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ABSTRACT

Kern River 650°F⁺ residuum (Kern Co, CA) and mixtures of Kern River 650°F⁺ residuum with solids were examined by micropyrolysis at nominal constant heating rates from 1 to 50°C/min. from temperatures of 100 to 700°C to establish evolution behavior, pyrolysate yields, and kinetics of evolution.

The profiles for all samples generally exhibited two regimes of evolution: 1) low temperature (due to distillation), and 2) high temperature (due to cracking and distillation). The pyrolysate yields of the residuum alone and residuum with solids exhibited, with increasing sample size, a broad maximum at 0.005 to 0.010 g of ~ 1000 mg pyrolysate/g residuum (relative to Green River oil shale Fischer Assay yield) as well as shifting of distribution from distillation to cracking regime.

For kinetic parameters, because much of the low temperature evolving data was due to volatilization and not cracking, determinations were limited mostly to the discrete method. The best fits exhibited very similar parameters for all the samples have principal E_{discrete} of 50 to 51 kcal/mol (accounting for ~30% of total energy) and A_{discrete} around 10^{12} to 10^{13} sec⁻¹.

These results indicate the use of heat carriers, such as alumina or dolomite, in pyrolysis processing of heavy oils may effect the overall yields of the pyrolysate, but will probably not effect the pyrolysis cracking rates

INTRODUCTION

Upgrading heavy oils can be approached from two directions -- hydrogen addition or carbon rejection [1]. Hydrogen addition processes are often desirable because of the high liquid yields (over 100% by volume in many processes). However, these processes are costly, requiring expensive reactors because of high temperatures (600 to 850°C) and pressures (1000 to 2000 psi) as well as requiring some type of hydrogen source (usually available at large refineries but not for small producers). Carbon rejection processes are also desirable because of cheaper construction and operating conditions. However, these processes can produce large quantities of very low grade materials (like asphaltenes or coke) which are not always high valued or readily disposable.

We have been examining both hydrogen addition and carbon rejection processes for the upgrading of heavy oils from California. One specific interest is adapting the Hot-Recycle-Solids (HRS) retorting process [2], which was developed for oil shale pyrolysis, to heavy oil upgrading. Figure 1 shows a schematic of the modified process. In the heavy oil case, ceramic balls or mineral solids replace spent shale as the heat transfer medium, and oil is introduced into the system through a spray-nozzle mechanism located at the top of the pyrolyzer. The pyrolyzer is operated at ~ 500°C. As in the case of shale retorting, the liquid product has a very short residence, swept out of the pyrolyzer by N₂ based-pyrolysis gas. During pyrolysis, coke is deposited on the heat carrier. As these solids enter into the pneumatic lift pipe, air is injected to facilitate combustion (and move the solids). Combustion continues as the solids pass through the other combustors. Eventually, the hot solids are recycled into the pyrolyzer, providing energy for the pyrolysis. In the HRS pilot plant, the extra heat is not utilized, but in a commercial unit, this heat would be used for a co-generation facility.

To support the development of heavy oil upgrading in the HRS process (and to possible up scaling) we have been studying the intrinsic pyrolysis behavior of specific heavy oils, such as Kern River crude, as well as possible modification of that behavior by the addition of solids. We have been utilizing the Pyromat II micropyrolyzer, which has been used previously for pyrolysis examination of kerogens [3], shales [4,5], coals [6], tar sands and heavy oils [5,7,8]. Here we re-

port the pyrolysis evolution behavior and cracking kinetics of Kern River 650°F⁺ residuum and Kern River 650°F⁺ residuum mixed with dolomite, alumina, and spent (combusted) oil shale.

EXPERIMENTAL

Sample preparation

The residuum was prepared from a batch (single plate) distillation of a barrel of Kern River crude oil (steam stripped) to a cut point of 650°F (343°C). The alumina ceramic balls were purchased from Schoofs Inc. (Moraga CA) and are α -Al₂O₃ heat treated to corundum. The 1/4 in. diameter alumina balls were coarsely crushed between two stainless steel plates using a hammer, followed by a ceramic plate pulverizer. Checking the particles under the microscope indicated a "granular" looking mixture. The dolomite was purchased from Ward's Natural Science Establishment (Rochester, NY), and sieved to -60 mesh before use. Green River oil shale (AP22) is from the Anvil Points mine and assays to 22 gal/ton. The spent shale was from the HRS retort using AP22 oil shale, run H-14. Only fines were used, which had less than 0.3 wt % carbon.

