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Abstract

Kern River 650°F+ residuum and Midway Sunset crude oil were examined by micropyrolysis at several constant-heating rates to determine pyrolysis cracking kinetics. Determined by the discrete distribution method, both feeds exhibited principal activation energies of 50 kcal/mol and frequency factors ~ 10^{13} sec^{-1}. Energy distributions were similar ranging from 45 to 57 kcal/mol. Determined by the shift-in-T_{max} method, E_{approx}, A_{approx} for Kern River 650°F+ and Midway Sunset were 48 kcal/mol, 1.3 X 10^{12} sec^{-1}, and 46 kcal/mol, 4.6 X 10^{11} sec^{-1}, respectively. These results are similar, but not identical to other kinetic parameters for heavy oils from type II source rocks.

Introduction

Both hydrogen addition and carbon rejection processes have advantages for upgrading heavy oils. One method of interest is adapting pyrolysis-retorting technology, such as the Hot-Recycle-Solids (HRS) process (1) developed for oil shale pyrolysis. In the heavy oil modification, ceramic balls or other 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 advantage is production of an upgraded synfuel (from pyrolysis) and a source of energy for co-generation (from combustion).

To support the development of heavy oil upgrading in the HRS process (and possible upscaling) the intrinsic pyrolysis behavior of specific heavy oils from California, as well as possible modification of that behavior by the addition of solids, has been studied (2). The method employed was the Pyromat II micropyrolyzer, which has been utilized previously for pyrolysis examination of kerogens (3), shales (4,5) coals (6), tar sands and heavy oils (5,7,8). Here, further studies on pyrolysis cracking kinetics of heavy oils, specifically Kern River 650°F$^+$ residuum and Midway Sunset crude oil, are reported.

Experimental

Kern River 650°F$^+$ residuum was produced from a single plate distillation of 13.6° API Kern River crude (Kern County, CA). 11.5° API Midway Sunset was obtained from secondary (steam) recovery in the Midway Sunset field (Taft, CA).

The Pyromat II micropyrolyzer has been described previously (4). A 2.5 mg. sample was pyrolyzed at nominal heating rates, using He as the carrier gas. Hydrocarbon evolution was measured by FID 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 an IBM PS/2 Model 70 386 personal computer interfaced with the pyrolysis unit.

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 set. If T_{max} (temperature of maximum rate of evolution) and profile shapes were not in agreement, more runs at these heating rates were performed. Evolution range was 250 to 650°C with a one-hour soak time to remove low temperature volatiles. Rate data were analyzed by using the regression analysis Program KINETICS (9), which contains several methods of accounting for reactivity distribution. The kinetic parameters used in this study were determined by the discrete distribution method (yielding $A_{discrete}$ and $E_{discrete}$) and, in limited cases, 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 used because of the large amount of low temperature data truncated to isolate evolution due to cracking.

Results

The Pyromat II pyrolysis profile of crude oils and residua general exhibit two evolution ranges. These ranges have been assigned previously (8) as being due to distillation of volatile material (maximum around 300 to 400°C at 50°C/min) and combination of distillation and cracking (maximum around 400 to 500°C at 50°C/min), respectively. Figure 1 shows the profiles comparing Kern River 650°F$^+$ residuum (dashed line) and Midway Sunset crude oil (solid line). Both have a maxima which are similar (distillation T_{max}, cracking T_{max}: Kern River - 483.7°C, 333.6°C; Midway Sunset - 479.2°C, 332.5°C). However, Midway Sunset shows volatile material which begins at a lower temperature than Kern River reflecting the distillation pretreatment of the 650°F$^+$ residuum. For purposes of dividing yields into components (i.e. isolation of volatiles produced by cracking only), these ranges are divided using a minimum point between the two maxima (420.0°C for Kern, 407.8°C for Midway). Note: this does not completely deconvolute the peaks. Distillation must be occurring through out the pyrolysis temperature range.

Figure 2 shows the activation energy distributions, frequency factors, and data with generated fits (from discrete distribution method) for the best kinetic data sets for Kern River 650°F$^+$ and Midway Sunset crude oil. Note the approximate parameters for the Kern River 650°F$^+$ were determined using the entire data set from 250°C to 650°C (2). The approximate parameters for the

Midway Sunset were determined on the same data range utilized for the discrete analysis.

Both samples show principal activation energies of 50 kcal/mol with similar energy distributions and frequency factors. The data and generated fits show reasonable agreement except at the low temperature range cut-off points. The least square residuals (Σ_1 = sum of squares normalized rate residuals, Σ_2 = sum of squares weighted integrated rate residuals) are the same for both sets.

The approximate parameters are slightly different for the two samples, and the difference could be due to all the data were used for Kern River 650°F$^+$, and only cracking data were used for Midway Sunset. The approximate program utilizes a fit of the top 10% of maximum to calculate the T_{max}. Recalculating the approximate values with a spreadsheet that only uses T_{max} values measured manually yields E_{approx} (kcal/mol), A_{approx} (1/sec) of 48.3, 3.27 X 10^{12} and 47.5, 2.075 X 10^{12}, for Kern River 650°F$^+$ and Midway Sunset, respectively. Weighted averages of the discrete distribution yield 48.8 and 48.6 kcal/mol for Kern River 650°F$^+$ residuum and Midway Sunset crude, respectively, which are in reasonable agreement with the corresponding speadsheet calculations.

