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7-16152

DOE/METC-86/4024
(DE86001066)

Identification of Data Gaps Found During the Development of a Zero-Order Model for a Fluidized-Bed Retort/Combustion Process

Technical Note

By
J.R. Ammer

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January 1986

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
MORGANTOWN ENERGY TECHNOLOGY CENTER
MORGANTOWN, WEST VIRGINIA

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January 1986

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EXECUTIVE SUMMARY

This technical note (TN) reports on the development of a zero-order ASPEN (Advanced System for Process Engineering) model for the fluidized-bed retort/combustion of an eastern oil shale. The objective of the work described was to identify data needs and to create a structure for future, more definitive models.

New Albany shale was the initial reference eastern shale at the Department of Energy (DOE)/Morgantown Energy Technology Center (METC). A literature search on this shale was conducted to find the physical property data required for the ASPEN model. This TN discusses the types of missing or incomplete data, the process being modeled, and how process variables are affected by varying input parameters. The TN also presents recommendations for increasing the reliability of the simulation.

1.0 INTRODUCTION

DOE/METC has initiated a long-range, in-house systems-analysis research program for oil shale. Systems analysis will be used to identify potential process improvements in the retorting of oil shale that could lead to enhanced operability, improved process economics, or that could mitigate environmental impacts. Systems models are intended eventually to describe the entire shale operation from mining and solids handling to retorting/combustion and spent shale disposal. In this systems analysis program, DOE/METC will simulate a number of oil shale process configurations for both eastern and western shales. The ASPEN code will be the primary simulation tool in this effort.

Fluidized-bed processing of shale offers a flexibility in retorting conditions that far exceeds those available with packed-bed retorting approaches. The advantages of the fluidized-bed process for retorting oil shale are as follows:

- A high in-bed heat transfer rate results in very rapid heating of cold, raw shale particles to retorting temperature.
- A large solids throughput is possible because the good mixing characteristics help create a high degree of bed uniformity and because the raw shale feedstock can attain the desired retorting temperature with a relatively short residence time in the retort.
- Operational flexibility exists because the fluidized-bed can handle a wide variety of oil shale types and particle sizes. For example, the shale fines generated by mining and processing operations tend to block the gas passages of packed-bed retorts but do not hinder fluidized-bed retorts.
- Secondary hydrocarbon cracking in the retort is minimized because of the short residence time of the gaseous retorted hydrocarbon products within the shale matrix.
- Process economics may be improved because the fluidized-bed retort is inherently smaller than packed-bed retorts for a given throughput and offers the potential for modular construction.

2.0 BACKGROUND

The Department of Chemical Engineering and Energy Laboratory at the Massachusetts Institute of Technology (MIT) modeled an oil shale fluidized-bed retorting process using the ASPEN process simulator (Fong and others 1981). Their modeling objectives were to determine the thermal balance of the overall process, solids recirculation ratio, effect of carbonate decomposition on heat requirements, and the sensitivity of various operating parameters on the performance of the process. This work was performed for a western oil shale, as a starting point from which to study eastern oil shale. A past study conducted at DOE/METC checked the reproducibility of the MIT model on the METC VAX system and began research on eastern oil shale.

Because eastern and western oil shales differ in many respects, a significant effort was needed to convert the existing MIT fluidized-bed ASPEN model to an oil shale fluidized-bed retort/combustion process model for eastern oil shale. Although the overall process flow sheet and ASPEN unit operation blocks were

very similar, the numeric values for the physical property input data for eastern shale were quite different from those values given for western shale. Some of the major differences affecting model results are the kerogen composition, which influences the stoichiometric yield of oil, gas, and residue (spent shale), and the composition of minerals and their related physical properties. These data are needed to create a realistic simulation of an eastern oil shale fluidized-bed retort/combustion process.

3.0 DISCUSSION

The following sections discuss the ASPEN flow sheet language and assumptions, the input parameters required by ASPEN, methods to improve the data, and a parametric study. Figure 1 shows a schematic diagram of the fluidized-bed oil shale retorting process modeled in this study. The block diagram for the ASPEN simulation flow sheet is shown in Figure 2. The major difference between the actual fluidized-bed process (Figure 1) and the simulation is that the section before the retort, which incorporates the crusher, cyclone, and preheater, is not modeled. In the ASPEN simulation, preheated shale is mixed with the recycled gas and recycled shale prior to entering the retort. The input language for the base case simulation is given in Appendix A.

3.1 ASPEN FLOW SHEET DESCRIPTION AND ASSUMPTIONS

- Feed Mixer Block

The feed stream of raw shale, FDSHALE, entered MIX1, an ASPEN mixer block, at 400°F where it is combined with the fluidizing gas, FLDZGAS, and the recycled hot shale, REC SHALE. The raw shale was modeled as three substreams: kerogen, minerals, and moisture. Two ultimate analyses of the raw shale, with a few assumptions, was averaged to determine the percent of kerogen, minerals, and moisture (Phillips and others 1984; Battelle 1984). All of the nitrogen, 75 percent of the oxygen, and 15 percent of the sulfur was assumed to be organic; all of the organic components (C, H, O, N, and S) was assumed to compose the kerogen. A mineralogical X-ray diffraction analysis was performed by the West Virginia University Geology Department on a sample of New Albany shale to determine the composition of the minerals. (See Table 1.) A FORTRAN block, FEEDRATE, was used to set the flow rate of the three substreams, kerogen, minerals, and moisture, such that the total flow of FDSHALE is 1,000 lb/hr. (A FORTRAN block is a section of FORTRAN statements generally used to set process variables in a once-through calculation.) SET-FLDZGAS, another FORTRAN block, was used to calculate the flow rate of the fluidizing gas, based on the flow rate of the feed stream and recycled shale stream. The composition of the fluidizing gas stream was assumed to be similar in composition to that of the product gas. Table 2 shows the composition of the fluidizing gas.

