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HYDROGEN PRODUCTION FROM COALMINE METHANE

Introduction. At present, the volume of hydrogen production in the world is estimated at 75 million tons/year. A 30% increase is expected in the next five years [1]. More effective oil refining, together with the advance in output of ammonia, methanol and synthetic liquid fuels have caused a steady increase in hydrogen consumption. Along with the conventional areas of demand, active hydrogen consumption is predicted in the energy sector, where hydrogen, due to its high energy saturation and environmental cleanliness, is considered as the most promising energy carrier (Fig. 1).

Bloomberg New Energy Finance offers three scenarios for achieving zero emissions by 2050. They differ as to the contribution of the primary energy resources (fossil fuels, renewable energy, nuclear energy) to the energy supply mix (Fig. 2). The "green" and "red" scenarios put forward RES and nuclear energy, respectively, as priority sources of clean electricity, while the share of fossil fuel is to be reduced to 7−10% from the current 85%. According to the "green" scenario, in 2050 the demand for hydrogen will approximately reach 1318 million tons per year, and its contribution to the structure of electricity consumption will increase from 0.002% to 22%. According to the "gray" scenario, where coal and gas
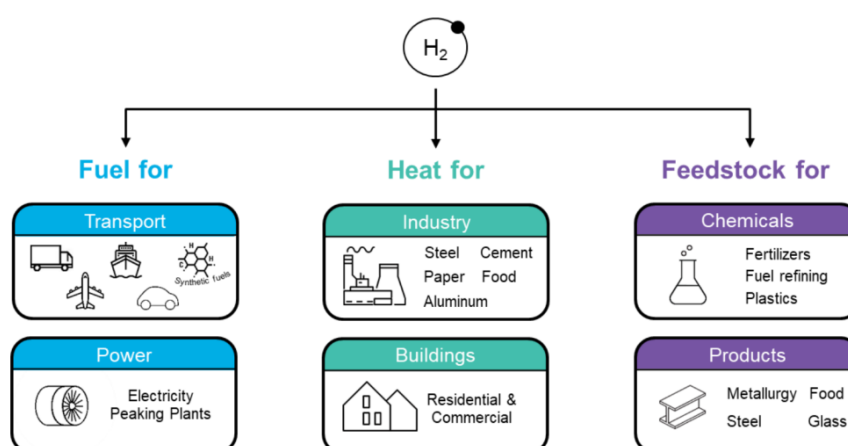

Fig. 1. Major areas of hydrogen application in hydrogen-oriented economy [2]
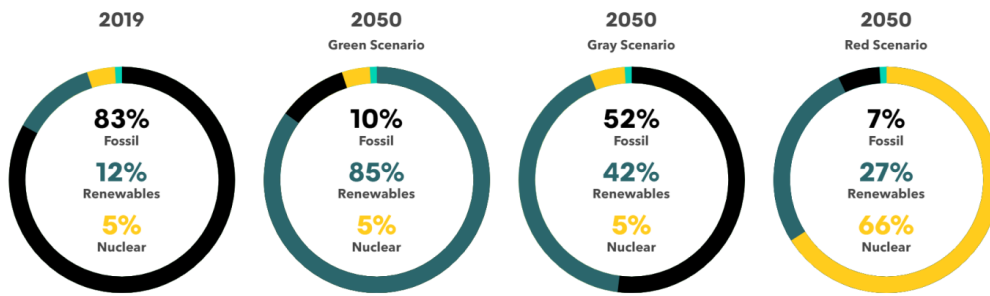
Fig. 2. Present and future contribution of the major energy resources to the energy supply structure,
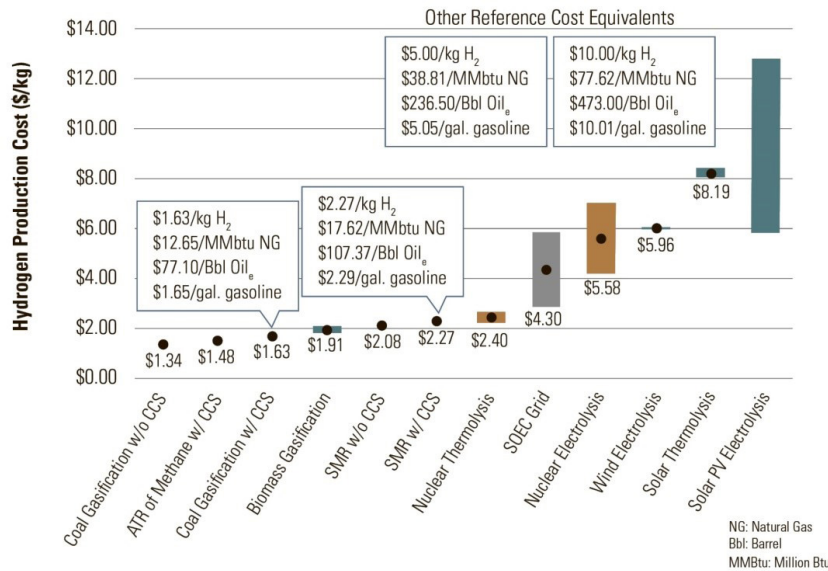depending on the energy development scenario [3]

Fig. 3. The cost of hydrogen depending on its production technology [7]

will still be used to generate electricity, and where CO_2 capture and storage technologies will be implemented, the demand for hydrogen will approximately reach 190 million tons a year in 2050.

On the one hand, coal is seen as the dirtiest fuel with a high carbon footprint. Into the bargain, the contribution of CBM emissions to greenhouse gases and global warming is quite significant. On the other hand, with the increasing role of hydrogen as an energy carrier, the coal industry has a very high potential for its production from both coal and methane.

At present, the cost of renewable hydrogen is significantly higher than the cost of hydrogen obtained using traditional technologies (Fig. 3). The cost of hydrogen produced specifically from coal is minimal even with the combined use of carbon capture and storage (CCS) technology. In Australia, the Latrobe Valley Project (also called the Hydrogen Energy Supply Chain Project) is being developed. It represents a pilot plant for the gasification of lignite to produce hydrogen [4]. The plan is to integrate H_2 production into CO_2 utilisation technologies, with its subsequent delivery to consumers in liquefied form (Fig. 4). In China, coal already plays a key role in the production of hydrogen (62% against the global contribution of 18%), and this trend continues to intensify [5]. The world's largest plant for the production of hydrogen from coal is located in Inner Mongolia (China) and includes two reactors for coal gasification, processing 2250 tons of coal per day [6].
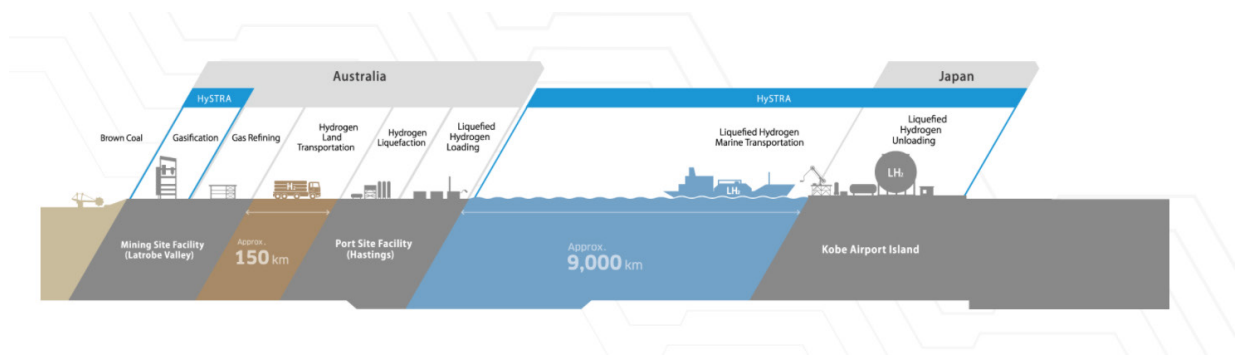
Fig. 4. Hydrogen energy supply chain pilot project between Australia and Japan: hydrogen production from brown coal [8]
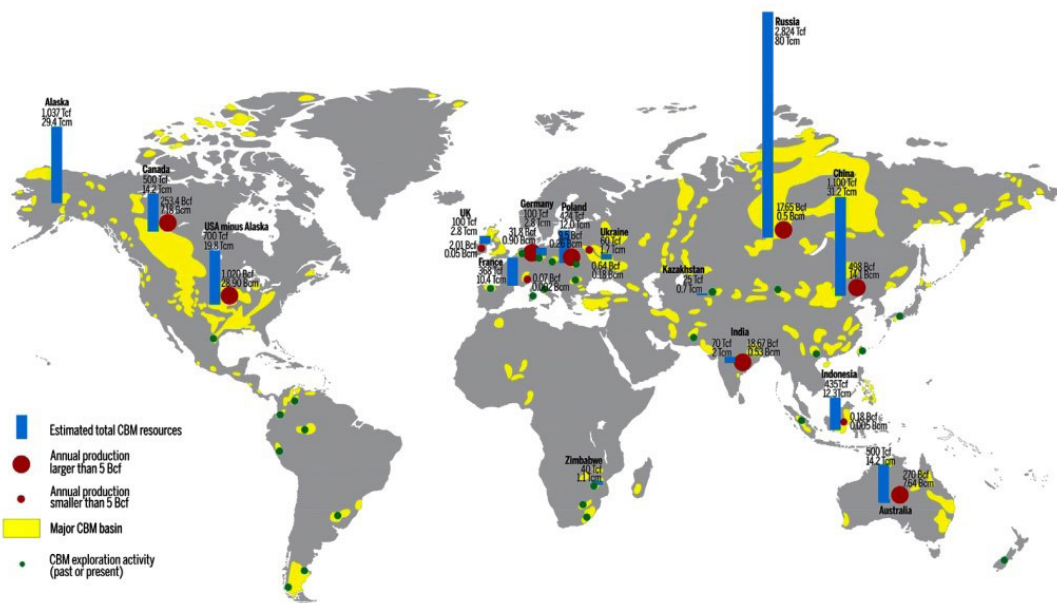

Fig. 5. Coal-bed methane and its production in the world [10]

This review looks at the scientific basis and promising technologies for hydrogen production from coal-bed methane and coal production.

Coal-bed Methane Resources

Coal beds contain significant hydrocarbon wealth, consisting mainly of methane (80−98%) and small amounts of carbon dioxide, nitrogen, ethane, propane, and butane. In November 2011, coal-bed methane (CBM) was recognised as an independent mineral and included in the All-Russian Classifier of Minerals and Subsoil Waters (code 111021111, additionally included by amendment No.1/2011) [9].

