# CHAPTER II
# THEORETICAL BACKGROUND AND LITERATURE REVIEW

## 2.1 Oil Recovery (James, 2013; Dawe, 2000)

Oil recovery can be classified into 3 stages, i.e. primary recovery, secondary recovery, and tertiary recovery or enhanced oil recovery (EOR). Primary recovery of oil results from natural energy of reservoir, which normally can recover up to 30% of original oil in place (OOIP). The techniques include gas-cap drive, natural water-drive, fluid and rock expansion, and gravity drainage. The secondary recovery (synonym of water flooding) is implemented after primary production declines, and oil can't be no longer produced by reservoir natural energy. The techniques can be water flooding, gas injection, or something that can maintain the reservoir pressure in order to give the displacement energy to displace oil toward producing wells. The secondary recovery can produce oil in the range of 25-40% of OOIP depending on the reservoir characteristic and in place fluid properties. The tertiary recovery or enhanced oil recovery is the third stage of oil production and normally will be done after water flooding. The EOR technique can recover oil ranging from 5-20% of OOIP after done the primary and secondary recovery.

In the tertiary oil recovery or EOR process, the energy that is injected into the well will change chemical and physical properties of oil and injected fluid especially physical properties, i.e. density and viscosity. EOR is widely used for recovering more oil from medium to heavy crude oil to maximize produced crude oil. EOR can be categorized into two main techniques, thermal recovery process and non-thermal recovery process.

### 2.1.1 Thermal Recovery Process

This technique supplies heat to a reservoir to reduce oil viscosity to increase the amount of produced oil from wells. The technique can account for the production around 70% of the total production from EOR. This process is normally used in heavy oil reservoir. The widely used thermal recovery processes are steam flooding, cyclic steam stimulation (CSS), in-situ combustion, and steam-assisted gravity drainage (SAGD).

### 2.1.1.1 Steam Flooding

Steam flooding is sometimes called continuous steam injection or steam drive. The technique uses hot steam to transfer heat to oil in a reservoir to decrease viscosity of oil at elevated temperature and then, the oil produced can be moved at a higher flow rate, thus, the amount of oil recovery is enhanced. The technique is appropriate for thick reservoir and low operating pressure. Too much heat will be lost or wasted if the reservoir is a thin type. In addition, this process is favored to operate at low pressure because of low boiling point of water.

### 2.1.1.2 Cyclic Steam Stimulation (CSS)

A CSS method or cyclic steam injection, huff-and-puff, or steam soak is a precursor of steam flood which needs high-quality feed water to inject into the formation through the well with one-to-two weeks at a high injection rate. Then, the well will be closed and becomes a soak period for a few weeks to let the heat from the steam penetrating through the reservoir to reduce the crude oil viscosity. When the time comes, the injection well will be turned into a producer for a few months to over a year. The cycle may be repeated and stopped when the production rate is decreasing to unacceptable level (uneconomical).

### 2.1.1.3 In-Situ Combustion

In-situ combustion or called fire flooding requires air to be injected into the reservoir to create the thermal energy and to reduce the oil viscosity at the front. If water is injected, this process is named "wet combustion". The in-situ combustion is the one process that can improve element of oil because oil produced is lighter than the initial crude oil. This technique gives a highest performance of oil recovery (around 90% of oil recovery from thermal process). In addition, it is an environmental friendly process because the combustion products, carbon dioxide ($CO_2$) and nitrogen ($N_2$) can be used in an immiscible/miscible process.

### 2.1.1.4 Steam-Assisted Gravity Drainage (SAGD)

Two horizontal wells are drilled by the upper horizontal well which is a steam injector and the lower horizontal well is a producer well. When steam is injected, steam will spread out and form a chamber near the injection well. Heat will transmit to the surrounding oil which makes oil movable because the

viscosity of oil is decreased. After that oil will be drained down by gravity to production well.

### 2.1.2 Non-Thermal Recovery Process

Non-thermal recovery process includes water flooding, chemical flooding, amicrobial process, and gas drive.

#### 2.1.2.1 Water Flooding

This technique can be done by injecting water into reservoir to support reservoir pressure to increase amount of oil produced. Water flooding is appropriate if the oil viscosity is in a range of 10-100 cP.

#### 2.1.2.2 Chemical Flooding

This technique requires addition of chemicals to displacing water. The chemicals will change physicochemical properties of displacing water which makes the displacing process more sufficient. Chemical flooding consists of surfactant flooding, polymer flooding, and foam process.

- Surfactant flooding. Surfactant is injected to reduce an interfacial tension of oil-water. It is always done with residue oil recovery in swept areas.

- Polymer flooding. It suits to low reservoir temperature because polymer trends to degrade at high temperature. Polymer flooding is often used in 2 different purposes; those are to viscosify the injection water with polymer to increase viscosity of displacing water to avoid viscous fingering effect. Examples of polymer are polyacrylamides, polysaccharide and xanthan gums. Another purpose is conformance adjustment used to reduce permeability of selected reservoir volume. A type of used polymer is gelled polymers formed by crosslinking.

- Foam process. A system consists of water, gas, oil, and foaming agent. When injected surfactant together with gas, foam is produced.

