

DIRECT HYDROGENATION
REACTIVITY
OF
HIGH VOLATILE
BITUMINOUS COALS

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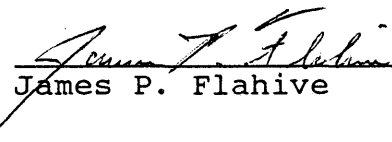
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Golden, Colorado

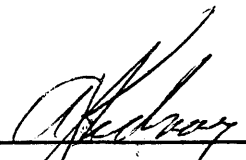
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ABSTRACT

Conversion profiles for nine high volatile bituminous U.S. coals were generated in a fast-heating tubing bomb reactor using 1-methylnaphthalene as a non-hydrogen donor solvent. Gaseous hydrogen was used as the hydrogen source.

Kinetic modelling demonstrated that a first order, irreversible model was statistically and mechanistically superior to a second order, irreversible model for describing the initial stages of the coal liquefaction reaction. Coal conversion was defined as the conversion to tetrahydrofuran, toluene, and hexane soluble products. Correlations of the toluene solubles kinetic constant were found with the following parent coal properties: O/C atomic ratio, % oxygen, and % carbon. The hexane solubles kinetic constant correlated against total sulfur and pyritic sulfur content. A two-parameter correlation was developed for toluene solubles kinetic constant, with the independent parameters being organic sulfur and O/C atomic ratio.

Two ancillary studies were performed. First, no catalytic effect stemming from the walls of the tubing bomb reactor was observed. Second, there was no apparent mass transfer limitation on the liquefaction reaction for coal particle sizes smaller than -20 mesh.

T-3546

DEDICATION

To Kevin Scott Flahive

TABLE OF CONTENTS

Section	Page
ABSTRACT	iii
LIST OF TABLES	vii
LIST OF FIGURES	viii
ACKNOWLEDGMENTS	x
1. INTRODUCTION	1
2. LITERATURE SURVEY	4
3. EXPERIMENTAL EQUIPMENT	9
3.1 REACTOR SYSTEM	9
3.2 ANALYTICAL EQUIPMENT	12
4. EXPERIMENTAL PLAN	14
5. EXPERIMENTAL PROCEDURE	15
5.1 COAL	15
5.1.1 Coal Characterization Data	15
5.1.2 Coal Preparation	15
5.2 REACTION PARAMETERS	21
5.3 EXPERIMENTAL RUN PROCEDURE	22
5.3.1 Start-up	22
5.3.2 Experimental Run Preparation	22
5.3.3 Run Procedure	23
5.4 ANALYTICAL PROCEDURE	23
6. RESULTS OF PHASE 1 EXPERIMENTS	27
6.1 CATALYTIC WALL EFFECT	27
6.1.1 Background	27

6.1.2	Discussion of Catalytic Wall Effect . .	28
6.2	COAL PARTICLE SIZE EFFECT	30
6.2.1	Background	30
6.2.2	Discussion of Particle Size Effect . .	31
6.3	GENERATION OF REACTIVITY DATA	31
6.3.1	Definition of Conversion	31
6.3.2	Selection Process of Suitable Coals . .	35
6.3.3	Correction of Reaction Time	37
7.	RESULTS OF PHASE 2 EXPERIMENTS	43
7.1	KINETIC MODELLING	43
7.2	SINGLE PARAMETER CORRELATIONS	48
7.2.1	Background	48
7.2.2	Discussion	61
7.3	MULTI-PARAMETER CORRELATIONS	75
8.	CONCLUSIONS	77
9.	RECOMMENDATIONS	79
	LITERATURE CITED	80
	APPENDIX	

LIST OF TABLES

Table 1.	Experimental Plan	14
Table 2.	Characterization Data for the Penn State Premium Coal Suite: Bituminous Coals	16
Table 3.	Characterization Data for the Argonne National Laboratory Premium Coal Suite	19
Table 4.	Reaction Parameters	21
Table 5.	Definitions of Conversions for Liquefaction Products	36
Table 6.	1 st and 2 nd Order Model Comparison: Total Conversion	45
Table 7.	1 st and 2 nd Order Model Comparison: Toluene Solubles	46
Table 8.	1 st and 2 nd Order Model Comparison: Hexane Solubles	47
Table 9.	Coefficients of Determination for Single Parameter Correlations: Total Conversion	62
Table 10.	Coefficients of Determination for Single Parameter Correlations: Toluene Solubles	63
Table 11.	Coefficients of Determination for Single Parameter Correlations: Hexane Solubles	64
Table 12.	Correlations of Kinetic Constant with Coal Properties	66

LIST OF FIGURES

Figure 1.	Schematic of Reaction System	10
Figure 2.	Schematic of Tubing Bomb Reactor	11
Figure 3.	Definitions of Solvent Soluble Products	25
Figure 4.	Catalytic Wall Effect on Yield	29
Figure 5.	Particle Size Effect on Yield	32
Figure 6.	Particle Size Effect on Rate	33
Figure 7.	Activation Energies of Representative Coals.	41
Figure 8.	Kinetic Model Comparison: UF	49
Figure 9.	Kinetic Model Comparison: FS	50
Figure 10.	Kinetic Model Comparison: WP	51
Figure 11.	Conversion Profile: St	52
Figure 12.	Conversion Profile: UF	53
Figure 13.	Conversion Profile: B	54
Figure 14.	Conversion Profile: T	55
Figure 15.	Conversion Profile: FS	56
Figure 16.	Conversion Profile: BW	57
Figure 17.	Conversion Profile: WP	58
Figure 18.	Conversion Profile: S	59
Figure 19.	Conversion Profile: SL	60
Figure 20.	Correlation of Toluene Solubles Kinetic Constant vs. % Oxygen	67
Figure 21.	Correlation of Toluene Solubles Kinetic Constant vs. % Carbon	68

Figure 22.	Correlation of Toluene Solubles Kinetic . . .	69
	Constant vs. O/C Atomic Ratio	
Figure 23.	Correlation of Hexane Solubles Kinetic . . .	70
	Constant vs. Total Sulfur	
Figure 24.	Correlation of Hexane Solubles Kinetic . . .	71
	Constant vs. Pyritic Sulfur	

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1. INTRODUCTION

The foundation of the West's technological advancement has been, and is, the availability of easily accessible, relatively cheap energy. Since the advent of the 20th century crude oil has been the primary fuel source of the civilized world.

Two factors now necessitate the supplementation of conventional crude oil resources; one, the political instability of the Middle East, which contains the vast majority of the free world's oil reserves and two, the dramatic increase in energy consumption needed to maintain a reasonable growth rate in the world's economy. The mere fact that the number of barrels of oil equivalent from coal reserves is 50 times greater than that from crude petroleum requires serious research into coal liquefaction

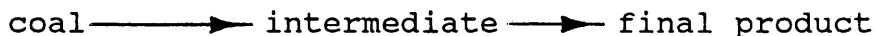
The possibility of producing liquid hydrocarbons from coal stems from coal's structural and compositional similarity to crude oil. However, coal is a very non-homogeneous substance whose precise structure and composition can only be approximated. Because of this uncertain nature of coal, much work has been put into determining the effects of various coal characteristics on coal liquefaction.

In the past 50 years, one thrust of coal liquefaction

research has been to relate coal liquefaction behavior to coal properties. These properties have varied in nature from petrographic to geographic to compositional.

The majority of these researchers have used, as their definition of coal liquefaction, the amount of solvent soluble product after an extended (40-60 minutes) reaction time. Furthermore, most correlational efforts have involved only one independent parameter, with the correlation being strictly empirical in nature.

Many researchers have postulated as a coal liquefaction mechanism the following rough equation:



The above mechanism suggests that at long reaction times the structure of the intermediate, rather than that of the coal, dominates the reaction and the subsequent yield. This equilibrium approach ignores the properties of the parent coal. Hence, any relationship that may exist between coal properties and the behavior of that coal under hydro-liquefaction conditions is minimized.

In this research, I shall attempt to correlate the parameters of the parent coal against the kinetic rate constant of the initial liquefaction reaction. This approach will isolate the properties of the coal itself,

rather than those of the intermediates. The correlational effort will involve two phases. The first will be the classic one-parameter correlations, in which the effects of various coal characteristics on liquefaction will be elucidated. The second phase will involve the determination of a two-parameter correlation. One parameter will express the catalytic nature of the coal mineral matter, and the other will involve the structure of the coal. This semi-theoretical approach will hopefully produce a correlation superior to a one-parameter correlation.

Two auxiliary studies have been conducted during the course of this research. The possibility that the metallic walls of a reactor have a catalytic effect on the liquefaction reaction has been postulated for many years. This thesis will attempt to prove or disprove the purported catalytic effect of the walls on the overall yield of the reaction. Finally, the mass transfer effects that the size of the coal particles have on the rate and yield will be directly examined.

2. LITERATURE SURVEY

Coal liquefaction has been an active topic of research for over 100 years. Berthelot was the first to study coal liquefaction in the late 1800's, and is generally credited with discovering that liquids could be generated from coal by the process of direct hydrogenation.

Since that time, coal liquefaction research has concentrated on two primary areas. These areas are: 1) the determination of a "universal" coal liquefaction mechanism, and 2) the evaluation of the effect various coal properties have on the liquefaction reaction.

The attempt to elucidate a single and universal mechanism for coal liquefaction stems from the ability to determine a mechanism for reactions between homogeneous chemical compounds. However, coal is far from a pure chemical compound. Coal is a very non-homogeneous substance. Its structure is an enigma, and any attempt to evaluate its structure is purely empirical. Furthermore, the structural and compositional changes between any two coals can be drastic.

In an attempt to model the coal liquefaction mechanism, it has become necessary to categorize certain products of the reaction. This is usually done through solvent extraction techniques. This method lumps products into

different groups of compounds based on their solubilities in various solvents (5,6,7). Schweighardt and Thames (5), among others, have labeled these groups as "Pre-asphaltenes", "Asphaltenes", and "Oils".

Storch (8) was the first to kinetically model the liquefaction reaction. Since then many other attempts have followed. Wisler used an n^{th} order model and found that for the first 60 minutes a second order model was adequate, while a first order model was more appropriate for the latter stages of the reaction (9). Furlong proposed a second order reversible model (23). Curran, Storch, and Gorin (10), on the other hand, stated that a second order model could not be justified. By the 1970's, complex reaction networks were proposed, and the appropriate kinetic constants calculated by regression techniques (2,3,4,11). In order to more theoretically relate coal kinetics to the liquefaction mechanism, various intermediates such as pre-asphaltenes and asphaltenes have been used as feedstocks (12,13,14). It was felt that the more homogeneous nature of these compounds could better facilitate the determination of the reactivity mechanism.

The type of solvent used in liquefaction studies has been a subject of discussion for 50 years. There are two categories of solvents: hydrogen donor and non-hydrogen solvents. Boomer and Saddington discovered that tetralin is

an excellent hydrogen donor in the absence of free hydrogen (15). Since that study in 1931 tetralin has been widely used in studies where hydrogen donor solvents were desired. However, when measuring the reactivity of coal one question has been raised in relation to hydrogen donor solvents. That question is: could not a hydrogen donor solvent so overpower the parent coal that any differences in coal liquefaction reactivities between two different coals would be masked? Many researchers, Curtis chief among them, have studied the effect various solvents have on liquefaction (16,17,18,19,20). The general consensus is that the amount of donatable hydrogen is in itself insufficient to define effectiveness as a solvent. Other factors, such as structure and heteroatomic species, have marked effects.

A related question to that of solvent type is the method of hydrogen transfer in coal liquefaction. Curran and Wiser postulated the production of free radicals from coal by thermolysis of the macromolecular structure, which are then capped by the most easily accessible hydrogen source (9,10). McMillan has recently proposed that "nonthermolizable linkages" are broken by hydrogen transfer via a direct bimolecular step from solvent-derived cyclohexadienyl radicals (39). Neavel stated that bond rupture is the limiting factor in hydrogen transfer, and that 25-30% of the parent coal is autohydrogenated (21). Orchin and Storch (22)

proposed that hydrogen gas is the primary source of free hydrogen, regardless of the solvent used.

The evaluation of the effects various coal properties have on the liquefaction reaction has been an important topic since 1920. Many people have attempted to find a correlation between coal liquefaction and coal rank, which is one of the most apparent coal properties (24,25,26). Each reached the conclusion that rank cannot predict liquefaction ability. Much work has been put into the maceral and petrographic content of coals and their effect (28,29,30,31). Correlations involving macerals, H/C ratios, sulfur content and other parameters have been postulated (29,32,37). Given et al., in their series of works, have conclusively stated that any one parameter is insufficient to describe coal reactivity (27,34,35,36).

One characteristic of the above correlational efforts is the definition of coal reactivity. In the vast majority of cases, equilibrium conversion was used as the definition of coal reactivity, in spite of the fact that the mechanism of coal liquefaction is accepted to be roughly as follows:

coal → intermediate → final product

Among those who have used equilibrium conversion as the definition of reactivity are Given et al., Orchin and

Storch, and others (22,26,27,33,35). A few have attempted to correlate against the rate constant of the kinetic model proposed for that research, whether this constant was measured directly (23,28), or computed from a system of differential equations that solve the mass balance of the system (11). Furlong, using a second order reversible model, demonstrated directly that the kinetic constant correlates against parent coal properties more accurately than equilibrium conversion (23).

3. EXPERIMENTAL EQUIPMENT

3.1 REACTOR SYSTEM

Figure 1 is a schematic of the reaction system utilized for this research. Altizer has an excellent description of this system (41). In brief, the system is comprised of a tubing bomb reactor, a temperature controlled fluidized sand bath, and a gas charge system.

The gas charge system is designed to facilitate precise control over both the reactor pressure and the initial gas composition. One can insure the purity of the initial gas composition by closing valve V3 and evacuating the reactor through valve V5 with a vacuum pump.

The fluidized sand bath is a Tecan, Model SBL2D. A Leeds & Northrup Electromax III temperature controller, connected to a Leeds & Northrup power pack, is used to insure proper temperature control. The temperature controller keeps the fluidized bath within ± 2 °C of the set point.

The type of reactor used is a tubing bomb reactor. Figure 2 is an illustration of this reactor. The body of the reactor is 1/2" OD 316 stainless steel. The bottom of the reactor has a 1/2" Swagelok cap, and the top has a Cajon VCR gasket fitting. The volume of the reactor is approximately 18 cc. The reactor head is comprised of a VCR

Figure 1. Schematic of Reaction System

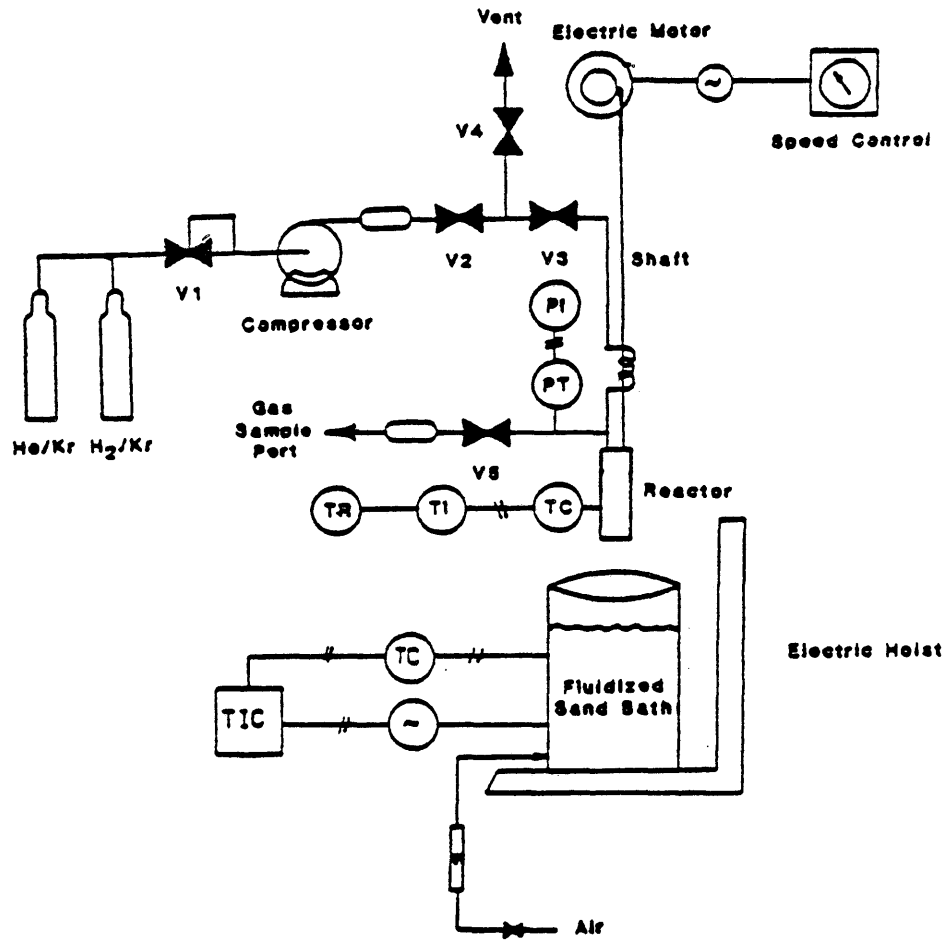
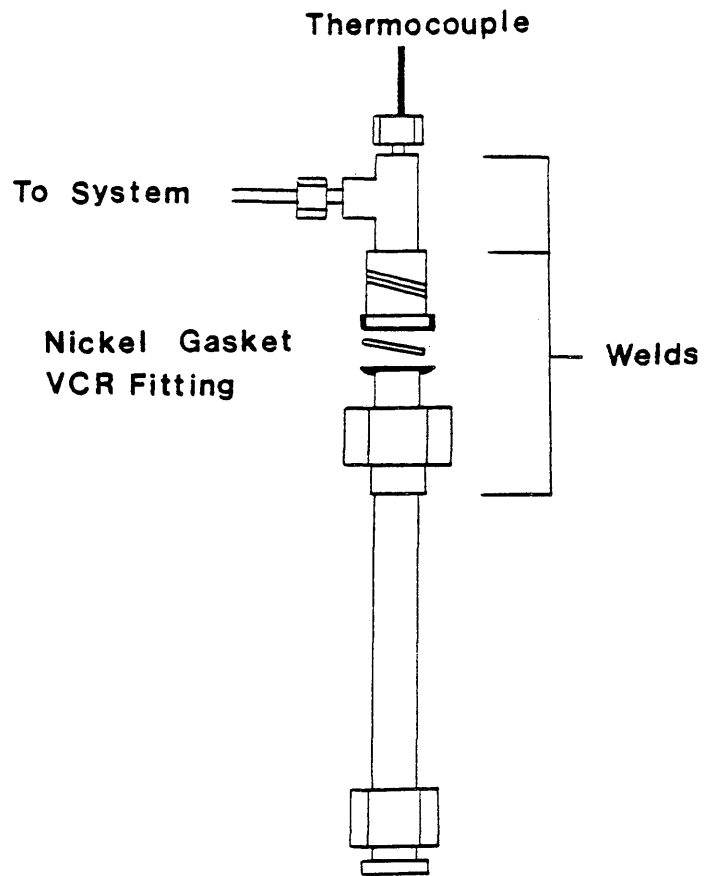


Figure 2. Schematic of Tubing Bomb Reactor



gland fitting and a Swagelok male run tee. The thermocouple used is a K type, sheathed in 1/16" stainless steel. An 1/8" Autoclave Engineers connector is attached to the gas feed line. The reactor is sealed by a disposable nickle gasket. Nine reactors were available for this research, but generally only five were utilized. The reactor is attached to an eccentrically-driven, vertical arm which was shaken at 120 rpm for this research.