- Retort

The new (combined) stream, PRYOLIN, from MIX1 entered the retort block (RETORT1), that was modeled using an ASPEN stoichiometric reactor, or RSTOIC block. Here, a predetermined stoichiometric equation causes all the kerogen to pyrolyze to form oil, gases, and residue. An analysis of the oil product from the retort was obtained from data on a fluidized-bed retort of an eastern oil shale (Jones and others 1984). Using data from

FIGURE 1. SCHEMATIC DIAGRAM OF THE FLUIDIZED-BED OIL SHALE RETORTING PROCESS

FIGURE 2. BLOCK DIAGRAM OF THE ASPEN SIMULATION OF AN OIL SHALE RETORTING PROCESS

TABLE 1. MINERALOGICAL X-RAY DIFFRACTION ANALYSIS
FOR KENTUCKY NEW ALBANY SHALE

COMPONENT	WEIGHT %
Illite ¹	70.8
Quartz (SiO ₂)	15.3
Kaolinite (Al ₂ Si ₂ O ₇ ·2H ₂ O)	7.2
Pyrite (FeS ₂)	3.6
Calcium-Sulfate (CaSO ₄)	1.1
Szomolnokite (FeSO ₄ ·H ₂ O)	1.0
K-Feldspar (KAlSi ₃ O ₈)	0.6
Calcite (CaCO ₃)	0.2
Dolomite (CaMg(CO ₃) ₂)/Ankerite Ca(Mg _{0.67} Fe _{0.33})(CO ₃) ₂	<u>0.2</u>
Total	100.0

¹Formula not given.

TABLE 2. COMPOSITION OF
FLUIDIZING GAS

COMPONENT	MOLE %
CH ₄	28
C ₂ H ₆	14
C ₃ H ₈	10
C ₄ H ₁₀	7
CO	7
H ₂	<u>34</u>
Total	100

studies conducted on fluidized-bed retorting of eastern oil shale (Carter and Taulbee 1984; Ahmed, Parker, and Archer 1982), which gave the percent of raw carbon released into the oil and gas (and therefore, the remaining percent of carbon would be left in the residue, the amount of oil that would be formed by pyrolyzing 100 lbs of oil shale was calculated. The gas composition was assumed as were the mole fractions for each component. Then, assuming the pyrolysis of 100 lbs. of kerogen, the amount of gas was calculated, for each component and overall. The remaining amount of each element, C, H, O, N, and S, was assumed to remain in the residue. Appendix B shows the calculation of the stoichiometric equation and Table 5 is a list of reactants and products formed during the retort. The only reaction involving minerals that was assumed to occur in the retort was the endothermic reaction of pyrite and water. A 35-percent reaction extent of pyrite was obtained from Phillips and others (1984):

A design specification, RECYCLE, forced the temperature in the retort outlet stream, PYROLOUT, to 950°F by varying the percentage of recycled spent shale, RECSHALE. (A design specification varies one process variable in an iterative manner until another variable attains a specified value.) The enthalpy model used to calculate the enthalpy of kerogen was developed by MIT (Fong and others 1981). This model uses Dulong's correlation and the ultimate analysis of kerogen to calculate the heat of combustion and the heat of formation, which are then used to calculate the enthalpy of kerogen.

- Post-Retort Cyclone

To simplify the simulation, and since data on shale particle size were not available, the cyclone in the process flow sheet was modeled using an ASPEN separator block, SSPLIT. This block separates the vapor phase oil and gases from the spent shale, SPTSHALE. A 100-percent separation of solids is assumed. The gaseous product stream, PRODUCT, is sent for gas cleaning and liquid upgrading; however, these processes were not modeled in this study. The spent shale stream, SPTSHALE, is recycled to the combustor.

- Combustor

Three ASPEN reactor blocks (BURNIT, COMBUST2, and COMBUST3) and a mixer block were used to model the combustor. BURNIT is an insert, i.e., a file consisting of standard ASPEN input statements that can be called like a FORTRAN subroutine. BURNIT is used to burn a nonconventional component such as spent shale into CO₂, H₂O, H₂S, and ash using air as the oxidant. In the simulation, spent shale, SPTSHALE, enters a mixer block where it is combined with air. This stream then enters the first reactor block, BURNIT, where the carbon in the spent shale is combusted. The stoichiometric coefficients for combusting the shale are based on the ultimate analysis of the spent shale. The reaction extent of the carbon combusted and excess amount of oxygen are user-specified. Ninety percent of the carbon was assumed to react, and 10-percent excess oxygen was specified.

Block COMBUST2 models the endothermic decomposition of dolomite into calcite, magnesium oxide, and carbon dioxide:

The stoichiometric equation and reaction extent are user-specified. The reaction extent is 100 percent. Physical property data for the minerals were obtained from the JANAF Thermochemical Tables (National Bureau of Standards 1971), from data collected by Los Alamos National Laboratory for an ASPEN oil shale properties data base, and from a publication on thermodynamic properties of minerals and related substances (Robie 1978). Data for the mineral muscovite were used for the mineral illite since the two minerals have similar molecular structures.

Block COMBUST3 models the endothermic decomposition of calcite into calcium oxide and carbon dioxide:

The percentage of calcite that reacts, which is determined by thermodynamic equilibrium, depends upon the temperature of the calcite and the partial pressure of carbon dioxide in the surrounding gas. The decomposition of dolomite and calcite are the only two reactions involving minerals that are assumed to occur in the combustor. A design specification, PQFLASH, forces this block to be adiabatic.

- Post-Combustor Cyclone

CYCLONE2, which models a cyclone using an ASPEN separator block, separates the flue gases, FLUEGAS, from the hot shale stream, BDSHALE. A 100-percent separation of solids is assumed.

- Recycle Splitter

In the block SPLITTER, a percentage of the hot spent shale, BDSHALE, is recycled to MIX1. The remaining shale, DSPSHALE, is disposed of. A design specification, RCYCLE, varies the amount of recycled shale, RECYCLE, until the temperature in the outlet stream from RETORT1 is 950°F.

