# MODELLING OF CO2 AND GREEN-HOUSE GASES (GHG) MISCIBILITY AND 

 INTERACTIONS WITH OIL TO ENHANCE THE OIL RECOVERY IN GAS FLOODING PROCESSESBy<br>Mohammed Kamal Emera<br>B.Sc., M.Sc., Pet. Eng.

THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY


Australian School of Petroleum
The University of Adelaide, Australia

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## THESIS SUBMITTED FOR THE DEGREE OF

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# To my father 

## To my mother

## To my son (Ahmed)

To my wife, my brothers, and my sisters
To Prof. Hemanta Sarma
To Prof. Helmy Sayyouh
To Prof. Saad Eid
To all my family, friends, and professors

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#### Abstract

\section*{1. Objective}

The objective of this research has been to develop more reliable models to predict the miscibility and interactions between $\mathrm{CO}_{2}$ or green-house gas (GHG) and oil (dead and live oils) over a wider range of conditions, based on data from different site sources, considering all the major variables affecting each modelled parameter, and for different injected gas compositions. The Genetic algorithm (GA), an artificial intelligence technique based on the Darwinian theory of evolution that mimics some of the natural processes in living organisms, was used to develop these models, based on GA software that has been developed in this work (as a modelling technique). While applications of GA have been used recently in the mathematical and computer sciences, its applications in the petroleum engineering, especially EOR research, have been limited.


## 2. Motivation to Investigate the Potential of GA-based Models

The detrimental effects of $\mathrm{CO}_{2}$ and/or GHG emissions from various industrial and human-activity sources on the environment are a major concern worldwide. This has resulted in an intensive global R\&D effort to lower or mitigate the damaging impact of GHG on the environment. One potentially attractive and effective means of lowering the GHG emissions could be to capture them from their major sources of emissions and then sequester them in depleted oil and gas reservoirs while also enhancing oil recovery.

Typically, a GHG stream, also referred to as "flue gas", contains high percentages of $\mathrm{CO}_{2}$ in addition to other gases, notably, $\mathrm{N}_{2}, \mathrm{NO}_{\mathrm{x}}$ and $\mathrm{SO}_{\mathrm{x}}$. The presence of high $\mathrm{CO}_{2}$ content in the flue gas, in particular, could make this option potentially viable, provided the miscibility and interaction properties between the injected gas and reservoir fluids are favorable. Therefore, it is critical to ascertain the likely miscibility and interactions parameters between the injected gas $\left(\mathrm{CO}_{2}\right.$ or flue gas) and oil at different conditions to
determine the optimal miscibility and interaction conditions that contribute to oil viscosity reduction and oil swelling. They in turn enhance oil recovery through improved gas flooding process performance due to higher oil mobility, volumetric sweep efficiency, and relative permeability to oil.

Often miscibility and interactions between injected gases and oils are established through "experimental methods", "new mathematical models" based on phase equilibria data and equations of state (EOS), and available "published models". Experimental methods are time-consuming and costly. Moreover, they can handle only limited conditions. Mathematical models require availability of a considerable amount of reservoir fluid composition data, which may not be available most of the time. Although, the published models are simpler and faster to use, one must however recognise that most of these models were developed and validated based on limited data ranges from site-specific conditions. Therefore, their applications cannot be generic. Another noteworthy point is that most of the interactions models have been developed using dead oil data and pure $\mathrm{CO}_{2}$ as an injected gas. Hence, they do not perform well for a wider range of live oils, as well as injected flue gases, which contain different components besides $\mathrm{CO}_{2}$.

Consequently, there is a need to have more reliable miscibility and interaction models, which can handle a much wider range of conditions and different data sources. Also, these models should be able to consider all the major variables, different injected gas compositions, and live oil in addition to dead oil.

## 3. GA-based Models Developed in This Research

- GA-based model for more reliable prediction of minimum miscibility pressure (MMP) between reservoir oil and $\mathrm{CO}_{2}$ : This model recognised the major variables affecting MMP (reservoir temperature, $\mathrm{MW}_{\mathrm{C} 5+}$, and volatiles and intermediates compositions). It has been successfully validated with published experimental data and compared to common models in the literature. It is noted that GA-based $\mathrm{CO}_{2}$-oil MMP offered the best match with the lowest error and standard deviation.
- GA-based flue gas-oil MMP model: For this model, the MMP was regarded as a function of the injected gas solubility into oil, which in turn is related to the injected gas critical properties (pseudocritical temperature and pressure) besides reservoir temperature and oil composition. A critical temperature modification factor was also used in developing this model. The GA-based model has also been successfully validated against published experimental data and compared to several models in the literature. It yielded the best match with the lowest average error and standard
deviation. Moreover, unlike other models, it can be used more reliably for gases with higher $\mathrm{N}_{2}$ (up to 20 mole\%) and different non- $\mathrm{CO}_{2}$ components (e.g., $\mathrm{H}_{2} \mathrm{~S}, \mathrm{~N}_{2}, \mathrm{SO}_{\mathrm{x}}$, $\mathrm{O}_{2}$, and $\mathrm{C}_{1}-\mathrm{C}_{4}$ ) with higher ratio (up to 78 mole\%).
- GA-based $\mathrm{CO}_{2}$-oil physical properties models: These models have been developed to predict $\mathrm{CO}_{2}$ solubility, impact on the oil swelling factor, $\mathrm{CO}_{2}$-oil density, and $\mathrm{CO}_{2}$ oil viscosity for both dead and live oils. These models recognised the major variables that affect each physical property and also properly address the effects of $\mathrm{CO}_{2}$ liquefaction pressure and oil molecular weight (MW). These models have been successfully validated with published experimental data and have been compared against several widely used models. The GA-based $\mathrm{CO}_{2}$-oil properties models yielded more accurate predictions with lower errors than other models that have been tested. Furthermore, unlike the other tested models, which are applicable to only limited data ranges and conditions, GA-based models can be applied over a wider data range and conditions.
- GA-based flue gas-oil physical properties models: These models predict flue gasoil properties such as, flue gas solubility, impact on the oil swelling factor, and flue gas-oil density and viscosity while recognising all the major variables affecting each property. Also, the GA-based models recognised the different injected flue gas compositions. These models have been successfully validated with published experimental data and have also been compared against other commonly reported $\mathrm{CO}_{2}$-oil models, which are often used for flue gas-oil physical properties prediction. The GA-based models consistently yielded a lower prediction error than the models that have been tested. Furthermore, unlike other models, which are applicable only over limited data ranges and conditions, GA-based models can be valid over a wider range of data under various conditions.

All the above-mentioned models, developed in this research, are particularly useful when experimental data are lacking and the project financial situation is a concern. In addition, these models can be useful as a fast track gas flooding project screening guide. Also, they can easily be incorporated into a reservoir simulator for $\mathrm{CO}_{2}$ or flue gas flooding design and simulation. Furthermore, they can serve as yet another useful tool to design optimal and economical experimental test protocols to determine the miscibility and interactions between the injected $\mathrm{CO}_{2}$ or flue gas and oils in gas flooding processes.

## Publications and Awards Based on This Research (2003-2006)

The following are the awards I have received and papers I have authored and/or coauthored based on my PhD research at The University of Adelaide, Australia:

## 1. Scholarships and Awards

- Postgraduate Student Energy Encouragement Award (2005) by the Australian Institute of Energy, Australia, $3^{\text {rd }}$ of November 2005.
- Santos Ltd International Post-Graduate Scholarship, Australia, 2003-2006.
- Chosen as a candidate for inclusion in the 2006-2007 ${ }^{\text {th }}$ Edition of Who's Who in Science and Engineering® scheduled to be published in September 2006 (http://www.marquiswhoswho.com/index.asp).
- The article (with Prof. Hemanta Sarma): (Emera, M.K. and Sarma, H.K.: "Use of Genetic Algorithm to Estimate $\mathrm{CO}_{2}$-Oil Minimum Miscibility Pressure-A Key Parameter in Design of $\mathrm{CO}_{2}$ Miscible Flood", Journal of Petroleum Science and Engineering, Vol. 46, Issue 1-2, No. 4, pp37-52, 2005) was adjudged the "hottest" article among the top 25 articles in Journal of Petroleum Science and Engineering (ELSEVIER) during the period (June to October 2005), one of the top 25 articles in the journal during the period (October 2005 to January 2006), and still the second hottest article during the period (January 2006-to date): \{http://top25.sciencedirect.com/?journal_id=09204105\}.


## 2. Publications:

## - Refereed Journal Papers

1. Emera, M.K. and Sarma, H.K.: "Use of Genetic Algorithm to Estimate $\mathrm{CO}_{2}$-Oil Minimum Miscibility Pressure-A Key Parameter in Design of $\mathrm{CO}_{2}$ Miscible Flood",

Journal of Petroleum Science and Engineering, Vol. 46, Issue 1-2, No. 4, pp37-52, 2005.
2. Emera, M.K. and Sarma, H.K.: "A More Reliable Model to Predict $\mathrm{CO}_{2}$ Solubility in oil and its effects on the Oil Physical Properties", In Press, Journal of Petroleum Science \& Technology, Dekker, USA, 2006.
3. Emera, M.K. and Sarma, H.K.: "Use of Genetic Algorithm to Predict Minimum Miscibility Pressure (MMP) between Flue Gases and Oil in Design of Flue Gas Injection Project", In press, SPE Reservoir Evaluation and Engineering Journal, 2006.

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4. Emera, M.K. and Sarma, H.K.: "Genetic Algorithm (GA)-based Correlations Offer More Reliable Prediction of Minimum Miscibility Pressures (MMP) between the Reservoir Oil and $\mathrm{CO}_{2}$ or Flue Gas", passed the pre-screening in the Journal of Canadian Petroleum Technology (JCPT), Canada, 2005.
5. Emera, M.K. and Sarma, H.K.: "A Novel Model to Predict $\mathrm{CO}_{2}$-oil Physical Properties for Dead and Live Oil", submitted to the Journal of Canadian Petroleum Technology (JCPT), Canada, 2005.

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7. Bon, J., Emera, M.K., and Sarma, H.K.: "An Experimental Study and Genetic Algorithm (GA) Correlation to Explore the Effect of $\mathrm{nC}_{5}$ on Impure $\mathrm{CO}_{2}$ Minimum Miscibility Pressure (MMP)", submitted to the SPE Reservoir Evaluation and Engineering Journal, 2006.

## - Conference Papers

8. Emera, M.K. and Sarma, H.K.: "A New Genetic Algorithm (GA) Model Predicts Green-House Gas (GHG) and Reservoir Oil Interaction Parameters More Accurately in Geosequestration Applications", SPE 100808 accepted for presentation in the Asia Pacific Oil and Gas Conference and Exhibition, to be held in Adelaide, Australia, September 11-13, 2006.
9. Bon, J., Emera, M.K., and Sarma, H.K.: "An Experimental Study and Genetic Algorithm (GA) Correlation to Explore the Effect of $\mathrm{nC}_{5}$ on Impure $\mathrm{CO}_{2}$ Minimum Miscibility Pressure (MMP)", SPE 101036 accepted for presentation at the Asia Pacific Oil and Gas Conference and Exhibition, to be held in Adelaide, Australia, September 11-13, 2006.
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13. Emera, M.K. and Sarma, H.K.: "A New Genetic Algorithm (GA)-Based Technique to Model the Effects of $\mathrm{CO}_{2}$ Injection on Crude Oil Properties", presented at the $13^{\text {th }}$ European Symposium on Improved Oil Recovery, Budapest, Hungary, April 25 - 27, 2005.
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## Statement of Originality

This work contains no material which has been accepted for the award of any other degree or diploma at any university or any tertiary institution and, to best of my knowledge and believe, this thesis contains no material previously published or written by another person, except where due reference has been made in the text.

I give consent to this copy of my thesis, when deposited in the University Library, being available for loan and photocopying.

Signed. Date.

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& \text { MMP to reduced } \mathrm{CO}_{2} \text {-oil MMP) and the weight average pseudocritical } \\
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\end{aligned}
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## Nomenclature

| $\alpha$ | Empirical parameter presented as a function of density and temperature and can be obtained by fitting the experimental data |
| :---: | :---: |
| $\beta$ | Mutation factor (0-1) |
| $\gamma$ | Oil specific gravity (oil density at $15.56{ }^{\circ} \mathrm{C}$ ), |
| $\gamma_{0}$ | Oil gravity, ${ }^{\circ} \mathrm{API}$ |
| $\Delta$ | Difference operator |
| $\Delta \mathrm{P}$ | Additional pressure, MPa |
| $\xi$ | Viscosity parameter of a mixture |
| $\theta$ | Ratio between gas volume at standard conditions to the volume at system T and P |
| $\lambda$ | Mutation factor (0-1) |
| $\mu$ | Gas ( $\mathrm{CO}_{2}$ or flue gas)-oil viscosity, mPa.s |
| $\mu^{*}$ | Viscosity of a gas mixture at low pressure, mPa.s |
| $\mu_{\text {d }}$ | Viscosity of dead oil at the specified temperature, mPa.s |
| $\mu_{\mathrm{i}}$ | Initial oil viscosity at the specified temperature, mPa.s |
| $\mu_{\mathrm{j}}^{*}$ | Viscosity of component j as a gas at low pressure, mPa.s |
| $\mu_{\text {m }}$ | Mixture viscosity, mPa.s |
| $\mu_{\text {o }}$ | Oil viscosity, mPa.s |
| $\mu_{\text {s }}$ | Solvent viscosity, mPa.s |
| $\rho$ | Gas ( $\mathrm{CO}_{2}$ or flue gas)-oil density, $\mathrm{g} / \mathrm{cm}^{3}$ |
| $\rho_{\text {c }}{ }^{\prime}$ | Pseudocritical density of a mixture, $\mathrm{g} / \mathrm{cm}^{3}$ |
| $\rho_{\text {i }}$ | Initial oil density at the specified temperature, $\mathrm{g} / \mathrm{cm}^{3}$ |
| $\rho_{\text {MMP }}$ | $\mathrm{CO}_{2}$ density at the MMP, $\mathrm{g} / \mathrm{cm}^{3}$ |
| $\rho_{\mathrm{r}}$ | Reduced density, fraction |
| $\Sigma$ | Sum operator |

ANN Artificial Neural Network
API $\quad$ Oil gravity ${ }^{\circ} \mathrm{API}$
Av. Average
B Ratio between oil volume at system T, and 1 atm to the volume at system T and P
b Characterization parameter obtained by measuring the viscosity of the oil at $30^{\circ} \mathrm{C}$ and 1 atm . $\left(\mu_{30}\right)$
$\mathrm{B}_{0} \quad$ Oil expansion factor
$\mathrm{C}_{\mathrm{g}} \quad \mathrm{GA}$ evaluation constant $=1.0$ for gas $\left(\mathrm{CO}_{2}\right.$ or flue gas) solubility, oil swelling factor, and gas ( $\mathrm{CO}_{2}$ or flue gas)-oil density models and $=100$ for gas ( $\mathrm{CO}_{2}$ or flue gas)-oil viscosity models and $=5000$ for MMP models
$\mathrm{C}_{\mathrm{i}} \quad$ Carbon number
Dev. Deviation (error), \%
EOS Equation of state
exp Exponential factor
Exp. Experimental
F Weighting composition parameter
$\mathrm{F}_{\text {impure }} \quad$ Impurity correction factor
Fit (i) Average fitness of chromosome i, where the chromosome has many fitness values based on the number of data available ( j )
$\mathrm{F}_{\mathrm{R}} \quad$ Mole percentage of $\mathrm{C}_{2}$ through $\mathrm{C}_{6}$ in the reservoir fluid, \%
GA Genetic algorithm
GHG Green-house gas
I
Interm. Intermediates components, $\mathrm{C}_{1}-\mathrm{C}_{4}, \mathrm{H}_{2} \mathrm{~S}$, and $\mathrm{CO}_{2}$, fraction
$\mathrm{K}_{\mathrm{i}} \quad$ Normalized partition coefficient for carbon number i
m Exponent
$\mathrm{MF}_{\mathrm{i}} \quad$ Critical temperature modification factor of injected gas component i
$\mathrm{M}_{\mathrm{inj}}$. Molecular weight of the injected gas
$\mathrm{M}_{\mathrm{j}} \quad$ Molecular weight of gas component j
MMP Gas-oil Minimum Miscibility Pressure, MPa
$\mathrm{MMP}_{\mathrm{CO} 2} \quad \mathrm{CO}_{2}$-oil Minimum Miscibility Pressure, MPa
MMP $_{\text {flue gas }} \quad$ Flue gas-oil Minimum Miscibility Pressure, MPa
MW
Average molecular weight of the oil
$\mathrm{MW}_{\mathrm{C} 5+} \quad$ Molecular weight of the $\mathrm{C}_{5+}$ components
MW ${ }_{\text {C7+ }} \quad$ Molecular weight of the $\mathrm{C}_{7+}$ components
$\mathrm{MW}_{\mathrm{CO} 2} \quad \mathrm{CO}_{2}$ molecular weight
$\mathrm{MW}_{\text {flue gas }}$ Flue gas molecular weight
$\mathrm{MW}_{\mathrm{i}} \quad$ Molecular weight of component i
n Non- $\mathrm{CO}_{2}$ components, components, or the GA population size
$\mathrm{nn} \quad$ Number of available data points
NPV Net present value
P (c) Crossover probability
P (m) Mutation probability
$\mathrm{P}_{\mathrm{b}} \quad$ Bubble point pressure, MPa
$\mathrm{P}_{\mathrm{c}} \quad$ Gas critical pressure, MPa
$\mathrm{P}_{\mathrm{C}, \mathrm{CO} 2} \quad \mathrm{CO}_{2}$ critical pressure, MPa
$\mathrm{P}_{\mathrm{C}, \text { inj. }} \quad$ Injection gas critical pressure, MPa
$\mathrm{P}_{\mathrm{Ci}} \quad$ Critical pressure of the gas component i, MPa
$\mathrm{P}_{\mathrm{cj}} \quad$ Critical pressure of component j
$\mathrm{P}_{\mathrm{cm}} \quad$ Mole average pseudocritical pressure, MPa
$\mathrm{P}_{\mathrm{CW}} \quad$ Weight average pseudocritical pressure, MPa
pen GA penalty value
Pfit( $\mathrm{i}, \mathrm{j}$ ) Fitness function of data number j of chromosome i , fraction
$\mathrm{P}_{\text {liq }} \quad$ Gas $\left(\mathrm{CO}_{2}\right.$ or flue gas) liquefaction pressure at the specified temperature, MPa
$\mathrm{P}_{\mathrm{pc}} \quad$ Flue gas weight average pseudocritical pressure, MPa
$\mathrm{P}_{\mathrm{r}, \mathrm{CO} 2} \quad$ Reduced $\mathrm{CO}_{2}$-oil MMP, fraction
$\mathrm{P}_{\mathrm{r} \text {, flue gas }} \quad$ Reduced flue gas-oil MMP, fraction
PR-EOS Peng-Robinson equation of state
$\mathrm{P}_{\mathrm{s}} \quad$ Saturation pressure, MPa
PV Pore volume
RBA Rising bubble apparatus
SA Simulated annealing
SF Oil swelling factor, fraction
$\mathrm{SF}_{\mathrm{i}} \quad$ Dong (1999) factor representing the strength of species $i$ in changing the apparent critical temperature of the mixture relative to the critical temperature of $\mathrm{CO}_{2}$

| STDEV | Standard deviation, \% |
| :---: | :---: |
| $\mathrm{T}_{\mathrm{ac}}$ | Mole average pseudocritical temperature with using factor $\mathrm{SF}_{\mathrm{i}}, \mathrm{K}$ |
| T | Gas critical temperature, ${ }^{\circ} \mathrm{C}$ |
| $\mathrm{T}_{\mathrm{C}, \mathrm{CO} 2}$ | Critical temperature of pure $\mathrm{CO}_{2}$ gas, ${ }^{\circ} \mathrm{C}\left(31.1{ }^{\circ} \mathrm{C}\right)$ |
| $\mathrm{T}_{\mathrm{C}, \mathrm{inj} .}$ | Injected gas critical temperature, K |
| $\mathrm{T}_{\mathrm{c} \text { flue gas }}$ | Flue gas critical temperature, ${ }^{\circ} \mathrm{C}$ |
| $\mathrm{T}_{\mathrm{ci}}$ | Critical temperature of gas component $\mathrm{i},{ }^{\circ} \mathrm{C}$ |
| $\mathrm{T}_{\mathrm{Ci}}$ | Critical temperature of gas component i, K |
| $\mathrm{T}_{\mathrm{cj}}$ | Critical temperature of component j |
| $\mathrm{T}_{\mathrm{CM}}$ | Mole average critical temperature, K |
| $\mathrm{T}_{\mathrm{cm}}$ | Mole average pseudocritical temperature, ${ }^{\circ} \mathrm{C}$ |
| $\mathrm{T}_{\text {CW }}$ | Weight average pseudocritical temperature with using the critical temperature modification factor $\left(\mathrm{MF}_{\mathrm{i}}\right),{ }^{\circ} \mathrm{C}$ |
| $\mathrm{T}_{\mathrm{cw}}$ | Weight average pseudocritical temperature, ${ }^{\circ} \mathrm{C}$ |
| $\mathrm{T}_{\mathrm{pc}}$ | Pseudocritical temperature (may be weight average or mole average), ${ }^{\circ} \mathrm{C}$ |
| $\mathrm{T}_{\mathrm{pc}}$ | Flue gas weight average or mole average pseudocritical temperature, ${ }^{\circ} \mathrm{C}$ |
| $\mathrm{T}_{\mathrm{r}}$ | Reduced reservoir temperature, ${ }^{\circ} \mathrm{C}$ |
| $\mathrm{T}_{\mathrm{R}}$ | Reservoir temperature, ${ }^{\circ} \mathrm{C}$ |
| $\mathrm{T}_{\text {Res }}$. | Reservoir temperature, K |
| Value $_{\text {cal }}$ | MMP, solubility, swelling, density, and viscosity predicted value |
| Value exp. | MMP, solubility, swelling, density, and viscosity experimental value |
| $\mathrm{V}_{\mathrm{c}}{ }^{\text {m }}$ | Pseudcritical volume of a mixture, $\mathrm{cm}^{3} / \mathrm{g}$ |
| $\mathrm{V}_{\mathrm{cC7} 7+}{ }^{\mathrm{m}}$ | Critical volume of the $\mathrm{C}_{7+}$ fraction, $\mathrm{cm}^{3} / \mathrm{g}$ |
| $\mathrm{V}_{\mathrm{cj}}$ | Critical volume of component $\mathrm{j}, \mathrm{cm}^{3} / \mathrm{g}$ |
| $\mathrm{V}_{0}$ | Oil volume fraction |
| Vol. | Volatiles ( $\mathrm{C}_{1}$ and $\mathrm{N}_{2}$ ) mole percentage, \% |
| Volatiles | Volatile components, $\mathrm{C}_{1}$ and $\mathrm{N}_{2}$, fraction |
| $\mathrm{V}_{\text {s }}$ | Solvent volume fraction |
| $\mathrm{w}_{\mathrm{i}}$ | Weight fraction of component $i$, fraction |
| $\mathrm{w}_{\text {ic } 2+}$ | Component i normalized weighting fraction in the $\mathrm{C}_{2+}$ fraction of oil |
| X | Gas concentration, mole \% |
| $\mathrm{x}_{\mathrm{CO} 2}$ | $\mathrm{CO}_{2}$ mole percentage in the injection gas, \% |
| $\mathrm{x}_{\mathrm{i}}$ | Mole fraction of gas component i |


| $x_{j}$ | Mole fraction of component j, fraction |
| :--- | :--- |
| y | Mole fraction of diluted component |
| $\mathrm{yCO}_{2}$ | Mole fraction of $\mathrm{CO}_{2}$ in the injected flue gas, fraction |
| $\mathrm{y}_{\mathrm{i}}$ | Mole fraction of the gas component i in the injected gas, fraction |

## CHAPTER 1

## Introduction

### 1.1. Introduction

Due to the imbalance between the demand and available supply, and the high cost of finding new reserves, it is very important for the oil industry to enhance recovery from existing sources of oil. One of the important methods of enhancing oil recovery is gas flooding (e.g., using $\mathrm{CO}_{2}$, hydrocarbon gases, methane, air, and nitrogen).

Among the various gas flooding processes, $\mathrm{CO}_{2}$ flooding has been received much attention in recent years. The detrimental effects of $\mathrm{CO}_{2}$ and/or green-house gas (GHG) emissions from various industrial and human-activity sources on the environment are a major concern worldwide. This has resulted in an intensive global R\&D effort to lower or mitigate the damaging impact of these gases on the environment. One potentially attractive and effective means of lowering these gases emissions could be to capture them from their major sources of emissions and then sequester them in depleted oil and gas reservoirs while also enhancing the oil recovery. Typically, a GHG stream, also referred to as "flue gas", contains high percentages of $\mathrm{CO}_{2}$ in addition to other gases (e.g., $\mathrm{C}_{1}-\mathrm{C}_{4}, \mathrm{~N}_{2}, \mathrm{NO}_{\mathrm{x}}$, and $\mathrm{SO}_{\mathrm{x}}$ ). The presence of high $\mathrm{CO}_{2}$ content in the flue gas, in particular, could make this option potentially viable, provided the miscibility and interaction properties between the injected gas and reservoir fluids are favorable.
$\mathrm{CO}_{2}$ or flue gas can displace oil using three displacement mechanisms: immiscible displacement, multi-contact miscibility, and first contact miscibility, as dictated by the pressure and temperature conditions. At a specific temperature and low pressures (below the gas-oil minimum miscibility pressure (MMP)), the displacement mechanism is immiscible displacement. While at pressures above the specified pressure (MMP), the displacement
mechanism is multi-contact miscible displacement. For impractically very high pressures, $\mathrm{CO}_{2}$ or flue gas displacement may be first contact miscible displacement (Jarrell et al. (2002) and Rathmell et al. (1971)). Theoretically, $\mathrm{CO}_{2}$ has the potential to recover all residual oil provided $\mathrm{CO}_{2}$ flood is carried out at or above the MMP at which $\mathrm{CO}_{2}$ and oil are miscible (Jarrell et al. (2002)).

For the multi-contact miscible displacement, $\mathrm{CO}_{2}$ is enriched with intermediates $\left(\mathrm{C}_{2}-\right.$ $\mathrm{C}_{6}$ ) from the oil, where there is initially a period of immiscible displacement until multiple contacts (mass transfers) enable some components of the oil and $\mathrm{CO}_{2}$ to be exchanged until the oil-enriched $\mathrm{CO}_{2}$ cannot be distinguished from the $\mathrm{CO}_{2}$-enriched oil (Jarrell et al. (2002) and Rathmell et al. (1971)). This process is described as a condensing/vaporizing mechanism as shown in Fig.1-1 (Zick (1986), Johns and Orr (1996), and Jarrell et al. (2002)).

## NOTE:

This figure is included on page 2 of the print copy of the thesis held in the University of Adelaide Library.

Fig.1-1. $\mathrm{CO}_{2}$ multi-contact miscibility process (after Jarrell et al. (2002).

Gas miscible flooding is among the more widely applied non-thermal EOR techniques. Among gas injection processes, $\mathrm{CO}_{2}$ or flue gas is preferred to hydrocarbon gases (HC) because of its lower cost, as well as the high displacement efficiency, and potential for
concomitant environmental benefits through its disposal in the petroleum reservoir. Conventional use of $\mathrm{CO}_{2}$ or flue gas for improving oil recovery is mostly for miscible flood applications where displacement of oil from reservoir pore volume is achieved by the injected gas solvent action. This solvent action prevents formation of an interface between the driving and driven fluids through the formation of a bank of liquid that is miscible with both the reservoir and injected fluids.

Key factors that affect gas miscible flooding are reservoir temperature, oil characteristics, reservoir pressure and the purity of injected gas itself. Field case histories from $\mathrm{CO}_{2}$ floods in the Permian Basin, West Texas suggest that $\mathrm{CO}_{2}$ purity should not be viewed as too rigid a constraint, as the use of low purity $\mathrm{CO}_{2}$ streams could also be economic and effective in enhancing oil recovery. In fact, certain impurities (e.g., $\mathrm{H}_{2} \mathrm{~S}$ and $\mathrm{SO}_{\mathrm{x}}$ ) could contribute towards attaining gas-oil miscibility at lower pressures and these components contribute to increased gas solubility in oil, which in turn increases oil mobility and relative permeability. In contrast, the presence of other components (e.g., $\mathrm{C}_{1}, \mathrm{~N}_{2}, \mathrm{O}_{2}$ ) increases MMP and is detrimental to the injected gas solubility in oil, which results in the decrease of its effect on oil viscosity reduction and oil swelling factor and in turn causes less effect on the oil mobility and relative permeability. However, from an operational perspective, it is often the remaining low percentages of non- $\mathrm{CO}_{2}$ gases that are more difficult and costly to remove, requiring expensive gas separation facilities. Safety and compression cost considerations also justify near-miscible gas flood applications for some reservoirs. Therefore, the potential of injecting flue gases containing both $\mathrm{CO}_{2}$ and non- $\mathrm{CO}_{2}$ components $\left(\mathrm{H}_{2} \mathrm{~S}, \mathrm{~N}_{2}, \mathrm{SO}_{\mathrm{x}}, \mathrm{O}_{2}\right.$, and $\mathrm{C}_{1}$ $\mathrm{C}_{4}$ ) could be an attractive option, provided the flue gas composition does not affect the process performance adversely and their overall impact on the miscibility and interactions with oil, separation/purification at the surface, and subsequent re-injection is evaluated and well understood.

### 1.2. Motivation to Investigate the Potential of GA-based Models

The knowledge of miscibility conditions and interactions between injected gas and reservoir oil in addition to their effect on oil recovery are very important for any gas flooding project. The major parameters that affect gas flooding are MMP and gas solubility in oil. Gas solubility results in oil viscosity reduction and oil swelling increase, which in turn, enhance the oil mobility and increase the oil recovery efficiency. A better understanding of these parameters is vital to any successful gas flooding project. Therefore, it is critical to ascertain the likely miscibility and interaction parameters between injected gas $\left(\mathrm{CO}_{2}\right.$ or flue gas) and oil at different conditions to determine the optimal miscibility and interaction conditions that
contribute to oil viscosity reduction and oil swelling. They, in turn, enhance the oil recovery through improved gas flooding process performance due to higher oil mobility, volumetric sweep efficiency, and relative permeability to oil.

Often the miscibility and interactions between the injected gas and oil are established through "experimental methods", "new mathematical models" based on phase equilibria data and equations of state (EOS), and available "published models". Experimental methods are time-consuming and costly. Moreover, they can handle only limited conditions. Mathematical models often demand the availability of a considerable amount of reservoir fluid composition data, which may not be available most of the time. Although, the published models or correlations are simpler and faster to use, however one must recognise that most of these models are developed and validated based on limited data ranges from site-specific conditions. Therefore, their applications cannot be generic. Another noteworthy point is that most of the interactions models have been developed using dead oil data and pure $\mathrm{CO}_{2}$ as an injected gas. Hence, they do not perform well for a wider range of live oils and also when flue gases are injected because such gases contain other components besides $\mathrm{CO}_{2}$.

Consequently, there is a need to have more reliable miscibility and interaction models, which can handle a much wider range of conditions and different data sources. Also, these models should be able to consider all the major variables, different injected gases compositions, and live oil in addition to dead oil.

## CHAPTER 2

## Research Objective and Thesis Overview

### 2.1. Introduction

As discussed in Chapter 1, there is a need to have more reliable miscibility and interaction models, which can handle a much wider range of conditions and different data sources. Also, these models should be able to consider all the major variables, different injected gas compositions, and live oil in addition to dead oil. Therefore, this research was designed to satisfy this research gap and present more reliable models for miscibility and interactions between injected gas $\left(\mathrm{CO}_{2}\right.$ or flue gas) and oil. This chapter explains the research objective and also presents an overview on the thesis outline.

### 2.2. Research Objective

The objective of this research has been to develop more reliable models to predict the miscibility and interactions between $\mathrm{CO}_{2}$ or flue gas and oil (dead and live oils) over a wider range of conditions, based on data from different site sources, considering all the major variables affecting each modelled parameter, and for different injected gas compositions. The proposed models are as follows:

1. For miscibility pressures (MMP):

- $\mathrm{CO}_{2}$-oil MMP for both dead and live oils,
- Flue gas-oil MMP, considering wider range of the injected gas composition.

2. For gas ( $\mathrm{CO}_{2}$ or flue gas)-oil interactions, for dead and live oils:

- $\mathrm{CO}_{2}$-oil solubility,
- Impact on oil swelling factor due to $\mathrm{CO}_{2}$,
- $\mathrm{CO}_{2}$-oil density,
- $\mathrm{CO}_{2}$-oil viscosity,
- Flue gas-oil solubility,
- Impact on oil swelling factor due to flue gas,
- Flue gas-oil density,
- Flue gas-oil viscosity.

Genetic algorithm (GA), an artificial intelligence technique based on the Darwinian theory of evolution that mimics some of the natural processes in living organisms, was used to develop these models, based on GA software that has been developed in this work (as a modelling technique). It is to be noted that applications of GA have been started recently in the mathematical and computer sciences and its applications in the petroleum engineering, especially EOR research, have been limited.

### 2.3. Thesis Overview

The outline of this thesis is as follows:

- Literature review of the factors affecting miscibility and interaction parameters of $\mathrm{CO}_{2}$ or flue gas and oil are presented. In addition, an explanation is introduced of the most widely used miscibility and interaction models (Chapter 3).
- Literature review of GA and its characteristics and advantages are presented. Also, the previous applications of this tool in petroleum engineering are reviewed (Chapter 4).
- Explanation about the GA modelling software that has been developed in this research as an efficient modelling technique (Chapter 5).
- Presentation of the developed models for MMP, $\mathrm{CO}_{2}$-oil MMP and flue gas-oil MMP, is introduced (Chapter 6).
- Presentation of the developed models for interactions between $\mathrm{CO}_{2}$ and oil (dead and live oils), notably, $\mathrm{CO}_{2}$ solubility in oil, impact on oil swelling factor, $\mathrm{CO}_{2}$-oil density, and $\mathrm{CO}_{2}$-oil viscosity is introduced. In addition, the models developed for interactions between flue gas and oil (dead and live oils), notably, flue gas solubility in oil, impact on oil swelling factor, flue gas-oil density, and flue gas-oil viscosity are presented (Chapter 7).
- The conclusions and recommendations developed based on this research are presented (Chapter 8).
- Appendices present the literature database used in this research for both miscibility and interaction models are included together with the developed GA software code.


## CHAPTER 3

## Literature Review-1: Modelling of the Miscibility and Interactions Between $\mathrm{CO}_{2}$ or Flue Gas and Oil in Gas Flooding Processes

### 3.1. Introduction

One potentially attractive and effective means of lowering $\mathrm{CO}_{2}$ and flue gas emissions could be to capture them from their major sources of emissions and then sequester them in depleted oil and gas reservoirs while also enhancing oil recovery. This option is potentially viable, provided the miscibility and other interactions between the injected gas and reservoir oil are favorable. Therefore, a better understanding of interactions between $\mathrm{CO}_{2}$ or flue gas and reservoir oil in addition to their effect on oil recovery are very important for any gas flooding project.

As an example, the presence of some components (e.g., $\mathrm{C}_{2}-\mathrm{C}_{4}, \mathrm{H}_{2} \mathrm{~S}, \mathrm{SO}_{\mathrm{x}}$ ) with $\mathrm{CO}_{2}$ in the flue gas is favorable for enhanced oil recovery because they contribute to increased gas solubility in oil, which in turn increases oil mobility and relative permeability. In addition, these components contribute towards reducing minimum miscibility pressure (MMP). In contrast, the presence of other components (e.g., $\mathrm{C}_{1}, \mathrm{~N}_{2}, \mathrm{O}_{2}$ ) is detrimental to the injected gas solubility in oil, resulting in the decrease of its effect on oil viscosity reduction and oil swelling factor, and in turn resulting in less effect on oil mobility and relative permeability. In addition, these components contribute towards increasing the MMP. Therefore, it is critical to ascertain the likely interactions between injected $\mathrm{CO}_{2}$ or flue gas (with different compositions) and oil to determine the optimal conditions that contribute to the gas-oil MMP reduction, viscosity reduction, and oil swelling to enhance oil recovery and increase the efficiency of gas flooding processes.

This chapter presents an overview on the available models for $\mathrm{CO}_{2}$-oil MMP and flue gas-oil MMP. In addition, this chapter covers the available models for $\mathrm{CO}_{2}$ and flue gas interactions with oil (e.g., gas solubility, impact on oil swelling factor, and gas-oil density and viscosity). An overview on the factors affecting the miscibility and interactions parameters is also presented.

### 3.2. Modelling of $\mathbf{C O}_{\mathbf{2}}$-Oil MMP and Flue Gas-Oil MMP

Often MMP is obtained by three methods: experimental tests, predicting of MMP using commonly available models or correlations in the literature, and predicting of MMP by equations of state (EOS) studies.

The most common experimental methods to determine MMP are slim tube and rising bubble apparatus (RBA) experiments. Slim tube experiments are the most commonly used experimental method in the oil industry. However, there are no standard and accurate test conditions and interpretation procedures for the slim tube experiments, as different organizations use different apparatus specifications and different interpretation procedures (Green and Willhite (1998)). In addition to the slim tube, RBA experiments are also used to determine MMP and their results correspond to those from the slim tube with less experimental time (Eakin and Mitch (1988), Dong et al. (2001b), and Elsharkawy et al. (1992)). In general, the experimental methods, especially slim tube tests, are expensive, time consuming, or may not be readily available. Thus, efforts are also made to predict gas-oil MMP using various methods such as the mathematical studies and the commonly available models in the literature.

The mathematical studies are developed based on using phase equilibria data and an EOS to determine the MMP (Jarrell et al. (2002)). This approach requires availability of a considerable amount of reservoir fluid composition data, which may not be readily available most of the time and hence is a tedious approach. Furthermore, the calculations are not easy and require the application of certain algorithms and computer modelling, which is not commonly available in many of the situations. Also, for the EOS calculations, the equilibrium constants should be determined accurately to provide an accurate prediction, which could be difficult to achieve where the EOS may not be adequately accurate. Therefore, the EOS calculations must be calibrated using experimental PVT data, which can be difficult (Green and Willhite (1998)). As examples of the mathematical determination of MMP, Johns and Orr (1996) developed a multi-component phase equilibrium approach using the method of characteristics in absence of dispersion. They presented an approach that can be used to find the key tie line that controls miscibility and predicts MMP from an EOS. Also, Wang and Orr
(1998) presented a method to determine the MMP for displacements with an arbitrary number of components and two phase flow that is based on an analytical theory for one-dimension and dispersion free flow of a multi-component mixture. Furthermore, Ahmed (1997) presented a generalized method to determine MMP for a multi-component miscible displacement of oil by $\mathrm{CO}_{2}$ and other different gas injection (hydrocarbon gas and nitrogen) by using the modified Peng Robinson EOS (PR-EOS) in conjunction with a miscibility function.

In addition to the mathematical calculations, the available published models also could be used to predict the MMP. Table 3-1 summarizes along with brief corresponding remarks, some of the commonly used MMP models available in the literature. As these models are used to predict $\mathrm{CO}_{2}$-oil MMP and flue gas-oil MMP, a brief overview of these properties follows.

### 3.2.1. $\mathrm{CO}_{2}$-Oil MMP

$\mathrm{CO}_{2}$-oil MMP is a function of oil composition and reservoir temperature (Holm and Josendal (1974), Alston et al. (1985), and Johnson and Pollin (1981)). All the previous studies and models stated that the reservoir temperature has a significant impact on the $\mathrm{CO}_{2}$-oil MMP. With regard to the oil composition, Rathmell et al. (1971) indicated that the presence of volatiles (e.g., $\mathrm{C}_{1}$ ) increases the MMP, while the presence of intermediates (e.g., $\mathrm{C}_{2}$ - $\mathrm{C}_{6}$ ) decreases the MMP. Metcalfe and Yarborough (1974) suggested that a model should take into consideration the presence of both the volatiles and intermediates in oil as well as the reservoir temperature for it to be considered a general model for MMP prediction. Alston et al. (1985), too, had conducted a series of slim tube tests to prove that the MMP is affected by the presence of $\mathrm{C}_{1}$ and other volatile components (e.g., $\mathrm{N}_{2}$ ) in the oil. They found that the presence of these components increases the MMP, however, the MMP is lowered by the presence of the intermediates in reservoir oil (e.g., $\mathrm{C}_{2}-\mathrm{C}_{4}, \mathrm{H}_{2} \mathrm{~S}$, and $\mathrm{CO}_{2}$ ). Furthermore, they stated that consideration of $\mathrm{C}_{5+}$ molecular weight $\left(\mathrm{MWc}_{5_{+}}\right)$is more important than the oil API gravity. Cronquist (1978), too, used the $\mathrm{MWc}_{5+}$ as a model variable in addition to the volatiles mole percentage ( $\mathrm{C}_{1}$ and $\mathrm{N}_{2}$ ) and temperature. Moreover, Enick et al. (1988) developed their model using the $\mathrm{MWc}_{5+}$ to present the effect of oil composition on the MMP.

### 3.2.2. Flue Gas-Oil MMP

The factors that affect flue gas-oil MMP are reservoir temperature, oil composition, and injected gas composition. As stated before for $\mathrm{CO}_{2}$-oil MMP, the flue gas-oil MMP is also
affected similarly by the reservoir temperature, $\mathrm{MW}_{\mathrm{C}_{5}+}$, and oil volatiles and intermediates components.

In addition, the existence of non- $\mathrm{CO}_{2}$ components (e.g., $\mathrm{H}_{2} \mathrm{~S}, \mathrm{SO}_{\mathrm{x}}$, and $\mathrm{C}_{2}-\mathrm{C}_{4}$ ) whose critical temperatures are higher than that of $\mathrm{CO}_{2}\left(31.1^{\circ} \mathrm{C}\right)$ causes an improvement in the flue gas solubility in reservoir oil (Dong (1999) and Zhang et al. (2004)). This results in an increased injected gas pseudocritical temperature and a lower MMP. On the other hand, the existence of the components (e.g., $\mathrm{N}_{2}, \mathrm{O}_{2}$, and $\mathrm{C}_{1}$ ) with lower critical temperatures causes a reduction in the flue gas solubility in reservoir oil and has the opposite effect.

Wilson (1960) stated that the pseudocritical temperature of the injected gas affects the MMP and it could be used as a variable in a miscibility model. Likewise, Rutherford (1962) found, empirically, that the hydrocarbon gas (HC)-oil MMP in HC miscible floods is a function of the pseudocritical temperature of the injected gas. Jacobson (1972) also suggested a similar scheme using the pseudocritical temperature as a model variable for acid gases $\left(\mathrm{CO}_{2}\right.$ with $\mathrm{H}_{2} \mathrm{~S}$ )-oil MMP prediction. However, instead of using actual values, apparent critical temperatures were used for non-HC components as model variables. Alston et al. (1985) followed a similar approach to model the flue gas-oil MMP using the injected gas pseudocritical temperature, where apparent critical temperatures for $\mathrm{C}_{2}$ and $\mathrm{H}_{2} \mathrm{~S}$ components (equal to $51.67^{\circ} \mathrm{C}$ for both of them) were also used to determine the pseudocritical temperature using the weight-fraction mixing rule. They found that the weight-fraction mixing rule gave better results than the mole-fraction method.

Similarly, Kovarik (1985) presented a model that was developed also based on the pseudocritical temperature. In addition to the weight-fraction mixing rule, the mole-fraction rule was used to determine the pseudocritical temperature and the author found that the two methods presented similar results. Moreover, Sebastian et al. (1985) also used the molefraction mixing rule to determine the injected gas pseudocritical temperature in developing their flue gas-oil MMP model. They also used an apparent critical temperature for $\mathrm{H}_{2} \mathrm{~S}$ $\left(51.67^{\circ} \mathrm{C}\right)$. Dong (1999) presented an approach similar to that of Sebastian et al. (1985) but instead of using apparent critical temperatures, a factor with non- $\mathrm{CO}_{2}$ components $\left(\mathrm{H}_{2} \mathrm{~S}, \mathrm{SO}_{2}\right.$, $\mathrm{O}_{2}, \mathrm{~N}_{2}$, and $\mathrm{C}_{1}$ ) was used in determining the injected gas pseudocritical temperature to represent the strength of these components in changing the apparent critical temperature of the injected flue gas relative to pure $\mathrm{CO}_{2}$.

