

# Retardation of Hydrocarbon Generation and Maturation by Water Pressure in Geologic Basins: An Experimental Investigation

**Clement N. Ugana, Colin E. Snape, and Will Meredith**

*Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, Nottingham, United Kingdom*

**Andrew D. Carr<sup>1</sup>**

*Advanced Geochemical Systems Ltd., Leicestershire, United Kingdom*

**Iain C. Scotchman**

*Statoil (UK) Ltd., London, United Kingdom*

**Robert C. Davis**

*Woodside Energy (USA) Inc., Houston, Texas, U.S.A.*

## ABSTRACT

Temperature-time-based first-order kinetic models are currently used to predict hydrocarbon generation and maturation in basin modeling. Physical chemical theory, however, indicates that water pressure should exert significant control on the extent of these hydrocarbon generation and maturation reactions. We previously heated type II Kimmeridge Clay source rock in the range of 310 to 350°C at a water pressure of 500 bar to show that pressure retarded hydrocarbon generation. This study extended a previous study on hydrocarbon generation from the Kimmeridge Clay that investigated the effects of temperature in the range of 350 to 420°C at water pressures as much as 500 bar and for periods of 6, 12, and 24 hr. Although hydrocarbon generation reactions at temperatures of 420°C are controlled mostly by the high temperature, pressure is found to have a significant effect on the phase and the amounts of hydrocarbons generated.

In addition to hydrocarbon yields, this study also includes the effect of temperature, time, and pressure on maturation. Water pressure of 390 bar or higher retards the vitrinite reflectance by an average of *ca.* 0.3% Ro compared with the values obtained under low pressure hydrous conditions across the temperature range investigated. Temperature,

<sup>1</sup>Present address: British Geological Survey, Keyworth, Nottingham, United Kingdom.

pressure, and time all control the vitrinite reflectance. Therefore, models to predict hydrocarbon generation and maturation in geological basins must include pressure in the kinetic models used to predict the extent of these reactions.

## INTRODUCTION

The growth of petroleum system modeling is caused by its ability to predict the timing of maturation and hydrocarbon generation in geologic basins and also advances in computer technology that allow for petroleum system models to be constructed and run in reasonable amounts of time. Although initially predicted using temperature-time calibrations, both maturation and hydrocarbon generation are now predicted using Arrhenius first-order parallel kinetic models derived mainly from laboratory pyrolysis studies. From the initial pioneering work on coals (Van Krevelen et al., 1951; Pitt, 1962), the subsequent 20 yr have resulted in sophisticated kinetic models that predict hydrocarbon composition and gas-oil ratios (di Primio and Horsfield, 2006) and hydrocarbon expulsion (Stainforth, 2009). These parallel kinetic models are inappropriate because they contain forced compensation effects produced by heat and mass transfer effects (Braun and Burnham, 1987; Burnham, 1993; Barth et al., 1996; Schenk and Dieckmann, 2004; Stainforth, 2009).

Arrhenius kinetics also ignores the fact that transition state and thermodynamic theories both show that water pressure reduces the reaction rates of endothermic volume expansion reactions, such as hydrocarbon generation and maturation (Laidler, 1987). The Arrhenius equation arises from empirical observations that ignore mechanistic considerations involved in the reaction. An increase in water pressure increases the activation energy caused by increased activation enthalpy because of the additional energy required to displace the pressurized water in the kerogen pore systems (Carr et al., 2009). Energy that is used to displace pressurized water is no longer available to be used to overcome the activation energy barrier because that energy (thermal) is leaving the kerogen and being transferred to the water column as potential energy. In addition, an increase in pressure reduces the entropy, thereby reducing the pre-exponential factor (Carr et al., 2009). The combined effect of increasing the enthalpy and reducing the entropy increases the Gibbs free energy ( $\Delta G$ ), meaning that the reactants instead of the products are favored, that is, less reaction occurs. Indeed, experiments conducted at temperatures between 310 and 350°C under 500-bar water pressure always produced lower yields than those obtained under nonhydrous or low-pressure hydrous conditions (Carr et al., 2009). The results at 450 to 500 bar water pressure are entirely consistent with the predic-

tions derived from transition state and thermodynamic theories.

Several workers using laboratory experimental studies (e.g., Price and Wenger, 1992; Dalla Torre et al., 1997) and data from geologic basins (McTavish, 1978, 1998; Hao et al., 1995; Huijun et al., 2004) found evidence that pressure retards either hydrocarbon generation or maturation. Other workers, however, did not find any laboratory evidence to support the retardation of either hydrocarbon generation or maturation (see Zou and Peng, 2001; Carr et al., 2009, for details).

Carr et al. (2009) suggested that the different conclusions reached by studies involving laboratory experiments could be explained by the different experimental methods used, with the vapor pressure and gold bag studies generally finding no evidence for pressure retardation. This lack of evidence for retardation may be caused by the combined effects of the compressibility of the vapor phase (thereby allowing volume expansion against the compressible vapor) and the malleability of the gold bag, which allows the volatiles generated by the maturation reactions to expand the gold bag, so that the internal pressure remains relatively constant against the externally applied pressure. In contrast, high pressure water pyrolysis experiments conducted in closed autoclave vessels in which the pressurized water is in direct contact with the sample being pyrolyzed (typical of the conditions in geologic basins) show significant retardation effects (Price and Wenger, 1992; Landais et al., 1994; Michels et al., 1995a, b; Carr et al., 2009).

Previously, Carr et al. (2009) showed that water pressure retarded hydrocarbon generation when Kimmeridge Clay samples were pyrolyzed in the temperature range of 310 to 350°C and at water pressures as much as 500 bar. However, as identified first by Lewan (1993, 1997) and found in our previous study (Carr et al., 2009), water first promotes bitumen-plus-oil and gas generation, and under laboratory conditions at 350°C, the maximum conversion to these products was observed at the steam pressure of approximately 160 bar before pressure retardation effects were observed at 500 bar. In this study, temperature in the range between 350 and 420°C, pressures of 45 to 500 bar, and periods of 6, 12, and 24 hr were used to evaluate the effects of temperature, pressure, and time on bitumen, bitumen-plus-oil, and gas yields as well as vitrinite reflectance ( $VR R_o$ ). The specific aim of this study was to evaluate pressure retardation effects in water at higher levels of maturity than has been previously investigated. This

**Table 1.** Geochemical data for the Kimmeridge Clay sample.

TOC* (%)	S1 (mg HC/g rock)	S2 (mg HC/g rock)	S3 (mg HC/g rock)	HI (mg HC/g TOC)	OI (mg CO <sub>2</sub> /g TOC)	PI S1/ (S1 + S2)	T <sub>max</sub> (°C)	% R <sub>o</sub>
25.5	3.17	174.47	2.67	684	10	0.02	416	0.36

\*TOC = total organic carbon; R<sub>o</sub> = vitrinite reflectance; HC = hydrocarbon; HI = hydrogen index; OI = oxygen index; PI = production index.

has necessitated using supercritical water at temperatures up to 420°C because only moderate maturities can be achieved in liquid water at 350°C in reasonable experimental periods. This study is the first in which high maturities were achieved under high-pressure hydrous conditions.

## EXPERIMENT

### Sample

The source rock investigated in this study is from the fresh samples of organic-rich Kimmeridge Clay Formation from the coastal outcrop at Kimmeridge Bay, Dorset, United Kingdom. The source rock is immature and oil prone with a hydrogen index (HI) of 684 mg HC/g TOC, T<sub>max</sub> of 416°C, and 0.36% R<sub>o</sub> (Table 1). Whole rock samples instead of kerogens were used in an attempt to reproduce the mineral-kerogen interactions that occur in source rock kitchens (Eglington et al., 1986).

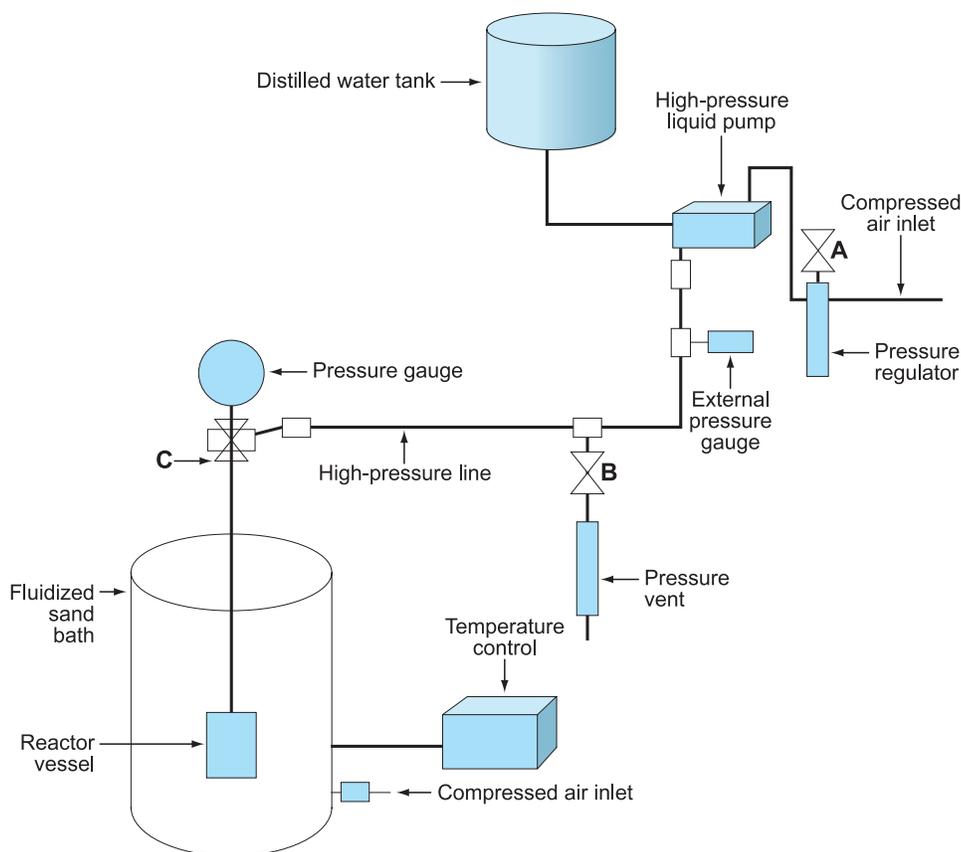
### Pyrolysis Experiments

Pyrolysis experiments were conducted on 4-g samples of Kimmeridge Clay source rock (180- to 425-μm particle size) at temperatures in the range of 350 to 420°C (temperature accuracy ±1°C) and durations of 6 to 24 hr under nonhydrous (no water added), low-pressure hydrous, and high-water pressure hydrous pyrolysis conditions. The pyrolysis equipment (Figure 1) used a Parr 4740 series Hastalloy (22 mL cylindrical) pressure vessel (rated to 648 bar at 350°C) connected to a pressure gauge rated to 690 bar. Previously, Carr et al. (2009) reported the results from a 22-mL Parr 4740 stainless steel vessel. The change in the vessel was required to achieve temperatures of 420°C while using a water pressure of as much as 500 bar.

