CRACKING AND COKING OF SHALE-OIL VAPORS

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ABSTRACT

The objective of our work on cracking and coking of shale oil vapor is first to quantify oil yield losses in the Hot-Solids-Recycle (HRS) oil shale process due to these reactions, and second, to determine if cracking and/or coking are favorable oil upgrading reactions that can be used advantageously in the HRS process. Cracking and coking of the produced shale oil vapor can relatively easily be incorporated into the HRS process, and a certain level of cracking and coking is unavoidable in the HRS process.

The first objective of quantifying oil yield losses for a simple fluidized-bed process has been accomplished, but oil quality effects of cracking and coking have only been studied under high-severity conditions, i.e. with oil destruction conversions much higher than the conversions typical of the HRS process.

INTRODUCTION

Figure 1 shows schematically the main process units of a generic HRS process: a pyrolyzer for heating raw shale to a pyrolysis temperature around 500°C with a stripping gas that usually also serves mixing purposes, and a combustor that raises the temperature of the pyrolysis residue for recycle as heat carrier to the pyrolyzer. Different process arrangements have been proposed for both the pyrolyzer and the combustor. For the pyrolyzer, Tamm et al. at Chevron (1982) proposed a fluidized bed where the stripping gas also served as the fluidizing gas. Cena and Taylor (1988) proposed that the fluidized-bed mixer be scaled down in size to accomplish only the mixing of raw and recycle shale while leaving most of the pyrolysis to a separate packed-bed pyrolyzer purged with a cross-flow stripping gas.
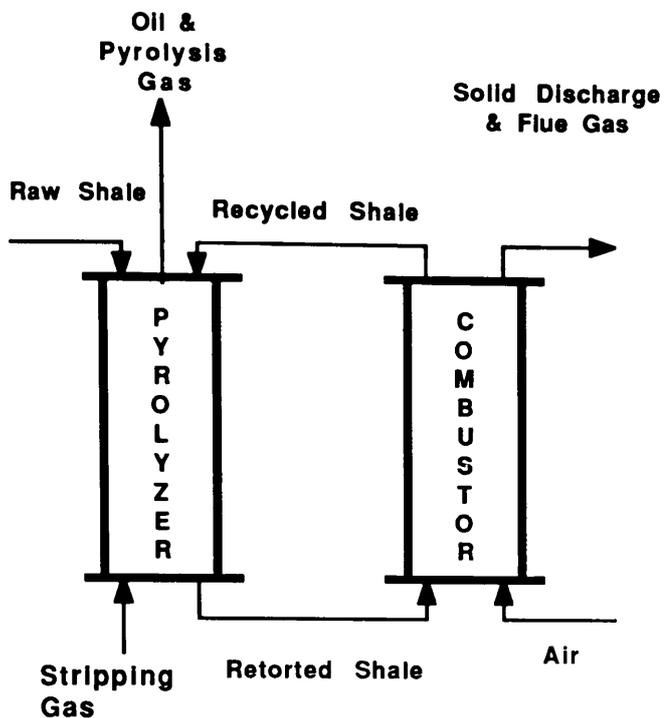
Figure 1.   Hot-Recycle-Solids (HRS) Process

Common to all HRS processes utilizing burned shale as heat carrier is contact between the oil product vapor and the burned shale. Such contact has been shown to produce coking of the oil vapor onto the surface of the burned shale. This was observed by, for example, Bissel, Burnham and Braun (1985) for Colorado oil shale, and by Udaja, Duffy and Chensee (1989) for several Australian oil shales. It was also observed that shale oil vapor undergoes chemical changes merely as a result of residence time at high temperatures (such as 500°C), i.e. in the absence of solid surfaces. The main manifestation of these changes is production of light hydrocarbon gas, defined in this paper as C_4 and lighter hydrocarbons, from the oil. This light gas production is commonly referred to as "cracking", whereas the surface-induced oil-loss mechanism is referred to as "coking" because coke is the main product. These definitions are not strict in a chemical sense because coking produces significant amounts of light gas, and cracking probably produces minute amounts of coke.

