1. Introduction

As the dominant greenhouse gas, carbon dioxide (CO_2) emission was the major cause that accounted for global warming and climate chance. Figure 1-1(a) shows that the amount of carbon dioxide in the atmosphere has increased along with human emissions over the past two hundred years (Lindsey, 2023). The amount of CO_2 in the atmosphere has indeed increased along with human emissions since the start of the Industrial Revolution in the 18th century. Emissions of CO_2, primarily from the burning of fossil fuels such as coal, oil, and natural gas, have risen steadily over time. The increase in CO_2 in the atmosphere is a major contributor to climate change and global warming. The Intergovernmental Panel on Climate Change (IPCC) estimates that human activities, primarily the burning of fossil fuels, are responsible for about 78% of the increase in CO_2 in the atmosphere since 1750 (Al‐Ghussain, 2019). The rise in CO_2 emissions has been particularly steep since the mid-20th century, with emissions increasing from about 5 billion tons per year in the mid-20th century to more than 35 billion tons per year by the end of the century (Levine and Steele, 2021). Figure 1-1(b) shows the total fossil energy consumption since the 1850s (Gilmore et al., 2022; Höök et al., 2012). The concentration of CO_2 in the atmosphere was relatively stable at around 280 parts per million (ppm) for thousands of years before the Industrial Revolution. However, since the start of the Industrial Revolution in the 18th century, human activities such as the burning of fossil fuels and deforestation have resulted in a significant increase in CO_2 emissions. As a result, the concentration of CO_2 in the atmosphere has risen from below 300 ppm in pre-industrial times to over 410 ppm in recent years (Drag et al., 2020). This increase in CO_2 concentration is a major contributor to climate change and global warming, as CO_2 acts as a greenhouse gas, trapping heat in the atmosphere and leading to an increase in average global temperatures. It can be seen that the global warming is closely related to human activities, especially the massive use of fossil fuels, which leads to a continuous increase in atmospheric CO_2 concentration. Noticeably, emission reduction has drawn more and more attention in the international community during the past decades.

In order to deal with these challenging threats, human society worldwide is actively responding and taking relevant measures. As a vital positive result and guideline for action, the Paris Agreement was reached and proposed to control the temperature increase within 1.5-2 °C by reducing carbon emissions and achieving climate and carbon neutrality (Rogelj et al., 2016; Stua et al., 2022). In order to fulfill the commitments, carbon reduction techniques such as carbon capture, utilization, and carbon storage (CCUS) have received significant interest globally.

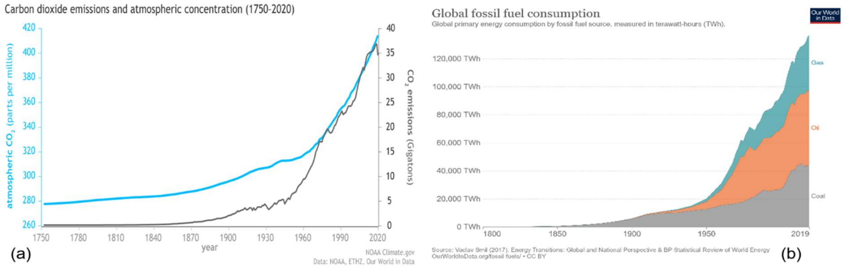

Figure 1-1. (a) CO_2 emissions and atmospheric concentration. (b) Global fossil fuel consumption.

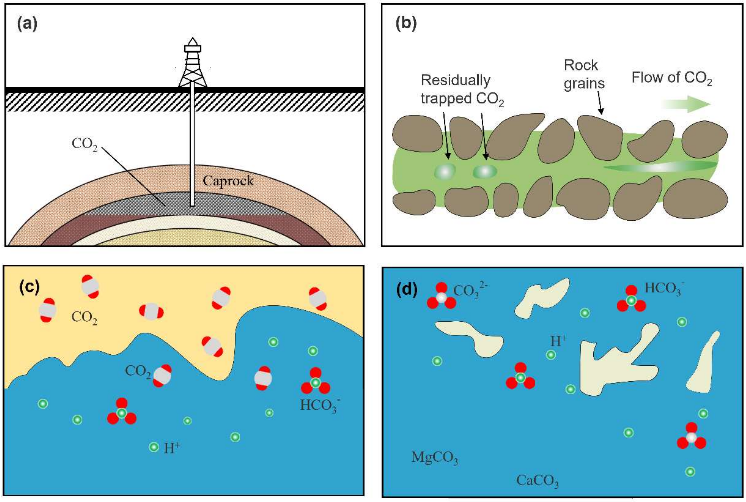

Figure 1-2. (a) structural trapping; (b) residual trapping; (c) solubility trapping; (d) mineral trapping.

