ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

Clean coal technologies in China based on methanol platform

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ARTICLE INFO

Keywords:
Clean coal technologies
Methanol economy
Methanol
Derivatives
Sustainable energy system

ABSTRACT

Coal is the most abundant fossil energy, however, coal industry is threatened by its environmental problems caused by the traditional way of utilization. In recent years, China has developed a series of clean coal technologies to transform black-dirty coal into clean fuels and chemicals. Shenhua Group, the largest coal company in China is leading the commercialization of modern clean-coal technologies for value-added chemicals and clean transportation fuels, in which CO_2 is captured in the process and ready for carbon capture, utilization and storage (CCUS). Industrial plants for coal based methanol production and conversion are flourishing in last decade. With the development of renewable H_2, methanol production could be realized by CO_2 hydrogenation to transform into "Methanol Economy", the sustainable energy development system. This paper will focus on the overview of research and development of methanol-based coal conversion technologies in China, such as methanol synthesis, methanol to olefins (MTO), chemicals (formaldehyde, acetic acid, aromatics, ethanol, ethylene glycol, etc.), gasoline (MTG), dimethyl ether (DME), polyoxymethylene dimethyl ethers (DMM*n*), methyl *tert*-butyl ether (MTBE), direct combustion (DMFC), and as energy carrier. Commercial and successfully demonstrated units in China on both the synthesis of methanol and its utilization are discussed in detail.

1. Introduction

Coal is the most abundant fossil energy source which was used to provide energy for heating and cooking for centuries, powered the steam engine, used for steel production, and provided coal chemicals for more than a century. Since the petroleum was introduced, coal gradually quit from the usage as transportation fuels and chemicals in the western world, and nowadays mainly used for power generation in coal powered plant. Currently, about 30% electricity is still generated from coal in the United States based on the data of Energy Information Administration (EIA). In China, the situation is different. The characteristic of China's energy reserves is rich in coal, deficient in petroleum oil and lean for natural gas. China has become the world top coal producer and consumer during the rapid economic development of three decades. According to EIA data, coal production in China in 2014 is 3.84 billion metric ton per year. Over 75% of electricity and 67.5% of primary energy are provided by coal which occupies a predominant role for energy in China. Besides using coal as a fuel for power plants, coal is also widely used in domestic and industrial heating, synthesis of ammonia, chemicals derived from coal tars, calcium carbide and coke oven gases. In the last decade, clean-coal technologies are flourishing marked by commercialization of a number of large coal conversion plants in China. Shenhua group took the lead to commercialize the first (600,000 metric ton/a) MTO plant in Baotou, Inner Mongolia, and the first direct coal liquefaction plant (one million metric ton/a) in Erdos, Inner Mongolia, China, and the largest indirect coal liquefaction plant (4 million metric ton/a) in Ningxia, China. Other coal conversion technologies are also commercialized in China, such as coal to synthetic natural gas (SNG), coal to gasoline, coal to dimethyl ether (DME), and coal to ethylene glycol. Finished demonstrations and commercial plants of coal to aromatics and polyoxymethylene dimethyl ethers (DMM*n*) are building up. Unlike other part of the world, ammonia synthesis and methanol synthesis are using coal rather than natural gas to provide energy and carbon. Most ammonia plants in China are integrated with methanol plants to adjust the production according to market, which provide a substantial portion of methanol production capacity.

Although the reserve of coal is larger than petroleum and natural gas, coal is usually associated with black and dirty. Coal is rich in carbon, and it will emit more carbon dioxide than natural gas and petroleum when generating same amount of energy. For coal fired power plant, most pollutants such as SOx, NOx are captured, and the emissions of particulate matter. However, CO_2 capture is costly for coal fired power plants. Coal conversion through gasification has the merit of capturing CO_2 in the process which greatly reduced the cost. The captured CO_2 could be used as the carbon source to synthesize methanol with the hydrogen produced by electrolysis of H_2O using renewable energy such as wind and solar [1,2].

