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SOLVENT TAILORING
IN COAL LIQUEFACTION

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Quarterly Report for the
Period November 1982-February 1983

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OBJECTIVE

The objective of this research program is to determine the effects of phase behavior of process components on coal liquefaction and of solvent composition on coal-dissolution behavior as well as their combined effects on second stage upgrading. Through understanding the fundamentals of coal dissolution, this research will provide data for tailoring solvents to attain higher reaction rates, increased conversion, and higher product selectivity.

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Abstract

A simple kinetic model, including a first-order catalyst deactivation rate, was applied to the upgrading of coal-derived feedstocks prepared from two solvent-refined coal fractions. A catalyst deactivation mechanism was proposed which involves the adsorption and surface reaction of coke precursors on active catalytic sites. The effect of feedstock composition, temperature, and pressure on kinetic parameters and, in particular, the catalyst deactivation rate, was determined.

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SUMMARY

In related past works, the effects of liquid feed vaporization on hydrotreater performance during coal liquefaction were investigated. It was found that liquid vaporization significantly affects hydrotreater performance during coal liquefaction. As a result of this finding, it was thought that liquid vaporization may also affect catalyst deactivation. Thus, the study of deactivation of hydrotreating catalysts was pursued.

The deactivation of hydrotreating catalysts in the presence of coal liquids, during liquefaction, is a complex phenomenon due to the existence of a wide variety of components in the feedstock. Several mechanisms can contribute to catalyst deactivation. These include fouling, poisoning, sintering, and loss of sulfur from the catalyst. Pore plugging can prevent the diffusion of reactants into the catalyst pores and hence, drastically reduce the rate of reaction.

A simple first-order, irreversible, series model was applied to the initial deactivation of catalyst in the upgrading of coal liquefaction products. The activity of the catalyst was incorporated into the rate expressions. An expression for the activity decline was derived by assuming that the initial deactivation occurs due to coke formation by the condensation of coke precursors present in the liquefaction products.

In addition to the development of a kinetic model, the effects of

feedstock characteristics, reaction temperature, and hydrogen partial pressure on the model parameters, particularly on the deactivation rate, were examined.

Two fractions of feedstock from the solvent refined coal (SRC) process were examined: a heavy fraction labelled SRC, and a light fraction labelled LSRC. Deactivation rate was found to be higher for the heavier fraction (consisting predominantly of preasphaltenes and insoluble organic matter) than for the lighter fraction (consisting predominantly of oil and asphaltenes). The higher deactivation rate for the heavier fraction was attributed to the presence of preasphaltenes.

The model appeared to satisfactorily represent the experimental data. The reliability of rate parameter estimates, with a few exceptions, was determined to be fairly good.

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NOMENCLATURE

a	= catalyst activity
A	= concentration of asphaltenes, wt. %
A_i	= i th reactant
$A_{i\ell}$	= species A_i in adsorbed state
B_i	= i th product
$B_{i\ell}$	= species B_i in adsorbed state
C	= coke
C_{A_i}	= concentration of species A_i in bulk phase, moles/cc
$C_{A_{i\ell}}$	= concentration of adsorbed species $A_{i\ell}$, moles/cc of catalyst
C_{B_i}	= concentration of species B_i in bulk phase, moles/cc
$C_{B_{i\ell}}$	= concentration of adsorbed species $B_{i\ell}$, moles/cc of catalyst
C_C	= coke concentration on catalyst surface, moles/cc of catalyst
C_ℓ	= concentration of vacant active sites, moles/cc of catalyst
C_p	= concentration of coke precursor in bulk phase, moles/cc
$C_{p\ell}$	= concentration of adsorbed coke precursor, moles/cc of catalyst
C_t	= concentration of vacant active sites on fresh catalysts, moles/cc of catalyst
G	= concentration of gases, wt. %
IOM	= concentration of insoluble organic matter, wt. %
k_1, k_2, k_3 k_4, k_n	= pseudo first order rate constant, hr^{-1}
k_{A_i}, k'_{A_i}	= adsorption and desorption rate constants, respectively, for species A_i
k_d	= deactivation rate constant, hr^{-1}

k_{dB_i}, k'_{dB_i}	= desorption and adsorption rate constants, respectively, for species B_i
k_p, k'_p	= adsorption and desorption rate constants, respectively, for coke precursor
k_{sA_i}, k'_{sA_i}	= intrinsic rate constants for forward and reverse reactions, respectively, of species A_i
k_{sp}	= intrinsic rate constant for coke formation reaction
ℓ	= vacant active site
m, n, p	= stoichiometric coefficient
O	= concentration of oil, wt. %
P	= coke precursor
$P\ell$	= coke precursor in adsorbed state
PA	= concentration of preasphaltenes, wt. %
r_A	= reaction rate of species A
$(r_A)_0$	= reaction rate of species A with fresh catalyst
r_{aA_i}	= rate of adsorption of species A_i
r_{aP}	= rate of adsorption of coke precursor
r_{dB_i}	= rate of desorption of species B_i
r_{sA_i}	= rate of surface reaction of species A_i
R_k	= ratio of 95% confidence interval to the estimate of the parameter
r_{sp}	= intrinsic rate of coke formation
T	= absolute temperature

