

INSTITUT TEKNOLOGI BANDUNG

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No : 1255/IT1.C05.1/DA.05/2021 22 Maret 2021 Perihal : **Undangan Ujian Proposal Penelitian Disertasi Sdr. Kartika Fajarwati Hartono NIM. 32219001.**

Kepada Yth.

- 1. Prof.Ir. Asep Kurnia Permadi, M.Sc., Ph.D. Pembimbing (Ketua)
- 2. Ir. Utjok W.R. Siagian, M.Sc., Ph.D. Pembimbing (Anggota)
- 3. Dr. Andri Luthfi Lukman Hakim Pembimbing (Anggota)
- 4. Prof. Ir. Doddy Abdassah, M.Sc., Ph.D. Penguji
- 5. Prof.Dr.Ir. H.P. Septoratno Siregar, DEA Penguji
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- 7. Zuher Syihab, S.T., Ph.D. Anggota KPPs/Kaprodi
- 8. Dr.-Ing. Bonar Tua Halomoan Marbun **Anggota KPPs**
- 9. Dr. Eng. Sutopo M.Eng. Anggota KPPs

6. Dr. Muslim Abdurrahman Penguji (Univ. Islam Riau)

Sehubungan dengan telah disetujuinya Proposal Disertasi mahasiswa Program Doktor Teknik Perminyakan FTTM-ITB, yaitu:

bersama ini kami sampaikan dengan hormat undangan pelaksanaan Ujian Proposal Penelitian Disertasi, yang akan dilaksanakan pada:

Demikian yang dapat kami sampaikan, atas perhatian yang diberikan kami ucapkan terimakasih.

Ketua KPPs,

Prof.Ir. Asep Kurnia Permadi, M.Sc, Ph.D. NIP. 19631112 199001 1 001

Tembusan Yth : Sdr. **Kartika Fajarwati Hartono**

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LAPORAN AKHIR PENILAIAN UJIAN PROPOSAL DISERTASI

Hasil Penilaian/Komentar:

Diusulkan ke Tahap III dengan susunan Tim Pembimbing sebagai berikut:

- 1. Prof.Ir. Asep Kurnia Permadi, M.Sc., Ph.D. (Promotor)
- 2. Ir. Utjok W.R. Siagian, M.Sc., Ph.D. (Ko-Promotor)
- 3. Dr. Andri Luthfi Lukman Hakim (Ko-Promotor)

Lain-lain (jika ada) :

Saran, masukan dan perbaikan sesuai dengan hasil sidang dan catatan dari seluruh peserta sidang (KPPS, Penguji dan Tim Pembimbing, Ka Prodi) pada lembar penilaian.

> Bandung, 30 Maret 2021 Ketua Tim Penilai dan Penguji Proposal Disertasi

Mumin

(Prof.Dr.Ir. H.P. Septoratno Siregar, DEA)

INSTITUT TEKNOLOGI BANDUNG FAKULTAS TEKNIK PERTAMBANGAN DAN PERMINYAKAN Gedung Basic Science Center B Lantai 4, Jalan Ganesa 10 Bandung 40132, Telp.: +6222 2506282 Fax.: +6222 2514922, E-mail: dekan@fttm.itb.ac.id, http://www.fttm.itb.ac.id

BERITA ACARA PENILAIAN UJIAN PROPOSAL DISERTASI MAHASISWA PROGRAM DOKTOR

Tanggal Ujian : **30 Maret 2021**

Catatan :

Catatan ini merupakan kompilasi dari catatan/isian (**terlampir**) dari masing-masing peserta sidang yang hadir.

1. Dr. Muslim Abdurrahman (Penguji, Universitas Islam Riau)

- 1) DOE Perlu ditinjau ulang, penggunaan surfactant dan ethanol dalam persentasi perlu ditambahkan.
- 2) Terlampir hasil review dari draft proposal.

2. Prof. Dr. Ir. H P Septoratno, DEA (Ketua Penguji)

- 1) Kalimat2 bhs Inggeris perlu diperbaiki
- 2) Apakah judul tidak terlalu umum, jadi scope penelitian luas sekali?
- 3) Pada kebaruan no 2 dan 3 ada solid precipitation? Apakah tdk sama?
- 4) Utk pengendapan padatan, apakah tdk akan dilakukan analisis SARA (Saturates, Asphaltenes, Resins and Aromatics)?

3. Prof. Ir. Doddy Abdassah, M.Sc., Ph.D (Penguji)

Perbaikan perbaikan harus dilakukan sesuai dengan yang saya sam-paikan pada Ujian Proposal ini. Saya tidak mencatatnya. Silakan diden-garkan dari rekamannya.

4. Dr. Ing. Bonar Tua Halomoan Marbun (Anggota KPPS)

- 1) Proposal bisa Saudari Kartika perbaiki sehingga sesuai dengan kaidahproposal dengan format dan novelty yang jelas.
- 2) Scope of work dantata waktu serta target publikasi bisa dibuat lebih realistis mengacukepada kondisi peralatan lab, dana, dan waktu yang tersedia.

5. Dr.Eng. Ir. Sutopo, M.Eng. (Anggota KPPS)

format penulisan diperbaiki

6. Ir.Utjok W. R. Siagian M.Sc., Ph.D (Anggota Pembimbing)

perbaikan sesuai diskusi saat presentasi

7. Dr. Andri Luthfi Lukman Hakim (Anggota Pembimbing)

- 1) Pertimbangan antara keseuaian Judul dengan Scope of Works
- 2) Phase Behaviour dan Phase Diagram untuk penjelasan yang lebihtepat sebagai target atau tujuan dalam penelitian ini.
- 3) Dalam Hipotesis,disampaikan mengenai kondisi presipitasi aspaltene bersifat reversible,perlu ditinjau ulang untuk penelitian ini, sebagai pertanyaan atau sebagaikomplimentari.
- 4) Metode Penelitian PVT, antara Fix volume atau konstanpressure.
- 5) Revisit DOE untuk "doability"

8. Prof. Ir. Asep Kurnia Permadi, M.Sc., Ph.D (Pembimbing Utama)

Banyak catatan. Saya turut mencatat Pertanyaan/Komentar/Masukan danakan berkomunikasi dengan Yang Bersangkutan

9. Zuher Syihab, ST., Ph.D (Anggota KPPS/KaProdi S2/S3 TM, ITB)

Disesuaikan dengan diskusi oleh Tim Penguji/KPPS dan tentunya TimPembimbing

Bandung, 30 Maret 2021

 2 which

 Ketua Sidang Zuher Syihab, S.T., Ph.D.

Catatan / Saran atas Presentasi Sdri Kartika Fajarwati Hartono

- 1. Dalam *Abstract* dan *Introduction/Background* belum ada menyampaikan penggunaan *etanol* dan *surfactant* untuk menurunkan MMP.
- 2. Point 1.3 (*purpose* & *objective*) membahas *effect of additives*, tetapi tidak ada dibahas dalam *introduction* dll
- 3. Hal 16 → penjelasan gambar 2.1 agar disesuaikan lagi dengan gambar yang ada
- 4. Hal 32 → apakah sudah ada penelitian penggunaan *surfactant* untuk ↓ MMP. Masukkan Referensinya
- 5. Apakah dilakukan screening jenis *surfactant* yang cocok bagaimana melakukannya dalam study ini.
- 6. Dalam Table 2.1 *viscosity* dan GC digunakan untuk menentukan MMP. Bagaimana penjelasannya.
- 7. Halaman 39, detail perhitungan persamaan MCO2 *Dissolved* perlu dicantumkan.
- 8. Halaman 41, *Reservoir Brine* digunakan untuk apa dipengujian MMP menggunakan Slim **Tube**
- 9. Dalam DOE penggunaan *alcohol* dan *surfactant* 10 %, 30 % dan 50 %. Jelaskan / tambahkan dasar penentuan % tersebut.
- 10. Jenis *surfactant* dan bagaimana memilih *surfactant* yang cocok untuk ↓ MMP juga perlu ditambahkan dalam proposal ini.
- 11. Uji *Swelling* 1,5 bulan & ST 1 bulan → perlu di cek ulang. Seharusnya Slim tube perlu waktu lebih lama pengujiannya.
- 12. Sample minyak, perlu data *oil composition (initial)* dan data komposisi saat *Dead Oil*. Perlu dicantumkan efek CO2 terhadap MMP jika perbedaan kondisi sampel minyak yang digunakan apakah live atau dead oil.

