

Chain Transfer During Coal Liquefaction: A Model System Analysis

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Introduction

Coal liquefaction is a complex set of chemical reactions involving coal and solvent that is usually summarized globally in terms of the reaction of solubility- or boiling point-defined product classes. This modelling approach is warranted because both identification and kinetics solution of the large number of elementary reactions governing coal liquefaction is formidable. Nevertheless, the number of elementary reaction families is far less than the actual number of governing elementary reactions, which permits a hybrid molecular/lumped analysis of coal liquefaction kinetics. This also allows some of the rigor of molecular chemistry to be brought to bear on the synthesis of novel coal liquefaction process concepts. The purpose of the present paper is to use a hybrid molecular/lumped analysis of coal liquefaction reaction families to suggest the possibility of optimal chain transfer solvents for the initial stages of coal fragmentation.

The liquefaction reaction families are organized in Figure 1. Bond homolysis, followed by radical capping, is a time-honored view of coal liquefaction that has recently been suggested [1] to constitute only a portion of the overall reaction set. Any coal- or solvent-derived radical can abstract hydrogen from a donor (within coal or from a solvent); these radicals can also induce cleavage of coal bonds through ipso substitution and radical-induced hydrogen transfer (RHT). Kinetically significant β -scission steps are also available to coal- and solvent-derived radicals. Radical recombination and radical addition to olefins, the reverse of bond homolysis and β scission, respectively, are also kinetically significant.

As regards coal liquefaction, steps 1-4 are desirable: they lead to molecular weight reduction. Steps 5 and 6 are undesirable, since they lead to molecular weight growth (these might be termed "primary" retrograde reactions). Increasing the rates of 1-4 relative to 5 and 6 during the initial stages of coal liquefaction would allow for better net fragmentation of the macrostructure. As developed below, this can amount to increasing the kinetic chain length during the initial stages of coal liquefaction.

The reaction families 1-6 collectively possess aspects of a kinetic chain process. Reaction 1 initiates, Reaction 2-4 (and 6) propagate, and Reaction 5 terminates a chain. The essential feature of the chain is its kinetic chain length, i.e., the rate of consumption of coal by steps 2-4 relative to that by step 1. At the condition of steady state, step 1 must be equal in rate to step 5, which is a primary retrograde reaction. As highlighted in Figure 1, a chain transfer solvent will catalyze the desirable kinetic cycle through hydrogen transfer steps, increasing the turnover of the propagation cycle by shuttling H atoms without net consumption of hydrogen; μ_2 is regenerated in the cycle. A chain transfer solvent will, by definition, have slow β -scission pathways available to μ_2 . Of course, μ_2 can terminate with itself or coal-derived radicals, and may also be less reactive than the original coal-derived radical, R , of Figure 1. Both of these factors would tend to lower the turnover or chain length, which motivates the need for quantitative kinetics analysis.

The classic Rice-Herzfeld (RH) formalism provides a convenient vehicle for the kinetics analysis of the foregoing chemistry. The reaction families of Figure 1 are organized according to the RH formalism in Figure 2, which includes unimolecular bond homolysis, bimolecular hydrogen transfer, unimolecular β scission and bimolecular termination steps for coal and coal-derived radicals. Additional bimolecular hydrogen transfer and recombination steps involve the chain transfer solvent. Note that the propagation cycle, i.e., the hydrogen transfer and β -scission steps, sum to include the RHT step, which is therefore implicitly included in this analysis.

In outline of the remainder of this communication, kinetics analysis of the scheme of Fig. 2 is aimed at resolving the attributes of solvents that will enhance turnover of the propagation cycle, i.e., the kinetic chain length. This analysis will also show, as suggested by McMillen [1], the existence of a solvent of optimal C-H bond strength. In particular, the solvent with the most easily donatable hydrogen is not the best liquefaction

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solvent. We will show that the intrinsic chemistry that controls the catalytic effect of the chain transfer solvent is determined by the difference in reactivities of the coal- and solvent-derived radicals.

