

ROLE OF PRESSURE ON EXTENT OF PETROLEUM GENERATION

Ronald HILL and Michael LEWAN

United States Geological Survey, Box 25046, MS 977, Denver Federal Center, Denver, CO 80225

Hydrous pyrolysis experiments were conducted on a thermally immature Devonian New Albany Shale source rock at 300, 326, and 356 °C for 72 hours under pressures from 0.1 to 2.1 kbar to evaluate the role of pressure on petroleum generation. Previous studies have shown that these conditions depict the full range of the two-step process for petroleum generation with kerogen to bitumen taking place at and below 330°C for 72-h durations and bitumen to oil taking place at and above 330°C for 72-h durations (Lewan, 1985). The experiments have been grouped into four pressure regimes as shown in Figure 1. The lowest-pressure regime (0.1-0.2 kbar) represents conventional hydrous pyrolysis experiments where pressures are predominantly controlled by the vapor pressure of water along its vapor-liquid curve. The highest-pressure regime (1.8-2.1 kbar) represents lithostatic pressures at subsurface depths of 7.4 to 8.6 km.

With the start of thermal maturation, the kerogen partially decomposes into soluble, viscous, resin- and asphaltene-rich bitumen. Decreasing kerogen content with corresponding increase in bitumen yield evinces this first overall reaction. As thermal maturation proceeds, the second of the two-step process commences with the decomposition of bitumen to free-flowing liquid hydrocarbon-rich oil that is compositionally similar to natural crude oils (Ishiwatari et al, 1976). Decreasing bitumen and constant kerogen content with increased oil yields evinces this second overall reaction.

Figure 1 shows the results of hydrous pyrolysis at the 4 different pressure regimes. The kerogen to bitumen reaction is prevalent at temperatures less than 330°C for 72h, whereas the bitumen to oil reaction is best represented at 330 and 356°C for 72h. These results indicate that while there might be some pressure effects on kerogen decomposition to bitumen, the most pronounced effects are on the decomposition of bitumen to oil. This decrease in oil generation as pressure increases might be a result of cross-linking reactions becoming more dominant than cracking reactions during the thermal decomposition of bitumen to oil. In addition to pressure-induced cross-linking in bitumen reducing oil yields, pressure might also decrease the rates of bitumen to oil cracking reactions through activation volume controls on reaction rates. An implication of the latter effect is that time-temperature-pressure conditions in some parts of a sedimentary basin could result in oil generation taking place at deeper depths and longer times that typically predicted in kinetic models.

