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Efficient methanol synthesis: Perspectives, technologies and optimization strategies

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A B S T R A C T

In economy nowadays, methanol is already a key compound widely employed as building block for producing intermediates or synthetic hydrocarbons, solvent, energy storage medium, and fuel. This status is expected to last in the near future or even improve to the point of making this compound a central participant in the worldwide economic landscape. For these reasons, every improvement to its production process, in terms of energy savings, optimization, etc., has potential to promote relevant economic benefits. Methanol production comprises three main steps: preparation of syngas, methanol synthesis and downstream separation. This paper aims at reviewing technologies and procedures for modeling and optimizing the second aforementioned phase: the synthesis reactor. Specifically, we focus on packed-bed units, which represent the most widespread technology. In the manuscript, we are going to describe and compare both steady-state and dynamic reactor models as well as analyze typical assumptions and implementation schemes. The kinetics of methanol synthesis is also reported in detail due to a long debate, present in the literature, concerning the real carbon source for methanol, the nature of the active sites and the effect of their morphology and oxidation state.

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1. Introduction

Large amounts of energy must be consumed to preserve humanity's actual living standards. Oil, natural gas and coal, still constitute our principal energy sources and offer the raw materials for producing a large variety of derivatives. Unfortunately, these resources are limited and not renewable on the human time scale, thus we will probably run out of coal, oil and natural gas within 3 centuries [1]. For this reason, all feasible alternatives must be investigated to seek feasible and long-term solutions. Besides the problem of power generation, an important question is/will be how to store and efficiently use energy. The utilization of hydrogen is an option that is being discussed worldwide. However, its storage and transportation raises serious (safety) problems, and no infrastructures are available. A feasible alternative could be liquid methanol. Methanol can serve as convenient energy storage medium, easily transportable fuel, solvent and building block for producing intermediates and synthetic hydrocarbons, also including polymers and single-cell proteins. Therefore, it might be a key compound in the global economy of the future.

The methanol economy [2], based on green-methanol synthesis pathways, has been proposed in contrast to the hydrogen economy, which requires a deep change in energy storage and transportation means. Methanol has an octane number of 113 and its energy density is about half of that of gasoline (by volume). The blend of 10%/90% methanol/gasoline can lead to an octane up to 130. Pure methanol engines can reach efficiency close to 43% and maintain it above 40% in a wide speed and load range [1]. Methanol can favor the transition from fossil fuels to renewable energies. Later on, we will briefly comment on green processes for methanol production.

Other than the traditional production pathway via synthesis gas, methanol could be manufactured in different and new ways. The carbon source may be natural gas (in this case, methanol could be directly produced at the gas well by direct oxidative transformation) or CO_2, which can be recovered from industrial sites and, eventually, from the atmosphere. This second production pathway would allow mitigating global warming due to the increasing presence of greenhouse gases in the atmosphere. All energy sources can be exploited for methanol production, thus the "Methanol Economy" offers a feasible means of using and storing all sources of energy (renewable, atomic, etc.). At this point, it is clear how important methanol may be for our future economy. Since improvements in methanol synthesis process are still feasible, there is great research interest in this field. New production technologies have been proposed after the first process start-up [3], which are principally aimed at reducing investment costs (relevant for methanol production). The modeling of methanol manufacturing process, and particularly the reactor model, allows improving energy savings and optimizing the production itself. Therefore, this review focuses on modeling strategies and optimization techniques for the methanol synthesis reactor.

1.1. History

Methanol was first isolated by Robert Boyle in 1661 via wood distillation while its chemical composition was first discovered by Dumas and Peligot in 1834. At that time, production volumes were still small, e.g. 10–20 L per ton of wood treated for charcoal manufacturing. Initially, it was used for lighting, cooking and heating purposes but it was quickly replaced by more economical fuels. On the other hand, methanol was increasingly required by the chemical industry. In 1905, Sabatier proposed the first synthetic pathway for producing methanol, which implied reacting CO and H_2. Based on this earlier discovery, the Badische Anilin und Soda Fabrik (BASF) patented a syngas-based methanol production process, where syngas was supplied via coal gasification. This process required a zinc/chromium oxide catalyst as well as high temperature and pressure (300–400 °C and 250–350 atm). It was first deployed in Leuna, Germany, in 1923. The following technology developments aimed at reducing the pressure and temperature levels in order to improve process economics. Thanks to the invention of the steam reforming of methane, which allowed producing a purer syngas, a more active Cu/ZnO catalyst could be employed, thus decreasing the process temperature and pressure to about 300 °C and 100 atm. This significant improvement was proposed by ICI (Imperial Chemical Industries) in 1966. Few years later, Lurgi developed a process with even lower operating pressure and temperature (230–250 °C and 40–50 atm). Subsequent developments further improved the process such that, nowadays, the production of methanol from carbon dioxide can be considered a mature technology. In fact, the actual methanol selectivity is over 99.8% with an energy efficiency of around 75%. Most of the current research efforts are now targeted to finding new ways to synthetize methanol using both diverse origin carbon dioxide/hydrogen feeds and different chemistries, e.g. the direct oxidation of methane.

Nowadays, methanol is used as primary feedstock for a large variety of chemicals. Among the most important, we can mention formaldehyde (it consumes about 70% of the methanol produced worldwide), methyl-tert-butyl ether (MTBE, 20%), acetic acid and dimethyl ether. In addition, a variety of intermediates employed in manufacturing many products of our daily life derive from methanol: paints, resins, silicones, adhesives, antifreeze, plastics, and so on. Methanol is also used as transportation fuel in addition to gasoline, and in the future, it will certainly play an increasing role in such field. In fact, the emissions (hydrocarbons, NOx, SOx and particulate) associated with it are reduced. However, before being able to use pure methanol as fuel, we still need to solve issues like metal corrosion (especially, aluminum, zinc and magnesium can be attacked) and/or cold engine start, which is related to the absence of highly volatile compounds. In any case, adding a certain percentage of methanol to gasoline improves the performance of internal combustion engines (ICE), thus mixtures of methanol and gasoline are already being marketed. In China, starting from 2009, national fuel blending standards of M85 (85% methanol, 15% gasoline) and M100 (100% methanol) went into effect, and M15 standard is in adoption. In Shanxi province alone, there are more than 1000 petrol stations, which are equipped to sell M15, and other 40 M85-M100 refueling points are present. The Shanxi government plans to expand rapidly the number of vehicles using methanol and the number of petrol stations. Therefore, China appears to play a leading role in the methanol market and, consequently, the global methanol demand is growing rapidly as shown in Fig. 1.

The development of fuel cell vehicles (FCV) will certainly involve the use of methanol as hydrogen carrier. Direct methanol fuel cells (DMFCs) are under development for a number of possible