Journal of CO_2 Utilization 27 (2018) 326–354

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

Review Article

State of art and perspectives about the production of methanol, dimethyl ether and syngas by carbon dioxide hydrogenation

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ARTICLE INFO

Keywords:
Carbon dioxide
Methanol
Dimethyl ether
Syngas
Hydrogenation
CCU systems

ABSTRACT

The conversion of carbon dioxide into feedstock for the chemical and process industry is the most efficient way to rapidly introduce renewable energy in this value chain. Carbon capture and utilization systems are getting the attention from researchers in the last years, also due to the introduction of carbon tax in many States. Through the hydrogenation of carbon dioxide methane, hydrocarbons, ethanol, formic acid, methanol, dimethyl ether and syngas can be produced. However, methanol dimethyl ether and syngas have the lower value of lost hydrogen during the reaction, equal to 0.33, 0.25 and 0, respectively. Then, these compounds are analyzed in this review. Carbon dioxide is an industrial waste, while hydrogen is generally obtained by the electrolysis of water using surplus renewable energies. Processes and reactors reported in literature regarding the production of methanol, dimethyl ether and syngas by hydrogenation of carbon dioxide are analyzed. For the capture of carbon dioxide adsorption, absorption, membranes, cryogenic systems can be developed. An important role will have ionic liquids, under study by many researchers. Future research efforts should focus on dry reforming processes, innovative carbon dioxide capture techniques and hydrogen availability at reduced cost, and wider dissemination of these scientific and technical concepts to enlarge social acceptance.

1. Introduction

The need of finding new solutions for a clean and sustainable energy is becoming a critical factor for the future of society [1]. It is necessary to increase the share of use of renewable energy (RE) and valorize alternative raw materials. In other words, it is necessary to develop processes and technologies for a resource- and energy-efficient process industry. In this context, an important role is assumed by carbon capture and storage (CCS) and by carbon capture and utilization (CCU). These technologies promote the sustainability and circular economy, encourage industrial symbiosis and economic growth and enable the storage of renewable energy. This is in agreement with European policy 2020 that aims to reduce the 20% of GHG emissions by 2020. In fact, the storage and the utilization of CO_2 to produce other compounds contribute to achieve this objective.

Many works are present in the literature regarding the use of carbon dioxide as waste or cheap available raw material [2–5] but only Olha and Prakash [6] and Centi et al. [7] with three different routes discuss the integration of renewable energy and carbon dioxide to produce methanol and other compounds. The introduction of RE into the chemical production chain thus opens new challenges and interesting research perspectives. In fact, in addition to other chemical compounds, carbon dioxide may be used to produce many fuels.

An important metric to compare the different fuels is the EX_C, as the carbon fuel exergy content per mole of carbon. The exergy of a fuel refers to the maximum reversible work that can be generated from it. In general, EX_C gives an indication of the moles of carbon atoms needed to store one unit (MJ) of exergy in the carbon fuel. Thus, choosing fuels with higher value of EX_C reduces the carbon demand for storing a unit of exergy. Al-musleh et al. [8] provide the value of the carbon fuel exergy for different fuels, considering other metrics as $EX_{H\rightarrow C}$ as the exergy stored in the carbon fuel relative to hydrogen exergy during the carbon fuel synthesis step and the EX_V as the carbon fuel exergy content per unit fuel volume under storage.

Gases, such as methane, ethane and dimethyl ether have the higher value of EX_C equal to 806 MJ/kmolC, 723 MJ/kmolC, 685 MJ/kmolC, respectively. Liquids, such as methanol, ethanol and iso-octane have the higher value of EX_C equal to 693 MJ/kmolC, 654 MJ/kmolC, 652 MJ/kmolC, respectively. This parameter identifies favorable carbon fuel candidates that can be evaluated by conducting rigorous simulations or experimentation. Methanol and dimethyl ether, having the highest values, are chosen to be analyzed in this study, in addition to syngas, being a source that can be used to produce these two chemical compounds. The innovative production technologies of them and the used reactors are analyzed. Also, respect to other literature works, attention is posed to political legislations that encourage the use of renewable

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https://doi.org/10.1016/j.jcou.2018.08.005
Received 8 June 2018; Received in revised form 28 July 2018; Accepted 8 August 2018
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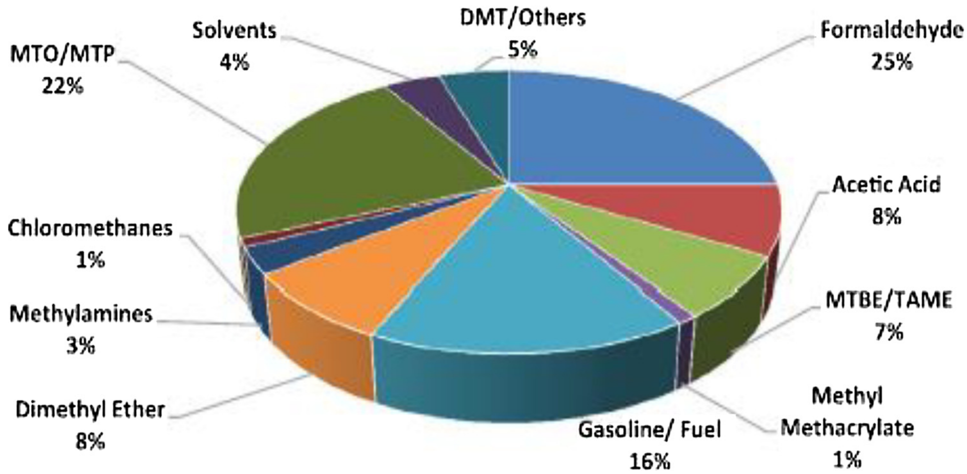

