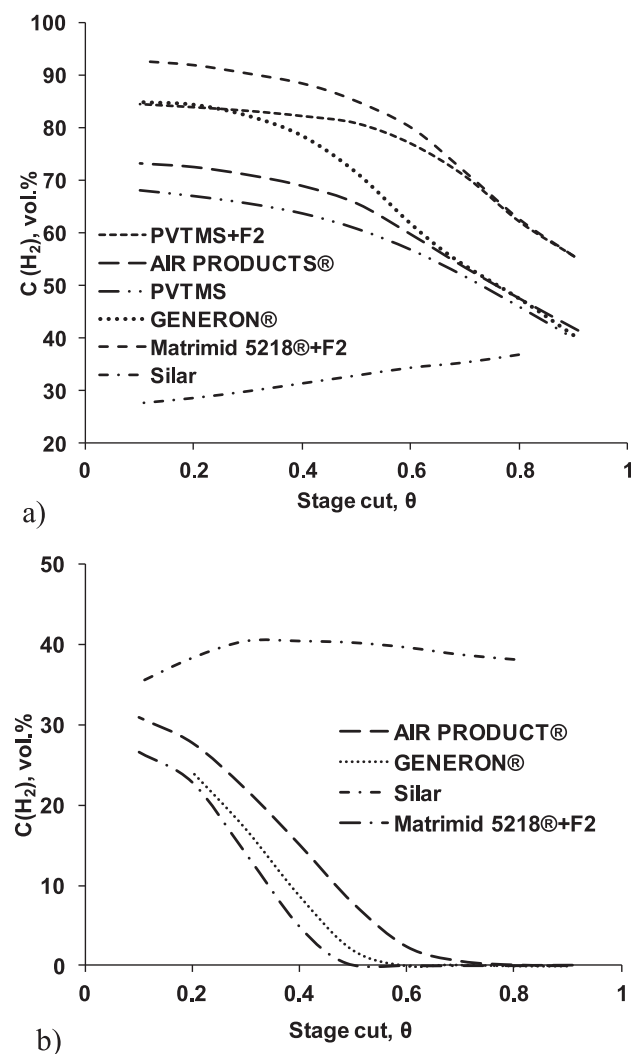
Fig. 2 — The dependence of H_2 concentration in permeate (a) and retentate (b) on stage cut (θ) for wet sewage sludge pyrolysis gas membrane separation.
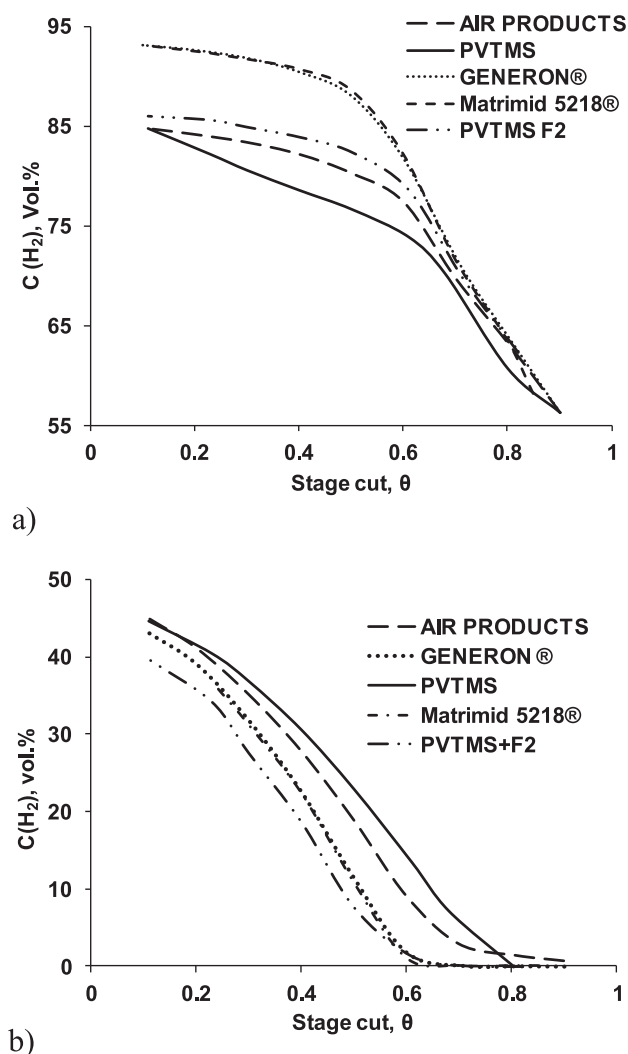
Fig. 3 – The dependence of H_2 concentration in permeate (a) and retantate (b) on stage cut (θ) for pyrolysis gas of pine tree membrane separation.

