PMod2 Version 1.xx for Windows XP/Vista/7/8/10

A Computer Program to
Calculate a Network of Pyrolysis Reactions
for a Specified Thermal History

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ABSTRACT

PMod2 is a copyrighted computer program for simulating pyrolysis reactions for a specified thermal history. The chemical reaction mechanism is defined by the user and, within limits, can be as simple or complex as desired. PMod2 can simulate (1) a closed system in which fluid products can undergo further reactions, (2) an open system in which fluid products are immediately expelled without further reactions, or (3) an expulsion system based on the Pepper/Corvi sorption model. This program is a useful tool for determining kinetic parameters from a variety of pyrolysis experiments. It is also useful in predicting pyrolysis results for prescribed thermal histories. In addition, PMod2 can do a Rock-Eval simulation at specified times during the main pyrolysis calculation.

INTRODUCTION

A comprehensive computer model, PMOD, was developed by Braun and Burnham[1] for simulating oil generation, cracking, and other chemical reactions occurring during the pyrolysis of petroleum source rocks, as well as compaction of the source rock and expulsion of a water phase and a single hydrocarbon fluid phase. The expulsion is done by either a simple, excess-volume model using constant densities for the fluid species or by a more rigorous, pressure-driven model using a modified Redlich-Kwong-Soave equation of state. The primary focus of PMOD is the prediction of the composition and timing of oil expulsion at geologic heating rates. Some features of the program are also very useful in interpreting laboratory pyrolysis experiments and deriving kinetic parameters for the chemical reactions. PMOD was originally a proprietary computer program available only to industrial sponsors of the petroleum geochemistry work at the Lawrence Livermore National Laboratory and to government contractors of the United States. It is now available, for a fee, from Energy Science and Technology Software Center, P. O. Box 1020, Oak Ridge, TN 37831.

The present work was undertaken to develop a similar, but less comprehensive, computer model with a PC user interface to enable an easier use of the program. The resulting model, PMod2, has only chemical reaction capabilities at this time, but that is sufficient for interpreting many laboratory pyrolysis experiments and for extrapolating to geologic thermal histories. Fluid pressure is not calculated or used in any of the calculations. Fluid expulsion is treated more simply than in PMOD. PMod2 can use (1) a closed system in which fluid products can undergo further reactions, (2) an open system in which expellable fluid products

are immediately expelled without further reactions, or (3) an expulsion system based on the Pepper/Corvi sorption model with continuing reactions until the fluids are expelled.

CHEMICAL REACTION MECHANISMS

PMod2 can handle diverse types of chemical reaction models. The choice of which model to use, out of the many possible, depends on both the preference of the user and the detail of chemical compositional information desired for a particular purpose. With respect to petroleum geochemistry, for example, the following questions may dictate the complexity of the chemical reactions needed: Will the gas contain separate species for methane and wet gas components? Will the oil contain different fractions and, if so, will they be based on chemical-type properties, boiling-point properties, or both? Table 1 shows examples of different types of chemical reaction mechanisms that can be used singly or in combination in PMod2 to build up more complicated mechanisms for the complete reaction network required to interpret a given set of pyrolysis experiments. Reactions having more than one reactant (e.g., synthesis-type reactions) have not yet been implemented in PMod2.

Table 1. Examples of reaction mechanisms that can be modeled with PMod2.

Parallel Mechanism:	Simple Example:
Precursor 1 → product type 1	heavy oil potential → heavy oil
Precursor 2 → product type 2	light oil potential → light oil
Precursor 3 → product type 3	gas potential → gas
Serial Mechanism:	Simple Example:
starting material → primary products	kerogen → oil + gas + residue
primary products → secondary products	oil → gas + residue
secondary products → tertiary products	residue → gas + inert carbon
Competing Pathways:	Simple Example:
starting material → intermediate	kerogen → bitumen
↓ ↓	↓ ↓
products	oil + gas + residue

All reactions are assumed to be independent of pressure and their temperature dependence is described by the Arrhenius equation:

$$k = A\, e^{-E/RT}$$

The rate of a reaction is expressed as a first-order or n^{th}-order function of the concentration of the reactant, W_i. For a first-order reaction:

$$\partial W_i / \partial t = -k\, W_i$$

For an n^{th}-order reaction:

$$\partial (W_i / W_o) / \partial t = -k\, (W_i / W_o)^n$$

or

$$\partial W_i / \partial t = -k\, W_o\, (W_i / W_o)^n$$

where W_o is the concentration of initial total organic carbon.