Pekanbaru, 01 April 2021

Dr. Eng. Muslim External Examiner

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HASIL PENILAIAN UJIAN PROPOSAL DISERTASI (TAHAP II) MAHASISWA PROGRAM DOKTOR

2. Telah mengevaluasi hasil kegiatan Semester I & II, maka pendapat kami tentang yang bersangkutan untuk diajukan ke tahap yang berikutnya (Tahap III) adalah:

3. Usulan/Catatan Perbaikan (jika ada):

paikan pada Ujian Proposal ini. Saya tidak mencatatnya. Silakan diden-

garkan dari rekamannya.

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persentasi perlu ditambahkan,

umum, jadi scope penelitian luas sekali? 3. Pada kebaruan no 2 dan 3 ada solid precipitation? Apakah tdk sama? 4. Utk pengendapan padatan, apakah tdk akan dilakukan analisis SARA (Saturates, Asphaltenes, Resins and Aromatics)?

Tidak menyetujui

3. Usulan/Catatan Perbaikan (jika ada):

/ 0 pts Auto-graded 0

format penulisan diperbaiki

Tidak menyetujui

3. Usulan/Catatan Perbaikan (jika ada):

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perbaikan sesuai diskusi saat presentasi

Disesuaikan dengan diskusi oleh Tim Penguji/KPPS dan tentunya Tim Pembimbing Auto-graded

akan berkomunikasi dengan Yang Bersangkutan.

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pressure. 5. Revisit DOE untuk "doability"

proposal dengan format dan novelty yang jelas. 2. Scope of work dan tata waktu serta target publikasi bisa dibuat lebih realistis mengacu kepada kondisi peralatan lab, dana, dan waktu yang tersedia.

Tanggal Ujian

 $: 30$ Maret 2021

PHASE BEHAVIOR AND INTERACTIONS OF CO² - CRUDE OIL SYSTEM IN ENHANCED OIL RECOVERY

RESEARCH PROPOSAL

By KARTIKA FAJARWATI HARTONO Student ID: 32219001 (Doctoral Program in Petroleum Engineering Department)

INSTITUT TEKNOLOGI BANDUNG March 2021

ABSTRACT

PHASE BEHAVIOR AND INTERACTIONS OF CO² - CRUDE OIL SYSTEM IN ENHANCED OIL RECOVERY

By

Kartika Fajarwati Hartono Student ID: 32219001 (Doctoral Program in Petroleum Engineering)

One of the most important parameters for designing CO² flooding project is determination of Minimum Miscibility Pressure (MMP) value. Therefore, accurate and robust determination of the MMP is required for the $CO₂$ flooding project. Several researchers have developed either experimental or simulation methods for determining MMP measurement techniques include slim tube test and core flood, rising bubble apparatus (RBA), pressure/composition (P/X) diagram, oil swelling/extraction test, and more recently is vanishing interfacial tension (VIT). From the previously published literatures, the slim tube test and VIT technique are most commonly used experimental methods for the MMP determinations. However, either slim tube test or VIT technique are still leaves the remaining question. The MMP measurement using VIT may be questionable with the technical criteria in determining the lowest IFT. It is then necessary to observe and to study the phase behavior and the effect of interactions between $CO₂$ and crude oil system comprehensively to determine the criteria and factors for determining the robust of minimum miscibility pressure. This research proposes to study phase behaviors and to investigate the interactions between $CO₂$ and crude oil system comprehensively including solubility, swelling, viscosity, and also the possibility of solid precipitation as the effect of interactions between $CO₂$ and crude oil.

This study will be carried out by several experimental methods to analyze phase behavior of CO² and crude oil samples. The analysis of phase behavior includes visualization tests and compositional analysis using Fluid Eval PVT and Gas Chromatograph (GC), respectively. In this study, the possibility of solid precipitation will be also analysed. Then, to convince the MMP obtained from mutual interactions of $CO₂ - crude$ oil, the displacement test using slim tube will be conducted.

From this research, we will obtain the threshold or onset pressure from phase behavior analysis and onset pressure of solid precipitation as the effect of interactions between $CO₂$ and crude oil system. It will very useful to apply $CO₂$ flooding in oilfields by considering this onset pressure.

Keywords: Minimum Miscibility Pressure (MMP), Phase Behavior, Interactions CO2-Crude Oil, Onset Pressure, Fluid Eval PVT

PHASE BEHAVIOR AND INTERACTIONS OF CO2 - CRUDE OIL SYSTEM IN ENHANCED OIL RECOVERY

By Kartika Fajarwati Hartono **Student ID: 32219001** (Doctoral Program in Petroleum Engineering)

Institut Teknologi Bandung

Approved **Promotor Team**

17 Maret 2021 Date ...

Promotor

ase

(Prof. Ir. Asep Kurnia Permadi, M.Sc., Ph.D)

Co-Promotor I

(Ir. Utjok W.R. Siagian, M.Sc., Ph.D)

Co-Promotor II

(Dr. Andri Luthfi Hakim, M.T)

FOREWORD

Alhamdulillahi rabbil'alamin, in the Name of Allah, Most Merciful. This research proposal entitled **"Phase Behavior and Interactions of CO² – Crude Oil System in Enhanced Oil Recovery"** is submitted as a part of the requirements for pursuing Doctoral Degree from Institut Teknologi Bandung.

Gratitude to Prof. Asep Kurnia Permadi, Ph.D., Ir. Utjok W.R. Siagian, M.Sc., Ph.D., Dr. Andri Lutfi Lukman Hakim. S.T., M.T as the promotor and co-promotors for giving me many inputs, suggestions, and encouragement that were very useful in the process of finding ideas and completion of this research proposal.

I would also like to express gratitude to Ir. Zuher Syihab, Ph.D as head of Magister Petroleum Engineering Department ITB for the supports and encouragement in completing my research proposal.

Thanks also to Indonesia Endowment Fund for Education (LPDP) and Universitas Trisakti for the financial support and the encouragement for pursuing Doctoral Degree.

In addition, thanks to Bapak Dr. Harry Budiharjo, S.T., M.T and all of my friends who support and give me the helpful inputs and suggestions.

I sincerely expect that this research will provide the contribution for petroleum engineering and science to solve the problems to increase oil production through EOR implementation.

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Chapter I Introduction

CO² flooding is one of Enhanced Oil Recovery (EOR) technique that has been considered not only effectively as enhances oil recovery but also reduces greenhouse gas emission (Dong et al., 2001; Ghorbani, et al., 2014; Moghadasi et al., 2018). CO² shows certain unique, interesting, and useful characteristics when it placed at a pressure and temperature above its critical pressure and critical temperature (i.e. supercritical state) (Saini, 2019). $CO₂$ displaces the residual oil by either miscible or immiscible displacement, depending on the reservoir condition. When $CO₂$ is injected to the reservoir, it occurs the physically and chemically interaction with reservoir rock and the existing hydrocarbon fluid. These interactions are the fundamental mechanisms to explain why and how injected $CO₂$ recovers the remained oil. These include: oil volume swelling, oil viscosity and density reduction, CO_2 -oil interfacial tension (IFT) reduction, and vaporization – extraction of the trapped of oil portions (mostly light components) (Hamouda & Chughtai, 2018; Moghadasi et al., 2018; Rezk & Foroozesh, 2019). All the mentioned phenomena are directly caused by CO₂ dissolution into the crude oil and thus closely related to the mutual interactions of crude oil-CO2. However, the effects of mutual interaction between $CO₂$ and crude oil on EOR mechanism has not been well understood (Zanganeh et al., 2012).

