1. Introduction

1.1. Motivation, objectives and scientific challenges

In the commercial exploitation of unconventional gas reservoir, for instance tight and shale gas reservoir, hydraulic fracturing plays a very important role. It is used to enhance the original permeability of unconventional reservoirs, which usually is very low even ultra-low. During hydraulic fracturing, the fracturing fluid, normally composed of water and some chemical additives, is pumped from surface down to perforation through injection well. The pressurized fluid breaks the rock in tension firstly surrounding perforations, and propagates into deep reservoir. To prevent the closure of opened fracture after removing pumping power, some proppant is injected along with fracturing fluid, when enough fracture has been created. The created artificial fracture performs as a high conductive channel connecting tight reservoir and production well for gas flow, which could enhance the gas production significantly in comparison with original reservoir. Thanks to the innovation of horizontal and directional drilling technology, currently, a horizontal well can be drilled into the reservoir over 1000m (Ma et al. 2016). As shown in Fig. 1.1, the horizontal well will be divided into 10 or more segments for fracturing. In this case, multi-fractures can be stimulated through only one well, which greatly improve production efficiency and makes the exploiting of unconventional reservoir more economic.

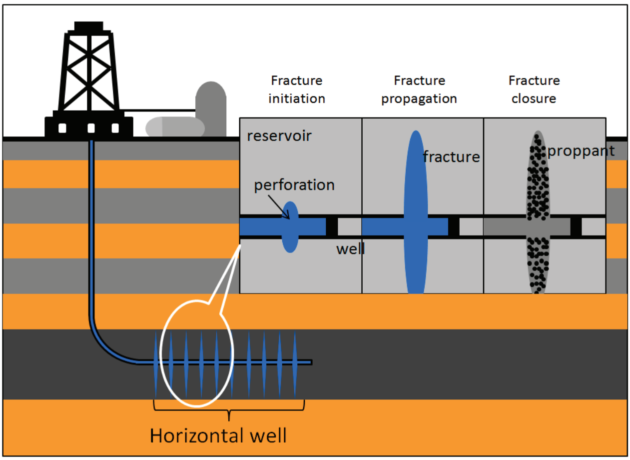

Figure 1.1. Demonstration of hydraulic fracturing in gas reservoir

Geothermal energy is kinds of thermal energy generated and stored inside the earth. Due to its excellent features like huge capacity and independency on weather conditions, geothermal energy as one of the important renewable resources attracts more and more attentions, especially hot dry rock (HDR), which is impervious crystalline basement rock with remarkable temperature (Armstead & Tester 1978). The HDR owning a vast capacity can be found almost everywhere deep beneath the earth's surface. But, extraction and utilization of this heat resource remains an enormous challenge. Enhanced geothermal system (EGS) technology has a goal to extract the heat out of HDR for electricity generating. As shown in Fig.1.2, the EGS is composed of at least two well, one for injection and one for production. The cold medium, usually pure water is pumped down to target geothermal reservoir, where the cold medium will be heated through energy exchange with HDR. Then the heated medium will be brought up to surface again for electricity generating. Such circulation makes the utilization of HDR resource possible. However, before circulation, the permeability of geothermal reservoir needs been enhanced for efficient heat mining, generally by using hydraulic fracturing. Like in unconventional reservoir, the hydraulic fracturing plays a very important role in EGS, and is used to create artificial fractures for improving the geothermal reservoir conductivity.

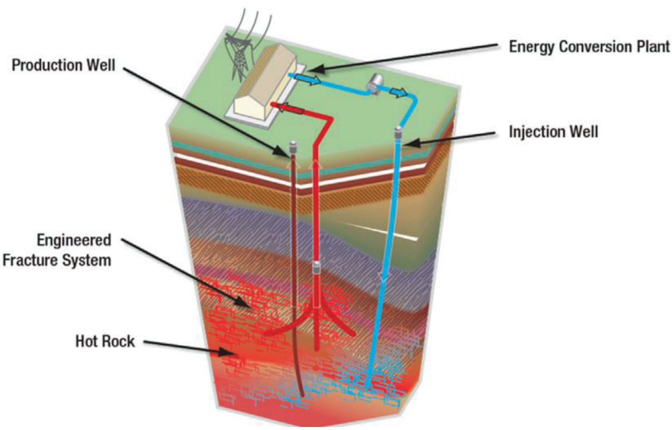

Figure 1.2. Demonstration of an enhanced geothermal system (Olasolo et al. 2016)