EXPERIMENTAL APPROACH

Our approach to studying cracking and coking is shown schematically in Figures 2A and B. Both pieces of equipment are bench-scale in size. The "long-exposure" apparatus was first used be Levy, Mallon and Wall (1986) to study Australian shale oil cracking, and the "short exposure" apparatus was used by Coburn, Taylor, Morris and Duval (1988) to study pyrolysis kinetics.

In the long-exposure apparatus, the oil feed is constant by use of injected Fischer-Assay shale oil that is vaporized into a carrier gas that flows through a packed bed of oxidized shale or quartz sand. This apparatus has the advantage of allowing accurate quantitative determination of oil, gas and coke yields, and provides enough oil for determination of oil properties. A disadvantage of this apparatus is that a relatively long experimental run time is required for a material-balanced yield determination, and the long run time translates to a long exposure time for the oxidized shale.
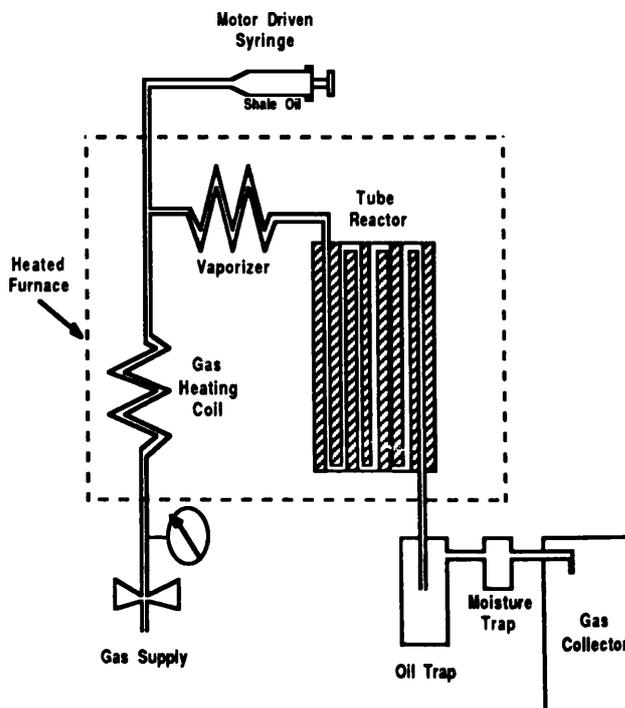

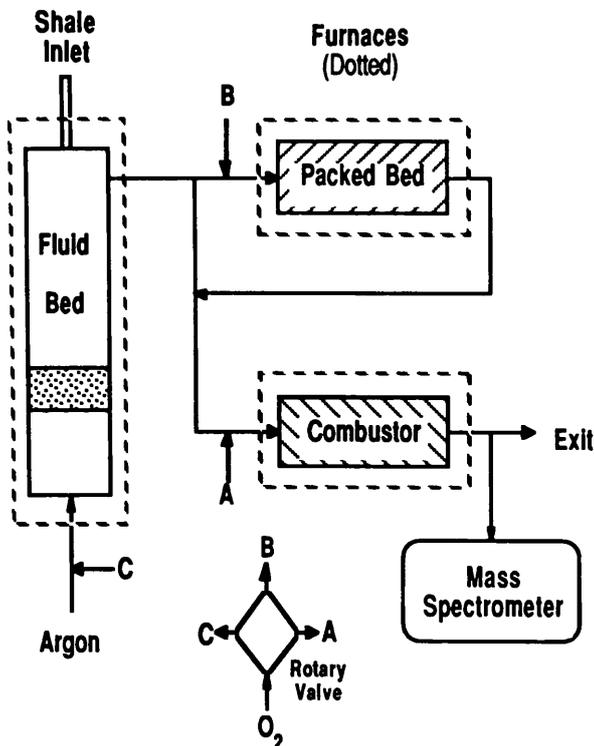**Figure 2A.   Long-Exposure Time Apparatus**

