



# **A STUDY OF OXIDATION REACTION KINETICS DURING AN AIR INJECTION PROCESS**

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***To my mothers love which always encourages me***

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# 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	–	<i>In situ</i> 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

$\alpha$	–	fractional weight change of the sample = $(w_0 - w_t)/(w_0 - w_\infty)$
$\beta$	–	Heating rate
E	–	activation energy of reaction
H	–	enthalpy to be released
k	–	specific reaction rate
R	–	universal gas constant
T	–	temperature
t	–	time
$w_\infty$	–	final sample weight
$w_0$	–	initial sample weight
$w_t$	–	sample weight at 't'
$\Delta t$	–	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<sub>5</sub> – n-C<sub>13</sub> compounds. Reservoir B oil also contains a substantial amount (i.e., 95 mole %) of lower carbon number n-C<sub>4</sub> – C<sub>19</sub> 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.

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\* 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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## 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 16<sup>th</sup> 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.

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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.