

SOURCE ROCK KINETICS ANALYSIS

GIPPSLAND BASIN WELLS

Prepared for:

Energy and Minerals Victoria

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1. INTRODUCTION

Two source rock samples from the **Burong-1** and **North Seaspray-1** wells in the Gippsland Basin were submitted for oil generation kinetics analysis. This work was carried out as part of a broader hydrocarbon characterisation study undertaken by Geotechnical Services Pty Ltd for Energy and Minerals Victoria in March 1997.

Two copies of this report have been sent to Mr. Kourosh Mehin at Energy and Minerals Victoria. Any queries pertaining to the data or interpretive content presented herein should be directed to either Dr. Paul Kralert or Dr. Birgitta Hartung-Kagi at Geotechnical Services Pty Ltd.

All data and information are proprietary to Energy and Minerals Victoria and are considered as highly confidential by all Geotechnical Services Pty Ltd personnel.

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2. ANALYTICAL PROCEDURE

Kinetic measurements were carried out using a modified Rock-Eval II micro-scale pyrolysis instrument (Delsi Instruments). Flame ionisation detector and oven thermistor outputs were captured and processed on an IBM-compatible 486DX/33 personal computer linked to the pyrolyzer via a Humble Instruments interface module and a PE Nelson 9000 Series A/D converter (sampling rate 1 Hz).

All samples selected for analysis were ground to a particle size of less than 125 μ m and solvent-extracted by ultrasonication with dichloromethane for 2 hr to remove free hydrocarbons (i.e. soluble organic matter).

Pyrolysis experiments were performed in duplicate at four different heating rates, *viz.* 5, 15, 25 and 50°C min⁻¹. Sample weights used ranged from 30 to 60 mg according to the organic carbon content of the rock. Initial and final isotherms were 300°C (5 min) and 550°C (1 min), respectively. In cases where T_{max} values recorded for duplicate experiments differed by more than 1°C, additional runs were made until the required level of reproducibility was attained.

Oil generation kinetics were calculated from the pyrolysis data obtained for each sample using the KINETICS[©] program (v. 2.4.3) developed by the Lawrence Livermore National Laboratory (USA). Computations were based on the discrete distributed activation energy (E_a) model, and involved an iterative non-linear regression analysis of reaction rate data derived from S_2 peak profiles. Calibration of the Rock-Eval oven temperature was achieved using solvent-extracted Green River Anvil Points shale (AP22) as a reference standard (principal $E_a = 54$ kcal mol⁻¹).



3. RESULTS

Calculated activation energy distributions for the **Burong-1 3777 ft** and **North Seaspray-1 3213 ft** samples are presented in tabular form in Tables 1 and 2, respectively. These data are also shown graphically in Figures 1 and 2.

Measured and calculated reaction rate profiles generated for the two source rocks at the four different heating rates used are given in Appendix A to show the level of goodness of the curve fits obtained. The contents of the original computational output files generated by the KINETICS[©] program are included for reference purposes in Appendix B.



Table 1

BURONG-1 3777 ft SWC

 $(TOC = 4.05\%, \ \%R_v = 0.38)$

Frequency factor $A = 1.06 \times 10^{13} \text{ s}^{-1}$

Percent of reaction	Activation energy <i>E</i> _a (kcal mol ⁻¹)
0.00	43
0.00	44
0.00	45
0.00	46
0.00	47
0.00	48
0.00	49
73.05	50
4.16	51
19.58	52
0.00	53
1.12	54
0.04	55
0.00	56
0.00	57
2.05	58







Figure 1

BURONG-1 3777 ft ROCK-EVAL DERIVED KINETICS

Table 2

NORTH SEASPRAY-1 3213 ft CORE

 $(TOC = 5.94\%, \ \%R_v = 0.39)$

Frequency factor $A = 3.53 \times 10^{12} \text{ s}^{-1}$

Percent of reaction	Activation energy E_a (kcal mol ⁻¹)		
0.00	42		
0.00	43		
0.00	44		
0.00	45		
0.00	46		
0.00	47		
11.83	48		
59.10	49		
13.44	50		
8.59	51		
0.71	52		
2.63	53		
1.19	54		
0.00	55		
0.00	56		
2.51	57		







Figure 2

4. INTERPRETATION

Burong-1 3777 ft SWC

The activation energy distribution is dominated by contributions at $E_a = 50$ kcal mol⁻¹ (73.0%) and, to a lesser extent, at $E_a = 52$ kcal mol⁻¹ (19.6%). The geochemical study prepared by Geotechnical Services Pty Ltd for Energy and Minerals Victoria in March 1997 indicated that this sample was a shaly coal or related lithotype. The relatively low E_a values obtained, coupled with the narrow spread of the distribution, suggest that the kinetic behaviour of the source rock is primarily influenced by the liptinite component of the sample. Oil generation for this source rock will commence at relatively low levels of thermal maturity.