Figure 2B. Short-Exposure Time Apparatus

Chemical Kinetics

The chemical reaction kinetics were obtained from experiments in the long-exposure time apparatus with quartz packing or without any packing. Several packed-bed temperatures, gas residence times and oil inlet concentrations were used in these experiments.
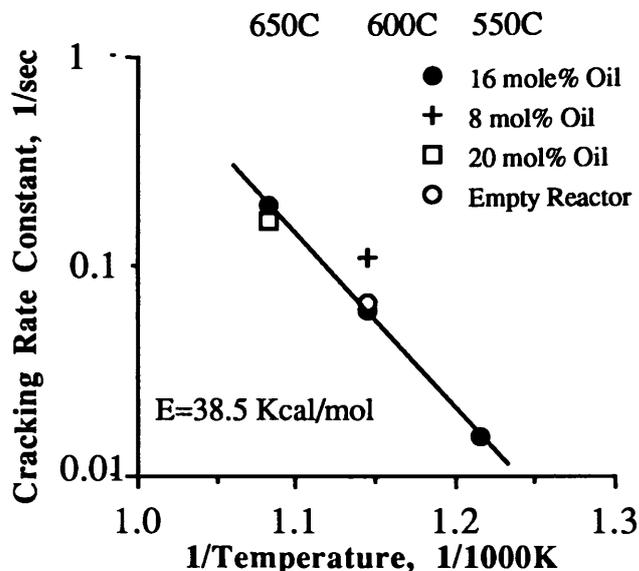

Figure 3. First-Order Cracking Rate Constant over Quartz in Long-Exposure Time Apparatus

The short-exposure time apparatus consists of a fluidized bed for pyrolyzing a small shale sample followed by a packed bed of oxidized shale for cracking and coking of the oil emerging from the fluidized bed. This apparatus is kinetic in nature; an oil vapor pulse 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 by oxidizing the hydrocarbons to $CO_2 + H_2O$ in a combustor, and analyzing the combustion products by a rapid mass spectrometer. Inlet and outlet pulses are measured in separate experiments. After an experiment (with flow through the packed bed), the coke deposited in the packed bed is quantitatively determined by burnoff and quantification of the combustion products. A disadvantage of the short-exposure time apparatus is the lumped quantitative analysis of hydrocarbons that does not distinguish between oil and gas. Hence, cracking kinetics cannot be determined from experiments in the short-exposure time apparatus. Also, the oil concentration in the gas entering the packed bed is much lower than typical HRS conditions.

A first-order rate constant for gas production, i.e. the cracking reaction, is plotted in Figure 3 in the Arrhenius form. This is a limited data set of all the experiments performed where the limitation is that the oil conversion to gas is significantly less than the ultimate conversion level discussed below (This implies very short gas residence times for the higher temperatures). The reason for this limitation is that the cracking reaction is known to deviate from first order at higher conversions (Bissel, Burnham and Braun, 1985). Deviation from first order is also apparent in our high-conversion experiments; the cracking conversion with long gas residence times approaches an asymptotic value of the order 40-50%, implying depletion of the

crackable components at this conversion level. From a practical point of view, however, the high conversion cases are less important because the cracking conversions of interest in the HRS process are much less than 20%.

The first order cracking rate constant k_{crac} in Figure 3 is given by:

[1] $k_{crac} = 2.53 \ 10^8 \ exp(-19350°K/T) \ (s)^{-1}$

where the activation energy of 38.5 Kcal/mol is similar to previously reported values in the range 36-40 kcal/mol (Bissel, Burnham and Braun, 1985).

The cracking rate constant in Figure 3 is seen to be relatively insensitive to oil inlet concentration in the range of practical importance, 8-20 mol% (assuming an average oil molecular weight of 300). However, the 8-mol% rate is inexplicably high in Figure 3. Also shown in Figure 3 is the result of an experiment without any packing, showing that the quartz used in the other experiments had no significant effect on the cracking rate. This does not necessarily mean that the cracking reaction is homogeneous, although from a process point of view it may be treated as such. A chemically more plausible explanation is that the cracking reaction occurs at least partially on the surface of the small amount of coke that forms on the quartz. Coke probably also forms in empty space by nucleation similar to soot formation in combustion reaction mixtures.

