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ADVANCED CHEMISTRY BASINS MODEL TECHNICAL REPORT

- Covering the period from December 4, 2001 – June 1, 2002
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- Issued June, 2002

EXECUTIVE SUMMARY

The advanced Chemistry Basin Model project has been operative for 36 months. During this period, about half the project tasks are on projected schedule. On average the project is slightly behind schedule (90%). This report has additional progress reports on related projects attached, to show the continuing method development at the program sites.

MILESTONE SCHEDULE/STATUS

The only milestone listed in the project is to have a prototype model operational on a workstation. That milestone was reached during the last year. The project is set to end in June, 2003.

TASK 1: MATURITY INDICATORS

Primary Responsibility	*Current Subtasks*	*Investigator*
Caltech	Develop algorithms	Tang

Summary

The first task is to "Develop a database of additional and better maturity indicators for paleo-heat flow calibration". Fundamental to this development is to perform a series of controlled kinetic experiments on maturity indicator evolution. The goals for the third task year are:

R0 suppression
Study the vitrinite reflectance suppression.

Compare thermal indicators
Compare different thermal indicators and test them under geological conditions.

Finish R0 Database
Establish the complete database for worldwide vitrinite reflectance kinetics.

Performance

For the past 6 months, our research work has focused on (1) kinetic parameters for methylphenanthrene Index (MPI), (2) completing the experimental work on diamondoid pyrolysis for high maturity parameter (oil cracking indicator), (3) kinetic modeling of hydrogen isotope fractionation for normal paraffin (maturity indicator), and (4) effect of biodegradation on biomarker maturity.

1. <u>Kinetic parameters for methylphenanthrene Index (MPI)</u>. Based on large number of geological data, we have developed quantitative MPI maturity kinetics that can be put into the basin modeling software. These new parameters are derived from

several different basins. The results have been correlated with vitrinite reflectance and then calculated based on MPI conversation and distribution activation energy calculations.

2. Kinetic modeling of hydrogen isotope fractionation. A numerical model based on fundamental chemical kinetic principles has been developed to simulate hydrogen and carbon isotope fractionation effects in individual *n*-alkanes during artificial maturation of a crude oil. Combining quantum chemistry computations with laboratory CSIA data, an enthalpy differential ($\Delta\Delta H$) of approximately 300 cal mol^{-1} was calculated for D versus H substitution in *n*-eicosane (n-C$_{20}$). A ? ? H^{o} value of *ca*. 50 cal mol^{-1} was likewise determined for ^{13}C/^{12}C. We have submitted the result to *Geochimica et Cosmochimica Acta.*

3. Complete the experimental work diamondoid pyrolysis. We have completed two heating rate pyrolysis experiment for diamondoid maturity development. The results are to be quantified against field data during the final year of the project. We are currently in dialog with several oil companies for the field data.

4. Effect of biodegradation on biomarker maturity. We have finalized our study of the effect of biodegradation on biomarker maturity. A comprehensive report has been documented and result will be published in *Geochimica et Cosmochimica Acta.*

TASK 2: COMPOSITIONAL MATURATION

Primary Responsibility	*Subtask*	*Investigator*
Caltech	Establish a reaction network	Tang

Summary

The second task is to "Develop maturation models capable of predicting the chemical composition of hydrocarbons produced by a specific kerogen as a function of maturity, heating rate, etc.; assemble a compositional kinetic database of representative kerogens." For the third year, the task list is:

Expand Reaction Network
Add additional generation models with kinetic parameters describing the breakdown of a typical range of kerogens. Analyze additional pyrolysis experiments to derive the needed parameters.

Verify the reaction network
Verify the reaction network and kinetic modeling by extrapolating to geologic conditions

Performance

Our main efforts are to develop kinetics for gas generation and oil cracking (GOR) prediction. For the gas generation, we have now completed experiments on five different types of kerogen for both primary and secondary generation. We have developed a new technology to study both primary and secondary gas generation. Our gas kinetics will include the detail gas information, such as C1, C2, and C3 species. Our kerogen type-specific gas kinetics will be extremely interesting to the future gas exploration and modeling program.

TASK 3: EQUATION OF STATE FLASH CALCULATION

Primary Responsibility	*Subtask*	*Investigator*
Caltech	EOS model	Meulbroek

Summary

The third task of the project is to "Develop a 4 phase equation of state-flash model that can define the physical properties (viscosity, density, etc.) of the products of kerogen maturation, and phase transitions that occur along secondary migration pathways."