Greek symbols

β	= catalyst loading
σ_E^2	= variance of experimental error
$\sigma_{E\ell}^2$	= lower limit on σ_E^2
σ_{Eu}^2	= upper limit on σ_E^2
σ_k^2	= variance of the estimate of the rate parameter

1. Introduction

Several processes have been developed over the past few decades for the conversion of coal to clean solid and liquid fuels. Hydrotreatment involving catalytic hydrogenation and hydrocracking of the heavy coal liquids using a hydrogen rich gas is generally utilized to upgrade the primary coal liquids. The activity of the catalysts used in the hydrotreating step generally diminishes with time and hence the product quality as measured, for example, by degree of asphaltene conversion to oil, or heteroatom removal, deteriorates. Over a limited period, this decline in catalytic activity can be offset by operating the unit at higher severity; however, the spent catalyst must eventually be replaced or regenerated. The cost of commercial hydrotreating catalysts has escalated significantly over the past few years and the economic feasibility of hydrotreating processes is affected by the life of the catalyst. In addition to this, a knowledge of the rate of catalyst deactivation is essential for the design of the hydrotreater and for estimating the process severity-time relationship required to achieve a constant conversion of reactants to products. The objective of this work was to examine the initial rapid deactivation of hydrotreating catalysts in upgrading coal liquids in light of the kinetics of the upgrading process. A mechanism for the deactivation was proposed and rate parameters in the deactivation rate model were related to feed properties and processing conditions.

Deactivation of hydrotreating catalysts in the presence of coal liquids is a very complex phenomenon due to the existence of a wide variety of components in the feedstock. A hydrotreating catalyst can suffer deactivation by many mechanisms including fouling, poisoning, sintering, and loss of sulfur from the catalyst. In addition, pore-plugging can reduce the intraparticle

diffusion of reactants into the catalyst pores and hence reduce the rate of reaction. The exact mechanism causing the deactivation may vary depending on the catalyst age. Sie (19) observed three distinct stages of deactivation in a study of hydrodesulfurization of a residual feedstock. A rapid decline in activity was observed during the initial and final stages and a gradual decline in activity was observed during the intermediate stage. The rapid initial activity decline was attributed to carbon deposition, while the slow decline was attributed to poisoning by metals such as vanadium and nickel.

Stiegel et al. (20) studied catalyst deactivation during coal liquefaction. They observed that the deposition of coke on the catalyst is rapid within the first few hours of processing and contributes to the initial decline in activity. Their results indicated that metal deposition is the major cause of longterm catalyst deactivation. Ocampo et al. (12) reported rapid and severe decline in the hydrogenation activity of hydrotreating catalysts in batch coal liquefaction experiments within the first few hours of processing. Mitchell (9) compared the hydrogenation and hydrocracking activities of fresh and deactivated catalysts and observed that both declined significantly after deactivation and that the hydrocracking activity declined more rapidly than the hydrogenation activity. Furimsky (6) observed significant quantities of coke formed on catalysts during hydrotreatment of bitumen and heavy gas oil in the initial period of processing.

The mechanism of coke formation on hydrotreating catalysts is complex and not well understood. Beuther et al. (2) proposed that the mechanism of coking was similar to the phenomenon of mesophase formation in carbonization of aromatic liquids except that the smaller mesophase crystals were converted rapidly to coke before they coalesced to form larger crystals. In its simplest form, coke formation on the catalyst can be viewed to result from the

adsorption of coke precursors on the active sites with subsequent participation in degradation reactions such as condensation, dehydrogenation, and polymerization, to form high molecular weight species (4). This mechanism is similar to that presented by Appleby et al. (1) in catalytic cracking of aromatic hydrocarbons and by Ruderhausen and Watson (15) in aromatization of cyclohexane.

The above studies indicate that rapid deactivation of hydrotreating catalyst during the initial period usually is attributed to formation of carbonaceous deposits (coke). Despite this, the majority of the kinetic studies on catalytic coal liquefaction and hydrotreating of coal liquids assume that the catalyst activity is constant throughout the course of the reaction. Only a few kinetic studies of coal liquefaction and coal liquids upgrading have taken into account the deactivation of the catalyst. Using petroleum materials, Weekman et al. (21) presented a model coupling the kinetics for catalyst decay with the conversion kinetics for the catalytic cracking of gas oil. Subsequently, Nace et al. (11) applied this model to study the effect of the properties of feedstocks and process conditions on gas-oil conversion, gasoline selectivities, and catalyst deactivation.

For the design, operation, and optimization of a hydrotreater in a coal liquefaction process, the kinetics of the major reactions as well as of catalyst deactivation require a better understanding. It may be postulated that the rate of the main reaction, in the presence of deactivation, may be expressed as $[r_A = (r_A)_0 \alpha]$ where α is the activity according to Khang and Levinspiel (8) and $(r_A)_0$ is the reaction rate with fresh catalyst.