#### 2.1.2.3 Microbial Process

In this technique, reservoir will be flushed to reach residual oil saturation and bacteria and nutrients are used to inject into a wellbore for a few

hours, and then surfactants, $H_2S$ and $CO_2$ are produced from metabolism to react with residue oil in the reservoir. Next is production stage at which it may continue for weeks or months.

### 2.1.2.4 Gas Drive

Gas drive or gas injection uses $CO_2$ and $N_2$, which are most famous gas injected into the reservoir to push more oil out at a production well. Some gases can dissolve into oil to reduce oil viscosity dramatically. The gas drive can be miscible includes gas flooding and immiscible gas flooding. The miscible gas flooding is more effective to recover residue oil than the immiscible gas flooding.

- Immiscible gas injection. Advantages of the method are to maintain pressure in reservoir, able to reduce the amount of residual oil saturation if that gas can dissolve into oil, and able to swell the oil.
- Miscible gas injection. Gas or mixed gas is injected to mix with reservoir fluid to improve flow properties (mobility) of mixed hydrocarbon phase. $CO_2$, hydrocarbon, or mixture is widely used.
  - Carbon dioxide flooding. The miscibility of $CO_2$ and oil forms high density phase which can extract hydrocarbons easier and heavier hydrocarbon, for example, $C_2$-$C_4$ components.
  - Hydrocarbon gas flooding. At high temperature, it can be done with first contact miscibility or injecting gas that is enriched with $C_2$-$C_6$ components.
  - Vaporizing gas drive. It can be done with multiple contact miscibility by bringing $C_2$-$C_6$ component out from crude oil.
  - Condensing gas drive. It can be done with multiple contact miscibility at oil-gas slug, which $C_2$-$C_6$ which will be condensing out from gas.

## 2.2 Carbon Dioxide Flooding (James, 2013)

$CO_2$ is injected into the reservoir to raise the amount of oil production because $CO_2$ is dissolved in the contacted oil in reservoir which results in decreasing

of oil viscosity and consequently makes the oil to move out easily from the reservoir to the production well. It can be done after the initial pressure of reservoir in primary recovery stage has declined. Sometime, $CO_2$ will be used in a water-alternating-gas (WAG) process to improve its efficiency in recovering residue oil from the reservoir. A parameter that plays very important role to determine how much gas can diffuse into liquid is called "diffusion coefficient".

## 2.3 Diffusion (Mehrer, 2009)

Diffusion is a process that uses to determine a concentration of substance or equilibrium concentration distribution in a system. By definition, it is a random movement of molecules of a specific species from a high concentration region to a low concentration region. Diffusion can be divided into 3 types, i.e. molecular diffusion, Brownian diffusion, and turbulent diffusion. The diffusion can be noticed by Fick's law and the diffusion coefficient can be determined.

- Fick's first law of diffusion. It relates a diffusive flux to concentration under an assumption of steady state, where the flux will go from high concentration region to low concentration region. Fick's first law of diffusion can be expressed as

$$J = -D\frac{\partial c}{\partial x} \tag{2.1}$$

where

J is a diffusion flux, unit area per unit time

D is diffusion coefficient of diffusivity, $length^2 time^{-1}$

C is concentration, amount of substance per unit volume

x is position, length

- Fick's second law of diffusion. It is used to predict how diffusion causes the concentration to change with time. Fick's second law of diffusion can be expressed as

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{2.2}$$

where

t is time in a unit of second

### 2.3.1 Diffusion Coefficient (Mehrer, 2009)

Diffusion coefficient or diffusivity, D is a proportionality constant between concentration gradient and molar flux. Physically, D implies that the mass of substance diffuses through a unit surface in a unit time at a concentration gradient of unity. In a system, such as gas-liquid, the diffusion might be occurred by higher diffusivity, the faster they diffuse into each other. The main parameters that impact to D are temperature and pressure. Moreover, molecular size and other properties of diffusing substance can also impact to D value.

### 2.3.2 Correlations which use to predict the diffusion coefficient summarized by Mehrotra *et al.*(1987) are shown in Table 2.1 below:

**Table 2.1** Summary of correlations (Mehrotra *et al.*, 1987)

| Correlation | Equation | Notation |
|---|---|---|
| Stroke-Einstein equation | For small and hard spherical molecule only $$D^0_{AB} = \frac{kT}{6\pi R_A \mu_B} \quad (2.3)$$ | - The diffusion coefficients will changes with the size of diffusing molecule. |
| Wilke-Chang equation | $$D^0_{AB} = 7.4 \times 10^{-8} \frac{(\phi_B M_B)T}{\mu_B V_A^{0.6}} \quad (2.4)$$ | - This correlation will be successful with limited application. |
| Eyring-Jhon equation | $$D^0_{AB} = \left(\frac{kT}{6\mu_B}\right)\left(\frac{N_0}{V_B}\right)^{1/3} \quad (2.5)$$ | |
| Othmer-Thakar equation | $$D^0_{AB} = \frac{1.4 \times 10^{-4}}{V_A^{0.6} \mu_B \mu_W (1.1\frac{L_R}{L_W})} \quad (2.6)$$ | |

