DEPENDENCE OF COAL HYDROLIQUEFACTION

REACTIVITY ON COAL PROPERTIES

by

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ABSTRACT

The kinetics of hydroliquefaction for five coals from the Penn State Premium Coal Bank were studied in a tubing bomb micro-reactor system using a non-hydrogen donor vehicle. The goal of this study was to investigate the relationships between fundamental coal properties and coal hydroliquefaction reactivities. For experimental studies 1-methylnaphthlene was used as the non-hydrogen donor vehicle. Runs were made at three temperatures (425, 400, 375°C), 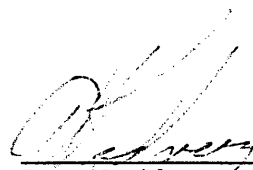five residence times (3, 5, 10, 15, 40 min), and 900 psi pressure. Five kinetic models were tested and a second order reversible model was determined to be the most adequate. Activation energies and rate constants for liquefaction of the five coals were also determined by using second order reversible model. Activation energies for conversion to THF solubles were correlated well with total carbon plus total hydrogen and activation energies for conversion to toluene solubles were highly correlated with free swelling index, total carbon, and total oxygen content. Rate constants were strongly correlated with total hydrogen content.

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1. INTRODUCTION

The goal of developing a fundamental understanding of the chemistry of coal has been occupying researchers for over half a century. Techniques avaliable for analysis of coal are not as yet powerful enough to give a detailed description of coal unit structures, since coal is an inhomogeneous mixture of organic and inorganic species. Today much research is focused on reactions typical of coal, but using homogeneous substances with known structures (model compounds) as well as instrumental techniques that give direct information about the structure of coal.

The main purpose of much of the research on coal is to produce an energy source for future usage as a substitute for petroleum. To achieve this goal one has to fully understand the characteristics and behavior of coal under certain conversion conditions. However, the research on coal conversion that has been done generally lacks fundamental definitions for reactivity. Coal hydroliquefaction reactivity is usually defined as the conversion rate to some solvent soluble classification at fixed temperature and time. It has been proven that this type of definition may give rise to incorrect conclusions about the characteristic behavior of coal for conditions other than those for which they were produced. Recently, new reports have been published expanding the question of how to define and correlate

coal liquefaction reactivity based on rate processes. Furlong showed that the rate of reaction served as a more sensitive relative reactivity ranking parameter than the conversion for coals with very similar composition (40). However, this definition was shown to be flawed by Shin (23), who pointed out that two coals with the same kinetic constants may also show different conversions at long reaction times.

In this study, activation energy is used as a more general reactivity parameter for coal hydroliquefaction. Correlation of coal properties with activation energies for conversion to THF and toluene solubles is carried out, and relationships to coal structure and the chemistry of coal liquefaction developed. Finally, reactivity ranking using activation energy as the parameter is shown to be independent of the choice of kinetic model.

2. LITERATURE SURVEY

Production of liquid fuels from coal has been a technical feasibility since the late 19th century. The possibility of producing a liquid-like material from coal was first demonstrated by Bertholet in 1869. Germany laid the foundations for most of the present day direct and indirect coal liquefaction techniques with the discovery and development of the Bergius hydrogen donor process in 1913, the Pott-Broche solvent extaction process in 1927, and the Fischer-Tropsch process for hydrocarbon synthesis from synthesis gas in 1925 (1).

2.1 Chemistry of Coal

The goal of developing a fundamental understanding of the chemistry and structure of coal has been occupying researchers for over half a century. Coal is a sedimentary rock which accumulated initially as peat. Virgin coal is composed principally of macerals (plant fossils) and subordinately of minerals, water, and gases in submicroscopic pores. Coal is an inhomogeneous mixture of carbon, hydrogen, oxygen, sulphur, and minor proportions of other elements (2). As shown in Figure 1, coal is considered to contain relatively small polycyclic aromatic and hydroaromatic rings as structural units, connected by ether and

methylene bridges to form a macromolecular structure (3).

Thus conversion of coal via depolymerization is believed to

proceed initially mainly through cleavage of these bridges.

2.2 Mechanism of Liquefaction

The reactivity of coal in liquefaction reactions is

influenced by its chemical structure. Hence, a knowledge of

the relationship between reactivity and chemical structure

is useful for the elucidation of the liquefaction mechanism.

To produce liquids from coal, the following chemical

changes need to be accomplished :

- Breaking large macromolecular structures into small-

er ones by bond rupture.
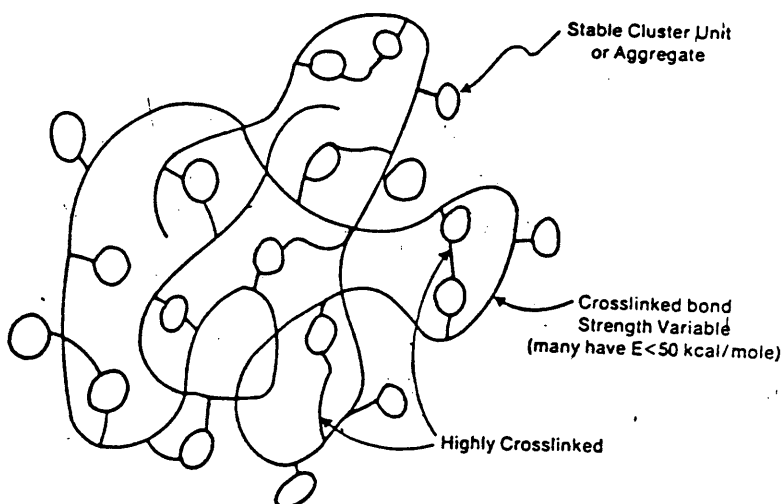
Figure 1.   The macromolecular network of coal (3)

- Addition of hydrogen to increase H/C atomic ratio.

- Removal of heteroatomic species (N, O, S) by trans-
formation into their hydrogenated gas state (H2O, H2S,
etc.).

- Removal of mineral matter.

Presently, there are no standard methods or techniques
to separate and characterize liquids from coal. However,
most investigators in coal liquefaction tend to characterize
coal-derived products by solubility distribution analysis,
chromatographic analysis, and distillation (4, 5, 6). Among
these three techniques, solubility distribution (solvent
extraction) is most commonly used by researchers to charac-
terize coal products and to define coal conversion. The
solvent extraction technique classifies coal-derived
products into lumped groups of compounds according to their
relative solubilities in different solvents such as tetrahy-
drofuran (THF), toluene, hexane, etc. Lumped groups which
are most widely named are "preasphaltenes" (soluble in polar
solvents such as THF or pyridine, but insoluble in non-polar
aromatic solvents such as benzene), "asphaltenes" (soluble
in benzene but insoluble in hexane), and "oils" (soluble in
hexane). The molecular weight of the molecules in the above
fractions are correspondingly smaller than the molecular
weight of the parent coal; the lower molecular weight
results from various bond-breaking reactions.

Pyrolysis of coal is presumed to be the first step in which the structure of coal is broken down to smaller fragments by thermal bond rupture. The resulting derived fragments (radicals) are assumed to capture hydrogen from hydrogen donor species such as tetralin, dihydrophenanthrene (DHP), from molecular hydrogen supplied either directly or indirectly by the gaseous reaction atmosphere, or from hydrogen-rich portion of the coal itself. A schematic representation of hydrogenation of coal in the presence of a hydrotreating catalyst and a donor solvent is shown in Figure 2.

The mechanism of direct hydroliquefaction is widely believed to proceed by a free-radical mechanism (7). Thermal cleavage of C-C, C-O and C-H bonds are assumed to initiate the free-radical processes, and it has been shown by Benjamin (8) that C-C cleavage can occur under the conditions of asphaltene formation.

2.2.1 Methylene and Ether Bridges

It has been generally accepted that there are ether and methylene bridges in coal, and that breaking these bonds initiates thermal conversion and thus the liquefaction of coal. To understand the contribution of these bridges to the mechanism of liquefaction, reactions using various model
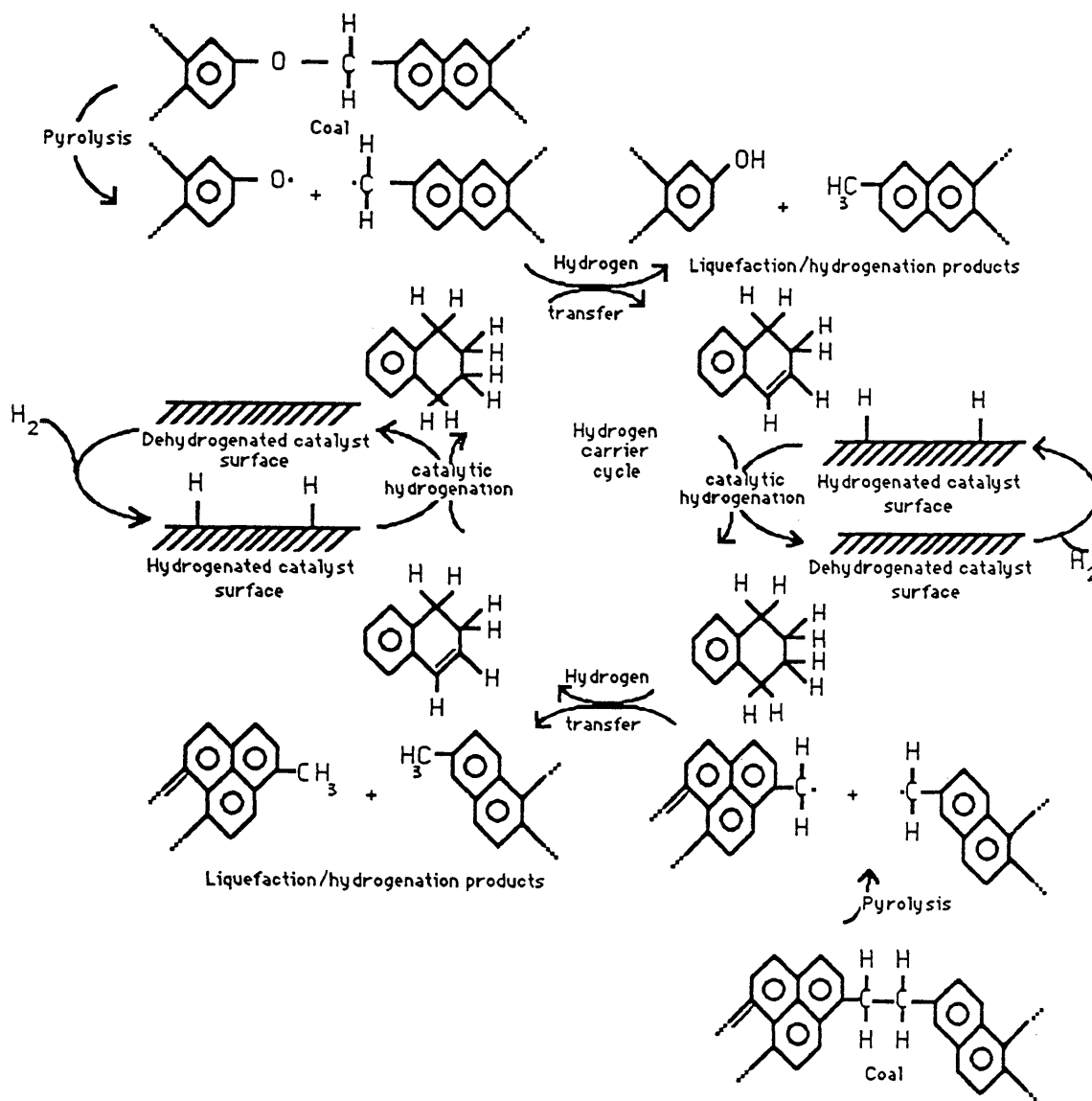
Figure 2. Schematic Representation of the Reaction
Cycles of Coal Hydrogenation (69)

compounds have been studied. As the simplest model for methylene connecting units in coal, thermolysis of Ar-CH2-X-Ar' (X=CH2, O, S) model compounds has been of particular interest. Poutsma (9) studied the thermolysis of both gaseous and liquid dibenzyl and concluded that the results for thermolysis of dibenzyl are consistent with a nonchain, free radical mechanism but only after appropriate account is taken for combination, disproportionation (another disappearance pathway for radicals), and rearrangement of the radicals involved. The effect of the number of methylene groups and substituents in etheric structures on the mechanism of thermolysis has been studied by many researchers (10, 11, 12, 13, 14, 15). Korobkov (10) showed that introducing methylene groups into a Ph-O-Ph structure drastically decreased its stability. He further found that introducing additional methylene groups into R-O-R structure had a two fold effect: In the nonsymmetrical structures such as Ph-CH2CH2-O-Ph, C-O bond strength remained low; in symmetrical structures, like Ph-CH2-O-CH2-Ph or Ph-CH2CH2- O-CH2CH2-Ph bond strength increased. Yoshida (16) found that the cleavage of ether bridges contributed to the formation of preasphaltenes. He also found that the conversion to hexane solubles in the mild liquefaction reaction (400°C, 30 min) correlated well with CH2 carbon content of coal. Yoshida further concluded that the formation of oil from

preasphaltenes was caused by scission of CH2 bridges and some napthenic CH2 bonds. He also determined that etheric oxygens in coal are distributed predominately as aromatic rather than aliphatic ethers. From an extensive model compound study, Benjamin (8) showed that structures that contain two-carbon aliphatic chains as bridges connecting aryl groups are cleaved from the central C-C bonds, not the bonds adjacent to the aryl rings. Benjamin further showed that preasphaltenes were formed in part by the scission of C-C bonds in ethylene bridges connecting aryl groups, and that the slower asphaltene and oil formation must be partly a result of ether bond cleavage and more C-C bond cleavage including bonds adjacent to aryl rings. Kamiya (17) proved that the conversion rate of 2, 2' dinapthyl ether was re-markably enhanced in the presence of hydrogen donor solvent. It was postulated by Kamiya that the enhancing effect of the hydrogen donor was due to hydrogen transfer to the aromatic nucleus of the diaryl ether from the hydrogen donor, and successively fast decomposition of the hydrogenated ether. From the study of pyrolysis of dibenzyl ether at 450°C, Schlosberg (18) found that in the absence of added hydrogen, increasing reaction severity (residence time) led to growth/polymerization reactions ultimately leading to coke.

2.2.2 Sulfur in Coal

Compounds of nitrogen and sulfur are also components of coal, and their removal is of economic importance in producing clean fuels from coal. Sulfur in coal exists as both inorganic (pyrite, FeS_2, etc.) and organic sulfur (thiophene etc.) compounds. The effect of pyrite (FeS_2) on coal liquefaction reactivity has been studied by many researchers. Guin (65) studied both the effect of elemental iron and ironsulfide (FeS_2) as a catalyst on the liquefaction reactivity of coal and rate of hyrodesulfurization. He reported that elemental iron had very little catalytic activity towards the liquefaction reactivity of coal, but it acted as a very strong sulfur scavenger by reacting with hydrogen sulfide (H_2S) to produce a nonstochiometric iron sulfide $FeS(1+X)$. Guin (65) further showed that iron sulfides catalyzed the coal liquefaction reaction resulting in higher oil yields, but they did not affect the removal of sulfur from the coal liquids. Mukherjee (68) also studied the effect of mineral content on liquefaction reactivity and reported that conversion to liquid products increased with increasing mineral matter, with iron pyrite identified as an active catalyst. Baldwin (66) suggested that pyrite may be acting as an indirect catalytic agent via formation of H_2S. It has been shown that most of the sulfur removal by catalytic hydrogenation was from a R-S-R type structure

rather than thiophene like structures (67).

2.2.3 Cross-linking

It is known that when coal is immersed in a solvent
the solvent penetrates into and causes swelling of the coal.
The degree of cross-linking can be estimated by the
swelling beheviour of the coal. Larsen (20) estimated the
degree of cross-linking (average molecular weight per
cross-link) by using data based on solvent swelling (amine
bases) and the interaction of the swelling molecules with
coal. In those swelling experiments, Larsen (21) further
showed that low rank coals, like lignite and subbituminous,
have a much higher tolerance to branched, bulky groups than
do the bituminous coals. Ouchi (22) stated that higher
conversions of lower rank coals probably results from the
fact that these coals contain more ether linkages which are
easily cleaved, and more polar functional groups such as
hydroxyl or carboxyl groups which contribute to the enhance-
ment of cleavage of C-C linkages.

2.3 Effect of Vehicle (Solvent) on Liquefaction

Much research has been carried out to determine the
effects of various vehicles (non-hydrogen donor and hydrogen
donor) on coal hydroliquefaction and the function of gase-
ous hydrogen as a hydrogen donor source. Shin (23) performed

experiments with 5 bitumious coals in 1-methylnapthalene
(1-MN), naphthalene, and phenanthrene (non H-donor
vehicles), and the relative reactivities of these coals was
assessed by toluene conversion. His data clearly showed
that the relative reactivities were independent of the
choice of non-H donor vehicle.

It was proposed by Ouchi that when the reactivity of
the coal was higher than that of the solvent, the coal
appeared to be predominantly hydrogenated directly by gase-
ous hydrogen (22). When reactivity of the coal approaches
that of the solvent, an alternative mechanism begins to
operate in which the solvent is hydrogenated initially to
form a donor solvent which then donates hydrogen to the
coal. If the solvent reactivity is greater than that of
coal, the second path predominates. In 1976, Neavel (24)
showed that free radicals formed pyrolytically were stabi-
lized in the early stages by autogenous hydrogen transfer,
and in later stages by abstraction of hydrogen from the
hydrogen-donating tetralin. Utz (25) studied short contact
time liquefaction in hydrogen-donor and gaseous hydrogen
vehicles and found that even though hydrogen consumption is
minimal during the early stages of liquefaction, hydrogen-
donor vehicle plays an important role in converting coal to
THF-soluble materials. Utz further found that H2 was a
competing source of hydrogen in short contact time liquefac-

tion, and that the rate of reaction of H2 with reactive coal fragments (free-radicals) was similar to that of tetralin. Winschel (26) showed that donor solvent quality (as measured by microautoclave coal conversion) increases with increasing hydroaromatic content and with decreasing aromaticity and paraffinicity.

Effect of Phenolic Compounds on Liquefaction

Among organic substances, phenols have a particularly individual set of chemical properties. ✓Earlier work (27) had shown that a major fraction of the oxygen in vitrinites and vitrains was present as phenolic OH.✓ As early as 1955, Brown (28) showed that a decrease in the intensity of the phenolic OH band was one of the first phenomena to be ob-served when vitrinites were pyrolysed at temperatures of 400-550°C. From these findings, Abdel-Baset suggested that dissociation of OH to produce free radicals might deepen hydrogenation of coal structures (29). It was confirmed that phenolic compounds are not effective solvents for coal dissolution in the absence of a hydrogen donor (30). Phenols do have a remarkably positive effect on coal liquefaction in the presence of tetralin, depending on the character of the coal and on the concentration of the phenols. Kamiya (30) found that the solvent refined coal obtained in the presence of phenol was low in hydrogen content and high in aromatic

hydrogen. These results are in agreement with the fact that coal conversion increases without the simultaneous increase of hydrogen consumption in the presence of phenols.

2.4 Kinetic Modelling

Initially work on kinetic modelling of coal liquefaction was done in the 1940's by Storch who defined the products of liquefaction by lumped groups in terms of solubility of the products in acetone and benzene (31). Curran (50) defined the kinetics of coal conversion by assuming that a certain portion of the coal dissociated at a faster rate than the remaining part. In 1968, Wiser (51) reported that second order reactions in the initial stages of liquefaction shifted gradually to first order reactions at longer reaction time. Many kinetic models have been proposed to involve entire reaction networks by assuming pseudo-first order reactions for each reaction step (35, 52). Following the assumption of various reaction paths among lumped coal-derived products, best-fit models were obtained for the experimental data by using regression schemes. In spite of the fact that the experimental data can be described satisfactorily, it is generally understood that these kinetic models do not necessarily represent the true reaction mechanism because more than one rate constant can be obtained from statistical analysis (42, 43, 44). Recently

Anthony (45, 46) proposed statistical kinetic models based on the concept of a distribution of activation energies. More recently Shin (53) developed a single-step liquefaction kinetic model by using a pseudo-equilibrium conversion concept.

