

METHANE AND ETHANE GENERATION FROM OIL CRACKING : FIRST ISOTOPIC MODELLING BASED ON ^{13}C LABELLED COMPOUNDS

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Recent papers have demonstrated that aromatic hydrocarbons are less stable than saturated ones during thermal cracking (Behar and Vandembroucke, 1996; Behar et al., 1999 and 2002, Dominé et al., 2002). Therefore the focus of the present work includes a molecular and kinetic isotopic study of secondary methane and ethane generated from aromatic compounds present in the low-molecular-weight fraction ($\text{C}_6\text{-C}_{14}$) of petroleum found in high pressure and high temperature (HP-HT) reservoirs. In addition the kinetic scheme will illustrate the isotopic fractionations taking place at temperatures ranging from 160°C to 220°C over several millions of years.

More than 200 isothermal pyrolysis experiments in gold sealed tubes have been carried out at three temperatures ranging from 395 to 450°C for periods of several hours to several months. As shown with some examples in the table below, attention has been paid to mass balances using different fractions, such as a gaseous fraction ($\text{C}_1\text{-C}_4$), a pentane extract ($\text{C}_6\text{-C}_{14}$ and $\text{C}_{15}\text{-C}_{20}$), a DCM extract (C_{20+}) and the residue, in order to get a better constrained isotopic model. A complete kinetic study on 10 non-labelled compounds has been performed first in order to establish the kinetic scheme for methane and ethane generation. These compounds include 2-ethyltoluene and 3-ethyltoluene, 3-ethylorthoxylylene and 4-ethylorthoxylylene, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene, 1,2,4,5-tetramethylbenzene, 1-methylnaphthalene, 1,5-dimethylnaphthalene and 2,4,5-trimethylnaphthalene. These components indeed represent the overall composition of the $\text{C}_6\text{-C}_{14}$ aromatic fraction of a typical oil and also represent different group positions, chain lengths, ring substitutions and ring effects. The influence of the previous factors was quantified by calculating activation energies (E_a) and frequency factors (A) for methane and ethane generation, using an Arrhenius plot.

In addition, an extensive isotopic study has been carried out in order to get a holistic mass balance for the $^{13}\text{C}/^{12}\text{C}$ of the different fractions. Important carbon isotope fractionations were observed in ethane and methane at different temperatures and various pyrolysis times. For example 5.6 and 7.5‰ enrichments were observed for methane and ethane, respectively

for 2-ethyltoluene when the pyrolysis time was increased from 10 to 432 hours at a temperature of 450°C. A 14.3‰ enrichment was observed for methane generated from 1,2,4-trimethylbenzene under similar conditions.

Syntheses of aromatic compounds, with a ^{13}C label in specific positions, have also been carried out successfully allowing us to study the carbon isotope fractionations occurring during methane and ethane generation. Indeed, a mixture of each labelled compound with its non-labelled counterpart, in order to start from a reasonable $\delta^{13}\text{C}$ value, will be pyrolysed and run through the above analytical protocol.

The results of the present study should lead to the first kinetic model of carbon isotope fractionation during methane and ethane generation from a given oil cracked under conditions met in high pressure and high temperature reservoirs.

Compound	2ET	124TMB	124TMB	124TMB
Conditions	395°C/144h	395°C/144h	450°C/10h	450°C/50h
C ₁	0.33	0.15	0.23	6.3
C ₂	0.37	0.014	0	0.33
C ₆ -C ₁₄	90	92	91	65
C ₁₅ -C ₂₀	1.9	1.7	3.6	13
C ₂₀₊	2.5	2.5	2.6	2.9
Residue	0	0	0	7.1
Sum	95	96	97	95
$\delta^{13}\text{C}$ (Compound)	in process	in process	in process	in process
$\delta^{13}\text{C}$ (C ₁)	-38.6	-41.1	-47.1	-35.6
$\delta^{13}\text{C}$ (C ₂)	-37.5	ND	ND	ND
$\delta^{13}\text{C}$ (C ₆ -C ₁₄)	in process	in process	in process	in process
$\delta^{13}\text{C}$ (C ₁₅ -C ₂₀)	-29.4	-29.7	-27.1	-29.4
$\delta^{13}\text{C}$ (C ₂₀₊)	-27.5	-27.9	-27.6	-28.2
$\delta^{13}\text{C}$ (Residue)	ND	ND	ND	-29.5

Table 1. Mass balances (% of initial charge) and $\delta^{13}\text{C}$ (‰) obtained during some closed system pyrolysis experiments of 2-ethyltoluene (2ET) and 1,2,4-trimethylbenzene (124TMB).

