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Production of fuels and chemicals based on the conversion of carbon dioxide biomass and methane

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ABSTRACT

In the circumstances of climate change caused by the rise in CO_2 emissions, the role of renewable energy sources, including those that generate carbon neutral cycles, is increasingly important. This mini-review addresses the pathways that should lead to the production of different types of fuels on the basis of conversions of methane (natural gas), biomass and even CO_2 that isstill considered as a component that cause climate change. Most of the chemical conversions are concerned with the involvement of hydrogen - an important constituent and are being targeted by scientists and energy companies to find the pathways, leading to the possibly cheapest production.

Introduction

The use of fossil fuels for production of electricity and in transport is a major and growing contributor to the emission of carbon dioxide - a greenhouse gas that contributes significantly to global warming and changing the world climate. The climate change is affecting, in one way or another, almost all countries, including Vietnam. One of the main problems that the world is now facing is how to satisfy the foreseen increase in energy demand using all available sources in the most efficient manner, and without increasing the emission of CO_2. In this consideration, together with other forms of renewable energy, such as solar and wind sources, the contribution of renewable fuels should be considerably increased.

Nowadays governments, scientists and energy companies are doing everything possible to accelerate the use of renewable forms of energy that do not increase CO_2 emissions, including biofuels. In fact, in recent years, solar and wind power has grown rapidly, supplying about 7% of the world's electricity; solar energy in the form of photovoltaic (PV) conversion increased by 28%/year and wind power - by 13%/year [1]. According to REN21 [1], biofuel is the largest renewable contributor to global final energy demand, providing nearly 13% of the total (mainly for heat and building), but the advanced biofuels provide only 3% of transport needs. Production of biofuels for transport increased 2.5% in 2017. The production and use of new transport fuels such as hydrotreated vegetable oil (HVO) have grown significantly over the last five years, and in 2017 HVO accounted for about 6% of total biofuel production by energy content. Progress also is being made in developing the technologies needed to produce advanced biofuels for aviation use, for example.

The last decade has witnessed the appearance of the concept the Methanol Economy, which has changed the perception of the role of CO_2 in chemistry and chemical engineering, leading to a number of advanced technologies in the reuse of CO_2 as a energycarrierand chemical raw materials.It is interesting and fascinating that the concept "the Methanol Economy" with CO_2 as an energy carrier can visualize the carbon cycle, in which biomass and methane also play their important roles in producing diverse products, including fuels and chemicals. On the basis of the carbon cycle in the diagram of the Methanol economy [2], the following reaction systems can be expressed for different chemical (thermal, thermo-catalytic) transformations (Fig.1):

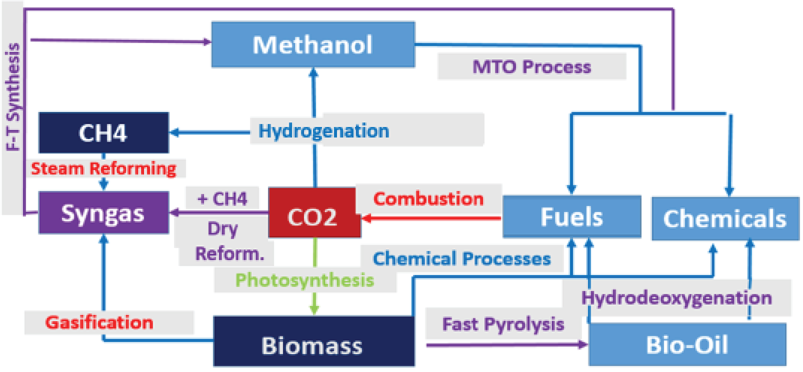

Figure1. Carbon Cycle including transformations of CO_2 biomass and methane to fuels and chemicals

