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TECHNICAL PROGRESS REPORT

KINETICS OF COAL PYROLYSIS AND DEVOLATILIZATION

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SUMMARY

This report presents some recent experimental results on the effect of coal rank on the chemical characteristics of the evolved tars and some results of a modeling effort on intraparticle heat transfer.

The characterization of the tars by FTIR and elemental analysis leads to the clear conclusion that the lower the rank of the coal, the greater the chemical differences between the tar and the parent coal. These differences are particularly noticeable in comparisons of the relative aromatic/aliphatic ratio as determined by infrared analysis and in the relative hydrogen content. The hydrogen content of the tars and the aliphatic C-H as measured by FTIR at 2920 cm^{-1} both show a strong correlation with coal rank for seven different coals.

The modeling study of intraparticle heat transfer has developed new indices for quantifying extent of "isothermality". These indices are valuable for determining the extent of agreement between volume averaged pyrolysis rates and the corresponding quantity calculated using the particle surface temperature for the entire volume.

Coal Rank Effects on Tar Characteristics

Recent efforts have been directed to determining effects of changing parent coal characteristics on the nature of the tars produced. The UTRC-EF is selected because it conveniently produces enough tars for subsequent analyses whereas multiple runs are required in the heated grid and flash lamp reactors. The heating conditions that maximized the tar yield for the PSOC 1451D samples were employed -- 930°C wall temperature and 510°C peak gas temperature -- for the sake of comparison, although it is recognized that various coal types may require different conditions to maximize tar yield.

The qualitative behavior of the various coal types can be summarized as follows: the phenomenological sequence of devolatilization remains invariant with coal type, but the chemical nature and yields of tars varies significantly with chemical characteristics of the parent coal. More specifically, intra-particle tar formation and the evolution of heavy molecular weight hydrocarbons precedes significant light gas evolution. However, the lower the rank characteristics of the parent coal, the more unlike the parent coal structures are the corresponding tar species (Figure 1).

Figures 2 and 3 compare the hydrogen and sulfur + oxygen levels of the tar species to those in the parent coals for the coals of various ranks. As the rank characteristics of the parent coal increase, as indicated by the %C, the elemental composition of the tars become more like the parent coal. The hydrogen and sulfur + oxygen ratios asymptote toward unity. However, the Rocky Mountain bituminous, subbituminous and lignite coals evolve tars of very

different compositions. Figure 4 indicates that the hydrogen levels of these low rank coal tars approach 9.0% or greater. The most striking difference in the IR absorbance spectra of the low rank coal tars relative to the higher ranks resides in the polymethylene absorbance region (2920 cm^{-1}). Low rank tars display much greater absorbance levels in this region per unit mass of sample than high rank tars. Assuming absorption coefficients of this band do not vary significantly with coal rank, such behavior implies increasing concentrations of $-\text{CH}_2$ levels with decreasing coal rank. Indeed the increase in $-\text{CH}_2$ -related absorbance correlates well with the increase in %H level of the tars, Figures 5 and 6.

Although the nature of the tars varies significantly with coal type, the particle devolatilization and gas phase reaction sequences did not. Table I shows the composition of tars from a subbituminous coal (PSOC 1520D) at various reactor temperatures. As for PSOC 1451D, the tar evolution process to the point of maximum tar yield appears to follow a distillation like process, that is, the hydrogen rich, more volatile species vaporize before the heavier, less hydrogen rich tar components. As reactor gas phase temperatures rise above 700°C , significant pyrolysis reactions of tars occur. Examination of the gaseous species indicate these reactions produce large increases in C_2H_2 , HCN, CO and C_2H_4 levels. Relative increases are significantly greater than those observed in gas phase reactions of high rank coal tars. Such observations qualitatively agree with those made by Tyler, Doolan, Calkins, and Nelson (1, 2, 3, 4). These gas phase reactions result in much

greater relative decreases in the overall polymethylene levels of the collected tars (Figure 7), again as observed by others (2, 3, 4). In short, the results indicate that phenomenologically, the coal devolatilization/pyrolysis process is invariant with coal characteristics but tar yields, tar chemical composition, and gas phase pyrolysis reactions of tars vary appreciably with coal type, implying different underlying physical-chemical processes are responsible for the observables.

Intra-Particle Heat Transfer Effects in Coal Pyrolysis

The above results indicate the importance of clearly defining the particle temperature profile, irrespective of the chemical or physical nature of the process, if fundamental rate parameters are to be developed. The obvious importance of heat transfer processes during the tar formation and evolution phase in itself necessitates a comprehensive examination of coupled heat transfer and physical-chemical kinetic processes.