Heat was applied by means of a fluidized sand bath controlled by a temperature gauge. Temperature was monitored by means of an additional K-type thermocouple connected externally to a computer that recorded the temperature every 10 s. Hydrous experiments were

conducted by the addition of 5 to 20 mL of water to the vessel, whereas the nonhydrous runs were conducted without water. The unextracted rock sample to be pyrolyzed was first weighed and transferred to the vessel, after which the volume of water needed for the experiment was added before the pressure vessel was assembled for the hydrous runs. For all experiments, the reaction vessel was flushed with nitrogen gas to replace air in the reactor head space, after which 2 bar pressure of nitrogen was pumped into the vessel to produce an inert atmosphere during the pyrolysis runs. The sand bath was connected to a compressed air source and was preheated to the required temperature and left to equilibrate. After equilibration, the pressure vessel was then lowered onto the sand bath and the experiment was left to run with constant air flow through the sand bath. The amount of water used for the experiments was varied to control the pressure at all temperatures, except for the high pressure (500 bar) runs at 350°C, where the added water was insufficient to generate the required pressure and additional water was pumped into the vessel to increase the pressure.

The high-pressure (500 bar) runs at 350°C were performed in a similar fashion to the low pressure hydrous experiments, with the vessel initially filled with 20 mL water. After lowering the pressure vessel onto the sand bath, the vessel was connected to the high-pressure line and allowed to attain its maximum vapor pressure (in about 20 min) before adding more water to increase the pressure. This is to ensure that excess water was not added to the vessel that could result in excessive pressure, thereby creating a safety issue. To apply a high liquid water pressure to the system with the aid of a compressed air-driven liquid pump, the emergency pressure release valve B was first closed (Figure 1), and valve A opened until a pressure slightly higher than the vapor pressure of the experiment was displayed on the external pressure gauge (to avoid losing any content of the vessel when the reactor valve C was opened). A high liquid water pressure was then applied to the system by first opening valve C and immediately gradually opening valve A to add more distilled water to the reaction vessel. When the required pressure was attained, valve C was closed to isolate the reactor from the high-pressure line, and valve A was also closed to prevent more water going to the



**FIGURE 1.** Schematic diagram of pyrolysis equipment.

pressure line. Then valve B was opened to vent the excess pressure in the line. The experiment was then allowed to run (leaving valve C tightly closed to avoid losing generated products) for the required time, after which the sand bath was switched off and left to cool to ambient temperatures before product recovery.

To attain a high pressure (e.g., 500 bar) at 350°C for 24 hr, the vessel was initially pressurized to about 440 bar, and the final pressure obtained was caused by thermal expansion of the additional water and generated gas. The volume of water giving a pressure of around 500 bar at 350°C was measured to be about 25 mL at ambient temperature from a blank run. The total internal volume of the empty pressure vessel and its associated pipe work (pressure gauge connected) was estimated to be about 34 mL by pressurizing with nitrogen gas to 2 bar and measuring the volume of gas released. The water in the hydrous experiments did not expand fully as expected considering the high temperatures used. This is because the head space of the reactor (gauge block), which is not immersed in the sand bath, is at a temperature lower than each of the experimental temperatures, and the extent of convection is not sufficient to overcome the reduced expansion that results from any temperature gradient that might exist above the reactor. Note that an overpressure between 40 and 60 bar was generated

because of gas generation for the 380 and 420°C high-pressure (390 bar and above) experiments.

To test whether any gas in the system was lost during pressurizing the vessel, a control experiment was conducted at 350°C for 50 min at 500 bar pressure using a light (35° API) crude oil, which is more thermally stable than the source rock being investigated. The short period used for the control experiment was to ensure that the oil did not thermally crack. The volume of gas collected after the control experiment was found to be equal to the volume of nitrogen pumped into the system at 2 bar before the experiment started. This indicated that gas was not lost during pressurization, pressure buildup in the vessel, or during gas sampling from the reactor after the experiments.

### Gas Analysis

The gaseous product was collected from the pressure vessel with the aid of a gas-tight syringe and transferred to a gas bag. Generated gases were analyzed immediately on a Carlo Erba HRGC 5300 gas chromatograph fitted with a FID detector operating at 200°C. Ten microliters of gas sample was injected at 100°C, with separation performed on a Varian Plot fused silica 25 m × 0.32 mm column, with helium as the carrier gas,

**Table 2.** Bitumen and hydrocarbon gas yields (milligrams per gram) total organic carbon from pyrolysis at 350°C for 6 and 12 hr.

<i>Experiment</i>	<i>Pressure (bar)</i>	<i>Time (hr)</i>	<i>CH<sub>4</sub></i>	<i>C<sub>2</sub>H<sub>4</sub></i>	<i>C<sub>2</sub>H<sub>6</sub></i>	<i>C<sub>3</sub>H<sub>6</sub></i>	<i>C<sub>3</sub>H<sub>8</sub></i>	<i>C<sub>4</sub>H<sub>10</sub></i>	<i>Total C<sub>1</sub>-C<sub>4</sub></i>	<i>Bitumen Plus Oil</i>
5 mL	45	6	3.31	0.18	3.20	0.59	2.61	1.27	11.16	975
10 mL	180	6	3.36	0.16	3.22	0.49	2.58	1.20	11.01	998
20 mL	210	6	2.84	0.05	2.50	0.16	1.85	0.71	8.11	997
485 bar	485	6	1.63	0.01	1.41	0.09	1.31	0.76	5.21	944
5 mL	45	12	6.22	0.13	6.70	0.66	5.13	2.04	20.88	881
10 mL	180	12	7.51	0.13	7.55	0.68	5.53	2.35	23.75	851
20 mL	210	12	6.82	0.04	6.67	0.32	5.16	2.63	21.64	818
470 bar	470	12	5.64	0.01	4.98	0.12	3.82	2.06	16.63	854

and an oven temperature program of 70 (2 min) to 90°C (3 min) at 40°C min<sup>-1</sup>, then to 140°C (3min) at 40°C min<sup>-1</sup>, and finally to 180°C (49 min) at 40°C min<sup>-1</sup>. Individual gas yields were determined quantitatively in relation to an external gas standard.

### Recovery of Generated Bitumen Plus Oil

After gas analysis, the pressure vessel was dismantled and the water in the vessel was decanted. For experiments where expelled oil was generated, the floating oil was separated from the water with the aid of a separating funnel, after which the vessel was transferred to a vacuum oven where the reacted source rock was vacuum dried at 45°C for 3 to 4 hr. The dried rock sample was then transferred to a pre-extracted cellulose thimble and Soxhlet extracted using 150 mL dichloromethane (DCM)-methanol mixture (93:7 vol/vol) for 48 hr. After extraction, the DCM-methanol mixture was gently evaporated (almost to dryness) by rotary evaporation and transferred to a pre-weighed glass vial with a Pasteur pipette. The vial was then left to air-dry to remove any DCM and/or methanol left in the sample. The generated product stuck to the side of the vessel (recovered by rinsing with DCM), and any expelled oil was combined with the Soxhlet extract and termed the “generated bitumen” or “bitumen plus oil.”

### Vitrinite Reflectance Measurement

Vitrinite reflectance measurements were obtained from extracted reacted rock residues and unreacted rock sample mounted in epoxy resin. Before reflectance measurements, samples were ground and polished using diamond solutions to produce a scratch-free polish. Measurements were made on a Leitz Ortholux microscope fitted with an MPV control and photometer head. The samples were examined in white light using oil-immersion objectives, whereas reflectance was measured using a

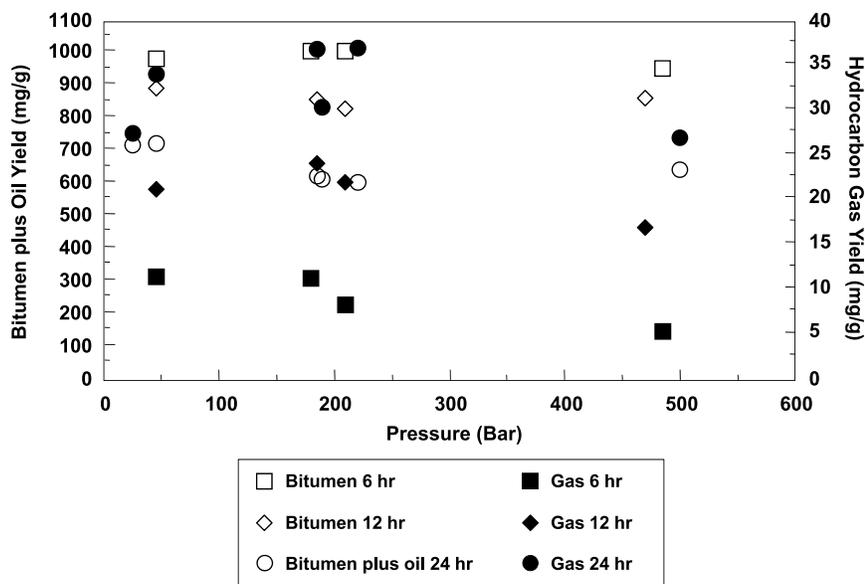
green filter with a peak transmission of 547 nm and a measuring aperture of 16 μm<sup>2</sup>. The results were expressed as arithmetic means (% R<sub>o</sub>).