As an important carbon emission reduction method, CCUS technologies can help with achieving the global greenhouse gas and climate change control targets. CCUS involves the capture of CO_2 from significant point sources, including power generation or industrial facilities that use either fossil fuels or biomass for fuel, while it can also be captured directly from the atmosphere. Depending on its location, carbon storage can be categorized as either onshore storage or offshore storage. Among them, terrestrial geologic storage includes injection into deep saline aquifers, oil and gas fields, and deep coal seams. If not being used on-site, the captured CO_2 is compressed and transported by pipeline, ship, rail, or truck to be used in a range of applications or injected into deep geological formations, which trap the CO_2 for permanent storage. The mechanisms of CO_2 storage in terrestrial geologic formation include structural trapping, residual trapping, solubility trapping, and mineral trapping (Figure 1-2) (Luo et al., 2023) (Alanazi et al., 2023). Structural traps refer to the accumulation of carbon dioxide in deep saline formations and depleted oil and gas reservoirs. The injected CO_2 usually moves upward, however, due to the existence of caprocks (Knopf and May, 2017), CO_2 leakage can be effectively avoided. As a physical trapping of CO_2 in the pores, structural trapping is the mechanism that traps the greatest amount of CO_2. Residual trapping involves the transport of carbon dioxide and water (Ge et al., 2022). As a response to the CO_2 injection, the water saturation of the pores will decline while the CO_2 saturation rises, leading the carbon dioxide to be trapped in the pore and pore throat space between the rock grains. In solubility trapping, a portion of the injected CO_2 will dissolve into the brine water leading to solubility trapping, which depends on the water salinity, reservoir temperature and pressure (Gilfillan et al., 2009). It should be pointed out that since the buoyancy is caused by density contrast, CO_2 could migrate upward in the terrestrial storage reservoirs consequently, hence an impermeable sealing layer is indispensable, such as cap rock. Mineral trapping is a geochemical reaction process, in which dissolved CO_2 initiates reactions with the formation rock minerals leading to the formation of carbonate minerals (Al-Khdheeawi et al., 2023; Xu et al., 2004).

1.1 Properties of CO_2

Pure CO_2 is a colorless, odorless, inert, and non-combustible gas (Cho, 2015). The molecular weight at standard conditions is 44.010 g/mol, which is one and a half times higher than air (Saravanan et al., 2021). CO_2 is a naturally occurring compound that exists in three different states of matter: solid, liquid, and gas. Its pressure and temperature determine the phase transitions of CO_2, and the phase diagram for CO_2 illustrates the conditions under which each state of matter exists. At low temperatures and pressures, CO_2 exists in a solid state, commonly known as dry ice. As the temperature increases, the solid CO_2 will eventually transition to a liquid state. This process is known as sublimation, and it occurs at a temperature of -78.5°C and a pressure of 0.518 MPa (Yamasaki et al., 2017). As the temperature and pressure continue to increase, the liquid CO_2 will eventually transition to a gaseous state. This process is known as vaporization, and it occurs at a temperature of -0.4°C and a pressure of 0.1013 MPa (Zhao and Lvov, 2016). The phase diagram for CO_2 is a graph that shows the conditions under which each state of matter exists. It is typically represented as a pressure-temperature plot, with lines separating the solid, liquid, and gaseous regions. The triple point of CO_2 is at a temperature of -78.5°C and a pressure of 0.518 MPa, where all three states of matter exist in equilibrium. It's important to note that these conditions are for standard temperature and pressure and that the phase transitions and phase diagram of CO_2 may vary under different conditions (Yamaguchi and Zhang, 2009). Also, CO_2 can exist in the supercritical state, which is a state where CO_2 is above its critical temperature and pressure and where the distinction between liquid and gas no longer exists. This state is of interest in industries such as power generation, extraction, and chemical synthesis. CO_2 is solid at low temperatures and pressures, but most dependent on temperature as shown in Figure 1-3. But by increasing the pressure and temperature, the liquid phase appears for the first time and coexists with the solid and vapour phases at the triple point. The liquid and the vapour phase of CO_2 coexist from the triple point and up to the critical point on the curve. Below the critical temperature, CO_2 can be either liquid or gas over a wide range of pressures. Above the critical temperature, CO_2 will exist as a gas regardless of the pressure. However, at increasingly higher supercritical pressures, the vapor becomes and behaves more like a liquid.