Fig. 1. Perspective of methanol demand by end use of $92.3{\cdot}10^6$ t in 2016 [9].

carbon dioxide. Carbon taxes and Emission Trading Scheme (ETS) are political means, used to promote the production of fuels from carbon dioxide and renewable energy. Literature works show that the hydrogenation of carbon dioxide is the most appealing way to produce methanol by technical and economic point of views and many compounds can be obtained, as shown in Fig. 1.

Different sources are used for carbon dioxide and hydrogen involved in the reaction.

However, future researches should be regarding alternative sources of molecular hydrogen in order to decrease the costs (the incidence of electrolyzer is about 65% of total costs). In addition to coke oven gas (COG) and chlorine alkali plant, syngas, methane steam reforming and petrochemical plants can be used to produce hydrogen. The same consideration can be treated for the carbon dioxide source: more integration with other chemical plants can be developed to recover CO_2 and to produce methanol and dimethyl ether (the latter can be obtained by methanol dehydration). The ammonia plant, for example, can be integrated to recover carbon dioxide and produce ammonia and methanol simultaneously. Iron, steel, cement plants are additional sources of carbon dioxide. An interesting technology under development is the co-electrolysis of carbon dioxide and water to produce methanol and syngas [10,11]. More attention should be posed about municipal and industrial wastes.

It is very important to study and diffuse the knowledge of the production of these fuels from renewable energy and by capturing carbon dioxide from other chemical processes. In fact, as reported by Jones et al. [12] the social acceptance of carbon dioxide utilization is very low and there is some skepticism about the long term environmental benefits. Then, better knowledge diffusion models are need. In this case, the social acceptance of policy and technology innovation is determined by the opinions and actions of stakeholders operating on three dimensions (i.e., socio-political, market, and community acceptance).

2. Production of useful chemical compounds from CO_2

CO_2 capture and storage (CCS) is an important technology to reduce the amount of greenhouse gas (GHG) emissions and mitigate the climate change in the future. Another option is the CO_2 capture and utilization (CCU). Although the CCU is an attractive approach, the market for the utilization of captured CO_2 is relatively small (11%–17%) compared to the total production of CO_2 [13,14]. However, compared to CCS, CCU reduces the CO_2 emissions and produces valuable fuels and chemicals [15]. An integration of CCS and CCU, known as CCUS, might be able to effectively utilize both advantages of the respective approaches, as enhancing both environmental and economic incentive [14]. In this context, the carbon dioxide is a waste that can be valorized and it is a key molecule to reduce the fossil consumption and to ensure the energy efficiency of processes. Also, the conversion of CO_2 into feedstock for the chemical/process industry is an efficient way to introduce the renewable energies in the chemical chain [7]. The main products, shown in Fig. 2, that can be obtained by CO_2 are: methane, syngas, hydrocarbons, methanol, ethanol, formic acid, dimethyl ether (DME) [16]. Hydrogenation of CO_2 is extensively researched in literature because it provides a direct route to methanol, methane, ethanol

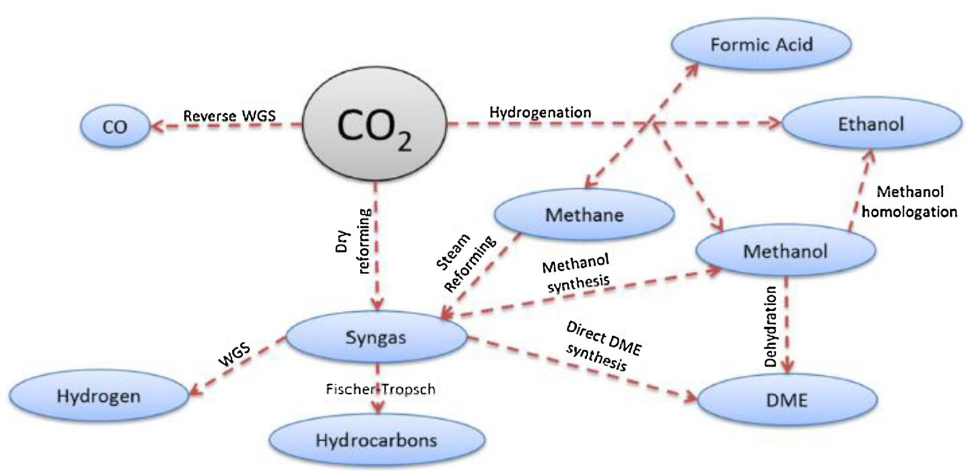

Fig. 2. Schematic representation of main reaction routes for CO_2 utilization [16].