CO$_2$-to-methanol conversion – an alternative energy storage solution

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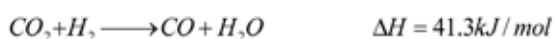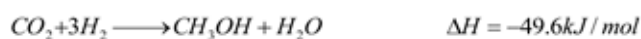
Introduction

Using carbon oxides in synthesis of fuels is an extensively researched subject, since studies devoted to this problem have been conducted as long as since the beginning of the previous century. The two major reactions were the Sabatier process, which consisted in carbon dioxide hydrogenation to methane, and the Fisher-Tropsch process, being extensively applied to obtain fuels through carbon monoxide hydrogenation.

On account of the contemporary environmental protection requirements, it is necessary to reduce emission of carbon dioxide, since it is commonly considered to be the main factor responsible for global climate changes. The CO$_2$ emission reduction technologies which are most frequently taken into consideration include CCS-based solutions which consist in carbon dioxide capture, transport and underground (predominantly) storage. However, 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. Nowadays, utilisation of carbon dioxide as chemical raw material is limited to several chemical processes, including mainly synthesis of urea, salicylic acid and polycarbonates. Additionally, CO$_2$ can be used in enhanced oil recovery (EOR).

For this reason, conversion of carbon dioxide to fuels appears as a good alternative for both carbon dioxide utilisation as well as storage of renewable and redundant electric energy.

Methanol synthesis from CO$_2$ and hydrogen

Most of the 40 million tonnes of methanol produced each year is the outcome of synthesis from fossil fuel-based syngas. Synthesis gas is predominantly a mixture of CO and H$_2$ with some additives like, for instance, carbon dioxide. The presence of carbon dioxide in syngas is advantageous from the perspective of methanol synthesis, since up to ca. 2% of such addition increases the reaction rate nearly one hundred times. However, higher concentrations of carbon dioxide are unfavourable, because the progress of methanol synthesis is disturbed [1]. An alternative method of methanol production is the synthesis from CO$_2$ and H$_2$, at the same time being a way to store energy. This method involves catalytic carbon dioxide reduction with hydrogen which proceeds according to the following reactions:

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O \qquad \Delta H = -49.6 kJ/mol$$