The crude oil and CO₂ are considered as immiscible if there is a distinct interface at their contact area. Miscibility refers to a specific thermodynamic condition, at which the interface between the crude oil and $CO₂$ phases disappears and both form a single liquid. For petroleum reservoir, miscibility is defined as that physical condition between two or more fluids that permits them to mix in all proportions without the existence of an interface (Holm, 1986). Hence, the minimum miscibility pressure (MMP) of a crude oil- $CO₂$ system at a specified temperature is defined as the lowest operating pressure at which the injected gas and the residual oil in place become miscible after a dynamic multi-contact process at the reservoir temperature (Abedini et al., 2014; Gu et al., 2013; Saini & Rao, 2010). If the reservoir pressure is lower than the MMP, the $CO₂$ injection is classified as an immiscible injection process. Otherwise, the CO² injection is considered to be a miscible displacement. Therefore, the robust determination of MMP value and the effects of mutual interactions between crude oil and $CO₂$ on EOR mechanism are very important parameter for designing CO² flooding project in enhanced oil recovery (EOR), whether the injection must be operated below or above the MMP value.

I.1 Background

The methods for determining MMP value have been developed by several either experimental or simulation methods and described in the literature. The MMP measurement techniques include the displacement test such as slim tube test and core flood, rising bubble apparatus (RBA), pressure/composition (P/X) diagram, oil swelling/extraction test, and more recently is vanishing interfacial tension (VIT) (Ayirala & Rao, 2011; Gu et al., 2013; Zhang et al., 2019).

The slim tube is the most common test and widely accepted as a standard to determine gas/oil miscibility and measure the MMP in the petroleum industry. However, the slim tube test is expensive and time consuming, it needs several weeks (4-5 weeks) to complete one miscibility measurement (Ghorbani et al., 2014; Riyami & Rao, 2015; Siagian & Grigg, 1998). Although the slim tube is widely accepted, there is no standard design, or a standard operating procedure, or a standard set of criteria for determining miscibility conditions using this technique (Elsharkawy et al., 1996; Zhang et al., 2019).

Rising bubble apparatus (RBA) is become alternative to the slim tube method due to time saving, low capital and operating cost, small material requirements, and direct visual observation (Ahmad et al., 2016; Elsharkawy et al., 1996; Zhou & Orr, 1995). Principally, RBA is used to determine the MMP by interpreting the dynamic behavior of a gas bubble as it rises through a transparent oil column at different pressures and temperatures (Hemmati-sarapardeh et al., 2013; K. Zhang et al., 2019). This method is qualitative whereas the miscibility is determined from visual observations of changes in shape and appearance of injected gas bubbles as they rise through reservoir crude oil contained in a visual high-pressure cell. Even though the RBA method is faster and cheaper than the slim tube method, the RBA simulates the vaporizing process alone in the miscibility development process and neglects the condensing process and also lack of quantitative supporting information. This causes an overestimated MMP of some crude oil $-CO₂$ systems, in which the condensing process also contributes to the miscibility development (Subhash C. Ayirala & Rao, 2007; Gu et al., 2013).

P/X diagrams for gas/oil miscibility are built by conducting phase – behavior measurements in high pressure visual cell at reservoir temperature. Different amounts of injection gas are added to crude oil, and the loci of bubble point and dewpoint pressure are determined to generate phase boundaries. However, this method is time consuming, expensive, and complicated, it needs large amounts of fluids (S C Ayirala & Rao, 2011; Hemmati-sarapardeh et al., 2013).

The determination of MMP by Swelling/Extraction method are also conducted by some researcher (Abdurrahman et al., 2015; Abedini et al., 2014; Hand & Pinczewski, 2007; Harmon & Grigg, 1988; Siagian & Grigg, 1998; Tsau et al., 2010). A swelling test is a simple and popular means commonly performed in the laboratory to study the volume of hydrocarbon that $CO₂$ can extract from crude oil by determining the swelling factors. This method is cheaper and faster than aforementioned methods. The extraction is the principal mechanism in the development of multicontact miscibility by vaporization (Siagian & Grigg, 1998). Abdurrahman et al (2015) also deduced based on their experiment that the swelling/extraction method is based on the principle that condensation, extraction – condensation, and extraction phenomenon occurred during miscibility of crude oil and CO² (Abdurrahman et al., 2015). Based on some literatures, the swelling/extraction test is capable to determine MMPs of crude oil – gas systems at high temperatures (K. Zhang et al., 2019). However, this method is required to compare with other methods to convince the mass transfer effect between crude oil and gas phases in multiple contact miscibility process as the fundamental of multiple contact miscibility.

More recently, vanishing interfacial tension (VIT) method has been used to determine the MMP, which based on the principle of interface absence or zero interfacial tension (IFT) at the point of fluid miscibility (Ahmad et al., 2016; Subhash C Ayirala & Rao, 2007; Rao, 1997; Ghorbani et al., 2014; Rao & Lee, 2003; Saini & Rao, 2010; Sequeira, et al., 2008). In the VIT method, the gas/oil IFT is measured at reservoir temperature and at varying pressures or enrichment levels of the gas phase. The gas/oil miscibility conditions are then determined by extrapolating the plot of IFT against pressure to zero IFT. The VIT technique is less costly, less time consuming, and consumes lower quantities of fluids compared with the slim tube (Ayirala $& Rao, 2011$). Due to its effectiveness in MMP measurement compared with the slim tube, lately, many petroleum industries use the VIT for determining MMP value. In spite of this technique has a direct and simple measurement to determine miscibility based on the fundamental definition of zero IFT at miscibility, it has critics for perceived absence of compositional path specification created during two-phase flow in porous media (Jessen& Orr, 2008; Orr & Jessen, 2007). The accuracy of the VIT technique for the MMP determination might be questionable with more fluid components involved (Zhang et al., 2019). In addition, in terms of the VIT technique, the choice of the lowest equilibrium IFT measured at the highest test pressure may affect the determined MMP. There have not been any technical criteria for correctly choosing the lowest equilibrium IFT to be used in the linier extrapolation. In fact, the measured equilibrium IFT versus test pressure data have been chosen arbitrarily to determine the MMP (Zhang & Gu, 2016). In previous study, generally, two distinct pressure ranges may exist for the measured equilibrium IFT versus pressure (Golkari & Riazi, 2017; Wang et al., 2010). The determined MMP from VIT technique is found to be close to slim tube test if the measured equilibrium IFT versus pressure in the first pressure range are linearly extrapolated to zero IFT (Escrochi et al., 2013; Zhang et al., 2019). Hakim (2020) in his dissertation, performed MMP determination from integrated measurement include swelling factor, IFT, and viscosity. He deduced that the MMP is determined by the intersection of the two lines (first pressure range and second pressure range). However, the MMP determined from the VIT technique is overestimated if much lower IFT measured at even higher pressure in the second pressure range are used. Consequently, the determination of MMP from the interfacial tension by means of linear extrapolation to zero IFT might be questionable with more fluid components involved.

The phenomena directly caused by $CO₂$ dissolution into the crude oil including oil viscosity reduction, oil swelling effect, and interfacial tension reduction have been studied. However, the effects of interaction between crude oil and $CO₂$ such as the possibility of solid precipitation is not fully studied so that the effects of interaction between crude oil and $CO₂$ on EOR mechanisms are not well understood. The injection of CO² into reservoir could lead to solid precipitation. By the change in reservoir fluid composition, temperature, and pressure might affect the thermodynamic equilibrium of the fluid behavior thus cause solid precipitation (Ali et al., 2015; Kokal & Sayegh, 1995; Zanganeh et al., 2012). This effects of interaction between $CO₂$ and crude oil might affects the accuracy of MMP measurement. Therefore, it is important to investigate how the effects of its interaction in MMP measurement particularly in VIT technique.

Against this background, it is then necessary to observe and to study the phase behavior and the effects of interactions between CO₂ and crude oil system itself comprehensively to determine the criteria and factors for determining the robust of minimum miscibility pressure. Based on the literature review, there is little research has been studied the phase behaviors and the effect of interactions between $CO₂$ and crude oil system comprehensively. Therefore, to fill the research gap, this research proposes to study the phase behaviors and the effects of interactions between $CO₂$ - crude oil system comprehensively including solubility, swelling, viscosity, and also the possibility of solid precipitation due to high pressure and high temperature.

I.2 Present Status of the Questions

Refers to the background and literature review as discussed in **sub-chapter I.1**, there is research gap proposed in this study. In the effort on obtaining reliable and comprehensive solution to fill the research gap above, the study must be able to answer several questions related to the determination the robust minimum miscibility pressure (MMP) as below:

- 1. How good and robust is the phase behavior method to obtain the robustness of multi-contact miscibility pressure or minimum miscibility pressure?
- 2. What are the important factors affecting the interactions between $CO₂$ hydrocarbon fluid, so that it will affect the determination of MMP value?
- 3*.* How the asphaltene/paraffinic crude oil or solid precipitation affecting the value of MMP?
- 4. By adding some additives to crude oil and $CO₂$, how is the effect of adding additives to the values of MMP?

