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Kinetic Models of Hydrocarbon Generation

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OBJECTIVES

We are carrying out an integrated program of laboratory experiments, kinetic modeling, and basin thermal history modeling in order to better understand the natural breakdown of organic matter into oil and gas. Our kinetic models of organic maturation are being used to better understand the coupling of generation, cracking, expulsion, and overpressuring in both the laboratory and geologic setting. Currently we are carrying out chemical experiments and developing more efficient chemical kinetic modeling schemes to obtain a better understanding of expulsion and cracking from lean source rocks and from hydrogen-poor (terrestrial) organic source material. We verify the chemical kinetic models by integrating them with thermal history models of hydrocarbon-producing sediments and comparing predicted and observed characteristics of the hydrocarbon occurrence in a variety of settings. We intend to apply this approach to evaluate the potential for deep gas resources in the Pacific Northwest and in the Louisiana Gulf Coast.

BACKGROUND INFORMATION

It is now widely appreciated that oil and gas generation is governed by chemical kinetics describing the breakdown of more complex organic matter. LLNL has been in the forefront of efforts to develop a quantitative description of this process. Gas can be generated either from cracking of oil that cannot migrate to a cooler reservoir above or from hydrogen-poor kerogens, including coal and residual oil-prone kerogens. Both processes occur at a greater depth (temperature) than oil generation.

Such depths will probably be greater in the convergent margin setting than in the deep basin setting because of the differences in the thermal regime. The precise kinetics of gas generation are less well known than for oil generation. Recent research at LLNL has suggested that oil-prone source rocks, when lean (less than 1%-2% total organic carbon), will be primarily gas producers because there isn't enough driving force to expel the oil before it is cracked to gas. Sediments in convergent margins are generally lean and gas-prone. It has been proposed that a significant amount of the hydrocarbons produced in the onshore and offshore U.S. gulf coast sedimentary basin originated from lean source rocks.

Models of gas generation should also include the calculation of overpressure (pore pressure in excess of hydrostatic) because it is a measurable phenomenon that can be used in calibrating the model, it is an important mechanism for preserving porosity in deeply buried sediments, and it is important to predict for the driller. We have developed a pseudo 1-D model of pore pressure that includes chemical generation kinetics, gas-oil equation-of-state calculations, and a simple compaction model of sediments. We are improving this model by incorporating the effects of thermal expansion of water, mineral transformations, and dehydration and couple these with calculations of the solubility of gas in water.

We use basin modeling (determinations of the time-temperature history of sediments) in combination with the chemistry to determine if, when, and where hydrocarbons are generated as well as to check the chemical models. In general, the level of detail of the basin model is determined by the quantity and quality of stratigraphic, age, structural, and physical property data available for the sediments. At one end of the range of complexity, thermal history modeling can involve using simple estimates of geothermal gradients, either assumed or based on bottom-hole temperatures, that are assumed to be constant through time. At the other end of the range are integrated 2-dimensional fluid-flow and conductive heat flow calculations that require a great deal of knowledge about physical properties and local structure.

PROJECT DESCRIPTION

In order to examine the characteristics of possible deep gas generation in a convergent margin we will develop a preliminary thermal model for sediments beneath the recently-obtained seismic line in Washington and Oregon using the seismic data and any other pertinent data available. Following this, we will make preliminary estimates of oil and gas generation in the convergent margin of the Pacific Northwest using existing organic geochemistry models. To carry out improvements (mentioned above) to PYROL, our general hydrocarbon modeling code, and to PMOD, a code similar to PYROL but with simpler PVT calculations and a highly flexible reaction scheme, we will acquire geochemical data and source rock samples for analysis and laboratory experiments and couple this work with detailed thermal history modeling in an area where a lot of data are available and the geologic history is relatively straightforward. These criteria are best met in areas of the onshore U. S. gulf coast where there has been extensive drilling, exploration, and recovery of hydrocarbons. A wealth of data is available for the

onshore gulf, where some tentative identification of source rocks has been made. This contrasts with the offshore gulf, where nonproprietary data is limited and the identification of source rocks for the hydrocarbons recovered there is a major unresolved problem. We choose the onshore gulf also because, like the convergent margin of the Pacific Northwest, some of the source rocks are thought to be lean and gas prone. With this approach, coupled with improved thermal history modeling of the convergent margin of Washington and Oregon, we can accomplish three major objectives:

