A STUDY OF OXIDATION REACTION KINETICS DURING AN AIR INJECTION PROCESS

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To my mothers love which always encourages me
# TABLE OF CONTENTS

List of Tables vi
List of Figures vii
Nomenclature ix
Abstract x
Statement of Originality xii
Acknowledgements xiii
Paper, Reports & Poster from this Study xv

## Chapter 1: INTRODUCTION

1.1 Background 1
1.2 Research Objectives 3
1.3 Overview of Chapters 4

## Chapter 2: RESEARCH BACKGROUND

2.1 Overview of Air Injection 5
2.2 Why Air Injection? 7
2.3 Is Air Injection Simple Gas Flood? 7
2.4 Candidate Reservoir Screening 8
   2.4.1 Field Screening 9
   2.4.2 Laboratory Screening 9
2.5 Air Injection Field Performance 10
2.6 Air Injection in Australian Basins 11
2.7 Summary of Current Research on Air Injection 14

## Chapter 3: THEORETICAL ASPECTS OF AIR INJECTION

3.1 Oxidation Reactions Associated with Air Injection 15
   3.1.1 Low Temperature Oxidation 15
   3.1.2 Pyrolysis 17
   3.1.3 High Temperature Oxidation 17
3.2 Air Injection of Light Oil versus In-situ Combustion of Heavy Oil 18
3.3 Factors Affecting the Oxidation Behaviour of Crude Oil 20
6.2 Discussions on Thermal Test Results 77
  6.2.1 Kenmore Oils 77
  6.2.2 Oils of Field B 78
6.3 Kinetic Parameters 80

Chapter 7: CONCLUSIONS AND RECOMMENDATIONS 82
  7.1 Conclusions 83
  7.2 Recommendations 84

REFERENCES 86
LIST OF TABLES

Table 2. 1  Reservoir Properties of Prospective Basins in Australia  12
Table 2. 2  Cooper-Eromanga Basin–Oil Reservoir Properties   13

Table 4. 1  Principal Thermo Analytical Methods     30
Table 4. 2  Oil and Cutting Samples      44

Table 5. 1  Specific Gravity and API-gravity     46
Table 5. 3  Thermal Tests Performed in this Study  49

Table 6. 1  Kinetic Parameters       81
LIST OF FIGURES

Fig. 2.1 Conceptual Representation of Air Injection Process 6
Fig. 3.1 Crude Oil Oxidation Regions 20

Fig. 4.1 Setup of Rheometer Physica MCR 301 29
Fig. 4.2 Clarus 500 GC–MS Apparatus Setup 29
Fig. 4.3 Schematic Diagram of a TGA Furnace Assembly 31
Fig. 4.4 View of the TA 2950 Thermogravimetric Analyser 32
Fig. 4.5 Schematic Diagram of a Heat Flux DSC Cell 33
Fig. 4.6 View of the DSC 2920 (TA Instruments) 33
Fig. 4.7 View of the DSC 2920 with Pressure Cell 34
Fig. 4.8 View of the High Pressure Cell of DSC 2920 34
Fig. 4.9 Super Heated Result of Kenmore Oil #34 with Rock #34 36
Fig. 4.10 Temperature Calibration of TGA Instrument by Nickel 38
Fig. 4.11 Temperature Calibration of TGA by Alumel 39
Fig. 4.12 DSC Baseline of DSC–2920 at 4500kPa in Air Environment 40
Fig. 4.13 Temperature Calibration Result for PDSC 41
Fig. 4.14 Reproducibility of TGA and DTG curve 42
Fig. 4.15 Reproducibility of TGA and DTG curve 42
Fig. 4.16 Reproducibility of Heat-flow Curve 43