The reservoir stimulation in unconventional gas reservoir shares some common characteristics with the one in HDR reservoir. For the inefficient conductivity, both reservoirs need be stimulated by pressurized fracturing fluid to enhance the original permeability before production. And the hydraulic fracturing process is a thermal-hydraulic-mechanic (THM) coupled process, involving heat flow, multi-component and -phase flow, mechanic response of reservoir rock. Besides, massively implementation of water-based fracturing in unconventional gas reservoir as well as DHR could induce water shortage or conflicts with other users, particularly in water-scare area (Vengosh et al. 2014). In addition to this, there are also some differences in reservoir stimulation and production. Firstly, the host rock type is different. Unconventional gas reservoir is found almost in porous sedimentary, whereas the HDR is consisted mostly of crystalline volcanic rock. Normally a signal fracture with two wings is stimulated in unconventional gas reservoir, if no natural fracture is contained in sedimentary. Due to high-density of naturally fractures, usually a complex fracture network is stimulated through hydraulic fracturing in volcanic rock. And the temperature in HDR often over 160°C (Lu 2018) is higher than in unconventional gas reservoir. Additionally, proppant is not necessary in reservoir stimulation of HDR, because during heat production, the injection fluid provides the pressure to support fracture wall.

Due to the low cost, availability and high specific heat, currently water is the mostly used working fluid for unconventional gas reservoir stimulation as well as HDR reservoir stimulation. In general, some chemical additives are added into fracturing fluid to improve its performance on fracture making ability and proppant carrying capacity. Hence, water-based fracturing often brings some environmental problem, like groundwater pollution and formation damage, water shortage, unsuitable in water-sensitive clay mineral (Ward et al. 2016, Schill et al. 2017, Sanaei et al. 2018). To address these problems, some alternative non-aqueous fracturing fluids have been proposed. Several important non-aqueous fracturing fluids, including foam-, oil-, alcohol-, Emulsion-based fracturing fluid, and liquid CO_2 and N_2, are summarized in Tab.1.1. In addition to the common characteristics, liquid CO_2 shows some unique advantages, including CO_2 sequestration, enhancing gas recovery by displacing the adsorbed methane, rapid clean-up etc. The CO_2 will presents as supercritical phase, if the temperature and pressure exceed 31.04°C and 71.82 bars at the same time (Vargaftik 1975). This condition could be easily met under fracturing in unconventional gas reservoir. For this reason, the CO_2 in fracture exists mostly as supercritical CO_2 during fracturing. Not only in unconventional gas reservoir, but in EGS the CO_2 can be used as working fluid to exact geothermal energy. Apparently, the CO_2 running EGS circulation is supercritical. However, supercritical CO_2 stills a concept in reservoir stimulation and geothermal energy production. Before commercial application of supercritical CO_2, some barriers, e.g. proppant transport, corrosive of CO_2 dissolution, transport etc. need be removed.

To gain deeper understanding on the CO_2 behavior in geo-energy exploitation, numerical methods on the base of THM coupled framework will be used to study CO_2-based hydraulic fracturing in tight gas reservoir, CO_2-based reservoir stimulation and heat extraction in HDR reservoir, respectively.

Table 1.1. Summary of potential advantages and disadvantages of several non-aqueous fracturing fluids (adapted from Gandossi 2013)