Eakin and Mitch (1988) used the injected gas pseudocritical pressure and the pseudocritical temperature in developing their model. They argued that the change of the rising bubbles' shape in the RBA and also the low value of the interfacial tension between the injected gas and oil would occur only near the critical point.
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Table 3-1. Commonly used $\mathrm{CO}_{2}$-oil MMP and flue gas-oil MMP models.

| Author | Model | Remarks |
| :---: | :---: | :---: |
| 1. $\mathrm{CO}_{2}$-oil MMP: |  |  |
| Holm and Josendal (1974) | A graphical model that is a function of the reservoir temperature and $\mathrm{MW}_{\mathrm{C} 5+}$. | Limitations: $-180 \leq \mathrm{MWc}_{5_{+}} \leq 240$ <br> - Temperature and pressure limits for every molecular weight (e.g., for $\mathrm{MWc}_{5+}=240$, the temperature limit is from $32.2^{\circ} \mathrm{C}$ to $82.2^{\circ} \mathrm{C}$ and the pressure limit is from 9.65 MPa to 22 MPa ). |
| National Petroleum <br> Council (NPC) <br> (1976) (after Klins (1984)) | The MMP was presented as a function of oil API gravity and reservoir temperature. <br> - For oil API gravity<27,$~ M M P=27.6 \mathrm{MPa}$, <br> - For $27^{\circ} \leq$ oil API gravity $\leq 30^{\circ}$, MMP $=20.7 \mathrm{MPa}$, <br> - For oil API gravity $>30^{\circ}$, MMP $=8.27 \mathrm{MPa}$. | For every reservoir temperature $\geq 49^{\circ} \mathrm{C}$, there is a correction for the corresponding MMP value: <br> - For $49^{\circ} \mathrm{C} \leq \mathrm{T}_{\mathrm{R}}<65.6^{\circ} \mathrm{C}, \Delta \mathrm{P}=+1.38 \mathrm{MPa}$, <br> - For $65.6^{\circ} \mathrm{C} \leq \mathrm{T}_{\mathrm{R}}<93.3^{\circ} \mathrm{C}, \Delta \mathrm{P}=+2.413$ MPa, <br> - For $93.3^{\circ} \mathrm{C} \leq \mathrm{T}_{\mathrm{R}}<121^{\circ} \mathrm{C}, \Delta \mathrm{P}=+3.45 \mathrm{MPa}$. Limitation: |

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|  |  | $-\mathrm{T}_{\mathrm{R}}<121{ }^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: |
| Cronquist (1978) <br> (after Stalkup (1984)) | $\mathrm{MMP}=0.11027 \times\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)^{\mathrm{Y}}$ <br> where, $\mathrm{Y}=0.744206+0.0011038 \times \mathrm{MW}_{\mathrm{C} 5+}+0.0015279 \times \mathrm{Vol} .$ | Limitations: <br> - Oil API gravity range from $23.7^{\circ}$ to $44^{\circ}$, <br> - $\mathrm{T}_{\mathrm{R}}$ range from 21.67 to $120^{\circ} \mathrm{C}$, <br> - MMP range from 7.4 to 34.5 MPa . |
| Lee (1979) | Developed based on equating the MMP with the $\mathrm{CO}_{2}$ vapour pressure when $\mathrm{T}_{\mathrm{R}}<\mathrm{CO}_{2}$ critical temperature, while using the corresponding model when $\mathrm{T}_{\mathrm{R}} \geq \mathrm{CO}_{2}$ critical Temperature. $\mathrm{MMP}=7.3924 \times 10^{\mathrm{b}}$ <br> where: $\mathrm{b}=2.772-\left(1519 /\left(492+1.8 \mathrm{~T}_{\mathrm{R}}\right)\right)$ | - If MMP< $\mathrm{P}_{\mathrm{b}}$, the $\mathrm{P}_{\mathrm{b}}$ is taken as MMP. |
| Yellig and <br> Metcalfe (1980) | $\begin{aligned} & \mathrm{MMP}=12.6472+0.015531 \times\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)+ \\ & 1.24192 \times 10^{-4} \times\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)^{2}-716.9427 /\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right) \end{aligned}$ | -If MMP $<\mathrm{P}_{\mathrm{b}}$, the $\mathrm{P}_{\mathrm{b}}$ is taken as MMP. Limitations: $35^{\circ} \mathrm{C} \leq \mathrm{T}_{\mathrm{R}}<88.9^{\circ} \mathrm{C}$ |
| Holm and Josendal (1982) | A graphical model that is a function of $\mathrm{C}_{5}$ to $\mathrm{C}_{30}$ hydrocarbons contents present in the $\mathrm{C}_{5+}$ fraction, density of pure $\mathrm{CO}_{2}$, and reservoir temperature. where, MMP is a linear function of the $\mathrm{C}_{5}-\mathrm{C}_{30}$ hydrocarbons contents present in the $\mathrm{C}_{5+}$ fraction and the density of $\mathrm{CO}_{2}$. | - Limitations: $\begin{aligned} & 53 \% \leq\left(\mathrm{C}_{5}-\mathrm{C}_{30}\right) / \mathrm{C}_{5+} \leq 90 \%, \\ & 6.9 \mathrm{MPa} \leq \mathrm{MMP} \leq 55 \mathrm{MPa}, \\ & 20^{\circ} \mathrm{C} \leq \mathrm{T}_{\mathrm{R}} \leq 182^{\circ} \mathrm{C}, \end{aligned}$ <br> If MMP $<\mathrm{P}_{\mathrm{b}}$, the $\mathrm{P}_{\mathrm{b}}$ is taken as MMP. |


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| 2. Flue gas-oil MMP: |  |  |
| :---: | :---: | :---: |
| Alston et al. (1985) | $\begin{aligned} & \frac{\mathrm{MMP}_{\text {flue gas }}}{\mathrm{MMP}_{\mathrm{CO} 2}}=\left(\frac{87.8}{1.8 \mathrm{~T}_{\mathrm{cw}}+32}\right)^{\left(\frac{1.935 \times 87.8}{1.8 \mathrm{~T}_{\mathrm{cw}}+32}\right)}, \\ & \text { where: } \mathrm{T}_{\mathrm{cw}}=\sum \mathrm{w}_{\mathrm{i}} \times \mathrm{T}_{\mathrm{ci}} \end{aligned}$ | $-\mathrm{H}_{2} \mathrm{~S}$ and $\mathrm{C}_{2}$ critical temperatures were modified to $51.67^{\circ} \mathrm{C}$. <br> -If MMP $<\mathrm{P}_{\mathrm{b}}$, the $\mathrm{P}_{\mathrm{b}}$ is taken as MMP Limitation: <br> -Used for not more than 8 mole\% of $\mathrm{N}_{2}$. <br> - Presented inaccurate prediction for flue gas containing $\mathrm{SO}_{2}$. |
| Sebastian et al. (1985) | $\begin{aligned} & \frac{\mathrm{MMP}_{\text {fluegas }}}{\mathrm{MMP}_{\mathrm{CO} 2}}=1.0-2.13 \times 10^{-2}\left(\mathrm{~T}_{\mathrm{CM}}-304.2\right)+ \\ & 2.51 \times 10^{-4}\left(\mathrm{~T}_{\mathrm{CM}}-304.2\right)^{2}-2.35 \times 10^{-7}\left(\mathrm{~T}_{\mathrm{CM}}-304.2\right)^{3} \end{aligned}$ <br> where, $\mathrm{T}_{\mathrm{CM}}=\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{x}_{\mathrm{i}} \times \mathrm{T}_{\mathrm{Ci}}$ | $-\mathrm{H}_{2} \mathrm{~S}$ critical temperature was modified to $325^{\circ} \mathrm{K}\left(51.67^{\circ} \mathrm{C}\right)$ <br> Limitation: <br> - Used for non- $\mathrm{CO}_{2}$ ratios up to 55 mole $\%$. <br> - Presented inaccurate prediction for flue gas containing $\mathrm{SO}_{2}$ and/or $\mathrm{N}_{2}$. |
| Kovarik (1985) | $\mathrm{MMP}_{\text {flue gas }}=0.2814 \times\left(548-\left(1.8 \mathrm{~T}_{\mathrm{pc}}+492\right)\right)+\mathrm{MMP}_{\mathrm{CO} 2}$ <br> where, $\mathrm{T}_{\mathrm{pc}}=\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{w}_{\mathrm{i}} \times \mathrm{T}_{\mathrm{ci}}$ <br> or $\mathrm{T}_{\mathrm{pc}}=\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{x}_{\mathrm{i}} \times \mathrm{T}_{\mathrm{ci}}$ | - The weight average fraction modelled the data similar to the mole average fraction. -Limitation: <br> Used for $\mathrm{C}_{1}$, as a non- $\mathrm{CO}_{2}$ component, with less than 20 mole\% ratio. |

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| Eakin and Mitch (1988) | $\begin{aligned} & \operatorname{lnP}_{\mathrm{r}, \mathrm{flue} \text { gas }}=\left(0.1697-\frac{0.06912}{\mathrm{~T}_{\mathrm{r}}}\right) \mathrm{y}_{\mathrm{C} 1}\left(\mathrm{MW}_{\mathrm{C} 7+}\right)^{\frac{1}{2}}+\left(2.3855-\frac{0.005955(\mathrm{M} \mathrm{~W}}{\mathrm{C} 7+} \text { ) }\right) \mathrm{y}_{\mathrm{C} 2+}+ \\ & \left(0.1776-\frac{0.01023}{\mathrm{~T}_{\mathrm{r}}}\right) \mathrm{y}_{\mathrm{N} 2}\left(\mathrm{MW}_{\mathrm{C} 7+}\right)^{\frac{1}{2}}+\left(0.01221\left(\mathrm{M} \mathrm{~W}_{\mathrm{C} 7+}\right)-\frac{0.0005899\left(\mathrm{MW}_{\mathrm{C} 7+}\right)^{\frac{3}{2}}}{\mathrm{~T}_{\mathrm{r}}}\right) \mathrm{y}_{\mathrm{CO} 2+}+ \\ & \left(\frac{101.429}{\mathrm{MW}_{\mathrm{C} 7+}}+\frac{0.00375\left(\mathrm{MW} \mathrm{M}_{\mathrm{C} 7+}\right)}{\mathrm{T}_{\mathrm{r}}}\right) \mathrm{y}_{\mathrm{H} 2 \mathrm{~S}} \end{aligned}$ <br> where, $\begin{aligned} & \mathrm{P}_{\mathrm{r}}=\frac{\mathrm{MMP}_{\text {flue gas }}}{\mathrm{P}_{\mathrm{cm}}}, \mathrm{P}_{\mathrm{cm}}=\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{x}_{\mathrm{i}} \mathrm{P}_{\mathrm{Ci}} \\ & \mathrm{~T}_{\mathrm{r}}=\frac{1.8 \mathrm{~T}_{\mathrm{R}}+492}{1.8 \mathrm{~T}_{\mathrm{cm}}+492}, \mathrm{~T}_{\mathrm{cm}}=\sum_{\mathrm{i}-1}^{\mathrm{n}} \mathrm{x}_{\mathrm{i}} \times \mathrm{T}_{\mathrm{ci}} \end{aligned}$ | - The MMP was considered to correspond to the critical point of the flue gas-oil mixture. <br> Limitations: <br> -This model does not take into consideration the presence of some non$\mathrm{CO}_{2}$ components, e.g., $\mathrm{SO}_{2}$ and $\mathrm{O}_{2}$. |
| :---: | :---: | :---: |
| Dong (1999) | $\frac{\mathrm{MMP}_{\text {flue gas }}}{\mathrm{MMP}_{\mathrm{CO} 2}}=\left(\frac{\mathrm{T}_{\mathrm{ac}}}{304.2}\right)^{4}$ <br> where, $\mathrm{T}_{\mathrm{ac}}=\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{SF}_{\mathrm{i}} \mathrm{x}_{\mathrm{i}} \mathrm{~T}_{\mathrm{Ci}}$ <br> The values of $\mathrm{SF}_{\mathrm{i}}$ for the different components are as follows: <br> - For $\mathrm{H}_{2} \mathrm{~S}, \mathrm{SF}_{\mathrm{i}}=0.7-$ For $\mathrm{SO}_{2}, \mathrm{SF}_{\mathrm{i}}=0.5$ <br> - For $\mathrm{C}_{1}, \mathrm{SF}_{\mathrm{i}}=2.5 \quad-$ For $\mathrm{O}_{2}, \mathrm{SF}_{\mathrm{i}}=5.0$ <br> - For $\mathrm{N}_{2}, \mathrm{SF}_{\mathrm{i}}=7.5 \quad-$ For $\mathrm{CO}_{2}, \mathrm{SF}_{\mathrm{i}}=1.0$ <br> - For other non- $\mathrm{CO}_{2}$ components, $\mathrm{SF}_{\mathrm{i}}=1.0$ | - The author used a factor $\left(\mathrm{SF}_{\mathrm{i}}\right)$ representing the strength of species $i$ in changing the apparent critical temperature of the flue gas relative to the critical temperature of $\mathrm{CO}_{2}$ (this factor was consistent with the components K-values). |

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| 3. For both $\mathrm{CO}_{\mathbf{2}}$-oil MMP and flue gas-oil MMP: |  |  |
| :---: | :---: | :---: |
| Johnson and Pollin (1981) | $\mathrm{MMP}-\mathrm{P}_{\mathrm{C}, \mathrm{inj} .}=\alpha_{\mathrm{inj} .}\left(\mathrm{T}_{\text {Res. }}-\mathrm{T}_{\mathrm{C}, \mathrm{inj} .}\right)+\mathrm{I}\left(\beta \times \mathrm{MW}-\mathrm{M}_{\mathrm{inj} .}\right)^{2}$ <br> where, $\begin{aligned} & \mathrm{I}=-11.73+6.313 \times 10^{-2} \times \mathrm{MW}-1.954 \times 10^{-4} \times \mathrm{MW}^{2}+ \\ & 2.502 \times 10^{-7} \times \mathrm{MW}^{3}+\left(0.1362+1.138 \times 10^{-5} \times \mathrm{MW}\right) \mathrm{API}-, \\ & 7.222 \times 10^{-5} \times \mathrm{API}^{2} \end{aligned}$ <br> $\beta=0.285$ and for pure $\mathrm{CO}_{2}, \alpha_{\mathrm{inj}}=0.13 \mathrm{MPa} /{ }^{\circ} \mathrm{K}$, <br> -For $\mathrm{N}_{2}$ impurity, $\alpha_{\text {inj. }}=0.0722\left(1.8+\frac{10^{3} \mathrm{y}}{\mathrm{T}_{\text {Res. }}-\mathrm{T}_{\mathrm{C}, \text { inj }}}\right)$, <br> - For $\mathrm{C}_{1}$ impurity, $\alpha_{\text {inj. }}=0.0722\left(1.8+\frac{10^{2} \mathrm{y}}{\mathrm{T}_{\text {Res. }}-\mathrm{T}_{\mathrm{C}, \text { inj }}}\right)$. | Limitations: <br> -Temperature range from 26.85 to 136.85 ${ }^{\circ} \mathrm{C}$, <br> - Used for less than 10 mole\% of non- $\mathrm{CO}_{2}$ components in the injected flue gas, -Used only for $\mathrm{C}_{1}$ and/or $\mathrm{N}_{2}$ as non- $\mathrm{CO}_{2}$ components. |
| Orr and Silva (1987) | $\rho_{\mathrm{MMP}}=-0.524 \times \mathrm{F}+1.189, \text { when: } \mathrm{F} \prec 1.467$ <br> $\rho_{\text {MMP }}=0.42$, when: $\mathrm{F} \succ 1.467$, <br> where, $\begin{aligned} & \mathrm{F}=\sum_{2}^{37} \mathrm{~K}_{\mathrm{i}} \times \mathrm{w}_{\text {ic } 2+} \\ & \log \left(\mathrm{K}_{\mathrm{i}}\right)=0.7611-0.04175 \times \mathrm{C}_{\mathrm{i}} \end{aligned}$ | -MMP could be obtained at the reservoir temperature and $\rho_{\text {MMP }}$. <br> - Used for $\mathrm{CO}_{2}$ and flue gas-oil MMP prediction. <br> Limitations: <br> - Does not take into consideration the presence of $\mathrm{C}_{1}$ and all other nonhydrocarbons in the oil composition |

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|  | $\mathrm{w}_{\mathrm{ic} 2+}=\frac{\mathrm{w}_{\mathrm{i}}}{\sum_{2}^{37} \mathrm{w}_{\mathrm{i}}}$ | - Can be used only when the carbon distribution from $\mathrm{C}_{2}$ to $\mathrm{C}_{37}$ is available. -Uncertain for $T_{R}>87.78^{\circ} \mathrm{C}$ for oils containing significant amount of dissolved gas. <br> If MMP $<\mathrm{P}_{\mathrm{b}}$, the $\mathrm{P}_{\mathrm{b}}$ is taken as MMP. |
| :---: | :---: | :---: |
| Enick et al. (1988) | A graphical model that was developed as a function of the reservoir temperature and $\mathrm{MW}_{\mathrm{C} 5+}$ with a graphical corrections for volatiles $\left(\mathrm{C}_{1}\right.$ and $\left.\mathrm{N}_{2}\right)$ and intermediates $\left(\mathrm{C}_{2}-\mathrm{C}_{4}\right)$ that exist in the oil and another correction factor for the non- $\mathrm{CO}_{2}$ components in injected flue gas streams which was developed based on their mole fraction. | Limitations: $\begin{aligned} & -35^{\circ} \mathrm{C} \leq \mathrm{T}_{\mathrm{R}} \leq 115^{\circ} \mathrm{C} \\ & -156 \leq \mathrm{MW}_{\mathrm{C} 5+} \leq 256 \end{aligned}$ $-7 \mathrm{MPa} \leq \mathrm{MMP} \leq 30 \mathrm{MPa}$ <br> - Can be used for up to 25 mole\% of non$\mathrm{CO}_{2}$ components in the flue gas. |
| Yuan et al. (2004) | For $\mathrm{CO}_{2}$-oil MMP: $\begin{aligned} & \mathrm{MMP}=\mathrm{a}_{1}+\mathrm{a}_{2} \mathrm{MW}_{\mathrm{C} 7+}+\mathrm{a}_{3} \mathrm{~F}_{\mathrm{R}}+\left(\mathrm{a}_{4}+\mathrm{a}_{5} \mathrm{MW}_{\mathrm{C} 7+}+\right. \\ & \left.\mathrm{a}_{6} \frac{\mathrm{~F}_{\mathrm{R}}}{\mathrm{MW}_{\mathrm{C} 7+}^{2}}\right) \mathrm{T}_{\mathrm{R}}+\left(\mathrm{a}_{7}+\mathrm{a}_{8} \mathrm{MW}_{\mathrm{C} 7+}+\mathrm{a}_{9} \mathrm{MW}_{\mathrm{C} 7+}^{2}+\mathrm{a}_{10} \mathrm{~F}_{\mathrm{R}}\right) \mathrm{T}_{\mathrm{R}}^{2} \end{aligned}$ <br> For flue gas-oil MMP $\left(\mathrm{CO}_{2}\right.$ with $\left.\mathrm{C}_{1}\right)$ : $\frac{\mathrm{MMP}_{\text {flue gas }}}{\mathrm{MMP}_{\mathrm{CO} 2}}=1.0+\mathrm{m}\left(\mathrm{x}_{\mathrm{CO} 2}-100\right)$ | For $\mathrm{CO}_{2}$-oil MMP: $\begin{aligned} & a_{1}=-1.4634 \mathrm{E}+03, \mathrm{a}_{2}=0.6612 \mathrm{E}+01 \\ & \mathrm{a}_{3}=-4.4979 \mathrm{E}+01, \mathrm{a}_{4}=0.2139 \mathrm{E}+01 \\ & \mathrm{a}_{5}=1.1667 \mathrm{E}-01, \quad \mathrm{a}_{6}=8.1661 \mathrm{E}+03 \\ & \mathrm{a}_{7}=-1.2258 \mathrm{E}-01, \mathrm{a}_{8}=1.2883 \mathrm{E}-03 \\ & \mathrm{a}_{9}=-4.0152 \mathrm{E}-06, \mathrm{a}_{10}=-9.2577 \mathrm{E}-04 \end{aligned}$ |

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For flue gas-oil MMP:
$a_{1}=-6.5996 \mathrm{E}-02, \quad a_{2}=-1.5246 \mathrm{E}-04$
$\mathrm{a}_{3}=1.3807 \mathrm{E}-03, \quad \mathrm{a}_{4}=6.2384 \mathrm{E}-04$
$\mathrm{a}_{5}=-6.7725 \mathrm{E}-07, \mathrm{a}_{6}=-2.7344 \mathrm{E}-02$
$\mathrm{a}_{7}=-2.6953 \mathrm{E}-06, \mathrm{a}_{8}=1.7279 \mathrm{E}-08$
$\mathrm{a}_{9}=-3.1436 \mathrm{E}-11, \mathrm{a}_{10}=-1.9566 \mathrm{E}-08$
Limitations:

- Used for flue gas containing $\mathrm{C}_{1}$ only as a
non-CO $\mathrm{C}_{2}$ component.
- Used for injection streams contain up to 40
mole $\%$ of $\mathrm{C}_{1}$


### 3.3. Modelling of $\mathrm{CO}_{2}$-Oil Physical Properties

As has been emphasized earlier, the properties of the $\mathrm{CO}_{2}$-oil mixtures play a critical role in the success (or failure) of a $\mathrm{CO}_{2}$ flood. Therefore, it is important that they are obtained as reliably and accurately as possible. These properties are usually obtained through some experimental studies or by employing some sort of modelling or correlation techniques. However, in many instances, an approach that combines both experimental and theoretical means is employed.

The experimental approach involves a set of high-pressure volumetric and vapour liquid equilibrium tests such as the constant composition expansion (or the flash test), the constant volume depletion, the differential liberation, the separator tests, and some special laboratory tests such as the swelling tests (Klins (1984) and Ahmed (1989)).

Mathematical studies derived by matching the experimental data and equations of state (EOS) provide more general PVT data and physical properties over a wider range of conditions (Dong and Paddock (1999) and Ahmed (1989)). The mathematical model efficiency depends on both the quality and quantity of the data, and the computation often require the use of certain algorithms and numerical modelling (Green and Willhite (1998)).

The available correlations or models can only be used to predict the gas-oil mixture physical properties within their validity ranges. Table 3-2 summarises, along with brief remarks, some commonly used models available in the literature. As these models take into account the following $\mathrm{CO}_{2}$-oil physical properties, a brief overview of these properties is warranted here.

### 3.3.1. $\mathrm{CO}_{2}$ Solubility

$\mathrm{CO}_{2}$ solubility is basically affected by the saturation pressure $\left(\mathrm{P}_{\mathrm{s}}\right)$, temperature $\left(\mathrm{T}_{\mathrm{R}}\right)$, and oil API gravity (Welker and Dunlop (1963), Simon and Graue (1965), Chung et al. (1988), and Srivastava et al. (1995)). As the solubility increases with the pressure and oil API gravity, its value decreases with the temperature. The other factors affecting $\mathrm{CO}_{2}$ solubility are oil composition and $\mathrm{CO}_{2}$ liquefaction pressure, where gaseous $\mathrm{CO}_{2}$ is more soluble in oil than the liquid $\mathrm{CO}_{2}$ (Dyer and Farouq Ali (1989), Chung et al. (1986), Kokal and Sayegh (1993), and DeRuiter et al. (1994)). Therefore, for temperatures less than the $\mathrm{CO}_{2}$ critical temperature ( $\mathrm{T}_{\mathrm{c}, \mathrm{CO} 2}$ ), the $\mathrm{CO}_{2}$ solubility increases with the pressure up to the liquefaction pressure, then levels off at pressures higher than the liquefaction pressure and becomes less sensitive to the pressure.

### 3.3.2. Oil Swelling Factor Due to $\mathbf{C O}_{2}$ Injection

Oil swelling factor is defined as the ratio of $\mathrm{CO}_{2}$-sarurated oil volume at the reservoir temperature and pressure to the oil volume at the reservoir temperature and oil bubble point pressure. The swelling factor is mainly a function of $\mathrm{CO}_{2}$ solubility (Welker and Dunlop (1963), Simon and Graue (1965), Sankur et al. (1986), and Briggs and Puttagunta (1984)). Hence, the liquefaction pressure affects the swelling factor. Furthermore, as $\mathrm{CO}_{2}$ solubility in light oil is higher than that in heavy oil, the lighter oil swells more than the heavier oil (Srivastava et al. (1995)). Besides $\mathrm{CO}_{2}$ solubility, the swelling factor is also a function of the molecular size of oil molecules (Simon and Graue (1965)).

### 3.3.3. $\mathrm{CO}_{2}$-Oil Density

The effect of $\mathrm{CO}_{2}$ solubility on oil density is generally small and is more apparent in lighter oils than in heavier oils (Holm and Josendal (1974), Grigg (1995), and Sayegh et al. (1990)). Srivastava et al. (1995) stated that $\mathrm{CO}_{2}$-oil density changes linearly with the temperature. DeRuiter et al. (1994) also found that the oil exhibits an increased density due to $\mathrm{CO}_{2}$ solubility increase. However, they stated that this density increase might be a result of an increase in the system pressure as the density was apparently not impacted by the change in the solubility above the $\mathrm{CO}_{2}$ liquefaction pressure (at temperature less than $\mathrm{T}_{\mathrm{c}, \mathrm{CO} 2}$ ).

### 3.3.4. $\mathrm{CO}_{2}$-Oil Viscosity

Oil viscosity decreases severely with increasing $\mathrm{CO}_{2}$ solubility, resulting in increasing oil mobility, consequently causing an increase in the oil recovery. At temperatures less than $\mathrm{T}_{\mathrm{c}, \mathrm{CO} 2}, \mathrm{CO}_{2}$-oil viscosity decreases with the saturation pressure up to the liquefaction pressure, then levels off and decreases slightly at pressures higher than liquefaction pressure. At higher pressures, the viscosity returns to increase again because of the effect of the pressure and oil compressibility (Srivastava et al. (1995), DeRuiter et al. (1994), and Sayegh et al. (1990)). It is also noted that the oil viscosity reduction due to $\mathrm{CO}_{2}$ is higher at lower temperatures than at higher ones. Also, the reduction in the $\mathrm{CO}_{2}$-oil mixture viscosity is higher for more viscous oil (heavier oil) than for lower viscous oil (lighter oil) (Welker and Dunlop (1963), Srivastava et al. (1995), and Rojas and Farouq Ali (1985)). For the composition effect on the $\mathrm{CO}_{2}$-oil viscosity, many studies reported that the mixture viscosity is generally a function of its composition (Chung et al. (1986) and Kokal and Sayegh (1993)).

### 3.4. Modelling of Flue Gas-Oil Physical Properties

Like the $\mathrm{CO}_{2}$-oil physical properties, flue gas-oil properties could also be determined through the experimental methods and the prediction methods (Mathematical calculations and available models).

Most of the available models (as shown in Table 3-2) are developed essentially for the $\mathrm{CO}_{2}$-oil physical properties but are still used for flue gas-oil physical properties. Consequently, they are unable to give an accurate prediction for flue gas-oil properties, especially for the flue gases, which contain higher ratios (more than 5-10 mole\%) of non- $\mathrm{CO}_{2}$ components (Monger (1987)). As these models are used to predict the flue gas-oil physical properties, a brief overview of these properties follows.

### 3.4.1. Flue Gas-Oil Solubility

Monger (1987) stated that the change in flue gas solubility is connected to the change in gas critical temperature. The flue gas solubility increases when the flue gas streams contain intermediate hydrocarbons, such as $\mathrm{C}_{2}-\mathrm{C}_{4}$, besides $\mathrm{SO}_{\mathrm{X}}$ and $\mathrm{H}_{2} \mathrm{~S}$ (cause higher flue gas critical temperature) (Zhang et al. (2004), Dong and Paddock (1999), and Monger (1987)). On the other hand, volatile gases such as $\mathrm{C}_{1}, \mathrm{~N}_{2}$, and $\mathrm{O}_{2}$ reduce the flue gas solubility (cause lower flue gas critical temperature) (Zhang et al. (2004), Graue and Zana (1981), and Dong and Paddock (1999)). In addition, as stated before for $\mathrm{CO}_{2}$ solubility, the flue gas solubility is affected by the saturation pressure, temperature, and oil API gravity (Welker and Dunlop (1963), Simon and Graue (1965), Chung et al. (1988), and Srivastava et al. (1995)).

The other factors affecting flue gas solubility are oil composition and flue gas liquefaction pressure. Gaseous flue gas is more soluble in the oil than the liquid flue gas as the solubility becomes less sensitive to the pressure effect (Dyer and Farouq Ali (1989), Chung et al. (1986), Kokal and Sayegh (1993), and DeRuiter et al. (1994)).

### 3.4.2. Oil Swelling Factor Due to Flue Gas Injection

Oil swelling factor is principally a function of the flue gas solubility (Welker and Dunlop (1963), Simon and Graue (1965), Sankur et al. (1986), and Briggs and Puttagunta (1984)). Thus, the existence of volatile gases (e.g., $\mathrm{C}_{1}, \mathrm{~N}_{2}$, and $\mathrm{O}_{2}$ ) in the flue gas streams causes lower oil swelling due to the lower gas solubility in oil (Sankur et al. (1986) and Nguyen and Farouq Ali (1998)). On the other hand, the existence of other components (e.g., $\mathrm{C}_{2}-\mathrm{C}_{4}, \mathrm{SO}_{\mathrm{X}}$, and $\mathrm{H}_{2} \mathrm{~S}$ ) causes higher oil swelling due to the higher gas solubility. Besides flue gas solubility, the swelling factor is a function also of the molecular size of oil molecules as stated above for the oil swelling due to $\mathrm{CO}_{2}$ injection (Simon and Graue (1965)).

### 3.4.3. Flue Gas-Oil Density

With respect to flue gas-oil density, although the flue gas injection effect on the oil density is small, it is more pronounced in lighter oils than in heavier oils (Holm and Josendal (1974), Grigg (1995), and Sayegh et al. (1990)). Srivastava et al. (1995) stated that the flue gas-oil density is a function of the temperature. DeRuiter et al. (1994) also found that the oil density increases due to the flue gas solubility increase. However, they stated that this density increase might be a result of an increase in the system pressure.

### 3.4.4. Flue Gas-Oil Viscosity

Oil viscosity decreases severely with increasing flue gas solubility, resulting in increasing oil mobility, consequently causing an increase in oil recovery. Thus, the existence of volatile gases (e.g., $\mathrm{C}_{1}, \mathrm{~N}_{2}$, and $\mathrm{O}_{2}$ ) in the flue gas streams causes less reduction in the flue gas-oil viscosity, while the existence of $\mathrm{C}_{2}-\mathrm{C}_{4}, \mathrm{SO}_{\mathrm{X}}$, and $\mathrm{H}_{2} \mathrm{~S}$ in the flue gas streams causes a greater reduction in the mixture viscosity due to the higher solubility of this stream in oil (Sankur et al. (1986), Frimodig et al. (1983), and Nguyen and Farouq Ali (1998)). The flue gas-oil viscosity is also a function of the temperature and saturation pressure (Srivastava et al. (1995), DeRuiter et al. (1994), and Sayegh et al. (1990)). Furthermore, the mixture viscosity reduction is higher for more viscous oil than for less viscous oil (Welker and Dunlop (1963), Srivastava et al. (1995), and Rojas and Farouq Ali (1985)). Also, many studies reported that the gas-oil mixture viscosity is generally a function of its composition (Chung et al. (1986) and Kokal and Sayegh (1993)).

| Authors | Model | Remarks |
| :---: | :---: | :---: |
| 1. $\mathrm{CO}_{2}$ solubility: |  |  |
| Welker and Dunlop (1963) | Graphical model, which is a function of the saturation pressure and oil API gravity at a constant temperature $\left(26.67^{\circ} \mathrm{C}\right)$. | Developed for dead oil with temperature equal to $26.67^{\circ} \mathrm{C}$ and oil gravity range from 20 to $40^{\circ} \mathrm{API}$ ( $0.93-0.825 \mathrm{gm} / \mathrm{cc}$ ). |
| Simon and Graue (1965) | Graphical model, which is a function of $\mathrm{CO}_{2}$ fugacity and temperature or saturation pressure and temperature at characterisation factor equal to 11.7, with a correction factor which is a function of the characterisation factor and temperature for characterization factors differ than 11.7. | Developed for dead oil with temperature range from $43.33^{\circ} \mathrm{C}$ to $121.1^{\circ} \mathrm{C}$, pressures up to 15.86 MPa , and oil gravity from 12 to $33^{\circ}$ API. |
| Mulliken and <br> Sandler (1980) | Used Peng-Robinson (1976) equation of state and a characterisation of the oil, which requires the specific gravity and the mean average boiling point or Watson K factor. | Developed based on the same data used by Simon and Graue (1965) with the same data range and oil type. |
| Mehrotra and Svrcek (1982) | $\mathrm{Sol}(\mathrm{m} 3 / \mathrm{m} 3)=\mathrm{C}_{1}+\mathrm{C}_{2} \mathrm{P}_{\mathrm{s}}+\mathrm{C}_{3}\left(\frac{\mathrm{P}_{\mathrm{S}}}{\mathrm{T}_{\mathrm{R}}+273.16}\right)+\mathrm{C}_{4}\left(\frac{\mathrm{P}_{\mathrm{S}}}{\mathrm{T}_{\mathrm{R}}+273.16}\right)^{2}$ where, $C_{1}=-0.0073508, C_{2}=-14.794, C_{3}=6428.5, C_{4}=4971.39$ | The solubility at $\mathrm{P}_{\mathrm{b}}$ equal to 1 atm is taken to be equal to zero (for dead oil). <br> Limitations: <br> - Pressures up to 6.38 MPa , <br> -Temperature range from 23.89 to $97.22^{\circ} \mathrm{C}$. |

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| Chung et al. (1986) | $\operatorname{Sol}(\mathrm{m} 3 / \mathrm{m} 3)=\frac{1}{\mathrm{C}_{1} \gamma{ }^{\mathrm{C}_{2}}{ }_{\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)} \mathrm{C}_{7}+\mathrm{C}_{3}\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right) \mathrm{C}_{4} \times \exp \left[-\mathrm{C}_{5} \mathrm{P}_{\mathrm{s}}-\frac{\mathrm{C}_{6}}{\mathrm{P}_{\mathrm{s}}}\right]}$ <br> where, $\begin{aligned} & \mathrm{C}_{1}=0.02770441, \mathrm{C}_{2}=4.0928, \mathrm{C}_{3}=3.20617 \times 10^{-6}, \mathrm{C}_{4}=1.6428, \\ & \mathrm{C}_{5}=0.098057, \mathrm{C}_{6}=5.38888, \mathrm{C}_{7}=-0.2499 . \end{aligned}$ | Limited to pressures up to 20.684 MPa and oil gravity from 10 to $20^{\circ} \mathrm{API}$ (for dead and heavy oils). |
| :---: | :---: | :---: |
| 2. Oil swelling factor (SF): |  |  |
| Welker and Dunlop (1963) | $\mathrm{SF}=1.0+\frac{1.96525 \times(\mathrm{Sol}(\mathrm{~m} 3 / \mathrm{m} 3))}{1000}$ | Developed for dead oil with temperature equal to $26.67^{\circ} \mathrm{C}$ and oil gravity range from 20 to $40^{\circ}$ API ( 0.93 to $0.825 \mathrm{~g} / \mathrm{cc}$ ). |
| Simon and Graue (1965) | Graphical model, which is a function of $\mathrm{CO}_{2}$ solubility, oil MW, and oil density at $15.56^{\circ} \mathrm{C}$. | - Developed for dead oil with temperature range from $43.33^{\circ} \mathrm{C}$ to $121.1^{\circ} \mathrm{C}$, pressures up to 15.86 MPa , and oil gravity from 12 to $33^{\circ}$ API. <br> - Gave lower accuracy at higher pressures. |
| Mulliken and Sandler (1980) | Used Peng-Robinson (1976) equation of state and a characterisation of the oil, which requires the specific gravity and the mean average boiling point or Watson K factor. The Peng-Robinson equation was applied twice, once to the $\mathrm{CO}_{2}$-saturated oil at saturation conditions and then again to the oil at 1 atm and the same temperature. | Developed based on the same data used by Simon and Graue (1965) with the same data range and oil type. |

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| 3. $\mathrm{CO}_{2}$-Oil density: |  |  |
| :---: | :---: | :---: |
| Quail et al. (1988) | $\rho=\left(\mathrm{C}_{1}-\mathrm{C}_{2}\left(\mathrm{~T}_{\mathrm{R}}+273.16\right)+\mathrm{C}_{3} \mathrm{P}_{\mathrm{s}} \frac{\exp \left(-\mathrm{C}_{4} \mathrm{Sol}(\text { mole fraction })\right)}{\left(1+\mathrm{C}_{5}\left(\mathrm{CH}_{4}, \text { mole fraction }\right)\right)}\right.$ <br> where, <br> The coefficients used for Senlac region heavy oil were found to be: $\begin{aligned} & \mathrm{C}_{1}=1.1571, \mathrm{C}_{2}=0.6534 \mathrm{E}-03, \mathrm{C}_{3}=0.7989 \mathrm{E}-03, \mathrm{C}_{4}=35.8 \mathrm{E}-04, \\ & \mathrm{C}_{5}=50.86 \mathrm{E}-03 . \end{aligned}$ | -Developed based on heavy oil data from Senlac region. <br> -Used for pressures up to 17.0 MPa. <br> -Can be used for other oils by measuring some experimental data to rectify its coefficients. |
| 4. $\mathrm{CO}_{2}$-Oil viscosity: |  |  |
| Welker and Dunlop (1963) | A graphical model, where the $\mathrm{CO}_{2}$-oil viscosity at $26.67^{\circ} \mathrm{C}$ is a function of the initial oil viscosity and saturation pressure. | $\mathrm{CO}_{2}$-dead oil viscosity prediction is limited to temperature of $26.67^{\circ} \mathrm{C}$, saturation pressures up to 5.516 MPa , and viscosity range from 4 to 5000 mPa .s. |
| Lohrenz-Bray- <br> Clark (1964) | $\left[\left(\mu-\mu^{*}\right) \zeta+10^{-4}\right]^{\frac{1}{4}}=0.1023+0.023364 \rho_{\mathrm{r}}+0.058533 \rho_{\mathrm{r}}^{2}-0.40758 \rho_{\mathrm{r}}^{3}+0.0093324 \rho_{\mathrm{r}}^{4}$ <br> where, $\zeta=\frac{\left(\sum_{j=1}^{n} x_{j} T_{c j}^{\frac{1}{6}}\right)}{\left(\sum_{j=1}^{n} x_{j} M_{j}^{\frac{1}{2}}\right)\left(\sum_{j=1}^{n} x_{j} P_{c j}^{\frac{2}{3}}\right)},$ | -Used basically for light oils and depends on the reservoir liquid composition. <br> - Sensitive to density calculation as it uses the $4^{\text {th }}$ power of reduced density. <br> - Sensitive to the critical volume of $\mathrm{C}_{7+}$. |

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|  | $\begin{aligned} & \mu^{*}=\frac{\sum_{j=1}^{n}\left(x_{j} \mu_{j}^{*} \sqrt{M_{j}}\right.}{\sum_{j=1}^{n}\left(x_{j} \sqrt{M_{j}}\right.}, \rho_{\mathrm{r}}=\frac{\rho}{\rho_{\mathrm{c}}^{\prime}}, \\ & \rho_{\mathrm{c}}^{\prime}=\frac{1}{\mathrm{v}_{\mathrm{c}}^{/ \mathrm{m}}}=\frac{1}{\sum_{\substack{\mathrm{j}=1 \\ j \neq C 7+}}^{\mathrm{n}}\left(x_{\mathrm{j}} \mathrm{v}_{\mathrm{cj}}^{\mathrm{m}}\right)+\mathrm{x}_{\mathrm{C} 7+} \mathrm{v}_{\mathrm{cC} 7+}^{\mathrm{m}}} \end{aligned}$ |  |
| :---: | :---: | :---: |
| Simon and Graue (1965) | A graphical model, where $\mathrm{CO}_{2}$-dead oil viscosity is a function of the saturation pressure and initial oil viscosity for $48.89^{\circ} \mathrm{C}$. Also, they presented a temperature correction, which is a function of the temperature and $\mathrm{CO}_{2}$ solubility of the specified oil. | Limitations: <br> - Temperature range from 43.33 to $121.1^{\circ} \mathrm{C}$, <br> - Pressures up to 13.79 MPa , <br> -Viscosity up to 1300 mPa .s. |
| Beggs and <br> Robinson (1975) | $\mu_{\mathrm{d}}=10^{\mathrm{X}}-1$ <br> where, $\mathrm{X}=10^{\left.\left(3.0324-0.02023 \gamma_{\mathrm{o}}\right)_{\left(1.8 \mathrm{~T}_{\mathrm{R}}\right.}+32\right)^{-1.163}}$ <br> For dissolved gas (e.g. $\mathrm{CO}_{2}$ ): $\mu=A \mu_{d}^{B}$ <br> where, | Neglected the dependence of oil viscosity on composition since oils of widely varying compositions can have the same gravity. Also, neglected the viscosity dependence on the pressure. |

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|  | $\begin{aligned} & A=10.715\left(\frac{\mathrm{Sol}(\mathrm{~m} 3 / \mathrm{m} 3)}{5.615}+100\right)^{-0.515} \\ & \mathrm{~B}=5.44\left(\frac{\mathrm{Sol}(\mathrm{~m} 3 / \mathrm{m} 3)}{5.615}+150\right)^{-0.338} \end{aligned}$ |  |
| :---: | :---: | :---: |
| Mehrotra and Svrcek (1982) | $\log \log (\mu)=a_{1}+a_{2} T_{R}+a_{3} P_{s}+\frac{a_{4}}{\left(T_{R}+273.16\right)} P_{s}$ <br> where, $a_{1}=0.815991, \quad a_{2}=-0.0044495, a_{3}=0.076639, a_{4}=-34.5133 .$ | Developed for $\mathrm{CO}_{2}$-saturated bitumen, based on the pressure and temperature. Limitation: <br> - Temperature range from $23.89^{\circ} \mathrm{C}$ to $97.22^{\circ} \mathrm{C}$, <br> - Pressures up to 6.38 MPa . |
| Chung et al. (1986) | The authors used Lederer (1933) equation, as follows: $\ln \left(\mu_{\mathrm{m}}\right)=\mathrm{x}_{\mathrm{o}} \ln \left(\mu_{\mathrm{o}}\right)+\mathrm{x}_{\mathrm{s}} \ln \left(\mu_{\mathrm{s}}\right)$ <br> where, $\begin{aligned} & x_{\mathrm{S}}=\frac{\mathrm{V}_{\mathrm{S}}}{\alpha \mathrm{~V}_{\mathrm{o}}+\mathrm{V}_{\mathrm{S}}}, \\ & \mathrm{x}_{\mathrm{o}}=1-\mathrm{x}_{\mathrm{s}} \end{aligned}$ <br> They presented a model for the parameter $\alpha$ as follows: $\alpha=0.255 \gamma^{-4.16} \mathrm{~T}_{\mathrm{r}}^{1.85}\left[\frac{\mathrm{e}^{7.36}-\mathrm{e}^{7.36\left(1-\mathrm{P}_{\mathrm{r}}\right)}}{\mathrm{e}^{7.36}-1}\right]$ | Limited to pressures up to 20.684 MPa and oil gravity from 10 to $20^{\circ} \mathrm{API}$ (for dead and heavy oils). |