3.2 IMPROVING THE DATA USED

The simulation could be improved by decreasing the number of assumptions made or improving the data as indicated:

- The organic percentages of oxygen, nitrogen, and sulfur in the raw shale were assumed from the ultimate analysis. The exact amounts of nitrogen and sulfur can be determined by performing an ultimate analysis on the demineralized organic matter of the oil shale. Subtracting carbon, hydrogen, sulphur, and nitrogen from the total raw shale would give the amount of organic oxygen.

- A mineralogical analysis was conducted on only one sample of New Albany shale. This analysis should be conducted on numerous samples so that the analysis is more representative of the oil shale.
- The three sources used for physical property data of the minerals were in good agreement; however, a problem still remains on what data to use for illite. Both Los Alamos National Laboratory and the Institute for Mining and Minerals Research (IMMR) at the University of Kentucky agree that muscovite is very similar to illite and that using the physical property data of muscovite for illite is reasonable. This assumption should be further investigated.
- The insert BURNIT, which is used to burn a nonconventional component such as spent shale, forms the products CO_2 , H_2O , H_2S , and ash. This insert would better represent the combustion of a nonconventional component in an oxidizing environment by having SO_2 and NO_x as products instead of H_2S .
- A list of minerals given in the mineralogical analysis of the raw shale, obtained from the West Virginia University Geology Department, was used as an initial set of constituents to describe the shale composition. This analysis was limited to nine major minerals, whose physical properties were found in the literature. As a first approximation, it was felt that this number of components was sufficient for the ASPEN model to generate gross material and energy balances around each of the process units. However, a more complete breakdown of the mineral composition of the shale would lead to future refinements to the simulation.
- The heat of reaction for kerogen decomposition as calculated by the MIT model showed a major discrepancy with values found in the literature (Carley 1975) for western oil shale. Therefore, this model should be checked against experimental data on eastern oil shale to determine its validity. Other ASPEN enthalpy calculation methodologies are available that may be more accurate; however, these were not used in this simulation.

3.3 UNKNOWN ASPEN INPUT PARAMETERS

The fluidized-bed retort/combustor process model will provide the framework to build a more rigorous and predictive model as additional information is obtained. However, for this model and future models to be representative of the fluidized-bed process, important input parameters must be well defined. Table 3 shows the list of input parameters for the ASPEN input language given in Appendix A. This section describes the parameters or models with unknown or uncertain values. The known input parameters and their sources, along with assumptions that were made, are discussed in Section 3.1 of this report.

The oil composition and oil physical properties must be better defined. In the MIT study, the product oil from the retort was represented as cyclohexene (C_6H_{10}). The heat of formation from the ASPEN data banks was overridden by calculating the heat of formation using Dulong's correlation and the ultimate analysis of the oil. This study represented the product oil from the retort as n-dodecane ($\text{C}_{12}\text{H}_{26}$). A better way to represent the oil may be to break down the product oil into cuts (pseudo components) based on the boiling point curve. The physical properties of the cuts can then be determined by using their

molecular weight, boiling point, and specific gravity. This model for oil shale liquids is currently being developed by Los Alamos National Laboratory.

TABLE 3. INPUT PARAMETERS/MODELS FOR EASTERN OIL SHALE
RETORT/COMBUSTION PROCESS

KNOWN	UNKNOWN
Ultimate Analysis of Raw Oil Shale (See Appendix B)	Product Oil Composition
Mineralogic Analysis of Raw Oil Shale (See Table 1)	Product Oil Physical Properties
Physical Properties for Each Mineral in This Simulation	Gas Composition
<ul style="list-style-type: none"> • Heat of Formation • Gibbs Free Energy of Formation • Heat Capacity Parameters • Molar Volume Parameters 	Ultimate Analysis of Retorted Oil Shale Ultimate Analysis of Oil Shale After Combustion Mineralogical Analysis of Oil Shale After Retort Mineralogical Analysis of Oil Shale After Combustion
Enthalpy Model for Kerogen	Stoichiometry and Extent of Mineral Reactions
Fluidizing Gas Composition	Stoichiometry and Extent of Kerogen Pyrolysis
Combustion Model (Insert)	Pyrolysis Model Hydrodynamic Model

Ultimate analyses and mineralogical analyses should be performed on the oil shale after retorting and after combustion. The stoichiometric equation for the pyrolysis of kerogen was based on many assumptions. (See Appendix B.) The ultimate analyses of the oil shale after retorting and after combustion can be used to strengthen the calculations of the stoichiometric equation by reducing the number of assumptions made. Since little is known of the reactions that take place between the minerals, mineralogical analyses may help determine the stoichiometric equations for these reactions.

All of the above data are determined at specific retorting/combustion conditions. If the oil shale fluidized-bed retort/combustion process model is to be used to

its fullest extent, the model must be predictive. This gives the modeler the opportunity to do a complete parametric study, varying input data and operating conditions, without making gross assumptions or needing experiments conducted at the set of conditions being modeled.

The best way to model the fluidized-bed retort/combustion process would be to use mechanistic models to predict the thermodynamic and kinetics of reactions and the hydrodynamics of the fluidized-bed system. Lawrence Livermore National Laboratory recently developed a pyrolysis model for the Mahogany Zone Green River oil shale (Burnham and Braun 1984). However, this model is based on experimentation for a range of pyrolysis conditions for the Green River oil shale and is not applicable for an eastern oil shale. It is in this direction that DOE/METC should set its goals, i.e., a predictive model of a fluidized-bed retort/combustion process for eastern shale. Two other models worth mentioning were also developed by Lawrence Livermore: RETORT (Braun 1981) and STBERSIM (Diaz and Braun 1984). RETORT simulates the chemicophysical processes involved in the vertical retorting of a rubblized bed of oil shale. STBERSIM simulates an aboveground oil shale retorting process that utilizes two reactors (a staged, fluidized-bed retort, and a lift-pipe combustor).