$$CO_2 + H_2 \longrightarrow CO + H_2O \qquad \Delta H = 41.3 kJ/mol$$

$$CO + 2H_2 \longrightarrow CH_3OH \qquad \Delta H = -90.9 kJ/mol$$

As an outcome of catalytic hydrogenation of carbon dioxide to methanol, water is formed as a by-product. The hydrogen is converted to water in 1/3, which proves to be a much higher value compared to classical methanol production from syngas. Moreover, the thermodynamic reaction of methanol synthesis from CO$_2$ and H$_2$ is less favoured than the reaction of synthesis from CO and H$_2$. The equilibrium yield of methanol obtained from CO$_2$ at 200°C is slightly below 40%, whereas with CO it is higher than 80% [2]. In itself, the conversion of CO$_2$ with H$_2$ to methanol is an exothermic reaction leading to a decrease in the number of particles, and therefore high pressures and low temperatures shift the equilibrium to the right (to CH$_3$OH). Separating the reaction products, i.e. water and methanol, will consequently increase the yield of the methanol formation reaction. The CuO/ZnO/Al$_2$O$_3$ catalyst which facilitates methanol synthesis from syngas has poor activity when carbon dioxide is hydrogenated at low temperatures (T<250°C) [3]. Increasing the temperature triggers activation of the reaction with CO$_2$, nevertheless the undesirable products (CO and H$_2$) are formed as a result of the inverse WGS reaction. Consequently, additional H$_2$ is consumed at the expense of reduced methanol production yield. Another issue to be mentioned is the water-induced acceleration of Cu and ZnO crystallisation, leading to rapid sintering and deactivation of the catalyst bed [4]. Moreover, other hydrogenation products such as higher alcohols and hydrocarbons are side products. For these reasons, it is crucial that a highly selective catalyst be applied. When using the mixture of H$_2$/CO$_2$ at the ratio of 3:1, the equilibrium yield of CO$_2$ conversion and the methanol selectivity at 250°C and 5 MPa equal 27 and 68% respectively. In order to obtain a high ratio of conversion, one must apply high pressure of ~30 MPa and temperature of ca. 125°C [5]. The data illustrating the dependence of the CO$_2$ conversion ratio from pressure and temperature have been provided in Figure 1.
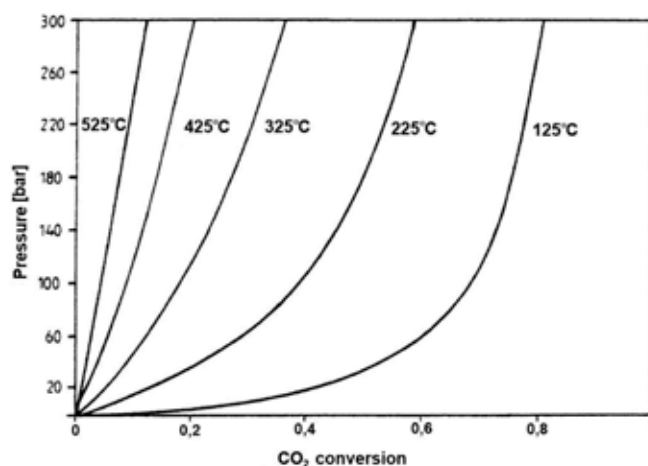

Fig. 1. Dependence of CO$_2$ conversion ratio in methanol synthesis from pressure and temperature. [5]

The data provided in Table 1 show that the CO$_2$ conversion ratio when using traditional fixed-bed tubular reactors is typically low regardless of the catalyst type used. High conversion can be

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achieved by using a recirculating reactor. Studies of the impact of operating parameters on gas conversion performed in a fixed-bed reactor using the $Cu/Zn/ZrO_2$ catalyst have shown a higher conversion ratio and higher selectivity compared to methanol produced at lower temperatures and higher pressure. Nevertheless these values were lower compared to a recirculating reactor. It can be seen from results provided in Table 1 that the most considerable effect on the ratio of CO_2 conversion to methanol is exerted by the type of reactor used.

<div align="right">Table 1</div>

Summary of studies on methanol synthesis from CO_2

Catalyst	Reactor type	T (°C) P (MPa)	CO_2 conversion ratio (%)	Selectivity to methanol (%)	Ref.
Effect of catalyst type					
$Cu/Zn/Ga/SiO_2$	Fixed-bed reactor	$T = 270$ $P = 2$	5.6	99.5	[6]
$Cu/Ga/ZnO$	Fixed-bed reactor	$T = 270$ $P = 2$	6	88	[6]
Cu/ZrO_2	Fixed-bed reactor	$T = 240$ $P = 7.6$	6.3	48.8	[7]
$Cu/Ga/ZrO_2$	Fixed-bed reactor	$T = 250$ $P = 2$	13.7	75.5	[8]
$Cu/B/Cr, Zr, Th/ZrO_2$	Fixed-bed reactor	$T = 170$ $P = 5$	25.9	72.9	[9]
$Au/Zn/ZrO_2$	Fixed-bed reactor	$T = 220$ $P = 8$	1.5	100	[10]
$Cu/Zn/ZrO_2$	Fixed-bed reactor	$T = 220$ $P = 2$	12	71.1	[11]
$Cu/Zn/Al/ZrO_2$	Fixed-bed reactor	$T = 240$ $P = 2$	18.7	47.2	[12]
$Pd/Zn/CNTs$	Fixed-bed reactor	$T = 250$ $P = 2$	6.3	99.6	[13]
$LaCr_{0.5}Cu_{0.5}O_3$	Fixed-bed reactor	$T = 250$ $P = 2$	10.4	90.8	[14]
Effect of reactor operating parameters					
$Cu/Zn/ZrO_2$	Fixed-bed reactor	$T = 250$ $P = 2$	19.4	29.3	[15]
$Cu/Zn/ZrO_2$	Fixed-bed reactor	$T = 240$ $P = 2$	17	56.2	[13]
$Cu/Zn/ZrO_2$	Fixed-bed reactor	$T = 220$ $P = 8$	21	68	[16]
Effect of reactor type					
$Cu/ZnO/ZrO_2/Ga_2O_3$	Recirculating reactor (CAMERE process)	$T = 600$ $P = 2,$ $R = 4$	61.81	89	[17]
$Cu/ZnO/ZrO_2/Ga_2O_3$	Fixed-bed reactor	$T = 600$ $P = 2,$ $R = 0$	16.04	79	[17]