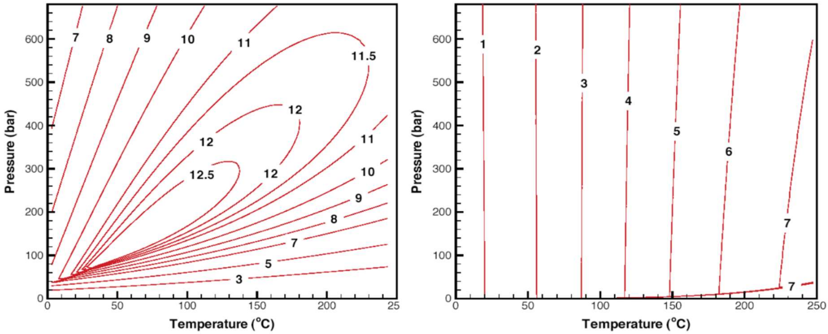

Figure 1-3. Diagram of the phase change of carbon dioxide.

The phase behavior is important to understand when a CO_2 flood is considered. However, the most essential behavior is how CO_2 interferes with reservoir fluids and reservoir rock when it flows through the reservoir under different temperature and pressure conditions. The simplest applications of thermodynamics are the phase transitions that a pure substance can undergo. The process involves a single substance that undergoes a physical change. A phase of a substance is a form of matter that is uniform throughout its chemical composition and physical state. A phase transition, the spontaneous conversion of one phase to another, occurs at a characteristic temperature for a given pressure. A phase diagram of a substance is a map of the ranges of pressure and temperature at which each phase of a substance is the most stable. The boundaries between regions, or the phase boundaries, show the values of P and T at which two phases coexist in equilibrium. A technique for constructing the CO_2 phase diagram would include charting the pressure and temperature conditions at which the three phases of matter (solid, liquid, and gas) exist in equilibrium. This is possible by using the Gibbs free energy and Clausius-Clapeyron equation. The Gibbs free energy is a thermodynamic quantity that indicates a system's work-doing capacity. In the case of CO_2, the Gibbs free energy is dependent on the system's pressure and temperature, and it varies during a phase transition. The Clausius-Clapeyron equation is a connection between the Gibbs free energy and the system's pressure and temperature. It asserts that the change in Gibbs free energy per unit volume is proportional to the change in both temperature and pressure. The slope of the phase boundary on the pressure-temperature phase diagram may be calculated using this equation. To produce the CO_2 phase diagram, it would be necessary to measure the system's pressure and temperature at many sites and then utilize these measurements to depict the phase boundaries. The Clausius-Clapeyron equation may then be utilized to compute the slope of the phase boundaries, which can be used to connect the data points and finish the phase diagram. It is also feasible to forecast the phase transitions of CO_2 using theoretical calculations, such as Density Functional Theory or Molecular Dynamics, and then create a phase diagram based on these predictions. It is crucial to remember that the phase diagram for CO_2 is a graph that depicts the conditions under which each form of matter exists and that it may alter under different situations, such as impurities or varying pressure and temperature ranges.

1.2 Types of geological utilization of CO_2

CO_2 utilization involves the direct conversion of CO_2 into valuable products, such as fuels or chemicals, and its use as a displacement/energy exchange medium in the geologic energy industry (Huang and Tan, 2014; Zhu, 2019). For example, CO_2 is used as a working fluid and injected into underground formations such as oil and gas reservoirs, aquifers, and hot dry rocks to enhance the production of underground energy reserves through displacement, dissolution, heat transfer, and fracture generation, while simultaneously achieving underground CO_2 storage (Li and Zhiwei, 2021; Xie et al., 2014). Consequently, CCUS technology in the conventional geological energy industry mainly includes CO_2-EGR (such as natural gas, coalbed methane, and shale gas), CO_2-EOR, CO_2-enhanced water recovery (CO_2-EWR), CO_2 fracturing, CO_2 geothermal systems, and CO_2 in-situ uranium leaching (CO_2-IUL) (Figure 1-4).

