MODELING DEVOLATILIZATION RATES AND YIELDS FROM VARIOUS COALS WITH FLASHCHAIN

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Keywords: Modeling, coal devolatilization, coal type effects

INTRODUCTION

Predicting the ultimate weight loss and tar yields from any coal type is largely a matter of distinguishing aliphatic, heteroatomic, and aromatic constituents. In FLASHCHAIN (1-3), this crucial partitioning is implemented with balances based on the ultimate analysis, carbon aromaticity, aromatic carbon number per momoneric unit, and other characterization data. This study shows that the ultimate analysis is the only sample-specific data needed for accurate predictions of ultimate tar and total yields with this theory, consistent with a previous parametric sensitivity study(3). Regression values of all other inputs are adequate. Along with evaluations of ultimate yields for coals across the rank spectrum, reliable transient predictions for rapid atmospheric devolatilization of any coal type are also demonstrated.

OVERVIEW OF THE THEORY

FLASHCHAIN invokes a new model of coal's chemical constitution, a four-step reaction mechanism, chain statistics, and the flash distillation analogy (4) to explain the devolatilization of various coal types. The theory's central premise is that the partitioning of the elements among aliphatic, heteroatomic, and aromatic constituents largely determines the devolatilization behavior of any coal type. The abundance of labile bridges in lignites promotes their extensive conversion to noncondensible gases, but their oxygen promotes the charring of bridges into refractory links, which inhibits fragmentation of the macromolecules into tar. Conversely, the paucity of labile bridges in low volatility coals suppresses gas yields. These coal also have too few labile bridges for extensive fragmentation, so their tar yields are also relatively low. High volatile bituminous coals generate an abundance of tar precursors, so a competition between flash distillation and repolymerization into larger, refractory fragments determines their tar yields.

Coal is modeled as a mixture of chain fragments ranging in size from a monomer to the nominally infinite chain. They are constructed from only four structural components: aromatic nuclei, labile bridges, char links, and peripheral groups. Aromatic nuclei are immutable units having the characteristics of the hypothetical aromatic cluster based on ^{13}C NMR analysis. They also contain all of the nitrogen in the coal. Nuclei are interconnected by two types of linkages, labile bridges or char links. Labile bridges are the key reaction centers. They represent groups of aliphatic, alicyclic, and heteroatomic functionalities, not distinct chemical bonds. Bridges contain all of the oxygen, sulfur, and aliphatic carbon, but no aromatic components. Being refractory, char links are completely aromatic with no heteroatoms. Peripheral groups are the remnants of broken bridges.

Connectedness among nuclei is another important aspect of coal rank. In FLASHCHAIN, the initial coal configuration is specified by the proportions of broken bridges and intact linkages. Since the number of linked nuclei denotes the fragment size, the fraction of broken bridges determines the initial fragment size distribution. This distribution is empirically related to extract yields in pyridine. Qualitatively, fragment distributions skewed toward smaller sizes correspond to coals with substantial amounts of readily extractable material.

All parameters in the constitution submodel are collected in Table 1 for diverse coal samples. Four are based on molecular weights: that of the aromatic nucleus, MW_A, is used to normalize those of labile bridges (MW_B/MW_A), char links (MW_C/MW_A), and peripheral groups (MW_P/MW_A). The tabulated values show that nuclei become more massive in coals of higher rank, and both the labile and refractory connections among them become smaller. The proportion of intact links in the whole coal, p(0), follows the tendency in the pyridine extract yields to remain constant for ranks through hv bituminous. It then rises precipitously for coals of higher ranks, consistent with their smaller extract yields because structures which are more tightly interconnected have fewer smaller fragments to be extracted. The fraction of labile bridges among intact links, $F^b(0)$, decreases from its value of unity for lignites in proportion to the carbon content.

The selectivity coefficient between scission and spontaneous char condensation, ν_B , also varies with rank. Since crosslink formation has been clearly related to CO_2 evolution, the values of ν_B are proportional to O/C ratios, but only for values below 0.2 or for carbon contents less than 83%. The latter restriction is consistent with the fact that precursors to CO_2 are either carboxyclic acid or ketone functionalities, which are present only in lower rank coals.

RESULTS

In the forthcoming simulations only the operating conditions of temperature, heating rate, and/or time were varied to match those in the experiments. A simulation of each thermal history requires from 2 to 5 minutes on a 386 personal microcomputer operating at 20 MHz with an 8-Bit Fortran compiler.

Figure 1 presents comparisons among the predicted and measured ultimate values of weight loss and tar yield based on the laboratory study of Xu and Tomita (5). The data are ultimate yields for atmospheric pyrolysis for a heating rate of 3000 K/s and a 4 s reaction time at 1037 K. The predicted weight loss is within 4 wt. % of the measured values in 13 of the 17 cases. The predictions also display the perturbations from a smooth, monotonic trend that is evident in the data. Similarly, predicted tar yields are within 4 wt. % of the observed values in 14 of the 17 cases, and also depict the rather erratic relation with carbon content that is observed. The only sample-specific inputs for these simulations are the reported ultimate analyses.

Weight loss and tar yields for transient devolatilization of 4 coal types throughout diverse thermal histories appear in Fig. 2. These cases represent ranks from subbituminous through lv bituminous. Throughout all of these cases, the FLASHCHAIN predictions are within experimental uncertainty.