The world coal-bed methane supplies are estimated at 113−201 trillion m³, of which 30 to 42 trillion m³ are considered to have good extraction potential [10]. The largest volumes of CBM are found in Russia, China, USA, Canada, Australia, Indonesia, Poland, Germany and France (Fig. 5).

In Russia, CBM reserves reach approximately 80 trillion m³ [11]. More than half of those resources are concentrated in the West Siberian (40%) and Tunguska (24%) coal basins, followed by Kuznetsk (16%), Leninsky (12%), Taimyr (5%) and Pechora (2%) basins (Fig. 6). Among the deposits potentially fit for industrial development, there are Kuznetsk and Pechora basins, since they are well-explored, and they have optimal coal-bed depth and sufficient gas content [12].
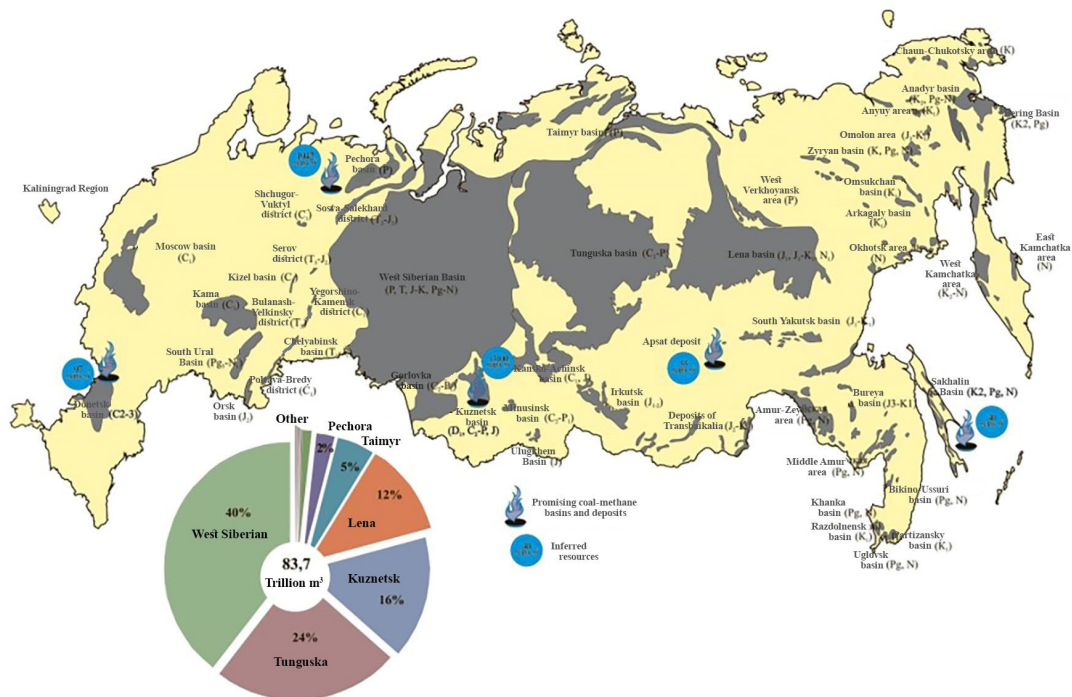
Fig. 6. Resources of coal-bed methane in Russia [12]

Coal industry methane: characterisation and classification

Coal-bed gas properties, in particular its origin, composition and quantity, are determined by the coal rank and vary greatly. The content of methane per ton of coal may vary from low (4–6 m³/ton) to high (15–20 m³/ton) (Fig. 7).

International and Russian classifiers offer several terminology sets to designate coal industry methane depending on the process flow stage. Currently, the most established are the four main terms describing the various stages of the coal mining process and referring to the differing methane content, and, accordingly, to the ratio of methane and air concentrations:

(1) VAM – Ventilation Air Methane. Methane contained in mine ventilation gas (ventilation methane). Methane concentration is less than 1%;

(2) CMM – Coal Mine Methane. Coal mine methane recovered by associated degassing (mine/degassing methane). Methane concentration is 25–60%;

(3) AMM – Abandoned Mine Methane. Methane from closed coal mines. When recovered by degassing, methane concentration can reach 60 to 80%;

(4) CBM – Coal Bed Methane. Methane from unrelieved coal beds extracted during preliminary drainage through the wells drilled from the surface. Methane concentration exceeds 80%.

Coal Industry Methane Situation in Russia

In Russia, coal-bed methane is extracted mainly as by-product, in the existing mine fields, by mine degassing systems. The only exception is the joint innovation project of the Administration of the Kemerovo Region and Gazprom PJSC for the extraction of coal-bed methane in Kuzbass, where methane is recovered as an independent mineral [14]. Coal bed methane (CBM) is used in gas-fired power plants that provide electricity to manufacturing facilities [15].

Projects for capturing gas from the degassing systems of existing mines (methane type is CMM, coal mine methane), its recovery and use are implemented only by a few coal industry companies. In particular, in 2020, SUEK reclaimed 4.8 million m³ (equivalent to 67,651 tons of CO_2) of methane, which
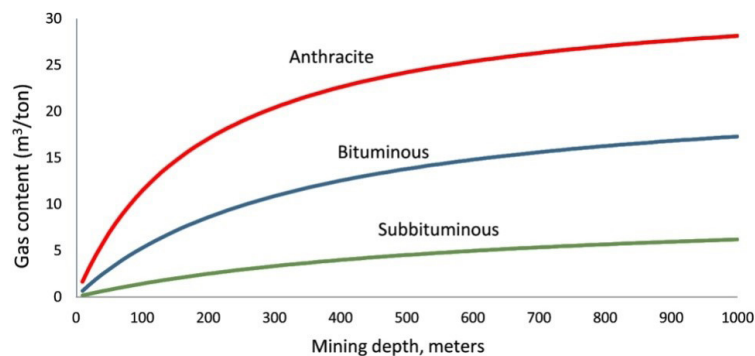
Fig. 7. Ratio between coal gas content, its grade and mining depth [13]

amounted to no more than 2% of total methane emissions. Higher rates were achieved at the enterprises of OA Vorkutaugol, where, according to data for 2018, 77.5 million m^3 of methane was processed, which was equal to 73% of the total volume of degassed methane [16]. Sibuglemet has outlined an environmental development strategy that includes a program for coal mine methane utilisation [17]. In Russia, methane recovered from the degassing systems of operating mines (CMM), as well as the CBM considered above, is mainly used for the generation of electrical and thermal energy.

Standing out is the issue of gas emission in the decommissioned mines and their adjacent areas. Their methane (AMM) concentrations may become hazardous for the population. For instance, in Primorye Territory [18], certain long-decommissioned mines have not been flooded properly, so the situation with methane seepages to the surface still remains unstable. Passive degassing through degassing wells has been found insufficient; forced degassing of the worked-out space of mines is required. At the same time, the concentration of methane in the mine fields can reach ~35%, and in degassing well emissions, up to 75% [18].

Regulatory documents [19] prohibit the use of degassing products with methane content below 25% in flare plants, 30% as fuel for boiler plants, 25% in gas engine plants and with methane content below 50%, for domestic needs.

Economically Sensible Utilisation of Methane into Hydrogen to Solve the Issue of Mine Safety and Greenhouse Gas Utilisation

The coal industry is a source of methane emissions, which has negative impact on the environment and is detrimental for mining safety.

Methane is an explosive gas. Especially hazardous is its air content within the range from 5 to 15%. Methane should be transported, collected or used in quantities within the range of at least 2.5 times of its lower explosive limit (2.0%) and at least 2 times of its upper explosive limit (30%) [20]. To date, the frequency and severity of methane explosions during coal mining, despite the measures taken, remains unacceptably high.

Methane is an intense greenhouse gas. The radiation efficiency of methane, which depends on the spectral characteristics of the molecule, is $1.37 \cdot 10^{-5}$ W·m^{-2}·ppb^{-1}, and its atmospheric lifetime can reach 12 ± 3 years. The global warming potential (GWP) of CH_4 is 84 times the GWP of CO_2 over a 20-year time horizon and 28 times over a 100-year time horizon. The average global concentration of methane in the surface layer of the atmosphere is growing: in 1750 it was 722 ± 25 ppb, in 2011 it was 1803 ± 2 ppb, and in 2021 it reached 1890 ± 2 ppb (Fig. 8).

In the gross structure of global greenhouse gas emissions, methane ranks second after CO_2 (Fig. 9). Its annual volume released is equal to about 8046 Mt of CO_2 equivalent in total, with the coal industry contributing 967 Mt of CO_2 equivalent (12%) or 34.5 Mt of CH_4. As noted above, CH_4 enters the atmos-
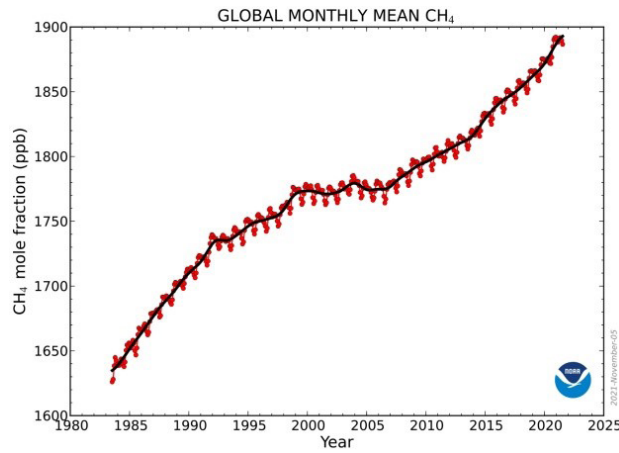
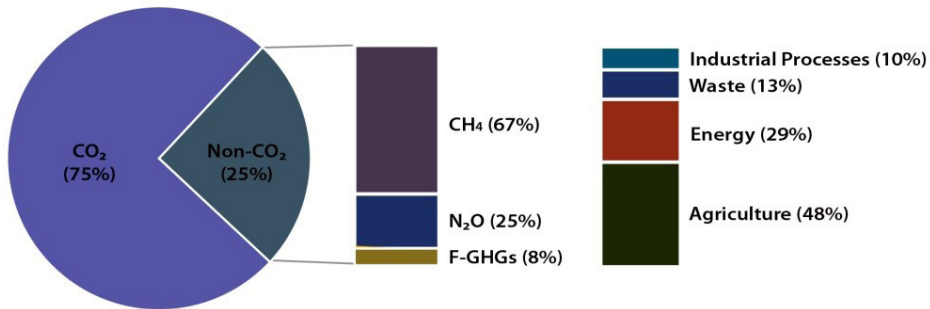Fig. 8. Dynamics of methane atmospheric concentration [21]