Residuum Only Samples: Test samples were drawn under a magnifying glass by insertion of a clean microliter syringe needle into a bulk sample. The syringe needle was mounted on a ring-stand for stability. Residuum was inserted into the micropyrolysis crucible under the magnifying glass to facilitate proper location of the test sample in the crucible. 0.010 to 0.020 g quartz wool were placed in crucible after the residuum was loaded.

Residuum/Solids Samples: The residuum and dolomite were weighed directly onto a watch glass then mixed together. To maximize sample homogeneity, each batch was large enough for approximately ten tests. Mixing was done on the watch glass under a microscope with sealed glass capillaries to minimize sample loss or contamination. Aliquots were drawn from the bulk sample under the microscope. The crucible was first loaded with ~ 0.010 g quartz wool. To avoid smearing the sample along the length of the test crucible, the aliquot was transferred from the glass mixing rods under a magnifying glass. Another 0.010 to 0.020 g of quartz wool were loaded into the crucible to keep the sample in place. The mixture appeared to have thixotropic behavior so freshly prepared mixtures were used.

MicroPyrolysis Tests

The Pyromat II micropyrolyzer has been described previously [4]. Samples were pyrolyzed at constant heating rates, using He as the carrier gas. Hydrocarbon evolution was measured by flame ionization detection. Temperature was measured by direct contact of a Type K thermocouple (0.040-in. 304 stainless steel sheath) with the sample. Data were stored and manipulated on a IBM PS/2 Model 70 386 personal computer interfaced with the pyrolysis unit.

Yields: Pyrolysis yield was determined for each sample by comparison to the yield from AP22 oil shale. This yield has been determined from Fischer Assay and Rock-Eval analysis to be 88 mg pyrolysate/g oil shale [9]. For most samples, the yield was determined from a single run at the nominal heating rate of 25°C/min. from 100 - 700°C. Some sample size replication studies were done to give an indication of the precision of test results. The AP22 standard was run at least twice daily, at the beginning and end of tests for the day. When trends in the data were not clearly defined, to assure more accurate yields, the standard was run immediately before and after each sample. With both calibration techniques, the standard values were averaged each day, providing a daily calibration factor. Individual profiles were normalized to total yield, and analyses were performed using Kaleidagraph Graphics software (Synergy Software, Reading PA). The yields measured in this study (~1000 mg/g sample) are far outside the range of the yield of AP22. As a result the values appear somewhat high, and are meant to be semiquantitative.

The Pyromat II pyrolysis profiles of crude oils and residua general exhibit two evolution ranges, assigned previously [8] as being due to distillation of volatile material and a combination of distillation and cracking. Figure 2 shows the two evolution ranges are characterized by maxima around 300 to 400°C and 450 to 500°C at the 50°C/min. heating rate. For purposes of classifying yields into components, these ranges were divided using a minimum point between the two maxima (division point in figure), although this does not deconvolute the peaks. Complete analyses of these ranges require examining the evolution from 100 to 700°C. In source rock and kerogen analyses, the temperature range is generally 250 to 650°F⁺, which partially eliminates the highly volatile materials. This is an acceptable practice for that type analysis because of the usual small amount of bitumen in the samples is of little interest in kerogen conversion kinetics.

However, in oil cracking experiments, this volatilization is an important part, so the chosen evolution range is necessary.