This formulation for an n^{th}-order reaction is strictly accurate only when W_o is the initial concentration of W_i. For a reactant species that has an initial concentration of zero (such as a species that is both generated and pyrolyzed in the reaction network), this n^{th}-order formulation is only an approximation and should be used with caution. Furthermore, an n^{th}-order reaction should be used only with a single activation energy, although the user is not prevented from using it with a distribution of activation energies.

The partial derivatives and the specified mass stoichiometry coefficients for the reactions are then used to formulate the complete derivative for each solid and fluid species remaining in the system or expelled from the system. The complete set of ordinary differential equations is numerically integrated by LSODE, the Livermore Solver for Ordinary Differential Equations[2]. The equations explicitly observe only mass balance, but judicious choice of the stoichiometry coefficients for all reactions can, at least approximately, satisfy elemental balance.

PMod2 can also simulate Rock Eval analysis of the remaining material at specific times during the main pyrolysis calculation. Either a rigorous or an approximate Rock Eval calculation can be done, as explained in more detail in Appendix A.

PROGRAM EXECUTION

The primary commands used in the program execution are discussed below. They permit the user to define the pyrolysis conditions, run the calculation, and examine the results. Each command is disabled until sufficient information has been supplied to invoke it.

Filename: Select drive, directory, and control file for storing I/O files. If the selected filename has already been used for a previous run, PMod2 permits the input files to be used or revised for the present run. The files used by PMod2 are defined in Appendix B. These are written by PMod2 and should not be modified by the user outside of the program. The nomenclature and file structures are similar to those used in PMOD.

Input: Enter input data for the chemical reactions, pyrolysis conditions, thermal history, and miscellaneous controls. In each case, the data may be optionally read from a previously made file.

Chemical: One or more chemical reactions can be defined in terms of the species names given in Appendix C. The choice of what species to use to describe a reaction is critical only to the extent that the species designated as fluids are assumed to be expellable and extractable, while the species designated as solids are assumed to be unexpellable and unextractable. Future versions of PMod2 may permit gradations of expellability and extractability ranging from one to zero for the oil species.

Mass balance for the each reaction is required. In addition, the user should formulate meaningful reactions to try to achieve at least an approximate elemental balance. For each reaction, rate parameters must be supplied, in terms of a single frequency factor and a discrete distribution of activation energies. The reaction scheme can range from a simple one

consisting of one or two reactions to a complex one consisting of up to 26 reactions with each reaction having up to 25 energies. Some examples of reactions schemes that may be useful in modeling pyrolysis experiments are shown in Appendix D. After the desired reactions have been entered, the species that are to constitute the initial, organic-carbon-containing material must be selected and the relative amounts of each specified. Usually, these will be the kerogen species, although for an oil cracking experiment they will be the initial oil species. Note that only the relative amounts of the initial species are needed here. The absolute amounts are calculated from the total organic carbon (TOC) supplied in the next section.

Physical: The initial mass fraction of total organic carbon is specified here. Secondly, the user can select an open or closed pyrolysis system. Future versions may implement the more complex compaction/expulsion systems used in PMOD. Finally, the use of unextracted or extracted material for the Rock Eval simulations can be selected.

Thermal: The thermal history is defined by supplying a list of times (starting with zero and increasing monotonically) and the desired temperature and either depth or pressure at each time. PMod2 assumes a linear change between consecutive time points. Up to 50 time points are permitted and consecutive times cannot be equal. In this version, the depth or pressure entry is not used in any of the calculations, but may be used in future versions.

Miscellaneous: Options for writing the output text file and the output binary file are given. The binary file can be used later for making an Excel file of the results and should contain enough points to give the desired resolution in Excel plots. In addition, a choice of calculating Tmax at each point in the output binary file is made. As discussed in Appendix A, the Tmax calculation is time-intensive and should only be used when necessary. Finally, the error tolerances for the optimization calculations are specified. Usually tolerances of 1.E-09 for the main calculation and 1.E-12 for the Tmax calculation are adequate.

