CORRELATION OF COAL LIQUEFACTION REACTIVITY WITH COAL PROPERTIES

R. M. Baldwin

Chemical and Petroleum-Refining Engineering Department
Colorado School of Mines
Golden, Colorado 80401

S. L. Durfee and K. J. Voorhees

Chemistry/Geochemistry Department
Colorado School of Mines
Golden, Colorado 80401

ABSTRACT

A narrow suite of bituminous coals chosen from the DOE/Penn State sample bank has been hydrogenated in a batch stirred autoclave. Rates of conversion to THF-solubles have been measured, and the data modeled using a pseudo-second order rate expression. Extent of conversion and rate of conversion of the coals in the suite have been correlated to coal compositional parameters and structural features. Recent data on reactivity correlations with information from pyrolysis/mass spectrometry and C-NMR are presented.

INTRODUCTION

The relationship between coal composition and hydrogenation reactivity has been studied extensively for over 60 years. As early as 1920, Bergius (1) recognized that coal with less than 85% carbon (daf) made poor liquefaction feedstocks. Francis (2) suggested that reactivity was related to rank, and many other researchers have attempted to correlate reactivity with rank (3,4,5). Neavel (6) has shown that a relationahip does exist between rank and rate of coal hydrogenation to benzene solubles. Fischer (7) and his co-workers at the Bureau of Mines in Bruceton developed mathematical models for coal liquefaction reactivity based on a petrographic analysis of the parent coal. This concept was expanded and greatly elaborated upon by Given et al. (8,9,10,11), who established reactivity ensamples by statistical factor analysis of a large number of samples. Recently, Furlong et al. (12) studied the use of different definitions for coal reactivity, and demonstrated the utility of a definition based on kinetic parameters when ranking coals of very similar properties.

All studies relating coal properties to coal hydrogenation reactivity are hampered by the crude tools available for chemical and structural analysis of the prime reactant. Pyrolysis, followed by mass spectroscopy (Py/MS) of the products at low energy levels provides a new tool for coal analysis that can provide data on structural features that previously could not be obtained (13). Voorhees et al. (14), and Meuzelaar et al. (15) have recently reported correlations of structural data from coal Py/MS and coal hydroliquefaction reactivity.

EXPERIMENTAL

A series of bituminous coals from the DOE/Penn State sample bank were hydrogenated in a batch stirred autoclave reactor into which coal was injected. Table 1 presents data on coal properties in the suite. All coals were low sulfur, in order to minimize catalytic effects due to H_2S and iron pyrite. Details of the run procedure and reaction equipment used have been presented elsewhere (12). Coal samples were pyrolysed using a Fisher Curie-Point pyrolyser in conjunction with an Extranuclear SpectrEL mass spectrometer. Curie point wires composed of Ni (510 C final temperature) and low energy (14 ev) electron impact were used throughout for data acquisition. Mass spectral data were collected on a Hewlett-Packard 2100 S computer, and the data then analysed using ARTHUR (Infrometrix Inc., Seattle, Wa.). Solid state ^{13}C-NMR was performed at the NSF Regional Center for NMR at Colorado State University, Department of Chemistry.

DISCUSSION AND RESULTS

Rate data on coal conversion to THF-solubles was reduced using a pseudo-second

order kinetic model of the form:

$$\frac{dC}{dt} = -k_f C^2 + k_r P^2$$

Here k_f and k_r (with units: mass fraction · min^{-1}) are the forward and reverse rate constants for the reaction:

$$C \underset{k_r}{\overset{k_f}{\rightleftharpoons}} P$$

As previously, coal (C) was defined in these expressions as THF-insoluble organic matter, which included unreacted coal as well as high-molecular-weight moieties and coke produced by free radical recombination and condensation reactions. Parameter P was defined as all products soluble in THF.