As it was expected high H_2 purity can be achieved by membrane methods only at low recovery degrees (see Table 10). On the other hand, as it is mentioned above, membrane methods of gas separation can be used for the pre-concentration of hydrogen at high H_2 recovery degrees for its further purification by PSA method. Thereby there are polymeric membranes and modules which can solve the problem of hydrogen pre-concentration of mixtures containing 35–49 vol.% of hydrogen. In any way since characteristics of membrane separation strongly depend on feed mixture composition a certain calculation is required for each specific case. As opposed to the separation of the bulk species, Table 10 also shows that the residual carbon monoxide might be an issue.

Although a decreasing of the H_2S fraction in permeate down to 0.3% vol. is considered feasible, it can be recovered completely at subsequent PSA stage. Also it is not sufficient to recover only the hydrogen from feed gas as permeate, as shown in Tables 8 and 9, CO concentration increases in retentate, so it can be used after preliminary treatment in chemical synthesis such as Fisher-Tropsch process or syngas production.

Nevertheless, presented calculations predict that H_2 concentration can be increased from 35 up to 70% vol. by application of commercially available membranes.

Membrane contactors for hydrogen recovery from gaseous mixtures of bioorigin

As it was mentioned above the problem of H_2/CO_2 separation (purification of biohydrogen) cannot be solved by standard membrane technology due to the low selectivity of membranes for this pair of gases. Nevertheless application of gas–liquid membrane contactors (GLMCs) allows to overcome this problem [82–85]. GLMC is a device where mass exchange between gas and liquid phases takes place via a membrane. Such combination of absorption and membrane separation techniques unites advantages of both methods and provides following features: possibility of application of wide range of industrial CO_2 absorbents (as physical as chemical); high selectivity of CO_2-containing gas mixtures separation; determined and constant geometry of mass exchange area; very wide range of possible velocities of gas and liquid streams; independence of gas and liquid streams from each other; high specific area of mass exchange; independence of gravity force direction (free orientation of module). Main drawback of GLMCs is additional mass transfer resistance due to the presence of a membrane. Application of porous membranes which demonstrate low mass transfer resistance in GLMCs is possible only in some particular cases. These GLMCs require accurate control of trans-membrane pressure drop in order to avoid formation of bubbles in liquid or penetration of liquid into membrane pores that leads to dramatic rising of mass transfer resistance in membrane. Some studies have shown

Component	GENERON®, $\theta = 0.71$		Air product®, $\theta = 0.70$	
	Concentration in permeate, %	Concentration in permeate, %	Concentration in permeate, %	Concentration in retentate, %
H_2	70.0	0.1	70.0	2.9
CO_2	12.8	0.5	11.7	1.0
CO	14.9	80.2	15.6	78.9
CH_4	2.0	13.9	2.3	12.8
C_2H_6	0.3	5.3	0.4	4.4

Table 8 – Calculation of pyrolysis pine tree gas membrane separation (stage cut corresponds to pre-concentration of H_2 up to 70% vol.).

Table 9 — Calculation of pyrolysis pine tree gas membrane separation (stage cut correspond to pre-concentration of H_2 up to 70% vol.).

Component	PVTMS, $\theta = 0.68$		Matrimid 5218®, $\theta = 0.72$	
	Concentration in permeate, %	Concentration in retentate, %	Concentration in permeate, %	Concentration in retentate, %
H_2	70.0	5.8	70.0	0.0
CO_2	11.9	1.8	12.1	0.0
CO	14.3	78.0	13.4	85.0
CH_4	3.2	10.7	3.9	10.3
C_2H_6	0.6	3.7	0.6	4.7

that liquid penetrates into membrane pores during the time even if proper trans-membrane pressure is maintained. Therefore application of non-porous membranes seems to be much more prospective.

Non-porous membranes demonstrate much higher mass transfer resistance compared to porous membranes. Nevertheless starting from a certain level of membrane permeance the dominant contribution of mass transfer resistance becomes related to liquid phase. Therefore in practical cases permeance of non-porous membranes could be enough high for its application. Wide investigation and application of GLMCs based on non-porous membranes is limited at present time due to the absence of commercially available high permeable non-porous membranes which additionally demonstrate stability in contact with CO_2 absorbents.