Calculate: Once the data input has been completed, the pyrolysis calculation can be started. This is done in a DOS console window by a Fortran program PYROSOLV. Occasionally, because of improper input data, PYROSOLV may fail to run correctly and control may never be returned to PMod2. In this case you are advised to exit the PMod2 calculation by clicking the “Exit” button. Then restart PMod2 with the same "filename" files and carefully recheck all input data. After a successful calculation, the results can then be examined in several ways, as discussed next.

Display: This command displays the output text file containing selected results of the PMod2 calculation. In general, however, a better method of examining the results is to create and display an Excel file of selected results.

Excel: An Excel file of selected results from the PMod2 calculation can be created and displayed. Excel plots can be made from that file. Some or all of the following items can be included in the Excel file:

1. All species variables (KER1, KER2, …, HO1, HO2, …, CHY, CHX, CH4,… etc.)
2. All expelled species (i.e., a fluid species variable preceded by an X, as XCH4)
3. Selected items listed in Appendix E

REFERENCES

1) Braun, R. L. and Burnham, A. K. (1992) PMOD: a flexible model of oil and gas generation, cracking, and expulsion. Org. Geochem. **19**, 161-172.

2) Hindmarsh, A. C. (1980) LSODE and LSODI: two new initial value ordinary differential equation solvers. *A.C.M. SIGNUM Newsletter* **15**, 10-11.

Appendix A: Rock Eval simulation

PMod2 can simulate Rock Eval analysis of the remaining material at specific times during a run. The user must be cautioned that TOC and Rock Eval results calculated by PMod2 are reported in terms of mass of **remaining** rock, not mass of initial, unreacted rock. This may run counter to desired units, but the calculations were done this way to more realistically simulate the Rock Eval results for partially matured source rocks.

Either a rigorous or an approximate Rock Eval calculation can be done. A rigorous Rock Eval simulation is always done for the text PRN file output, but it is done for output to the binary PLT file only when a Tmax calculation is specified for the PLT file. To account for serial reaction effects, the rigorous simulation is done by numerically integrating the rate equations. This is a time-intensive calculation, since it is tantamount to doing a separate, full PMod2 run within the main run each time the rigorous Rock Eval output is wanted. When no Tmax calculation is specified for the PLT file, only the quicker, approximate Rock Eval calculation is done for output to the PLT file.

In a rigorous Rock Eval simulation, the remaining material is heated from 300 to 625 C at 25 C/min and the rates and integrals of hydrocarbon evolution are calculated. From this, S1, S2, and Tmax are obtained. S1 consists of the volatile oil present and S2 consists of the potential for oil and hydrocarbon gas from the solid organic matter.

In an approximate Rock Eval calculation, S1 again consists of the volatile oil present, but S2 is only estimated from the stoichiometry coefficients of the reaction network without a detailed integration of the reaction rates. We exclude contributions to S2 from any residual species (e.g., RESC), since without a detailed rate calculation the extent of pyrolysis of the residual is unknown. Furthermore, no estimate is made for TMAX.

When possible, several Rock Eval diagnostics are calculated from S1, S2, TOM, and their derivatives. When unextracted material is specified for the Rock Eval calculation,

oil and gas potential: $OGP = S2/TOM$

production index: $PI = S1/(S1 + S2)$

expulsion efficiency: $PEE = (S2o - S2 + S1o - S1) / (S2o - S2 + S1o)$

In the above equations, TOM is the total organic matter at the start of the Rock Eval calculation and the subscript “o” refers to zero time. When extracted material is specified for the Rock Eval calculation,

oil and gas potential: $OGP = S2 / TOMIOM$,

where TOMIOM is the solid organic matter, assuming that all oil species are extractable. In this case, no estimates are made for PI or PEE

Appendix B: Files used by PMod2

The following files are used for PMod2 input and output, where '`filename`' is the base name supplied by the user:

`'filename'.con`	Control file of commands for PMod2
`'filename'.prn`	Output text file of selected results of calculation
`'filename'.plt`	Output binary file of detailed results of calculation
`'filename'.kem`	Input file of chemical reaction parameters
`'filename'.fiz`	Input file of physical properties and initial TOC
`'filename'.his`	Input file of thermal history
`'filename'.mis`	Input file of miscellaneous parameters

