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PROCESS AND ANALYTICAL STUDIES OF ENHANCED LOW SEVERITY CO-PROCESSING USING SELECTIVE COAL PRETREATMENT

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ABSTRACT

This report describes progress on research during the sixth quarter of this contract dealing with applications of coal pretreatment techniques in coal hydroliquefaction. The objectives of the project are to investigate various coal pretreatment techniques and to determine the effect of these pretreatment procedures on the reactivity of the coal. Reactivity enhancement will be evaluated under both direct hydroliquefaction and co-processing conditions. Coal conversion utilizing low rank coals and low severity conditions (reaction temperatures generally less than 350 °C) are the primary focus of the liquefaction experiments, as it is expected that the effect of pretreatment conditions and the attendant reactivity enhancement will be greatest for these coals and at these conditions.

This document presents a comprehensive report summarizing the findings on the effect of mild alkylation pretreatment on coal reactivity under both direct hydroliquefaction and liquefaction co-processing conditions. Results of experiments using a dispersed catalyst system (chlorine) are also presented for purposes of comparison. In general, mild alkylation has been found to be an effective pretreatment method for altering the reactivity of coal. Selective (oxygen) methylation was found to be more effective for high oxygen (subbituminous) coals compared to coals of higher rank. This reactivity enhancement was evidenced under both low and high severity liquefaction conditions, and for both direct hydroliquefaction and liquefaction co-processing reaction environments. Non-selective alkylation (methylation) was also effective, although the enhancement was less pronounced than than found for coals activated by O-alkylation. The degree of reactivity enhancement was found to vary with both liquefaction and/or co-processing conditions and coal type, with the greatest positive effect found for subbituminous coal which had been selectively O-methylated and subsequently liquefied at low severity reaction conditions.

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INTRODUCTION

If coal liquefaction is ever to become an economical source of liquid fuels, liquefaction processes must be developed which can compete with energy sources presently in use. Development of low severity (temperature, pressure and reaction time) liquefaction processes is one such alternative that has recently received increased emphasis. Liquefaction processes which operate at lower temperatures and pressures (temperatures below 350 °C and pressures below 10 MPa) require lower capital costs while maintaining a high degree of selectivity to liquid products. The production of undesired hydrocarbon gases is minimized, resulting in reduced hydrogen consumption and improved economics over high severity liquefaction processes. The main disadvantage of using lower severity liquefaction processes is the increased reaction (residence) time required due to the fact that at lower severity the rate of coal dissolution is slower. Maximization of coal conversion is normally not the primary concern when low severity liquefaction is employed as the first stage of a two stage liquefaction process. In two stage processes, the first stage is geared towards obtaining a satisfactory dissolution rate and a liquid product distribution where asphaltenes are preferred over the less reactive preasphaltenes. This results in an intermediate coal-derived product stream which is less refractory and more amenable to subsequent upgrading in a higher severity catalytic second stage.

The disadvantages of low severity liquefaction in terms of coal reactivity could be offset by pretreatment of the coal prior to first stage processing. This would result in improved operating characteristics for the first stage process while still maintaining a product composition which is suitable for subsequent upgrading in the second stage process. The objective of this research program was to investigate a variety of coal pretreatment methods, and determine the effect of these processes on the reactivity of coal. Coal reactivity measurements were made at both low and high severity conditions, and in both liquefaction and coprocessing reaction environments. This report presents the results of experiments performed to investigate use of mild alkylation and addition of a dispersed catalyst as coal pretreatment steps. Different liquefaction conditions were used in order to determine which pretreatment methods would be most suitable as precursors to first stage, low severity liquefaction processes. Both bituminous and subbituminous coal samples were chosen in order to observe how the effectiveness of different pretreatment methods varied with coal rank. Two different liquefaction solvents were used, resulting in two separate sets of reactivity data. The first solvent was dihydrophenanthrene (DHP), which was chosen in order to determine the effect of coal pretreatment on reactivity under direct hydrogenation conditions. The second solvent utilized was Cold Lake atmospheric residuum, in order to simulate operation and measure coal reactivity under coal/oil co-processing conditions. The pretreated samples were liquefied at different combinations of these reaction variables, resulting in two sets of liquefaction data for different ranks of coal, reaction times, and temperatures. Coal reactivities were compared in terms of the extent to which the coal was converted to THF soluble material during liquefaction, and comparisons were made between the pretreated and the untreated coals at each set of liquefaction conditions.