3.2 ANALYTICAL EQUIPMENT

The laboratory work of this research involved two primary steps: 1) running the coal for a specified time at a specific temperature and pressure, and 2) determining conversion by solvent soluble products. The second step consisted of sonication, centrifugation, and drying. A Branisonic ultrasonic bath, an IEC Damon Model ICX centrifuge, and a Precision Scientific Oven were used for the second step, respectively. The first two solvents used (THF and Toluene) were distilled off via a rotary evaporator produced by Buchi.

All weight measurements were done on a Mettler PC-2000 electronic balance. A Labconco glove box was utilized to prepare the coal samples. All the coal was bottled under a CO₂ atmosphere, as was the coal that was ground to 100 mesh for the particle size effect study. Prepared coals were

sealed in glass bottles and stored in a Labconco, Model
55300 vacuum dessicator until ready for use

4. EXPERIMENTAL PLAN

The experimental work and analysis were separated into two distinct sections. The first phase evaluated the catalytic effect of the wall of the reactor and the particle size of the coal on conversion. For these two studies one coal was used. Phase 1 also involved generating reactivity data for nine bituminous coals. In Phase 2, a kinetic model was developed. Standard single parameter correlations were developed, along with multi-parameter correlations. Table 1 is a brief outline of the two phases.

Table 1. Experimental Plan

	<u>Phase 1</u>	<u>Phase 2</u>
Goal	*investigate wall effect . # of coals used: one	*develop kinetic model
	*investigate size effect # of coals used: one	*develop single parameter correlations
	*generate reactivity data # of coals used: nine	*develop multi- parameter correlation

5. EXPERIMENTAL PROCEDURE

5.1 COAL

Ten coals were used for this project. The coal used for the wall and particle size effect studies was from the Argonne National Laboratories. The remaining nine coals, used for the correlational study, were from the Penn State Premium Coal Suite. These coals are handled under carefully monitored conditions. The coal is bottled under an inert argon atmosphere, and extreme care is taken to prevent any exposure of the coal to air.

5.1.1 Coal Characterization Data

Table 2 contains the characterization data for the nine Penn State coals. Table 3 has the data for the Argonne coal. These data were provided by the laboratories in question, with one exception. It was discovered that the moisture content of many Penn State coals - specifically, those coals with high moisture contents - was erroneous. This was a result of the mode of preparation used by Penn State to bottle the coals. Personal conversation (40) with the researchers at Penn State confirmed the erroneous nature of the moisture data. Therefore, any coals with a reported moisture content greater than 5% were sent to Huffman Laboratories, Inc. for moisture determination.

Table 2. Characterization Data for the Penn State
Premium Coal Suite: Bituminous Coals

<u>Coal</u>	<u>I.D. number</u>	<u>Origin</u>	<u>Rank</u>
Stigler(St)	PSOC-1376P	Oklahoma	HVAB
Upper Freeport(UF)	PSOC-1361P	Pennsylvania	HVAB
B-Seam(B)	PSOC-1390P	Colorado	HVAB
Tebo(T)	PSOC-1369P	Missouri	HVAB
Fort Scott(FS)	PSOC-1375P	Oklahoma	HVAB
Bevier-Wheeler(BW)	PSOC-1364P	Missouri	HVBB
Weir-Pittsburgh(WP)	PSOC-1368P	Missouri	HVBB
Sudduth(S)	PSOC-1388P	Colorado	HVCB
Lower Sudduth(SL)	PSOC-1389P	Colorado	HVCB

Table 2 (cont). Characterization Data for the Penn
State Premium Coal Suite; Bituminous
Coals

<u>Coal</u>	<u>Fixed Carbon, %</u>	<u>Volatile Matter, %</u>	<u>Vitrinite Reflectance, %</u>	<u>O/C Ratio</u>	<u>H/C Ratio</u>
St	65.22	34.78	1.11	.085	.74
UF	58.31	41.69	0.83	.079	.84
B	58.66	41.34	0.76	.092	.80
T	52.52	47.48	0.54	.019	.79
FS	52.23	47.77	0.65	.055	.73
BW	56.40	43.60	0.44	.057	.82
WP	54.80	45.20	0.55	.033	.83
S	55.65	44.35	0.51	.214	.81
SL	49.46	50.54	0.48	.269	.93

Table 2 (cont). Characterization Data for the Penn
State Premium Coal Suite; Bituminous
Coals

<u>Coal</u>	<u>Elemental Analysis (daf, wt.%)</u>					
	<u>H</u>	<u>C</u>	<u>O</u>	<u>Stot</u>	<u>Sorg</u>	<u>Spyr</u>
St	4.87	78.68	8.91	6.00	1.04	4.62
UF	5.70	81.94	8.70	2.12	0.79	1.28
B	5.47	82.08	10.11	0.63	0.61	0.01
T	5.52	84.01	2.20	7.03	2.44	3.98
FS	4.98	81.71	5.99	5.53	2.22	3.09
BW	5.41	79.25	6.02	8.32	3.42	4.75
WP	5.42	78.11	3.48	11.95	2.19	8.72
S	4.93	72.85	20.79	0.34	0.27	0.06
SL	5.30	68.16	24.53	0.66	0.60	0.04

Table 3. Characterization Data for the Argonne National
Laboratory Premium Coal Suite

<u>Coal</u>	<u>Origin</u>	<u>Rank</u>	<u>Elemental Analysis (d.a.f, wt. %)</u>			
			<u>C</u>	<u>H</u>	<u>O</u>	<u>S_{tot}</u>
Stocton	WV	HVBB	81	5.5	11	0.6

5.1.2 Coal Preparation

The Stockton coal was shipped from Argonne National Labs in 5 or 10 gram nitrogen-purged, amber glass ampules. In performing experiments with this coal the ampule was opened and the coal charged directly to the reactors. Oxidation was prevented by loading the reactor with vehicle immediately after the coal had been charged. The Penn State coals arrived in 30 to 35 gram argon-purged ampules. Five to ten grams were used, with the remaining coal being bottled under CO₂ atmosphere. These bottles were sealed with paraffin wax and stored in the vacuum dessicator.

5.2 REACTION PARAMETERS

Table 4 is a list of the reaction conditions under which this research was conducted. These conditions were essentially identical to those used by Shin in his master's thesis, and represent optimal conditions for liquefaction data (1).

Table 4. Reaction Parameters

Coal feed: 1 gram

Coal size: -60 mesh for Penn state coals
-20 mesh for Stockton coal, wall catalytic effect
-20 and -100 mesh, Stockton coal, particle size effect

Vehicle: 1-methylnaphthalene

Vehicle/coal ratio: 1/1 by weight

Temperature: 425 °C

Pressure: 900 psig (initial), 99.5% H₂, .5% Kr

Shaking speed: 120 rpm

Reaction times: 3,5,10,20,40 minutes

5.3 EXPERIMENTAL RUN PROCEDURE

5.3.1 Start-up

1. Introduce air flow into the sand bath and set the temperature controller to the desired reaction temperature.
2. Test fluidized bed temperature with a K-type thermocouple. Adjust temperature controller to attain desired temperature.

5.3.2 Experimental Run Preparation

1. Charge the reactor with 1.00 grams of coal, 1.00 grams of vehicle, and two 1.0 gram stainless steel balls.
2. Seal the reactor with a nickle gasket in the VCR fitting
3. Attach reactor to the eccentric arm and evacuate the reactor by closing valve V3 and opening valve V5.
4. Once reactor is purged, close V5, open V3 and charge the reactor with 900 psig H₂ gas via the metering valve, V2. Close V2 and V3.
5. Monitor pressure for approximately 2 minutes to check for leaks. If a leak is present, isolate the leak with Snoop liquid detector and correct the problem.

5.3.3 Run Procedure

1. Turn on eccentric arm.
2. After allowing the reactor to shake for 20 seconds, raise the fluidized sand bath to the reactor.
Reaction time commences when the sand bath contacts the reactor.
3. At the end of the reaction time, lower the sand bath and cool the reactor to 100-120 °C by compressed air. Then quench with ice water for 30 seconds.
4. Turn off the eccentric arm.
5. Bleed off gas by opening V5.
6. Remove reactor from eccentric arm.

5.4 ANALYTICAL PROCEDURES

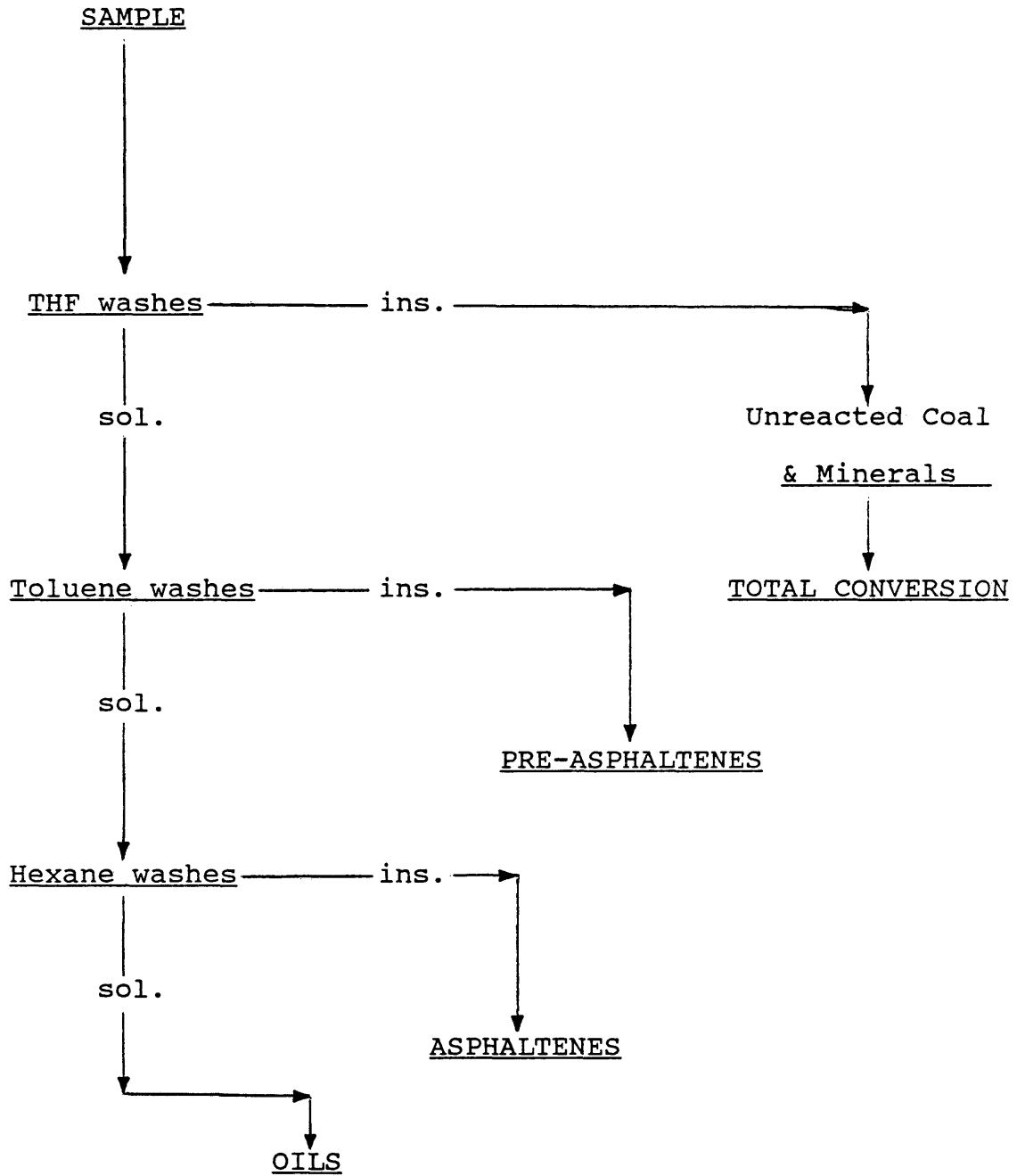
After the reaction, 100% of the reaction products and unreacted coal were gathered into a 250ml centrifuge tube by washing the reactor with tetrahydrofuran (THF). These products were then isolated into the solvent soluble products "Pre-asphaltenes", "Asphaltenes", and "Gas + Oils" by the technique described below.

Schweighardt and Thames (2) have documented the solvent separation analysis used in this research. THF, being the strongest solvent, was used to insure a 100% recovery of the reaction products and unreacted coal from the reactor.

Figure 3 is a diagram of the solvent soluble products definitions. The technique for solvent fractionation is as follows:

1. Place 15 ml of THF into the reactor and sonicate for six to eight hours.
2. Wash the contents of the reactor with approx. 200 ml of THF into a 250 ml centrifuge tube. Dry the reactor, and then weigh the reactor to confirm 100% recovery.
3. Sonicate the centrifuge tube containing the THF plus reaction products plus unreacted coal for 10 minutes.
4. Centrifuge the tube at 2400 rpm for 12 minutes.
5. Decant the supernatant into a 500 ml Erlenmeyer flask.
6. Repeat steps 3-5 twice, each time adding 100 ml of fresh THF to the centrifuge tube.
7. Dry the tube in an oven at 150 °C for eight hours. Cool the tube, and weigh. The weight of the "THF Insolubles" is determined by the difference of the tube + products minus the tare weight of the tube.
8. Distill the THF washes at 80 °C and ambient pressure to isolate the THF solubles.

Figure 3. Definitions of Solvent Soluble Products



9. Wash the distillation flask with Toluene into a new centrifuge tube, and repeat steps 3-7 using 150 ml of fresh Toluene each time. Determine the weight of the "Toluene Insolubles".
10. Distill the Toluene washes at 50 °C and under vacuum to isolate the Toluene solubles.
11. Wash the distillation flask with Hexane into a new tube, and repeat steps 3-7 using 75 ml. of fresh Hexane each time. Determine the weight of the "Hexane Insolubles"

6. RESULTS OF PHASE 1 EXPERIMENTS

6.1 CATALYTIC WALL EFFECT

6.1.1 Background

For many years it has been postulated that the metallic walls of the reactors used in coal liquefaction studies produced a catalytic effect on the liquefaction reaction. Due to the high surface area to volume ratio of small-scale laboratory reactors, this effect (if present) could be very significant in the subsequent liquefaction experiments. Orchin and Storch (22) ran their reactions with a glass liner in the reactor; however, when an experiment was run without the liner, they noticed an increase in the liquefaction yields. They could not definitely state that the walls of the reactor lent a catalytic effect, for they did not know whether it was the walls, or some residual catalyst retained on the walls from previous experiments, that produced the added yields. Kanda, Ouchi, and Yoshimoto used red mud, which contained a high amount of iron sulfide, as an externally added catalyst in their research (12,13,14). It is easy to extrapolate how the walls of the reactor, usually made of an iron alloy, could produce iron sulfide and hence a catalytic effect.

One of the ancillary studies performed during this research was the direct evaluation of any effect the walls

of the reactor may have on the yield. This was accomplished by making four 40 minute runs in a new, previously unused reactor. If the walls did lend a catalytic effect, then the initial runs should have shown a higher yield, while the later runs, being performed in a used reactor, would not have the benefits of a fresh catalytic surface and hence the yield would be expected to decline with each subsequent run. Furthermore, these runs were compared to four runs made in reactors that had been exposed to over 150 runs each, and where the walls of the reactor were heavily fouled with carbonaceous residues. Conversion was defined as

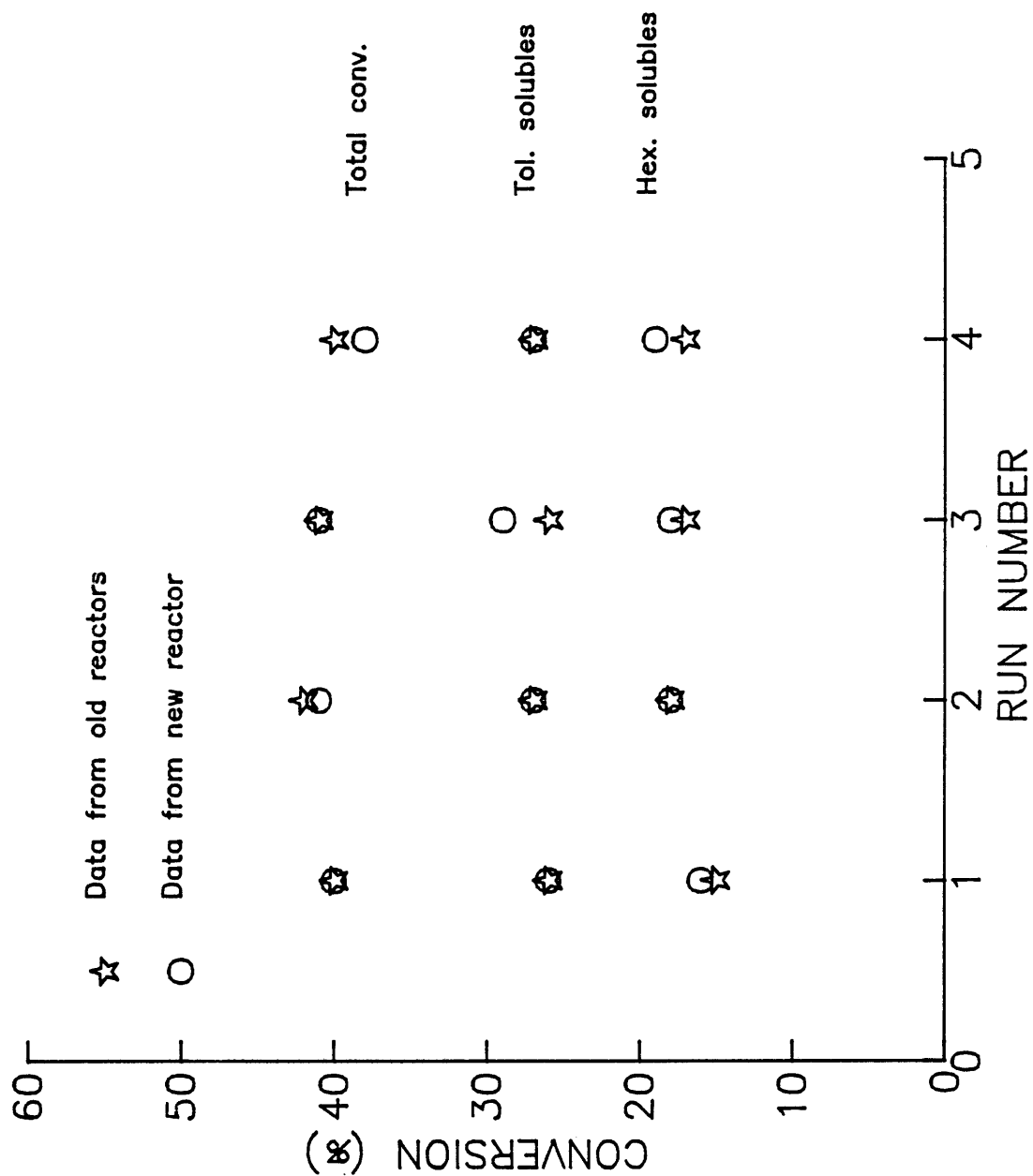
$$\text{Conv. (wt\%)} = \frac{\text{Total coal} - \text{Solvent(s) insolubles}}{\text{Total coal}} \times 100$$

The coal used for this study was the Stockton Seam coal, from the Argonne National Laboratory Premium Coal Collection.