Analysis

Kinetics analysis of the steps of Figure 2 is phrased in terms of the RH transformation of reactant ($A_1 = \mu_1 H$) through free-radical intermediates β_1 and μ_1 to products $\beta_1 H$ and Q_1 . Chain transfer occurs through the addition of A_2 ($\mu_2 H$), which can donate hydrogen to β_1 , or to μ_1 in the case of slow β scission. The thus-derived μ_2 radical can abstract hydrogen from A_1 or terminate with another radical. Individually, A_2 is stable and, in particular, μ_2 does not have a kinetically significant β -scission path. This results in no net consumption of the catalyst A_2 .

The long-chain rate of consumption of A_1 ,

$$r_{A_1} = k_{11}A_1\beta_1 + k'_{21}A_1\mu_2 - k'_{12}A_2\mu_1 \quad (1)$$

can be written in terms of observable species' concentrations by invoking the pseudo-steady state approximation on radical concentrations. The β_1 and μ_1 balances provide the concentrations μ_1 and μ_2 in terms of β_1 . The equality of initiation and termination rates then provides the final information needed to express β_1 (and, thus, μ_1 and μ_2) in terms of A_1 , A_2 and the rate constants for elementary steps.

The thus-derived rate expression for the pyrolysis of A_1 in the presence of a chain transfer solvent (A_2) is:

$$r_{A_1}(A_1, A_2) = \left(\frac{\alpha_1 A_1}{k_t}\right)^{\frac{1}{2}} \frac{k_{11}A_1(1 + \hat{k}'\theta'S_2)}{D^{\frac{1}{2}}} \quad (2)$$

where,

$$D = (1 + \hat{k}'S_2(\gamma_3 + \gamma_5\hat{k}'S_2) + M_1(1 + \hat{k}'\theta'S_2)(\gamma_1 + \hat{k}'S_2(\gamma_3\phi' + \gamma_4 + 2\gamma_5\phi'\hat{k}'S_2) + M_1^2(1 + \hat{k}'S_2)^2(\gamma_2 + \hat{k}'\phi'S_2(\gamma_4 + \gamma_5\hat{k}'\phi'S_2))) \quad (3)$$

In Eqs. 2 and 3, $M_1 = k_{11}A_1/k_1$, $\hat{k}' = k_{12}/k'_{21}$, $\theta' = k'_{21}/k_{11}$, $\phi' = k_{12}/k'_{12}$, $S_2 = A_2/A_1$ and γ_i is a termination rate constant relative to that for β_1 self-termination.

The influence of the chain transfer solvent A_2 is emphasized by considering the enhancement $E_1 = r_{A_1}(A_1, A_2)/r_{A_1}(A_1)$ of the rate of consumption of A_1 caused by the addition of A_2 . Recognizing $r_{A_1}(A_1)$, the rate in the absence of a chain transfer additive, to be:

$$r_{A_1}(A_1) = \left(\frac{\alpha_1 A_1}{k_t}\right)^{\frac{1}{2}} \frac{k_{11}A_1}{(1 + (\gamma_1)M_1 + (\gamma_2)M_1^2)^{\frac{1}{2}}} \quad (4)$$

E_1 reduces as:

$$E_1 = \frac{(1 + \hat{k}'\theta'S_2)(1 + (\gamma_1)M_1 + (\gamma_2)M_1^2)^{\frac{1}{2}}}{D^{\frac{1}{2}}} \quad (5)$$

The chain transfer solvent therefore effects rate enhancement through modified rates of chain propagation (\hat{k}' , θ' , S_2) and chain termination (γ_1 , $\gamma_2, \dots, \gamma_5$, ϕ'). θ' indicates the ease of H abstraction from A_1 by μ_2 and β_1 radicals, and \hat{k}' is a cross-coupling parameter which compares the propensity of β_1 radicals to abstract H from A_2 with that of μ_2 radicals to abstract H from A_1 . ϕ' describes relative time constants for H abstraction from the shuttle molecule by μ_1 and β_1 radicals, respectively.