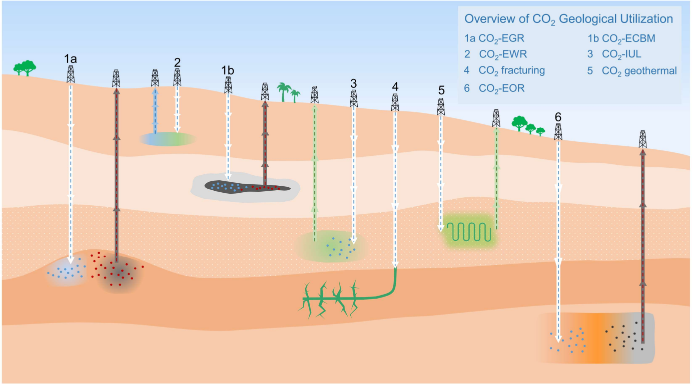

Figure 1-4. Overview of CO_2 geological utilization.

1.2.1 CO_2-EOR

CO_2-EOR, which involves injecting CO_2 into oil reservoirs to enhance oil recovery, was initially developed in the US, China, and Canada (Hill et al., 2020; Luo et al., 2022).

1.2.1.1 Mechanisms of CO_2-EOR

The interaction between CO_2 and crude oil is one of the most important mechanisms for CO_2-EOR in conventional reservoirs. In the experimental studies, the CO_2-crude oil interaction is mainly investigated by observing the change of physical properties of crude oil due to CO_2 injection under bulk condition or conducting coreflooding experiments (Chen et al., 2022; Cui et al., 2017). The relevant experimental apparatus and operation process have relatively matured (Ghedan, 2009; Hawthorne et al., 2014). For the unconventional reservoirs, e.g., Bakken tight formation, the same mechanisms of oil-CO_2 interaction are proved by PVT and coreflooding tests, and the CO_2 is much easier to become miscible with oil than other gases, including CO_2-enriched flue gas, natural gas, nitrogen, and CO_2-enriched natural gas (Alfarge et al., 2017; Zhou et al., 2023).

(1) Viscosity and density reduction

The phenomenon of CO_2 reducing the viscosity and density of crude oil is a multi-faceted process involving intricate interactions between CO_2 and the chemical constituents of the oil (Syed et al., 2022). When CO_2 is introduced into the oil reservoir, it dissolves within the crude oil and undergoes a chemical reaction with the water present, leading to the formation of carbonic acid (Zhou et al., 2023). This acid subsequently interacts with various compounds within the crude oil, inducing alterations in its chemical composition. A pivotal effect of CO_2

dissolution in the oil is the increase in acidity (Nešić, 2007). The carbonic acid reacts with basic compounds in the oil, resulting in the generation of acidic components. This rise in acidity significantly influences the viscosity of the oil by weakening the intermolecular forces among its constituent molecules. Consequently, the oil experiences reduced cohesion, facilitating more effortless flow. Moreover, the changes induced by increased acidity in the chemical structure of the oil lead to a reduction in its density. This effect complements the viscosity reduction process and contributes to further lowering the oil's resistance to flow. In addition to the chemical interactions, CO_2 operates on a molecular level, particularly interacting with the long-chain hydrocarbons responsible for the high viscosity of heavy crude oil (Li et al., 2019). CO_2 molecules position themselves between these hydrocarbon chains, disrupting the cohesive forces that bind them together. This intercalation effect weakens the overall attractive forces between the hydrocarbon chains, resulting in a substantial decrease in the oil's viscosity (Moultos et al., 2016). Furthermore, CO_2 induces a swelling effect on the oil. CO_2 molecules infiltrate the molecular structure of the oil, leading to the formation of microscopic bubbles. As a consequence, small channels are created within the oil, facilitating smoother flow and thereby further reducing its viscosity.

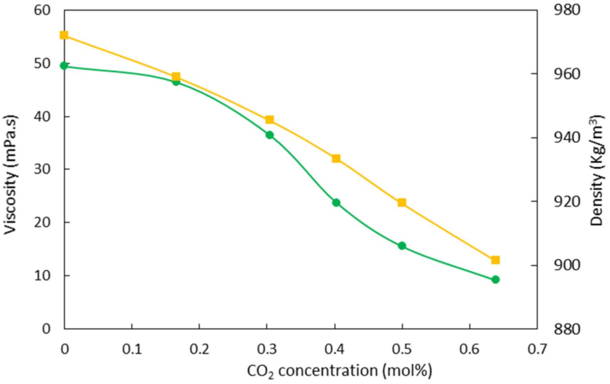

Figure 1-5. Oil viscosity and oil density with different CO_2 concentrations.