Fracturing fluids	Potential advantages	Potential disadvantages	Status of applications
Foam-based	-Water usage reduced -Reduced amount of chemical additives. -Reduction of formation damage. -Better clean-up of the residual fluid	-Low proppant concentration in fluid, -Higher costs. -Difficult rheological characterization -Higher surface pumping pressure required.	Some commercial applications
Oil-based (LPG)	-Water usage much reduced or completely eliminated. -Fewer chemical additives are required. -Flaring reduced. -Truck traffic reduced. -Abundant by-product of the natural gas industry. Increased the productivity of the well. -Excellent fluid properties -Full fluid compatibility with shale reservoirs -No fluid loss. -Recovery rates (up to 100%) possible. -Very rapid clean up	-Involves the manipulation of large amounts of flammable propane, hence potentially riskier than other fluids and more suitable in environments with low population density. -Higher investment costs. -Success relies on the formation ability to return most of the propane back to surface to reduce the overall cost.	Some commercial applications in unconventional reservoir
Alcohol-based (Methanol)	-Water usage much reduced or completely eliminated. -Methanol is not persistent in the environment. -Excellent fluid properties -Very good fluid for water-sensitive formations.	-Methanol is a dangerous substance to handle: a. Low flash point, hence easier to ignite. b. Large range of explosive limits. c. High vapour density. d. Invisibility of the flame.	It has been used in low permeability reservoir
Emulsion based	-Depending on the type of components used to formulate the emulsion, these fluids can have potential advantages such as: a. Water usage much reduced or completely eliminated. b. Fewer (or no) chemical additives are required. -Increased the productivity of the well; better rheological properties	-Potentially higher costs.	It has been used on unconventional reservoir
Liquid CO_2	-Potential environmental advantages: a. Water usage much reduced or completely eliminated. -Fewer chemical additives -Some level of CO_2 sequestration achieved. -Reduction of formation damage. -Form more complex micro-fractures. -Enhance gas recovery by displacing the methane adsorbed in the shale formations. -Rapid clean-up. -More controlled proppant placement and higher proppant placement within the created fracture width.	-Proppant concentration must necessarily be lower and proppant sizes smaller, hence decreased fracture conductivity. -CO_2 must be transported and stored under pressure (typically 2 MPa, -30°C). -Corrosive nature of CO_2 in presence of H_2O -Unclear (potentially high) treatment costs.	Liquid CO_2 as fracturing fluid is commercially used in unconventional applications Supercritical CO_2 usage appears to be at the concept stage.
Liquid N_2	-Water usage much reduced or completely eliminated. -Fewer chemical additives are required. -Reduction of formation damage. -Self-propping fractures can be created by the thermal shock, hence need for proppant reduced or eliminated	-Can replace hydraulic fracturing only for small to medium treatments -Proppant is not carried into the fracture. Instead, propellant fracturing relies upon shear slippage to prevent the fracture from fully closing back on itself. -Potentially induce seismic events.	The use of liquid nitrogen is less typical

Because of a relatively new concept, CO_2 for reservoir stimulation and production is still in the preliminary study stage. Rare applications has been conducted and planned in commercial projects. In spite of this, there remain several important numerical models have been proposed to simulate CO_2 fracturing in unconventional gas reservoir. Jiang et al. (2014) developed a multi-Continuum multi-component model to study the CO_2 performance on enhanced gas recovery in a shale gas reservoir with complex fracture network. In this reservoir, different structures, involving matrix, major hydraulic fracture and large-scale natural fractures, were described by embedded discrete fracture model. Lee and Ni (2015) analyzed CO_2 behavior in discrete fracture network, wherein the flow and CO_2 migration was simulated by using flow code THOUGH2/ECO2N. The TOUGH series code is primarily developed at Lawrence Berkeley National Laboratory (LBNL) (Pruess 2004) and as one of the popular multi-component and -phase programs has been widely used to study the multi-flow in unconventional gas reservoir. Fang et al. (2014) used a 2D commercial program, universal distinct element code (UDEC) to compare the fracture-making ability of different fluids: water, slick water and CO_2. The above-mentioned models focus only on the flow and CO_2 behavior in predefined fracture or complex fracture network. Yet, the fracture initiation and propagation have not been considered. Then, Peng et al. (2017) conducted the simulation on supercritical CO_2 fracturing by using bonded particle model, in which the rock material was modeled as a collection of round particles and the microcracks was modeled by breakage of bound between particles. The bonded particle model performs very well in characterizing fracture initiation and propagation on micro level, but for large scale project it is still inefficient. More recently, the 2D damaged-based model (Liu et al. 2018, Wang et al. 2018, Zhang et al. 2019) was proposed to investigate supercritical CO_2 fracturing. In this model, the fracture pattern was characterized by the damage induced by rock-gas interaction due to CO_2 injection. During fracture propagation, equivalent permeability of corresponding fracture was updated according to value of damage. However, this model is still limit to solve the fracture field scale fracture propagation and proppant transport. Comparing with unconventional gas reservoir, the study on CO_2 as working fluid to exploit geothermal energy starts relatively late. Since Brown (2000) firstly proposed the CO_2-EGS concept, some preliminarily works has been conducted. The numerical simulator for CO_2-EGS could be principally divided into three categories. One focused only on supercritical CO_2 performance in operation of naturally permeable or already stimulated geothermal reservoir, in which the reservoir stimulation and gas-interaction was ignored (Pruess and Azaroual 2006, Pruess 207, Randolph and Saar 2010, Luo et al. 2014, Shi et al. 2018). The gas flow and heat exchange efficiency of supercritical CO_2 EGS have been discussed in these models. Because the CO_2 dissolving in water exhibits acids, the CO_2 dissolution can chemically react with surrounding minerals, further causing mineral dissolution or precipitation, which has potential influence on the productiveness of geothermal reservoir. Thus another category of simulators was proposed to interpret the effects of chemical interaction on EGS performance (Xu and Pruess 2010, Wan et al. 2011, Borgia et al. 2012, Cui et al. 2018). Additionally, mechanical interaction of hot rock plays also a very important role in heat extraction. In the third category, the mechanical response of hot rock has been considered during CO_2 injecting into a discrete fracture network, in which the cracks width was local pressure- and stress-dependent (Sun et al. 2017, Li et al. 2019a). However, the reservoir stimulation before production has not been considered in these models.