2. Kinetic Modelling

Introduction

In this work the kinetics of the upgrading of two fractions from the solvent refined coal (SRC) process were represented by a simple first-order, irreversible, series model with the reaction components being identified according to a solubility scheme. Thus, the reactions involved in the upgrading process were represented as

This first order irreversible scheme is only one of many models which could be proposed to represent the upgrading process (7,18). Many of these proposed models lead to simultaneous series and parallel reaction pathways; however, it is sometimes difficult to determine the one "best" model by regression analysis alone (3). In any event, the methodology outlined in this work could be adapted to any of the several models proposed in the literature, if desired. Roughly speaking, as the reactions proceed to the right, the components have lower viscosities, lower molecular weights, fewer heteroatoms, and are less aromatic. The exact definition of the components according to solubility classification is given in the experimental section. To represent the decline in catalyst activity an activity function was coupled with the main reaction kinetics according to the method of Khang and Levenspiel (8). With this methodology the activation energies and the frequency factors for the model parameters were determined using two coal-derived feedstocks. In addition to the development of a kinetic model, the effects of feedstock characteristics, reaction temperature, and hydrogen partial pressure on the model parameters, particularly on the deactivation rate, were examined in this work.

Deactivation Mechanism

In this section a possible mechanism for catalyst deactivation is proposed. Because of the large number of unknown parameters, a rigorous solution of the model was not performed and the quasi-steady state approximation was used to obtain an approximate solution for the activity.

Consider the main reactions:

followed by the coking reaction

where A_i , B_i , P and C represent the i^{th} reactant, i^{th} product, coke precursor, and coke, respectively.

Assuming that the mechanism for the main reactions involves adsorption of reactant on vacant active sites represented by ℓ , surface reaction of adsorbed species, and desorption of product, the individual steps can be represented as

Similarly the mechanism for the coking reaction can be represented as sorption of coke precursor followed by irreversible surface reaction of adsorbed species to form coke;

The surface reactions can be condensation and dehydrogenation; or polymerization reactions.

The rate expressions for the various steps represented by equations (3) to (7) can be written as:

$$r_{aA_i} = k_{A_i} C_{A_i} C_\ell - k'_{A_i} C_{A_i} \ell \quad (8)$$

$$r_{sA_i} = k_{sA_i} C_{A_i}^m \ell - k'_{sA_i} C_{B_i}^n C_\ell^{(m-n)} \quad (9)$$

$$r_{dB_i} = k_{dB_i} C_{B_i}^n \ell - k'_{dB_i} C_{B_i}^n C_\ell \quad (10)$$

$$r_{aP} = k_p C_p C_\ell - k'_p C_p \ell \quad (11)$$

$$r_{sP} = k_{sP} C_p^P \ell \quad (12)$$

The rates of change of various species are

$$\frac{1}{\beta} \frac{dC_{A_i}}{dt} = - r_{aA_i} \quad (13)$$

$$\frac{dC_{A_i} \ell}{dt} = r_{aA_i} - r_{sA_i} \quad (14)$$

$$\frac{dC_{B_i} \ell}{dt} = \frac{n}{m} r_{sA_i} - r_{dB_i} \quad (15)$$

$$\frac{1}{\beta} \frac{dC_{B_i}}{dt} = r_{dB_i} \quad (16)$$

$$\frac{1}{\beta} \frac{dC_P}{dt} = -r_{aP} \quad (17)$$

$$\frac{dC_{P\ell}}{dt} = r_{aP} - r_{sP} \quad (18)$$

$$\frac{dC_C}{dt} = \frac{1}{p} r_{sP} \quad (19)$$

where β is the catalyst loading. In writing equations (6) and (7) the assumption was made that the same active sites are involved for the main reactions as well as the coking reaction.

The site balance equation can be written as

$$C_t = C_\ell + pC_C + \sum_{i=1}^N C_{A_i\ell} + \sum_{i=1}^N C_{B_i\ell} + C_{P\ell} \quad (20)$$

The exact transient solution for the concentrations C_{A_i} , C_{B_i} , C_P , $C_{A_i\ell}$, $C_{B_i\ell}$, $C_{P\ell}$, C_C , and C_ℓ can be obtained by solving equations (13) to (20) along with appropriate initial conditions. To simplify matters, the steady-state approximation was made for the surface species such that

$$\frac{dC_{A_i\ell}}{dt} = \frac{dC_{B_i\ell}}{dt} = \frac{dC_{P\ell}}{dt} = 0 \quad (21)$$

Equations (20) and (21) taken together imply that

$$\frac{-dC_\ell}{dt} = p \frac{dC_C}{dt} \quad (22)$$

So that upon integration one obtains

$$C_t = pC_c + C_\ell \quad (23)$$

Eq (23) is a necessary consequence of the quasi-steady state assumption since for its validity one must have small concentrations of the adsorbed species, $C_{A_i\ell}$, $C_{B_i\ell}$, and $C_{P\ell}$.

Catalyst activity is defined here as the fraction of total sites not covered by coke.

$$a = \frac{C_t - pC_c}{C_t} = \frac{C_\ell}{C_t} \quad (24)$$

Differentiating equation (24) with respect to time and substituting equations (12) and (19) yields

$$-\frac{da}{dt} = \frac{1}{C_t} k_{sp} C_{P\ell}^p \quad (25)$$

The unknown concentration of adsorbed coke precursor may be obtained by using equations (11), (12), and (18), and the steady-state approximation to obtain

$$k_p C_p C_\ell - k_p' C_{P\ell} - k_{sp} C_{P\ell}^p = 0 \quad (26)$$

The activity as a function of time may be obtained by simultaneous solution of eqs (17), (24), (25) and (26). At this point a further approximation was made by assuming that the coke precursor adsorption is fast compared to the coking surface reaction (14). Mathematically, this means that

$k_p \gg k_p, k_{sp}$ in eq (26) and that $C_{p\ell} = K_p C_p C_\ell$ where K_p is the relevant adsorption equilibrium constant. Under these conditions eq (25) becomes

$$\frac{-da}{dt} = k_{sp} K_p^p C_t^{p-1} C_p^p a^p \quad (27)$$

The coke precursor concentration was assumed to remain roughly constant for a given feed and thus eq (27) is represented as

$$\frac{-da}{dt} = k_d a^p \quad (28)$$

with $k_d = K_p^p k_{sp} C_t^{p-1} C_p^p$. As a concession to reduce the number of model parameters it was assumed that first-order deactivation occurs.