EXPERIMENTAL PROCEDURE

1. EXPERIMENTAL DESIGN

The objective of this program is to investigate the manner in which selected pretreatment methods affect the reactivity enhancement of differently ranked coals. Reactivity enhancement was measured by liquefaction of the pretreated coal at both low and high severity reaction conditions using both co-processing and direct liquefaction solvents. As shown in Table I, each combination of reaction severity and mode of processing (direct liquefaction or co-processing) was run at short and longer reaction times to observe how the enhancement by pretreatment varied with reaction time.

Two coals, Illinois #6 bituminous and Wyodak sub-bituminous, were selected so that pretreatment effects could be compared as a function of coal rank. A matrix of reactivity experiments, shown in Table II, was completed to evaluate the effect of each variable listed in Table I. Both pretreated and untreated coals were used in completing the matrix so that the effect of the pretreatment method at each combination of liquefaction conditions could be directly determined.

TABLE II

Matrix of Liquefaction Reaction Parameters

COAL	SOLVENT	REACTION TEMP (C)	REACTION TIME (min)
WYODAK	DHP	350	5
			30
		425	5
			30
	COLD LAKE ATM. RESIDUUM	350	5
			30
		425	5
			30
ILLINOIS #6	DHP	350	5
			30
		425	5
			30
	COLD LAKE ATM. RESIDUUM	350	5
			30
		425	5
			30

2. MATERIALS

2.1 Coals

The experimental design used involved using Illinois #6 bituminous and Wyodak subbituminous coals. An analysis of the coal properties is shown in Table III. All coal samples used in the pretreatment experiments and subsequent liquefaction experiments were obtained from the Argonne Premium Coal Bank in 5 g ampoules of -100 mesh coal. Each ampoule was nitrogen purged to prevent oxidation of the sample prior to use. Ampoules were kept intact until the instant they were needed; any coal left beyond the amount required for each pretreatment process was discarded. This procedure assured that the coals used in all experimental work were essentially free of oxidation.

2.2 Solvents

Two different solvents were used in the liquefaction reactivity experiments. Dihydrophenanthrene (DHP) was chosen as the liquefaction solvent based upon its excellent hydrogen donor capabilities. The DHP sample used was obtained from the Aldrich Chemical Co., with a purity of 94.0% by weight. Cold Lake atmospheric petroleum residuum was used to simulate coal reactivity liquefaction performance under co-processing conditions. Cold Lake residuum

TABLE III

Feed Coal Properties

Ultimate Analysis (wt% maf basis)	Illinois #6 Bituminous	Wyodak Subbituminous
Carbon	77.7	75.0
Hydrogen	5.0	5.4
Nitrogen	1.4	1.1
Organic Sulfur	2.4	0.5
Chlorine	0.1	0.0
Fluorine	0.0	0.0
Oxygen	13.4	18.0
Total	100.0	100.0

is a low grade petroleum solvent, containing about 85 wt% 455 °C material as shown in Table IV. In order to facilitate its use in the coal liquefaction experiments, 100 g samples of Cold Lake residuum were hydrotreated using an Autoclave Magnedrive II 300 cm^3 batch reactor. Hydrotreating involved the addition of 10.0 g of Shell 324 Ni/Mo catalyst which was sulfided in-situ by the addition of 2.00 g of methyl sulfide. The reactor was then charged with 15.5 MPa hydrogen gas, and heated to 400 °C for 1 hr. After hydrotreating, the catalyst was separated via centrifugation, resulting in a less viscous and more manageable coprocessing solvent. The hydrotreated Cold Lake residuum was distilled using a micro-spinning band distillation column; distillation data are listed in Table IV.

2.3 Reaction Gas

The reaction gas used for the coal liquefaction experiment was hydrogen, which was obtained in industrial grade from General Air Services, Inc.

3. COAL PRETREATMENT METHODS

For each of the pretreatment methods used, the quantity of coal pretreated and scheduling of the pretreatment process were chosen to minimize coal waste and aging prior to

TABLE IV

Properties of Cold Lake Atmospheric Residuum

Distillate Yields

Distillate Boiling Range	WEIGHT PERCENT DISTILLED	
	As Received	After Hydrotreatment
Water	0.0	0.0
IBP - 177 °C	0.0	0.0
177 - 455 °C	25.1	32.0
455 + °C	74.9	68.0
Total	100.0	100.0

Ultimate Analysis

	WEIGHT PERCENT	
Component	As Received	After Hydrotreatment
Carbon	88.3	-
Hydrogen	8.1	-
Nitrogen	1.0	-
Oxygen	1.7	-
Sulfur	0.9	-
Ash	0.0	-
Total	100.0	-

the liquefaction experiments. Pretreated coals were analyzed using Fourier transform infra-red spectroscopy (FTIR) and elemental analysis. Each pretreatment procedure and FTIR analysis of the pretreated coal was performed by Ms. Onranong Nguanprasert. Elemental analysis of each pretreated sample was performed by Huffman Laboratories, of Golden, Colorado.