Despite major advances in fundamental understanding of rapid coal devolatilization in the last 15 years, there remains great need for quantitative data and mathematical models to interpret and predict how coal type, transport-kinetics coupling including intra-particle and boundary layer processes, particle swelling and agglomeration, and heating rate affect volatiles compositions and release rates and char yields and morphology. The chemical and physical complexity of "tars" (volatiles and extracts of MW >

70d), and the rapid deformation of softening coals during critical stages of devolatilization present special challenges, especially since engineering applications will be facilitated by simplified mathematics. Development and testing of responsive models and data bases for rapid devolatilization under conditions pertinent to suspension firing of pulverized coal are major program goals. Potential applications include inputs to major computer codes for design and operation of commercial coal furnaces.

The protocol for model development involves identifying contributory physico-chemical phenomena, developing or adapting models to describe each in isolation, and then constructing predictive devolatilization models by judiciously superimposing the component models, taking care to treat interaction effects. Selected experiments are performed to acquire critical data for model implementation and testing.

' Building on previous DOE-supported work, including models by Oh (5) and Fong (6), Hsu (7) has conceptualized softening coal devolatilization as volatiles driven extension of one large central bubble with simultaneous thinning and eventual perforation of a concentric bladder of foam-like metaplast (Fig. 8). Hsu's model offers promise for predicting swelling kinetics, tar release rates, and novel features of char morphology such as cenosphere development, shrinkage, and blow hole formation. A significant data base to facilitate model implementation was recently obtained in collaboration with Dr. T. Fletcher of the Combustion Research Group at Sandia

National Laboratory. Further algebraic and numerical work is required to advance this model to the testing and application stages.

Hajaligol, et al. (8) have formulated new indices for quantifying intra-particle heat transfer effects in coal devolatilization, by computing the extent of agreement between: volume averaged pyrolysis rate constant (Eq. 1) [or volume averaged pyrolysis weight loss (Eq. 2)], and the corresponding quantity calculated using the particle surface temperature for the entire particle volume.

Rate Constant Isothermality Index

$$\hat{\eta}_r(\tau) = \frac{3 \int_0^1 k_0 e^{-\frac{\beta}{\beta\epsilon + \epsilon^2\theta(\xi, \tau)}} \xi^2 d\xi}{k_0 e^{-\frac{\beta}{\beta\epsilon + \epsilon^2\theta_s(\tau)}}} \quad (1)$$

Conversion Isothermality Index

$$\hat{\eta}_c(\tau) = \frac{1 - 3 \int_0^1 \exp\left[-\int_0^{\tau'} \phi e^{-\frac{\beta}{\beta\epsilon + \epsilon^2\theta(\xi, \tau)}} d\xi\right] d\xi}{1 - \int_0^{\tau'} \phi e^{-\frac{\beta}{\beta\epsilon + \epsilon^2\theta_s(\tau)}} d\tau} \quad (2)$$

The analysis predicts domains of particle size and surface heating rate where 95% particle "isothermality" occurs according to these criteria (Fig. 9), and that heat of pyrolysis effects become negligible when rates of chemical enthalpy release at the particle surface are less than heat penetration rates (parameter δ , Fig. 10). The "rate" index is the most stringent (Fig. 9) and, as expected, defines more narrow domains of compliant particle sizes and heating rates as apparent activation energy increases. Both isothermality indices exhibit significant temporal variations (Figs. 11 and 12).

Modeling implications are that the "isothermality of a devolatilizing coal particle depends on time and on the devolatilization feature of interest. Despite good agreement between surface and centerline temperatures, volatiles yields release rates predicted from surface temperature alone, may still be in serious error. Even very large heats of pyrolysis may exert little effect on particle isothermality if intra-particle heat transmission is sufficiently rapid while chemical kinetics are sufficiently slow. Conversely, a modest heat of pyrolysis may effect particle isothermality if the associated pyrolysis/devolatilization chemistry is rapid.

Nomenclature

d_p	Particle Diameter, Cm
E	Activation Energy, Cal/g-mole
h_{eff}	Effective Heat Transfer Coefficient, Cal/(Cm ² -Sec-C)

