

COKING AND CRACKING REACTIONS OF OIL VAPOR OVER HOT OXIDIZED OIL SHALE

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ABSTRACT

The investigation of cracking and coking reactions of shale oil vapor in the presence of hot oxidized oil shale is conducted both for its intrinsic importance and in support of the modeling effort on the oil shale process. The model includes mass transfer of vapor through the gas film surrounding the shale particles with countercurrent flow of cracked low-molecular weight products, diffusion through the pore system, adsorption onto the internal surfaces, chemical reaction of the adsorbate, and desorption of oil and light gas. Results from two experimental configurations are related to the model calculations, and the application of coking and cracking in the retort process to upgrade oil product are discussed.

INTRODUCTION

Hot-Recycle-Solids (HRS) oil shale processes^(1,2) provide the heat for reaching pyrolysis temperatures through recycle of a burned shale stream. The intimate contact between primary oil vapors and recycled burned solids results in oil property changes that are mostly favorable but can also result in oil yield loss to coke and noncondensable gases. Previous work at LLNL^(3,4) and at CSIRO in Australia^(5,6) has shown that partial coking of shale oil vapors over oxidized shale minerals can have a favorable oil upgrading effect due to cracking of heavy oil to lighter components. Hence the degree of coking in HRS oil shale processes may provide an opportunity to improve oil quality and at the same time control the undesirable loss of product to excess coking and cracking. As a guide to this optimization we have developed a coking model that is based on the HRS pilot plant process developed at LLNL.

The coking process is quite complex because of its heterogeneous character coupled with its dependence on both oil properties and surface properties⁽³⁾. In many respects it resembles catalytic petroleum crackers in that both processes involve the contact of oil vapors with a hot porous solid. Similar to the deactivation of many solid catalyst, the surface reactions on oxidized shale have been shown⁽⁴⁾ to change with coke buildup leading to a slowdown of the overall coking rate with time.

In the model we assume that the oil is a mixture of three pseudocomponents each with a different boiling point. The diffusion rates and the adsorption equilibria are different for the three components, but the intrinsic coking kinetics are assumed to be the same since experimental data on intrinsic coking rates of specific oil components are not available. We also assume that the three oil components undergo the same coking reaction on the surface to produce coke and light gas with the same stoichiometry (2/3 coke and 1/3 gas). No production of lighter oil components from adsorbed heavy oil has been included since basic kinetic data do not exist. Even with these simplifying assumptions the current model has several adjustable parameters which are determined by matching the model to experimental results.

In our previous study⁽⁴⁾ we used a simple packed-bed reactor with a constant oil feed. With that apparatus, the oil upgrading effect was established: Fig. 1 shows a sample result that compares the boiling point distribution of the feed oil with the product oil distribution after 27% of the oil is coked. The partially coked oil is considerably lighter, and hence more valuable, than the starting oil. In modeling this effect, we make use of the fact that the result in Fig. 1 can be predicted by postulating that coke originates from the heavy end of the boiling point distribution without production of any light oil components. Such an explanation is no doubt a simplification of the real coking/cracking reactions that probably both produce and remove light oil. Nevertheless, this result provides a basis for the simple reaction stoichiometry adopted for the model. In the same study⁽⁴⁾ we determined the intrinsic coking rate of shale oil adsorbed on a non-porous quartz surface. This coking rate was determined on a well-

coked surface, because the fresh surface is covered with coke in a fraction of the total elapsed time of each experiment. For this same reason, the apparatus used in Ref. 4 did not allow determination of coking kinetics over fresh-oxidized porous shale surfaces. In order to relax this limitation we took a different experimental approach in our current work.

EXPERIMENTAL APPROACH

The apparatus shown schematically in Fig.2 consists of a fluidized bed for pyrolyzing a small shale sample followed by a packed bed of oxidized shale where coking reactions occur. An oil-vapor pulse from the fluidized bed enters the packed bed at the inlet and emerges as an altered oil pulse from the outlet. The hydrocarbon concentrations of both of these pulses are determined in separate experiments by oxidizing the oil pulse to $\text{CO}_2 + \text{H}_2\text{O}$ in a combustion tube and monitoring the combustion products by a rapid mass spectrometer. Coke deposited in the packed bed is quantitatively determined by subsequent oxygen addition and burnoff with quantification of the combustion products. A disadvantage of this apparatus relative to the apparatus of Ref. 4 is that the products are destroyed and cannot be used for studying oil property changes. Another experimental limitation is that only dilute vapors (i.e., low oil concentrations) can be studied.