6.1.2 Discussion of Catalytic Wall Effect

Figure 4 is a plot of the yields of the reaction vs. the experiment number. As can be seen, all four runs are within experimental error (± 3 percentage points) of the runs made in the old reactors. Therefore, it can be deduced that the metallic walls of the reactor have no effect on the liquefaction yield. However, this does not refute the work

Figure 4. Catalytic Wall Effect on Yield



and conclusions of those that postulate that iron sulfides positively contribute to the liquefaction reaction. Rather, it suggests that the iron walls of the reactor are a very poor source of iron sulfides and other catalytic materials at liquefaction conditions.

6.2 COAL PARTICLE SIZE EFFECT

6.2.1 Background

It is a well established fact that the particle size of a solid undergoing a chemical reaction has an effect on the rate of the overall reaction. This is a consequence of the mass transfer limitation associated with intraparticle and interparticle diffusional effects. Many researchers have studied the effect of coal particle size on the liquefaction mechanism. Curran, Storch, and Gorin used two mesh sizes in their runs (10). One set of runs was performed with coal ground to 28 x 48 mesh, and another set run with coal ground to 100 x 200 mesh. They reported no difference in the results. Similarly, Neavel ran two sets of experiments, one at -20 mesh and the other at -200 mesh (21). He too concluded that mesh size has no effect on the yields.

The evaluation of the effect particle size has on both the ultimate yield and the rate was the second ancillary study performed during this research. As in the previous study, the Stockton coal was used. Runs were made at five

minutes and 40 minutes with the coal at -20 mesh. Fresh coal was then slowly ground, under a CO₂ atmosphere in the glove box, to -100 mesh. Again, runs were made at five and 40 minutes with this coal.

6.2.2 Discussion of Particle Size Effect

Figure 5 is a plot of the yields of the reaction at 40 minutes, and Figure 6 is a plot of the yields at five minutes. It can be concluded that mass transfer has no limiting effect for coal liquefaction reactions involving particle sizes smaller than -20 mesh. This is true not only for the ultimate yield (40 minutes), but more importantly for the rate of the liquefaction reaction (five minutes), on which mass transfer has the greatest ramification.

6.3 GENERATION OF REACTIVITY DATA

The major thrust of this research was the generation of conversion profiles for the bituminous coals from the Penn State Premium Coal Collection. Over 140 runs were made in the course of this study. The data were converted to weight % conversion vs. time (adjusted for the non-isothermal heat-up period) on a dry, ash-free (d.a.f) basis.

6.3.1 Definition of Conversion

The general definition of conversion used for this research was:

Figure 5. Particle Size Effect on Yield

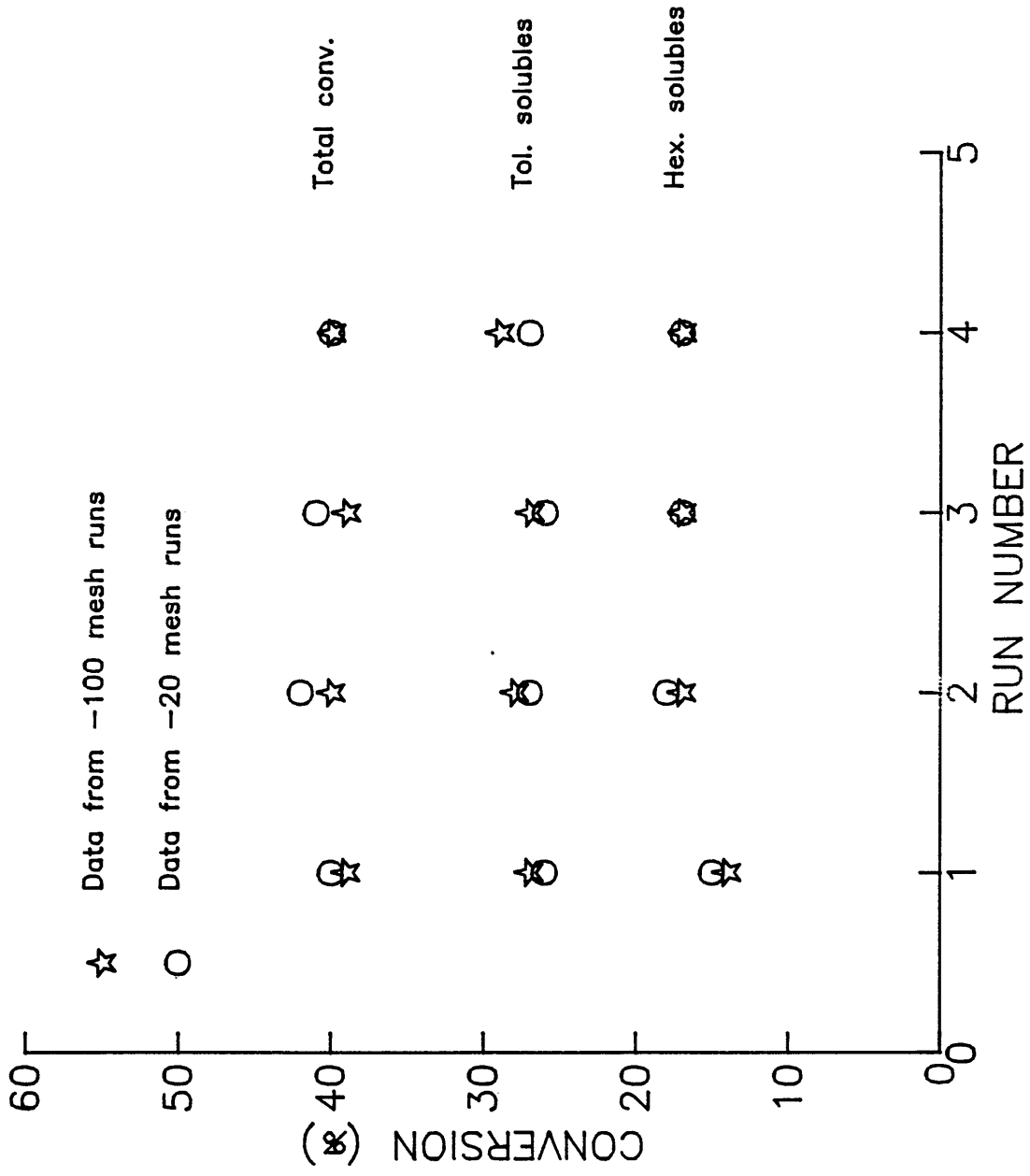
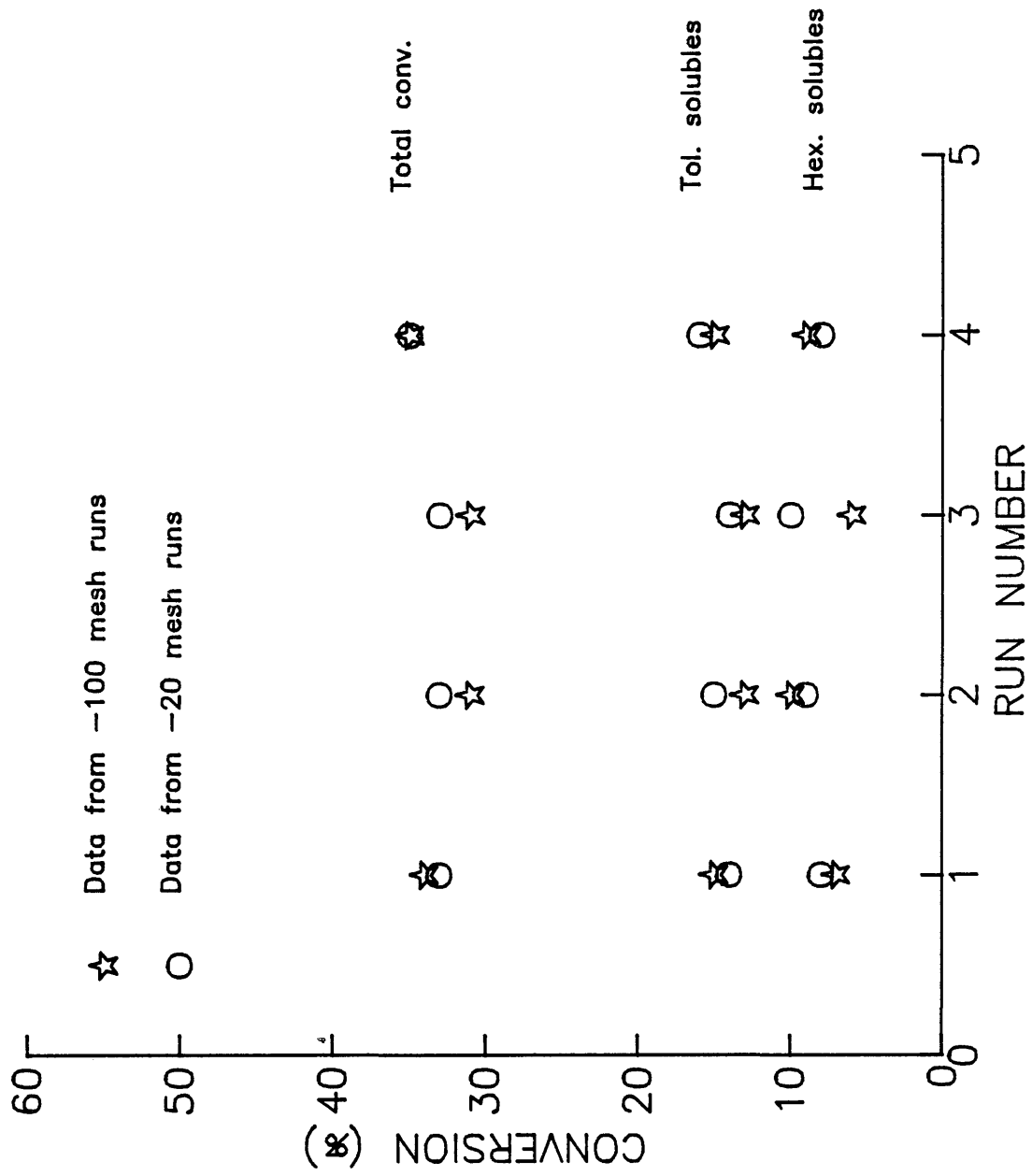


Figure 6. Particle Size Effect on Rate



$$\text{Conv. (wt\%)} = \frac{\text{Organic matter that has reacted to solvent soluble products}}{\text{Total organic matter}} \times 100$$

If one assumes the amount of mineral matter does not change, and the moisture does not convert to solvent soluble products, then

$$\text{Total organic matter} = \text{Total coal} - \text{ash} - \text{moisture}$$

This changes all conversion data to a dry, ash-free (d.a.f) basis.

The organic matter converted to solvent soluble products is defined as:

$$\begin{aligned} \text{Organic matter converted} &= \text{Solvent sol.} - \text{intrinsic sol.} \\ &\quad - \text{moisture} \\ &= \text{Total coal} - \text{solvent insol.} \\ &\quad - \text{intrinsic sol.} - \text{moisture} \end{aligned}$$

For this research, several coals from each rank classification were tested for intrinsic solubility in THF and Toluene. In all cases, the intrinsic solubility was less than 1 %. Therefore, the intrinsic solubility term of the above equations was dropped.

The final equation for conversion used in this research was:

$$\text{Conv.} = \frac{\text{Total coal} - \text{solvent insolubles} - \text{moisture}}{\text{Total coal} - \text{ash} - \text{moisture}} \times 100$$

As mentioned in section 5.4, Analytical Procedures, the liquefaction products were separated into five groups by solvent extraction techniques. Those groups were: Total conversion, Toluene solubles, Hexane solubles, Pre-asphaltenes, and Asphaltenes. Gas + Oils is equivalent to Hexane solubles. Table 5 gives the definitions of these liquefaction reaction products.

6.3.2 Selection Process of Suitable Coals

The question of whether to limit this research to bituminous coals or to include sub-bituminous ones was raised during the course of this research. Kuriki, Hayamiza, et al., in their work on characterization of coal by ^1H NMR and ^{13}C NMR, found a definite distinction between bituminous and sub-bituminous coals (40). Shin (41) provided evidence indicating that within the operating parameters of this research, it is invalid to compare a bituminous coal and a sub-bituminous coal run under the same solvent. He deduced, by reasons which cannot be expanded upon in this thesis for lack of time and space, that sub-bituminous and

Table 5. Definitions of Conversions for Liquefaction Products

*Basis: Dry, ash-free (d.a.f) coal

*Abbreviations: THF - tetrahydrofuran M - % moisture
 Tol - toluene A - % ash in coal
 Hex - hexane
 ins - insolubles

*Definitions:

$$\text{Total conversion} = \frac{1.00 - \text{THF ins} - M}{1.00 - M - A} \times 100$$

$$\text{Toluene solubles} = \frac{1.00 - \text{THF ins} - \text{Tol ins} - M}{1.00 - M - A} \times 100$$

$$\text{Hexane solubles} = \frac{1.00 - \text{THF ins} - \text{Tol ins} - \text{Hex ins} - M}{1.00 - M - A} \times 100$$

$$\text{Pre-asphaltenes} = \text{Total conversion} - \text{Toluene solubles}$$

$$\text{Asphaltenes} = \text{Toluene solubles} - \text{Hexane solubles}$$

$$\text{Gas + Oils} = \text{Hexane solubles}$$

lignite coals run under an inert, non-hydrogen donor solvent yield faulty results. Therefore, only the results of the bituminous coals of the Penn State suite are reported here. Detailed chemical data for the nine coals are shown in Table 2.

6.3.3 Correction of Reaction Time

The coals run during this research were run at a fluidized bath temperature of 425 °C. However, approximately three minutes was needed for the reactor to reach this temperature. Since the data was to be analyzed assuming isothermal conditions, the reaction time had to be corrected to take into account the non-isothermal nature of the beginning of each run.

Altizer (39) described in detail one method for correcting the apparent reaction time to an equivalent isothermal reaction time. In brief, a first order response is assumed for the heating rate of the reactor, and the activation energy of the coal is used to alter the time. The pertinent equations are:

Temperature profile during heat-up period $T = T^{\circ} + \Delta T [1 - \exp(-t/\tau)]$

where T° = Ambient temperature

ΔT = Step change

t = uncorrected reaction time

τ = time constant

$$\text{Isothermal time : } t^* = \frac{\int_0^3 \exp(-E/RT) dt}{\exp(-E/RT^*)}$$

where t^* = Isothermal time (min.)

E = Activation energy (cal/mol)

R = 1.98719 cal/mol K

T^* = 698 K (425 °C)

For this reactor system, Shin has shown the time constant to be 0.5 minutes (1).

Within the bituminous coals run during this research, there were three sub-categories: HVAB, HVBB, and HVCB. One coal from each of these categories was run at 375 °C and 400 °C to determine an activation energy through an Arrhenius plot. This activation energy was used as a representative activation energy for the remaining coals in that sub-category. The coals chosen for this purpose were Upper Freeport for HVAB, Weir-Pittsburgh for HVBB, and Lower Sudduth for HVCB.

An iterative procedure was utilized to determine the final isothermal time. This procedure was:

1. Determine the kinetic constant (k) from the profiles made at 425, 400, and 375 °C. The kinetic model used will be discussed later. Determine an activation energy through an Arrhenius plot.
2. Through the isothermal time equation, find the 1st value of isothermal time (evaluate the integral via numerical integration).
3. Correct the reaction profile with the new isothermal time.

Steps 1 through 3 were repeated until the isothermal time did not change.

The above technique worked well for Weir-Pittsburgh and Lower Sudduth. The Arrhenius plot for these two coals were linear. However, the Arrhenius plot for Upper Freeport was not linear. This is not uncommon in coal research. Several researchers have stated that at least two activation energies are necessary to describe the kinetics of coal liquefaction (9,10,21). The first activation energy is low, reflecting the autohydrogenolysis of the parent coal. The second activation energy is much higher, indicative of the external hydrogen transfer necessary to continue the liquefaction reaction, and of the strong bonds broken in this phase of the reaction. The low activation energy apparent at low temperatures and the high activation energy

at high temperatures were used to modify the isothermal time equation as follows:

$$\text{Isothermal time at } 425 \text{ } ^\circ\text{C} \quad t^* = \frac{\int_0^{t^0} \exp(-E_1/RT) dt}{\exp(-E_1/RT^*)} + \frac{\int_{t^0}^3 \exp(-E_2/RT) dt}{\exp(-E_2/RT^*)}$$

where t^0 = Time when $T = 400 \text{ } ^\circ\text{C}$ (0.8 min.)