The development presented above shows that the deactivation rate constant is a function of the concentration and adsorptivity of the coke precursor. In the case of complex coal liquids such as those examined in this work, the reactants and products for the main reactions were taken to be soluble fractions each containing an essentially infinite number of individual compounds. It is likely that coke precursors are present in all of these classes, although not necessarily to the same extent. Strictly speaking, then, C_p would not be a constant since the compound classes are functions of time; however, since the precursor species are unknown at this time, a general model incorporating this time dependence would not be useful. Thus, in the following application to coal liquids C_p was assumed to be constant at some average value, which, as demonstrated herein, would be representative of the coke precursor concentration

in a given feed material. The k_d factor for a given feed material would reflect the average coke precursor concentration for that particular feed and also give an indication of the coke forming propensity and processability of the particular feed under consideration. In the experimental work discussed in the following section, two different coal-derived feed materials were considered with regard to deactivation behavior.

3. Experimental

Equipment

The experiments were conducted in a microreactor constructed of 316 stainless steel tubing, 3/4 inch O.D. with a 0.065 inch wall thickness and a volume of 46 cc (5). This volume provides under normal operating conditions, at least 100% excess hydrogen for the upgrading reactions. The reactor was sealed at one end with a swagelok cap, charged with reactants, and closed with a gas connection assembly consisting of a metering valve, 1/4 inch tubing, and reducing unions. Hydrogen gas was introduced into the tubing bomb through the metering valve.

Reaction temperature was maintained by immersing the tubing bomb in a fluidized sand bath equipped with a Techne TC 40 temperature controller. The tubing bomb was agitated at 360 rpm, with 1-1/2 inch vertical stroke by means of a variable speed motor equipped with crank shaft, bushing, couplings and extension rods.

Materials

The solvent used for preparing the feed blends was a Koppers heavy residue creosote oil, hydrogenated to 8.0 wt.% hydrogen. Two different materials from SRC pilot plants were utilized to prepare two feedstocks by blending each material with the solvent at a level of 50 wt. percent. One material, labeled SRC, was a shiny black solid prepared from Kentucky #9 coal processed at the Ft. Lewis, Washington, SRC pilot plant. The second material, a lighter fraction of SRC, labeled LSRC, was produced as a stream from the critical solvent deashing process at the Wilsonville, Alabama, SRC pilot plant using Kentucky #9/14 coal (13). The properties of these two materials and the solvent are given in Table I. Both materials, SRC and LSRC, were ground to -200 mesh for preparation of the feed blends. The product distributions for the feed

TABLE I
Analyses of Solvent and SRC Materials

	Solvent	LSRC	SRC
Elemental content, wt.%			
Carbon	91.48	84.0	87
Hydrogen	8.01	6.58	6.2
Oxygen	<0.5	--	--
Nitrogen	0.29	1.8	2.1
Sulfur	0.03	--	--
Ash, %		Trace	0.6
Distillation, °F			
277	0.0		
336	0.4		
396	1.4		
435	2.3		
464	3.3		
500	6.3		
583	21.6		
648	25.9		
675	35.8		
747	64.0		
820	100.0		

materials are given in Table II. It is worth noting that LSRC is, as its name implies, a less residual material than SRC, being comprised largely of oil and asphaltenes, whereas, the SRC is comprised mainly of preasphaltenes and ICM.

The catalyst used in the upgrading experiments was Shell 324, a nickel molybdenum catalyst, supported on Al_2O_3 . Prior to loading, the catalyst was ground to -325 mesh and presulfided with 10% H_2S in H_2 at 400 C for 2 hours. The sulfur content of the presulfided catalyst was approximately 10 wt. %. The following chemicals were used as received: benzene (Fisher, ACS certified), pentane (Aldrich, 99%), methylene chloride and methanol (Fisher, ACS certified).

Procedure

In a typical experiment, the tubing bomb was charged with a uniform mixture of 4.5 g of SRC or LSRC, 4.5 g of solvent, and 1 g of powdered catalyst. Two 3/16 inch diameter steel balls were placed in the reactor to aid in mixing and to negate mass transfer phenomena. The reactor was tested and then charged with 1250 psig hydrogen at ambient temperature.