The application of MCs with non-porous membranes based on poly(vinyltrimethylsilane) (produced by Kuskovo Chemical Factory, Russia) and aqueous potassium carbonate as CO_2 absorbent was demonstrated in pilot-scale biogas separation process [86] and lab-scale biohydrogen separation [85]. Mathematical model of mass transfer in GLMC with chemical absorbent of CO_2 was developed in Ref. [86], obtained result of theoretical calculations were in good agreement with experimental data.

Purification of biohydrogen by separation system (Fig. 4) based on GLMCs with non-porous membranes and chemical CO_2 absorbent in liquid phase (aqueous potassium carbonate) was studied theoretically using the model developed in Ref. [86].

Separation characteristics of the system were investigated by variation of such operating parameters as H_2 concentration in feed (60—80 vol.%), relative velocity of feed stream, relative velocity of liquid absorbent, permeance of membrane (0.34—3.6 $m^3(STP)/(m^2 \cdot h \cdot atm)$). Results of theoretical study of H_2/CO_2 gas mixture separation show the possibility of effective hydrogen purification, such system provides high separation factors and low losses of hydrogen.
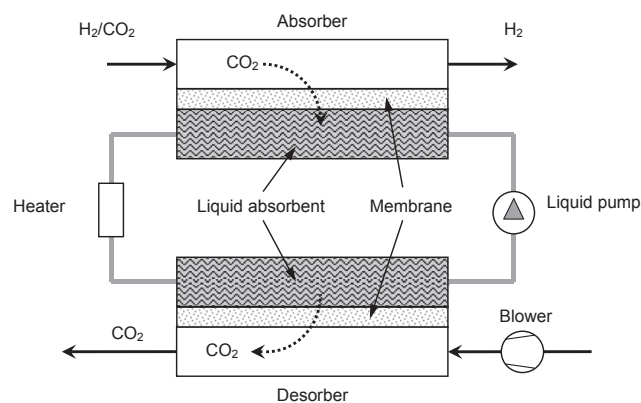
Obtained dependencies of hydrogen concentration in product stream on velocity of liquid absorbent are non-linear and have extremums (Fig. 5). Such behavior provides easy optimization of separation process for particular composition of feed mixture. Possibility of the system characteristics adjustment is especially important for the application in biohydrogen purification since bioreactor productivity and composition of feed may vary during the time.

The influence of membrane permeance is shown in Fig. 6. Concentration of H_2 in product stream increases strongly when membrane permeance rises from 0.34 up to approximately 1.5 $m^3(STP)/(m^2 \cdot h \cdot atm)$, after this value weak increase of H_2 concentration is observed. It means that mass transfer resistance in membrane is dominant in the initial region and becomes comparable to resistance in liquid phase in the second region. These results allow to establish the value of 1.5 $m^3(STP)/(m^2 \cdot h \cdot atm)$ as sufficient level of membrane permeance for realization of biohydrogen purification process.

Industrial non-porous membranes based on polyvinyltrimethylsilane which demonstrate H_2 and CO_2 permeance around 2.7 $m^3(STP)/(m^2 \cdot h \cdot atm)$ were used for assembling of laboratory scale GLMCs. Mass transfer characteristics of the modules were experimentally investigated and found to be in good agreement with results of modeling.

Table 10 — Calculation of gas separation by membrane at maximum pre-concentration of H_2 (one stage), (pressure drop 10/0.1 atm, feed flow 10 $m^3(STP)/h$).

| Component	GENERON®, $\theta = 0.08$, wet sewage sludge pyrolysis gas		PVTMS, $\theta = 0.07$, biosyngas	
	Concentration in permeate, %	Concentration in retentate, %	Concentration in permeate, %	Concentration in retentate, %
H_2	90.0	42.0	84.0	35.3
CO_2	8.1	12.1	12.7	14.9
CH_4	0.01	1.2	0.3	1.1
N_2	0.1	3.6	0.1	5.5
H_2S	—	—	0.08	1.1
CO	0.7	22.2	1.5	42.1
H_2C_6	0.1	12	—	—
O_2	1	0.5	—	—

Fig. 4 – **Biohydrogen separation by gas–liquid membrane contactor system.**

Combined membrane systems for hydrogen recovery from gaseous mixtures of technogenic and bio origin

Combined membrane systems for hydrogen recovery from gaseous mixtures is known enough long time ago [87], but for variety of hydrogen-containing mixtures it continues to up-growth. So, in Refs. [67,68] the combined unit including membrane and PSA blocks for separation of multicomponent gaseous mixture separation is described. This unit consisted of membrane modules (hollow fiber type and disk-type) and lab-scale PSA block (volume of adsorbent about 1 dm^3) is assigned for study of membrane and PSA combination for separation aims. Simple scheme of this unit with example of combination for biosyngas separation is presented in Fig. 7.