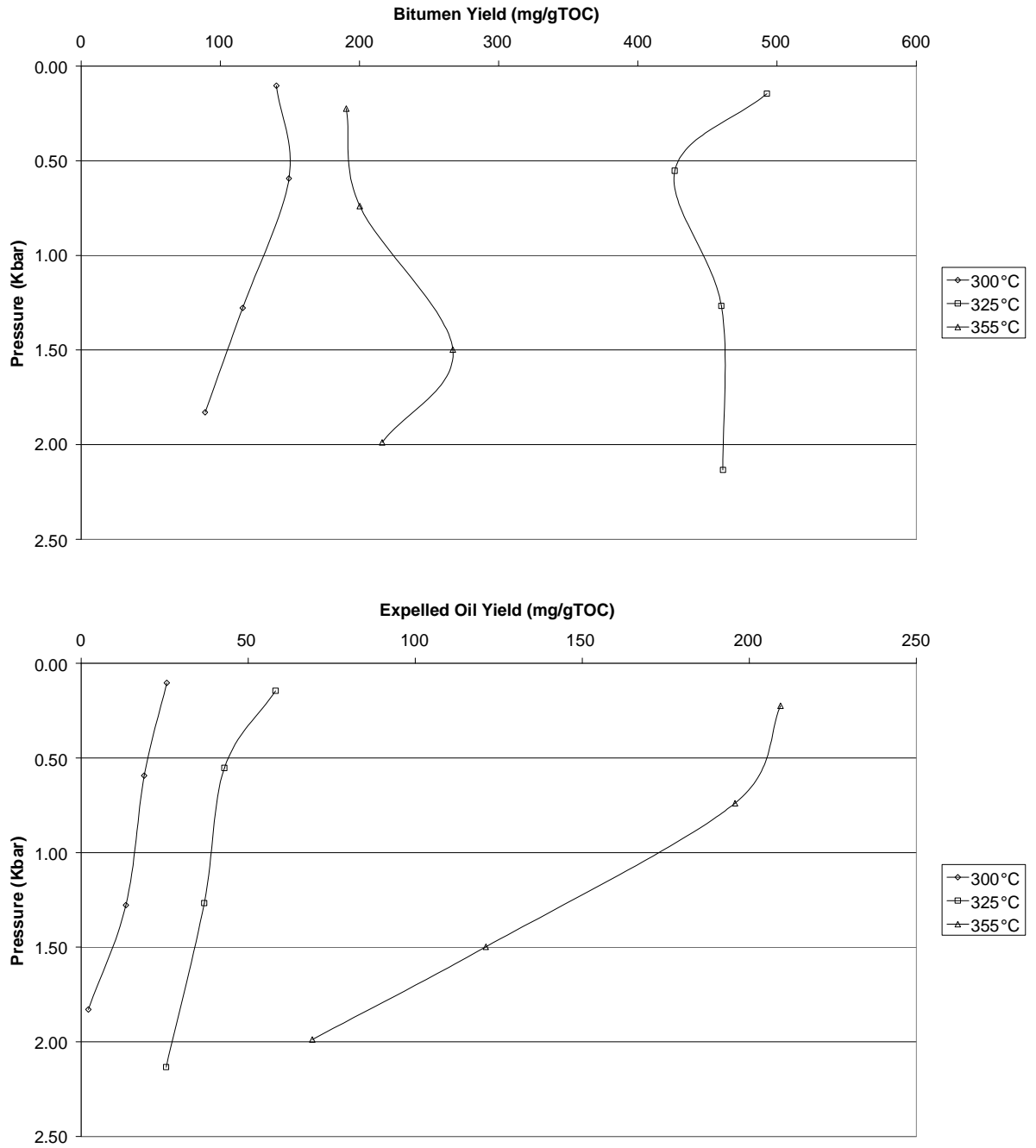


Figure 1. Changes in bitumen and expelled oil yield as a function of temperature and pressure.

REFERENCES

- Lewan, M., 1985. Evaluation of petroleum generation by hydrous pyrolysis experimentation. *Philosophical Transactions of the Royal Society* 315, 123-134.
- Ishiwatari, R., Ishiwatari, M, Kaplan, I. R., and Rohrback, B., 1976. Thermal Alteration of young kerogen in relation to petroleum genesis. *Nature* 264, 347-349.

RETARDATION OF OIL CRACKING IN HIGH-PRESSURE LIQUID WATER

C.E. SNAPE¹, W. MEREDITH¹, C. UGUNA¹, A.D. CARR², I.C. SCOTCHMAN³ and R.C. DAVIS⁴

¹Nottingham Fuel & Energy Centre, School of Chemical, Environmental and Mining Engineering (SChEME), University of Nottingham, University Park, Nottingham NG7 2RD

²Advanced Geochemical Systems, Burton-on-the-Wolds, Leicestershire, UK

³Statoil, Statoil House, 11A Regent Street, London, SW1 4ST, U.K

⁴Woodside Energy Ltd., 240 St. Georges Terrace, Perth 6000, Western Australia

Oil cracking in geological basins is generally simulated using laboratory pyrolysis experiments in which the oil is heated in either a vapour or a mixed water-vapour phase in a closed system. However, in geological basins, oils exist in water-saturated conditions with the water being either hydrostatically pressured or over-pressured. Previous investigations into the effects of pressure, mainly in gold bags, have indicated that pressure effects are not significant. In contrast, studies under inert gas pressure have suggested the cracking is retarded. The overall aim of this investigation has been to investigate the effect that liquid water pressure has on oil cracking in geological basins. Using a stainless steel pressure vessel rated up to 500 bar (*ca.* 7000 psi, 50 MPa) at 350°C, cracking of an oil was compared under anhydrous, normal hydrous conditions, a full vessel of water at the steam pressure of 150 bar and liquid water pressures of 310 and 470 bar.

