

Catalytic carbon dioxide hydrogenation as a prospective method for energy storage and utilization of captured CO₂

Lucyna Więclaw-Solny^a, Andrzej Wilk^a, Tadeusz Chwoła^a, Aleksander Krótki^a, Adam Tatarczuk^a, Janusz Zdeb^{b,*}

^aInstitute for Chemical Processing of Coal, Zamkowa 1, 41-803 Zabrze, Poland

^bTAURON Wytwarzanie S. A., Promienna 51, 43-603 Jaworzno, Poland

Abstract

The article addresses the problem of carbon dioxide utilization through conversion with hydrogen to gaseous fuels. It describes methods which can be used to obtain Substitute Natural Gas (SNG) with as well as reactors where methanation process can be guided. There has been highlighted different economic and technical issues linked with carbon dioxide utilisation for production of methane. The last part of the article introduces global and local projects involved in developing this technology.

Keywords: utilization, power to gas, methane, CO₂, methanation, PtG

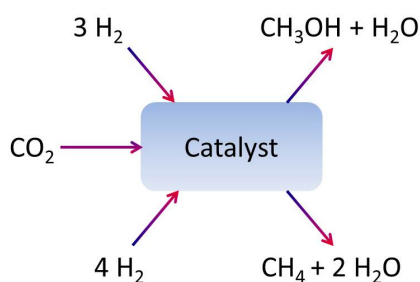


Figure 1: Diagram illustrating the reaction of carbon dioxide with hydrogen

1. Introduction

The scientific domain of methane synthesis was pioneered by Paul Sabatier and Jean-Baptiste Senderens who found in 1902 that methane can be obtained through synthesis from hydrogen and carbon monoxide or carbon dioxide in the presence of reduced nickel (at 200–300°C) or reduced cobalt (at 270–300°C). Carbon monoxide may also be utilized as a raw material in fuel synthesis by way of the Fischer-Tropsch reaction, where carbon monoxide is used to produce liquid

fuels. This technology had been widely applied in industry until cheap petroleum emerged in the 1950s. Currently, on account of the growing prices of petroleum, the reduction of costs of fuel production based on the Fischer-Tropsch synthesis as well as the contemporary requirements of environmental protection, the technology in question is gaining interest again. The main fuels produced as an outcome of the direct reaction between carbon dioxide and hydrogen are methane or methanol. The type of the fuel thus acquired depends on the catalyst applied, as shown in Fig. 1.

The most frequently used CO₂ capture emission reduction technologies (CCS-based) are these which consist in carbon dioxide capture [1], transport and typically underground storage, or alternatively its utilization as an agent for Enhanced Oil Recovery (EOR). However, as proved by the aforementioned reactions (Fig. 1), carbon dioxide may also function as a single carbon building molecule in organic synthesis, therefore, CCU technologies are increasingly often considered as the CCS substitute.

The use of carbon dioxide as a raw material is currently limited to the following several reactions:

1. Synthesis of urea
2. Synthesis of salicylic acid
3. Synthesis of polycarbonates

Carbon dioxide conversion is also an efficient method used to solve other problems highlighted under the contemporary energy and climate policy, such as renewable energy storage and utilization of surplus electric energy [2].

*Corresponding author

Email address: Janusz.Zdeb@tauron-wytwarzanie.pl (Janusz Zdeb)

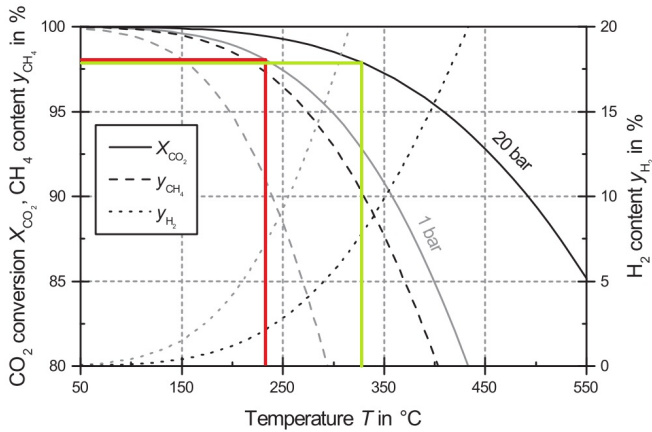


Figure 2: Equilibrium conversion ratio and concentrations of H₂ and CH₄ (H₂/CO₂= 4, no inerts) [4]

