Kinetics of Tar Sand Pyrolysis Using a Distribution of Activation Energy Model

Liang C. Lin
Milind D. Deo
Francis V. Hanson
Alex G. Oblad
Department of Fuels Engineering
University of Utah
Salt Lake City, UT 84112

Tar sands are bitumen-impregnated rocks. Tar sand deposits are found worldwide except in Australia. The total resource is estimated to be 360 × 10^{12}L in place (Probstein, 1982). The United States has an estimated resource of 4.5 × 10^{12}L, including measured and speculative resources. Most of the tar sand deposits in the United States are in the state of Utah (IOCC, 1984; Oblad et al., 1987).

Tar sand bitumen may be recovered by two basic methods: *in-situ* thermal recovery or surface mining followed by recovery processes (Oblad et al., 1987). The study of pyrolysis kinetics is essential to fully understand thermal processing of the resource, by either the *in-situ* or surface-recovery methods. The objectives of this work were to obtain the kinetic data for the pyrolysis of tar sands and develop a satisfactory model to explain the experimental data.

Pyrolysis of tar sands involves the breakdown up of bitumen, the organic constituent of tar sands. Kinetic studies of the pyrolysis of bitumen have been analyzed by conventional techniques such as single first-order kinetics (Barbour et al., 1976; Lin, 1988) and *n*th-order kinetics. Other methods, such as the first-order kinetic network (Phillips et al., 1985) and the Friedman technique (Lin, 1988), have also been used. The wide variations observed in kinetic parameters, obtained by conventional means, have been reported elsewhere (Lin, 1988). The failure of these conventional rate expressions to exactly fit the behavior of a complex reaction is an indication of a wide spectrum of conversion rates (Golikeri and Luss, 1972; Braun and Burnham, 1987). Such a reaction scheme often may be analyzed by the distribution of activation energies model, proposed by Anthony and Howard (1976), for coal devolatilization and hydrogasification.

In this work, a distinct bimodal distribution was observed in experimental weight loss profiles. The first low-temperature weight loss peak was attributed to distillation and low severity cracking reactions, and high severity cracking was proposed for the high-temperature weight loss peak. The experimental data were modeled, using a modified Anthony-Howard model, where the various heating rates used and the bimodal nature of the experimental data were effectively incorporated. The activation energies for the two mechanisms, 83 and 121 kJ/mol, respectively, were consistent with the type of mechanisms proposed for each of the weight loss peaks. A higher standard deviation of mean activation energy at low temperature was explained by the possibility of a wider variety of reactions in this regime. It was observed that the heating rate had little effect on the nature of reactions at low temperatures. At higher temperatures, however, the variety of reactions appeared to decrease with an increase in the heating rate.

Experimental Details

Tar sand samples from the Whiterocks (Utah) deposit were crushed and screened. The bitumen content of the raw tar sand sample was about 8%, and the bitumen content of the 30–45 U.S. mesh sample used in this study was 6.7%. It was observerd that after crushing and screening, finer samples contained less bitumen saturation. A 30–45 U.S. mesh sample was chosen, since its bitumen content was high enough to represent the raw sample and its size was small enough so that intrinsic kinetic studies could be conducted.

The experiments were conducted in a DuPont 951 thermogravimetric analyzer and a DuPont 990 thermal analyzer. Nitrogen, at a flow rate of 100 mL/min was used as a carrier gas. The sample was placed in a desiccator overnight to remove water before the pyrolysis study. About 45 mg of tar sand sample was used in each run. The air in the pyrolysis unit was flushed out by nitrogen before temperature programming. Heating rates of 2, 5, 10 and 20°C/min were used in this study. Weight loss vs. temperature was recorded for each of the four

---

Correspondence concerning this paper should be addressed to M. D. Deo.