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|  | where, $\begin{aligned} & \mathrm{T}_{\mathrm{r}}=\left(1.8 \mathrm{~T}_{\mathrm{R}}+492\right) / 547.57 \\ & \mathrm{P}_{\mathrm{r}}=\mathrm{P}_{\mathrm{s}} / 7.384 \end{aligned}$ <br> The relationship between $\mathrm{x}_{\mathrm{s}}$ and the $\mathrm{CO}_{2}$ solubility $(\mathrm{Sol}(\mathrm{m} 3 / \mathrm{m} 3))$ and the swelling factor can be obtained as: $\begin{aligned} & \mathrm{x}_{\mathrm{S}}=\frac{1}{\alpha\left(\frac{5.615 \times \theta}{\text { B.Sol }(\mathrm{m} 3 / \mathrm{m} 3)}\right)+1}, \\ & \mathrm{x}_{\mathrm{S}}=\frac{\text { B.SF }-1}{\alpha+\text { B.SF }-1} \end{aligned}$ |  |
| :---: | :---: | :---: |
| Quail et al. (1988) | $\mu=\left(10{ }^{\mathrm{C}_{1}\left(\mathrm{~T}_{\mathrm{R}}+273.16\right)^{\mathrm{C}_{2}}}+\mathrm{C}_{3} \mathrm{P}_{\mathrm{s}}-1\right) \frac{\left.\exp \left(-\mathrm{C}_{4} \text { Sol (mole fraction }\right)\right)}{\left(\mathrm{C}_{5}\left(\mathrm{CH}_{4}, \text { mole fraction }\right)+1\right)}$ <br> where, <br> For Senlac region of Saskatchewan, Canada: $\begin{aligned} & C_{1}=5.1942 \mathrm{E} 08, C_{2}=-3.3163, C_{3}=62.612, C_{4}=6.374, \\ & C_{5}=10.309 . \end{aligned}$ | -Developed based on heavy oil data from Senlac region. <br> -Modified Beggs-Robinson (1976) to account for $\mathrm{CO}_{2}$ dissolved in Saskatchewan heavy oils. <br> Limitations: <br> - Viscosity range from 7.1 to $2600 \mathrm{mPa} . \mathrm{s}$, <br> - Pressures up to 17.0 MPa , <br> - Temperatures up to $140^{\circ} \mathrm{C}$. |

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| Puttagunta et al. (1991) | $\ln (\mu)=15.9058\left(\frac{\mathrm{~b}}{\left(1+\frac{\mathrm{T}_{\mathrm{R}}-30}{303.15}\right)^{\mathrm{S}}}+\mathrm{C}\right)+\mathrm{x}_{\mathrm{O}}\left(\mathrm{P}_{\mathrm{s}}-0.1\right) \times \exp \left(\mathrm{dT}_{\mathrm{R}}\right)-\mathrm{C}_{\mathrm{O}} \mathrm{X} \cdot \exp \left(-\mathrm{ET}_{\mathrm{R}}\right)$ <br> where, $\begin{aligned} & \mathrm{b}=\log \left(\mu_{30}\right)-C \\ & \mathrm{~S}=0.006694 \times b+3.5364, x_{0}=0.032759 \times b+0.056443, \\ & d=-0.0015646 \times b+0.0061814, C=-3.002 \end{aligned}$ <br> - For dissolved gases $\left(\mathrm{CO}_{2}\right)$ : $\mathrm{C}_{\mathrm{O}}=0.200435 \times \mathrm{b}-0.087217, \mathrm{E}=0.0028338 \times \mathrm{b}+0.0023982 .$ | Developed for dead and heavy oils, so its prediction appeared to be better for heavy oil than for light oil. <br> - The model requires the oil viscosity at 1 atm and $30^{\circ} \mathrm{C}$. |
| :---: | :---: | :---: |
| Kokal and Sayegh (1993) | This model was developed based on the dead oil and the authors used Lederer (1933) equation, as follows: $\ln \left(\mu_{\mathrm{m}}\right)=\mathrm{x}_{\mathrm{o}} \ln \left(\mu_{\mathrm{o}}\right)+\mathrm{x}_{\mathrm{s}} \ln \left(\mu_{\mathrm{s}}\right)$ <br> where, $\begin{aligned} & x_{S}=\frac{V_{S}}{\alpha V_{O}+V_{S}}, \\ & x_{0}=1-x_{S}, \end{aligned}$ <br> $\mathrm{x}_{\mathrm{s}}$, in terms of the swelling factors, and oil expansion factor $\left(\mathrm{B}_{\mathrm{o}}\right)$ : | -The pressure dependence of the oil viscosity was considered insignificant and was ignored. <br> - $\mathrm{CO}_{2}$ viscosity is a function of the pressure and temperature and can be obtained from the viscosity tables. |

3. Modelling of the Miscibility and Interactions Between $\mathrm{CO}_{2}$ or Flue Gas and Oil in Gas Flooding Processes

| $\begin{aligned} & \mathrm{x}_{\mathrm{S}}=\frac{\mathrm{B}_{\mathrm{o}} \mathrm{SF}-1}{\alpha+\mathrm{B}_{\mathrm{o}} \mathrm{SF}-1}, \\ & \mathrm{~B}_{\mathrm{O}}=\frac{\rho_{\mathrm{o}}\left(\mathrm{~T}_{\mathrm{R}}, 1 \mathrm{~atm}\right)}{\rho_{\mathrm{o}}\left(\mathrm{~T}_{\mathrm{R}}, \mathrm{P}\right)} \end{aligned}$ <br> Assuming $\frac{\rho_{\mathrm{O}}\left(\mathrm{T}_{\mathrm{R}}, 1 \mathrm{~atm}\right)}{\rho_{\mathrm{O}}\left(\mathrm{T}_{\mathrm{R}}, \mathrm{P}\right)}=1$ and after some simplifications: $\mathrm{x}_{\mathrm{S}}=\frac{1}{\left[1+\frac{\alpha(1-\text { Sol (mole fraction) }) \mathrm{MW}_{\mathrm{oil}}}{\text { Sol (mole fraction) } \mathrm{MW}_{\mathrm{CO} 2}}\right]}$ <br> - For oil viscosity, it was modelled as a function of temperature as follows: $\log \log \left(\mu_{\mathrm{o}}+0.7\right)=\mathrm{b}_{1}+\mathrm{b}_{2} \log \left(\mathrm{~T}_{\mathrm{R}}+273.16\right)$ <br> where, <br> $b_{1}$ and $b_{2}=$ constants based on the oil system used. |  |
| :---: | :---: |

### 3.5. Summary

This chapter presents an overview of the available models, which were developed to predict the miscibility and interactions between $\mathrm{CO}_{2}$ or flue gas and oil (MMP and other interactions such as gas solubility, oil swelling factor, gas-oil density and viscosity). Most of these models can be applied over a small range of conditions and most of them ignored some of the basic variables affecting the modelled parameters. In addition, some of these models were developed based on dead oil rather than live oil data. Therefore, their predictions, especially for the live oil, are not adequate. For example, the Alston et al. (1985) flue gas-oil MMP model performance for flue gas streams that contain $\mathrm{N}_{2}$ is inadequate; especially for injected gas streams containing more than 8 mole $\%$ of $\mathrm{N}_{2}$. Furthermore, their model is unable to deal with the existence of $\mathrm{SO}_{2}$ in the flue gas. For the Sebastian et al. (1985) flue gas-oil MMP model, its prediction accuracy was overly sensitive to the existence of $\mathrm{N}_{2}$ and/or $\mathrm{SO}_{2}$ in the injected flue gas. Also, the existence of high fractions of non- $\mathrm{CO}_{2}$ components (more than $55 \mathrm{~mole} \%$ ) in the injected flue gas caused a lower accuracy in its prediction.

For gas-oil physical properties models, most of the available models are developed basically for $\mathrm{CO}_{2}$ injection, and the majority of them have been developed for $\mathrm{CO}_{2}$-dead oil physical properties. Also, these models are limited in their application within certain data ranges and they are unable to accurately predict the effect of the injected gas on the live oil properties. The Simon and Graue (1965) models, for example, are limited to saturation pressure of 15.86 MPa and oil viscosity up to $1300 \mathrm{mPa} . \mathrm{s}$ and they predict mixture viscosity incorrectly, especially for lighter oils. The Emanuel (1985) model yields significant errors in the prediction of $\mathrm{CO}_{2}$-oil viscosity and it has been developed basically for heavy oils. Chung et al (1986) models also are limited to a saturation pressure of 20.7 MPa . Welker and Dunlop (1963) models are limited to an oil gravity range from 20 to $40^{\circ} \mathrm{API}$ for temperature limited to $26.67^{\circ} \mathrm{C}$. In particular, the preceding models do not adequately address the liquefaction pressure (at the specified temperature) effect on the solubility. Also, because these models have been developed for $\mathrm{CO}_{2}$-oil physical properties, they are unable to give an accurate prediction for the flue gas-oil physical properties, especially for the flue gases, which contain a higher ratio of non- $\mathrm{CO}_{2}$ components (more than 5-10 mole\%).

## CHAPTER 4

## Literature Review-2: Genetic Algorithm (GA)- One of the Artificial Intelligence Techniques

### 4.1. Introduction

The genetic algorithm (GA), one of the artificial intelligence techniques, was invented by John Holland (1975) to mimic some of the natural processes observed in natural evolution. It is an example of the random method of optimisation and search. The random method is more popular because it allows to search, randomly, about the optimum value at many points on the search space at a time and to save the best values (Goldberg (1989)).

Other optimisation and search methods are calculus-based and enumerative (Goldberg (1989)). The calculus-based method that search for a local optimum is subdivided into two main classes: direct, which moves in the direction related to the local gradient and explore the function to get the local optimum (hill climbing) and indirect, which depends on putting the objective function gradient as equal to zero and then solving the non-linear group of equations resulting from it. Both of these subclasses of the calculus-based method show lack in robustness because they are local in searching for optimum values and they search for the optimum in the near neighbourhood of a current position in the search space. Furthermore, they depend on the existence of derivatives. The enumerative method starts to search the objective function value at each point on the search space, going from one point to the other. This method also is not robust because of the lack of its efficiency, as many practical search spaces are too large to search point by point (one at a time).

Compared to the preceding optimisation methods, the GA shows a higher robustness and efficiency as an optimisation technique. Therefore, GA applications in petroleum engineering have been introduced recently as an optimisation tool. An overview is presented
to give an idea about GA, its advantages, a description of the GA tool, how to enhance its performance, and its previous applications in petroleum engineering, as follows.

### 4.2. What is the GA?

GA is a computer based stochastic search procedure that was developed based on the Darwinian theory of evolution. The GA depends on the mechanics of natural selection, natural genetics, and rule of survival of the fittest (Goldberg (1989)). It can be used over wider ranges of optimisation and search procedures, including those that are difficult to handle by most of the conventional techniques (Jefferys (1993)). This tool involves a random generation of potential design solutions encoded on a string similar to the chromosomes of the biological system. This procedure accompanied by an evaluation method according to an objective function and constraints. Then, a refinement of the solution is applied using reproduction operators (e.g., crossover and mutation) to get the best solution of the problem comparable to which occur in nature. This refinement process is repeated until a stopping criterion is met, indicating the optimum solution (Goldberg (1989)).

### 4.3. The Advantages of the GA

The GA offers the following advantageous features over the traditional optimisation methods:

1. The GA can deal with all types of objective and constraint functions (e.g., linear-nonlinear, convex-concave, continuous-discrete, differentiable-non differentiable functions, etc). On the other hand, some traditional methods are restricted to specific objective functions (e.g., Newton's methods need the objective function to be differentiable) (Mostafa (2000)).
2. The GA maintains a population of points and manipulates them to get better populations. Hence, the GA can explore many positions on the search space at the same time, which increases the chance of global optimum discovery, instead of going from point to the other (one point at each time) on the search space (traditional methods) (Goldberg (1989) and Mostafa (2000)).
3. The GA works by exploration (search for population of points not single point) and exploitation (search on the optimum at each position) of the search space, in contrast to most traditional optimisation methods, which are based on exploitation (Goldberg (1989) and Mostafa (2000)).
4. It works on encoding of the problem parameters on strings (not with the parameters themselves), which increases the GA robustness (Goldberg (1989) and Mostafa (2000)).
5. It performs very well for complicated and large optimisation problems (Badru (2003) and Abourayya (2001)).
6. This algorithm is computationally uncomplicated and powerful in its search for optimum values (Stender (1993)).
7. The GA solutions are less likely to be untruthful, as the problem does not need to be "bowed" to fit the solution method (Jefferys (1993) and Goldberg (1989)).
8. The GA uses probabilistic rules not deterministic rules (Goldberg (1989)).

### 4.4. The GA Tool Description

The operation of the GA starts with a population of random chromosomes to present different random solutions of a specific problem. It then starts to test and evaluate these chromosomes based on a certain evaluation function. By applying certain reproduction techniques, the GA continues to improve the population of solutions until a stopping criterion is reached, indicating the optimum solution. These general steps in performing the GA operation are shown in Fig. 4-1. A detailed overview on different components of the general steps of the GA tool is presented as follows.

### 4.4.1. Initial Population

The initial population is a set of random solutions for a specified problem represented as strings of chromosomes. There are different types of chromosomes (single dimension or multidimensional chromosomes) and each chromosome contains a number of genes, which encode the problem parameters on the chromosome string. As shown in Fig. 4-2, the common approaches to encode the problem parameters are binary strings, real numbers, and letters or characters (Marczyk (2004)). For the binary encoding system, a sequence of 1 's and 0's encodes the solution parameters on the chromosome. This method is simple to generate and manipulate and easy for reproduction operators applications. On the other hand, this method is not efficient for large-scale problems with large search space, as these problems will need too large binary strings. In addition, there may be a precision loss in the parameters values because of the conversion to the binary system. For the other encoding methods (real number, letters, or characters), the solution is encoded on the chromosome with real numbers, letters, or characters, respectively. These methods, especially the real encoding method, are more efficient as they need less computer memory and there is no loss in precision due to the
conversion to binary numbers or other values. In addition, they are simple and easy to apply, especially, for large-scale problems with large search space, as long strings will not be required in this case (Michalewicz (1992)).


Fig. 4-1. A standard flow chart of the GA (after Cvetkovic (2000) and Mostafa (2000)).

After designing and encoding the specified problem parameters on the GA chromosome, the population size should be selected. If the population size is too small, the reproduction operators will have low opportunity to be applied and only a limited part of the search space will be explored. On the other hand, if the population size is too large, there will be unnecessary slow performance of the GA (Mostafa (2000)). The typical population size is between 30 to 100 individual chromosomes (Karr (1991)).


Fig. 4-2. The parameter encoding methods on the GA chromosome (After Abourayya (2001) and Marczyk (2004)).

### 4.4.2. Evaluation

The evaluation function plays the same role of the environment "Survival of the fittest", ranking the problem solutions in terms of their fitness, as each chromosome is assigned a value called the fitness value according to the problem objective function. The closer the chromosome to the optimum, the higher is the fitness value (Cvetkovic (2000)). There are three fitness methods: fitness as evaluation (converting the chromosome evaluation into fitness values), windowing (assign each chromosome a fitness value equal to the amount that it exceeds the minimum chromosome evaluation value in the population), and linear normalisation (order chromosomes in a descending evaluation) (Davis (1991)).

### 4.4.3. Selection Techniques

The selection process provides the chromosomes, which are chosen from the population to produce the new offspring for the next generation (using the reproduction operators) to improve the population fitness (make the problem solution move in the direction of the optimum solution). Individual chromosomes are chosen according to their fitness values and the fittest chromosomes have the higher probability to be chosen (Davis (1991)). The most common selection methods are roulette wheel selection, tournament selection, scaling selection, elitist selection, rank selection, generational selection, steady state selection, and hierarchical selection (Marczyk (2004)). A brief overview of these methods follows.

### 4.4.3.1. Roulette Wheel Selection

Roulette wheel method is a random selection method that depends on the selection of each parent (selected chromosome) according to its fitness. Thus, the chance of a chromosome to be selected from the population is proportional to the amount by which its fitness is different than the other population chromosomes. The fittest chromosome has a higher probability, but there is no certainty to be selected. On the other hand, there is a low probability for the lower fitness chromosomes to be selected, as these chromosomes may contain some useful features (genes). Over a number of generations, the lower fitness chromosomes will be driven out and the fittest chromosomes will survive (Marczyk (2004), Abourayya (2001), and Mostafa (2000)).

Hypothetically, this method can be presented as a roulette wheel game, as each chromosome has a slice area on the wheel proportional to its fitness (the higher fitness chromosomes has the higher slice area, as shown in Fig. 4-3). From Fig. 4-3, Chromosome 5 is the fittest chromosome and occupies the largest slice on the roulette wheel, whereas chromosomes 1 and 4 have the lowest fitness and have correspondingly smaller slices within the roulette wheel. In this selection technique, the chromosome that roulette wheel spinner lands on its slice is chosen as the parent to produce the next offspring. Therefore, the higher slice area of the chromosome, the higher is the probability for the wheel spinner to land on its slice, and consequently, to be chosen as a parent to produce the next offspring (Marczyk (2004), Abourayya (2001), and Mostafa (2000)).

## NOTE:

This figure is included on page 38 of the print copy of the thesis held in the University of Adelaide Library.

Fig. 4-3. Roulette wheel showing the proportional of each chromosome slice area with its fitness value (after Abourayya (2001)).

### 4.4.3.2. Tournament Selection

In the tournament selection method, the population is divided into subgroups randomly without duplication of the chromosomes between these groups. The chromosomes from each group compete against each other and the fittest chromosome is chosen to reproduce the next generation offspring (Marczyk (2004)). This selection method is slower than other methods (e.g., roulette wheel method) because of executing many random selections (Abourayya (2001)).

### 4.4.3.3. Scaling Selection

When the average population fitness is high and the selection pressure increases (when all chromosomes have high fitness values and there are a small differences between them, after applying the reproduction process to many generations), the scaling method can be helpful in making the best selection. Therefore, this method could be used in combination with other selection methods (Marczyk (2004)).

### 4.4.3.4. Elitist Selection

Elitist selection method confirms the selection of the fittest chromosomes from each generation. This method is not purely used in most of the situations, but instead a modified
form is used, as the best or few of the best chromosomes from each generation are selected as a back up (if there is no better chromosomes are produced) (Marczyk (2004)).

### 4.4.3.5. Rank Selection

In the rank selection method, a numerical ranking is appointed to each population chromosome based on its fitness. Thus, the selection procedure is applied based on the chromosomes ranking, not on their fitness differences. This technique helps in preventing fittest chromosomes from dominance early at the expense of the less fit chromosomes, which may have a good genes on them (Marczyk (2004)).

### 4.4.3.6. Generational Selection

In the generational selection method, the selected chromosomes from each generation become the whole next generation. Hence, no chromosomes are preserved between generations (Marczyk (2004)).

### 4.4.3.7. Steady-State Selection

For steady-state selection method, the selected chromosomes from each generation return back to the previous generation replacing some of the lower fitness chromosomes to form the next generation. Hence, some chromosomes are preserved between generations (Marczyk (2004)).

### 4.4.3.8. Hierarchical Selection

In the hierarchical selection method, the chromosomes pass through multiple selection criteria in each generation. Hence, it uses faster and lower level evaluation for the majority of chromosomes that show little or no promise and only uses more rigorous and more computationally expensive fitness evaluation for the fittest chromosomes who survive to the higher levels (Marczyk (2004)).

### 4.4.4. Reproduction Operators

After the selection process and selecting the fittest chromosomes to produce the new generation, reproduction operators start to work on the selected chromosomes to produce the new offspring. The purpose of the reproduction operators is to allow the possibility of producing new and fittest chromosomes to improve the population fitness (the group of solutions). The most common reproduction operators are: crossover, mutation, deletion, and inversion operators. An overview on these operators follows.

### 4.4.4.1.Crossover

Crossover operator is defined as producing new chromosomes (offspring) from the current generation (population) through selecting two chromosomes (parents) and exchanges some of the genes between each parent and the other. Thus, the new offspring takes its features from its parents with a probability that the new offspring will get good parts from its parents and have higher fitness to improve the solution (Cunha (1999)). The crossover is applied with a certain probability (crossover rate), which determine how often the crossover will be performed. For crossover probability equal to one, all the new offspring will be produced by crossover. On the other hand, if this probability is equal to zero, whole new offspring will be produced from exact copies of the parents' chromosomes (Abourayya (2001)). There are different types of the crossover operator as follows.

### 4.4.4.1.1. One-Point Crossover

In this type of crossover, a random point is selected on the two parent chromosomes and then an exchange in the genes between the two parents occurs between this point and the end of each parent chromosome to produce two new offspring (Cunha (1999) and Marczyk (2004)). An example of the one-point crossover method is presented in Fig. 4-4, as two parents' chromosomes are swapped after a randomly selected point (e.g., between the third gene and fourth gene), creating two new offspring that hold mixture of properties (genes) from each parent.


Fig. 4-4. One-point crossover operator example (after Marczyk (2004) and Cunha (1999)).

### 4.4.4.1.2. Two-Points Crossover

The difference between two-points crossover and the one-point crossover operator is that instead of selecting one point on each parent chromosome (as in the one-point crossover), two points are selected randomly and the genes between these two points are swapped between the two parents to produce two new chromosomes (children) (Davis (1991)). An example of the two-points crossover method is presented in Fig. 4-5, as two parents' chromosomes are swapped between randomly selected two points, creating two new offspring that hold mixture of properties from each parent.


Fig. 4-5. Two-points crossover operator example (after Davis (1991) and Cunha (1999)).

### 4.4.4.1.3. Uniform Crossover

For uniform crossover operator, each gene on the two children (offspring) is chosen randomly from one of the two parents analogous position genes (Davis (1991), Cunha (1999), and Marczyk (2004)). Fig. 4-6 presents an example of the uniform crossover operator.

## NOTE:

This figure is included on page 42 of the print copy of the thesis held in the University of Adelaide Library.

Fig. 4-6. Uniform crossover operator example (after Cunha (1999)).

### 4.4.4.2.Mutation

In the mutation reproduction operator, one chromosome gene is selected randomly and then its value is changed. The change in the gene value also occurs randomly. The benefit of the mutation technique is to prevent the GA from falling into local optimum positions by destruction of one gene on the chromosome and change its value randomly. The mutation occurs with a certain probability, which should be a low probability to prevent the GA from losing the good solutions. This probability is determined based upon experimental evaluation (Cunha (1999)). Fig. 4-7 presents an example of the mutation operator.

For real number coded chromosomes, genes values could be replaced using a memory factor. This is different than the binary coding in which the gene value will be 0 's or 1 's. Hence, for the real number coding methods, the new gene value could be:

New Value $=\lambda \times$ Old Value $+\beta \times$ Random Value, $0 \leq \lambda \leq 1$ and $0 \leq \beta \leq 1$

### 4.4.4.3.Deletion

After producing the new offspring, chromosomes have a probability of being inserted back inside the population. There are many methods to reinsert the chromosomes (parents and/or offspring) in the population as follows.

## NOTE:

This figure is included on page 43
of the print copy of the thesis held in
the University of Adelaide Library.

Fig. 4-7. Mutation operator example (after Cunha (1999)).

### 4.4.4.3.1. Generation Replacement

In this deletion method, the new offspring replaces the old population (parents) (Fonseca (1995) and Davis (1991)). Therefore, many of the best individuals may be lost (Mostafa (2000)).

### 4.4.4.3.2. Steady State Replacement

In this method, the new offspring has the opportunity to compete with its parents. A lower number of offspring (typically, one or two) has the possibility to be inserted into the population replacing: random members from the population, their own parents, the oldest members in the population, or the lower fitness members in the population. This replacement occurs unconditionally or only if the offspring is better than the replaced chromosomes (Fonseca (1995)).

### 4.4.4.3.3. Steady State without Duplicates

This method is similar to steady state replacement, except that the offspring, which is a duplicate of any chromosome in the population, is removed (Davis (1991)).

### 4.4.4.4. Inversion Operator

Inversion operators swap the information inside the chromosome. This operator is used to reorder the genes inside the chromosome to increase the potential for evolution especially
when the objective function changes with time. In this operator, two points are randomly selected and the genes between them are interchanged (Cunha (1999)). Fig. 4-8 presents an example of the inversion operator.

NOTE:
This figure is included on page 44 of the print copy of the thesis held in the University of Adelaide Library.

Fig. 4-8. Inversion operator example (after Cunha (1999)).

### 4.5. Performance Enhancement of the GA Tool

There are several methods to enhance GA performance. This enhancement can be made through adapting the GA operator probabilities (e.g., crossover and mutation probabilities), selecting a suitable encoding technique for each problem, and/or using hybrid algorithms (GA with other optimisation techniques) to take advantages of both of them.

Because the crossover and mutation are the most important operators in the GA, thus adapting their execution by controlling their probabilities is vital to enhance the GA performance. One method to do this is through using higher crossover and mutation probabilities for lower fitness chromosomes and lower probabilities for higher fitness ones. This method will help improve the exploration (exploring different area on the search space) and exploitation (get the optimum value in the selected area) performance in the GA. Also, to adapt the crossover and mutation operators, the GA can start its run with a higher value of the crossover probability to explore a wider area on the search space while starting with a lower mutation probability. This happens because the mutation is not very useful at the start of the GA run, as the algorithm needs to explore wider area on the search space. As the GA run proceeds, the crossover probability starts to be lower and mutation probability starts to be
higher, resulting in gradual convergence of the best solutions in the explored regions. Then, the GA can find the optimum solution from these regions (Mostafa (2000)).

When selecting the suitable encoding schemes, the binary encoding method is useful for certain problems but, on the other hand, it has some disadvantages that increase with large search space problems. The real number encoding method is also useful for some problems like those problems with large search space, but may be not the best option for other problems. Therefore, selecting the convenient encoding scheme for each problem can enhance the GA performance (Mostafa (2000)).

To enhance the GA performance using a hybrid algorithm of GA and other optimisation techniques, a quick algorithm, which can be applied to the specified problem, can be used to present its results as initial results for the GA population instead of using a random population. This can enhance the GA convergence rate. On the other hand, the GA can start the search process to explore the search space and determine the area, which contains the optimum solution. Then, a local optimisation method (e.g., gradient method), which can be applied to the specified problem, can be used to find the optimum solution in this explored area. This method also can enhance the convergence rate of the GA (Mostafa (2000)).

### 4.6. GA Applications in Petroleum Engineering

GA applications in petroleum engineering have started recently as an optimisation tool in the production engineering, reservoir engineering, drilling, stimulation, logging, and gas storage. This section presents an overview on some of the GA applications in petroleum engineering as follows.

### 4.6.1. Use of GA in Production Engineering

GA was used, as an efficient optimisation technique, to develop an optimisation model for the Kuparuk River field production, located on the North Slope of Alaska. The GA-based model included well performance, surface lines, and facility models. This model was used to compute the oil rate and to optimise the wells and gas lift allocations to production (Stoisits et al. (1999)). In addition, the GA was used to optimise a gas lift process in the oil wells to increase the quantity of the produced liquid. This tool was used to optimise the gas injection rate distribution for every well considering a restriction of the gas supply for the field (Martinez et al. (1994)). Also, Palke and Horne (1997) used the GA to optimise the net present value (NPV) of the flow streams by optimising the wellbore configuration considering the gas lift configuration and change of the parameters with time.

Furthermore, the GA was used to optimise the oil and gas condensate production system through selection of the optimum size of the well tubing (single size or dual size), the depth at which the tubing size should change (in case of dual size tubing), choke size, number of separators, and separator pressures (Tavakkolian et al. (2004)).

### 4.6.2. Use of GA in Gas Storage

GA was used to provide an optimum treatment design for the stimulation processes in a gas storage field in Ohio. Also, it presented an optimum stimulation combination of the candidate wells using several economic parameters (Mohaghegh et al. (1998)). In addition, the GA was used in combination with reservoir simulation for a natural gas storage field development-planning problem (Johnson et al. (2000)).

### 4.6.3. Use of GA in Hydraulic Fracturing

To maximise post fracture production, GA was used to optimise the fracture treatment. A combination of data mining with GA, as a fracture optimisation tool, was used to provide the optimum fracture design (Oberwinkler et al. (2004)). Also, GA was used to select fracturing materials and optimise fracturing treatment parameters (e.g., proppant volume and concentration, pumping rate, and pad percentage) in low permeability and complex reservoirs in China (Wang et al. (2004)). In addition, Rahman et al. (2002) used the GA to find optimum values for fracture treatment parameters and fracture geometry that are formation friendly, in order to achieve the maximum possible NPV from a gas reservoir.

### 4.6.4. Use of GA in Well Test Interpretation

GA was used to select the appropriate reservoir model between the candidate models based on a given set of pressure transient data. In addition, it has been used to determine the unknown model parameters (permeability, skin, etc.). The GA was applied, as a hybrid algorithm with conventional gradient-based algorithms, to a number of noisy pressure transient tests and demonstrated to be robust and competent (Guyaguler et al. (2001)). Furthermore, the GA was used to determine the optimum interpretation for early-time transient pressure data, influenced by wellbore storage effects. Based on this optimum interpretation, the optimum reservoir parameters can be obtained (Yin and Zhai (1998)).

### 4.6.5. Use of GA in Reservoir History Matching and Reservoir Description

GA was used to perform reservoir characterisation by matching the reservoir simulation model to production data (history matching). This method used GA combined with geo-
statistical modelling to present multiple reservoir descriptions to the reservoir team for further analysis (Romero et al. (2000)). Also, to recognise the reservoir characteristics, tracer breakthrough profiles were used besides numerical techniques, which combined the GA, finite element methods, and a streamline approach (Guerreiro et al. (1998)). Furthermore, a hybrid algorithm of GA and the simulated annealing (SA) method was applied to the history matching of a typical multi-layer cross sectional reservoir model and a field multi-layer and multi-well model. This algorithm proved to be less sensitive to the starting point and more robust and efficient than other optimisation methods (Tongchun and Sezgin (1997)).

Also, GA was used to develop an automated history-matching program for core flooding simulation model to interpret water displacement experiments. This program was used to optimise several coefficients for normalized $\mathrm{K}_{\mathrm{r}} / \mathrm{K}_{\mathrm{rw}}$ and capillary pressure curves for each litho-facies (Tokuda et al. (2004)). In 2003, Sun and Mohanty also used the GA to get the optimum match between the simulation data and experimental data for low injection rate primary drainage.

### 4.6.6. Use of GA in Directional Drilling and Well Placement Optimisation

GA was used to determine the optimum (minimum) drilling depth of directional and horizontal wells in 3D. This depth was determined at the optimum values of kick-point, inclination angle, angle build-up, and drop-off rate (Shokir et al. (2004)). Also, GA was used to optimise well type (vertical, horizontal, or multilateral), location, and trajectory to maximise reservoir performance in a giant oil field located in Saudi Arabia (Yeten (2003)). Furthermore, to determine optimum well locations, GA in combination with a quality map and other algorithms was successfully used (Badru (2003)).

### 4.6.7. Use of GA in Field Development

To find the best strategy for a field development problem, reservoir simulation and GA in combination with other methods (e.g., Polytope, Tabu search, and memory strategy) were used. The objective function consisted of a cash flow analysis for production profiles determined from the simulation runs considering a particular set of parameters. This approach can speed up the field development plan and consider a wider range of hypotheses (Filho (1997)).

### 4.7. Summary

Based on the Darwinian theory of evolution, the GA is a computer based stochastic search procedure, which depends on the mechanics of natural selection, natural genetics, and the rule of survival of the fittest. The GA involves a random generation of potential design solutions encoded on a string comparable to chromosomes of the biological system. This procedure is accompanied by an evaluation method according to the objective function and constraints. An evaluation function, which depends on the problem objective, is used in this technique. Also, some reproduction operators (e.g., crossover and mutation) are used to explore a wider area on the search space in order to find the best solution for the specified problem. By controlling the crossover and mutation probabilities, modifying the encoding technique based on the solved problem, and using a hybrid algorithm of the GA with other suitable optimisation methods, the GA performance and convergence rate can be enhanced.

Recently, the GA has been used in many applications in petroleum engineering as an efficient optimisation tool. For example, it has been used in the production engineering, gas storage, hydraulic fracturing, well test interpretation, reservoir engineering, drilling engineering, and field development applications. However, its applications in the EOR techniques are rather scant.

## CHAPTER 5

## Methodology: Genetic Algorithm (GA) Software Design

### 5.1. Introduction

As discussed in Chapter 4, GA is one of the artificial intelligence techniques with the ability to mimic some of the processes observed in natural evolution. GA is particularly suited to problems with non-linearity, variables discontinuity, large search space and all kinds of objective and constraint functions. Recently, this tool is used as an optimisation engine to solve different scientific problems. Also, GA has been used in petroleum engineering applications, mainly, as an optimisation tool to solve different problems in reservoir engineering, production engineering, logging, stimulation, and drilling engineering. The GA applications in the petroleum engineering have been started in the last two decades.

In this research, new GA modelling software was designed to present a more reliable technique to model the minimum miscibility pressure (MMP) and other physical properties of $\mathrm{CO}_{2}$ or flue gas mixtures with oil during gas injection processes. The objective was that if a robust and efficient modelling method was used, as well as considering major variables affecting each modelled parameter, the produced models could be more reliable with a higher accuracy. An overview of the GA software design methodology is presented in this chapter, as follows.

### 5.2. Using the GA as a Modelling Technique

Many fitting models can be solved analytically, without using iterative methods. For example, the analytical solution is obvious in some cases like the simple linear regression model ( $\mathrm{Y}=\mathrm{A}+\mathrm{BX}$ ). However, in most cases the model is more complicated and the analytical solution is indistinct or the problem becomes non-analytical. In such cases, the iterative
methods should be used even if they are not strictly needed. From the available iterative methods to develop correlations or models, multiple regression analysis is most common. For example, the model (type of equation) is proposed, and then by using the regression analysis method the coefficients of this model can be determined by minimizing the misfit function, which is a function of the difference between observed and model predicted values. Thus, this process is an optimisation process of the model coefficients to determine the best coefficients that can give an accurate model (Chambers (2001)).

GA can usefully be used for two more common distinct purposes. One of them is selection of parameters to optimise the performance of a system. Most published work has been concerned with this use of the GA for optimisation processes. The second potential use is testing and fitting of quantitative models. This second use of the GA has received much less attention.

### 5.3. GA Software Design

The GA modelling technique is an iterative process, where a descriptive model is built and literature data is collected and used to test the model. In this technique, the parameters of the model are determined to minimise the misfit between the model predicted data and the experimental data (optimise the fitness function).

In this study, the GA software was designed using FORTRAN language. It contained a main body and six functions and subroutines, as follows:

1. Main software body,
2. Randomisation function,
3. Evaluation subroutine,
4. Selection subroutine,
5. Reproduction subroutine,
6. Reinsertion (Deletion) subroutine,
7. Maximum chromosome fitness subroutine.

Fig. 5-1 presents the flowchart in developing the GA software followed by an overview on each segment. The GA software code is presented in Appendix-11.


Fig. 5-1. Flowchart of the developed GA software design.

### 5.3.1. Initial Population

Real-coded two-dimension chromosomes were used to encode the model's coefficients (model's structure were assumed for the GA software based on the relationship between dependent and independent variables, as well as testing some of the standard model's types that can adequately represent the relationship between the variables such as the power-law type model). This encoding method is efficient and has many advantages (e.g., needs less computer memory, no loss in precision by converting to binary or other values, simple, and easy to apply, especially for large scale problems with large search space). Then, each gene (model coefficient) takes a random value to build an initial random population with a population size equal to 100 chromosomes. This population size was determined based on an experimental evaluation and it was consistent with the range reported in the literature ( 30 to 100 chromosomes in the population). A number of iterative runs of the software were carried out using the historical optimum coefficients values as an initial population for the next GA run to enhance the accuracy of the optimal values. This approach is termed as a hybrid genetic-genetic algorithm. The initial chromosome design, including the number of genes for each chromosome, was different for each application based on the specified model.

### 5.3.2. Evaluation Function

After building the initial population, each chromosome (solution) in the population was evaluated according to a fitness function value that depended on the objective function (e.g., minimise the misfit between the predicted and the experimental values). This fitness method is called "fitness is evaluation" and its value was calculated as follows:

$$
\begin{equation*}
\operatorname{PFit}(\mathrm{i}, \mathrm{j})=\mathrm{C}_{\mathrm{g}} /\left(\mathrm{C}_{\mathrm{g}}+\left(\mid \text { Value }_{\text {cal. }}(\mathrm{i}, \mathrm{j})-\text { Value }_{\text {exp. }}(\mathrm{i}, \mathrm{j}) \mid\right)\right) \tag{5-1}
\end{equation*}
$$

where,
$\mathrm{i}=1, \mathrm{n}$ (population size), $\mathrm{j}=1, \mathrm{nn}$ (number of the used data)

$$
\begin{equation*}
\operatorname{Fit}(\mathrm{i})=\left(\sum_{\mathrm{j}=1}^{\mathrm{nn}} \operatorname{PFit}(\mathrm{i}, \mathrm{j})\right) / \mathrm{nn} \tag{5-2}
\end{equation*}
$$

If any variable had a value that was out of its limits (non logical value, such as a negative MMP, or out of the pre-specified constraints), the fitness value was reduced by a certain amount called a penalty function, as follows:

PFit $(\mathrm{i}, \mathrm{j})($ new $)=\operatorname{PFit}(\mathrm{i}, \mathrm{j})(\mathrm{old}) \times(1-$ pen $)$
where,
pen= penalty value
PFit ( $\mathrm{i}, \mathrm{j}$ ) (new)= fitness value after applying the penalty function
PFit ( $\mathrm{i}, \mathrm{j}$ ) (old)= fitness value before applying the penalty function

The evaluation function mapping was modified for each application based on the specified model.

### 5.3.3. Selection Technique

To produce a new offspring (new chromosomes or solutions to discover new area on the search space), two parents (chromosomes from the old population) were selected based on certain criteria. To produce two new children (offspring) by the reproduction operators, the selection technique used was the roulette wheel parent selection method. This method was selected because it is faster than other methods (e.g., tournament parent selection) and also it gives a probability for lower fitness chromosomes (proportional to their fitness values) to be selected as parents, as these chromosomes may have some good features (genes) on them. The roulette wheel selection algorithm was as follows.

1. Determine the total fitness of the entire population members (add all the population chromosomes fitness),
2. Generate a random number ( n ) between zero and the total population fitness value,
3. Choose the first chromosome whose fitness, added to the fitness of the preceding population members, is greater than or equal to $n$.

### 5.3.4. Reproduction Operators

After the parents' selection, the GA reproduction operators start to produce the new offspring. The most important operators are the crossover and mutation. Then, after the offspring production, reinsertion of some of the chromosomes from the offspring and their parents were decided based on a selected deletion method. The selected reproduction operators were applied as follows:

### 5.3.4.1. Crossover

Crossover is very useful as an exploration method to explore different areas on the search space in searching for the global optimum. A one-point crossover with probability ( $\mathrm{P}(\mathrm{c})$ ) equal to $100 \%$ has been used as a simple and faster crossover method. This probability means that every offspring chromosome was produced after a crossover operation to produce
new chromosomes, which have different characteristics than their parents (not duplicates of their parents to explore new areas on the search space). There are two new chromosomes were produced, which have mixtures of their parents' features.

### 5.3.4.2. Mutation

After the crossover and production of two children (new) chromosomes, one gene was selected from each child chromosome to mutate its value by adding a random value to its old one, in the course of searching for better population convergence (mutation probability $(\mathrm{P}(\mathrm{m})$ ) was selected to be equal to $100 \%$, which means that from every produced chromosome, one gene was subject to the mutation process). The change in the gene value (by mutation) was developed as follows:

$$
\begin{equation*}
\text { New Value }=\lambda \times \text { Old Value }+\beta \times \text { Random Value, } 0 \leq \lambda \leq 1 \text { and } 0 \leq \beta \leq 1 \tag{5-4}
\end{equation*}
$$

where,
$\beta$ and $\lambda$ are the mutation coefficients (had different values based on the specified model)

The values of $\beta$ and $\lambda$ were selected based on the GA software performance (experimental evaluation), where $\beta$ was increased and $\lambda$ was decreased to detect any improvement in the population fitness value. Otherwise, the process was reversed. Furthermore, this technique enabled the use of a part of the last reached solution.

The mutation operator is expected to find the best solution in a certain area (hill climbing), which was explored by the crossover. In addition, it is also expected to prevent the GA from falling into local optimum positions.

### 5.3.4.3. Deletion

After producing the two children chromosomes, they were evaluated, prior to being used, to obtain their fitness values (using the evaluation function). Then, the best two chromosomes (e.g., the most fit two chromosomes) from the two parents and the two children were reinserted back into the population to improve the group of solutions. This deletion technique is called "steady state replacement", as the two offspring chromosomes competed with their parents' chromosomes.

### 5.3.5. Stopping Criterion

The stopping criterion was set when the difference between the best chromosome fitness in the population and the average population fitness is less than or equal to a certain accuracy and the best chromosome in the population (the chromosome that has the highest fitness) gives the problem solution (the best model that minimise the misfit between the predicted and experimental data).

The software run was repeated to confirm that there was no better solution than the produced one, when the new run starts with different random initial population.

### 5.4. Summary

The GA can be used for two distinct purposes: (i) selection of parameters to optimise the performance of a system, and (ii) testing and fitting of quantitative models. Although the former has been widely addressed, the latter has received much less attention. GA software was developed as a stochastic modelling technique in the course of this research. The objective function of this software was to find the optimum models that minimise the misfit between predicted and experimental values (optimise the fitness function). Thus, using such an efficient modelling technique, and considering the major variables affecting each model, can result in optimum models with better accuracy.

## CHAPTER 6

## GA-based Minimum Miscibility Pressure (MMP) Models for $\mathrm{CO}_{2}$ and Flue Gases

### 6.1. Introduction

MMP is defined as the minimum pressure that is required to attain the miscibility between an injected gas (e.g., $\mathrm{CO}_{2}$ or flue gas) and oil at reservoir conditions. The MMP is the single most important parameter in the design of a miscible gas flood. A reliable estimation of the MMP helps the operator to develop injection conditions and to plan suitable surface facilities. In view of its importance, the operator is strongly advised to determine the MMP for site-specific candidate gas-oil system under representative reservoir conditions. The injected $\mathrm{CO}_{2}$ could be a pure gas or a mixture of $\mathrm{CO}_{2}$ and other impurities (non- $\mathrm{CO}_{2}$ components), which is referred to in this work as "flue gas". From an operational perspective, the existence of non- $\mathrm{CO}_{2}$ components in the injected flue gas should not be treated as a rigid impediment, as the separation of such components from the gas is difficult and costly. Thus, the current trend is to use the flue gas stream as it is, provided such impurities are below certain optimum levels, which determine the amount of the contaminants (non- $\mathrm{CO}_{2}$ components) in $\mathrm{CO}_{2}$ that can be allowed for miscible displacement of the oil reservoirs. In addition, some of these non- $\mathrm{CO}_{2}$ components are useful to decrease the MMP.

There is a need for more reliable $\mathrm{CO}_{2}$-oil MMP and flue gas-oil MMP models, which consider effects of all major variables on the MMP of the $\mathrm{CO}_{2}$ or flue gas in oil. In this research, more reliable models developed using the GA modelling software are presented. Also, this research presents a comparison of the efficiency of these models against that of other commonly used models, which are presented in Table 3-1. In addition, a sensitivity analysis, using @Risk ${ }^{\mathrm{TM}}$ (commercial software from the Palisade Company), is presented to explore the major variables affecting the MMP.

## 6.2. $\mathrm{CO}_{2}$-Oil MMP

For $\mathrm{CO}_{2}$-oil MMP, the main factors affecting this value are reservoir temperature and oil composition. How these factors affect the MMP is presented in the developed GA-based $\mathrm{CO}_{2}$-oil MMP model which follows. In addition, a discussion of the model results and a comparison between this model and other available models in the literature is presented.

### 6.2.1. GA-based $\mathrm{CO}_{2}$-Oil MMP Model

Metcalfe and Yarborough (1974) stated that any model to be considered as a general model for $\mathrm{CO}_{2}$-oil MMP prediction should take into consideration the effect of the volatiles and intermediates besides the reservoir temperature effect. Moreover, Alston et al. (1985) stated that the $\mathrm{MW}_{\mathrm{C} 5+}$ is better for the modelling purpose than the oil API gravity.

Therefore, the proposed GA-based $\mathrm{CO}_{2}$-oil MMP model addressed both arguments and used the following variables:

1. Reservoir temperature $\left(\mathrm{T}_{\mathrm{R}}\right)$,
2. $\mathrm{MW}_{\mathrm{C} 5+}$,
3. Oil volatiles mole fraction $\left(\mathrm{C}_{1}\right.$ and $\left.\mathrm{N}_{2}\right)$,
4. Oil intermediates mole fraction $\left(\mathrm{C}_{2}-\mathrm{C}_{4}, \mathrm{H}_{2} \mathrm{~S}\right.$, and $\left.\mathrm{CO}_{2}\right)$.