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EFFECT OF SOURCE, MATURITY AND BIODEGRADATION ON THE D/H RATIO OF AUSTRALIAN NATURAL GAS

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Compound specific isotope analysis (CSIA) of stable carbon isotopes for individual C₁ to C₅ gaseous hydrocarbons has been routinely used for over two decades to determine the origin of natural gas (James, 1983, 1990; Schoell, 1983; Boreham et al., 2001). Here we report gas–gas correlations based on the more recent CSIA application of the hydrogen isotopic composition (D/H ratio) of Australian natural gas (Boreham 2004). The influence of source, maturity and in-reservoir alteration (biodegradation) on the C₁ to C₅ gaseous hydrocarbons is documented and, in combination with complementary carbon isotope data, provides a powerful tool for the study of the origin and correlation of the natural gas.

Source influence in natural gases from Australian sedimentary basins shows a wide range in hydrogen isotopes with $\Delta D \sim 160$ ‰ for both methane (δD -290 to -135 ‰) and *iso*-butane (δD -255 to -94 ‰). On the other hand, the carbon isotopic range is an order of magnitude less (Boreham et al., 2001). The source rock ages of Australian natural gases studied herein include the latest Proterozoic in the Amadeus Basin and most of the Phanerozoic from Ordovician (Amadeus Basin) to Early Eocene (Bass Basin). Gases generated from older marine source rocks are most enriched in D whereas gases sourced from younger terrestrial coals are amongst the most depleted in D. On the other hand, for carbon the marine-sourced gases are the most depleted in the heavier isotope (¹³C; Boreham et al., 2001).

Maturity attenuates the isotopic signature of natural gases for methane and results in carbon isotopic variations approaching those of source effects (Boreham et al., 2001). A Cooper Basin maturation sequence from mature oil-associated wet gas to highly overmature dry gas shows ΔD enrichments of ~ 50 ‰ for methane (δD -162 to -116 ‰), with smaller isotopic enrichments observed for the wet gas components. Overall, maturity has a much lower δD variation than that associated with source and biodegradation effects.

Biodegradation of natural gas produces a drier gas, due to the addition of biogenic methane and selective removal of wet gas components in the order propane > *n*-butane \sim *n*-pentane > *i*-pentane > ethane \geq *i*-butane (Boreham et al., 2001). Addition of biogenic methane to natural gases from the Carnarvon Basin results in little change in $\delta D_{\text{methane}}$, unlike the large depletion in ¹³C_{methane} (Figure 1). Almost complete biodegradation of the wet gas components

leads to δD enrichments of up to 225 ‰ (Figure 1); slightly larger than the ΔD source effects. The strong positive correlation between hydrogen and carbon isotopes for the individual wet gas components implies a kinetic control on the isotopic composition, which is consistent with a biological-mediated process.

Examples will be given from the across Australia (e.g. Otway Basin and the North West Shelf) where the hydrogen isotopic composition of natural gas offers the only conclusive means of resolving multiple petroleum systems.

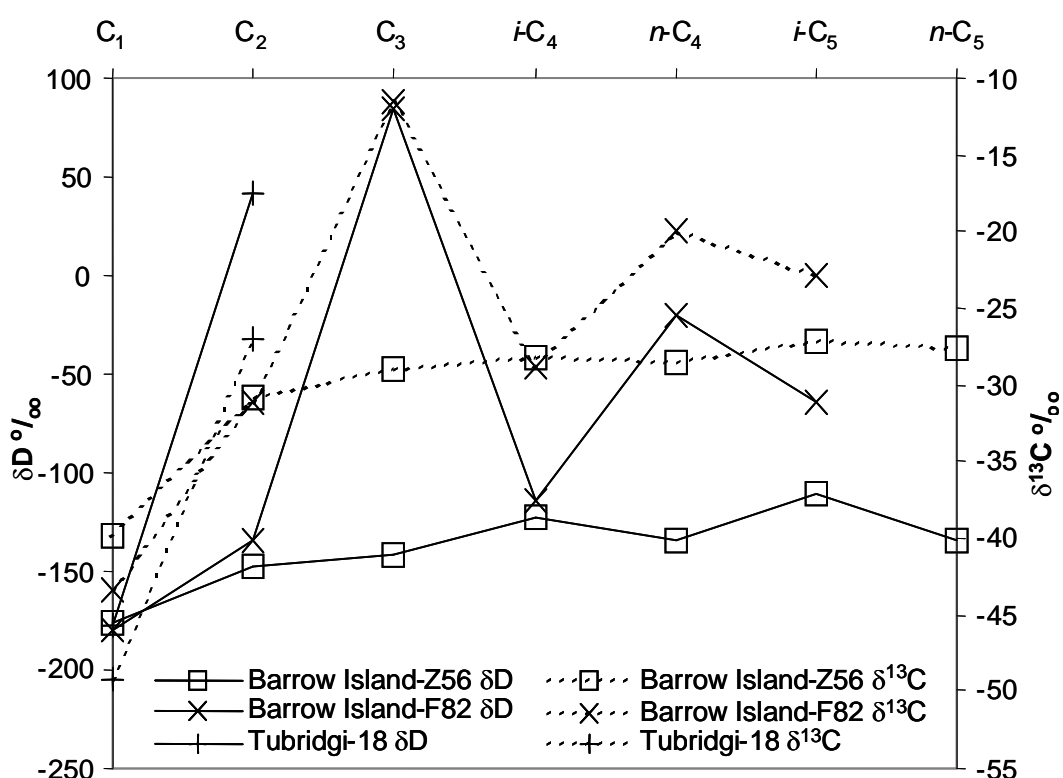


Figure 1. Hydrogen and carbon isotopic composition of individual gaseous hydrocarbons from a biodegradation sequence from the Carnarvon Basin, Western Australia. The gases have the same Late Jurassic mixed marine-terrestrial source.

