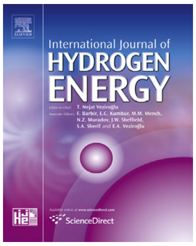
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 40 (2015) 3438–3451

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



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

M.G. Shalygin [a], S.M. Abramov [b], A.I. Netrusov [b], V.V. Teplyakov [a],*

[a] A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (TIPS RAS), Moscow, Russia
[b] M.V. Lomonosov Moscow State University (MSU), Biological Faculty, Moscow, Russia

ARTICLE INFO

Article history:
Received 4 August 2014
Received in revised form
27 November 2014
Accepted 19 December 2014
Available online 2 February 2015

Keywords:
Hydrogen recovery
Membranes
Membrane contactors
Pressure-swing adsorption

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

---

* *Corresponding author*. Tel.: +7 4952585304; fax: +7 4956338520.
E-mail address: tepl@ips.ac.ru (V.V. Teplyakov).

http://dx.doi.org/10.1016/j.ijhydene.2014.12.078

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].