North Seaspray-1 3213 ft core

This sample was taken from an interval comprised of argillaceous siltstone with sandy lenses, interbedded with thin coal laminae. The low principal activation energy value of 49 kcal mol⁻¹ (59.1%) is atypical of data reported for most coals and indicates that the kinetic character of the sample is largely governed by the more thermally labile organic component of the rock. Oil generation is expected to occur at relatively low sediment maturities.



5. BIBLIOGRAPHY

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APPENDIX A

REACTION RATE PLOTS







Figure A1





Figure A2

TC 2 Infil



APPENDIX B

OUTPUT FILES

BURONG-1 3777ft SWC

Code Version: 2.43 Output File: BURONGA.OUT

Number of data

(total) (used)

63

86

81

94

Group

63 1.0000E+00

86 1.0000E+00

81 1.0000E+00

94 1.0000E+00

weight

Data file

A05BURD1.LLL A15BURH1.LLL A25BURF1.LLL A50BURI1.LLL

Title line of data files: A05BURD1

A15BURH1

A25BURF1

A50BURI1

Friedman-type analysis at fraction reacted = x									
(Valid only if data extend to nearly complete reaction)									
х	ln[A(1-x)^n]	A(for n=1)	E	E std.err.					
		(s^-1)	(cal/mol)	(cal/mol)					
.1	2.8953E+01	4.167E+12	49067.	1741.					
.2	2.7655E+01	1.280E+12	47382.	2002.					
.3	2.8567E+01	3.644E+12	48871.	2051.					
.4	2.9084E+01	7.130E+12	49869.	1655.					
.5	2.9352E+01	1.118E+13	50615.	1923.					
.6	2.8973E+01	9.569E+12	50490.	2766.					
.7	2.8789E+01	1.061E+13	50814.	3017.					
.8	2.8047E+01	7.583E+12	50614.	3204.					
.9	2.5131E+01	8.212E+11	47912.	6239.					

Mean approximate A and E over fraction-reacted interval from 0 to x (Valid only if data extend to nearly complete reaction)

x	А	Е	E std.err.
	(s^-1)	(cal/mol)	(cal/mol)
.1	1.0962E+14	49340.	782.
.2	2.3938E+13	48769.	1489.
.3	8.6780E+12	48398.	1538.
.4	5.7822E+12	48710.	1583.
.5	5.0044E+12	49345.	1545.
.6	3.4400E+12	49680.	1721.
.7	2.1883E+12	50003.	2009.
. 8	9.5732E+11	50010.	2662.
.9	3.1486E+11	50277.	3156.



	Interpolat Tmax	ion f						s. log(Heat e = 25 C/m	ing rate): hin	
	Interpolation from linear fit of FWHH vs. log(Heating rate): FWHH = 54.02 C at Heating rate = 25 C/min									
								vs. log(He e = 25 C/m	ating rate): nin	
	Data 1 2 3	Heati (C/ 4.915 1.464 2.672	.ng r (min) 50E+0 13E+0 28E+0	ate 0 4 1 4 1 4	Tmax (C) 137.45 159.90 170.91		Exp.FWHH (C) 52.83 53.36 55.85	(C) 47.47 50.32 52.00	Exp./Calc. 1.11285 1.06036	.8449 .8267 .8354
and the set	A(s^-1) E(cal/mol) S(%E) n(order)	= =	4.99 8.85	71E+04 32E-01	ł (st	d.	err. = 1.	046E+03)		



```
Discrete (option 1)
Fitting method:
                     Relative Rates
Least squares of:
Error tolerance for initial search:
                                          1.0000E-01
                                          1.0000E-02
Error tolerance for final convergence:
Thermal history: Constant heating rate (max. rel. std. dev. = 1.212E-03)
                                          9.0060E+11
Initial minimum frequency factor(s^-1):
Initial maximum frequency factor(s^-1):
                                          9.0060E+13
Results
                     1.0615E+13 s<sup>-1</sup>
Frequency factor =
                Activation energy (cal/mol)
   Percent
                           43000.
      .00
      .00
                           44000.
      .00
                           45000.
      .00
                           46000.
                           47000.
      .00
                           48000.
      .00
                           49000.
      .00
    73.04
                           50000.
    4.16
                           51000.
    19.58
                           52000.
      .00
                           53000.
                           54000.
     1.12
                           55000.
      .04
                           56000.
      .00
                           57000.
      .00
     2.05
                           58000.
Least squares exit: successful completion
Sum of squares of weighted normalized rate residuals:
                                                          7.1905E-02
Sum of squares of weighted integrated rate residuals:
                                                          8.5992E-03
```