Fig. 5.1 Viscosity Temperature Profile of Kenmore Crude Oil 47
Fig. 5.2 Hydrocarbon Distribution of Kenmore Crude Oil 47
Fig. 5.3 Viscosity Temperature Profile of Field B Crude Oil 48
Fig. 5.4 Hydrocarbon Distribution of Crude Oil B 48
Fig. 5.5 TGA of Kenmore Cutting #31 in Air and N2 Environments 50
Fig. 5.6 PDSC of Kenmore Cutting in Air and O2 Environments 51
Fig. 5.7 TGA of Kenmore Oil #32 in Air and N2 Environments 52
Fig. 5.8 DSC of Kenmore Oil #32 in Air at Atmospheric Pressure 53
Fig. 5.9 PDSC of Kenmore Oil #32 in Air and O2 Environments 54
Fig. 5.10 TGA of Kenmore Oil #32 and Cutting #31 in Air Environment 55
Fig. 5.11 PDSC of Kenmore Oil #32 and Cutting #31 in Air and O2 56
Fig. 5.12 TGA of Kenmore Cutting #34 in Air and N2 Environments 57
| Fig. 5.13  | PDSC of Kenmore Rock #34 in Air Environment | 57  |
| Fig. 5.14  | TGA of Kenmore Oil #34 in Air and N₂ Environments | 58  |
| Fig. 5.15  | DSC of Kenmore Oil #34 in Air at Atmospheric Pressure | 59  |
| Fig. 5.16  | PDSC of Kenmore Oil #34 in Air and O₂ Environments | 60  |
| Fig. 5.17  | TGA of Kenmore Oil #34 with Cutting #34 in Air and N₂ | 61  |
| Fig. 5.18  | TGA of Kenmore Oil #34 with Cutting #34 in N₂ Environment | 61  |
| Fig. 5.19  | TGA of Kenmore Oil #34 with Cutting #34 in Air | 62  |
| Fig. 5.20  | PDSC of Kenmore Oil #34 and Cutting #34 in Air and O₂ | 63  |
| Fig. 5.21  | TGA of Cutting Samples of Field B in Air Environment | 64  |
| Fig. 5.22  | PDSC of E#22 Rock Cutting in Air Environment | 65  |
| Fig. 5.23  | TGA of E #13 Oil in Air and N₂ Environments | 66  |
| Fig. 5.24  | PDSC of E #13 in Air Environment | 67  |
| Fig. 5.25  | TGA of E #13 Oil and Cutting E#22 in Air Environment | 68  |
| Fig. 5.26  | TGA of W #3 Oil in Air and N₂ Environments | 69  |
| Fig. 5.27  | TGA of W #5 Oil in Air and N₂ Environments | 70  |
| Fig. 5.28  | DSC of W #3 Oil in Air Environment | 71  |
| Fig. 5.29  | PDSC of W #5 in Air Environment | 72  |
| Fig. 5.30  | Details of TGA of W #3 Oil in Air Environment | 73  |
| Fig. 5.31  | TGA of W #3 Oil and Cutting E#22 in Air Environment | 73  |
| Fig. 5.32  | TGA of W #5 Oil and Cutting E#22 in Air Environment | 74  |
| Fig. 5.33  | PDSC of W #3 with Rock Cuttings in Air Environment | 75  |
| Fig. 5.34  | PDSC of W #5 with Rock Cuttings in Air Environment | 75  |
NOMENCLATURE

Abbreviations

API  –  American Petroleum Indication
ARC  –  Accelerating Rate Calorimetry
DTA  –  Differential Thermal Analysis
DTG  –  Derivative Thermogravimetry
EGA  –  Evolved Gas Analysis
EOR  –  Enhanced Oil Recovery
GC  –  Gas Chromatography
HC  –  Hydrocarbon
HPAI – High Pressure Air Injection
HTC – High Temperature Combustion
IOR  –  Improved Oil Recovery
ISC  –  In situ Combustion
LTO  –  Low Temperature Oxidation
NTGR  –  Negative Temperature Gradient Region
PDSC  –  Pressurised Differential Scanning Calorimetry
RTO  –  Ramped Temperature Oxidation
SARA  –  Saturates, Resins, Aromatics, Asphaltenes
TG/TGA  –  Thermogravimetry/Thermogravimetric Analysis