## RESULTS

The pyrolysis of Kimmeridge Clay Formation source rock at 350 to 420°C between 6 and 24 hr was used to investigate the effects of temperature, pressure, and time on both hydrocarbon generation and maturation.

### Effect of Water, Pressure, and Time on Product Yield at 350°C

Experiments conducted at 350°C for 6 hr were used to investigate kerogen conversion to bitumen, whereas the 12- and 24-hr experiments were used to investigate bitumen cracking to oil. Table 2 and Figure 2 show the amounts of gas and bitumen generated in 6 and 12 hr. Bitumen yield increased from 975 mg/g at 45 bar to a maximum of 998 mg/g and 997 mg/g at 180 and 210 bar, respectively, for the 6-hr run, and the data are consistent with those of Carr et al., (2009), who also reported maximum bitumen generation from an identical Kimmeridge Clay sample at 320°C for 24 hr under low-pressure hydrous conditions. At 485 bar for 6 hr, the bitumen yield decreased by about 5% when compared with the yields obtained at 180 and 210 bar. The total C<sub>1</sub>-C<sub>4</sub> gas yield was maximum and identical at 45 and 180 bar, but decreased by about 27% at 210 bar. At 485 bar, the total C<sub>1</sub>-C<sub>4</sub> gas yield further decreased by about 50% when compared with the 180-bar experiment. The higher yields of gas and bitumen obtained under low pressure are caused by water promoting hydrocarbon generation. The increased bitumen and hydrocarbon gas yields obtained during low-pressure hydrous pyrolysis have been widely reported (Lewan, 1997; Price and



**FIGURE 2.** Bitumen, bitumen-plus-oil, and hydrocarbon gas yields (mg/g total organic carbon) obtained by pyrolysis at 350°C.

Wenger, 1992). The lower yields obtained at high pressure are caused by the water retarding hydrocarbon generation. Increasing the run time to 12 hr resulted in a decrease in the bitumen yield and an increase in the gas yield under all experimental conditions in relation to the 6-hr data. The reduced bitumen and increased gas yield obtained for the 12-hr experiment are the results of the bitumen starting to crack to oil. The total C<sub>1</sub>-C<sub>4</sub> gas yield was maximum and about the same under 45-, 180-, and 210-bar conditions but decreased with increase in pressure to 470 bar. The bitumen yields initially decreased from 45 bar to a minimum at 210 bar and then increased with increase in pressure to 470 bar. The increase in bitumen and decrease in gas yield observed with increase in pressure for 12 hr are caused by water pressure retarding the cracking of bitumen to oil and gas. The liquid product from the 12-hr experiments was also classified as bitumen because the source rock had not started expelling oil at this stage, and the nongaseous product was also solid as the 6-hr product.

At 350°C for 24 hr, the experiment is well into the oil-generating stage, and the liquid product (termed bitumen plus oil) was a combination of oil expelled during the experiment and unexpelled oil and bitumen extracted from the source rock after the experiments. The expelled oil generated from the experiments was not treated separately for two reasons. First, the small particle size (180–425 μm) of the sample made it difficult to separate the expelled oil adsorbed on the rock because any attempt to separate the oil from the rock by washing with solvent also dissolves the generated bitumen. Second, because of the small amount of sample used for the experiments (4 g), the expelled oil generated was also small, which would produce an increased experimental error if treated separately.

The bitumen-plus-oil and gas yields obtained from the 24-hr experiments at 350°C are presented in Figure 2 and Table 3. The bitumen-plus-oil yields at 24 hr are significantly lower, and the total C<sub>1</sub>-C<sub>4</sub> gas yields significantly higher when compared with the 350°C 6-hr data. This reduction in bitumen-plus-oil yield at 350°C for 24 hr compared with 350°C for 6 hr is caused by cracking of the generated bitumen to lighter oil and gas. The nonhydrous and 45-bar products at 350°C for 24 hr is solid bitumen because of the lack of expelled oil during the experiment, unlike the product from hydrous (185 and 220 bar) and high (500 bar)-water pressure experiments, which is a viscous liquid comprising of expelled oil, extracted unexpelled oil, and bitumen. The bitumen-plus-oil yield decreased as the conditions changed from nonhydrous to low-pressure hydrous (185 and 220 bar) conditions, but at 500-bar pressure, a reversal in the trend was observed with the bitumen-plus-oil yield increasing slightly.

The total C<sub>1</sub>-C<sub>4</sub> gas yields at 24 hr increased from nonhydrous to a maximum under low-pressure hydrous (185 and 220 bar) conditions, before decreasing when the water pressure was raised to 500 bar. The unsaturated ethene and propene yields decrease from the value obtained under nonhydrous pyrolysis to become either zero (below the detection limit) at 500 bar in the case of ethene or 0.11 mg/g in the case of propene. Methane, ethane, propane, and butane yields reach maxima at either 185 or 220 bar of pressure when compared with the 500-bar experiment (Table 3).

### Effect of Water, Pressure, and Time on Product Yield at 380°C

At 380°C for 6 and 12 hr, the experiment is well into the oil-generating stage, with the bitumen already

**Table 3.** Bitumen-plus-oil and hydrocarbon gas yields (milligrams per gram) total organic carbon from pyrolysis at 350°C for 24 hr.

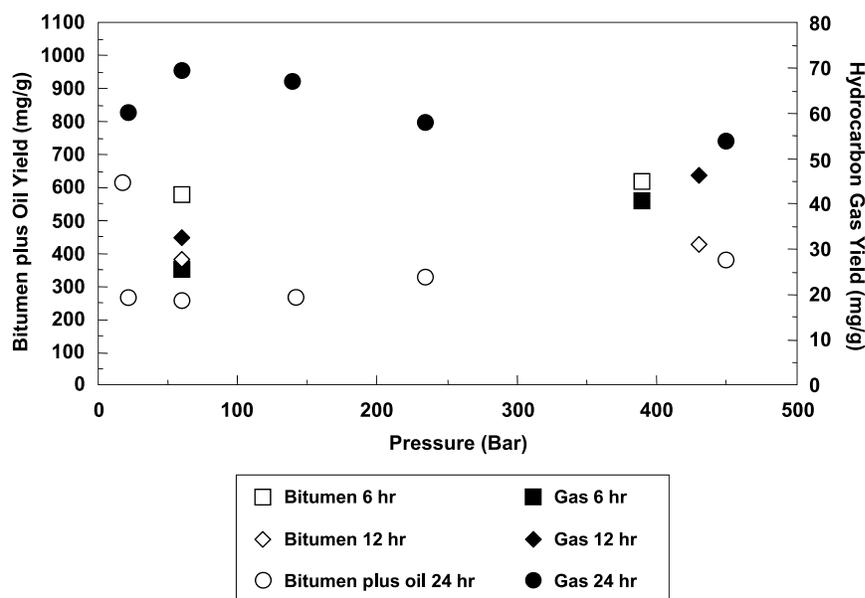
Experiment	Pressure (bar)	Time (hr)	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	Total C <sub>1</sub> -C <sub>4</sub>	Bitumen Plus Oil
Nonhydrous	22	24	7.19	0.10	8.46	0.67	7.47	3.36	27.25	709
5 mL	45	24	9.38	0.06	10.68	0.71	8.89	4.17	33.89	714
10 mL	185	24	9.89	0.04	10.83	0.78	9.44	5.59	36.57	614
20 mL	220	24	12.62	0.01	11.46	0.26	8.51	3.72	36.58	597
500 bar	500	24	8.82	0.00	8.23	0.11	6.35	3.12	26.63	632

cracking to oil and gas, whereas for the 24-hr experiment, virtually all the bitumen is cracked to oil and gas. Liquid products obtained at 380°C for 6 and 12 hr will be referred to as “bitumen plus oil” because the product is highly viscous and is a mixture of oil and bitumen yet to be cracked to oil, whereas the 24-hr product will be referred to as “oil” because the product is less viscous when compared with the 6- and 12-hr product. The cracking of the bitumen at 6 and 12 hr resulted to lower bitumen-plus-oil yield and higher gas yield when compared with the bitumen yield obtained at 350°C for 6 hr at the end of bitumen generation. The bitumen-plus-oil and C<sub>1</sub>-C<sub>4</sub> gas yields obtained at 380°C for 6 and 12 hr are shown in Figure 3 and Table 4. The bitumen-plus-oil yield decreased while the gas yield increased with increase in residence time because of cracking of the generated bitumen. The bitumen-plus-oil and gas yields from the 6- and 12-hr data show the same trend, both the bitumen-plus-oil yield and the C<sub>1</sub>-C<sub>4</sub> gas yield increased from low supercritical water pressure (60 bar) to high supercritical water pressure (390 bar).

