

CORRELATION OF BITUMINOUS COAL HYDROLIQUEFACTION ACTIVATION
ENERGY WITH FUNDAMENTAL COAL CHEMICAL PROPERTIES

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ABSTRACT

The rate and extent of direct coal hydroliquefaction for 5 bituminous coals from the Argonne Premium Sample Bank have been measured. Data were obtained in batch microautoclave tubing bomb reactors at three temperatures (375, 400, 425 °C) and 5 residence times (3, 5, 10, 15, 40 minutes) in 1-methylnaphthalene vehicle under a hydrogen blanket. Data on rate of conversion of coal to THF and toluene solubles were modeled with a simple reversible rate expression, and activation energies for conversion to each solvent solubility class determined.

Data on carbon and proton distribution in the coals were obtained by ^1H -NMR (Combined Rotational and Multiple Pulse Spectroscopy) and ^{13}C -NMR (CPMAS/Dipolar Dephasing). A strong correlation of activation energy with the aliphatic hydrogen content of the coal was found for conversion to THF solubles. Toluene solubles activation energies were found to be highly correlated ($R^2 > 90\%$) with total oxygen, and protonated aliphatic carbon. ^{13}C -NMR data indicated a high degree of correlation between protonated aliphatic carbon and total oxygen for only the bituminous coals from the Argonne suite, suggesting the importance of etheric oxygen in crosslinking structures for determination of bituminous coal reactivity.

Introduction

The relationship between coal chemical and structural features and coal reactivity has been the subject of considerable research for well over 70 years, dating from the original observations of Bergius (1) regarding the influence of carbon content on hydroliquefaction yield. Early studies of the influence of coal properties on coal reactivity were focused on an attempt to find a single parameter or group of parameters capable of correlating physical, chemical, and geochemical properties with the degree of conversion to some solvent soluble products under a fixed set of reaction conditions (2-8). Given et al. (9-12) developed multiparameter statistical correlations for coal reactivity for an extensive suite of U.S. coals. These correlations were partitioned according to the geographical location of the coal in order to increase the significance of the relationships. Other researchers have attempted to correlate coal hydroliquefaction reactivity with the mineral matter in coal, most notably pyrite, and other physical and chemical properties (13-18). Neavel (19) and Furlong et al. (20) introduced the concept of using reaction rate as a reactivity parameter while Shin et al (21) attempted to combine reaction rate and reaction extent into a single reactivity parameter which could then be correlated to coal properties. Gutmann (22) correlated reaction rate constants with the sulfur content of lignite coals. Other reactivity

relationships based on information from instrumental techniques such as pyrolysis/mass spectrometry have been developed by Baldwin et al. (23).

All of the above attempts to relate coal liquefaction reactivity to coal properties have suffered from two severe limitations. First, the parameters employed as reactivity definitions have generally fallen into two categories: 1) reactivity as defined by a point-yield definition at fixed time and temperature (e.g. toluene solubles at 60 minutes, 450 °C) or; 2) reactivity as defined by a reaction profile with time at fixed temperature. While both of these "traditionally" used reactivity definitions can be correlated with liquefaction reactivity, the correlations developed are not truly universal in that they may not hold at different time and/or temperature levels. This point is demonstrated conclusively below. The second major limitation of prior studies is that the correlations have not been developed in terms of fundamental structural and chemical properties of coal. In many cases, derived coal properties such as volatile matter, fixed carbon, rank, heating value, etc. have been used as the independent variables in multi-parameter statistical models. As pointed out by Neavel (24), such correlations are of limited significance.

The above discussion highlights the need for a reactivity parameter that is independent of both time and temperature, yet which can be correlated with basic coal chemical properties. Further, detailed knowledge of the chemical structure of coal is needed so that the reactivity correlations developed have some significance in terms of the chemistry of the liquefaction process. We have attempted to address both of these problem areas by using activation energy as a reactivity definition, and by exploring the use of structural information from two new NMR techniques (¹H-NMR/CRAMPS and ¹³C-NMR/CPMAS with dipolar dephasing) which do permit determination of fundamental chemical structural features important in coal liquefaction reactivity.