3.4 PARAMETRIC STUDY

Using the data and assumptions made in the previous sections, a parametric study determined the effects of input parameters on process variables such as combustor temperature and recycle ratio. Parameters included in this study were the heat capacity of illite, the stoichiometric equation, the heat of formation of the product oil from the retort, and the amount of carbon in the residue that was combusted. The retort temperature in these sensitivity studies was fixed at 950°F. Table 4 shows these parameters and the combustor temperature and recycle ratio for each run and the following text discusses the variations utilized.

TABLE 4. PARAMETRIC STUDY

PARAMETER VARIED	COMBUSTOR TEMPERATURE (°F)	ΔT FROM BASE CASE	RECYCLE RATIO ¹
Base Case	2,236		.246
Illite Heat Capacity	2,485	+249	.185
Stoichiometric Equation (Kerogen Pyrolysis)	2,034	-202	.315
Percent Carbon Combusted	2,046	-190	.286
Heat of Formation of Raw Oil	2,120	-116	.452
All Parameters (Excluding Illite Heat Capacity)	1,749	-487	.710

$$^1\text{Recycle Ratio} = \frac{\text{mass flow rate of recycled burned shale}}{\text{mass flow rate of raw feed shale}}$$

Base Case Run -- The base case ASPEN input language is given in Appendix A. A design specification was set around the retort to force the temperature in the outlet stream to 950°F by varying the recycle ratio of hot spent shale to raw feed shale. Another design specification around the combustor varied the temperature of the combustor to force the combustor to adiabatic conditions. The temperature of the combustor for the base case run was 2,236°F with a recycle ratio of 0.234. Since this temperature was higher than expected, the following parametric studies were conducted to determine the cause.

Heat Capacity -- The heat capacity for the major mineral component, illite (Table 1), had the greatest effect on combustor temperature. Communication with Los Alamos and IMMR helped obtain data on muscovite which is similar in molecular structure to illite. Mobil, who did an analysis for IMMR, identified the major clay mineral in a New Albany shale as muscovite. When the heat capacity data of illite from a past study at METC was used (the base case used the physical property data of muscovite), the combustor temperature increased by 249°F. This was expected since the heat capacity for illite is less than that of muscovite. (See Figure 3.) This was approximately a 35 percent reduction in heat capacity from the base case. Therefore, less heat is absorbed when the heat capacity of illite is used and the combustor temperature increases.

Stoichiometric Equation -- The stoichiometric equation in the retort was varied to determine its effect on combustor temperature. The base case run had a ratio of 43 percent of pounds-of-residue-formed per pound-of-kerogen-consumed. The new stoichiometric equation used for the parametric study had a ratio of 34 percent. For 1,000 lbs of raw shale feed (the feed stream rate used in this simulation), 90 lbs less residue was formed than in the base case. The net effect was a reduction in temperature of 202°F and an increase in the recycle ratio. This shows the need to accurately define the pyrolysis reactions that take place in the retort.

Percent Carbon Combusted -- As less carbon is burned, the combustor temperature decreases. Therefore, it is necessary to determine the percent of carbon that is burned. Lowering the carbon from 90 percent (base case) to 70 percent reduced the combustor temperature by 190°F. By performing ultimate analyses on the oil shale before and after combustion, this percentage could be accurately defined.

Heat of Formation of Raw Oil -- This parameter was very interesting because, although increasing the heat of formation had the smallest effect on the combustor temperature (a 116°F reduction), it had the greatest effect on the recycle ratio. (See Table 4.) By increasing the heat of formation of the oil, more heat was required in the retort because more heat was needed to pyrolyze the shale.

All Parameters Varied -- All the parameters in the sensitivity study were varied (except the heat capacity of illite for which the heat capacity of muscovite was used) to determine the result this would have on reducing the abnormally high combustor temperature. The total effect was a reduction in the combustor temperature from 2,236°F to 1,749°F, and an increase in the recycle ratio from 0.246 to 0.71. This shows that wide variation in the base case simulation results can be caused by changing only a few parameters. Therefore, the importance of obtaining data to accurately define input parameters must be stressed.

FIGURE 3. COMPARISON OF THE HEAT CAPACITY OF MUSCOVITE AND ILLITE

4.0 CONCLUSIONS AND RECOMMENDATIONS

The effort to develop a model of a fluidized-bed retort/combustion process showed that accurate data are very important. By varying assumptions made on some input variables, the process variables differed significantly, showing that for any set of assumptions, different results could be obtained. However, the results of this type of simulation would not be significant because too many assumptions were made. Therefore, it is necessary to stress the importance of obtaining accurate data to reduce the number of assumptions in order to increase the level of confidence in the simulation results. By implementing the recommendations in Sections 3.2 and 3.3, a more realistic and accurate model of a fluidized-bed retort/combustion process for an eastern oil shale will be developed.