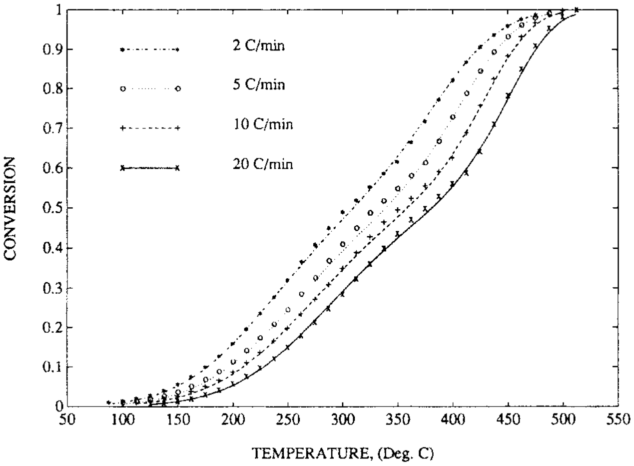

Figure 1. Conversion as a function to temperature for various heating rates.

heating rates. Conversions for the four different heating rates are shown in Figure 1. These are compared with the predicted conversions in the same figure.

Theoretical Considerations

With the constituents of the organic matter complex such as coal, oil shale, and tar sand, the pyrolysis reaction cannot always be adequately described by the simple pseudo-*n*th-order equation, if a single activation energy and preexponential factor are used for the reaction rate. The same formalism can be retained if a distribution of activation energies is assumed, as in the Anthony-Howard (1976) model. In this model, the complex reaction is represented by a number of parallel first-order reactions, each having its own rate constant k_i. For simplification, it is also assumed that the rate constants k_i differ only in their activation energies and have the same preexponential factors. If the number of reactions occurring is large enough, then the activation energy can be represented by a continuous distribution function.

Using this formalism, for a fixed heating rate, and appropriate simplifications. The following equation is obtained for the derivative of conversion with respect to the temperature.

$$\frac{dX}{dT} = \frac{A}{H}\int_0^{\infty} \exp\left[-\frac{E}{RT} - \frac{ART^2}{HE} \cdot \exp\left(-\frac{E}{RT}\right)\left(1 - \frac{2RT}{E}\right)\right] D(E)\, dE \quad (1)$$

A Gaussian distribution is assumed for the distribution function $D(E)$, with a mean activation energy E_0 and standard deviation σ.

Since the experimental results of tar sand pyrolysis show distinct bimodal distributions, indicating two primary weight loss mechanisms, a modification of Eq. 1 is needed. For each heating rate,

$$\left(\frac{dX}{dT}\right)_{total} = a_1\left(\frac{dX}{dT}\right)_1 + a_2\left(\frac{dX}{dT}\right)_2 \quad (2)$$

where a_1 is a coefficient that expresses the fractional contribution of the first weight loss, and a_2 expresses the fractional contribution of the second weight loss. Hence,

$$a_1 + a_2 = 1 \quad (3)$$

The use of Eq. 2 to analyze kinetic data is straightforward. With a fixed heating rate, the experimental data dX/dT were fitted into Eq. 2 using two groups of A, E_0, and σ as parameters corresponding to the two weight loss peaks. Availability of the weight loss data for different heating rates can be used to obtain the values of E_0 and approximate values of A for the two peak groups by using the following equation (Braun and Burnham, 1987).

$$\ln\left(\frac{H}{T_{max}^2}\right) = -\frac{E_0}{RT_{max}} + \ln\left(\frac{AR}{E_0}\right) \quad (4)$$

The plot of $\ln(H/T_{max}^2)$ vs. $1/T_{max}$ should result in a straight line with a slope of $-E_0/R$ and an intercept of $\ln(AR/E_0)$. For each of the peak groups, E_0 and approximate values of A were determined. These values were then modified to obtain sets of a_i, A, E_0, and σ for each of the peaks for each of the heating rates, so as to obtain the best fit for the experimental data.