Fig. 9. Composition and volumes of greenhouse gas emissions [22]
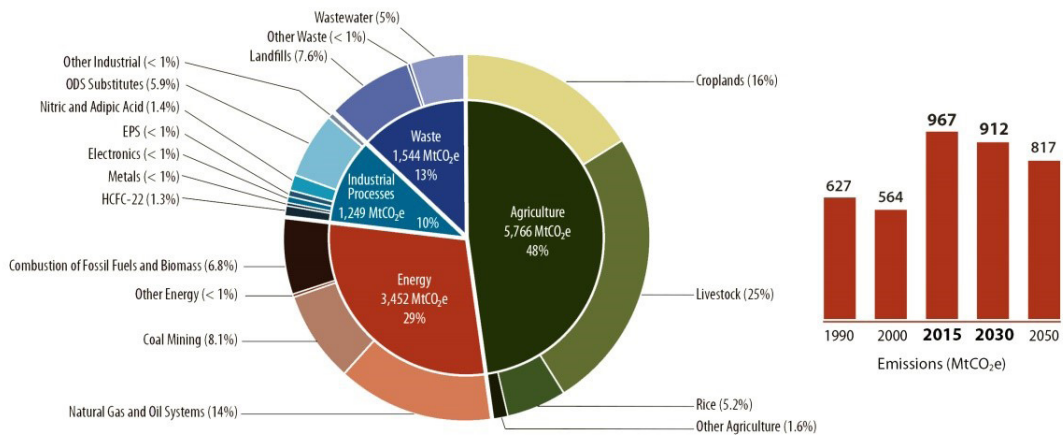
Fig. 10. Sources of emissions of greenhouse gases other than CO_2 (a)
and the volume of methane emissions in the coal industry by years (b) [22]

phere from coal beds as a result of natural erosion, ground fissures or coal mining. It is believed [22] that 98% of the coal industry methane emissions occur during the underground mining. The contribution of the coal industry to the emissions of greenhouse gases other than CO_2 is 8.1% (Fig. 10).

According to the International Energy Agency (IEA) figures over the year 2020, China ranks first in terms of methane emissions from coal industry facilities with 22.31 Mt [23]. Emissions in the Russian Federation are lower and reach only 5.7 Mt; still, they exceed coal industry methane emissions of the EU (2.74 Mt), USA (2.10 Mt), India (1.27 Mt), Indonesia (1.18 Mt) and Australia (1.13 Mt). Given the present-day rates of coal production, a further increase in the release of methane into the atmosphere can be predicted.

The target indicators of the environmental safety of the coal industry (CI) are set up in policy papers of the Russian Federation. According to [18], the emission factor of CI pollutants into the atmosphere in 2019 amounted to 2.5 kg per ton of production; of those, less than 5% of harmful substances were captured and neutralised.

Global Experience of Coal Industry Methane Involvement in the Fuel and Energy Sector and Chemical Industry

According to the Global Methane Initiative (GMI) database, there are more than 300 coal mine / dump methane (CMM) utilisation projects [24]. These projects have different statuses (starting, operating, completed) and are being implemented in 15 countries of the world, of which China, the USA and Germany are the leaders. As of 2021, there were 260 active projects, of which 152 projects were related to CMM utilisation, 4 projects were related to VAM (coal mine ventilation air methane) and 104 projects were related to AMM (abandoned mine methane) (Fig. 11).

Mainly, these are projects for CMM and AMM use for heat and power generation (Fig. 11). Low-concentration methane-air mixtures (VAM) are also used to generate electricity or, more often, are simply burned with the release of carbon dioxide into the atmosphere [20, 25−27]. For example, during coal mining in China, Shanxi Province, a number of projects (TUNLAN, MALAN, DUERPING) are being implemented to minimise coal mine methane (CMM, VAM) emissions and its optimal utilisation [28].

The principles of a multifaceted approach to efficient methane capture and recycle into energy through combustion are illustrated in Fig. 12. We should emphasise that in this case, another greenhouse gas, CO_2, will enter the atmosphere instead of CH_4.

At the laboratory level, a number of VAM utilisation technologies are being developed (Fig. 13), in particular, low-temperature and more environmentally friendly catalytic combustion processes [30−32].

Production of Hydrogen from Coal-Bed Methane

A distinctive feature of CBM is its significant flow rate fluctuations and composition heterogeneity. Methane content depends on the type of gas (VAM, CMM, AMM, CBM) and varies over a very wide
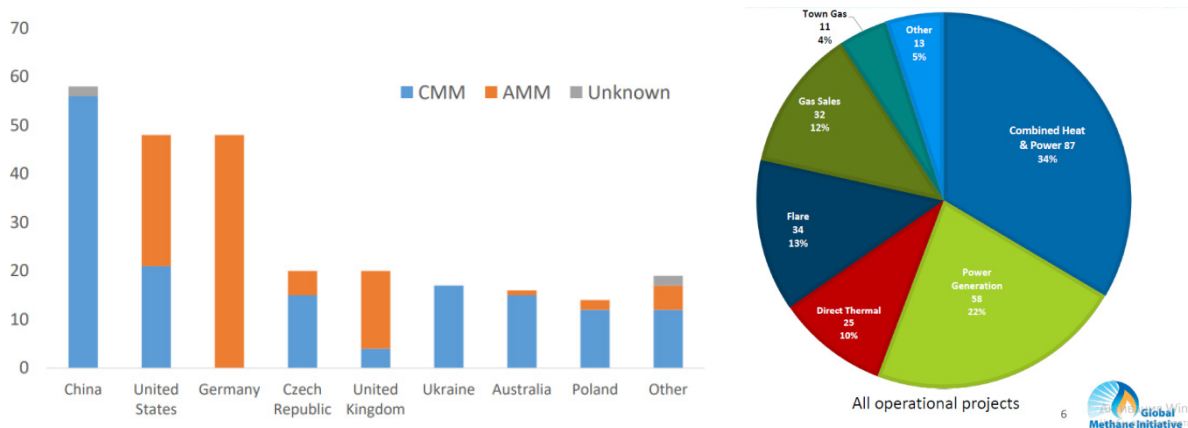

Fig. 11. The number coal industry methane utilisation projects for several countries and the types of projects for coalmine methane / CMM degassing methane usage [24]
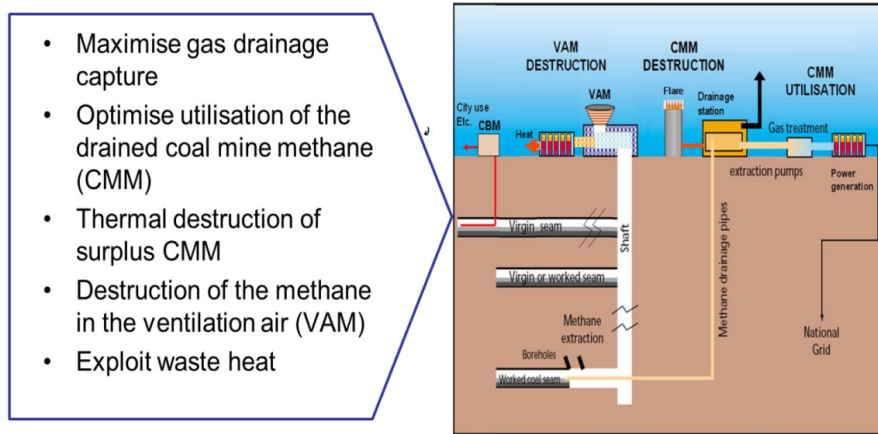
Fig. 12. Illustration of coal mining processes with practically zero methane emissions [29]
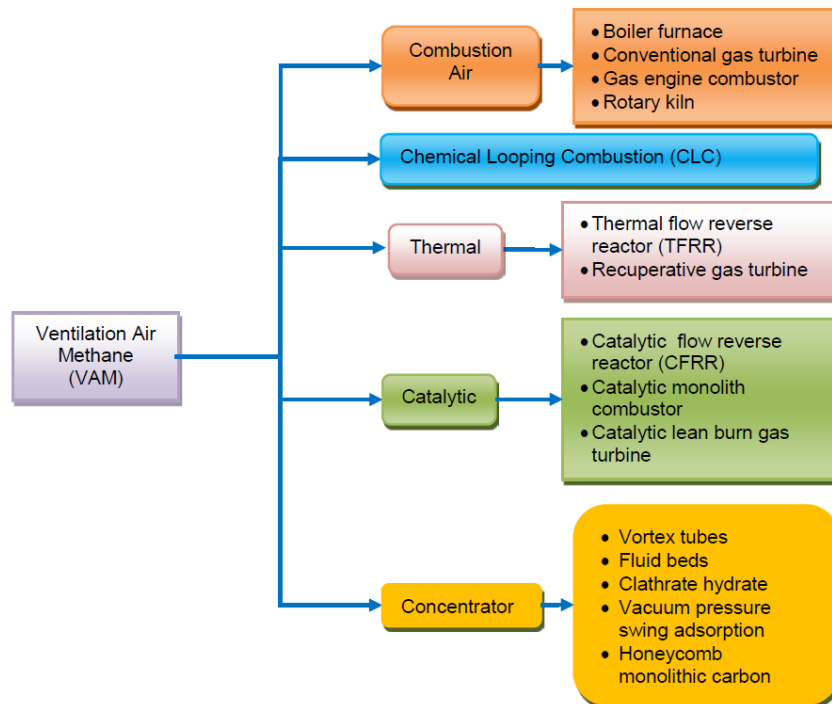

Fig. 13. VAM utilisation methods [31]

range, which imposes certain restrictions on the use of traditional technologies employed in natural gas processing. Thus, there are two main options. The first is conditioning (purification, concentration) of the gas until it becomes suitable for further chemical processing by traditional methods to produce hydrogen. The second option is the processing of the existing methane-air mixture.