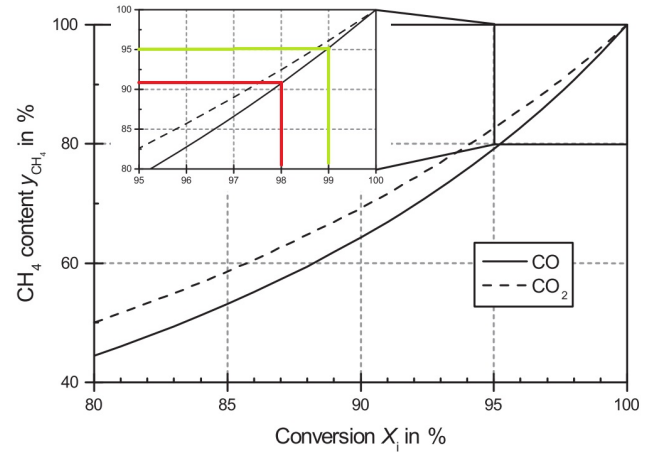
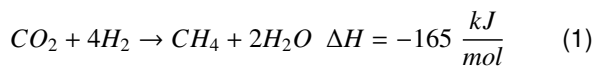


Figure 3: Dependence between CO or CO₂ conversion and CH₄ content in dry SNG (without inert gases, H₂/CO=3, H₂/CO₂= 4) [4]

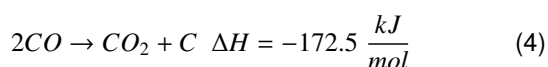
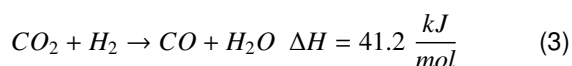
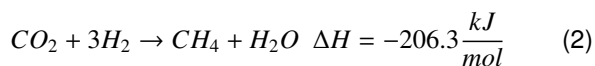
2. Synthesis of methane (Power to Gas)

Methanation is a chemical reaction where carbon monoxide and/or carbon dioxide is converted to the methane. Methane production by the way of the Sabatier reaction is a popular process of carbon dioxide conversion used to produce chemical components was found in 1902. However, methane production based on this reaction has never been implemented on a large industrial scale due to high availability and low price of natural gas. This technology has significantly grown in importance within the recent years on account of the shift observed in the global energy and climate policy as well as the need for efficient methods of carbon dioxide utilization and storage of surplus electric energy from renewable sources.

The Sabatier reaction is a simple reaction of hydrogen with carbon dioxide taking place at moderate temperatures and pressures in the presence of metallic catalysts, leading to formation of methane and water. The reaction may be noted as the following equation [3]:



What basically also takes place in the course of the methanation processes is some additional reactions of CO hydrogenation as well as the reverse water gas shift (RWGS) conversion of carbon monoxide, but also, to a certain extent, the Boudouard reaction [4]:



The hydrogenation reactions of both carbon monoxide and carbon dioxide are strongly exothermic. As a consequence

of the foregoing, high temperatures limit the conversion ratio for CO, and particularly for CO₂. As was shown on Fig. 2, temperatures below 230°C (at the pressure of 1 bar) or 325°C (at the pressure of 20 bar) are required in order to reach 98% CO₂ conversion ratio.