Current state of research on methanol synthesis from carbon dioxide

It is considered to have been a milestone in the research on methanol synthesis from carbon dioxide that Lurgi AG and Sud-Chemie developed a highly active and selective catalyst for methanol from CO_2 and hydrogen at the temperature of 260°C. The catalyst's activity dropped at the same rate as in conventional catalysts for methanol synthesis from syngas. Another important fact to mention was the commissioning of the first pilot system for methanol production from CO_2 and H_2 (50 kg/h) using the $Cu/ZnO-SiO_2$ catalyst, which took place in Japan [18]. In 2009, the Mitsui corporation started their own pilot system for methanol production based on CO_2 with the capacity of 100 t per annum, using waste carbon dioxide and hydrogen from chemical syntheses [19]. The first commercially managed system of methanol production from carbon dioxide and hydrogen received from water electrolysis using geothermal energy was established in Iceland in 2012. The plant built by Carbon Recycling International produces more than 5 million litres of methanol per annum, consuming 5,500 tonnes of carbon dioxide for that purpose [20].

Conclusions

There are several PtL (*power to liquid*) research projects conducted at present, and they also cover large-scale systems. As for methanol synthesis, the first commercial system running with the capacity of 4000 tones per year has already been commissioned. CO_2-to-methanol synthesis is characterised by relatively low selectivity, and besides the main product, the higher alcohols and hydrocarbons are produced (where the selectivity ranges from 50 to 100% depending on process conditions), which makes it necessary that the final product is purified, for instance, by distillation. The carbon dioxide conversion ratio may reach as high as to 70% when products of the reaction are condensed and gaseous raw materials are recycled. A significant advantage of the technology is the utilisation of hydrogen in the reaction. In this respect, methanol synthesis is beneficial, since in terms of stoichiometry, 2/3 of hydrogen are reacted to the main product, and only 1/3 to water. The H_2/CO_2 ratio resulting from the stoichiometry is also favourable in methanol synthesis, as it comes to 3:1, whereas in SNG synthesis it is 4:1.

The reaction of carbon dioxide with hydrogen leading to formation of methanol is exothermic, however, the amount of energy which must be removed is more than three times smaller than in the aforementioned SNG synthesis.

The overall yield of the energy storage and reuse process (power-to-power) is rather beneficial. With methanol synthesis, if the product does not require being transported or converted to another form, the maximum yield which may be achieved equals 44.7% [21].
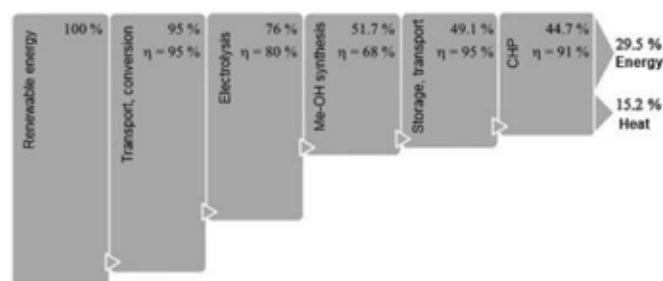
Fig. 2. Process chain for energy storage in methanol form. [21]

Furthermore, a crucial aspect of the methanol production technology is the progressing development of the electrolysis technology aimed at yield increase and cost reduction. Owing to 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 [21].