Results and Discussion

The bitumen conversions vs. temperature for heating rates of 2, 5, 10, and 20°C/min are shown in Figure 1. Each of the curves was divided into three sections, and each section was fitted to a fourth-degree polynomial. From these, the derivatives were constructed, Figure 2. Two major weight loss peaks were observed. As the heating rate increased, the following two results were observed:

1. The peaks shifted to higher temperatures.
2. The intensity of the first (low-temperature) peak decreased and the intensity of the second (high-temperature) peak increased.

When the derivative, dX/dT, is plotted vs. conversion instead of temperature, as shown in Figure 3, it can be seen that the first peaks line up at a conversion of about 0.34 and the second peaks

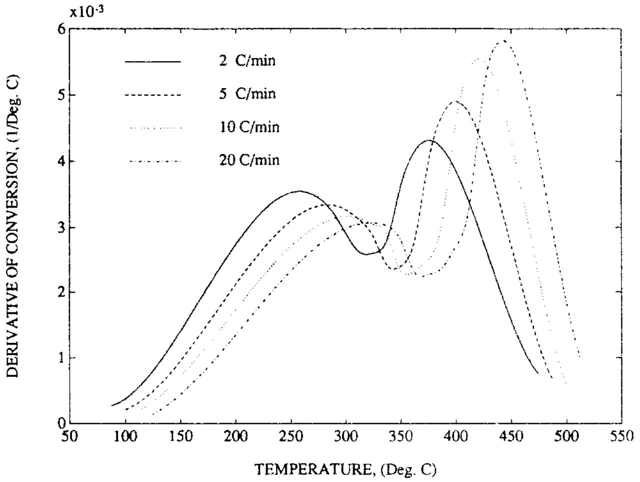

Figure 2. Derivative of conversion as a function of temperature for various heating rates.

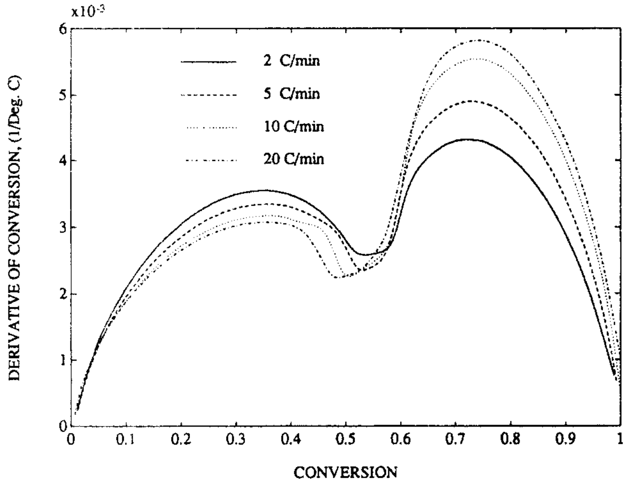

Figure 3. Derivative of conversion as a function of conversion for various heating rates.

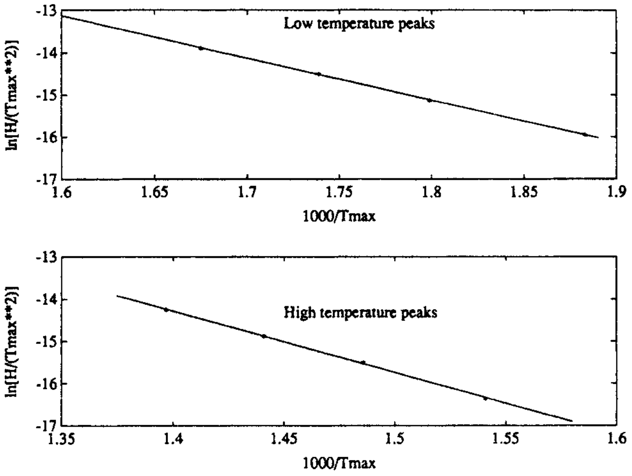

Figure 4. Plots to evaluate E_0 and approximate A: low- and high-temperature peaks.

line up at a conversion of about 0.73. The alignment of the weight loss peaks reveals that the intrinsic mechanism of pyrolysis reaction was not changed by the heating rates although the relative intensities were influenced.