k_0	Reaction Frequency factor, sec^{-1}
$\dot{m}$	Surface Heating Rate, $^{\circ}\text{K}/\text{sec}$
N_{Bi}	Biot Number; $h_{\text{eff}} d_p / 2$
$\dot{q}_0$	Surface Heat Flux Density, Cal/sec
R	Gas Constant; $1.987 \text{ Cal}/\text{gmole}^{\circ}\text{K}$
r	Radius, Cm
R_0	Particle Radius, Cm
T	Temperature, $^{\circ}\text{K}$
T_0	Initial Temperature, $^{\circ}\text{K}$
T_s	Surface Temperature, $^{\circ}\text{K}$
$T_{s,f}$	Final Surface Temperature, $^{\circ}\text{K}$
T_{∞}	Ambient Temperature, $^{\circ}\text{K}$
t	Time, Sec
V	Particle Volume, Cm^3
ρ	Particle Density, g/cm^3
λ	Particle Thermal Conductivity, $\text{Cal}/(\text{Cm}\cdot\text{Sec}\cdot^{\circ}\text{C})$
α	Particle Thermal Diffusivity, Cm^2/Sec
ΔH_{γ}	Heat of Pyrolysis, Cal/g
θ	Dimensionless Temperature; $\frac{T - T_{s,f}}{T_0 - T_{s,f}}$
θ_s	Dimensionless Surface Temperature; $\frac{T_s(t) - T_{s,f}}{T_0 - T_{s,f}}$
θ_{CL}	Dimensionless Center Temperature; $\frac{T_{CL}(t) - T_{s,f}}{T_0 - T_{s,f}}$

Θ_∞ Dimensionless Ambient Temperature;

$$\frac{T_\infty - T_{s,f}}{T_\infty - T_{s,f}}$$

τ Dimensionless Time; $\frac{\alpha t}{R_o^2}$

ξ Dimensionless Length; r/R_o

$\eta_r, \hat{\eta}_r$ Dimensionless Temperature Index

$\eta_r, \hat{\eta}_r$ Dimensionless Rate Index (See Text)

$\eta_c, \hat{\eta}_c$ Dimensionless Conversion Index (See Text)

E Dimensionless Parameter; $R T_{s,f} / E$

β Dimensionless Parameter; $\frac{R T_{s,f}^2}{E(T_\infty - T_{s,f})}$

δ Dimensionless Parameter; $\frac{-\Delta H_{ry} \rho d_p^2 k_o e^{-E/RT_{s,f}}}{4 \lambda (T_\infty - T_{s,f})}$

γ Dimensionless Heating Rate;

$$\frac{\dot{m} d_p^2}{4 \alpha (T_\infty - T_{s,f})}$$

Φ Dimensionless Heat Flux Density;

$$\frac{\dot{q}_o}{2 \pi \lambda d_p (T_\infty - T_{s,f})}$$

Table I

Heat Transfer Characteristics of Reactors

<u>Reactor</u>	<u>Conditions</u>	<u>Modes of Heat Transfer</u>	<u>Magnitude (w/cm²)</u>	<u>Measurement Technique</u>
UTRC-HG	Vacuum 1 atm helium	Radiation	0.1-1.0	Measure current and voltage-compute power and normalize WRT to screen surface area
		Radiation+ Conduction	1.0-4.0	
UTRC-EF	1 atm argon	Radiation+ Convection	2-25	Windowed and non-windowed water-cooled flux probes
UTRC-FL	Vacuum 1 atm argon	Radiation	100-1000	Rapid response pyroelec- tric detectors
PSU-EF	1 atm	Convection+ Radiation	50-100	Measure wall and gas temperatures and estimate power density to particle

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Figure 1

PRIMARY TAR $\longleftrightarrow$ PARENT COAL: STRUCTURAL COMPARISONS

Figure 2

%H(TAR) / %H(COAL) vs. COAL RANK

(PSOC XXXXD coals) 20-30 micron, particles,
peak reactor gas temperature = 510C

Figure 3

% (S+O) - TAR / % (S+O) - COAL VS. COAL RANK

(PSOC XXXXD coals) 20-30 micron particles,
reactor peak gas temperature = 510C

Figure 4

% HYDROGEN IN TAR VS. COAL RANK

(PSOC XXXXD coals) 20-30 micron, particles,
peak gas temperature = 510C

Figure 5

2920 CM-1 ABSORBANCE OF TARS vs. COAL RANK

(PSOC XXXXD coals) 20-30 micron particles,
peak gas temperature = 510C

Figure 6

ABSORBANCE (2920 / CM) vs. % H (DAF) IN TARS

(PSOC XXXXD coals) 20-30 micron particles, peak gas temp. = 510C

Figure 7

-CH₂- STRETCH ABSORBANCE (2920 CM⁻¹) VS. GAS TEMPERATURE

Triangle = PSOC 1451D, square = PSOC 1520D, 20-30 microns

Figure 8
SHELL THINNING - PERFORATION MODEL

Schematic cross-sections of morphology changes in a softening coal during pyrolysis and their corresponding effects on swelling.

Figure 9

ISOTHERMAL REGIONS DEFINED
BY DIFFERENT INDICES

Figure 10

EFFECT OF HEAT OF PYROLYSIS ON INDICES

Figure 11

EFFECTS OF HEATING RATE ON THE RATE INDEX FOR 100 μ m PARTICLE DIAMETER

Figure 12

EFFECTS OF HEATING RATE ON THE CONVERSION INDEX FOR 100 μ m PARTICLE DIAMETER

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