I.3 Purpose and Objectives

The main objective of this research is to study the phase behavior and mutual interactions between $CO₂$ and crude oil system comprehensively in all stages in order to obtain robust minimum miscibility pressure (MMP) until achieving miscibility of $CO₂$ and crude oil. The mutual interactions of $CO₂$ and crude oil system is very important and crucial for implementing CO₂ flooding project. Therefore, for that purpose, the objectives of this research are:

- 1. To obtain the robustness of minimum miscibility pressure (MMP) through comprehensive phase behavior methods compare to the preceding methods.
- 2. To investigate the important factors affecting the mutual interactions between CO₂ and crude oil system through their phase behavior.
- 3. To observe the onset pressure of solid precipitation (asphaltene/paraffinic crude oil) as the effect of CO² and crude oil interactions.
- 4. To investigate the effects of additives to $CO₂$ and crude oil on MMP reduction.

1.4 Hypotheses

To answer the present status of the question in **sub-chapter 1.2,** below are some hypotheses:

1. The MMP of a given crude – oil system is defined as the minimum pressure at which $CO₂$ can achieve the multi contact miscibility with the crude oil (Wang et al., 2010). During this process, the composition of solutions $(CO₂$ and crude oil) are changed through a mass transfer between $CO₂$ and crude oil. This mass transfer phenomenon drives miscibility in two ways. First, miscibility is achieved through in situ vaporization of the intermediate molecular weight hydrocarbons from the reservoir oil into the CO2. Second, miscibility is developed by in situ transfer of $CO₂$ into the reservoir oil. In fact, $CO₂$ will be diffused into the crude oil. At a high equilibrium pressure, the initial strong light components extraction was observed and considered as an important physical phenomenon, in which the light components of the crude oil were extracted.

Based on the phenomenon occurred in multi contact miscibility, the extraction and vaporization are the principle mechanism in the development of multi contact miscibility. Therefore, the comprehensive visual PVT including $CO₂$ solubility, oil swelling and extraction, viscosity, density, and the possibility of solid precipitation are representative and reliable method to convince the position of multi-contact miscibility pressure. Gas chromatograph (GC) and density measurement are also can be considered as complementary measurement to obtain a "clear" minimum miscibility pressure (MMP) measurement.

2. The miscibility and the interactions of $CO₂$ and hydrocarbon fluid was found to be a strong function of pressure and temperature. However, the composition of hydrocarbon fluid is also important to determine the miscibility of $CO₂$ – crude oil. As aforementioned, the composition of the fluid is the main concern in the determination of MMP using the recently VIT technique. Therefore, the effect of the composition in determination of MMP need to be further experiment using phase behavior measurement.

Pressure, temperature, and composition of reservoir fluid also affect the solid precipitation. Theoretically, the injected CO₂, when it contacts the reservoir oil, can cause changes in the fluid behavior and equilibrium conditions which favor precipitation of organic solids, mainly asphaltenes (Srivasfava et al., 1999). Hence, this study also proposes to observe the mutual interaction of $CO₂$ and crude oil in solid precipitation.

- 3. In the MMP measurement using interfacial tension technique (IFT), asphaltene and paraffinic precipitation does not affect the MMP estimation. This is based on the observation conducted by Wang et.al (2010), shows that the asphaltene precipitation is almost reversible when the saturation pressure is suddenly reduced (Wang et al., 2010). However, this phenomenon is necessary to be proved further by phase behavior measurement to convince the onset pressure of solid precipitation.
- 4. The addition of additives in crude oil $-$ CO₂ have the effect and impact in reducing the MMP. Alcohol, such as ethanol and propanone have been proven to give positive effects in reducing the MMP (Hakim, 2020; Yang et al., 2019) (Permadi et al., 2021). Another additive that can be considered as solvent for reducing MMP is surfactant. It is due to the capability of surfactants to lower the $CO₂$ – crude oil IFT. $CO₂$ - soluble surfactants itself do not have the issue in dissolution as they are dissolved in $CO₂$ and migrate together with $CO₂$ (Mclendon et al., 2014; Xing et al., 2012; X. Zhang et al., 2019).

1.5 Scope of Research

The scope of this research will be defined and limited to the following several conditions:

- 1. The crude oil samples are taken from Indonesian oil fields.
- 2. The crude oil samples are light-dead oil (specific gravity between $32^{\circ}API -$ 50°API).
- 3. The MMP results from the PVT measurement will be compared to established apparatus: slim tube test.
- 4. The solvents used to investigate in reducing MMP values are ethanol and surfactant at various concentration of the solution.

Chapter II Literature Review

This literature review covers the flow of thought and scientific development in the determination of the topic and ideas of this study. Through the literature review, the proposed novelty and originality in this research is expected to fill the gap among other researchers. The important thing to understand and to review of the references for determining the research gap is understanding the fundamental science and phenomenon that exist related to the issues reviewed.

II.1 CO² Injection Fundamentals

When $CO₂$ is injected to the reservoir, it interacts physically and chemically with reservoir rock and the existing hydrocarbon fluid. Such interactions are the base mechanisms to explain why and how injected $CO₂$ recovers the remained oil in place (Moghadasi et al., 2018). Mostly, these mechanisms are categorized as follows:

- 1. Oil volume swelling
- 2. Oil and water density reduction
- 3. Oil viscosity reduction
- 4. Interfacial tension reduction between the reservoir rock and oil, which has previously inhibited oil flow through the pores
- 5. Vaporization and extraction of the trapped of oil portions (mostly light component)

CO² has uniqueness. When CO² placed at a pressure and temperature above its critical pressure and critical temperature (i.e. supercritical state), as can be seen in Figure II.1, CO₂ shows certain unique, interesting, and useful characteristics (Saini, 2019). It has high solubility in oil, causing the oil to swell and consequently reducing the oil viscosity and density. Figure II.1 shows the supercritical region in $CO₂$ phase diagram, which is beyond the critical point of $CO₂$ (1070.3 Psi) and critical temperature (87.76°F) . Due to its high solubility in crude oils, it is considered as one of the main oil recovery mechanisms in both miscible and immiscible $CO₂$ injections. The importance of each mechanism depends on the pressure and temperature of the reservoir. At high pressures, $CO₂$ can vaporize the light and intermediate components of the oil, which is considered as one of the oil recovery mechanisms, particularly at high pressure reservoir (Rezk & Foroozesh, 2019; Rudyk et al., 2017). Figure II.2 is the illustration of oil recovery mechanisms during CO² injection in the reservoir. The dark colour and grey colour represent the original oil and the oil after interaction with the injected $CO₂$, respectively. First of all, oil produced by direct CO² displacement (a) then CO² dissolved in the crude oil caused oil swelling (b). As mentioned before, at high pressure, $CO₂$ can vaporize crude oil due to $CO₂$ extraction of light and intermediate oil components. Oil swelling can cause coalescing of disconnected oil ganglia.

Figure II.1 CO² Phase Diagram (Saini, 2019)

In CO² flooding process, the oil and CO² relative permeabilities and the residual oil saturation can be related to the crude oil – $CO₂$ interfacial tension through a dimensionless number, which compares either capillary force with thee viscous force in the horizontal displacement processes or the capillary force with the gravity force in the gravity drainage process (Nobakht et al., 2007). Nobakht et al (2007), performed the experimental study to examine the detail effects of viscous and capillary forces on the CO² EOR under the actual reservoir conditions. They measured equilibrium interfacial tension between light crude oil and CO² at different equilibrium pressures. It has been found that the interfacial tension of a crude oil – $CO₂$ system is significantly reduced when $CO₂$ is injected into an oil reservoir at a high reservoir pressure, so it leads to favourable recovery factors.