Figure 4 shows the coking rate calculated from the same experiments as those of Figure 3. These coking rates have been obtained from the experimentally determined coke yields, the solids exposure time, and the surface area of the quartz (0.0023 m^2/g). The absence of any oil-concentration effect in Figure 4 is evidence of chemical kinetics control. The calculated coking rate is also insensitive to solids exposure time implying that the buildup of coke does not slow down with time (as is the case with oxidized shale shown in a subsequent section). Whether the first monolayer of coke forms with the rate of Figure 4 is not known because all results were obtained with, relatively speaking, thick layers of coke. However, the conversions of oil to coke

are quite small in these experiments when compared with the conversions of oil to gas.
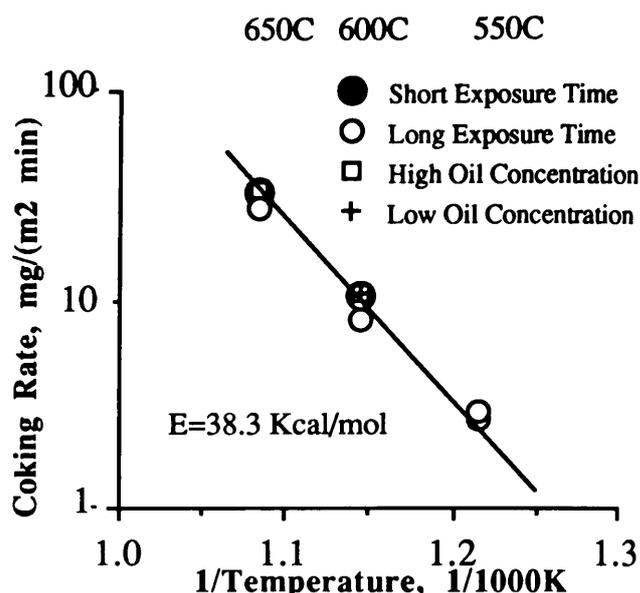

Figure 4.   Coking Rate over Quartz in Long-Exposure Time Apparatus

The coking rate R_{coke} shown in Figure 4 is given by:

[2] $R_{coke} = \ 3.63 \ 10^{10} \ exp(-19270°K/T)$
$$mg/(m^2 \ min)$$

where the activation energy of 38.3 Kcal/mol is almost identical to the cracking activation energy. This is further evidence of the two reactions having similar chemistry; probably a free-radical so-called beta-scission mechanism typical of thermal cracking (Gates, Katzer and Schuit, 1979).

Mass Transfer

Recycle shale in an HRS process operating on Colorado oil shale is expected to have a total surface area of about 5 m^2/g, or about 2000 times higher than the nonporous quartz used in the experiments discussed above. Use of oxidized shale in the packed bed of the long-exposure time apparatus had a profound effect on

oil destruction; total oil losses were much greater at all conversion levels, and the ultimate conversion, that was approximately 40% in the absence of large surfaces, increased to 80% with oxidized shale present. A very important question is whether the coking rate of Eq[2] can be directly used to predict coking on oxidized shale in an HRS process. At 500°C the coking rate predicted by Eq[2] is 0.55 mg/(m^2 min) which translates to 2.7 mg/(g shale min) for shale with a surface area of 5 m^2/g. The observed overall coking rate is of this same order at 500°C: In experiments performed in the short-exposure time apparatus (with the oxidized shale present in the fluid bed instead of the packed bed), the coke yield was found to be 2.5-3.5 mg/g shale and somewhat dependent on the combustion conditions used to generate the oxidized shale. This suggests chemical kinetics control at 500°C (an approximate exposure time of 1 minute is implied in this argument), but other bench-scale results showed almost the same coking rate at 600°C, definitely implying mass-transfer control at higher temperature.

Another observation of mass-transfer effects is shown in Figure 5. Here, the coke yield is given as a function of shale-surface exposure time as determined in a series experiments at 600°C in the long- exposure time apparatus. Interestingly, the observed coking rate, i.e. the slope of the curve in Figure 5 changes with time, and is much less than the chemical coking rate at 600°C. The observation of the "slow down" of the coking rate is not new; Voorhis (1945) observed the same pattern on natural cracking catalysts, and modeled the rate simply with a reaction rate constant declining with time. Here, however, a different modeling approach is taken that involves modeling the mass transfer between the vapor phase and the solid surface. We believe that mass transfer is important in the overall kinetics at 500°C, and becomes dominant at higher temperatures.

