

## The Effect Of Pressure On The Kinetics Of Kerogen Pyrolysis

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### Introduction

The determination of the kinetics of oil generation is usually done in the laboratory using shales of interest and subjecting the material to high temperatures to accelerate the conversion. Kinetics are determined at these high temperatures, low pressures and extrapolated back to the geological conditions believed to exist at the time of generation. The validity of the extrapolation of these rate constants over a wide range of temperatures<sup>1,2</sup> and pressures<sup>2</sup> has recently been studied.

Other authors have addressed the issue of pressure. Teichmuller and Teichmuller<sup>3</sup> have suggested that high pressure retards the coalification process based on field measurements of vitrinite reflectance. Also using vitrinite reflectance measurements from the offshore of northwestern Europe, McTavish developed a correlation quantitatively relating pressure to vitrinite reflectance.<sup>4</sup> More recently, Sajgo et al<sup>5</sup> compressed alginite and lignite into disks and determined the effect of pressure on their thermal alteration. They observed significant retardation at 1 kbar equivalent to about 50°C (i.e., the high pressure case had to be raised 50° to obtain the same extent of conversion). Price and Wenger have performed aqueous pyrolysis experiments on Phosphoria shale and report a similar retardation.<sup>6</sup>

The role of pressure in the generation of hydrocarbons has also been addressed theoretically by Perlovsky and Vinkovetsky<sup>7</sup> who presented a treatment involving an activated volume to suggest that increased pressure will retard the hydrocarbon generation reactions. In another theoretical paper, Neto<sup>8</sup> hypothesized that reactions only occur when reactants are within a critical distance between each other. He predicted a pressure dependence on the kinetics but did not quantify it.

Monthieux et al<sup>9</sup> studied the effect of reactor configuration, water, and pressure in the artificial maturation of coal. He found the effect of pressure (as well as water) to be minimal if the experiments were done in a confined system, with the pressure provided externally.

In an effort to elucidate the role of pressure in oil generation, we have done experiments to quantify the effect of pressure on the kinetics of maturation. Our approach was to quantify the pressure effect by determining an activated volume. We examined two shales: Bakken, a type II marine shale and Monterey, a type IIS

marine shale.

## Experimental/Analytical

The samples to be heated were prepared in small gold tubes (~25mm long x 4mm O.D.) welded at one end before adding sample. Typically, 200 mg of ground shale were loaded into the tubes along with 25 mg sea water. The tubes were then welded shut under an argon atmosphere. The tubes were inserted into a pressure vessel and placed in a furnace. A thermocouple inserted in the end of the pressure vessel measured the temperature of the sample. It had been previously calibrated against a thermocouple inserted down the inside of the vessel. The vessel was then pressurized with argon causing the gold tube to collapse tightly around its contents. Experiments for a given shale were done varying the time, temperature, and pressure to which the sample was subjected. After heating, the samples were removed and the gold tubes punctured. The shale was removed and typically allowed to air dry, removing water and light hydrocarbons. The shale was then extracted using dichloromethane until the extract was visually colorless.

Conversion was defined based on Rock-Eval  $S_2$  data:

$$\text{Conversion} = 1 - (S_2 \text{ (sample)} / S_2 \text{ (raw)})$$

The Rock-Eval parameters for the raw (initial, unheated) sample were also done on rock extracted by the above procedure.

## Results

### Bakken data

The results of a series of runs with the gold tubes at different pressures are shown in Figure 1, plotting  $S_2$  and conversion versus pressure. The line is a quadratic best fit to the data.

In order to quantify the effect of pressure, we needed to put the data on a consistent kinetic basis. We chose to use a distributed, Gaussian activation energy functional form to fit the data. Data at 4000 psi were input to the Lawrence Livermore KINETICS<sup>10</sup> program. Figure 2 shows the fit obtained at 4000 psi allowing the program to optimize A, E, and s. Because we wanted to compare parameters as a function of pressure, the input values for the A factor and the breadth (standard deviation) of the distribution, s, were then fixed and not allowed to vary during subsequent optimizations at different pressures. Hence, we obtained as a function of pressure different activation energies. Figure 3 is a plot at high pressure showing an example of the fit obtained. Also included in Figure 3 is the sensitivity to a change in activation energy of 200 cal/mole. A total of more than 60 runs were made with the Bakken shale.