It is essential to consider that the specific mechanisms governing the CO_2-induced reductions in viscosity and density can vary based on the unique chemical composition and physical properties of the oil and the reservoir. Parameters such as the initial viscosity of the crude oil, the presence of specific compounds, as well as reservoir temperature and pressure conditions, all play vital roles in determining the extent of viscosity and density reduction. Figure 1-5 shows the viscosity and density of the CO_2–oil system in the study conducted by Hou et al., and it can be seen that the viscosity and density decrease with the increase in CO_2 concentration (Hou et al., 2021a). Rezk and Foroozesh studied the phase behavior and mutual interactions between light crude oil and CO_2 under high pressures and high temperatures conditions. The swelling factor (SF) measurements demonstrated an increasing trend with pressure up to a specific extraction pressure. Beyond this point, the SF began to decrease, even reaching values below one. Furthermore, the measurements of oil viscosity revealed that the dissolution of CO_2 in the oil sample led to a significant reduction in the mixture's viscosity, by up to 61% (Rezk and Foroozesh, 2019). Mansour et al. conducted a study on the application of (CO_2) miscible flooding in Egyptian oil fields using swelling experiments. In Figure 1-6 (Mansour et al., 2019), the results of (CO_2)-oil viscosity versus (CO_2)-saturation pressure at reservoir temperature are shown for ten wells: S.ID (1), S.ID (2), S.ID (3), S.ID (4), S.ID (5), S.ID (6), S.ID (7), S.ID (8), S.ID (9), and S.ID (10). Each solid line in the figure represents a sample, illustrating the variation in (CO_2)-oil viscosity with different percentages of carbon dioxide (CO_2) from saturation pressure (bubble-point pressure) to minimum miscibility pressure (MMP). The findings indicate that the addition of carbon dioxide (CO_2) significantly reduced the (CO_2)-oil viscosity in each sample. Wei et al. conducted a series of experiments on cyclical CO_2 injection into tight reservoirs in Lucaogou, Jimusar Basin. With PVT experiments and minimum miscibility pressure (MMP) measurement, they observed that as the CO_2 concentration increased, CO_2 dissolving in tight oil tended to be saturated, and the density and viscosity of tight oil decreased slowly (Wei et al., 2017). Furthermore, they suggested that even if the pore pressure was higher than MMP, the injected CO_2 may not be able to form a miscible phase with crude oil due to the extremely tight porous media.

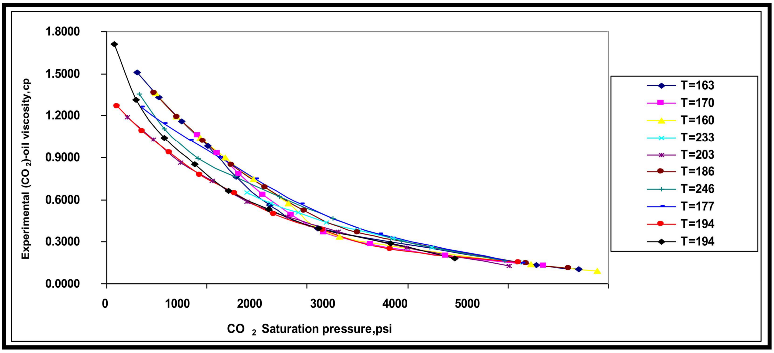

Figure 1-6. (CO_2)-Oil viscosity and (CO_2)-saturation pressure.

(2) Oil swelling

CO_2 injection exhibits a notable swelling effect on crude oil (Sohrabi et al., 2009). Following CO_2 injection, as it dissolves in the oil, the specific volume, reservoir volume factor, and compressibility coefficient of the crude oil increase. The expansion of the oil occurs due to CO_2 molecules entrapping tiny air bubbles within its molecular structure, creating narrow pathways that improve viscosity and facilitate flow. As a result, the compressibility of the crude oil and oil well productivity are enhanced.