Prior to liquefaction studies using pretreated coals, each method was repeated a number of times and the subsequent coal samples analyzed. Once the pretreatment process was deemed reproducible, a fresh batch of coal was pretreated, samples were withdrawn for analysis and the balance of the pretreated coal was stored under vacuum for use in liquefaction reactivity experiments.

3.1 Determination Of Extent Of Alkylation

The extent of alkylation for each pretreatment method was determined by elemental analysis of the alkylated coal in order to determine the hydrogen to carbon ratio. Hydrogen to carbon ratios of the untreated coals were determined using information supplied by the Argonne National Laboratory (1). The extent of alkylation due to the pretreatment method was calculated using the following equation:

$$X = 100*(C3 - C1)/(C2 - C3)$$

where:

X is the extent of alkylation (grams of alkyl groups added per 100 grams of parent MAF coal),

C1 is the normalized weight fraction of carbon in the untreated feed coal ((wt % C)/(wt %C + wt %H)),

C2 is the normalized weight fraction of carbon in the alkyl group being introduced into the coal,

C3 is the normalized weight fraction of carbon in the alkylated coal.

The extent of alkylation can also be defined in terms of the number of alkyl groups added per 100 carbon atoms of moisture and ash free (MAF) coal:

$$A = (X * MWC)/(MWA * MFC)$$

where:

A is the extent of alkylation in terms of number of alkyl groups added per 100 carbon atoms of MAF coal,

X is the extent of alkylation (grams of alkyl groups added per 100 grams of MAF coal),

MWC is the molecular weight of carbon (12.01),

MWA is the molecular weight of the alkyl group being incorporated into the coal,

MFC is the mass fraction of carbon in the untreated coal on a MAF basis.

An example of how these equations are used is shown below, given the elemental analysis data for the raw and alkylated coal in the following table:

MAF BASIS

SAMPLE	WT % CARBON	WT % HYDROGEN	C/(C+H) RATIO	
RAW WYODAK	75.01	5.35	0.9334	< C1
METHYL GROUP	12.01	3.03	0.7985	< C2
TREATED WYODAK	72.33	5.36	0.9310	< C3
X =	1.82	A =	1.94	

The untreated Wyodak coal has a composition of 75.01 weight percent carbon and 5.35 weight percent hydrogen, as seen in the first row. The third column uses these two values to calculate the normalized weight percent carbon (C1). For methyl group addition, the normalized weight percent carbon for a methyl (-CH3) group is shown in the second row (C2). Using the carbon and hydrogen analysis results from the treated coal sample, C3 is calculated in the third row. These values are then used to calculate the extent of alkylation (X), with the resulting value of 1.82 grams of alkyl groups per 100 grams of MAF coal.

The extent of alkylation in terms of alkyl groups added per 100 carbon atoms (A), can be calculated using 75.01 weight percent carbon as the value for MFC in the untreated coal, 12.01 for the value of MWC, and 15.04 for the value of MWA. The resulting value for A is 1.94 methyl groups added per 100 carbon atoms.

3.2 Reductive Alkylation

Coal pretreatment by reductive alkylation was based upon the work of Sternberg (2). The recipe used was based upon approximately 5 g of raw coal. If 2 ampoules of feed coal were required (10 g), then all of the accompanying reagents required to alkylate a 5 g batch of coal were doubled. The most coal alkylated at any one time was 4 ampoules (about 20 g) in a single alkylation experiment. For each 5 g of coal to be alkylated, 120 ml of tetrahydrofuran (THF) were added to a round-bottomed, three necked flask. Approximately 4.4 g of potassium metal and 0.304 g of naphthalene were added to the THF, the flask was sealed and purged continually with a stream of nitrogen, and the mixture was magnetically stirred for 24 hr. The observation was made that soon after the addition of the potassium and naphthalene, the slurry took on a dark olive-green hue. This result was expected according to Sternberg's paper, and it was found that if the slurry remained clear, the reagents had been added in the wrong proportions and the subsequent alkylation experiment would be unsuccessful.