At present, the primary numerical method for hydraulic fracturing includes finite element method (FEM), distinct element method (DEM), finite difference method/finite volume method (FDM/FVM) and boundary element method (BEM). They have their own advantages and disadvantages. FEM is a very popular method in solid mechanic, because of the complete theory. On base of EFM, the extended finite element method (XFEM) is developed mainly to solve the fracture propagation, which can be used to simulate hydraulic fracturing (Zhao et al. 2014, Wang 2015, Zhou et al. 2015,Yan et al. 2016). In this method, an enrichment function is introduced to describe continue and discontinue deformation around fracture as well as fracture tip. As a consequence, re-mesh at fracture tip is not necessary and improve the competing efficient. However, XEFM is currently not suitable for 3D problem. In DEM, the pore rock material is represented by a collection of micro particles (Al-Busaidi et al. 2005, Yoon et al. 2015, Damjanac and Cundal 2016). The mechanic response between micro particles is transferred by the assumed springs in both normal and tangential directions, which performs as tensile/compress and shear strength on macro level. The fluid can flow in the pores between particles even break the assumed springs, to create a hydraulic fracture. DEM is very visible method to simulate shear and tensile fracture. But it is not efficient for field scale simulation if small particles are chosen. FDM/FVM is often used to solve fluid as well as heat flow (Wei and Zhang 2013, Wang et al. 2014). It is one of the most popular methods in simulation of reservoir flow, due to its complete theory and well development. In this method, the stress and pressure of element is represented by the one averaged on the center point of control volume, rather than from the grid point. Therefore, the converted scalar stress loses much information about direction. On the other side, it is also limit to solve the propagation direction, as the fracture parts is pre-defined during model generation. The basic idea of BEM is converting area integration to curve integration, or converting volume integration to area integration with the help of Green's function (Olson 2004, Olson 2009, Wu and Olson 2013, Wu and Olson 2015). Then the whole problem is converted to boundary problem. Through integration on discrete boundary can achieve the stress as well as deformation distribution inter domain. By treating the fracture wall as inter discrete boundary, this method could be used to simulate hydraulic fracturing. Dimension reduction improves the computing efficient significantly. Despite, the precondition, homogenous mechanic properties within the domain, limits its application.

The main scientific challenge of this thesis is development of suitable numerical models to study the mechanic and hydraulic behavior in utilization of supercritical CO_2 in corresponding geo-energy production. More concretely, develop THM coupled model to characterize fracture network growing during hydraulic fracturing in deep geothermal reservoir; study the reservoir stimulation, heat exaction and CO_2 sequestration in deep geothermal reservoir with pre-existing formation water based on CO_2-EGS concept; develop THM coupled model for hydraulic fracturing in unconventional gas reservoir, involving at least fracture model, proppant transport model as well as temperature sensitive fracturing fluid (CO_2, thickened CO_2 and guar gum); improve the fracture-making ability and proppant-carrying capacity of CO_2 in unconventional gas reservoir; compare the performance of supercritical CO_2 with traditional working fluid, like water and guar gum in geo-energy production.

1.2. Thesis outline

In this work, the models are developed on the fundament of popular THM framework TOUGH2MP-FLAC3D, in which both codes are developed on the base of FDM. In order to overcome its shortness for information loss, iso-parameter method is applied to interpret the local stress state. As Fig. 1.3 shown, different specific models are integrated in this THM framework, to study the CO_2 performance in different reservoir, including HDR reservoir and unconventional gas reservoir. Generally, in HDR reservoir, especially in volcanic rock types, usually a fracture network is stimulated by hydraulic fracturing. Therefore, an anisotropic continuum damage-permeability model is introduced into describe the equivalent anisotropic permeability as well as porosity for stimulated HDR reservoir. The feasibility of such models have been verified by measured stress, damage, permeability in series triaxial tests as well as a small scale field testing in hard rock. Then the developed model is applied in a specific planned Dikili EGS to study the performance of CO_2 in reservoir stimulation and heat extraction, comparing with water. To solve the hydraulic fracturing in unconventional gas reservoir, another model, containing fracture model (single fracture model), proppant model (proppant transport and placement), and fracturing fluid model (water, guar gum, pure CO_2 and thickened CO_2) has been integrated into the THM framework and verified, separately. In these model, the fracture initiation, propagation, proppant transport and placement, fracture closure even gel break can be simulated based on different working fluids in unconventional gas reservoir, because the temperature-sensitive properties of fracturing fluid, like viscosity, density, enthalpy etc. has been integrated in these models. Then the performance of different fluid, thermal effect as well as proppant transport has been compared using the newly developed models.