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ADVANCED MUD LOGGING TECHNOLOGY 'FLAIR' – NEW HORIZONS IN PETROLEUM GEOCHEMISTRY

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Characterization and prediction of reservoir fluids based on mud logging information is not a novel idea or approach, and the basic interpretation approaches have been already presented 20 years ago (Haworth et al., 1985; Whittaker, 1991; Kandel et al., 2001). However, until recently, standard mud logging technologies did not offer the resolution and sensitivity necessary to approach a quantitative aspect of fluid facies description (Blanc et al., 2003). Developments by Geoservices of the Flex (constant volume and temperature) extractor and Flair detector (GC/MS) provide tools to (1) increase sensitivity to analyze C1-C7 hydrocarbon gases down to 1 ppm, and (2) allow for specificity to analyze components up to m/z 100, such as benzene, methylcyclohexane or distinguish between ethane and ethylene during drilling operations. Moreover, a very short cycle time (60 sec) allows for a full chromatographic analysis up to C7, including differentiation of several C_n isomers. Finally, a reliable and reproducible degassing efficiency can be obtained that allows for a quantitative evaluation of the actual content of light hydrocarbon components in the mud system and provides the capability for correction of the mud composition for recycled components and contaminants (details of the technology elsewhere in this volume).

Shell has been using the Flair technology worldwide since 2004 and has tested its application in various geologic settings (deepwater turbidites, carbonates, shallow deltaic systems) and drilling environments (onshore, offshore, high pressure and temperature; oil-based and water based drilling muds). While its primary application, to date, has been for exploration wells, it has been also successfully used as a logging while drilling (LWD) tool in wells drilled horizontally in different directions to appraise extent of structures/reservoirs.

The traditional wetness, balance and character ratios (Haworth et al., 1985) are successfully used, along with oil-water contact (OWC) or biodegradation ratios such as i-C₄/n-C₄ or i-C₅/n-C₅. However, new ratios such as Benzene/n-C₆, Methylcyclohexane/n-C₆ or Ethene/Ethane are being successfully utilized. In addition to the qualitative hydrocarbon facies evaluation and ratio-based interpretations, we have observed a very good correlation between C1 through C5 composition of the actual hydrocarbons sampled from a given

reservoir with the C1-C5 normalized mud gas data from the same formation (Table 1). This phenomenon has been observed on more than 10 wells from around the world and hydrocarbon types varying from dry gas to heavy oil. A number of case studies will be demonstrating the value of the technology and its impact on E&P operations. For example:

- Flair data clearly indicating tops of formations and changes in lithology/porosity.
- Flair data used in a detailed correlation/identification of subtle flow barriers and correlation to facies change.
- The correlation with IsoTubes, wireline hydrocarbon samples and well test samples.
- Determination of changes in HC composition, from gassy shows to heavy HC's, OWC, GWC and GOC.
- Fingerprinting of HC types between wells and within the same well allowing possible correlation of pay zones across a given field.
- Flair used as a LWD tool - assistance in decision-making while drilling.

Table 1. Correlation between C1-5 hydrocarbons between mud gas data from various techniques and the actual hydrocarbon fluids recovered from formations.

Region	Africa		Gulf of Mexico					Middle East	
	HC	FF	HC	FF	Trad	HC	FF	HC	FF
<i>C1</i>	73.2	72.3	81.4	80.8	94.6	78.5	76.1	90.1	88.3
<i>C2</i>	9.0	9.1	7.6	8.2	3.7	9	10	5.8	6.1
<i>C3</i>	7.9	7.9	5.6	5.7	1.3	5.5	6.6	2.1	2.3
<i>i-C4</i>	3.1	3.4	1	1.1	0.4	1.2	1.2	0.5	0.7
<i>n-C4</i>	4.1	4.4	2.5	2.3	0	2.5	2.9	0.8	1.2
<i>i-C5</i>	2.6	2.7	0.9	0.9	0	1.3	1.1	0.4	0.7
<i>n-C5</i>	0.1	0.1	1	0.9	0	1.3	1.2	0.4	0.6

NOTE: HC – C1 through C5 normalized composition of hydrocarbons recovered from reservoir; FF – C1 through C5 normalized mud gas composition from Flair; Trad – C1 through C5 normalized mud gas composition from traditional mud logging equipment.

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