Kinetic Analysis: The method of kinetic analysis using the Pyromat II has been described in detail elsewhere [4]. Kinetics were determined from multiple runs at constant heating rates (nominally) -- three 50°C/min., one 7°C/min., and two 1°C/min. runs were performed for each kinetic data set. If T_{max} values (temperature of maximum rate of evolution) and profile shapes were not in agreement, more runs at these heating rates were performed. Rate data were analyzed by using the regression analysis program KINETICS (Lawrence Livermore National Laboratory, Livermore CA) [10], which contains several methods of accounting for a reactivity distribution. The kinetic parameters used in this study were determined by the discrete distribution method (yielding $A_{discrete}$ and $E_{discrete}$), and, on a limited basis, by the shift-in- T_{max} method (yielding A_{approx} and E_{approx}). Other methods usually employed, the modified Friedman and modified Coats-Redfern, could not be reliably used because of the large amount of low temperature data truncated to isolate evolution due to cracking.

RESULTS

Kern River 650°F⁺ and mixtures of Kern River 650°F⁺ residuum with various solids were examined first for evolution profile behavior at the nominal heating rates of 25 and 50°C/min., then at multiple heating rates to determine pyrolysis kinetic parameters.

Evolution Behavior

Residuum Only: Previous studies indicated the pyrolysis yield may be affected by sample size [4,7]. Figure 3 shows the total pyrolysis yield of Kern River 650°F⁺ residuum at several sample sizes, ranging from less than 1.0 mg to over 15 mg. Although there is considerable scatter in the data, particularly at small sample sizes, the yields appears constant for samples sizes greater than 5 mg, but decrease with decreasing sample size for samples less than 5 mg. The extrapolated yield from measurements using a 5 or more mg sample is ~ 1100 mg pyrolysate/g or residuum. The extrapolated yield to zero sample size following the curvature generated by the decreasing sample size effect is ~ 900 mg pyrolysate/g residuum.

Sample sizes above 15 to 20 mg generally cause analysis problems with the Pyromat II micropyrolyzer because part of the sample is outside of the homogeneous heating regime of the furnace, and the high organic carbon evolution is outside the linear response range of the flame ionization detector. Measurements were made on the residuum at 23.4 and 34.9 mg sample size. Both gave pyrolysate yields of less than 900 mg pyrolysate/g residuum. This indicated the best operational sample size based on total yield alone is in the range of 5 to 15 mg.

The integration of the bimodal distribution seen in the evolution profiles (Figure 2) was divided into volatilization and cracking yields. Figure 3 shows the behavior of these components with respect to sample size. The cracking yield behaves similar to the total yield -- increases with increasing sample size until ~ 5 mg, then remains constant until very large sample size. Volatilization yield, however, seems to be invariant with sample size. The extrapolated yields from the constant yield range are 600 and 450 mg pyrolysate/g residuum for the volatilization and cracking, respectively.

Figure 4 shows the evolution profiles of Kern River 650°F⁺ residuum from 100 to 700°C at the nominal heating rate of 25°C/min. at different samples sizes all at roughly the same yield. The bimodal distribution appears to systematically shift towards the cracking regime as the sample size increases.

Residuum with Dolomite: Figure 5 shows the total pyrolysis yields for Kern River 650°F⁺ residuum mixed with varying ratios of dolomite. Most of the mixtures show a similar behavior to that of the residuum alone -- yields increase with increasing sample size until ~ 5 mg of residuum, then stay constant. Large sample sizes were not examined with the dolomite mixtures.

Although there are some differences in total yields, varying the dolomite to residuum ratio appears to have no obvious effect. Perhaps mixtures with the ratio of 4.0 give the maximum pyrolysate yield at a specific sample size, but the scatter in the measurements preclude any definite conclusions about this. The scatter comes about when preparing the mixtures, particularly lower

dolomite to residuum ratios. As the sample sits, it appears to have thixotropic properties, which hinder representative sampling.

The data in Figure 5 were divided into volatilization and cracking yields as in Figure 3 for the residuum alone. The behavior was found consistent with what was seen for the residuum alone in Figure 3.

Figure 6 shows the evolution profiles of the dolomite and residuum mixtures at the ratio of 3.5 to 1 for different sample sizes at the nominal heating rate of 25°C/min. As seen with the pyrolysis of the residuum alone, the profile appears to shift towards the cracking range as the sample size increases.