Theoretically, when $CO₂$ is injected into an oil reservoir, there is a minimum pressure level – below that value $CO₂$ and oil are no longer miscible (Moghadasi et al., 2018). Increasing the pressure leads to an increase in $CO₂$ density, which reduces the density difference between crude oil and $CO₂$. As a result, the IFT between crude oil and CO2 vanishes, then they will reach mutual solubility in each other. This minimum pressure is named as minimum miscibility pressure (MMP) (Lashkarbolooki et al., 2017). Basically, oil recovery is higher when $CO₂$ and oil are miscible. Before discussing about the MMP in more detail, a brief discussion on the basic definition and general theory of miscibility is necessary.

Figure II.2 Illustration Oil Recovery Mechanism during CO² Injection in Reservoir (Rezk & Foroozesh, 2019)

II.2 Gas – Oil Miscibility

The term miscibility is often used to refer the ability of a liquid solute to dissolve in a liquid solvent, whereas, solubility is a more general term, often referring to the ability of a solid solute to dissolve in a liquid solvent (Saini, 2019). By definition, miscibility or infinite mutual solubility can be described as *"physical condition between two fluids that will permit them to mix in all proportions without an interface being formed by the materials"* (Holm, 1986)*.* Two fluids that mix together in all proportions within a single fluid phase are miscible (Rao & Lee, 2002). As discussed before, the pressure at which miscibility occurs is defined as MMP. Depending of the nature of contacts occurring between injected $CO₂$ and reservoir oil for establishing miscibility, the pressure is referred to as first contact minimum miscibility pressure (FC-MMP) or multiple contact – minimum miscibility pressure. The MC-MMP is simply referred as the MMP.

First-contact miscibility (FCM) refers to a condition wherein injected CO₂ and reservoir oil are mixed in all proportions upon first contact, making a single homogenous solution. Multiple-contact miscibility (MCM) generally, $CO₂$ and crude oil are not miscible on the first contact. Indeed, miscibility occurs dynamically upon multiple contacts within the reservoir. The phase behavior of multiple – contact miscibility, theoretically, can be shown on a ternary or pseudo – ternary diagram in Figure II.3. During this process, the composition of solutions (injection and reservoir fluids) are changed through a mass transfer between $CO₂$ and crude oil. This mass transfer phenomenon drives miscibility in two ways (Jia et al., 2018):

- (i) Vaporizing Gas Drive (VGD): Miscibility is achieved through in situ vaporization of the intermediate molecular weight hydrocarbons from the reservoir oil into the CO2.
- (ii) Condensing Gas Drive (CGD): Miscibility is developed by an in-situ transfer of $CO₂$ into the reservoir oil. In fact, $CO₂$ will be diffused into the crude oil.

When CO₂ interacts with reservoir oil, a dynamic miscibility zone would be developed. Therefore, a $CO₂$ – enriched crude oil is produced from the producing wells. Figure II.3 shows that the injection solvent and reservoir oil are not miscible, as the line connecting them passes through the two-phase region. However, as solvent invades through the porous media and contacts the reservoir oil, some components of oil will vaporize and transfer to the gas phase (solvent) (Moghadasi et al., 2018).

Miscibility (Moghadasi et al., 2018) Figure II.3 Phase Behavior on Ternary Diagram for Multiple Contact
II.3 Mutual Interactions and Oil Recovery of CO² – Crude Oil System

Successful CO² flooding is largely dependent on the strong mutual interactions between the reservoir crude oil and the injected $CO₂$ (Cao & Gu, 2013a). These interactions determine the overall performance of the $CO₂ - EOR$ Process. As mentioned before, CO² is highly soluble in a light crude oil and the solubility of CO² in the crude oil depends on the reservoir pressure, reservoir temperature, and oil composition (Zhang et al., 2018). The dissolution of $CO₂$ in the crude oil makes the oil swell, reduces the interfacial tension (IFT) and oil viscosity, thus enhances oil recovery (Whitson $&$ Brule, 2000). The interfacial interactions mainly include the interfacial tension (IFT), wettability, and interfacial mass transfer and these mutual interactions determine the performance of $CO₂$ flooding (Nobakht et al., 2008). The stated before, miscibility is achieved through two-way mass transfer between the crude oil - $CO₂$ and it is indicates that the interfacial mass transfer plays an important role in achieving the dynamic miscibility through multiple-contact miscibility (Hamouda & Chughtai, 2018; Siagian & Grigg, 1998). Hence, it is very important to study and understand how a crude oil and $CO₂$ interact with each other under the actual reservoir conditions.

After CO² is injected into an oil reservoir, it contacts and interacts with the reservoir oil and thus changes the reservoir equilibrium conditions and fluid properties, which may lead to the precipitation of the heavy organic solids, such as asphaltenes (Ali et al., 2015; Buriro & Shuker, 2013; Cao & Gu, 2013c; Kokal & Sayegh, 1995). Asphaltene precipitation can change the wettability of the reservoir matrix and consequently affect the flood performance (Srivasfava et al., 1999). Crude oil generally contains different hydrocarbon compounds such as aromatics, waxes, resins, and asphaltenes. Asphaltenes are heaviest components of crude oil. On the basis of solubility, asphaltene is defined as a part of petroleum that is not soluble in n-alkenes but completely miscible in aromatic hydrocarbons such as toluene or benzene (Cao & Gu, 2013b; Golkari & Riazi, 2017). Asphaltene molecules tend to aggregate and create larger agglomerates. The tendency of asphaltene molecules toward association and precipitation is related to their molecular structure, but it is not determined clearly because of the complex nature of asphaltene molecules (Zanganeh et al., 2012). The asphaltene precipitation may occur if a sufficient amount of $CO₂$ is dissolved into the crude oil. Gas injection generally increases the risk of asphaltene precipitation. Precipitation occurs if the concentration of gas in the oil (or gas pressure) exceeds a threshold value (Escrochi et al., 2013). It become one of the major technical issues in CO² flooding for a field application. Therefore, it is important to determine the onset pressure of asphaltene precipitation for a given crude oil $-$ CO₂ system.

II.4 Position of the Present Study

The position of the present study represents some thought and ideas which is based on the fundamental science that written in the previous sub-chapter. The fundamental science and position of the present study are expected to fill the gap among other researches, so that the novelty and its scientific contributions can be perceived. Based on publications from several researchers, some thought and ideas can be stated as follows:

- 1. Rao, D.N. (1997), developed Vanishing Interfacial Tension (VIT) technique for measuring Minimum Miscibility Pressure (MMP) which based on the principle of interface absence or zero interfacial tension (IFT) at the point of fluid miscibility. The VIT technique is less costly, less time consuming, and consumes lower quantities of fluids compared with the slim tube. Due to its effectiveness in MMP measurement compared with the slim tube, lately, many petroleum industries use the VIT for determining MMP value. In spite of this technique has a direct and simple measurement to determine miscibility based on the fundamental definition of zero IFT at miscibility, it has critics for perceived absence of compositional path specification created during twophase flow in porous media.
- 2. Rao, D.N and Lee, J.L. (2003), proposed the application of the new Vanishing Interfacial Tension (VIT) to evaluate miscibility conditions for Terra Nova field. They proposed to determine MMP and MMC through VIT technique then compared to Slim tube and Rising Bubble Apparatus (RBA). The concept of determination MMP based on the fundamental definition of zero IFT (Figure II.4) is still questionable. During their research, solid phase from Tera Nova

crude oil was appeared but there was no discussion further about the solid phase, particularly for onset pressure.

Figure II.4 Minimum Miscibility Pressure (MMP) Determination from VIT Technique (Rao & Lee, 2003)

- 3. Orr, F.M and Jessen, K (2007), criticized the VIT technique proposed by Rao et al. whereas the MMP is taken to be the pressure at which the IFT plotted as a function of pressure extrapolates to zero IFT. They argued that the determination of MMP from VIT technique perceived absence of compositional path specification and the associated "perceived weakness" at mimicking the interactions of flow and phase equilibrium observed in a slim tube displacement experiment. They also argued that the compositions resulting from the VIT experiment do not agree with the compositional path created during two-phase flow in porous media. The VIT approach can give estimates of the MMP that are close the actual MMP or that are significantly in error depending on the compositions of mixtures created in the equilibrium cell. Orr and Jessen also said that additional experimental information would be required to select the optimal cell mixture composition that would give a reasonably accurate estimate of the MMP by the VIT technique. However, Orr and Jessen presented an analysis of the VIT technique-based EOS calculation
- 4. Ayirala, S and Rao, D. N (2007), compared miscibility determination from gasoil interfacial tension to Peng Robinson Equation of State (EoS) computational

model. This study was performed to answer the arguments from Orr and Jensen. From their results, there was still remaining question about the determination of MMP through VIT technique. There have not been any technical criteria for correctly choosing the lowest equilibrium IFT to be used in the linier extrapolation. In fact, the measured equilibrium IFT versus test pressure data have been chosen arbitrarily to determine the MMP. Consequently, the detailed effects of some factors on the determined MMP from the VIT technique remain ambiguous.