The first option can be implemented for gases with high methane concentration (i.e. CBM, AMM). In this case, with rational methods of deoxygenation, separation and concentration, 100% gaseous methane is obtained, which can be pumped into an existing natural gas pipeline or chemically processed by convertion into useful products, primarily hydrogen, or into synthesis gas, carbon nanomaterials, C_1-oxygenates, C_2 and aromatic hydrocarbons (Fig. 14) [33–42].
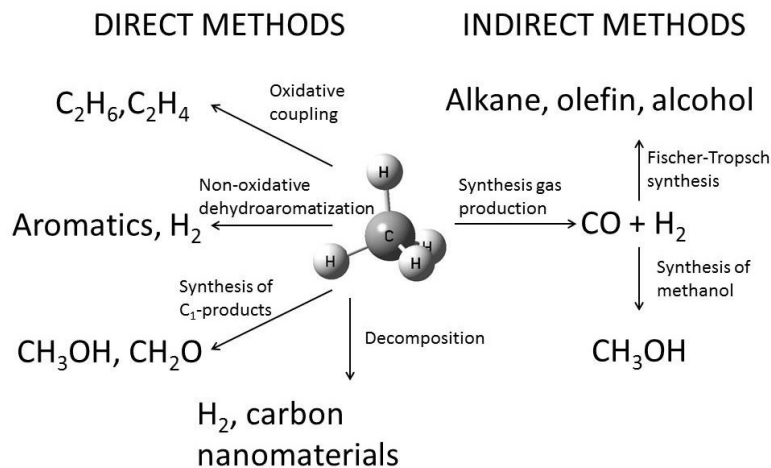
DIRECT METHODS INDIRECT METHODS

Fig. 14. Methods of direct and indirect conversion of methane into useful products [43]

The second option is for obtaining hydrogen from less methane-concentrated gases (SMM, AMM) and it will require development and mastering of technologies for processing gas of variable composition, including methane (30−80%), air, water vapour, and carbon dioxide. This option is attractive because, in essence, there is a reaction mixture containing methane and oxygen, and the most promising methods in this case are the methods of partial and combined catalytic reforming of methane into a hydrogen-containing gas. An extremely important issue of today is the development of catalytic processes that will provide high and stable conversion of a methane and air mixture of variable composition [33−42, 44−53, 54−62].

To obtain hydrogen from highly concentrated coal bed gases (CBM, AMM), it is advisable to improve the gas quality by removing impurities (e.g. nitrogen, oxygen, water vapour, carbon oxides), which will make it possible to process them by standard gas chemistry methods. The most technically challenging stage, namely separation of methane from nitrogen, is possible with molecular sieves, pressure swing adsorption (PSA), solvent absorption, cryogenic or membrane technologies [63]. Following the removal of nitrogen, the most technically complex and expensive procedure is the removal of oxygen, deoxygenation. Commercial technologies are available for extraction of carbon dioxide from coal-bed gas, including amine scrubbing, membrane technology, and selective adsorption. Dehydration of coal gas is mainly performed on molecular sieves.

For purification and concentration of the ventilation air methane (VAM), special adsorbents are being developed that are distinguished by high capacity and methane selectivity, as well as by their resistance to water vapour (Fig. 15) [64, 65].

Worth mentioning is the method of non-catalytic CMM deoxygenation by passing gas through heated dead rock, which allows simultaneous use of two types of coal mine by-products [66]. At higher temperatures, oxygen will interact with carbon contained in the dump waste and the intermediate product which primarily consists of oxides of silicon (23.8 wt. %), aluminum (17.7 wt. %), iron (0.8 wt. %) and titanium (1.0 wt. %). Both temperature and gas flow rate have been shown to affect deoxygenation efficiency. Complete removal of oxygen from the CMM simulating mixture ($CH_4 = 43\%$, $O_2 = 12\%$, $N_2 = 45\%$) was achieved at a temperature of 650°C and a rate of 15 l/h. In this case, the loss of methane due to its decomposition amounted to maximum 0.2% [66].

Methane Decomposition

The production of hydrogen by decomposition of methane is an effective way to avoid releasing carbon dioxide into the atmosphere [44−56]. A huge amount of research has been devoted to this meth-
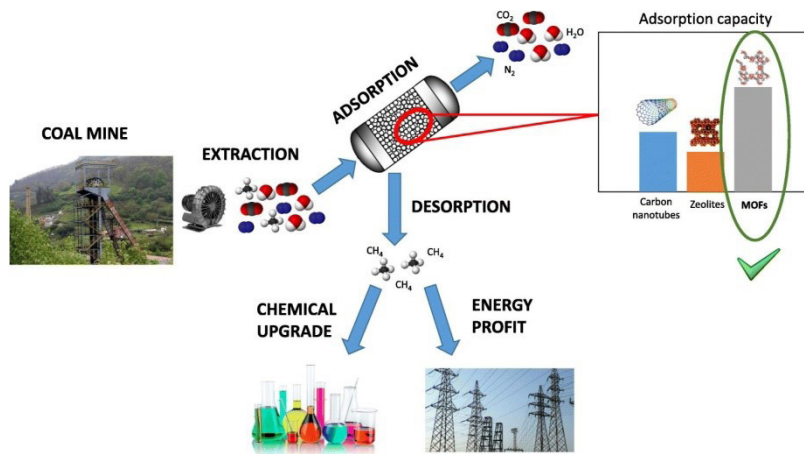
Fig. 15. VAM processing, concentration of methane from diluted mine ventilation system streams [64]
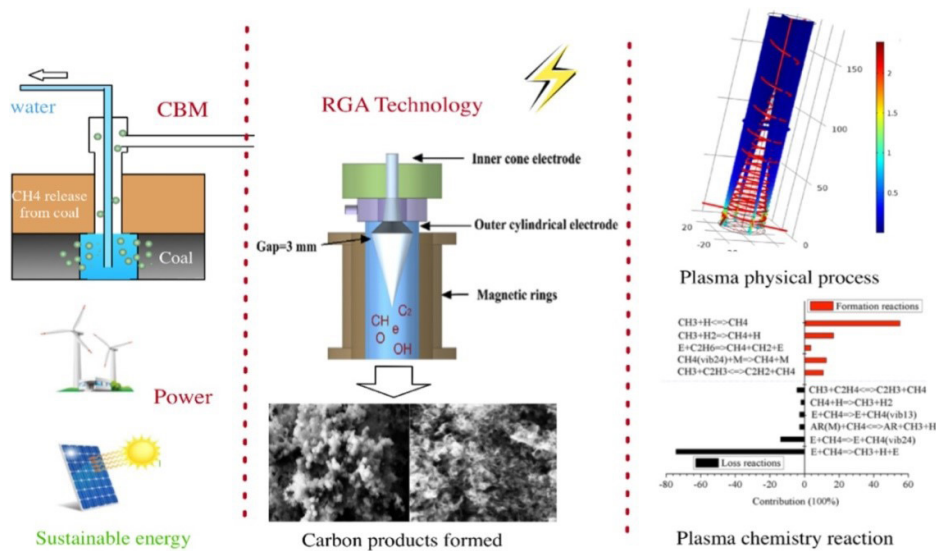

Fig. 16. Schematic representation of hydrogen production
from coal-bed methane using rotating gliding arc (RGA) plasma [67]

od and several innovative catalytic technologies are being developed, since the principal advantage of this method is the production of pure hydrogen with the simultaneous production of a wide range of unique carbon materials: carbon nanofibers (CNF), carbon nanotubes (CNTs), graphene, various types of amorphous carbon etc.

$$CH_4 \rightarrow C + H_2$$
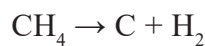
The opportunity of obtaining hydrogen and the second useful product, graphene, via methane pyrolysis in an electric arc plasma has been considered [67, 68]. Among the advantages of the method, the authors mention the possibility to use CBM as a raw material without its preliminary purification. The method allows for the presence of small impurities of nitrogen and carbon dioxide; in the plasma, those are effectively converted into active radical species, which, in turn, have some catalytic effect in the conversion of CBM (Fig. 16).
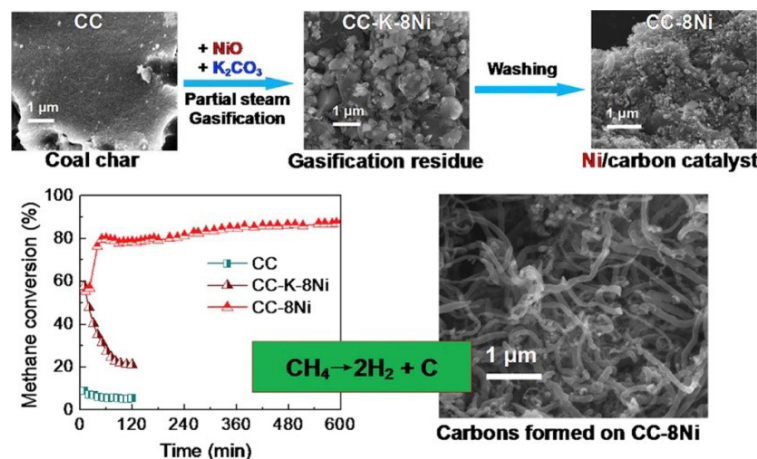
Fig. 17. Production of hydrogen by decomposition of methane on nickel-carbon catalysts
obtained in situ during the steam gasification of coal char [70]

Lots of studies are devoted to the production of hydrogen. Catalytic systems based on wastes (by-products, semi-products) of the coal industry look advantageous from the point of view of creation of low-waste technologies [69−71]. For instance, a strategy has been proposed for preparing Ni/C catalysts for methane decomposition by adding nickel oxide and K_2CO_3 during the steam gasification of coal char (Fig. 17). Gasification yields Ni^0 nickel crystallites, with the concurrent production of hydrogen rich gas and nickel-carbon composite materials. In general, these catalysts achieve high methane conversion (up to 80−87% at 850°C) with the combined formation of hydrogen and filamentous carbon.

Methane Reforming

Methane reforming is one of the major traditional methods of hydrogen production in gas chemistry. It consists of three stages: (1) reforming of methane with the formation of a $CO + H_2$ mixture (synthetic gas); (2) conversion of CO to obtain H_2 and CO_2; (3) purification from CO_2. This is the cheapest and most energy efficient method, but in order to avoid CO_2 emissions, capture and storage technologies will be required [72, 73]. Each of these methods has its own advantages and disadvantages and yields gas with different hydrogen content. As a rule the exact method is chosen depending on the further use of the resulting synthetic gas. From Table 1 it can be seen that the maximum hydrogen content is achieved in the case of steam reforming of methane, while the minimum content is achieved in carbon dioxide reforming.