The system was standardized on an Anvil Points, Green River Formation oil shale with a grade of about 24 gallons/ton. Shale sample drops varied from 0.5 to 1.6 grams each. Most of the experiments included a series of sample drops into the fluidized bed with the resulting oil pulses passing through the packed bed followed by burnoff of both beds at the end of each series of drops. Consequently the first oil pulse in each series encountered a freshly oxidized shale surface whereas subsequent oil pulses saw an increasingly coked surface. The size of the packed bed was varied, so that the coke yield would differ relative to the oil pulse. Shorter beds were used for small particles because small particles showed a greater overall coking tendency than did large particles.

COKING MODEL

The basis for the current coking model is a computer code developed at LLNL⁽⁷⁾ for heterogeneous reactions in a porous sphere. This code is quite rigorous; i.e., it incorporates the Stefan-Maxwell relationships for describing diffusion of gas species in the multi-component system. The code also allows for a film resistance around the particle, but this resistance proved to be insignificant for the cases studied here. This general code and the numerical scheme employed for its solution are not discussed in this paper. Rather the emphasis here is on the relationship of the experimental data to the results obtained from the code.

Table 1. Oil Component Properties Used in Model

Component	Boiling Point °C	Molecular Weight	Fraction Wt%	Diffusivity @ 500° C cm ² /s
1	200	155	50	0.27
2	400	338	25	0.17
3	500	451	25	0.15

Properties of the three oil pseudocomponents are specified in Table 1. This selection of components implies a three-point discretization of the continuous boiling-point curve of the shale oil. More components could easily be added. Molecular diffusivities predicted by theory⁽⁸⁾ are also given in Table 1. The effective diffusivities for porous shale are based on the ϵ^2 model⁽⁹⁾. A typical porosity (ϵ) and total surface area of oxidized Green River formation oil shale are 0.3 and 5 m²/g, respectively.

The adsorption equilibrium relationships are based on the Langmuir isotherm⁽⁹⁾ and are given by:

$$K_i \cdot P_i^* = \frac{\theta_i}{1 - (\theta_1 + \theta_2 + \theta_3)}, \quad i = 1, 2, 3 \quad (1)$$

where

K_i = Equilibrium constant of component i (kPa^{-1} , function of temperature)

P_i^* = Equilibrium vapor pressure of component i (kPa)

θ_i = Surface coverage factor for component i ($[\text{Oil}_i, \text{ads}] / [\text{Oil}_{\text{max,ads}}]$)

K_i correlates to the heat of adsorption ΔH_i according to the van't Hoff relationship:

$$K_i = k_0 \exp\left(\frac{\Delta H_i}{RT}\right) \quad (2)$$

where

$$\frac{\Delta H_i}{R} = 10 \cdot T_{\text{boiling point}} \quad (\text{Trouton's rule for heat of condensation})$$

The equilibrium relationships, Eqs. 1 and 2, contain two adjustable parameters: the pre-exponential factor k_0 in Eq. 2 and the total number of sites for adsorption $[\text{Oil}_{\text{max,ads}}]$ appearing in the definition of θ_i .

A third adjustable parameter is the preexponential factor A appearing in the first-order coking rate, Eq. 3, for the intrinsic coking rate on a freshly oxidized surface. The activation energy is assumed to be the same as for the coking rate on a coked surface from Ref. 4 shown for reference in Eq. 4:

$$\frac{d[\text{Oil}_i, \text{ads}]}{dt} = -A \cdot \exp\left(-\frac{19270 \text{ K}}{T}\right) \cdot [\text{Oil}_i, \text{ads}] \quad (\text{mineral surface}) \quad (3)$$

$$\frac{d[\text{Oil}_i, \text{ads}]}{dt} = -10^9 \cdot \exp\left(-\frac{19270 \text{ K}}{T}\right) \cdot [\text{Oil}_i, \text{ads}] \quad (\text{coked surface}) \quad (4)$$

The model uses a weighted average of Eqs. 3 and 4 for the case of a partially coked surface.