Henry's Law Coefficients
Determine Henries Law coefficients controlling maturation product interaction with the aqueous phase.

Verify class divisions
Refine and verify component class divisions

Asphaltenes (cont)
Integrate equation of state and/or other thermodynamic models to predict de-asphaltene processes.

Progress

As reported previously, the "Henry's law coefficient" methodology has been downgraded in priority. Although methodologies have been developed to estimate these coefficients (see Appendix), we have concluded that a mixed-equation of state approach provides sufficient accuracy to calculate phase equilibria, given the uncertainties in composition inherent in the problem. Current efforts consist of expanding the 2-phase perl/COM code described previously into three phases (liquid, vapor, and aqueous). This task should be finished by calendar year's end. As described in the last report, an interface to this code has been built on top of MS Excel. Code release will occur as soon as an installer is completed. Current plans are to release the code and interface as open source over the next reporting period.

An ongoing effort to define appropriate oil component classes is due to be complete at the end of the summer. The method being investigated is to divide the broad oil classes that are defined by the maturation routines (Task 2) along two dimensions. Each 'macro' component will be sub-divided by carbon number. Each resulting component will then be sub-divided by chemical class (saturates, aromatics, etc). The result will be a robust specification method that should markedly improve flash accuracy.

Finally, a collaboration has been established to define the thermodynamic process of deasphaltanization.

Remaining Work

- The physical connections between the basin model and the EOS have been completed (see below). However, testing in a real problem is not yet finished.
- The EOS / Flash model has to incorporate the models produced under Tasks 5 (primary migration). Specifically, asphaltene precipitation models have to be linked.
- Final linking of the maturation fluid specification and the EOS fluid specification.

TASK 4: CONVENTIONAL BASIN MODELING

Primary Responsibility	*Subtask*	*Investigator*
Cornell	2-D model	Cathles
Cornell	add maturity indicators	Cathles

Summary: The fourth task of the project is to "Build a conventional basin model and incorporate new maturity indicators and data bases in a user-friendly way". The third year projects include:

Test code
Incorporate additional kinetic data bases

Performance

A prototype is developed and largely tested. As reported previously, regridding schemes have been dropped as too complex to be useable. All specified model abilities, including compaction, faults, salt, seals are all incorporated as promised. PC prototype is well tested.

Prototype maturity indicators have been incorporated into the model from according to kinetic schemes and trial data supplied by PEER for:

- Vitrinite R_0
- 22S/22S+22R C_{32} Hopane
- 20S/20S+20R C_{29} Sterane
- R28TA/R28TA+aR29MA tri-aromatic Steroid

The vitrinite kinetics can be read from set of kinetic options using a windows file-read navigator. The other maturity indicators have been tested against data we have in the Gulf of Mexico.

Remaining Work:
The following additional maturity indicators need to be added to the model:

- Apatite fisson track

- Illitization
- MPI
- MDI

TASK 5: PRIMARY MIGRATION

Primary Responsibility	*Subtask*	*Investigator*
Cornell	2-D model	Cathles
Cornell	Prototype algorithm	Cathles

Summary

The fifth task of the project is to “Develop an algorithm which combines the volume change and viscosities of the compositional maturation model to predict the chemistry of the hydrocarbons that will be expelled from the kerogen to the secondary migration pathways.”

Chemical Feedback ? Flow
Establish any necessary feedback from chemical to finite difference flow model.

Performance

A prototype primary migration model was build as “scratchpad” in the PC prototype DOE Basin Model early in the project. Independently, Yuling Zhang has been working on a C++ version that is integrated to maturation models and the EOS code (for properties such as viscosity). Asphaltene precipitation will be incorporated in this code based on a colloid precipitation model.

The primary migration model has yet not been integrated with secondary migration in the PC model. However, incorporation has been included in he code architecture. Plans are to abstract “capacitor-chemical filter” parameters from the scratchpad calculator and modify the timing and chemistry of hydrocarbon delivery to the secondary migration algorithm.

Remaining Work

- Integrate capillary model with EOS physical property models.
- Add asphaltene precipitation.
- Adapt best available rock property model from Revil’s work.
- Abstract simple capacitor (hydrocarbon expulsion delay) and chemical filter parameters.
- Build delay-filter model into PC code.