E_1 = Activation energy below $400 \text{ } ^\circ\text{C}$

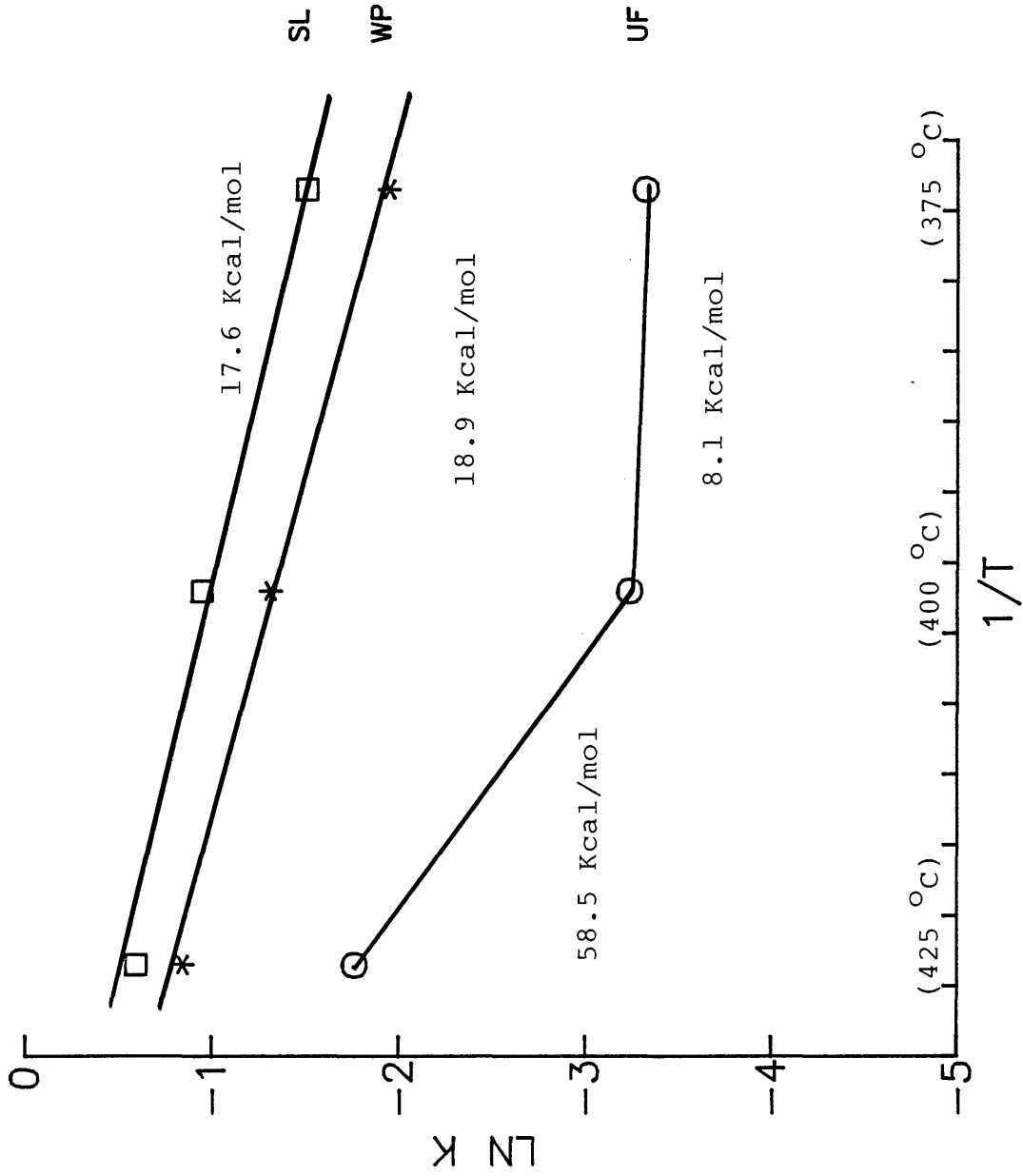
E_2 = Activation energy above $400 \text{ } ^\circ\text{C}$

$$\text{Isothermal time at } 400 \text{ and } 375 \text{ } ^\circ\text{C} \quad t^* = \frac{\int_0^3 \exp(-E_1/RT) dt}{\exp(-E_1/RT_1)}$$

where $T_1 = 648 \text{ K}$ or 673 K

Figure 7 is a plot of the activation energies computed for the three coals. Szladow and Given concluded that the majority of coals have activation energies between 25-40 kcal/mol (42). Anthony and Howard (43), cognizant of the fact that coal liquefaction is a combination of many reactions, devised a method in which an average activation energy, along with the statistical distribution of the

Figure 7. Activation Energies of Representative Coals



individual activation energies about the norm, was computed. Shin, however, has shown this technique minimizes the inherent reactivity differences between two radically different coals, and is not consistent with the simpler Arrhenius approach (41).

7. RESULTS OF PHASE 2 EXPERIMENTS

7.1 KINETIC MODELLING

The question of the most appropriate kinetic model for coal liquefaction has been debated for many years. In this research, two models were tested: first order irreversible and second order irreversible. All three levels of conversion (Total conversion, Toluene solubles, and Hexane solubles) were tested. Only the first four data points were utilized (0, 3, 5, and 10 minutes). The reason for the exclusion of the 20 and 40 minute data points will be elaborated upon later. The equations of the models tested are:

	<u>Rate Expression</u>	<u>Integrated Form</u>
1 st order	$dx/dt = k(a-x)$	$x = a [1-\exp(-kt)]$
2 nd order	$dx/dt = k(a-x)^2$	$x = \frac{ka^2t}{kta + 1}$

where x = coal conversion (d.a.f, wt %)

a = pseudo- equilibrium conversion (wt %)

k = kinetic constant

(min^{-1} for 1st order, (wt \% min^{-1} for
2nd)

t = isothermal time (min)

The conversion data for each coal was statistically regressed for the two models by MINITAB. Tables 6, 7, and 8 compare the results for the 1st and 2nd order models. The choice for the final model was based upon statistics (coefficient of determination), "a" values, and mechanistic arguments.

The statistics of each model, based on the r^2 values, are essentially identical. In most cases, the differences between the r^2 values is $\pm 5\%$. The majority of coals have an r^2 value above 90% for both models. Accordingly, both models are statistically valid.

The values of the pseudo-equilibrium conversion, "a", are radically different for the two models. Theoretically, "a" represents the conversion at infinite time. Therefore, there are two bounds to "a": "a" must be greater than or equal to the conversion at 40 minutes (which is a good approximation of infinite time), and "a" must be less than 100%. For the 1st order model "a" was a fitting parameter fed into the regression routine. Thus, all the 1st order values of the equilibrium conversion meet the two criteria. But the 2nd order equilibrium conversion values are purely statistical by nature. Of the 27 2nd order values of "a", only 12 meet the necessary criteria. In this regard the 1st

Table 6. 1st and 2nd Order Model Comparison: Total Conversion

r²: coefficient of determination (%)

a: pseudo-equilibrium conversion (wt %)

k: kinetic constant (min⁻¹ for 1st order, (wt % min)⁻¹ for 2nd)

<u>Coal</u>	<u>1st order</u>			<u>2nd order</u>		
	<u>r²</u>	<u>a</u>	<u>k</u>	<u>r²</u>	<u>a</u>	<u>k</u>
St	93.4	75.0	.307	95.7	70.4	.0216
UF	89.5	69.2	.273	95.1	84.8	.0049
B	64.1	55.0	.349	84.7	64.1	.0105
T	97.3	85.0	.536	100.0	90.1	.0179
FS	93.5	85.0	.439	96.0	103.2	.0065
BW	97.1	37.6	.309	97.9	37.9	.0235
WP	97.2	85.0	.429	100.0	90.9	.0125
S	78.7	35.0	.626	90.8	35.0	.3804
SL	91.1	44.0	.551	97.8	44.1	.1052

Table 7. 1st and 2nd Order Model Comparison: Toluene Solubles

<u>Coal</u>	<u>1st Order</u>			<u>2nd Order</u>		
	<u>r²</u>	<u>a</u>	<u>k</u>	<u>r²</u>	<u>a</u>	<u>k</u>
St	89.6	43.6	.129	97.0	28.3	.0356
UF	98.9	45.0	.171	98.6	41.5	.0089
B	98.7	37.6	.156	99.9	42.9	.0049
T	91.9	67.1	.155	99.9	52.9	.0132
FS	99.6	49.3	.178	99.1	50.5	.0055
BW	99.2	35.0	.290	99.3	38.2	.0134
WP	99.6	65.0	.129	100.0	75.2	.0020
S	80.3	28.4	.297	96.6	25.1	.1990
SL	99.4	32.0	.435	100.0	36.4	.0198

Table 8. 1st and 2nd Order Model Comparison: Hexane Solubles

<u>Coal</u>	<u>1st Order</u>			<u>2nd Order</u>		
	<u>r²</u>	<u>a</u>	<u>k</u>	<u>r²</u>	<u>a</u>	<u>k</u>
St	84.2	18.4	.0891	95.0	8.9	.1671
UF	99.3	31.3	.142	98.4	196.1	.0001
B	98.5	26.0	.213	97.7	67.6	.0011
T	91.4	39.0	.108	99.0	29.1	.0136
FS	99.5	33.1	.137	98.5	-40.8	.0014
BW	97.9	31.0	.146	99.8	29.1	.0105
WP	99.2	40.0	.0909	96.2	-33.3	.0018
S	88.1	23.5	.185	98.5	18.6	.0706
SL	97.4	23.3	.177	99.9	22.5	.0175

order model is preferable to the 2nd order.

Theoretically, 1st order kinetics is more compatible to the known coal liquefaction mechanism. The primary driving force behind the initial stages of coal liquefaction is the pyrolysis of the weak aliphatic and etheric bonds in the coal structure. While it is necessary for these radicals to be capped by hydrogen, implying a rate expression dependent on the hydrogen concentration, there is a sufficient excess of hydrogen to enable one to consider the hydrogen concentration as constant. Hence, one can assume the rate expression to be first order in the weak bonds in the coal structure for the initial stages of the reaction.

The 1st order model was chosen for purposes of reactivity correlations from the above arguments. Figures 8, 9, and 10 illustrate how the 1st order model compares to the data for Upper Freeport, Fort Scott, and Weir-Pittsburgh at the Toluene Solubles conversion level. The conversion profiles for the nine bituminous Penn state coals are shown in Figures 11 through 19.

7.2 SINGLE PARAMETER CORRELATIONS

7.2.1 Background

Several single parameter correlations were attempted against a variety of coal properties. Both linear and non-linear correlations were tried, with the coefficient of