(1) refine our ability to characterize the generation of gas at moderate and deep levels in lean and rich source rocks of all types.

(2) apply the refined modeling capabilities to better characterize the gas reservoir potential at deep levels in convergent margins.

(3) attempt to solve major unresolved problems about hydrocarbon generation and migration in the onshore and offshore U.S. gulf coast.

RESULTS

PYROL was originally developed to aid in the understanding of chemical processes involved in retorting of lacustrine oil shale of the Green River Formation. Use of the model in the geologic setting was tested in the Uinta Basin (Sweeney et al., 1987). With recent laboratory and modeling work we have developed preliminary chemical kinetic parameters to model oil and gas generation in the prolific marine kerogen of the La Luna Formation and have tested this approach in the Maracaibo Basin (Sweeney et al., 1990).

Our experimental program is designed to use the simplest and most efficient methods to better understand the chemical processes and to determine the chemical kinetic parameters needed to model generation and cracking of hydrocarbons in conditions relevant to both the laboratory and nature. We continue to develop and improve our modeling capabilities with PYROL and now with PMOD so that they can more accurately predict the characteristics of oil generation, expulsion, and cracking to gas from marine and terrestrial kerogens. To guide further development, these models are continually being tested by comparing predictions with data under laboratory and natural conditions.

Chemical Analyses and Modeling

We have recently completed (Reynolds et al., 1990) a series of pyrolysis - triple quadrupole mass spectrometry (Py - TQMS) experiments, at heating rates of 10°C/min, on 15 different shale source rocks. Included in this group was a terrestrial source rock, referred to as JNUS, with a relatively low TOC of 1.5%. The evolution profile for the C_1-C_4 hydrocarbons is shown in Fig. 1. The T_{max} of each species, shown for each profile, is shown to be highest for methane, CH_4. All of the shale samples produce roughly the same total volumes of C_1-C_4, with CH_4 usually making up the largest volume of the species. The important result for the JNUS sample was that its pyrolysis yields are similar to pyrolysis yields for both the

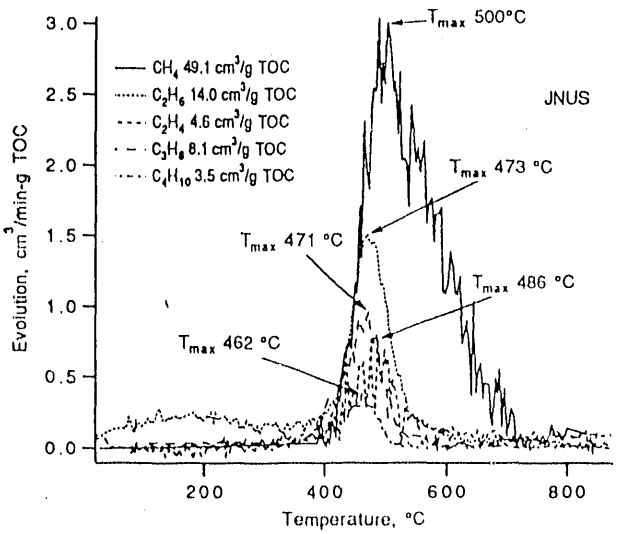

Figure 1. CH_4, C_2H_6, C_3H_8, and C_4H_{10} evolution profiles for a lean terrestrial kerogen at 10°C/min heating rate. T_{max} for each profile is indicated.