Residuum with Alumina: Figure 7 shows the total pyrolysis yields of mixtures of alumina and residuum at different sample sizes at the 25°C/min. heating rate. Only a limited number of ratios were examined. The behavior at small samples sizes is similar to residuum alone -- increasing yield with increasing sample size. However, the yield has a definite maximum and begins to decrease for sample sizes above 7 mg of residuum. Total yields of samples above 10 mg of residuum are much lower than at smaller residuum samples sizes.

Residuum with Spent Shale: Figure 7 also shows the total pyrolysis yields of mixtures of spent shale and residuum at selected ratios. The behavior is similar to that of the residuum and alumina mixtures where there is a maximum at ~ 10 mg residuum sample size. Samples larger than that show much reduced total yield compared to smaller sample sizes.

Comparison of Evolution Behavior: Figure 8 shows evolution profiles of residuum alone, residuum with dolomite, alumina, and spent shale at solids to residuum ratio of ~ 4.5 to 1 and residuum sample size of ~ 4 mg. The profiles of the residuum alone and residuum with alumina are very similar. The profiles of the residuum with dolomite and residuum with spent shale are shifted various amounts toward cracking temperatures compared to the residuum alone.

Kinetic Parameters

Kinetic determinations for the residuum and the residuum mixed with solids were more difficult to perform than kinetics on previously examined residua and tar sand bitumens. The problem lies primarily with the co-evolution of volatile matter from distillation and from cracking in the high temperature evolution range. In the work-up of the Kern River 650°F⁺ profiles, the cut-off point was taken at the division assigned in Figure 2, so the high temperature data was assigned to cracking only. This caused two problems: 1) removal of the low temperature data did not leave, in many cases, enough data for the shift-in- $T_{\max}$ calculations to be performed, and 2) evolution which is assigned to cracking is really a combination of cracking and distillation [8]. This latter issue can never be completely resolved by these methods. Attempts to deconvolute the two generation mechanisms is touched upon briefly below and will be reported in detail later.

Residuum only: Table 1 shows the kinetic parameters for several determinations for Kern River 650°F⁺ residuum. The sample size was 4 mg for all determinations, and all the samples were soaked at 250°C prior to pyrolysis. Note, the shift-in- $T_{\max}$ values (approximate) were calculated by including the entire evolution range. All the discrete values were determined by truncating the profiles at the point indicated in Figure 2. Because of the large amount of truncation, our other parameters methods, Coats-Redfern and Friedman, would not produce meaningful values [11], so they were not considered.

Set D12 and D13 show the best discrete analysis fits considering both Σ_1 (least squares analysis of weighted normalized rate residuals) and Σ_2 (least squares analysis of weighted integrated rate residuals). However, it is important to note that the activation energy-frequency factor combination governs reactivity, not just activation energy alone. Therefore, these and the other data sets were examined to see if the differences are due to compensating factors. All discrete determinations were recalculated holding $A = 1.02 \times 10^{13} \text{ sec}^{-1}$ (from D12) and $A = 6.0408 \times 10^{13} \text{ sec}^{-1}$ (from D13) constant. Using the D12-A value, all the activation energy distributions were almost identical to that of D12. The principal E_{discrete} was 50 kcal/mol (see Appendix Table 1). The least squares of the residuals, however, were all higher than those for D12. Using the D13-A value, all the activation energy distributions were within experimental error to that of D13. The

principal E_{discrete} was $53 \text{ kcal/mol} \pm 1 \text{ kcal}$ (see Appendix Table 2). The least squares of the residuals, however, were all higher than those for D13.

The magnitude of changes in the residuals for the various kinetic sets upon recalculation with fixed A values (residuals from Table 1 minus the residuals from recalculated parameters holding A fixed) were lower for the D12-A value recalculations than the D13-A value recalculations (see Appendix Table 3). This suggests the D12 parameters may indeed be the better set for comparison.

Figure 9 shows the results of the kinetic determinations at multiple heating rates for Kern River 650°F^+ residuum using the D12 and D13 parameters. Shown on the left side of the figure are the parameters from the discrete method. Shown on the right side of the figure are the rate data and corresponding fits generated by the discrete parameters. The evolution ranges selected were the cracking regime, as seen by the truncation of the early evolving data on the right side of the figure.