Conversion of CO_2 to methanol

Key process in the Methanol Economy is the conversion of CO_2 into methanol through hydrogenation. This process is usually performed on different catalysts (homogeneous and heterogeneous) at low temperatures and high pressures [3]. On the typical conventionalcatalyst Cu-Zn/Al_2O_3 modified with different elements, the optimum reaction temperature is about 250 °C and the pressure is between 1 and 100 atm. Several mechanisms of the reaction have been proposed, however, there is still much debate among the various authors. At the present time there are not technological processes to be commercialized, but some companies (*BASF and bse Engineering*) are collaborating to upgrade the process scale to the industrial production[4]. The new process developed by *bse Engineering* enables the sustainable use of CO_2 and electricity current with small-scale delocalized production units built where the two components are generated, i.e. near power plants using renewable sources of energy as well as large-scale industrial plants producing CO_2. The excess current will be used to produce hydrogen through discontinuous electrolysis. In the second step, methanol is produced from CO_2 and hydrogen, thus leading to a valorizing of excess current and CO_2 off-stream gas. At the signing ceremony of exclusive joint development agreementbetween two companies Christian Schweitzer, Managing Director of *bse Engineering* said:"After four years of developing the global process concept, we are now ready to enter the licensing phase of this process, with construction of the first plants starting soon".

Conversion of methanol to fuels and chemicals:

Inthe Methanol Economy, methanol is considered as the base material for production of fuels and chemicals through the Methanol-to-Olefin process (MTO). So far, this process has been mainly carried out to convert methanol obtained from natural gas into olefins and fuel (gasoline, diesel). This is a trend that has been developed recently in China to produce fuels and chemicals from their poor quality coal through the gasification processinto syngas.Various forms of zeolite have been reported as effective catalysts for this process [5]. Some companies have commercialized this process primarily with the starting material methanol obtained from syngas. Since March 2018 UOP and Chinese partners startedthe operation of olefins production plant with capacity of 833,000 tons per year [6].

Conversion of CO_2 to methane

Another important direction of CO_2 conversion is methanation. Methanation is the classical reaction (H_2 + CO) to remove carbon monoxide for hydrogen cleaning, but methanation of CO_2 is of recent interest. Catalytic methanation reactors typically work at temperatures of 200-550°C and pressures ranging between 1 and 100 bar. Catalysts used in the methanation process are based on the metals of sub-group VIII (eg Ru, Rh, Pd, Co, Fe, Ni) supported on different oxide materials (Al_2O_3, TiO_2, CeO_2, MgO, NiO-$MgAl_2O_4$, NiO-K_2O-$MgAl_2O_4$, SiO_2, Cr_2O_3, ZrO_2, Al_2O_3-

CaO, La_2O_3). However, the nickel-based catalyst remains to be frequently used because of the relatively high activity, good selectivity towards CH_4 and low raw material prices. Among the studied Ni-based catalysts, the 12Ni$_3$Fe catalyst exhibited the highest CO_2 conversion of 84.3 % and nearly 100% CH_4 selectivity at 50,000 mL g^{-1} h^{-1} and 420°C. The enhancement effect of adding Fe on CO_2 meth anation was attributed to the dual effect of suitable electronic environment and increased reducibility generated by Fe species [7].

Energy production by this way is the basis of the Power-to-Gas concept (P2G). The P2G process uses electrolysis to convert excess electricity from fluctuating sources into hydrogen. It can either be used immediately or turned into methane by using carbon dioxide in a subsequent step. For this purpose, *ZSW* is currently developing electrolysers and synthesis reactors. Converting electricity to gas allows solar and wind power to be stored in the gas grid for several months. Hydrogen and methane can be used to power climate-friendly fuel cell vehicles or natural gas vehicles. The gas has a methane content of 99% meaning that it exceeds statutory requirements for gas feed-in. It was made possible by a membrane technology that was used to process the gas after methanisation. In Stuttgart there is a demonstration Power-to-methane plant (250 kW power input as capacity) founded by *ZSW* [8]. Audi's 6 MW plant in Werlte (Germany) is the world's largest P2G plant currently in operation.The plant began feeding Audi e-gas to the grid in the fall of 2013 and produces about 1,000 metric tons of e-gas per year, chemically binding some 2,800 metric tons of CO_2 comingfrom a waste-biogas plant. This roughly corresponds to the amount that a forest of over 220,000 beech trees absorbs in one year. Water and oxygen are the only by-products [9].