Application of Eq. 5 to coal liquefaction reaction families suggests several chemistry-driven simplifications. In many cases β scission is fast relative to H abstraction ($M_1 \rightarrow 0$) which permits the simplification of Eq. 5 to:

$$E_1 = \frac{(1 + \hat{k}'\theta'S_2)}{(1 + \hat{k}'S_2(\gamma_3 + \gamma_5\hat{k}'S_2))^{\frac{1}{2}}} \quad (6)$$

In this instance β_1 and μ_2 are the most abundant reaction intermediates. For the reasonable limiting case of equal termination rate constants save the statistical factor of 1/2 for self collision, the denominator simplifies to a perfect square and allows E_1 to be written as:

$$E_1 = \frac{(1 + \hat{k}'\theta'S_2)}{(1 + \hat{k}'S_2)} \quad (7)$$

Thermochemical Constraint

Further inspection of the controlling dimensionless groups \hat{k}' and θ' shows them to be relative rate constants for a family of hydrogen abstraction reactions. The Evans-Polanyi relation $E^* = E_0 + \alpha\Delta H_R^1$ for exothermic reactions (EXO) [2] should then provide a reasonable estimate of E_1 in terms of reaction enthalpies and, ultimately, comparative bond strengths [3-9]. The dependence of these dimensionless groups on the relevant bond strengths is illustrated in Table 1, where θ' is shown to be a function of $d_{\beta_1-H}^0$ and $d_{\mu_2-H}^0$ and \hat{k}' a function of $d_{\beta_1-H}^0$, $d_{\mu_2-H}^0$ and $d_{\mu_1-H}^0$.

Eqs. 6 and 7 for E_1 , and the expressions in Table 1 for θ' and \hat{k}' , allow illustration of the dependence of E on $d_{\mu_2-H}^0$, $d_{\beta_1-H}^0$, and $d_{\mu_1-H}^0$. For a model where coal species are lumped as pseudo component 1, and with the chain transfer solvent as pseudo component 2, it is reasonable to consider β_1H and μ_1H as fixed by the coal type and μ_2H to be a design parameter. This renders E_1 dependent on $d_{\mu_2-H}^0$ and T for a given coal. This dependence is illustrated in Figure 3 for $T = 400^\circ C$ and $d_{\beta_1-H}^0 = 87$ kcal/mol, the bond strength for fission of toluene, β_1H , into H and β_1 . Inspection of Figure 3 reveals an extremum in the dependence of E_1 on $d_{\mu_2-H}^0$. For low $d_{\mu_2-H}^0$, the easily formed μ_2 radicals are also very stable. Here μ_2-H acts as an inhibitor and lowers the rate. At the high $d_{\mu_2-H}^0$ extreme, highly reactive μ_2 radicals are formed only with great difficulty. In the limit $d_{\mu_2-H}^0 \rightarrow \infty$ the additive acts as an inert diluent, and $E_1 \rightarrow 1$. In an intermediate regime of $d_{\mu_2-H}^0$ the enhancement $E_1 > 1$. Thus Figure 3 summarizes the homogeneous equivalent of the classic Balandin Volcano curve illustrating the principle of Sabatier.

The effect of unequal termination rate constants (Eq. 6) is illustrated in Figure 4. When, for example, μ_2 radicals terminate with one one-thousandth the rate constant of β_1 radicals ($\gamma = 0.001$), the enhancement is amplified by a factor of about 4.

Sensitivity to Parameters

Eq. 7 allows more careful delineation of the conditions for enhancement and the location of the maximum of Fig. 3. Clearly $E_1 > 1$ for $\theta' > 1$, or $d_{\mu_2-H}^0 > d_{\beta_1-H}^0$. This indicates that the formation of a less-stable μ_2 radical, relative to the β_1 radical, will increase the rate relative to neat pyrolysis. Likewise, for $\theta' < 1$, the rate will decrease. But the magnitude of the effect will depend upon the rate of forming the μ_2 radicals, as shown by the derivative of E_1 with respect to $\hat{k}'S_2$. i.e.,

$$\frac{\partial(E_1)}{\partial(\hat{k}'S_2)} = \frac{(\theta' - 1)}{(1 + \hat{k}'S_2)^2} \quad (8)$$

This is positive for $\theta' > 1$ and negative for $\theta' < 1$. Thus the group $\hat{k}'S$ attenuates the effect dictated by the value of θ' . Finally, the curves parametric in $d_{\mu_1-H}^0$ in Figure 3 intersect at $\theta' = 1$, which corresponds to $d_{\mu_2-H}^0 = d_{\beta_1-H}^0$, for all values of $d_{\mu_1-H}^0$.