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APPENDIX A: ASPEN INPUT FILE FOR THE BASE CASE

```

NEW
;
;      CODES FOR VAX/VMS
;
;:MAIL (ON A BATCH JOB; DO YOU WANT TO BE NOTIFIED Y/N) = Y
;:CODE (PROJECT) = C9
;:OLDID = WORG
;:NEWID = WORG
;:BUILD A NEW INPUT TRANSLATOR (Y/N) = N
;:PDF LENGTH (400 MAX) = 120
;:QUEUE ( B:BATCH 2, S:SYS$BATCH, H:HIGH SPEED ) = B
;:SUBMIT (Y IF IMMEDIATE, N IF SPECIFYING TIME) = N
;:KEY = INSERT      ARG = INSERTLIB
;:END VAX/VMS PROCS
;
;
;      ASPEN MODEL FOR RETORT PROCESS OF EASTERN OIL SHALE
;
TITLE 'EASTERN OIL SHALE RETORTING AND COMBUSTION SIMULATION'
;
DESCRIPTION 'FLOWSHEET FOR EASTERN OIL SHALE RETORT AND COMBUSTOR;
            KEROGEN PYROLYSIS IN THE RETORT; CARBON COMBUSTION
            AND MINERAL REACTIONS IN THE COMBUSTOR'
;
IN-UNITS ENG
OUT-UNITS ENG
;
HISTORY MSG-LEVEL  PROPERTIES=2
;
;      THE FOLLOWING IS A LIST OF ALL COMPONENTS AND THEIR CHEMICAL FORMULA
;
COMPONENTS      N2          NITROGEN/
                O2          OXYGEN/
                H2          HYDROGEN/
                SO2         SULFUR-DIOXIDE/
                H2O         WATER/
                H2S         HYDROGEN-SULFIDE/
                NH3         AMMONIA/
                CO          CARBON-MONOXIDE/
                CO2         CARBON-DIOXIDE/
                CH4         METHANE/
                C2H6        ETHANE/
                C3H8        PROPANE/
                C4H10       ISOBUTANE/
                OIL         N-DODECANE/ ; ASSUMED FORMULA FOR OIL C12H26
                KEROGEN/
                RESIDUE/
                ILLITE/      ; MINERALS
                SILICA/

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KAOLINITE/
 IRONOX/
 ALUMINA/
 IRON/
 HEMATITE/
 CALCITE/
 PYRITE/
 DOLOMITE/
 FELDSPAR/
 CAO/
 MGO/
 CASO4 CALCIUM-SULFATE/
 SZOMOL

;
 ATTR-COMPS KEROGEN GENANAL/
 RESIDUE PROXANAL ULTANAL SULFANAL

;
 ; THE FOLLOWING SPECIFIES THE MODELS TO BE USED TO CALCULATE
 ; THE SPECIFIED PROPERTIES FOR THE LISTED COMPONENTS

;
 NC-PROPS KEROGEN ENTHALPY ENTHLUSR 1/
 DENSITY DNSTYGEN
 NC-PROPS RESIDUE ENTHALPY HCJ1BOIE/
 DENSITY DCHARIGT

;
 PROPERTIES SYSOPO GLOBAL

;
 PROP-DATA
 COMP-LIST KEROGEN
 CVAL DENGEM 1 1 9.45E+02 ;
 CVAL ENTUA 1 1 78.3/ 2 8.9/ 3 6.4/ 4 2.6/ 5 3.8

;
 ; COMP-LIST OIL
 ; CVAL DHFORM 1 1 6.966E+07

;
 ; THE FOLLOWING IS A LIST OF THE MOLECULAR WEIGHT, STANDARD ENTHALPY OF
 ; FORMATION AT 298.15K AND THE STANDARD FREE ENERGY OF FORMATION AT 298.15K
 ; FOR THE MINERALS

;
 PROP-DATA
 PROP-LIST MW / DHSFRM / DGSFRM
 PVAL DOLOMITE 184.42 / -2.327861D9 / -2.153945D9
 PVAL CALCITE 100.09 / -1.207473D9 / -1.127830D9
 PVAL SILICA 60.06 / -0.911466D9 / -0.857051D9
 PVAL CAO 56.08 / -0.634719D9 / -0.603569D9
 PVAL MGO 40.32 / -0.601643D9 / -0.569344D9
 PVAL FELDSPAR 278.33 / -3.801614D9 / -3.577244D9
 PVAL ILLITE 398.31 / -5.976740D9 / -5.600671D9
 PVAL ALUMINA 101.96 / -1.676395D9 / -1.582937D9
 PVAL IRON 55.85 / 0 / 0
 PVAL IRONOX 71.85 / -2.722257D8 / -2.516141D8
 ; PVAL HEMATITE 159.69 / -8.260556D8 / -7.440739D8
 ; PVAL MAGNETITE 231.54 / -1.121644D9 / -1.018192D9

PVAL PYRITE 119.98 / -1.782000D8 / -1.669000D9
PVAL KAOLINITE 258.16 / -4.119600D9 / -3.799700D9
PVAL MAGNESITE 84.32 / -1.105000D9 / -1.029000D9
PVAL SZOMOL 170.00 / -8.000000D8 / -1.500000D9 ; ASSUMED

; THE FOLLOWING IS A LIST OF THE PURE SOLID HEAT CAPACITY
; PARAMETERS AND THE TEMPERATURE RANGE FOR THE MINERALS
;

PROP-LIST	CPSP01									
PVAL DOLOMITE	1.562932D5	8.055403D1			0 0	-2.160389D9	298	2000		
PVAL CALCITE	1.045863D5	2.193883D1			0 0	-2.595816D9	298	1200		
PVAL SILICA	0.439447D5	3.884094D1			0 0	-0.968407D9	298	1200		
PVAL CAO	0.396554D5	0.452174D1			0 0	-0.695009D9	298	2888		
PVAL MGO	0.490149D5	0.314429D1			0 0	-1.144671D9	273	3098		
PVAL FELDSPAR	2.672434D5	5.400972D1			0 0	-7.138494D9	273	3000		
PVAL ILLITE	2.34247D5	4.563D2	-1.738D-1	-2.06010D4	2.85415D5	298	1250			
PVAL ALUMINA	9.544080D4	3.755260D1			0 0	-2.187185D9	298	1500		
PVAL IRON	1.728818D4	2.670668D1			0 0		298	1500		
PVAL IRONOX	4.45597D4	1.9999D1	-0.51128D-2	-7.5278D2	-6.66D0	298	1400			
; PVAL HEMATITE	3.985288D4	2.536965D2	-1.36898D-1	0		0	298	1400		
; PVAL MAGNETITE										
PVAL PYRITE	4.257162D4	5.592496D1			0 0		298	1500		
PVAL KAOLINITE	2.461400D5	3.812006D1			0 0		298	1500		
; PVAL MAGNESITE	4.491932D4	1.395501D2	-5.319513D-2	0	-5.644941D8	200	1000			
PVAL SZOMOL	6.000000D4	7.400000D1			0 0		273	1500	; ASSUMED	

; THE FOLLOWING IS A LIST OF THE PURE SOLID MOLAR VOLUME
; PARAMETERS FOR THE MINERALS
;

PROP-LIST	VSPOLY							
PVAL DOLOMITE	6.435D-2	0	0	0	0	0	0	2D3
PVAL CALCITE	3.694D-2	0	0	0	0	0	0	2D3
PVAL SILICA	2.269D-2	0	0	0	0	0	0	2D3
PVAL CAO	1.676D-2	0	0	0	0	0	0	2D3
PVAL MGO	1.125D-2	0	0	0	0	0	0	2D3
PVAL FELDSPAR	1.002D-1	0	0	0	0	0	0	2D3
PVAL ILLITE	1.407D-1	0	0	0	0	0	0	2D3
PVAL ALUMINA	2.616D-2	0	0	0	0	0	0	2D3
PVAL IRON	7.109D-3	0	0	0	0	0	0	2D3
PVAL IRONOX	1.200D-2	0	0	0	0	0	0	2D3
PVAL HEMATITE	3.027D-2	0	0	0	0	0	0	2D3
; PVAL MAGNETITE								
PVAL PYRITE	2.401D-2	0	0	0	0	0	0	2D3
PVAL KAOLINITE	8.906D-2	0	0	0	0	0	0	2D3
; PVAL MAGNESITE	2.776D-2	0	0	0	0	0	0	1D3
PVAL SZOMOL	3.500D-2	0	0	0	0	0	0	2D3 ; ASSUMED

FLWSHEET

MIX1	IN=FDSHALE FLDZGAS REC SHALE	OUT=PYROLIN
RETORT1	IN=PYROLIN	OUT=PYROLOUT
CYCLONE1	IN=PYROLOUT	OUT=PRODUCT SPT SHALE
COMBUST2	IN=HOT SHALE	OUT=DOLDECOM
COMBUST3	IN=DOLDECOM	OUT=CALDECOM DUMMY HEAT1
CYCLONE2	IN=CALDECOM	OUT=FLUEGAS BDSHALE
SPLITTER	IN=BDSHALE	OUT=REC SHALE DSP SHALE

;
 DEF-STREAM-CLASS OIL SHALE SUBS=MIXED CISOLID NC
 DEF-STREAMS OIL SHALE ALL/ CONVEN FLDZGAS AIR/ HEAT HEAT1
 ;

;
 ; THE FOLLOWING FORTRAN BLOCK SETS THE TOTAL FLOW OF THE FEED STREAM
 ;

FORTRAN FEEDRATE