2.5   Correlation of Coal Reactivity

Many researchers have attempted to find satisfactory correlations between properties of parent coal and coal liquefaction behavior. Bergius (54) in 1920 recognized that coals with over 85% carbon (d.a.f. basis) made poor liquefaction feedstocks; but it was later found that coal rank was not adequate in assesing the liquefaction behavior of a coal (55). In Germany, the Institute of Technical Chemistry compared the relative ease of coal liquefaction to a benzene-soluble product (no catalyst or organic carrier solvent was used) and their results indicated that in the range from 52% to 84% carbon content by weight (moisture free), conversion tends to increase with increasing H/C or O/C ratios of feed (32). Fischer and his co-workers (56) in 1942 carried out an extensive research program to determine the relationship between petrographic composition of coal with coal liquefaction reactivity, but their study was a limited success. It was later found that coals of the same overall carbon content may have different maceral distributions

(57). In 1951, one of the earliest models for the liquefaction of bituminous Dutch coals using anthracene oil and beta-naphtol as solvents was proposed by Oele et al (33). The rate data obtained by these researchers were correlated with a reversible model, assuming that forward reaction was zero order and that reverse reaction was first order with respect to the fraction of extracted material.

Hill et al. (34) proposed the following kinetic expression for the liquefaction of high-volatile bituminous coal in tetralin:

$$dX/dt = k(1-X)$$

where "X" is the fraction of coal liquefied and "k" is the first order rate constant which was modeled as a function of conversion:

$$k = k_o(1-aX)$$

Here, "k_o" is a pseudo second-order rate constant and "a" is the reciprocal of the maximum liquefiable fraction at a given temperature.

It is often observed that the fraction of bituminous coal liquefied in tetralin, determined by soxhlet extraction using benzene, increases with increasing temperature and finally reaches an "equilibrium" value beyond which

it remains constant. The time required to reach this "equilibrium" value is seen to decrease with increasing temperature, while the "equilibrium" value attained increases with increasing temperature. Cronauer et al. (35) observed an increase in this "equilibrium" value for a given coal with increasing hydrogen-donor capacity of the solvent used to liquefy the coal.

In the second half of 1970's Given et al. completed extensive liquefaction reactivity research with more than one hundred different coals. Correlation studies on these coals provided insight into the nature of coal reactivity (36,37,38,39). The results of their work can be summarized as follows:

- Attempts to correlate coal properties solely with a rank parameter, such as carbon content, are not adequate.

- Geographic origin is one of the key factors affecting coal liquefaction behavior.

- The liquefaction behavior of coals can vary widely depending on their chemical and petrographic characteristics.

- Sulfur content is one of the major factors in defining coal reactivity populations.

As a measure of coal reactivity, Given used the percentage of coal converted to ethyl acetate soluble products for a reaction time of 60 minutes.

The concept of point-yield conversion at a given residence time as the definition of reactivity has been used by many researchers. However this definition of reactivity does not provide any insight into the kinetic behavior of the coal. Previously, only a few reports have been published correlating kinetic parameters with coal properties. Correlation of basic coal properties with kinetic parameters was initiated by Furlong (58) and Gutmann (63). Furlong (40) later proposed that a kinetically defined reactivity would have a more direct correlation with parent coal properties rather than a reactivity defined by a single point conversion. Furlong further showed that a kinetic definition for reactivity was superior in ranking relative reactivities among closely related coals (58). More recently Shin (53) proposed a different concept which combined both static and dynamic reactivity definitions as a measure of the liquefaction reactivity of coal. He developed this idea further and correlated liquefaction activation energies for toluene solubles with coal properties, choosing a first-second order reversible model as the best kinetic model from five proposed models (23).

Most of the research done earlier was intended to separate coal liquids into "kinetically similar lumped groups" such as by solubility in various solvents or using liquid-solid chromatography (LSC) or distillation. Many

researchers have attempted to quantitatively relate coal
liquefaction yields to basic coal properties (e.g., volatile
matter, H/C atomic ratio, reactive macerals, fixed carbon,
sulfur content, etc.). Neavel (47) studied interrelation-
ships between coal compositional parameters and reported
that many derived properties (density, reflectance, specific
energy, free index, and volatile matter) of coal have a
strong interrelationship with the elemental properties of
the coal. Neill (59, 60) also determined that a high corre-
lation existed between aromaticity and the carbon content of
coal. Neavel (61) pointed out the necessity of correlation
with basic properties of the coal, and not with derived
properties. Although correlation between coal fundamental
properties and liquefaction yield has been thoroughly stud-
ied, only a few correlational studies have been made con-
cerning the kinetic behavior of coal in direct hydrolique-
faction. Prasad (62) collected the reported values for
activation energies from other researchers and concluded
that there appeared to be a direct correlation between
activation energy and elemental (H/C) ratio of the coal.
Gutman (63) calculated the kinetic rate constants for 10
lignite coals by assuming a series first-order model, and
found that kinetic constants had some correlation with
combustible sulfur contents of the coals. Shin (23) recent-
ly found a strong correlation between activation energy (THF

solubles) and aliphatic hydrogen content. He also reported
satisfactory correlations between activation energy (toluene
solubles), total oxygen (wt%) and protonated aliphatic
carbon (wt%). Most recently Neill (48) found that, from a
set of 26 high volatile bituminous coals with sulfur con-
tents ranging from 2.8 to 7.9% by weight, there was a tend-
ency for total conversion to decrease with increasing rank.
In addition no correlation of asphaltenes, oils, gas, rank
or sulfur content were seen. Shadle (49) recently found
that no correlation existed between liquefaction yields from
26 high-sulfur coals and structural features, and stated
that high sulfur coals were more heterogenous than had been
expected.

3. EXPERIMENTAL

3.1 Equipment

3.1.1. Tubing-Bomb Reactor System

An existing tubing bomb reaction apparatus was used to carry out the experimental portion of this research. A schematic of this apparatus is shown in Figure 3. This unit, used for coal liquefaction reactions, was previously employed by Altizer and is described in detail in his thesis (50). The system consists of four subsystems: gas feed subsystem, gas sampling subsystem, heating, and reactor subsystems.

The gas feed subsystem is designed to permit precise control of feed gas pressure to the reactor. The reactor subsystem is evacuated first through valve V5 with valve V3 closed, insuring the integrity of the gas mixture fed to the reactor. The gas sampling subsystem consists of a one liter surge tank with a Swagelok female quick connect sample port, allowing sampling of the reaction product gases. Valve V5, a Whitey micro-metering valve, allows for the reactor tube to be pressurized accurately. The heating system, designed to rapidly attain the desired reaction temperature, utilizes a Tecam Model SBL2D fluidized bed sand bath. The bath temperature is controlled by a Leeds & Northrup Electromax III temperature controller connected to a Leeds & Northrup model
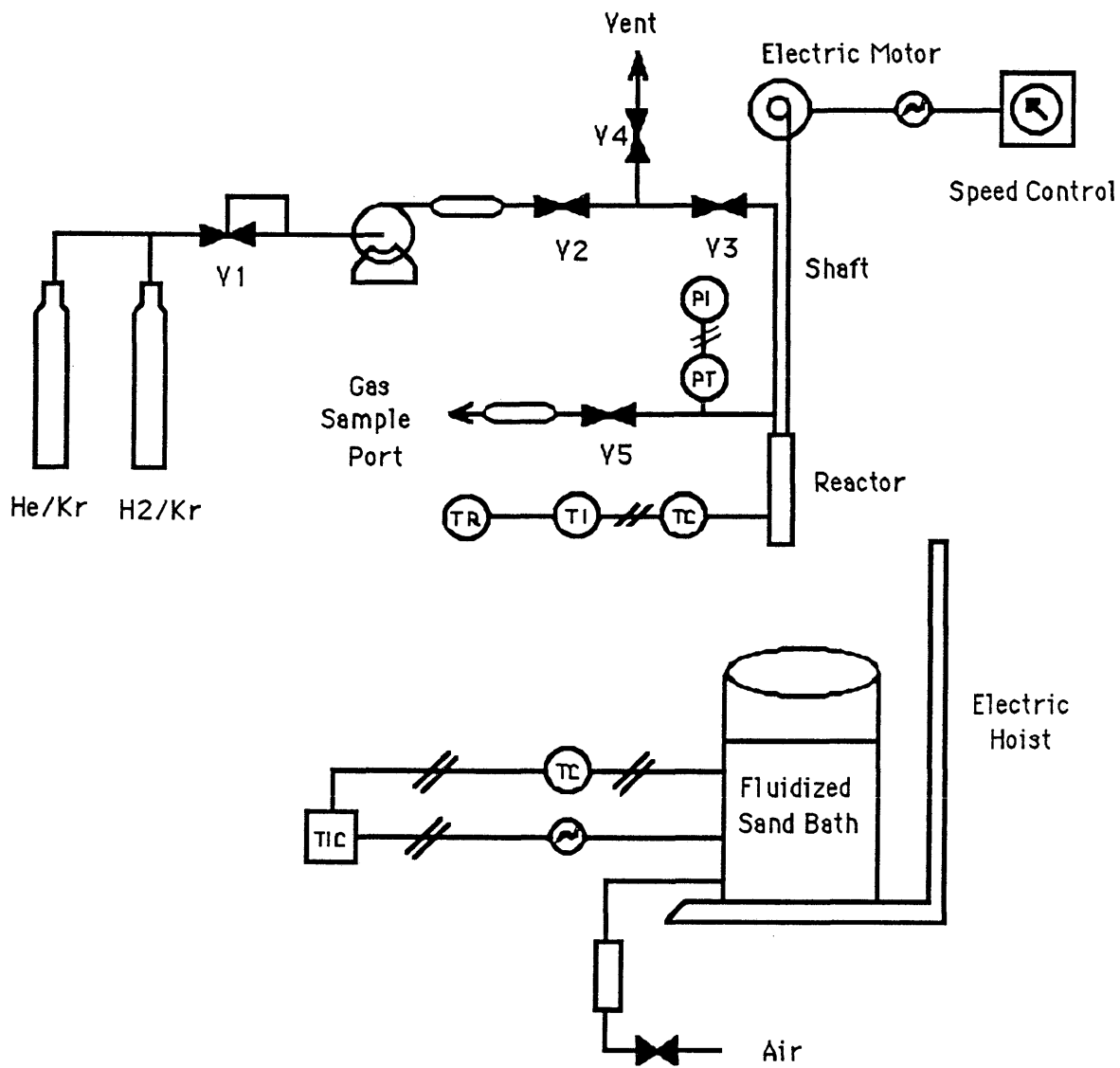
Figure 3. Schematic of Reaction System

1106 zero voltage power supply. The reactor contents were found to attain the desired temperature within 3 minutes after immersion into fluidized bed sand bath.

A drawing of the tubing-bomb reactor assembly is shown in Figure 4. The body of the reactor consists of 1/2" OD 316 stainless steel tubing, closed at the bottom by a swagelok 1/2" cap and welded at the top to a Cajon VCR gland-type gasket fitting. The reactor head is a combination of a VCR gland fitting, a Swagelok male run tee, a K type thermocouple in a 1/16" stainless steel sheath, and a 1/8" Autoclave Engineers union on the gas feed line. Reactor volume is approximately 20 cc for the tubing-bomb. Ten reactors of the described configuration were fabricated for experimental use. A disposable nickel gasket was used for sealing purposes. This "zero-clearance" type of fitting has been found to be far superior to other closure systems employed in this laboratory (Swagelok compression fitting) in terms of re-use and ease of pressure seal. The reactor is agitated vertically by use of an eccentric arm driven at a rate of approximately 120 rpm.

3.1.2 Analytical Equipment

Analytical procedures used in this research were idenical to those employed by Shin (23). The solvent separation analysis requires that the samples be dispersed using a

Thermocouple

To System

Nickel gasket

VCR Fitting

Welds
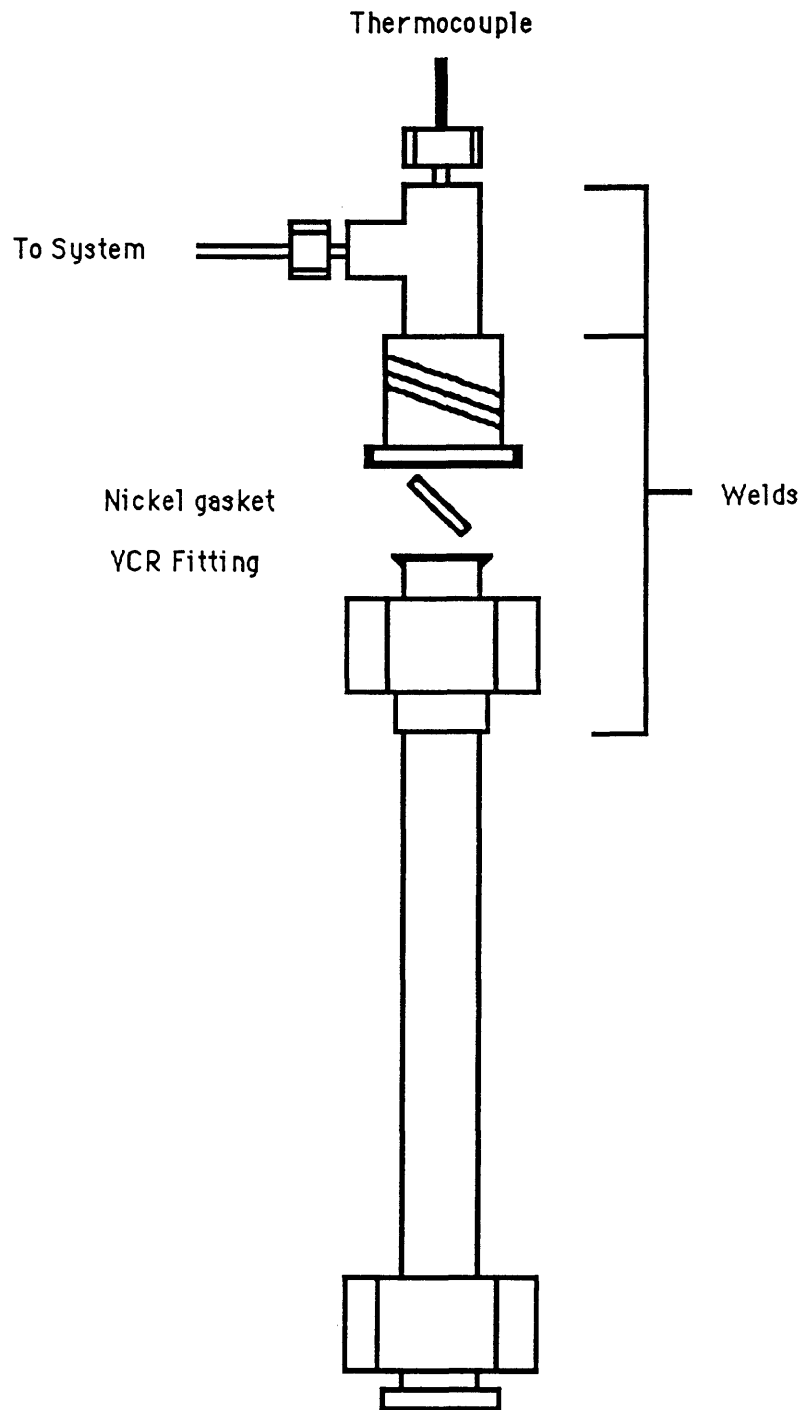
Figure 4. Tubing-bomb Reactor

sonic bath, centrifuged, and dried. To perform these steps,
a Branisonic Ultrasonic bath, an IFC Dacmon Model ICX cen-
trifuge, and a Precision Scientific Oven were used. Two
rotary evaporators manufactured by Buchi were used for
solvent recovery of THF from the soluble liquefaction
products. A Mettler PC 2000 top-loading electronic balance
with a precision of 0.01 gram was used for reactor charge
and liquid product weights.

A model 111H Carle analytical gas chromatograph was
used in conjunction with a model 3390A Hewlet-Packard inte-
grator for gas analysis.

3.2 Coals and Chemicals

3.2.1 Coals

Five different bituminous coals ranging from high
volatile to low volatile were used in this study. Fifteen
coal samples were purchased from the Penn State Premium Coal
Sample Bank. Every effort was made by Penn State Premium
Coal Bank to obtain coal samples from the most recently
exposed areas of a coal mine and samples were stored in
containoers under an inert gas. Nine of the samples pur-
chased (ground to -60 mesh or 250 micron) arrived in ampules
and six samples (ground to -20 mesh) were shipped in cans.
Prior to experimentation, all samples were ground to -100
mesh (150 micron). This was performed in a Labconco glove

box under a nitrogen blanket in order to avoid oxidation.
The ground samples were then sealed in small amber borosili-
cate glasses and stored in a Labconco Vacuum dessicator.
From fifteen coal samples, five were chosen and used for
the experiments. Preliminary characterization data for
these coals are given in Tables 1 and 2.

3.2.2 Chemicals

The chemicals utilized in this research were obtained
from Aldrich Chemical Company and were used as received
without further purification. A gaseous mixture of 99 mole
% hydrogen and 1 mole % krypton tracer was used as feed gas
(Liquid Air Corporation).

3.3 Experimental Procedures

3.3.1 Run Procedure

Start-Up

1. Air is introduced to the sand bath to induce fluid-
ization. Bath temperature is set to the desired reaction
temperature and monitored with a type K thermocouple.

2. Air flowrate is adjusted during heat up to prevent
excessive bubbling of the sand bath.

3. Approximately 3 hours is required for the sand
bath to reach the proper operating temperature.

Run Preparation

1. The reactor is charged with 1.0 gram of coal, 1.0

Table 1. Characterization Data of Penn State Coal Sample

Bank (Ultimate Analysis)

Coal Seam	State	Rank	Ultimate Analysis				Ash
			C	H	O	Stot	
Weir-Pittsburg	MO	HVAB	78.4	5.7	1.7	12.5	17.9
Bevier-Wheeler	MO	HVBB	78.0	5.7	6.7	8.0	20.5
Lower Sudduth	CO	HVCB	68.2	5.3	24.5	0.7	31.3
Splashdam	VA	MVB	87.5	5.4	4.8	0.8	12.4
Lower Freeport	PA	LVB	89.1	4.6	3.8	1.7	21.6

Note:

1. All the values are on a moisture and ash-free   basis
(wt%), except for "ash", which is in dry wt%.

2. Data furnished by Penn State Coal Bank.

Table 2. Characterization Data of Penn State Coal Sample

Bank (Proximate Analysis)

Coal Seam	State	Rank	Moisture	Ash	V.M	F.C
Weir-Pittsburg	MO	HVAB	6.3	16.8	37.2	39.8
Bevier-Wheeler	MO	HVBB	9.3	18.6	34.8	37.4
Lower Sudduth	CO	HVCB	5.8	29.5	32.7	32.0
Splashdam	VA	MVB	1.6	12.2	27.0	59.2
Lower Freeport	PA	LVB	0.5	21,5	16.6	61.4

Note:

1. All the values are based on "as received" basis (wt%).

2. Data are furnished by Penn State Coal Bank.

gram of the vehicle, and two small stainless mixing balls.

2. The reactor is then sealed into the VCR fitting using the nickel gasket.

3. The reactor system is then attached to the eccentric arm. Following this, the reactor and gas surge tank are evacuated. Valve V3 is closed during evacuation. After the reactor is evacuated, valve V5 is closed, preventing backflow of air into the reactor.

4. Reactor is then charged with the reaction gas to the desired pressure by opening the metering valve V2 smoothly. Then V2 and V3 are closed.

5. Following pressurization, the system is monitored for gas leaks by observing the system pressure.

Reaction Procedure

1. First eccentric arm is activated.

2. Reaction is started by raising the fluidized bed to the indicated level immersing the reactor. Time zero is defined as when the reactor is first immersed in the sand bath.

3. The sand bath is lowered after the allotted reaction time, and reaction is then terminated by first quenching the reactor with cold air, and then quenching the reactor in ice water.

4. Gas is then bled to the gas sampling bottle by opening V5 slowly. The sample bottle consists of an evacu-

ated 75 ml stainless steel pressure vessel.

Unit Shut Down

1. Turn off the panel controls and shut off the gas cylinder.

2. Vent the remaining gas in the system to blowdown.

3.3.2 Solvent Separation Analysis

The liquid products from the reactor were collected into a 250 ml centrifuge tube by washing the reactor with THF. Product recovery from the reactor was 100 %. Following this, the reaction slurry was analyzed via the solvent separation analysis previously mentioned. A schematic diagram of solvent separation procedure is shown in Figure 5. The solvent separation is performed as follows:

1. Wash the reactor with 150 ml of THF solvent to recover the reaction products (liquid + solid) from the reactor.

2. Immerse the centrifuge tube containing the reaction products plus THF for 10 minutes in a ultrasonic bath containing water.

3. Centrifuge the sample at 3000 rpm for 15 minutes.

4. After centrifugation, the solvent and soluble products are decanted into 500 ml flasks previously labeled with the run number.