To quantify the effect of pressure for a reaction with rate constant k, one typically plots  $\ln k$  versus  $PV_a/RT$ , where P is the system pressure, R the universal

gas constant and T is the absolute temperature.<sup>11</sup> The parameter  $V_a$  is the activated volume. It is the pressure analog to the Arrhenius activation energy and for simple or elementary reactions, represents the change in volume of the activated complex relative to the reactants. In more complex systems, as we have, the methodology is still valid but the activated volume is best thought of as a parameter which quantifies the pressure sensitivity of the system.

As we mentioned, we have reduced our kinetic data in the form of a distributed Gaussian activation energy. As the pressure is varied, we expect this distribution to shift, i.e., the center of the activation energy distribution, E, will vary with pressure. Because this activation energy tends to track  $\ln k$ , we can relate E to the activated volume,  $V_a$ :

$$E = P V_a + E_0$$

where E is the center of the activation energy distribution determined from the kinetics program at a given pressure and  $E_0$  is the center of the distribution at very low pressures. Hence, we plot in Figure 4 the determined activation energy as a function of pressure. The solid line is a least squares fit through the Bakken data—the slope yields a value of 32.8 cc/mole for the activated volume of the Bakken.

#### What is conversion?

Conversion in these experiments is based on the  $S_2$  peak in a Rock-Eval analysis after extraction. Hence, material which is very heavy yet soluble in methylene chloride is considered product and removed. This material would tend to increase  $S_2$  if it weren't extracted. We did a series of experiments in which no extraction was done on the samples after reaction. In these experiments, we still define conversion as before, based on  $S_2$ , but now the reacted material contains those molecules (or pieces of kerogen) which have been released from the starting material but are very large, soluble molecules (as well as smaller product molecules which show up as  $S_1$ ). During Rock-Eval, this material will decompose leading to a higher  $S_2$  and hence lower calculated conversion. We constrain the data to have the same activation energy as the extracted case and determine a new A factor. The A factor for the unextracted runs at low pressure is  $7.2 \times 10^{15} \text{ sec}^{-1}$  compared to the extracted case of  $9.5 \times 10^{16} \text{ sec}^{-1}$ .

The effect of pressure for the unextracted case was examined at one high pressure ( $P = 25000 \text{ psi}$ ). Using the aforementioned methodology, we obtained an activated volume of 12.8 cc/mole.

#### Monterey data

To examine the dependence on kerogen type, we measured the pressure dependence of a high sulfur type IIS kerogen, a Monterey formation shale. The experiments were run as described earlier although only 14 runs were done and two

pressures were used. The KINETICS program determined the following parameters:

P = 2000 psi

P = 15000 psi

A =  $7.5 \times 10^{15} \text{ sec}^{-1}$

E = 54376 cal/mole

E = 54866 cal/mole

s = 3.46 %

This led to an activated volume of 22.9 cc/mole as indicated in Figure 4.

## Discussion

The activated volumes obtained in this work range from 13-33 cc/mole. Activated volumes are known for simple elementary free radical reactions, e.g.,  $V_a$  for H-atom abstraction reactions range 10-20 cc/mole. For material as complex as kerogen, the authors are unaware of any measurements of activated volume for decomposition. Typical values for the activation volume in polymerization reactions are in the range - (15-25) cc/mole.<sup>11</sup> Because bonds are forming, the activation volumes are negative meaning the rates accelerate with increasing pressure. The polymerization reactions, however, are similar mechanistically in that they are free radical reactions involving initiation, propagation, and termination. It is reasonable to expect that the pyrolysis of kerogen (essentially a de-polymerization reaction) would have a similar, albeit positive, activation volume because of the similar kinds of reactions occurring. The activated volume we measured for the Bakken was 32.8 cc/mole and 22.8 cc/mole for the Monterey.