5. Saini, D and Rao, D. N (2010), performed an experimental study to reinforce the use of VIT techniques as a robust experimental method for determining the MMP of Terra Nova EOR project and its possible use to validate the EOS models for using them in compositional model. The determination of MMP based on the concept of the lowest equilibrium IFT to be used in the linear extrapolation to zero as can be seen in Figure II.5. The remaining question is the same as the previous reviews: there have not been technical criteria for correctly choosing the lowest equilibrium IFT to be used in the linier extrapolation. There is ambiguous in the determination of Multi-contact Miscibility or MMP and First Contact Miscibility (FCM) based on the lowest equilibrium IFT to be used in the linier extrapolation to zero IFT.

Figure II.5 Minimum Miscibility Pressure (MMP) Determination from VIT Technique for Recombined Live Oil Sample at 289°F (Saini & Rao, 2010)

- 6. Ayirala, S and Rao, D. N (2011), conducted laboratory experiment related to gas/oil IFT for various types of developed miscibility. This experiment was aimed to answer the critics from Orr and Jessen (2007&2008) to the Vanishing Interfacial Technique (VIT) for perceived absence of compositional – path specification and the associated "perceived weakness" at mimicking the interactions of flow and phase equilibrium observed in a slim tube displacement experiment. They also argued that the compositions resulting from the VIT experiment do not agree with the compositional path created during two-phase flow in porous media. Therefore, the study was conducted by Ayirala and Rao had objectives to carry out IFT measurements in standard gas/oil systems of known miscibility conditions at elevated pressures and temperatures; to study the effect of compositional path on gas/oil miscibility determined from the VIT technique; to investigates the presence of multiple stage contacts between fluid phases in the VIT technique. However, they use VIT technique only to determine the multiple stage in the process of $CO₂$ flooding. The results also still have the remaining questions for choosing the lowest equilibrium IFT, including how determine the multiple contact stage (MCM) and first contact stage (FCM) from only the VIT technique.
- 7. Gu, Y., Hou P., and Luo W., (2013), examined the specific effects of four important factors on the measured Minimum Miscibility Pressure (MMP) and First Contact Miscibility. The following four important factors are experimentally studied to evaluate and compare their detailed effects on the measured MMP and FCM: temperature, oil composition, gas composition, and initial gas-oil ratio (GOR) in volume. They applied VIT technique to determine the MMPs and the first contact miscibility pressure. The result shows that in each IFT test, the measured equilibrium IFT is reduced almost linearly with the equilibrium pressure in two pressure ranges as can be seen in Figure II.6. The MMP of each light crude oil – $CO₂$ systems is thus determined from the measured equilibrium IFT's in range I by applying the VIT technique The FCMP (P_{max}) of each light crude oil – CO₂ system is extrapolated from the measure equilibrium IFT's in range II. However, they use only VIT technique to determine the MMP and FCMP and still have the remaining questions for

choosing the lowest equilibrium IFT considered as MMP value because there are no technical criteria for correctly choosing the lowest equilibrium IFT to be used in the linier extrapolation. The results of the experiment on plot of IFT vs Pressure (Figure II.6) are different with Rao's et al in Figure II.4 and Figure II.5. Figure II.6 shows the MMP is overestimated if much lower equilibrium IFT measured at even higher test pressures in the second pressure range are used. It is aligned with Orr and Jessen argument that VIT estimates of the MMP obtained by extrapolating IFTs from low values of the IFT are least accurate for gas/oil systems that have a FCMP much higher than the MMP (Jessen $\&$ Orr, 2007).

Figure III.6 Measured Equilibrium IFTs at Different equilibrium pressures for (a) dead oil – pure CO₂ and (c) Live Oil – Pure CO₂ System for T = 294.15 K; 313.15 K; 326.15 K (Gu et al., 2013)

8. Cao, M and Gu, Y (2013), did the experimental to study the temperature effects on the phase behavior, mutual interactions, and oil recovery of light crude oil $-CO₂$ system. They did PVT test to measure the saturation pressures and the oil swelling factors for temperature $T_{lab} = 27$ °C and $T_{res} = 53$ °C. They also observed the possibility of asphaltene precipitation due to $CO₂$ injection. However, they did not provide the compositional result of crude oil, such as Gas Chromatograph (GC), before and after $CO₂$ injection. The composition of crude oil before and after CO² injection is useful to observe the detail of oil swelling and extraction process during $CO₂$ injection.

9. Hemmati-Sarapardeh, A., Ayatollahi, S., Ghazanfari, M.H., and Masihi, M., (2013), conducted experimental determination of Interfacial Tension (IFT) and miscibility of the $CO₂$ – crude oil system by function of temperature, pressure, and composition effects. They used VIT technique to determine the MMP and First-Contact Miscibility Pressure (P_{max}) of crude oil/CO₂ systems at different temperatures and pressures. They also performed the SARA analysis for asphaltene precipitation as the effect on the crude oil/CO² IFT behavior. However, the experiment did not conduct and compare by either visual observation or slim tube/core flood. In addition, there is no further explanation and criteria in choosing the lowest IFT to be considered as the MMP as can be seen in Figure II.7.

Figure IV.7 Measured MMP (*) and First Contact Miscibility (x) of Crude Oil A/CO2 System from VIT Technique (Hemmati-sarapardeh et al., 2013)

10. Zhang, K and Gu, Y., (2016), performed six series of dynamic interfacial tension (IFT) tests of dead and live crude oil $-$ CO₂ systems at five different initial gas – oil ratios (GOR). They proposed two new quantitative technical criteria to determine the MMPs from VIT technique: the linier correlation coefficient (LCC) criterion and the critical interfacial thickness (CIT) criterion. Nevertheless, the determined MMPs from dynamic interfacial tension (IFT) tests had not compared and verified yet by the MMP of the former system such as core flood or slim tube tests.

- 11. Zhang, K., Tian, L., and Liu L., (2018), proposed a new analysis of pressure dependence of the equilibrium interfacial tensions of different light crude oil CO² systems. They performed three series of the dynamic IFT tests for a dead light crude oil–pure CO_2 system, a live light crude oil–pure CO_2 system, and a dead light crude oil–impure CO² system at different equilibrium pressures from the literature are used. The modified Peng–Robinson equation of state (PR-EOS) is tuned by using measured pressure–volume–temperature (PVT) data to predict the equilibrium two-phase compositions of the three light crude oil– CO² systems. The analysis was conducted by comparing IFT method with PR-EOS. The result shows that CO2 dissolution is a dominant mass-transfer process, which accounts for 90% of the total compositional change.
- 12. Zhang, K., Jia, N., Zeng, F., Li, S., and Liu, L., (2019), reviewed the determination of MMP for ten existing experimental methods and their three important technical aspects, including the experimental design, operating procedure, and MMP criterion. They reviewed that the miscibility developments in the VIT technique were controversial and may be questionable with more fluid components involved (K. Zhang et al., 2019). Rao and Lee (2002) and Ayirala and Rao (2011) deduced that the multiple contact miscibility could be reached through the vaporizing, condensing, or combined vaporizing/condensing process (Subhash C. Ayirala & Rao, 2011; Rao & Lee, 2002), while Orr and Jessen (2007) insisted that only single-contact miscibility was modelled (Orr & Jessen, 2007).
- 13. Permadi A. K., Pratama E. A., Hakim A. L. L., Abdassah, D., (2021), observed the effect of carbonyl and hydroxyl compounds on swelling, IFT, and viscosity. They also performed the MMP determination through simultaneous observations of swelling, viscosity, and interfacial tension (Permadi, Pratama, Hakim, & Abdassah, 2021). However, there is no technical criteria in choosing the lowest equilibrium IFT to be used in the linier extrapolation to be considered as the minimum miscibility pressure (MMP).