Experimental

Five bituminous coals from the Argonne Premium coal collection were liquefied in 1-methylnaphthalene vehicle. Characterization data for the Argonne coals are shown in Tables 1 and 2. Experimental runs were carried out in batch tubing bomb microautoclave reactors at 375, 400, and 425 °C, and at 3, 5, 10, 15, and 40 minute residence times. All runs were performed in a hydrogen atmosphere under a cold pressure of 6.2 MPa. Data on the rate and extent of coal conversion to THF and toluene solubles were collected using a standard solvent fractionation procedure. Further details concerning experimental methods have been reported elsewhere (25).

The experimental program consisted of two phases. During the first phase, an examination of the effect of vehicle on the measured liquefaction reactivities was carried out using 3 aromatic compounds (1-methylnaphthalene, naphthalene, and phenanthrene). The second phase of the project concerned

measurement of the data, kinetic modeling, and correlation with coal properties.

Proton NMR data for the Argonne coals was obtained from the National Science Foundation Regional Center for NMR at Colorado State University, utilizing the technique of Combined Rotational and Multiple Pulse Spectroscopy (CRAMPS). Basic data on the proton distribution in these coals are shown in Table 3. Information on the carbon distribution via dipolar dephasing of ^{13}C -NMR data was obtained from Dr. R.L. Pugmire at the University of Utah, and these data are presented in Table 4.

Discussion of Results

Effect of Vehicle on Liquefaction Reactivity In order to properly evaluate and compare the inherent reactivities of different coals, a non-hydrogen donor liquefaction vehicle was required so that reactivity differences between similar coals within a given rank or sub-rank could be magnified. The first phase of this experimental program was thus concerned with an evaluation of the effect of three aromatic vehicles on relative reactivities. Liquefaction experiments were performed on the 5 Argonne bituminous coals in 1-methylnaphthalene (1-MN), naphthalene, and phenanthrene, and the relative reactivities of these coals assessed by toluene conversion at 5 and 40 minutes. Figure 1 presents the results of the 40 minute runs. These data clearly indicate that the relative reactivities are independent of choice of vehicle, and that conversions in 1-methylnaphthalene are equivalent to the other two aromatic vehicles. Data from the 5 minute runs led to similar conclusions. Because of the added ease of operation afforded by 1-MN, this material was utilized as the liquefaction vehicle in all subsequent experiments.

Rate Data and Modeling Rate data for conversion of the Argonne coals to THF and toluene solubles were measured. Reproducibility of the data was checked by performing duplicate experiments on the Illinois #6 coal. Various kinetic models were investigated for purposes of data fitting, including the following:

- first-order irreversible
- first-order reversible
- second-order irreversible
- second-order reversible
- first order (forward)/second order (reverse)
- Anthony-Howard model (26)

Rate data from the liquefaction experiments were fit to each of these models for all 5 coals, and model discrimination performed using a goodness-of-fit (R^2) criterion. Statistical results from data fitting indicated that the best model overall from among these candidates was the first/second reversible model. The analysis of variance from regression modeling of the Illinois #6 coal (the replicated data set) gave very low values for the pure error mean square, indicating that the data were highly reproducible. A parity plot for toluene solubles conversion for Illinois #6 coal and the first/second-order reversible kinetic model is shown in Figure 2. As can be seen, the model provides a satisfactory descriptive expression for the data being observed.