Many models structures were tested, but the power-law type model proved to be better in expressing the relationship between the $\mathrm{CO}_{2}$-oil MMP and the major affecting variables. The GA-based model was presented as follows:

1. For oil with bubble point pressure $\left(\mathrm{P}_{\mathrm{b}}\right)>0.345 \mathrm{MPa}$ :

MMP $=7.43497 \times 10^{-5} \times\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)^{1.1669} \times\left(\mathrm{MW}_{\mathrm{C} 5+}\right)^{1.201} \times\left(\frac{\text { Volatiles }}{\text { Interm. }}\right)^{0.109}$
2. For stock tank oil with $\mathrm{P}_{\mathrm{b}} \leq 0.345 \mathrm{MPa}$ (for oil with zero volatiles fraction and nonzero intermediates fraction):

$$
\begin{equation*}
\text { MMP }=7.43497 \times 10^{-5} \times\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)^{1.1669} \times\left(\mathrm{MW}_{\mathrm{C} 5+}\right)^{1.201} \times\left(\frac{1}{\text { Interm. }}\right)^{0.023} \tag{6-2}
\end{equation*}
$$

3. For stock tank oil with $\mathrm{P}_{\mathrm{b}} \leq 0.345 \mathrm{MPa}$ (for oil with zero volatiles and intermediates fractions):

MMP $=7.43497 \times 10^{-5} \times\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)^{1.1669} \times\left(\mathrm{MW}_{\mathrm{C} 5+}\right)^{1.201}$

If the predicted MMP is less than $\mathrm{P}_{\mathrm{b}}$, the $\mathrm{P}_{\mathrm{b}}$ is taken as the MMP, because the slim tube experiments cannot be done at pressures less than $\mathrm{P}_{\mathrm{b}}$ as $\mathrm{CO}_{2}$ will be mixed with the free gas that exists below $\mathrm{P}_{\mathrm{b}}$; this will be detrimental to the miscibility process and the MMP determination.

The GA-based model to predict $\mathrm{CO}_{2}$-oil MMP was tested against the available literature experimental data and commonly used models. It was found that this GA-based model yielded the best prediction of the MMP. After the application of $\mathrm{P}_{\mathrm{b}}$ modification (applied for two data points of Rathmell et al. (1971)), the GA-based model presented an average error equal to $5.5 \%$ and standard deviation equal to $7.4 \%$. On the other hand, Alston et al. (1985) model presented $8.34 \%$ average error and $10.2 \%$ standard deviation. For Glaso (1985) model, it presented $12.6 \%$ average error and $18.0 \%$ standard deviation. Fig. 6-1 presents the GA-based $\mathrm{CO}_{2}$-oil MMP model prediction results, while Table 6-1 and Fig. 6-2 present a comparison between GA-based, Alston et al., and Glaso models (the higher accuracy models).

Table 6-2 presents the data range that used to develop and validate the GA-based $\mathrm{CO}_{2}$-oil MMP model. The literature experimental data, the model prediction results, and the comparison between GA-based model and all other commonly used $\mathrm{CO}_{2}$-oil MMP models are presented in Appendix-1.

### 6.2.2. Discussion for the GA-based $\mathrm{CO}_{2}$-oil MMP

In order of their effects, this model was developed based on the reservoir temperature, $\mathrm{MW}_{\mathrm{C} 5+}$, volatiles $\left(\mathrm{C}_{1}\right.$ and $\left.\mathrm{N}_{2}\right)$, and intermediates $\left(\mathrm{C}_{2}-\mathrm{C}_{4}, \mathrm{H}_{2} \mathrm{~S}\right.$, and $\left.\mathrm{CO}_{2}\right)$. This order of importance is shown in Fig. 6-3, which presents the sensitivity analysis for the $\mathrm{CO}_{2}$-oil MMP and describes its dependence on each variable. The reservoir temperature gives the highest impact, as the MMP increases with the temperature increase. Following the reservoir temperature, $\mathrm{MW}_{\mathrm{C} 5+}$ causes an increase in the MMP as its value increases. From this figure, it can be seen that effects of the volatiles and intermediates components are equal and in the opposite directions, where the volatiles cause an increase in the MMP, while the intermediates effect is the same but they cause a decrease in the MMP. Hence, based on the sensitivity
analysis that is presented in Fig. 6-3, the intermediates effect on the MMP cannot be ignored for zero volatiles oils or generally for stock tank oils with $\mathrm{P}_{\mathrm{b}}$ less than 0.345 MPa . For stock tank oils with zero volatiles and intermediates, the MMP model was developed based on the $\mathrm{T}_{\mathrm{R}}$ and $\mathrm{MW}_{\mathrm{C} 5+}$.


Fig. 6-1. GA-based $\mathrm{CO}_{2}$-oil MMP model prediction results within $90 \%$ accuracy.

Table 6-1. Comparison between the GA-based $\mathrm{CO}_{2}$-oil MMP model and other commonly used literature models.

| Model | Average Error, \% | Standard Deviation, \% |
| :---: | :---: | :---: |
| GA-based | 5.47 | 7.4 |
| Alston et al. (1985) | 8.34 | 10.2 |
| Glaso (1985) | 12.6 | 18 |
| Cronquist (1978) | 14.32 | 16.27 |
| Yellig and Metcalfe (1980) | 14.9 | 19.53 |
| Holm and Josendal (1974) | 15.37 | 18.9 |
| Lee (1979) | 16.8 | 24.6 |



Fig. 6-2. Comparison between GA-based $\mathrm{CO}_{2}$-oil MMP model, Alston et al. (1985), and Glaso (1985) models results within $90 \%$ accuracy.

Table 6-2. Data range used to develop and validate of the GA-based $\mathrm{CO}_{2}$-oil MMP model.

| Variables | Data range |
| :---: | :---: |
| Temperature, ${ }^{\circ} \mathrm{C}$ | $32.2-137.22$ |
| $\mathrm{MW}_{\mathrm{C} 5+}$ | $136.17-247.8$ |
| Volatiles, mole fraction | $0-0.5336$ |
| Intermediates, mole fraction | $0.002-0.3937$ |
| Experimental MMP, MPa | $6.9-34.49$ |



Fig. 6-3. Sensitivity analysis presents effect of each parameter ( $\mathrm{T}_{\mathrm{R}}, \mathrm{MW}_{\mathrm{C} 5+}$, volatiles (Vol.), and intermediates (Intm)) on the $\mathrm{CO}_{2}$-oil MMP.

In developing the $\mathrm{CO}_{2}$-oil MMP model, the developed GA modelling software has proved to be an efficient tool for testing and fitting of the quantitative models. For example, the GA software was used to redevelop the Glaso model using the same equation model and conditions that were presented by Glaso (1985), and the GA-based Glaso model was presented as follows:

- When $\mathrm{F}_{\mathrm{R}}$ (mole percentage of intermediates, $\mathrm{C}_{2}-\mathrm{C}_{6}$ ) $\geq 18$-mole $\%$ :

$$
\begin{align*}
\mathrm{MMP}= & 0.474265308-0.018174974 \times \mathrm{MW}_{\mathrm{C} 7+}+\left(278.6388 \times 10^{-11} \times \mathrm{MW}_{\mathrm{C} 7+}^{3.023}\right. \\
& \times \mathrm{e}^{\left.803.9 \times \mathrm{MW}_{\mathrm{C} 7+}^{-1.189}\right) \times\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)} \tag{6-4}
\end{align*}
$$

- When $\mathrm{F}_{\mathrm{R}}<18$-mole \%:

$$
\begin{align*}
\text { MMP }= & 9.690285-0.018174974 \times \mathrm{MW}_{\mathrm{C} 7+}+\left(278.6388 \times 10^{-11} \times \mathrm{MW}_{\mathrm{C} 7+}^{3.023}\right. \\
& \times \mathrm{e}^{\left.803.9 \times \mathrm{MW}_{\mathrm{C} 7+}^{-1.189}\right) \times\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)-0.44796015 \times \mathrm{F}_{\mathrm{R}}} \tag{6-5}
\end{align*}
$$

The GA-based Glaso model presented an average error equal to $7.86 \%$ (compared to $12.6 \%$ average error by the original Glaso model) with a standard deviation of $11.15 \%$ (compared to $18 \%$ standard deviation by the original Glaso model). Thus, among these models (GA-based, Glaso, and GA-based Glaso), the GA-based model gave the best accuracy.

However, it must be recognised that an error in any model could result from two sources: an error in the modelling process and/or an error in the data itself. The GA-based model developed in this study honoured all the data as reported, without any filtering or massaging as Alston et al. (1985) have done, where they interpreted the data to satisfy their miscibility criterion of $90 \%$ recovery at the solvent breakthrough. As a general observation, caution must be applied with regard to the uncertainties and accuracies in the data gathered from the literature and experiments. In particular, the following common points are highlighted:

1. Slim tube data: As no standard slim tube test methodology and apparatus were used in data reported in the literature, reliable comparison of results becomes a challenge.
2. While there are different experimental procedures and interpretations, consequently, there is no standard definition of the miscibility criterion. Different definitions of the miscibility criterion are used by different authors, and also by different organisations. Furthermore, it could be not correct to simply take a minimum recovery value at 1.2 pore volume (PV) gas injection as a criterion to determine the MMP because the shape of the recovery curve with injection pressure is a function of the test temperature. For that matter, it is also not correct to take for example $90 \%$ or $94 \%$ recovery value as a criterion for miscibility.
3. $\mathrm{CO}_{2}$ compressibility factor is a strong function of the pressure and temperature values. Therefore, any errors in maintaining these values will result in errors in the volumetric calculation of the $\mathrm{CO}_{2}$ injection. This, in turn, will result in uncertainty in determining the MMP.
4. Slim tube experiments are often conducted in steps of pressure increment exceeding one MPa (even 3.45 MPa in some experiments) to obtain the recovery curve as a function of the pressure. This obviously precludes a more accurate inference of the MMP from the recovery curve.

Notwithstanding above general observations and shortcomings in the literature data used in this study, the GA-based $\mathrm{CO}_{2}$-oil MMP was successful in yielding the best prediction of the $\mathrm{CO}_{2}$-oil MMP among all the available models tested during the course of this study.

### 6.3. Flue Gas-Oil MMP

Flue gas-oil MMP is affected by the same factors affecting $\mathrm{CO}_{2}$-oil MMP, as well as the injected gas purity (existence of non- $\mathrm{CO}_{2}$ components). The existence of these non- $\mathrm{CO}_{2}$ components may cause a decrease or increase in the MMP based on their nature and composition. The following subsections present a more reliable GA-based flue gas-oil MMP model that considers the effect of existence of different non- $\mathrm{CO}_{2}$ components in the injected flue gas. In addition, a discussion of the model results and a comparison between this model and other available models in the literature are also presented.

### 6.3.1. GA-based Flue Gas-Oil MMP Model

As stated earlier in Chapter 3, the existence of certain non- $\mathrm{CO}_{2}$ gas components (e.g., $\mathrm{H}_{2} \mathrm{~S}, \mathrm{SO}_{\mathrm{x}}$, and $\mathrm{C}_{2}-\mathrm{C}_{4}$ ), whose critical temperatures are higher than that of $\mathrm{CO}_{2}$, in the injected flue gas causes an improvement in the flue gas miscibility in reservoir oil. This results in a lower MMP and higher injected gas pseudocritical temperature. On the other hand, the existence of other components (e.g., $\mathrm{C}_{1}$ and $\mathrm{N}_{2}$ ), whose critical temperatures are lower than that of $\mathrm{CO}_{2}$, has a reverse effect and causes an increase in the MMP. Furthermore, many studies reported that the injected gas pseudocritical temperature affects the flue gas-oil MMP and it could be used as a variable in the miscibility models.

In this study, the proposed GA-based flue gas-oil MMP model was regarded as a function of the injected flue gas solubility in oil, which in turn is based on the injected gas pseudocritical properties (temperature and pressure), $\mathrm{CO}_{2}$ critical properties (temperature and pressure), and $\mathrm{CO}_{2}$-oil MMP (which could be determined from laboratory work or from available models including the GA-based $\mathrm{CO}_{2}$-oil MMP model). The weight fraction method was used in developing of this model. In addition, a critical temperature modification factor $\left(\mathrm{MF}_{\mathrm{i}}\right)$ was used to modify the injected gas pseudocritical temperature to present the best fit among the pseudocritical properties and the MMP. This factor was used, with different
values, for the components: $\mathrm{SO}_{2}, \mathrm{H}_{2} \mathrm{~S}, \mathrm{C}_{2}, \mathrm{C}_{1}$, and $\mathrm{N}_{2}$. The GA-based flue gas-oil MMP model and the $\mathrm{MF}_{\mathrm{i}}$ values are as follows:

$$
\left.\left.\begin{array}{rl}
\frac{\mathrm{P}_{\mathrm{r}, \text { flue gas }}}{\mathrm{P}_{\mathrm{r}, \mathrm{CO} 2}}= & 6.606-29.69 \times\left(\frac{1.8 \mathrm{~T}}{1.8 \mathrm{CW}}+32\right. \\
\mathrm{C}, \mathrm{CO} 2+32 \tag{6-6}
\end{array}\right)+109.5 \times\left(\frac{1.8 \mathrm{~T}_{\mathrm{CW}}+32}{1.8 \mathrm{C}_{\mathrm{C}, \mathrm{CO} 2}+32}\right)^{2}-213.363 \times\left(\frac{1.8 \mathrm{~T}}{\mathrm{CW}+32}{ }^{1.8 \mathrm{~T}_{\mathrm{C}, \mathrm{CO} 2}+32}\right)^{3}\right)
$$

where,
$\mathrm{P}_{\mathrm{r}, \text { flue gas }}=\frac{\mathrm{MMP}_{\text {flue gas }}}{\mathrm{P}_{\mathrm{CW}}}$
$\mathrm{P}_{\mathrm{CW}}=\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{w}_{\mathrm{i}} \mathrm{P}_{\mathrm{Ci}}$
$\mathrm{P}_{\mathrm{r}, \mathrm{CO} 2}=\frac{\mathrm{MMP}_{\mathrm{CO} 2}}{\mathrm{P}_{\mathrm{C}, \mathrm{CO} 2}}$
$\mathrm{T}_{\mathrm{CW}}=\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{MF}_{\mathrm{i}} \mathrm{w}_{\mathrm{i}} \mathrm{T}_{\mathrm{ci}}$
$\mathrm{P}_{\mathrm{b}}$ modification was applied, also, for this model.

Values of $\mathrm{MF}_{\mathrm{i}}$ were as below:

| Components | $\mathbf{M F}_{\mathbf{i}}$ |
| :---: | :---: |
| $\mathrm{SO}_{2}$ | 0.3 |
| $\mathrm{H}_{2} \mathrm{~S}$ | 0.59 |
| $\mathrm{CO}_{2}$ | 1.0 |
| $\mathrm{C}_{2}$ | 1.1 |
| $\mathrm{C}_{1}$ | 1.6 |
| $\mathrm{~N}_{2}$ | 1.9 |

All other injected gas components $\quad 1.0$

Compared to all other commonly used models, the GA-based flue gas-oil MMP model presented the best match (excellent accuracy) with the experimental data. As evident from Table 6-3, the GA-based model gave an average error equal to $4.6 \%$ and standard deviation equal to $6.2 \%$. Alston et al. (1985) model gave a $14.1 \%$ average error and $43.3 \%$ standard
deviation, while Sebastian et al. (1985) model gave a $13.1 \%$ average error and $22.0 \%$ standard deviation. The GA-based flue gas-oil MMP model results are shown in Fig. 6-4 and a comparison between this study, Alston et al., and the Sebastian et al. model is presented in Fig. 6-5.

From Fig. 6-5 and Appendix-2, it is found that the maximum error of Alston et al. model was $311.6 \%$ (for the injected flue gas composed of $80 \mathrm{~mole} \%$ of $\mathrm{CO}_{2}$ and 20 mole \% of $\mathrm{N}_{2}$ ). Even after ignoring this data point from the model's validation (because Alston et al. model should not be used when $\mathrm{N}_{2}$ concentration in the flue gas exceeds 8 mole\%), the GAbased model presented the best prediction with nearly the same average error and standard deviation, which proved that the GA-based model was not sensitive to the existence of higher concentrations of $\mathrm{N}_{2}$ (tested up to 20 mole\% of $\mathrm{N}_{2}$ ). Fig. 6-6 and Table 6-4 present the comparison between GA-based, Alston et al., and Sebastian et al. model predictions after excluding this data point, which is identified within the ellipse in Fig. 6-5.

Table 6-5 presents the data range that was used to develop and validate the GA-based flue gas-oil MMP model. The literature experimental data, the model prediction results, and the comparison between the GA-based model and all other commonly used flue gas-oil MMP models are presented in Appendix-2.

### 6.3.2. Discussion for the GA-based Flue Gas-Oil MMP

Based on the above results and noting the caveat that must be applied with regard to the uncertainties in data accuracy gathered from various literature sources and experiments, the GA-based flue gas-oil MMP model was successful in yielding the best prediction of the flue gas-oil MMP among the models tested during the course of this study.

Based on the sensitivity analysis that is presented in Fig. 6-7, it was shown that the pseudocritical temperature has a major impact on the MMP, as any increase in the pseudocritical temperature causes a decrease in the MMP. On the other hand, the injected gas pseudocritical pressure, also, has a significant impact on the MMP, as any increase in the pseudocritical pressure causes an increase in the MMP.

A critical-temperature modification factor was used in developing the GA-based flue gas-oil MMP model to present a better relationship between the MMP and the pseudocritical properties of the injected flue gas and $\mathrm{CO}_{2}$. The difference between this relationship before and after using this factor in the model development is explained in Fig. 6-8 and Fig. 6-9, respectively. With the exception of $\mathrm{C}_{2}$, the critical temperature modification factor was qualitatively proportional to the equilibrium constants of the injected gas non- $\mathrm{CO}_{2}$ components $\left(\mathrm{SO}_{2}, \mathrm{H}_{2} \mathrm{~S}, \mathrm{C}_{1}\right.$, and $\left.\mathrm{N}_{2}\right)$.

Furthermore, it was evident that the GA-based flue gas-oil MMP model gave a better prediction accuracy with different types of non- $\mathrm{CO}_{2}$ components that may co-exist with $\mathrm{CO}_{2}$ in the flue gas streams (e.g., $\mathrm{H}_{2} \mathrm{~S}, \mathrm{~N}_{2}, \mathrm{SO}_{\mathrm{x}}, \mathrm{O}_{2}$, and $\mathrm{C}_{1}-\mathrm{C}_{4}$ ). This model was successfully tested, with higher prediction accuracy, for the presence of up to 78 mole\% of non- $\mathrm{CO}_{2}$ components and up to 20 mole $\%$ of $\mathrm{N}_{2}$ in the injected gas. On the other hand, the Alston et al. (1985) model performance for flue gas streams that contain $\mathrm{N}_{2}$ was inadequate; especially for injected gas streams containing more than 8 mole\% of $\mathrm{N}_{2}$. Furthermore, the Alston et al. model was unable to deal with the existence of $\mathrm{SO}_{\mathrm{x}}$ in the flue gas. For the Sebastian et al. model, its prediction accuracy was overly sensitive to the existence of $\mathrm{N}_{2}$ and/or $\mathrm{SO}_{\mathrm{x}}$ in the injected flue gas. Also, the existence of high fractions of non- $\mathrm{CO}_{2}$ components (more than 55 mole\%) caused a lower accuracy in its prediction. For the other tested models, their average errors were much higher than the foregoing models (GA-based, Alston et al., and Sebastian et al. models).

Table 6-3. Comparison between the GA-based flue gas-oil MMP model and other commonly used literature models for all the data.

| Model | Average Error, \% | Standard Deviation, \% |
| :---: | :---: | :---: |
| GA-based | 4.6 | 6.16 |
| Alston et al. (1985) | 14.1 | 43.26 |
| Sebastian et al. (1985) | 13.1 | 22.1 |
| Dong (1999) | 29.6 | 55 |
| Kovarik (1985) | 34.6 | 54 |
| Eakin and Mitch(1988) | 60.8 | 74 |



Fig. 6-4. GA-based flue gas-oil MMP model prediction results within $90 \%$ accuracy.


Fig. 6-5. Comparison between the GA-based flue gas-oil MMP model, Alston et al. (1985), and Sebastian et al. (1985) models results within $95 \%$ accuracy.


Fig. 6-6. Comparison between the GA-based flue gas-oil MMP, Alston et al. (1985), and Sebastian et al. (1985) models within $95 \%$ accuracy for all the data except the identified data point within the ellipse in Fig. 6-5 (composed of 80 mole $\%$ of $\mathrm{CO}_{2}$ and $20 \mathrm{~mole} \%$ of $\mathrm{N}_{2}$ ).

Table 6-4. Comparison between the GA-based flue gas-oil MMP model and other commonly used models for all the data except the identified data point within the ellipse in Fig. 6-5 (composed of $80 \mathrm{~mole} \%$ of $\mathrm{CO}_{2}$ and 20 mole $\%$ of $\mathrm{N}_{2}$ ).

| Model | Average Error, \% | Standard Deviation, \% |
| :---: | :---: | :---: |
| GA-based | 4.64 | 6.21 |
| Alston et al. (1985) | 9.4 | 18.23 |
| Sebastian et al. (1985) | 12.7 | 21.66 |
| Dong (1999) | 29.8 | 55 |
| Kovarik (1985) | 35 | 54 |
| Eakin and Mitch (1988) | 60.8 | 74 |

Table 6-5. Data range used to develop and validate of the GA-based flue gas-oil MMP model.

| Variables | Data range |
| :---: | :---: |
| Temperature, ${ }^{\circ} \mathrm{C}$ | $40.8-112.2$ |
| $\mathrm{MW}_{\mathrm{C} 5+}$ | $166.2-267.5$ |
| Volatiles, mole fraction | $0-0.486$ |
| Intermediates, mole fraction | $0.0131-0.403$ |
| $\mathrm{~T}_{\mathrm{CW}},{ }^{\circ} \mathrm{C}$ | $-9.26-55.1$ |
| $\mathrm{P}_{\mathrm{CW}}, \mathrm{MPa}$ | $5.27-8.1$ |
| Experimental $\mathrm{CO}_{2}$-oil MMP, MPa | $8.28-30.2$ |
| Experimental flue gas-oil MMP, MPa | $6.55-34.01$ |
| Non- $\mathrm{CO}_{2}$ components | $\mathrm{H}_{2} \mathrm{~S}, \mathrm{~N}_{2}, \mathrm{SO}_{\mathrm{x}}, \mathrm{O}_{2}$, and |
|  | $\mathrm{C}_{1}-\mathrm{C}_{4}$ |
| Non- $\mathrm{CO}_{2}$ components, mole fraction | $0.03-0.78$ |
| $\mathrm{~N}_{2}$, mole fraction | $0-0.2$ |
| $\mathrm{H}_{2} \mathrm{~S}$, mole fraction | $0-0.5$ |
| $\mathrm{SO}_{\mathrm{x}}$, mole fraction | $0-0.3$ |



Fig. 6-7. Sensitivity analysis presents the effect of each variable ( $\mathrm{T}_{\mathrm{CW}} / \mathrm{T}_{\mathrm{C}, \mathrm{CO} 2}$ and $\mathrm{P}_{\mathrm{CW} \text {, flue gas }} / \mathrm{P}_{\mathrm{C}, \mathrm{CO} 2}$ ) on the MMP ratio (flue gas-oil MMP/ $\mathrm{CO}_{2}$-oil MMP).


Fig. 6-8. The relationship between reduced MMPs ratio (reduced flue gas-oil MMP to reduced $\mathrm{CO}_{2}$-oil MMP) and the weight average pseudocritical temperature before using the critical temperature modification factor $\left(\mathrm{MF}_{\mathrm{i}}\right)$.


Fig. 6-9. The relationship between reduced MMPs ratio (reduced flue gas-oil MMP to reduced $\mathrm{CO}_{2}$-oil MMP) and the weight average pseudocritical temperature after using the critical temperature modification factor $\left(\mathrm{MF}_{\mathrm{i}}\right)$.

### 6.4. Summary

Two new GA-based models were proposed for more reliable prediction of the minimum miscibility pressure (MMP) between the reservoir oil and $\mathrm{CO}_{2}$ or flue gas.

The key input parameters in the GA-based $\mathrm{CO}_{2}$-oil MMP model, in order of their impact, were the reservoir temperature, $\mathrm{MW}_{\mathrm{C} 5+}$, and volatiles $\left(\mathrm{C}_{1}\right.$ and $\left.\mathrm{N}_{2}\right)$ to intermediates $\left(\mathrm{C}_{2}-\mathrm{C}_{4}, \mathrm{H}_{2} \mathrm{~S}\right.$, and $\left.\mathrm{CO}_{2}\right)$ mole ratio. For stock tank oils with $\mathrm{P}_{\mathrm{b}}$ less than 0.345 MPa and zero volatiles composition, the model considered the effect of the reservoir temperature, $\mathrm{MW}_{\mathrm{C} 5+}$, and the intermediates $\left(\mathrm{C}_{2}-\mathrm{C}_{4}, \mathrm{H}_{2} \mathrm{~S}\right.$, and $\left.\mathrm{CO}_{2}\right)$ mole fraction. In case of stock tank oils ( $\mathrm{P}_{\mathrm{b}}$ less than 0.345 MPa ) that contain no volatiles or intermediates in their compositions, the MMP was regarded as a function of the reservoir temperature and $\mathrm{MW}_{\mathrm{C} 5+}$. This model, which has been successfully validated with published experimental data and compared to common models in the literature, offered the best match with the lowest error (5.5\%) and standard deviation (7.4\%).

For the GA-based flue gas-oil MMP model, the MMP was regarded as a function of the injected gas solubility into the oil, which in turn is related to the injected gas pseudocritical properties (pseudocritical pressure and temperature). A critical temperature modification factor was used with some components $\left(\mathrm{C}_{1}, \mathrm{C}_{2}, \mathrm{~N}_{2}, \mathrm{H}_{2} \mathrm{~S}\right.$, and $\left.\mathrm{SO}_{2}\right)$ to present the best fit among the pseudocritical properties and the MMP. The weight fraction method was used in developing of this model. The GA-based model has also been successfully validated against published experimental data and compared to several models in the literature. It yielded the best match with the lowest average error ( $4.6 \%$ ) and standard deviation ( $6.2 \%$ ). Moreover, unlike the other models, it can be used more reliably for gases with high $\mathrm{N}_{2}$ (up to 20 mole\%) and non- $\mathrm{CO}_{2}$ components up to 78 mole\% (e.g., $\mathrm{H}_{2} \mathrm{~S}, \mathrm{~N}_{2}, \mathrm{SO}_{\mathrm{x}}, \mathrm{O}_{2}$, and $\mathrm{C}_{1}-\mathrm{C}_{4}$ ).

## CHAPTER 7

## GA-Based Physical Properties Models for $\mathrm{CO}_{2}$-oil and Flue Gas-oil Mixtures

### 7.1. Introduction

Knowledge of the physical and chemical interactions between $\mathrm{CO}_{2}$ or flue gas and reservoir oil in addition to their effect on oil recovery are very important for any gas flooding project. The major parameter that affects gas flooding is gas solubility in oil because it results in oil viscosity reduction and an increase in oil swelling, which in turn, enhances the oil mobility and increases the oil recovery efficiency. Therefore, a better understanding of this parameter and its effects on oil physical properties is vital to any successful $\mathrm{CO}_{2}$ or flue gas flooding project.

The injected gas effects on oil physical properties are determined by laboratory studies and available modelling packages. Laboratory studies are expensive and time consuming, particularly when one needs to cover a wider range of data. On the other hand, the available modelling packages can only be used in certain situations, and hence, may not be applicable in many situations.

The objective of this chapter is to develop more reliable models to predict the effects of $\mathrm{CO}_{2}$ and flue gas on oil properties (gas solubility in oil, oil swelling factor, and gas-oil mixture density and viscosity) for both dead and live oils using the GA software. Also, this chapter presents a comparison between these models and the available models in the literature, which were presented in Chapter 3 (Table 3-2).

## 7.2. $\quad \mathrm{CO}_{2}$-Oil Physical Properties

The available models for $\mathrm{CO}_{2}$-oil physical properties in the literature were developed based on a limited data conditions. The majority of them do not consider all major variables that affect each parameter model. Furthermore, most of the available packages were developed based on the dead oil data and there are no reliable models to predict the $\mathrm{CO}_{2}$ effects on the live oil physical properties. Therefore, more reliable GA-based $\mathrm{CO}_{2}$-oil physical properties models were developed to predict the $\mathrm{CO}_{2}$-oil physical properties for both dead and live oils over a wider range of conditions. The physical properties accounted for in the models developed in this study are the $\mathrm{CO}_{2}$ solubility, oil swelling factor, and $\mathrm{CO}_{2}$-oil density and viscosity. This section presents the GA-based models developed in this study together with a comparison of their accuracy with the available models reported in the literature. Also, a sensitivity analysis using @ Risk ${ }^{\mathrm{TM}}$ software (Palisade Company) for the major factors affecting each physical property is also presented.

### 7.2.1. GA-based $\mathrm{CO}_{2}$-Oil Physical Properties

The GA-based models were presented as follows.

### 7.2.1.1.GA-based $\mathrm{CO}_{2}$ Solubility in Oil

GA-based models for $\mathrm{CO}_{2}$ solubility in oil (dead and live oils) were proposed as a function of the saturation pressure, temperature, oil specific gravity, oil composition (through oil MW), and $\mathrm{CO}_{2}$ liquefaction pressure. Each model (for solubility in dead and live oils) was categorised based on the $\mathrm{CO}_{2}$ state (liquid or gaseous). The GA-based models proposed for $\mathrm{CO}_{2}$ solubility in dead and live oils were presented as follows:

### 7.2.1.1.1. GA-based $\mathrm{CO}_{2}$ Solubility in Dead Oil Model

For a more reliable prediction of the $\mathrm{CO}_{2}$ solubility in dead oil, a GA-based model is presented as follows:

1. When $\mathrm{CO}_{2}$ is in the gaseous state, for temperatures greater than $T_{c, \mathrm{CO}}$ (for all pressures) and temperatures less than $T_{c, C O 2}$ (for pressures less than the $\mathrm{CO}_{2}$ liquefaction pressure):

Sol $($ mole fraction $)=2.238-0.33 y+3.235 y^{0.6474}-4.8 y^{0.25656}$
where,

$$
\mathrm{y}=\gamma\left(0.006897 \times \frac{\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)^{0.8}}{\mathrm{P}_{\mathrm{S}}}\right)^{\exp \left(\frac{1}{\mathrm{MW}}\right)}
$$

For this model, the $\mathrm{CO}_{2}$ solubility at $\mathrm{P}_{\mathrm{b}}$ (equal to 1 atm for the dead oil case) is taken to be equal to zero.

The GA-based $\mathrm{CO}_{2}$ solubility model for the dead oil depends, primarily, on the saturation pressure and temperature. The solubility increases with an increase in saturation pressure. On the other hand, it increases with a decrease in temperature. Also, the solubility depends, to a lesser degree, on the oil specific gravity and oil molecular weight. Fig. 7-1 presents the sensitivity analysis of the factors that affect $\mathrm{CO}_{2}$ solubility in dead oil.
2. When $\mathrm{CO}_{2}$ is in the liquid state, for temperatures less than $T_{c, \mathrm{CO} 2}$ and pressures greater than the $\mathrm{CO}_{2}$ liquefaction pressure:

Sol $($ mole fraction $)=0.033+1.14 y-0.7716 y^{2}+0.2176 y^{3}-0.02183 y^{4}$
where,
$y=\gamma\left(\frac{P_{S}}{P_{\text {liq }}}\right) \operatorname{exp(\frac {1.8T_{R}+32}{MW})}$

The GA-based solubility model in this case depends on the ratio between the saturation pressure and the $\mathrm{CO}_{2}$ liquefaction pressure, temperature, oil molecular weight, and oil specific gravity. Because the solubility of $\mathrm{CO}_{2}$ when it is in the liquid state is less sensitive to the saturation pressure effect and the $\mathrm{CO}_{2}$ becomes less soluble in oil, the GA-based model used the ratio between the saturation pressure and the $\mathrm{CO}_{2}$ liquefaction pressure as a variable instead of using the saturation pressure.

As shown in Table 7-1, Fig. 7-2, and Fig. 7-3, the GA-based $\mathrm{CO}_{2}$ solubility in dead oil model offered a better accuracy compared to models of Simon and Graue (1965), Mehrotra and Svrcek (1982) (their models have been developed for bitumen), and Chung et al. (1986). In addition to the higher accuracy and compared to the other available models, the GA-based model could be applied over a wider range of conditions. Table 7-2 presents a summary of the experimental data range used in this study for developing and testing of the $\mathrm{CO}_{2}$ solubility
in dead oil model. The experimental data details of the $\mathrm{CO}_{2}$ solubility in dead oil and the prediction results from the GA-based $\mathrm{CO}_{2}$ solubility model are presented in Appendix-3.

Table 7-1. Comparison between the GA-based $\mathrm{CO}_{2}$ solubility in dead oil model and other $\mathrm{CO}_{2}$ solubility literature models.

| Model | No. of <br> data | Average Error, <br> \% | STDEV, <br> $\mathbf{\%}$ | $\mathbf{R}^{\mathbf{2}}$ |
| :---: | :---: | :---: | :---: | :---: |
| GA-based | 106 | 4.0 | 5.6 | 0.985 |
| Simon and Graue (1965) | 49 | 5.7 | 10.8 | 0.97 |
| Mehrotra and Svrcek (1982) | 106 | 32.6 | 36.6 | 0.756 |
| Chung et al. (1986) | 106 | 83.7 | 150.3 | 0.0096 |



Fig. 7-1. Sensitivity analysis of the factors affecting $\mathrm{CO}_{2}$ solubility in dead oil.


Fig. 7-2. GA-based $\mathrm{CO}_{2}$ solubility in dead oil model prediction results.


Fig. 7-3. Comparison results between the GA-based $\mathrm{CO}_{2}$ solubility in dead oil, Simon and Graue (1965), and Mehrotra and Svrcek (1982) models.

Table 7-2. Experimental data range used in this study for developing and testing of the GAbased $\mathrm{CO}_{2}$ solubility in dead oil model.

| Variable | Experimental data range |
| :---: | :---: |
| Oil API gravity, ${ }^{\circ} \mathrm{API}$ | Wider range (12-37.0) |
| $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Up to 27.4 |
| $\mathrm{~T}_{\mathrm{R}},{ }^{\circ} \mathrm{C}$ | Up to 140 |
| MW | Up to 490 |

### 7.2.1.1.2. GA-based $\mathrm{CO}_{2}$ Solubility in Live Oil

For a reliable prediction of the $\mathrm{CO}_{2}$ solubility in live oils, a GA-based model was presented as follows:

1. When $\mathrm{CO}_{2}$ is in the gaseous state, for temperatures greater than $T_{c, \mathrm{CO}}$ (for all pressures) and temperatures less than $T_{c, \mathrm{CO}}$ (for pressures less than the $\mathrm{CO}_{2}$ liquefaction pressure):

Sol $($ mole fraction $)=1.748-0.5632 y+3.273 y 0.704-4.3 y 0.4425$
where,

$$
\mathrm{y}=\gamma\left(0.006897 \times \frac{\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)^{1.125}}{\mathrm{P}_{\mathrm{s}}-\mathrm{P}_{\mathrm{b}}}\right) \exp \left(\frac{1}{\mathrm{MW}}\right)
$$

For this model, it is considered that the $\mathrm{CO}_{2}$ solubility at $\mathrm{P}_{\mathrm{b}}$ is equal to zero.

As shown in Fig. 7-4, the GA-based $\mathrm{CO}_{2}$ solubility in live oil model also depends on the difference between the saturation pressure and $\mathrm{P}_{\mathrm{b}}$, temperature, oil specific gravity, and oil molecular weight. However, as noted in this figure, the saturation pressure effect on the $\mathrm{CO}_{2}$ solubility in live oil is higher than that in dead oil. The temperature effect, on the other hand, is lower in the live oil case.
2. When $\mathrm{CO}_{2}$ is in the liquid state, for temperatures less than $T_{c, \mathrm{CO}}$ and pressures greater than the $\mathrm{CO}_{2}$ liquefaction pressure:

The same model that developed for the solubility in dead oil when $\mathrm{CO}_{2}$ is in the liquid state (as given in Equation 7-2) was also used for the solubility in live oil.

As shown in Table 7-3, Fig. 7-5, and Fig. 7-6, the GA-based $\mathrm{CO}_{2}$ solubility in live oil model offered a much better accuracy compared to the models of Simon and Graue (1965), Mehrotra and Svrcek (1982), and Chung et al. (1986), as these models were developed basically based on dead or heavy oils data. In addition, the GA-based model could be applied over a wider range of conditions. Table 7-4 presents a summary of the experimental data range used in this study for developing and testing of the $\mathrm{CO}_{2}$ solubility in live oil model. The experimental data details of the $\mathrm{CO}_{2}$ solubility in live oil and the prediction results from the GA-based $\mathrm{CO}_{2}$ solubility in live oil model are presented in Appendix-3.

Table 7-3. Comparison between the GA-based $\mathrm{CO}_{2}$ solubility in live oil and other $\mathrm{CO}_{2}$ solubility literature models.

| Model | No. of <br> data | Average Error, <br> $\boldsymbol{\%}$ | STDEV, \% | $\mathbf{R}^{\mathbf{2}}$ |
| :---: | :---: | :---: | :---: | :---: |
| GA-based | 74 | 4.0 | 5.5 | 0.98 |
| Simon and Graue (1965) | 45 | 24.7 | 26.5 | 0.956 |
| Mehrotra and Svrcek (1982) | 74 | 36.7 | 46.3 | 0.3616 |
| Chung et al. (1986) | 74 | 76.4 | 127.87 | 0.0471 |



Fig. 7-4. Sensitivity analysis of the factors affecting $\mathrm{CO}_{2}$ solubility in live oil.


Fig. 7-5. GA-based $\mathrm{CO}_{2}$ solubility in live oil model prediction results.


Fig. 7-6. Comparison results between the GA-based $\mathrm{CO}_{2}$ solubility in live oil, Simon and Graue (1965), and Mehrotra and Svrcek (1982) models.

Table 7-4. Experimental data range used in this study for developing and testing of the GAbased $\mathrm{CO}_{2}$ solubility in live oil model.

| Variable | Experimental data range |
| :---: | :---: |
| Oil API gravity, ${ }^{\circ}$ API | Wider range $(15-70)$ |
| $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Up to 32.75 |
| $\mathrm{~T}_{\mathrm{R}},{ }^{\circ} \mathrm{C}$ | Up to 123.9 |
| MW | Up to 391.55 |

7.2.1.2. GA-based Oil (Dead and Live Oils) Swelling Factor Due to $\mathrm{CO}_{2}$ Injection

A GA-based oil swelling factor (SF) model (for dead and live oils) was proposed as a function of the $\mathrm{CO}_{2}$ solubility and oil molecular size (equal to ratio between oil MW and oil density at $15.56^{\circ} \mathrm{C}$ (oil specific gravity)). The oil was classified based on its molecular weight to two groups: heavier oil (for $\mathrm{MW} \geq 300$ ) and lighter oil (for $\mathrm{MW}<300$ ).

### 7.2.1.2.1. Heavier Oil ( $M W \geq 300$ )

$\mathrm{SF}=1+0.3302 \mathrm{Y}-0.8417 \mathrm{Y}^{2}+1.5804 \mathrm{Y}^{3}-1.074 \mathrm{Y}^{4}-0.0318 \mathrm{Y}^{5}+0.21755 \mathrm{Y}^{6}$
where,
$\mathrm{Y}=1000.0 \times\left(\left(\left(\frac{\gamma}{\mathrm{MW}}\right) \times \operatorname{Sol}(\text { mole fraction })^{2}\right)^{\exp \left(\frac{\gamma}{\mathrm{MW}}\right)}\right)$

As shown in Fig. 7-7, the GA-based oil swelling factor for the heavier oil is affected primarily by the $\mathrm{CO}_{2}$ solubility, increasing with the $\mathrm{CO}_{2}$ solubility increase. On the other hand, there is a lesser impact of the oil molecular size as the swelling factor decreases with the oil molecular size increase.

### 7.2.1.2.2. Lighter Oil ( $M W<300$ )

$$
\begin{equation*}
\mathrm{SF}=1+0.48411 \mathrm{Y}-0.9928 \mathrm{Y}^{2}+1.6019 \mathrm{Y}^{3}-1.2773 \mathrm{Y}^{4}+0.48267 \mathrm{Y}^{5}-0.06671 \mathrm{Y}^{6} \tag{7-5}
\end{equation*}
$$

Also, from Fig. 7-8, the GA-based oil swelling factor for the lighter oil (oil MW<300) is, basically, affected by the $\mathrm{CO}_{2}$ solubility, but the effect of the solubility is less than its effect on the heavier oil. On the other hand, there is a lesser impact also of the oil molecular size, although its effect is higher on lighter oil than on heavier oil.

### 7.2.1.2.3. GA-based Oil Swelling Factor Model Test

For the dead oil swelling factor, Table 7-5, Fig. 7-9, and Fig. 7-10 present a comparison between the GA-based oil swelling factor model accuracy for the dead oil swelling factor and the model by Simon and Graue (1965). As shown, the GA-based model offered a better accuracy than that of Simon and Graue model. Also, it could be applied over a wider range of conditions. Table 7-6 presents a summary of the experimental data range used in this study for developing and testing of the GA-based oil swelling factor (due to $\mathrm{CO}_{2}$ injection) model for dead oil. The experimental data details of the dead oil swelling factor and the prediction results from the GA-based oil swelling factor model for dead oil are presented in Appendix-4.


Fig. 7-7. Sensitivity analysis of the factors affecting dead and live oils swelling factor (due to $\mathrm{CO}_{2}$ ) for oils with MW $\geq 300$.


Fig. 7-8. Sensitivity analysis of the factors affecting dead and live oil swelling factor (due to $\mathrm{CO}_{2}$ ) for oils with MW $<300$.

Table 7-5. Comparison between the GA-based and Simon and Graue (1965) oil swelling models prediction results for dead oil.

| Model | No. of <br> data | Average Error, <br> $\boldsymbol{\%}$ | STDEV, <br> $\boldsymbol{\%}$ | $\mathbf{R}^{\mathbf{2}}$ |
| :---: | :---: | :---: | :---: | :---: |
| GA-based | 85 | 0.61 | 0.94 | 0.994 |
| Simon and Graue (1965) | 83 | 1.0 | 1.7 | 0.970 |



Fig. 7-9. GA-based oil swelling factor (due to $\mathrm{CO}_{2}$ ) model prediction results for dead oil.


Fig. 7-10. Comparison results between the GA-based and Simon and Graue (1965) oil swelling factor (due to $\mathrm{CO}_{2}$ ) models prediction results for dead oil.

Table 7-6. Experimental data range used in this study for developing and testing of the GAbased oil swelling factor (due to $\mathrm{CO}_{2}$ ) model for dead oil.

| Variable | Experimental data range |
| :---: | :---: |
| Oil API gravity, ${ }^{\circ}$ API | Wider range (12-37) |
| $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Up to 27.4 |
| $\mathrm{~T}_{\mathrm{R}},{ }^{\circ} \mathrm{C}$ | Up to 121.1 |
| MW | Up to 463 |

For the live oil swelling factor, Table 7-7, Fig. 7-11, and Fig. 7-12 present a comparison between the GA-based oil swelling factor model and the model by Simon and Graue (1965). As shown, the GA-based model gave a better accuracy than that of Simon and Graue model. In addition, this model could be applied over a wider range of conditions. Table 7-8 presents a summary of the experimental data range used in this study for testing of the GA-based oil swelling factor (due to $\mathrm{CO}_{2}$ injection) model for the live oil. The experimental data details for the live oil swelling factor and the prediction results from the GA-based oil swelling factor model for the live oil are presented in Appendix-4.