Based on the above literature review which begins with MMP measurement using the IFT concept (whereas MMP is defined as the lowest IFT to be used in the linear extrapolation to zero IFT) that still have the remaining questions, it is necessary to look back at the literature review which refers to the fundamental phenomena of CO² flooding to obtain the robust MMP measurement. As mentioned before, one of the fundamental phenomena that occur in CO² flooding is vaporization/extraction. The vaporization/extraction phenomena can be explained through the detailed observation of $CO₂ - oil$ phase behavior. Therefore, the subsequent review is to look and observe at the possibility of measuring MMP from the phase behavior of $CO₂ - crude$ oil system.

- 14. Siagian, U.W.R. and Grigg, R.B., (1998), performed two sets of experiments: one was a series of $CO₂$ – oil extraction experiments and the other was a series of slim tube tests for comparison with results obtained from the extraction experiments. The experiments were aimed to investigate the effect of pressure, temperature, and oil composition on extraction of hydrocarbons by CO² from crude oils. The result shows that the MMP prediction was lied in range of upper and lower phase of extraction capacity. The result of the experiment also indicated that the miscibility mechanism of $CO₂ -$ oil system is vaporizing gas drive (Siagian & Grigg, 1998). However, the experiment had not completed by visual observation to observe the extraction process of $CO₂ - oil$ system.
- 15. Tsau J.S., Bui. L.H., and Willhite, G.P., (2010), conducted the experiment to determine the MMP value through swelling/extraction test. The tests are conducted in a visual PVT cell with a large sample size (40-100cc). The result describes a small volume high pressure view cell that was developed to investigate the mass transfer process occurring in swelling/extraction tests when CO2 dissolves in the oil phase. Based on their experiment, they proposed to estimate the MMP using plot of swelling factor versus pressure. Nevertheless, they did not compare the MMP as the result of swelling test to

the established apparatus such as slim tube in the same graph as previously studied by Siagian and Grigg (1998).

- 16. Abedini A., Mosavat, N., and Torabi, F., (2014), determined the MMP of crude oil–CO² systems through analysing the experimental data of swelling/extraction tests. The results showed that the oil swelling factor increases with the equilibrium pressure, reaches the maximum value at light hydrocarbon extraction pressure, and then reduces with further increase in equilibrium pressure. The MMP of the crude oil $-$ CO₂ systems at a specific temperature was estimated by finding the intersection of the linear regression correlation corresponding to each of the regions. The results from their experiments show the agreement with those previously reviewed (Tsau et al and Siagian). The MMP prediction value obtained from the swelling test was also compared to the Vanishing Interfacial Tension (VIT) technique. The VIT technique is consists of two range, they called Range I as solubility mechanism and Range II as extraction mechanism. Comparing the MMP values estimated by VIT with those determined by swelling/extraction data at the same temperature shows that there exists a good agreement between the results. However, Abedini et al did not consider the effects of crude oil composition parameter in their experiment. As Orr and Jessen (2007) mentioned that The VIT approach can give estimates of the MMP that are close the actual MMP or that are significantly in error depending on the compositions of mixtures created in the equilibrium cell. Their experiment also had not completed by visual observation to observe the extraction process of $CO₂ - oil$ system.
- 17. Abdurrahman, M., Permadi, A.K., and Bae, W.S., (2015), performed the slim tube experiments and swelling tests on determining the MMP. They identified the relationship through a plotting technique of the swelling tests data. In addition to their experimental works, they also performed numerical simulation and visual observation during the experiments. The results show that the MMP value resulted from the swelling test is in good agreement with those the slim tube experiment and the simulation. Similar to Abedini et al (2014), they did not consider the effects of crude oil composition parameter in their experiment.
- 18. Rezk, M.G. and Foroozesh, J., (2019), investigated the phase behavior and mutual interactions between a light crude oil and $CO₂$ at high pressure and high temperatures (HPHT). They performed a series of PVT tests, viscosity, and IFT measurements at various conditions. However, they did not perform the displacement test such as slim tube or core flood and had not investigated the possibility of organic precipitation due to mutual interactions of $CO₂ - crude$ oil system in high pressure and high temperature.
- 19. Hakim, A. L.L., (2020), in his dissertation performed the MMP determination by simultaneously measurement of three parameters: Interfacial tension, swelling factor, and viscosity. He proposed to estimate the MMP using a plot of those parameters: IFT, Swelling Factor, and Viscosity vs Pressure. Based on the experiment results, he concluded that the MMP occurred when $IFT = 0$ is not truly correct because when pressure at which the IFT equals to zero, by miscibility definition, it is not MMP but miscible condition. Again, this leaves the remaining question for choosing the lowest equilibrium IFT considered as the MMP. He did not conduct the fluid composition analysis before and after CO² injection to show the vaporization/extraction phenomenon.
- 20. Permadi, A.K., Pratama E.A., Hakim, A.L.L., Widi, A.K., Abdassah. D., (2021), performed the experiment to investigates the effects of carbonyl and hydroxyl compounds addition on CO₂ injection through hydrocarbon extraction processes. The experiment was conducted using swelling test and interfacial tension (IFT) test at 131° F and 158° F working temperature. The MMP then estimated by the intersection plot between condensation-extraction straight line curves. However, their swelling test result shows different phenomenon with an increasing trend of swelling factor continuously without followed by condensation curves, as can be seen in Figure II.8. This phenomenon is required to observed further by varying other parameters to obtain the MMP values from the swelling test.

Figure V.8 Swelling Test Results at (a) 131° F and (b) 158° F (Permadi et al., 2021)

Based on the above review, there are still little research that has been studied the phase behaviors and interactions between CO² and crude oil system comprehensively. It is necessary to see and to study the phase behavior and the interactions between CO² and crude oil system itself comprehensively to determine the criteria and factors for determining the robust multi-contact minimum miscibility pressure or MMP. Hence, to fill the research gap, this research proposes to study phase behaviors and interactions between CO² and crude oil system including solubility, swelling, viscosity, the fluid composition, and also the possibility of solid precipitation due to high pressure and high temperature.

II.5 Novelty and Originality

Reviewing and comparing the research work published in the literature as mentioned in **chapter I and sub-chapter II.4**, this proposed present study is expected to answer the previous investigations that have not been addressed. Therefore, this study is expected to fill the gap among the previous reported researches, including:

1. Determination of Multi-Contact Minimum Miscibility Pressure (MMP) and First-contact Miscibility Pressure (FCMP) through comprehensive visual phase behavior of $CO₂ - Crude Oil System in High Pressure High Temperature$ (HPHT), including solubility, viscosity, swelling factor, interfacial tension (IFT), and fluid compositional (Gas Chromatograph) so that it will obtained the "crystal" clear the MMP value. Most of previous investigators have determined the MMP through standalone technique such as Vanishing Interfacial Tension then compared to conventional displacement test (slim tube/core flood).

- 2. Determination of onset pressure solid precipitation as the effects of interactions between $CO₂$ and crude oil. The phenomena are caused by $CO₂$ dissolution into the crude oil have been discussed yet there is little research have studied the effects of interaction between $CO₂$ and crude oil. Therefore, the effects of interactions between $CO₂$ and crude oil on EOR mechanisms are not well understood.
- 3. Determination of onset or threshold pressure in all stages including vaporization pressure, extraction pressure, MMP, the onset pressure of solid precipitation / paraffinic, and miscibility pressure as the effect of the interactions between $CO₂$ and crude oil in high pressure and high temperature. It will provide the clear and new insight about the mechanisms of the interactions between $CO₂$ and crude oil in all stages. Also, it will provide the new and original interpretation compared to the previous investigations. In addition, there is little research has been studied about the mechanisms of the interactions between $CO₂$ and crude oil in all stages. The threshold pressure is very important and useful in designing CO² EOR Project.
- 4. The use of surfactant for lowering MMP. It has been widely known that the surfactant has the ability in lowering the interfacial tension (IFT). However, there is just little research has been studied how the effect of surfactant in lowering the MMP.
- 5. The use of ethanol for lowering the MMP. Some of the previous researchers have performed the effects of ethanol on lowering the IFT. It can be deduced and proved that the ethanol has the impact on lowering the IFT. However, it requires for further investigation in order to find the optimum concentration of ethanol when it is mixed with $CO₂$ as the injected gas on the MMP.