Scheme in Fig. 7 was experimentally tested by using model mixture $He/CO_2/O_2$ – 42,5%/32%/25,5% where He was used instead of H_2 (for safety reason) and O_2 instead of CO. CO_2 and O_2 were measured with on-line concentration registration:
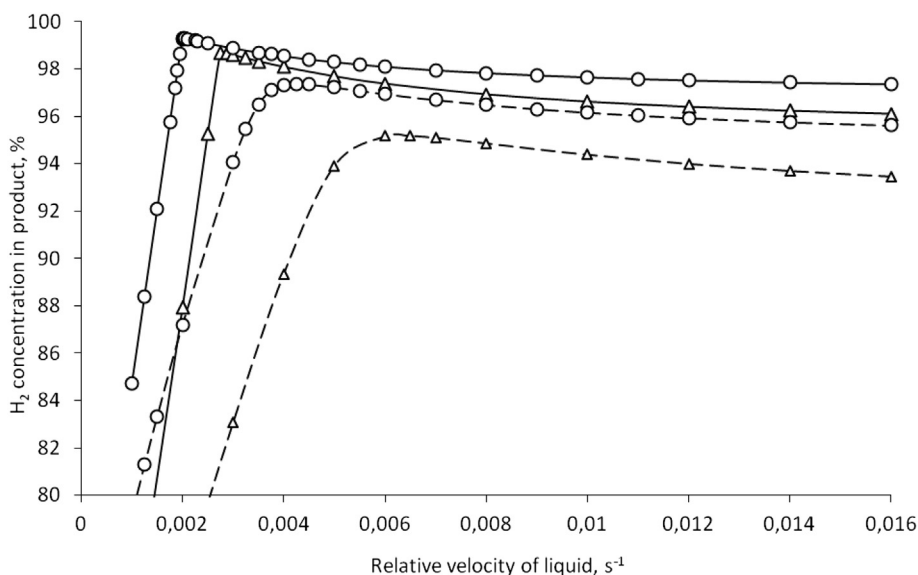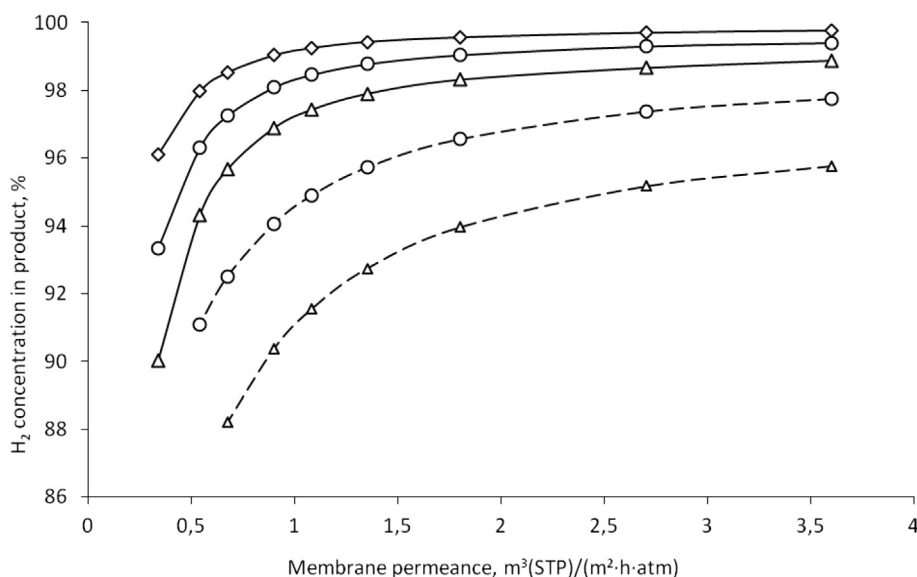
Riken Infrared Gas analyzer-R1-550A (for CO_2) and PKG-4K-MK-C-2A (for O_2); He is a balance. Product gas productivity was 45.6 l/h. Gas pressure in membrane block was varied in the range of 4–10 bar; in PSA block it was varied in the range 4–7 bars. Obtained experimental data are presented in Table 11.