Relevant coal model compound data are summarized in Table 2. The enhancement of dibenzyl ether (DBE), $d_{\mu_1-H}^0 = 78.85$ kcal/mol and $d_{\beta_1-H}^0 = 87$ kcal/mol) was observed in each of diphenylmethane, triphenylmethane, fluorene, dihydroanthracene, dihydrophenanthrene, and bibenzyl. The chain transfer solvents span a range of both C-H bond strengths [3-10] and termination rate constants. For example, triphenylmethyl radicals are known to be persistent due to steric hindrance to self collision. In this case, $\gamma_5 \rightarrow 0$ and $\gamma_3 \ll 1$, and therefore the effect on DBE pyrolysis is predicted by the uppermost curve of Fig. 4.

Actual coal liquefaction data are consistent with the existence of an optimal chain transfer solvent. McMillen's analysis of the coal conversion data of Curtis [11] in terms of the C-H bond dissociation energy of the liquefaction solvent is summarized in Figure 5. McMillen's observation that the 'optimal' solvent was not that which most easily donated hydrogen (low $d_{\mu_2-H}^0$) supported the hypothesis that the traditionally accepted view of coal liquefaction comprising bond scission and radical capping was incomplete. The likelihood of radical hydrogen transfer (RHT) as a mechanism for the fragmentation of strong bonds was noted. The behavior in Figure 5 is also consistent with the notion of an optimal chain transfer solvent. This suggests that the chain transfer scheme of Fig. 1 may contribute to the overall observable kinetics of coal liquefaction. Further delineation of the contributions of chain transfer, fission, RHT, etc. awaits more detailed accounting of the differences between coal and its model compounds.

¹ For endothermic reactions (ENDO) $E^* = E_0 + (1 - \alpha)\Delta H_R$

Conclusions

In summary, kinetic coupling of reaction cycles involving coal and solvent species can result in the presence of an optimal solvent for coal liquefaction. The present analysis permits qualitative prediction of this behavior using the hybrid molecular/lumped chain transfer scheme outlined in Fig. 1. Model compound data are consistent with these predictions.

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Table 1: Thermochemical Relationships

Dimensionless Group [D]	- RT ln D = ΔE*		
	EXO/EXO	ENDO/EXO	EXO/ENDO
$\theta' = \frac{k_{21}}{k_{11}}$	$[(1 - \alpha)d_{\mu_2H}^0 - \alpha d_{\beta_1H}^0 - (1 - 2\alpha)d_{\mu_1H}^0]$	$[\alpha(d_{\beta_1H}^0 - d_{\mu_2H}^0)]$	—
$\hat{k} = \frac{k_{12}}{k_{21}}$	$[\alpha(d_{\beta_1H}^0 + d_{\mu_1H}^0 - 2d_{\mu_2H}^0)]$	$[\alpha d_{\beta_1H}^0 - d_{\mu_2H}^0 + (1 - \alpha)d_{\mu_1H}^0]$	$[\alpha d_{\mu_1H}^0 - d_{\mu_2H}^0 + (1 - \alpha)d_{\beta_1H}^0]$

Table 2: Experimental Observations of DBE Enhancement in Chain Transfer Solvents

Solvent	E	$d_{\mu_2H}^0$	Explanation	Conclusions
Diphenylmethane	0.8	84±2	($\theta' = 0.57$)	$\gamma_5 \sim 0.25$
Triphenylmethane	1.5	75±4	$\gamma < 1$ due to steric hindrance ($\theta' = 0.025$)	$\gamma_5 \sim 0.0003$
Fluorene	1.3	81	$\gamma < 1$ due to steric hindrance ($\theta' = 0.33$)	$\gamma_5 \sim 0.3$
Dihydroanthracene	0.40	77±2	($\theta' = 0.077$)	$\gamma_5 \sim 0.04$
Dihydrophenanthrene	0.37	83	($\theta' = 0.47$)	$\gamma_5 \sim 2$
Bibenzyl	0.65	85±3	($\theta' = 0.69$)	$\gamma_5 \sim 1.5$