5. Steps 1 trough 4 are repeated three times with
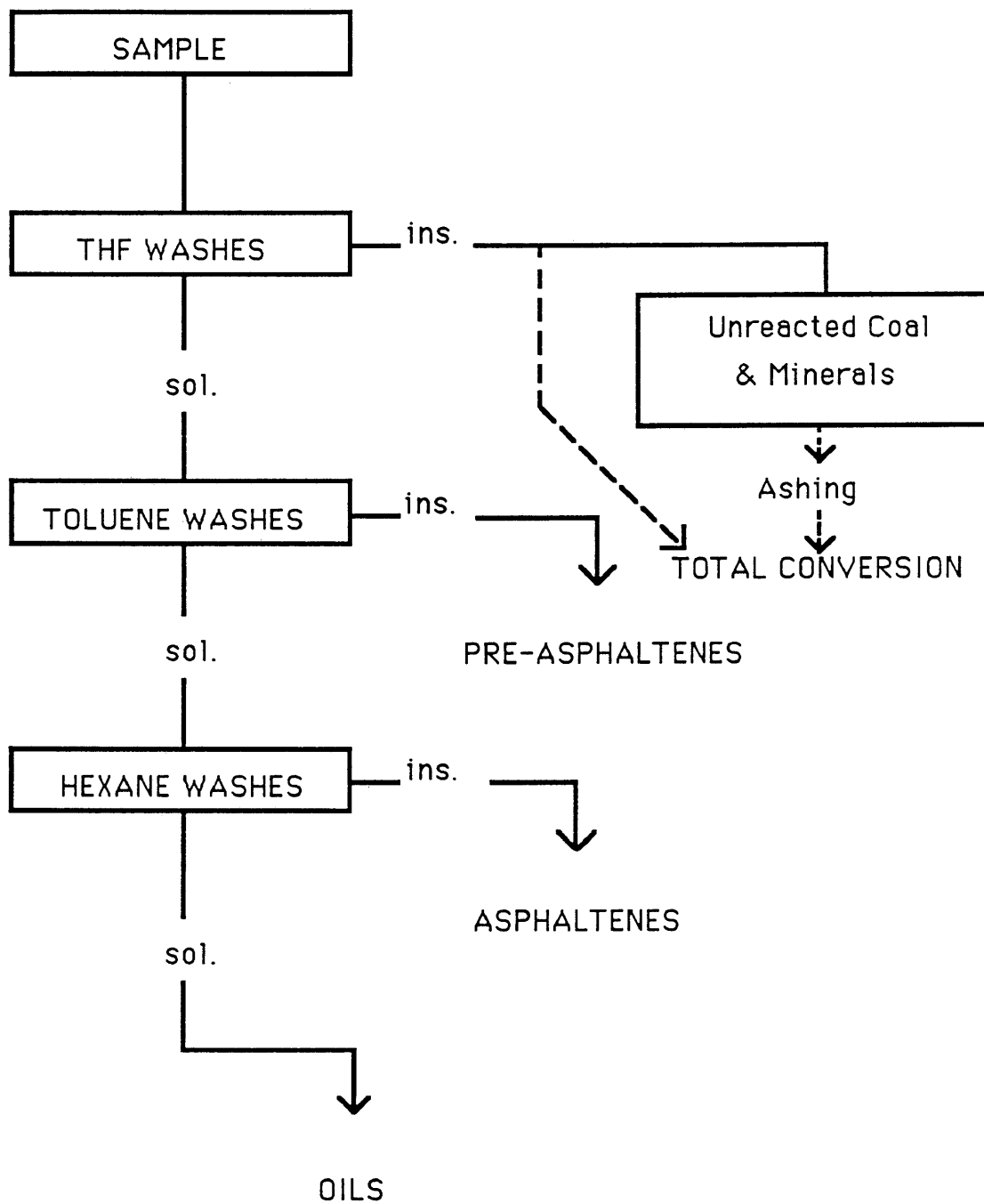
Figure 5.   Schematic of Solvent Separation Procedure

fresh THF, to insure complete removal of THF solubles.

6. The centrifuge tubes containing the residue are dried over-night at 100°C, and then weighed to a precision of 0.01 grams to determine the weight of "THF insolubles".

7. The THF washes (THF + soluble products) are evaporated at 80°C and 1 atm in a rotary evaporator to separate the THF solvent from the reaction products.

8. Steps 2 through 6 are repeated using toluene and the THF soluble material separated in step 7 to determine the weight of "toluene insolubles".

9. The toluene washes are then evaporated in a rotary evaporator to separate toluene solvent at 50°C under vacuum.

10. Steps 2 through 6 are again repeated using hexane solvent with the "toluene soluble" material separated in step 9, to determine the weight of "hexane insoluble" product.

4. EXPERIMENTAL DESIGN

4.1 Basic Argument

     As cited in an earlier discussion, extra care is
required to determine the intrinsic rate of chemical reac-
tion in the absence of other confounding rate effects. This
is done by eliminating side-effects, such as those imposed
when using a hydrogen donor solvent. As evidenced by many
researchers, different hydrogen donor solvents have differ-
ent hydrogen donor abilities which can affect the conversion
level and intrinsic conversion rate of a particular coal due
to differing rates of hydrogen transfer from the donor
vehicle (26). For this reason, a non-hydrogen donor sol-
vent was preferred as the reaction system vehicle. For the
reactions performed with a non-hydrogen-donor vehicle, the
role of the vehicle is to aid in dissolving the liquid
products and to reduce the viscosity of the liquid products,
allowing the recovery to be performed more easily.

     However, using molecular hydrogen as a hydrogen
source in coal liquefaction is questionable since the hydro-
gen molecule has a strong bond energy (104 Kcal/mole H2).
Thus the mechanism of hydrogen gas as a hydrogen source, and
the different roles between the hydrogen-donor solvents and
molecular hydrogen gas in different surroundings should be
further discussed. Vernon (64) studied the role of hydrogen

gas as a hydrogen source using dibenzyl and diphenyl as model compounds (which are suitable representatives of strong and weak carbon-carbon bonds in coal). Product yields (benzene, ethylbenzene, and its ratio) were compared between reaction with tetralin only and reaction with tetralin and hydrogen gas. Vernon reported that the ratio of benzene/ethylbenzene was much higher in the presence of gas phase molecular hydrogen than when compared to the system of tetralin only. Thus it can be concluded that hydrogen gas serves as a hydrogen source in the presence of a radical initiator. Vernon's results support the hypothesis that hydrogen gas helps cleave strong bonds in coal by attacking those bonds. In summary, hydrogen gas can act as a homogenous hydrogen-donor, meaning that its functionality during the reaction is directly influenced by the chemical properties of a coal.

4.2 Detailed Experimental Matrix

The following experimental design matrices were planned in order to satisfy the objectives of this research. In this research, identically equal reaction and separation techniques were used as with Shin (23), who previously used the same reactor system. Thus, the data from this work could be appended to Shin's results, providing a larger data base in order to correlate kinetic parameters with coal properties.

* Stage 1. Measurement of Rate Data

    - Coals   : 5 Penn State Coals

    - Solvent   : Aromatic (1-MN)

    - Reaction times   : 3, 5, 10, 15, 40 min

    - Reaction temperatures: 375, 400, 425°C

    - Cold pressure   : 900 psi (H2 gas)

* Stage 2. Kinetic Modelling

    - Development and determination of the best model
for all coals.

    - Calculation of activation energy.

* Stage 3. Correlational Efforts

    - Correlation of activation energy and kinetic
parameters.

5. RESULTS AND DISCUSSION

5.1 Definition of Conversion

The following definition of conversion was used to calculate reaction conversion .

$$\text{Conversion(wt\%)} = \frac{\begin{bmatrix} \text{Organic fraction in coal converted} \\ \text{to solvent solubles by the reaction} \end{bmatrix}}{\begin{bmatrix} \text{Total organic fraction in coal} \end{bmatrix}} \times 100$$

By assuming that the amount of mineral matter in coal does not change during the reaction and that the amount of mineral matter can be represented by the amount of ash measured by Penn State Coal Bank, the following relations can be developed:

$$\begin{bmatrix} \text{Total organic fraction} \\ \text{in coal} \end{bmatrix} = \text{Total coal} - (\text{Ash amount} + \text{Moisture content})$$

$$\begin{bmatrix} \text{Organic fraction con-} \\ \text{verted by reaction only} \end{bmatrix} = \text{Solvent solubles} - \begin{bmatrix} \text{Intrinsic} \\ \text{solubles} \end{bmatrix}$$

Solvent solubles = Dry coal - Solvent insolubles(dry)

Intrinsic solubles = Solubility of coal in a solvent at room temperature without reaction

$$\text{Conversion(wt\%)} = \frac{(D - SI) - I}{T - (A + M)} \times 100$$

Where, T = Total Coal

        A = Ash amount

        M = Moisture content

        S = Solvent solubles

        I = Intrinsic solubles

        D = Dry coal

        SI = Solvent insolubles (Dry)

The intrinsic solubilities in toluene and THF for the 5 coals studied were obtained from separation analysis at room temperature. These were found to be very small (2-5 wt%) and were subsequently neglected since these values were in the range of experimental error.

5.2 Measurement of Kinetic Data

    Rate data for conversion to THF and toluene solubles were measured for the 5 Penn State coals at three different temperatures. Conversion rate data to THF and toluene solubles are shown graphically in Figures 6 through 15. Numerical data for these figures are tabulated in Appendix 1 As can be seen from Figures 6 through 10, conversion to THF solubles was relatively rapid compared to conversion to toluene solubles. Conversion to THF solubles for Weir
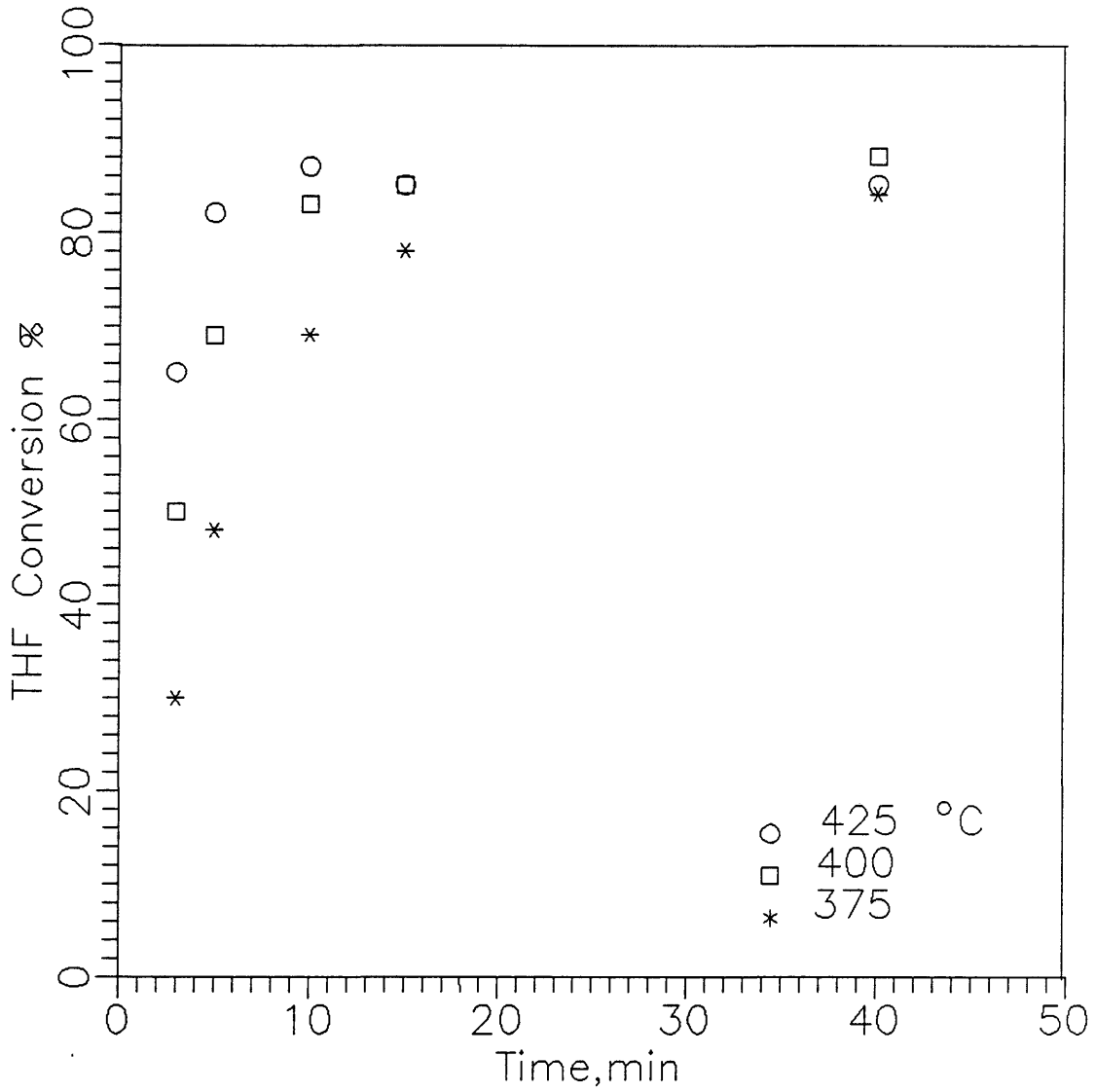
Figure 6. Conversion to THF solubles vs. Time

Coal : Weir Pittsburg
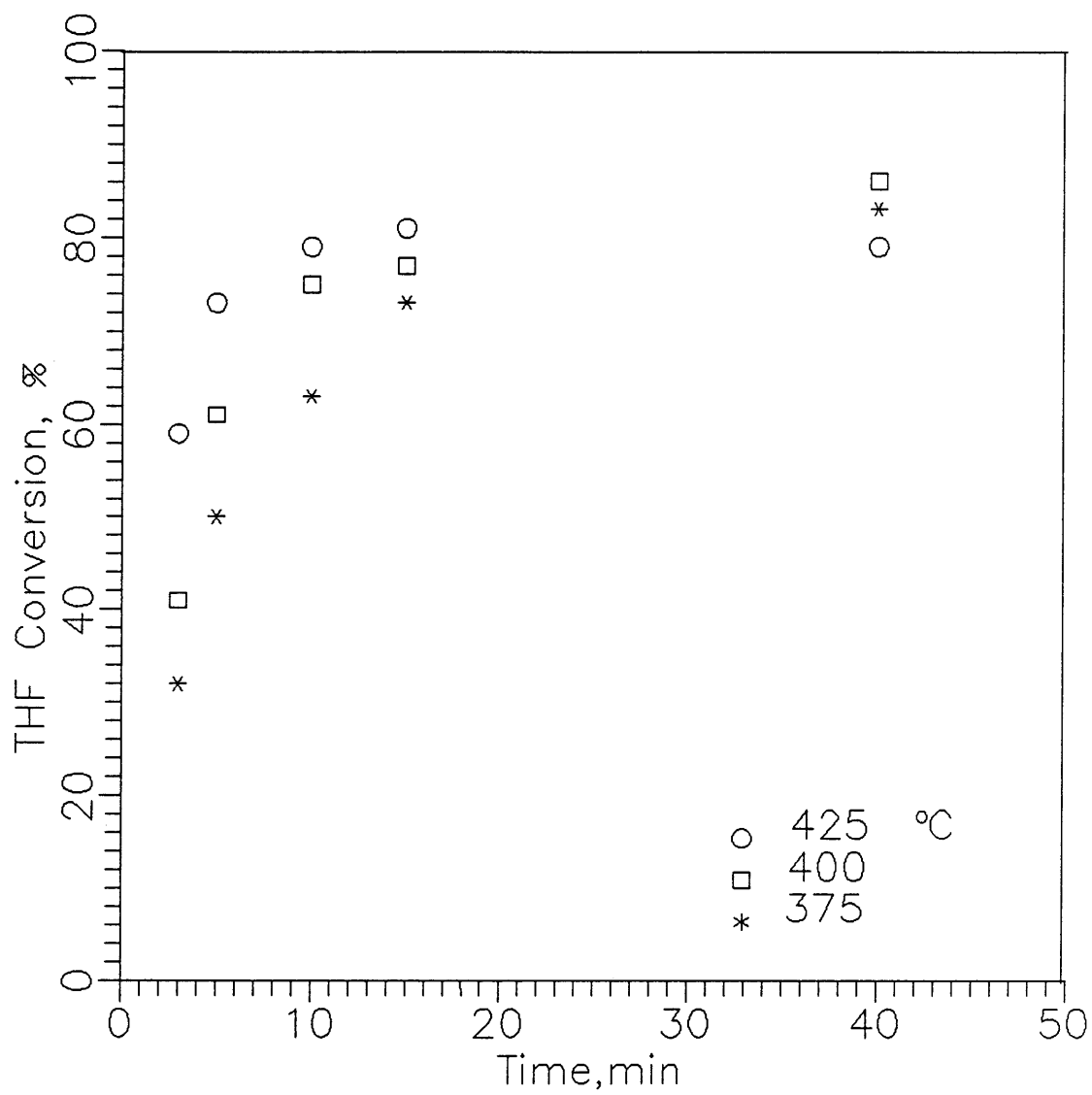
Figure 7. Conversion to THF solubles vs. Time

Coal : Bevier-Wheeler
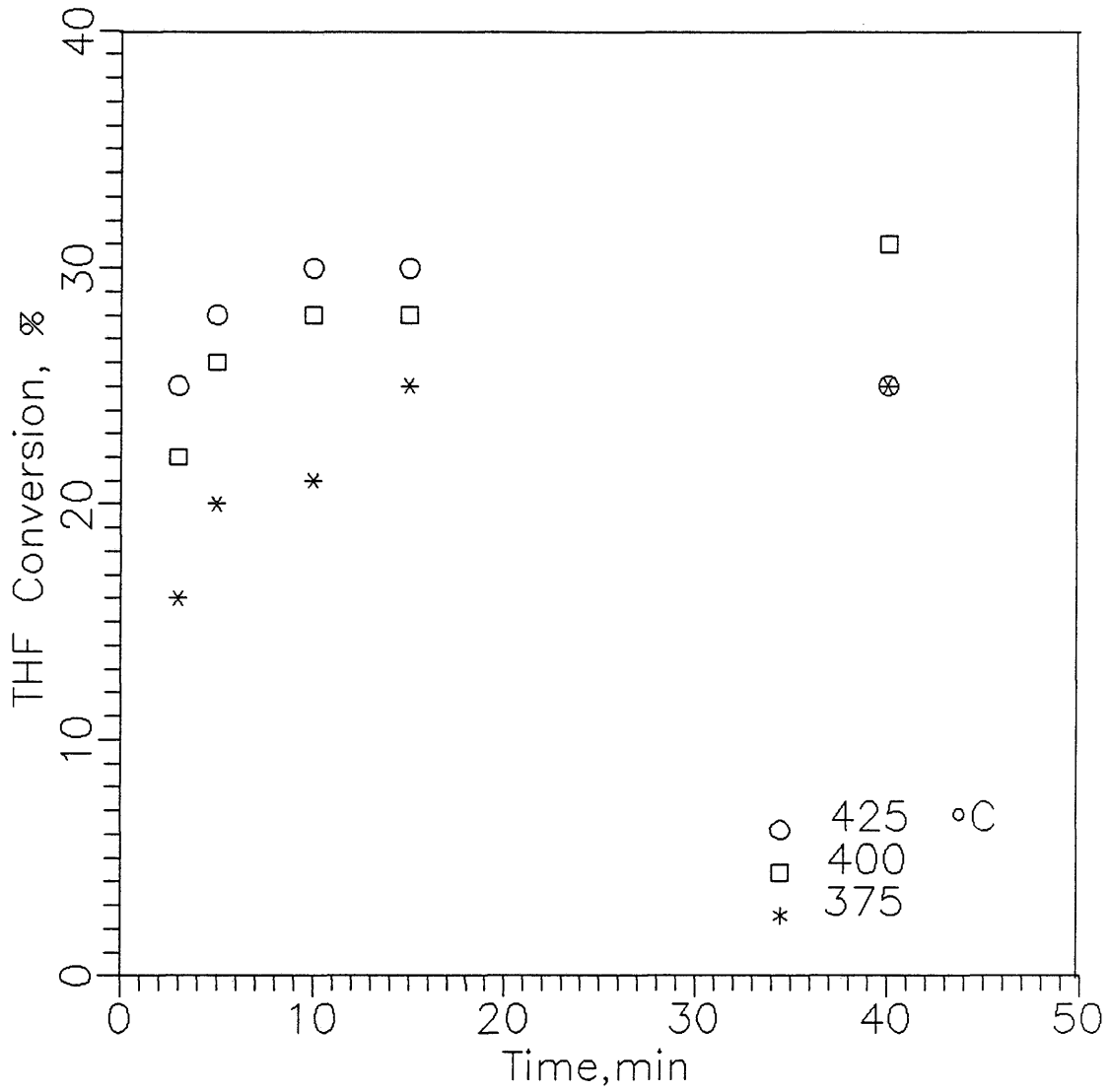
Figure 8. Conversion to THF solubles vs. Time