Problems related to developing efficient and economical systems for carbon dioxide conversion into useful materials, even though challenging, seem very prospective in times of continuously rising fuel prices and needs for the carbon dioxide emission reduction. The estimated quantity of carbon dioxide currently consumed for purposes of chemical syntheses accounts for a negligible fraction of the total amount of carbon dioxide released into the atmosphere. The amount of CO_2 released which can be utilised ranges between 5-7% [22]. The foregoing naturally involves specific costs to be incurred, like those related to chemical conversion of carbon dioxide and other reagents or carbon dioxide purification, storage and transport.

The process of purifying CO_2 from process gas can be costly, and so it may constitute the restricting stage. In different chemical syntheses, presence of impurities such as oxygen, sulphur or nitrogen oxides in the stream of CO_2 causes poisoning of the catalyst and consequently disqualifies it in terms of application.

Nevertheless, the most important factor constrains the evolution of processes in which carbon dioxide is consumed as the source of carbon atoms for purposes of chemical syntheses is the process economy. So far, the cost analysis conducted for the products received from syngas and CO_2 has shown unprofitability of CO_2 utilisation, since the said products would need to be offered at far higher prices compared to the goods available in the market and produced by classical methods.

Figure 3 provides a comparison of product costs for synthesis products received from CO_2 and market prices of the same products received using traditional methods. The diagram clearly implies that methanol, acetic acid or sodium carbonate production costs for carbon dioxide-based production are much higher than prices of the same goods produced by classical methods, which makes the former uncompetitive under the current economic and technological conditions.
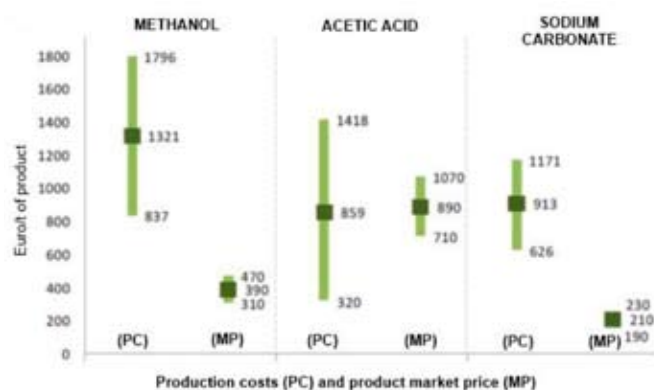

Fig. 3. Comparison of production costs for CO_2-based processes [23]

Figure 4 provides a comparison of values of the carbon footprint involved in production of methanol, acetic acid and Na_2CO_3 by application of traditional methods and with utilisation of CO_2. The environmental advantages resulting from the use of carbon dioxide in the synthesis processes of the said products are evident. However, for the sake of improved competitiveness in the market of chemical products, the prerequisite is the technological development of carbon dioxide-based processes, consequently leading to a drop in investment and operating costs as well as evolution of support mechanisms dedicated to such processes.
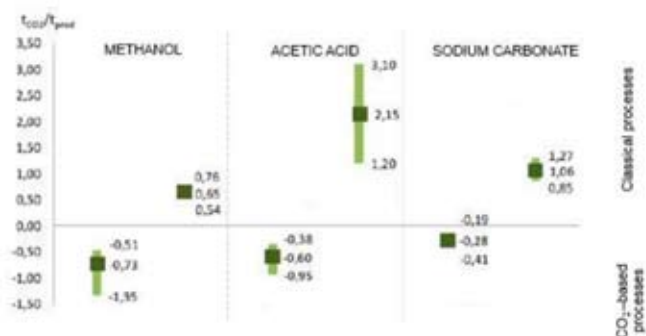