Traditional Correlations As mentioned above, the traditional parameters that have been used for coal liquefaction reactivity correlations are point-yield conversion and a kinetic rate constant. We thus began our correlational efforts by exploring similar types of relationships. Figure 3 presents three correlations using the point-yield reactivity definition. Here, conversion to toluene solubles at 5 minutes is used as the yield parameter. As shown, a very strong correlation ($R^2=98\%$) exists between toluene conversion at 5 minutes and 425°C and total oxygen plus total carbon in the coal. However if this same correlation is extended to a different time (40 minutes) at the same temperature, a much weaker correlation ($R^2=61\%$) results. If the temperature is changed to 375°C while time is held constant (5 minutes), essentially no correlation ($R^2=0$) exists. Figure 4 shows the same sort of effect, but using a kinetic constant (from the first/second model) as the reactivity parameter. A very strong correlation is found at 425°C between the rate constant for conversion to THF solubles and the total carbon content of the coal ($R^2=94$). Since the rate constant is time independent, this is a valid reactivity parameter as long as the temperature is not altered. However, if the temperature is reduced to 400 and then to 375°C , the same correlation weakens significantly and then disappears, with R^2 falling to 54% and 12% respectively at the lower temperatures. This graphically illustrates the inadequacy of both of these "traditional" reactivity parameters, which are either time and/or temperature dependent.

The above discussion demonstrates the need for a reactivity parameter that is time and temperature independent. This leads logically to consideration of activation energy as a fundamental reactivity parameter, since:

- activation energy includes temperature effects;
- activation energy should reflect more closely the chemical nature of the parent coals;
- activation energy is obtained by measuring time and temperature effects, but the result is time and temperature independent.

Activation Energy Correlation Intuitively, the behavior noted above might be interpreted as a shift in the controlling mechanism for the liquefaction reaction, with one type of chemical functionality dominating the reaction at one set of conditions. This would be accompanied by a gradual shift to different reaction pathways and hence different chemical functionalities at other temperatures and times. This concept of a distribution of reaction pathways was the basis for the development of the Anthony-Howard model (26). However, when this expression was applied to our rate data little variation in the derived activation energies between the different coals was found. A strong dependency of the derived activation energies with coal type was found, however, for the first/second rate model. These data are presented in Table 5. Exceedingly good fits to the expected Arrhenius temperature dependency were found for the toluene and THF rate constants, as indicated by the

coefficients of determination (R^2) in Table 5. It is important to recognize that these activation energies are not fundamental parameters, but the large differences in activation energies found for these 5 coals suggest that this parameter should be useful as a relative reactivity indicator.

Before initiating correlation of reactivity with coal properties, it is important to determine which of the coal characteristics available are independent parameters, and which are highly correlated with other characteristics and thus are simply derived properties. Eight coal characteristics, including basic data from proximate and ultimate analysis along with the proton NMR (CRAMPS) information, were first investigated in this manner. Volatile matter and total carbon were found to be strongly correlated with aliphatic carbon content, while total carbon was found to be highly correlated with carbon aromaticity. Total sulfur, ash, and aromatic (and hence aliphatic) hydrogen content of the coal were found not to be related with any of the other properties of the coal.

Table 6 presents the results of correlation of the liquefaction activation energies for the 5 bituminous coals with the independent coal properties. The activation energy for coal conversion to toluene solubles was found to be strongly ($R^2=93\%$) correlated with the total oxygen content of the coal, while the activation energy for conversion to THF solubles was found to be highly correlated ($R^2=95\%$) with aliphatic hydrogen content. These correlations are shown graphically in Figures 5 and 6. Correlation of activation energies for conversion to toluene and THF solubles were not found to be highly correlated with any of the other coal properties in Table 6, suggesting that the relationships found between reactivity and these two coal properties are unique.

Data from the ^{13}C -NMR were next investigated, and simple single-parameter correlations of these properties with THF and toluene activation energies attempted. Intercorrelations between the various ^{13}C -NMR properties and other coal characteristics were first investigated in a manner similar to the above. The only intercorrelation found from this data set was for total oxygen and protonated aliphatic carbon (sp^3 -hybridized and CH or CH_2). The correlation between these two parameters for the 6 Argonne bituminous coals (including Blind Canyon) was almost 99%, however when the data for the subbituminous and lignite coals was added, the correlation no longer held. These data are shown graphically in Figure 7. This finding may have strong implications with respect to coal structure, and the differences in reactivity found between low rank and high rank coals in general. The activation energy for conversion to toluene solubles was found to be very highly correlated ($R^2=93\%$) with protonated aliphatic carbon. No other correlations of coal properties from the ^{13}C -NMR data and toluene or THF activation energies were found.