This study is conducted in high pressure and high temperature condition using oil samples from Indonesia so that it is expected that the results of this study will be useful for Indonesian reservoirs. The proposed novelty in this study is also represented in research matrix. It can be seen in **table II.1**.

Table II.1 Research Matrix

Chapter III Method of Study

This study will be carried out by several experimental methods to analyze phase behavior of CO² and crude oil samples. The analysis of phase behavior includes visualization tests and compositional analysis using Fluid Eval PVT and Gas Chromatograph (GC), respectively. A Fluid Eval PVT system will be used to analyze the $CO₂$ – crude oil system phase behavior under various conditions. The PVT apparatus with visual observation is used for measuring the solubility of $CO₂$ in the oil, oil swelling due to $CO₂$, viscosity of the $CO₂$ – oil mixture, interfacial tension (IFT) of CO_2 – crude oil, and gas chromatograph is used for analyzing the composition of fluid. In this study, the possibility of solid precipitation either asphaltene or paraffinic as the effects of interaction between CO² and crude oil will be analyzed as well. Therefore, the variables of Pressure (P) and Temperature (T) is very important in this study. The purpose of this study is determining the minimum miscibility pressure (MMP) from comprehensive phase behavior and investigate the effects of interactions between $CO₂$ and crude oil. Then to convince the MMP obtained from phase behavior, the displacement test using slim tube will be carried out. Overall, the process and the method in this study can be described through the flowchart in Figure III.1.

III.1 Materials

The crude oil samples used in this experiment are dead light oil from Indonesian oil field. The CO² gas with high purity (99.9%) will be used for the injection gas as well. The additive solvents used for investigating the reduction of MMP are alcohol (ethanol) and surfactant. It should be noted that the temperature used in this experiment is $140^{\circ}F$ (60 $^{\circ}C$). The measurements will be re-conducted at $158^{\circ}F$ (70 $^{\circ}$ C) to investigate the temperature effects in interaction between CO₂ – crude oil.

III.2 Experimental Apparatus

The experimental apparatus used in this study are fluid eval PVT (it can be seen in Figure III.2), Interfacial Tension (IFT) apparatus, Gas/Liquid Chromatograph, and Displacement test apparatus (slim tube). This fluid eval PVT is used for measuring the solubility of CO_2 in the oil, oil swelling due to CO_2 dissolution, viscosity of the $CO₂$ – oil mixture, and it can be used to observe the possibility of solid precipitation.

III.2.1 Visual Fluid Eval PVT

The fluid eval PVT is used for measuring the solubility of $CO₂$ in the oil, oil swelling due to $CO₂$ dissolution, and viscosity of the $CO₂ -$ oil mixture. The $CO₂$ solubility in oils and the oil swelling are measured by contacting a certain amount of CO² with a certain amount (mass) of oil at high Pressure and high temperature (HPHT) conditions in a PVT cell, and the pressure of the system is recorded continuously. Then mass dissolved $CO₂$ is calculated through mas balance equation (Mosavat et al., 2014). The mass balance equation can be written as:

 $M_{CO2,~dissolved} = M_{CO2,~free~at~initial~state} - M_{CO2,~free~at~final~state}$

The swelling factor (SF) itself, can be calculated using equation below (Welker & Dunlop, 1963)

$$
SF = \frac{V_{o,final} (P_{test}, T_{test})}{V_{o,initial}(P_{test}, T_{test})}
$$

Where V_{ofinal} is the volume of oil fully saturated with $CO₂$ at the test pressure and temperature, and V_{ofinal} is the initial oil volume (free of CO₂) at atmospheric pressure and the test temperature.

The Visual Fluid Eval PVT is connected to an electromagnetic viscosimeter that is used to measure the viscosity of oil saturated with CO₂. The viscosity measurements were carried out by analyzing the two-way travel time a piston a moving between two coils due to magnetic field. The absolute viscosity of the mixture was measured automatically and recorded in the attached computer.

III.2.2 Compositional Analysis

The compositional analysis is aimed to analyze the composition of original oil sample and remaining oil after the swelling test. This analysis is referred to GPA Standard 2261 *"Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography"*

Figure III.1 Flowchart of this Study

Figure III.2 Visual Fluid Eval PVT Setup

III.2.3 Displacement Test

The displacement test used in this study is slim tube. Four high pressure cylinders were used to store and deliver the crude oil, reservoir brine, CO₂, and tap water, respectively. These four transfer cylinders and the high-pressure core holder were placed inside an air bath, which is kept at the constant test temperature. The MMP result of slim tube will be compared to MMP results from phase behavior. The slim tube apparatus system itself can be seen in Figure III.3.

III.3 Design of Experiment (DOE)

The Design of Experiment (DOE) is a systematic approach to investigate an experiment process. The design of experiment on this study contains several parameters to answer the present study of the questions and hypothesis and also to accomplish the research objectives. Overall, the experiment will be carried out as seen in the flowchart of this study (Figure III.1). The variables and parameters used in this study can be seen in Design of Experiment in table III.1 for more detail.

Based on Design of Experiment (table III.1), the whole of experiments requires approximately 8-9 months with 80 times of experiments. The experiments consist of five steps, there are: basic properties of crude oil measurements; PVT analysis and observation of onset pressure for solid precipitation; compositional analysis; solvent addition for MMP reduction; and displacement test (slim tube test).

Figure VI.3 Slim tube Apparatus System

Chapter IV Contribution and Significance of the Research

The contributions and significance of this research are related to the research gap and novelty proposed in this study. The data and results produced from this study give the comprehensive investigation to the oil recovery mechanisms in any $CO₂$ – EOR project through phase behavior and mutual interaction between phases in $CO₂$ and oil system. It is highly important to have better understanding of the behavior of CO² and oil phases mechanisms at all stages at various reservoir conditions in order to obtain robust prediction of multi-contact and first-contact minimum miscibility pressure and other threshold pressure from the interactions of $CO₂ - oil$ system. The robust prediction of multi-contact and first-contact minimum miscibility pressure and other threshold pressure from the interactions of $CO₂ - oil$ system is very useful for the application of $CO₂$ flooding for oilfields.

This research also gives the contribution and significance in determining of onset pressure from solid (asphaltene/paraffine) precipitation. One of the major technical issues in CO² flooding for field application is to determine the possibility of asphaltene/paraffinic precipitation and its effects on the tertiary oil recovery. The asphaltene and paraffinic precipitation may occur if a sufficient amount of $CO₂$ is dissolved into the crude oil. On the other words, the precipitated asphaltenes and paraffinic may be deposited onto porous medium and plug the flow of fluid. Therefore, it is very important to determine the onset pressure of asphaltene precipitation for a given crude oil $-$ CO₂ system. It should be noted that if the determined onset pressure is lower than the actual reservoir pressure, the asphaltene/paraffinic precipitation may occur during $CO₂$ flooding and it will affect the CO² EOR. Overall, the contribution of this research can be illustrated in Figure III.1. Figure III.1 also represent the expected results for this study. From this research, we will obtain the threshold pressure from phase behavior and interactions between CO2 and crude oil system comprehensively. It will very useful to apply CO² flooding in oilfields by considering this threshold pressure.

Figure VIIV.1 Threshold Pressure for CO² Flooding EOR

IV.1 Research Output

The output for this research can be seen in table III.1. Most of research output are targeted to publish in reputable International Journal (Quartile I and Quartile II). The results obtained from the research will also be presented to International Conference, such as Society of Petroleum Engineer (SPE) Conference and International Conference on Earth, Mining, and Energy and proposed patent at Directorate General of Intellectual Property, Republic of Indonesia. The timeline for publication can be seen in Table IV.1 as well.

IV.2 Research Schedule and Timeline

Based on methods and Design of Experiment proposed above, the experimental study require approximately 12 months (1 year). The expected completion time for experimental study time is January 2022 then continue to publish the research output and patent. As mentioned above, the results of this study will be presented to International Conference and published to reputable International Journal (indexed by Scopus/Thomson). The publications are estimated require 4-8 months (submissions until published article). The overall schedule and timeline of this research can be seen in table IV.2

Table III.2 Research Timeline

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