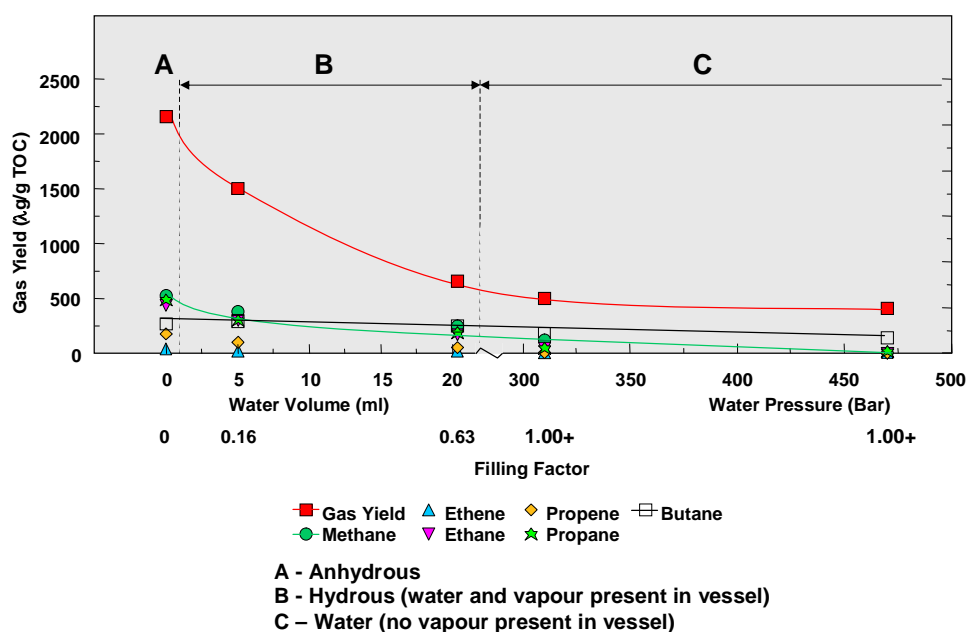


Figure 1. Total C₁-C₄ and individual hydrocarbon gas yields from the oil cracking tests.

The principal findings are:

- (i) cracking of oil to C₁-C₄ hydrocarbons is retarded significantly by high-pressure liquid water (Figure 1), and the magnitude of this effect is much more pronounced than in other studies using gold bags or inert gas pressure and there is evidence that pressure alters the dryness of the gas;
- (ii) increasing the water filling factor also reduced the hydrocarbon gas yield at constant steam pressure (Figure 1) but also reduced the boiling point range of the oil, indicating a major change in product selectivity; and
- (iii) In tandem with the vastly reduced hydrocarbon gas yields at high pressure, some polymerisation to increase both the boiling point range and asphaltene content of the oil was evident, consistent with volume reduction processes being favoured at high pressure.

To provide further initial insights into these phenomena identified, a corresponding set of experiments was conducted on *n*-hexadecane at 350°C where, previously, only gold bags have been used to investigate pressure effects (Jackson *et al.*, 1993. The product distribution from the anhydrous pyrolysis was entirely consistent with previous studies (Ford, 1986) with the conversion being low (*ca.* 2 %) due to the relatively low temperature of 350°C used to ensure being below the supercritical temperature of water. Overall, apart from the inherent lower conversions, the experiments revealed very similar trends as for the oil, notably the vast suppression in C₁-C₄ hydrocarbon yields in the water pressure experiments, which was accompanied by a marked decrease in the yield of C₅-C₈ hydrocarbons in the liquid product, together with the suppression of alkene formation at high liquid water pressures. Further, the re-arrangement of *n*-alkanes to high molecular mass (>C₁₆) branched chain alkanes was suppressed by the combination of increasing water content in the vessel and the increasing liquid water pressure. Increasing the amount of *n*-hexadecane 4 fold at 500 bar had no significant effect on the gas yield, confirming that over-pressurisation was not occurring within the autoclave, with the water being undersaturated with respect to hydrocarbon gas at 350°C. These results provide further evidence that oils cannot crack to a significant extent under the water pressure regimes found in geological basins.

REFERENCES

- Ford, T.J. 1986. Liquid-phase thermal decomposition of hexadecane: reaction mechanisms. *Ind. & Eng. Chem. Fund.* 25, 240-243.
- Jackson, K.J., Burnham, A.K., Braun, R.L. and Knauss, K.G. 1995. Temperature and pressure dependence of *n*-hexadecane cracking. *Organic Geochemistry* 23, 941-953.

QUANTITATIVE ASSESSMENT OF GAS GENERATION, ORIGIN, AGE, AND PALEO FORMATION TEMPERATURE IN PETROLEUM SYSTEM

YONGCHUN TANG*¹, QISHENG MA¹ and SHENG WU¹

¹*Power, Environmental and Energy Research Center, California Institute of Technology, Pasadena, California, USA*