Model

The cracking and coking model that we have derived can be expressed as follows for a stationary solid phase and a flowing gas phase:

[3a] $v \dfrac{\partial C}{\partial x} = - k\, a\, (C-C^*) - k_{crac}\, C$

[3b] $\dfrac{\partial C_s}{\partial t} = k\, \varepsilon\, (C-C^*) - k_{coke}\, C_s^2$

[3c] $k_{crac}=$ $2.53 \times 10^8 \exp(-19350°K/T)\ (s)^{-1}$

[3d] $k_{coke}=$ $3.07 \times 10^{14} \exp(-19270°K/T)$
$m^2/(mol\ oil\ s)$

[3e] $C^*=$ $m\, C_s / (1.0 - C_s/C_{s\,max})$

[3f] $k =$ $\dfrac{k_0}{1.0 + \alpha \displaystyle\int_0^t k_{coke}\, C_s^2\, dt}$

where,
C   =   oil concentration in gas phase
        (mol oil/m^3 gas)
C_s =   oil concentration on solid phase
        (mol oil/m^2 surface)
v   =   interstitial fluid velocity
k   =   mass transfer coefficient
a   =   shale surface area/reactor volume
ε =   void space
x   =   distance coordinate along axis
t   =   time

The physics behind Eqs[3] is simply an interchange of oil between the vapor phase (concentration C) and the solid phase (concentration C_s) where the rate of interchange is modeled by a mass-transfer coefficient k acting on the driving potential difference (C-C*), where C* is in equilibrium with C_s. This mass-transfer coefficient is assumed to decline with coke buildup on the surface in accordance with Eq[3f]. A possible physical explanation of this gradual impediment of the mass-transfer is that the coke on the surface undergoes slow chemical changes resulting in the release of H$_2$ (and some light hydrocarbons). This outgassing produces a gas flux that impedes the diffusion of large oil molecules to the surface.

The adsorption/desorption characteristics of oxidized shale are modeled by a Langmuir-type relationship given in Eq[3e]. The slope m is a fitted parameter, but the maximum adsorbate concentration $C_{s\,max}$ is assumed to correspond

to a monolayer of adsorbed oil on the surface. A weak temperature dependance is also introduced through a van't Hoff relationship:

$$[4] C_{s\ max} = 6.61\ 10^{-9}\ \exp(4620°K/T)\ mol/m^2$$

The coking reaction order is two in Eq [3b] in accordance with coking literature (Gates, Katzer and Schuit, 1979).

Table 1. Numerical Values of Model Parameters Used in Calculations

Parameter	Value	Unit
k_o	$0.4\ 10^{-4}$	m/s
α	$0.45\ 10^8$	m^2/mol oil
m	$0.2\ 10^5$	m^2/m^3 void
a	$0.43\ 10^7$	m^2/m^3 rct.
ϵ	0.41	m^3void/m^3rct
v_{inlet}	2.0(HRSval)	m/s

With the model parameters given in Table 1, the results of Figures 5 and 6 were obtained. Figure 5 shows that the model has the correct trend in predicting the observed coking rate. The mismatch for long exposure times is unimportant for the HRS process where exposure times are of the order of one or a few minutes. The model correctly predicts a very high coking rate initially.

The short-exposure time results of Figure 6 also provide verification of the model, but here there is also a significant mismatch between the model outlet pulse and the measured outlet pulse. As Figure 6 shows, the model responds faster than the experiment, possibly due to too low a value for $C_{s\ max}$ and too high a value for the mass transfer coefficient k. For the HRS process however, this mismatch is not too serious because it is a result of the very low oil concentrations used in the experiment of Figure 6. There are also some difficulties in interpreting the experimental data because the oil and gas are indistinguishable from each other. The mismatch between the shapes of outlet pulses translates to