Table 1

**H_2/CO ratio in synthetic gas obtained through various methane
reforming processes and its main applications [74]**

Methane reforming process	H_2/CO ratio in the reforming gas	Usage
Steam reforming with further CO conversion with steam	> 3	Production of H_2 and ammonia
Steam reforming	2-3	Methanol synthesis
Steam reforming or partial oxidation	2-2.5	Fischer-Tropsch synthesis for gasoline and light olefins production
Steam reforming or partial oxidation	1/7-2	Fischer-Tropsch synthesis for the production of paraffins and diesel fuel
Carbon dioxide reforming	< 1	Production of acetic acid and polycarbonates

Steam Reforming of Methane

Steam reforming of methane (1) is an endothermic process carried out in the presence of catalysts at temperatures of 800 to 1000˚C, pressures of 0.3 to 2.5 MPa, and a high ratio of H_2O to $CH_4 = 2.5-3.0$. This process yields synthetic gas with a high hydrogen content $H_2/CO = 3$. However, it has certain disadvantages, as it requires big capital investments, has low energy efficiency, and displays rapid catalyst deactivation due to coke formation and hydrogen sulfide poisoning.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta_r H^\circ_{298} = +226 \text{ kJ/mol}. \tag{1}$$
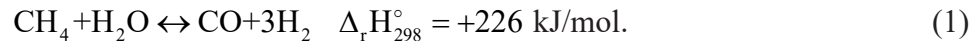
The proprietary technologies of hydrogen production by steam reforming over catalysts are offered by many companies, e. g. Linde Engineering [75], Air Liquide Engineering & Construction [76], Haldor Topsoe [77]. In particular, according to the SMR-X™ technology offered by Air Liquide Engineering & Construction, hydrogen production occurs without the associated production of steam, which distinguishes it from the traditional steam reforming of methane by its higher thermal efficiency and lower CO_2 emissions [76]. In the steam reforming process, the desulphurated hydrocarbon feedstock (natural gas, off-gas, NGL or naphtha) is heated, mixed with steam and converted to hydrogen, carbon monoxide and carbon dioxide (Fig. 18). The mixture of CO with steam undergoes conversion and yields extra hydrogen and CO_2 (2). The hydrogen is then separated by adsorption.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta_r H^\circ_{298} = -41 \text{ kJ/mol}. \tag{2}$$
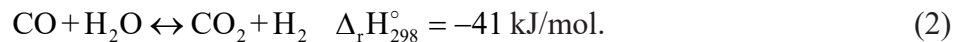
Despite the fact that the process of hydrogen production by steam reforming of methane has been successfully put into practice, further work is underway to optimise the characteristics of the catalyst and the process as a whole. Advanced methods for improving the methane steam reforming process also include its coupling with CO_2 adsorption [78, 79], the employment of microreactor units [80, 81] or chemical cycling technologies using complex oxide materials as oxygen carriers instead of molecular oxygen from the gas phase: $LaFe_{1-x}Co_xO_3$ [82], Ce-Fe-Zr-O/MgO [83], Fe_2O_3/Al_2O_3 with additions of Ce and Ca [84], $SrFeO_{3-\delta}$ [85]. In [86], calcite modified with nickel and iron was proposed as an affordable and efficient oxygen carrier. As seen on the diagram in Fig. 19, during its reaction CH_4 interacts with lattice oxygen $Ca_2Fe_2O_5$ and NiO to form H_2, CO_2, CO and C. The process yields a mixture of CaO and Ni_3Fe, whose oxidation closes the cycle. The treatment of oxide materials in the reactor with water vapour yields additional portions of hydrogen due to the conversion of carbonaceous deposits (3). A high selectivity of hydrogen production (93%) at methane conversion of 96% is reported.

$$C + H_2O = H_2 + CO. \tag{3}$$
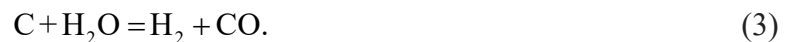
The use of bifunctional materials with a core-shell structure, combining the adsorbent and catalyst features, for steam reforming of methane makes it possible to increase the yield of hydrogen and to reduce the carbon footprint of production [79, 87, 88]. $CaO-Ca_9A_{16}O_{18}@Ca_5A_{16}O_{14}/Nic$ material has been developed containing 13 wt. % CaO, with a core-to-shell ratio ($CaO-Ca_9A_{16}O_{18}$ to $Ni/Ca_5A_{16}O_{14}$) of 0.2 (Fig. 20). The material offers 100% CO_2 sorption within 60 reaction-regeneration cycles.

Partial Oxidation of Methane

The composition of CMM varies over a wide range, but its main components are methane and air, which is fully suitable for hydrogen production by the reaction of partial oxidation of methane. The partial oxidation of methane (4) is a weakly exothermal process ($\Delta_r H^\circ = -44$ kJ/mol), which is carried out over catalysts at temperatures of 800 to 900˚C and pressure of 2 to 4 MPa. This process yields synthetic gas with molar ratio of $H_2/CO = 2$, which is favorable for its further conversion into methanol or
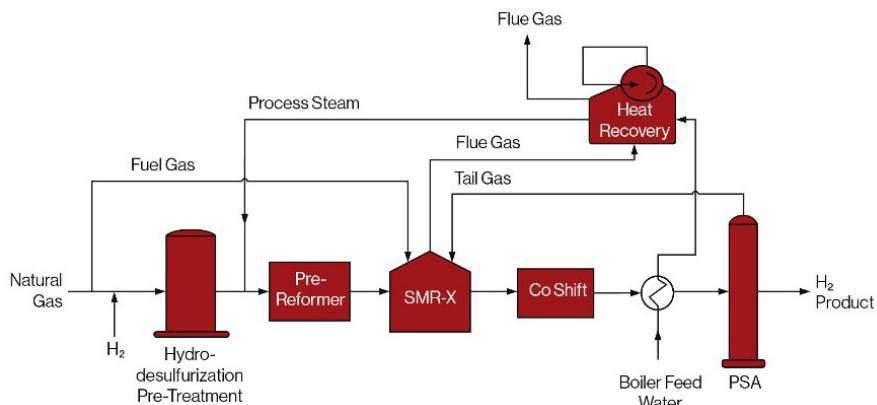
Fig. 18. Hydrogen production by steam reforming of methane without steam removal via SMR-X™ [76]
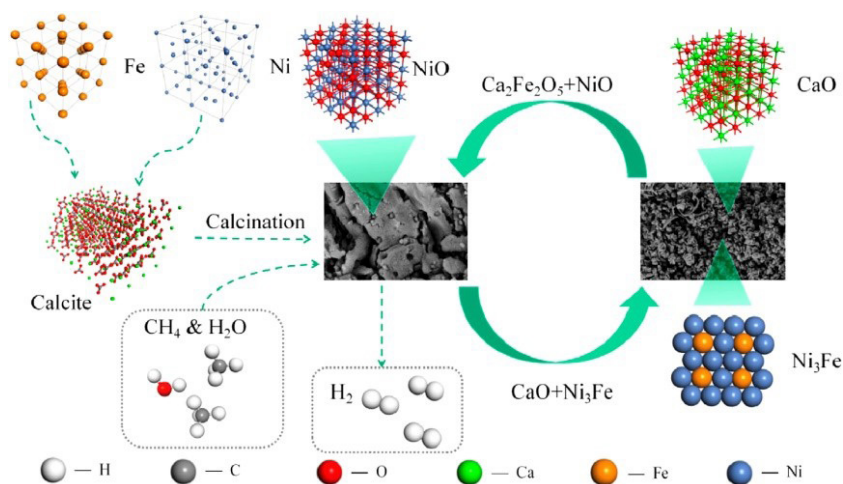

Fig. 19. Flowchart of hydrogen production by steam reforming of methane in the chemical cycling mode [86]

hydrocarbons by the Fischer-Tropsch reaction, but not sufficiently advantageous in terms of hydrogen production. It does not require extra heat supply, but is characterised by low stability and safety due to the high probability of mixture ignition, the formation of overheating zones, sintering, and catalyst deactivation.

$$CH_4 + 0.5_2O \leftrightarrow 2CO + 3H_2 \cdot \Delta_r H^\circ_{298} = -44 \text{ kJ/mol.} \tag{4}$$
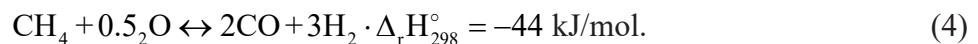
Partial oxidation of methane, as well as its steam reforming, in addition to hydrogen, yields carbon oxides and water. Using methane-air mixture (CMM) for hydrocarbon feedstock, in contrast to the use of natural gas, eliminates the need for the air separation unit producing oxygen for the reaction. After the reaction, converted gas is cooled to form high pressure steam, and CO_2 is removed in the amine treatment plant. Membrane, adsorption or cryo technologies are used to release hydrogen.

Partial oxidation can be carried out without a catalyst. In this case, the process temperature will exceed 1000°C. A technology for non-catalytic "matrix" reforming of hydrocarbon gases, including methane, into synthesis gas and hydrogen was proposed [89]. Carrying out the CMM conversion reaction in a burner with porous filler ensures the simultaneous production of heat and hydrogen, which can be used
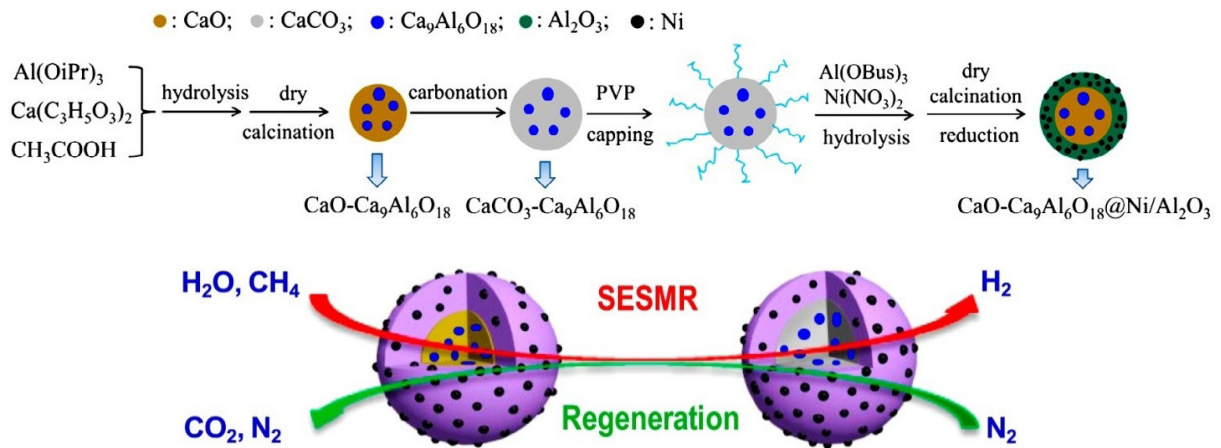
Fig. 20. Process design of bifunctional material and its mode of operation
in the hydrogen process by methane steam reforming reaction [79]
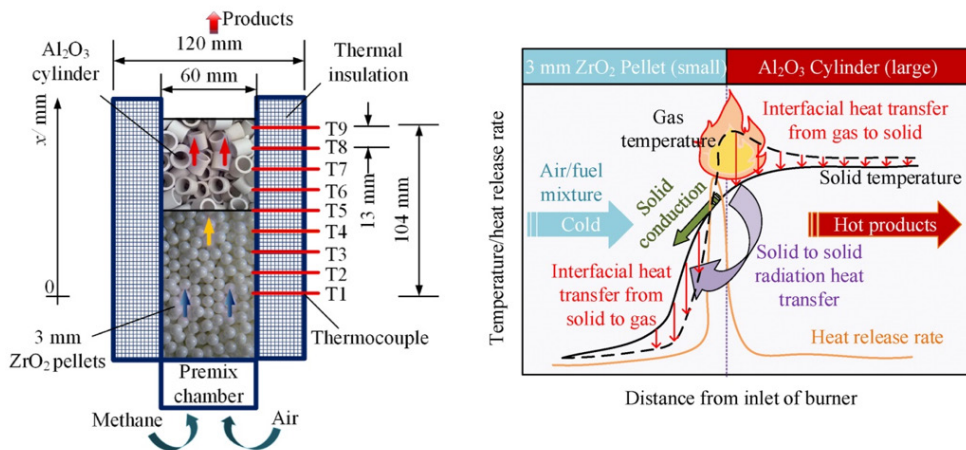