Figure 1

Coal Liquefaction Reaction Families

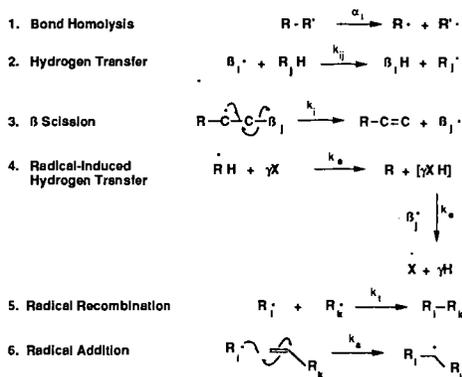
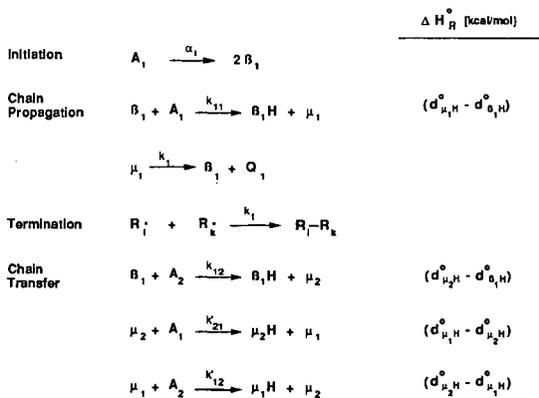


Figure 2

Rice-Herzfeld Pyrolysis Mechanism

Including Chain Transfer Elementary Steps



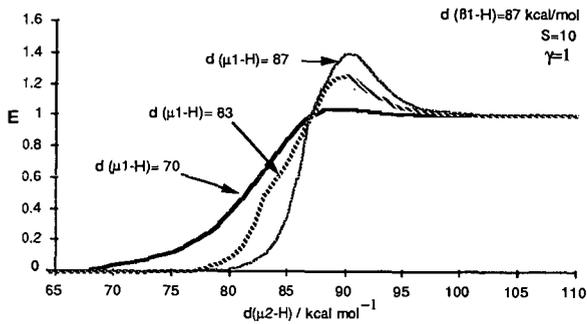


Figure 3 Rate Enhancement due to Hydrogen Transfer Solvent

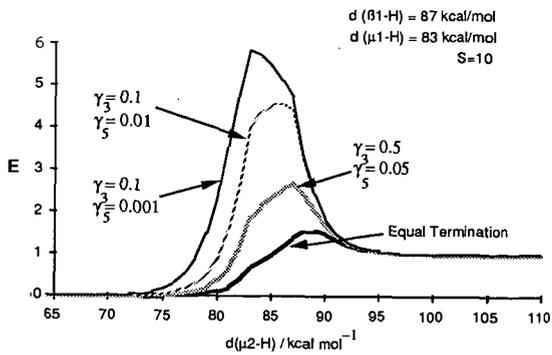


Figure 4 Rate Enhancement due to Chain Transfer Solvent:
Effect of Unequal Termination Rate Constants

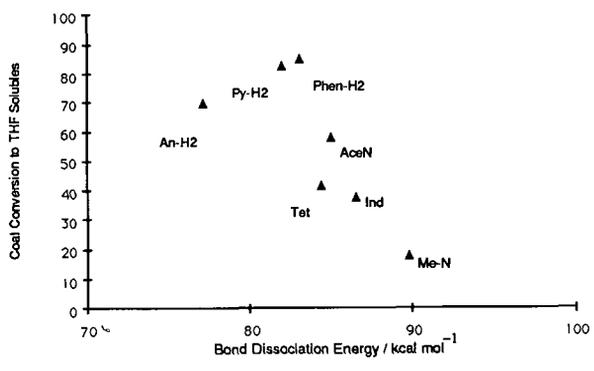


Figure 5 Coal Liquefaction Efficiency