The strong intercorrelation found between protonated aliphatic

carbon and total oxygen for the 6 bituminous Argonne coals can be interpreted structurally in terms of etheric groups in the cross-linking structures between aromatic clusters. While based on a rather limited data set, this relationship and the correlation found between total oxygen and toluene activation energy would seem to suggest that the carbon-oxygen bonds in crosslinking structures are of extreme importance in determining coal reactivity. Data from the ^{13}C -NMR also provides an estimate of the relative abundance of etheric carbon-oxygen structures (All-O in Table 4). However, when this parameter is correlated with the toluene activation energy a less than adequate ($R^2=77\%$) relationship is found as shown in Figure 8. One coal (Stockton) in this data set represents a significant outlier, and if this coal is removed from the regression, the adequacy of the relationship improves to 97%. Due to the limited number of coals in this study, these observations and conclusions must be treated as tentative at this time. Further research on a wider suite of bituminous coals is needed.

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Table 1. Characterization Data of Argonne Premium Coals
(Elemental & Proximate Analysis)

Coal Seam	State	Rank	Elemental Analysis*				Proximate Analysis**		
			C	H	O	Stot	Ash	V.M	F.C
Illinois #6	IL	HVB	77	5.7	10	5.4	14.8	35.4	44.7
Pittsburgh #8	PA	HVB	83	5.8	9	1.6	9.7	34.9	53.6
Lewiston- Stockton	WV	HVB	81	5.5	11	0.6	20.1	28.6	49.4
Upper Freeport	PA	MVB	87	5.5	4	2.8	13.1	25.1	60.7
Pocahontas #3	VA	LVB	91	4.7	3	0.9	5.3	17.1	77.1

* All the values are given based on wt % (d.a.f basis), except for sulphur which is in dry wt %. These data furnished by Argonne National Laboratory, Argonne, Illinois.

** All the values are given based on as received basis (wt %). These data measured by Huffman Laboratories, Inc., Golden, Colorado

Table 2. Characterization Data of Argonne Premium Coals
(Carbon-13 N.M.R and Proton N.M.R)

Coal Seam	State	Rank	Carbon-13 N.M.R.*		Proton N.M.R. **			
			C-tot	C-arom	C-alip	H-tot	H-arom	C-alip
Illinois #6	IL	HVB	6.42	4.42	2.00	5.7	2.74	2.96
Pittsburgh #8	PA	HVB	6.92	5.17	1.75	5.8	2.21	3.59
Lewiston-Stockton	WV	HVB	6.75	5.00	1.75	5.5	1.68	3.82
Upper Freeport	PA	MVB	7.25	5.92	1.33	5.5	2.10	3.40
Pocahontas #3	VA	LVB	7.58	6.75	0.83	4.7	2.57	2.13

* All the values based on moisture and ash-free atomic basis (wt % divided by m.w of carbon). Aromaticity data measured by Utah University using C-NMR (CPMAS). These data were furnished by Dr. Ronald Pugmire.

** All the values based on moisture and ash-free atomic basis (wt % divided by m.w of hydrogen). Proton NMR data measured by NSF Regional NMR Center (Colorado State University, Fort Collins, Colorado) using H-NMR (CRAMPS).

Table 3. Aliphatic and Aromatic Hydrogen Contents of Argonne Coals: Proton-NMR (CRAMPS)

coal	aromatic H (%)	aliphatic H (%)
Illinois #6	48.0	52.0
Pittsburgh #8	38.1	61.9
Stockton	30.6	69.4
Upper Freeport	38.2	61.8
Pocahontas	54.6	45.4

Proton spectra obtained at a proton Larmor frequency of 187 MHz using a BR-24 pulse sequence. The 90 pulse width was 1.1 us and the cycle time of 36 tau was 108 us. Samples were spun at the magic angle at a nominal rate of 2 KHz.