Figure 8. Kinetic Model Comparison: UF

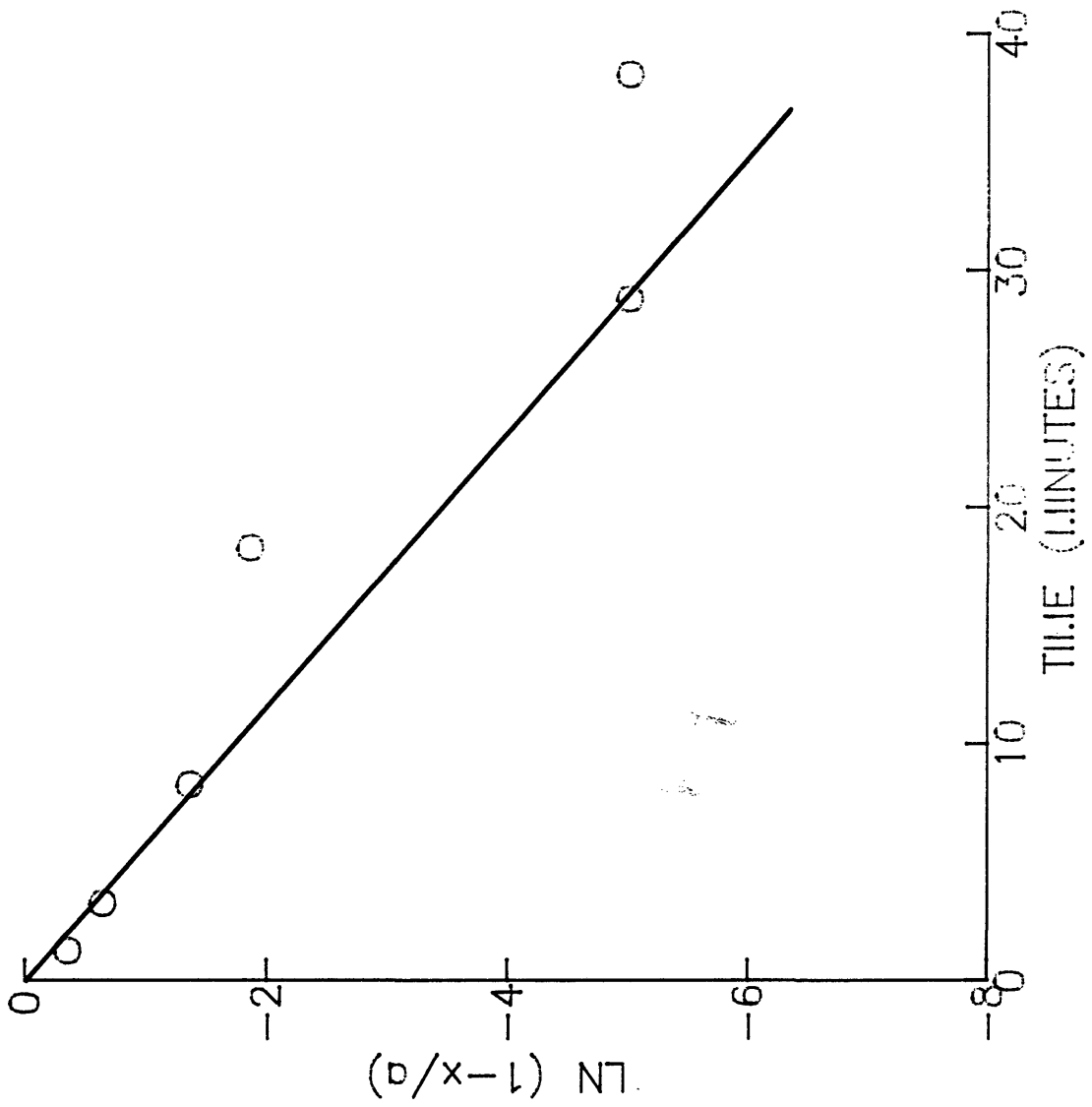


Figure 9. Kinetic Model Comparison: FS

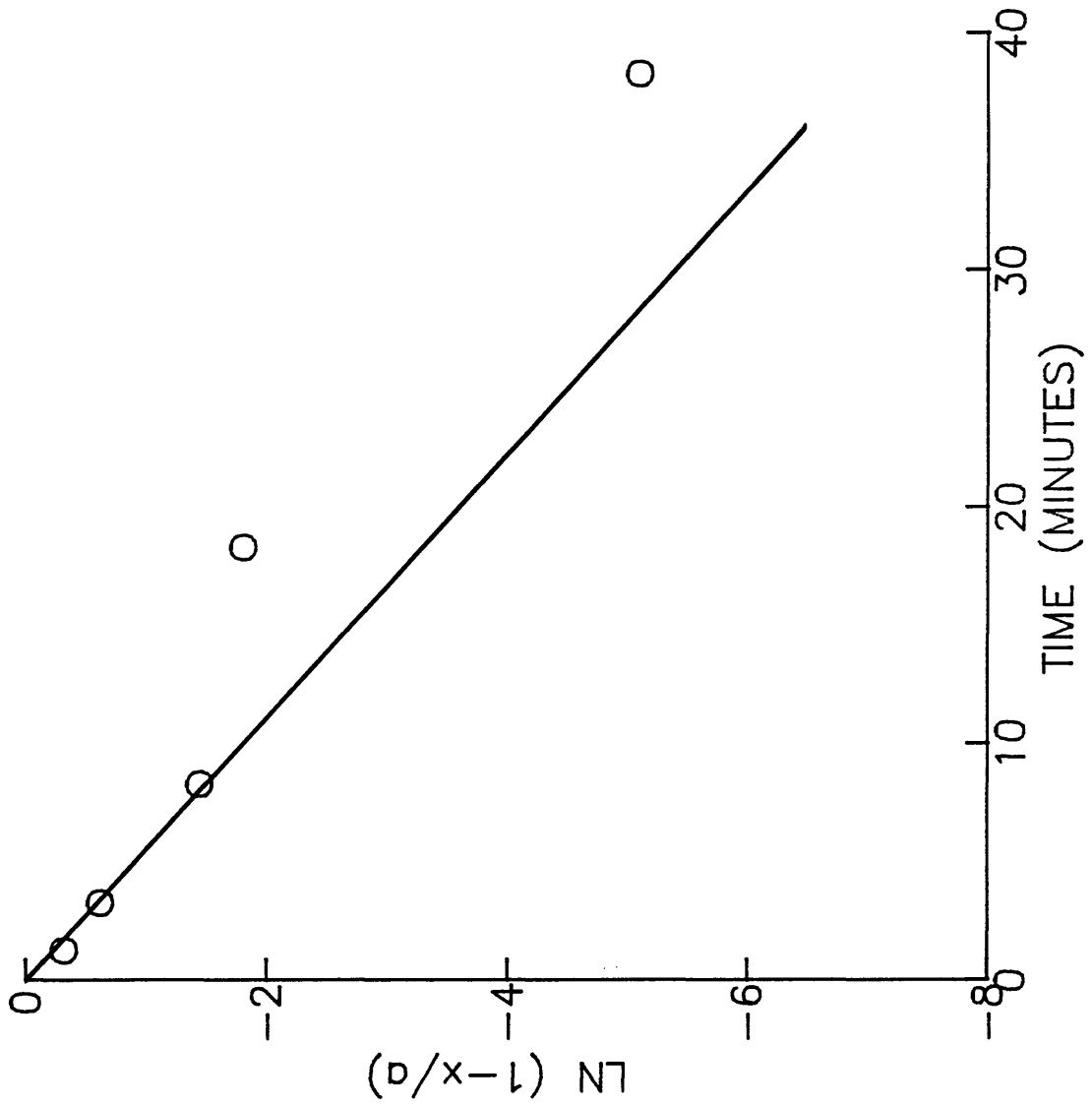


Figure 10. Kinetic Model Comparison: WP

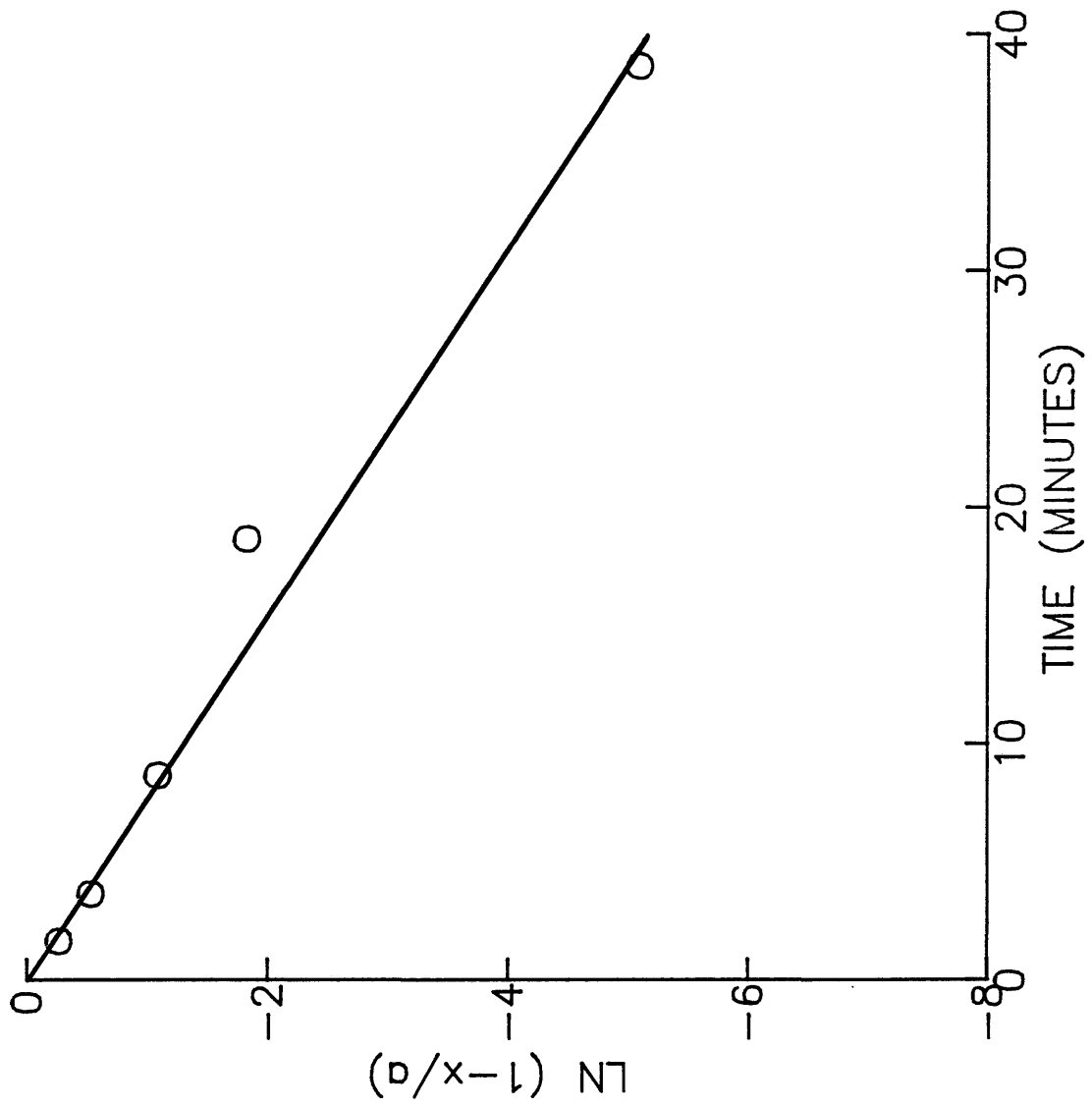
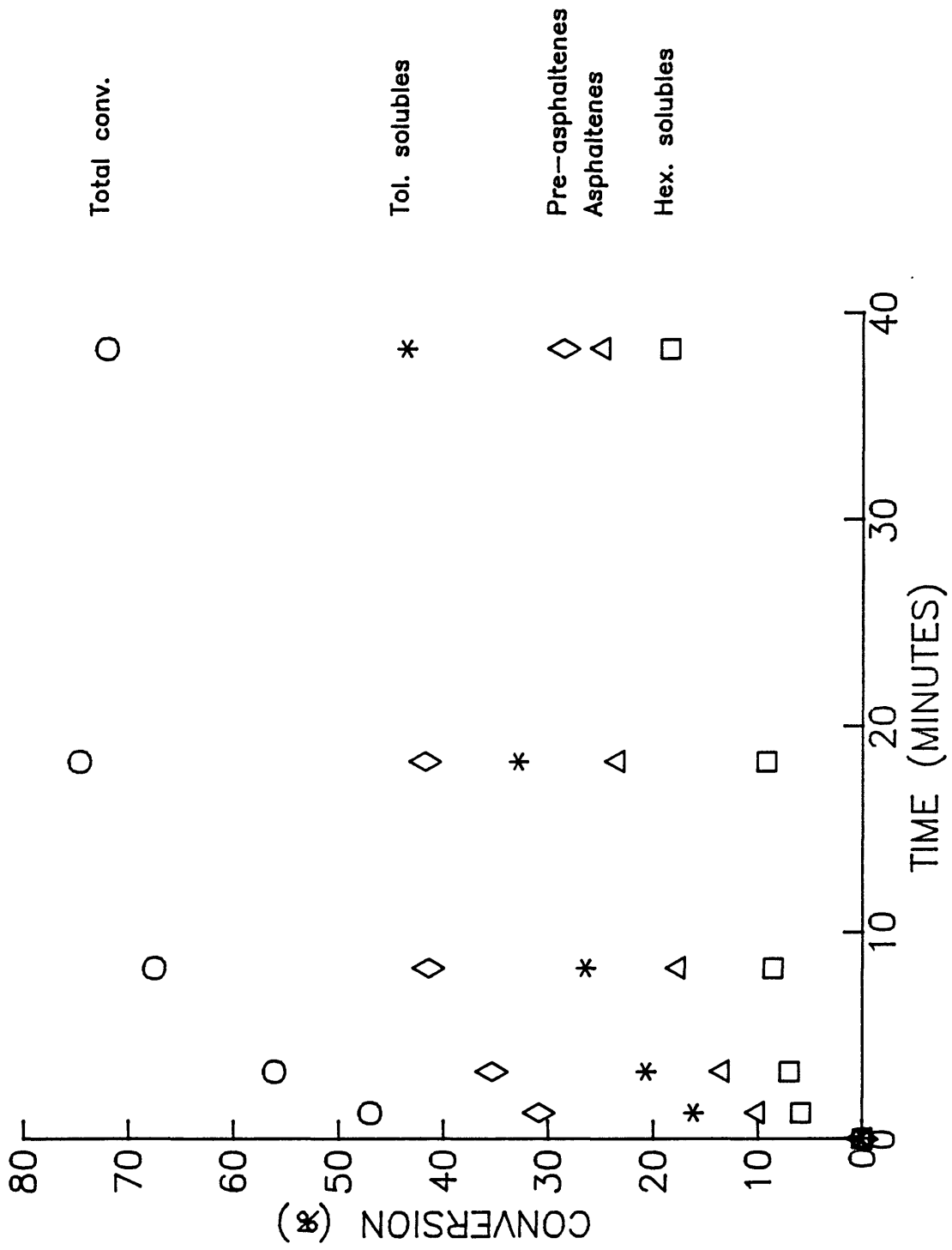


Figure 11. Conversion Profile: St



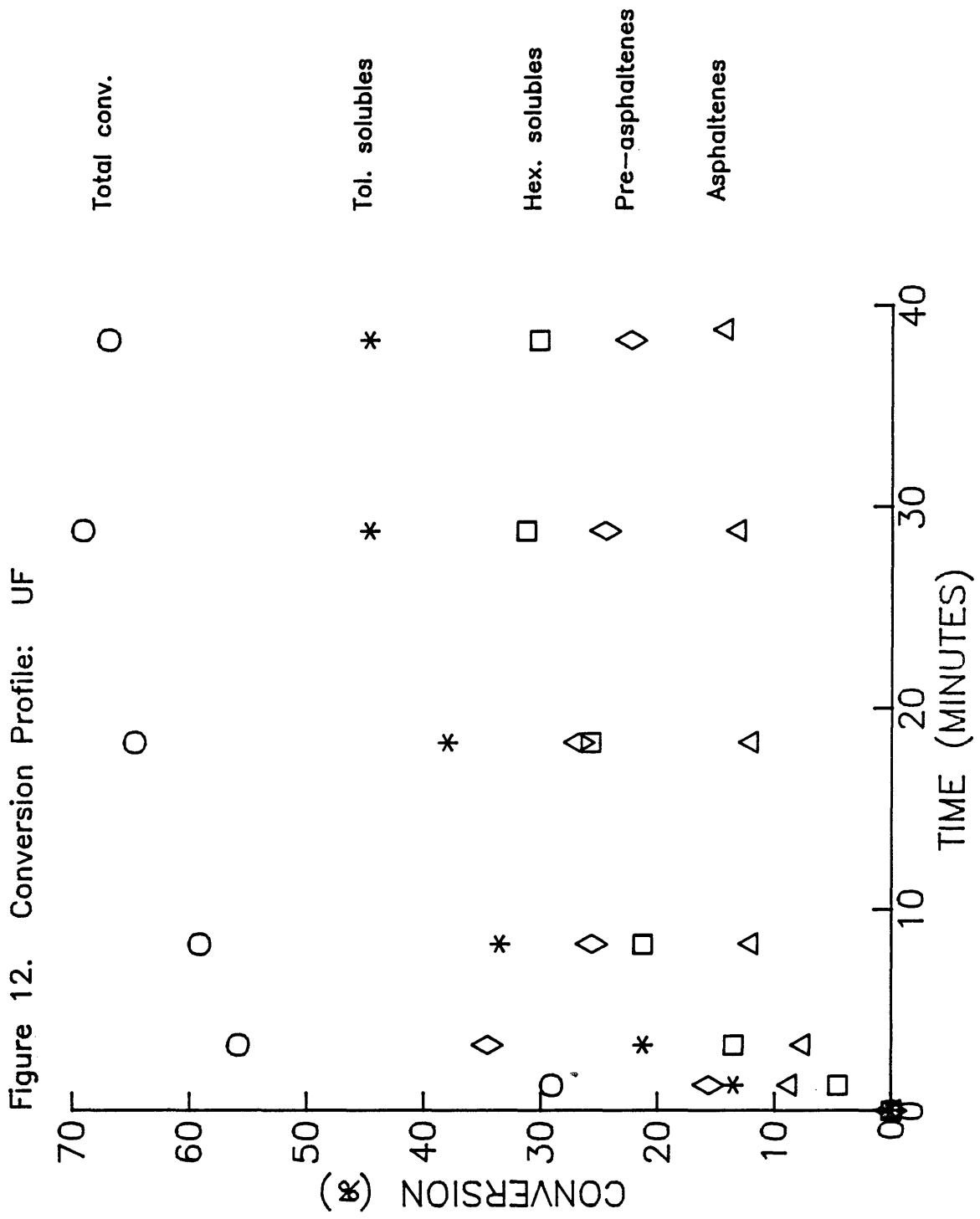
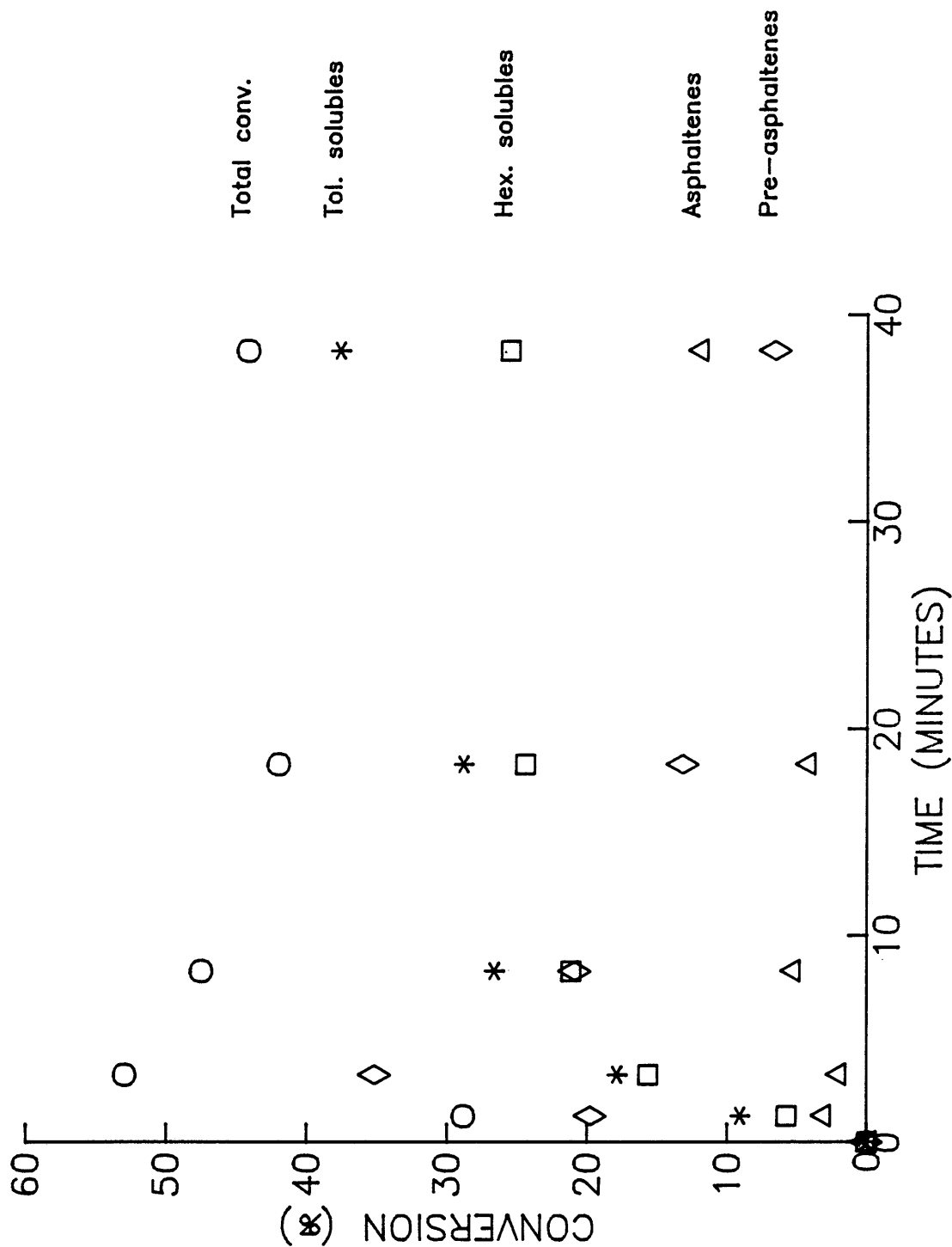


