A STUDY OF OXIDATION REACTION KINETICS DURING AN AIR INJECTION PROCESS

SHYAMOL CHANDRA DAS

A thesis submitted for the degree of
Master of Engineering Science

Australian School of Petroleum
Faculty of Engineering, Computer & Mathematical Science
The University of Adelaide
Adelaide, Australia

April 2009

To my mothers love which always encourages me

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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 = $(w_0\text{-}w_t)/(w_0\text{-}w_\infty)$
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
w_0	–	initial sample weight
w_t	–	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-C_5 – n-C_{13} compounds. Reservoir B oil also contains a substantial amount (i.e., 95 mole %) of lower carbon number n-C_4 – C_{19} 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.

I give consent to this copy of my thesis, when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library catalogue, the Australasian Digital Theses Program (ADTP) and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

Shyamol Chandra Das

April 2009

ACKNOWLEDGEMENTS

The most important thing that must be said about working on this research project is that it has been one of the most rewarding experiences of my life. It has given me the opportunity to meet many wonderful people who have provided me much-appreciated support during my study. For this they deserve the following acknowledgement.

My faith in academia is greatly increased by my supervisor Professor Hemanta Sarma. I gratefully acknowledge the continuous support, technical advice and guidance I have received from him during this study. His professionalism and responsibility always inspired me to work promptly. Also, I have received continuous moral support and individual non-academic advice from him in which I had the opportunity to ask him at any time. I could not ask for better supervisors.

For the financial support, I thank the Australian School of Petroleum; The University of Adelaide provided me the SANTOS scholarship. I would like to thank Beach Petroleum Limited and Santos Limited for their support during this study, as well as Mark Pitkin and Sarah McDonnell for their advice and technical assistance.

I recognize the laboratory support of Dr. Milena Ginic-Markovic and Dr. Rachel Pillar, School of Chemistry, Physics and Earth Sciences, Flinders University for their assistance in performing the thermal analyses of this work.

Further, I deeply appreciate my fellow researchers for their entertaining discussions and encouragement as well the assistance I have received in different tasks throughout the project. Here I must mention two names Prasant Jadhawar and Saju Menacherry for their great support during the course of work, especially in writing period, also thanks to all at third floor multicultural and serious researchers.

All the staff at the ASP, I would rather not mention any name in particular because it has been a wonderful relationship with everyone and I am thankful for their support towards the completion of this work.

Research is never an easy task. I am very grateful to my parents who since an early age guided me through life. Special credit towards the completion of this thesis goes to my mother and my family for their patience and encouragement; also I would like to thank my brothers for putting up with me for higher goals.

Finally, my deepest thanks extended to my friend Naseem, who always inspired motivation and excellence in any work undertaken for achieving my goals, and that I have to admire her.

PAPER, REPORTS & POSTER FROM THIS STUDY

Sarma H. and Das S., 2009. "*Air Injection Potential in Kenmore Oilfield in Eromanga Basin, Australia: A Screening Study Through Thermogravimetric and Calorimetric Analyses"*, Paper SPE-120595 presented at the 16th SPE Middle East Oil & Gas Show and Conference; Bahrain International Exhibition Centre, Kingdom of Bahrain, 15-18 March.

Das S. and Sarma H., 2008. "*Screening of Selected Australian Reservoirs for Air Injection Process Candidate Reservoir: Kenmore Oilfield, Eromanga Basin"*, report submitted to Beach Petroleum Limited, June 5.

Das S., and Sarma H., 2008. "*Screening Study of Field B for Air Injection Process"*, report submitted to Santos Limited, November 15.

Das S. 2008. "*Burn and Earn: Air Injection EOR Technique for Australian Light-Oil Reservoirs*", poster presented at the AIE National Postgraduate Student Energy Awards, Sydney, Australia, November 18.