The following files are used in post-processing calculations to make graphs and to make additional text files of user-selected results from the detailed output binary file:

`'filename'.pyp`	Control file of commands for making a graph
`'filename'.pyt`	Control file of commands for making a text file
`'filename'.txt`	Text file of user-selected results from output binary file

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Appendix C: Species names* permitted for internal use in PMod2

Solid organic matter (unexpellable and unextractable);

KER1	KER2	KER3	KER4	KER5	KER6	KER7	KER8
COKE1	COKE2	COKE3	COKE4	COKE5			

Oil species (expellable:optional and extractable);

HO1	HO2	HO3	MO1	MO2	MO3
LO1	LO2	LO3	NA1	NA2	NA3

Gas species

CHY	CHX	CH4	H2	N2
CO2	CO	H2S	NH3	H2O

*****Alternative names may be assigned to these species for external use (e.g., in a user's plotting program). The alternative names must not contain any spaces.

Appendix D: Examples of chemical reaction schemes

Kerogen pyrolysis and oil cracking can be treated by a variety of simple-to-complex models. A separate set of rate parameters, including a discrete distribution of activation energies, can be given for each reaction. Mass stoichiometry coefficients must also be supplied for reactions having more than one product. This can sometimes be avoided by an initial partitioning of the reactant and using two or more separate reactions for the reactant parts.

Model A: One kerogen precursor, one oil species, one gas species, one residual species.

1. KER1 → MO1 + CHX + RESC
2. MO1 → CHX + RESC

In this model a single species is used for kerogen. Oil and gas will be generated with the same rate parameters. Reaction stoichiometry must be supplied for the kerogen pyrolysis as well as for the oil cracking reaction.

Model B: Two kerogen precursors, one oil species, one gas species, one residual species.

1. KER1 → MO1
2. KER2 → CHX
3. MO1 → CHX + RESC

In Model B the initial kerogen is partitioned into two kerogen species, one generating oil and one generating gas at a different rate (if desired). Reaction stoichiometry must be supplied only for the oil cracking reaction. This model is easily extended to more oil and gas species, by initially partitioning the kerogen into additional species and including more cracking reactions for the other oil species and even for the hydrocarbon gas. An alternative way of treating several oil and gas species is shown in the next model.

Model C: One kerogen precursor, two oil species, two gas species, four residual species.

1. KER1 → HO1 + LO1 + CHX + CH4 + KER2
2. HO1 → LO1 + CHX + CH4 + KER3
3. LO1 → CHX + CH4 + KER4
4. CHX → CH4 + KER5
5. KER2 → CHX + CH4 + KER3
6. KER3 → CHX + CH4 + KER4
7. KER4 → CH4 + KER5

In Model C a single species, KER1, is again used for the initial kerogen. Each reaction generates oil products (HO1, LO1) and/or gas products (CHX, CH4), as well as a solid organic residue (KER2, KER3, KER4, or KER5). The differences among the residual species is presumably the hydrogen composition, although PMod2 cannot explicitly take that into account.

Appendix E: Additional items included in output files

TEMP	Temperature, ^{o}C
PRES	Pressure, MPa
VITR	Vitrinite reflectance, Easy%Ro
KER	Reactive kerogen within rock
KER9	Unreactive kerogen within rock
OIL	Sum of all oil species within rock
GAS	Sum of all gas species within rock
XOIL	Sum of all oil species expelled from rock
XGAS	Sum of all gas species expelled from rock

Appendix F: Rock Eval items included in output files

TOM	Total organic matter, including unexpelled oil (g organic matter / g rock)
TOMIOM	Total organic matter, excluding unexpelled oil (g organic matter / g rock)
S1	Rock Eval parameter [mg oil / g rock]
S2	Rock Eval parameter [(mg oil + HC gas) / g rock]
OGP	Oil and Gas Potential [(mg oil + HC gas) / g TOM]
PI	Production index [S1 / (S1 + S2)]
PEE	Petroleum expulsion efficiency [S2o - S2 + S1o - S1) / (S2o - S2 + S1o)]
Tmax	Calculated at 25 C/min