The discrete distribution shows a maximum at 50 and 53 kcal/mol for D12 and D13, respectively, accounting for $\sim 30\%$ of the total energy distribution. Activation energies at 45, 47, and 49 kcal/mol for D12 and 47, 49, 51 and 52 kcal/mol for D13 also have substantial intensities. The fits of the data generated by the discrete parameters show relatively good agreement, although deviation occurs around the truncation points on the low temperature side. The low values of residuals for both parameter sets reflect the good agreement of the fits with the data (see above).

Residuum with Solids: Figure 9 shows results of the kinetic determinations at multiple heating rates for dolomite mixed with Kern River 650°F^+ residuum at 3.5 to 1, and 6.5 to 1 ratios. The principal E_{discrete} , A_{discrete} , and the energy distributions are very similar to those of the residuum alone and are within experimental error of the parameters of D12.

Figure 9 also shows results of the kinetic determinations for spent shale mixed with Kern River 650°F^+ residuum. The same trend is seen with the residuum alone -- the activation energy distribution from the discrete method shows a principal energy within experimental error of the residuum, and the distribution exhibits intense lower energy contributions.

Table 1 also lists the kinetic parameters determined by the approximate or shift-in- $T_{\max}$ method using the entire evolution range. The E_{approx} and A_{approx} values are considerably lower than those calculated by the discrete method. Even though the values generally do not agree perfectly, considering that the $T_{\max}$ used in the approximate method is on the same maximum that is used for the discrete calculation the corresponding values should be in better agreement. The possible reason for the differences comes from the approximate method uses a hyperbolic fit of the top 10% of the data on the maximum to calculate a $T_{\max}$. In the cases here, this includes data which is after the division point (see Figure 2) which shows the fit to give a different $T_{\max}$ than observed.

DISCUSSION

Effects of Solids on Kinetic Parameters: Clearly, from Figure 9, the kinetic parameters determined by the discrete method for Kern River 650°F⁺ residuum and Kern River 650°F⁺ residuum mixed with dolomite or spent shale are within experimental error. The principal activation energies fall within 50 to 51 kcal/mol, with frequency factors between 1 to 9 X 10¹³ sec⁻¹. Even though there is an evolution profile change due to dolomite or spent shale as seen in the yield determinations (Figures 3 to 8), this apparently has little or no effect on the cracking kinetics.

Although little has been done on the open system pyrolysis kinetics of heavy crude oil residua, the effect of added mineral matter on laboratory pyrolysis of shale has been studied in some detail -- alumina, bentonite, kaolinite, calcite, illite, montmorillonite, quartz, and dolomite [12-15]. Evidence indicates that mineral matter may affect pyrolysis through pyrolysate yield and compound distribution changes similar to what we observed for Kern River 650°F⁺ residuum. What is not clear in the shale case is the effect of mineral matter on kinetic parameters. Dembicki [15] found that added mineral matter affected the kinetic parameters found for pyrolysis of kerogen concentrates, but it is not clear if the study was looking at real effects or statistical scatter, since the $T_{\max}$ was not affected significantly [16,17]. Other comparison studies between isolated kerogens and corresponding source rocks have shown, for some cases, little differences in the derived kinetic parameters [18]. More recently, Reynolds and Bumham [3] found little or no effect on kinetic parameters when comparing whole shales with mineral free kerogen concentrates of samples from Green River, Ohio, Rundel, Drauphne, and Phosphoria deposits.

The results shown in Figure 9 are consistent with the evolution profile behavior discussed above. The effects on the profiles caused by the mixing of the residuum with dolomite or spent shale were seen primarily in the lower temperature ranges -- shifting the evolution due to distillation of volatiles in the sample. This part of the profile is truncated in the discrete analysis so this information is lost.

Clearly, there must be co-evolution of compounds due to distillation and cracking in the ranges examined for cracking kinetics. Attempts have been made to deconvolute these mechanisms in the Rock Eval analysis of bitumen impregnated shale samples [19-23] and in Pyromat II analysis of tar sand and shales [5,7,8]. Further work is in progress utilizing other kinetic methods (such as two Gaussian fits) and asphaltene separations to resolve this issue.