Using conversion (X) defined as the fraction of coal reacted to THF-soluble materials, the mass balance may be rewritten as a function of the conversion:

$$\frac{1}{k_f} \frac{dX}{dt} = (-X)^2 - \left[\frac{1}{K}\right] X^2$$

Here C = 1 - X, P = X, and K, the equilibrium constant for the reaction, is given by k_f/k_r. Data for each of the 11 coals which were successfully run were processed by non-linear parameter estimation methods (16) to obtain values for the parameters k_f and k_r in the second-order model. These data are given in Table 2 as are values for the equilibrium constant K. Also in Table 2 are values for the 60 min conversion to THF-soluble materials (X(60)).

Data on the aliphatic-to-aromatic carbon ratios in the parent coal samples plotted against kinetic reactivity (k_f) are shown in Figure 1. With one exception, the correlation is one of increasing reactivity with increasing aliphatic to aromatic carbon ratio. This was to be expected, as it has been well established that the more aliphatic coals convert more readily in comparison with the more aromatic coals. The correlation with rate of conversion (Figure 1) is fairly good, thus substantiating the importance of aliphatic carbon-carbon bonds in coal hydrogenation. Aliphatic/aromatic carbon ratio also correlates fairly well with extent of reaction (X(60)), but not with reactivity as measured by the pseudo-equilibrium constant (K) from Table 2. Overall however, the correlation of aliphatic to aromatic carbon is the best with reactivity as defined in a kinetic fashion by the forward rate constant.

Coals from the reactivity suite shown in Table 1 were run in triplicate on the Py/MS, and an average spectrum obtained which represented a composite spectrum for 9 of the 11 coal hydrogenated. Data from Py/MS of the coal suite were reduced by ARTHUR, and a statistical factor analysis performed on the entire data set. From the factor analysis, 4 factors were identified which accounted for over 72% of the variation in the data set. The factors and the percent of total variation explained were as follows:

FACTOR	VARIATION ACCOUNTED FOR	CUMULATIVE VARIATION
1	24.3%	24.3%
2	23.1%	47.4%
3	14.8%	62.1%
4	10.0%	72.2%

These factors were utilized in Karhunen Loeve (K-L) plots obtained from ARTHUR, in order to ascertain whether any clustering into reactivity groupings could be obtained. As shown in Figure 2, a plot of K-L factor 3 vs K-L factor 2 does produce such a clustering, with the higher reactivity coals in the suite falling towards the upper right hand corner of the plot, and the less reactive coals clustering in the lower left. These data may indicate the utility of pyrolysis/mass spectrometry as a rapid screening tool for coal reactivity.

The data set from Py/MS of the coal suite can be rotated towards any other factor, and composite spectra calculated which demonstrate relationships between chemical moieties in the spectrum and the chosen factor. Such correlations have

recently been reported by Baldwin (17) on a suite of coals with a very broad geographical and rank distribution. Further analysis of this data set was performed by rotating the composite spectra towards reactivity, with reactivity defined in each of the three manners listed above (k_f, X(60), and K). The results of these analyses are presented in Figures 3-5. As before, the only meaningful correlation seems to be when reactivity is defined as a kinetic reactivity. Figure 3 indicates that a strong positive correlation exists between a homologous series of high molecular weight naphthalenes and coal reaction rate. Further analysis of Py/MS data set is continuing, and will be presented later.

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Table 1 Parent coal analyses

Coal				Ultimate analysis (wt % dmmf (Parr))					Maceral comp. (vol % dmmf)			Sulphur (wt % daf)	
PSOC No.	Rank	Seam	State	C	H	N	O	Min. matter	vit	iner.	lipt.	pyr.	tot.
001	hvAb	Upper Elkhorn	KY	84.36	5.46	1.54	8.64	4.71	54.8	21.7	23.5	0.10	0.81
056	hvCb	Arizona No. 2	AZ	77.37	5.90	1.34	15.39	6.92	83.9	12.8	3.3	0.01	0.45
071	hvCb	Rogers	WA	78.00	5.88	1.68	14.44	7.41	86.5	7.7	5.8	0.07	0.58
107	hvBb	Brazil Block	IN	81.97	5.07	1.37	11.59	6.42	62.4	14.6	23.0	0.11	0.53
151	hvCb	Lower Blue	NM	78.37	5.87	1.24	14.51	5.80	78.6	10.8	10.6	0.05	0.47
437	hvAb	Utah B	UT	80.26	6.20	1.47	12.07	5.63	92.1	6.0	1.9	0.11	0.51
444	hvBb	Colorado E	CO	78.87	6.47	1.57	13.09	2.46	94.4	3.9	1.7	0.06	0.46
456	hvAb	Blind Canyon	UT	79.49	6.43	1.58	12.50	4.91	88.7	10.2	1.1	0.06	0.37
577	hvCb	(unnamed)	TX	79.97	5.68	1.32	13.04	25.51	87.2	11.7	1.1	0.17	1.17

