CHAPTER
4
CARBON DIOXIDE AS RESOURCE FOR METHANOL PRODUCTION

Amirul Hafiiz Ruhaimi and Muhammad Arif Ab Aziz

4.1 INTRODUCTION

As the world is currently facing a rapid industrialisation growth rate and an increase in world population, this has directly affected the rate of global greenhouse emissions. According to the report associated with this matter, the emission of carbon dioxide (CO_2) in the atmosphere has gradually increased since the 1990s until the latest data recorded in 2016. In the 1990s, the annual emission was recorded at about 0.9%; up until the 2000s, the emission has increased to 3.0% (Peters et al., 2020). Moving to 2010, the annual emission rate has reduced back to 0.9%, and according to the data from 2014 to 2016, the rate goes even lower. The trend seems promising in preventing serious environmental problems associated with excessive greenhouse gas emissions, such as global warming and climate instability. This intercorrelation was related to the CO_2 gas, where if the concentration of CO_2 in the atmosphere increased up to a certain ppm, its properties and durability would influence the global temperature. CO_2 possesses the ability to adsorb and re-radiate heat; thus, with other significant properties of long-lived gas, it will amplify the greenhouse effect, which will then influence the increase of the earth's temperature (Lindsey, 2023; Ruhaimi et al., 2022).

Due to this concern, numerous investigations have been conducted at both bench-scale and industrial levels to address the issues of carbon emissions. These studies encompass carbon reduction through gas separation (capture) techniques, carbon utilisation, and geological storage, which together constitute the carbon capture, utilisation, and storage (CCUS) approach. The primary goal of CCUS is to reduce global anthropogenic CO_2 emissions and mitigate their current and future environmental and societal impacts. Within this framework, the principle of carbon capture and utilisation (CCU) involves converting captured CO_2 into valuable products, while carbon capture and storage (CCS) focuses on the geological storage of compressed CO_2 in onshore and offshore reservoirs, often filling voids created by fossil fuel extraction. A critical component of CCUS lies in the capture stage, where CO_2 is separated from emission streams using techniques such as membrane cryogenics, absorption, and adsorption. These methods have shown promising results across different gas streams with varying concentrations and compositions, including pre-combustion, post-combustion, and oxy-fuel combustion processes (Figure 4.1) (Ruhaimi et al., 2021). Among these, absorption is one of the most established and widely applied methods; however, its limitations have restricted large-scale implementation, prompting further investigations into alternative separation techniques.

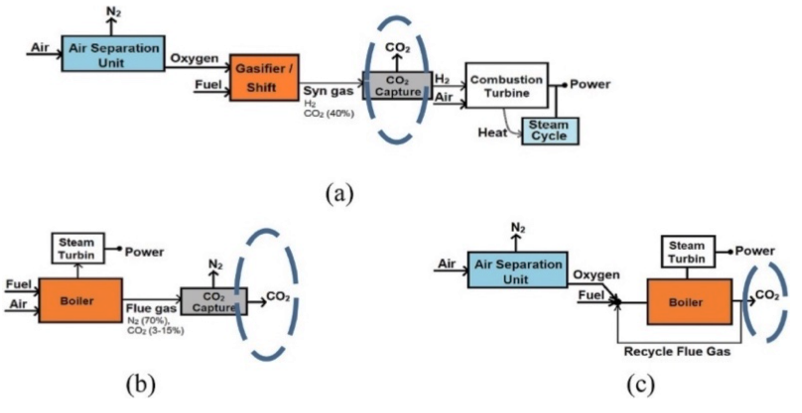

Figure 4.1 Schematic illustration of carbon capture: (a) Pre-combustion, (b) Post-combustion, and (c) Oxy-fuel combustion (Source: Rajabloo et al., 2023)

4.2 CARBON CAPTURE AND UTILISATION

The carbon utilisation routes offer advantages using both catalytic and non-catalytic pathways. One was to provide better economic and industrial feasibility compared to CCS. Even though both routes, CCU and CCS, have similar main limitations, which are high separation, conversion, and compression costs, the CCU will generate a return in price as the product is generated (Ruhaimi et al., 2022). The continuous product produced will compensate for the cost invested in the capture and conversion process, thus reducing the overall processing cost. Compared to CCS, the operating cost was heavily invested in the compression process and transportation of the captured CO_2, with only a minor cost return. In recent studies, the catalytic captured CO_2 utilisation has been classified as reactive capture of CO_2 (RCC), which involves process integration and combination of multiple processes, and at the same time, some others are removed (e.g., does not require a release of CO_2 from capture medium) (Siegel et al., 2023). Thus, an intermediate storage process of captured CO_2 is not required.

Catalytic CO_2 utilisation has become a headline nowadays as it is capable of generating a primary chemical compound that can be used on a wide industrial scale. Considering the promising potential of CO_2 as a chemical feedstock, its versatility has encouraged tremendous studies to utilise CO_2 as a raw material in fabricating valuable chemical molecules. Examples of possible products developed from CO_2 catalytic reactions, particularly via the gas-phase CO_2 hydrogenation pathway, are C_1 and C_2^+ compounds. C_1 products contain one-carbon compounds, e.g., carbon monoxide (CO), CO_2, methane (CH_4), and methanol (CH_3OH). The other two or higher carbon species-containing compounds were categorised under the C_2^+ product. Some of the C_1 compounds were able to undergo an extended process for further conversion, forming a C_2^+ product (Figure 4.2). Comparing both individual synthesis processes, the C_1 product synthesis process is less challenging, whereas in C_2^+, there are several process complexities faced, e.g., a high C-C bond coupling barrier and multiple competing reactions the between C_2^+ and C_1 products (Ye