The gas produced in the course of methanation processes must fulfil specific requirements: its properties should be similar to those of the natural gas in the distribution system. Typically, natural gas contains more than 80% of methane. Other natural gas components, such as ethane, propane and butane, increase the calorific value of gas compared to pure methane. On the other hand, natural gas may also contain nitrogen and carbon dioxide which decrease its calorific value.

A standard methanation process based on application of the nickel catalyst is characterized by selectivity of nearly 100%. Absence of higher hydrocarbons may lower the calorific value of Substitute Natural Gas (SNG) compared to natural gas. Fig. 3 shows that for 98% CO₂ conversion, the methane content in the gas is slightly above 90%, whereas for 99% conversion, the content of CH₄ is about 95%. The presence of inert components or the over stoichiometric ratio of H₂/CO₂ may reduce concentrations of methane in the gas, wherefore high requirements are imposed upon methanation reactors. For the classical synthesis of methane from CO and H₂, the methane contents in the post-process gas is several per cent higher at analogic conversion ratios.

The methanation process may proceed in both biological and catalytic methanation reactors. The block diagram provided in Fig. 4 illustrates the concepts underlying the reactors used for SNG production from carbon dioxide. A comparison between individual parameters of methanation reactors has been provided in Table 1.

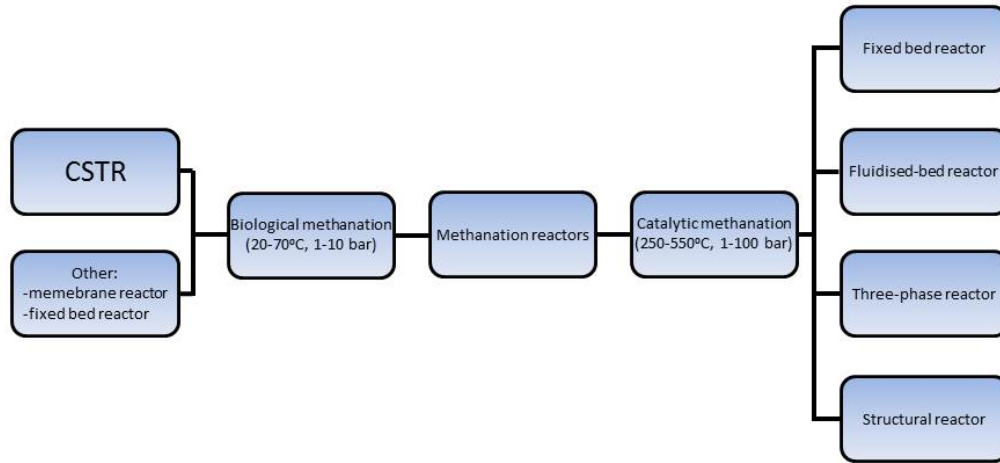


Figure 4: Breakdown of reactors used in methanation processes [4]

Table 1: Comparison of parameters of selected methanation reactors [4]

| Reactor type | Isothermal CSTR | Isothermal suspension reactor | Adiabatic fixed-bed reactor |
|-------------------------------|---------------------------|------------------------------------|-----------------------------|
| Phases present in the reactor | Liquid, gaseous | Liquid, gaseous, solid | Gaseous, solid |
| Number of reactor stages | 1 | 1–2 | 2–6 |
| Temperature, °C | 20–70 | 300–350 | 300–550 |
| Pressure, bar | <10 | 20 | >5 |
| Concept maturity | Laboratory/pilot scale | Laboratory/pilot scale | Commercial scale |
| Tolerance for impurities | High | Low/moderate | Low |
| Process materials | Proteins, buffer solution | Heat transferring liquid, catalyst | Catalyst |
| GHSV* | ≪100 | 500–1,000 | 2,000–5,000 |

*GHSV = Reactant Gas Flow Rate/Reactor Volume, h⁻¹ (ensuring CO₂ conversion ratio of 90%)