Conversion of CO_2 to synthesis gas

CO_2 can be transformed not only into methanol and methane, but also can interact with methane to produce synthesis gas through the process of dry reforming (DRM). This process is quite attractive due to the advantages of environmental protection [10]. It is known that CH_4 is 21 times more potent than CO_2 in increasing the atmospheric temperature. Dry reforming of methane (DRM) has gained much attention in recent years for its remarkable performance, converting CH_4 and CO_2 to synthesis gas. Thus, the DRM process not only reduces CH_4 and CO_2 emissions into the atmosphere, but also converts them to a valuable product, syngas. Various types of catalysts are reported in the literature for the DRM process, such as noble metals, spinels, perovskites, hydrotalcite, pyrochlore, and supported base metals. From an industrial point of view, supported nickel is the most appropriate catalyst for the DRM process due to its availability and low cost, but Ni-based catalysts are more susceptible to deactivation in high-temperature reactions than noble metal catalysts. This situation leads to the need to develop Ni-based catalysts with improved activity and stability. This can be done by using appropriate supports and preparation methods and adding modifiers, such as alkaline or noble metals. A number of papers have been published on improving the activity and stability of the catalysts, using: a bimetallic catalyst ($Ni–Co/Al_2O_3$) promoted with Sr or MgO, a Ni–Co/glass fiber spinel structure, a $Ni/(Al_2O_3/ZrO_2/Ce_2O_3/La_2O_3)$ modified with K and Li, an aerogel catalyst, a Rh-promoted Ni catalyst, an atomic layer dispersion method, and different modified Ni-based catalysts [11].

Conversions of Biomass to fuels and chemicals

The production of first generation biofuels (ethanol, biodiesel) has been said much. However, due to certain disadvantages, this development is slowing down; in recent years, the annual production of these fuels (conventional biofuels) has not increased, instead, the production of advanced biofuels has increased sharply. Advanced biofuels are produced from sustainable sources that are not considered competitive with food production systems or lead to loss of plant carbon by deforestation. Biofuels, which are produced from non-food crops or waste products, for example, plants grown on poor soil, or used cooking oils, animal fats through the first generation technology can also be called sustainable biofuels, sometimes classified as advanced biofuels although processing technology is not advanced. Thus, the main raw materials for producing advanced biofuels are agro-forestry wastes, grass and wood.

Biomass conversion to bioethanol is being carried out with the use of hydrolyzing enzymes and modified microorganisms. The process consists of three steps: pretreatment, hydrolysis and fermentation. Biomass is pretreated to improve the access of enzymes, then undergoes enzymatic hydrolysis to convert polysaccharides into monomer streams such as glucose and xylose. Next, sugar is fermented into ethanol using various microorganisms. In these three steps, the physico-chemical pretreatment of biomass is the most difficult due to the "recalcitrance" of lignocelluloses.

Advanced (sustainable) biofuels belong to the second generation biofuels. There are many chemical methods that produce these fuels [see review 12]. The first is to perform high-temperature gasification, which produces synthesis gas and continues to treat through the conventional Fischer-Tropsch synthesis (F-T synthesis) process for obtaining either alcohols or hydrocarbons depending on the reaction conditions and the catalysts used. Hydrotreating and esterification followed by hydrogenation/hydroisomerization of vegetable oils (HVO) is the conventional method of converting fatty acids and triglycerides into first generation biodiesel. The technology has been commercialized and implemented by UOP and its partners to produce high quality non-oxygenated green fuels that can be used in aircraft engines. The purpose of this process now is to produce HVO-products from sustainable raw materials, i.e.non-edible vegetable oils or non-compete with food production.