Table 2 Estimated second-order rate parameters

Coal (PSOC No.)	k_f*	k_r*	K	a	X (60)
001	0.0672 ± 0.0103	0.0094 ± 0.0069	7.17	0.728	0.724
056	0.1655 ± 0.0319	0.0107 ± 0.0080	15.51	0.797	0.828
071	0.1358 ± 0.0253	0.0068 ± 0.0066	20.01	0.817	0.837
107	0.0839 ± 0.0064	0.0018 ± 0.0023	45.94	0.871	0.810
151	0.1673 ± 0.0265	0.0143 ± 0.0076	11.71	0.774	0.801
437	0.1997 ± 0.0253	0.0082 ± 0.0046	24.34	0.831	0.850
444	0.1057 ± 0.0162	0.0002 ± 0.0039	485.33	0.957	0.872
456	0.2174 ± 0.0363	0.0055 ± 0.0051	39.81	0.863	0.884
577	0.1369 ± 0.0169	0.0157 ± 0.0063	8.74	0.747	0.769

* 95% confidence limits on k_f and k_r estimates.

Rate constants have units of (mass fraction min^{-1})

FIGURE 1

ALIPHATIC/AROMATIC CARBON RATIO VS FORWARD RATE CONSTANTS

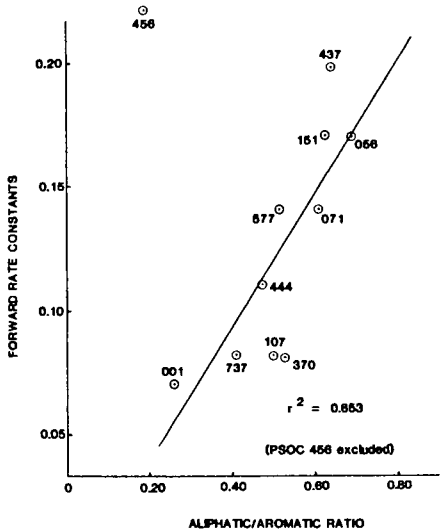


FIGURE 2

KARHUNEN-LOEVE PLOT

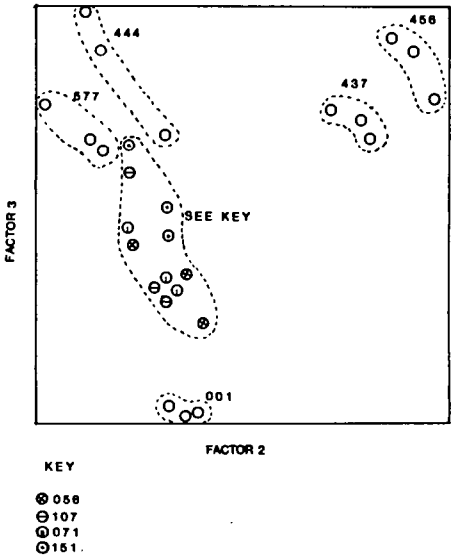


FIGURE 3

FACTOR SPECTRUM, KINETIC REACTIVITY

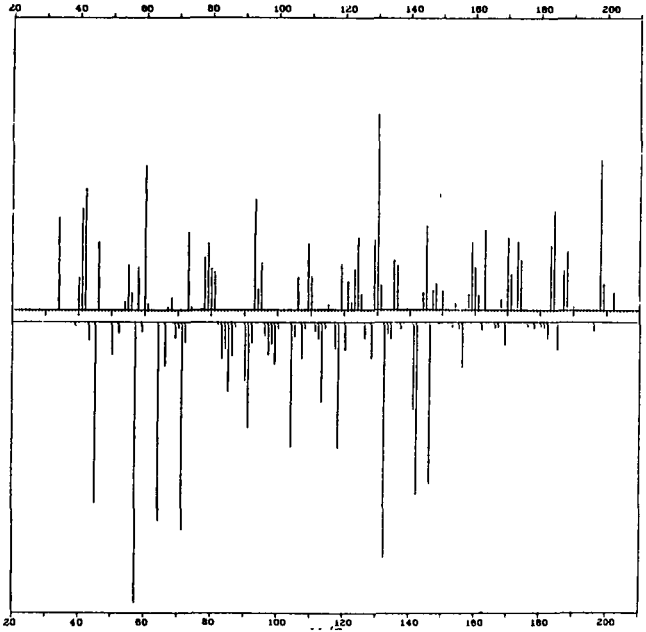


FIGURE 4

FACTOR SPECTRUM, X(60) REACTIVITY

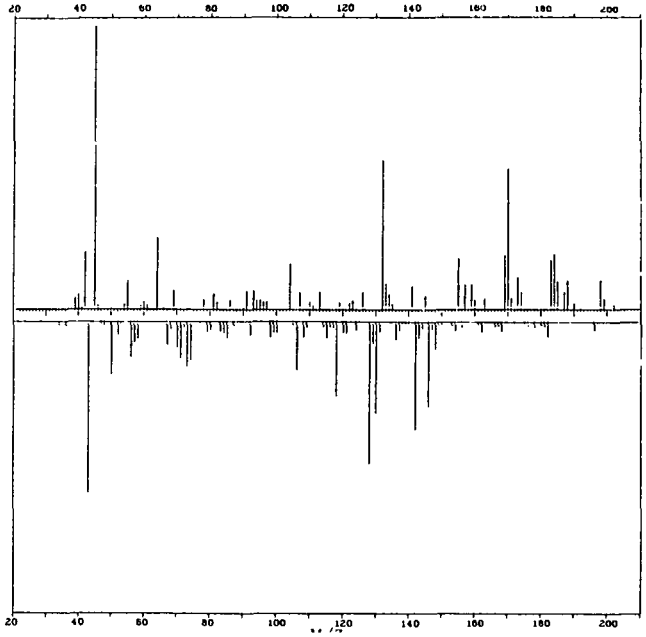
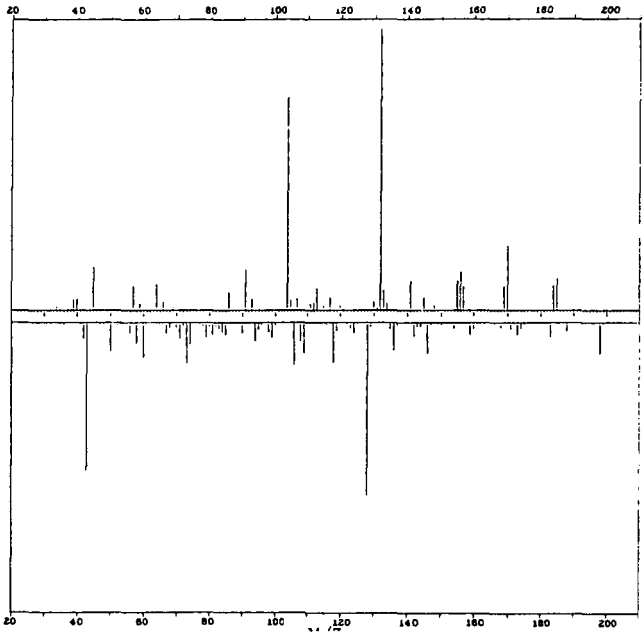


FIGURE 5

FACTOR SPECTRUM, EQUILIBRIUM REACTIVITY