2.1. Catalytic methanation

Catalytic methanation reactors typically work at temperatures of 200–550°C and under pressures ranging between 1 and 100 bar. The catalysts used in the methanation process are based on metals of sub-group VIII (e.g. Ru, Rh, Co, Fe, Ni) based on different oxides (Al₂O₃, TiO₂, CeO₂, MgO, NiO-MgAl₂O₄, NiO-K₂O-MgAl₂O₄, SiO₂, Cr₂O₃, ZrO₂, Al₂O₃-CaO, La₂O₃). However, the nickel-based catalyst remains to be most frequently used because of the relatively high activ-

ity, good selectivity compared to CH₄ and low raw material price. Nevertheless, as a consequence of application of the nickel-based catalyst, it is necessary to ensure high feed gas purity (particularly when halides and sulphur compounds are present).

The methanation reaction is highly exothermic. On total CO₂ conversion, about 2 MW of heat must be released per each cubic meter of the catalyst bed (comparing with the methanol synthesis it is about 0.6 MW/m³). To counteract thermodynamic limitations of the reaction as well as to prevent the catalyst bed from sintering the methanation reactors must ensure appropriate heat removal.

There are several reactor concepts which can develop such high heat exchange, including fixed-bed reactors, fluidised-bed reactors, three-phase reactors and structural reactors.

The fixed-bed reactors are predominantly composed of a series of adiabatic reactors (from 2 to 5) featuring a multi-stage cooling system and frequently also gas recirculation. On account of the adiabatic operation mode in this reactor, the catalyst must be resistant to a considerable range of temperatures (250–700°C). The main issue linked with this solution is coking and sintering of the catalyst.

In fluidized-bed reactors, a mixture of solid particles in a fluidized state ensure nearly isothermal conditions, what help to control the process. Efficient heat removal is the main advantage of this concept, as it allows for a single struc-

turally uncomplicated reactor to be used. Unfortunately there is also an issue which limited application of the fluidized bed. Fluidized bed reactor has an abrasive wear of both the catalyst and the reactor components, which may consequently lead to deactivation of the catalyst. Moreover, a fluidized-bed reactor is limited by the gas flow rate. It must neither be too low so that optimum fluidization conditions are ensured, nor too high in order not to blow catalyst particles off. The potential formation of gas bubbles in the bed may lead to incomplete CO₂ conversion.

Another concept to be highlighted is based on three-phase methanation reactors. A three-phase suspension reactor is generally filled with suspended matter comprising a liquid phase (heat transfer oil, e.g. dibenzyltoluene) in which catalyst particles are suspended as a result of the gas flow. The presence of a high thermal capacity liquid phase ensures efficient and accurate heat control of the process. The heat of reaction may be completely removed from the reactor, owing to which it can operate under nearly isothermal conditions. Main operating issues encountered in these type of reactor are the mass penetration resistances between the liquid and the gaseous phase as well as decomposition and evaporation of oil.

Structural reactors were designed to eliminate the disadvantages of typical adiabatic fixed-bed reactors. These reactors have a monolithic inner metal structure, what intensified heat removal from the reactor interior as well as low resistances of gas flow through the bed. Structural reactors are compact units which are also characterized by a very high surface-to-capacity ratio. Their main disadvantage is a complicated process of the catalyst settling on a metallic bed and some difficulties involved in replacement of deactivated catalyst.

2.2. Biological methanation

Biological methanation (BM) is an alternative process of CO₂ conversion to methane. In this process, methanogenic microorganisms perform the function of a biological catalyst. Methane is produced directly from carbon dioxide and hydrogen by microorganisms which acquire energy through hydrogenotrophic methanogenesis of CO₂ and H₂. This reaction has been known since 1906. Biological methanation usually takes place at temperatures ranging between 20 and 70°C. The ratio of conversion CO₂ and H₂ to methane depends on the type and quantity of microorganisms, the reactor design, pressure, pH value and temperature. The reaction proceeds in the aqueous phase, therefore the main disadvantage is the variance of solubility of individual substrates (for CO₂ is about 23 times more soluble than hydrogen).