**Table 2.1** Summary of correlations (Mehrotra *et al.*, 1987) (cont'd)

| Correlation | Equation | Notation |
|---|---|---|
| Sridhar-Potter equation | For gas-liquid and liquid-liquid diffusivity $$D^0_{AB} = \frac{0.088 V_{C_B}^{4/3} RT}{\mu_B V_0 V_{C_A}^{2/3} N_0^{2/3}} \quad (2.7)$$ | |
| Umesi-Danner equation | For pure gas diffusing into pure liquid system $$D^0_{AB} = 2.75 \times 10^{-8} \frac{T}{\mu_B} (\bar{R}_B / \bar{R}_A^{2/3}) \quad (2.8)$$ | |
| Akgerman-Gainer equation | For gas-liquid diffusion coefficient $$D^0_{AB} = \left(\frac{kT}{\varepsilon_A \mu_B}\right) \left(\frac{N_0}{V_B}\right)^{1/3} \left(\frac{M_B}{M_A}\right)^{1/2} \exp\left(\frac{E_{\mu B} - E_{\mathcal{D} AB}}{RT}\right) \quad (2.9)$$ | $E_{\mu B} - E_{D_{AB}}$ $$= E_{BB}^j [1$$ $$- (\frac{E_{AA}^j}{E_{BB}^j})^{1/(\varepsilon_A + 1)}]$$ $E_{BB}^j$ $$= \frac{R \ln\left(\frac{\mu_2}{\mu_1}\right) + \frac{R}{2} \ln\left(\frac{T_1}{T_2}\right)}{\frac{1}{T_1} - \frac{1}{T_2}}$$ $E_{AA}^j = 5875.3 M_A^{-0.186}$ |

**Nomenclature**

$D^0_{AB}$ = the diffusivity in an infinite dilute solution, cm$^2$/s

k = the Boltzmann's constant, $1.38 \times 10^{-23}$ J/K

T = the absolute temperature, K

$\mu_B$ = the viscosity of solvent B, g/cm·s (for equation 2.3, 2.5, 2.7, 2.9)

$\mu_B$ = the viscosity of solvent B, mPa·s (for equation 2.4, 2.6, 2.8)

$\mu_w$ = the viscosity of water, mPa·s

$R_A$ = the radius of the diffusion molecule of solute A, cm

$\phi_B$ = the parameter of association of solvent B

$M_A$ = the molar mass of solute A, g/mol

$M_B$ = the molar mass of solvent B, g/mol

$V_A$ = molar volume of solute A at a boiling point under normal conditions, cm$^3$/mol

$V_B$ = molar volume of solvent B at boiling point under normal conditions, cm$^3$/mol

$N_0$ = Avogadro's number, $6.023 \times 10^{-23}$ mol$^{-1}$

$L_B$ = latent heat of vaporization of solvent B, J/mol

$L_W$ = latent heat of vaporization of water, J/mol

$V_{CA}$= molar volume of solute A at a critical boiling point under normal conditions, cm$^3$/mol

$V_{CB}$= molar volume of solvent B at a critical boiling point under normal conditions, cm$^3$/mol

R = universal gas constant

$V_0 = 0.31 V_{CB}$

$\bar{R}_A$ = the radius of gyration of solute A, Å

$\bar{R}_B$ = the radius of gyration of solvent B, Å

$\varepsilon_A$ = number of B molecules around a central A molecule, $\varepsilon_A = 6 \left( \frac{V_A}{V_B} \right)^{1/6}$


## 2.4 Experimental Methods for the Gas-Liquid Diffusivity

The diffusion coefficient of gas-crude oil was experimentally measured using various methods including pressure decay, constant pressure dissolving gas volume (CPDGV), X-ray computed assisted tomography, dynamic pendant drop volume analysis (DPDVA).

### 2.4.1 Pressure Decay Method

Riazi (1996) developed a model to predict a position of gas-liquid interface and pressure of gas changed with time by using visible constant-volume constant-temperature or PVT cell as shown in Fig. 2.1. It contained non-equilibrium gas-oil mixture with known initial composition at constant temperature. Pressure, composition of each phase and volume are changed as a function of time until the system reaches its equilibrium.
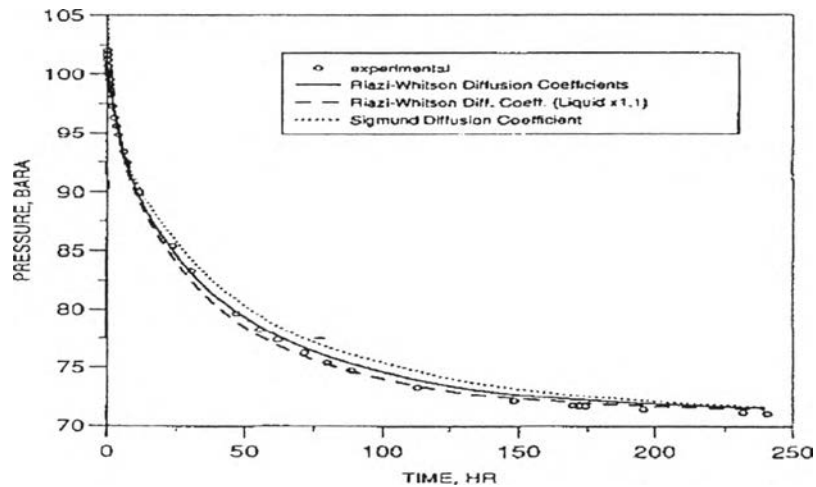
$$0 \leq z \leq L$$