RESULTS

The fitted parameters are: $k_0 = 3 \cdot 10^{-7} \text{ kPa}^{-1}$, $[\text{Oil}_{\text{max,ads}}] = 0.6 \text{ mg/m}^2$, and $A = 10^{10} \text{ s}^{-1}$. This set of parameters produces the match of model results (shown as drawn curves) to experimental results (shown as individual points) in Figs. 3 and 4. For plotting the exposure time in these figures, the actual oil pulses have been approximated by assuming rectangular oil pulses instead of the true pyrolysis-kinetic pulses used in both experiment and model calculations.

Figure 3 shows that oxidized shale particle size has a strong effect on overall coking rate and that the overall coking rate declines significantly at a coke coverage of approximately 3 mg/g. The slowdown is particularly strong for the 1-mm particles because the initial overall coking rate for this small particle size is not dominated by pore diffusion. The model matches the slowdown by switching from a combination of Eq. 3 and Eq. 4 to Eq. 4 kinetics only at a coke coverage of 3 mg/g. (There is an order of magnitude change in intrinsic coking rate between the two equations.) The coke coverage of 3 mg/g is equivalent to 0.6 mg/m^2 and corresponds approximately to a monolayer. It is significant that the matching of the model produced the same monolayer limit for the maximum adsorbed oil concentration on the surface.

The two sets of 5-mm particle data in Fig. 3 show the importance of differential reactor conditions. The diamond series used a larger bed than the triangle series, and the consequence is a significant

depletion of cokable reactants across the bed (hence less coke per g of oxidized shale) for this series of experiments.

Figure 4 shows the results of varying the temperature of the oxidized-shale bed. Increasing temperature increases the overall coking rate but not in proportion to the increase in intrinsic coking rate that Eqs. 3 and 4 predict. Pore diffusion is only partially responsible for limiting the overall coking rate increase with temperature; another effect particularly important at low oil coverage of the surface is the reduced adsorbate equilibrium concentration on the surface which is modeled by the equilibrium constant in Eq. 2. (The surface is assumed to be in equilibrium with the local oil vapor within the pore system.)

Figure 4 also shows a result of varying oil concentration at a constant temperature of 502 °C. Oil concentration is seen to have a significant effect on the overall coking rate for the 5-mm particles.

Figure 5 contains model results that address the question of coking at higher oil concentrations. The maximum oil concentration expected in HRS oil shale processes is a few hundred mg oil/l. (The exact concentration depends on the amount of stripping gas.) Fig. 5 shows that increasing oil concentration increases the coke yield but with a proportionality much less than first-order; this result has also been confirmed by experiment. Comparison of Fig. 5(a) and Fig. 5(b) reveals that the increased coke yield with higher oil concentration is due mostly to increased coking in the large particles. This is explained by pore diffusion responding to a higher driving force. The pore-diffusion effect is also evident in the coke profiles of the larger particle sizes: a coke wave penetrates gradually into the 5- and 7.5-mm particles. A distinct coke layer extending from the surface partway into the particle has also been observed visually in partially coked shale bed samples.

CONCLUSIONS AND FUTURE PLANS

We compared experimental data with a model based on physical and chemical phenomena that govern coking of oil vapors over a porous medium. We conclude that mass transfer, phase equilibria and intrinsic chemical kinetics are all important in determining the overall coking rates for oil shale processes where the product-oil vapor contacts an oxidized recycle solid stream. We have used our model to extrapolate the experimental data to higher oil concentrations typical of the HRS processes and to larger particle sizes. Although these extrapolations remain to be confirmed in a newly constructed laboratory apparatus, we are relatively confident that oil losses to coke in the HRS process can be kept to a level of 10-15% of primary oil produced (assuming recycle ratios of 2 to 3). We have also concluded that the physical adsorption step is at least partially responsible for the observed selectivity toward high-boiling components in the heterogeneous coking process. It is likely that the high-boiling components also have higher reactivities than the low-boiling components, and we intend to study possible differences in reactivity as a function of molecular structure. Different reactivities also lead to the question of reaction products: adsorbed oil will no doubt produce lighter oil, not just coke and noncondensable gas. Hence cracking reactions for oil adsorbed on the surface should be added to the two competing processes, coking and desorption, included in this study.