The oil and gas yield obtained at 380°C for 24 hr are shown in Figure 3 and Table 5. Increasing the ex-

perimental time to 24 hr resulted in the oil yield further decreasing and the gas yield increasing when compared with the 6- and 12-hr data and is a result of the bitumen cracking to oil. The C<sub>1</sub>-C<sub>4</sub> gas yield increased for the 24-hr experiment going from nonhydrous to 60- and 140-bar hydrous conditions. At 235 bar supercritical water pressure, the C<sub>1</sub>-C<sub>4</sub> gas yield decreased, and a further reduction in gas yield was observed at the 450-bar supercritical water pressure. The gas yield obtained at 380°C follows the same trend as the 350°C data, with the yield increasing initially at low pressures (60 and 140 bar) in the presence of water before decreasing with increase in pressure. The oil yield is similar under nonhydrous and 45-bar hydrous conditions but increased slightly for the 140-bar experiment. Increasing the supercritical water pressures of the experiments to 235 and 450 bar by increasing the volumes of water added to the experiments to 10 and 20 mL, respectively, caused the oil yield to increase significantly, with the increase most significant at 450 bar.

The individual gas compositions in the 24-hr experiments show a maximum under either 45- or 140-bar hydrous conditions. The results at 6 and 12 hr are

**Figure 3.** Bitumen-plus-oil and hydrocarbon gas yields (mg/g total organic carbon) obtained by pyrolysis at 380°C.

**Table 4.** Bitumen-plus-oil and hydrocarbon gas yields (milligrams per gram) total organic carbon from pyrolysis at 380°C for 6 and 12 hr.

<i>Experiment</i>	<i>Pressure (bar)</i>	<i>Time (hr)</i>	<i>CH<sub>4</sub></i>	<i>C<sub>2</sub>H<sub>4</sub></i>	<i>C<sub>2</sub>H<sub>6</sub></i>	<i>C<sub>3</sub>H<sub>6</sub></i>	<i>C<sub>3</sub>H<sub>8</sub></i>	<i>C<sub>4</sub>H<sub>10</sub></i>	<i>Total C<sub>1</sub>-C<sub>4</sub></i>	<i>Bitumen Plus Oil</i>
5 mL	60	6	7.25	0.09	8.11	0.80	6.54	2.97	25.76	580
20 mL	390	6	14.21	0.03	12.82	0.45	9.42	3.83	40.76	615
5 mL	60	12	9.20	0.06	10.41	0.66	8.63	3.92	32.88	385
20 mL	430	12	17.09	0.00	14.84	0.30	10.50	3.69	46.42	427

generally lower than the 24-hr experiment values regardless of whether low-hydrous (60 bar) or high-supercritical water pressure was used. The exceptions appear to be methane, ethane, and propene, all of which seem to be the same at 12 hr as at 24 hr. Comparisons between the 6- and 12-hr values show increases for the saturated C<sub>1</sub> to C<sub>3</sub> gases, whereas butane seems to remain relatively constant.

#### Effect of Water, Pressure, and Time on Product Yield at 420°C

As for the 380°C product, the liquid product of the 420°C pyrolysis at 6 and 12 hr is also called “bitumen plus oil” and that obtained for 24 hr is called “oil.” The bitumen-plus-oil and C<sub>1</sub>-C<sub>4</sub> gas yields for 6 and 12 hr from the 420°C pyrolysis are presented in Figure 4 and Table 6, whereas the oil and C<sub>1</sub>-C<sub>4</sub> gas yields for the 24-hr pyrolysis are shown in Figure 4 and Table 7. Although no quantitative measure of the viscosity of the oil generated existed, the oil produced by the experiments at 420°C appears to be less viscous than the oil generated at 380°C, and the 380°C oil also appears less viscous than that generated at 350°C for identical periods. The bitumen-plus-oil yield decreased whereas the gas yield increased with the increase in experimental period from 6 to 12 hr. Increase in residence time to 24 hr also resulted in a decrease in oil yield and increase in gas yield as observed for the 380°C runs. The bitumen-plus-oil and the total C<sub>1</sub>-C<sub>4</sub> gas yields for the 6- and 12-hr runs were lower for the 60-bar experiments than those obtained

from the supercritical water pressure (430–435 bar) runs, a characteristic that was also observed in the 380°C experiments. The 24-hr data show that the gas yield increased with increase in water content and pressure to a maximum at 450 bar, a trend that is opposite to that observed at 380°C. However, the oil yield followed the same trend as at 380°C, increasing from nonhydrous (25 bar) and low pressures (60 and 150 bar) hydrous conditions to a maximum at 450 bar.

The individual gas compositions show increases in all the saturated components as the time of the experiment was increased from 6 to 12 hr and then to 24 hr. Ethene, although present in the 60-bar hydrous gases, is always absent from the 430- to 450-bar supercritical water pressure runs. Propene shows a slight reduction with increasing time for 6 to 24 hr. Methane shows the largest increase as the experiment was extended from 12 to 24 hr, with the amount of increase decreasing as the carbon number of the saturated gas component increased.

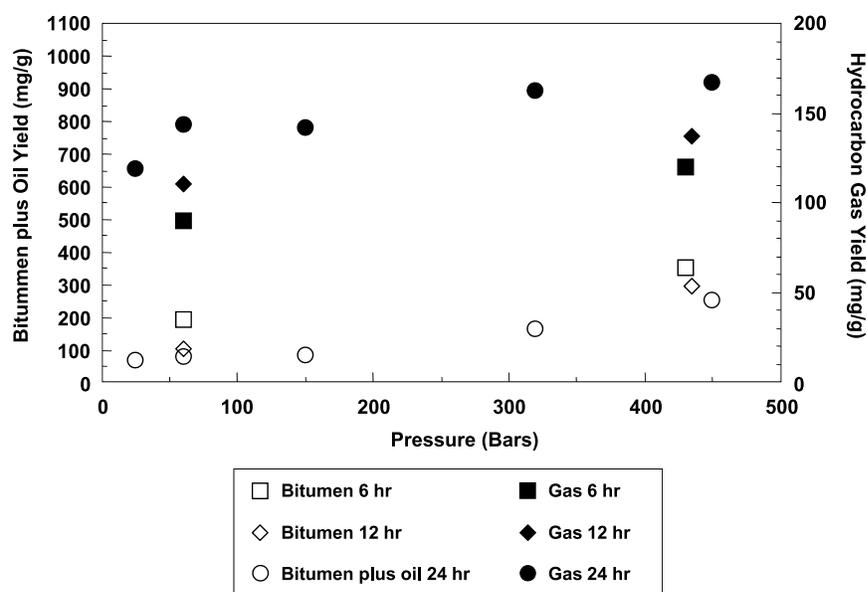
#### Vitrinite Reflectance

The VR values obtained from the source rock residues for experiments conducted at temperatures in the range of 310 to 420°C are shown in Figures 5 and 6 and in Table 8. The 310 and 320°C samples were taken from the experiments described in Carr et al. (2009). The mean VR values are based on only 1 to 7 counts because the Kimmeridge Clay source rock was deposited under anaerobic conditions with very little terrigenous kerogen. Such small numbers of primary particles of vitrinite, as

**Table 5.** Oil and hydrocarbon gas yields (milligrams per gram) total organic carbon from pyrolysis at 380°C for 24 hr.

<i>Experiment</i>	<i>Pressure (bar)</i>	<i>Time (hr)</i>	<i>CH<sub>4</sub></i>	<i>C<sub>2</sub>H<sub>4</sub></i>	<i>C<sub>2</sub>H<sub>6</sub></i>	<i>C<sub>3</sub>H<sub>6</sub></i>	<i>C<sub>3</sub>H<sub>8</sub></i>	<i>C<sub>4</sub>H<sub>10</sub></i>	<i>Total C<sub>1</sub>-C<sub>4</sub></i>	<i>Bitumen Plus Oil</i>
Nonhydrous	22	24	17.35	0.17	19.24	1.00	15.58	6.84	60.18	264
5 mL	60	24	20.82	0.02	23.15	0.87	18.24	6.68	69.78	255
7 mL	140	24	20.21	0.02	21.44	0.59	17.39	7.50	67.15	276
10 mL	235	24	19.34	0.04	18.61	0.77	13.91	5.51	58.18	329
20 mL	450	24	16.88	0.00	16.10	0.27	12.74	8.13	54.12	381

**FIGURE 4.** Bitumen-plus-oil and hydrocarbon gas yields (mg/g total organic carbon) obtained by pyrolysis at 420°C.



opposed to other types of kerogen, are not unusual for the Kimmeridge Clay.

The VR data for the 24-hr experiment at 350°C show that the mean reflectance value increased significantly by 0.6%  $R_o$  as the experimental conditions changed from nonhydrous to 185-bar hydrous conditions. At 220-bar hydrous conditions, a slight decrease in VR was observed relative to the 185-bar VR. Increasing the water pressure to 500 bar resulted in VR of 0.66%  $R_o$  lower than the maximum value obtained under 185-bar hydrous conditions.

At 380°C for 6 hr, the VR decreased from 1.23%  $R_o$  at low pressure (60 bar) to 1.07%  $R_o$  at 390 bar. However, the 12-hr result shows that VR increases from 0.99%  $R_o$  at low pressure (60 bar) to 1.19%  $R_o$  at 430 bar. Comparison of the 6- and 12-hr VR values indicates that the source rock was at a similar level of maturity between 6 and 12 hr. However, extending the run time to 24 hr at 380°C showed that the VR increased compared with the 6- and 12-hr values for identical heating conditions. The VR values increased with increases in water content and pressure to a maximum of 1.61%  $R_o$  at 235 bar. At 450 bar, the measured VR was lower (1.48%  $R_o$ ), with

the trend at 380°C for 24 hr mirroring that observed at 350°C for 24 hr.