Comparison with Other Crude Oils: Table 2 compares discrete kinetic parameters determined here with those previously determined by Pyromat micropyrolysis on other heavy crude oils and tar sand bitumen [5,7,8]. Also included are kinetic parameters on some asphaltenes derived from these sources [8]. Using the D12 result from above, the principal E_{discrete} value of Kern River 650°F⁺ residuum appears in the range of the principal E_{discrete} values of other materials. Altamont and Sunny Side Asphaltenes have higher principal E_{discrete} values as well as having sharper distributions. This reflects the source rock origin of the Uinta basin materials being type I, whereas the other materials come from type II and II_s source rocks.

CONCLUSIONS

Kern River 650°F⁺ residuum exhibited the following pyrolysis behavior:

- 1) decreasing yield with decreasing sample size for samples < 0.005 g,
- 2) constant yield for sample sizes in the range 0.005 g to 0.015 g,
- 3) decreasing yield with increasing sample size for sample > 0.015 g,
- 4) shift of pyrolysis profile to evolution in cracking range up to ~ 0.005 g samples,
- 5) principal E_{discrete} is ~ 50 kcal/mol and $A_{\text{discrete}} \sim 1 \times 10^{13} \text{ sec}^{-1}$.

Kern River 650°F⁺ residuum mixed with heat carriers exhibited the following pyrolysis behavior:

- 1) sample yield trends similar to residuum alone,
- 2) shift in pyrolysis profile to evolution in cracking range up to ~ 0.005 g similar to the residuum alone for alumina and greater than residuum alone for dolomite and spent shale,
- 3) principal E_{discrete} 50 to 51 kcal/mol and A_{discrete} 1×10^{12} to 10^{13} sec^{-1} .

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APPENDIX

Appendix Tables 1, 2, and 3.

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Table 1. Kinetic parameters for Kern River 650°F⁺ residuum

Determination	D01	D02	D03	D12	D13	D14	D15	D16
Soak Time, (min.) ^a	15	15	15	60	60	60	60	60
T _{max} , in °C (25°C/min) ^b	465.5	465.5	468.2	468.0	464.9	468.6	467.0	467.3
E _{approx} , (kcal/mol) ^c	48.2 (1.4)	48.1 (1.4)	46.3 (2.6)	47.6 (0.3)	50.2 (2.0)	47.1 (0.0)	48.3 (0.8)	48.2 (0.7)
Λ _{approx} (1/sec)	2.17 X 10 ¹²	2.03 X 10 ¹²	5.14 X 10 ¹¹	1.33 X 10 ¹²	9.25 X 10 ¹²	9.18 X 10 ¹¹	2.43 X 10 ¹²	2.13 X 10 ¹²
E _{discrete} (kcal/mol) ^d	50 (32)	51 (27)	49 (33)	50 (31)	53 (29)	49 (34)	50 (26.3)	50 (31)
Λ _{discrete} (1/sec)	1.04 X 10 ¹³	2.93 X 10 ¹³	4.45 X 10 ¹²	1.02 X 10 ¹³	6.04 X 10 ¹³	4.43 X 10 ¹²	1.16 X 10 ¹³	1.02 X 10 ¹³
Σ ₁ ^e	0.248	0.207	0.238	0.178	0.174	0.229	0.203	0.180
Σ ₂ ^f	0.011	0.008	0.006	0.007	0.011	0.009	0.008	0.006

a. Preheating time of sample held at 250°C. b. extrapolated from approximate parameters. c. () error in kcal/mol. d. principal activation energy of distribution, () percent of distribution. e. Least squares analyses of weighted normalized rate residuals. f. Least squares analysis of weighted integrated rate residuals.

Table 2. Kinetic (Discrete Method) Comparisons with Selected Oils.