Table 7-7. Comparison between the GA-based and Simon and Graue (1965) oil swelling models prediction results for live oil.

| Model | No. of <br> data | Average <br> Error, \% | STDEV, <br> $\mathbf{\%}$ | $\mathbf{R}^{\mathbf{2}}$ |
| :---: | :---: | :---: | :---: | :---: |
| GA-based | 52 | 0.866 | 1.29 | 0.99 |
| Simon and Graue (1965) | 35 | 1.2 | 2.0 | 0.98 |



Fig. 7-11. GA-based oil swelling factor (due to $\mathrm{CO}_{2}$ ) model prediction results for live oil.


Fig. 7-12. Comparison results between the GA-based and Simon and Graue (1965) oil swelling factor (due to $\mathrm{CO}_{2}$ ) models prediction results for live oil.

Table 7-8. Experimental data range used in this study for testing of the GA-based oil swelling factor (due to $\mathrm{CO}_{2}$ ) model for live oil.

| Variable | Experimental data range |
| :---: | :---: |
| Oil API gravity, ${ }^{\circ}$ API | Wider range (15-50) |
| $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Up to 30.72 |
| $\mathrm{~T}_{\mathrm{R}},{ }^{\circ} \mathrm{C}$ | Up to 137.22 |
| MW | Up to 391.55 |

### 7.2.1.3.GA-based $\mathrm{CO}_{2}$-Oil (Dead and Live Oils) Density

The GA-based $\mathrm{CO}_{2}$-oil density model for dead and live oils considered the effects of the saturation pressure, temperature, oil specific gravity, and initial oil density at the specified temperature on the mixture density. The following is the proposed GA-based $\mathrm{CO}_{2}$-oil density model for both dead oil and live oils:

$$
\begin{equation*}
\rho=\rho_{\mathrm{i}}-0.10276 \mathrm{y} 0.608+0.1407 \mathrm{y} 0.6133 \tag{7-6}
\end{equation*}
$$

where,

$$
\mathrm{y}=\frac{\gamma \rho_{\mathrm{i}}\left(\mathrm{P}_{\mathrm{s}}-\mathrm{P}_{\mathrm{b}}\right)^{1.25}}{1.8 \mathrm{~T}_{\mathrm{R}}+32}
$$

As evident from the sensitivity analysis presented in Fig. 7-13, the GA-based $\mathrm{CO}_{2}$-oil density increases with the initial oil density and saturation pressure increase, and consequently, with the $\mathrm{CO}_{2}$ solubility increase. On the other hand, there is a lower impact of the temperature and nearly no impact of the oil specific gravity.

For the $\mathrm{CO}_{2}$-dead oil density, as evident from Table 7-9, Fig. 7-14, and Fig. 7-15, the GA-based model yielded a much lower error than the Quail et al. (1988) model. In addition, this model could be applied over a wider range of conditions. Table 7-10 presents a summary of the experimental data range used in this study for developing and testing of the GA-based $\mathrm{CO}_{2}$-oil density model for $\mathrm{CO}_{2}$-dead oil density. The details of the experimental $\mathrm{CO}_{2}$-dead oil density data and the prediction results of the GA-based $\mathrm{CO}_{2}$-oil density model for the $\mathrm{CO}_{2^{-}}$ dead oil density are presented in Appendix-5.

Table 7-9. Comparison between the GA-based and Quail et al. (1988) models results for the $\mathrm{CO}_{2}$-dead oil density prediction.

| Model | No. of <br> data | Average <br> Error, \% | STDEV, \% | $\mathbf{R}^{\mathbf{2}}$ |
| :---: | :---: | :---: | :---: | :---: |
| GA-based | 136 | 0.29 | 0.43 | 0.9952 |
| Quail et al. (1988) | 129 | 3.0 | 4.8 | 0.293 |



Fig. 7-13. Sensitivity analysis of the factors affecting $\mathrm{CO}_{2}$-oil (dead and live oils) density.


Fig. 7-14. GA-based $\mathrm{CO}_{2}$-oil density model prediction results for $\mathrm{CO}_{2}$-dead oil density.


Fig. 7-15. Comparison results between the GA-based and Quail et al. (1988) $\mathrm{CO}_{2}$-oil density models prediction results for $\mathrm{CO}_{2}$-dead oil density.

Table 7-10. Experimental data range used in this study for developing and testing of the GAbased $\mathrm{CO}_{2}$-oil density model for $\mathrm{CO}_{2}$-dead oil density.

| Variable | Experimental data range |
| :---: | :---: |
| Oil API gravity, ${ }^{\circ}$ API | Wider range (10-41) |
| $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Up to 34.5 |
| $\mathrm{~T}_{\mathrm{R}},{ }^{\circ} \mathrm{C}$ | Up to 140 |
| MW | Up to 490 |

Also, for the $\mathrm{CO}_{2}$-live oil density, as evident from Table 7-11, Fig. 7-16, and Fig. 7-17, the GA-based model yielded a much lower error than the Quail et al. (1988) model. Also, this model could be applied over a much wider range of conditions. Table $\mathbf{7 - 1 2}$ presents a summary of the experimental data range used in this study for testing of the GA-based $\mathrm{CO}_{2}-$ oil density model for the $\mathrm{CO}_{2}$-live oil density. The details of the experimental $\mathrm{CO}_{2}$-live oil density data and the prediction results of the GA-based $\mathrm{CO}_{2}$-oil density model for $\mathrm{CO}_{2}$-live oil density are presented in Appendix-5.

Table 7-11. Comparison between the GA-based and Quail et al. (1988) $\mathrm{CO}_{2}$-oil density models prediction results for $\mathrm{CO}_{2}$-live oil density.

| Model | No. of <br> data | Average <br> Error, \% | STDEV, \% | $\mathbf{R}^{\mathbf{2}}$ |
| :---: | :---: | :---: | :---: | :---: |
| GA-based | 50 | 1.05 | 1.76 | 0.9932 |
| Quail et al. (1988) | 50 | 17.0 | 22.5 | 0.6465 |



Fig. 7-16. GA-based $\mathrm{CO}_{2}$-oil density model prediction results for $\mathrm{CO}_{2}$-live oil density.


Fig. 7-17. Comparison results between the GA-based and Quail et al. (1988) $\mathrm{CO}_{2}$-oil density models prediction results for $\mathrm{CO}_{2}$-live oil density.

Table 7-12. Experimental data range used in this study for testing of the GA-based $\mathrm{CO}_{2}$-oil density model for $\mathrm{CO}_{2}$-live oil density.

| Variable | Experimental data range |
| :---: | :---: |
| Oil API gravity, ${ }^{\circ}$ API | Wider range (14.9-70) |
| $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Up to 32.92 |
| $\mathrm{~T}_{\mathrm{R}},{ }^{\circ} \mathrm{C}$ | Up to 96.1 |
| MW | Up to 391.55 |

### 7.2.1.4. GA-based $\mathrm{CO}_{2}$-Oil (Dead and Live Oils) Viscosity

A GA-based $\mathrm{CO}_{2}$-oil (dead and live oils) viscosity model was developed based on the $\mathrm{CO}_{2}$ solubility, initial oil viscosity, saturation pressure, temperature, and oil specific gravity. The effect of the $\mathrm{CO}_{2}$ liquefaction pressure was included in this model through the $\mathrm{CO}_{2}$ solubility variable. The proposed GA-based $\mathrm{CO}_{2}$-oil (dead and live oils) viscosity model was presented as follows:

$$
\begin{equation*}
\mu=\mathrm{y} \mu_{\mathrm{i}}+\mathrm{A}\left(\frac{\text { Sol (mole fraction) }}{\mu_{\mathrm{i}}}\right) \tag{7-7}
\end{equation*}
$$

where,
$y=x^{B}$ \&
$\mathrm{x}=\left(\mathrm{C} \times \mu_{\mathrm{i}}\left(\frac{\mathrm{P}_{\mathrm{S}}}{1.8 \mathrm{~T}_{\mathrm{R}}+32}\right) \mathrm{D}\right)^{(\gamma \times \text { Sol(mole fraction) })}$

The coefficients of this model for dead and live oils were presented as follows:

|  | A | B | C | D |
| :---: | :---: | :---: | :---: | :---: |
| Dead oil | -9.5 | -0.732 | 3.14129 | 0.23 |
| Live oil | 0 | -0.587 | 305.873 | 1.15 |

Based on the sensitivity analysis presented in Fig. 7-18 (for dead oil) and Fig. 7-19 (for live oil), the GA-based viscosity reduction ( $\mathrm{CO}_{2}$-oil viscosity/initial oil viscosity) depends, basically, on the $\mathrm{CO}_{2}$ solubility, as well as the initial oil viscosity, saturation pressure, oil specific gravity, and temperature. The impact of the $\mathrm{CO}_{2}$ solubility, saturation pressure, oil specific gravity, and temperature on the viscosity reduction is higher on live oil than on dead oil. However, the initial oil viscosity impact is lower for live oil than for dead oil.

For $\mathrm{CO}_{2}$-dead oil viscosity, compared to other models (Beggs and Robinson (1975) and Mehrotra and Svrcek (1982)), the GA-based $\mathrm{CO}_{2}$-dead oil viscosity model appeared to yield more accurate results (see Table 7-13 and Figs. 7-20 and 7-21). Also, it could be used successfully for a wider range of conditions (e.g., has been applied for up to $12086 \mathrm{mPa} . \mathrm{s}$ ). Table $\mathbf{7 - 1 4}$ presents a summary of the experimental data range used in this study for developing and testing of the $\mathrm{CO}_{2}$-dead oil viscosity model. The details of the experimental $\mathrm{CO}_{2}$-dead oil viscosity data and the prediction results from the GA-based $\mathrm{CO}_{2}$-dead oil viscosity model are presented in Appendix-6.

Table 7-13. Comparison between the GA-based and other $\mathrm{CO}_{2}$-dead oil viscosity literature models.

| Model | No. of <br> data | Average <br> Error, \% | STDEV, \% | $\mathbf{R}^{\mathbf{2}}$ |
| :---: | :---: | :---: | :---: | :---: |
| GA-based | 130 | 6.0 | 8.8 | 0.9998 |
| Beggs and Robinson (1975) | 130 | 56.8 | 62.7 | 0.8743 |
| Mehrotra and Svrcek (1982) | 130 | 94.3 | 95.2 | 0.18 |



Fig. 7-18. Sensitivity analysis of the factors affecting dead oil viscosity reduction due to $\mathrm{CO}_{2}$ injection.


Fig. 7-19. Sensitivity analysis of the factors affecting live oil viscosity reduction due to $\mathrm{CO}_{2}$ injection.


Fig. 7-20. GA-based $\mathrm{CO}_{2}$-dead oil viscosity model prediction results.


Fig. 7-21. Comparison results between the GA-based and Beggs and Robinson (1975) $\mathrm{CO}_{2^{-}}$ dead oil viscosity models.

Table 7-14. Experimental data range used in this study for developing and testing of the $\mathrm{CO}_{2}{ }^{-}$ dead oil viscosity model.

| Variable | Experimental data range |
| :---: | :---: |
| Oil API gravity, ${ }^{\circ}$ API | Wider range (10-37) |
| $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Up to 34.5 |
| $\mathrm{~T}_{\mathrm{R}},{ }^{\circ} \mathrm{C}$ | Up to 140 |
| MW | Up to 530 |
| Oil viscosity, mPa.s | Up to 12086 |

For $\mathrm{CO}_{2}$-live oil viscosity, again, compared to other models (Beggs and Robinson (1975) and Mehrotra and Svrcek (1982)), the GA-based $\mathrm{CO}_{2}$-live oil viscosity model appeared to yield more accurate results (see Table 7-15 and Figs. 7-22 and 7-23). Also, it could be used successfully for a wider range of conditions. Table $\mathbf{7 - 1 6}$ presents a summary of the experimental data range used in this study for developing and testing of the GA-based $\mathrm{CO}_{2}$-live oil viscosity model. The details of the experimental $\mathrm{CO}_{2}$-live oil viscosity data and the prediction results from the GA-based $\mathrm{CO}_{2}$-live oil viscosity model are presented in Appendix-6.

Table 7-15. Comparison between the GA-based and other $\mathrm{CO}_{2}$-live oil viscosity literature models.

| Model | No. of <br> data | Average <br> Error, \% | STDEV, <br> \% | $\mathbf{R}^{\mathbf{2}}$ |
| :---: | :---: | :---: | :---: | :---: |
| GA-based | 52 | 6.6 | 9.75 | 0.9996 |
| Beggs and Robinson (1975) | 52 | 56.25 | 91.4 | 0.8734 |
| Mehrotra and Svrcek (1982) | 52 | 65.1 | 79.5 | 0.4387 |



Fig. 7-22. GA-based $\mathrm{CO}_{2}$-live oil viscosity model prediction results.


Fig. 7-23. Comparison results between the GA-based and Beggs and Robinson (1975) $\mathrm{CO}_{2^{-}}$ live oil viscosity models.

Table 7-16. Experimental data range used in this study for developing and testing of the $\mathrm{CO}_{2^{-}}$ live oil viscosity model.

| Variable | Experimental data range |
| :---: | :---: |
| Oil API gravity, ${ }^{\circ}$ API | Wider range (15-50) |
| $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Up to 24.34 |
| $\mathrm{~T}_{\mathrm{R}},{ }^{\circ} \mathrm{C}$ | Up to 137.22 |
| MW | Up to 391.55 |
| Oil viscosity, mPa.s | Up to 941 |

### 7.2.2. Discussion For the GA-based $\mathrm{CO}_{2}$-Oil Physical Properties

It was obvious that although various models in the literature were applicable in some conditions, they could not be applied universally because of their data and application limitations. Also, most of the available models in the literature were developed based on dead and/or heavy oil data and they presented unreliable prediction for live oil data. The Simon and Graue (1965) models, for example, were developed based on dead oil data and were limited to a saturation pressure of 15.9 MPa and oil viscosity up to 1300 mPa .s, and they predicted $\mathrm{CO}_{2^{-}}$ oil viscosity incorrectly, especially for lighter oils. The Chung et al. (1986) models also were developed based on heavy and dead oil data, and were limited to a saturation pressure of 20.7 MPa and oil gravities from 10 to $20^{\circ}$ API. The Emanuel (1985) model yielded significant errors in the prediction of $\mathrm{CO}_{2}$-oil viscosity, and it has been developed basically for heavy oils. Although the Lohrenz-Bray-Clark (1964) viscosity model has been proposed for light oils, it was sensitive to density calculation, in which it used the $4^{\text {th }}$ power of reduced density. Welker and Dunlop (1963) models were limited to $20-40^{\circ}$ API oil for temperature equal to $26.67^{\circ} \mathrm{C}$. Furthermore, the preceding models do not account for the effects of the $\mathrm{CO}_{2}$ liquefaction pressure on the $\mathrm{CO}_{2}$ solubility, in particular.

Unlike other models, the GA-based models proposed in this study predicted $\mathrm{CO}_{2}$-oil physical properties ( $\mathrm{CO}_{2}$ solubility, oil swelling factor, and $\mathrm{CO}_{2}$-oil density and viscosity) for both dead and live oils with a higher accuracy. These models, also, could be applied over a wider range of oil gravities, pressures up to 34.5 MPa , oil MW>490, oil viscosities up to 12000 mPa .s and temperatures up to $140^{\circ} \mathrm{C}$. Furthermore, the GA-based models considered all major variables that affect each physical property.

For $\mathrm{CO}_{2}$ solubility prediction, the GA-based $\mathrm{CO}_{2}$ solubility models used saturation pressure, temperature, oil gravity, oil MW, and $\mathrm{CO}_{2}$ liquefaction pressure. The GA-based oilswelling factor model used oil molecular size (e.g., ratio between oil molecular weight and original oil density at $15.56^{\circ} \mathrm{C}$ ) and $\mathrm{CO}_{2}$ solubility. For prediction of $\mathrm{CO}_{2}$-dissolved oil density, the GA-based model used saturation pressure, temperature, oil specific gravity, and initial oil density at the specified temperature. Furthermore, for prediction of $\mathrm{CO}_{2}$-oil viscosity, the initial oil viscosity, $\mathrm{CO}_{2}$ solubility, saturation pressure, temperature, and oil specific gravity were used.

The GA-based models have been validated with published experimental dead and live oils data and available models in the literature. Each GA-based model presented in this study (for dead and live oils) has demonstrated superior performance in terms of its accuracy and covered wider ranges of data. In particular, the GA-based models for live oils presented a
higher accuracy with a higher difference between their predictions and other literature models predictions. Furthermore, these models could be integrated, easily, into a reservoir simulator for $\mathrm{CO}_{2}$ flooding design and simulation.

### 7.3. Flue Gas-Oil Physical Properties

The available model packages that have been developed basically for $\mathrm{CO}_{2}$-oil physical properties prediction may not be appropriate for flue gas-oil physical properties, and as a consequence, yield inaccurate predictions in most cases. Therefore, there is a need for more accurate models, which consider the effects of different non- $\mathrm{CO}_{2}$ components on the flue gasoil physical properties. The GA software developed in this study was used as a modelling tool to determine reliable models for the flue gas-oil physical properties prediction. The following subsections discuss the GA-based models developed in this study, notably, flue gas solubility, impact on oil swelling factor, and flue gas-oil density and viscosity. They also present a comparison between GA-based models and the other commonly used models in the literature (as presented in Table 3-2), which were developed basically for the $\mathrm{CO}_{2}$-oil physical properties and tested here for the flue gas-oil properties. In addition, these subsections also present a sensitivity analysis using @ Risk ${ }^{\mathrm{TM}}$ software for major factors affecting each physical property.

### 7.3.1. GA-based Flue Gas-Oil Physical Properties

The GA-based models are as follows:

### 7.3.1.1.GA-based Flue Gas Solubility in Oil

GA-based flue gas-oil solubility models have been developed based on the saturation pressure, temperature, oil specific gravity, oil composition (through oil MW), flue gas composition (through flue gas MW), and injected flue gas critical properties (pseudocritical pressure and temperature). Hence, these models took into account the effect of non- $\mathrm{CO}_{2}$ components on the flue gas solubility. These models also considered the effect of the flue gas liquefaction pressure. GA-based models proposed for the flue gas solubility in dead and live oils are as follows.

### 7.3.1.1.1. GA-based Flue Gas Solubility in Dead Oil

For a reliable prediction of the flue gas solubility in dead oil, the following GA-based model is proposed:

1. When flue gas is in the gaseous state, for temperatures greater than $T_{c, f l u e}$ gas (for all pressures) and temperatures less than $T_{c, f l u e}$ gas (for pressures less than the flue gas liquefaction pressure):
$\operatorname{Sol}($ molefraction $)=1.2357-12.866 y+65.48 y^{2}-159.5 y^{3}+192.39 y^{4}-109.74 y^{5}+23.17 \mathrm{y}^{6}$
where,
$\mathrm{y}=\left(\frac{\gamma}{\mathrm{MW}_{\text {flue gas }}}\right)\left(\frac{\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)^{0.4}}{\left(\mathrm{P}_{\mathrm{s}} / \mathrm{P}_{\mathrm{CW}}\right)}\right) \exp \left(\frac{1}{\left(\left(1.8 \mathrm{~T}_{\mathrm{CW}}+32\right) \times \mathrm{MW}\right)}\right)$
where,
$\mathrm{T}_{\mathrm{CW}}=\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{MF}_{\mathrm{i}}{ }_{\mathrm{W}} \mathrm{i}_{\mathrm{i}} \mathrm{T}_{\mathrm{i}}$
$\mathrm{P}_{\mathrm{CW}}=\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{w}_{\mathrm{i}} \mathrm{P}_{\mathrm{Ci}}$
$\mathrm{MW}_{\text {flue gas or oil }}=\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{y}_{\mathrm{i}} \mathrm{MW}_{\mathrm{i}}$
$\mathrm{MF}_{\mathrm{i}}$ is the critical temperature modification factor for the gas components as presented before in Chapter 6.

For this model, the flue gas solubility at $\mathrm{P}_{\mathrm{b}}$ (equal to 1 atm for the dead oil case) was considered to be equal to zero.

The GA-based flue gas solubility model for the dead oil depends, primarily, on the saturation pressure, temperature, flue gas liquefaction pressure, flue gas critical properties (pseudocritical temperature and pressure), and oil specific gravity. Also, it depends, to a lesser degree, on the flue gas molecular weight and oil molecular weight. Fig. 7-24 presents the sensitivity analysis of the factors that affect flue gas solubility in dead oil.
2. When flue gas is in the liquid state, for temperatures less than $T_{c, f l u e}$ gas $a n d$ pressures greater than the flue gas liquefaction pressure:

The model proposed for the $\mathrm{CO}_{2}$ solubility when $\mathrm{CO}_{2}$ is in the liquid state (Equation 72) could be also used for the flue gas solubility as the saturation pressure effect on the solubility when flue gas or $\mathrm{CO}_{2}$ are in the liquid state is less pronounced. Hence, the GA-
based flue gas solubility model depended on the ratio between the saturation pressure and the flue gas liquefaction pressure, temperature, oil molecular weight, and oil specific gravity.


Fig. 7-24. Sensitivity analysis of the factors affecting flue gas solubility in dead oil.

### 7.3.1.1.2. GA-based Flue Gas Solubility in Live Oil

For a reliable prediction of the flue gas solubility in live oil, the following GA-based model is proposed:

1. When flue gas is in the gaseous state, for temperatures greater than $T_{\text {cfflue gas }}$ (for all pressures) and temperatures less than $T_{c, f l u e}$ gas (for pressures less than the flue gas liquefaction pressure):

Sol $($ mole fraction $)=0.8521-5.89 y+21.5 y^{2}-35.32 y^{3}+4.57 y^{4}+52.1 y^{5}-40.79 \mathrm{y}^{6}$
where,

$$
\left.\mathrm{y}=100 \times \gamma \times\left(\frac{\left(145.04 \times \mathrm{P}_{\mathrm{CW}}\right)}{\left(1.8 \mathrm{~T}_{\mathrm{CW}}+32\right)}\right)^{1.6} \times\left(\frac{\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)^{0.2}}{\mathrm{MW}_{\text {flue gas }} \times\left(145.04 \times\left(\mathrm{P}_{\mathrm{s}}-\mathrm{P}_{\mathrm{b}}\right)\right)^{1.2}}\right) \exp _{\mathrm{MW}}\right)
$$

For this model, the flue gas solubility at $\mathrm{P}_{\mathrm{b}}$ was considered to be equal to zero.

As shown in Fig. 7-25, the GA-based flue gas solubility in live oil model also depends on the saturation pressure, temperature, flue gas liquefaction pressure, flue gas critical properties (pseudocritical temperature and pressure), oil specific gravity, flue gas molecular weight, and oil molecular weight. However, the flue gas critical properties effect is higher for the gas solubility in live oil than for the solubility in dead oil.
2. When flue gas is in the liquid state, for temperatures less than $T_{c, f l u e}$ gas $a n d$ pressures greater than the flue gas liquefaction pressure:

The same model used for the $\mathrm{CO}_{2}$ solubility in dead oil when $\mathrm{CO}_{2}$ is in the liquid state (as given in Equation 7-2) can also be used for the flue gas solubility in live oil.

### 7.3.1.1.3. GA-based Flue Gas Solubility Models Test

As shown in Table 7-17, Fig. 7-26, and Fig. 7-27, the GA-based flue gas solubility in dead and live oil models offered a much better accuracy compared to models of Simon and Graue (1965), Mehrotra and Svrcek (1982) (have been developed for bitumen), and Chung et al. (1986). In addition they could be applied over a wider range of conditions. Table 7-18 presents a summary of the experimental data range used in this study for developing and testing of the flue gas solubility in dead and live oils models. The details of the experimental flue gas solubility data and the prediction results from the GA-based flue gas solubility in oil models are presented in Appendix-7.


Fig. 7-25. Sensitivity analysis of the factors affecting flue gas solubility in live oil.


Fig. 7-26. GA-based flue gas solubility models prediction results for dead and live oils.


Fig. 7-27. Comparison results among the GA-based flue gas solubility in oil (dead and live oils), Simon and Graue (1965), Chung et al. (1986), and Mehrotra and Svrcek (1982) models.

Table 7-17. Comparison between the GA-based flue gas solubility in oil (dead and live oils) and other literature solubility models.

| Model | Average Error, <br> $\mathbf{\%}$ | STDEV, <br> $\mathbf{\%}$ | $\mathbf{R}^{\mathbf{2}}$ |
| :---: | :---: | :---: | :---: |
| GA-based | 6.2 | 8.8 | 0.9504 |
| Simon and Graue (1965) | 35.9 | 46.3 | 0.3914 |
| Mehrotra and Svrcek (1982) | 36.3 | 51.4 | 0.3068 |
| Chung et al(1986) | 98.6 | 167.6 | 0.0007 |

Table 7-18. Experimental data range used in this study for developing and testing of the flue gas solubility (in dead and live oils) models.

| Variable | Experimental data range |
| :---: | :---: |
| Oil API gravity, ${ }^{\circ} \mathrm{API}$ | Wider range (14-55) |
| $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Up to 41.37 |
| $\mathrm{~T}_{\mathrm{R}},{ }^{\circ} \mathrm{C}$ | Up to 141.1 |
| MW | Up to 450 |
| Flue gas composition | $\mathrm{CO}_{2}, \mathrm{~N}_{2}, \mathrm{C}_{1}-\mathrm{C}_{5+}$, for up to 20 <br> mole $\% \mathrm{~N}_{2}$, and non $-\mathrm{CO}_{2}$ <br> components up to 40 mole $\%$ |

7.3.1.2. GA-based Oil (Dead and Live Oils) Swelling Factor Due to Flue Gas Injection

The previous model that was developed for oil swelling factor due to $\mathrm{CO}_{2}$ injection (Equations 7-4 and 7-5) was used also for the oil swelling factor due to flue gas injection. The effect of the injected gas composition (including the existence of non- $\mathrm{CO}_{2}$ components) was implicitly included in this model in the gas solubility variable.

For the sensitivity analysis of the GA-based oil swelling factor model, as shown in Fig. 7-28, the oil swelling factor for the heavier oil (oil MW $\geq 300$ ) depends primarily on the flue gas solubility, increasing as the flue gas solubility increases. On the other hand, there is a lesser impact of the oil molecular size as the swelling factor decreases with the higher oil molecular size. Also, from Fig. 7-29, the oil swelling factor for the lighter oil (oil MW<300) depends basically on the flue gas solubility with a lesser impact of the oil molecular size.


Fig. 7-28. Sensitivity analysis of the factors affecting dead and live oils swelling factor for oils with $\mathrm{MW} \geq 300$.


Fig. 7-29. Sensitivity analysis of the factors affecting dead and live oils swelling factor for oils with MW<300.

Table 7-19, Fig. 7-30, and Fig. 7-31 present a comparison between the GA-based oil swelling factor (for dead and live oils) model and the model by Simon and Graue (1965). The GA-based model offered a higher accuracy and could also be applied over a wider range of conditions. Table 7-20 presents a summary of the experimental data range used in this study for testing of the GA-based swelling factor model for dead and live oils. The details of the experimental oil swelling factor (due to flue gas injection) data and the prediction results are presented in Appendix-8.

Table 7-19. Comparison between the GA-based model and Simon and Graue (1965) oil swelling factor models (for dead and live oils).

| Model | Average <br> Error, \% | STDEV, \% | $\mathbf{R}^{\mathbf{2}}$ |
| :---: | :---: | :---: | :---: |
| GA-based | 0.48 | 0.77 | 0.992 |
| Simon and Graue (1965) | 0.68 | 0.95 | 0.992 |



Fig. 7-30. GA-based oil swelling factor (due to flue gas) model prediction results (for dead and live oils).


Fig. 7-31. Comparison results between GA-based and Simon and Graue (1965) oil swelling factor (due to flue gas) models (for dead and live oils).

Table 7-20. Experimental data range used in this study for testing of the GA-based oil (dead and live oils) swelling factor (due to flue gas) model.

| Variable | Experimental data range |
| :---: | :---: |
| Oil API gravity, ${ }^{\circ}$ API | Wider range (14-42) |
| $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Up to 31.72 |
| $\mathrm{~T}_{\mathrm{R}},{ }^{\circ} \mathrm{C}$ | Up to 110 |
| MW | Up to 450 |
| Flue gas composition | $\mathrm{CO}_{2}, \mathrm{~N}_{2}, \mathrm{C}_{1}$, for up to 84.4 |
|  | mole $\% \mathrm{~N}_{2}$, for non $-\mathrm{CO}_{2}$ |
|  | components up to 85.1 mole $\%$ |



Fig. 7-32. Sensitivity analysis of the factors affecting flue gas-oil (dead and live oils) density.

### 7.3.1.3. GA-based Flue Gas-Oil (Dead and Live Oils) Density

The previous model that was developed for the $\mathrm{CO}_{2}$-oil density (Equation 7-6) was used also for the flue gas-oil density, as the effect of the gas solubility is less pronounced on the gas-oil density. From the sensitivity analysis presented in Fig. 7-32, the flue gas-oil density increases with the increase in initial oil density and saturation pressure. Also, there is a lesser impact of the temperature and oil specific gravity.

From the comparison in Table 7-21, Fig. 7-33, and Fig. 7-34, the GA-based model yielded a much lower error than Quail et al. (1988) model. Also, it appeared to be valid over a wider range of conditions. Table $\mathbf{7 - 2 2}$ presents a summary of the experimental data range used in this study for testing of the GA-based flue gas-oil (dead and live oils) density model. The data details of the experimental flue gas-oil density and the prediction results from the GA-based gas-oil density model for the flue gas-oil density are presented in Appendix-9.

Table 7-21. Comparison between the GA-based model and Quail et al. (1988) model for the flue gas-oil density prediction.

| Model | Average <br> Error, \% | STDEV, <br> \% | $\mathbf{R}^{\mathbf{2}}$ |
| :---: | :---: | :---: | :---: |
| GA-based | 0.6 | 0.8 | 0.9963 |
| Quail et al. (1988) | 10.5 | 15.2 | 0.9366 |

Table 7-22. Experimental data range used in this study for testing of the GA-based flue gasoil (dead and live oils) density model.

| Variable | Experimental data range |
| :---: | :---: |
| Oil API gravity, ${ }^{\circ} \mathrm{API}$ | Wider range (14-42) |
| $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Up to 22.41 |
| $\mathrm{T}_{\mathrm{R}},{ }^{\circ} \mathrm{C}$ | Up to 76.7 |
| MW | Up to 440 |
| Flue gas composition | $\mathrm{CO}_{2}, \mathrm{~N}_{2}, \mathrm{C}_{1}, \mathrm{C}_{4}$, for up to 84.4 |
|  | mole $\% \mathrm{~N}_{2}$, for non- $-\mathrm{CO}_{2}$ |
|  | components up to $85.1 \mathrm{~mole} \%$ |



Fig. 7-33. GA-based flue gas-oil density model prediction results.


Fig. 7-34. Comparison results between the GA-based and Quail et al. (1988) flue gas-oil density models.

### 7.3.1.4. GA-based Flue Gas-Oil (Dead and Live Oils) Viscosity

For a reliable prediction of the flue gas-oil viscosity, a GA-based flue gas-oil viscosity model (for dead and live oils) was developed based on the flue gas solubility, saturation pressure, temperature, initial oil viscosity, oil specific gravity, and flue gas composition. The GA-based model was presented as follows:

$$
\begin{equation*}
\mu=\mathrm{y} \mu_{\mathrm{i}}+\mathrm{A}\left(\frac{\text { Sol (mole fraction) }}{\mu_{\mathrm{i}}}\right) \tag{7-10}
\end{equation*}
$$

where,
$y=x^{B}$
$\mathrm{x}=\left(\left(\mathrm{MW}_{\text {flue gas }} \times \mathrm{y}_{\mathrm{CO} 2}\right)^{\mathrm{C}} \times \mu_{\mathrm{i}} \times\left(\frac{145.04 \times \mathrm{P}_{\mathrm{S}}}{\left(1.8 \mathrm{~T}_{\mathrm{R}}+32\right)}\right)^{\mathrm{D}}\right)^{(\gamma \times \text { Sol(mole fraction) })}$

The model coefficients for dead and live oils were developed as follows:

|  | A | B | C | D |
| :---: | :---: | :---: | :---: | :---: |
| Dead oil | -9.5 | -0.732 | 0.45 | 0.23 |
| Live oil | 0 | -0.587 | 0.1 | 1.15 |

Based on the sensitivity analysis presented in Fig. 7-35 (for dead oil) and Fig. 7-36 (for live oil), the GA-based viscosity reduction (flue gas-oil viscosity/initial oil viscosity) depends, basically, on the flue gas solubility, as well as the initial oil viscosity, saturation pressure, oil specific gravity, flue gas composition, and temperature. The impact of the flue gas solubility on the viscosity reduction is much greater for dead oil than for live oil.

For the model test, compared to other models (Mehrotra and Svrcek (1982) and Beggs and Robinson (1975)), the GA-based flue gas-oil viscosity model appeared to yield more accurate results (see Table 7-23, Fig. 7-37, and Fig. 7-38). Table 7-24 presents a summary of the experimental data range used in this study for developing and testing of the flue gas-oil (dead and live oils) viscosity model. The details of the experimental flue gas-oil viscosity data
and the prediction results from the GA-based flue gas-oil viscosity model are presented in Appendix-10.

Table 7-23. Comparison between the GA-based model and other flue gas-oil viscosity literature models.

| Model | Average <br> Error, \% | STDEV, <br> \% | $\mathbf{R}^{\mathbf{2}}$ |
| :---: | :---: | :---: | :---: |
| GA-based | 2.7 | 5.0 | 0.997 |
| Beggs and Robinson (1975) | 12.8 | 18.0 | 0.991 |
| Mehrotra and Svrcek (1982) | 96.6 | 110.63 | 0.516 |



Fig. 7-35. Sensitivity analysis of the factors affecting dead oil viscosity reduction due to flue gas injection.


Fig. 7-36. Sensitivity analysis of the factors affecting live oil viscosity reduction due to flue gas injection.


Fig. 7-37. GA-based flue gas-oil (dead and live oils) viscosity model prediction results.


Fig. 7-38. Comparison results between the GA-based and Beggs and Robinson (1975) flue gas-oil (dead and live oils) viscosity models.

Table 7-24. Experimental data range used in this study for developing and testing of the GAbased flue gas-oil (dead and live oils) viscosity model.

| Variable | Experimental data range |
| :---: | :---: |
| Oil API gravity, ${ }^{\circ} \mathrm{API}$ | Wider range $(14-50)$ |
| $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Up to 21.4 |
| $\mathrm{~T}_{\mathrm{R}},{ }^{\circ} \mathrm{C}$ | Up to 137.22 |
| MW | Up to 450 |
| Oil viscosity, mPa.s | Up to 1677 |
| Flue gas composition | $\mathrm{CO}_{2}, \mathrm{~N}_{2}, \mathrm{C}_{1}-\mathrm{C}_{5+}$, for up to 30 |
|  | mole $\% \mathrm{~N}_{2}$, for non- $-\mathrm{CO}_{2}$ |
|  | components up to 85.1 mole $\%$ |

### 7.3.2. Discussion for the GA-based Flue Gas-Oil Physical Properties

It is evident that the environmental considerations in favour of reducing GHG (flue gas) emissions have given a greater impetus on utilizing (or disposing) flue gases through EOR processes. In addition, gas flood operators, too, are increasingly putting a greater emphasis on using flue gases for EOR, because the experience in the West Texas region has shown that the cost of $\mathrm{CO}_{2}$ separation and compression could be significant and it has been found that too much emphasis on the $\mathrm{CO}_{2}$ purity is disproportionate to the overall economic benefits. Therefore, it is of significant interest to study the interactions between the flue gas and oil to determine the effect of the flue gas injection on the oil physical properties.

As noted earlier, all of the available models were developed, basically, for $\mathrm{CO}_{2}$ injection and the majority of them have been developed for $\mathrm{CO}_{2}$-dead oil physical properties. Also, these models are limited in their application to certain data ranges (as presented above in Section 7.2.2) and they are unable to accurately predict the effect of the injected gas on the live oil properties. Furthermore, these models do not adequately address the effect of the liquefaction pressure (at the specified temperature) on the solubility, in particular. Also, because these models have been developed based on $\mathrm{CO}_{2}$-oil physical properties, they are unable to give an accurate prediction for the flue gas-oil physical properties, especially when the flue gas contains higher non- $\mathrm{CO}_{2}$ content (more than 5-10 mole\%) and $\mathrm{N}_{2}$ content higher than 5mole \%.

This study presents reliable models to predict flue gas-oil physical properties and investigate the interactions between the flue gas and oil taking into consideration all major variables affecting the flue gas-oil mixture physical properties. For the flue gas solubility prediction, the GA-based model considered the effects of the saturation pressure, temperature, oil specific gravity, oil and flue gas compositions, and injected flue gas critical properties. The GA-based oil swelling factor model considered the effects of the oil molecular size and the flue gas solubility, which implicitly took into account the effects of the flue gas composition. To predict the mixture density, the GA-based flue gas-oil density model considered the effects of the saturation pressure, temperature, oil specific gravity, and initial oil density at the specified temperature. For the flue gas-oil viscosity model, the effects of the initial oil viscosity, saturation pressure, temperature, flue gas solubility, oil specific gravity, and flue gas composition were included.

The GA-based models have been validated with published experimental dead and live oils data and compared with available models in the literature. Each GA-based model presented in this study has demonstrated superior performance in terms of its accuracy and covers wider ranges of conditions. In particular, the GA-based models have consistently
presented higher accuracy for flue gases with higher content of non- $\mathrm{CO}_{2}$ components and for flue gas-live oils mixture properties.

### 7.4. Summary

A key parameter in a gas ( $\mathrm{CO}_{2}$ or flue gas) flooding process is the gas solubility; for, it contributes to oil viscosity reduction and oil swelling, which together, in turn, enhance the oil mobility and oil relative permeability. Often injected gas-oil mixture physical properties parameters are established through time-consuming experimental means or using models available in the literature. However, one must recognise that such models for predicting the injected gas-oil physical properties are valid usually for certain data ranges or site-specific conditions. Furthermore, it is to be noted that there is no reliable model available to predict injected gas-live oil physical properties, as most of the available models were developed based on dead oil data. Also, the commonly used literature models do not adequately address the effect of the liquefaction pressure (at the specified temperature) on the solubility, in particular. In addition, because these models have been developed based on the $\mathrm{CO}_{2}$-oil physical properties, they were unable to give an accurate prediction of the flue gas-oil physical properties, especially for flue gases, which contain higher amounts of non- $\mathrm{CO}_{2}$ components.

In this study, a GA-based technique has been used to develop more reliable models to predict $\mathrm{CO}_{2}$ solubility, oil swelling factor, $\mathrm{CO}_{2}$-oil density, and $\mathrm{CO}_{2}$-oil viscosity for both dead and live oils. These models recognised not only all major variables that affect each physical property, but also considered the effect of the $\mathrm{CO}_{2}$ liquefaction pressure. The GAbased models have been successfully validated with published experimental data and compared with several widely used models. The GA-based models have yielded more accurate predictions with lower errors than the other tested models. Furthermore, unlike the literature models, which were applicable to only limited data ranges and conditions, the GAbased models could be applied over a wider range and conditions.

This study also proposed new models to predict the flue gas-oil physical properties. In particular, these models developed for the flue gas-oil properties such as flue gas solubility, impact on the oil swelling factor, and flue gas-oil density and viscosity. These GA-based models utilised all major variables affecting each parameter model including the injected flue gas composition and the flue gas critical properties. In addition, the critical temperature modification factor $\left(\mathrm{MF}_{\mathrm{i}}\right)$ was also used in developing these models. The GA-based flue gasoil physical properties models have been successfully validated with published experimental data and have also been compared against other commonly reported $\mathrm{CO}_{2}$-oil models that are
often used for the flue gas-oil processes. The GA-based models consistently yielded a lower prediction error than the tested models. Furthermore, unlike the other models, which were applicable only over limited data ranges and conditions, the GA-based models could be valid over a much wider range of conditions. They also can be used, successfully, for a wide range of the injected flue gas compositions.

## CHAPTER 8

## Conclusions and Recommendations

### 8.1. Introduction

GA software was developed in this study and was successfully used as a modelling technique. This software has been tested and validated for developing models that minimise the misfit between the experimental and predicted values and has been proved to be an efficient modelling technique within the range of conditions examined.

Using the GA software, two more reliable models for $\mathrm{CO}_{2}$-oil MMP and flue gas-oil MMP have been developed, and then, their predicted values have been compared against those obtained by the commonly used models in the literature. Experimental data available in the public domain were used in development and validation of these models. Furthermore, a package of GA-based models has been developed and successfully validated using data available in the public domain to predict the $\mathrm{CO}_{2}$ flooding effects on the oil physical properties (for dead and live oils properties), notably, $\mathrm{CO}_{2}$ solubility, oil swelling factor, $\mathrm{CO}_{2}{ }^{-}$ oil density, and $\mathrm{CO}_{2}$-oil viscosity. Another package of GA-based models has been developed and successfully validated using data available in the public domain to predict the flue gas flooding effects on the oil physical properties (for dead and live oils properties), notably, flue gas solubility, oil-swelling factor, flue gas-oil density, and flue gas-oil viscosity.

Based on the data used in this study and keeping in mind the limitations of this data, the following conclusions and recommendations are made.

### 8.2. Conclusions

1. The GA technique proved to be an efficient method in testing and developing of the quantitative models.
2. The factors that affect $\mathrm{CO}_{2}$-oil MMP were in the following order, in terms of their impact, the reservoir temperature, $\mathrm{MW}_{\mathrm{C}+}$, and ratio between the volatiles and intermediates. When there are no volatiles fractions in the oil, the intermediates effect on the MMP cannot be ignored.
3. The GA-based $\mathrm{CO}_{2}$-oil MMP model yielded the best prediction with the lowest average error among all other tested models.
4. The flue gas-oil MMP model was a function of the injected flue gas solubility into reservoir oil. The injected gas solubility, in turn, depends on the gas critical properties (pseudocritical temperature and pressure).
5. Compared to other commonly used models, the GA-based flue gas-oil MMP model offered the best prediction with excellent accuracy.
6. GA-based flue gas-oil MMP model could be used for higher $\mathrm{N}_{2}$ content (tested up to $20 \mathrm{~mole} \%$ ) and for different non- $\mathrm{CO}_{2}$ components (e.g., $\mathrm{H}_{2} \mathrm{~S}, \mathrm{~N}_{2}, \mathrm{SO}_{\mathrm{x}}, \mathrm{O}_{2}$, and $\mathrm{C}_{1}-\mathrm{C}_{4}$ ) with higher fractions (tested up to 78 mole\%).
7. Use of the critical temperature modification factor $\left(\mathrm{MF}_{\mathrm{i}}\right)$ in developing the flue gas-oil MMP model improved the relationship between the flue gas-oil MMP, $\mathrm{CO}_{2}$-oil MMP, and the pseudocritical properties of the injected flue gas and pure $\mathrm{CO}_{2}$.
8. The GA-based package of models developed in this study for $\mathrm{CO}_{2}$-oil mixture physical properties prediction presented a more reliable prediction with higher accuracy than the other literature models tested in this study.
9. This study presented high-accuracy models to predict the $\mathrm{CO}_{2}$-live oil mixture properties that based directly on the $\mathrm{CO}_{2}$-live oil mixture data. In contrast, many of the currently available models were based on dead and/or heavy oil properties and they are still used for live oils.
10. Unlike most of the other models, the GA-based models account for all major variables that affect $\mathrm{CO}_{2}$-oil physical properties, including the $\mathrm{CO}_{2}$ liquefaction pressure effect.
11. Besides the higher prediction results with outstanding accuracy, the GA-based models were capable of covering a wider range of oil properties, with regard to oil gravities, pressures up to 34.5 MPa , oil $\mathrm{MW}>490$, oil viscosities up to 12000 mPa .s, and temperatures up to $140^{\circ} \mathrm{C}$.
12. This study presented new models developed basically to study the effects of injected flue gas on the oil physical properties, and consequently on enhanced oil recovery process performance.
13. The GA-based package of models developed in this study presented a more reliable prediction of the flue gas-oil mixture physical properties with higher accuracy than the other literature models, which were developed basically for $\mathrm{CO}_{2}$ and tested in this study for the flue gas-oil properties.
14. Unlike most of the other models, the GA-based models account for all major variables that affect the flue gas-oil physical properties, including the effects of the oil and injected flue gas compositions and the injected gas liquefaction pressure.
15. Besides the higher prediction results with outstanding accuracy than other models, the GA-based models are capable of covering a wider range of oil properties for dead and live oils and also for different flue gas compositions.
16. When data from standard or similar experimental procedures are used, the accuracy of the GA-based models could be further enhanced.
17. In the absence of any measured site-specific miscibility and interactions data and when the project financial situation is a concern, the GA-based models could be used as an effective and convenient predictive tool to guesstimate the miscibility and interaction parameters for initial design calculations. They can be used as a fast track gas flooding project screening guide. In addition, they could contribute towards designing a more efficient and economical experimental programs. Also, they can easily be incorporated into a reservoir simulator for $\mathrm{CO}_{2}$ or flue gas flooding design and simulation.