From Figure 4 for the Bakken, one can see that a pressure of 20000 psi would cause an activation energy increase of about 1 kcal/mole. If we assume that temperature would not effect the measured activated volume (determined around 300 °C) then it is valid to consider the effect of this on the maturation of kerogen at much lower temperatures. Figure 5 shows the effect a 1 kcal/mole difference between two kerogens would have under maturation conditions. We have taken the heating rate to be 1°/million years and have used the parameters obtained for the Bakken. At 50% conversion there is an offset of 7° between the two generation curves. This temperature offset is about the same as the extrapolation uncertainty from the determination of the high temperature rate constants. Hence the role of pressure is small. Note that Figure 1 indicates a significant change in  $S_2$  as the pressure increases from 2000 to 30000psi. Although  $S_2$ , the amount of pyrolyzed volatiles expelled in Rock-Eval, increases over a factor of 2, the conversion only drops from around 80% to 58%. It is the conversion, not  $S_2$ , which is the important kinetic parameter.  $S_2$  is a measure of what is still left behind unreacted and must be related to the initial or raw value to obtain the conversion.

The results of Sajgo et al and Price and Wenger would suggest an offset in

temperature of more than 35 ° when applied to a similar maturation situation. The discrepancy between these results and ours is disconcerting. We see a relatively minor effect with pressure whereas they see differences amounting to an increase of more than 5000 cal/mole in the activation energy at 15000 psi compared to 2000 psi. Sajgo et al examined lignite, a type III kerogen material whereas we have investigated types II and IIS. Price and Wenger examined the Phosphoria, a type IIS shale. We do not believe kerogen type is the cause of the differences. The reactor configuration used by Sajgo was quite different than our experimental apparatus. However, one set of our experiments was quite similar in configuration to that of Price and Wenger.

We have measured the activated volume for the pyrolysis of two shales. We have done a large number of experiments in different configurations under a range of experimental conditions (in addition to those discussed here). Our results support our belief that pressures below 2 kbar (30000psi) play a minor role in kerogen pyrolysis.

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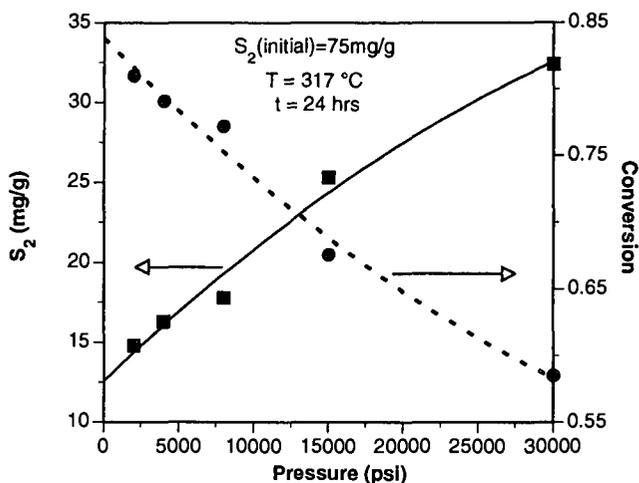


Figure 1. S<sub>2</sub> and conversion as a function of pressure.