$$z = z_0 + L_0 \ if \ z \geq L_0$$

$$z = z_0 \ if \ z \leq L_0$$

**Fig. 2.1** Schematic and dimensions of a constant-volume cell (PVT cell) (Riazi, 1996).

The studied system was methane-n-pentane at initial pressure of 102 bar (1480 psia) and temperature at 37.8 °C. At first, 35% n-pentane (by volume of cell) was filled in the cell, then vacuum was applied, and the liquid volume at saturated condition was made to determine the initial moles of n- pentane. Next, high pressure methane was introduced slowly into PVT cell until the pressure in PVT cell reached 102 bar. The pressure of gas is recorded along with time as shown in Fig. 2.2. The author determined diffusion coefficient of methane-n-pentane system by using Fick's second law (equation 2.2), the results were satisfactorily matched among the models within ±5% of literature value.

**Fig. 2.2** Variation of pressure for $C_1$-n-$C_5$ as a function of time with constant volume diffusion experiment at 37.8 °C (Riazi, 1996).

Zhang *et al.* (2000) adapted Riazi (1996) technique to determine diffusion of carbon dioxide ($CO_2$) and methane ($CH_4$) in heavy oil (Venezuela oil with viscosity of 5.0 Pa·s) at constant temperature 21 °C and initial to final pressures of 3471 kPa to 3420 kPa for methane-oil system and 3510 kPa to 2856 kPa for carbon dioxide-oil system. The advantage of this technique is that it does not require the data of interface position change with time. The results of pressure were recorded as a function of time as shown in Fig. 2.3 and Fig. 2.4.
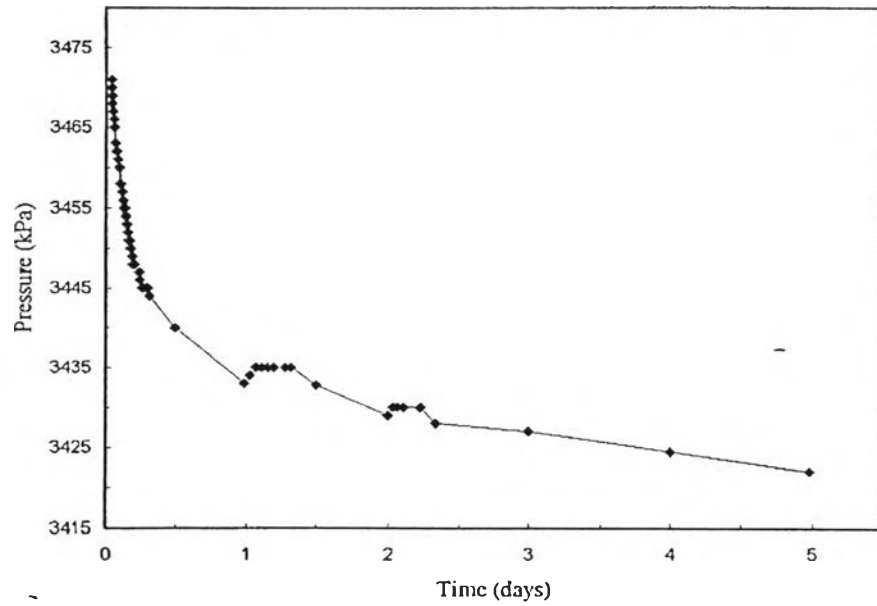
**Fig. 2.3** Measured pressure data versus time plot for methane-oil system (Zhang *et al.*, 2000).
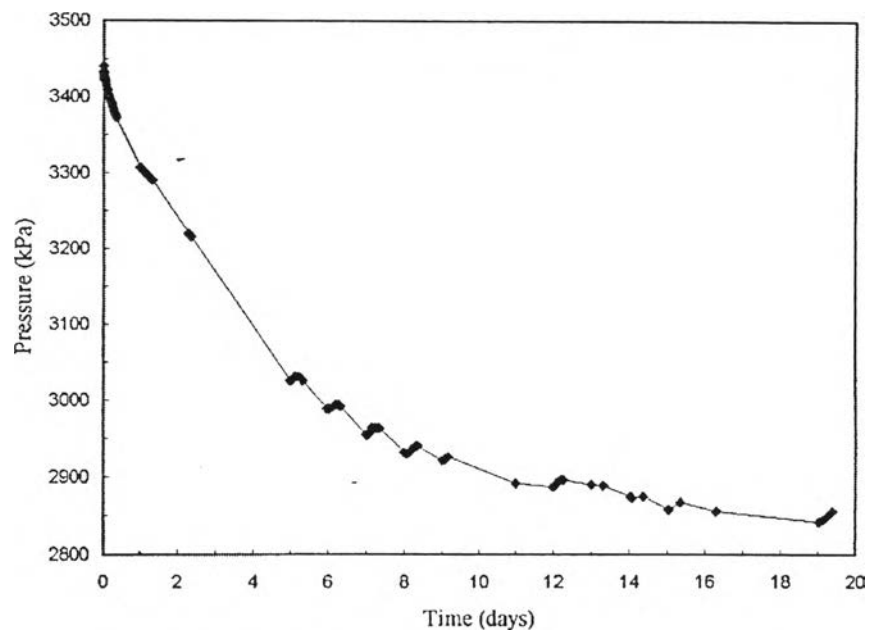