### 8.3. Recommendations

The GA-based models proposed in this study to predict the miscibility and interactions between the injected gas ( $\mathrm{CO}_{2}$ or flue gas) and oils (dead and live oils) are based on data in the public domain. There is a scarcity of data for certain cases, for example, there is a need for more data especially in cases where the injected flue gas has higher $\mathrm{N}_{2}$ content and also for flue gas-oil mixture viscosity. In view of this, it is envisaged that:

1. The flue gas-oil viscosity model could be improved further with a larger database and more reliable data for it to be applied over a wider range of data and conditions.
2. There is a need for flue gas-oil miscibility and interactions models for injected gas with higher fraction of $\mathrm{N}_{2}$ (more than $20 \mathrm{~mole} \%$ ), as the displacement process
changes from a condensing-vaporizing drive to a vaporizing drive as the $\mathrm{N}_{2}$ concentration is increased.
3. Improvement of the GA software by using different operators, (e.g., two-point crossover or uniform crossover, testing different parent selection techniques, etc) to get better performance in developing of the quantitative models should be attempted.
4. Based on its many advantages indicated in Chapter 4, the applications of the GA technique could also be extended forward developing of the quantitative models.
5. Where possible, standardised data or data from similar experimental setup should be used; for example, currently the MMP data reported in the literature and used in this study came from various sources using different experimental protocols, and hence, the inconsistencies among them are unavoidable.
6. The GA-based models results can be tested/confirmed, experimentally, using one experimental run (especially, for MMP).

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## Appendices

The following appendices present the literature database used in this research for developing and testing of the GA-based models and also the GA software code is presented:

Appendix-1: for $\mathrm{CO}_{2}$-oil MMP experimental data validation.
Appendix -2: for flue gas-oil MMP experimental data validation.
Appendix -3: for $\mathrm{CO}_{2}$ solubility experimental data validation.
Appendix -4: for oil swelling factor (due to $\mathrm{CO}_{2}$ ) experimental data validation.
Appendix -5: for $\mathrm{CO}_{2}$-oil density experimental data validation.
Appendix -6: for $\mathrm{CO}_{2}$-oil viscosity experimental data validation.
Appendix -7: for flue gas solubility experimental data validation.
Appendix -8: for oil swelling factor (due to flue gas) experimental data validation.
Appendix -9: for flue gas-oil density experimental data validation.
Appendix -10: for flue gas-oil viscosity experimental data validation.
Appendix -11: the GA software code.
Appendix-1
Table A-1-1. Experimental data from the literature used for developing and testing of the $\mathrm{CO}_{2}$-oil MMP model.

| Reference | TR, ${ }^{\circ} \mathrm{C}$ | $\mathbf{M W}_{\mathbf{C 5}+}$ | Vol., \% | Interm. \% | Vol./ Interm. | $\mathrm{C}_{2}-\mathrm{C}_{6}, \%$ | $\mathbf{M W}_{\text {C7+ }}$ | Experimental (ММР), МРа |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Alston et al. (1985) | 54.4 | 185.83 | 5.4 | 38.4 | 0.141 | - | - | 9.48 |
| Alston et al. (1985) | 61.1 | 185.83 | 5.4 | 38.4 | 0.141 | - | - | 10.35 |
| Alston et al. (1985) | 54.4 | 185.83 | 5 | 7.5 | 0.667 | - | - | 10.35 |
| Alston et al. (1985) | 54.4 | 185.83 | 22.9 | 38.4 | 0.596 | - | - | 10.35 |
| Alston et al. (1985) | 57.8 | 202.61 | 0.5 | 1.2 | 0.417 | - | - | 11.72 |
| Alston et al. (1985) | 54.4 | 235.56 | 5.4 | 35.5 | 0.152 | - | - | 12.76 |
| Alston et al. (1985) | 67.8 | 203.81 | 31 | 22.9 | 1.354 | 23 | 210 | 16.9 |
| Alston et al. (1985) | 112.2 | 213.5 | 32.7 | 28.1 | 1.164 | 28 | 220 | 24.15 |
| Alston et al. (1985) | 99 | 190.7 | 40.14 | 2.95 | 13.607 | 3 | 195 | 30.28 |
| Alston et al. (1985) | 110 | 180.6 | 32.51 | 35.64 | 0.912 | 36 | 185 | 20.21 |
| Alston et al. (1985) | 71.1 | 221 | 41.27 | 6.99 | 5.904 | 7 | 227 | 23.45 |
| Alston et al. (1985) | 102.2 | 205 | 51.28 | 9.84 | 5.211 | 10 | 210 | 28.17 |
| Alston et al. (1985) | 80 | 240.7 | 53.36 | 8.6 | 6.2 | 9 | 245 | 26.76 |
| Graue and Zana (1981) | 71.1 | 207.9 | 4.4 | 13.9 | 0.317 | 24.68 | 227.94 | 15.52 |
| Dicharry et al. (1973) | 54.4 | 171.2 | 29.48 | 31.82 | 0.928 | 40.05 | 197.4 | 11 |
| Gardner et al. (1981) | 42.8 | 196.1 | 19.35 | 26.8 | 0.722 | 33.12 | 221 | 10.62 |
| Thakur et al. (1984) | 118.3 | 171.1 | 34.2 | 28.6 | 1.1958 | 28.58 | 192 | 23.45 |
| Metcalfe (1982) | 32.2 | 187.77 | 10.5 | 14.28 | 0.735 | 24.44 | 206 | 6.9 |
| Metcalfe (1982) | 40.6 | 187.77 | 10.5 | 14.28 | 0.735 | 24.44 | 206 | 8.28 |
| Metcalfe (1982) | 57.2 | 187.77 | 10.5 | 14.28 | 0.735 | 24.44 | 206 | 11.86 |

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| Metcalfe (1982) | 49 | 187.25 | 34.34 | 22.82 | 1.505 | 26.39 | 200 | 11.04 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Holm and Josendal (1974) | 57.2 | 182.6 | 31.88 | 3.48 | 9.161 | $11^{\text {a }}$ | 196 | 13.79 |
| Holm and Josendal (1974) | 57.2 | 182.6 | 0 | 5.11 | 0 | 16.9 | 197 | $13.10^{\text {b }}$ |
| Holm and Josendal (1974) | 87.8 | 182.6 | 0 | 5.11 | 0 | 16.9 | 197 | $17.24{ }^{\text {b }}$ |
| Holm and Josendal (1974) | 54.4 | 170.5 | 0 | 1.57 | 0 | 9.3 | 178 | $12.07{ }^{\text {b }}$ |
| Rathmell et al. (1971) | 42.8 | 204.1 | 17.07 | 20.95 | 0.815 | 28.83 | 222 | 10.35 |
| Rathmell et al. (1971) | 39.4 | 199.7 | 27.84 | 21.81 | 1.276 | 26.83 | 223 | $13.79{ }^{\text {c }}$ |
| Rathmell et al. (1971) | 85.6 | 247.8 | 44.53 | 18.34 | 2.428 | 13.4 | 268 | $34.49{ }^{\text {d }}$ |
| Dong et al. (2001) | 59 | 205 | 5.45 | 11.35 | 0.48 | $18.93{ }^{\text {a }}$ | $220{ }^{\text {a }}$ | 12.8 |
| Shelton and <br> Yarborough (1977) | 34.4 | 212.56 | 16.78 | 10.76 | 1.56 | 17.7 | 227 | 10 |
| Henry and Metcalfe (1983) | 48.9 | 205.1 | 12.5 | 22.62 | 0.5526 | 31 | 227 | 10.59 |
| Bon and Sarma (2004) | 137.22 | 136.17 | 24.68 | 39.37 | 0.6269 | 30.59 | 149.6 | $19.38{ }^{\text {e }}$ |
| Bou-Mikael (2002) | 73.89 | 231 | 0 | 0.002 | 0 | 0.0025 | 231.4 | 22.83 |
| Metcalfe (1982) | 65.6 | 187.25 | 34.34 | 22.82 | 1.505 | 26.39 | 200 | 13.45 |
| - = Not available, $\mathrm{a}=$ approximate value, $\mathrm{b}=\mathrm{P}_{\mathrm{b}}$ less than $0.345 \mathrm{MPa}, \mathrm{c}=\mathrm{P}_{\mathrm{b}}$ equal to 10.62 MPa , $\mathrm{d}=\mathrm{P}_{\mathrm{b}}$ equal to 29.2 MPa, $\quad \mathrm{e}=\mathrm{P}_{\mathrm{b}}$ equal to $16.2 \mathrm{MPa}, \quad$ Vol.=Volatile, $\quad$ Interm. $=$ Intermediates. |  |  |  |  |  |  |  |  |

[^0]Appendix-1
Table A-1-2. The GA-based $\mathrm{CO}_{2}$-oil MMP model prediction results and comparison of its accuracy against other commonly used models accuracy.

| $\begin{array}{\|c} \text { Experimental } \\ \mathrm{MMP}, \\ \mathrm{MPa} \end{array}$ | GA-based $\mathrm{CO}_{2}$-oil MMP |  | Alston et al. (1985) |  | Glaso (1985) |  | Cronquist (1978) |  | Yellig and Metcalfe (1980) |  | Holm and Josendal (1974) |  | Lee (1979) |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | MMP, MPa | Error\% | MMP, MPa | Error\% | MMP, MPa | Error\% | MMP, MPa | Error\% | MMP, MPa | Error\%\| | MMP, MPa | Error\% | MMP, MPa | Error\% |
| 9.48 | 9.34 | 1.50 | 8.84 | 6.83 | - | - | 11.7 | 22.96 | 11.25 | 18.6 | 12.8 | 34.91 | 11.65 | 22.81 |
| 10.35 | 10.35 | 0.09 | 9.70 | 6.2 | - | - | 12.7 | 22.65 | 12.31 | 19.0 | 12.1 | 16.67 | 13.11 | 26.7 |
| 10.35 | 11.07 | 6.98 | 10.92 | 5.51 | - | - | 11.6 | 12.38 | 11.25 | 8.7 | 12.8 | 23.67 | 11.65 | 12.6 |
| 10.35 | 10.93 | 5.69 | 10.75 | 3.91 | - | - | 13.3 | 28.38 | 11.25 | 8.7 | 12.8 | 23.67 | 11.65 | 12.6 |
| 11.72 | 12.30 | 4.87 | 12.53 | 6.9 | - | - | 12.9 | 9.63 | 11.78 | 0.5 | 13.4 | 14.71 | 12.36 | 5.44 |
| 12.76 | 12.53 | 1.83 | 13.61 | 6.7 | - | - | 15.2 | 19.4 | 11.25 | 11.8 | 14.0 | 9.73 | 11.65 | 8.72 |
| 16.90 | 16.28 | 3.66 | 16.95 | 0.33 | 13.6 | 19.6 | 18.5 | 9.22 | 13.33 | 21.1 | 15.6 | 7.76 | 14.68 | 13.1 |
| 24.15 | 27.59 | 14.22 | 28.11 | 16.37 | 20.9 | 13.42 | 30.4 | 25.71 | 20.02 | 17.1 | - | - | 28.32 | 17.23 |
| 30.28 | 27.76 | 8.33 | 28.64 | 5.42 | 30.0 | 0.96 | 25.2 | 16.67 | 17.97 | 40.6 | 20.6 | 31.82 | 23.64 | 21.93 |
| 20.21 | 21.54 | 6.57 | 19.82 | 1.92 | 19.1 | 5.46 | 24.4 | 21.0 | 19.67 | 2.7 | 21.4 | 5.8 | 27.50 | 36.1 |
| 23.45 | 22.03 | 6.07 | 24.91 | 6.24 | 23.6 | 0.7 | 22.9 | 2.44 | 13.83 | 41.0 | 17.2 | 26.47 | 15.52 | 33.83 |
| 28.17 | 28.18 | 0.02 | 29.45 | 4.53 | 25.2 | 10.6 | 31.0 | 9.92 | 18.48 | 34.4 | 22.4 | 20.44 | 24.76 | 12.12 |
| 26.76 | 27.42 | 2.48 | 32.30 | 20.7 | 24.4 | 8.7 | 31.1 | 16.35 | 15.15 | 43.4 | 22.1 | 17.53 | 17.88 | 33.18 |
| 15.52 | 14.88 | 4.12 | 15.01 | 3.26 | 14.8 | 4.9 | 16.0 | 2.93 | 13.83 | 10.9 | 16.6 | 6.67 | 15.52 | 0.013 |
| 11 | 10.40 | 5.79 | 9.87 | 10.3 | 11.4 | 3.6 | 12.9 | 17.21 | 11.25 | 2.3 | - | - | 11.65 | 5.9 |
| 10.62 | 9.70 | 8.71 | 10.07 | 5.15 | 10.0 | 6.00 | 11.5 | 8.1 | 9.24 | 13.0 | 11.1 | 4.55 | 9.36 | 11.9 |
| 23.45 | 22.38 | 4.58 | 19.97 | 14.83 | 20.4 | 12.8 | 24.9 | 6.27 | 20.98 | 10.5 | - | - | 30.63 | 30.6 |
| 6.90 | 7.37 | 6.93 | 7.63 | 10.63 | 8.2 | 18.8 | 8.6 | 24.32 | 7.08 | 2.7 | 9.7 | 40.0 | 7.57 | 9.73 |
| 8.28 | 8.83 | 6.67 | 8.98 | 8.55 | 9.4 | 14.0 | 10.0 | 20.26 | 8.82 | 6.6 | 10.8 | 30.0 | 8.96 | 8.26 |
| 11.86 | 11.84 | 0.22 | 11.73 | 1.15 | 11.9 | 0.47 | 12.7 | 7.0 | 11.70 | 1.4 | 13.3 | 12.2 | 12.24 | 3.2 |
| 11.04 | 11.12 | 0.74 | 11.35 | 2.9 | 10.6 | 3.8 | 13.4 | 21.9 | 10.32 | 6.4 | 11.9 | 8.13 | 10.52 | 4.71 |

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| 13.79 | 15.07 | 9.24 | 15.73 | 14.0 | $17.3{ }^{\text {d }}$ | 25.6 | 14.5 | 5.03 | 11.70 | 15.2 | 13.3 | 3.5 | 12.24 | 11.25 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $13.10^{\text {a }}$ | 12.67 | 3.28 | 11.64 | 11.21 | 12.4 | 5.32 | 11.4 | 12.94 | 11.70 | 10.7 | 13.3 | 1.58 | 12.24 | 6.6 |
| $17.24{ }^{\text {a }}$ | 18.89 | 9.53 | 16.71 | 3.1 | 16.8 | 2.46 | 15.8 | 8.6 | 16.31 | 5.4 | 18.6 | 8.0 | 20.13 | 16.75 |
| $12.07{ }^{\text {a }}$ | 11.48 | 4.91 | 9.89 | 18.02 | 18.3 | 52.0 | 10.3 | 14.53 | 11.25 | 6.8 | - | - | 11.65 | 3.5 |
| 10.35 | 10.31 | 0.36 | 11.00 | 6.30 | 10.0 | 3.31 | 11.8 | 13.8 | 9.24 | 10.7 | 10.9 | 5.33 | 9.36 | 9.54 |
| 13.79 | $\begin{gathered} 9.9^{b} \\ (10.62) \end{gathered}$ | $\begin{gathered} 28.3 \\ (23.0) \end{gathered}$ | $\begin{gathered} \mathbf{1 0 . 5 8}^{\text {b }} \\ (\mathbf{1 0 . 6 2}) \end{gathered}$ | $\begin{gathered} 23.24 \\ (23) \\ \hline \end{gathered}$ | 9.5 | 31.20 | 11.7 | 14.9 | $\begin{gathered} 8.6^{\mathrm{b}} \\ (10.62) \end{gathered}$ | $\begin{gathered} \hline 37.6 \\ (23.0) \\ \hline \end{gathered}$ | 10.6 | 23.5 | $\begin{gathered} \hline 8.76^{b} \\ (10.62) \end{gathered}$ | $\begin{array}{\|c\|} \hline 36.5 \\ (23.0) \\ \hline \end{array}$ |
| 34.49 | $\begin{gathered} 27.35^{\mathrm{c}} \\ (29.20) \\ \hline \end{gathered}$ | $\begin{gathered} \hline 20.7 \\ (15.3) \\ \hline \end{gathered}$ | 31.75 | 7.93 | 23.6 | 31.54 | 32.1 | 6.9 | $\begin{gathered} 16^{\mathrm{c}} \\ (29.20) \\ \hline \end{gathered}$ | $\begin{array}{\|c\|} \hline 53.7 \\ (15.3) \\ \hline \end{array}$ | - | - | $\begin{gathered} 19.47^{\mathrm{c}} \\ (29.20) \\ \hline \end{gathered}$ | $\begin{array}{\|l\|} \hline 43.54 \\ (15.3) \\ \hline \end{array}$ |
| 12.80 | 12.90 | 0.78 | 13.26 | 3.6 | 12.5 | 2.20 | 13.7 | 7.21 | 11.98 | 6.5 | 13.8 | 7.73 | 12.63 | 1.34 |
| 10.00 | 9.77 | 2.27 | 11.04 | 10.36 | 8.7 | 13.0 | 10.6 | 5.8 | 7.58 | 24.2 | 10.2 | 2.07 | 7.92 | 20.8 |
| 10.59 | 11.12 | 5.03 | 11.65 | 10.0 | 11.1 | 4.86 | 12.6 | 19.0 | 10.32 | 2.5 | 12.1 | 14.0 | 10.52 | 0.68 |
| 19.38 | 18.45 | 4.80 | $\begin{gathered} 14^{\mathrm{d}} \\ (16.2) \end{gathered}$ | $\begin{gathered} 27.85 \\ (16.4) \\ \hline \end{gathered}$ | 23.7 | 22.45 | 21 | 8.4 | 24.07 | 24.3 | - | - | 38.47 | 98.6 |
| $22.83{ }^{\text {a }}$ | 22.89 | 0.26 | 21.86 | 4.2 | 30.1 | 31.94 | 18.11 | 20.63 | 14.24 | 37.6 | 18.48 | 19 | 16.23 | 28.9 |
| 13.45 | 14.42 | 7.25 | 14.38 | 6.95 | 13.0 | 3.04 | 16.8 | 25.1 | 12.99 | 3.4 | 14.9 | 10.77 | 14.15 | 5.2 |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Average error, after $\mathrm{P}_{\mathrm{b}}$ modification, \% |  | 5.47 |  | 8.34 |  | 12.6 |  | 14.32 |  | 14.9 |  | 15.37 |  | 16.8 |
| STDEV, after $\mathrm{P}_{\mathrm{b}}$ modification, \% |  | 7.4 |  | 10.2 |  | 18.0 |  | 16.3 |  | 19.5 |  | 18.9 |  | 24.6 |
| a | =These data points have a $\mathrm{P}_{\mathrm{b}}$ less than 0.345 MPa , |  |  |  |  |  |  | c | $=\mathrm{MMP}$ value should be $29.2 \mathrm{MPa}\left(\mathrm{P}_{\mathrm{b}}\right.$ modification), |  |  |  |  |  |
| b | $=\mathrm{MMP}$ value should be $10.62 \mathrm{MPa}\left(\mathrm{P}_{\mathrm{b}}\right.$ modification), |  |  |  |  |  |  | d | $=\mathrm{MMP}$ value should be $16.2 \mathrm{MPa}\left(\mathrm{P}_{\mathrm{b}}\right.$ modification). |  |  |  |  |  |

Appendix-2
Table A-2-1. Literature experimental data used for developing and testing of the GA-based flue gas-oil MMP model and the model prediction results.

| Reference | Flue gas composition (Mole, \%) | $\mathrm{T}_{\mathbf{C W}},{ }^{\circ} \mathrm{C}$ | Pure $\mathrm{CO}_{2}$-oil MMP, MPa | Experimental flue gas-oil MMP, MPa | GA-based MMP, MPa | GA-based error, \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Alston et al. (1985) | 92.5\% $\mathrm{CO}_{2}, 7.5 \% \mathrm{C}_{1}$ | 26.69 | 9.48 | 10.35 | 10.79 | 4.3 |
| Alston et al. (1985) | 90\% $\mathrm{CO}_{2}, 10 \% \mathrm{C}_{1}$ | 25.10 | 11.13 | 13.10 | 13.59 | 3.7 |
| Alston et al. (1985) | 92.25\% $\mathrm{CO}_{2}, 7.75 \% \mathrm{n}-\mathrm{C}_{4}$ | 43.15 | 24.15 | 19.69 | 18.21 | 7.5 |
| Alston et al. (1985) | 95\% $\mathrm{CO}_{2}, 5 \% \mathrm{n}-\mathrm{C}_{4}$ | 38.92 | 23.45 | 18.62 | 18.71 | 0.5 |
| Alston et al. (1985) | $90.5 \% \mathrm{CO}_{2}, 9.5 \% \mathrm{C}_{3}$ | 37.28 | 23.45 | 18.62 | 18.91 | 1.5 |
| Alston et al. (1985) | 87.5\% $\mathrm{CO}_{2}, 6.3 \% \mathrm{~N}_{2}, 6.2 \% \mathrm{n}-\mathrm{C}_{4}$ | 29.20 | 25.14 | 23.17 | 24.42 | 5.4 |
| Alston et al. (1985) | $86.4 \% \mathrm{CO}_{2}, 10.7 \% \mathrm{C}_{1}, 2.9 \% \mathrm{n}-\mathrm{C}_{4}$ | 29.76 | 24.28 | 23.10 | 23.72 | 2.7 |
| Graue and Zana (1981) | 95\% $\mathrm{CO}_{2}, 4.9 \% \mathrm{C}_{1}, 0.1 \% \mathrm{~N}_{2}$ | 28.07 | 15.52 | 16.83 | 16.69 | 0.8 |
| Dicharry et al. (1973) | 90\% $\mathrm{CO}_{2}, 10 \% \mathrm{C}_{1}$ | 25.10 | 11.04 | 12.76 | 13.47 | 5.6 |
| Metcalfe (1982) | $75 \% \mathrm{CO}_{2}, 25 \% \mathrm{H}_{2} \mathrm{~S}$ | 35.27 | 8.28 | 7.53 | 7.49 | 0.5 |
| Metcalfe (1982) | $50 \% \mathrm{CO}_{2}, 50 \% \mathrm{H}_{2} \mathrm{~S}$ | 40.02 | 8.28 | 6.55 | 7.36 | 12.4 |
| Metcalfe (1982) | 90\% $\mathrm{CO}_{2}, 10 \% \mathrm{C}_{1}$ | 25.10 | 8.28 | 11.04 | 10.10 | 8.4 |
| Metcalfe (1982) | 45\% $\mathrm{CO}_{2}, 10 \% \mathrm{C}_{1}, 45 \% \mathrm{H}_{2} \mathrm{~S}$ | 33.01 | 8.28 | 8.83 | 8.07 | 8.6 |
| Metcalfe (1982) | 60\% $\mathrm{CO}_{2}, 20 \% \mathrm{C}_{1}, 20 \% \mathrm{H}_{2} \mathrm{~S}$ | 21.47 | 8.28 | 14.07 | 12.34 | 12.3 |
| Metcalfe (1982) | $67.5 \% \mathrm{CO}_{2}, 10 \% \mathrm{C}_{1}, 22.5 \% \mathrm{H}_{2} \mathrm{~S}$ | 28.82 | 11.72 | 12.41 | 12.63 | 1.8 |
| Metcalfe (1982) | $45 \% \mathrm{CO}_{2}, 10 \% \mathrm{C}_{1}, 45 \% \mathrm{H}_{2} \mathrm{~S}$ | 33.01 | 11.72 | 10.38 | 11.43 | 10.2 |
| Metcalfe (1982) | 60\% $\mathrm{CO}_{2}, 20 \% \mathrm{C}_{1}, 20 \% \mathrm{H}_{2} \mathrm{~S}$ | 21.47 | 11.72 | 17.24 | 17.49 | 1.4 |
| Metcalfe (1982) | 90\% $\mathrm{CO}_{2}, 10 \% \mathrm{C}_{2}$ | 31.47 | 11.04 | 10.07 | 10.29 | 2.2 |


| Metcalfe (1982) | 90\% $\mathrm{CO}_{2}, 10 \% \mathrm{C}_{3}$ | 37.61 | 11.04 | 9.31 | 8.84 | 5.1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Metcalfe (1982) | $90 \% \mathrm{CO}_{2}, 10 \% \mathrm{C}_{4}$ | 44.35 | 11.04 | 7.90 | 8.08 | 2.3 |
| Metcalfe (1982) | 80\% $\mathrm{CO}_{2}, 20 \% \mathrm{C}_{2}$ | 31.92 | 11.04 | 9.66 | 9.88 | 2.3 |
| Metcalfe (1982) | 80\% $\mathrm{CO}_{2}, 20 \% \mathrm{C}_{3}$ | 44.17 | 11.04 | 7.93 | 7.92 | 0.1 |
| Metcalfe (1982) | 90\% $\mathrm{CO}_{2}, 10 \% \mathrm{C}_{2}$ | 31.47 | 13.45 | 13.04 | 12.54 | 3.8 |
| Metcalfe (1982) | 90\% $\mathrm{CO}_{2}, 10 \% \mathrm{C}_{3}$ | 37.61 | 13.45 | 11.04 | 10.77 | 2.4 |
| Metcalfe (1982) | 90\% $\mathrm{CO}_{2}, 10 \% \mathrm{C}_{4}$ | 44.35 | 13.45 | 8.97 | 9.85 | 9.8 |
| Metcalfe (1982) | 80\% $\mathrm{CO}_{2}, 20 \% \mathrm{C}_{2}$ | 31.92 | 13.45 | 12.88 | 12.04 | 6.5 |
| Metcalfe (1982) | 80\% $\mathrm{CO}_{2}, 20 \% \mathrm{C}_{3}$ | 44.17 | 13.45 | 10.50 | 9.65 | 8.0 |
| Metcalfe (1982) | 80\% $\mathrm{CO}_{2}, 20 \% \mathrm{C}_{1}$ | 18.35 | 8.28 | 14.83 | 13.86 | 6.5 |
| Metcalfe (1982) | 68\% $\mathrm{CO}_{2}, 22 \% \mathrm{H}_{2} \mathrm{~S}, 10 \% \mathrm{C}_{1}$ | 28.74 | 8.28 | 10.28 | 8.94 | 13.0 |
| Metcalfe (1982) | $40 \% \mathrm{CO}_{2}, 40 \% \mathrm{H}_{2} \mathrm{~S}, 20 \% \mathrm{C} 1$ | 24.99 | 8.28 | 12.06 | 10.80 | 10.4 |
| Metcalfe (1982) | $75 \% \mathrm{CO}_{2}, 25 \% \mathrm{H}_{2} \mathrm{~S}$ | 35.27 | 11.72 | 10.35 | 10.62 | 2.6 |
| Metcalfe (1982) | $50 \% \mathrm{CO}_{2}, 50 \% \mathrm{H}_{2} \mathrm{~S}$ | 40.02 | 11.72 | 8.97 | 10.43 | 16.4 |
| Metcalfe (1982) | 90\% $\mathrm{CO}_{2}, 10 \% \mathrm{C}_{1}$ | 25.10 | 11.72 | 15.17 | 14.31 | 5.7 |
| Metcalfe (1982) | 80\% $\mathrm{CO}_{2}, 20 \% \mathrm{C}_{1}$ | 18.35 | 11.72 | 18.74 | 19.63 | 4.8 |
| Metcalfe (1982) | $55 \% \mathrm{CO}_{2}, 25 \% \mathrm{H}_{2} \mathrm{~S}, 20 \% \mathrm{C}_{1}$ | 22.18 | 11.72 | 16.45 | 17.04 | 3.6 |
| Zick (1986) | $\begin{gathered} 22.18 \% \mathrm{CO}_{2}, 23.49 \% \mathrm{C}_{1}, 23.5 \% \\ \mathrm{C}_{2}, 27.4 \% \mathrm{C}_{3}, 3.38 \% \mathrm{C}_{4} \\ \hline \end{gathered}$ | 44.66 | 30.19 | 16.55 | 16.75 | 1.2 |
| Cardenas et al. (1984) | $79.2 \% \mathrm{CO}_{2}, 8.8 \% \mathrm{~N}_{2}, 12 \% \mathrm{n}-\mathrm{C}_{4}$ | 33.70 | 25.14 | 23.17 | 20.19 | 12.9 |
| Dong et al. (2001b) | 94.1\% $\mathrm{CO}_{2}, 3.1 \% \mathrm{~N}_{2}, 2.8 \% \mathrm{C}_{1}$ | 23.64 | 12.80 | 14.50 | 16.79 | 15.7 |
| Dong et al. (2001b) | $90.1 \% \mathrm{CO}_{2}, 9.9 \% \mathrm{C}_{1}$ | 24.95 | 12.80 | 16.01 | 15.74 | 1.7 |
| Dong (1999) | 60\% $\mathrm{CO}_{2}, 10 \% \mathrm{~N}_{2}, 30 \% \mathrm{SO}_{2}$ | 15.49 | 12.01 | 23.00 | 23.58 | 2.5 |
| Dong et al. (2001b) | $89.8 \% \mathrm{CO}_{2}, 5.1 \% \mathrm{~N}_{2}, 5.1 \% \mathrm{C}_{1}$ | 18.00 | 12.80 | 20.51 | 21.93 | 6.9 |
| Dong (1999) | $90 \% \mathrm{CO}_{2}, 5 \% \mathrm{O}_{2}, 5 \% \mathrm{~N}_{2}$ | 15.73 | 12.01 | 23.00 | 22.74 | 1.1 |
| Dong (1999) | 85\% $\mathrm{CO}_{2}, 15 \% \mathrm{~N}_{2}$ | 1.62 | 12.01 | 33.01 | 34.10 | 3.3 |
| Dong (1999) | 65\% $\mathrm{CO}_{2}, 15 \% \mathrm{~N}_{2}, 20 \% \mathrm{SO}_{2}$ | 5.05 | 12.01 | 34.01 | 32.59 | 4.2 |
| Dong (1999) | $\mathbf{9 0 \%} \mathrm{CO}_{2}, \mathbf{1 0 \%} \mathrm{H}_{2} \mathrm{~S}$ | 32.70 | 12.01 | 11.60 | 11.25 | 3.1 |
| Dong (1999) | $\mathbf{8 0 \%} \mathrm{CO}_{2}, \mathbf{2 0 \%} \mathrm{H}_{2} \mathrm{~S}$ | 34.38 | 12.01 | 11.40 | 10.97 | 3.7 |

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| Dong (1999) | $70 \% \mathrm{CO}_{2}, \mathbf{3 0 \%} \mathbf{H}_{2} \mathrm{~S}$ | 36.19 | 12.01 | 10.40 | 10.80 | 3.8 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Dong (1999) | $\mathbf{9 0 \%} \mathrm{CO}_{2}, \mathbf{1 0 \%} \mathrm{SO}_{2}$ | 31.58 | 12.01 | 10.50 | 11.53 | 9.8 |
| Dong (1999) | $\begin{gathered} \hline 80 \% \mathrm{CO}_{2}, 5 \% \mathrm{O}_{2}, 5 \% \mathrm{~N}_{2}, 10 \% \\ \mathrm{SO}_{2} \end{gathered}$ | 17.01 | 12.01 | 22.50 | 21.49 | 4.5 |
| Dong et al. (2001a) | 94.4\% $\mathrm{CO}_{2}, 5.6 \% \mathrm{C}_{2}$ | 31.29 | 16.50 | 16.01 | 15.61 | 2.5 |
| Dong et al. (2001a) | 70.8\% $\mathrm{CO}_{2}, 29.2 \% \mathrm{C}_{2}$ | 32.37 | 16.50 | 14.50 | 14.19 | 2.2 |
| Dong et al. (2001a) | $\mathbf{6 0 \%} \mathrm{CO}_{2}, 40 \% \mathrm{C}_{2}$ | 32.92 | 16.50 | 13.60 | 13.50 | 0.8 |
| Dong et al. (2001a) | 46.3\% $\mathrm{CO}_{2}, 53.7 \% \mathrm{C}_{2}$ | 33.69 | 16.50 | 11.90 | 12.60 | 5.9 |
| Dong et al. (2001a) | $\mathbf{9 7 \%} \mathrm{CO}_{2}, \mathbf{3 \%} \mathrm{C}_{3}$ | 33.02 | 16.50 | 14.80 | 14.87 | 0.5 |
| Dong et al. (2001a) | $\mathbf{9 4 . 9 \%} \mathrm{CO}_{2}, \mathbf{5 . 1 \%} \mathrm{C}_{3}$ | 34.40 | 16.50 | 14.30 | 14.26 | 0.3 |
| Dong et al. (2001a) | 88.4\% $\mathrm{CO}_{2}, 11.6 \% \mathrm{C}_{3}$ | 38.66 | 16.50 | 13.00 | 12.96 | 0.3 |
| Dong et al. (2001a) | 84.1\% $\mathrm{CO}_{2}, 15.9 \% \mathrm{C}_{3}$ | 41.48 | 16.50 | 12.40 | 12.37 | 0.2 |
| Dong et al. (2001a) | 80.4\% $\mathrm{CO}_{2}, 19.6 \% \mathrm{C}_{3}$ | 43.91 | 16.50 | 11.40 | 11.89 | 4.3 |
| Dong et al. (2001a) | 75.7\% $\mathrm{CO}_{2}, 24.3 \% \mathrm{C}_{3}$ | 46.99 | 16.50 | 11.00 | 11.20 | 1.8 |
| Dong et al. (2001a) | $\mathbf{6 8 . 3 \%} \mathrm{CO}_{2}, 31.7 \% \mathrm{C}_{3}$ | 51.85 | 16.50 | 10.30 | 9.85 | 4.4 |
| Dong et al. (2001a) | 63.4\% $\mathrm{CO}_{2}, 36.6 \% \mathrm{C}_{3}$ | 55.07 | 16.50 | 9.10 | 9.11 | 0.1 |
| Holm and Josendal (1974) | $90 \% \mathrm{CO}_{2}, 10 \% \mathrm{C}_{1}$ | 25.10 | 13.10 | 16.21 | 16.00 | 1.3 |
| Stalkup (1984) | 80\% $\mathrm{CO}_{2}, 20 \% \mathrm{C}_{1}$ | 18.35 | 8.28 | 13.79 | 13.86 | 0.5 |
| Stalkup (1984) | $\mathbf{8 0 \%} \mathrm{CO}_{2}, 20 \% \mathrm{~N}_{2}$ | -9.26 | 8.28 | 28.97 | 29.16 | 0.66 |
| Average Error, \% = |  |  |  |  |  | 4.6 |

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| $\begin{gathered} \mathrm{CO}_{2} \text {-oil } \\ \text { MMP, } \\ \text { MPa } \end{gathered}$ | Flue gas composition (Mole, \%) | Experimental flue gas-oil MMP, MPa | GA- <br> based <br> MMP, <br> MPa | GAbased error, \% | Sebastian <br> et al. <br> MMP <br> MPa | Sebastian et al. error, \% | Alston et al. MMP, MPa | Alston et al. error, \% | Dong MMP, MPa | Dong error, \% | Kovarik MMP (mole), MPa | Kovarik (mole) error, \% | Eakin \& Mitch MMP, MPa | Eakin \& Mitch error, \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 9.48 | $\begin{gathered} 92.5 \% \mathrm{CO}_{2}, \\ 7.5 \% \mathrm{C}_{1} \\ \hline \end{gathered}$ | 10.35 | 10.79 | 4.3 | 11.38 | 10.0 | 10.91 | 5.5 | 11.20 | 8.3 | 13.9 | 34.6 | - | - |
| 11.13 | $\begin{gathered} 90 \% \mathrm{CO}_{2}, 10 \% \\ \mathrm{C}_{1} \\ \hline \end{gathered}$ | 13.1 | 13.59 | 3.7 | 14.19 | 8.3 | 13.60 | 3.8 | 13.88 | 5.9 | 17.0 | 29.8 | - | - |
| 24.15 | $\begin{gathered} 92.25 \% \mathrm{CO}_{2}, \\ 7.75 \% \mathrm{nC}_{4} \\ \hline \end{gathered}$ | 19.69 | 18.21 | 7.5 | 19.86 | 0.8 | 17.11 | 13.1 | 27.27 | 38.5 | 19.5 | 0.8 | - | - |
| 23.45 | $\begin{gathered} 95 \% \mathrm{CO}_{2}, 5 \% \\ \mathrm{nC}_{4} \\ \hline \end{gathered}$ | 18.62 | 18.71 | 0.5 | 20.64 | 10.8 | 18.26 | 2.0 | 25.37 | 36.2 | 20.5 | 10.1 | - | - |
| 23.45 | $\begin{gathered} 90.5 \% \mathrm{CO}_{2}, \\ 9.5 \% \mathrm{C}_{3} \end{gathered}$ | 18.62 | 18.91 | 1.5 | 20.56 | 10.4 | 19.05 | 2.3 | 25.43 | 36.6 | 20.4 | 9.6 | - | - |
| 25.14 | $\begin{gathered} 87.5 \% \mathrm{CO}_{2}, \\ 6.3 \% \mathrm{~N}_{2}, 6.2 \% \\ \mathrm{nC}_{4} \end{gathered}$ | 23.17 | 24.42 | 5.4 | 27.22 | 17.5 | 22.66 | 2.2 | 45.16 | 94.9 | 27.1 | 17.1 | - | - |
| 24.28 | $\begin{gathered} 86.4 \% \mathrm{CO}_{2}, \\ 10.7 \% \mathrm{C}_{1}, 2.9 \% \\ \mathrm{nC}_{4} \end{gathered}$ | 23.1 | 23.72 | 2.7 | 29.21 | 26.4 | 23.95 | 3.6 | 32.08 | 38.8 | 28.8 | 24.6 | - | - |
| 15.5 | $\begin{gathered} 95 \% \mathrm{CO}_{2}, 4.9 \% \\ \mathrm{C}_{1}, 0.1 \% \mathrm{~N}_{2} \\ \hline \end{gathered}$ | 16.83 | 16.69 | 0.8 | 17.55 | 4.3 | 17.00 | 1.0 | 17.46 | 3.7 | 18.6 | 10.2 | 20.4 | 21.2 |
| 11.0 | $\begin{gathered} 90 \% \mathrm{CO}_{2}, 10 \% \\ \mathrm{C}_{1} \end{gathered}$ | 12.76 | 13.47 | 5.6 | 14.07 | 10.2 | 13.48 | 5.6 | 13.76 | 7.8 | 16.9 | 32.6 | 18.8 | 47.1 |
| 8.28 | 75\% $\mathrm{CO}_{2}, 25 \%$ | 7.53 | 7.49 | 0.5 | 7.42 | 1.4 | 7.13 | 5.4 | 7.16 | 4.9 | -0.3 | 104.1 | 17.5 | 131.7 |


| Appendix-2 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{H}_{2} \mathrm{~S}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 8.28 | $\begin{gathered} \hline 50 \% \mathrm{CO}_{2}, 50 \% \\ \mathrm{H}_{2} \mathrm{~S} \\ \hline \end{gathered}$ | 6.55 | 7.36 | 12.4 | 6.68 | 1.9 | 6.27 | 4.3 | 6.17 | 5.9 | -9.0 | 237.7 | 20.9 | 218.3 |
| 8.28 | $\begin{gathered} 90 \% \mathrm{CO}_{2}, 10 \% \\ \mathrm{C}_{1} \end{gathered}$ | 11.04 | 10.1 | 8.4 | 10.55 | 4.4 | 10.11 | 8.4 | 10.32 | 6.5 | 14.2 | 28.3 | 20.4 | 84.5 |
| 8.28 | $\begin{gathered} 45 \% \mathrm{CO}_{2}, \\ 10 \% \mathrm{C}_{1}, 45 \% \\ \mathrm{H}_{2} \mathrm{~S} \\ \hline \end{gathered}$ | 8.83 | 8.07 | 8.6 | 8.65 | 2.0 | 7.22 | 18.3 | 8.04 | 8.9 | -1.5 | 117.3 | 20.0 | 126.9 |
| 8.28 | $\begin{gathered} 60 \% \mathrm{CO}_{2}, 20 \% \\ \mathrm{C}_{1}, 20 \% \mathrm{H}_{2} \mathrm{~S} \\ \hline \end{gathered}$ | 14.07 | 12.34 | 12.3 | 12.29 | 12.7 | 11.12 | 21.0 | 11.47 | 18.5 | 12.9 | 8.0 | 21.8 | 55.2 |
| 11.7 | $\begin{gathered} 67.5 \% \mathrm{CO}_{2}, \\ 10 \% \mathrm{C}_{1}, 22.5 \% \\ \mathrm{H}_{2} \mathrm{~S} \end{gathered}$ | 12.41 | 12.63 | 1.8 | 13.54 | 9.1 | 12.00 | 3.4 | 12.93 | 4.2 | 9.8 | 21.4 | 21.1 | 70.3 |
| 11.7 | $\begin{gathered} 45 \% \mathrm{CO}_{2}, \\ 10 \% \mathrm{C}_{1}, 45 \% \\ \mathrm{H}_{2} \mathrm{~S} \\ \hline \end{gathered}$ | 10.38 | 11.43 | 10.2 | 12.26 | 18.1 | 10.22 | 1.5 | 11.39 | 9.8 | 1.9 | 81.5 | 21.7 | 108.6 |
| 11.7 | $\begin{gathered} \hline 60 \% \mathrm{CO}_{2}, 20 \% \\ \mathrm{C}_{1}, 20 \% \mathrm{H}_{2} \mathrm{~S} \\ \hline \end{gathered}$ | 17.24 | 17.49 | 1.4 | 17.41 | 0.9 | 15.75 | 8.6 | 16.25 | 5.8 | 16.4 | 5.0 | 23.1 | 33.9 |
| 11.0 | $\begin{gathered} 90 \% \mathrm{CO}_{2}, 10 \% \\ \mathrm{C}_{2} \\ \hline \end{gathered}$ | 10.07 | 10.29 | 2.2 | 11.01 | 9.4 | 10.43 | 3.6 | 11.05 | 9.7 | 11.1 | 10.3 | 17.6 | 75.2 |
| 11.0 | $\begin{gathered} 90 \% \mathrm{CO}_{2}, 10 \% \\ \mathrm{C}_{3} \end{gathered}$ | 9.31 | 8.84 | 5.1 | 9.61 | 3.2 | 8.89 | 4.6 | 12.02 | 29.1 | 7.8 | 15.9 | 17.8 | 91.4 |
| 11.0 | $\begin{gathered} 90 \% \mathrm{CO}_{2}, 10 \% \\ \mathrm{C}_{4} \end{gathered}$ | 7.9 | 8.08 | 2.3 | 8.89 | 12.6 | 7.64 | 3.2 | 12.62 | 59.8 | 5.9 | 25.3 | 16.5 | 108.9 |
| 11.0 | $\begin{gathered} 80 \% \mathrm{CO}_{2}, 20 \% \\ \mathrm{C}_{2} \end{gathered}$ | 9.66 | 9.88 | 2.3 | 10.99 | 13.8 | 9.88 | 2.3 | 11.06 | 14.6 | 11.1 | 14.5 | 18.2 | 88.2 |
| 11.0 | $\begin{gathered} 80 \% \mathrm{CO}_{2}, 20 \% \\ \mathrm{C}_{3} \end{gathered}$ | 7.93 | 7.92 | 0.1 | 8.42 | 6.2 | 7.67 | 3.3 | 13.07 | 64.7 | 4.5 | 43.1 | 16.9 | 113.3 |
| 13.5 | $\begin{gathered} 90 \% \mathrm{CO}_{2}, 10 \% \\ \mathrm{C}_{2} \end{gathered}$ | 13.04 | 12.54 | 3.8 | 13.42 | 3.0 | 12.71 | 2.5 | 13.47 | 3.3 | 13.5 | 3.7 | 18.3 | 40.8 |


| Appendix-2 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 13.5 | $\begin{gathered} \hline 90 \% \mathrm{CO}_{2}, 10 \% \\ \mathrm{C}_{3} \end{gathered}$ | 11.04 | 10.77 | 2.4 | 11.71 | 6.2 | 10.83 | 1.9 | 14.65 | 32.7 | 10.2 | 7.1 | 17.5 | 58.2 |
| 13.5 | $\begin{gathered} 90 \% \mathrm{CO}_{2}, 10 \% \\ \mathrm{C}_{4} \end{gathered}$ | 8.97 | 9.85 | 9.8 | 10.83 | 20.8 | 9.31 | 3.9 | 15.38 | 71.6 | 8.3 | 7.3 | 17.8 | 99.1 |
| 13.5 | $\begin{gathered} 80 \% \mathrm{CO}_{2}, 20 \% \\ \mathrm{C}_{2} \\ \hline \end{gathered}$ | 12.88 | 12.04 | 6.5 | 13.39 | 4.0 | 12.04 | 6.5 | 13.48 | 4.7 | 13.5 | 4.6 | 19.6 | 51.9 |
| $13.5{ }^{(29)}$ | $\begin{gathered} 80 \% \mathrm{CO}_{2}, 20 \% \\ \mathrm{C}_{3} \\ \hline \end{gathered}$ | 10.5 | 9.65 | 8 | 10.26 | 2.2 | 9.34 | 11.0 | 15.92 | 51.7 | 6.9 | 34.0 | 18.3 | 73.9 |
| 8.28 | $\begin{array}{\|c\|} \hline 80 \% \mathrm{CO}_{2}, 20 \% \\ \mathrm{C}_{1} \\ \hline \end{array}$ | 14.83 | 13.86 | 6.5 | 13.38 | 9.8 | 13.84 | 6.7 | 12.71 | 14.3 | 19.9 | 34.3 | 18.4 | 24.3 |
| 8.28 | $\begin{gathered} 68 \% \mathrm{CO}_{2}, 22 \% \\ \mathrm{H}_{2} \mathrm{~S}, 10 \% \mathrm{C}_{1} \\ \hline \end{gathered}$ | 10.28 | 8.94 | 13 | 9.58 | 6.8 | 8.50 | 17.3 | 9.15 | 10.9 | 6.5 | 36.9 | 18.4 | 79.1 |
| 8.28 | $\begin{gathered} 40 \% \mathrm{CO}_{2}, 40 \% \\ \mathrm{H}_{2} \mathrm{~S}, 20 \% \mathrm{C}_{1} \\ \hline \end{gathered}$ | 12.06 | 10.8 | 10.4 | 11.27 | 6.5 | 9.16 | 24.0 | 10.32 | 14.4 | 6.0 | 50.5 | 20.3 | 68.5 |
| 11.7 | $\begin{gathered} 75 \% \mathrm{CO}_{2}, 25 \% \\ \mathrm{H}_{2} \mathrm{~S} \end{gathered}$ | 10.35 | 10.62 | 2.6 | 10.52 | 1.7 | 10.10 | 2.4 | 10.15 | 1.9 | 3.1 | 69.7 | 19.0 | 84.1 |
| 11.7 | $\begin{gathered} 50 \% \mathrm{CO}_{2}, 50 \% \\ \mathrm{H}_{2} \mathrm{~S} \\ \hline \end{gathered}$ | 8.97 | 10.43 | 16.4 | 9.46 | 5.5 | 8.88 | 0.9 | 8.74 | 2.5 | -5.6 | 162.2 | 20.5 | 129.0 |
| 11.7 | $\begin{gathered} 90 \% \mathrm{CO}_{2}, 10 \% \\ \mathrm{C}_{1} \end{gathered}$ | 15.17 | 14.31 | 5.7 | 14.95 | 1.5 | 14.32 | 5.6 | 14.62 | 3.7 | 17.6 | 16.0 | 21.1 | 39.0 |
| 11.7 | $\begin{gathered} 80 \% \mathrm{CO}_{2}, 20 \% \\ \mathrm{C}_{1} \\ \hline \end{gathered}$ | 18.74 | 19.63 | 4.8 | 18.95 | 1.1 | 19.61 | 4.6 | 18.01 | 3.9 | 23.4 | 24.6 | 24.1 | 28.5 |
| 11.7 | $\begin{array}{\|c\|} \hline 55 \% \mathrm{CO}_{2}, 25 \% \\ \mathrm{H}_{2} \mathrm{~S}, 20 \% \mathrm{C}_{1} \\ \hline \end{array}$ | 16.45 | 17.04 | 3.6 | 17.04 | 3.6 | 15.06 | 8.5 | 15.83 | 3.8 | 14.6 | 11.0 | 21.2 | 28.6 |
| 30.2 | $\begin{gathered} 22.18 \% \mathrm{CO}_{2}, \\ 23.49 \% \mathrm{C}_{1}, \\ 23.5 \% \mathrm{C}_{2}, \\ 27.45 \% \mathrm{C}_{3}, \\ 3.38 \% \mathrm{C}_{4} \\ \hline \end{gathered}$ | 16.55 | 16.75 | 1.2 | 33.54 | 102.7 | 18.56 | 12.1 | 63.56 | 284.0 | 32.8 | 98.2 | 21.1 | 27.2 |
| 25.1 | $\begin{gathered} 79.2 \% \mathrm{CO}_{2}, \\ 8.8 \% \mathrm{~N}_{2}, 12 \% \\ \hline \end{gathered}$ | 23.17 | 20.19 | 12.9 | 25.76 | 11.2 | 19.02 | 17.9 | 58.21 | 151.2 | 25.8 | 11.5 | - | - |