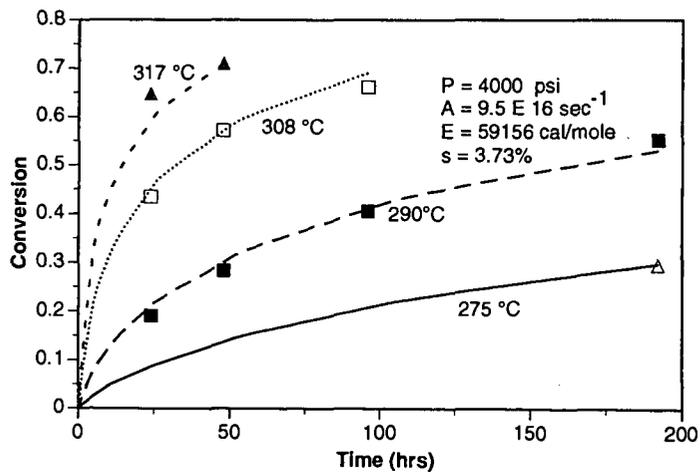
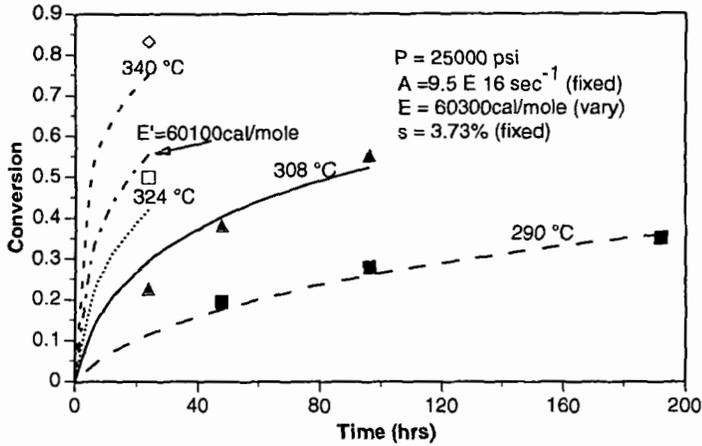
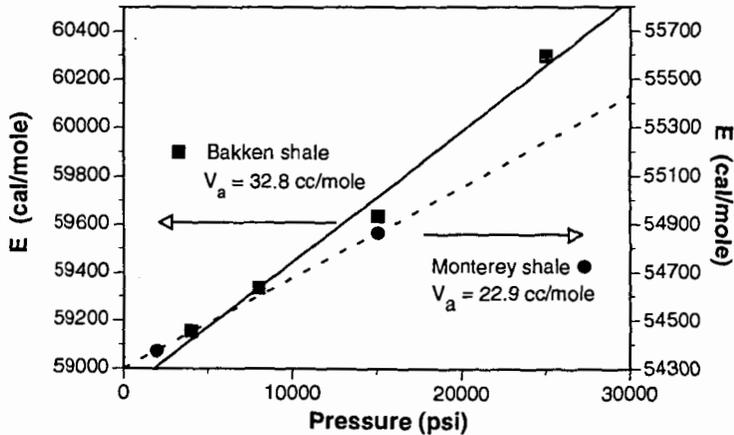


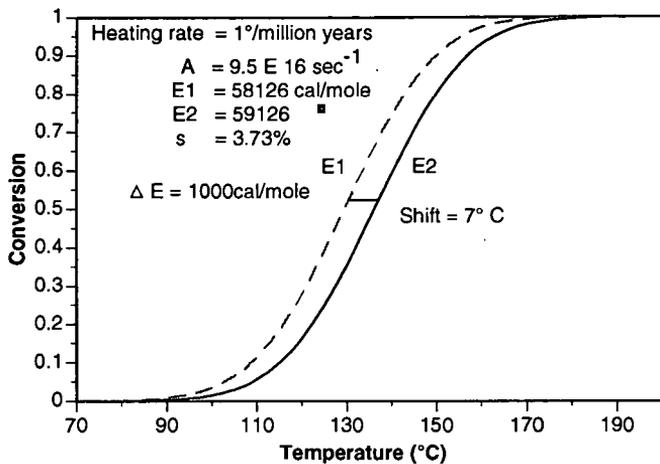
Figure 2. Determination of kinetic parameters using the KINETICS program. Curves are best fit to the experimental points by varying A, E, and s.



**Figure 3.** High pressure example of the fit obtained from the KINETICS program. Curves are fit to data varying only the activation energy. A and s are determined from the 4000 psi run. To get an idea of sensitivity, we also show for the 324°C case, a curve having the center of its activation energy distribution decreased by 200 cal/mole.



**Figure 4.** A plot of the center of the activation energy distribution,  $E$ , as a function of pressure. The temperature ranged from 250-360°C for the Bakken and from 270-300°C for the Monterey.



**Figure 5.** The effect of 1 kcal/mole on the kinetics of oil generation from kerogen.