Coal : Lower Freeport
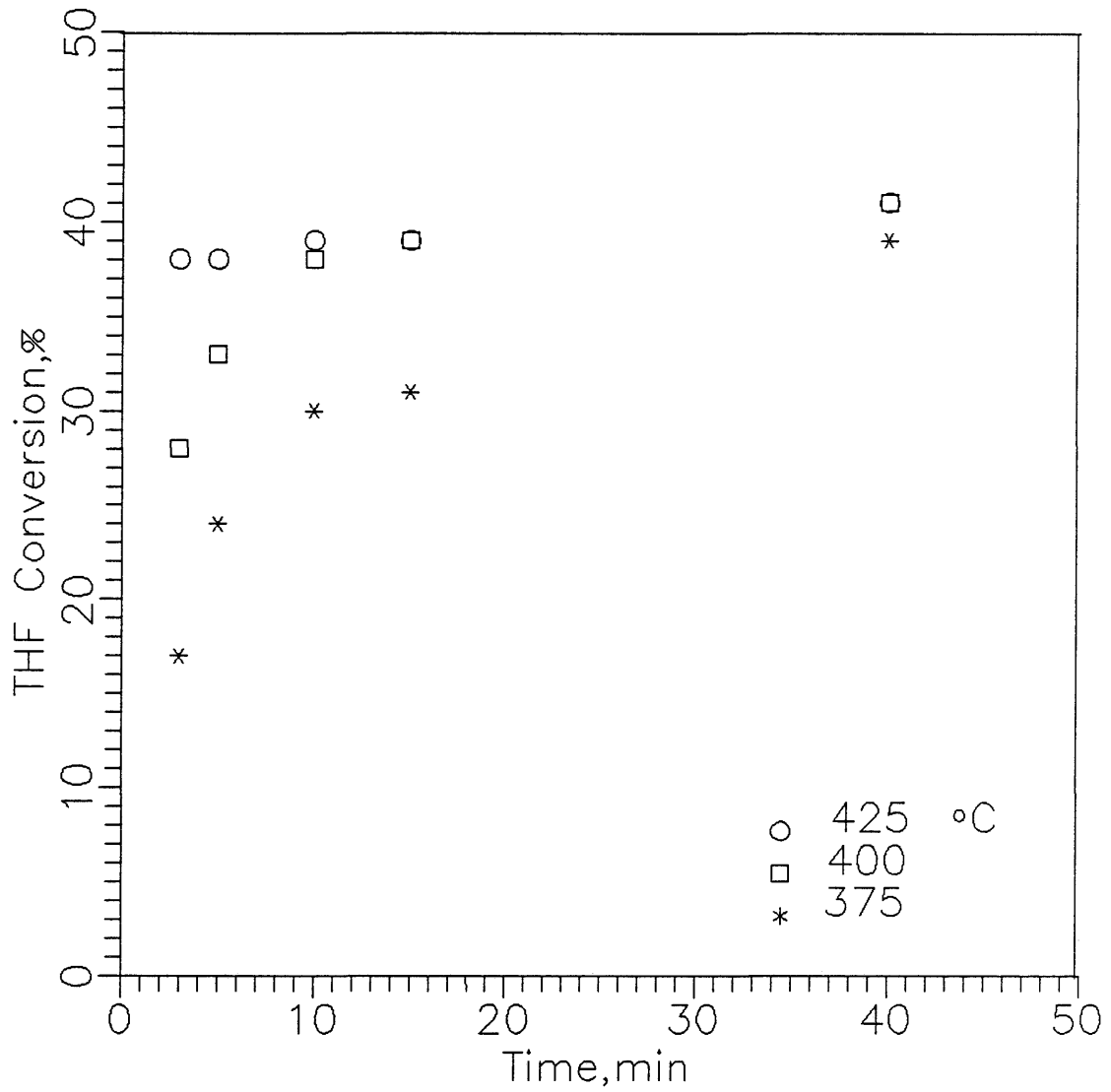
Figure 9. Conversion to THF solubles vs. Time

Coal : Lower Sudduth
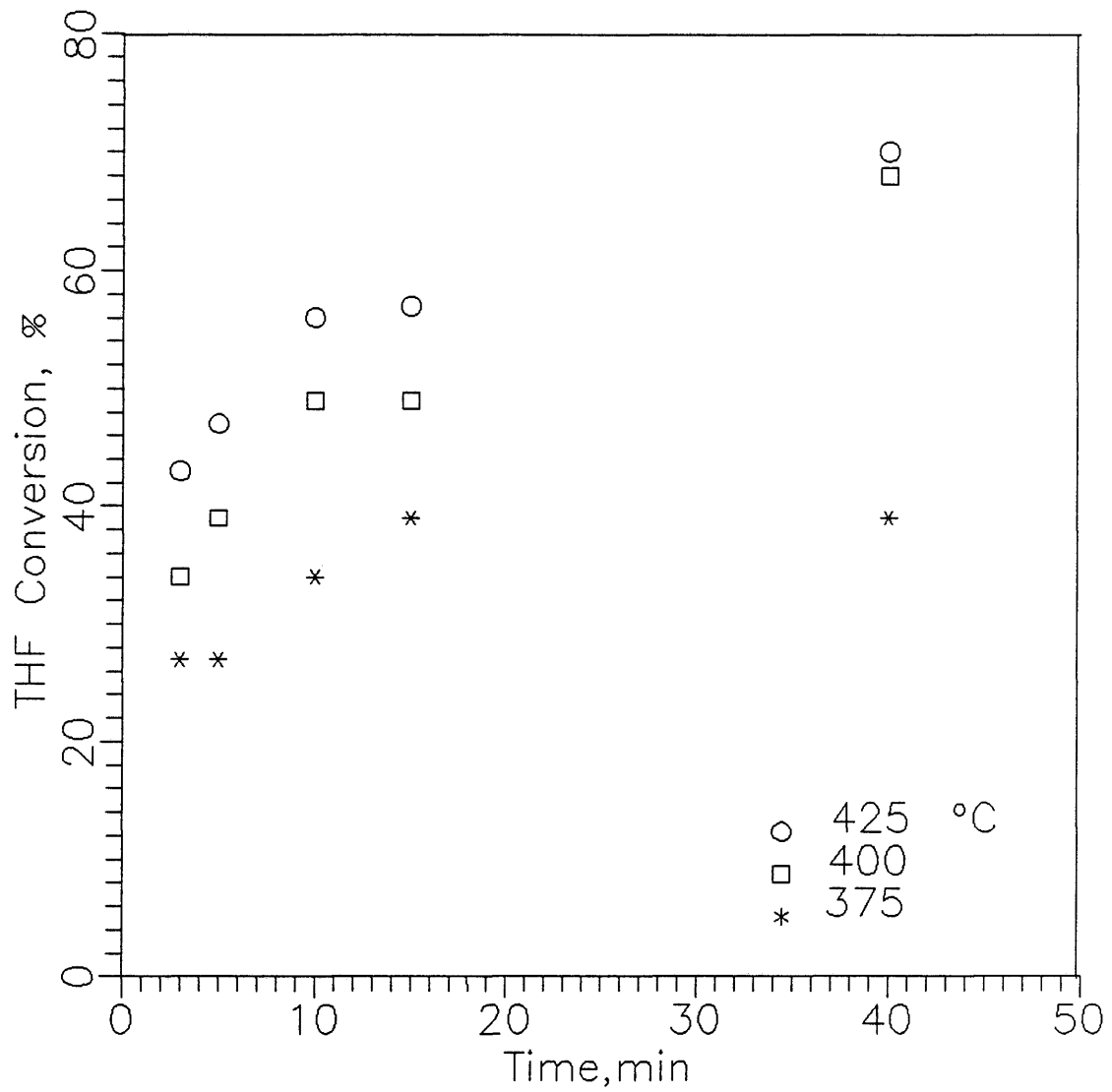
Figure 10. Conversion to THF solubles vs. Time

Coal : Splashdam
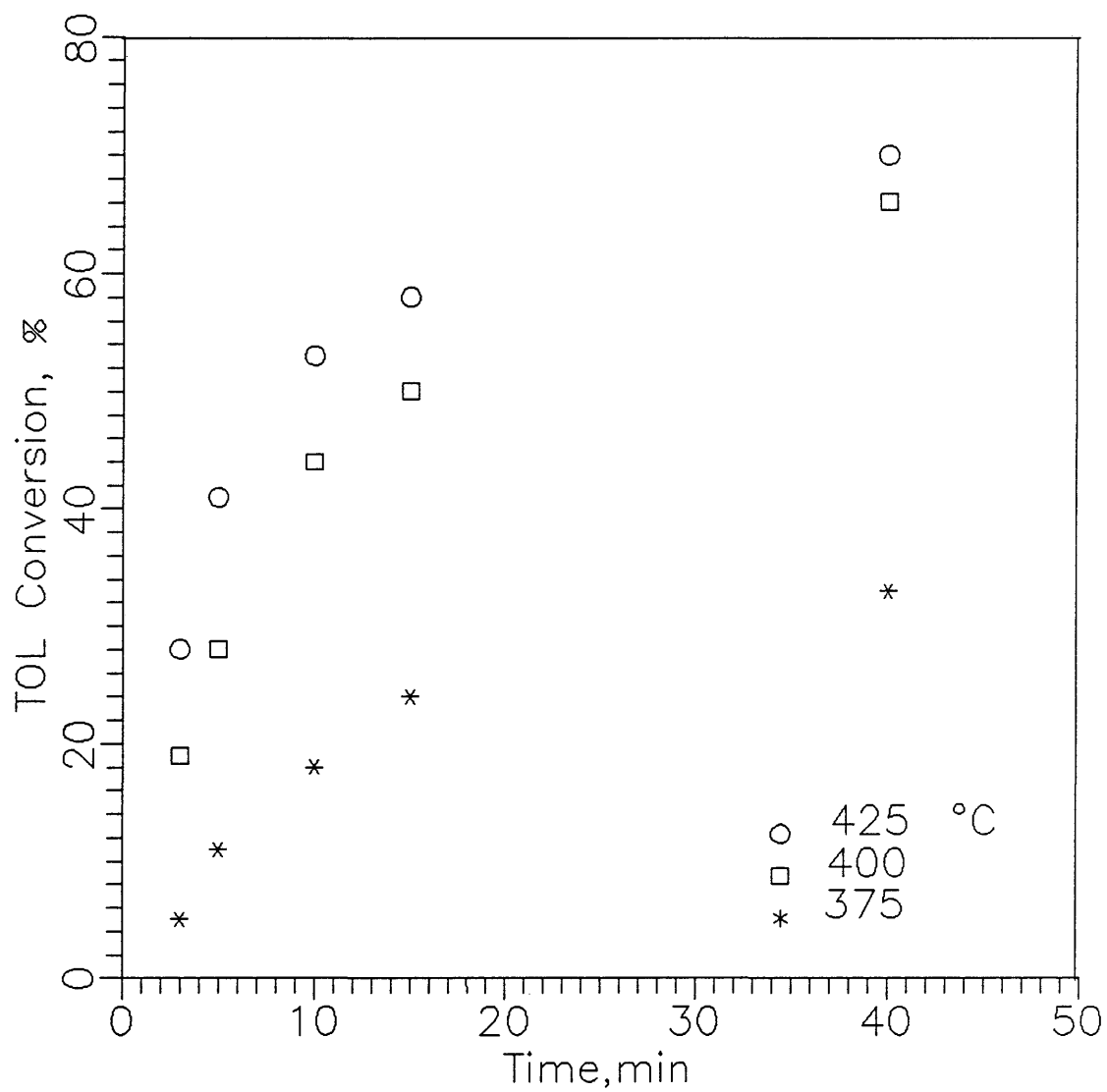
Figure 11. Conversion to Toluene solubles vs. Time

Coal : Weir Pittsburg
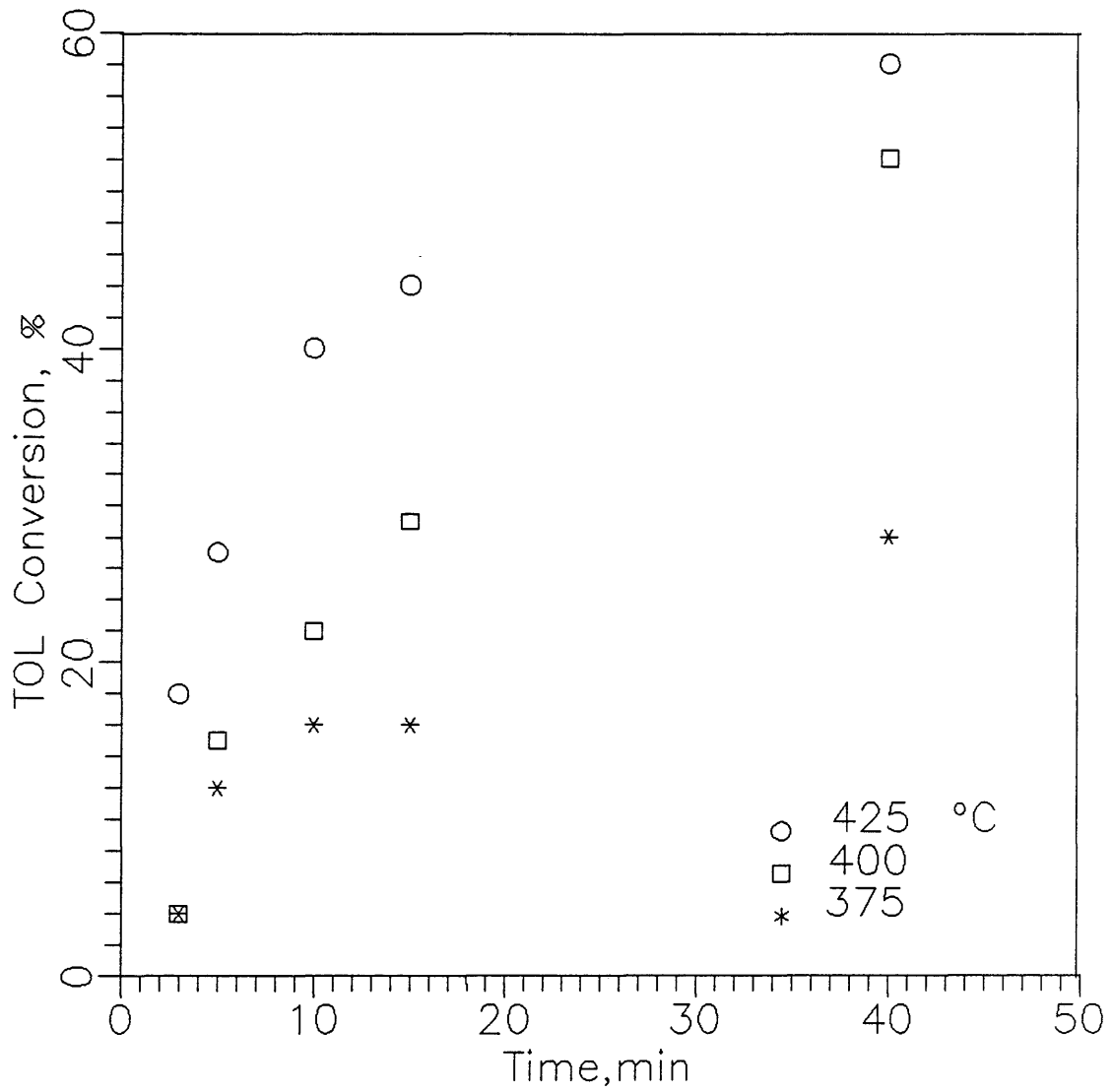
Figure 12. Conversion to Toluene solubles vs. Time

Coal : Bevier-Wheeler
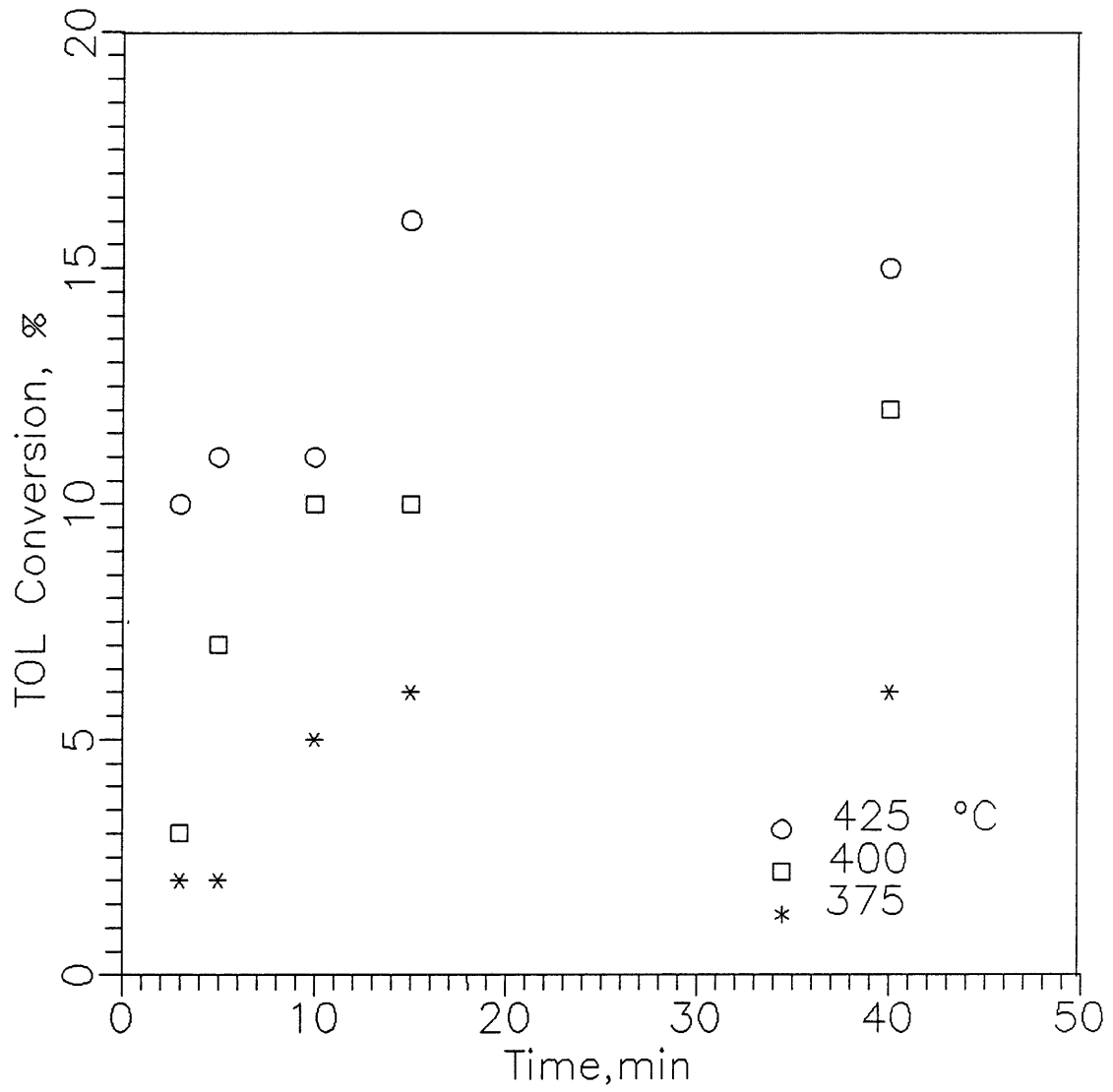
Figure 13. Conversion to Toluene solubles vs. Time