The plot of ln (H/T_{max}^2) vs. $1{,}000/T_{max}$ for both the low- and the high-temperature peaks peaks is presented in Figure 4. From this, a mean activation energy of 83 kJ/mol and an approximate preexponential factor of 1.7×10^5 1/s were obtained. For the high-temperature peaks, a mean activation energy of 121 kJ/mol and an approximate preexponential factor of 6.5×10^6 1/s were obtained.

An observation of the bitumen conversion vs. temperature, Figure 1, indicates that the low-temperature weight loss is about 50% of the total weight loss for a 20°C/min heating rate, and about 54% of the total for a 2°C/min heating rate. The inflection point is considered indicative of the shift in weight loss mechanism. Thus, the approximate values of a_l for various heating rates were obtained. The limits of the integration in Eq. 1, 0 and ∞, can be substituted by $E_0 - 3\sigma$ and $E_0 + 3\sigma$, since 99.7% of the area of a Gaussian distribution function is covered in these limits (Johnson and Bhattacharyya, 1985). The parameters obtained by the best fit of Eq. 2 to experimental data are listed in Table 1.

It is reassuring to note that the best fit a_l are very close (around 50%) to those observed visually in Figure 2. The lower mean activation energies and frequency factors seem to be characteristic of distillation and light cracking reactions attributed to the first primary weight loss peak. Higher apparent mean activation energies of 121 kJ/mol for the high-temperature peak are consistent with the activation energies for other fossil fuels, such as oil shale, heavy oils and coal. These fall in the temperature range where major cracking can occur. In general, the standard deviations for the activation energies for the low-temperature peaks are higher compared to those for the high-temperature peaks. This suggests that the reactions occurring at lower temperatures have a wider distribution of activation energies than those at higher temperatures. The fact that the standard deviation remains the same, for the low-temperature peaks at all heating rates, suggests that the nature of these reactions does not change when the heating rate is altered. This fact is also revealed by the similar shapes of the low-temperature peaks. However, this is not the case for the high-temperature peaks. Here, the standard deviations of the mean activation energy differ by 6% of E_0 for a heating rate of 2°C/min to 2% of E_0 for a heating rate of 20°C/min. This is indicated by the broader-shorter weight loss peak for the lower heating rates and the narrower-taller peaks for higher heating rates, in Figure 2. It is postulated that when the heating rates are low, a wider spectrum of reactions can be attributed to the high-temperature peak than when the heating rates are high.

Use of the obtained kinetic parameters to predict the experimental data results in reasonable fits. This is observed for the conversions in Figure 1 and for the derivative of conversions for a specific heating rate (10°C/min) in Figure 5. The nature of the fit for other heating rates is similar.

Thus a modified Anthony-Howard distribution of activation energies model, incorporating the bimodal nature of the experimental data and different heating rates, was used successfully to explain the set bimodal distributions observed for the nonisothermal TGA weight loss analyses obtained during the pyrolysis of

Table 1. Kinetic Parameters for the Pyrolysis of Whiterocks Tar Sand

	E_0, kJ/mol		σ, % of E_0		A, 10^6 1/s		
H °C/min	Low Temp.	High Temp.	Low Temp	High Temp.	Low Temp.	High Temp.	a_l
2	82.97	121.08	12.0	6.0	0.2914	3.266	0.53
5	82.97	121.08	12.0	4.2	0.3017	3.920	0.52
10	82.97	121.08	12.0	2.6	0.3428	4.262	0.52
20	82.97	121.08	11.2	2.0	0.3943	4.638	0.50