At 420°C, the VR increased with increasing time, and a much higher VR was also achieved compared with the 380°C values. The 420°C values for 6 and 12 hr show lower VR values at high pressure (430 bar) than at low pressure (60 bar). The 24-hr experiments also show the same trend as the 350 and 380°C data. The VR increased from 1.98%  $R_o$  under nonhydrous conditions to a maximum of 2.09% and 2.18%  $R_o$  in the 60- and 320-bar experiments, whereas a lower value of 1.71%  $R_o$  was recorded at 450 bar.

## Experimental Mass Balances

Mass balances were performed for the different temperature experiments at low and high pressures. Tables 9–11 list the mass balances obtained at 350°C for 6 hr, 350°C for 24 hr, and 380 to 420°C for 24 hr, respectively. As previously mentioned in the experiment section, the initial rock contains 25% carbon, and using 4 g of sample for the experiments equates to 1 g or 1000 mg

**Table 6.** Bitumen-plus-oil and hydrocarbon gas yields (milligrams per gram) total organic carbon from pyrolysis at 420°C for 6 and 12 hr.

Experiment	Pressure (bar)	Time (hr)	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	Total C <sub>1</sub> -C <sub>4</sub>	Bitumen Plus Oil
5 mL	60	6	27.53	0.05	28.69	0.97	22.63	8.09	87.96	186
15 mL	430	6	43.69	0.01	36.86	0.55	28.84	10.82	120.77	351
5 mL	60	12	35.78	0.02	35.12	0.77	28.24	9.84	109.77	103
15 mL	435	12	50.35	0.00	39.90	0.39	33.33	13.51	137.48	296

**Table 7.** Oil and hydrocarbon gas yields (milligrams per gram) total organic carbon from pyrolysis at 420°C for 24 hr.

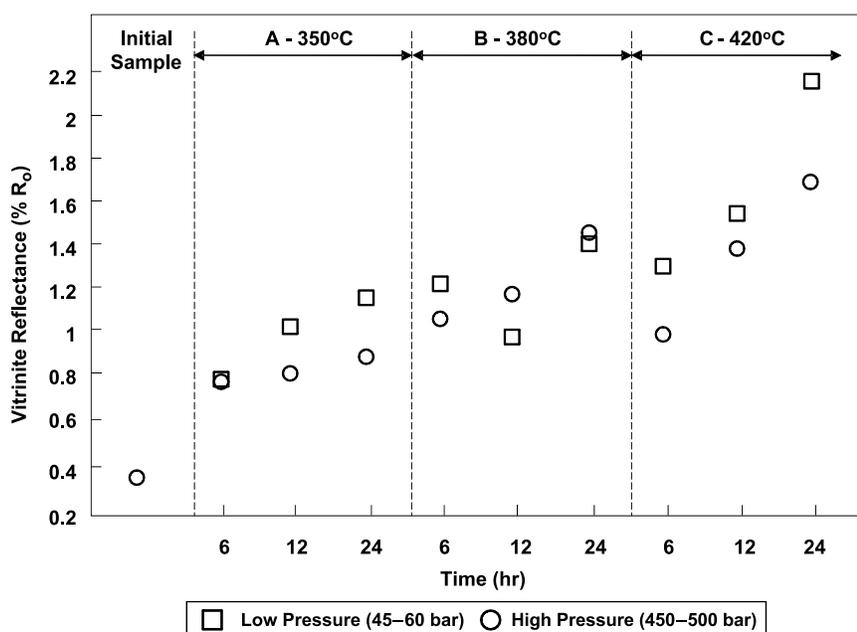
Experiment	Pressure (bar)	Time (hr)	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	Total C <sub>1</sub> -C <sub>4</sub>	Bitumen Plus Oil
Nonhydrous	25	24	36.33	0.20	35.48	1.34	31.21	14.12	118.68	84
5 mL	60	24	45.83	0.00	44.62	0.55	38.05	15.17	144.22	78
7 mL	150	24	47.53	0.02	42.57	0.32	37.11	14.52	142.07	83
10 mL	320	24	57.35	0.05	48.31	0.48	39.83	15.80	161.82	167
15 mL	450	24	61.08	0.00	47.72	0.31	41.33	16.96	167.40	252

of starting carbon. At 350°C for 6 hr (bitumen-generation stage), where the products are mainly gas and bitumen, almost all of the starting carbon was recovered after the experiments for both the 45- and 485-bar experiments.

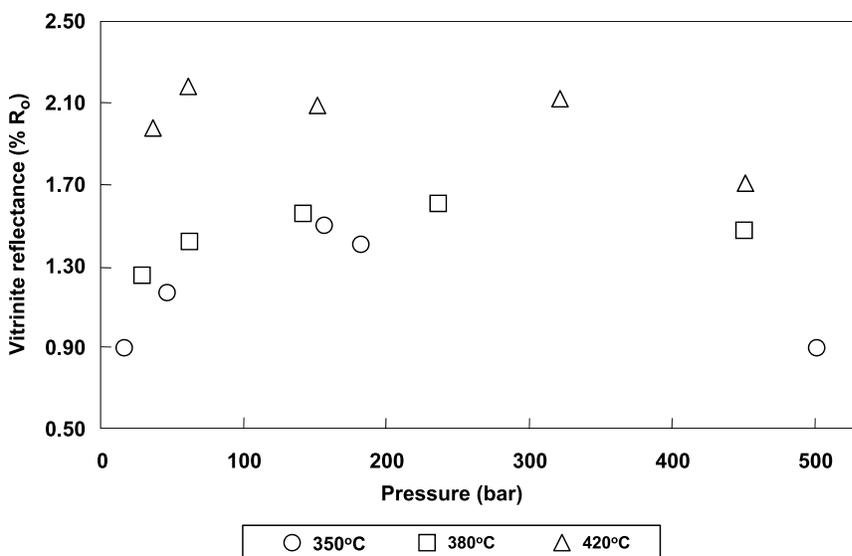
Increasing the residence time of the experiment to 24 hr at 350°C (bitumen cracking to oil stage) where the products are gas, bitumen, and oil, 80% of the starting carbon was recovered for both the low- and high-pressure experiments. This is caused by the loss of the lighter liquid products during sample drying and Soxhlet extraction of the recovered rock after the pyrolysis experiments. The observed increase in the carbon content of residual rock from 192 mg (low pressure) and 180 mg (high pressure) at 350°C for 6 hr to 277 mg (low pressure) and 265 mg (high pressure) at 350°C for 24 hr is caused by the onset of coke or pyrobitumen formation as the bitumen is cracked to oil.

At 380°C for 24 hr, only about 70% of the starting carbon was recovered for the 235- and 450-bar experiments, 10% less when compared with the amount re-

covered at 350°C for 24 hr. This is caused by more loss of lighter liquid product at 380°C as the liquid product obtained is less viscous than the 350°C for 24 hr products. The carbon content of the residual rock also increased further at 380°C for 24 hr, indicating that more pyrobitumen or coke formed with increased cracking of the generated bitumen and oil. The recovered carbon for the 420°C experiments for 24 hr is 79 and 70% for the 320- and 450-bar experiments, respectively. The lower amount of carbon recovered when compared with the starting carbon is also a result of the loss of lighter liquid products as observed for the 350 and 380°C experiments for 24 hr. The carbon content of the residual rock also increased further with temperature when compared with the 380°C experiment and is also caused by more pyrobitumen or coke formed with increased cracking of the generated bitumen and oil at 420°C. The fact that similar amounts of total carbon were recovered for both the low- and high-pressure experiments at all three temperatures, apart from the

**FIGURE 5.** Vitrinite reflectance ( $R_0$ ) results for the 6-, 12-, and 24-hr experiments at low (45–60 bar)– and high (450–500 bar)–water or supercritical water pressures.

**FIGURE 6.** Vitrinite reflectance ( $R_o$ ) results for the 24-hr experiments undertaken at 350, 380, and 420°C in the pressure range of 15 (nonhydrous) to 450 and 500 (water or supercritical water pressure) bar.



380 and 420°C runs where slightly more carbon was recovered at low pressure, indicates that product recovery was good.

Note that the carbon content of the residual rock was always higher for the low-pressure compared with the high-pressure experiments for 24 hr at 350, 380, and 420°C, with the effect most significant at 380 and 420°C. This is because of a high water pressure retarding the cracking of the generated bitumen or oil to gas and insoluble pyrobitumen or coke. The high pyrobitumen or coke content of the residual rock from the low-pressure runs is consistent with bitumen-plus-oil or oil yield being lower, whereas the low pyrobitumen or coke content of high-pressure residual rock is also consistent with bitumen-plus-oil or oil yield being higher.

## DISCUSSION

Carr et al. (2009) showed that the pyrolysis of Kimmeridge Clay samples under 500 bar of water pressure at 310 and 320°C for 7 and 24 hr resulted in retardation of hydrocarbon (bitumen and gas) generation. At 350°C and 500 bar of water pressure for 24 hr, retardation of hydrocarbon generation still occurred, although the increase in temperature initiated some cracking of the bitumen to oil and gas. In the experimental results reported in this study, the results from the 350°C experiments follow the same general trends as those reported by Carr et al. (2009), although the different Kimmeridge Clay sample and the different water-rock ratio in the pressure vessel (with different internal volume) used in this study resulted in values slightly different to those reported in the previous study. To understand the ef-

fects of temperature, pressure, and time on hydrocarbon generation, the temperature and pressure effects will be discussed separately from time and pressure effects.