Appendix－2

|  | $\stackrel{\infty}{\sim}$ | $\stackrel{+}{\stackrel{\rightharpoonup}{\oplus}}$ | n | $\stackrel{m}{n}$ | $\stackrel{\sim}{\square}$ | $\stackrel{\wedge}{\infty}$ | + | $\stackrel{\text { rin }}{\text { in }}$ | $\frac{18}{\text { in }}$ | $\infty$ | $\stackrel{\rightharpoonup}{\dot{1}}$ | -i. | $\stackrel{ \pm}{\bullet}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\stackrel{\text { Y }}{ \pm}$ | $\stackrel{\underset{\infty}{\infty}}{\stackrel{1}{2}}$ | $\begin{aligned} & \bullet \\ & \pm \end{aligned}$ | $\stackrel{\text { ソ }}{\underset{\sim}{c}}$ | $\begin{aligned} & \stackrel{0}{\infty} \\ & \stackrel{1}{0} \end{aligned}$ | $\stackrel{\infty}{\dot{\omega}}$ | $\stackrel{N}{\infty}$ | $\stackrel{9}{\square}$ | $\underset{\sim}{\infty}$ | $\stackrel{0}{2}$ | へِّ | $\begin{aligned} & \text { N } \\ & \underset{\sim}{n} \end{aligned}$ | $\stackrel{\bullet}{\infty}$ |
|  | $\cdots$ | $\stackrel{\rightharpoonup}{\bullet}$ | $\stackrel{\uparrow}{\sigma}$ | N | $\stackrel{N}{\rightrightarrows}$ | $\underset{\sim}{\text { Ǹ }}$ | $\underset{\substack{\mathrm{O}}}{\substack{2 \\ \hline}}$ | $\begin{aligned} & n \\ & \sim \\ & \sim \end{aligned}$ | $\underset{\substack{n \\ \hline}}{ }$ | $\underset{\infty}{\infty}$ | $\begin{aligned} & \dot{q} \\ & \underset{\sim}{n} \end{aligned}$ | $\underset{\sim}{\mathrm{N}}$ | べ |
|  | $\stackrel{?}{\leftrightharpoons}$ | $\stackrel{\oplus}{\infty}$ | 9 | $\stackrel{n}{n}$ |  | $\underset{\sim}{\sim}$ | $\begin{aligned} & \infty \\ & \underset{\mathrm{U}}{ } \end{aligned}$ | $\infty$ | $\stackrel{\text { N }}{\text { N }}$ | $\stackrel{7}{7}$ | is | $\stackrel{\dot{U}}{\underset{\sim}{x}}$ | $\stackrel{\bullet}{\bullet}$ |
|  | $\hat{\sim}$ | $\cdots$ | $\stackrel{\infty}{\dot{\ominus}}$ | $\stackrel{\text { \％}}{+}$ | $\bar{i}$ | $\cdots$ | $\stackrel{n}{=}$ | $\xrightarrow{\text { N }}$ | $\overrightarrow{6}$ | $\stackrel{\odot}{\circ}$ | $\stackrel{3}{\square}$ | in | $\stackrel{\sim}{r}$ |
|  | $\stackrel{n}{n}$ | $\begin{aligned} & \underset{\sim}{2} \\ & \stackrel{\rightharpoonup}{2} \end{aligned}$ | $\underset{a}{\square}$ | $\stackrel{N}{\sim}$ | $\underset{\underset{\sim}{\mathrm{N}}}{\stackrel{\rightharpoonup}{+}}$ | oి. | $\begin{aligned} & \underset{\sim}{\circ} \\ & \text { in } \end{aligned}$ | $\stackrel{ \pm}{=}$ | $\stackrel{r}{\hat{O}}$ | $\begin{aligned} & \hat{\theta} \\ & \stackrel{\rightharpoonup}{\theta} \end{aligned}$ | $\begin{aligned} & \hat{0} \\ & \stackrel{O}{0} \end{aligned}$ | $\begin{gathered} \text { NT } \\ \underset{\sim}{n} \end{gathered}$ | － |
|  | $\stackrel{\square}{\circ}$ | $\stackrel{ }{-}$ | $\underset{\underset{N}{\text { i }}}{ }$ | $\stackrel{\sim}{n}$ | $\stackrel{\sim}{n}$ | $\stackrel{O}{\dot{G}}$ | $\stackrel{\underset{N}{N}}{ }$ | $\stackrel{\text { ì }}{ }$ | $\hat{6}$ | $\cdots$ | ざ | $\stackrel{i}{i}$ | $\stackrel{n}{8}$ |
|  | $\begin{aligned} & \infty \\ & \infty \\ & n \end{aligned}$ | $\underset{\sim}{n}$ | è | $\stackrel{n}{2}$ | $\begin{aligned} & \stackrel{\sim}{n} \\ & \underset{\sim}{n} \end{aligned}$ | $\stackrel{n}{\underset{\gamma}{\gamma}}$ | $\stackrel{n}{n}$ | $\stackrel{̣}{9}$ | $$ | $$ | $\stackrel{N}{\sim}$ | $\underset{\sigma}{\ddagger}$ | － |
|  | กิ． | $\bigcirc$ | $\begin{aligned} & 0 \\ & \dot{0} \end{aligned}$ | $\stackrel{m}{ \pm}$ | $\stackrel{\rightharpoonup}{\dot{\omega}}$ | en | O® | $\hat{0}$ | $\cdots$ | $\stackrel{ \pm}{\square}$ | $\stackrel{\stackrel{\rightharpoonup}{\mathrm{i}}}{ }$ | $\xrightarrow{\text { ¢ }}$ | $\stackrel{\sim}{0}$ |
|  | $\begin{aligned} & \text { Y } \\ & \underset{\sim}{n} \end{aligned}$ | $\xrightarrow[~ N]{\infty}$ | $\stackrel{\circ}{\infty}$ | $\stackrel{\infty}{n}$ | $\underset{\substack{\text { O} \\ \vdots}}{ }$ | $\underset{\sim}{\dot{\sim}}$ | $\stackrel{\underset{\sim}{\mathrm{i}}}{\substack{\text {. }}}$ | $\stackrel{\ddots}{g}$ | $\stackrel{\stackrel{\rightharpoonup}{\mathrm{C}}}{\mathrm{~B}}$ | $\stackrel{+}{6}$ | $\stackrel{N}{O}$ | $\stackrel{\stackrel{\rightharpoonup}{\mathrm{i}}}{\substack{2}}$ | $\stackrel{\infty}{+}$ |
|  | $\stackrel{\sim}{i}$ | $\stackrel{ }{-}$ | $\stackrel{n}{n}$ | فู | $亏$ | $\stackrel{m}{\infty}$ | $\stackrel{\text { }}{+}$ | $\vec{m}$ | へ | $\stackrel{\infty}{\infty}$ | $\stackrel{\infty}{\circ}$ | $\stackrel{10}{8}$ | $\stackrel{\sim}{i}$ |
|  | $\stackrel{\imath}{\mathrm{o}}$ | $$ | $\begin{aligned} & \stackrel{\infty}{n} \\ & \underset{\sim}{n} \end{aligned}$ | $\stackrel{\aleph}{\underset{\sim}{N}}$ | $\underset{\text { તi }}{\underset{\text { N }}{2}}$ | $\underset{\sim}{\dot{m}}$ | $\begin{gathered} \stackrel{n}{n} \\ \stackrel{\sim}{n} \end{gathered}$ | $\stackrel{N}{\underset{\sim}{̣}}$ | $\hat{\mathbf{O}}$ | $\stackrel{\infty}{\Theta}$ | $\stackrel{n}{n}$ | $\underset{\sim}{\underset{\sim}{*}}$ | 7 <br> $i \stackrel{1}{2}$ <br> 1 |
|  | $\stackrel{n}{\square}$ | $\underset{\theta}{0}$ | ก | ñ | $\underset{\sim}{\sim}$ | $\underset{\sim}{\underset{m}{\circ}}$ | $\begin{aligned} & \underset{\sim}{j} \\ & \hline \end{aligned}$ | $\stackrel{e}{\square}$ | $\stackrel{\underset{\exists}{7}}{\square}$ | $\stackrel{ \pm}{\bullet}$ | $\stackrel{n}{0}$ | $\begin{aligned} & \text { Nì } \\ & \text { Ǹ } \end{aligned}$ | － |
| U̇ |  | $\begin{aligned} & i \\ & 0_{0} \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  |  | $\begin{gathered} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{gathered}$ | $\begin{aligned} & \hline 0 \\ & 0 \\ & i n \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\begin{array}{\|l\|l} \hline 0 \\ 0 \\ \vdots \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 \\ 0 & \\ 0 \end{array}$ |  |  |
|  | $\begin{aligned} & \infty \\ & \underset{\mathrm{U}}{ } \end{aligned}$ | $\stackrel{\infty}{\underset{\mathrm{I}}{ }}$ | $\stackrel{O}{\mathrm{i}}$ | $\stackrel{\infty}{\mathrm{i}}$ | $\stackrel{O}{\mathrm{i}}$ | $\stackrel{O}{\mathrm{i}}$ | $\stackrel{O}{\mathrm{O}}$ | $\stackrel{\underset{\mathrm{i}}{\mathrm{i}}}{ }$ | $\stackrel{\stackrel{\rightharpoonup}{\mathrm{i}}}{ }$ | $\stackrel{\stackrel{\rightharpoonup}{\mathrm{i}}}{ }$ | $\stackrel{\text { i }}{\text { i }}$ | $\stackrel{\ominus}{\mathrm{i}}$ | n |

Appendix－2

| $\stackrel{F}{7}$ | $\begin{aligned} & \infty \\ & i \\ & i \end{aligned}$ | $\stackrel{\uparrow}{\mathrm{O}}$ | $\stackrel{\ominus}{0}$ | $\stackrel{\bullet}{\dot{ \pm}}$ | ત̀ | $\stackrel{\ominus}{\dot{+}}$ | $\stackrel{\mathrm{N}}{\mathbf{N}}$ | $\stackrel{\dot{\theta}}{\stackrel{\rightharpoonup}{\theta}}$ | $\underset{\infty}{\infty}$ | $\underset{\substack{ \pm \\ \hline}}{ }$ | $\xrightarrow{\mathbf{N}}$ | ， | ＇ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| in | 추N | $\begin{aligned} & \text { in } \\ & \text { Ni } \end{aligned}$ | $\stackrel{\ominus}{\mathrm{N}}$ | $\underset{\underset{\bullet}{ \pm}}{\stackrel{\rightharpoonup}{6}}$ | $\underset{\sim}{n}$ | $\bar{\theta}$ | $\bar{\theta}$ | $\underset{\sim}{\infty}$ | $\begin{gathered} 0 \\ \underset{\sim}{\infty} \end{gathered}$ | $\begin{aligned} & 10 \\ & \infty \\ & \hline 0 \end{aligned}$ | $\stackrel{N}{\infty}$ | ＇ | ＇ |
| అ | ત̀ | $\underset{\sim}{\underset{\sim}{n}}$ | in | $\stackrel{3}{7}$ | $\stackrel{\infty}{\square}$ | $\stackrel{0}{\infty}$ | $\stackrel{\underset{\rightharpoonup}{\nabla}}{\boldsymbol{\rightharpoonup}}$ | $\begin{aligned} & \underset{i}{~+~} \\ & \text { Ñ } \end{aligned}$ | $\stackrel{\ominus}{\dot{\theta}}$ | $\frac{\square}{i n}$ | $\underset{\sim}{-}$ | $\stackrel{?}{7}$ | $\infty$ |
| $\stackrel{1}{6}$ |  | $\underset{\sim}{e}$ | $\begin{aligned} & 0 \\ & 10 \end{aligned}$ | $\stackrel{\Theta}{ \pm}$ | $\begin{aligned} & \infty \\ & \underset{\sim}{\mathbf{U}} \end{aligned}$ | $\stackrel{?}{=}$ | $\stackrel{\rightharpoonup}{\theta}$ | 10 | T | 17 | $\stackrel{\theta}{0}$ | $\hat{\theta}$ | $\begin{gathered} \pm \\ \text { Ni } \end{gathered}$ |
| $\stackrel{\mathbf{N}}{\mathbf{\square}}$ | $\frac{\vdots}{N}$ | $\begin{aligned} & \text { è } \\ & \text { è } \end{aligned}$ | $\stackrel{\text { n }}{ \pm}$ | 융 | $\stackrel{\dot{\sigma}}{\circ}$ | $\begin{aligned} & \text { Ǹ } \\ & \text { Nin } \end{aligned}$ | $\stackrel{\ominus}{\mathrm{N}}$ | $\dot{\infty}$ | $\begin{aligned} & 0 \\ & \infty \\ & 0 \\ & \hline 0 \end{aligned}$ | $\begin{aligned} & 6 \\ & 10 \\ & \square \end{aligned}$ | $\stackrel{\infty}{\infty}$ | $\cdots$ | $\underset{-}{\theta}$ |
| $\begin{aligned} & \text { en } \\ & \text { no } \\ & \underline{0} \end{aligned}$ | $\begin{aligned} & \infty \\ & \stackrel{n}{n} \\ & \stackrel{0}{2} \end{aligned}$ |  | ف̀ | $\begin{aligned} & \text { N } \\ & \text { N } \end{aligned}$ | $\begin{aligned} & \underset{N}{N} \\ & \infty \end{aligned}$ | $\begin{aligned} & \infty \\ & \infty \\ & \infty \\ & \infty \end{aligned}$ | $\stackrel{\underset{\sim}{\nabla}}{\square}$ | $\begin{gathered} \underset{N}{N} \\ \underset{N}{N} \end{gathered}$ | $\stackrel{\stackrel{\rightharpoonup}{\mathrm{N}}}{\dot{\sim}}$ | $\begin{aligned} & \text { N} \\ & \text { Ǹ } \end{aligned}$ | $\begin{aligned} & \pm \\ & \text { N゙ } \\ & \underset{\sim}{n} \end{aligned}$ | $\stackrel{\underset{i}{n}}{i}$ | $\begin{aligned} & \text { N } \\ & \underset{\sim}{m} \end{aligned}$ |
| $\stackrel{\circ}{\text { c }}$ | $\stackrel{1}{0}$ | $\stackrel{\infty}{+}$ | N | $\stackrel{\rightharpoonup}{\text { N }}$ | $\stackrel{0}{0}$ | $\underset{i}{n}$ | $\stackrel{-}{-}$ | $\stackrel{\infty}{0}$ | $\stackrel{\text { ¹ }}{\sim}$ | $\cdots$ | $\stackrel{\text { ？}}{\square}$ | $\stackrel{?}{8}$ | $\cdots$ |
| $\stackrel{\hat{N}}{\underset{\sim}{\dot{C}}}$ | $\begin{aligned} & \text { Nे } \\ & \end{aligned}$ | $\begin{aligned} & \stackrel{\infty}{+} \\ & \stackrel{1}{\mathbf{i}} \end{aligned}$ | $\begin{aligned} & \text { m} \\ & i n \end{aligned}$ | $\begin{aligned} & \vec{\sigma} \\ & \underset{\square}{7} \end{aligned}$ | $\begin{aligned} & \underset{\mathbf{N}}{\mathbf{N}} \end{aligned}$ | $\stackrel{\underset{\mathrm{N}}{\underset{\sim}{c}}}{\mathbf{i}}$ | $\begin{aligned} & n \\ & \underset{=}{=} \end{aligned}$ | $\hat{\theta}$ | $\stackrel{\infty}{\stackrel{\infty}{0}}$ | $\begin{aligned} & -\infty \\ & \infty \end{aligned}$ | $\underset{\sim}{\dot{\theta}}$ | $\begin{aligned} & \pm \\ & \infty \\ & \end{aligned}$ | $\begin{aligned} & \underset{n}{\theta} \\ & \underset{\theta}{n} \end{aligned}$ |
| $\stackrel{\ominus}{\top}$ | $\stackrel{\text { Ǹ }}{N}$ | $\underset{\sim}{\underset{\sim}{e}}$ | ò | $\pm$ | $\bar{\infty}$ | $\stackrel{\ominus}{\circ}$ | $\stackrel{\ominus}{\theta}$ | $\pm$ | $\underset{6}{\mathrm{O}}$ | $\stackrel{Y}{\underset{ \pm}{+}}$ | $\stackrel{\square}{\text { ci}}$ | $\stackrel{\circ}{\text { ¢ }}$ | $\stackrel{1}{8}$ |
| $\begin{aligned} & \stackrel{\rightharpoonup}{\oplus} \\ & \underset{\sim}{\bullet} \end{aligned}$ | $\begin{aligned} & \text { è } \\ & \text { Mé } \\ & \underset{\sim}{n} \end{aligned}$ | $\stackrel{\rightharpoonup}{\underset{\sim}{e}}$ | $\begin{aligned} & \text { N } \\ & \infty \\ & \underset{\sim}{n} \end{aligned}$ | $\begin{aligned} & \text { N } \\ & \text { No } \\ & \end{aligned}$ | $\begin{aligned} & \stackrel{\ominus}{\bullet} \\ & \dot{ \pm} \end{aligned}$ | $\begin{aligned} & \underset{\sim}{\infty} \\ & \underset{\sim}{n} \end{aligned}$ | $\begin{aligned} & \text { e } \\ & \text { ㅂ } \end{aligned}$ | $\underset{\nabla}{\theta}$ | $\stackrel{10}{\theta}$ | $\stackrel{\text { ले }}{\stackrel{1}{e}}$ | $\stackrel{e}{\theta}$ | $\begin{aligned} & \infty \\ & \underset{\sim}{\infty} \\ & \end{aligned}$ | $\begin{aligned} & \text { Ǹ } \\ & \end{aligned}$ |
| $\stackrel{N}{\mathrm{~N}}$ | $\stackrel{\infty}{\bigcirc}$ | $9$ | 10 | $\stackrel{\cong}{8}$ | $\stackrel{\cong}{8}$ | $\stackrel{\text { r }}{\sim}$ | $\stackrel{\square}{7}$ | $\cdots$ | $\stackrel{ \pm}{*}$ | $\stackrel{\square}{0}$ | $\stackrel{?}{\square}$ | $\stackrel{10}{8}$ | ¢ |
| $\stackrel{\rightharpoonup}{ \pm}$ | $\begin{aligned} & n \\ & \end{aligned}$ | $\begin{aligned} & \mathbf{v} \\ & \mathbf{i} \end{aligned}$ | $\begin{aligned} & \underset{\infty}{\infty} \\ & \underset{ \pm}{+} \end{aligned}$ | $\begin{aligned} & \stackrel{0}{N} \\ & \underset{ \pm}{\square} \end{aligned}$ | $\begin{aligned} & 0 \\ & \text { Ò } \\ & \mathbf{~ Y} \end{aligned}$ | $\stackrel{N}{\mathrm{~N}}$ | $\hat{\infty}$ | $\stackrel{N}{\underset{\sim}{1}}$ | $\begin{aligned} & \infty \\ & \infty \\ & 0 \end{aligned}$ | $\stackrel{\square}{\square}$ | $\stackrel{\sim}{\square}$ | $\begin{aligned} & \infty \\ & \infty \\ & \end{aligned}$ | － |
| $\stackrel{10}{7}$ | $\begin{aligned} & 0 \\ & \dot{\eta} \end{aligned}$ | $\stackrel{9}{9}$ | $\stackrel{\infty}{ \pm}$ | $\stackrel{\text { r }}{ \pm}$ | $\cdots$ | $\stackrel{ \pm}{\text { ® }}$ | $\stackrel{ \pm}{\square}$ | F | $\stackrel{m}{\theta}$ | $\square$ | הֲ | $\stackrel{9}{7}$ | $\hat{\mathbf{N}}$ |
|  |  |  |  |  |  | $\left\lvert\, \begin{array}{ll} 0 & 0 \\ 0 & 0 \\ 0 & 6 \\ 0 & 9 \\ \hdashline \dot{j} & n \\ \infty & n \end{array}\right.$ | $$ |  |  |  | $\begin{aligned} & 0 \\ & \theta \\ & ⿱ 丷 ⿱ 一 ⿱ ㇒ ⿴ 囗 ⿱ 一 一 寸 \end{aligned}$ |  |  |
| $\begin{aligned} & \text { ne } \\ & \underset{0}{2} \end{aligned}$ | 109 | 109 | 109 | in | in | 1096 | nọ | 109 | －109 | 109 | $\stackrel{\rightharpoonup}{9}$ | $\underset{\substack{\infty \\ \infty}}{ }$ | $\stackrel{\infty}{\text { N }}$ |

Appendix-2

| Average error for all the data points, \% | 4.6 |  | 13.2 |  | 14.1 |  | 29.6 |  | 34.6 |  | 60.8 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| STDEV for all the data points, \% | 6.16 |  | 22.1 |  | 43.26 |  | 55.0 |  | 54.0 |  | 74.0 |
| Average error for all the data points except the last point, \% | 4.64 |  | 12.7 |  | 9.4 |  | 29.8 |  | 35.0 |  | 60.8 |
| STDEV for all the data points except the last point, \% | 6.21 |  | 21.66 |  | 18.23 |  | 55.0 |  | 54.0 |  | 74.0 |

Appendix-3
Table A-3-1. Experimental data used for developing and testing of the GA-based $\mathrm{CO}_{2}$ solubility in dead oil model and the model prediction results.
Error, \%GA-based $\mathrm{CO}_{2}$fraction
0.1990 0.3060 0.4538
0.4218 0.6342 n 0.4230 0.5401
 0.3149 ® $\stackrel{\infty}{6}$ 응 0.5025 0.1966 + n 0.5748 તิ $\stackrel{\infty}{+}$ Experimental $\mathrm{CO}_{2}$ fraction
0.196
 $\underset{\substack{\text { Pirf, } \\ \text { MPa }}}{ }$ $\mathbf{T}_{\mathrm{R}},{ }^{\circ} \mathbf{C}$
43.33
43.33
43.33
9333
93.33
71.11
71.11
71.11
71.11
48.89
48.89
48.89
48.89
48.89
48.89
121.1
12.1
121.1
121.1
48.89
48.89 0.950941 0.950941
0.950941 0.950941
0.950941 0.950941 $\stackrel{\rightharpoonup}{\circ}$ 0.858617景 0.858617
0.858617 0.858617 O

 0.944593 0.944593 | N |
| :---: |
|  | No

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Appendix-3
 0.6228
0.6634
0.3097
0.5233
0.3325
0.5250
0.6260
0.2316
0.5561
0.6533
0.1826
0.4034
0.5723
0.6908
0.2998
0.5357
0.0980
0.1880
0.2874
0.4506
0.602
0.629
0.625
0.609
0.0984
0.2923
0.4336
0.4810
0.1093
0.3118






Simon and Graue (1965)
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Appendix-3









Appendix-3


Table A－3－2．Experimental data used for developing and testing of the GA－based $\mathrm{CO}_{2}$ solubility in live oil model and the model prediction results．
Error，$\%$
3.5
4.1
0.6
2.4
0.5
0.0
5.8
0.4
0.6
2.6
7.2
4.7 GA－based $\mathrm{CO}_{2}$ Experimental $\mathrm{CO}_{2}$


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＊＊＊Data in bold were used to test the model． $\operatorname{Sol}(\mathrm{scf} / \mathrm{bbl}) / 379.3+350 \frac{\gamma}{\mathrm{MW}}$
$0.0 .0148 \mathrm{Sol}\left(\mathrm{sm}^{3} / \mathrm{m}^{3}\right)$
$0.0148 \mathrm{Sol}\left(\mathrm{sm}^{3} / \mathrm{m}^{3}\right)+350 \frac{\gamma}{\mathrm{MW}}$ $\operatorname{Sol}(\mathrm{scf} / \mathrm{bbl}) / 379.3+350 \frac{\gamma}{\mathrm{MW}}$
$0.0148 \mathrm{Sol}\left(\mathrm{sm}^{3} / \mathrm{m}^{3}\right)+350 \frac{\gamma}{\mathrm{MW}}$ $\operatorname{Sol}(\mathrm{scf} / \mathrm{bbl}) / 379.3+350 \frac{\gamma}{\mathrm{MW}}$
$0.0 .0148 \mathrm{Sol}\left(\mathrm{sm}^{3} / \mathrm{m}^{3}\right)$
$0.0148 \mathrm{Sol}\left(\mathrm{sm}^{3} / \mathrm{m}^{3}\right)+350 \frac{\gamma}{\mathrm{MW}}$
$\mathrm{Sol}($ mole fraction $)=\quad \mathrm{Sol}(\mathrm{scf} / \mathrm{bbl}) / 379.3 \quad$ ．Also from sm3／m3 to mole fraction by：
Sol（mole fraction）
MW

127.0
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 Simon et al．（1978） | $\infty$ |
| :--- |
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|  |
| 0 |
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| B | Simon et al．（1978）





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Appendix-3





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Srivastava et al. (1995)
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Turek et al. (1984)
Turek et al. (1984)
Chaback (1988)
Chaback (1988)
Chaback (1988)
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Chaback (1988)
Chaback (1988)
Chaback (1988)
Chaback (1988)
Novosad and Costain
(1990)
Novosad and Costain
Appendix-3


| 0.2 | 0.2019 |
| :--- | ---: |
| 0.27 | 0.2740 |
| 0.34 | 0.3471 |
| 0.4 | 0.4088 |
| 0.433 | 0.4449 |
| 0.48 | 0.4997 |
| 0.52 | 0.5454 |
| 0.61 | 0.6261 |
| Average Error, | \% $=$ |

* These data have pressures greater than $\mathrm{CO}_{2}$ liquefaction pressure at the specified temperature and Equation 7-2 was used to predict the $\mathrm{CO}_{2}$ solubility for them
**Data in bold were used to test the model.
Appendix-4
Table A-4-1. Experimental data used for developing of the GA-based oil swelling factor (due to $\mathrm{CO}_{2}$ ) model and testing of this model for dead oil swelling factor data.

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Simon and Graue (1965)
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Simon and Graue (1965)
Srivastava et al. (1995)
Srivastava et al. (1995)
Srivastava et al. (1995)
Srivastava et al. (1995)
Srivastava et al. (1995)
Appendix-4




| Srivastava et al. (1995) | 440 | $\mathbf{0 . 9 7 1 8 4}$ |
| :---: | :---: | :---: |
| Srivastava et al. (1995) | $\mathbf{4 4 0}$ | $\mathbf{0 . 9 7 1 8 4}$ |
| Srivastava et al. (1995) | $\mathbf{4 2 4}$ | $\mathbf{0 . 9 7 3 8 5}$ |
| Srivastava et al. (1995) | $\mathbf{4 2 4}$ | $\mathbf{0 . 9 7 3 8 5}$ |
| Srivastava et al. (1995) | $\mathbf{4 2 4}$ | $\mathbf{0 . 9 7 3 8 5}$ |
| Srivastava et al. (1995) | $\mathbf{4 2 4}$ | $\mathbf{0 . 9 7 3 8 5}$ |
| Srivastava et al. (1995) | $\mathbf{4 2 4}$ | $\mathbf{0 . 9 7 3 8 5}$ |
| Nguyen and Farouq Ali | $\mathbf{4 5 0}$ | $\mathbf{0 . 9 5 2 8 6}$ |
| (1998) |  |  |
| Nguyen and Farouq Ali | $\mathbf{4 5 0}$ | $\mathbf{0 . 9 5 2 8 6}$ |
| (1998) |  |  |
| Nguyen and Farouq Ali | $\mathbf{4 5 0}$ | $\mathbf{0 . 9 5 2 8 6}$ |
| (1998) |  |  |
| Nguyen and Farouq Ali | $\mathbf{4 5 0}$ | $\mathbf{0 . 9 5 2 8 6}$ |
| (1998) |  |  |
| Simon and Graue (1965) | $236^{*}$ | 0.85862 |
| Simon and Graue (1965) | $236^{*}$ | 0.85862 |
| Simon and Graue (1965) | $236^{*}$ | 0.85862 |
| Simon and Graue (1965) | $236^{*}$ | 0.85862 |
| Simon and Graue (1965) | $236^{*}$ | 0.85862 |
| Bou-Mikael (2002) | $246^{*}$ | 0.84985 |
| Bou-Mikael (2002) | $246^{*}$ | 0.84985 |
| Bou-Mikael (2002) | $246^{*}$ | 0.84985 |
| Bou-Mikael (2002) | $246^{*}$ | 0.84985 |
| Bou-Mikael (2002) | $246^{*}$ | 0.84985 |
| Bou-Mikael (2002) | $246^{*}$ | 0.84985 |
| Srivastava et al. (1995) | $280^{*}$ | 0.91231 |
| Srivastava et al. (1995) | $280^{*}$ | 0.91231 |
| Srivastava et al. (1995) | $280^{*}$ | 0.91231 |
| Srivastava et al. (1995) | $280^{*}$ | 0.91231 |

Appendix-4

| 280* | 0.91231 | 0.618 | 1.289 | 1.276 | 1.00 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 205* | 0.83827 | 0 | 1 | 1.000 | 0.00 |
| 205* | 0.83827 | 0.1915 | 1.064 | 1.054 | 0.98 |
| 205* | 0.83827 | 0.2601 | 1.1 | 1.083 | 1.52 |
| 205* | 0.83827 | 0.3200 | 1.14 | 1.110 | 2.60 |
| 205* | 0.83827 | 0.3708 | 1.157 | 1.137 | 1.72 |
| 205* | 0.83827 | 0.4719 | 1.207 | 1.208 | 0.05 |
| 205* | 0.83827 | 0.5638 | 1.2857 | 1.2857 | 0.00 |
| GA-based STDEV, \% = 0.94 |  |  |  | Average Error, \% | 0.61 |
| er than 300 and Equation $\mathbf{7 - 5}$ was used to predict the oil-swelling factor for them. test the model. |  |  |  |  |  |
| ntal data used for testing of the GA-based oil swelling factor (due to $\mathrm{CO}_{2}$ ) model for the live oil swelling factor data. |  |  |  |  |  |
| MW | $\gamma$ | $\mathrm{CO}_{2}$ Solubility, mole fraction | Experimental live oil swelling factor | GA-based live oil swelling factor, fraction | Error, \% |
| 339.8 | 0.9659 | 0 | 1 | 1 | 0.00 |
| 339.8 | 0.9659 | 0.2 | 1.034 | 1.028 | 0.56 |
| 339.8 | 0.9659 | 0.4 | 1.08 | 1.079 | 0.14 |
| 339.8 | 0.9659 | 0.6 | 1.195 | 1.181 | 1.13 |
| 391.6 | 0.9663 | 0 | 1 | 1 | 0.00 |
| 391.6 | 0.9663 | 0.094 | 1.008 | 1.007 | 0.14 |
| 391.6 | 0.9663 | 0.242 | 1.033 | 1.034 | 0.13 |
| 391.6 | 0.9663 | 0.442 | 1.081 | 1.083 | 0.17 |
| 391.6 | 0.9663 | 0.584 | 1.153 | 1.146 | 0.59 |
| 356.3 | 0.9665 | 0 | 1 | 1 | 0.00 |
| 356.3 | 0.9665 | 0.346 | 1.067 | 1.060 | 0.67 |
| 356.3 | 0.9665 | 0.504 | 1.103 | 1.119 | 1.46 |

Appendix-4






GA-based STDEV, \%=1.29

* These data points have oil MW lower than 300 and Equation $\mathbf{7 - 5}$ was used to predict oil-swelling factor for them.
**The data points in bold were used to test the model.

$$
\begin{gathered}
1.265 \\
1 \\
1.005 \\
1.046 \\
1.091 \\
1.143 \\
1.302 \\
1.417 \\
1 \\
1.083 \\
1.175 \\
1.330
\end{gathered}
$$

Average Error, \%
Table A-5-1. Experimental data used for developing of the GA-based $\mathrm{CO}_{2}$-oil density model and testing of this model for $\mathrm{CO}_{2}$-dead oil density data.
Error, \%
 AA-based $\mathrm{CO}_{2}$-oil
density, gm/cc 0.9500 ふ 0.9568 0.9625 0.9649 0.9677 0.8114 $\stackrel{2}{\infty}$ 0.8149 0.8175 N
$\underset{\sim}{\infty}$
O. 0.9678 సे 0.9772 응 $\stackrel{+}{\infty}$ $\stackrel{\leftrightarrow}{\infty}$ 0.9077 $\stackrel{\circ}{\circ}$ $\stackrel{\circ}{\circ}$ Experimental $\mathrm{CO}_{2^{-}}$ density, gm/cc oil density, gm/cc
0.9500
0.9510 0.9570 0.9600 0.9660 0.9700 0.8114 0.8203 0.8257 0.8285 0.9678 0.9739 0.9800 N.
$\stackrel{\infty}{\infty}$
${ }_{0}$ 0.9870 0.9885 0.9077 응ㅇㅇㅇ
Appendix-5
Appendix-5

 0.9687
0.9771
0.92417
0.9243
0.9298
0.9258
0.9289
0.9290
0.9390
0.9392
0.9499
0.9030
0.9056
0.9058
0.9075
0.9178
0.9199
0.9615
0.9681
0.9708
0.9694
0.9792
0.9800
0.9882
0.9599
0.9605
0.9613
0.9635
0.9681
0.9729

Appendix-5
능


 | Miller and Jones (1984) | 0.9659 | 23.9 | 10.41 | 0.6373 |
| :--- | :---: | :---: | :---: | :---: |
| Miller and Jones (1984) | 0.9659 | 23.9 | 13.89 | 0.6427 |
| Miller and Jones (1984) | 0.9659 | 23.9 | 20.86 | 0.6538 |
| Miller and Jones (1984) | 0.9659 | 60.0 | 0.10 | 0 |
| Miller and Jones (1984) | 0.9659 | 60.0 | 2.86 | 0.2455 |
| Miller and Jones (1984) | 0.9659 | 60.0 | 4.27 | 0.3414 |
| Miller and Jones (1984) | 0.9659 | 60.0 | 5.75 | 0.4419 |
| Miller and Jones (1984) | 0.9659 | 60.0 | 8.17 | 0.5374 |
| Miller and Jones (1984) | 0.9659 | 60.0 | 13.82 | 0.6943 |
| Miller and Jones (1984) | 0.9659 | 60.0 | 20.79 | 0.6951 |
| Miller and Jones (1984) | 0.9659 | 60.0 | 27.76 | 0.7200 |
| Miller and Jones (1984) | 0.9659 | 60.0 | 34.49 | 0.7362 |
| Miller and Jones (1984) | 0.9659 | 93.3 | 0.10 | 0 |
| Miller and Jones (1984) | 0.9659 | 93.3 | 4.69 | 0.3213 |
| Miller and Jones (1984) | 0.9659 | 93.3 | 5.69 | 0.3892 |
| Miller and Jones (1984) | 0.9659 | 93.3 | 13.00 | 0.5852 |
| Miller and Jones (1984) | 0.9659 | 93.3 | 19.27 | 0.6833 |
| Miller and Jones (1984) | 0.9659 | 93.3 | 26.45 | 0.7257 |
| Miller and Jones (1984) | 0.9659 | 93.3 | 32.34 | 0.7513 |
| Miller and Jones (1984) | $\mathbf{0 . 9 3 4}$ | $\mathbf{2 3 . 9}$ | $\mathbf{0 . 1 0}$ | $\mathbf{0}$ |
| Miller and Jones (1984) | $\mathbf{0 . 9 3 4}$ | $\mathbf{2 3 . 9}$ | $\mathbf{4 . 1 3}$ | $\mathbf{0 . 4 9 1 3}$ |
| Miller and Jones (1984) | $\mathbf{0 . 9 3 4}$ | $\mathbf{2 3 . 9}$ | $\mathbf{8 . 6 3}$ | $\mathbf{0 . 6 4 3 9}$ |
| Miller and Jones (1984) | $\mathbf{0 . 9 3 4}$ | $\mathbf{2 3 . 9}$ | $\mathbf{1 4 . 4 2}$ | $\mathbf{0 . 6 5 9 6}$ |
| Miller and Jones (1984) | $\mathbf{0 . 9 3 4}$ | $\mathbf{2 3 . 9}$ | $\mathbf{2 8 . 2 8}$ | $\mathbf{0 . 7 0 1 5}$ |
| Miller and Jones (1984) | $\mathbf{0 . 9 3 4}$ | $\mathbf{6 0 . 0}$ | $\mathbf{0 . 1 0}$ | $\mathbf{0}$ |
| Miller and Jones (1984) | $\mathbf{0 . 9 3 4}$ | $\mathbf{6 0 . 0}$ | $\mathbf{1 . 6 5}$ | $\mathbf{0 . 1 5 7 1}$ |
| Miller and Jones (1984) | $\mathbf{0 . 9 3 4}$ | $\mathbf{6 0 . 0}$ | $\mathbf{5 . 4 8}$ | $\mathbf{0 . 4 4 5 1}$ |
| Miller and Jones (1984) | $\mathbf{0 . 9 3 4}$ | $\mathbf{6 0 . 0}$ | $\mathbf{7 . 0 0}$ | $\mathbf{0 . 5 1 1 4}$ |
| Miller and Jones (1984) | $\mathbf{0 . 9 3 4}$ | $\mathbf{6 0 . 0}$ | $\mathbf{1 0 . 3 2}$ | $\mathbf{0 . 6 2 9}$ |
| Miller and Jones (1984) | $\mathbf{0 . 9 3 4}$ | $\mathbf{6 0 . 0}$ | $\mathbf{1 3 . 7 6}$ | $\mathbf{0 . 6 7 1 3}$ |
|  |  |  |  |  |

Appendix-5


| 0.9334 | 0.9276 |
| :---: | :---: |
| 0.8817 | 0.8817 |
| 0.8830 | 0.8833 |
| 0.8835 | 0.8855 |
| 0.8848 | 0.8873 |
| 0.8846 | 0.8880 |
| 0.8857 | 0.8893 |
| 0.8876 | 0.8912 |
| 0.8879 | 0.8949 |
| 0.8897 | 0.8981 |
| 0.9010 | 0.9011 |
| 0.8390 | 0.8390 |
| 0.8300 | 0.8413 |
| 0.8310 | 0.8447 |
| 0.8370 | 0.8455 |
| 0.8490 | 0.8464 |
| 0.8510 | 0.8474 |
| 0.7890 | 0.7890 |
| 0.7900 | 0.7907 |
| 0.7918 | 0.7919 |
| 0.7934 | 0.7930 |
| 0.7953 | 0.7941 |
| 0.7976 | 0.7950 |
| 0.7997 | 0.7960 |
|  | \%= |

Appendix-5

| Error, $\%$ |
| :---: |
| $\mathbf{0 . 0 0}$ |
| $\mathbf{0 . 6 8}$ |
| $\mathbf{0 . 7 2}$ |
| $\mathbf{1 . 3 0}$ |
| 0.00 |
| 1.38 |
| $\mathbf{3 . 7 0}$ |
| $\mathbf{4 . 4 5}$ |
| $\mathbf{0 . 0 0}$ |
| $\mathbf{0 . 0 6}$ |
| $\mathbf{0 . 1 9}$ |
| $\mathbf{0 . 3 3}$ |
| $\mathbf{0 . 4 7}$ |
| $\mathbf{0 . 4 6}$ |
| $\mathbf{0 . 5 1}$ |
| $\mathbf{0 . 0 0}$ |
| $\mathbf{0 . 3 3}$ |
| $\mathbf{0 . 4 9}$ |
| $\mathbf{0 . 6 5}$ |
| $\mathbf{0 . 8 7}$ |
| $\mathbf{1 . 3 2}$ |
| $\mathbf{0 . 0 0}$ |
|  |
| 1.05 |


| Reference | $\gamma$ | TR, ${ }^{\circ} \mathrm{C}$ | $\mathbf{P}_{\mathbf{b}}, \mathrm{MPa}$ | $\mathrm{P}_{\mathrm{s}}$, MPa | $\mathrm{CO}_{2}$ Solubility, mole fraction | Initial oil density, gm/cc | Experimental $\mathrm{CO}_{2}$-oil density, gm/cc | GA-based $\mathrm{CO}_{2}$-oil density, gm/cc |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Sankur et al. (1986) | 0.9659 | 48.89 | 4.00 | 4.00 | 0 | 0.9403 | 0.9403 | 0.9403 |
| Sankur et al. (1986) | 0.9659 | 48.89 | 4.00 | 6.10 | 0.2 | 0.9403 | 0.9499 | 0.9434 |
| Sankur et al. (1986) | 0.9659 | 48.89 | 4.00 | 10.38 | 0.4 | 0.9403 | 0.9547 | 0.9478 |
| Sankur et al. (1986) | 0.9659 | 48.89 | 4.00 | 22.07 | 0.6 | 0.9403 | 0.9451 | 0.9574 |
| Bou-Mikael (2002) | 0.8348 | 73.89 | 18.52 | 18.52 | 0 | 0.7328 | 0.7328 | 0.7328 |
| Bou-Mikael (2002) | 0.8348 | 73.89 | 18.52 | 20.70 | 0.2028 | 0.7328 | 0.7452 | 0.7349 |
| Bou-Mikael (2002) | 0.8348 | 73.89 | 18.52 | 23.06 | 0.3987 | 0.7328 | 0.7648 | 0.7365 |
| Bou-Mikael (2002) | 0.8348 | 73.89 | 18.52 | 28.16 | 0.6042 | 0.7328 | 0.7739 | 0.7395 |
| Srivastava et al. (2000) | 0.8448 | 61.00 | 3.50 | 3.50 | 0 | 0.7972 | 0.7972 | 0.7972 |
| Srivastava et al. (2000) | 0.8448 | 61.00 | 3.50 | 5.20 | 0.2234 | 0.7972 | 0.7997 | 0.7992 |
| Srivastava et al. (2000) | 0.8448 | 61.00 | 3.50 | 7.20 | 0.3937 | 0.7972 | 0.8024 | 0.8009 |
| Srivastava et al. (2000) | 0.8448 | 61.00 | 3.50 | 8.30 | 0.4749 | 0.7972 | 0.8044 | 0.8017 |
| Srivastava et al. (2000) | 0.8448 | 61.00 | 3.50 | 9.50 | 0.5603 | 0.7972 | 0.8064 | 0.8026 |
| Srivastava et al. (2000) | 0.8448 | 61.00 | 3.50 | 10.10 | 0.5967 | 0.7972 | 0.8067 | 0.8030 |
| Srivastava et al. (2000) | 0.8448 | 61.00 | 3.50 | 12.80 | 0.7201 | 0.7972 | 0.8089 | 0.8048 |
| Srivastava et al. (2000) | 0.8708 | 63.00 | 4.90 | 4.90 | 0 | 0.8064 | 0.8064 | 0.8064 |
| Srivastava et al. (2000) | 0.8708 | 63.00 | 4.90 | 7.20 | 0.2643 | 0.8064 | 0.8116 | 0.8090 |
| Srivastava et al. (2000) | 0.8708 | 63.00 | 4.90 | 9.20 | 0.3944 | 0.8064 | 0.8146 | 0.8106 |
| Srivastava et al. (2000) | 0.8708 | 63.00 | 4.90 | 10.40 | 0.4773 | 0.8064 | 0.8168 | 0.8115 |
| Srivastava et al. (2000) | 0.8708 | 63.00 | 4.90 | 11.90 | 0.5629 | 0.8064 | 0.8197 | 0.8125 |
| Srivastava et al. (2000) | 0.8708 | 63.00 | 4.90 | 14.40 | 0.6471 | 0.8064 | 0.8251 | 0.8142 |
| Delaney and Fish (1980) | 0.8203 | 96.11 | 15.79 | 15.79 | 0 | 0.7300 | 0.73 | 0.7300 |
| Delaney and Fish (1980) | 0.8203 | 96.11 | 15.79 | 18.68 | 0.197 | 0.7300 | 0.74 | 0.7322 |



Table A-6-1. Experimental data used for developing and testing of the GA-based $\mathrm{CO}_{2}$-dead oil viscosity model and the model prediction results.