Fig. 21. Composition of a two-layer reactor (a) for the conversion of a methane-air mixture
into a hydrogen-containing gas and its principle of operation (b) [90]

as the main raw material for solid oxide fuel cells (SOFC) (Fig. 21). Structural optimisation of two-layer "matrix" burners has made it possible to obtain gas with a maximum hydrogen concentration of 12.3% by means of partial CMM reforming. It was demonstrated [90] that the process efficiency depends on the geometry of porous fillers, flow rate, and the temperature of preheating of the reaction mixture. The efficiency of the device is approximately 50%.

With catalysts, the process temperature required to achieve high methane conversion and product yields may be below 1000°C. To intensify the process, membrane reactors are being developed that combine the functions of air separation and catalytic partial oxidation of methane [91–94]. In this event, the air oxygen passes through the oxygen-permeable membrane and is used to oxidise methane to synthetic gas (Fig. 22). The use of air reduces operating costs and minimises the hazards associated with the handling of pure oxygen. An additional advantage of catalytic membrane reactors is the uniform distribution of the temperature profile, which solves the problem of overheating the inlet part of the catalyst bed, where gas phase oxygen is consumed for the complete oxidation of methane.
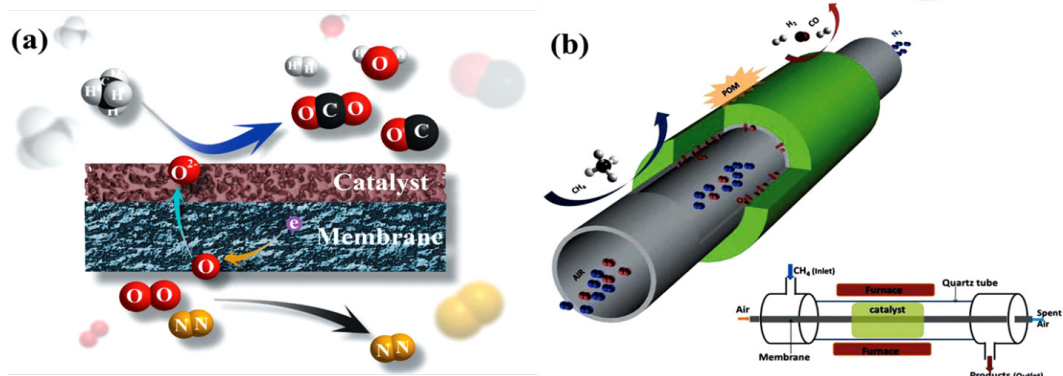
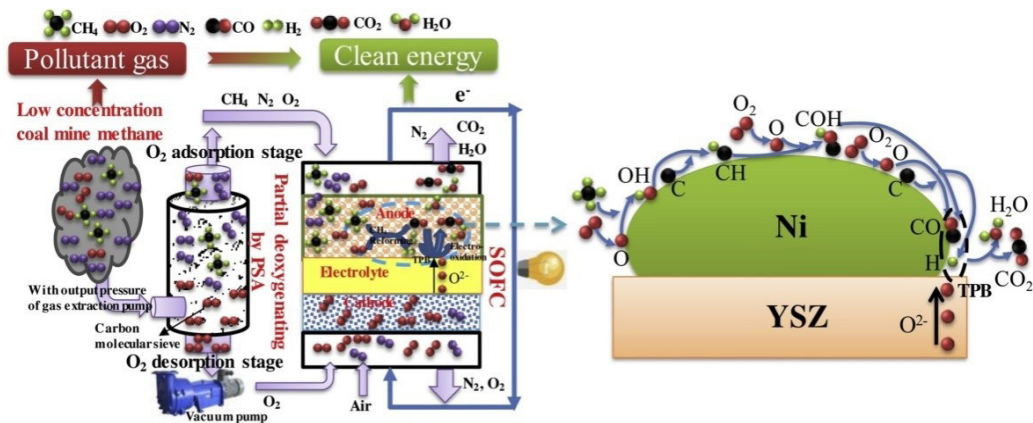Fig. 22. Layout of a membrane reactor for partial oxidation of methane [74]

Fig. 23. Flowchart of methane-air mixture (CMM) utilisation using SOFC [95]

A process of CMM oxidative conversion in an SOFC electrochemical cell with a catalytically active anode [95, 96], with the removal of oxygen from the CMM mixture by the PSA method was proposed to control the composition of the mixture and prevent the risk of explosion (Fig. 23).

Carbon Dioxide (Dry) Methane Reforming

Carbon dioxide (dry) reforming of methane (5) is an endothermic process carried out in the presence of catalysts at temperatures of 900 to 1000°C. Its essential advantage is the simultaneous utilisation of the two major greenhouse gases, CO_2 and CH_4. However, the process requires heat supply and can be complicated by a high rate of carbon deposits formation and catalyst deactivation. This technology, unlike steam reforming and partial oxidation of methane, is not yet employed on an industrial scale.

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta_r H^\circ_{298} = +261 \, kJ/mol. \tag{5}$$
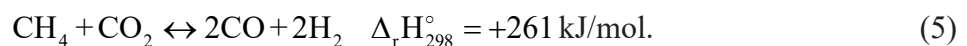
Since this process is characterised by side reactions of carbon deposits formation which are more pronounced than those occurring in other reforming processes [6−9], catalysts with improved composition and structure are being developed to reduce the deactivation rate [97].

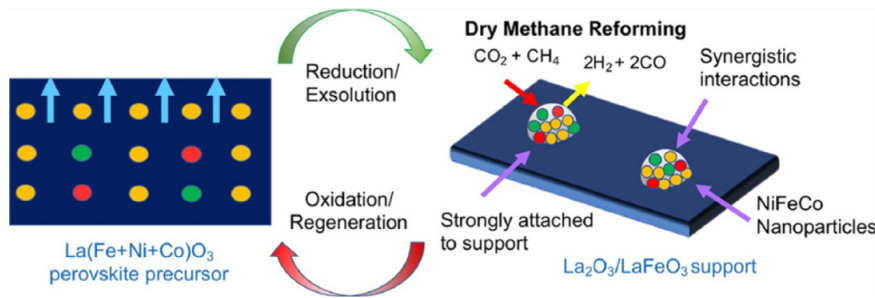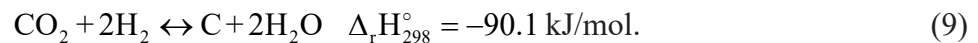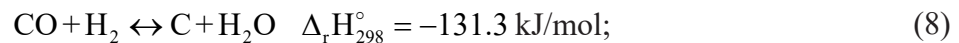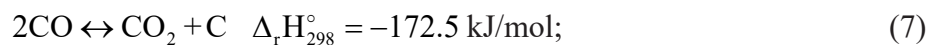$$CH_4 \leftrightarrow C + 2H_2 \quad \Delta_r H^\circ_{298} = +74.6 \, kJ/mol; \tag{6}$$

Fig. 24. Generation of catalytically active NiFeCo nanoparticles upon reduction
of La (Fe,Ni,Co) O$_3$ for carbon dioxide conversion of methane [98]

$$2CO \leftrightarrow CO_2 + C \quad \Delta_r H_{298}^{\circ} = -172.5 \, \text{kJ/mol;} \tag{7}$$

$$CO + H_2 \leftrightarrow C + H_2O \quad \Delta_r H_{298}^{\circ} = -131.3 \, \text{kJ/mol;} \tag{8}$$

$$CO_2 + 2H_2 \leftrightarrow C + 2H_2O \quad \Delta_r H_{298}^{\circ} = -90.1 \, \text{kJ/mol.} \tag{9}$$

An increase in the dispersion ability of the active component and the strength of its interaction with the oxide matrix of the carrier makes it possible to enhance the system resistance to carbonisation. A well-established approach is based on the in-situ formation of catalytically active particles by activating complex oxides in a reducing or reaction medium. The targeted thermal activation of complex oxides/hydroxides leads to the destruction of their original structure, and to nucleation, growth, and formation of metal nanoparticles and clusters stabilised on the oxide surface of the carrier (Fig. 24).

Combined Methods

To overcome certain shortcomings inherent with the traditional methods of methane conversion, alternative combined methods for processing coal-bed methane are being developed. Under the 7th Framework European Program, Design and Manufacture of Catalytic Membrane Reactors by Developing New Nanoarchitectured Catalytic and Selective Membrane Materials (DEMCAMER), we have developed catalysts for autothermal reforming and dimerisation of coal mine methane [33, 34, 39, 40, 42, 57−62]. A large study cycle on catalytic membranes and microreactors has been completed. Pilot tests of the ATR process with a PdNi/Ce$_{0.5}$Zr$_{0.5}$O$_2$/Al$_2$O$_3$ catalyst developed by the Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences in a combined ATR and membrane reactor have shown hydrogen productivity of 650 to 850 Nm^3/h.