**Fig. 2.4** Measured pressure data versus time plot for $CO_2$-oil system (Zhang *et al.*, 2000).

The pressure-time curves need to be fitted to eliminate the pressure fluctuation at room temperature during the day and night and eliminate the need for experimentally measuring $P_{eq}$ provided sufficient pressure history is recorded to obtain reliable values of the regression parameters by using numerical non-linear regression method (equation 2.10).

$$P(t) = m_1 \exp\left(-\frac{t}{k_1}\right) + m_2 \exp\left(-\frac{t}{k_2}\right) + P_{eq} \qquad (2.10)$$

where the value of $m_1$, $k_1$, $m_2$, $k_2$, and $P_{eq}$ were determined by non-linear regression of the experimental data.

Fig.2.5 and Fig.2.6 show the fit curve that obtained from the calculation of equation 2.10
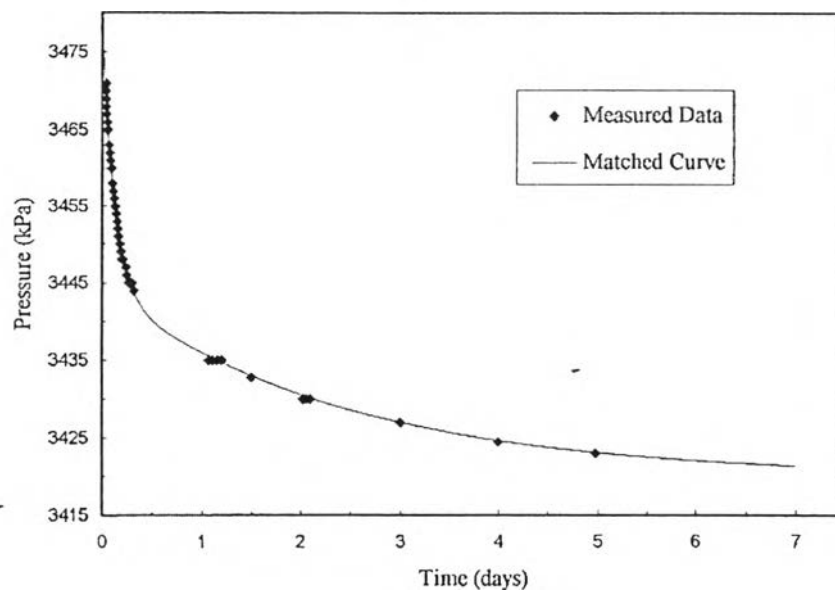


**Fig. 2.5** Using equation 2.10 matching for measured data for methane–oil system ($m_1 = 23.97$ kPa, $k_1 = 2.44$ day, $m_2 = 35.88$ kPa, $k_2 = 0.1245$ day) (Zhang *et al.*, 2000).
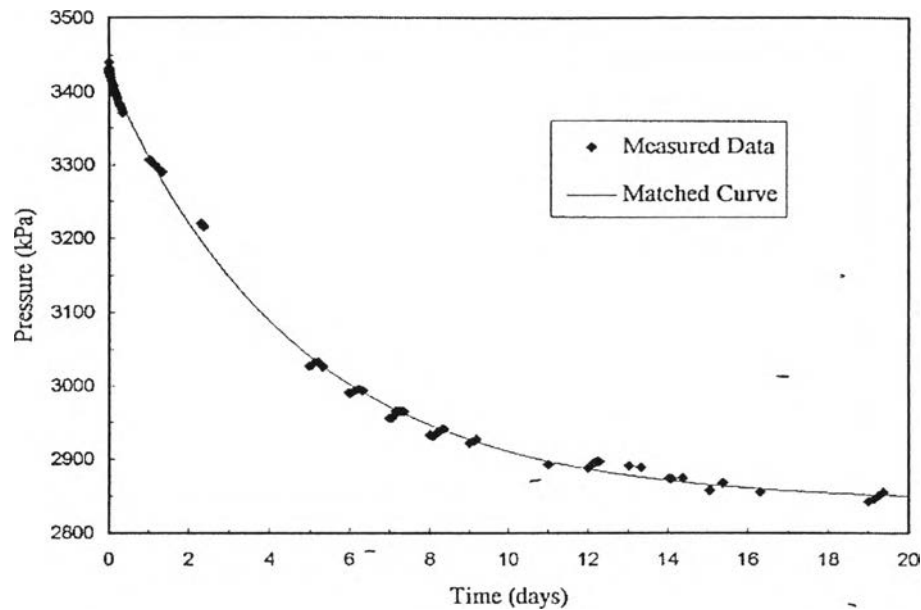
**Fig. 2.6** Using equation 2.10 matching for measured data for $CO_2$ – oil system ($m_1$ = 575.9 kPa, $k_1$ = 4.83 day, $m_2$ = 11.07 kPa, $k_2$ = 4.73 day) (Zhang *et al.*, 2000).