### Hydrocarbon Generation: Temperature and Pressure Effects

In this section, the results mainly from the 24-hr experiments will be discussed. At 350°C, the decrease in bitumen-plus-oil yield and the increase in gas yield going from 22-bar (nonhydrous) to 185- and 220-bar hydrous conditions are the results of water promoting the cracking of bitumen to oil and gas. Within source rocks in geologic basins and laboratory pyrolysis experiments, the conversion of kerogen into thermogenic hydrocarbons can be described by three somewhat overlapping stages (Erdmann and Horsfield, 2006). Thus, at 350°C for 6 hr, the kerogen is converted into bitumen and gas, with the bitumen itself converting into both oil and gas and the minor conversion of oil into gas after 12 hr (stages 1, 2, and 3, respectively, of Erdmann and Horsfield, 2006). The observed increase in bitumen-plus-oil yield and decrease in gas yield observed at 500 bar for 24 hr were caused by water pressure retarding the cracking of bitumen to oil and gas (stage 3 of Erdmann and Horsfield, 2006). Under 185 and 220 bar hydrous conditions, water promoted bitumen cracking to oil by donating hydrogen to the bitumen, a trend similar to that observed by Carr et al. (2009) during pyrolysis of the Kimmeridge Clay at 350°C using 155- and 180-bar hydrous conditions. At 500-bar water pressure, bitumen cracking is retarded because of the lack of sufficient vapor space in the vessel to accommodate the volume expansion required by cracking of bitumen to oil and gas. This contrasts to the 185- and 220-bar hydrous experiments

**Table 8.** Vitrinite reflectance values for the matured source rock after pyrolysis at 350, 380, and 420°C.

<i>Experiment</i>	<i>Pressure (bar)</i>	<i>Time (hr)</i>	<i>Temperature (°C)</i>	<i>Mean VR (% R<sub>o</sub>)*</i>	<i>Other Values (% R<sub>o</sub>)</i>
Nonhydrous	15	7	310	0.56 (1)	
10 mL	90	7	310	0.58 (1)	
500 bar	500	7	310	0.43 (2)	
Nonhydrous	18	24	320	0.58 (2)	0.13 (2) B, 0.31 L
10 mL	115	24	320	0.72 (2)	0.54 B
20 mL	125	24	320	0.89 (3)	
5 mL	45	6	350	0.77 (2)	
500 bar	500	6	350	0.80 (3)	0.43 B, 1.43 (7) I
5 mL	45	12	350	0.82 (2)	
20 mL	210	12	350	1.00 (1)	
470 bar	470	12	350	1.04 (3)	0.68 (2) B, 1.28 (2) I
Nonhydrous	22	24	350	0.90 (2)	1.29 I
5 mL	45	24	350	1.17 (3)	
10 mL	185	24	350	1.50 (2)	
20 mL	220	24	350	1.41 (1)	
500 bar	500	24	350	0.90 (8)	0.48 (15) B
5 mL	60	6	380	1.23 (2)	
20 mL	390	6	380	1.07 (3)	
5 mL	60	12	380	0.99 (2)	
20 mL	430	12	380	1.19 (2)	
Nonhydrous	22	24	380	1.25 (6)	
5 mL	60	24	380	1.42 (3)	1.73, 1.84, 1.77 I
7 mL	140	24	380	1.56 (2)	
10 mL	235	24	380	1.61 (2)	
16 mL	305	24	380	1.36 (2)	2.13 I
20 mL	450	24	380	1.48 (2)	1.86 (2) I
5 mL	60	6	420	1.34 (2)	
15 mL	430	6	420	1.02 (2)	
5 mL	60	12	420	1.56 (3)	
15 mL	435	12	420	1.40 (1)	
Nonhydrous	25	24	420	1.98 (6)	
5 mL	60	24	420	2.18 (7)	
7 mL	150	24	420	2.09 (2)	
10 mL	320	24	420	2.12 (2)	
15 mL	450	24	420	1.71 (3)	

\*Mean random reflectance value, % R<sub>o</sub> (no. of readings); B = bitumen; I = inertinite.

**Table 9.** Mass balance (product and residue in milligrams of carbon) for pyrolysis at 350°C for 6 hr.

<i>Experiment</i>	<i>Pressure (bar)</i>	<i>Total C<sub>1</sub>-C<sub>4</sub></i>	<i>Bitumen</i>	<i>Residual Rock</i>	<i>Total Recovered</i>	<i>(%) Recovery</i>
5 mL	45	9	780	192	981	98
485 bar	485	4	755	180	939	94

**Table 10.** Mass balance (product and residue in milligrams of carbon) for pyrolysis at 350°C for 24 hr.

<i>Experiment</i>	<i>Pressure (bar)</i>	<i>Total C<sub>1</sub>-C<sub>4</sub></i>	<i>Bitumen Plus Oil</i>	<i>Residual Rock</i>	<i>Total Recovered</i>	<i>(%) Recovery</i>
10 mL	185	29	491	277	797	80
500 bar	500	21	506	265	792	79

where enough compressible vapor space still exists in the system to accommodate the generated gases and give the higher gas yields obtained under low-pressure hydrous conditions. The retardation effect of pressure on gas generation from bitumen cracking mirrors was observed at 500 bar for 24 hr at 320°C (Carr et al., 2009). This result is consistent with previous studies (Brooks et al., 1971; Hesp and Rigby, 1973) in which water and inert gas pressure retarded the cracking of oil to gas.

The results for the 380°C experiments at 24 hr follow the same trend as the 350°C experiments. At 380°C, the conversion of bitumen into oil and gas (stage 2) and the conversion of oil into gas (stage 3) become increasingly important. Water initially promoted bitumen cracking, in that the yield decreases as the conditions change from nonhydrous (22 bar) to low-pressure hydrous conditions (<235 bar). The maximum effect of water was observed between 60 and 140 bar, producing more gas and less oil, before cracking was retarded by the increase in supercritical water pressure to 235 and 450 bar. At 450 bar, the total hydrocarbon C<sub>1</sub>-C<sub>4</sub> gas yield (54.12 mg/g) was about 20% lower than the gas yield (69.78 and 67.15 mg/g) obtained at low pressures (60 and 140 bar, respectively), whereas the oil yield remained about 50% higher than that from the low-pressure (<235 bar) experiments.

The retardation effect of pressure on oil cracking at 420°C is more significant than at 380°C, when the oil remaining at high pressures (450 bar) is compared with that obtained at low pressures for both sets of temperatures. This effect can be calculated by subtracting the bitumen plus oil yield at 380°C, 140 bar and 420°C, 150 bar (where maximum promotional effect of water was observed) from the values at 450 bar. At 420°C, the difference is 169 mg/g, whereas at 380°C, the difference

is 105 mg/g. In addition, subtracting the bitumen-plus-oil yield (597 mg/g) at 220 bar and 350°C (where maximum promotional effect of water was observed) from the 500 bar value (632 mg/g) gives a difference of only 35 mg/g, showing that the retardation effect of 450 to 500 bar of water or supercritical water pressure increases as the temperature increases. This occurs because the products obtained at higher temperatures (380 and 420°C) contain mainly oil (which is more thermally stable and more difficult to crack), whereas the 350°C products contain more bitumen than oil.

The increase in total C<sub>1</sub>-C<sub>4</sub> gas yields at 420°C with increasing water pressure is in contrast to the 350 and 380°C data, which show that water pressure retarded bitumen cracking to oil and gas. At 420°C, the increase in gas and bitumen-plus-oil yield with increase in water pressure to 450 bar resulted from the promotional effect of water on bitumen cracking to oil and gas, and not pressure promoting gas generation. The 450-bar pressure attained at 420°C was insufficient to prevent gas generation from bitumen cracking to oil, with the effect that chemical effect of water dominated the retardation of pressure because of the higher temperature and lower pressure conditions used. Pressures higher than 450 bar would need to be used before the retardation effect of pressure on bitumen cracking to oil and gas can be observed, which will be our future work. This indicates that at 450 bar, the retardation effect of water pressure on gas generation from bitumen cracking becomes less significant as the temperature increases from 350 to 420°C. However, 450 bar of pressure does significantly retard the cracking of the oil formed from bitumen cracking as the temperature increases from 350 to 420°C, resulting in more oil than in the low-pressure hydrous runs.

**Table 11.** Mass balance (product and residue in milligrams of carbon) for pyrolysis at 380 and 420°C for 24 hr.

<i>Experiment</i>	<i>Temperature (°C)</i>	<i>Pressure (bar)</i>	<i>Total C<sub>1</sub>-C<sub>4</sub></i>	<i>Oil</i>	<i>Residual Rock</i>	<i>Total Recovered</i>	<i>(%) Recovery</i>
10 mL	380	235	46	263	425	734	74
20 mL	380	450	43	305	321	669	67
10 mL	420	320	128	134	527	789	79
20 mL	420	450	134	202	369	703	70

The increase in hydrocarbon gas yield with increase in pressure to 450 bar observed at 420°C have been reported previously under anhydrous conditions (Hill et al., 1994, 1996). Hill et al. (1996) observed a slight decrease in gas yield from 90 to 210 bar and then an increase to 690 bar and then a decrease again at 2000 bar for oil cracking at 350 to 400°C, whereas for coal pyrolysis (Hill et al., 1994), both gas yield and VR increased with pressure to 690 bar before decreasing at 2000 bar at 300 and 340°C. The increase in gas yield (enhanced hydrocarbon generation) observed in this study at 420°C resulted from the promotional effect of water as the effect of 450-bar pressure attained became less dominant at 420°C. The increase in gas yield with pressure observed for oil cracking and coal pyrolysis (Hill et al., 1994, 1996) might be caused by the effect of pressure being less significant under high pressure–confined anhydrous conditions when compared with high-pressure hydrous conditions reported previously (Michels et al., 1995b; Landais et al., 1994). Michels et al. (1995b) and Landais et al. (1994) attributed the higher retardation effect observed under high-pressure hydrous conditions to the nature of the pressurizing medium (pyrolyzed sample in contact with pressurized water). The retardation of VR observed in this study at 430 to 500 bar is a result of the rock being in contact with pressurized water, whereas the increase in VR to 690 bar observed by Hill et al. (1994) might be caused by the fact that the pressure operating on the coal samples inside the gold bag has been reduced by the hydrocarbons generated inside the bag as well as the absence of water inside the bag.