Figure 13. Conversion Profile: B



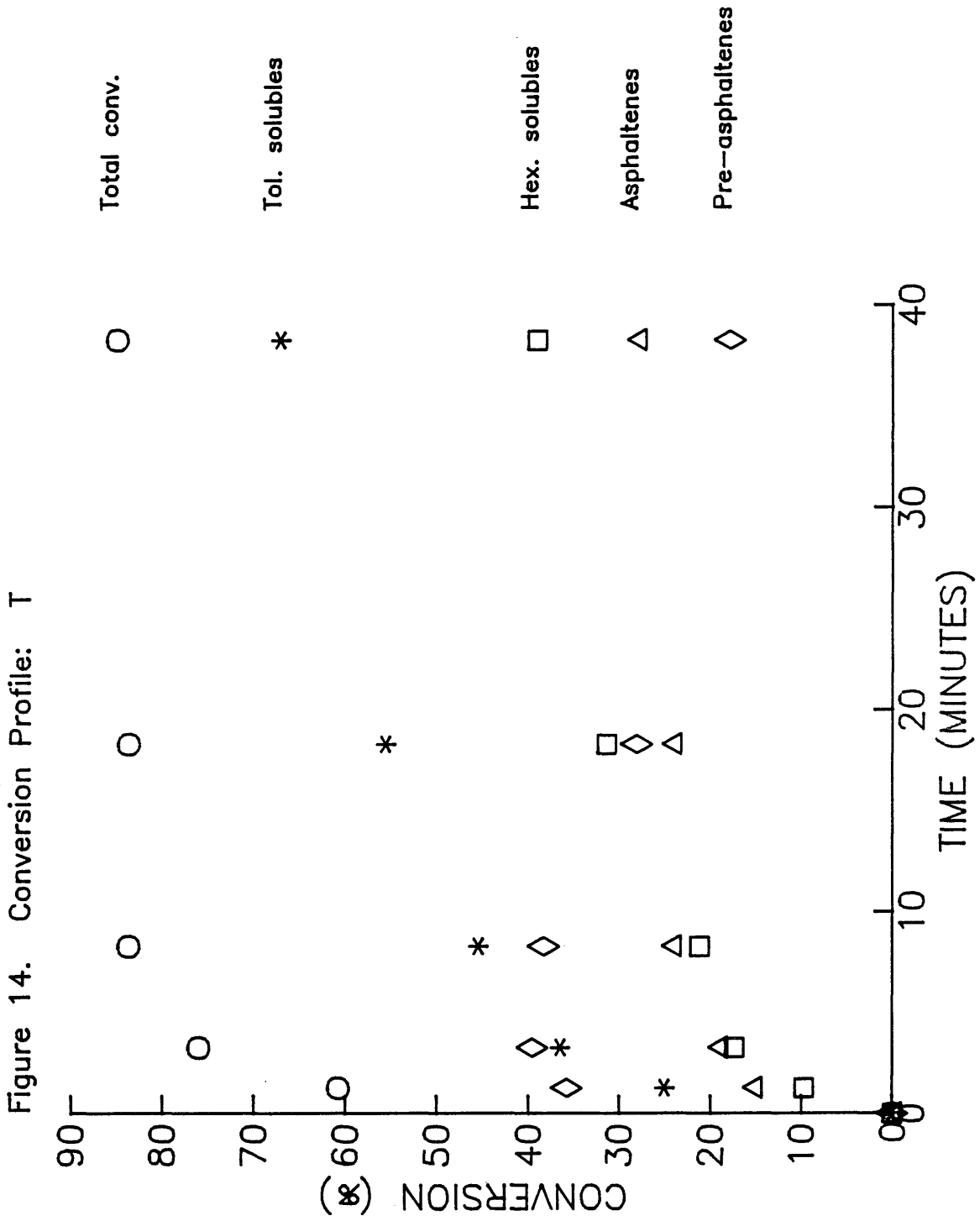


Figure 15. Conversion Profile: FS

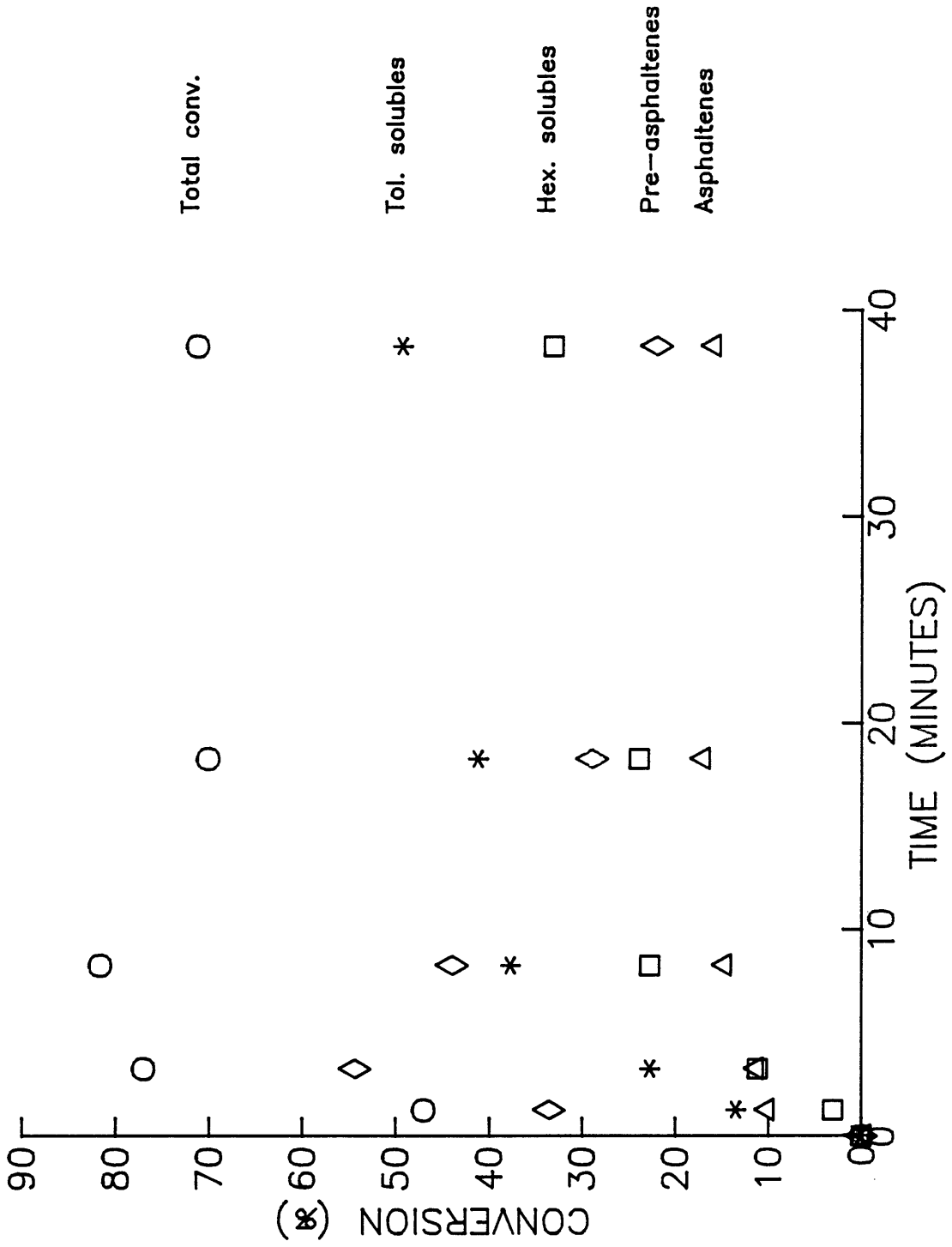
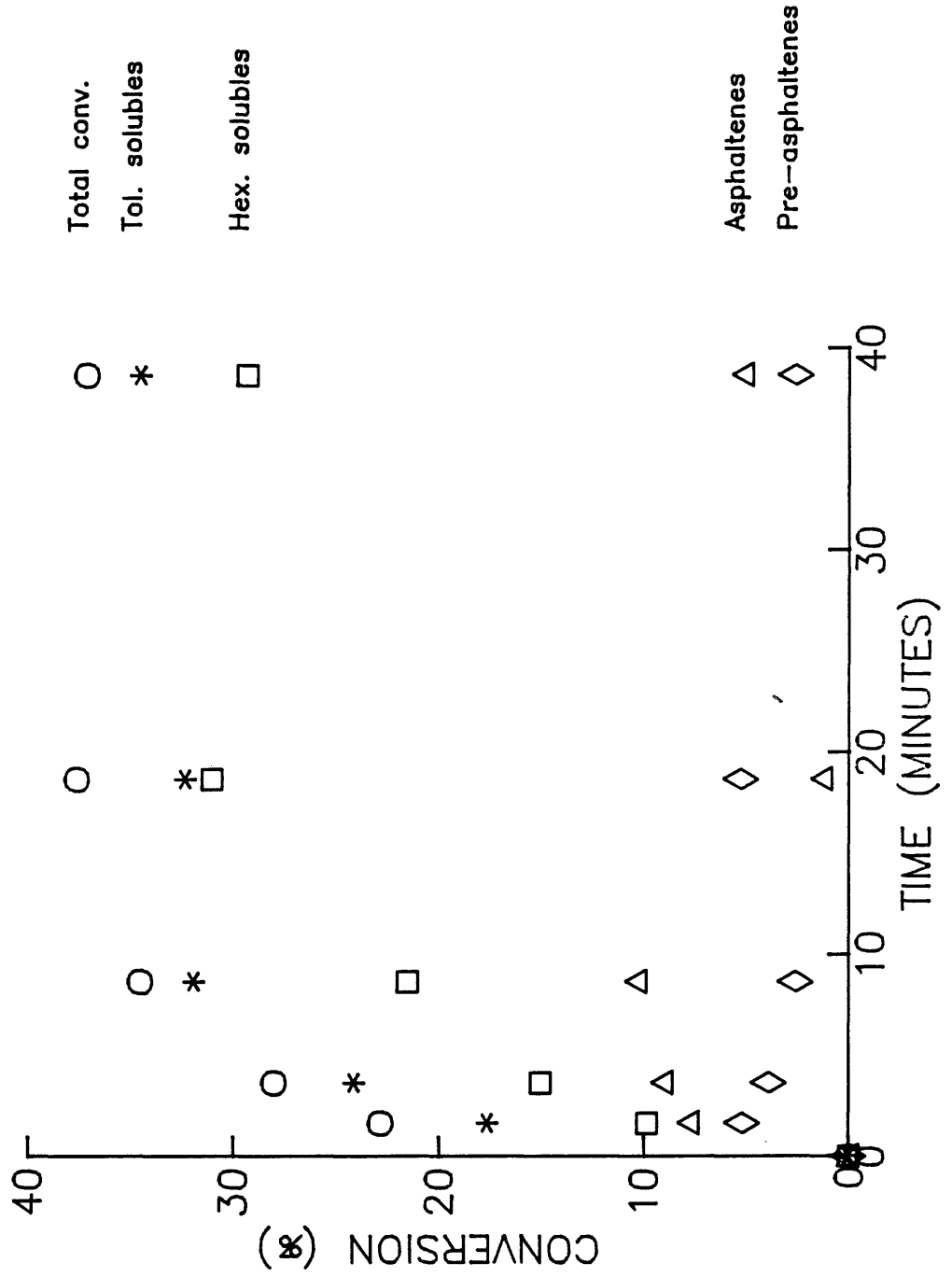


Figure 16. Conversion Profile: BW



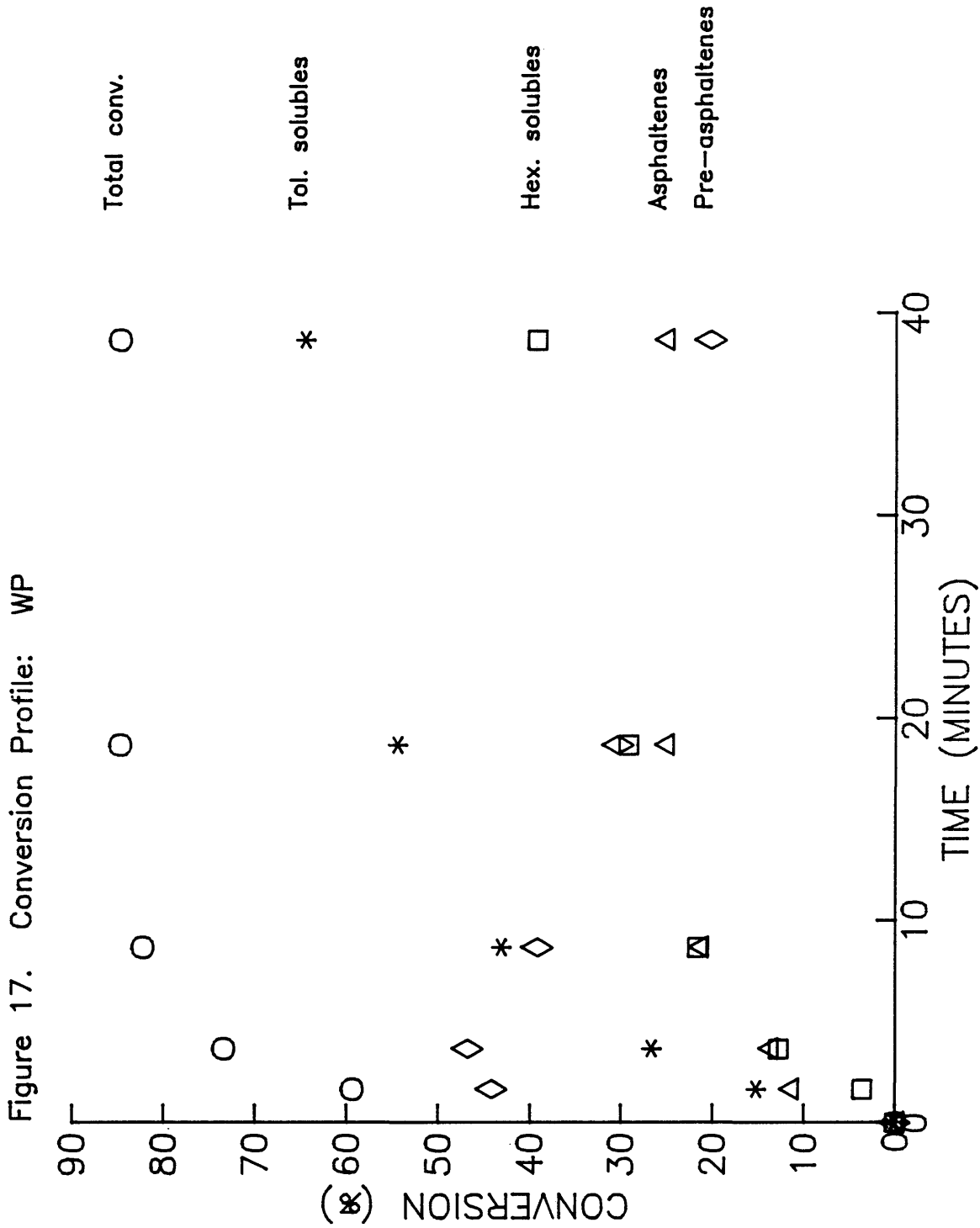


Figure 18. Conversion Profile: S

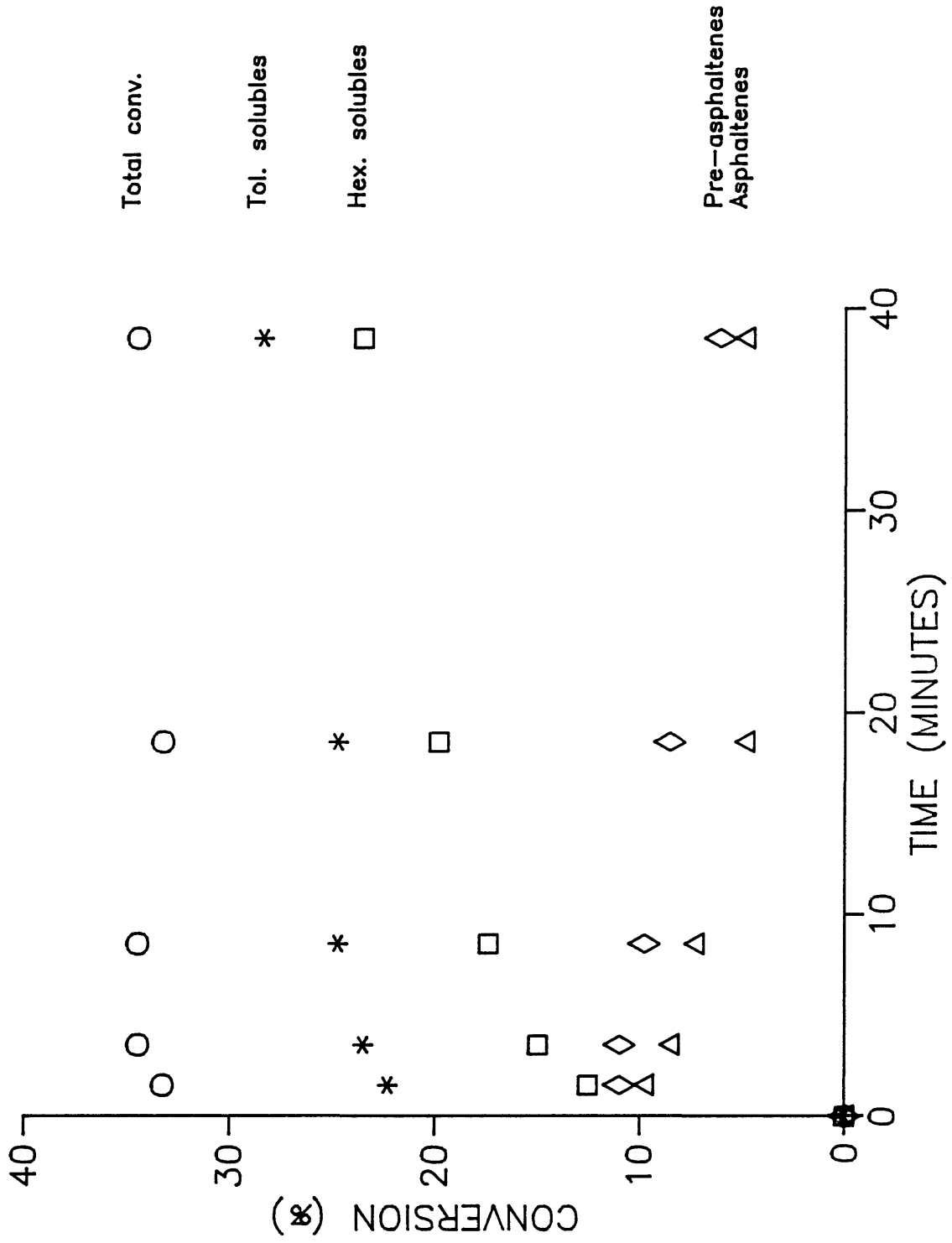
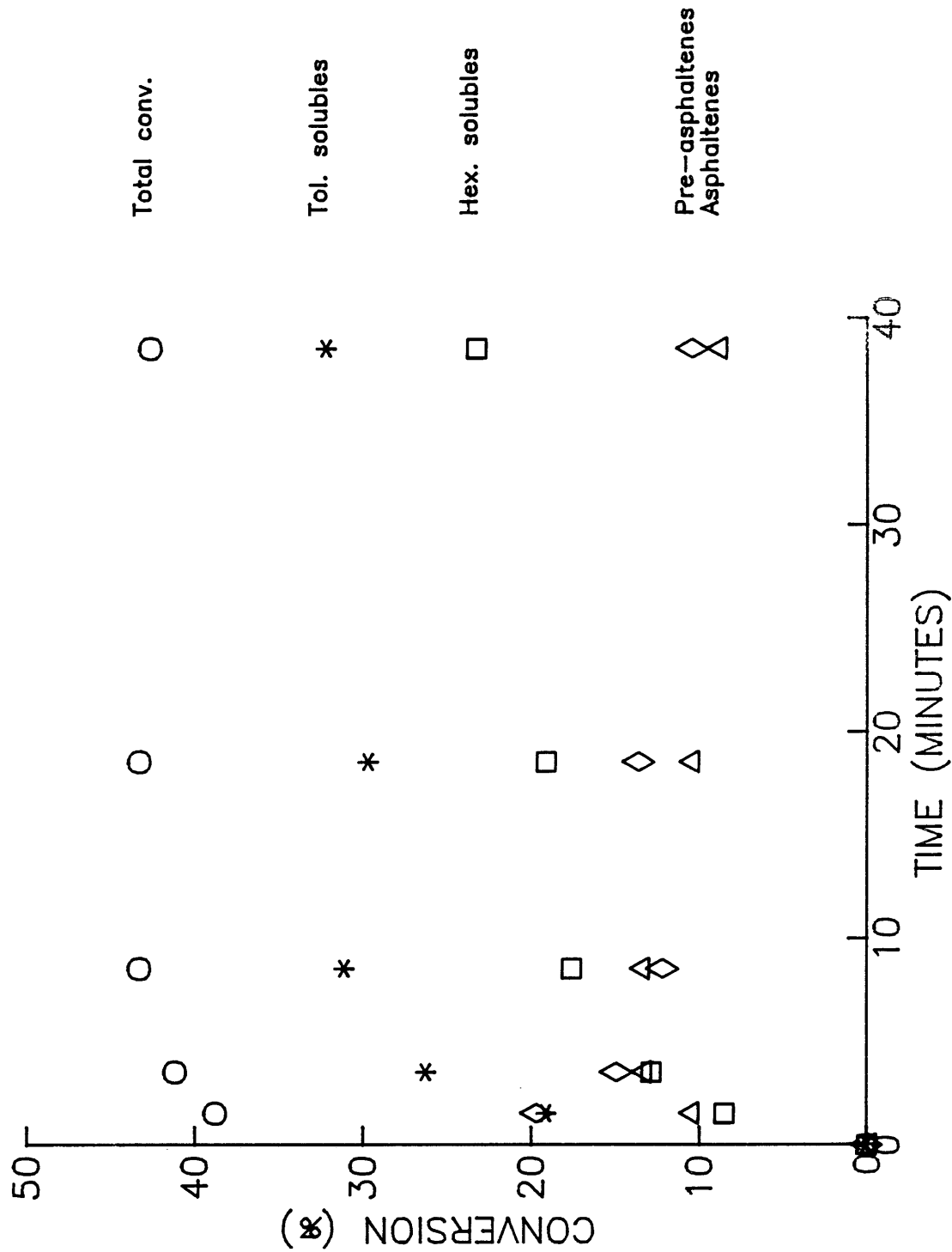


Figure 19. Conversion Profile: SL



determination, r^2 , being the criterion on which the correlations were judged.