Spectra measured by the National Science Foundation Regional NMR Center, Colorado State University, Fort Collins, Co.

Table 4. Carbon Structural Distribution of the Argonne Coals

	Illi #6	Pitt #8	Stockton	Upper F. Pocahontas
Aliphatic-total(SP3)	28%	28%	25%	19%
Ali-H	18	13	18	8
Ali-N	10	15	7	11
(Ali-O)	(5)	(3)	(4)	(2)
Aromatic-total(SP2)	72%	72%	75%	81%
Aro-Ring	72	72	75	81
Aro-R-H	26	27	27	28
Aro-R-N	46	45	48	53
Aro-R-N-P	6	6	5	4
(Aro-R-N-A	18	17	21	20
Aro-R-N-B	22	22	22	29
Aro-Carbonyl	0	0	0	0

Ali-H=fraction of total carbon that is sp³-hybridized and CH or CH₂.
 Ali-N=sp³-hybridized and CH₃ or nonprotonated, Ali-O=sp³-hybridized and bonded to oxygen. Aro-R-H=sp²-hybridized and protonated.
 Aro-R-N=sp²-hybridized and nonprotonated, Aro-R-N-P=sp²-hybridized and phenolic or phenolic ether, Aro-R-N-A=sp²-hybridized and alkylated, Aro-R-N-B=sp²-hybridized and at a bridgehead position.

Data on carbon distribution obtained from Dr. R.J. Pugmire, University of Utah.

Table 5. Activation Energies of 5 Bituminous Argonne Coal

Coal Seam	Toluene solubles		THF solubles	
	E (Kcal/m)	R-Square (%)	E (Kcal/m)	R-Square (%)
Illinois #6	20.9	99.8	17.5	99.5
Pittsburgh #8	15.5	95.2	24.5	96.3
Lewiston-Stockton	26.8	94.3	29.5	98.3
Upper Freeport	9.9	97.0	20.1	99.3
Pocahontas #3	4.3	100	7.5	98.3

Table 6. Correlation of Activation Energy with Coal Properties

o Adjusted Coefficient of Determination (%)

Coal Property	Activation Energy (toluene solubles)	Activation Energy (THF solubles)
C-aliphatic	64.8	32.0
C-aromatic	67.9	21.9
H-total	23.8	42.4
H-aliphatic	32.5	95.1 -----
O-total	93.2 -----	36.2
S-total	0.0	0.0
Ash	72.8	37.1
H-tot/C-tot	50.7	29.2
O-tot/C-tot	91.6	29.9
O-tot + C-tot	27.4	0.0

Figure 1. Solvent Effect on Reactivity Ranking
(Reaction Time: 40 min)

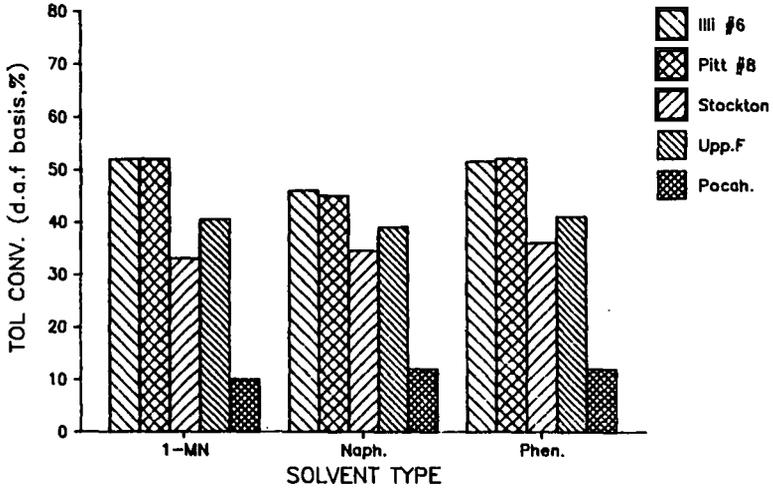


Figure 2. Parity Plot (toluene solubles)