Discussion

Parameters shown in Figure 2 indicate that the two materials have cracking kinetic parameters which are within experimental error. Table 1 compares these results with kinetic determinations by the discrete method from data measured by the Pyromat II micropyrolyzer on Boscan 1000°F$^+$ (Orinoco Belt, Venezuela) (8) and Hondo 650°F$^+$ (Hondo Field, CA) (9) residua. The T_{max} at 25°C/min was extrapolated from the approximate method.

These results for Kern River 650°F$^+$ residuum and Midway Sunset Crude oil are similar to those of other heavy oils produced from type II source rocks (2).

Both the Boscan and Hondo residua have slightly higher principal activation energies. In addition, the activation energy distribution for Hondo 650°F+ (not shown) (5) exhibits little contribution to the total from energies below 50 kcal/mol. The distribution for Boscan 1000°F+ is similar to those of Kern 650°F+ and Midway Sunset, reflecting the more volatilization at lower temperatures than Hondo.

Conclusions

Kern River 650°F+ residuum and Midway Sunset crude oil have very similar 1) evolution profiles from 100 to 700°C at the 50°C/min heating rate, and 2) very similar cracking kinetic parameters as determined by the discrete distribution and approximate analyses method. The results for these feeds are similar, but not identical to the kinetic parameters found for Boscan 1000°F+ and Hondo 650°F+ residua.

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Figures

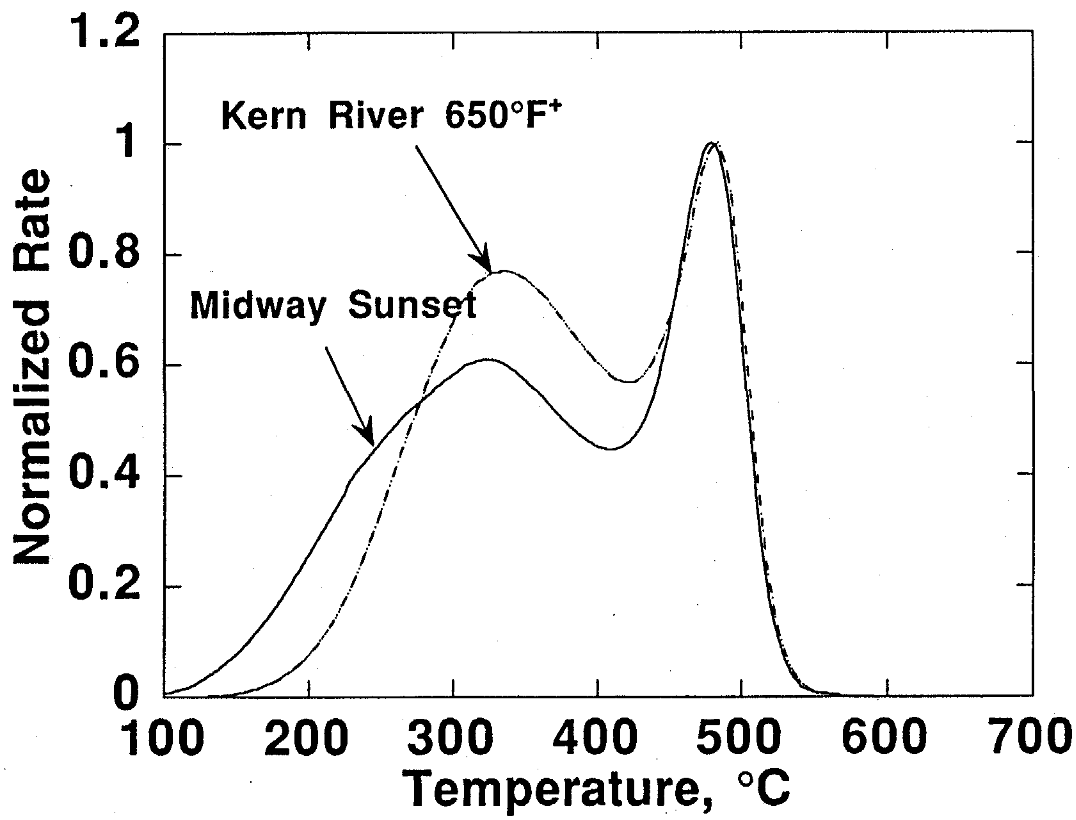
Figure 1. Evolution profiles for Kern River 650°F^{+} residuum and Midway Sunset crude oil at the nominal heating rate of 50°C/min. from 100 to 700°C.