Sample	E _{discrete} kcal/mol ^a	A _{discrete} sec ⁻¹	T _{max} °C ^b
Kern 650°F ⁺	50 (38)	7.4 X 10 ¹²	469.3
Kern Asphaltenes ^c	52 (35)	2.8 X 10 ¹³	476.6
Boscan 1000°F ⁺	53 (41)	7.3 X 10 ¹³	467.0
Boscan Asphaltenes ^d	53 (50)	3.4 X 10 ¹³	473.6
Altamont Asphaltenes ^c	55 (70)	2.7 X 10 ¹³	488.7
Hondo 650°F ⁺	53 (35)	1.4 X 10 ¹⁴	465.0
Hondo Asphaltenes ^c	51 (40)	1.8 X 10 ¹³	471.0
Sunny Side Asphaltenes ^f	56 (49)	7.8 X 10 ¹³	480.5
Kentucky Asphaltenes ^f	53 (42)	4.6 X 10 ¹³	480.5

a. principal activation energy, percent of total in (). b. extrapolated from approximate parameters at 25°C/min. c. 650°F⁺ isooctane insolubles. e. 343°C⁺ isooctane insolubles. f. tar sand bitumen isooctane insolubles.

Appendix Table 1. Calculated activation energy distribution (% of total) from discrete distribution method holding $A = 1.0156 \times 10^{13} \text{ sec}^{-1}$ for Kern River 650°F⁺ residuum at the 4 mg sample size.

Determination Energy, kcal/mol	D01	D02	D03	D12	D13	D14	D15	D16
45	21.43	21.48	21.42	19.08	19.67	18.94	18.86	19.07
46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
47	11.70	11.18	11.73	12.73	12.30	12.30	12.92	12.66
48	3.76	4.04	3.99	4.80	4.61	5.05	4.04	4.75
49	15.57	15.51	13.75	10.75	12.81	10.48	12.07	11.10
50	30.77	31.99	30.94	30.57	30.41	30.65	30.96	30.77
51	12.95	11.62	14.57	17.76	15.79	18.24	16.80	17.33
52	2.50	3.06	2.16	2.02	2.20	1.97	2.04	2.09
53	0.49	0.13	0.74	1.45	1.32	1.54	1.43	1.36
54	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
55	0.00	0.00	0.00	0.24	0.12	0.21	0.14	0.25
56	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
57	0.83	0.98	0.70	0.60	0.00	0.00	0.00	0.00
58	0.00	0.00	0.00	0.00	0.79	0.62	0.73	0.62
59	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
61	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Σ_1^a	0.258	0.305	0.241	0.178	0.245	0.235	0.217	0.181
Σ_2^b	0.012	0.014	0.007	0.007	0.013	0.014	0.082	0.007

a. Sum of squares of weighted normalized rate residuals. b. Sum of squares of weighted integrated rate residuals.

Appendix Table 2. Calculated activation energy distribution (% of total) from discrete distribution method holding $A = 6.0408 \times 10^{13} \text{ sec}^{-1}$ for Kern River 650°F⁺ residuum at the 4 mg sample size.

Determination Energy, kcal/mol	D01	D02	D03	D12	D13	D14	D15	D16
45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
47	0.00	0.27	0.00	0.00	17.80	0.00	0.00	0.00
48	25.46	0.00	25.56	22.48	0.00	22.26	22.40	22.44
49	0.00	11.29	0.00	0.00	13.68	0.00	0.00	0.00
50	4.26	5.58	4.16	8.22	2.67	7.92	8.32	8.23
51	16.57	7.52	16.55	12.18	11.76	12.44	11.62	12.18
52	16.53	25.15	14.32	13.98	16.98	13.59	15.75	14.38
53	30.67	21.99	32.40	34.07	28.78	34.36	33.29	33.94
54	2.03	5.89	2.40	3.69	3.89	4.03	3.33	3.50
55	3.37	1.23	3.56	4.39	3.58	4.34	4.27	4.33
56	0.00	0.40	0.00	0.00	0.00	0.00	0.00	0.00
57	0.00	0.00	0.00	0.18	0.10	0.25	0.14	0.09
58	0.00	0.00	0.00	0.23	0.25	0.14	0.19	0.28
59	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
60	1.11	0.68	1.06	0.00	0.00	0.00	0.00	0.00
61	0.00	0.00	0.00	0.59	0.50	0.68	0.70	0.61
Σ_1^a	0.597	0.225	0.711	0.430	0.174	0.522	0.407	0.402
Σ_2^b	0.032	0.009	0.043	0.025	0.011	0.040	0.017	0.202

a. Sum of squares of weighted normalized rate residuals. b. Sum of squares of weighted integrated rate residuals.