Autothermal Reforming of Methane

Autothermal reforming of methane (ATR CH$_4$) is deemed to be the most promising catalytic process for hydrogen production.

$$2CH_4 + 1/2O_2 + H_2O \rightarrow 2CO + 5H_2.$$

ATR CH$_4$ is a combination of several exothermic (10−12) and endothermic (13) processes, which makes it energy efficient compared to other processes of methane conversion into a hydrogen-containing gas.

$$CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2 \quad \Delta_r H_{298}^{\circ} = -35.6 \, \text{kJ/mol}^{-1}; \tag{10}$$
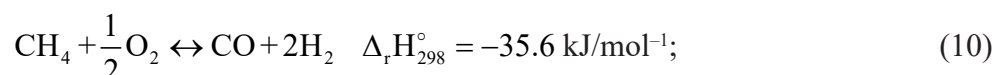
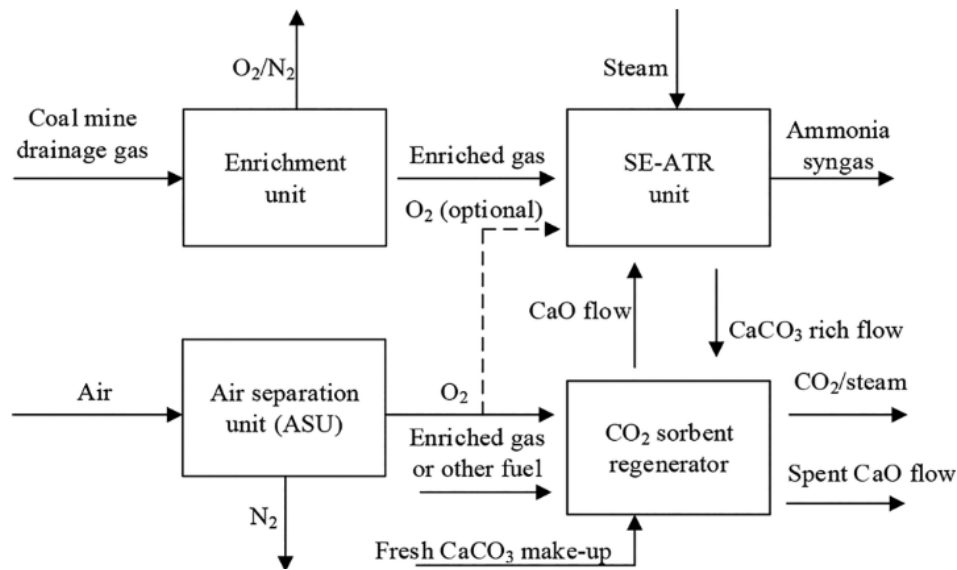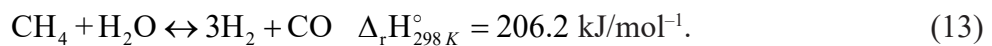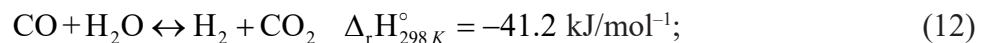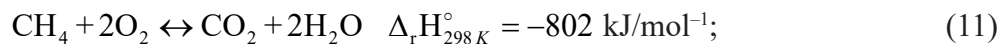Fig. 25. Utilisation of CMM by ATR, with preliminary concentration of methane and in situ utilisation of CO_2 [101]

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \quad \Delta_r H^\circ_{298\,K} = -802 \text{ kJ/mol}^{-1}; \tag{11}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta_r H^\circ_{298\,K} = -41.2 \text{ kJ/mol}^{-1}; \tag{12}$$

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \quad \Delta_r H^\circ_{298\,K} = 206.2 \text{ kJ/mol}^{-1}. \tag{13}$$

Along with the optimum power balance, this process is characterised by a fairly high yield of H_2 and by resistance to the formation of carbon deposits, due to the presence of oxygen in the reaction mixture. For this process, the methane-air mixture from the degassing system of the mine does not require special preparation, only water vapour dosage [99].

Topsoe offers SynCOR™ technology based on autothermal reforming [100]. SynCOR™ units are more compact compared to steam reformers. They can operate at a steam/carbon ratio of 0.6, which reduces capital and operating costs. Effective catalysts are being developed for better autothermal methane reforming performance in terms of hydrogen yield or volume concentration of hydrogen in hydrogen-containing gas [57–62].

Within the novel process flow of sorption-enhanced autothermal reforming, SE-ATR (sorption-enhanced autothermal reforming), methane is first recovered from the gas flow of the coal mine drainage system, and then it is reformed autothermically with CO_2 capture (Fig. 25). From the experimental results of the enrichment process [101] it is evident that a single-stage adsorption process involving carbon-containing sorbents can boost the concentration of the vent gas from 4.5% to 31.7%, and the concentration of methane, from 20.3% to 79.3% respectively. Autothermal reforming of a 30% CH_4 and air mixture over a nickel catalyst, yields gas mixture with H_2 concentration of about 45 to 47% (for dry gas).

Steam-Carbon Dioxide Reforming of Methane

Steam-carbon dioxide reforming of methane (14) is an environmentally friendly process making it possible to simultaneously utilise three greenhouse gases (carbon dioxide, methane, water vapour) and to produce hydrogen within synthetic gas (a mixture of H_2 and CO). The process is characterised by the possibility of flexible regulation of the H_2/CO ratio by varying the feedstock composition $CH_4/CO_2/H_2O$ [102].
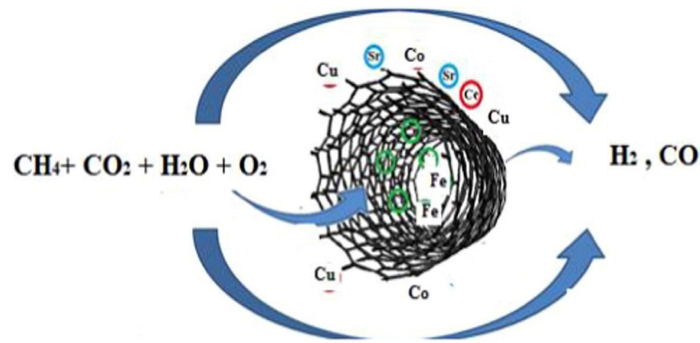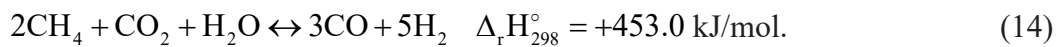
Fig. 26. Tri-reforming of methane into hydrogen-containing gas in the presence of a metal-carbon catalyst [105]

$$2CH_4 + CO_2 + H_2O \leftrightarrow 3CO + 5H_2 \quad \Delta_r H^{\circ}_{298} = +453.0 \text{ kJ/mol.} \tag{14}$$

Linde is developing a DRYREF™ synthetic gas process powered by a BASF SYNSPIRE™ G1-110 catalyst. With DRYREF technology, production costs are significantly reduced due to steam consumption reduction.

Tri-Reforming of Methane

Tri-reforming of methane combining endothermic reactions of steam and carbon dioxide reforming with exothermic reactions of partial and complete oxidation deserves special attention. This method has a number of advantages, such as (1) high energy efficiency: energy costs are compensated by the intrinsic energy of the initial hydrocarbon feedstock; (2) good process versatility: by changing the ratio between the initial reagents, it is possible to obtain a product of a given component composition; (3) lesser coke formation as side process; (4) chemical utilisation of CO_2. Also of interest is the possibility of using carbonaceous materials for methane tri-reforming (Fig. 26). For example, a mixture of $CH_4:CO_2:H_2O:O_2:N_2 = 1:0.34:0.23:0.5:2.12$ at 750°C in the presence of a 5% Ni@MWCNT/5%Ce catalyst increases conversion of the reagents, that is, 96.8% CH_4, 38.7% CO_2. The H_2/CO mole ratio in the reaction products is 1.9 [103]. In [104], CBM is modeled by a mixture with the composition CH_4/CO_2/H_2O/O_2/$N_2 = 1.0/0.45/0.45/0.1/0.4$. Its processing at 800°C in the presence of a Ni-Mg-ZrO$_2$ catalyst achieves a high conversion of methane (99%) and CO_2 (65%) with good performance in terms of H_2/CO = 1.5.

Dehydroaromathisation of Methane

Another important aspect is the production of hydrogen by aromatisation of methane over zeolite catalysts (15). From six molecules of methane, nine molecules of hydrogen are formed, together with one by-product benzene molecule which is a valuable chemical product. The non-oxidising nature of the process ensures high selectivity of the target products formation (minimum 70%). We have found that Mo-zeolite catalysts are the most active systems [106], and performed research in order to identify the nature of the active centers and to improve the catalyst formula with the aim to increase the systems' carbonisation resistance [35–38, 41, 43].

$$6CH_4 \rightarrow C_6H_6 + 9H_2 \quad \Delta_r H^{\circ}_{1000} = +620.7 \text{ kJ/mol.} \tag{15}$$
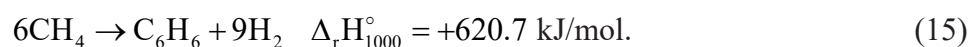
The influence of the method of preparation of metal-zeolite catalysts on their physicochemical and catalytic properties has been demonstrated [94, 95]. Thus, the introduction of an iron precursor at the stage of zeolite synthesis makes it possible to obtain a catalyst in one stage and ensures the stabilisation of nanosized clusters inside the porous space of the ZSM zeolite. Strong interaction with the carrier
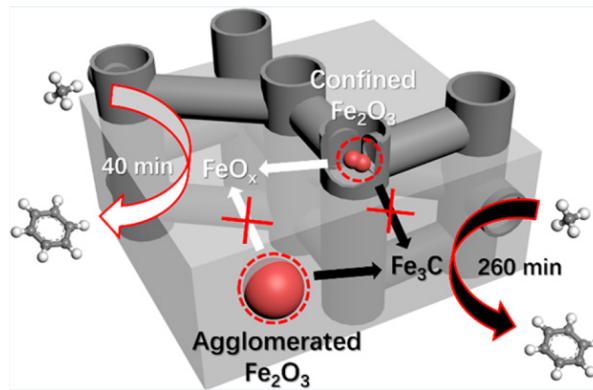
Fig. 27. Active sites of the Fe/ZSM-5 catalyst and their relationship
with the induction period of the methane dehydroaromatisation reaction [107]
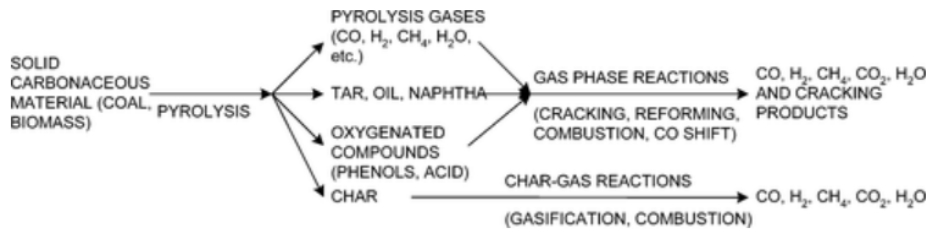
Fig. 28. Sequence of reactions during coal gasification [6]

prevents such centers from sintering, complete reduction, and carbonisation under the influence of the reaction environment. On the contrary, the Fe-containing centers used for the "impregnation" sample are large particles of iron oxide prone to agglomeration, slow activation, and rapid decontamination due to the formation of carbon deposits (Fig. 27).