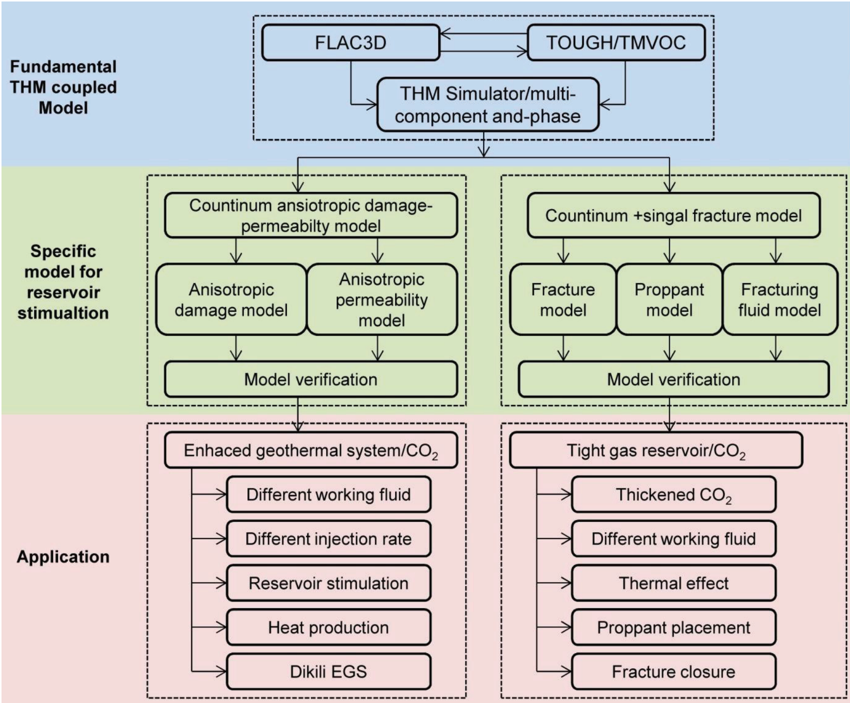

Figure 1.3. Research content and flowchart

The content of this thesis is divided into five chapters. In chapter 2, the state-of-the-art of CO_2 engineered application in geo-production will be studied through literature study. The advantages and disadvantages will be compared systematically. Besides, it is trying to point the critical barrier for industrial application and the potential solutions.

As the property of CO_2 is very temperature and pressure sensitive and many complex mechanic responses are involved in energy production, the new developed models should be integrated under a THM coupled framework. Therefore, the fundamentals of used THM framework (TOUGH2MP-FLAC3D), including theoretical background, governing equation, numerical algorithm as well coupling process, are introduced in chapter 3 in detail.

Attempting to learn the behavior of supercritical CO_2 in unconventional gas reservoir, a specific numerical model able to characterize fracture propagation and leak-off will be developed in chapter 4. In this model, a pre-defined potential fracture plane is inserted in the middle of host reservoir elements perpendicular to minimum stress. On this potential fracture plane, different specific models, including fracture model, proppant transport model and multi flow model, are integrated in the popular THM framework TOUGH2MP-FLAC3D. Then, the feasibility of these implemented models will be verified separately by analytical solution, experimental results and other simulated results. In this chapter, different fracturing fluids (mainly temperature-dependent viscosity property) is defined firstly, including pure CO_2, different thickened CO_2s and guar gum. Other properties, like density and enthalpy, is assumed equal to the base fluid of fracturing fluid. Then, different fracturing fluids, pure CO_2, two thickened CO_2s, pure water and guar gum, will be injected into a fictitious model with the properties of a typical tight gas reservoir, to compare their performances in fracture making-ability. Additionally, since the property of CO_2 is closely correlated to temperature, the fracturing by using CO_2 will be carried out under different thermal condition. Finally, proppant with different density is used to address the weakly proppant-carrying ability of CO_2.