The physical properties and generation processes that control natural gas accumulation are distinctly different from those related to oil generation, and require the development of new tools and strategies in order to create effective gas exploration programs. In contrast to the large amount of geochemical information that is preserved in crude oil, natural gas is compositionally very simple and requires creative approaches for maximizing the value of the available data. In the past few years, we have developed two techniques that allow fundamental questions of gas generation, origin, age of formation, temperature of gas generation, and accumulation to be quantitatively addressed. First model is based on first principle (Quantum Chemistry) to predict the most critical properties for gas generation and accumulation such as isotope fractionation patterns, temperature and maturity of the gas source rock, gas quality (e.g., wetness), and the gas to oil ratio (GOR). The experimental foundation of this model is the laboratory pyrolysis, e.g. by integrating with basin modeling tool, one can extrapolate gas isotopic fractionation under laboratory condition to geological frameworks. Second method is to develop a novel optical isotope measurement so we can detect the $^{13}\text{CDH}_3$ concentration in the natural gas system. We have synthesized the $^{13}\text{CDH}_3$ compound which has obtained all detail line spectrum. The concentration of $^{13}\text{CDH}_3$ relative to the normal carbon ($\delta^{13}\text{C}$) and (δD) may provide critical information about gas generation condition, environment, age and temperature of gas generation. Based on the Gibb's free energy calculation from first principle (quantum mechanics density function theory), we have quantified the thermodynamic equilibrium of isotopmers. At the current stage, it is not clear whether the natural gas will be randomly populated or it might exactly follow the equilibrium conditions. However, the relative concentration change in $^{13}\text{CDH}_3$ will provide us with valuable information about gas formation temperature (paleothermometer). For example, if we choose a gas with a carbon isotopic composition of -47‰ and a deuterium isotopic composition of -120‰, then this gas could potentially be generated by one of three different sources. One possibility might be from a mixture of biogenic and shale gases. Secondly, it is possible to generate such isotopic compositions from early shale gases. Lastly, this could also be generated from secondary

cracking of oil. This uncertainty could be further resolved if we can measure the concentration of $^{13}\text{CDH}_3$. By determining the gas formation temperature and integrating with other geologic data, it is possible to determine other information about the origin of the gas (Figure 1).

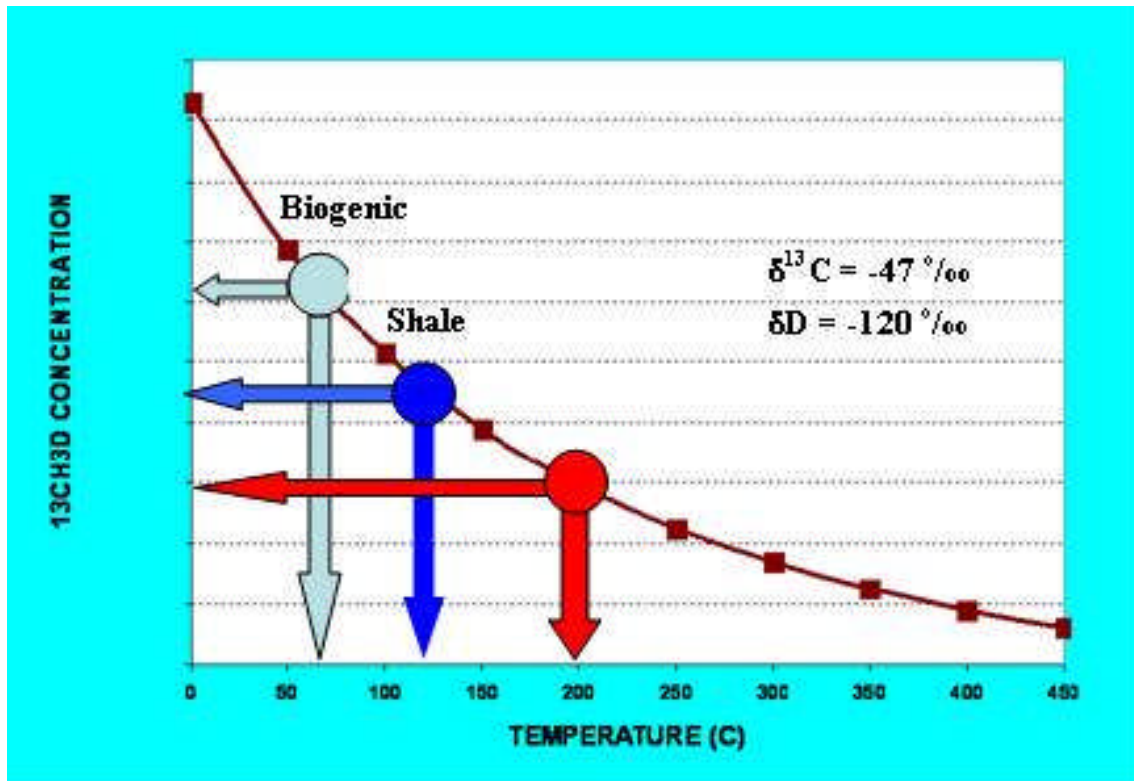


Figure 1. Applications of doubly-substituted methane isotopomer to distinguish the origin of natural gas