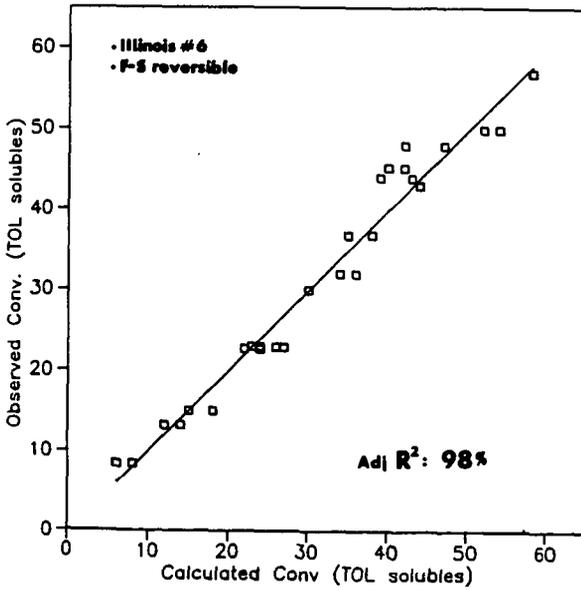


Figure 3. Example I

Point-Yield Reactivity vs. Total C+O

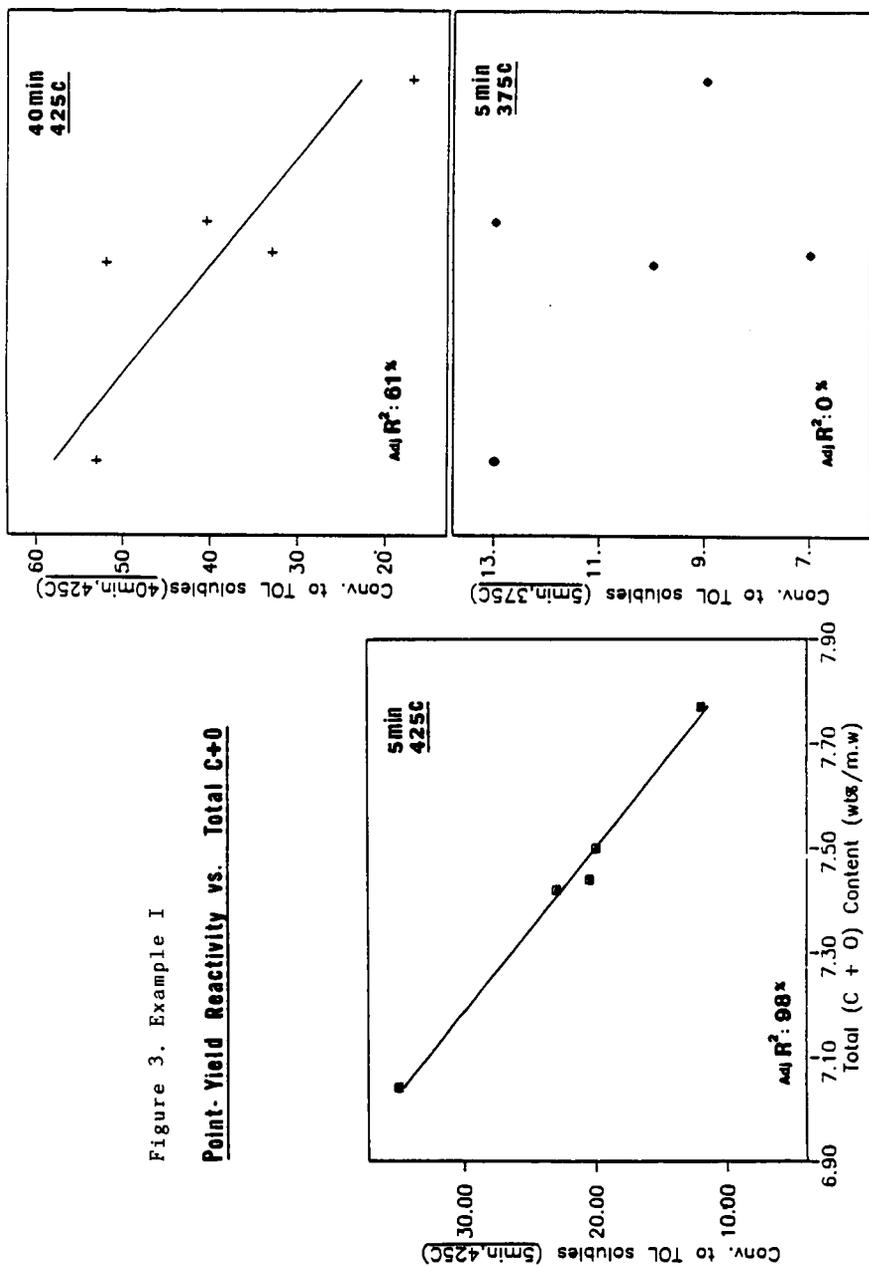