```

  DEF FNC SVAR FDSHALE NC      VARIABLE=MASS-FLOW
  DEF FCI SVAR FDSHALE CISOLID VARIABLE=MASS-FLOW
  DEF FMX SVAR FDSHALE MIXED   VARIABLE=MASS-FLOW
F      FANC=15.23
F      FAMX=3.0
F      FACI=1D2-FANC-FAMX
F      TOTAL=1000.
F      FNC=TOTAL*FANC/1D2
F      FCI=TOTAL*FACI/1D2
F      FMX=TOTAL*FAMX/1D2
  EXECUTE BEFORE MIX1

```

;
 STREAM FDSHALE

```

  SUBSTREAM NC TEMP=400. PRES=14.7 MASS-FLOW=1.5D2
  MASS-FRAC KEROGEN 1D0 / RESIDUE 1D-10
  COMP-ATTR KEROGEN GENANAL (100. 0. 0. 0. 0. 0. 0. 0. 0. 0.)
  COMP-ATTR RESIDUE ULTANAL (0.0 79.1 5.5 3.9 0. 2.0 9.6)/
      SULFANAL (0. 0. 2.0)/
      PROXANAL (0. 79.1 20.9 0.)

```

```

  SUBSTREAM CISOLID TEMP=400. PRES=14.7 MASS-FLOW=8.2D2
  MASS-FRAC DOLOMITE 0.002 / CALCITE 0.002 / SILICA 0.153 /
      FELDSPAR 0.006 / ILLITE 0.708 / KAOLINITE 0.072/
      PYRITE 0.036 / CASO4 0.011 / SZOMOL 0.01
  SUBSTREAM MIXED TEMP=400. PRES=14.7
  MASS-FLOW H2O 0.3D2

```

;
 STREAM SPT SHALE

```

  SUBSTREAM NC PRES=14.7 MASS-FLOW=0.5D2
  MASS-FRAC RESIDUE 1D0
  COMP-ATTR RESIDUE ULTANAL (0.0 79.1 5.5 3.9 0. 2.0 9.6)/
      SULFANAL (0. 0. 2.0)/
      PROXANAL (0. 79.1 20.9 0.)
  SUBSTREAM CISOLID PRES=14.7 MASS-FLOW=1.2D7
  MOLE-FRAC CALCITE 0.20/ CAO 0.10/ SILICA 0.30/
      FELDSPAR 0.13/ MGO 0.17 / ILLITE 0.10

```