Symbols

α  –  fractional weight change of the sample = (w₀-wₜ)/(w₀-w∞)
β  –  Heating rate
E  –  activation energy of reaction
H  –  enthalpy to be released
k  –  specific reaction rate
R  –  universal gas constant
T  –  temperature
t  –  time
w∞  –  final sample weight
w₀  –  initial sample weight
wₜ  –  sample weight at ‘t’
Δt  –  time interval
m, n  –  reaction order
ABSTRACT

Air injection is an enhanced oil recovery (EOR) process in which compressed air is injected into a high temperature, light-oil reservoir. The oxygen in injected air is intended to react with a fraction of reservoir oil at elevated temperature resulting in in-situ generation of flue gases and steam, which, in turn, mobilize and drive the oil ahead towards the producing wells. To understand and determine the feasibility of the air injection process application to a given reservoir, it is necessary to understand the oxidation behaviour of the crude oil.

The aim of this study is to screen two Australian light-oil reservoirs; Kenmore Oilfield, Eromanga Basin, and another Australian onshore oil and gas field “B”* for air injection EOR process, and to understand the oxidation reaction kinetics during air injection. It is carried out by the thermogravimetric and differential scanning calorimetric (TGA/DSC) studies to investigate the oxidation mechanism during an air injection process. There has not been any TGA/DSC evaluation conducted to date with regard to air injection for Australian light-oil reservoirs.

A series of thermal tests was performed to investigate the oxidation behaviour of two selected reservoirs in both air and oxygen environments. The first step undertaken in this study is thermogravimetric and calorimetric characterization of crude oils to (i) identify the temperature range over which the oil reacts with oxygen, (ii) examine the oxidation behaviour within the temperature identified, and (iii) evaluate the mass loss characteristics during the oxidation. This study also examines the effect of pressure on oxidation at different temperature ranges and the effect of core material (rock cutting) on oxidation reactions. Finally, kinetic data are calculated from thermal tests results by literature described method.

Kenmore and Field B both are high temperature and light-oil reservoirs. Hydrocarbon distribution indicates that Kenmore oil contains 84 mole% of lower carbon number n-C5 – n-C13 compounds. Reservoir B oil also contains a substantial amount (i.e., 95 mole %) of lower carbon number n-C4 – C19 compounds. These lighter components may contribute favourably towards efficient oxidation. However, a high content of lighter ends in the oil may also result in a lower fuel load. Generally, low molecular weight oil gives fastest mass loss from heavy crude oil.
Thermal tests on Kenmore oil showed two distinct exothermic reactivity regions in temperatures of 200-340°C and 360-450°C, with a 85-95% mass loss when the temperature reached 450°C. Reservoir B oil showed a wider exotherm range between approximately 180°C-260°C with 90-95% mass loss by temperature 350°C. In the high temperature range, the combustion reactions of Reservoir B oil are weaker than Kenmore oil. This is due to insufficient fuel available for oxidations in high temperature region. Reservoir B oil has more chance to auto ignite; but it has less sustainability to the ignition process. Based on the sustainability study of the ignition process, between the two reservoirs, Kenmore is the better candidate for air injection.

Based on the thermal tests, it is concluded that for light-oil oxidation, vaporization is the dominant physical phenomenon. At low temperature range, the addition of the core material enhanced the exothermic reactions of the oil. The elevated pressure accelerated the bond scission reactions. The largest amount and highest rate of energy generation occurred at the low temperature range. Activation energies (E) are calculated from thermal test results and the value of ‘E’ in oil-with-core combined tests is smaller than the oil-only test. This indicates that the rock material has a positive impact on the combustion process. Moreover, the compositional analysis result addresses the composition of oils, which can help understand the oxidation behaviour of light-oils.

* For confidentiality reasons, the field name is coded as Field B at the request of the operating company.
STATEMENT OF ORIGINALITY

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

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