Recently, fast pyrolysis (Rapid Thermal Pyrolysis - RTP) method, producing bio-oil, followed by the reaction of hydrodeoxygenation to remove (completely or partially) oxygen in the bio-oil has been developed. The RTP stage is carried out at relatively low temperatures (below 500 °C), atmospheric pressure, which may not require a catalyst, however, for products obtained in the catalytic pyrolysis, the hydro-deoxygenation (HDO) process will be more favorable, with higher efficiency [13]. The HDO stage should be performed under conditions of hydrogen presence and usually under certain pressure. The Vietnam Petroleum Institute [14] has started research on RTP and HDO technologies. Agricultural wastes (straw, rice husk, corn cobs) have been tested for fast pyrolysis. Bio-oil derived from RTP process with high efficiency (50-60%), then upgraded by catalytic processes such as cracking or HDO and hydrogenation. The first results in this work demonstrate the potential for the production of new biofuel from materials based on agricultural wastes in our country.In recent years, the search for catalysts and technology for HDO of products obtained fromfast pyrolysis of biomass has been of interest to many researchers. Authors [15] have reviewed a series of projects over the past five years on the conversion of bio-oil on various catalyst systems such as MoO_3/SiO_2, Ni/SiO_2, Fe/C, Fe/SiO_2, $Ni\text{-}Fe/SiO_2$, $Pd\text{-}Fe/Al_2O_3$, Pt/MgO, $Pt\text{-}Ni/Al_2O_3$, Ru/ TiO_2 …In particular, the authors [16] performed the direct HDO of wood sawdust to liquid alkanes on catalyst $Pt/NbPO_4$ at 190°C and hydrogen pressure 5 MPa and obtained the total alkanes yield (in mass) about 20% (approximately 1/2 potential alkanes).

Production of Hydrogen

Hydrogen plays a decisive role in the processes of fuels and chemicals production described above. At present time, approximately 96% of hydrogen is derived from fossil fuels (steam reforming, catalytic reforming, thermal cracking…) and only 4% is produced via electrolysis. It should be emphasized that hydrogen production today is actually a large net generator of CO_2 emissions, with 13.7 kg of CO_2 produced for every kg of H_2, on average.

Hydrogen can be produced from biomass through gasification process. Although the cost of hydrogen production in this process is now higher than that in the process of hydrogen production from natural gas (via steam reforming), it could be reduced with the scale of production. It has been indicated that the conventional gasification results in about 50% hydrogen yield, but if using CaO as a carbon dioxide absorber, the yield can be increased up to 75% [17].

The current trend is to produce hydrogen from water through electrolysis. Hydrogen for the world's first methanol production plant in Iceland (G.A.Olah Plant) is supplied from a geothermal power plant. In recent years, with the continuous technological advances, global solar power capacity has increased at a rapid rate (28% per year) with reduced production costs. Energy companies are planning to use hydrogen from complexes, including a photovoltaic (PV) energy plant and an electrolysis unit for the processes of fuels and chemicals production developed. Rodriguez et al. [18] demonstrated that the cost of hydrogen is largely defined by the PV component (which accounts for up to 97% of the total cost) while materials selection for the electrolysis cell has only minor effects. Thus PV cells operating with solar concentrators can be expected to lead to considerable cost savings. The authors estimate that optimized systems can achieve costs below $2.90 per kg of hydrogen produced, including compression and distribution costs. This compares favorably with the U.S. Department of Energy’s stated goal of reducing the cost of hydrogen production to $2.00–$4.00 per gallon of gasoline equivalent delivered and dispensed by 2020.

Capturing and Utilization of CO_2

According to many statistics, the current emission of CO_2 into the atmosphere has reached about 35 billion tons/year and continues to increase. Professor G. Olah and coworkers indicated that it is possible to capture atmospheric CO_2 to produce methanol, however, in practice, the capture of CO_2 from flue gases of CO_2-emitting plants (power plants, cement plants) is definitely more efficient.Another source of CO_2 that needs to be considered is CO_2 in natural gas reservoirs, in which the CO_2 content is high or very high, for example, in some of the gas deposits discovered in Vietnam.The present technologies for capturing CO_2 from flue gases (e.g. gas absorption into solvents or onto sorbents, membrane permeation, cryogenic distillation) remain costly and impose significant energy penalties for CO_2 stripping and sorbent regeneration. Identifying membranes with high selectivity and permeability remains a great challenge. Photocatalytic processes capable of removing CO_2 and simultaneously converting it to marketable hydrocarbon products deserve attention.