In chapter 5, in order to study the critical engineering process, reservoir stimulation and heat extraction in deep geothermal reservoirs, a 3D simulator based on a continuum anisotropic model and anisotropic permeability model will be developed under the THM framework of FLAC3D-TOUGH (TMVOC). In geothermal energy exploitation, the stress state change due to fracturing fluid injection could induce an anisotropic damage in geothermal reservoir, which further triggers an anisotropic permeability. Macroscopically, it performs as fracture propagation. In addition to this, the impact of effect stress will be considered in this model as well. It is believed that usually a fracture network is stimulated in the geothermal reservoir with brittle rocks, especially volcanic rock. This damage model and permeability will be verified by triaxial test in laboratory and cyclic fracturing test in flied. The influence factor will be discussed by a series of case studies on a 2D simple model. On a real case from Dikili geothermal project, the reservoir stimulation and heat extraction with different productions rates by using supercritical CO_2 will be conducted and compared with the results by using water, in which pre-existing formation water is taken considered. Besides, the ancillary benefit of CO_2 sequestration will be discussed in the lifetime of CO_2-EGS under different injection rate.

2. Engineered applications of CO_2 in geo-energy

2.1. The carbon dioxide challenge in climate change

Carbon dioxide (CO_2) is a chemical compound composed of one carbon and two oxygen atoms. It is an important composition of the earth's atmosphere, accounting for about 0.03%. This CO_2 has two important functions. One is the resource for plant photosynthesis, to convert the light power to bio power, at the same time releasing oxygen gas. Another one is the greenhouse gas to keep earth's temperature in a suitable range, with a minor day-night difference. However, large amount of CO_2 in atmosphere will cause global warming, further bring some worse problem, like more extreme weather events, species extinction, sea level rise etc. As shown in Fig. 2.1, the global averaged temperature is closely correlated to the CO_2 concentration in atmosphere. Along with the CO_2 concentration increasing from 280ppm in 1850 (pre-industrial) up to 408ppm in 2018, global averaged temperature has warmed about 1.2°C. The global warming trend will continue, if nothing is done in the future. Therefore, the goal to hold the global average warming within 2°C comparing with pre-industrial level is set in the Pairs Agreement and adopted by many nations (IPCC, 2018).

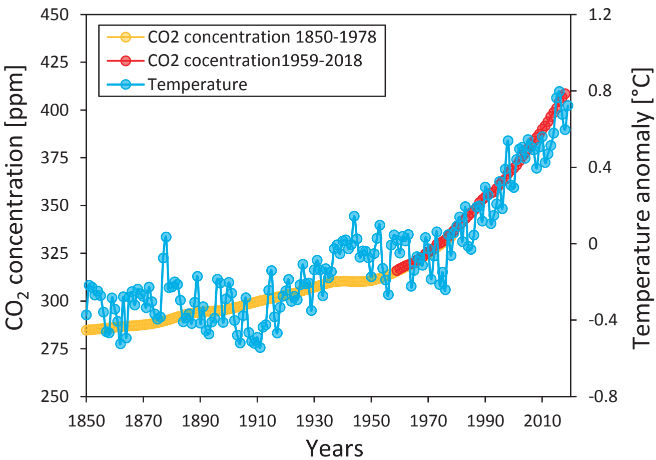

Figure 2.1. Correlation of global temperature and atmosphere CO2 concentration in 1850-2018, Temperature data is from HADCRUTv3, CO2 data is from NOAA ESRL (1859-2018)(NOAA ESRL 2019) (Etheridge et al. 1998) and Low Dome ice core (1850-1978) (Etheridge et al. 1998)

There are many resource of CO_2. It can be released through natural and human activities, for instance, volcanic activity, some organic compounds, breathing processes of humans and other animals etc. For a long time, the CO_2 concentration in atmosphere is dynamic equilibrium due to plant photosynthesis. Since the beginning of industrial revolution, a large amount of CO_2 has been released into atmosphere in a short period, because of massive combustion of fossil fuel, like oil, natural gas and coal etc. Such a huge amount of CO_2 breaks the dynamic equilibrium and raises the concentration level of CO_2 in atmosphere. This is the main reason for global warming from pre-industrial. How to reduce CO_2 releasing and ease the ensuing problems is very popular topic nowadays. Various methods for CO_2 storage and utilization has been proposed and projected since 21st century, for example, carbon capture utilization and storage (CCUS), CO_2-EOR/EGR, CO_2-EGS, CO_2 fracturing etc.