The differences obtained at the three temperatures reflect the relative effects that temperature and pressure have on endothermic reactions from both thermodynamic (equilibrium) and kinetic standpoints. The extent to which any reaction will proceed at a given temperature and pressure is controlled by the Gibbs free energy ( $G$  in equation 1), which when negative favors the products and the reaction proceeds, whereas a positive value favors the reactants, that is, no reaction occurs. The Gibbs free energy is given by

$$\Delta G = \Delta H - T \cdot \Delta S \quad (1)$$

where  $\Delta G$  is the Gibbs free energy (kJ/mol),  $\Delta S$  is entropy (J/mol K),  $\Delta H$  is enthalpy (kJ/mol), and  $T$  is the absolute temperature. The effect of increasing the temperature at any pressure increases the  $T \cdot \Delta S$  term in equation 1, resulting in the increased probability that the  $T \cdot \Delta S$  term becomes larger than the enthalpy, with the result that  $G$  is negative and the reaction proceeds. The entropy ( $S$ ) term in equation 1 is a measure of the disorder of the system, and the pressure reduces the mobility in the system, thereby reducing the entropy (Carr et al., 2009). Increasing the pressure at any temperature therefore reduces the  $T \cdot \Delta S$  term, increasing

the probability that the  $G$  term will either be less negative or even positive, and if positive then the reaction cannot proceed.

From a kinetic standpoint, the rate at which a reaction proceeds is controlled by the activation energy in the Arrhenius first-order kinetic model. From the transition state theory, the activation energy is given by:

$$E_a = H^\ddagger + R \cdot T \quad (2)$$

where  $H^\ddagger$  is the activation enthalpy, which is given by:

$$\Delta H^\ddagger = \Delta U^\ddagger + \Delta pV^\ddagger \quad (3)$$

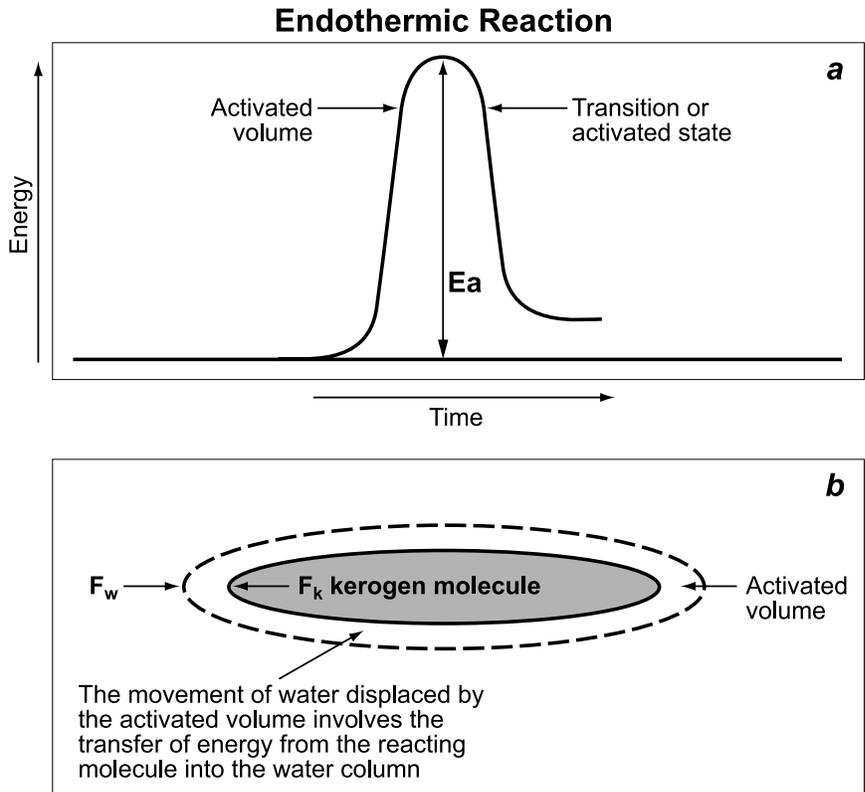
where  $\Delta U^\ddagger$  is the internal energy at activation (kJ/mol), and  $\Delta pV^\ddagger$  is the work (kJ/mol) against the force of the water that occurs as the volume of the activated complex increases. Internal energy includes the potential, kinetic, and thermal energies of the activated complex.

Pressure increases the activation energy caused by the energy required to create space for the hydrocarbons against the pressure. As shown in panels A and B of Figure 7, the expansion of the activated complex (activated volume) involves the transfer of energy ( $pV$  work in equation 3) from the kerogen into the water column, which increases the activation energy above the values determined by conventional kinetics using either Rock-Eval or microscale sealed vessel (MSSV) pyrolysis.

Theoretical considerations and the experimental results presented in this study and in Carr et al. (2009) indicate that both temperature and pressure exert significant controls on the extent of endothermic reactions, such as hydrocarbon generation and maturation reactions. Increasing temperature produces an increase in total hydrocarbon yield and maturation, whereas increases in pressure have the opposite effect, that is, hydrocarbon generation yields and maturation values are lower as reaction rates are retarded.

In the transition state theory, reaction rates are controlled by the activation volume ( $\Delta^\ddagger V^\circ$ ), which is the volume difference between the activated complex and reactant. If  $\Delta^\ddagger V^\circ$  is negative, then the reaction rate constant increases with increasing pressure. Conversely, if volume increases when the activated complex is formed, then pressure should slow the reaction rates. Hill et al. (1996) using gold bags to study oil cracking calculated  $\Delta^\ddagger V^\circ$  values of +47 cm<sup>3</sup>/mol in the 90- to 483-bar range at 400°C, whereas between 345 and approximately 690 bar at 350 and 380°C, and 483 and 690 bar at 400°C,  $\Delta^\ddagger V^\circ$  is -14 cm<sup>3</sup>/mol. Raising the pressure to between 690 and 2000 bar at temperatures between 350 and 400°C,  $\Delta^\ddagger V^\circ$  is +5 cm<sup>3</sup>/mol. Al Darouich et al. (2006) also using gold bags to study oil cracking, calculated  $\Delta^\ddagger V^\circ$  values in the range of 40 to 140 cm<sup>3</sup>/mol. Given the

**FIGURE 7.** (A) Diagram illustrates the relationship between the activation energy, activation volume, and the transition or activated state for an endothermic reaction. (B) Schematic diagram shows the activation volume of the kerogen that forces the surrounding pore medium (water in this study) to move. Energy (thermal) must be transferred from the kerogen into the incompressible water to force the water to move away ( $pV$  work in equation 2), thereby enabling the kerogen to expand into its activated state. The higher the pressure, the more energy is transferred from the kerogen into the water column, and this energy is lost from the kerogen and the reaction is retarded.



relatively large size of the molecules in kerogen and petroleum, it would not be unrealistic to expect quite large changes upon activation, depending upon the exact nature of the activated complex. The situation is complicated by the fact that  $\Delta^{\ddagger}V^{\circ}$  (like all volume parameters) is pressure dependent, and no theory exists to rationalize this variation.

To resolve this apparent ambiguity, we must also consider the complex thermodynamic effects in operation arising from equilibria based on competitive reactions. If the pseudo-equilibrium yield of methane for bitumen generation from kerogen is vastly reduced as shown by the reduced methane yields in the 310 and 320°C experiments reported by Carr et al. (2009), then the proportion of reactant ( $A_0$ ) forming methane reduces correspondingly. Thus, taking the hypothetical case of a four-fold reduction in the methane yield at the point of maximum bitumen generation and a two-fold reduction from the lower reaction rate, then the thermodynamic effect would approximately give rise to approximately 50% less methane. Given these issues, the derivation of a kinetic model based on calculated activation volumes would appear to be exceedingly difficult, and a better approach might involve the modification by pressure of the activation energy and preexponential factors in the Arrhenius model using equations given in the transition state theory (see equations 2 and 3 and in Carr et al., 2009).

### Hydrocarbon Generation: Time and Pressure Effects

At all three temperatures (350, 380, and 420°C), extending the heating time from 6 to 12 hr and then to 24 hr reduced the bitumen-plus-oil or oil yield and increased the gas yield at the same (or similar) pressure. In the 420°C experiments at high pressures (430–450 bar), for example, the gas yield increases from 120.77 mg/g after 6 hr to 137.48 mg/g after 12 hr, and to 167.40 mg/g after 24 hr. The difference between the 6- and 12-hr values is 16.71 mg/g, whereas that between 12 and 24 hr is 29.92 mg/g, indicating that although the duration of the experiment doubled, the yield has not doubled. As discussed previously, this is caused by the liquid product becoming more thermally stable as the product is composed more of oil caused by cracking of the bitumen with increase in residence time. Initially, this might be considered as being caused by the effect of the reaction nearing completion after 24 hr, but the presence of significant amounts of oil in the 420°C 450-bar sample indicates that the reactant has not been completely converted into products (gases).