After charging with hydrogen, the tubing bomb was attached to the vertical shaft on the agitation assembly, agitated at ambient temperature for 5 minutes at 660 rpm, and submerged into the preheated fluidized sand bath. The heat-up time was about 1 minute. At the end of the specified reaction, the tubing bomb was removed from the sand bath, immediately quenched in tap water, and checked for any leaks. The gases were collected in a gas sampling bag and the volume determined from water displacement. Gases were analyzed using a Varian 1800 gas chromatograph for C_1 - C_5 gases and for hydrogen. The slurry products were collected in a beaker, and the product distribution was determined according to a standard solvent separation scheme (5). The slurry

TABLE II
Product Distributions of Feed Materials

Fraction, wt. %	Solvent	LSRC	SRC
Oil	99.5	53.7	0.6
Asphaltenes	0.5	24.7	1.6
Preasphaltenes	0.0	18.0	69.9
IOM	0.0	3.6	27.9

products were separated into four fractions, namely, (1) oils--pentane solubles, (2) asphaltenes--pentane insolubles and benzene solubles, (3) preasphaltenes--insoluble in pentane and benzene, soluble in a solution of 90 vol % methylene chloride/10 vol % methanol, and (4) IOM--insoluble in pentane, benzene and 90 vol % methylene chloride/10 vol % methanol. The data were then used to determine the normalized product distribution as weight % oils, preasphaltenes, asphaltenes, gases and insoluble organic matter.

Upgrading Kinetics

As noted in the above section, coal-derived products may be separated via a solubility scheme into various classes of compounds, viz. oils (O), asphaltenes (A), preasphaltenes (P), and insoluble organic matter (IOM). These classes are listed in the general order of increasing molecular weight, viscosity, and heteroatom content. It was also noted that this lumping procedure, while leaving much to be desired, has nonetheless received wide application in coal liquefaction kinetic studies and a variety of kinetic models have been proposed. For the first-order irreversible kinetic model used in this work, the associated set of rate equations in matrix form, including the deactivation function, is given by

$$\frac{d}{dt} \begin{bmatrix} \text{IOM} \\ \text{PA} \\ \text{A} \\ \text{O} \\ \text{G} \\ \alpha \end{bmatrix} = (a) \begin{bmatrix} -k_1 & 0 & 0 & 0 & 0 & 0 \\ k_1 & -k_2 & 0 & 0 & 0 & 0 \\ 0 & k_2 & -k_3 & 0 & 0 & 0 \\ 0 & 0 & k_3 & -k_4 & 0 & 0 \\ 0 & 0 & 0 & k_4 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -k_d \end{bmatrix} \begin{bmatrix} \text{IOM} \\ \text{PA} \\ \text{A} \\ \text{O} \\ \text{G} \\ 1 \end{bmatrix} \quad (29)$$

The initial conditions for the set of equations represented by the above matrix are given as the composition of the feedstocks, presented in Table II, together with the condition that $\alpha = 1$ at $t = 0$. The coal derived product commonly termed solvent refined coal, typically contains various amounts of the first four species in the kinetic schemes as shown in Table II.

Parameter Estimation

The rate parameters, k_1 , k_2 , k_3 , k_4 , and k_d were estimated using algorithms for parameter estimation using differential equations. Two different algorithms were used in this work based on the methods of steepest descent and quasilinearization (17); both methods gave the same solution. These are iterative procedures which start with initial trial values. Iterations were carried out until the correction required for each parameter was less than 0.05% of the value obtained in the previous iteration. The parameter estimation methods do not guarantee convergence to the global minimum. In other words, the optimal parameter estimates obtained from these methods are the most probable estimates and they are neither unique nor global. Initial values for the parameters, k_n , taken from different regions of the convergent vector space were used to test whether the search routine would converge to the same solution. This was done to assure that at least the solution of parameter values represented a local minimum. Another caution to be used with these methods is that a good fit of the kinetic model to the experimental measurements of concentration-time profiles does not verify the validity of the proposed model because a good fit can always be obtained by introducing a sufficiently large number of parameters into the model.

Reliability of the Parameter Estimates

The result of parameter estimation is an estimate of the true value of the parameter which is, of course, unknown. A measure of the accuracy of the estimate is usually given by its standard deviation. The reliability of the experimental conversion values was tested by obtaining triplicates for one set of conversion values (425 C, SRC, 1250 psig, 5 min.) and computing the standard deviation. The standard deviations were less than 2%. To provide a measure of the reliability of the rate parameter estimates, the procedure recommended by Seinfeld and Gavalas (16) was used. This involved assuming a normal distribution for the uncertainty in the experimental conversion values, with the normal distribution having a zero mean, and the variance σ_E^2 . First, since exact values for σ_E^2 are not known, a lower limit of $\sigma_{E_L}^2 = 1\%$ and an upper limit of $\sigma_{E_U}^2 = 3\%$ were assumed. An expression presented by Seinfeld and Gavalas (16) was used to estimate the standard deviation for each rate parameter ($\sigma_{k_i}^2$, for k_1 's and k_d), based on the lower limit, $\sigma_{E_L}^2$, and the upper limit estimate, $\sigma_{E_U}^2$. The ratio of the 95% confidence interval for each rate parameter to the estimated value of the parameter, R_k , was computed. This ratio (R_k) provides a relative indication of the reliability of the estimated value for the rate parameter. For example, the R_k values for k_4 are higher than those of any other rate parameter (k_1, k_2, k_3, k_d) at 375 C. This implies that the reliability of the estimate for k_4 at this temperature is lower than those for the other parameters.

The overall goodness of the fit is indicated by the sum of squares of the error, i.e., the sum of squares of the deviation between the predicted and the experimental values. The sums of the squares of the errors were computed and listed in the appropriate tables for all sets of estimates of the rate parameters.