The dependent variables used in the correlational effort were: kinetic constant (k), conversion at 40 minutes (x_{40}), conversion at three minutes (x_3), and the area under the conversion profile (AREA). This latter variable was devised by Shin (1), and supposedly incorporates both the rate and the ultimate yield of the liquefaction reaction. It was computed by first modelling the conversion profile to a non-linear equation ($x = A + BC^t$) via a non-linear regression package, and then analytically integrating the equation to yield the area.

Three levels of conversion (Total conversion, Toluene solubles, and Hexane solubles) were tested against the four dependent variables. Although correlations of a non-linear form were attempted, these were scrapped in favor of linear correlations for reasons of simplicity and improved statistics. Tables 9, 10, and 11 are the r^2 values of the correlations of the three levels of conversion vs. 11 coal parameters.

7.2.2 Discussion

A number of observations are apparent from the single parameter correlations. First, neither the conversion at three minutes nor the AREA parameter correlate against any level of conversion. An r^2 of 54.3 % for the correlation of

Table 9. Coefficients of Determination for Single
Parameter Correlations: Total Conversion

Coal Property	Dependent Variable			
	<u>k</u>	<u>x₄₀</u>	<u>x₃</u>	<u>AREA</u>
V.M.	43.5	0.3	4.7	0.0
% O	25.2	48.5	16.1	47.4
O/C	28.1	48.5	13.0	44.5
H/C	6.7	15.0	6.3	18.0
% C	28.2	28.7	2.7	29.7
% H	9.4	2.0	1.5	1.0
R _o	35.2	10.3	0.1	9.4
S _{tot}	5.6	38.4	31.7	34.8
S _{pyr}	6.3	42.2	35.1	37.7
S _{org}	4.8	9.9	5.9	9.4
F.C.	43.5	0.3	4.7	0.0

where V.M. = volatile matter (d.a.f, wt. %)

O/C, H/C = atomic ratio

R_o = vitrinite reflectance (d.a.f, wt. %)

S_{tot} = total sulfur (d.a.f, wt. %)

S_{pyr} = pyritic sulfur (d.a.f, wt. %)

S_{org} = organic sulfur (d.a.f, wt. %)

F.C. = fixed carbon (d.a.f, wt. %)

% O, % C, % H = % oxygen, carbon, hydrogen

Table 10. Coefficients of Determination for Single
Parameter Correlations: Toluene Solubles

Coal <u>Property</u>	Dependent Variable			
	<u>k</u>	<u>x₄₀</u>	<u>x₃</u>	<u>AREA</u>
V.M.	28.7	1.7	13.3	5.8
% O	65.1	58.6	3.2	54.3
O/C	69.1	54.2	4.7	49.1
H/C	51.3	8.4	2.8	4.2
% C	68.6	33.0	8.8	27.9
% H	1.0	9.8	2.0	13.1
R _o	33.6	0.1	20.9	0.6
S _{tot}	20.6	49.4	0.8	50.1
S _{pyr}	24.5	48.3	0.2	46.7
S _{org}	3.7	22.9	2.4	28.2
F.C.	28.7	1.7	13.3	5.8

Table 11. Coefficients of Determination for Single
Parameter Correlations: Hexane Solubles

Coal Property	Dependent Variable			
	<u>k</u>	<u>x₄₀</u>	<u>x₃</u>	<u>AREA</u>
V.M.	4.7	23.4	2.9	29.1
% O	39.2	45.7	21.4	33.0
O/C	35.4	41.7	22.0	30.5
H/C	13.3	0.3	7.6	0.7
% C	9.7	24.8	17.0	23.4
% H	0.5	26.4	1.7	45.2
R _O	7.7	19.7	23.0	33.9
S _{tot}	65.3	39.8	9.1	19.9
S _{pyr}	71.0	31.3	12.5	11.7
S _{org}	25.2	39.6	0.5	37.1
F.C.	4.7	23.4	2.9	29.1

Toluene solubles AREA vs. % oxygen is the best correlation for either x_3 or AREA. Second, the conversion at 40 minutes only weakly correlates against the coal parameters. An r^2 of 58.6 % for the correlation of Toluene solubles x_{40} vs. % oxygen is the best x_{40} correlation. Third, the Total conversion does not correlate against any dependent variable. Only the Toluene solubles and Hexane solubles correlate to any appreciable degree. This is not unusual. Gutmann, among others, has produced correlations against the Oil yield of the liquefaction reaction (11,35). Others have used the Pre-asphaltenes and Asphaltenes for their correlational studies (28,33). Shin (1) also found no significant correlations for any coal properties when THF solubles (Total conversion) was used as the conversion parameter. Very seldom is Total conversion used for correlational purposes.

The kinetic constant, k , produces the best correlations from both a statistical and mechanistic viewpoint. The Toluene solubles kinetic constant correlates against oxygen content, carbon content, an O/C atomic ratio. Hexane solubles kinetic constant correlates against total sulfur and pyritic sulfur. Table 12 is a listing of these correlations and their r^2 values. Figures 17 through 21 are the plots of these correlations.

Mechanistically, the kinetic constant should be a

Table 12. Correlations of Kinetic Constant with Coal Properties

* $y = mx + b$ where $y = \text{kinetic constant (min}^{-1}\text{)}$
 $x = \text{coal property}$

<u>Coal Property</u>	<u>Conversion Level</u>	<u>Correlation</u>	<u>r²</u>
% O	Toluene solubles	$y = .105 + .0110x$	65.1
% C	Toluene solubles	$y = 1.55 - .0171x$	68.6
O/C	Toluene solubles	$y = .113 + 1.02x$	69.1
S_{tot}	Hexane solubles	$y = .183 - .0085x$	65.3
S_{pyr}	Hexane solubles	$y = .179 - .0123x$	71.0

Figure 20. Correlation of Toluene Solubles Kinetic Constant vs. % Oxygen

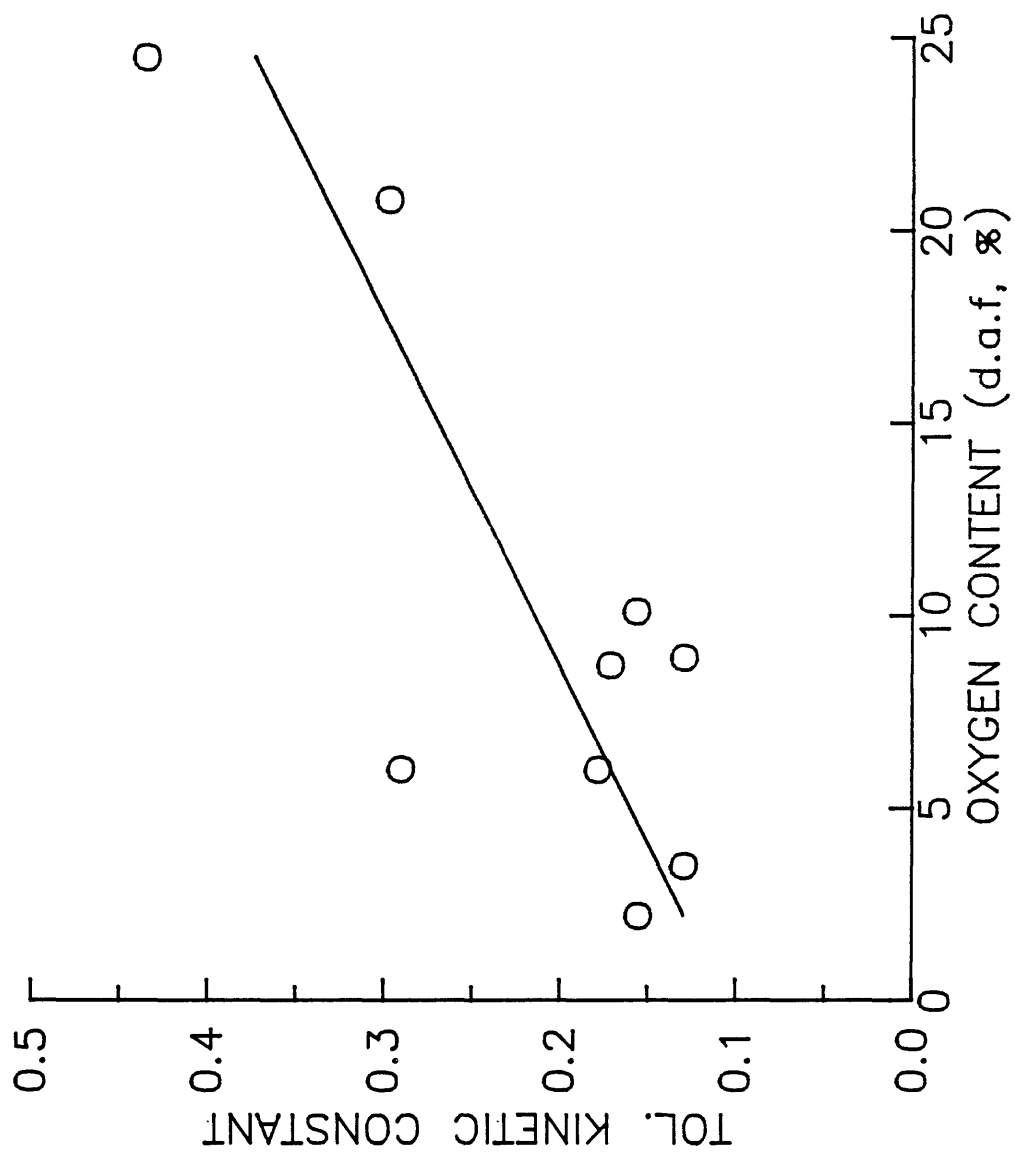


Figure 21. Correlation of Toluene Solubles Kinetic Constant vs. % Carbon

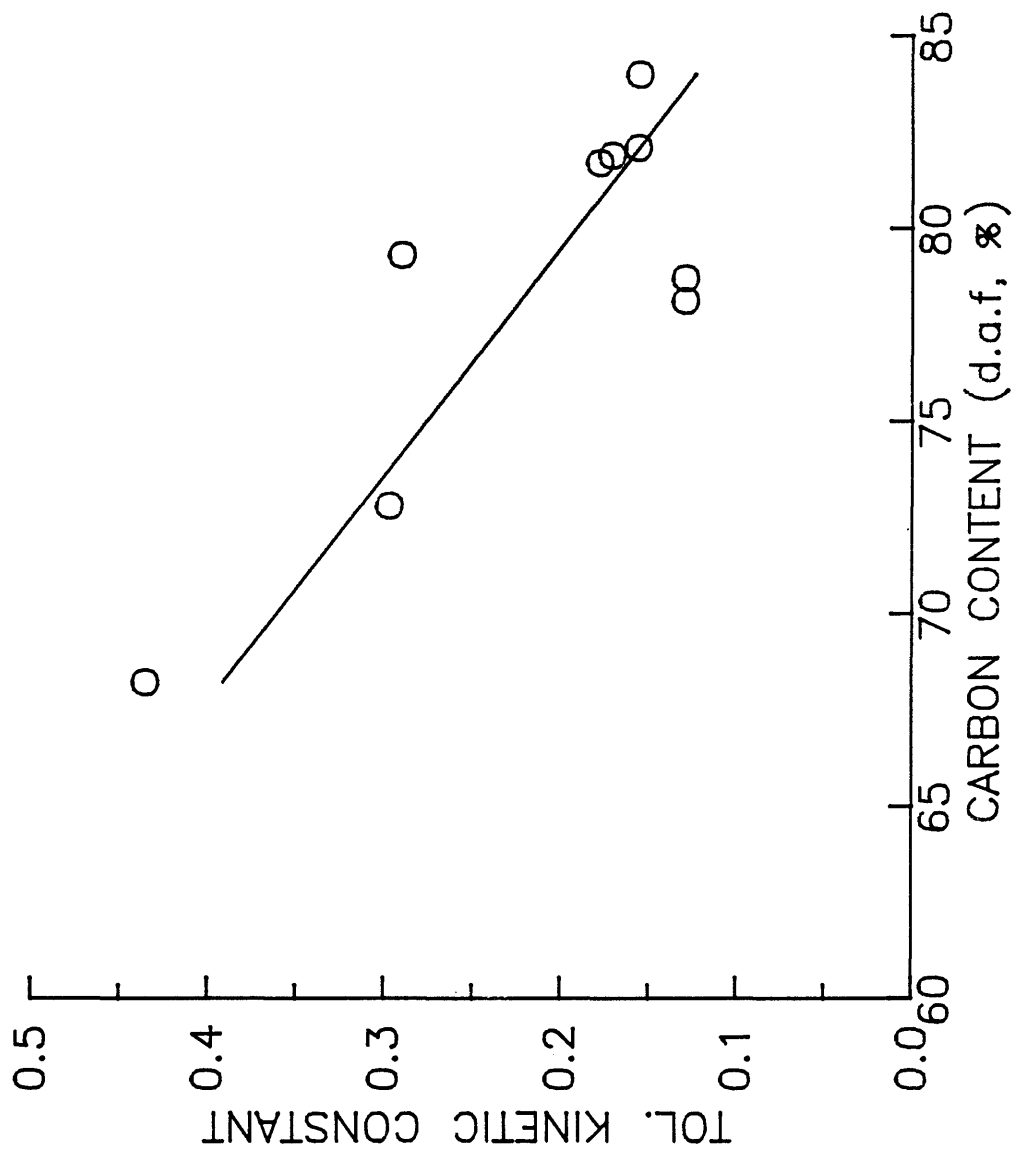


Figure 22. Correlation of Toluene Solubles Kinetic Constant vs. O/C Atomic Ratio

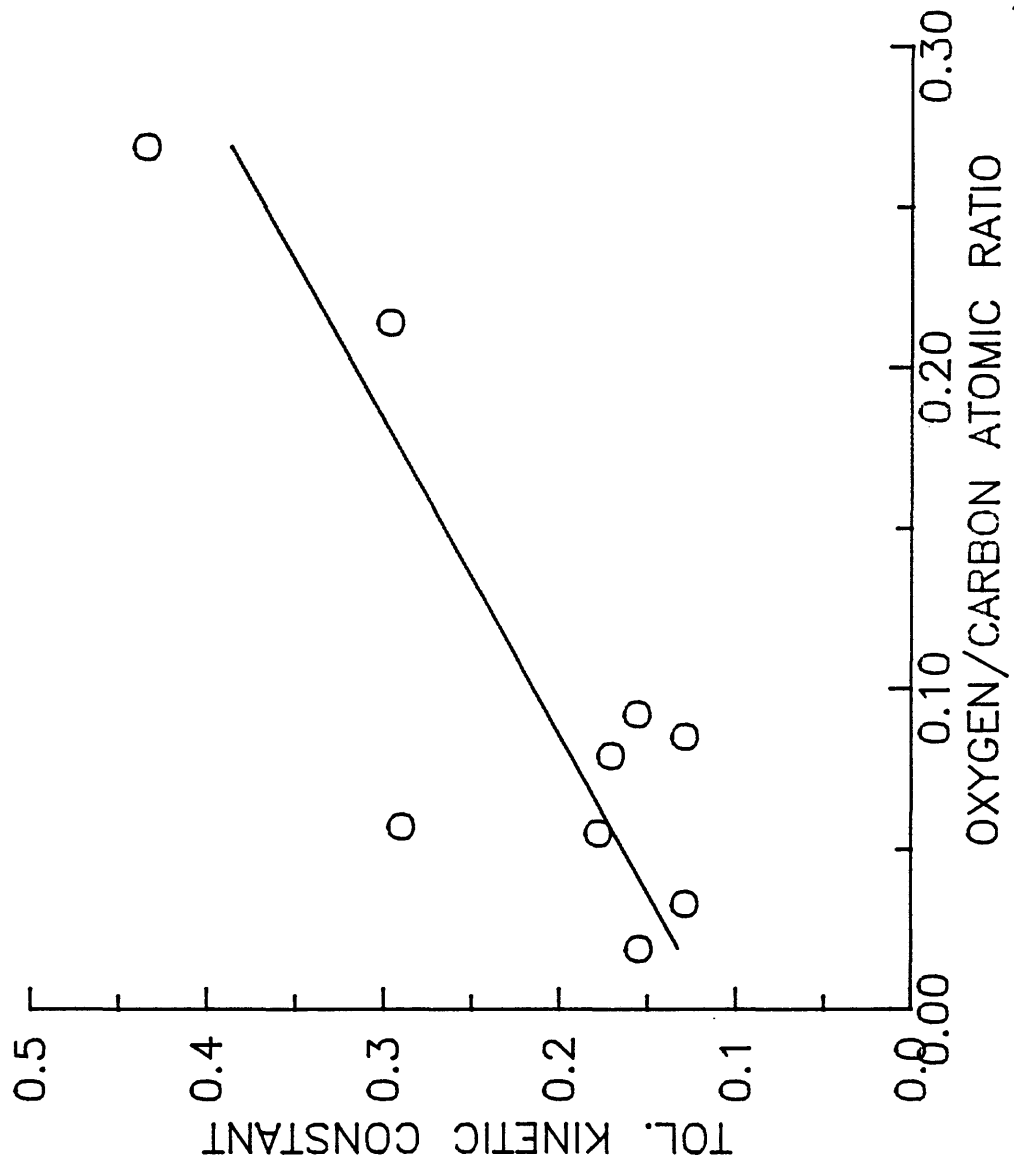


Figure 23. Correlation of Hexane Solubles Kinetic Constant vs. Total Sulfur Content