Coal : Lower Freeport
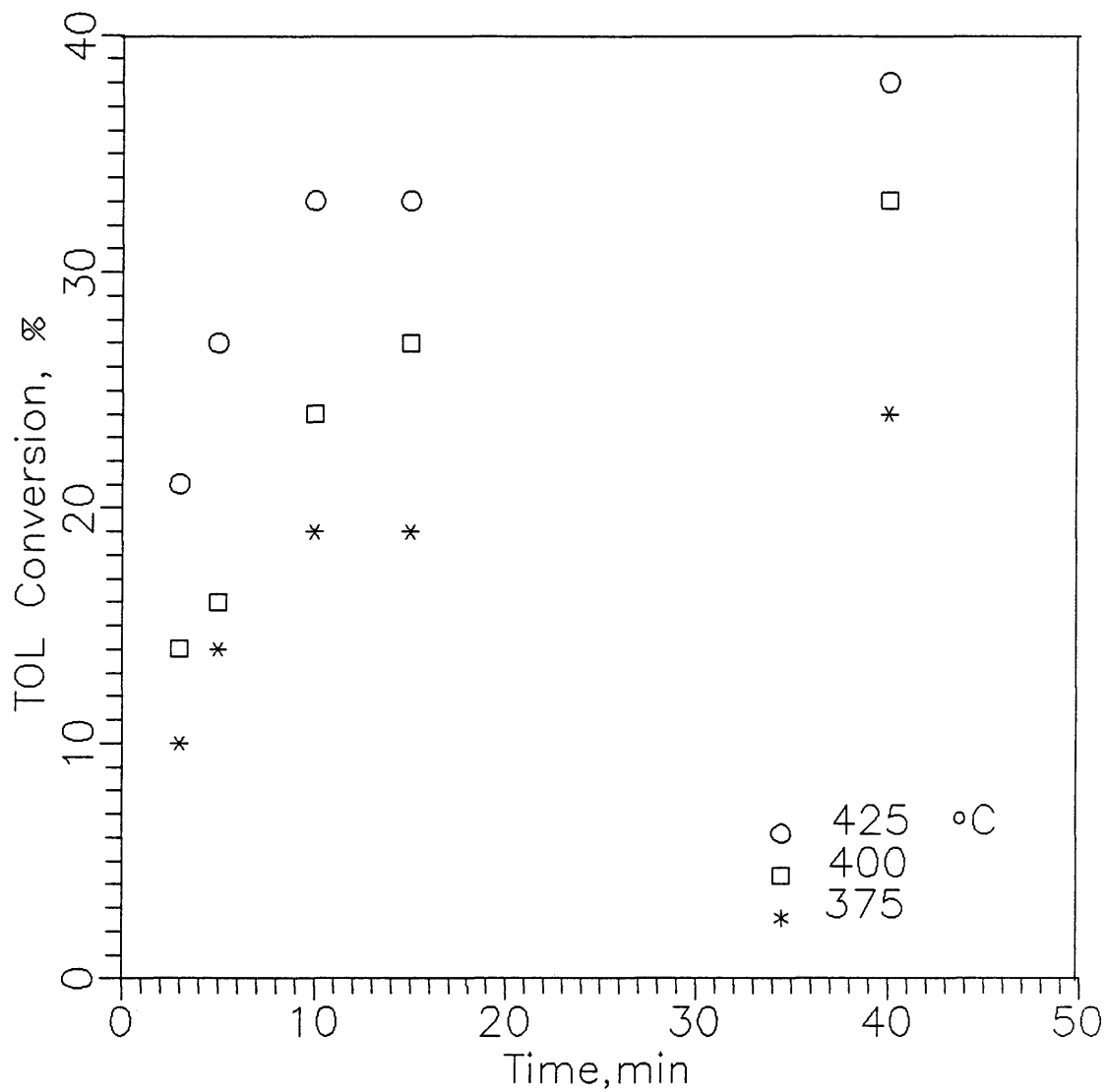
Figure 14. Conversion to Toluene solubles vs. Time
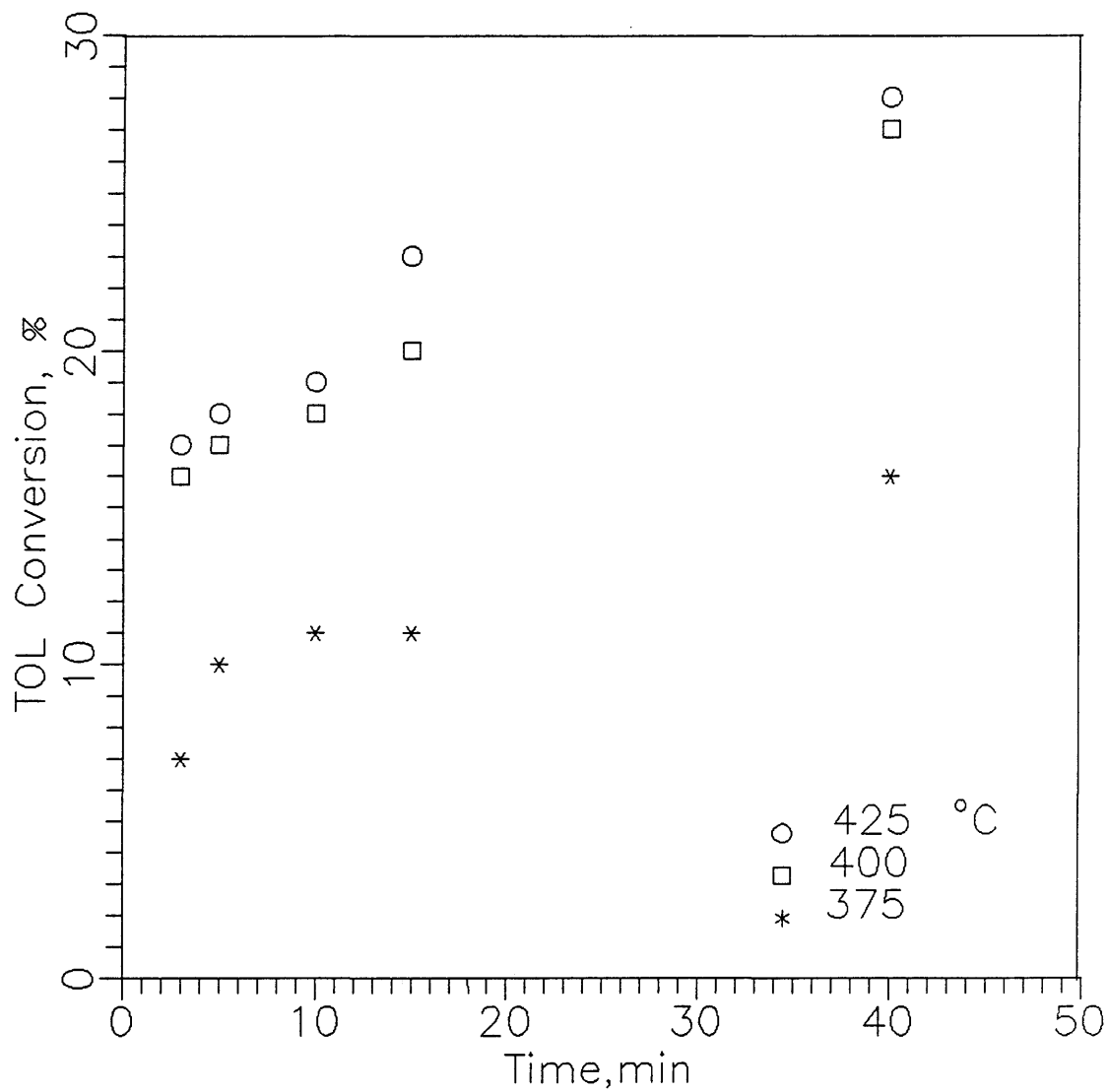
Coal : Lower Sudduth

Figure 15. Conversion to Toluene solubles vs. Time

Coal: Splashdam

Pittsburg, Bevier-Wheeler, Lower Freeport, and Lower Sudduth

coals (Figures 6, 7, 8, 9) shows almost the expected behav-

ior, in that the conversion reaches an equilibrium value in

early stages of the reaction for high reaction temperatures

(425°C). For Splashdam coal (Figure 10) conversion to THF

solubles increases continuously during the reaction at high

temperature. Regressive reactions introducing reversibility

into the data become more appreciable at higher reaction

temperature as seen in Figures 6 through 10. It is known

that this reversible (regressive) reaction is caused by a

recombination of primary free radicals initially produced

thermally from coal. Conversion data to THF solubles show

that reversible reactions start dominating at higher temper-

ature (425°C). This behevior can be correlated to the

free swelling index of the coal, as shown in Table 3. The

swelling index reflects the degree of cross-linking in coal,

i.e. as the free swelling index decreases, the degree of

cross-linking increases (47). As noted previously, these

linking bonds will be more rapidly and completely cleaved

thermally at higher temperature. From this reasoning coal

with a higher cross-linking density will produce more pri-

mary radicals that will in turn recombine if they are not

quenched rapidly. The radical quenching rate is much

slower in an aromatic vehicle (1-MN) than in a donor vehicle

(tetralin). As a result reversible reactions are much more

Table 3. Free Swelling Index of Coals

Coal	Free Swelling Index
Splashdam	8.0
Weir-Pittsburg	5.5
Bewier-Wheeler	5.0
Lower-Freeport	1.0
Lower-Sudduth	0.0

----

likely to occur in an aromatic solvent.

5.3 Kinetic Modelling

Measured kinetic data for 5 coal samples from Penn State Coal Bank were fitted to various kinds of kinetic models tabulated in Table 4. As a data fitting criteria, standard error of estimate values (SEE) were calculated for each model, and these values are presented in Table 5 for THF solubles, and in Table 6 for toluene solubles. The following definition of SEE was used.

$$SEE = \frac{\sqrt{\sum^{n} (X - X^{*})^{2}}}{n}$$

where, X = experimental values of coal conversion (wt%)

X* = estimated values of coal conversion by the model(wt%)

n = the number of data points

To calculate the values of standart error of estimate (SEE) for a particular model, the procedure outlined in Table 7 was used. The computer program utilized for these calculations is presented in Appendix 3. As can be seen from Table 5, the first and second order irreversible models were least suitable for fitting the data, since the average value of

Table 4. Kinetic Models

- -

Model	Rate Expression	integrated Form
1st order irreversible	$\dfrac{dx}{dt} = k(a-x)$	$x = a\left[1 - \exp(-kt)\right]$
2nd order irreversible	$\dfrac{dx}{dt} = k(a-x)^2$	$x = \dfrac{ka^2 t}{kta + 1}$
1st order reversible	$\dfrac{dx}{dt} = k_f(a-x) - k_r x$	$x = x_e\left[1 - \exp(-k_f at/x_e)\right]$
2nd order reversible	$\dfrac{dx}{dt} = k_f(a-x)^2 - k_r x^2$	see appendix
1st-2nd order reversible	$\dfrac{dx}{dt} = k_f(a-x) - k_r x^2$	see appendix

- -

Where, X = Coal conversion (d.a.f basis, wt%)

  x_e = Equilibrium conversion (d.a.f basis, wt%)

  a = Ultimate conversion (d.a.f basis, wt%)

  k = Kinetic constent (k_f = forward, k_r = reverse)

  t = Reaction time (minute)

Table 5. Statistical Comparison of Kinetic Models

(THF Solubles)

Coal	Temp	First Irr.	Sec. Irr.	First Rev.	Sec. Rev.	F-S. Rev.
Weir	425	1.24	1.81	0.82	1.8	0.81
	400	0.7	2.32	0.52	2.34	0.5
	375	1.1	2.67	0.62	2.59	0.58
Bevier	425	2.28	1.4	0.4	1.15	0.38
	400	1.56	2.01	1.18	2.02	1.22
	375	1.69	1.61	1.11	1.62	1.16
Low.Sud	425	1.05	0.54	0.48	0.38	0.44
	400	0.84	0.3	0.43	0.32	0.44
	375	1.54	0.49	0.97	0.5	1
Splash.	425	2.97	1.33	2.23	1.3	2.28
	400	2.91	1.52	2.71	1.75	2.81
	375	5.9	3.93	1.14	1.12	1.27
Low.Fre	425	1.03	0.32	0.47	0.31	0.47
	400	1.51	1.28	0.84	0.86	0.85
	375	1.7	0.95	0.76	0.46	0.58
SEE=		1.868	1.499	0.979	1.235	0.986

Table 6. Statistical Comparison of Kinetic Models

(TOL Solubles)

===

Coal	Temp.	Fir.Irr	Sec.Irr.	Fir.Rev	Sec.rev	F-S.rev
Weir	425	1.46	1.34	1.19	1.3	1.23
	400	1.07	1.37	0.63	1.33	0.68
	375	2.13	5.61	0.41	1.4	0.33
Bevier	425	0.9	1.43	0.82	1.43	0.85
	400	1.01	2.18	1.05	2.18	1.08
	375	1.9	1.36	0.99	1	1.07
Low.Sud	425	1.1	0.44	0.66	0.45	0.68
	400	1.46	0.41	0.66	0.39	0.73
	375	2.52	1.48	0.54	0.49	0.61
Splash.	425	1.65	0.88	1.25	0.89	1.28
	400	1.9	1.09	1.32	1.08	1.35
	375	1.85	1.3	0.7	0.71	0.76
Low.Fre.	425	0.96	0.64	0.72	0.62	0.73
	400	0.96	0.54	0.36	0.39	0.35
	375	1.03	0.7	0.42	0.44	0.45
SEE =		1.46	1.385	0.781	0.94	0.812

===

Table 7.   Algorithm   for the Calculation of SEE

```
          ┌──────────────────────────┐
          │ Read experimental        │
          │ conversion , X           │
          └────────────┬─────────────┘
                       │
                       ▼
    ┌────────────────────────────────────┐
    │ Start scanning values for          │
    │ ultimate conversion (a), initial   │◄──────────────┐
    │ value has to be higher than        │               │
    │ equilibriium conversion, Xe        │               │
    └─────────────────┬──────────────────┘               │
                      │                                   │
                      ▼                                   │
    ┌────────────────────────────────────┐               │
    │ Start scanning values for          │               │
    │ equilibrium  conversion Xe in the  │         Choose │
    │ vicinity of the observed value     │           an   │
    │ from the  experimental data        │       Increment│
    └─────────────────┬──────────────────┘               │
                      │                                   │
                      ▼                                   │
    ┌────────────────────────────────────┐               │
    │ Start scanning values for reaction │               │
    │ rate constent, K_f                 │               │
    └─────────────────┬──────────────────┘               │
                      │                                   │
                      ▼                                   │
        ┌──────────────────────────┐                     │
        │ Calculate , X*  and  SEE │                     │
        └────────────┬─────────────┘                     │
                     │                                    │
                     ▼                                    │
                   ◇ Is                     NO            │
                   the SEE    ─────────────────────────────
                   smallest
                     │
                    YES
                     │
                     ▼
          ┌──────────────────────────┐
          │ obtain values for        │
          │ SEE =                    │
          │ a    =                   │
          │ Xe   =                   │
          │ K_f  =                   │
          └──────────────────────────┘
```

SEE was higher compared to reversible models for both THF and toluene solubles. From the five kinetic models investigated, the second order reversible model was determined to be the best. From a statistical point of view, the second order reversible model does represent conversion data to toluene solubles very well, but first order and first-second order reversible models fit conversion data to THF solubles better than the second order reversible model. Theoretcally, the rate of the forward reaction should depend on the concentration of radicals produced and hydrogen atom, especially in the absence of a strong hydrogen donor vehicle. The reverse reaction should be second order since two species are involved in the recombination reaction.

Calculated activation energy, kinetic constants, ultimate conversion, and equilibrium conversion based upon second order reversible model are given in Tables 8 and 9. The Arrhenius plots for each of the five coals are given in Figures 16 and 17. Activation energies obtained vary from 15 to 46 kcal/mol for second order reversible model. This wide range of values indicates that the activation energy determined is a characteristic value of the coal. Activationenergies are listed in Table 10 for each coal for three reversible models tested. The table indicates the important finding that ranking of coals with respect to reactivity using activation energy as the ranking parameter is essen-

Table 8. Activation Energy(THF Sol) and Kinetic Constants

MODEL: Second Reversible

==

Coal	E(kcal/m)	R-sq(%)	Freq.F	k(kin)	a(%)	Xe(%)
			(1/min)	(1/min)		
Weir	28.7	100	1.46E+07	0.014	89	87
				0.007		88
				0.003		88
Bevier	21.6	98.1	5.40E+04	0.0097	97	82
				0.0047		86
				0.0029		86
Low.Sud.	44.1	99.4	4.80E+12	0.0671	42	40
				0.0174		41
				0.0057		41
Splash.	15.3	96.7	3.68E+02	0.0059	71	70
				0.0034		70
				0.0025		38
Low.Fre.	27.7	100	2.40E+07	0.0483	32	28
				0.0234		31
				0.0103		25

==

Table 9.   Activation Energy(TOL Sol) and Kinetic Constants

MODEL: Second Reversible

==

Coal	E(kcal/m)	R-sq(%)	Freq.F	k(kin)	a(%)	Xe(%)
Weir	36.5	95.5	1.31E+09	0.0038	71	70
				0.0021		70
				0.0005		35
Bevier	29.9	98.6	7.20E+06	0.0032	59	58
				0.0012		58
				0.0006		29
Low.Sud.	24.5	92.7	4.80E+05	0.0111	39	38
				0.0041		35
				0.0028		23
Splash.	22.2	88.5	1.20E+05	0.0113	29	28
				0.0092		26
				0.0033		14
Low.Fre.	45.9	99.9	6.40E+12	0.0233	17	15
				0.0070		12
				0.0018		6

==

Table 10. Coal ranking with respect to Activation Energy

(TOL Solubles)

(E, Kcal/mol)

===

RANK	Fir.Rev	Activ. Energy	Sec.Rev	Activ. Energy	F-S Rev	Activ. Energy	$\mathcal{O}$
1	Low.Fre.	38.4	Low.Fre.	45.9	Low.Fre.	37.1	3.8
2	Weir.	26.9	Weir.	36.5	Weir.	28.9	12.5
3	Bevier	21.0	Bevier	29.9	Bevier	23.2	6.7
4	Splash	17.7	Low.Sud.	24.5	Splash	17.2	4.8
5	Low.Sud.	16.1	Splash	22.2	Low.Sud.	17.0	94.5

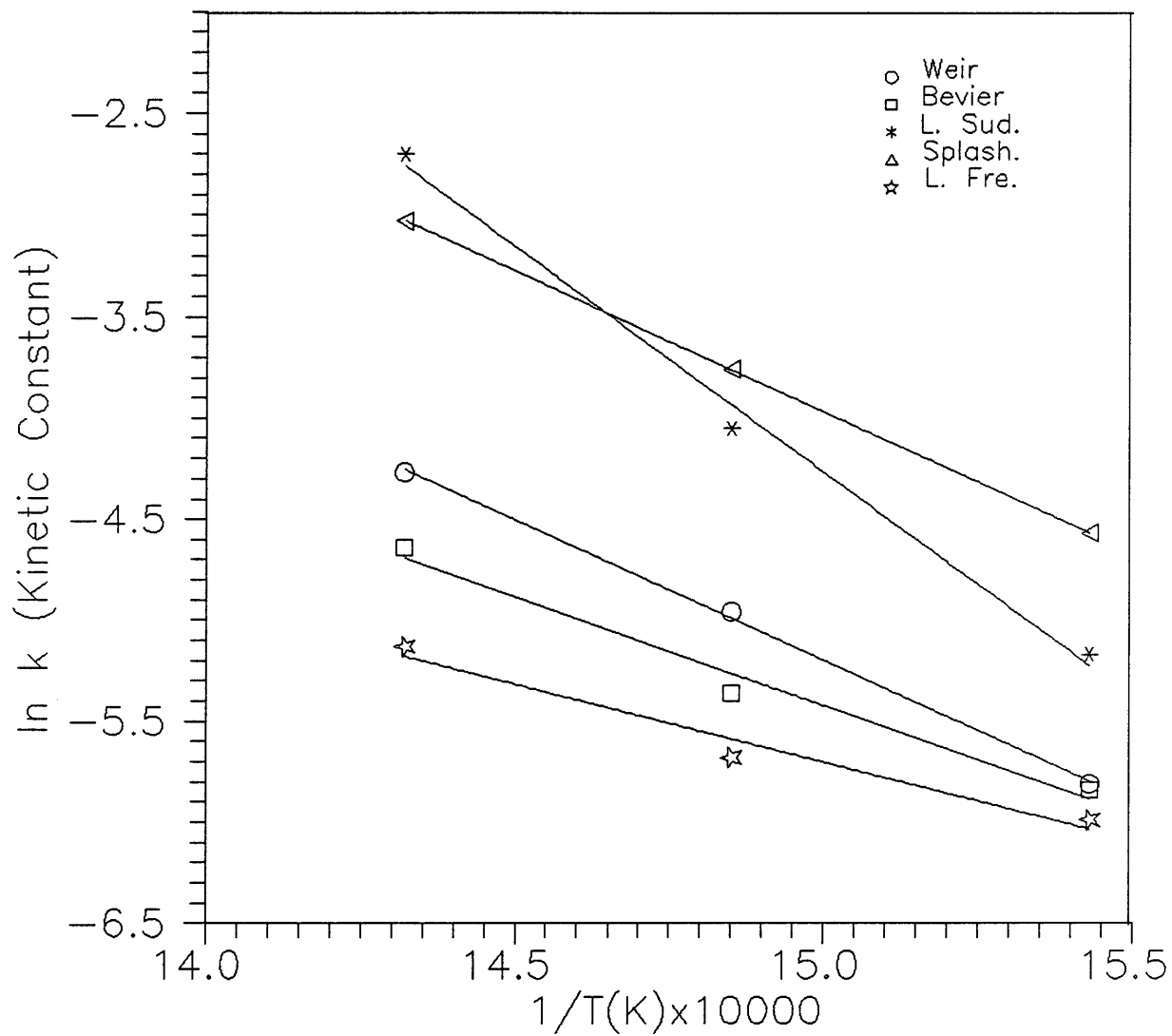===

Figure 16.   Arrhenius Plot (THF Solubles)