Appendix Table 3. Calculated differences in residuals comparing normal parameter fit with forced fit using fixed A for Kern River 650°F⁺ residuum at the 4 mg sample size.

Determination	D01	D02	D03	D12	D13	D14	D15	D16
$A = 1.1056 \times 10^{13} \text{ sec}^{-1}$								
Σ_1^a	0.080	0.127	0.063	0.000	0.067	0.057	0.039	0.003
Σ_2^b	0.005	0.007	0.000	0.000	0.006	0.007	0.001	0.000
$A = 6.0408 \times 10^{13} \text{ sec}^{-1}$								
Σ_1^a	0.423	0.051	0.537	0.256	0.000	0.348	0.233	0.228
Σ_2^b	0.021	-0.002	0.032	0.014	0.000	0.029	0.006	0.191

a. Sum of squares of weighted normalized rate residuals. b. Sum of squares of weighted integrated rate residuals.

FIGURE LEGENDS

Figure 1. Diagram of the Hot-Recycled-Solids Oil Shale Retort at Lawrence Livermore National Laboratory modified for heavy oil upgrading.

Figure 2. Evolution profile for Kern River 650°F⁺ residuum at the nominal heating rate of 50°C/min.

Figure 3. Pyrolysis yields of Kern River 650°F⁺ residuum as a function of sample size at the nominal heating rate of 25°C/min.

Figure 4. Evolution profiles of Kern River 650°F⁺ residuum at selected sample sizes at the nominal heating rate of 25°C/min.

Figure 5. Pyrolysis yields of Kern River 650°F⁺ residuum mixed with various amounts of dolomite as a function of residuum sample size at the nominal heating rate of 25°C/min.

Figure 6. Evolution profiles of Kern River 650°F⁺ residuum mixed with dolomite (3.51 dolomite to residuum ratio) at selected residuum sample sizes at the nominal heating rate of 25°C/min.

Figure 7. Pyrolysis yields of Kern River 650°F⁺ residuum mixed with alumina or spent shale (4.5 solid to residuum ratio) at selected residuum sample sizes at the nominal heating rate of 25°C/min.

Figure 8. Evolution profiles of Kern River 650°F⁺ residuum alone or residuum mixed with dolomite, alumina, or spent shale (4.5 solid to residuum ratio) at residuum sample size of ~ 5 mg at the nominal heating rate of 25°C/min.

Figure 9. Discrete distribution kinetic parameters (activation energy distribution, frequency factor, and calculate fits compared with experimental data) for Kern River 650°F⁺ residuum (D12 and D13), residuum and dolomite mixtures (3.5 and 6.5 dolomite to residuum ratio) and residuum and spent shale (6.5 shale to residuum ratio).

Figure 1. Schematic diagram of the Hot Recycled-Solids Oil Shale Retort at Lawrence Livermore

Figure 2. Evolution profile for Kern River 650°F⁺ residuum at the nominal heating rate of 50°C/min.

Figure 3. Pyrolysis yields of Kern River 650°F⁺ residuum as a function of sample size at the nominal heating rate of 25°C/min.

Figure 4. Evolution profiles of Kern River 650°F⁺ residuum at selected sample sizes at the nominal heating rate of 25°C/min.

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Figure 7. Pyrolysis yields of Kern River 650°F⁺ residuum mixed with alumina or spent shale (4.5 solid to residuum ratio) at selected residuum sample sizes at the nominal heating rate of 25°C/min.

Figure 8. Evolution profiles of Kern River 650°F⁺ residuum alone or residuum mixed with dolomite, alumina, or spent shale (4.5 solid to residuum ratio) at residuum sample size of ~ 5 mg at the nominal heating rate of 25°C/min.

Figure 9. Discrete distribution kinetic parameters (activation energy distribution, frequency factor, and calculate fits compared with experimental data) for Kern River 650°F⁺ residuum (D12 and D13), residuum and dolomite mixtures (3.5 and 6.5 dolomite to residuum ratio), and spent shale (6.5 shale to residuum ratio).