```

STREAM FLDZGAS
  SUBSTREAM MIXED TEMP=400. PRES=14.7 V=1.0 &
    FLASH-OPTION=1-PHASE MASS-FLOW=2D3
  MOLE-FRAC CO 5.5D-3/ H2 2.6D-2/ CH4 2.1D-2/ C2H6 1.1D-2/
    C3H8 7.6D-3/ C4H10 5.7D-3/
;
;THIS FORTRAN BLOCK CALCULATES THE FLOW RATE OF THE FLUIDIZING GAS BASED ON THE
;FLOW RATE OF THE FEED AND RECYCLED SHALE STREAMS
;
FORTRAN SET-FLDZGAS
  DEF F1 SVAR FLDZGAS MIXED VARIABLE=MOLE-FLOW
  DEF F2 SVAR FDSHALE NC VARIABLE=MASS-FLOW
  DEF F3 SVAR FDSHALE CISOLID VARIABLE=MASS-FLOW
  DEF F4 SVAR REC SHALE NC VARIABLE=MASS-FLOW
  DEF F5 SVAR REC SHALE CISOLID VARIABLE=MASS-FLOW
  DEF T1 SVAR FLDZGAS MIXED VARIABLE=TEMPERATURE
  DEF P1 SVAR FLDZGAS MIXED VARIABLE=PRESSURE
F      W=F2+F3+F4+F5
F      PD=(W/6DO)/0.6/156/30
F      UF=4DO
F      VG=PD*UF*3.6D3
F      VO=(T1+460)*10.73/(P1)
F      V1=VG/VO
F      F1=V1
  EXECUTE BEFORE MIX1
;
STREAM AIR
  SUBSTREAM MIXED TEMP=400. PRES=14.7 V=1.0 &
    MOLE-FLOW=1D3 FLASH-OPTIONS=1-PHASE
  MOLE-FRAC N2 0.79/ O2 0.21
;
;THIS STREAM GIVES INITIAL GUESSES TO ASPEN TO ALLOW IT TO TEAR THE STREAMS
;
STREAM CALDECOM
  SUBSTREAM CISOLID TEMP=2000. PRES=14.7 MASS-FLOW=1D3
  MASS-FRAC CALCITE .01/ SILICA .15/ FELDSPAR .01/ ILLITE .71/
    KAOLINITE .07/ PYRITE .03/ CASO4 .01/ SZOMOL .01
  SUBSTREAM MIXED TEMP=2000. PRES=14.7 MASS-FLOW=1D3
  MASS-FRAC H2O 0.2/ CO2 0.2/ H2S 0.2/ N2 0.2/ O2 0.2
;
BLOCK MIX1 MIXER
  PARAM NPK=1 KPH=1 PRES=14.7
;
BLOCK RETORT1 RSTOIC
  PARAM PRES=14.7 Q=0. NPK=1 KPH=1
;
  STOICH 1 NC KEROGEN -15.23/ RESIDUE 6.4875/ MIXED CO 4.291D-3/ CO2 4.5517D-3/
    H2 1.9873D-2/ CH4 2.1227D-2/ C2H6 1.1325D-2/ C3H8 7.7226D-3/
    C4H10 5.8589D-3/ NH3 4.7048D-3/ H2S 5.8779D-3/ OIL 3.9564D-2
  CONV 1 NC KEROGEN 1DO
;

```



```

STOICH  2 CISOLID PYRITE -1/ MIXED H2O -2/ CISOLID IRONOX 1/
MIXED H2S 2/ O2 0.5
CONV    2 CISOLID PYRITE 0.35
;
BLOCK  CYCLONE1      SSPLIT
  FRAC MIXED PRODUCT 1. / SPTSHALE 0.
  FRAC NC PRODUCT 0. / SPTSHALE 1.
  FRAC CISOLID PRODUCT 0. / SPTSHALE 1.
;
;BLOCK  COMBUST1      RSTOIC
;  PARAM TEMP=1400 PRES=14.7 NPK=1 KPH=1
;  STOICH 1 NC RESIDUE -1D2/ MIXED O2 -8.6132/
;          H2O 1.9000/ CO2 7.4083/ NO2 0.3143/ SO2 0.0156
;  CONV   1 NC RESIDUE 1DO
;  THE ARGUMENTS FOR THS INSERT ARE:
;          %1 - TWO CHARACTER UNIQUE ID FOR THE PROCESS
;          %2 - STREAM ID (MIXEDNC) OF THE FUEL TO BE BURNED
;          %3 - STREAM ID (MIXED) OF THE OXIDANT (AIR) STREAM IN
;  (WARNING: FLOWRATE IS SET BY INSERT, COMPOSITION BY USER)
;          %4 - STREAM ID (MIXEDNC) OF THE PRODUCTS OF COMBUSTION
;          %5 - STREAM ID (HEAT) OF THE HEAT GENERATED
;          %6 - ID ON THE NC COMPONENT TO BE BURNED
;          %7 - TEMPERATURE OF THE POC STREAM (%4)
;          %8 - STOICHIOMETRIC RATION OF O2 TO FUEL
;          %9 - CONVERSION OF FUEL (%6)
;
INSERT AA BURNIT SPTSHALE AIR HOTSHALE Q RESIDUE * 1.1 0.9
;
BLOCK  COMBUST2 RSTOIC
  PARAM PRES=14.7 Q=0. NPK=1 KPH=1
  STOICH 1 CISOLID DOLOMITE -1DO/ CALCITE 1DO/ MGO 1DO/
  MIXED CO2 1DO
  CONV   1 CISOLID DOLOMITE 1DO
;
BLOCK  COMBUST3  REQUIL
  PARAM NR=1 EPS=1D-20 PRES=14.7 Q=0. KODE=2 NPK=1 &
  KPH=1 CONMB=1D-8 RELKEQ=1D-4
  STOI  1  CALCITE -1 1/ CAO 1 1/ CO2 1 0/ DOLOMITE 0 1/ ILLITE 0 1/
  MGO 0 1/ SILICA 0 1/ FELDSPAR 0 1/ KAOLINITE 0 1/ IRONOX 0 1/
  PYRITE 0 1/ CASO4 0 1/ SZOMOL 0 1 ;HEMATITE & MAGNETITE
  FRAC   CISOLID 1DO/ NC 1DO
  BOPT  RESTART=0
;
BLOCK  CYCLONE2      SSPLIT
  FRAC MIXED          FLUEGAS 1./ BDSHALE 0.
  FRAC NC             FLUEGAS 0./ BDSHALE 1.
  FRAC CISOLID        FLUEGAS 0./ BDSHALE 1.
;
BLOCK  SPLITTER      FSPLIT
  FRAC REC SHALE      0.700
  BLOCK-OPTIONS      HMB-RESULTS=2
;

```