NORTH SEASPRAY-1 3213ft CORE Output File: NSEASPRA.OUT Code Version: 2.43 Number of data Group Data file (total) (used) weight 86 1.0000E+00 86 A05NSSA1.LLL 1.0000E+00 86 86 A15NSSD1.LLL 81 81 1.0000E+00 A25NSSB1.LLL 94 1.0000E+00 94 A50NSSB1.LLL Title line of data files: A05NSSA1 A15NSSD1 A25NSSB1 A50NSSB1 Friedman-type analysis at fraction reacted = x (Valid only if data extend to nearly complete reaction) A(for n=1)E std.err. $\ln[A(1-x)^n]$ Ε х (s^{-1}) (cal/mol) (cal/mol) 1228. 2.6324E+01 3.006E+11 45677. .1 48027. 1655. .2 2.7838E+01 1.538E+12 .3 2.8233E+01 2.607E+12 48828. 1524. 49997. 2.8818E+01 1792. 5.459E+12 .4 6.964E+12 50456. 1593. 2.8879E+01 .5 50847. 2465. 2.8814E+01 8.159E+12 .6 2396. .7 2.9082E+01 1.422E+1351895. 2528. .8 2.8898E+01 1.776E+13 52597. 2.463E+14 57701. 4118. .9 3.0835E+01 Mean approximate A and E over fraction-reacted interval from 0 to x (Valid only if data extend to nearly complete reaction) E std.err. Α Ε х (s^{-1}) (cal/mol) (cal/mol) 1488. 43428. .1 1.0400E+12 45001. 1393. .2 1.2093E+12 .3 46202. 1540. 1.3784E+12.4 47215. 1505. 1.5005E+12 .5 1.5415E+12 48111. 1647. .6 1.5147E+12 48982. 1735. .7 1.0610E+12 49460. 2231. 2102. 1.0426E+12 50693. .8 .9 1.1773E+12 52946. 2830.



- Interpolation from parabolic fit of Tmax vs. log(Heating rate): Tmax = 475.89 C at Heating rate = 25 C/min
- Interpolation from linear fit of FWHH vs. log(Heating rate): FWHH = 58.74 C at Heating rate = 25 C/min
- Interpolation from linear fit of Asymmetry vs. log(Heating rate):
 Asymmetry = .867 at Heating rate = 25 C/min

- 500-10	- Approximate fit of disk data to a single first-order reaction:								
	Data	Heating rate	Tmax	Exp .FWHH	Cal.FWHH	Exp./Calc.	Asymmetry		
		(C/min)	(C)	(C)	(C)				
	1	4.9026E+00	441.89	57.61	49.50	1.16369	.8250		
	2	1.4606E+01	464.65	59.03	52.59	1.12244	.9035		
	3	2.6665E+01	477.65	58.35	54.41	1.07249	.8333		
	4	5.2976E+01	492.29	59.19	56.60	1.04578	.8836		

			2.3691E+12 4.8499E+04	(std.	err.	=	5.143E+02)
	S(%E)	=	1.3361E+00				
-	n(order)	=	1.0000e+00				



```
Discrete (option 1)
Fitting method:
Least squares of:
                      Relative Rates
Error tolerance for initial search:
                                            1.0000E-01
                                            1.0000E-02
Error tolerance for final convergence:
                     Constant heating rate (max. rel. std. dev. = 1.202E-03)
Thermal history:
Initial minimum frequency factor(s<sup>-1</sup>): 2.3691E+11
Initial maximum frequency factor(s^-1):
                                            2.3691E+13
Results
                      3.5275E+12 s<sup>-1</sup>
Frequency factor =
                 Activation energy (cal/mol)
   Percent
                            42000.
       .00
       .00
                            43000.
                            44000.
       .00
       .00
                            45000.
                            46000.
       .00
       .00
                            47000.
                            48000.
    11.83
    59.10
                            49000.
    13.44
                            50000.
     8.59
                            51000.
                            52000.
       .71
                            53000.
      2.63
      1.19
                            54000.
                            55000.
       .00
       .00
                            56000.
      2.51
                            57000.
Least squares exit: successful completion
Sum of squares of weighted normalized rate residuals:
                                                            1.2533E-01
Sum of squares of weighted integrated rate residuals:
                                                            3.0579E-02
```