In order to determine the diffusivity, the derived simple equation 2.11 was used.

$$D_{AB} = \frac{4z_0^2}{k_1 \pi^2}$$  (2.11)

The diffusion coefficient of both methane-oil and carbon dioxide system were compared with the value from other experiments and found that their values of diffusion coefficient were close to other investigators.

### 2.4.2 Constant Pressure Dissolving Gas Volume (CPDGV)

Jamialahmadi *et al.* (2006) studied mechanisms of diffusion processes of enhanced oil recovery and effects of solute concentration and solution viscosity on the diffusivity using methane-dodecane system and methane-Iranian crude oil system. All properties including viscosity, surface tension, and density were calculated using Peng-Robinson equation of state.

For the methane-dodecane system, when increasing temperature, both density and viscosity are decreased and the diffusivity of this system is increased, which can be seen in Fig. 2.7 and Fig. 2.8. The diffusion coefficient was calculated from equation 2.12.

$$D(T, P) = a_0 \mu^{a_1} \tag{2.12}$$

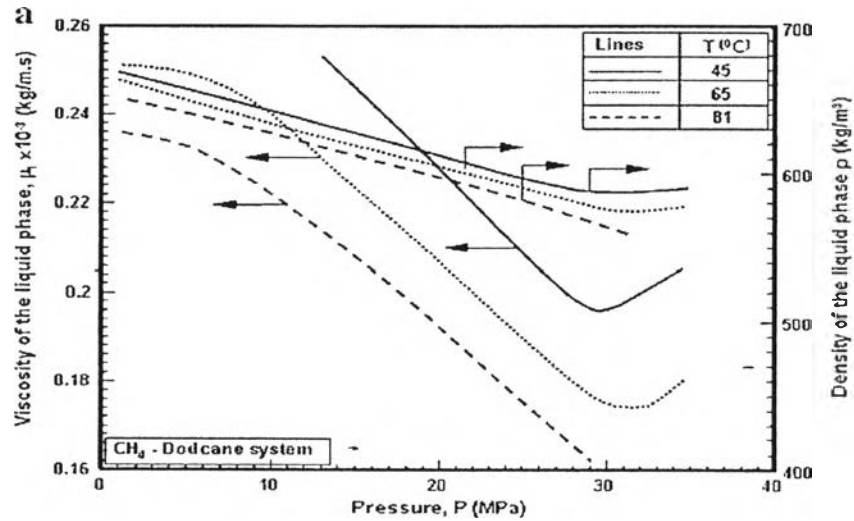where: $a_0$, e, and $a_1$ are parameters obtained from experimental data.



**Fig. 2.7** Variation of viscosity and density of the solution with pressure for the methane-dodecane system (Jamialahmadi *et al.*, 2006).
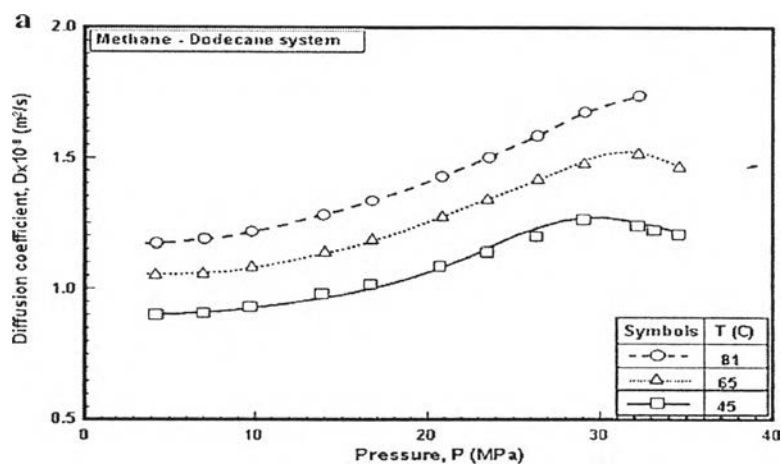


**Fig. 2.8** Diffusion coefficient of methane in dodecane as a function of pressure for different temperatures (Jamialahmadi *et al.*, 2006).

It was concluded that when gas phase was disappeared at one pressure (gas is completely dissolved into liquid phase), the maximum value of diffusivity is

observed. Furthermore, when pressure is increased, the density and viscosity increase, diffusivity decreases.