2.2. Properties of CO_2

As the phase diagram shown in Fig. 2.2, CO_2 can exist in the form of solid, liquid and gas phase, respectively, which is associated with temperature and pressure condition. At extreme low temperature and high pressure, it exists as solid phase. With gradually increased temperature, the solid CO_2 will transfer to liquid CO_2. Exactly on the boundary of solid and liquid phase (melting line), it could exists in a mixture form of solid and liquid phase under equilibrium state. With further decreased pressure, CO_2 will transform again from liquid phase to gas phase. On their boundary (saturation line), liquid and gas phase coexist in equilibrium state. Likewise, gas and solid phase could reach the equilibrium state on sublimation line. Especially, there is a point called triple point with temperature of -56.6°C and pressure of 0.52MPa, where is three-phase coexistence (Wu et al. 2005). Besides, there is another special point called critical point (temperature is 31.1°C and pressure is 7.29MPa) (Vargaftik 1975). When the temperature and pressure both exceed them of critical point, CO_2 will enter supercritical state, where CO_2 owns the characters of both liquid CO_2 and gas CO_2. Specifically, the supercritical CO_2 has a high density close to liquid and low viscosity close to gas, which performs very well as fracturing fluid or working fluid at reducing friction during operation.

The density and viscosity of CO_2 is correlated to both pressure and temperature. As shown in Fig. 2.3, the density of CO_2 falls down with increased temperature (constant pressure) or decreased pressure (constant temperature). At low temperature (T<10°C) and high pressure (P>350bar), the density of CO_2 is comparable with water, even higher. Inversely, at high temperature (T>70°C) and low pressure (P<100bar), the density of CO_2 could low as 200kg/m³. The common density of supercritical CO_2 from 900kg/m³ to 400kg/m³ shows a high compressibility. In comparison with density, the viscosity shows a comparable correlation with temperature and pressure. In spite of this, the viscosity is very low. The viscosity of supercritical CO_2 (0.9×10^{-4} -0.25×10^{-4} Pa·s) is only about 9%-2.5% of water viscosity (about 1.0×10^{-3} Pa·s).

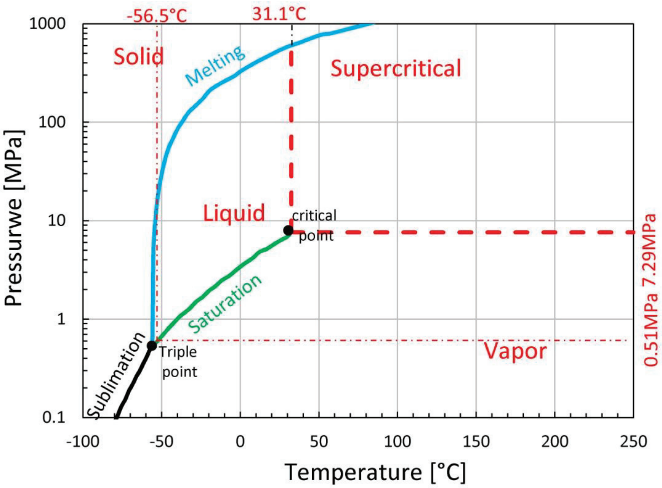

Figure 2.2. Phase diagram of CO_2 (data from Altumin 1975)

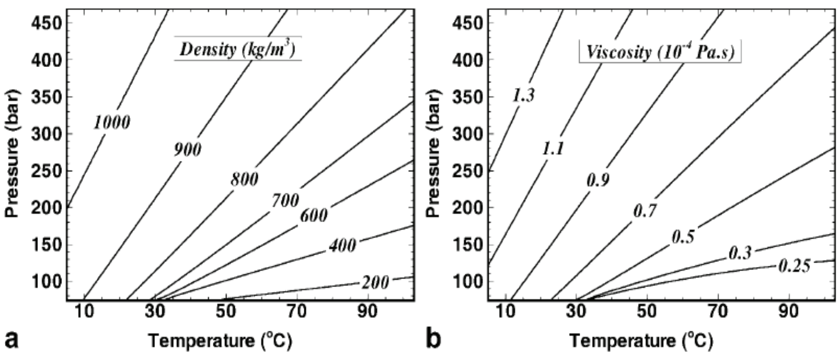

Figure 2.3. Temperature- and pressure-dependent density and viscosity of CO_2 (pressure and Garcia 2002)

The enthalpy of CO_2 is also both temperature- and pressure-dependent. The specific enthalpy of CO_2 and water are compared in Fig. 2.4 under different temperature and pressure. Under the same temperature and pressure, the specific enthalpy per unite mass of water is higher than CO_2. The difference is much significant under high temperature. The specific enthalpy shows a much complex correlation with temperature and pressure, especially around the critical point, where the state of CO_2 changes dramatically. This dramatic change also causes that the density as well viscosity varies rapidly even in a narrow temperature and pressure range near the critical point. Such character makes state computation of CO_2 very complex.