The biological methanation reactions are typically conducted in continuous flow stirred tank reactors (CSTR). Raising the stirring rate improves the hydrogen transfer into the liquid phase, but at the same time, it also increases the quantity of energy consumed in the process. There are two main concepts of how the methanation process should proceed: in a separate reactor or in situ, which intensifies methane production in the course of anaerobic fermentation. When the

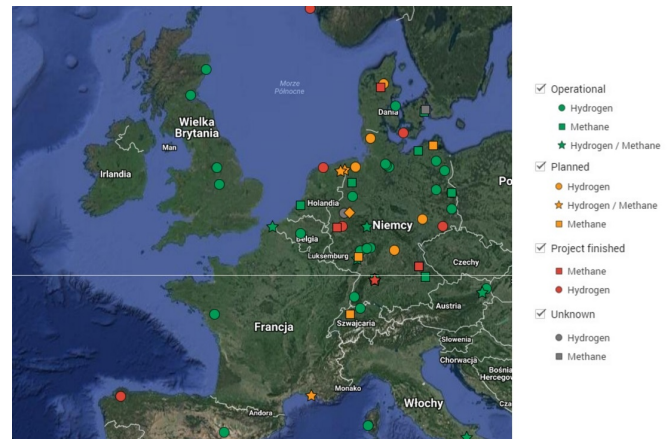


Figure 5: Power to Gas projects implemented in Europe [5]

former method is applied, the gas obtained contains 13-98% of methane, depending on the process efficiency. However, it ensures high conversion ratio only and exclusively at low gas flow rates. The latter makes it possible to increase the CH₄ concentration in biogas thus obtained from 52 to 74%, at the same time reducing the carbon dioxide content. Despite promising outcomes, both biological methanation methods have not yet evolved past the preliminary testing phase.

2.3. Current state of research on methane synthesis from carbon dioxide

The research on carbon dioxide hydrogenation has been conducted since the beginning of the 20th century. However, on account of the easily accessible and cheap natural gas, industrial-scale production of SNG was not cost-effective. The trend reversed as the need occurred for seeking ways to utilise carbon dioxide and store surplus electric energy from renewable sources. In Europe, there is a number of experimental Power to Gas (PtG) systems already commissioned or planned to be installed, powered by renewable energy and delivering gas products, e.g. hydrogen or methane. One of the most important of those PtG plants is the 6 MWe pilot system built by Audi in Werlte, Germany in 2013 [6]. For purposes of CO₂ methanation, Audi's E-gas pilot system uses hydrogen produced in the water electrolysis process as well as some portion of energy from renewable sources. The system only produces SNG when the renewable energy is at oversupply, and therefore its operating time is far smaller than that of industrial plants. In order to produce ca. 1,000 tonnes of SNG per annum, about 2,800 t of CO₂ is consumed [7, 8]. The European Power to Gas projects have been listed in Fig. 5.

2.4. Domestic research projects concerning methane synthesis from carbon dioxide

The leading Polish project pertaining to utilisation of carbon dioxide was initiated by TAURON Wytwarzanie S.A. in