Oil swelling also leads to the breakdown of the oil structure, contributing to viscosity reduction (Salleh et al., 2019). The relatively weak intermolecular forces holding oil molecules together are weakened by the introduction of CO_2 molecules, leading to a decrease in oil viscosity. The extent of swelling is directly proportional to the amount of injected CO_2, reservoir pressure and temperature, and the oil's composition. Oils with more polar or polar functional groups exhibit greater expansion compared to nonpolar oils. Furthermore, increasing injection pressure and/or temperature also enhances the magnitude of swelling. The rate at which the oil expands is influenced by various variables, including the oil's composition, pressure, temperature, and CO_2 injection rate. Habibi et al. visualized the CO_2-oil interface at 50 ℃ and 2000 psi in the visual cell to investigate the CO_2-oil interactions at reservoir conditions. Figure 1-7 presents the CO_2-oil interface at the specified reservoir temperature. In panel (a), the initial setup involved 235mL of oil with a molar quantity of 0.78, placed in a cell at atmospheric pressure, without the presence of CO_2, and maintained at 50 ℃. Subsequently, in panel (b), 6.4 mol of CO_2 was injected into the system to increase the pressure from 0 to 13.8 MPa. Notably, as depicted in panel (c), after a duration of 5 hours, further CO_2 dissolution into the oil phase resulted in the significant swelling of the oil (Habibi et al., 2017). These observations provide compelling evidence of CO_2's remarkable ability to dissolve into and expand the oil under reservoir conditions, which is of great importance for understanding the behavior of CO_2-oil interactions in such settings. Su et al. investigated the effects of CO_2 on crude oil and found that increasing the mole fraction of CO_2 from 0 to 0.45% resulted in a considerable increase in specific volume, reservoir volume factor, and compressibility coefficient of the crude oil (Yang et al., 2022). Similarly, Zhang et al. injected CO_2 into crude oil, leading to an expansion coefficient increase from 1.00 to 1.19 after adding 45% CO_2. Additionally, Pu et al. conducted visual tests on the CO_2 huff-n-puff process for enhanced oil recovery in tight reservoirs, affirming that the oil swelling factor and CO_2 solubility both increased with pressure (Pu et al., 2016). These studies collectively provide valuable insights into the significant effects of CO_2 on crude oil expansion and its implications for enhanced oil recovery in various reservoir conditions.

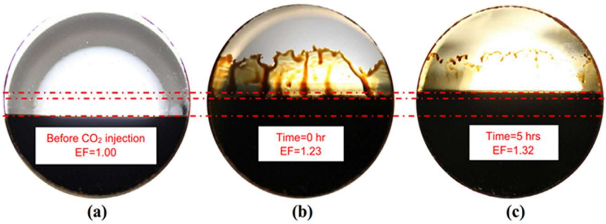

Figure 1-7. CO_2-oil interface at reservoir temperature. (a) Oil (235mL, 0.78 mol) in a cell at atmospheric pressure and no CO_2 atreservoir temperature, 50°C. (b) CO_2 (6.4 mol) injected to increasethe pressure from 0 to 13.8 MPa. (c) After 5 h, further CO_2 dissolution into the oil phase causes oil to swell.

(3) Light components extraction and density reduction

When carbon dioxide is injected into an oil reservoir, the injection pressure of CO_2 is usually higher than the saturation pressure of the crude oil to ensure sufficient interaction between CO_2 and the light components present in the crude oil, causing asphaltenes to precipitate (Nobakht et al., 2008; Tan et al., 2023). Additionally, at high pressures, CO_2 undergoes dissolution and adsorption with the crude oil. CO_2 forms a solution with the light components of the crude oil, such as methane and ethane, or gets adsorbed onto the surface of CO_2 (Bello et al., 2023). Moreover, a phase equilibrium is achieved between CO_2 and the light components of the crude oil. Under this phase equilibrium condition, the light components transfer from the oil phase to the gas phase, enabling the extraction of these light components. It causes the oil to become acidic because the CO_2 dissolves in the oil (Latsky et al., 2018). It is possible for this carbonic acid to react with the oil, which would result in the oil becoming more acidic. Therefore, the CO_2 has the ability to extract lighter components from the oil, such as the dissolved gases methane, ethane, propane, and butane. These lighter components can be extracted from the oil.

In the study conducted by Ding demonstrated the capability of CO_2 to extract all crude oil components, especially the light components (Ding et al., 2013). Figure 1-8 shows that CO_2 effectively extracts a wide range of oil components (C5-C33), similar to the original oil. With increasing pressure (20, 30, 36, and 46 MPa), the content of light components (C5-C9 and C10-C14) in the extracted oil decreases (41.8%, 31.4%, 34.8%, 34.2%), while the content of heavy components (C15-C19, C20-C24, and C25-C33) increases (12.8%, 18.9%, 17.4%, 17.1%). This suggests improved CO_2 extraction capacity for heavy components at higher pressures. In Figure 1-8b, residual oil components remain consistent (C5-C33), and with increasing pressure, the content of light components decreases (27%, 23.8%, 23.6%, 35.5%), while the content of heavy components increases (20.5%, 21.6%, 23%). Despite the enhanced capacity for heavy