TASK 6: SECONDARY MIGRATION

Primary Responsibility	*Subtask*	*Investigator*
Cornell	Develop prototype	Cathles

Summary

The sixth task of the project is to "Develop an algorithm that predicts the flow of hydrocarbons along secondary migration pathways, accounts for mixing of miscible hydrocarbon components along the pathway, and calculates the phase fractionation that will occur as the hydrocarbons move upward down the geothermal and fluid pressure gradients in the basin."

Test simulations
Carry out test simulations to refine chemical methods and debug.

Performance

A prototype has been completed and tested of secondary migration both on the PC and on our workstations. The PC version has been tested only for vertical flow, but the workstation version has been tested for 2D and 2D flow (into faults, through holes in salt, etc.). The model implements a two-pass algorithm: it first matures the solid hydrocarbon phases, and then migrates and matures the mobile hydrocarbon phases. Solid precipitation from the mobile phases is allowed and accounted for in mass balance calculations. Mass balance on all hydrocarbon phases in 100% accurate. Application has been made in offshore Louisiana, and interesting publishable results obtained.

Hydrocarbon phase separation (flashing) to oil and gas has not yet been tested, however we have successfully integrated EOS code and flash capabilities into the PC prototype. Flash calculations and gas washing will be modeled as a third pass. Volume changes associated with phase separation will propel gas at greater velocities than oil, and the relative motion will "wash" the oil chemically.

A critical need is the proper definition of oil components from the macro-components of the maturation-migration model. This is needed to carry out the flash calculations.

A critical need for testing and evaluation is to incorporate the kinetic databases for the various kerogen classes as soon as possible.

Remaining Work

- Implement non-vertical flow on PC prototype.
- Add flash calculations and gas washing.
- Incorporate database for kerogen maturation (5 kerogens from each of 3 kerogen classes).
- Write manual.

TASK 7: INTEGRATION ON PC

Primary Responsibility	*Subtask*	*Investigator*
Geogroup	connect external code	Manhardt

Summary

The final task for the project is to "Integrate the above components into a functional model implemented on a PC or low cost workstation."

port to PC

- Complete transfer from workstation to PC environment
- Establish umbrella shell.

Performance

Prototype is completed, but not all parts are present.

Remaining Work

- Simplify the models and the interface.
- Spin off installable code that can be delivered to the public domain.
- Write manuals of software operation.

Overall Status and Plans

This task is on schedule. We are aiming at delivering a compiled code, with source code available upon request. Because of the DLL integration, only compiled code can be made available over the net. Given the tight schedules for the other tasks, and the limited personnel funded for this project, this task should be considered very tight.

CONCLUSION

The overall project is producing good results, and has kept to scheduled tasks. Although the overall scheduling has slipped, the strong showing during the initial stages of the project (achieving results well ahead of schedule) has allowed the project to remain on schedule.

Appendix A

FIRST PRINCIPLE PREDICTIONS OF VLE PHASE DIAGRAMS
(ACTIVITY COEFFICIENT MODELS FOR QUANTUM MECHANICS)

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The Wilson and UNIQUAC equations are two of the primary models used to calculate the activity coefficients. For these two models the required parameters are thought to have significant physical meaning. New computational methods to estimate these parameters, and thus to predict vapor-liquid equilibrium phase diagrams from first principles, are presented. This study focuses on the computation of the interaction parameters necessary for the activity coefficient models. Cohesive energy density Molecular Dynamics simulations were used to describe the liquid phase, and quantum calculations, at the LMP2 level, were used to calculate the binary interaction energies. Previous studies have used gas phase molecular mechanics cluster simulations and have proven successful for polar/polar mixtures where coulomb terms dominate the energetics. We tackled the broader problem, mixtures of all types of polarity. We find that linear averages of pairwise interaction energies are inappropriate. Boltzmann weighted averages are more sound and provide better parameters. Unscaled, the Boltzman averaged energies calculated from the quantum calculations do not give the appropriate phase diagrams with the UNIQUAC model. When the energies are scaled by a factor of $2/z$, where z is a variable coordination number, the correct shape of the phase diagram is predicted for most systems. The Wilson model frequently predicts the correct shape of the phase diagram without any modification. With slight modifications, the Wilson model can accurately predict the compositions and pressures of many binary systems. The systems studied, and successfully modeled, include polar/polar, nonpolar/nonpolar and polar/nonpolar pairs.