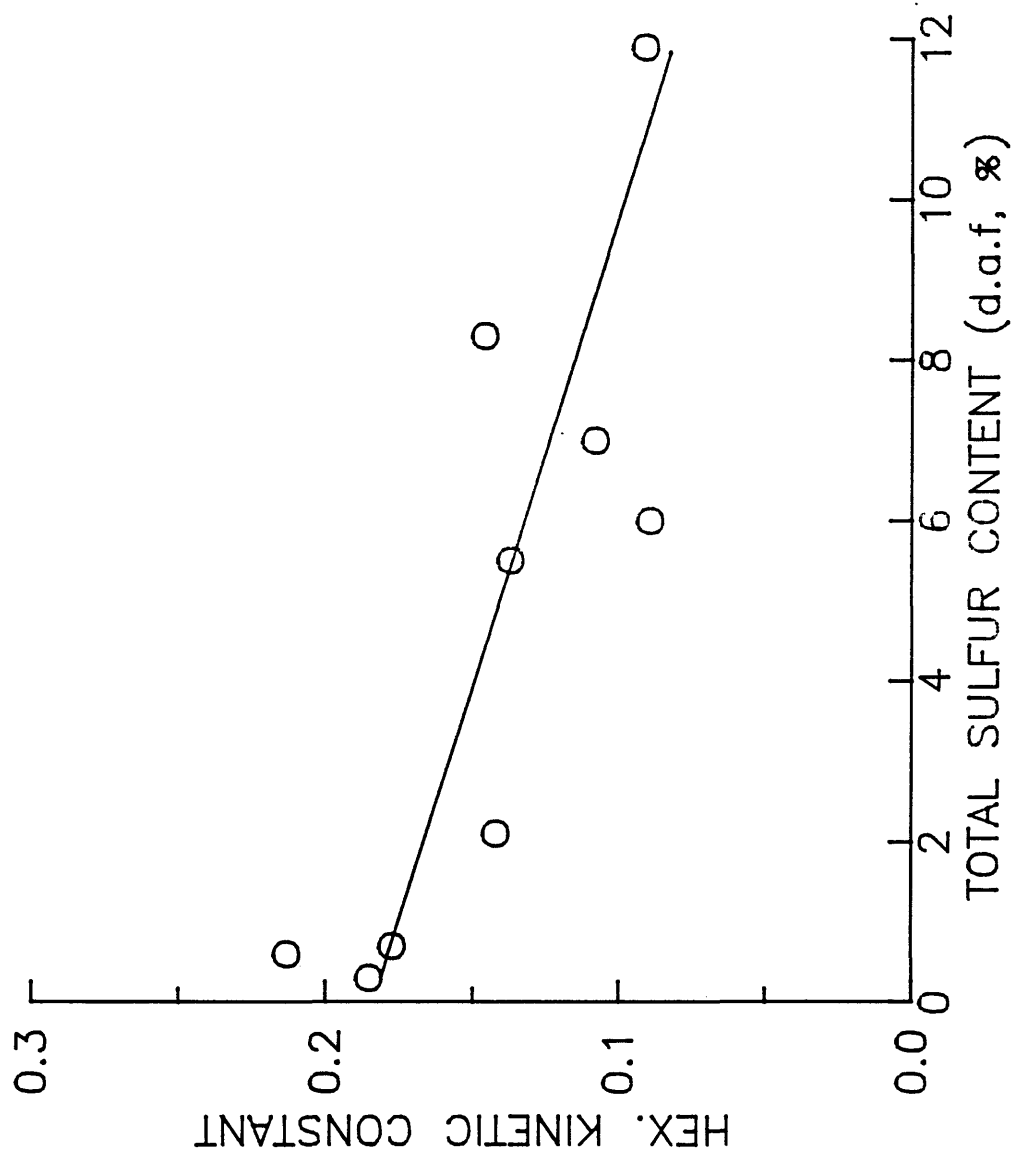
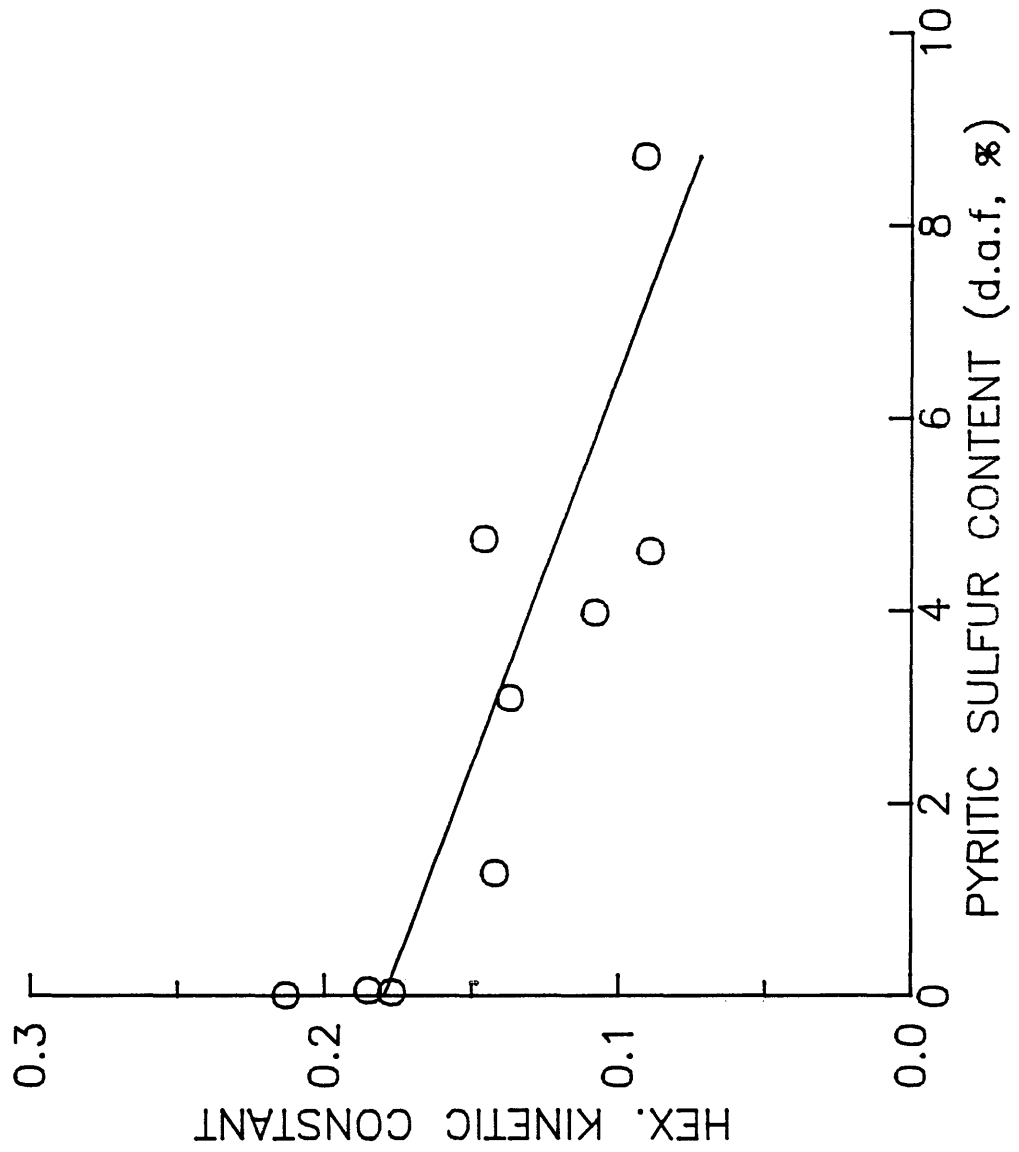


Figure 24. Correlation of Hexane Solubles Kinetic Constant vs. Pyritic Sulfur Content



better dependent variable for coal properties. As mentioned in the Introduction, the commonly accepted liquefaction mechanism is:

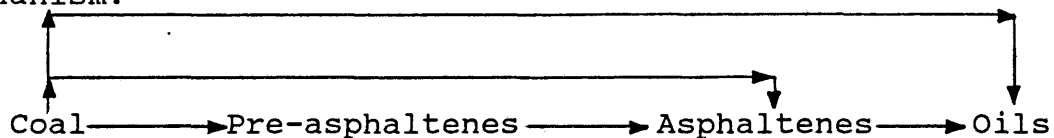


If one is to find a relationship with the parent coal properties, then it is necessary to study the beginning of the liquefaction reaction. Concentrating on the equilibrium conversion, or the entire conversion profile, will make the properties of the intermediates (whatever they may be) the dominant factors in the reaction, rather than the properties of the parent coal. It is for this reason that only the first four data points (0, 3, 5, and 10 minutes) were used for the evaluation of the kinetic constant. It is believed that in this manner, the parent coal properties can be best isolated and their effect on the liquefaction mechanism best elucidated.

The products of the coal liquefaction reaction have been, by convention, categorized as follows:

<u>Solvent Solubles</u>	<u>Product Classification</u>
THF solubles	Pre-asphaltenes + Asphaltenes + Oils
Toluene solubles	Asphaltenes + Oils
Hexane solubles	Oils

The above definitions demonstrate that as the polarity of the solvent decreases, the molecular weight and polarity of the products soluble in that solvent also decreases. One can conclude that each liquefaction product classification is produced directly from the parent coal and the preceding classification. This results in the following liquefaction mechanism:



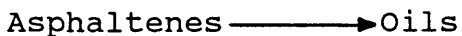
The specific correlations for the Toluene solubles and Hexane solubles are substantiated by theoretical investigations performed by other researchers. Ouchi et al. (13) used Pre-asphaltenes as a feedstock to determine the structural changes involved with the reaction



This reaction is analogous to the production of Toluene solubles. He determined that during the initial stages of the liquefaction reaction, the coal is broken down to lower molecular weight species by breaking the ether linkages that connect the structural aromatic units of the parent coal. This could explain the correlation between the O/C atomic

ratio, and the % oxygen, to the Toluene solubles kinetic constant.

The sulfur in the coal, when in the form of iron pyrite, is regarded as a hydrogenation catalyst that promotes hydrogen transfer to the coal. There are two theories that support the correlation between sulfur content (total and pyritic) to Hexane solubles kinetic constant. First, the Hexane solubles are the most hydrogenated product of the liquefaction reaction. One can extrapolate how sulfur content, which catalytically enhances hydrogen transfer, should correlate against the most hydrogenated product. Kanda et al. (12) produced evidence that in the later stages of the reaction



the conversion reaction occurs within the coal structure itself. This is accomplished chiefly through the saturation of aromatic rings, which requires a high amount of hydrogen. Furthermore, the activation energy involved in the saturation of aromatics is greater than the activation energy associated with capping aliphatic radicals. A catalyst that promotes hydrogen transfer, and hence lowers the required energy, should enhance this type of reaction. Thus, the correlation of Hexane solubles to pyritic sulfur,

with an r^2 of 71.0 %, is expected.

7.3 MULTI-PARAMETER CORRELATIONS

Multi-parameter correlations were attempted for all three levels of conversion. The 11 coal properties used for the single parameter correlations were used as the prospective independent variables for this study. The multi-parameter correlations were developed using stepwise linear regression using the STEPWISE function of the MINITAB statistics package.

The attempt to find multi-parameter correlations at the Total conversion and Hexane solubles levels failed completely. The STEPWISE function, utilizing an f-test as the criterion for adding independent variables to the correlations, could not find any additional parameters that produced a statistically significant improvement in the correlations. Thus, the best correlation for Total conversion is with volatile matter, with an r^2 of 43.6 %. For Hexane solubles, the best correlation is against pyritic sulfur, as mentioned in the previous section.

The development of a multi-parameter correlation for Toluene solubles was much more successful. The stepwise routine found no less than five coal parameters which statistically enhanced the correlation. However, the two

most relevant parameters are O/C atomic ratio and organic sulfur. Together, they produce a two parameter correlation with an adjusted r^2 of 95.3 %. This empirical correlation is:

$$y = -.0467 + 1.606x_1 + .0671x_2$$

where y = Toluene solubles kinetic constant (min^{-1})

x_1 = O/C atomic ratio

x_2 = % organic sulfur

This correlation is theoretically confirmed by several researchers. The di-sulfide bonds in the coal structure (S-S) are very weak compared to normal aliphatic bonds, and therefore rupture easily. These bonds are directly related to the organic sulfur content. The O/C ratio is, as previously mentioned, a measure of the ether linkages, which have been reported to be the bonds broken during the production of Asphaltenes (12,13). The O/C ratio has also been a parameter used in independent liquefaction correlations (35). Therefore, though this multi-parameter correlation is empirical by nature, it does have a mechanistic background.

8. CONCLUSIONS

The following conclusions are exclusive to the experimental system employed during this research and the coals utilized for the same.

1. There is no discernable catalytic effect on the yield of the liquefaction reaction from the walls of the reactor.
2. A coal particle size smaller than or equal to -20 mesh produces no mass transfer limitations on either the rate or the yield of the reaction.
3. A first order, irreversible model is superior to a second order, irreversible model for describing the initial stages of the liquefaction reaction based on statistics and mechanistic reasoning.
4. The kinetic constant is statistically and theoretically more suitable to describe the parent coal properties than the equilibrium conversion, the conversion at three minutes, or the area under the conversion profile.

5. Total conversion does not correlate against any of the 11 coal parameters used in this study.
6. Toluene solubles (Asphaltenes + Oils) correlate against:
 - Oxygen content
 - Carbon content
 - O/C atomic ratio
7. Hexane solubles (Oils) correlate against:
 - Total sulfur content
 - Pyritic sulfur content
8. No multi-parameter correlations were found for Total conversion of Hexane solubles.
9. A multi-parameter correlation was found for Toluene solubles, involving two parameters: O/C atomic ratio and organic sulfur content.

9. RECOMMENDATIONS

1. Determine the coal particle size at which mass transfer becomes a dominant factor.
2. Determine a theoretically valid vehicle for use with sub-bituminous and lignite coals, and generate conversion data for these coals.
3. Obtain more coals, both bituminous and sub-bituminous, and continue work on single parameter and multi-parameter correlations. Evaluate if the bituminous and sub-bituminous coals can be treated under the same set of correlations, or if they must be separated into distinct classifications.

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APPENDIX

Kinetic Data

Stocton Seam (Mesh = -20)

(All conversions are in d.a.f, wt. %)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
5	33	14	8	19	6
	33	15	9	18	6
	33	14	10	19	4
	35	16	8	19	8
40	40	26	15	14	11
	42	27	18	15	9
	41	26	17	15	9
	40	27	17	13	10

Stocton Seam (Mesh = -100)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
5	34	15	7	19	8
	31	13	10	18	3
	31	13	6	18	7
	35	15	9	20	8
40	39	27	14	12	13
	40	28	17	12	11
	39	27	17	12	10
	40	29	17	11	12

Stocton Seam (Catalytic Wall Effect)

Run #	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
1	40	26	16	14	10
2	41	27	18	14	9
3	41	29	18	12	11
4	38	27	19	11	8

Stigler (HVAB)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
1.28	47.0	16.2	5.9	30.8	10.3
3.28	56.1	20.7	7.0	35.4	13.7
8.28	67.5	26.4	8.5	41.1	17.9
18.28	74.7	32.9	9.2	41.8	23.7
38.28	72.1	43.6	18.4	28.6	25.1

Upper Freeport (HVAB)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
1.28	29.1	13.5	4.6	15.6	8.9
3.28	55.8	21.3	13.5	34.5	7.8
8.28	59.1	33.5	21.3	25.6	12.3
18.28	64.7	38.0	25.7	26.7	12.3
28.78	69.1	44.7	31.3	24.5	14.5
38.28	66.9	44.7	30.2	22.3	14.5

Upper Freeport (T = 400 °C)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
2.04	20.9	10.5	2.9	10.4	7.6
4.04	34.6	11.3	3.5	23.3	7.8
9.04	59.1	10.1	4.6	49.0	5.5
19.04	62.5	17.9	7.9	44.6	10.0
39.04	73.6	33.5	17.9	40.1	15.6

Upper Freeport (T = 375 °C)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
2.04	23.5	5.7	.1	17.8	5.6
4.04	36.9	4.6	.1	32.3	4.5
9.04	33.5	10.1	1.2	23.4	8.9
19.04	48.0	12.4	2.3	35.6	10.1
39.04	72.5	15.7	4.6	56.8	11.1

B-Seam (HVAB)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
1.28	28.8	9.1	5.8	19.8	3.3
3.28	53.0	17.8	15.6	35.1	2.2
8.28	47.5	26.6	21.1	20.9	5.5
18.28	42.0	28.8	24.4	13.2	4.4
38.28	44.2	37.6	25.5	6.6	12.1

Tebo (HVAB)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
1.28	60.7	25.0	9.7	35.7	15.3
3.28	76.0	36.5	17.4	39.5	19.1
8.28	83.7	45.4	21.2	38.3	24.2
18.28	83.7	55.6	31.4	28.1	24.2
38.28	85.0	67.1	39.0	17.9	28.1

Fort Scott (HVAB)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
1.28	47.0	13.5	3.1	33.5	10.4
3.28	77.0	22.7	11.2	54.3	11.6
8.28	81.7	37.7	22.7	43.9	15.0
18.28	70.1	41.2	23.9	28.9	17.3
38.28	71.3	49.3	33.1	22.0	16.2

Bevier-Wheeler (HVBB)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
1.66	22.8	17.6	9.8	5.2	7.8
3.66	28.0	24.1	15.0	3.9	9.1
8.66	34.5	31.9	21.5	2.6	10.4
18.66	37.6	32.3	31.0	5.3	1.3
38.66	37.1	34.5	29.3	2.6	5.2

Weir-Pittsburgh (HVBB)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
1.66	59.3	15.2	3.6	44.1	11.6
3.66	73.4	26.7	12.8	46.8	13.9
8.66	82.3	43.1	21.6	39.2	21.5
18.66	84.8	54.5	29.2	30.3	25.3
38.66	84.8	64.6	39.3	20.2	25.3

Weir-Pittsburgh (T = 400 °C)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Pre- <u>Asphaltenes</u>
1.66	40.3	10.4	29.9
3.66	57.0	12.8	44.2
8.66	76.0	24.1	51.9
18.66	84.8	29.2	55.6
38.66	86.1	40.6	45.5

Weir-Pittsburgh (T = 375 °C)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Pre- <u>Asphaltenes</u>
1.66	24.1	.1	24.0
3.66	36.8	1.4	35.4
8.66	59.5	3.9	55.6
18.66	74.7	14.0	60.7
38.66	83.6	25.4	58.2

Sudduth (HVCB)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
1.54	33.2	22.3	12.5	11.0	9.8
3.54	34.5	23.5	15.0	11.0	8.5
8.54	34.5	24.7	17.4	9.8	7.3
18.54	33.2	24.7	19.8	8.5	4.9
38.54	34.5	28.4	23.5	6.1	4.9

Lower Sudduth (HVCB)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Hexane <u>Solubles</u>	Pre- <u>Asphaltenes</u>	<u>Asphaltenes</u>
1.54	38.8	19.1	8.5	19.7	10.6
3.54	41.2	26.3	12.9	14.9	13.4
8.54	43.3	31.2	17.6	12.2	13.5
18.54	43.3	29.7	19.1	13.6	10.6
38.54	42.7	32.2	23.3	10.4	9.0

Lower Sudduth (T = 400 °C)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Pre- <u>Asphaltenes</u>
1.54	31.2	20.6	10.6
3.54	35.7	23.6	12.1
8.54	43.3	31.2	12.1
18.54	41.8	29.7	12.1
38.54	46.3	35.7	10.6

Lower Sudduth (T = 375 °C)

Time (min.)	Total <u>Conv.</u>	Toluene <u>Solubles</u>	Pre- <u>Asphaltenes</u>
1.54	17.6	11.5	6.1
3.54	22.1	11.5	10.6
8.54	28.2	19.1	9.1
18.54	31.2	19.1	12.1
38.54	32.7	19.1	13.6