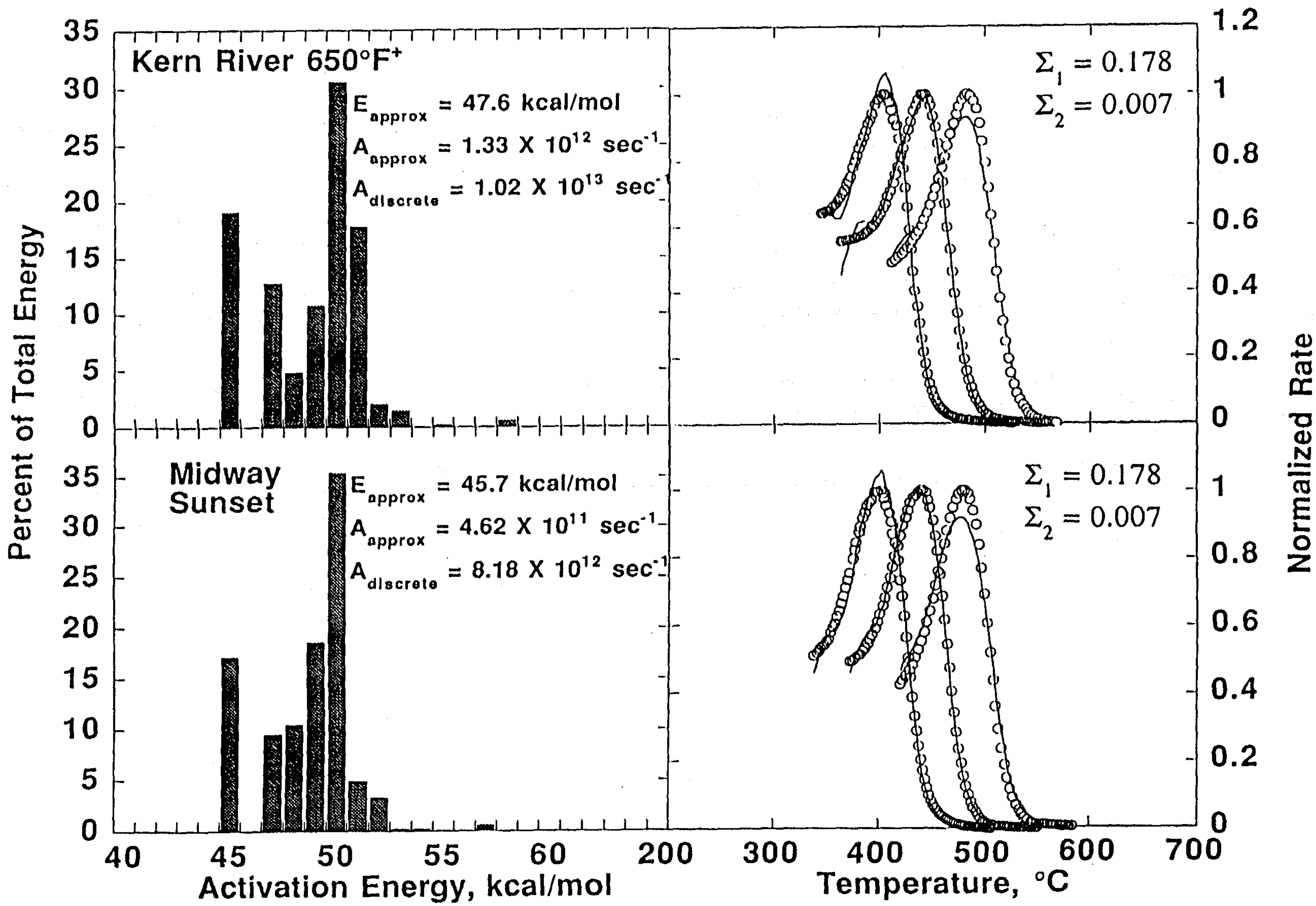
Figure 2. Cracking kinetic parameters for Kern River 650°F^{+} residuum and Midway Sunset crude oil on left side of figure. Experimental data with calculated fits from the discrete distribution parameters on right side of figure.

Table 1. 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 (32)	1.02×10^{13}	468.0
Midway Sunset Crude	50 (36)	8.18×10^{12}	465.0
Boscan 1000°F+	53 (41)	7.3×10^{13}	467.0
Hondo 650°F+	53 (35)	1.4×10^{14}	465.0

a. principal activation energy, percent of total in (). b. calculated from approximate parameters at 25°C/min.


Kern River 650°F+
Midway Sunset
Normalized Rate
Temperature, °C
0
0.2
0.4
0.6
0.8
1
1.2
100
200
300
400
500
600
700


Kern River 650°F+
E approx = 47.6 kcal/mol
A approx = 1.33 X 10^12 sec^-1
A discrete = 1.02 X 10^13 sec^-1
Σ1 = 0.178
Σ2 = 0.007
Midway Sunset
E approx = 45.7 kcal/mol
A approx = 4.62 X 10^11 sec^-1
A discrete = 8.18 X 10^12 sec^-1
Σ1 = 0.178
Σ2 = 0.007
Percent of Total Energy
Activation Energy, kcal/mol
Temperature, °C
Normalized Rate