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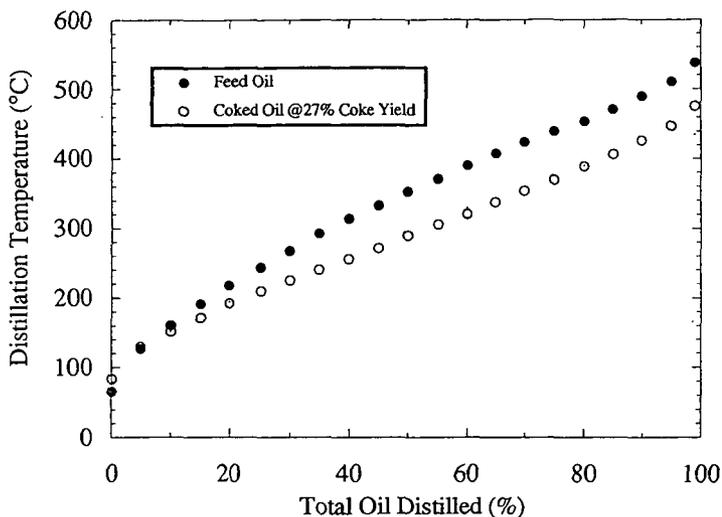


Figure 1 Effect of coking on shale oil boiling point distribution.

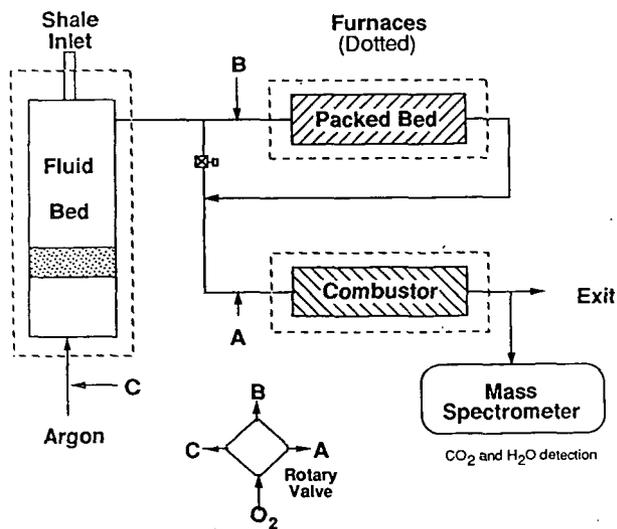


Figure 2 Apparatus for studying coking kinetics.

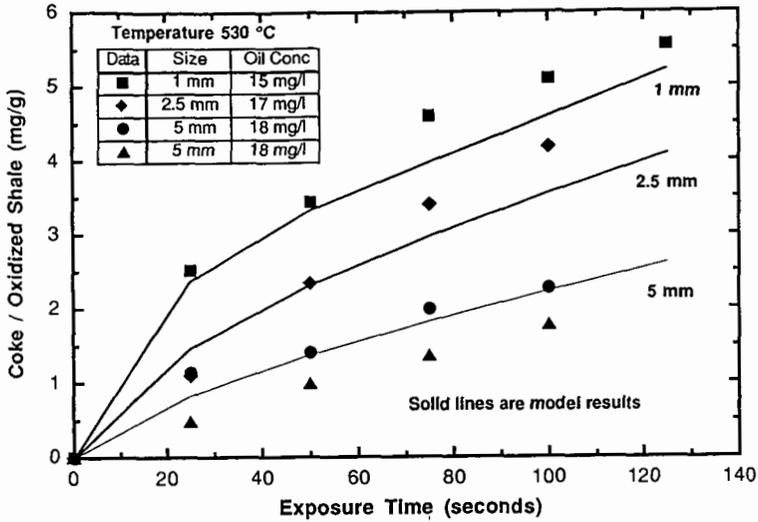


Figure 3 Particle-size effect on coke buildup.