Model:Second Reversible
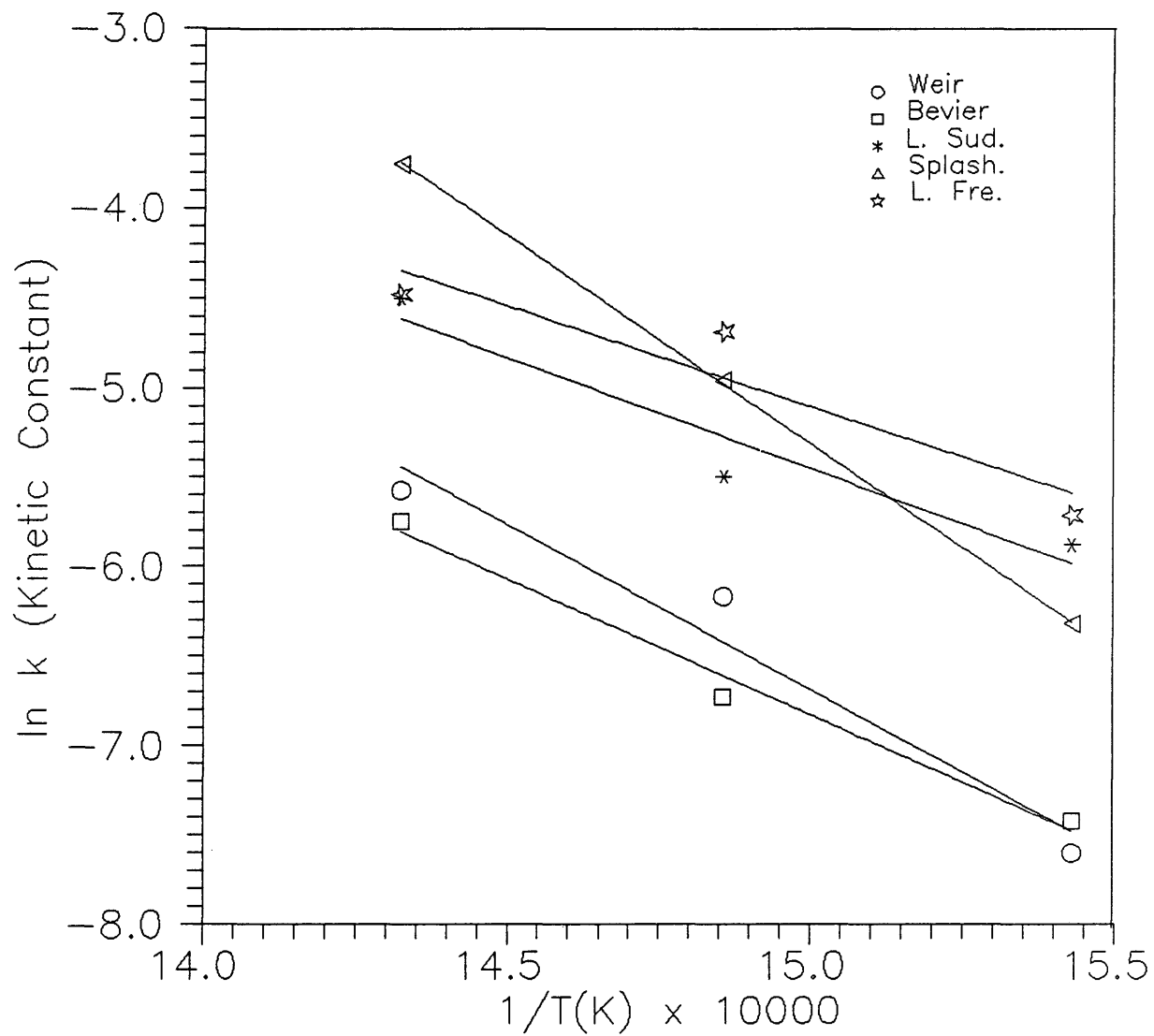
Figure 17.   Arrhenius Plot (Toluene Solubles)

cially independent of the choice of kinetic model used to determine the activation energy. Irrespective of the kinetic model choosen, the coals have the same relative reactivity ranking. This finding indicates that activation energies can be used as fundamental indicators of relative reactivity.

5.4 Correlations

5.4.1 Traditional Correlations

Point-Yield Conversion

Point-yield conversions (fixed time and temperature) were first tried to correlate activation energies with coal properties by using linear regression analysis. Multiple correlation coefficients for correlations of the yield of toluene solubles with the carbon plus oxygen contents of the parent coals are presented in Table 11. As shown conversion to toluene solubles is correlated well with total carbon plus oxygen (wt%/m.w) for the 5, 10, and 15 minutes residence times at 425°C. However, at temperatures of 400 and 375°C, significantly weaker correlations were found. The weakness of the point-yield conversion technique in describing coal reactivity is also illustrated graphically in Figures 18 through 20.

Kinetic Constant

Rate constants for coal conversion to THF and toluene solubles at 425, 400, 375°C were next used as correlational

Table 11. Multiple Correlation Coefficient of

Point-Yield Conversion

(Toluene Solubles vs. Total C+O Content)

===

Temp($^{\circ}$C)	Reaction Time (min)				
	3	5	10	15	40
425	72.2	90.6	97.9	98.4	58.2
400	11.3	61.3	78.7	87.6	94.7
375	0	34.7	63.2	80.7	89.6

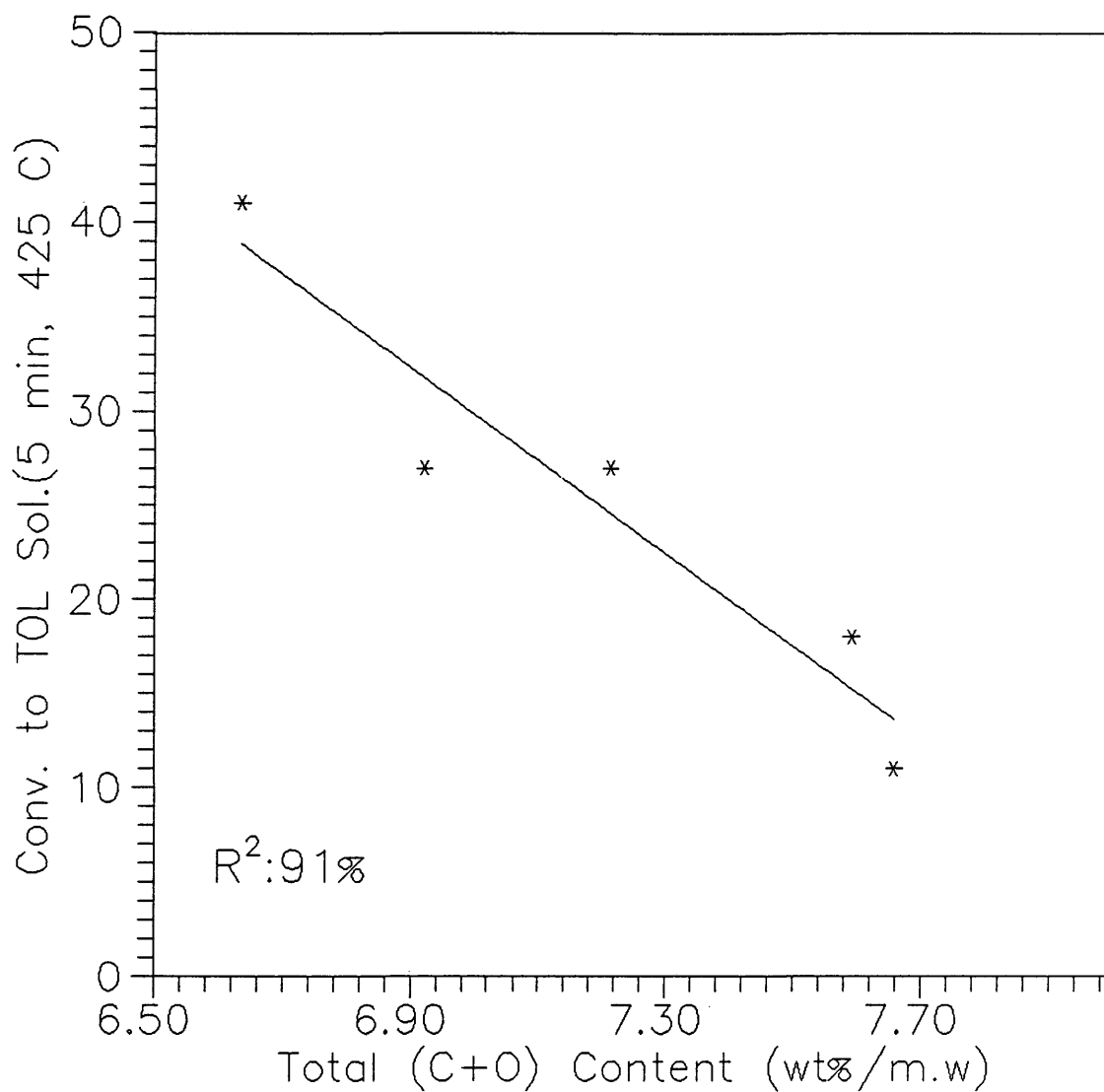===

Figure 18. Conversion to Toluene Solubles vs. (C+O) Content

(5 min, 425°C)
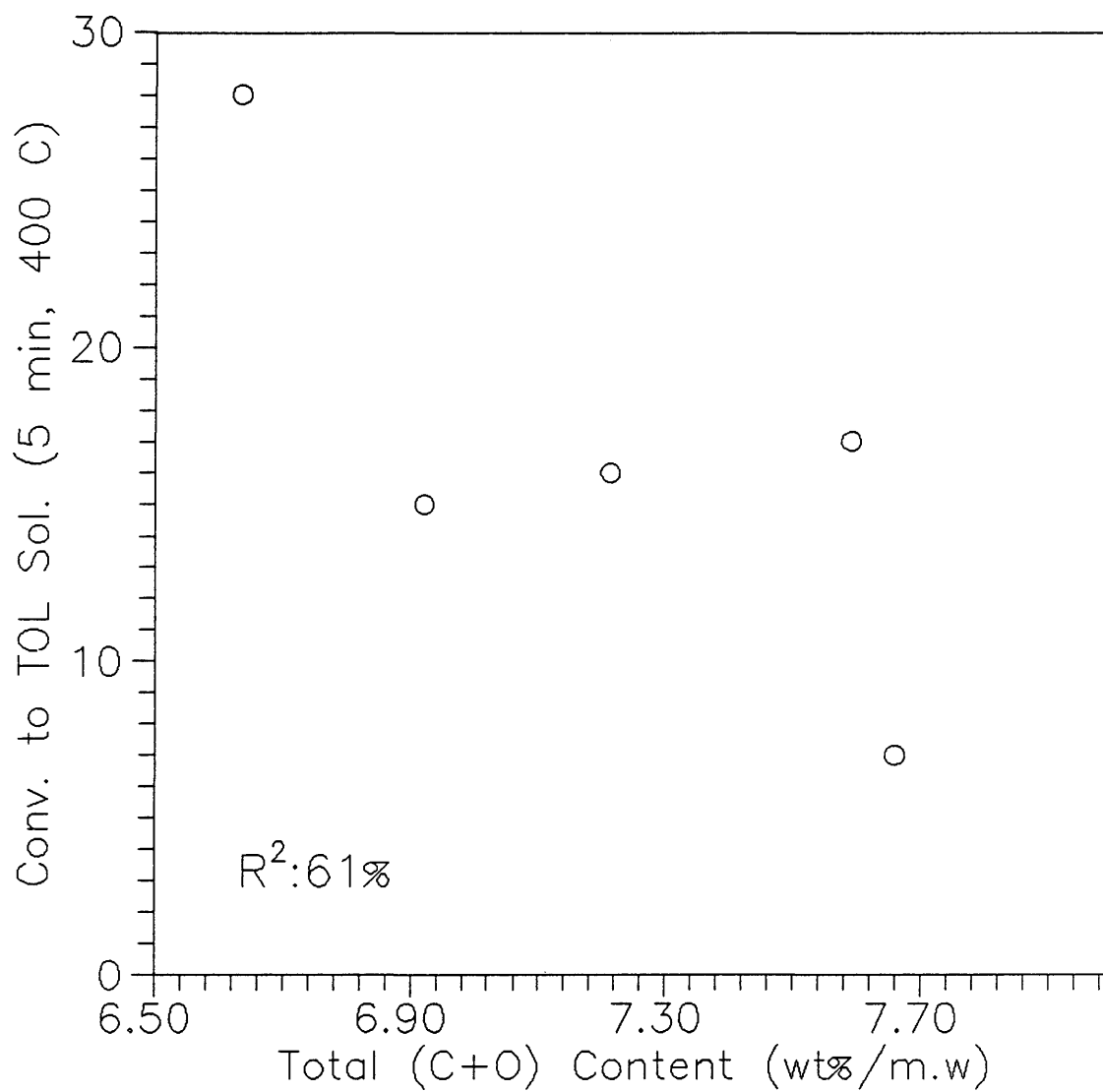
Figure 19. Conversion to Toluene Solubles vs.(C+O) Content

(5 min, 400°C)
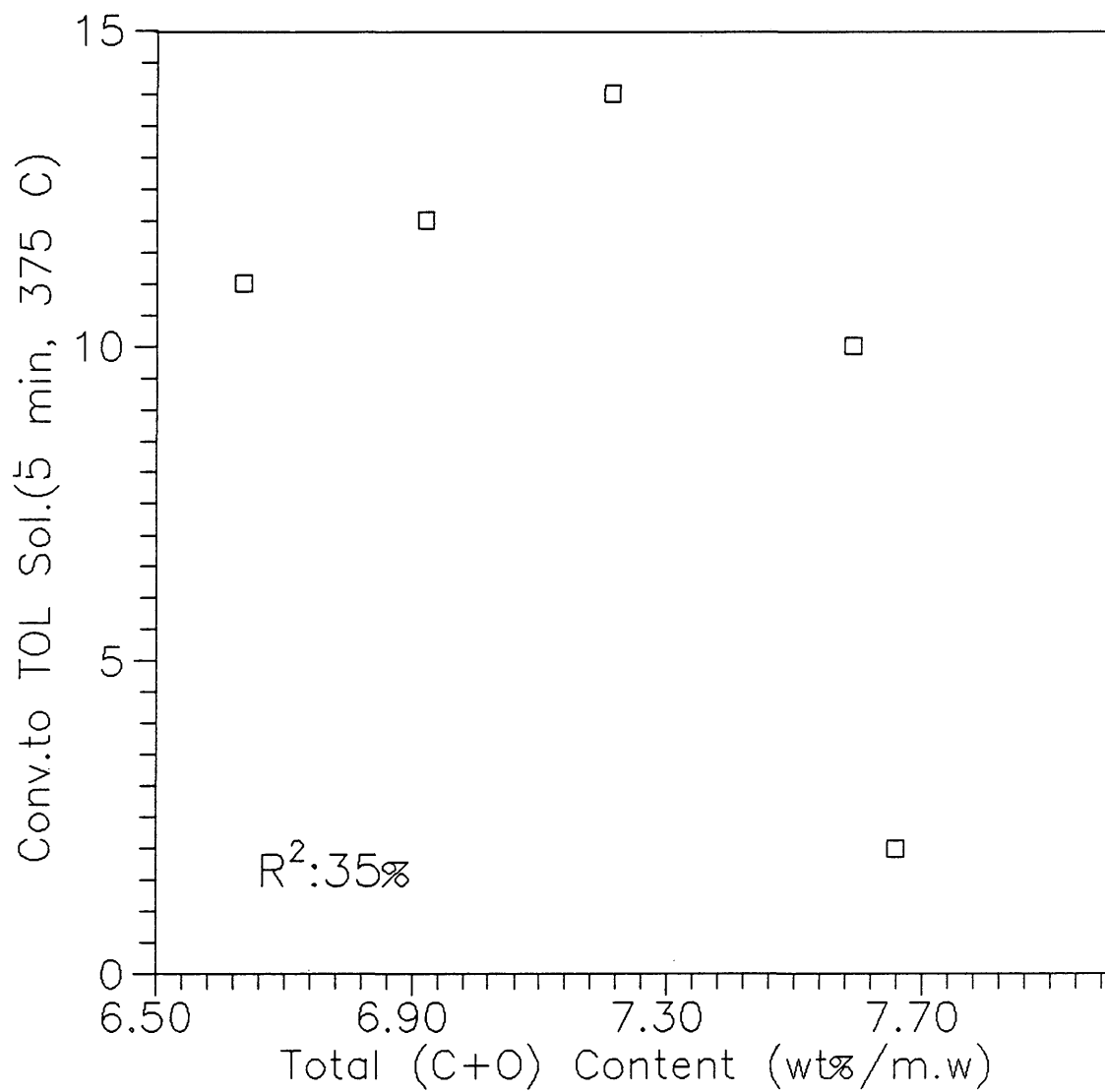
Figure 20. Conversion to Toluene Solubles vs.(C+O) Content
(5 min, 375°C)

parameters. Rate constants for conversion to toluene solu-
bles at 425°C gave a very strong correlation (R-sq value
99%) with the total hydrogen content of the coal as shown in
Figure 21. However the same strong correlations were not
found at lower temperatures, as shown in Figures 22 and 23.
Rate constants for conversion to toluene solubles showed
progressively better correlations with total carbon plus
oxygen as temperature decreased. Correlation coefficients
were 72%, 81%, 83% at temperatures 425, 400, 375°C respec-
tively.