Methanol is the smallest alcohol. Compared to other alcohols, it

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http://dx.doi.org/10.1016/j.cattod.2017.05.070
Received 30 December 2016; Received in revised form 9 May 2017; Accepted 27 May 2017
0920-5861/

Please cite this article as: Xu, X., Catalysis Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.05.070

does not have a carbon–carbon bond. Contrast to other C1 molecules, methanol is a stable liquid at ambient conditions. This feature establishes a special position for methanol in C1 chemistry, both as a finished chemical product and an intermediate for a variety of chemicals and fuels. Methanol is easily synthesized on copper-based catalysts from synthesis gas which can be derived from natural gas, coal or any carbonaceous materials. Methanol can also be easily decomposed into synthesis gas or reformed into H_2, so besides the wide usage as a bulk chemical product, methanol is also an excellent energy carrier. Compared to the Fischer-Tropsch synthesis, coal conversion through methanol platform is more flexible on adapting to the fuels and chemicals needs of different regions. With subsequent methanol conversion processes, methanol platform is more sustainable to support the society than the current petrochemical platform.

In last ten years, coal conversion through methanol platform has been proven to be successful both technologically and economically. In this paper, we would not intend to review the methanol platform or individual processes of methanol conversion technologies, rather to focus on the clean coal technologies which have been commercialized or demonstrated to be successful in China. We hope the successes of the clean coal technologies in China would spur the commercialization activities around the globe.

2. Methanol synthesis techniques

Chemically-synthesized methanol could be traced to 1923, chemists of BASF successfully synthesized methanol from synthesis gas (syngas), a mixture of hydrogen (H_2) and carbon monoxide (CO), together with small amount of carbon dioxide (CO_2). The reaction was performed on zinc-chromium (Zn-Cr) catalyst under harsh condition, 30–35 MPa and 300–400 °C Eq. (1)–(3). Starts from 1960s, Imperial Chemical Industries (ICI) Katalco developed methanol synthesis catalyst using copper-zinc (Cu/ZnO) under low pressure, 5 MPa and a relative mild temperature of 200–300 °C. Thereafter, copper-based methanol catalyst (Cu/ZnO/Al_2O_3) became dominant for methanol synthesis in industrial basis to this day. Recently, researchers' interest on copper-based methanol synthesis catalysts is still very active [3–5].

Methanol synthesis: $2H_2 + CO \rightarrow CH_3OH$ (1)

Water-gas shift: $CO + H_2O \rightarrow CO_2 + H_2$ (2)

Methanol synthesis: $3H_2 + CO_2 \rightarrow CH_3OH + H_2O$ (3)

In the process of coal to methanol, syngas is derived from coal and water via gasification process Eq. (4). The produced syngas usually possesses a lower ratio of hydrogen to carbon, which is not efficient to be used directly on methanol synthesis. Water-gas shift (WGS) is used to adjust the H_2/CO ratio suitable to methanol synthesis. CO_2 and sulfur are removed in subsequent steps to ensure sulfur and other pollutants in ppb level. Apart from coal gasification method, syngas can also be obtained from natural gas, coke-oven gas and ammonia synthesis plant, then methanol was produced following above-mentioned procedures. The integrated methanol production with ammonia plant becomes attractive when syngas is a waste feed in ammonia plant or the price of methanol become high enough to gain profit.

Coal gasification: $3C + O_2 + H_2O \rightarrow H_2 + 3CO$ (4)

Industrial methanol production in China was initiated since 1950s [6]. Driven by economy and the growing demand in methanol derivatives, such as olefins, formaldehyde, acetic acid, dimethyl ether (DME), aromatics, gasoline, methyl *tert*-butyl ether (MTBE), etc., China nowadays has become the largest methanol producer in the world. Fig. 1 summarizes methanol production capacity of China comparing with global methanol capacity through recent years [7]. Table 1 lists the mega-methanol commercial units, in which each unit possess methanol