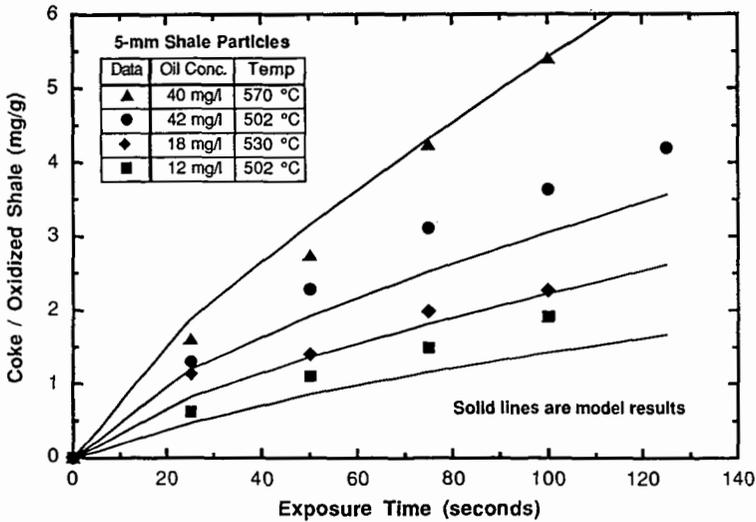


Figure 4 Temperature and oil-concentration effects on coke buildup.

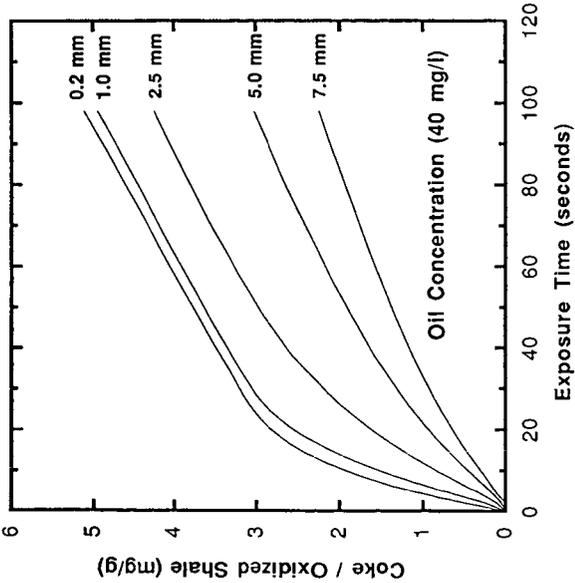


Figure 5 (a)

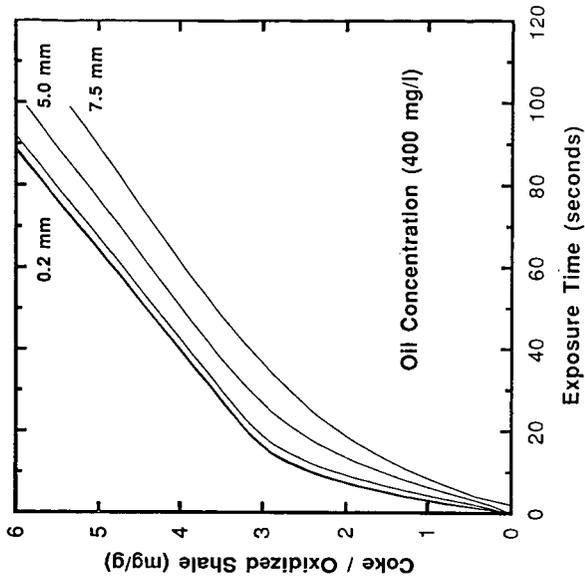


Figure 5 (b)

Figure 5 Model-predicted coke buildup with constant oil vapor concentration at (a) 40 mg oil/l, (b) 400 mg oil/l.