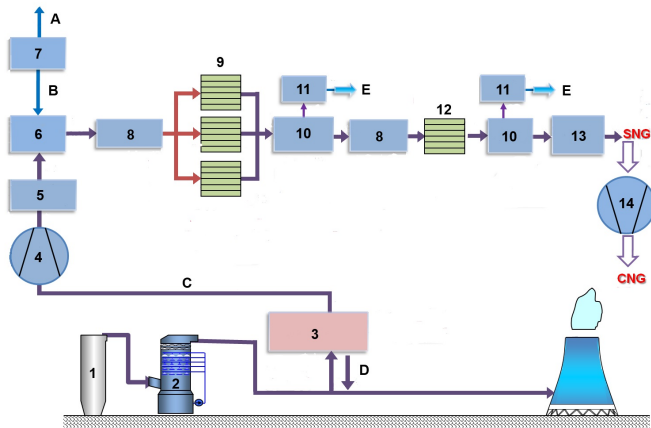


Figure 6: Block diagram of the CO₂-SNG system: A-oxygen, B-hydrogen, C-carbon dioxide, D-treated flue gas, E-condensate; 1-boiler, 2-flue gas desulphurisation, 3-CO₂ removal system, 4-CO₂ compressor, 5-deep CO₂ treatment, 6-gas mixer, 7-electrolyser, 8-gas pre-heater, 9-methanation reactor (first stage), 10-condenser, 11-condensate separator, 12-methanation reactor (second stage), 13-gas drying unit, 14-SNG compressor [9]

2014 under the title of “CO₂ methanation system for electricity storage through SNG production” (CO₂-SNG), and it is financed from the EU funds by the European Institute of Technology (EIT) via the Knowledge and Innovation Community (KIC). The project goal is the development of the CO₂ and H₂ methanation technology for purposes of storage of surplus electricity from renewable energy sources. The project consists in erection and testing of a pilot system for CO₂ conversion to methane.

In the CO₂-SNG system, carbon dioxide obtained from the existing TAURON's pilot CO₂ capture system is to be pre-compressed and subject to a deep treatment process (to remove even trace amounts of SO_x and other compounds which may poison the catalyst) [10]. The gas thus prepared will be mixed with hydrogen from electrolysis. Moreover, also oxygen, as a by-product, will be formed in the electrolysis process. After preliminary preparation, the gas mixture (mainly composed of CO₂ and H₂) will flow to a gas pre-heater installed upstream the first stage of the methanation reactor. The pre-heated gas will then flow to the first stage of the methanation reactor where the CO₂ hydrogenation process is to proceed in a suitable catalyst, thus leading to formation of methane and water. The gas leaving the first methanation reactor stage will be delivered to a condenser where, by cooling it with heat transfer oil to an appropriate temperature, the steam fraction present in the gas will be condensed. The gas will then be reheated and transferred to the second stage of the methanation reactor. Having left the second methanation reactor stage, the gas mixture mainly containing methane and steam will flow to the condenser where water will be separated again. Downstream the condensing section, the gas will be additionally dried. Once the drying is complete, pure SNG (Substitute Natural Gas) is to be obtained, which may then be delivered to a compressor

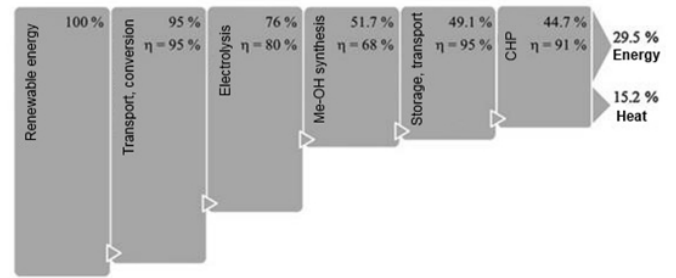


Figure 7: Process chain for energy storage [11]

in order to produce CNG (Compressed Natural Gas) ready to power motor vehicles. A simplified block diagram of the system has been provided in Fig. 6.

3. Conclusions

The methanation technology has been known for many years as a method of carbon dioxide conversion to chemical raw materials or fuels. Similarly to other technologies of conversion, e.g. to methanol, it is a relatively mature concept. There are several Power to Liquid research projects conducted at present, and they also cover large scale systems. As far as SNG synthesis is concerned, the capacity of the largest pilot system is about 1000 tons per annum.