### 2.4.3 X-Ray Computed Assisted Tomography

Song *et al.* (2010) evaluated the feasibility of determining experimental diffusion coefficients of carbon dioxide in heavy oil by using X-ray computed assisted tomography (CAT) shown in Fig. 2.9. All CT scan images were acquired using a scanner.
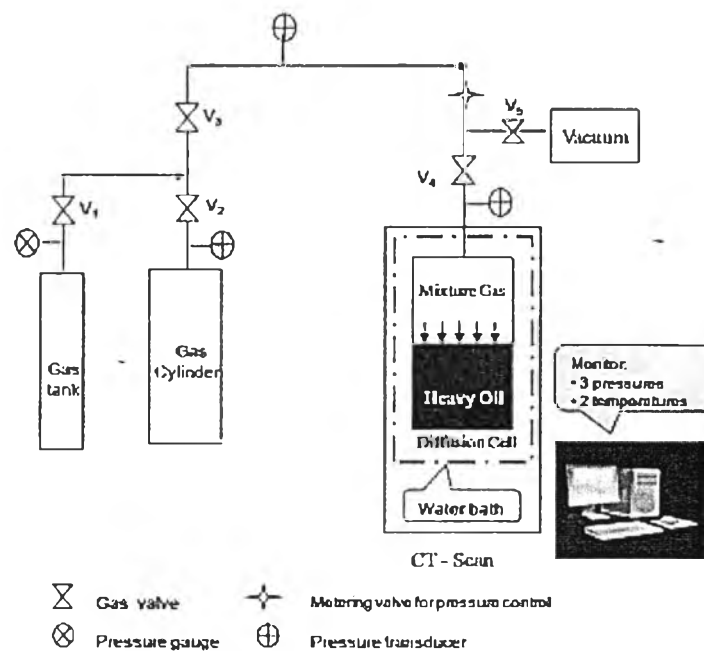


**Fig. 2.9** Schematic diagram of the experimental setup for gas diffusivity (Song *et al.*, 2010).

The investigators found that at the beginning of injection of carbon dioxide into heavy oil, interface between gas and crude is clear and becomes more unclear as the diffusion of $CO_2$ continues. Moreover, at the interface, the area and extent of gradual changing of color are enhanced with the diffusion distance indicating that carbon dioxide can slowly dissolve into the heavy oil even pressure is constant. It was concluded that the higher operating pressure, the higher diffusion coefficient.

The diffusivity of carbon dioxide is a strong function of time and distance of diffusion and the concentration of carbon dioxide at the initial stage is lower than the

concentration at final stage of the diffusion process. In addition the X-Ray CAT technique is a powerful tool to monitor carbon dioxide diffusing in heavy oil and has more accuracy to determine diffusion coefficient.

### 2.4.4 Dynamic Pendant Drop Volume Analysis (DPDVA)

Yang and Gu (2006) estimated the solvent diffusion coefficient and oil swelling factors of carbon dioxide, methane, ethane, propane, and their mixtures in heavy oil by using the dynamic pendant drop volume analysis (DPDVA). A high pressure windowed cell is filled with a test solvent at a given pressure and temperature and then, heavy oil is introduced to form a pendant oil drop inside the windowed cell. Solvent dissolution into the pendant oil drop by its volume is increasing until it reaches the saturation with solvent as shown in Fig. 2.10.
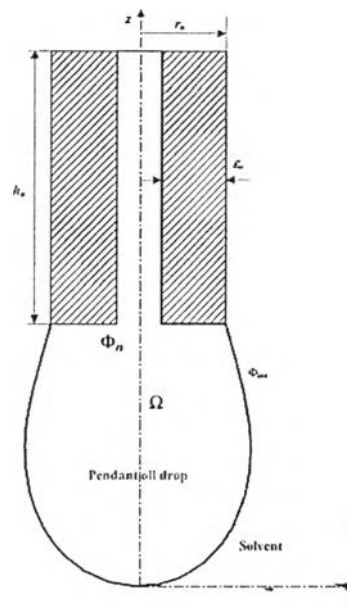


**Fig. 2.10** Schematic diagram of an axisymmetric pendant oil drop surrounded by a solvent in the cylindrical coordinate system (r,z) (Yang and Gu, 2006).

It was found that the liquid volume of $CO_2$ - heavy oil system increase 7% after 1,200 s. passed at 4 MPa and 23.9 °C. In addition, at the beginning of the test, volume of pendant oil drop increases very quickly and approaches a constant volume at the end of test as seen in Fig. 2.11.
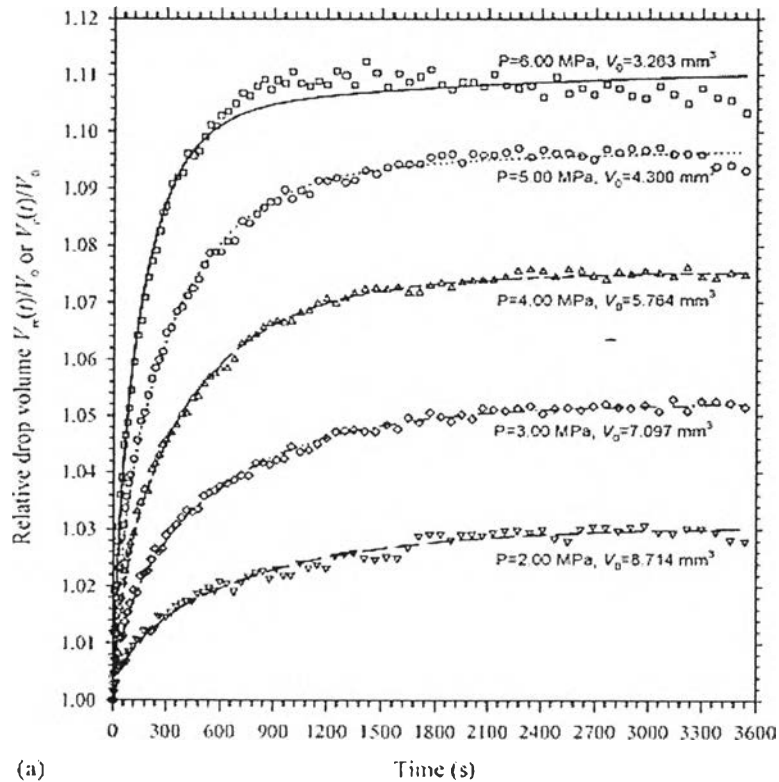
(a)