Nominal devolatilization rates for 8 coals for atmospheric devolatilization at 10^4 K/s appear in Fig. 3. The curves are the rate constants in single first order reactions which match the FLASHCHAIN predictions. These simulations indicate that devolatilization occurs over a narrower temperature range for higher rank coals, although the variation is rather modest. Rate variations with rank segregate into two categories. For ranks from lignite through hv bituminous, rank variation are modest, especially during the later stages of devolatilization at high temperatures. Nominal rates for these ranks vary by a factor of 3 at 715 K, but by only 40% at 1000 K. The temperature at which devolatilization commences also varies, from 600 K for the lignite to 680 K for the hv bituminous coals. (Of course, these temperatures will shift for different heating rates.) Low volatility coals comprise the second category. They begin to devolatilize at much higher temperatures and sustain significantly slower rates than the other ranks. Even so, the variations among very diverse coal samples are never as substantial as those from varying the heating rate by a single order of magnitude.

DISCUSSION

This reaction model delivers reliable yields of gas and tar for any coal at any operating conditions, yet it requires only a few minutes per simulation on a personal microcomputer. Throughout the entire rank spectrum, this theory quantitatively represents observed yields using only the sample-specific ultimate analyses and regression values of all other input data. To date, predictions for some 40 different coal samples covering the entire rank spectrum have been evaluated against measured transient and/or ultimate yields. In all but a few cases, the model predictions are within experimental uncertainty. Transient cases in the evaluations are also satisfied. The predictions show that devolatilization rates are very insensitive to rank through hvA bituminous, but then fall off for low volatility coals.

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Table 1. Structural Model Parameters

%C, daf	MW_A	C_A	MW_M/MW_A	MW_C/MW_A	MW_P/MW_A	p(0)	$F^b(0)$	ν_B	ν_E
66.5	125	9.7	1.859	.836	.511	.911	1.000	.150	2.40
69.0	134	10.6	1.602	.721	.442	.911	1.000	.150	2.23
69.5	135	10.7	1.563	.704	.430	.911	0.983	.150	2.19
74.1	148	11.6	1.307	.588	.359	.911	0.858	.329	2.03
75.5	152	11.9	1.258	.566	.347	.911	0.821	.202	2.05
79.9	165	12.9	1.044	.470	.288	.911	0.702	.370	2.00
82.5	176	13.7	0.901	.406	.247	.911	0.632	.500	1.93
84.0	180	14.1	0.838	.377	.230	.911	0.591	.500	1.90
87.4	169	13.4	1.079	.485	.297	.911	0.329	.500	2.48
87.5	182	14.2	0.886	.399	.243	.911	0.366	.500	2.19
88.7	183	14.4	0.866	.390	.239	.920	0.329	.500	2.21
89.6	186	14.6	0.836	.376	.230	.937	0.301	.500	2.21
89.9	181	14.4	0.897	.404	.247	.943	0.291	.500	2.33
94.3	178	14.5	1.005	.452	.097	1.000	0.154	.500	2.86

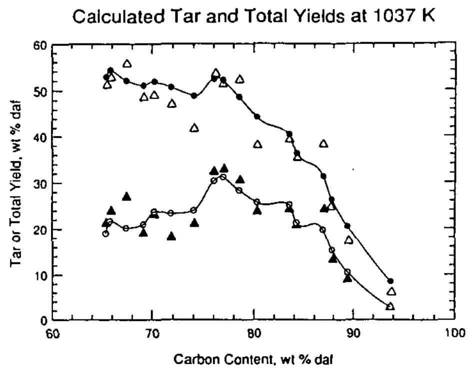

Figure 1. An evaluation of ultimate weight loss and tar yields for atmospheric devolatilization based on the study of Xu and Tomita (5). FLASHCHAIN predictions appear as the circles connected by solid lines, and the measured values appear as the contrasting triangles.

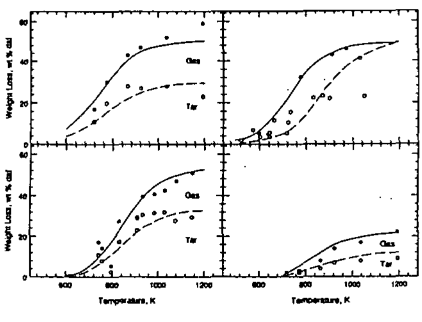

Figure 2. Representative FLASHCHAIN predictions for transient atmospheric devolatilization of four diverse coal types. (a) Total and tar yields from a subbituminous coal for 4 s isothermal reaction after heating at 3000 K/s to various temperatures, reported by Xu and Tomita (6). (b) Ultimate and transient weight loss from Ill. #6 for a heating rate of 1000 K/s reported by Freihaut and Proscia (7). (c) Transient total and tar yields from Pit. #8 during heatup at 1000 K/s and slow cooling from various temperatures, reported by Oh. et al. (8). (d) Same as (a) for a lv bituminous coal.

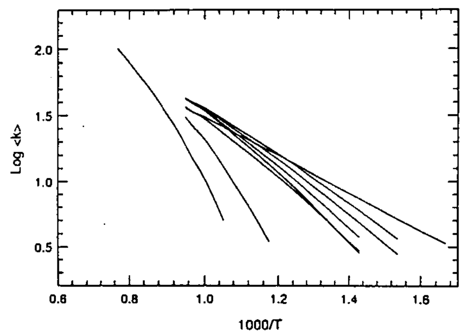

Figure 3. Arrhenius diagram of nominal devolatilization rates during transient heating at 10^4 K/s for the 8 coals tested by Xu and Tomita (6). In clockwise descending order, lines are for coals of increasing rank.