SNG synthesis is known of higher selectivity towards the target product compared to alternative methods of fuel synthesis from CO₂. This type of synthesis makes it possible to obtain almost only methane, which decreases the costs related to the final product treatment. What SNG synthesis also offers is the favourable carbon dioxide conversion ratio, as it comes to 99%. However, a major disadvantage of the technology is the need for hydrogen to be used in the reaction. In the methanation process, half of the hydrogen reacts to SNG, whereas the other half forms a by-product, namely water. The H₂/CO₂ ratio resulting from the reaction stoichiometry in SNG synthesis is also less favourable compared to methanol synthesis, for instance, as it is 4:1 and 3:1 respectively.

The reaction of carbon dioxide with hydrogen leading to formation of methane is highly exothermic. The foregoing makes the design of SNG synthesis reactors more complex, yet at the same time, it may constitute an additional source of heat which can be utilized in other processes.

The overall yield of the energy storage and reuse process (power-to-power) is relatively more beneficial. With SNG synthesis, the energy stored in methane accounts for 53.2% of the initial energy, and the maximum quantity recoverable as thermal and electric energy corresponds to 33.7% [11]. Among the most significant advantages of SNG synthesis, one should emphasize the possibility of utilizing the existing system of natural gas pipelines, which translates into simplicity of the energy carrier transport over long distances as well as the opportunity of using it at the right place and time.

A crucial aspect of both the SNG production technology and other methods of carbon dioxide hydrogenation is the progressing development of the electrolysis technology aimed at yield increase and cost reduction. Developing more efficient hydrogen production methods, general costs may drop considerably while energy balance may become more favourable.

Data provided in publications imply that large-scale chemical energy storage will become a necessity when the share of renewable energy exceeds 50%, which means that there is enough time to develop a suitable storage technology [11].

Problems related to developing efficient and economically sound technologies for CO₂ conversion into chemical raw materials or fuels, even though very challenging, seem crucial in times of continuously rising fuel prices and the need for the carbon dioxide emission reduction. The estimated quantity of carbon dioxide currently consumed for purposes of certain chemical syntheses is a negligible fraction of the total amount of carbon dioxide discharged into the atmosphere. The amount of CO₂ released which can be utilized ranges between 5 and 7% [12]. The foregoing naturally stems from the necessity of bearing high costs related to chemical conversion of both carbon dioxide and other reagents as well as costs of carbon dioxide separation, treatment, storage and transport. As in the case of many chemical syntheses, the very process of treatment of the CO₂ reclaimed from process gas may be costly, and so it may constitute the restricting stage due to the necessity of removing impurities, such as oxygen, sulphur or nitrogen oxides, which may poison the catalysts in use.

Therefore, the most important factor which constrains the evolution of processes in which carbon dioxide is consumed for purposes of chemical syntheses is the process economy. At present, the costs related to products obtained using CO₂ are still far higher than those involved in producing them by traditional methods of chemical synthesis (without utilization of captured carbon dioxide).

The current involvement of such major corporations as Audi, BASF or Bayer suggests that one should be moderately optimistic as far as further evolution of CO₂ utilization processes is concerned. High costs involved in the technological development of the processes, i.e. costs of investment in testing and pilot systems, require that not only domestic and EU-based public funding sources, but also industrial partners become involved.

The limited interest displayed by individual economic sectors with a certain potential for waste CO₂ utilization (e.g. chemical industry) is partially caused by reluctance to use new technologies and the increased risk involved in their application, as well as by the fact that, in many cases, the advantages of environmental protection are not accompanied by clearly noticeable economic benefits which, after all, are the drivers of industry. The limitations to the use of CO₂ for production of chemical raw materials also result from the magnitude of the market as well as from absence of investment incentives. What seems to be clear, however, is that integrated and interdisciplinary collaboration of chemists, en-

gineers and biologists may play a significant role in development and promotion of more prospective processes based on utilization of carbon dioxide.

Acknowledgments

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Project: CO₂ METHANATION SYSTEM FOR ELECTRICITY STORAGE THROUGH SNG PRODUCTION (CO₂-SNG)

Reference: 30_2014_IP108_CO₂-SNG

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