5.4.2 Correlation of Activation Energy

Activation energy was also utilized as a reactivity
definition, and correlated with coal properties such as
total carbon, total hydrogen, total oxygen etc. To analyze
activation energy dependence of coal properties a regression
method called stepwise regression was used. This method
performs a linear regression step by step to find the best
subset of predictors with respect to the F-Statistic.
Testing the weight of the variables, total carbon, total
oxygen, total hydrogen, nitrogen and sulfur content of coal
in predicting activation energy (THF solubles) was tested.
The stepwise regression method determined that only carbon
and hydrogen were significant (95 % confidence) in predict-
ing activation energy for coal conversion to THF solubles.
Results of this analysis are shown in Table 12. Activation
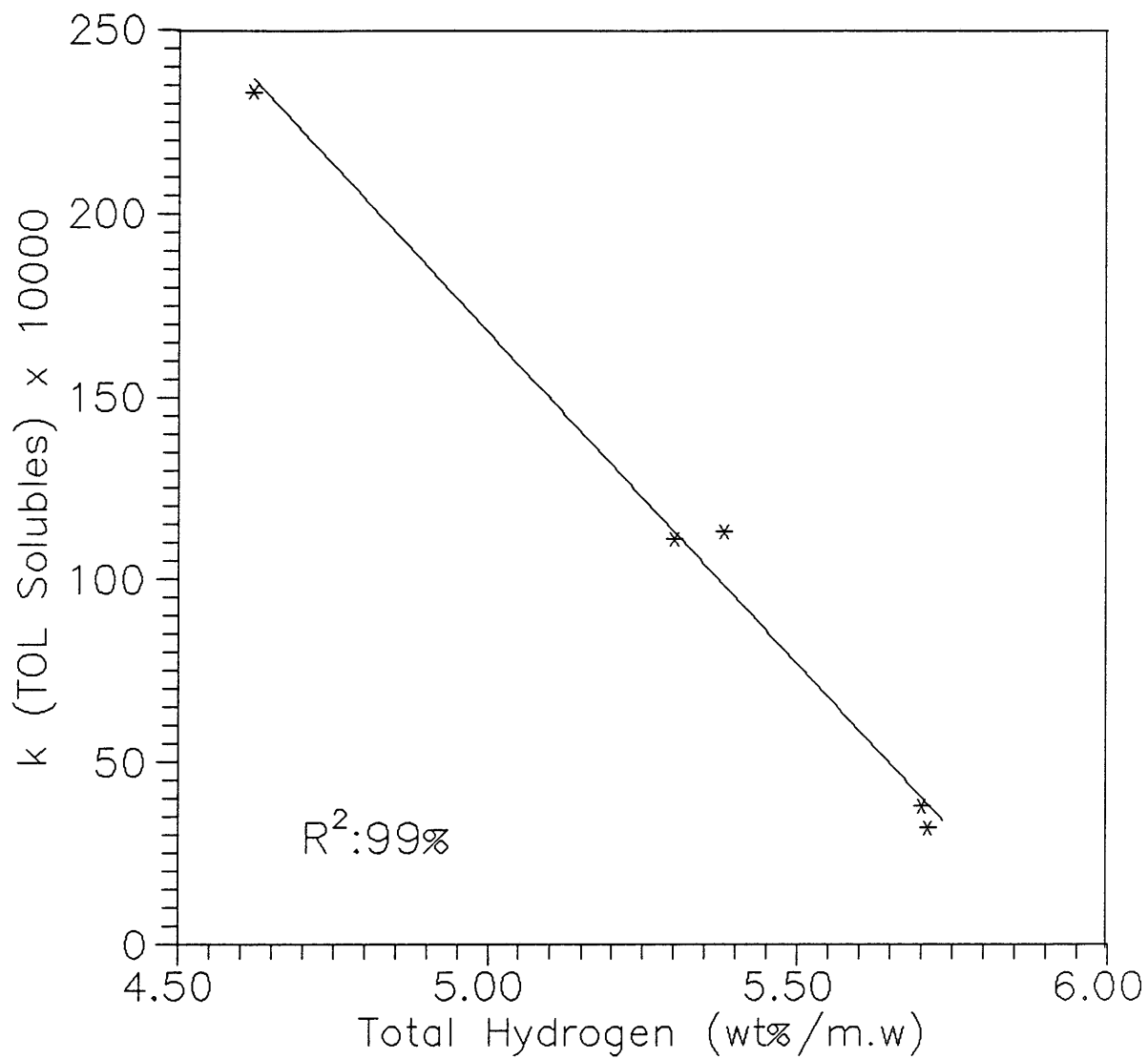
Figure 21.   Correlation of Kinetic Constant (Toluene Sol.)

vs. Total Hydrogen (wt%/m.w)

Temperature: 425°C
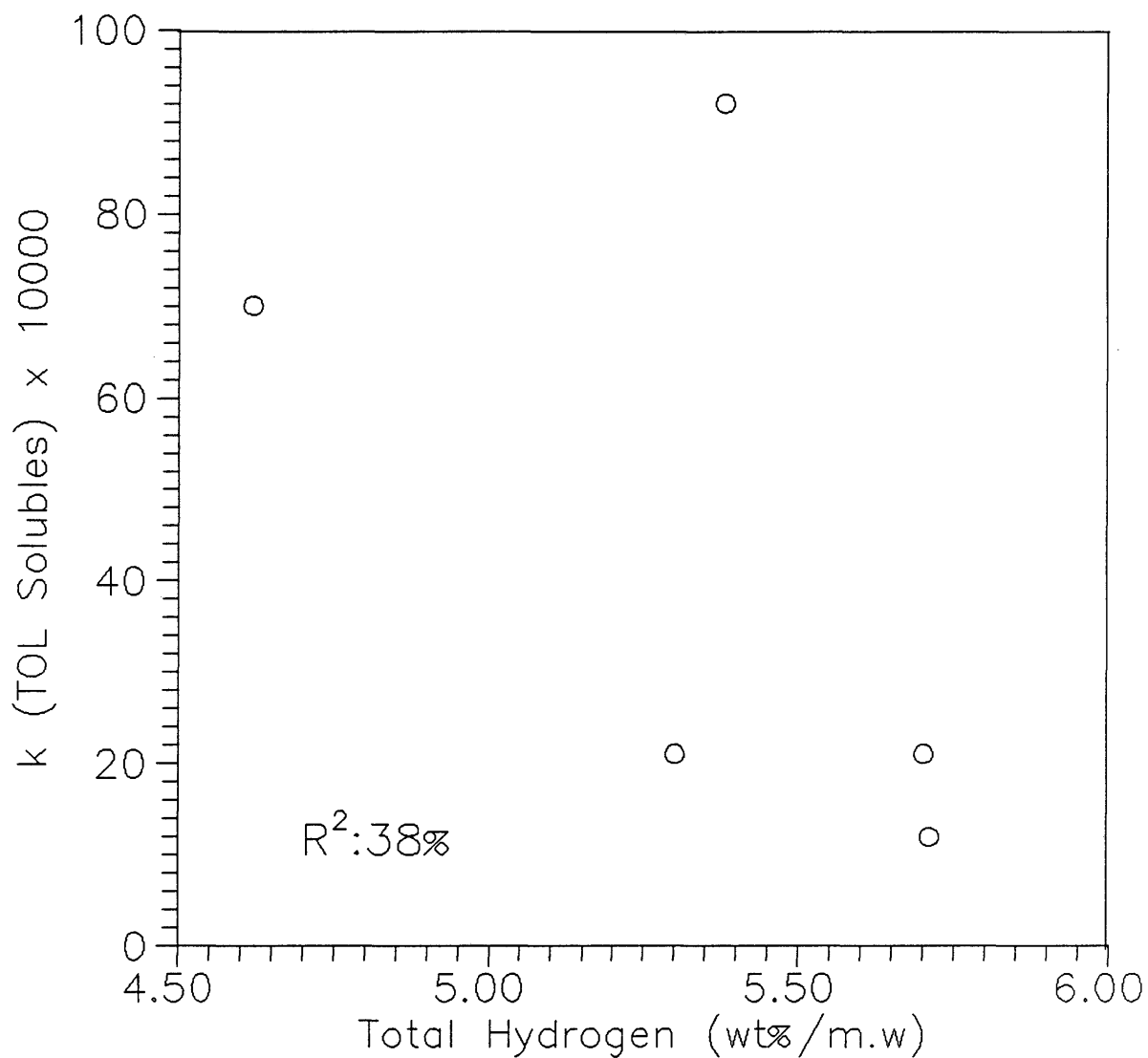
Figure 22.   Correlation of Kinetic Constant (Toluene Sol.)

vs. Total Hydrogen (wt%/m.w)

Temperature:400°C
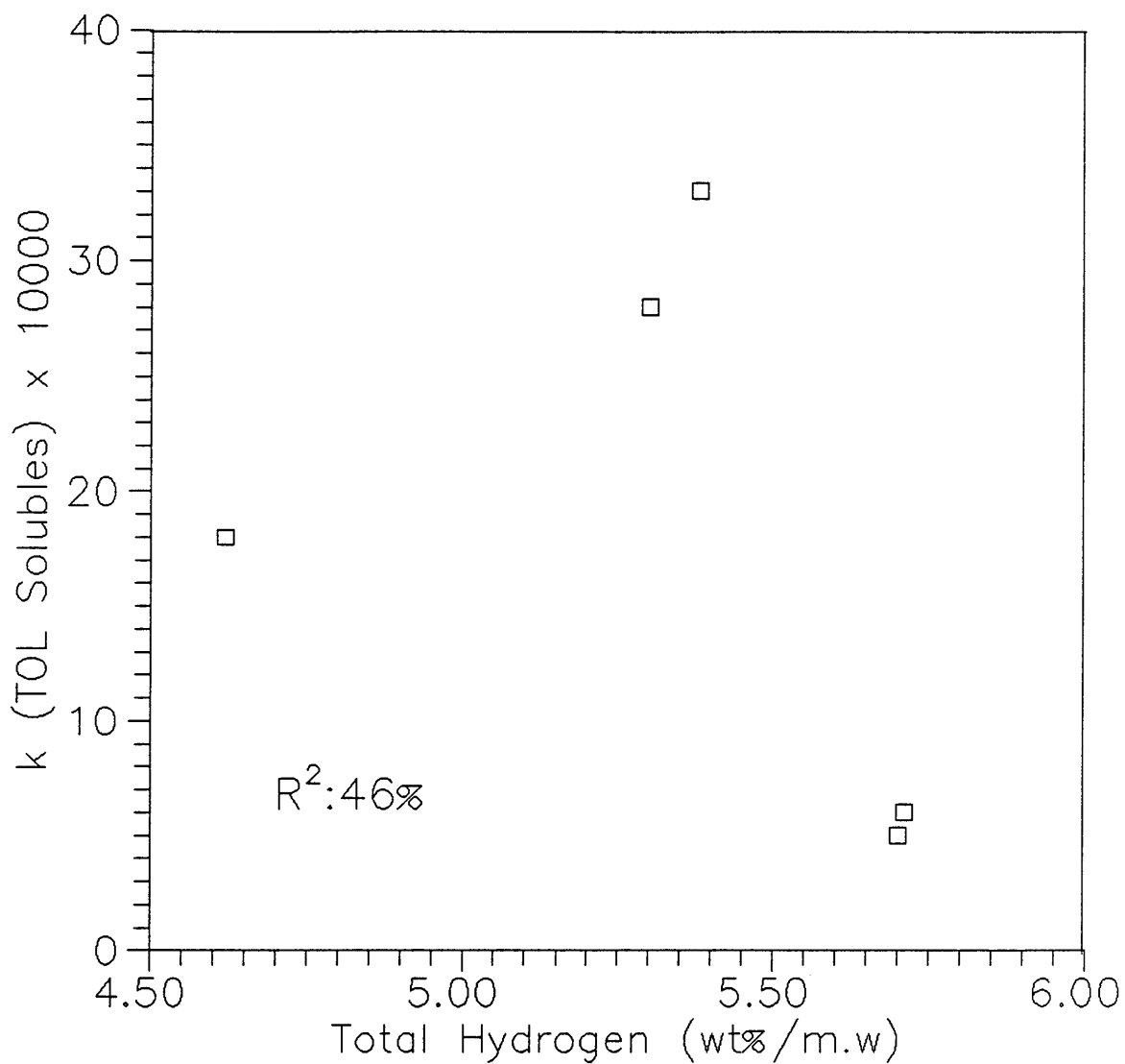
Figure 23.   Correlation of Kinetic Constant (Toluene Sol.)

vs. Total Hydrogen (wt%/m.w)

Temperature:375°C

Table 12.   Stepwise Regression of Coal Properties in

Predicting Activation Energy (THF)

===

STEP	1	2
Constant	105.3	224.2
C%	-11.6	-16.5
T-Ratio	-2.05	-5.12
H%		-16.2
T-Ratio		-3.18
*St.dev	8.01	3.99
R-sq	58.23	93.10

===

*: Estimated Standard deviation of the Regression

Line.

energy for coal conversion to THF solubles was highly corre-
lated with total carbon plus total hydrogen (R-sq 93%) and
the free swelling index plus total carbon (R-sq 82%). These
relationships are also illustrated in Figure 24.

$E(THF) = 225.2 - 16.4 (C+H)$ R-sq:93%

$E(THF) = 55.6 - 2.66 (Index+C)$ R-sq:82%

where, E = Activation energy, kcal/mole

C, H = Carbon and Hydrogen content (wt%/m.w, d.a.f)

Index= Free swelling index

Activation energy for coal conversion to toluene solubles
was found to be strongly correlated with the following
variables:

$E(TOL) = 55.7 - 3.36 [I+(C*O)]$ {R-sq:98.1%}

$E(TOL) = 53.8 - 3.30 [I+(H*O)]$ {R-sq:95.8%}

where, E = Activation energy, kcal/mole

I = Free Swelling Index

C, O, H = Carbon, Oxygen and Hydrogen content
(wt%/m.w, d.a.f)

These two correlations are presented graphically in Figures
25 and 26. Frequency factor was also correleted with coal
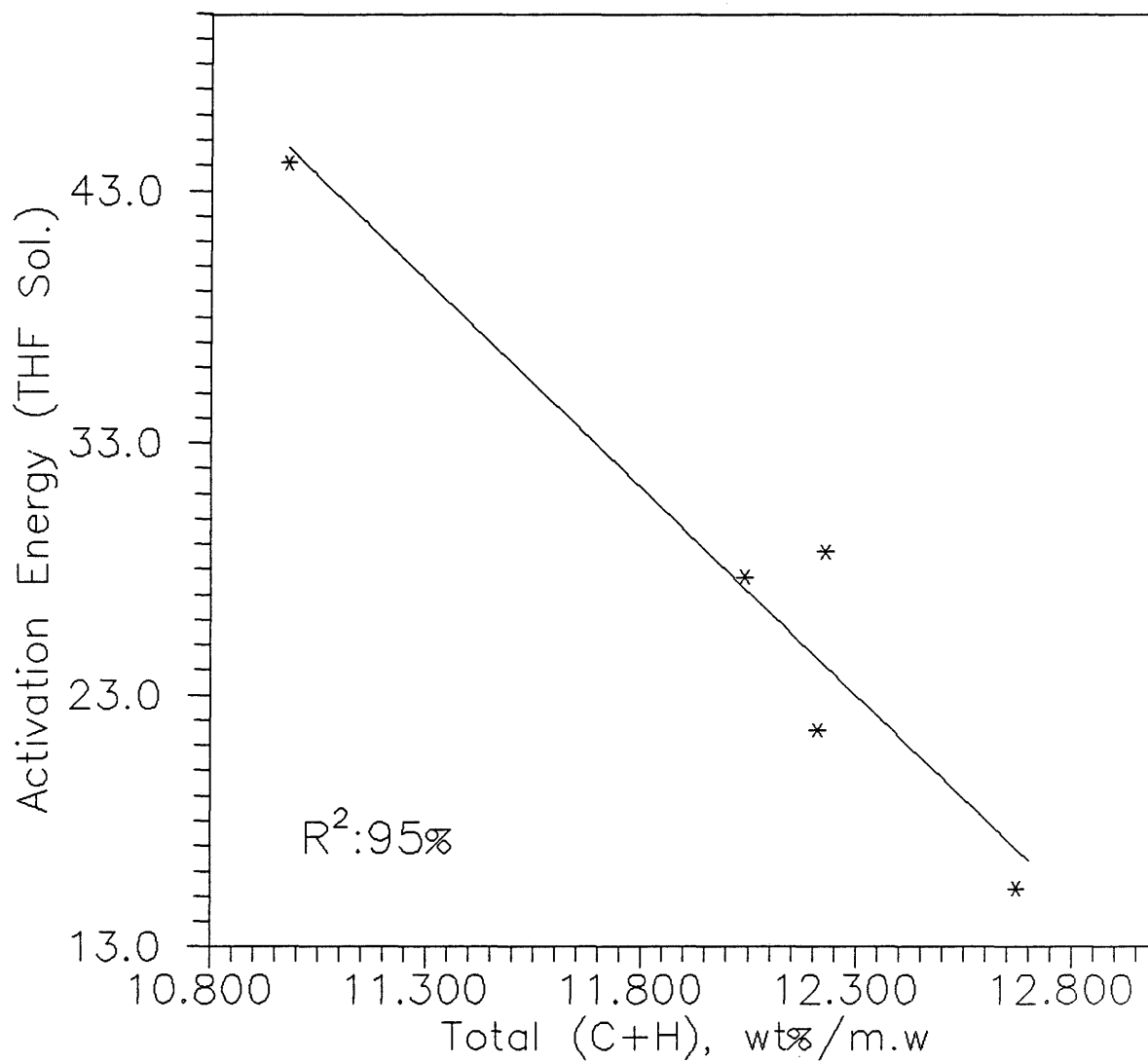
Figure 24.   Correlation of Activation Energy (THF Sol.)
             vs. C+H (wt%/m.w, d.a.f)
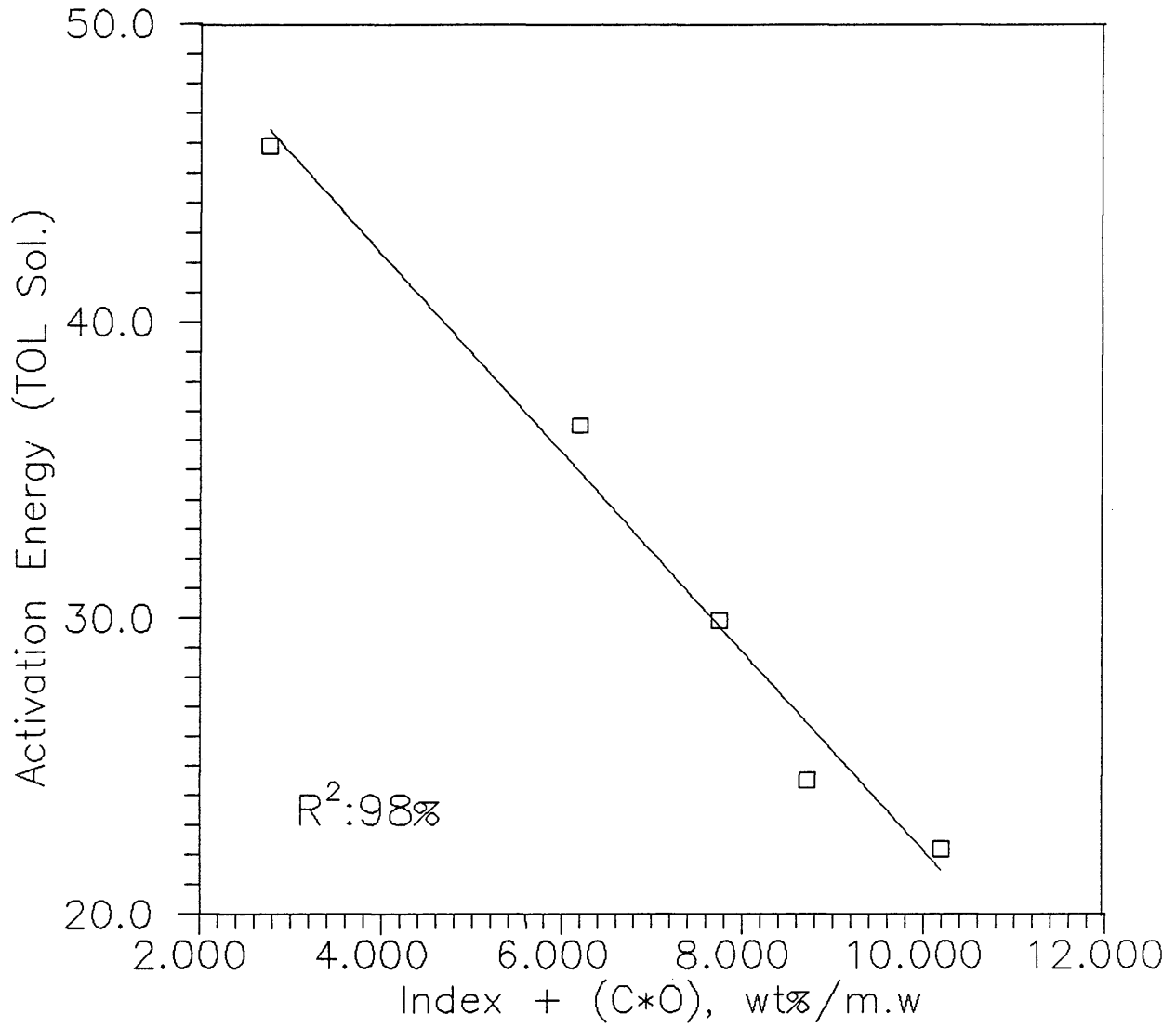
Figure 25. Correlation of Activation Energy vs.Index+(C*O)