4. Results and Discussion

Experiments were carried out at three different temperatures (375 C, 425 C, 475 C), two different pressures (1250 and 500 psig), and using two different feedstocks prepared with LSRC or SRC. Reaction conditions and product distributions for each set are given in Table III. Triplicates were obtained for one run (425 C, with SRC as the feedstock) at a reaction time of 5 minutes to determine the experimental reproducibility. A standard deviation of less than ± 2 wt. % was obtained for each product fraction. It should be noted, however, that the experimental error might be higher than ± 2 wt. % at longer reaction times because volatile losses were may be greater during product separation.

The experimental data and fitted curves are presented in Figures 1-5. Rapid oil formation occurred in the first five to ten minutes of reaction. Generally, a maximum was observed in asphaltene concentration at a reaction time of less than ten minutes, and this maximum appeared at shorter reaction times with increasing temperature. This observation is consistent with the assumption that the asphaltene fraction is an intermediate product. At 475 C the weight percentage of oils and of asphaltenes remained nearly constant after about fifteen minutes of reaction. It is worth noting that the maximum yield of oils from the SRC feedstock was only about 55%.

Effect of Temperature:

Experiments were performed at three temperature levels -- 375 C, 425 C, and 475 C -- to determine the effect of temperature on the conversion rate parameters, k_n , and the deactivation rate parameter, k_d (equation 29). The rate parameters determined from least squares analysis are given in Table IV. An examination of the sums of squares of the errors in Table IV shows that the model predicts the product distributions satisfactorily at all reaction

TABLE III
Summary of Product Distributions

Feed Stock	Temperature, C	Pressure, psig	Time, min.	IOM, %	Preasphal- tenes, %	Asphal- tenes, %	Oil, %	Gases, %
SRC	375	1250	0	12.3	20.1	19.8	47.8	
			5	9.7	17.4	22.8	50.0	0.1
			10	9.0	17.5	22.4	51.0	0.1
			15	7.6	17.0	23.8	51.2	0.4
			30	6.0	13.7	26.2	53.6	0.5
			45	4.7	10.6	28.5	55.6	0.6
			60	3.2	10.0	28.0	57.9	0.9
			90	2.0	6.2	27.4	63.2	1.2
SRC	425	1250	0	12.3	20.1	19.8	47.8	
			5	3.2	12.1	26.0	57.7	1.0
			5	3.5	14.1	24.7	56.8	0.9
			5	3.4	12.4	26.5	56.5	1.2
			10	3.6	10.5	28.1	57.4	0.4
			15	2.2	8.0	29.6	58.2	2.0
			30	0.8	3.8	26.7	65.5	3.2
			41	0.5	3.4	24.5	68.1	3.5
			60	0.3	2.0	19.3	74.9	3.5
			90	0.1	1.9	17.4	76.5	4.1
SRC	475	1250	0	12.3	20.1	19.8	47.8	
			5	2.8	4.3	22.9	65.0	5.0
			10	2.3	3.0	17.3	71.1	6.3
			15	2.0	2.5	16.3	72.2	7.0
			30	1.8	2.3	13.8	74.3	7.8
			45	1.3	1.9	12.6	74.9	9.3
			60	0.8	1.4	10.5	75.0	12.3
			90	0.4	1.0	9.9	74.0	14.7
LSRC	425	1250	0	1.8	9.0	12.6	76.6	
			5	1.4	3.5	16.0	79.0	0.1
			10	1.1	1.5	14.9	82.3	0.2
			15	0.9	0.8	12.7	85.2	0.4
			30	0.4	0.2	7.2	91.6	0.6
			45	0.2	0.1	4.3	94.3	1.1
			60	0.1	0.1	2.8	95.7	1.3
			90	0.1	0.1	1.5	96.3	2.0
SRC	425	500	0	12.3	20.1	19.8	47.8	
			5	6.8	13.6	25.8	53.5	0.3
			10	5.7	9.8	27.7	56.3	0.5
			15	5.1	8.6	27.5	58.1	0.7
			45	4.0	7.2	27.0	61.0	0.8
			90	3.3	6.1	26.4	63.2	1.0

Figure 1

Experimental and Fitted Product Distribution With SRC Based Feed At 375 C and 1250 psig.

Figure 2

Experimental and Fitted Product Distribution With SRC Based Feed At 425 C and 1250 psig

Figure 3

Experimental and Fitted Product Distribution With SRC Based Feed At 475 C

Figure 4

Experimental and Fitted Product Distribution With LSRC Based Feed At 425 C

Figure 5

Experimental and Fitted Product Distribution With SRC Based Feed At 500 PSIG and 425 C