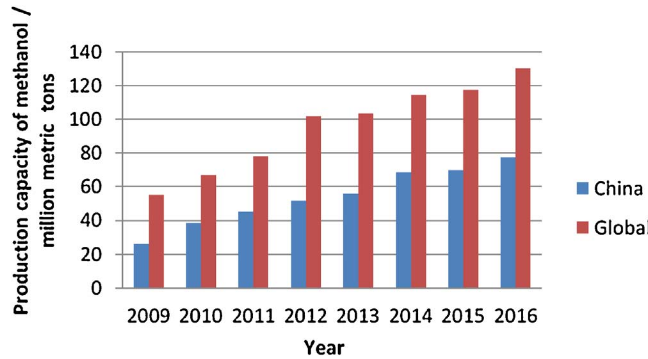

Fig. 1. Production capacity of methanol between China and global 2009–2016 [8].

capacity over one million metric ton/a.

According to the statistical data of Aisa Chem, worldwide methanol production capacity in 2015 is 103.2 million metric ton, and China with 65.7 million metric ton holds the top spot [9]. Due to the characteristic of energy reserves and impact on local policy in China, around 70% of the methanol was produced from coal. Statistic data in 2015 (Fig. 2a) show that produced methanol in China were mainly converted to olefins (35.5%), DME (9.2%), MTBE (3.4%), MTG (3.8%), methylamine (2%) and methane chloride (3.1%); oxidized to formaldehyde (24.4%) and acetic acid (4.5%); directly as fuel or additive in gasoline (11.2%).

Since the rapid development of methanol conversion plants, projected methanol derivative sharing ratio changed greatly. Large increase in coal to chemicals was projected based on the under-construction and planned methanol conversion plants. The share in coal to chemicals will increase to 61.4% (Fig. 2b), which mainly due to the expansion of MTO/MTP capacity and MTA commercialization.

3. Methanol derivatives

3.1. Methanol to olefins (MTO)

Methanol to Olefins (MTO), an acid catalyzed reaction, is one of the most effective ways to transfer methanol to high-value added chemicals Eq. (5). Began in 1977, Mobil found molecular sieve ZSM-5 active in MTO reaction and obtained propylene ($C_3^{=}$) and butylene ($C_4^{=}$) olefins as major products due to relative large pore size (about 5.5 Å). Thereafter, SAPO-34 had relative smaller pore size (4.3 Å) and optimized acidity by comparing with ZSM-5, that was discovered to be a high-selective MTO catalyst, especially for ethylene ($C_2^{=}$) and $C_3^{=}$ products. Universal Oil Products (UOP) cooperated with Norsk Hydro (Hydro) developed MTO technique using crude/fine methanol as feed. The first test performed in 1995 with a continuous run of 90 days and obtained $C_2^{=}$, $C_3^{=}$, and $C_4^{=}$ in yield of 40%, 30%, 9%, and byproducts, respectively [10]. With the improvement of technology, combined olefin synthesis technique of UOP with total's olefin cracking process, the selectivity to low carbon olefins in MTO could reach 85–90%.

$n\mathrm{CH_3OH} \rightarrow C_2^{=} + C_3^{=} + C_4^{=} + n\mathrm{H_2O}$ (5)

China is also very active in MTO research, back to 1980s, Dalian Institute of Chemical Physics (DICP) took the lead in developing their own dimethyl ether/methanol to olefin techniques (denoted as DMTO) using ZSM-5 and SAPO-34 molecular sieves as catalysts. They also initiated the world leading technique from syngas to olefins via DME pathway (SDTO) [11]. The two-step technique allows nearly full conversion of CO and a 5–8% of saving at total cost comparing to one-step MTO method. In 2004, DICP together with SYN Energy Technology Co., Ltd. and Sinopec (Luoyang Petrochemical Engineering Corporation) launched the first 10,000 metric ton scale of MTO plant in the world, which could achieve a throughput of methanol in 50 metric ton/d. In 2009, Shenhua group built up the first commercial unit of MTO plant