Figure 4. Example II
Kinetic Constant vs. Total Carbon

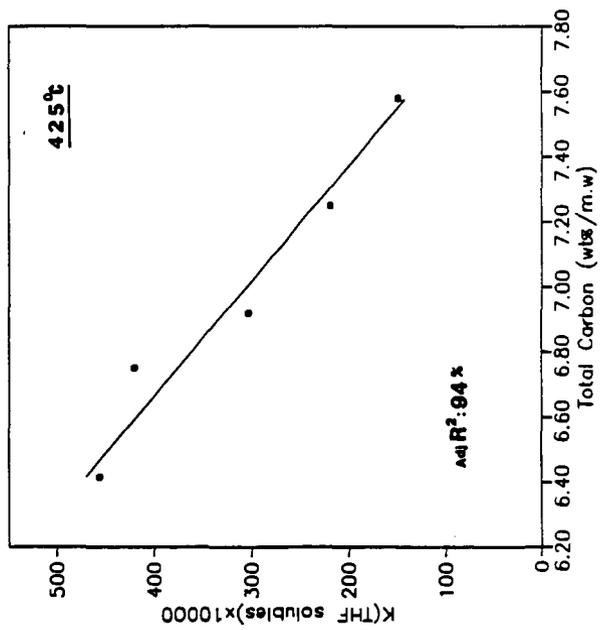
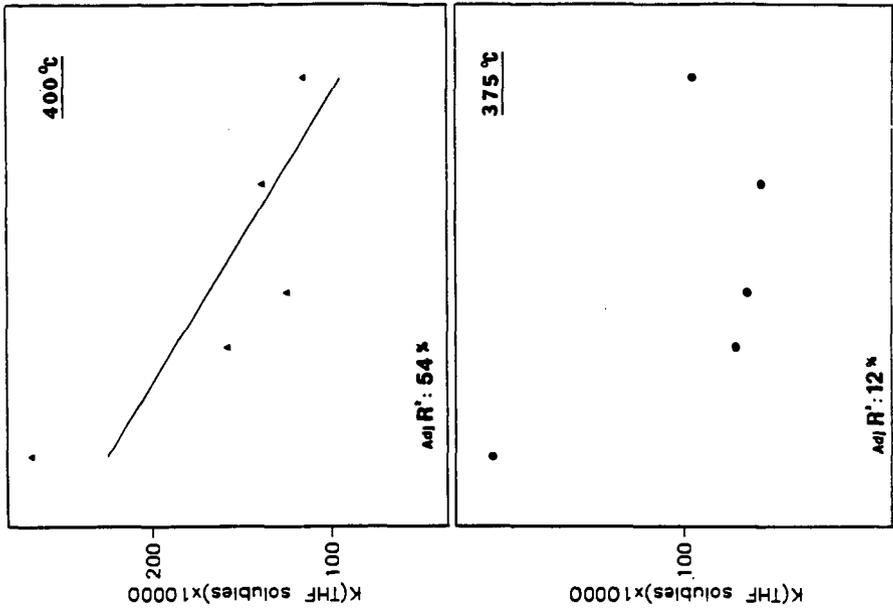