**Fig. 2.11** Comparison between the calculated and measured relative volumes of the dynamic pendant oil drops at T = 23.9 °C with drop formation time, $t_f$ = 8 s. The empty symbols represent the measured relative drop volumes, whereas the lines represent the calculated relative drop volumes with the determined diffusion coefficient and oil swelling factor of heavy oil-carbon dioxide system, P = 2.00, 3.00, 4.00, 5.00, and 6.00 MPa (Yang and Gu, 2006).

The result is important for $CO_2$ miscible flooding process, which shows the effect of increasing residual oil recovery. Furthermore, it is noticed that solvent diffusion coefficients of the four pure solvent-heavy oil systems increase with pressure because when pressure increase, the solubility of solvent in heavy oil is decreased and the reduction of viscosity results in the increasing of diffusion coefficient of the solvent in heavy oil also. The measured diffusion coefficient is shown in Fig. 2.12.
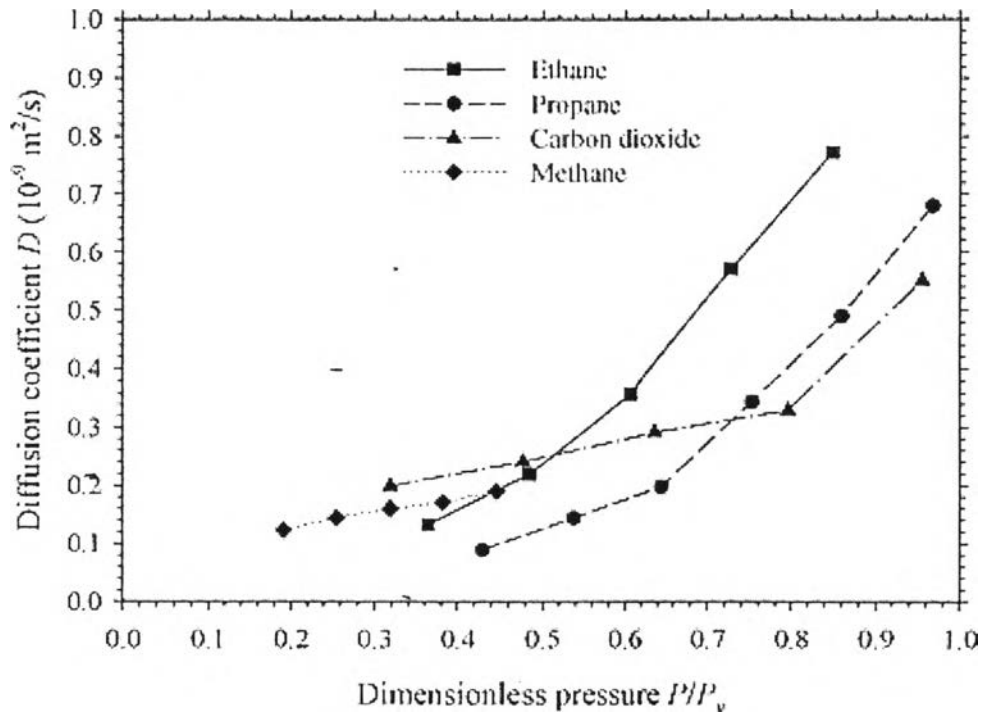
**Fig. 2.12** The measured diffusion coefficients of carbon dioxide, methane, ethane, and propane in Lloydminster heavy oil vs. the dimensionless pressure at T = 23.9 °C (Yang and Gu, 2006).

Yang and Gu (2006) concluded that the latest developed dynamic pendant drop volume analysis (DPDVA) can be applying to estimate the diffusion coefficient and oil swelling factors for carbon dioxide, methane, ethane, propane, and their mixtures in heavy oil. The experimental results for pure solvent showed that the diffusion coefficient increases when the pressure increases. For the mixture system, when pressure close to the dew-point pressure of three solvent mixtures, their viscosity of solvent mixture-saturated heavy oil may be decrease dramatically because of propane on the mixture. Swelling factors of oil both pure and mixture solvent systems also increased when pressure increased and the largest oil swelling of the mixtures occurred when the pressure was close to their dew-point pressure.

The main purpose of this work is to determine diffusion coefficient of carbon dioxide ($CO_2$ - 99.99% purity) in Lan Krabue crude by using a Parr reactor. Pressure decay method is used to measure pressure as a function of time passes, and the gathered data are used to calculate the diffusion coefficient of $CO_2$ in Lan Krabue

crude. In this study, two different pressures (300 psi and 700 psi), two different temperatures (30 °C and 40 °C), and two different APIs of Lan Krabue crude (API 14.1 and 21.3) which supported by PTTEP Public Company Limited were studied as parameters that can be effected to the value of diffusion coefficient of $CO_2$ in Lan Krabue crude.