The liquid product yields at 420°C also show the same pattern between 430 and 450 bar, with the bitumen-plus-oil yield decreasing from 351 mg/g for 6 hr to 296 mg/g for 12 hr and the oil yield also decreasing to 252 mg/g for 24 hr. The rate at which the bitumen-plus-oil

phase is converted into gas during the 12 hr (difference between 24 and 12 hr experiments being 44 mg/g) does not seem to have doubled the rate at which it declined during the 6 hr between 12 and 6 hr (55 mg/g). The results again suggest that with increasing time, fixed temperature, and high water pressure as the reaction progresses, the rate of the reaction decreases because of enhanced thermal stability of the oil generated, which is less reactive than the starting kerogen and the intermediate bitumen. The results suggest that with increasing time at fixed temperature and water or supercritical water pressure, the rate may decrease because of the shift in the Gibbs free energy from negative toward zero, at which point the reaction is in equilibrium.

The results at 380°C show the same pattern of reduction in liquid product yield with increase in residence time, with the yields between 6 and 12 hr being greater than those between 12 and 24 hr at a similar pressure. Although the extension of the heating time allows increased amounts of bitumen and oil to be cracked to gas, pressure has a far more significant effect on oil than bitumen cracking. The small increase in the gas yield at 420°C for 24 hr is not considered to be caused by the reaction nearing completion because the combined bitumen and gas yields obtained at 320°C under 115 bar hydrous conditions are greater than 1000 mg/g (Carr et al., 2009), whereas at 420°C and 450 bar after 24 hr, the combined yields (bitumen plus oil and gas) obtained 420 mg/g. As the bulk of the mass in the bitumen and oil is converted to pyrobitumen or coke, the total organic carbon content of the residual rock increases from the minimum value obtained at the end of bitumen generation (see Carr et al., 2009) (Tables 7, 10). Clearly, the reactions at 450 to 500 bar at the three temperatures used in this study are still continuing, but they appear to be slowing down with increasing time because of the effects of pressure.

### Vitrinite Reflectance

The VR data show four distinct trends, two of which are currently accepted as factors controlling the maturation of source rocks. First, increasing the temperature under either low-pressure (45–320 bar) hydrous conditions or high–water or supercritical water pressure conditions (450–500 bar) increases VR (Table 8; Figures 5, 6). Second, the effect of time also increases the VR, although some of the values such as the 380°C, 6 and 12 hr, 45- to 60-bar results are lower than the high-pressure values (Table 8; Figure 5). Third, pyrolysis under hydrous conditions always increases VR above the values obtained under nonhydrous conditions (Table 8; Figure 6). This increase in VR under hydrous conditions is consistent with the findings of Behar et al. (2003) who observed that the VR of lignite samples pyrolyzed

under hydrous conditions was on average 0.2%  $R_o$  higher than when the lignites were pyrolyzed under nonhydrous conditions. The reason for this increase in VR under hydrous conditions is uncertain but might be caused by increased hydrocarbon yield that enhances structural reorganization (aromatization) of the vitrinite, thereby increasing the reflectance.

Fourth, and most significantly, high liquid or supercritical water (450–500 bar) pressure retards VR at 350 to 420°C, the VR values at 390 to 500 bar are lower than the values obtained under low-pressure hydrous (60–320 bar) conditions (Table 8; Figure 6). The 380°C values for 12 hr do not follow this trend possibly because of the change in appearance produced by pyrolysis and low abundances of vitrinite in the original source kerogen. The case of retardation of VR under water pressure is supported by the results obtained by the pyrolysis of two high-volatile coals (0.7%  $R_o$ ) with high vitrinite contents at 350°C under 500 bar, which showed that the VR was always reduced relative to the coals pyrolyzed under low-pressure hydrous conditions (Ugana, 2007). The lower VR values under 450 to 500 bar pressure are probably related to the retardation of hydrocarbon generation in the same samples. The retention of volatiles (both hydrocarbon and nonhydrocarbon) in the kerogens pyrolyzed under 450- to 500-bar pressure as observed in the retardation of hydrocarbon generation in these samples prevents reorganization of the structure required to produce the polycyclic aromatic molecules that account for the higher reflectance in samples in the oil and gas windows (Carr, 1999).

Seewald and Eglinton (1994) and Seewald et al. (2000) investigated the function of aqueous fluids on vitrinite maturation by hydrous pyrolysis. Although pyrolysis using high-pH pore fluids yielded vitrinite with a reflectance of 1.06 to 1.19%  $R_o$ , pyrolysis with low-pH pore fluids gave vitrinite with a reflectance of 1.39%  $R_o$ . Seewald et al. (2000) examined the function of  $H^+$  activity in the evolution of vitrinite maturation during aqueous pyrolysis.  $H^+$  activity is much influenced by the physical state of water (vapor, liquid, supercritical). In addition, other problems with VR being retarded by water pressure exist. Khorsani and Michelsen (1994) found the evidence for the retardation of VR by pressure in geologic basins to be inconclusive and suggested that retardation was caused by reflectance differences produced by variations in both the chemical composition and structural heterogeneity of vitrinite. This issue about chemical differences between different types of vitrinite exists, as does the  $H^+$  activity, and both contribute to variability of the individual values obtained from the different experiments. Overall, the chemical variability and  $H^+$  activity are only secondary effects compared with the overall control exerted by the temperature-pressure-time conditions.

## Implications for Hydrocarbon Generation and Maturation in Geologic Basins

Sealed pyrolysis vessels, such as MSSV, and gold bag and hydrous pyrolysis methods have been widely used to evaluate the hydrocarbon yields and the maturity obtained from source rocks in the laboratory to understand these systems. Clearly, the results generated from the laboratory cannot precisely simulate the processes as in geologic basins because of the necessity of using higher temperatures during short periods to provide the necessary data. The source rocks in geologic basins occur in relatively low temperature (<250°C) high–water pressure (>500 bar) environments, whereas the laboratory pyrolysis work reported in this study involves high-temperature (>350°C), low–water pressure environments. This means that laboratory pyrolysis studies will always favor enhanced hydrocarbon generation and maturation. Although hydrocarbon generation and maturation will still occur in the high-pressured conditions in geologic basins, the rates at which these reactions proceed are slower because of low temperatures when compared with laboratory conditions. As such, the rates at which these reactions proceed cannot be accurately modeled using an Arrhenius kinetic model, which ignores the effects of pressure.

Both thermodynamic and transition state theories, as well as the experimental results reported in this study, show that hydrocarbon generation and maturation are retarded under liquid water and supercritical water pressures. Clearly, either previously published kinetic models for hydrocarbon generation and maturation will have to be modified to include the effects of pressure, or entirely new models need to be written in which the activation energies and preexponential factors are modified by pressure. Another alternative might involve building databases for the activation volumes (see equation 5 in Carr et al., 2009) for the reactions under the range of source rock temperatures and pressures in geologic basins. The use of such pressure-controlled kinetic models will have implications for the predictions of volumes of hydrocarbon generated, timing of hydrocarbon generation, that is, the critical point in the petroleum system model, and the maturity in the deeper parts of the basins being modeled.

One of the effects of including pressure in the kinetic models used to predict hydrocarbon generation and maturation is that for a fixed transformation ratio or maturity, the thermal history used to model these values will have to be increased compared with kinetic models that do not include the effects of pressure. Incorporating the pressure effect into the kinetic models used in basin modeling will enable the models to include the elevated thermal histories predicted by crustal modeling for basin formation, but which are mostly ignored in petroleum system modeling with thermal

calibration using the VR data and the Easy% $R_o$  model of Sweeney and Burnham (1990). This approach results in models with considerable periods of constant heat flow during both subsidence and uplift events in the history of the basin (Carr, 2003; Carr and Scotchman, 2003), although the laws of physics and thermodynamics clearly indicate that such constant thermal histories cannot be correct.

## Effect of Water Phase

The initial concern before conducting these experiments at higher maturity was the effect that supercritical water may have on the experimental results. However, the same result trend was observed under normal and supercritical water. Water initially promoted hydrocarbon generation and source rock maturation under low-pressure hydrous conditions, or low-pressure supercritical water conditions, before pressure retardation occurs. This indicates that the phase change going from liquid water to supercritical water is not significant. Thus, results obtained at lower temperatures (320 and 350°C) should be comparable to those obtained at 380 and 420°C.

## CONCLUSIONS

The hydrocarbon generation yield data presented in this and previous study by Carr et al. (2009) show that hydrocarbon generation is retarded both by liquid and supercritical water at 450 to 500 bar. Maturation as measured by VR is also retarded at high (390–500 bar) pressures. The kinetic models used to model hydrocarbon generation or maturation in geologic basins must be modified to include the effects of pressure, or entirely new models must be developed in which the effects of temperature, pressure, and time can be integrated into the models. The effects of pressure will always increase the temperature required to produce a given transformation ratio.

Whether pressurized water or supercritical water is present does not seem to be a major factor in the rate of hydrocarbon generation from source rocks, although the presence of water at temperatures below 373°C means that most hydrocarbon generation in the source kitchens in geologic basins will involve water instead of supercritical water. However, because of the promotional effects of water on source rock maturation where maximum  $R_o$  is obtained at 150 to 300 bar pressure, the pressure range for observing retardation effects here has only been approximately 200 to 300 bar when conducting experiments close to 500-bar pressure. Much more work is required to investigate the effects of these factors on hydrocarbon generation and maturation, including the use of higher water pressures to extrapolate to the highest basin pressures required in basin modeling.

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Conference conveners Marek Kacewicz (left), Ken Peters (back), and Dave Curry (right) and The Geysers field trip organizer Noelle Schoellkopf.



The Conference Icebreaker reunited many old friends. Wally Dow (left) and Les Magoon (right), co-editors of AAPG Memoir 60 on "The Petroleum System—From Source to Trap" in 1994 share some time with Ken Peters, one of the conference organizers. Les Magoon presented an evening keynote lecture for the meeting on the 'History of the Petroleum System Concept'.