TABLE IV

A Comparison of the Rate Constants for Three
Different Reaction Temperatures

Temperature C	Rate Parameter hr ⁻¹	Sum of Square of error (b)	Variance		95% Confidence interval		Ratio of (d) to (a), R _K	
			$\sigma_{E\ell}^2 = 1\%$ Lower Limit	σ_K^2 Upper Limit (c)	$\sigma_{Eu}^2 = 3\%$ Lower Limit	$1.96\sigma_K$ Upper Limit (d)	$\sigma_{E\ell}^2 = 1\%$ Lower Limit	$\sigma_{Eu}^2 = 3\%$ Upper Limit (e)
25	375	15.3						
	k ₁ 1.5		0.019	0.0558	0.267	0.463	18	31
	k ₂ 1.554		0.004	0.0119	0.123	0.214	8	14
	k ₃ 0.504		0.0004	0.0013	0.041	0.071	8	14
	k ₄ 0.018		0.0001	0.0004	0.022	0.038	122	212
	k _d 0.312		0.0039	0.0117	0.122	0.212	39	68
	425	58.5						
	k ₁ 8.364		0.7	2.097	1.64	2.839	20	34
	k ₂ 8.082		0.108	0.324	0.644	1.116	8	14
	k ₃ 2.442		0.0024	0.007	0.095	0.165	4	7
	k ₄ 0.15		0.0003	0.001	0.036	0.063	24	42
	k _d 1.71		0.0031	0.009	0.109	0.190	6	11
	475	21.5						
	k ₁ 17.676		2.922	8.765	3.35	5.8	19	33
	k ₂ 33.21		4.985	15.0	4.38	7.58	13	23
	k ₃ 13.218		0.064	0.191	0.50	0.86	4	7
	k ₄ 1.194		0.003	0.009	0.107	0.19	9	16
	k _d 6.864		0.03	0.09	0.34	0.589	5	9

temperatures. Generally, there was a low reliability for estimates of parameters k_1 and k_4 , as indicated by the 95% confidence intervals and the R_k values. The R_k values for k_1 , k_4 , and k_d are high at 375°C, indicating a low level of reliability for these parameters at this temperature.

The deactivation rate constant, k_d , increases with temperature in the same manner as the kinetic rate constants, k_i . Arrhenius plots for the rate constants are presented in Figure 6. The activation energies and the frequency factors are given in Table V. A satisfactory fit was obtained as indicated by the R-square values being nearly one, and the standard error in the activation energy being small. The standard errors for the frequency factor are high, varying from 5% to as much as 95%. Generally, a very poor fit was obtained for k_1 with respect to both product distribution and the Arrhenius plot. The activation energy was nearly the same, of the order of 30 kcal/mole, for all the reactions including the deactivation reaction, indicating that significant mass transfer resistances probably do not exist under the conditions studied. Since the activation energy for the deactivation step is of the same order of magnitude as that of the main reactions, increasing the reaction temperature to increase the rate of the conversion reactions, eqns (29), would also result in an increase in the rate of deactivation. Thus, little benefit would be derived from a temperature increase, considering the overall effects of catalyst deactivation.

Effect of Pressure

Kinetic data were obtained at two levels of pressure, 1250 psig and 500 psig, to examine the effect of pressure on the conversion rate constants, k_i , and the deactivation rate parameter, k_d . In the models developed herein, the effect of hydrogen pressure has been incorporated implicitly into the rate constants. Intuitively it is expected that a decrease in hydrogen pressure

TABLE V
Activation Energies and Frequency Factors

Rate Parameter	R-Square, lnk vs 1/T	Activation Energy, Cal./Mole Estimate	Standard Error	Frequency Factor, hr ⁻¹ Estimate/Standard Error
k ₁	0.9673	24096	4432	2.0124x10 ⁸ /1.93x10 ⁸
k ₂	1.000	29687	91	1.383x10 ¹⁰ /0.088x10 ¹⁰
k ₃	0.9963	31589	1926	1.8397x10 ¹⁰ /1.38x10 ¹⁰
k ₄	0.9994	41373	972	1.2622x10 ¹² /0.634x10 ¹²
k _d	0.9997	29986	502	3.5358x10 ⁹ /1.07x10 ⁹

Figure 6

Arrhenius Plot of Rate Constants

would cause an increase in the rate of condensation over that of hydrogenation. Hence, more coke formation would be expected with a lower hydrogen pressure. Thus, it is expected that a decrease in hydrogen pressure would be reflected in an increase in the deactivation rate constant, k_d .

Experimental and calculated product distributions are given in Figure 2 and 5 using the rate parameters in Table VI. The agreement between model product concentrations and experimentally determined values is satisfactory as indicated by the low values for the sum of squares of the error. The reliability of estimates for parameters was reasonably good for all rate parameters except for k_4 , for which the reliability was generally poor. The main conversion reactions, as expected, were affected by a decrease in pressure. The values for k_1 and k_4 were lower at 500 psig than those at 1250 psig initial H_2 pressure. Conversely, the values for k_2 and k_3 were slightly higher at 500 psig than those at 1250 psig. The reasons for this behavior are unknown. The reliability of estimates for parameters is reasonably good for all rate parameters, except for k_4 . The most significant point is that k_d was increased by a factor of 3 when the hydrogen pressure was reduced by a factor of 2.5. This result suggests an inverse relationship between k_d and the hydrogen pressure. This supports current practice in the petroleum industry where high hydrogen pressures are used to reduce catalyst deactivation rates.