Figure 5. Correlation of Activation Energy (toluene solubles) vs. Oxygen Content

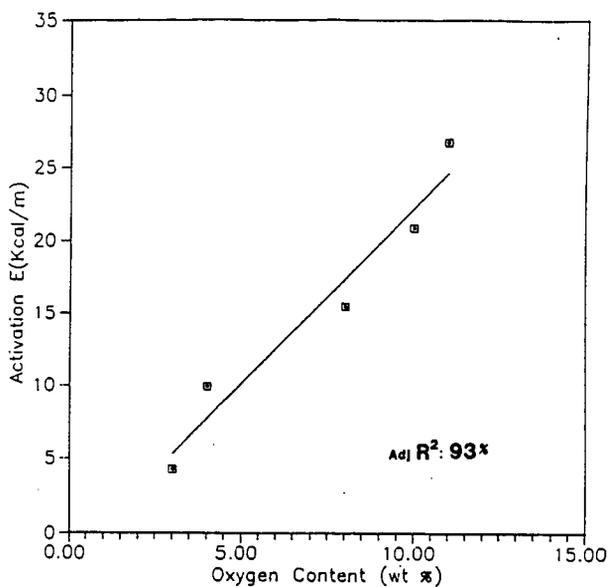


Figure 6. Correlation of Activation Energy (THF solubles) vs. Aliphatic Hydrogen

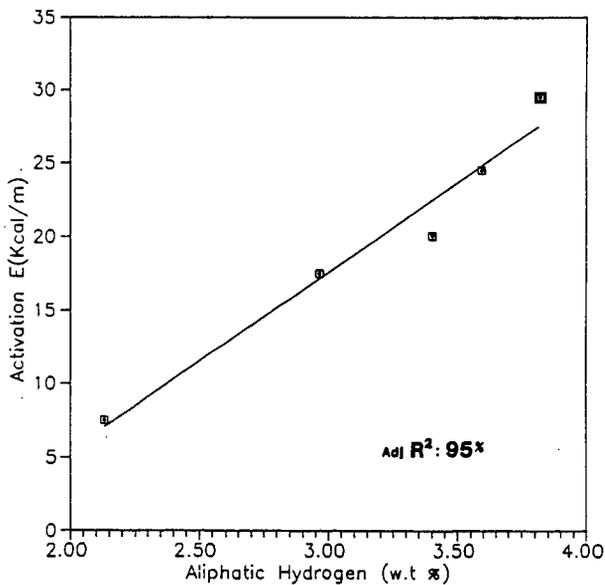


Figure 7. Interrelationship between Total Oxygen and Linking Aliphatic Carbon Content

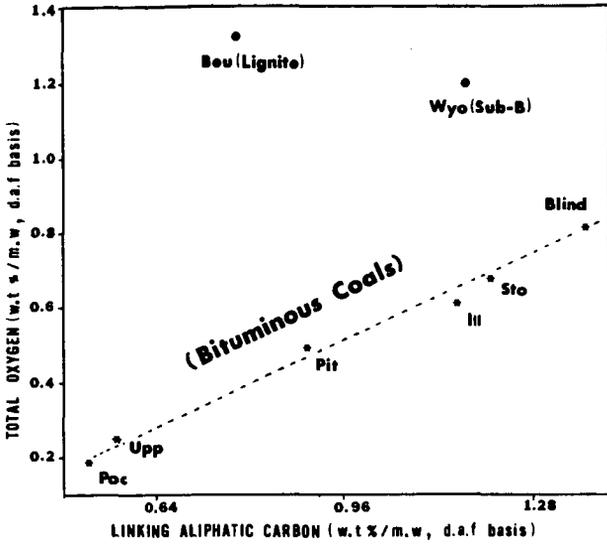


Figure 8. Correlation of Activation Energy (toluene solubles) vs. Aliphatic Carbon-Oxygen