Argonne (Burnham et al., 1989) and Brent (Espitalie et al., 1988) coals. These results suggest that TOC of the source rock does not greatly affect the relative yield (normalized to TOC). These methane evolution profiles are also similar to that calculated from vitrinite with our VITRIMAT kinetics (Burnham and Sweeney, 1989).

Although we have not developed a detailed maturation model for Type III kerogens, our VITRIMAT model does represent a starting point. We have tested the ability of VITRIMAT to calculate the increase in T_{max} of methane and total hydrocarbons with increased vitrinite reflectance (%R_o). Recently, Whelan et al. (1990) investigated methane evolution as a function of thermal maturity for two sets of isolated terrigenous kerogens using thermogravimetric Fourier transform infrared spectroscopy (TG-FTIR) techniques. The bold and solid lines in Fig. 2 give the predicted dependence of methane T_{max} on %R_o for geological maturation at 1 °C/m.y. and T_{max} measurement at 30 °C/min. The bold line used the correlation between %R_o and H/C and the solid line used the correlation between %R_o and weight percent C. The lines are parallel but generally lower than the experimental values for two kerogens. The calculated relationship between %R_o and T_{max} of total hydrocarbons (not shown) starts about 10 °C lower but merges with the methane curve when %R_o reaches about 1.5. In contrast, the measured relationship for total hydrocarbons (as corrected for temperature calibration and heating rate) reported by Teichmuller and Durand (1983) falls about 50 °C below our calculated relationship. Although these discrepancies indicate that

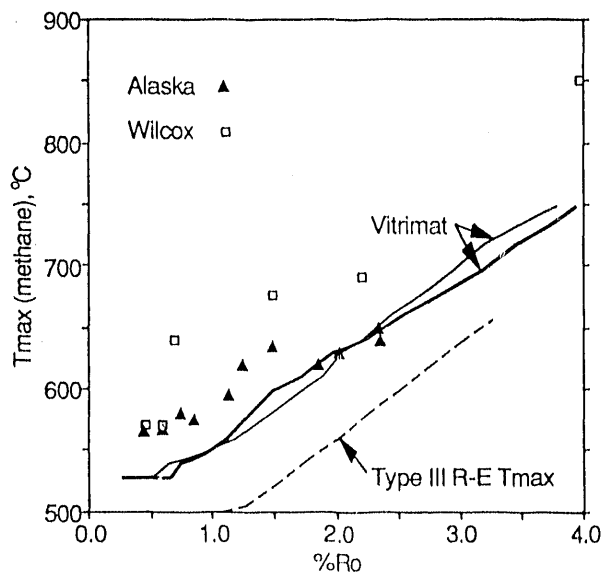

Figure 2. Comparison of calculated and measured T_{max} of methane as a function of vitrinite reflectance. Data from Whelan et al. (1990).

further measurements and model refinement are needed, the qualitative agreement between VITRIMAT and these experiments is encouraging.

Another area of uncertainty in our current modeling is the stability of oil at great depths. In recent work in collaboration with Dr. R.L. Mallinson of the University of Oklahoma Chemical Engineering Department, we constructed a detailed free-radical model of butane cracking and used it to assess the importance of pressure on the cracking rate at geological conditions. Butane is large enough to have many of the chemical properties of oil but small enough to model in a detailed fashion. We used the model to investigate the cracking rate at temperatures from 200°C to 600°C and at pressures from atmospheric to 100 MPa. For a typical geothermal gradient of 25°C/km, a depth of 7 km corresponds to 200°C and about 80 MPa. Model calculations over this wide range of conditions show that the effect of pressure depends strongly on temperature. The overall rate of butane cracking is dramatically increased by elevated pressures at 600°C but shows the opposite behavior at 200°C. Simulations at temperatures of 300-375°C, the lowest at which the reaction is fast enough to be characterized by laboratory experiments, show that pressure can either accelerate or inhibit the reaction rate depending on the precise temperature and extent of reaction.