 Initial dead oil Experimental $\mathrm{CO}_{2}{ }^{-}$
 3.6 $\stackrel{n}{n}$ $\because$ 2.5 2.2 $\cdots=$ 0 $\infty$ $\checkmark$ $5 \cdot$ 01 viscosity, mPa.s
 $\mathrm{CO}_{2}$ solubility,
mole fraction

$\square$

$\mathbf{T}_{\mathrm{R}},{ }^{\circ} \mathrm{C}$

0.8383
0.8383
0.8383
0.8383
0.8383
0.8383
0.8383
0.9123
0.9123
0.9123
0.9497
0.9497
0.9497
0.9497
0.9497
0.9529
0.9529
0.9529
0.9529
0.9529
0.9529
0.9529
Reference
Sim et al. $(1996)$
Sim et al. $(1996)$
Sim et al. $(1996)$
Sim et al. $(1996)$
Sim et al. $(1996)$
Sim et al. $(1996)$
Sim et al. $(1996)$
Srivastava et al. $(1995)$
Srivastava et al. $(1995)$ Srivastava et al. (1995)

 Kokal and Sayegh (1993) Kokal and Sayegh (1993) Kokal and Sayegh (1993)

 Miller and Jones (1984) Miller and Jones (1984)

 Miller and Jones (1984)
Appendix-6







Miller and Jones (1984) Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Sayegh et al. $(1990)$
Sayegh et al. $(1990)$
Sayegh et al. (1990)
Sayegh et al. (1990)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Chung et al. (1986)
Appendix-6
Chung et al. (1986)
Chung et al. $(1986)$
Chung et al. $(1986)$
Chung et al. (1986)
Chung et al. $(1986)$
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Miller and Jones (1984)
Kokal and Sayegh (1993)
Kokal and Sayegh (1993)
Kokal and Sayegh (1993)
Kokal and Sayegh (1993)
Srivastava et al. $(1995)$
Srivastava et al. (1995)
Appendix-6









## Srivas

| Srivastava et al. (1995) <br> Srivastava et al. (1995) |  |
| :---: | :---: |
|  |  |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (108) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984 |
|  | Miller and Jones (198) |
|  | Chung et al. (1986) |
|  | Chung et al. (1986) |
|  | Chung et al. (1986) |
|  | Chung et al. (1986) |
|  | Chung et al. (1986) |
|  | Chung et al. (1986) |
|  | Chung et al. (1986) |
|  | Chung et al. (1986) |
|  | Chung et al. (1986) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984) |
|  | Miller and Jones (1984) |

Appendix-6


Average Error, \%=

775
775
1450
1450
1450
1450
1450
1450
1450
1677
1677
1677
1677
12086
12086
12086
12086
12086
GA-based STDEV, $\%=8.8$


* The data points in bold were used to test the model.
Appendix-6
Table A-6-2. Experimental data used for developing and testing of the GA-based $\mathrm{CO}_{2}$-live oil viscosity model and the model prediction results.
Error, \%

Appendix-6
Appendix-7
Table A-7-1. Experimental data used for developing and testing of the GA-based flue gas solubility in dead and live oils models and the models prediction results.

| $\mathbf{P}_{\mathrm{b}}$ MPa | $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Experimental <br> flue gas solubility, mole fraction | GA-based <br> Solubility, mole fraction | $\begin{gathered} \text { Error, } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: |
| 4.0 | 10.8 | 0.20 | 0.1918 | 4.1 |
| 4.0 | 21.5 | 0.40 | 0.2653 | 33.7 |
| 4.0 | 31.6 | 0.50 | 0.3956 | 20.9 |
| 7.6 | 10.3 | 0.24 | 0.2440 | 1.7 |
| 7.6 | 13.8 | 0.43 | 0.4793 | 10.7 |
| 7.6 | 17.2 | 0.53 | 0.6025 | 14.8 |
| 7.6 | 10.3 | 0.15 | 0.1577 | 5.2 |
| 7.6 | 17.2 | 0.38 | 0.3832 | 0.8 |
| 7.6 | 20.7 | 0.44 | 0.4790 | 8.9 |
| 7.6 | 27.6 | 0.53 | 0.5975 | 12.1 |
| 2.6 | 6.2 | 0.28 | 0.3206 | 14.5 |
| 2.6 | 10.3 | 0.46 | 0.5524 | 20.1 |
| 2.6 | 13.8 | 0.58 | 0.6427 | 10.8 |
| 2.6 | 4.7 | 0.16 | 0.1502 | 6.1 |
| 2.6 | 10.3 | 0.34 | 0.3247 | 5.0 |

Appendix－7

N゙

| $\stackrel{\circ}{0}$ |
| :---: |
|  |  |


$85 \% \mathrm{CO}_{2}, 5 \% \mathrm{C}_{1}, 10 \% \mathrm{~N}_{2}$
$85 \% \mathrm{CO}_{2}, 5 \% \mathrm{C}_{1}, 10 \% \mathrm{~N}_{2}$
$85 \% \mathrm{CO}_{2}, 5 \% \mathrm{C}_{1}, 10 \% \mathrm{~N}_{2}$
$85 \% \mathrm{CO}_{2}, 5 \% \mathrm{C}_{1}, 10 \% \mathrm{~N}_{2}$
$80.2 \% \mathrm{CO}_{2}, 0.35 \% \mathrm{~N}_{2}, 15.31 \% \mathrm{C}_{1}$,
$2.34 \% \mathrm{C}_{2}, 1.1 \% \mathrm{C}_{3}, 0.22 \% \mathrm{iC}_{4}$,
$0.19 \% \mathrm{C}_{4}, 0.29 \% \mathrm{C}_{5+}$
$80.2 \% \mathrm{CO}_{2}, 0.35 \% \mathrm{~N}_{2}, 15.31 \% \mathrm{C}_{1}$,
$2.34 \% \mathrm{C}_{2}, 1.1 \% \mathrm{C}_{3}, 0.22 \% \mathrm{iC}_{4}$,
$0.19 \% \mathrm{CC}_{4}, 0.29 \% \mathrm{C}_{5+}$
$80.2 \% \mathrm{CO}_{2}, 0.35 \% \mathrm{~N}_{2}, 15.31 \% \mathrm{C}_{1}$,
$2.34 \% \mathrm{C}_{2}, 1.1 \% \mathrm{C}_{3}, 0.22 \% \mathrm{iC}_{4}$,
$0.19 \% \mathrm{CC}_{4}, 0.29 \% \mathrm{C}_{5+}$
$83.2 \% \mathrm{CO}_{2}, 13.5 \% \mathrm{C}_{1}, 3.3 \% \mathrm{C}_{2}$
$83.2 \% \mathrm{CO}_{2}, 13.5 \% \mathrm{C}_{1}, 3.3 \% \mathrm{C}_{2}$
$83.2 \% \mathrm{CO}_{2}, 13.5 \% \mathrm{C}_{1}, 3.3 \% \mathrm{C}_{2}$
$60 \% \mathrm{CO}_{2}, 40 \% \mathrm{C}_{2}$
$60 \% \mathrm{CO}_{2}, 40 \% \mathrm{C}_{2}$
$60 \% \mathrm{CO}_{2}, 40 \% \mathrm{C}_{2}$
$60 \% \mathrm{CO}_{2}, 40 \% \mathrm{C}_{2}$
$60 \% \mathrm{CO}_{2}, 40 \% \mathrm{C}_{2}$

| $\begin{aligned} & \text { Z } \\ & \text { Zo } \\ & \text { o } \\ & \text { io } \\ & \text { in } \end{aligned}$ | $\begin{aligned} & z_{0}^{N} \\ & 0 \\ & 0_{0}^{\prime} \\ & \text { i } \end{aligned}$ |
| :---: | :---: |
| $\begin{aligned} & \stackrel{\ddots}{2} \\ & \stackrel{0}{\infty} \end{aligned}$ | $\begin{aligned} & \dot{u} \\ & \stackrel{0}{0} \\ & \infty \\ & \text { in } \end{aligned}$ |
| $\begin{gathered} \text { i } \\ 0 \\ 0 \\ 8 \\ 8 \end{gathered}$ | $\begin{gathered} \hat{1} \\ \text { ou } \\ 0 \\ \text { fo } \end{gathered}$ |
| む゙ | $\dot{\sim}$ |




Graue and Zana
（1981）
Graue and Zana
（1981）
Graue and Zana
（1981）
Graue and Zana
（1981）
Bon and Sarma
（2004）

Bon and Sarma
（2004）

Bon and Sarma
（2004）
Unpublished data
Unpublished data
Unpublished data
Dong et al．（2001a）
Dong et al．（2001a）
Dong et al．（2001a）
Dong et al．（2001a）
Dong et al．（2001a）
Srivastava et al．
（1999）
Srivastava et al．
（1999）
Srivastava et al．
（1999）
 0.5449
0.0996
0.1970
0.3282
0.4398
0.6251
0.6770
0.1790

0.3346

$\mathbf{0 . 4 6 4 4}$

$\mathbf{0 . 5 3 0 5}$

$\mathbf{0 . 5 6 8 8}$
$\mathbf{0 . 1 7 0 0}$
$\mathbf{0 . 3 8 1 8}$
$\mathbf{0 . 5 8 5 0}$
$\mathbf{0 . 6 7 2 9}$
$\mathbf{0 . 2 6 8 8}$
$\mathbf{0 . 4 1 7 0}$
0.5999
0.1998
0.3657
0.4594
0.1729
0.2019




Appendix-7

Appendix-7



| $\underset{i}{O} \stackrel{O}{\dot{\lambda}} \underset{\sim}{O} \underset{i}{\circ} \underset{\sim}{\circ} \underset{\sim}{0}$ |  |  |  |  |  | $\stackrel{\odot}{\text { ¢ }}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  |


$84.5 \% \mathrm{CO}_{2}, 10.6 \% \mathrm{C}_{\mathbf{1}}, 4.9 \% \mathrm{nC}_{4}$
$\mathbf{8 4 . 5 \%} \mathrm{CO}_{2}, \mathbf{1 0 . 6 \%} \mathrm{C}_{\mathbf{1}}, 4.9 \% \mathrm{nC}_{4}$
$\mathbf{8 4 . 5 \%} \mathrm{CO}_{\mathbf{2}}, \mathbf{1 0 . 6 \%} \mathrm{C}_{\mathbf{1}}, 4.9 \% \mathrm{nC}_{4}$
 $80 \% \mathrm{CO}_{2}, 20 \% \mathrm{~N}_{2}$ $80 \% \mathrm{CO}_{2}, 20 \% \mathrm{~N}_{2}$ $80 \% \mathrm{CO}_{2}, 20 \% \mathrm{~N}_{2}$ $\mathbf{9 0 \%} \mathrm{CO}_{2}, \mathbf{1 0} \% \mathrm{~N}_{2}$ $\mathbf{9 0 \%} \mathrm{CO}_{2}, 10 \% \mathrm{~N}_{2}$





| $\stackrel{\rightharpoonup}{\hat{\theta}}$ | $\stackrel{\rightharpoonup}{6}$ | $\begin{aligned} & 0 \\ & \frac{0}{6} \\ & \hline 0 \end{aligned}$ | N | 冎 | $\stackrel{\circ}{7}$ | ¢ | $\stackrel{9}{7}$ | $\stackrel{7}{7}$ | $\stackrel{8}{7}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\stackrel{\infty}{\circ}$ | $\propto$ | $\stackrel{\infty}{+\infty}$ |  | $\begin{aligned} & \text { N} \\ & \text { N} \\ & \text { N } \end{aligned}$ | సి | సి | $$ | $$ | $\begin{aligned} & \stackrel{\rightharpoonup}{C} \\ & \underset{O}{2} \end{aligned}$ |  |


|  |
| :---: |
|  |  |
|  |  |

Appendix-7
181
두ㅇㅕㅕㄹ ج 0.3985
0.4989
0.6069

| 3 | 0.4000 |
| :--- | :--- |
| .8 | 0.5000 |
|  | 0.6000 |
|  |  |
| Average |  |

8.3
10.8
14.1
0.1
0.1
0.1
$90 \% \mathrm{CO}_{2}, 10 \% \mathrm{~N}_{2}$
$90 \% \mathrm{CO}_{2}, 10 \% \mathrm{~N}_{2}$
$90 \% \mathrm{CO}_{2}, 10 \% \mathrm{~N}_{2}$
GA-based STDEV, \%=8.8
48.9
48.9
48.9
$\begin{array}{lll}\text { Taylor (1984) } & \mathbf{0 . 8 6 5 4} & 222 \\ \text { Taylor (1984) } & \mathbf{0 . 8 6 5 4} & \mathbf{2 2 2} \\ \text { Taylor (1984) } & \mathbf{0 . 8 6 5 4} & \mathbf{2 2 2}\end{array}$

* The data points in bold were used to test the model.
Appendix-8
Table A-8-1. Experimental data used for testing of the GA-based oil (dead and live oils) swelling factor model for oil swelling factor (due to flue gas injection) data.

|  |  | 10 6 6 6 | $\begin{aligned} & \text { 긴 } \\ & \stackrel{1}{8} \end{aligned}$ | $$ | $\bigcirc$ | $\begin{aligned} & \text { n } \\ & \underset{0}{3} \end{aligned}$ | $\stackrel{\infty}{\underset{\sim}{c}}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\sum$ |  | 8 | 8 | $\stackrel{8}{7}$ | $\stackrel{8}{7}$ | $\stackrel{8}{7}$ | $\stackrel{8}{7}$ | $\stackrel{\stackrel{1}{7}}{\stackrel{1}{7}}$ |


Reference
Sankur et al. (198

 Nguyen and Farouq Ali (1998) Nguyen and Farouq Ali (1998) Nguyen and Farouq Ali (1998) Nguyen and Farouq Ali (1998)
Nguyen and Far Nguyen and Farouq Nguyen and Farouq Ali (1998) Nguyen and Farouq Ali (1998) Nguyen and Farouq $\stackrel{\infty}{2}$ Nguyen and Farouq


 $70 \% \mathrm{CO}_{2}, 30 \% \mathrm{~N}_{2}$
$70 \% \mathrm{CO}_{2}, 30 \% \mathrm{~N}_{2}$
$70 \% \mathrm{CO}_{2}, 30 \% \mathrm{~N}_{2}$
$15.6 \% \mathrm{CO}_{2}, 84.4 \% \mathrm{~N}_{2}$
$15.6 \% \mathrm{CO}_{2}, 84.4 \% \mathrm{~N}_{2}$
$15.6 \% \mathrm{CO}_{2}, 84.4 \% \mathrm{~N}_{2}$
$15.6 \% \mathrm{CO}_{2}, 84.4 \% \mathrm{~N}_{2}$
$15.6 \% \mathrm{CO}_{2}, 84.4 \% \mathrm{~N}_{2}$
$14.9 \% \mathrm{CO}_{2}, 85.1 \% \mathrm{C}_{1}$
$14.9 \% \mathrm{CO}_{2}, 85.1 \% \mathrm{C}_{1}$
$14.9 \% \mathrm{CO}_{2}, 85.1 \% \mathrm{C}_{1}$
$14.9 \% \mathrm{CO}_{2}, 85.1 \% \mathrm{C}_{1}$
$14.9 \% \mathrm{CO}_{2}, 85.1 \% \mathrm{C}_{1}$
$15.6 \% \mathrm{CO}_{2}, 84.4 \% \mathrm{~N}_{2}$

$15.6 \% \mathrm{CO}_{2}, 84.4 \% \mathrm{~N}_{2}$ | 0.1303 |
| :---: |
| 0.1933 |
| 0.2305 |
| 0.0 |
| 0.047 |
| 0.07 |
| 0.092 |
| 0.122 |
| 0.0 |
| 0.096 |
| 0.177 |
| 0.209 |
| 0.274 |
| 0.0000 |
| 0.0509 |


 Ali (1998)
Nguyen and Farouq
Ali (1998)
Nguyen and Farouq
Ali (1998)
Nguyen and Farouq
Ali (1998)
Srivastava and Huang
(1997)
Srivastava and Huang
(1997)
Srivastava and Huang
(1997)
Srivastava and Huang
(1997)
Srivastava and Huang
(1997)
Srivastava and Huang
(1997)
Srivastava and Huang
(1997)






 $\begin{gathered}\text { Srivastava and Huang } \\ \text { (1997) } \\ \text { Srivastava and Huang } \\ \text { (1997) } \\ \text { Srivastava and Huang } \\ \text { (1997) } \\ \text { Graue and Zana } \\ \text { (1981) } \\ \text { Graue and Zana } \\ \text { (1981) } \\ \text { Graue and Zana } \\ \text { (1981) } \\ \text { Graue and Zana } \\ (1981)\end{gathered}$
Graue and Zana
(1981)
Graue and Zana
(1981)
Graue and Zana
(1981)
Graue and Zana
(1981)
Graue and Zana
$(1981)$
185

1.096
1.0
1.020
1.040
1.068
1.083
1.086
1.0
1.0136
1.0273
1.044
1.055

Appendix- 8

| Wattenbarger (1991) <br> Mohammed and <br> Wattenbarger (1991) <br> Brinlee and Brandt <br> (1982) | $\mathbf{0 . 8 2 5 0 7}$ | $\mathbf{1 3 3 . 3}$ |
| :---: | :---: | :---: |
| Brinlee and Brandt <br> (1982) | $\mathbf{0 . 8 3 4 8 1}$ | $\mathbf{1 1 2 . 2 8}$ |
| Brinlee and Brandt <br> (1982) | $\mathbf{0 . 8 3 4 8 1}$ | $\mathbf{1 1 2 . 2 8}$ |
| Brinlee and Brandt <br> (1982) | $\mathbf{0 . 8 3 4 8 1}$ | $\mathbf{1 1 2 . 2 8}$ |
| Brinlee and Brandt <br> $(1982)$ | $\mathbf{0 . 8 3 4 8 1}$ | $\mathbf{1 1 2 . 2 8}$ |
|  |  |  |
| * The data points in bold were used to test the model. |  |  |

Table A-9-1. Experimental data used for testing of the GA-based gas-oil mixture density model for flue gas-oil (dead and live oils) density data.
은 읍 O O
 Experimental $\rho, \mathrm{gm} / \mathrm{cc}$
0.9403
0.9595
0.9467
0.782

0.785

0.793

0.801
0.751
0.758
0.76
0.76
0.751
0.755
0.749
0.742
0.9635
0.9653




| Flue gas composition |
| :---: |
| $\mathbf{8 2 \%} \mathrm{CO}_{2}, \mathbf{1 8 \%} \mathrm{~N}_{2}$ |
| 82\% $\mathrm{CO}_{2}, \mathbf{1 8 \%} \mathrm{~N}_{2}$ |
| 82\% $\mathrm{CO}_{2}, 18 \% \mathrm{~N}_{2}$ |
| 95\% $\mathrm{CO}_{2}, 5 \% \mathrm{C}_{1}$ |
| $\mathbf{9 5 \%} \mathrm{CO}_{2}, \mathbf{5 \%} \mathrm{C}_{1}$ |
| $\mathbf{9 5 \%} \mathrm{CO}_{2}, \mathbf{5 \%} \mathrm{C}_{1}$ |
| 95\% $\mathrm{CO}_{2}, 5 \% \mathrm{C}_{1}$ |
| $\mathbf{9 0 \%} \mathrm{CO}_{2}, 10 \% \mathrm{nC}_{4}$ |
| $90 \% \mathrm{CO}_{2}, 10 \% \mathrm{nC}_{4}$ |
| 90\% $\mathrm{CO}_{2}, 10 \% \mathrm{nC}_{4}$ |
| 90\% $\mathrm{CO}_{2}, 10 \% \mathrm{nC}_{4}$ |
| 80\% $\mathrm{CO}_{2}, 20 \% \mathrm{nC}_{4}$ |
| 80\% $\mathrm{CO}_{2}, 20 \% \mathrm{nC}_{4}$ |
| 80\% $\mathrm{CO}_{2}, 20 \% \mathrm{nC}_{4}$ |
| 80\% $\mathrm{CO}_{2}, \mathbf{2 0 \%} \mathrm{nC}_{4}$ |
| 15.6\% $\mathrm{CO}_{2}, 84.4 \% \mathrm{~N}_{2}$ |
| 5.6\% $\mathrm{CO}_{2}, 84.4$ |


 Sankur et al. (1986)

 Graue and Zana (186I) (1981) Graue and Zana (1981) Graue and Zana
$(1981)$ Chaback (1988) Chaback (1988) Chaback (1988) Chaback (1988) Chaback (1988) Chaback (1988) Chaback (1988) Chaback (1988) Srivastava and Huang (1997) Srivastava and
187

 | 0.9661 | 0.9700 |
| :--- | ---: |
| 0.9671 | 0.9718 |
| 0.9675 | 0.9739 |
| 0.9635 | 0.9635 |
| 0.9585 | 0.9680 |
| 0.9595 | 0.9700 |
| 0.9616 | 0.9718 |
| 0.9602 | 0.9739 | 0.9635

0.9635
0.9635
0.9635
0.9635
0.9635
0.9635
0.9635 GA-based STDEV, $\%=0.8$

$15.6 \% \mathrm{CO}_{2}, \mathbf{8 4 . 4 \%} \mathrm{~N}_{2}$ $15.6 \% \mathrm{CO}_{2}, \mathbf{8 4 . 4 \%} \mathrm{~N}_{2}$ $14.9 \% \mathrm{CO}_{2}, \mathbf{8 5 . 1} \% \mathrm{C}_{1}$ $14.9 \% \mathrm{CO}_{2}, \mathbf{8 5 . 1} \% \mathrm{C}_{1}$ $14.9 \% \mathrm{CO}_{2}, \mathbf{8 5 . 1} \% \mathrm{C}_{1}$ $14.9 \% \mathrm{CO}_{2}, \mathbf{8 5 . 1} \% \mathrm{C}_{\mathbf{1}}$ $14.9 \% \mathrm{CO}_{2}, \mathbf{8 5 . 1} \% \mathrm{C}_{1}$ 28.0
28.0
28.0
28.0
28.0
28.0
28.0
28.0 0.97184
0.97184
0.97184
0.97184
0.97184
0.97184
0.97184
0.97184 Huang (1997) Huang (1997) Srivastava and Huang (1997) Srivastava and Huang (1997)
Huang (1997)
Srivastava and
Huang (1997)
Srivastava and
Huang (1997) Huang (1997) Srivastava and
Huang (1997)
Appendix-10

| Reference | $\gamma$ | TR, ${ }^{\circ} \mathrm{C}$ | $\mathrm{P}_{\mathrm{s}}, \mathrm{MPa}$ | Flue gas solubility, mole fraction | Flue gas composition | Experimental Flue gas-oil viscosity ( $\mu$ ), mPa.s | GAbased $\mu$, mPa.s | $\begin{gathered} \text { Error, } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Bon and Sarma (2004) | 0.7796 | 137.2 | 16.3 | 0.0 | $\begin{gathered} 80.2 \% \mathrm{CO}_{2}, 0.35 \% \mathrm{~N}_{2}, \\ 15.31 \% \mathrm{C}_{1}, 2.34 \% \mathrm{C}_{2}, \\ 1.1 \% \mathrm{C}_{3}, 0.22 \% \mathrm{iC}_{4}, \\ 0.19 \% \mathrm{nC}_{4}, 0.29 \% \mathrm{C}_{5+} \\ 80.2 \% \mathrm{CO}_{2}, 0.35 \% \mathrm{~N}_{2}, \end{gathered}$ | 0.139 | 0.139 | 0.0 |
| Bon and Sarma (2004) | 0.7796 | 137.2 | 19.0 | 0.2 | $\begin{gathered} 15.31 \% \mathrm{C}_{1}, 2.34 \% \mathrm{C}_{2}, \\ 1.1 \% \mathrm{C}_{3}, 0.22 \% \mathrm{iC}_{4}, \\ 0.19 \% \mathrm{nC}_{4}, 0.29 \% \mathrm{C}_{5+} \\ 80.2 \% \mathrm{CO}_{2}, 0.35 \% \mathrm{~N}_{2}, \end{gathered}$ | 0.13 | 0.127 | 2.46 |
| Bon and Sarma (2004) | 0.7796 | 137.2 | 21.4 | 0.4 | $\begin{gathered} 15.31 \% \mathrm{C}_{1}, 2.34 \% \mathrm{C}_{2}, \\ 1.1 \% \mathrm{C}_{3}, 0.22 \% \mathrm{iC}_{4}, \\ 0.19 \% \mathrm{nC}_{4}, 0.29 \% \mathrm{C}_{5+} \end{gathered}$ | 0.119 | 0.113 | 5.25 |
| Dong et al. (2001a) | 0.8348 | 67.0 | 8.5 | 0.0 | 60\% $\mathrm{CO}_{2}, 40 \% \mathrm{C}_{2}$ | 0.76 | 0.760 | 0.0 |
| Dong et al. (2001a) | 0.8348 | 67.0 | 10.5 | 0.239 | $60 \% \mathrm{CO}_{2}, 40 \% \mathrm{C}_{2}$ | 0.54 | 0.555 | 2.77 |
| Dong et al. (2001a) | 0.8348 | 67.0 | 11.9 | 0.362 | 60\% $\mathrm{CO}_{2}, 40 \% \mathrm{C}_{2}$ | 0.46 | 0.460 | 0.03 |
| Dong et al. (2001a) | 0.8348 | 67.0 | 12.3 | 0.395 | $\mathbf{6 0 \%} \mathrm{CO}_{2}, \mathbf{4 0 \%} \mathrm{C}_{2}$ | 0.43 | 0.436 | 1.47 |
| Nguyen and Farouq Ali (1998) | 0.9529 | 23.0 | 0.1 | 0.0 | $90 \% \mathrm{CO}_{2}, 10 \% \mathrm{~N}_{2}$ | 1058 | 1058 | 0.0 |
| Nguyen and Farouq Ali (1998) | 0.9529 | 23.0 | 1.0 | 0.1665 | $90 \% \mathrm{CO}_{2}, 10 \% \mathrm{~N}_{2}$ | 375 | 382.65 | 2.04 |
| Nguyen and Farouq Ali (1998) | 0.9529 | 23.0 | 2.0 | 0.2421 | $90 \% \mathrm{CO}_{2}, 10 \% \mathrm{~N}_{2}$ | 230 | 234.57 | 1.98 |
| Nguyen and Farouq Ali (1998) | 0.9529 | 23.0 | 3.0 | 0.2854 | $90 \% \mathrm{CO}_{2}, 10 \% \mathrm{~N}_{2}$ | 180 | 175.92 | 2.26 |
| Nguyen and Farouq Ali (1998) | 0.9529 | 23.0 | 0.1 | 0.0 | $80 \% \mathrm{CO}_{2}, 20 \% \mathrm{~N}_{2}$ | 1058 | 1058 | 0.0 |


|  |
| :---: |
|  |
|  |

## Appendix-11

## The GA Software Code

|  | GA software code developed in this study for developing of the quantitative models |
| :---: | :---: |
|  | ********************************************************************** <br> dimension (put the dimensions based on the number of data points and the population size) <br> common k,n,kk,y,nn <br> call seed(2.0) |
| c**** | *********************************************************************** <br> Open input file (to enter the experimental data and other input data) and output file (for the results). <br> open(unit=1,file=file.inp') <br> open(unit=2,file='file.out') |
| $c^{* *}$ | ************************************************************************** |
| c | The software input section: |
| c | Enter number of the proposed model coefficients (k), number of the model variables $(\mathrm{kk})$, and the number of the data available ( nn ) <br> $\operatorname{read}(1, *) \mathrm{k}, \mathrm{kk}, \mathrm{nn}$ <br> write( $\left.{ }^{*}, *\right)$ 'enter the population size' <br> read(*,*)n |
|  | Read the experimental data model (from the input file) for the variables, which will be used to develop the model. |
| c | Enter the initial population values based on random real coded numbers (building the chromosomes). $\begin{aligned} & \text { do } 11 \mathrm{j}=1, \mathrm{n} \\ & \mathrm{x}(\mathrm{j}, \mathrm{i})=(\operatorname{abs}(\operatorname{md}())) \end{aligned}$ |
| 11 | continue |
|  | The end of software input section: |
| cccc | ****************************** |
|  | Evaluation function: to assign each chromosome an average fitness value based on the accuracy of its prediction (the higher the fitness value, the higher the prediction accuracy. $\mathrm{k} 1=1$ $\mathrm{k} 2=\mathrm{n}$ <br> call eval(x,k1,k2,nn,fit,dcal, and other affecting variables) |
| c | ****************************** |
|  | Parent selection technique: based on the roulette wheel selection method. call parent ( $\mathrm{p}, \mathrm{k}, \mathrm{n}, \mathrm{q}, \mathrm{u}, \mathrm{fit}, \mathrm{x}, \mathrm{m}$ ) |
| c | ) |
| c c c c | Apply the reproduction operators (crossover and mutation) to produce a new offspring (two new children) from the two parents selected to improve the population fitness and consequently improve the group of the problem solutions (improve the model results). <br> call crmut( $\mathrm{x}, \mathrm{k}, \mathrm{n}$ ) <br> $\mathrm{k} 1=\mathrm{n}+3$ <br> $\mathrm{k} 2=\mathrm{n}+4$ |

c $* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *$
c Evaluate the two produced two children (the new offspring).
call eval(x,k1,k2,nn,fit,dcal, and other affecting variables)
$\mathrm{c} * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *$
c Get the best two chromosomes between the two parents and the two children to reinsert
c them back into the population.
call max1(fit,k,n,m,x)
c $* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *$
c Get the best chromosome's average fitness in the population (the best solution).
call max2(fit,k,n,bav,x)
$\mathrm{c} * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *$
c Get the average population fitness (the average fitness of all the population
c chromosomes).
sum=0.0
do $275 \mathrm{j}=1$, n
sum=sum+fit(j)
275 continue
av=sum/n
write(*,*)'av fitness of the population=',av
c $* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *$
c Compare between the best chromosome's average fitness and the average population
c fitness to test the stopping criterion.
diff=abs(bav-av)
c $* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *$
c If the difference between the best fitness and the average fitness is less than a certain
c accuracy ( 0.00001 ) then write the results and finish the software, otherwise return
c back to select more parents and produce more offspring to improve the problem
c solution.
if(diff.le.0.00001)go to 22
go to 2
c $* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *$
c The software output section:
22 write( $2, *$ )'The GA software output for GA-based model:'
write $(2, *)^{\prime}$ '1. the best chromosome's average fitness in the population is:',bav
write $\left(2,{ }^{*}\right)^{\prime} 2$. the coefficients of the proposed model, (for example, a,b,c)'
write (2,*)' $\mathrm{a}={ }^{\prime}, \mathrm{x}(\mathrm{n}, 1)$
write(2,*)'b=', x(n,2)
write (2,*)'c=',x(n,3)
c The end of output format section.
c $* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *$
stop
end
c End of the main software body.

c A function to develop the random values for the initial random population.
function $\operatorname{rnd}()$
call random (g)
rnd $=2.0^{*}(\mathrm{~g}-0.5)$
c This function was used to determine random values (between -1.0 to +1.0 )
return
end

c
A subroutine to evaluate the population chromosomes (to determine the chromosome's
c
c
average fitness value) using an objective function, which developed based on the proposed model.
subroutine eval(x,k1,k2,nn,fit,dcal, and other affecting variables)
do $555 \mathrm{j}=\mathrm{k} 1, \mathrm{k} 2$
sum=0.0
do 88 l=1,nn
dcal( $\mathrm{j}, \mathrm{l})=$ "design the objective function and develop the model equation based on the relationship between the modelled parameter and the major affecting variables"
Determine the average fitness value for each chromosome based on the difference
between the predicted value and the observed value.
fdiff=abs(dcal(j, 1 )-d(1,l))
sfit $(\mathrm{j}, \mathrm{l})=\mathrm{C}_{\mathrm{g}} /\left(\mathrm{C}_{\mathrm{g}}+\mathrm{fdiff}\right)$
Use penalty functions to prevent presentation of abnormal values (e.g., negative values for the MMP).
$\operatorname{if}(\mathrm{dcal}(\mathrm{j}, \mathrm{l}) . \mathrm{lt} .0 .0) \mathrm{sfit}(\mathrm{j}, \mathrm{l})=\mathrm{sfit}(\mathrm{j}, 1)^{*}(1-0.001)$
if(fdiff.gt.0.02)sfit( $\mathrm{j}, \mathrm{l})=\mathrm{sfit}(\mathrm{j}, \mathrm{l}) *(1-0.001)$
sum=sum+sfit $(\mathrm{j}, \mathrm{l})$
continue
Present the chromosome's average fitness value.
fit $(\mathrm{j})=\mathrm{sum} / \mathrm{nn}$
write(*,*)'the value of fit(j)='
write(*,*)fit(j)
continue
return
end
*******************************************************************************)
This subroutine was used to determine two parents from the population by using
roulette wheel parent selection technique (the parents chromosomes is used to
determine a new offspring to improve the population fitness (improve the problem solution).
subroutine parent(p,k,n,q,u,fit,x,m)
dimension $p(105), q(105)$, fit(105), $x(105,30), m(2)$
real u,prop,sum
sum1 $=0.0$
do $133 \mathrm{j}=1$, n
sum=sum1+fit(j)
sum1 $=$ sum
continue
prop $=0.0$
do $40 \mathrm{j}=1$,n
$\mathrm{p}(\mathrm{j})=\mathrm{fit}(\mathrm{j}) / \mathrm{sum}$
continue
do $50 \mathrm{l}=1, \mathrm{n}$
$\mathrm{q}(\mathrm{l})=\mathrm{prop}+\mathrm{p}(\mathrm{l})$
prop $=q(1)$
continue
do $80 \mathrm{iz}=1,2$
$u=0.5^{*}(\operatorname{rnd}()+1.0)$
$j=1$
if(u.le.q(j))go to 99
do $100 \mathrm{j}=2, \mathrm{n}$
if ((u.gt.q(j-1)) .and. (u.le.q(j)))go to 99
continue

```
99 if((iz.eq.2.0).and.(j.eq.m(1)))go to 202
    \(\mathrm{m}(\mathrm{iz})=\mathrm{j}\)
    do \(119 \mathrm{jj}=1, \mathrm{k}\)
    \(\mathrm{x}(\mathrm{n}+\mathrm{iz}, \mathrm{jj})=\mathrm{x}(\mathrm{m}(\mathrm{iz}), \mathrm{jj})\)
119
    continue
    fit( \(\mathrm{n}+\mathrm{iz})=\mathrm{fit}(\mathrm{m}(\mathrm{iz}))\)
80 continue
    return
    end
\(\mathrm{c} * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *) ~\)
c This subroutine was used to apply the reproduction operators (crossover and mutation)
c on the selected two parents to produce two children (new offspring).
    subroutine \(\operatorname{crmut}(\mathrm{x}, \mathrm{k}, \mathrm{n})\)
    dimension \(x(105,30)\), anew (105)
    do \(29 \mathrm{jj}=1\), k
    \(\mathrm{x}(\mathrm{n}+3, \mathrm{jj})=\mathrm{x}(\mathrm{n}+1, \mathrm{jj})\)
    \(x(n+4, j \mathrm{j})=\mathrm{x}(\mathrm{n}+2, \mathrm{j})\)
29 continue
    lrcf=k*abs(rnd())+1
    do \(47 \mathrm{lt}=\mathrm{lrcf}, \mathrm{k}\)
    \(\mathrm{x}(\mathrm{n}+3, \mathrm{lt})=\mathrm{x}(\mathrm{n}+2, \mathrm{lt})\)
    \(x(n+4,1 t)=x(n+1, l t)\)
    continue
    do \(3 \mathrm{j}=\mathrm{n}+3, \mathrm{n}+4\)
    \(\operatorname{lrmt}=\mathrm{k} * \mathrm{abs}(\operatorname{rnd}())+1\)
    anew \((\mathrm{j})=\operatorname{rnd}()\)
    \(\mathrm{x}(\mathrm{j}, \operatorname{lrmt})=\lambda * \mathrm{x}(\mathrm{j}, \operatorname{lrmt})+\beta^{*}\) anew \((\mathrm{j})\)
    \(\lambda\) and \(\beta\) values are between 0 and 1 and their values are selected based on the software
c
3
    pormance (experimental evaluation).
    continue
    return
    end
c
    selected parents and the two produced children chromosomes and reinsert the best two
    chromosomes to the population again.
    subroutine max1(fit,k,n,m,x)
    dimension fit(105), \(\mathrm{x}(105,50), \mathrm{a}(105,50), \mathrm{m}(2)\)
    nn=3
    do 200 loop \(=1, \mathrm{nn}\)
    \(\mathrm{jj}=\mathrm{n}+4\)-loop
    do \(101 \mathrm{l}=\mathrm{n}+1\), jj
    if(fit(l).lt.fit(l+1))go to 101
    temp=fit(l)
    do \(6 \mathrm{jj}=1\), k
    \(\mathrm{a}(1, \mathrm{j})=\mathrm{x}(1, \mathrm{j})\)
6
    continue
    fit \((1)=f i t(1+1)\)
    do \(11 \mathrm{j}=1, \mathrm{k}\)
    \(\mathrm{x}(\mathrm{l}, \mathrm{j})=\mathrm{x}(\mathrm{l}+1, \mathrm{j} \mathrm{j})\)
    continue
    fit \((1+1)=\) temp
```

```
    do 13 jj=1,k
    x(l+1,jj)=a(l,jj)
    continue
    continue
    continue
    do 9 iz=1,2
    do 1 jj=1,k
    x(m(iz),jj)=x(n+iz+2,jj)
1
9
c
c
c
    This subroutine was used to determine the best (max.) chromosome's average fitness
    from the population and send this chromosome to test the stopping criteria.
    subroutine max2(fit,k,n,bav,x)
    dimension fit(105),a(105,30),x(105,30)
    nn2=n-1
    do 301 loop2=1,nn2
    jj2=n-loop2
    do 102 l=1,jj2
    if(fit(1).lt.fit(l+1))go to 102
    temp2=fit(1)
    do 7676 jj=1,k
    a(1,jj)=x(l,j)
    continue
    fit(l+1)=temp2
    do 1234 jj=1,k
    x(l+1,jj)=a(1,jj)
    continue
    continue
    continue
    bav=fit(n)
c
bav=best chromosome average fitness(max. average fitness).
    write(*,*)' best average fitness at end of max2= ',bav
    write(*,*)' best average chromosome at end of max2= ',(x(n,jj),jj=1,k)
    return
    end
```


[^0]:    *Data in bold were used to test the model

[^1]:    *Data in bold were used to test the model

[^2]:    Error, \%
     GA-based oil swelling factor, fraction
    1.000
    1.026
    1.048
    1.096
    1.251
    1.000
    1.084
    1.191
    1.000
    1.049
    1.105
    1.206
    1.302
    1.000
    1.048
    1.117
    1.190
    1.000
    1.030
    1.064
    1.084 Experimental oil swelling factor
    1.025
    1.039
    1.092
    1.245
    1 S $\stackrel{\circ}{2}$ $\stackrel{N}{2}$ ㄷ. $\pm$ $\xrightarrow{\circ}$ $-\overline{0}$ N 1.092
    $\mathrm{CO}_{2}$ Solubility, mole fraction
    0
    0.196
    0.294
    0.455
    0.667
    0
    0.423
    0.625
    0
    0.313
    0.495
    0.667
    0.717
    0
    0.299
    0.508
    0.632
    0
    0.215
    0.366
    0.43