```

DES-SPEC PQFLASH
  DEFINE HD STRM-ATTR-VAR STREAM=HEAT1 ATTRIBUTE=HEAT VARIABLE=DUTY
  SPEC HD TO 0.
  TOL-SPEC 1000.
  VARY BVAR COMBUST3 SENTENCE=PARAM VARIABLE=TEMP
  LIMITS 400. 3000.
;
DES-SPEC RCYCLE
  DEFINE T SVAR PYROLOUT MIXED VARIABLE=TEMP
  SPEC T TO 950.
  TOL-SPEC 0.1
  VARY BVAR SPLITTER SENTENCE=FRAC VARIABLE=FRAC ID1=REC SHALE
  LIMITS 0.05 0.90
;
TEAR CALDECOM
REPORT BLOCKS STREAMS FLOWSHEET

```

APPENDIX B: CALCULATIONS FOR STOICHIOMETRY OF NEW ALBANY SHALE

Composition of New Albany Shale:

Product Oil from the Retort:

<u>Analysis</u>	<u>Wt %</u>
Carbon (organic)	11.93
Hydrogen (organic)	1.36
Oxygen (organic)*	.97
Nitrogen (organic)*	.39
Sulfur (organic)*	.58
Minerals	81.77
Moisture	3.00
	<u>100.00</u>

<u>Analysis</u>	<u>Wt%</u>
Carbon	83.2
Hydrogen	9.8
Oxygen	2.0
Nitrogen	1.1
Sulfur	3.9
	<u>100.0</u>

From studies on fluidized-bed retorting:

- 45 to 47 percent raw carbon → oil (this study assumes 47 percent).
- 5 to 10 percent raw carbon → gas (this study assumes 10 percent).
- Remaining 43 percent raw carbon → residue.

For each 100 lbs of raw shale feed:

Carbon in oil = $.47 \times 11.93 = 5.61$ lbs.

Carbon in gas = $.10 \times 11.93 = 1.19$ lbs.

Carbon in residue = $.43 \times 11.93 = 5.13$ lbs.

Using the product oil analysis, if carbon is 83.2 percent by weight, then

$$\text{Total wt. of oil} = 5.61 \text{ lbs carbon} / .832 = 6.74 \text{ lbs oil}$$

Using the product oil analysis, the pounds of C, H, O, N, and S can be obtained for the oil.

A gas composition was assumed as follows:

<u>Compound</u>	<u>Wt%</u>
CH ₄	17.0
C ₂ H ₆	17.0
C ₃ H ₈	17.0
C ₄ H ₁₀	17.0
H ₂	2.0
NH ₃	4.0
H ₂ S	10.0
CO	6.0
CO ₂	10.0
	<u>100.0</u>

*The percentage of oxygen, nitrogen, and sulfur that is organic is assumed.

The weight percentages of C, H, O, N, and S were obtained by using the molecular weights of each component. The total pounds of gas were calculated by:

$$\text{Total weight of gas} = 1.19 / .596 \text{ (wt\% of carbon)} = 2.00 \text{ lbs}$$

The pounds of C, H, O, N, and S were then calculated by using the total pounds of gas and the weight percentages of C, H, O, N, and S in the gas.

The composition of the residue or spent shale was calculated by taking the pounds of C, H, O, N, and S in the oil and gas and subtracting this from the Kerogen analysis.

Organic Residue (Spent Shale) Analysis	<u>Wt%</u>
Carbon	79.1
Hydrogen	5.5
Oxygen	9.6
Nitrogen	3.9
Sulfur	<u>2.0</u>
	100.0

TABLE 5. STOICHIOMETRIC TABLE

Reactant -- 100 lbs Raw Shale		Products		
	Weight	Gas	Weight	Moles
<u>Kerogen</u>				
Organic Carbon	11.93 lbs	CH ₄	.34 lbs	2.1×10^{-2}
Organic Hydrogen	1.36 lbs	C ₂ H ₆	.34 lbs	1.1×10^{-2}
Organic Oxygen	.97 lbs	C ₃ H ₈	.34 lbs	7.7×10^{-3}
Organic Nitrogen	.39 lbs	C ₄ H ₁₀	.34 lbs	5.9×10^{-3}
Organic Sulfur	.58 lbs	H ₂	.04 lbs	2.0×10^{-3}
	15.23 lbs	NH ₃	.08 lbs	4.7×10^{-3}
		H ₂ S	.20 lbs	5.9×10^{-3}
		CO	.12 lbs	4.3×10^{-3}
		CO ₂	.20 lbs	4.6×10^{-3}
			2.00 lbs	
<u>Minerals</u>				
Quartz (SiO ₂)	12.51 lbs			
Illite	57.89 lbs			
Kaolinite (Al ₂ Si ₂ O ₇ ·2H ₂ O)	5.89 lbs			
Calcite (CaCO ₃)	.16 lbs	Oil	6.74 lbs	3.96×10^{-2}
Calcium-Sulfate (CaSO ₄)	.90 lbs			
Pyrite (FeS ₂)	2.94 lbs	Residue	6.49 lbs	
Dolomite (CaMg(CO ₃) ₂)	.16 lbs		15.23 lbs	
Szomolnokite (FeSo ₄ ·H ₂ O)	.82 lbs			
Feldspar (KAlSi ₃ O ₈)	.50 lbs	Minerals	81.77 lbs	
	81.77 lbs			
Moisture	3.00 lbs	Moisture	3.00 lbs	
Total	100.00 lbs			

DOE/METC-86/4024

**Identification of Data Gaps Found During
the Development of a Zero-Order Model for
Fluidized-Bed Retort/Combustion Process**

DOE