Effect of Feedstock

Experiments were performed to investigate the effect of feedstock composition, particularly the level of preasphaltenes concentration, on conversion rate parameters, k_n , and the deactivation rate parameter, k_d . A comparison of the rate parameters obtained with each feedstock is given in Table VII. Experimental and fitted product distributions with the LSRC feedstock are plotted in Figure 4. Based on the low values for the sum of

TABLE VI

A Comparison of the Rate Constants for Two Different
Initial Hydrogen Pressures

Temperature C	Rate Parameter hr ⁻¹ (a)	Sum of Square of error (b)	Variance		95% Confidence interval		Ratio of (d) to (a), R _K				
			$\sigma_{El}^2=1\%$	σ_K^2	$\sigma_{Eu}^2=3\%$	$\sigma_{El}^2=1\%$	$1.96\sigma_K$	$\sigma_{Eu}^2=3\%$	$\sigma_{El}^2=1\%$	R_K	$\sigma_{Eu}^2=3\%$
			Lower Limit	Upper Limit	Lower Limit	Upper Limit	Lower Limit	Upper Limit	Lower Limit	Upper Limit	
			(c)		(d)		(e)				
1250		58.5									
	k ₁	8.364	0.7	2.097	1.64	2.839	20	34			
	k ₂	8.082	0.108	0.324	0.644	1.116	8	14			
	k ₃	2.442	0.0024	0.007	0.095	0.165	4	7			
	k ₄	0.15	0.0003	0.001	0.036	0.065	24	42			
	k _d	1.71	0.0031	0.009	0.109	0.190	6	11			
500		7.3									
	k ₁	6.873	0.353	1.06	1.164	2.02	17	29			
	k ₂	9.888	0.163	0.49	0.792	1.37	8	14			
	k ₃	3.137	0.012	0.036	0.215	0.37	7	12			
	k ₄	0.083	0.003	0.01	0.113	0.20	136	241			
	k _d	5.040	0.042	0.124	0.4	0.69	8	14			

TABLE VII

A Comparison of the Rate Constants for the
Two SRC Feedstocks

Temperature C	Rate Parameter hr ⁻¹	Sum of Square of error	Variance		95% Confidence interval		Ratio of (d) to (a),	
			$\sigma_{El}^2=1\%$	σ_K^2	$\sigma_{Eu}^2=3\%$	$1.96\sigma_K$	$\sigma_{El}^2=3\%$	R_K
			Lower Limit	Upper Limit	Lower Limit	Upper Limit	Lower Limit	Upper Limit
	(a)	(b)	(c)		(d)		(e)	
<hr/>								
SRC		58.5						
	k ₁	8.364	0.7	2.097	1.64	2.839	20	34
	k ₂	8.082	0.108	0.324	0.644	1.116	8	14
	k ₃	2.442	0.0024	0.007	0.095	0.165	4	7
	k ₄	0.15	0.0003	0.001	0.036	0.065	24	42
	k _d	1.17	0.0031	0.009	0.109	0.190	6	11
<hr/>								
LSRC		2.1						
	k ₁	3.237	4.600	13.8	4.203	7.28	130	225
	k ₂	12.567	4.802	14.4	4.295	7.44	34	59
	k ₃	2.622	0.014	0.043	0.235	0.41	9	16
	k ₄	0.020	0.00004	0.0001	0.012	0.021	60	103
	k _d	0.244	0.022	0.066	0.19	0.503	119	206

squares of the error shown in Table VII and the excellent agreement in the plots shown in Figure 4, a satisfactory fit was obtained. Apparently, k_3 (conversion of asphaltenes to oil) is essentially the same with both feedstocks, whereas k_2 is greater by a factor of 1.5 with LSRC than with SRC. This higher value for k_2 might be due to the difference in the reactivities of the preasphaltenes present in the two feedstocks. It should be noted, however, that the reliability of the k_2 value for LSRC is low; thus, the significance of the difference in k_2 values becomes questionable. The lower value of k_4 for LSRC indicates a lower rate of gas production. The IOM in LSRC would seem to be less reactive than that in SRC by a factor of about 2.5. It should be noted that the preasphaltene and IOM contents of LSRC are much lower than those of SRC; therefore, k_1 and k_2 have somewhat less significance for LSRC than for SRC.

The deactivation rate parameter, k_d , is higher with SRC than with LSRC by a factor of about six. The rapid formation of preasphaltenes from IOM of SRC (higher k_1 value) and the slower conversion of preasphaltenes to asphaltenes (lower k_2 value) with SRC suggest that the preasphaltenes of SRC are probably responsible for its high value of k_d . Although less deactivation was observed here with a feedstock containing a lower concentration of preasphaltenes, no definitive conclusions can be made at this stage. More data are needed, and work along these lines is being continued.

5. Conclusion

A simple kinetic model was applied to the initial deactivation of catalyst in the upgrading of coal liquefaction products by introducing the activity of the catalyst into the rate expressions. An expression for the activity decline was derived assuming the initial deactivation is due to coke formation by condensation of coke precursors present in the liquefaction products. The model appeared to represent the experimental data satisfactorily. The reliability of the estimates of the rate parameters generally appeared to be good although the reliability appeared to be low in a few cases. Care must thus be taken in applying the proposed model and in interpreting the results presented. The pseudo first-order rate constants follow the Arrhenius relation with the activation energies being equal to about 30 kcal/mole. The temperature dependency of the deactivation rate parameter also follows the classical Arrhenius relation for the conditions of the reactions used in these studies. The catalyst deactivation rate constant, k_d , increases with decreasing hydrogen pressure.

The deactivation rate constant was higher for the heavier feedstock (SRC) which contained predominantly preasphaltenes and insoluble organic matter, than for the feedstock consisting mainly of asphaltenes and oil (LSRC). It appears that high concentrations of preasphaltenes in the feedstock cause an increase in the deactivation rate.

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