Applications to Geologic Settings

We used the thermal history model of Armentrout and Suek (1985) for the Mist Field in Oregon to compare predictions of their time-temperature index (TTI) model to those of our preliminary kinetic model for oil and gas generation (Burnham and Sweeney, 1990), which uses the same methane generation kinetics as in VITRIMAT. We assumed Type III (terrestrial) kerogen for the source organic material in the Cowlitz and pre-Cowlitz formations. The preliminary results show that most of the present-day generation of hydrocarbons, especially gas, in the Mist Field is occurring at depths greater than 15000 ft, far below the depths of production in the relatively shallow reservoir sandstones. This result, which is somewhat more quantitative than the previous work, agrees in principle with the suggestion of Amentrout and Suek (1985) that the gas in the field had migrated there from greater depths.

In another preliminary study, we have been trying to develop a thermal history, constrained by vitrinite maturation data and using our vitrinite maturation model (Sweeney and Burnham, 1990), for the Phillips State #1 well in Pierce County, Washington. The vitrinite-depth profile is unusual in that (Fig. 3) there is a sudden increase of about 0.3% R_O in reflectance at a depth of about 2200 m (7200 ft) and near-surface values of reflectance are relatively high, with values greater than 0.45% R_O. The slope of the %R_O data versus depth is relatively low, indicating a relatively low geothermal gradient. The "jumps" in %R_O near the surface and at 2200 m depth can be explained by invoking episodes of uplift and erosion, but inordinately large amounts (up to 5000 m) of missing section are needed at both levels because of the apparently low geothermal gradients. Initial modeling with a one dimensional thermal conduction code that does not account for fluid flow revealed that the

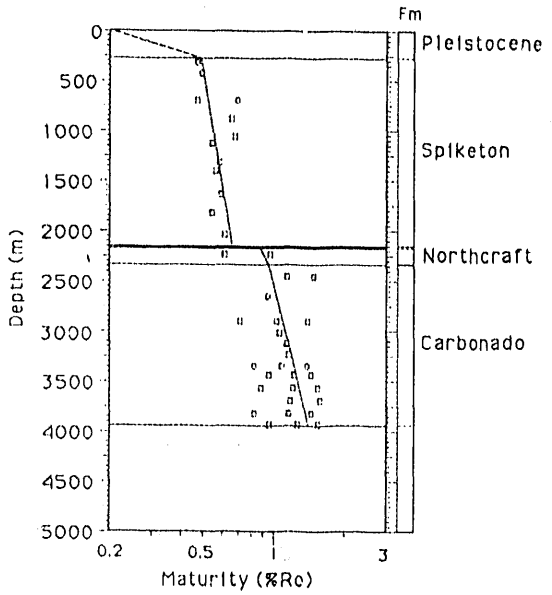

Figure 3. Vitrinite reflectance profile for the Phillips State #1 well, Pierce Co., WA

%Ro profile observed in the Phillips State #1 well, Pierce Co. Washington, could not be satisfactorily simulated with a 1-D conduction model. This is a fundamental problem for the Pacific Northwest area, since the Phillips State #1 vitrinite profile is typical. Recent modeling by Dr. C.Y. Wang - University of California, Berkeley, with a finite element code that incorporates coupled fluid flow and heat conduction - suggests that sudden release of pressure from overpressured argillaceous units lying below rapidly deposited sandy units may allow a sudden, temporary, periodic release of warm fluids into the sediments above, thereby affecting the %Ro values but not the local gradient of %Ro with depth. This preliminary work is being refined to more closely approximate the conditions in the Phillips State #1 well.