As it can be seen from Table 11, the combined system provides high quality products in comparison with separate single processes (PSA or membrane). Considered scheme is not optimal, but better one as compared with PSA only. In whole it was estimated that hydrogen recovery degree may achieve up to 80–97% for biosyngas in the case of hydrogen pre-concentration level up to 70% at the membrane stage. As a result, the hydrogen of 99.9% purity can be obtained after PSA stage. So, obtained results demonstrate that the investigation of effective recovery of H_2 needs to be focused on improving of membrane selectivity and optimization of PSA step. It is known that at present time the industrial PSA contains 4–16 adsorbed columns with 2–4 layers of different adsorbents. Proposed scheme can help to simplify these processes by introducing membrane block for preliminary concentrating of desired product and decreasing of undesirable impurities to provide the durability of process itself and additionally under lower pressure (<10 bar). It should be noted that successful results demonstrated by using commercial membranes are not limit properties and can be improved by development of high selective membranes and more efficient adsorbents.

Conclusion

Authors made an attempt to outline main problems connected with H_2 recovery (as energy carrier and environmentally friendly reagent) from different sources of biogenic and technogenic origin. Particularity of biogenic routes and main exhaust technogenic mixtures which can be considered for hydrogen recovery are discussed. It should noted, that the

Fig. 5 – **Concentration of H_2 in product stream at membrane permeance 2.7 m^3(STP)/(m$^2\cdot$h$\cdot$atm) depending on velocity of liquid, initial concentration of H_2 in feed ($\bigcirc$ – 70%, $\triangle$ – 60%) and relative velocity of feed stream (–– 0.1 s^{-1}, - - - 0.15 s^{-1}).**

Fig. 6 — Concentration of H_2 in product stream at optimal velocity of liquid depending on membrane permeance, initial concentration of H_2 in feed ($\lozenge$ − 80%, $\bigcirc$ − 70%, $\triangle$ − 60%) and relative velocity of feed stream (−− 0.1 s^{-1}, - - - 0.15 s^{-1}).
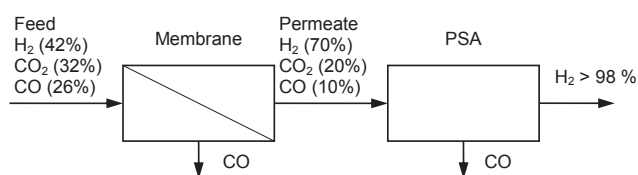
Fig. 7 — Scheme of combined membrane/PSA method for H_2 recovery (calculated data): feed is model biosyngas mixture; concentrating of H_2 as a permeate up to 70%; PSA provide H_2 (98%) as a product.

solution of formulated tasks demands multidisciplinary interaction of specialists in the field of biomass treatment, chemistry and petroleum refining, membrane technology and engineering, and energy producers as well. Membrane gas separation processes as lower energy consuming ones for H_2 recovery from gaseous sources which are as rule multicomponent gas mixtures were considered in this paper. Paper

demonstrated results of published knowledge in this area and own theoretical and experimental data on estimation of commercially and lab-scale polymeric membranes for separation of H_2 from mixtures with CO_2, CO, N_2, CH_4, H_2S, calculation of standard membrane processes. Hydrogen recovery from H_2/CO_2 mixtures can be effectively realized by application of gas–liquid membrane contactors with non-porous membranes. Combination of membrane (H_2 preconcentrating) and PSA (H_2 conditioning) systems that hydrogen recovery degree may achieve up to 80–97% for biosyngas and in the case of hydrogen pre-concentration level up to 70% at the membrane stage. As a result, the hydrogen of 99.9% purity can be obtained at the PSA stage. The obtained data correspond to well known membranes and adsorbents and can be considerably improved by using of new membrane materials and adsorbents.

Acknowledgments

Table 11 — Separation of gas mixture by different methods.

Stream	Composition of gas mixture, % vol.		
	O_2	CO_2	He
Feed	25.5	32.0	42.5
Product gas after	10	29	61
membrane module GENERON®	10	21	69
Product gas after PSA module, without membrane module	11.0	0.07	89.0
Product gas after combined system membrane module/ PSA	1.8	~0	98.2

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