Researchers from the University of Liverpool [19] have made a significant breakthrough in the direct conversion of CO_2 and CH_4 into liquid fuels and chemicals (e.g. acetic acid, methanol, ethanol and formaldehyde) with high selectivity at ambient conditions (room temperature and atmospheric pressure). This is the first time chemists have overcome a significant challenge of converting these two stable and inert molecules directly into liquid or chemical fuels without catalysts and high temperatures, high pressures and consume little energy. The one-step room-temperature synthesis of liquid fuels and chemicals from the direct reforming of CO_2 with CH_4 was achieved by using a novel atmospheric-pressure non-thermal plasma reactor with a water electrode and a low energy input. These results clearly show that non-thermal plasmas offer a promising solution to overcome the thermodynamic barrier for the direct transformation of CH_4 and CO_2 into a range of strategically important platform chemicals and synthetic fuels at ambient conditions. Introducing a catalyst into the plasma chemical process, known as plasma-catalysis, could tune the selectivity of target chemicals.

References

1. http://www.ren21.net/wp-content/uploads/2018/06/17-8652_GSR2018_FullReport_web_-1.pdf
2. G.A.Olah, et al, Beyond Oil and Gas: The Methanol Economy; Wiley-VCH: Weinheim, Germany, Second Edition (2009).
3. Ho Si Thoang, Renewable Fuels and "Methanol Economy"- The Presence and Perspectives,National Conference on Catalysis and Adsorption, Quy Nhon, August (2017)
4. https://www.basf.com/global/en/media/news-releases/2017/08/p-17-293.html
5. Wei Wang, et al, Catalysis Today,113, 102–114(2006)
6. https://www.chemengonline.com/worlds-largest-single-train-methanol-to-olefins-plant-now-operating/?printmode=1
7. Zhenhua Li, et al, Applied Organometallic Chemistry, 32(5):e4328. May 2018 DOI: 10.1002/aoc.4328
8. https://www.zsw-bw.de/en/research/renewable-fuels/topics/power-to-gas.html
9. http://biocat-project.com/news/biocat-project-visits-audi-e-gas-plant-in-werlte/
10. M. Usman, et al, Dry Reforming of Methane: Influence of Process Parameters – A Review, Renewable Sustainable Energy Rev., 45, 710–744 (2015)
11. Shalini Arora, et al, An overview on dry reforming of methane: strategies to reduce carbonaceous deactivation of catalysts.DOI: 10.1039/C6RA20450C (Review Article), RSC Adv., 6, 108668-108688 (2016)
12. Ho Sy Thoang, Vietnam Journal of Catalysis and Adsorption, 7, issue 1, 2 (2018)
13. Y. H. Wang,et al, Bioresources Technology, http://doi.org/10.1016/j.biortech.2011.12.132Get rights and content
14. Binh M. Q. Phan, et al, Biomass and Bioenergy Journal, 62, 74 (2014).
15. Y. Hong, et al, Catalysis Letters, 146 (9), 1621 (2016).
16. Q. Xia, et al, Nature Communication, 7, Article No.11162 (2016), DOI 10.1038/ncomms 11162.
17. https://www.researchgate.net/publication/225640604_Hydrogen_production_from_biomass
18. Claudia A. Rodriguez, et al, DOI: 10.1039/C4EE01453G (Analysis) Energy Environ. Sci., 7, 3828-3835 (2014)
19. https://phys.org/news/2017-10-breakthrough-co2-ch4-liquid-fuels.html

Li Wang et al, Angewandte Chemie (2017). DOI: 10.1002/ange.201707131