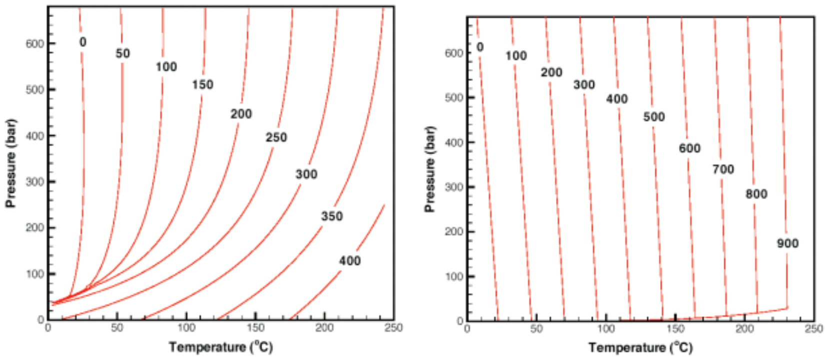

Figure 2.4. Temperature-and pressure-dependent specific enthalpy of CO_2 and water in unites of KJ/kg (Pruess 2006)

CO_2 is one of acid gas. A series of chemical reactions will take place, after CO_2 dissolving in formation water. Firstly, the dissolved CO_2 will form carbonic acid H_2CO_3, which is type of weak acid and its chemical properties is not particularly stable. The carbonic acid H_2CO_3 will break into HCO_3^- and H^+, in which HCO_3^- can further break into CO_3^{2-} and H^+. These chemical reactions are given in following, in which the hydrogen ion H^+ makes the solution acidic. Besides, all the chemical reactions are reversible. At the beginning, above-mentioned substances reach the chemical dynamic equilibrium. Once other associated substances are incorporated or chemical equilibrium condition is broken, the substance will vary and reaches new equilibrium state. Macroscopically, the process of re-equilibrium performs as precipitation or dissolution mineral, which is the reaction mechanism for long-term CO_2 geological storage (Liu 2014).

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \tag{2.1}$$

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_{3(aq)} \tag{2.2}$$

$$H_2CO_{3(aq)} \leftrightarrow HCO_{3(aq)}^- + H_{(aq)}^+ \tag{2.3}$$

$$HCO_{3(aq)}^- \leftrightarrow CO_{3(aq)}^{2-} + H_{(aq)}^+ \tag{2.4}$$

2.3. Phase path of CO_2 in engineering processes

A typical phase paths of CO_2 in a fracturing-treatment cycle in unconventional gas reservoir is illustrated in Fig. 2.5. Position 1 is tank for fracturing. As CO_2 in tank is commonly stored and transported in liquid phase, the Position 1 should locate at least on the saturation line or over the saturation line. Position 2 is pump or wellhead. Before injection, CO_2 need be pressurized by pump. The temperature of CO_2 increases slightly in process 1-2, under the effect of environment temperature. Then the pressurized CO_2 is injected into well bottom or perforation (Position 3). The CO_2 in Position 1, 2, 3 exists mostly in liquid phase, while Position 3 can also exist in supercritical phase, which is affected by many factors, like injection rate, injection depth, formation temperature, heat conductivity etc. Position 4 is hydraulic fracture. In this process 3-4, CO_2 will be heated by heat exchange trough fracture wall, but pressure will fall a bit, for the reason of friction effect of fracture wall roughness. It should be mentioned that the temperature of CO_2 in fracture (Position 4) is not constant, rather increase gradually from perforation to fracture tip. The temperature at fracture tip is infinitely close to formation temperature. Generally, injection well will be shut in for fracture closure and proppant support, in which the temperature increases gradually but still low than formation temperature. After that, CO_2 will reach Position 5, where the CO_2 has a relatively low pressure and high temperature, in comparison with it at Position 4. The CO_2 in both Position 4 and 5 exist normally in supercritical phase. Finally, CO_2 will flow back to surface in gas phase at the ambient condition (Position 6). Especially, in process 3-5, some CO_2 leaks into formation due to pressure difference and exists as supercritical phase in hot reservoir.