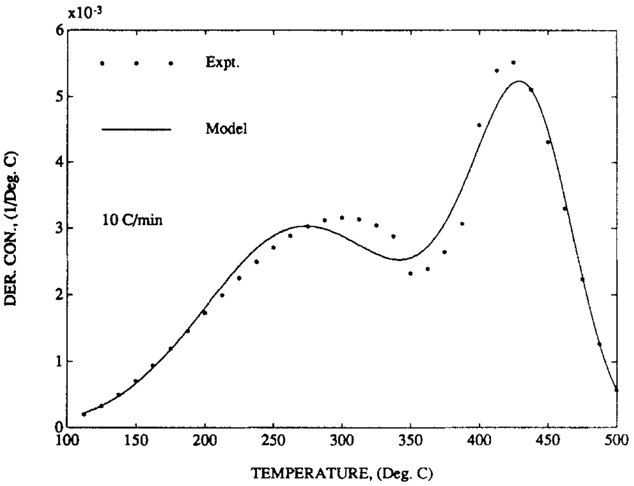

Figure 5. Plot comparing performance of model with experimental results at 10°C/min.

the Whiterocks (Utah) tar sands. The activation energies and their distributions were consistent with the mechanisms postulated—distillation and low severity cracking at low temperatures and high severity cracking at higher temperatures.

Acknowledgment

The financial support of the U.S. Department of Energy through the Laramie Project Office of the Morgantown Energy Technology Center is gratefully acknowledged.

Notation

a_1 = fractional contribution of low-temperature region
a_2 = fractional contribution of high-temperature region
A = preexponential factor, 1/s
$D(E)$ = Gaussian distribution of activation energy
E = activation energy, kJ/mol
E_0 = mean activation energy, kJ/mol
H = heating rate °C/min
R = universal gas constant, 8.314 J/mol K
T = temperature, K or °C
T_{max} = temperature where a peak maximum occurred, K or °C
X = bitumen conversion
σ = standard deviation of mean activation energy, kJ/mol

Literature Cited

Anthony, D. B., and J. B. Howard, "Coal Devolatilization and Hydrogasification," *AIChE J.*, **22**, 625 (1976).

Barbour, R. V., S. M. Dorrence, T. L. Vollmer, and J. D. Harris, "Pyrolysis of Utah Tar Sand Products and Kinetics," *172nd Natl. Meet. Am. Chem. Soc.*, San Francisco, **21**, 279 (1976).

Braun, R. L., and A. K. Burnham, "Analysis of Chemical Reaction Kinetics Using a Distribution of Activation Energies and Simpler Models," *Energy Fuels*, **1**, 153 (1987).

Golikeri, S. V., and D. Luss, "Analysis of Activation Energy of Grouped Parallel Reactions," *AIChE J.*, **18**, 277 (1972).

IOCC, "Major Tar Sands and Heavy Oil Deposits of the United States," Interstate Oil Compact Commission, Oklahoma City, OK (1984).

Johnson, R., and G. Bhattacharyya, *Statistics Principles and Methods*, Wiley, New York (1985).

Lin, L. C., "The Kinetics of the Pyrolysis of Tar Sands and of the Combustion of Coked Sand," Ph.D. Diss., Univ. Utah, Salt Lake City (1988).

Oblad, A. G., J. W. Bunger, F. V. Hanson, J. D. Miller, H. R. Ritzma, and J. D. Seader, "Tar Sand Research and Development at the University of Utah," *Ann. Rev. Energy*, **12**, 283 (1987).

Phillips, C. R., N. I. Haidar, and V. C. Poon, "Kinetic Model for the Thermal Cracking of Athabasca Bitumen—The Effect of the Sand Matrix," *Fuel*, **64**, 678 (1985).

Probstein, R. F., *Synthetic Fuels*, McGraw-Hill, New York (1982).

Manuscript received Apr. 9, 1990, and revision received July 16, 1990.