Fig. 4. Comparison of carbon footprint for methanol, acetic acid and Na_2CO_3 produced by application of traditional methods and using CO_2 [23]

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 CO_2 utilisation processes is concerned, since the high costs involved in the technological development of the processes (costs of investment in testing and pilot systems) require that not only public funds be allocated from science financing budgets based on domestic and EU sources, but also that industrial partners become involved, and that the approach towards CO_2 utilisation for commercial purposes should change. Both the distrust and the limited interest displayed by individual economic sectors with a certain potential for CO_2 utilisation (e.g. chemical industry) is partially caused by reluctance to use new technologies, or to be more precise, by 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 driving industry. The limitations to the use of CO_2 in 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, engineers and biologists may play a significant role in development and promotion of more prospective processes based on utilisation of carbon dioxide.

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Nominacje w konkursie PRIX GALIEN Polska'2016

13 września br. kapituła Prix Galien Polska pod przewodnictwem prof. Cezarego Szczylika ogłosiła listę nominowanych w 4 kategoriach konkursowych. W tym roku w konkursie pojawiło się 18 zgłoszeń – wiele na bardzo wysokim poziomie, spośród których kapituła wybrała nominowanych. Zwycięzców polskiej edycji tego najbardziej prestiżowego na świecie konkursu w zakresie medycyny i farmacji poznamy już 16 listopada br. podczas uroczystej gali, która w tym roku odbędzie się w Hotelu Hilton w Warszawie. *(kk)*

więcej na www.miesiecznikchemik.pl

(http://biotechnologia.pl/, 15.09.2016)

Zebranie sprawozdawczo-wyborcze Sekcji Dydaktycznej Wrocławskiego Oddziału PTChem

15 września 2016 roku w Sali Wałbrzyskiej Wydziału Chemicznego Politechniki Wrocławskiej odbyło się Zebranie Sprawozdawczo-Wyborcze Sekcji Dydaktycznej Wrocławskiego Oddziału Polskiego Towarzystwa Chemicznego.

Zebranych powitała przewodnicząca SD PTCh Krystyna Gans, która złożyła sprawozdanie z działalności Sekcji w upływającej kaden-cji. Przewodnicząca Zebrania, dr Krystyna Chmieleńska, przeprowadziła głosowanie nad wnioskiem o udzielenie absolutorium Zarządowi Sekcji, którego zebrani udzielili jednogłośnie.

Komisja wyborcza przeprowadziła wybory na przewodniczącego Sekcji, a następnie na członków Zarządu. Przewodniczącą Sekcji Dydaktycznej Wrocławskiego Oddziału PTChem ponownie wybraną została Krystyna Gans. Członkami Zarządu wybrani zostali: dr inż. Iwona Rutkowska – Wydział Chemiczny Politechniki Wrocławskiej; mgr inż. Ilona Kocel – Liceum Ogólnokształcące w Krotoszynie; mgr Stanisława Dudek – Gimnazjum nr 9 we Wrocławiu; mgr Dorota Czarnecka – Gimnazjum w Bogatyni.

W części merytorycznej zebrania wygłoszono dwa referaty: „Zmiany w oświacie" – *mgr inż. Krystyna Piosik,* Gimnazjum w Sułowie oraz „Współczesny kandydat na studia – strategia rozwoju procesu dydaktycznego na uczelni wyższej" – *dr inż. Iwona Rutkowska,* Wydział Chemiczny Politechniki Wrocławskiej

Zwieńczeniem Zebrania była dyskusja nad zmianami w nauczaniu, podczas której podnoszono konieczność podejmowania zadań oraz propozycji zmian do realizacji w przyszłości w związku z wdrażaną właśnie reformą oświaty.

(Inf. Krystyna Gans, 01 października 2016 r.)