Coal Mine Methane Co-processing with Coal

Very attractive is the method of coal mine methane co-processing with fossil coal. Hydrogen production via coal gasification is advantageous due to the low cost of raw materials, but is regarded as problematic due to the low H_2/CO ratio in the resulting synthetic gas yield. Therefore, modern applications are focused on the process of partial oxidation of coal to produce a gas mainly consisting of hydrogen and carbon monoxide (reactions 16−20) rather than on direct pyrolysis yielding a wide mixture of hydrocarbons (Fig. 28).

$$C + 1/2O_2 \rightarrow CO \quad \Delta_r H^\circ_{298} = -111 \text{ kJ/mol;} \tag{16}$$

$$CO + 1/2O_2 \rightarrow CO_2 \quad \Delta_r H^\circ_{298} = -283 \text{ kJ/mol;} \tag{17}$$

$$C + H_2O \leftrightarrow CO + H_2 \quad \Delta_r H^\circ_{298} = +131 \text{ kJ/mol;} \tag{18}$$

$$C + CO_2 \leftrightarrow 2CO \quad \Delta_r H^\circ_{298} = +172 \text{ kJ/mol;} \tag{19}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta_r H^\circ_{298} = -41 \text{ kJ/mol.} \tag{20}$$
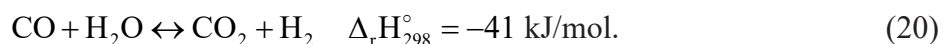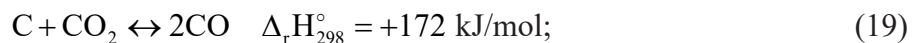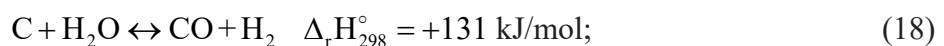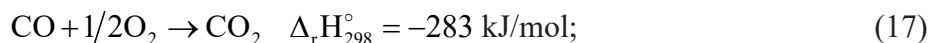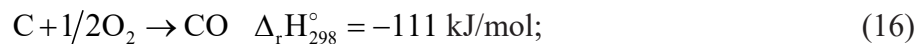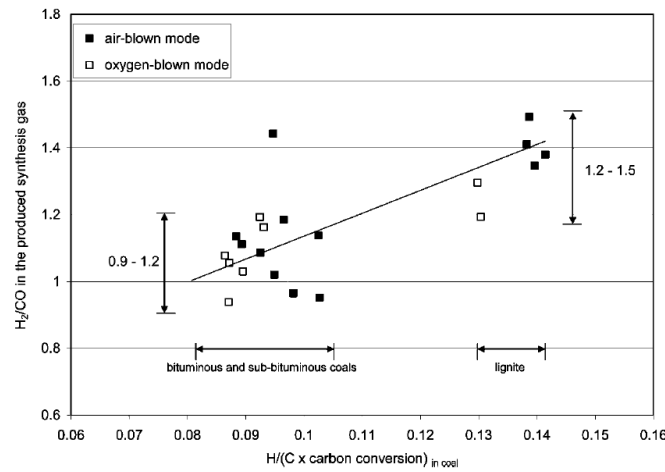
Fig. 29. Relationship between the composition of hydrogen-containing gas (H_2/CO)
produced by gasification and the degree of metamorphism, i. e. the C/H ratio in the coal composition [108]
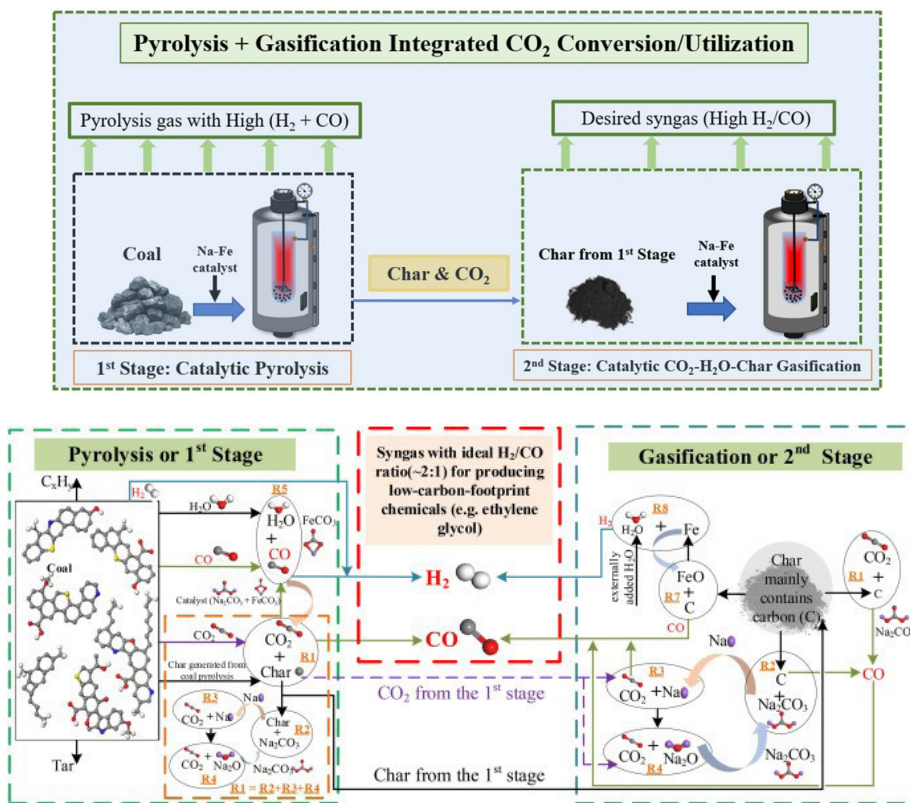
Fig. 30. Flow-chart of two-stage processing of coal into hydrogen-containing gas [109]

For various grades of coal, i.e. those of different composition and, accordingly, different reactivity, the H_2/CO ratio of the gas obtained as a result of coal gasification will be in the range of 0.9 to 1.5 (Fig. 29).

In [109], improved technologies for production of hydrogen-containing gas from coal are proposed, which ensure a high yield of hydrogen with simultaneous utilisation of CO_2 (Fig. 30). It is noted that the use of the $FeCO_3$-Na_2CO_3 catalyst reduces carbon dioxide formation by 75%, which means an overall
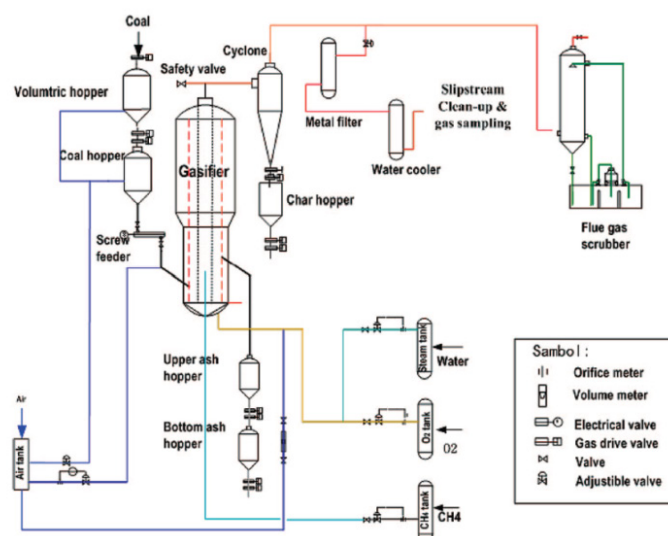
Fig. 31. Layout of a plant for producing hydrogen-containing gas by co-gasification of coal and methane [108]

reduction in the carbon footprint by 87%. In addition, the resulting gas is characterised by a high $H_2/CO = 2$ ratio.

The research results [108, 110] have revealed that coal gasification in the presence of coal mine methane makes conversion of coal more efficient, yielding gas of optimal composition ($H_2/CO = 2$) for further use. At the same time, coal ash and coal char formed during gasification have a catalytic effect and increase the yield of products in methane reforming reactions. The diagram of the installation for coal gasification is shown in Fig. 31. When coal is gasified with a mixture of $H_2O + CH_4$, a decrease in the molar ratio of H_2/CO [111] is observed. The composition of the hydrogen-containing gas obtained from coal is characterised by a high CO_2 content. This imposes restrictions on the use of standard cleaning methods, such as PSA method. Therefore, absorption of CO_2 and subsequent methanation of residual amounts of carbon oxides is considered as an effective approach [6].

Conclusion

Given the increasing role of hydrogen as energy carrier, coal industry has a very strong potential for its production. Coal bed methane is an important unconventional hydrocarbon feedstock with a high economic potential. In the recent years, research and development of technologies for production of hydrogen from coal mine methane have come to the fore. Also, under development are technologies for production of hydrogen from all types of coal mine methane (VAM, CMM, AMM and CBM), differing in methane concentration and methane-to-air ratio. For highly concentrated CMM, AMM and CBM, concentration technologies with purification and processing according to conventional gas chemistry technologies will be most advantageous. Lesser concentrated CMM and AMM can be also used without prior concentration. Hybrid methods of processing natural coal and coal-bed methane have great potential. They offer effective energy savings, significant economic benefits and cleaner production. Among hybrid and combined technologies, very attractive is the technology of hydrogen production by joint gasification of fossil coal and different types of coal-bed methane. It might reduce the cost of hydrogen below one dollar per kilogram.

We have studied the production of hydrogen from coal-bed methane by creating new domestic catalytic materials and technologies [33–42, 44–53, 54–62]: (1) autothermal and combined reforming; (2) "Green Plus" hydrogen obtained by catalytic conversion of methane into hydrogen and carbon nanomaterials; (3) "Green Plus" hydrogen obtained by dehydroaromatisation of methane into hydrogen

and benzene. We define the last two methods of hydrogen production as "Green Glus" grade, because, firstly, the method is "green", as it does not lead formation of carbon dioxide, and secondly, it is "plus" because it yields additional valuable products, namely carbon nanomaterials and benzene.

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