different areas under the curves, ie. different coke yields; the experimental coke yield is 2.9 mg/(g shale), while the model coke yield is only 1.8 mg/(g shale).
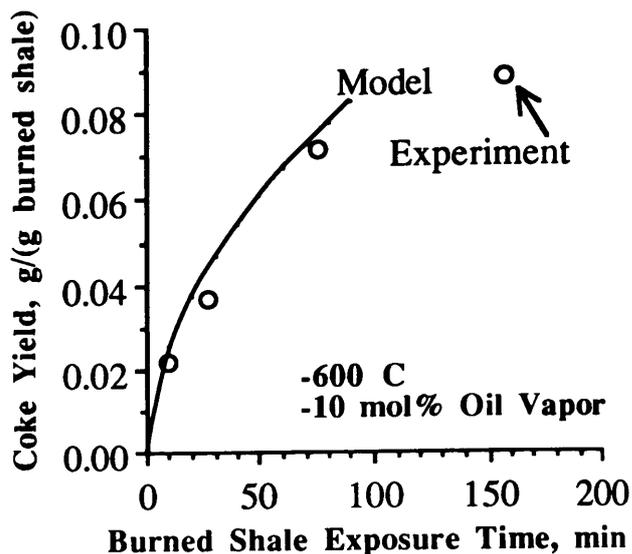

Figure 5. Comparison of Model Results to Experiments in Long-Exposure Time Apparatus
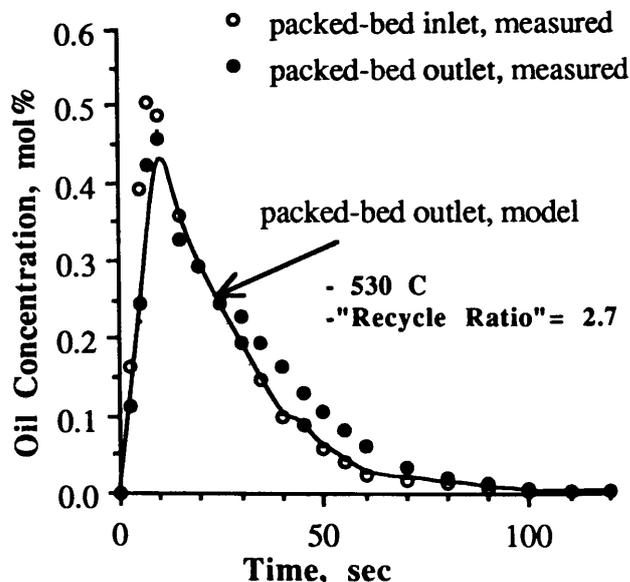

Figure 6. Comparison of Model to Experiments in Short-Exposure Time Apparatus

Prediction of Process Behavior

As an example of application of the model, a fluidized-bed pyrolyzer was simulated by discretizing Eqs [3] and assuming that both the solid phase and the vapor phase have plug-flow characteristics axially, and perfectly-mixed characteristics radially. With these assumptions the oil concentration profile in the bed is simply determined from the pyrolysis kinetics as given by Wallman, Tamm and Spars (1981), for example. A solids residence time of 5 minutes and an oil concentration of 10 mol% at the top of the bed are assumed for the fluidized bed under study.
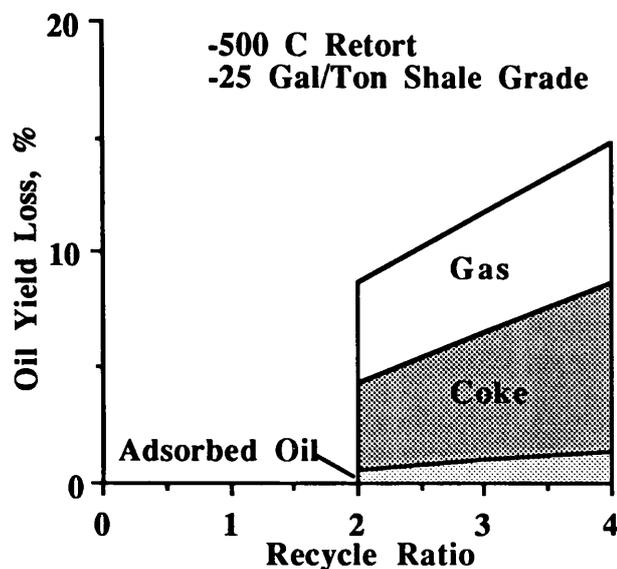