(Toluene Solubles)
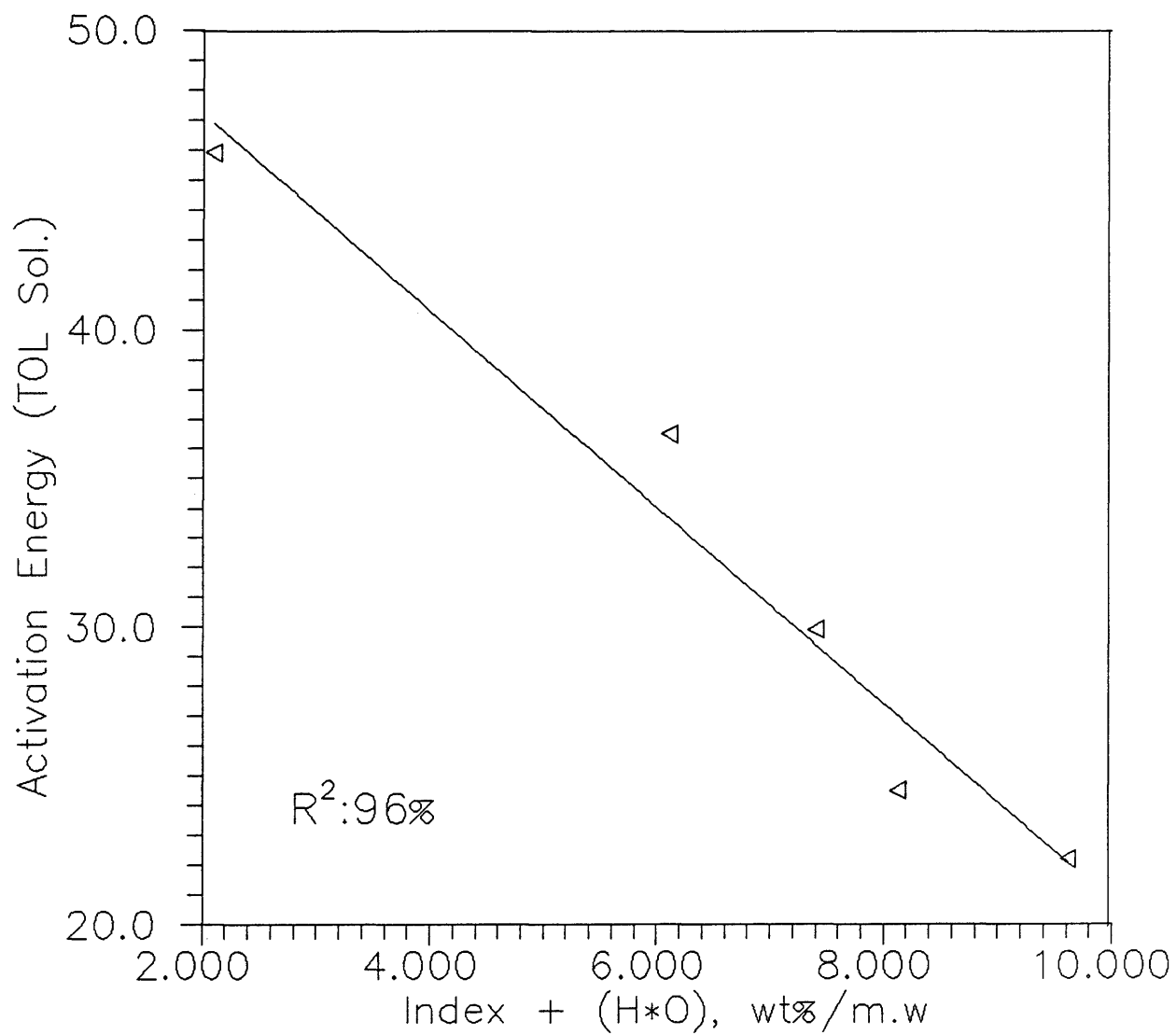
Figure 26. Correlation of Activation Energy vs. Index+(H*O)

(Toluene Solubles)

properties. This parameter was found to be highly correlat-

ed with the following variables:

$Ln(k_O)(THF) = 39.2 - 2.20\ (Index+C)$ R-sq:86%

$Ln(k_O)(TOL) = 36.2 - 2.53\ [Index+(C*O)]$ R-sq:98%

where, k_O = Frequency factor (1/min)

      Index = Free swelling index

      C,O   = Total Carbon and Oxygen (wt%/m.w, d.a.f)

Since both frequency factor and activation energy are higly

correlated with the same variables, a predictive equation

for the rate constant may be developed by using the Arrheni-

us equation:

$Ln\ k = Ln\ k_O - E/RT$

$Ln\ k(THF\ Sol)=[39.2-2.20\ (I+C)] - 1/RT\ [55.6-2.66(I+C)]$

$Ln\ k(TOL\ Sol)=\{36.2-2.53[I+(C*O)]\}-1/RT\{55.7-3.36[I+(C*O)]\}$

where, k = Kinetic constant (1/min)

     I = Free swelling index

    C,O = Total Carbon and Oxygen (wt%/m.w, d.a.f)

By using these two predicting equations for rate constants

to THF and toluene solubles, observed values and predicted

values were correlated. The predicted rate constant for THF

solubles was correlated well with the observed value (R-sq

90%), but correlation for toluene solubles was not as good

(R-sq 51%). These results are presented in Figures 27 and
28 in the form of parity plots. Correlations for activation
energy and frequency factor with coal properties are shown
in Table 13. The finding that activation energies for
conversion to THF and toluene solubles depend strongly on
the free swelling index, total carbon, and total oxygen
contents could give some insight into the chemical structure
of coal. The activation energy for a chemical reaction
shows the level of energy required to initiate the reaction.
It is known that the reaction of coal liquefaction is initi-
ated by breaking the bridging bonds between macromolecular
units first, since they are the weakest bonds in coal.
Hence, activation energy should be higher for coals which
are more strongly cross-linked. From the correlation of
activation energy for conversion to THF solubles, we see
that this parameter is correlated with free swelling index
which is in turn directly related to the degree of cross-
linking in coal. However activation energy was not uniqely
correlated with free swelling index alone. Independent
variables found to be significant include total carbon and
hydrogen too. It thus could be suggested that the activa-
tion energy for coal conversion to THF solubles was corre-
lated with the cross-linking of aliphatic carbon. For the
toluene solubles, activation energy was a function of oxygen
content in addition to free swelling index, carbon, and
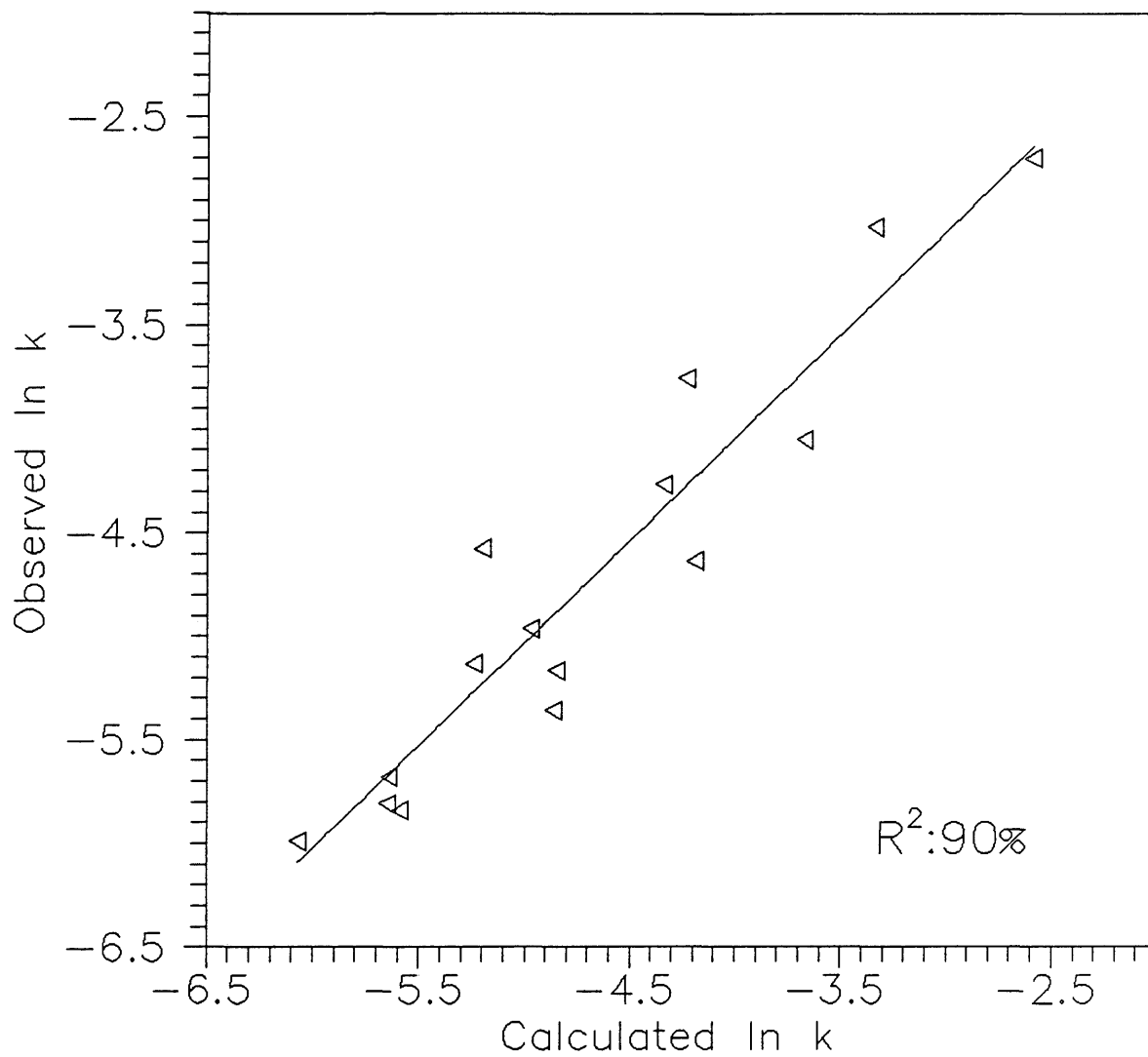
Figure 27. Correlation of Observed and Calculated Rate
Constants (THF Solubles)
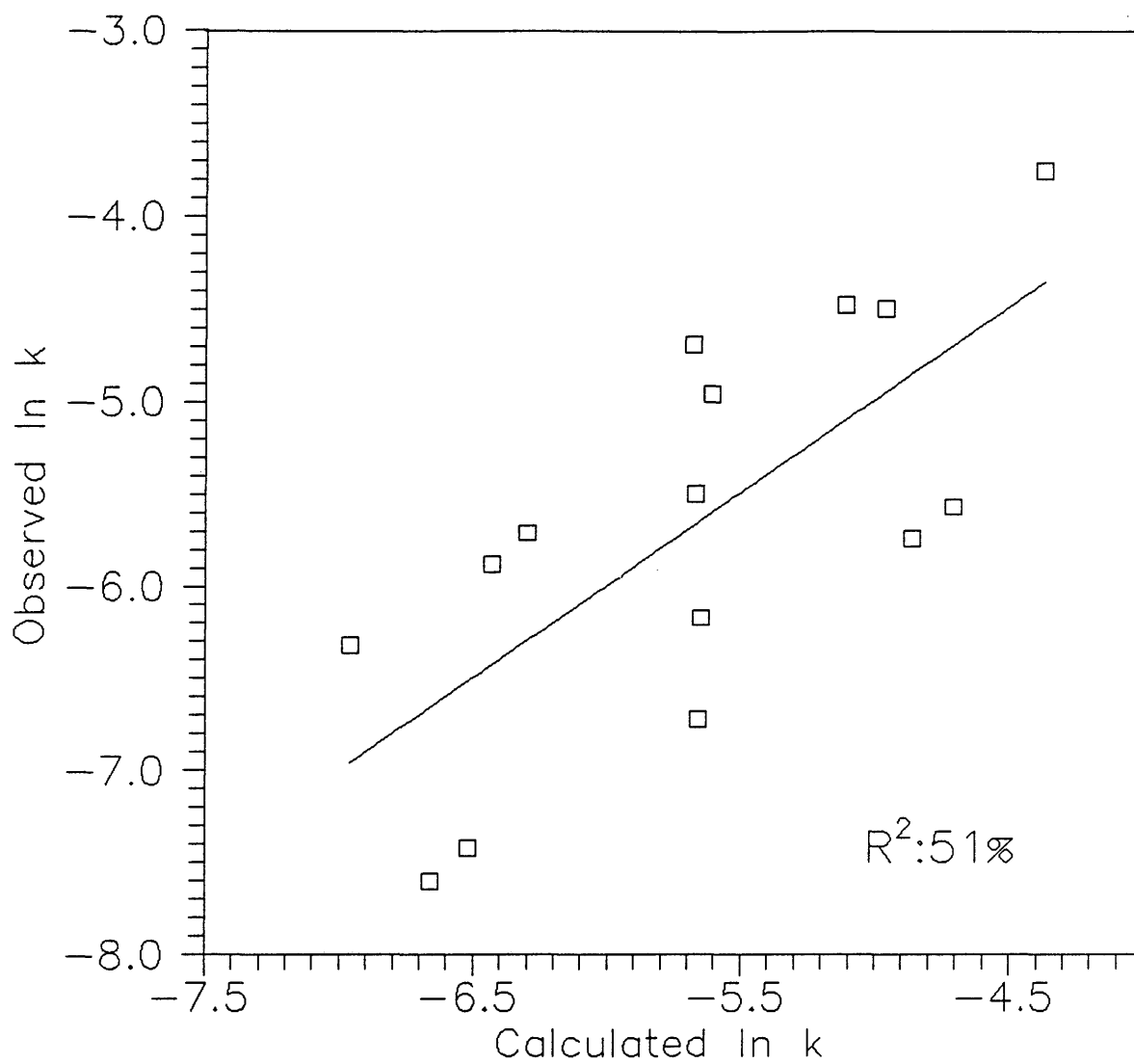
Figure 28.   Correlation of Observed and Calculated Rate
Constants (Toluene Solubles)

Table 13.   Correlations of Activation Energy, Frequency

Factor with Coal Properties

Multiple Correlation Coefficients

Property*	E(Tol)	E(THF)	k0(Tol)	k0(THF)	lnk0(Tol)	lnk0(THF)
C	18	58	34	64	22	53
H	29	3	83	0	39	5
O	25	62	8	96	22	60
N	26	4	80	1	34	6
S	7	2	10	19	3	3
C+H	1	93	0	86	1	93
C*H	0	89	4	75	1	91
C*H	26	58	7	94	23	56
I+C	6	82	11	56	7	86
I+(C*H)	4	82	12	60	6	86
I+(H*O)	96	2	80	8	98	4
I+(C*O)	98	2	74	10	98	3

* Property values (wt%/m.w, d.a.f)

where, E = Activation energy (kcal/mole)

       k0= Frequency factor (1/min)

       I = Free Swelling Index

hydrogen. This implies that activation energy for conversion to toluene solubles is a function of aliphatic carbon and oxygen, hence suggesting the importance of aliphatic ether groups in cross-linking structures.

6. CONCLUSIONS

* Activation energy obtained using a second order reversible kinetic model was not linearly correlated with a single property of coal, but it is strongly correlated with combinations of fundamental properties e.g. (C+H) or [I+(C*O)].

* It was shown that the reactivity ranking of coals by activation energy was independent of the kinetic model used.

* Total carbon, hydrogen, and free swelling index were found to be important properties in predicting activation energy for conversion of coal to THF solubles.

* A universal correlation for rate constants including temperature effects was derived. The total carbon and free swelling index were very important properties in predicting the rate constant for conversion to THF solubles.

7. RECOMMENDATIONS

\# For more general results the method and correlations used in this study should be tested by applying to a greater number of coal samples.

\# Activation energy dependence should be tested with other coal functionalities e.g. aliphatic carbon, hydrogen content and aromatic carbon, hydrogen content.

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APPENDIX

1. Kinetic data for five Penn State Coal Bank samples

2. Solutions of kinetic models

    o First-second order reversible model

    o Second order reversible model.

3. Computer program for the calculation of SEE.

Appendix 1-1. Kinetic Data for Weir-Pittsburg Coal

Conversion: d.a.f. basis wt %

TEMP(C)	CONVERSIONSION	REACTION TIME, MIN				
		3 min	5 min	10 min	15 min	40 min
425	THF Conve	65	82	87	85	85
	TOL Conve	28	41	53	58	70
400	THF Conve	50	69	83	85	88
	TOL Conve	19	28	44	50	66
375	THF Conve	30	48	69	78	84
	TOL Conve	5	11	18	24	33

Appendix 1-2. Kinetic Data for Bevier-Wheeler Coal

Conversion: d.a.f. basis, wt%

===

TEMP(C)	CONVERSION	REACTION TIME,MIN				
		3 min	5 min	10 min	15 min	40 min
425	THF Conv	59	73	79	81	79
	TOL Conv	18	27	40	44	58
400	THF Conv	41	61	75	77	86
	TOL Conv	4	15	22	29	52
375	THF Conv	32	50	63	73	83
	TOL Conv	4	12	16	16	28

===

Appendix 1-3. Kinetic Data for Lower Sudduth Coal

Conversion: d.a.f. basis, wt%

==

TEMP(C)	CONVERSION	REACTION TIME,MIN				
		3 min	5 min	10 min	15 min	40 min
425	THF Conv	38	38	39	39	41
	TOL Conv	21	27	33	33	38
400	THF Conv	28	33	38	39	41
	TOL Conv	14	16	24	27	33
375	THF Conv	17	24	30	31	39
	TOL Conv	10	14	19	19	24

==

Appendix 1-4. Kinetic Data for Splashdam Coal

Conversion: d.a.f. basis, wt%

===

TEMP(C)	CONVERSION	REACTION TIME,MIN				
		3 min	5 min	10 min	15 min	40 min
425	THF Conv	43	47	56	57	70
	TOL Conv	17	18	19	23	28
400	THF Conv	34	39	49	49	68
	TOL Conv	16	17	18	20	27
375	THF Conv	27	27	34	39	39
	TOL Conv	7	10	11	11	16

===

Appendix 1-5. Kinetic Data for Lower Freeport Coal

Conversion: d.a.f. basis, wt%

===

TEMP(C)	CONVERSION	REACTION TIME, MIN				
		3 min	5 min	10 min	15 min	40 min
425	THF Conv	25	28	30	30	25
	TOL Conv	10	11	11	16	15
400	THF Conv	22	26	28	28	31
	TOL Conv	3	7	10	10	12
375	THF Conv	16	20	21	25	25
	TOL Conv	2	2	5	6	6

===

Appendix 2. Solutions of Kinetic Models

      o First-Second Order Reversible Model

$$X = \frac{a.Xe.[1-\exp(-Q.t)]}{a+(a-Xe).\exp(-Q.t)}$$

where, a : Ultimate conversion

        X : Equilibrium conversion

        t : Time

        k_f : Forward kinetic constant

        $Q = k_f.(2a-Xe)/Xe$

      o Second Order Reversible Model

$$X = \frac{a}{(1-Q^2)} . \left\{1+Q.\left[\frac{1-P.\exp(R.t)}{1+P.\exp(R.t)}\right]\right\}$$

where , P = a/(a-2Xe)

        Q = (a-Xe)/Xe

        R = 2k.a.Q

Appendix 3. Computer Program for the Calculation of SEE

```
      PROGRAM SEC-REVERSIBLE
      DEMENSION XSTA(1000),DIF(1000),T(5),X(5),Q(1000),R(1000)
     +          ,P(1000)
C              XSTA=CONVERSION FROM MODEL
C              DIF=DIFFERENCE BETWEEN CONVERSIONS FROM MODEL
C              AND EXPERIMENT
C              T(I)=TIME
C              X(I)=EXPERIMENTAL CONVERSION
      REAL KIN,KF,N,K,I
C     ****************************************************

      WRITE(*,*)'ASSUME INITIAL,B,AND FINAL,F,ULTIMATE CONV'
      READ(*,*)B,F
C     ****************************************************

      WRITE(*,*)'ASSUME INITIAL,XIN,AND FINAL,XF,EQUILI CONV'
      READ(*,*)XIN,XF
C     ****************************************************

      WRITE(*,*)'ASSUME INITIAL,KIN,AND FINAL,KF,KINETIC CONS'
      READ(*,*)KIN,KF
C     ****************************************************

      OPEN(UNIT=2,FILE='TIME425TH1.DAT',STATUS='OLD')
      OPEN(UNIT=3,FILE='SREVV425TH1.OUT',STATUS='NEW')
      N=5.0

      DO I=1,5
      READ(2,*) T(I),X(I)
      ENDDO

      DO A=B,F
      DO E=XIN,XF
      DO K=KIN,KF,0.001

      SUM1=0.0
      DO I=1,5
      Q(I)=(A-E)/E
      R(I)=2*K*A*Q
      P(I)=A/(A-2*E)

      XSTA(I)=A/(1-Q(I)**2)*(1+Q(I)*((1-P(I)*EXP(R(I)*T(I)))/
     +        (1+P(I)*EXP(R(I)*T(I)))))
      DIF(I)=(X(I)-XSTA(I))**2
      SUM1=SUM1+DIF(I)
      ENDDO
      STOPL=SQRT(SUM1)
      SOLN=STOPL/N
```

```
      WRITE(3,60)SOLN,A,E,K
60    FORMAT(1X,F8.4,1X,F5.2,1X,F8.4,1X,F8.4)
      ENDDO
      ENDDO
      ENDDO
      STOP
      END
```