We have been using the PYROL code to calculate overpressures developed by the combined effects of sediment compaction and hydrocarbon generation and cracking in the Uinta Basin, Utah. Overpressures have been measured in the Brotherson 1-11B4 well below depths of about 2800 m, continuing to increase to depths of about 3500 m, and leveling off below that. A paradox is that geologic and thermal indicator data suggest that the basin has been uplifted by 1-2 km within the past 10 m.y. and that the sources of overpressuring should have been shut off during that time, allowing the overpressures to dissipate. Our modeling (Fig. 4) suggests that very low permeabilities are needed to account for the overpressures and that it is easier to maintain the observed excess pressure if uplift begins 3 Ma instead of 10 Ma. In our model, the pore pressure reaches a point at which hydrofracturing occurs (which we assume to be when pore pressure reaches 0.8 lithostatic) at about 44 Ma (t = 14 m.y.), during the peak rate of hydrocarbon generation.

FUTURE WORK

We have obtained, from V. Nuccio of the USGS, 20 coal samples from the San Juan Basin that all contain the same original organic matter but range in maturity from 0.4 $\%R_O$ to 1.3 $\%R_O$. These should be excellent samples to carry out a series of pyrolysis experiments for determination of the kinetic parameters for Type III kerogen. The results will be compared to other data, such as that from the Py-TQMS experiments mentioned above, to gain a better understanding of the

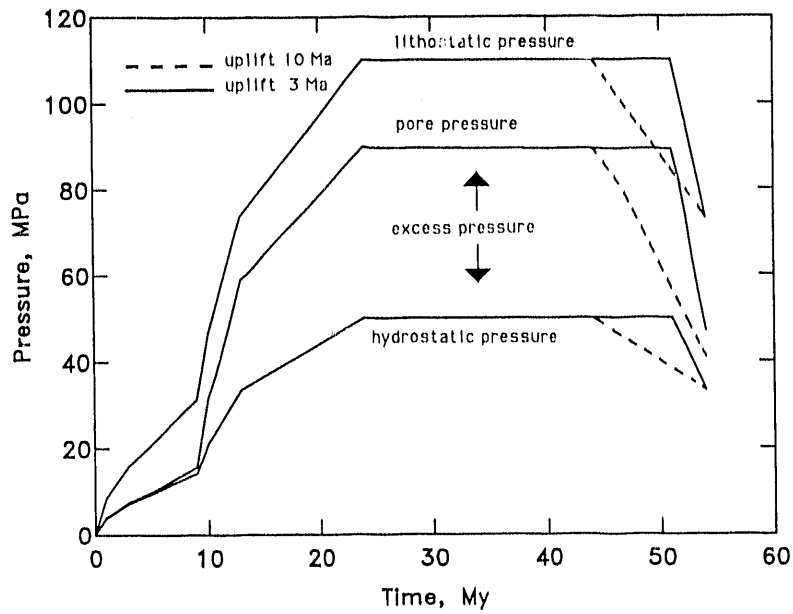

Figure 4. Plot of calculated pressure vs. time for the Brotherson 1-11B4 well, 3400 m depth, Uinta Basin. Note that excess pore pressure at present (right side of plot) is lower when uplift occurs at 10 Ma.

matter of different types and richness.

We will carry out sealed bomb pyrolysis experiments on n-hexadecane to validate the results of the free-radical kinetic calculations concerning the effects of pressure on cracking. We will look at cracking rates as a function of pressure in the temperature range of 300-375°C, which has been determined by the calculations to be the critical range to see the effect.

The finite-element code of C.Y. Wang will be used try investigate the role that fluid flow might play in development of the anomalous vitrinite-depth profiles observed in the Pacific Northwest. We also intend to use the code, at least in the 1-D mode, to evaluate the importance of fluid flow in other settings, such as in deep sediment of the Louisiana onshore Gulf Coast.

The final goal of the project is to couple the best available chemical kinetic cracking model with our best estimate of the thermal history for areas like the Pacific Northwest and the Louisiana Gulf Coast to make quantitative assessments of potential deep gas reserves in these areas. Work in both of these regions will be coordinated with ongoing complementary sedimentary basin assessment work being carried out by the USGS.

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