Figure 7. Predicted Oil Cracking/
Coking Loss In Fluidized
Bed HRS Process

Figure 7 shows the effect of changing recycle ratio in the fluidized-bed HRS process. The results show that oil yield losses in the categories coke and adsorbed oil increase proportionally to recycle ratio. This is because coke and adsorbed oil are approximately independent of recycle ratio at 2.2 mg coke/(g recycle shale) and 0.4 mg adsorbed oil/(g recycle shale). The cracking loss also increases with recycle ratio because the coking reaction is assumed to produce 1/3 gas and 2/3 coke, but there is also a "homogeneous" cracking contribution of approximately 2.5% oil

yield loss. Any extra cracking associated with quenching of a very hot recycle solid such as would be required at recycle ratios less than two is not included in the model. Hence, the cracking loss should not be extrapolated to recycle ratios lower than 2.
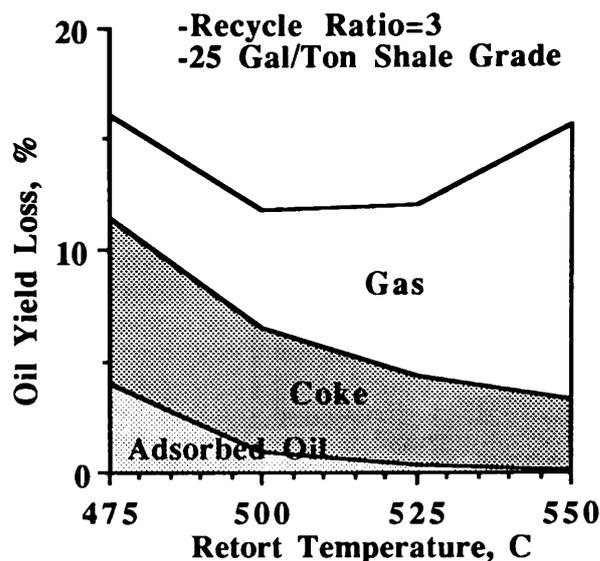

Figure 8. Predicted Oil Cracking/
Coking Loss In Fluidized
Bed HRS Process

Figure 8 shows the effect of changing pyrolysis temperature in the fluidized bed. Interestingly, the results show a broad oil loss minimum in the temperature range 500-525°C. The increase in oil loss at higher temperature is due to increased "homogeneous" cracking (the cracking rate increases rapidly with temperature), whereas the loss at lower temperature is a result of increased coking and adsorbed (unstripped) oil. This is mainly a result of the pyrolysis zone moving deeper into the fluidized bed because of slower pyrolysis kinetics. A longer contact between the emerging oil vapors and the down-flowing solids leads to more coke and adsorbed oil. Part of the adsorbed oil could be recovered by increasing the size of the stripping section of the bed, i.e. making the bed taller (A more efficient stripping gas may have the same effect). Nonetheless, the results in Figure 8 clearly show that retorting Colorado oil shale in an HRS process should not be carried out at temperatures

below 500°C unless there is a specific reason to coke part of the oil product.

Oil Quality Considerations

The oil produced in some high-severity experiments in the long-exposure time apparatus has been analyzed by means of GC simulated distillation and by a so-called GC finger print analysis. As might be expected, high-severity cracking and/or coking leaves a much lighter oil than the primary shale oil. However, we do not know if this effect is of any significance at the typical HRS severities of 10-15% total oil yield loss. Some differences between cracking and coking relating to oil properties have also been observed; Cracking for example, destroys more aliphatic hydrocarbons than does coking. Hence, coking is preferable to cracking for this particular upgrading effect because aliphatic hydrocarbons are desirable in the product oil.

FUTURE WORK

We will refine the cracking and coking model with more experiments in the short-exposure time apparatus, and then incorporate cracking and coking into the OSP model of the full HRS process (fluidized-bed mixer + packed-bed pyrolyzer). Verification against pilot-plant data will also be done.

We will also pursue the oil-upgrading considerations of cracking and coking in the laboratory. By analyzing oils from low-severity experiments in the bench-scale apparatus we will determine if there is an incentive to optimize the HRS process in a way different from simply maximizing the oil yield. Coking to a certain extent may be favorable in terms of some oil properties such as the pour point, for example. This work will also influence our pilot-plant program because oil quality is as important as oil yield for an overall oil shale process.

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