After the 24 hr digestion period, 5 g of coal was added to the THF slurry directly from a newly opened ampoule. The flask was then resealed and the mixture was magnetically stirred for another 72 hr under a nitrogen blanket. At that time, the flask containing the slurry was removed from the magnetic stirrer, and any undissolved lumps of potassium were removed from the slurry using a metal spatula. A mixture of 10 ml of ethyl iodide in 30 ml of THF was then added drop-wise over a 30 minute period while the flask was stirred. Once the drop-wise addition had been completed, the flask was magnetically stirred for 2 hr.

The mixture in the flask was then roto-evaporated to remove a majority of the THF. The coal residue was then transferred to centrifuge tubes where it was slurried with methanol and then centrifuged at high speed for 30 min. The methanol was decanted off, and the slurrying and subsequent centrifugation were repeated three more times to insure that the ethyl iodide had been completely washed away.

The remaining treated coal was then extracted with water using a soxhlet extractor for 24 hr in order to remove any remnant water soluble reagent ions. The treated coal was dried in a vacuum oven overnight at 50 ^{o}C at a vacuum of less than 10 torr, followed by further drying at 100 ^{o}C at a high vacuum (less than 0.1 torr) for 24 hr. The alkylated coal sample was then transferred to a sample jar and stored in a vacuum desiccator for future use.

3.3 Oxygen Alkylation

Coal pretreatment via oxygen alkylation (O-alkylation) was conducted using the method first developed by Liotta (3). Coal was O-alkylated in batches of 5, 10, or 20 g and the treated coal samples were used promptly in liquefaction studies so as to minimize storage time after alkylation.

To alkylate 5 g of raw, undried coal, 120 ml of THF was added to a round-bottomed, three necked flask which was magnetically stirred. Fresh coal was slowly added to form a coal-THF slurry A mixture of 40 percent aqueous tetrabutyl-ammonium hydroxide was then added drop-wise until the pH of the slurry was neutral (pH = 7.0). The slurry was stirred for 2 hr under a nitrogen blanket, at which time methyl iodide was added to the flask in a molar amount equal to twice the number of moles of tetrabutylammonium iodide added previously. The slurry was then stirred overnight under a nitrogen blanket.

The slurry was roto-evaporated under vacuum in order to remove all of the volatiles, leaving only alkylated coal behind. The pretreated coal was soxhlet extracted with water for 24 hr in order to remove all traces of water soluble reagents. The extracted coal was dried overnight in a vacuum oven at 50 oC and a vacuum of less than 10 torr, followed by subsequent high vacuum drying at 100 °C for another 24 hr at a vacuum of less than 0.1 torr. The O-alkylated coal was bottled and stored in a vacuum desiccator for future use.

3.4 Chlorine Catalyst/Mild Alkylation Pretreatment

For pretreatment by catalyst dispersion, the procedure developed by Armstrong (4) was used as a guideline. Depending upon the quantity of coal needed, the quantity of coal pretreated in any one batch varied between 5 g and 20 g. As stated in the previous two pretreatment procedures, the recipe developed was for 5 g of raw coal.

For each 5 g of coal pretreated, 40 ml of methanol and 0.40 ml of concentrated hydrochloric acid were mixed together in a three necked, round bottomed flask. The coal sample was then slowly added to the methanol/hydrochloric acid solution and the slurry was magnetically stirred for 3 hr. Next, the slurry was roto-evaporated, removing the majority of the methanol from the coal. The coal sample was then dried at 50 °C in a vacuum oven overnight at a vacuum of less than 10 torr, followed by vacuum drying at 100 °C for 24 hr under a vacuum of less than 0.1 torr. The pretreated coal was then transferred to a sample jar, and stored in a vacuum desiccator for future use.

4. COAL LIQUEFACTION MEASUREMENTS

4.1 Equipment Description

Reactivity enhancement of the pretreated coals was monitored by measuring coal conversion to THF soluble products in a pair of microautoclave tubing bomb reactors. Two identical reactors were built and configured so that two liquefaction experiments could be conducted simultaneously under the same reactivity conditions. This set-up assured that the only true variable between the two liquefaction runs was the pretreatment method used for the coal being liquefied within the tubing bomb reactors; all other variables such as reaction time and temperature would be exactly matched.

Each of the reactors consisted of a body constructed from a 5" length of 1/2" O.D. 316 stainless steel tubing which was sealed on the bottom with a Swagelock 1/2" nut and end plug, as shown in Figure 1. The top of the reactor body consisted of a Cajon VCR female gland fitting welded to the tubing body. The fitting was designed for repeated sealing by means of a sacrificial nickel gasket. All welding of the stainless steel components was performed by Russell D. White, of Boulder, Colorado.

FIGURE 1

Liquefaction Reactor Assembly

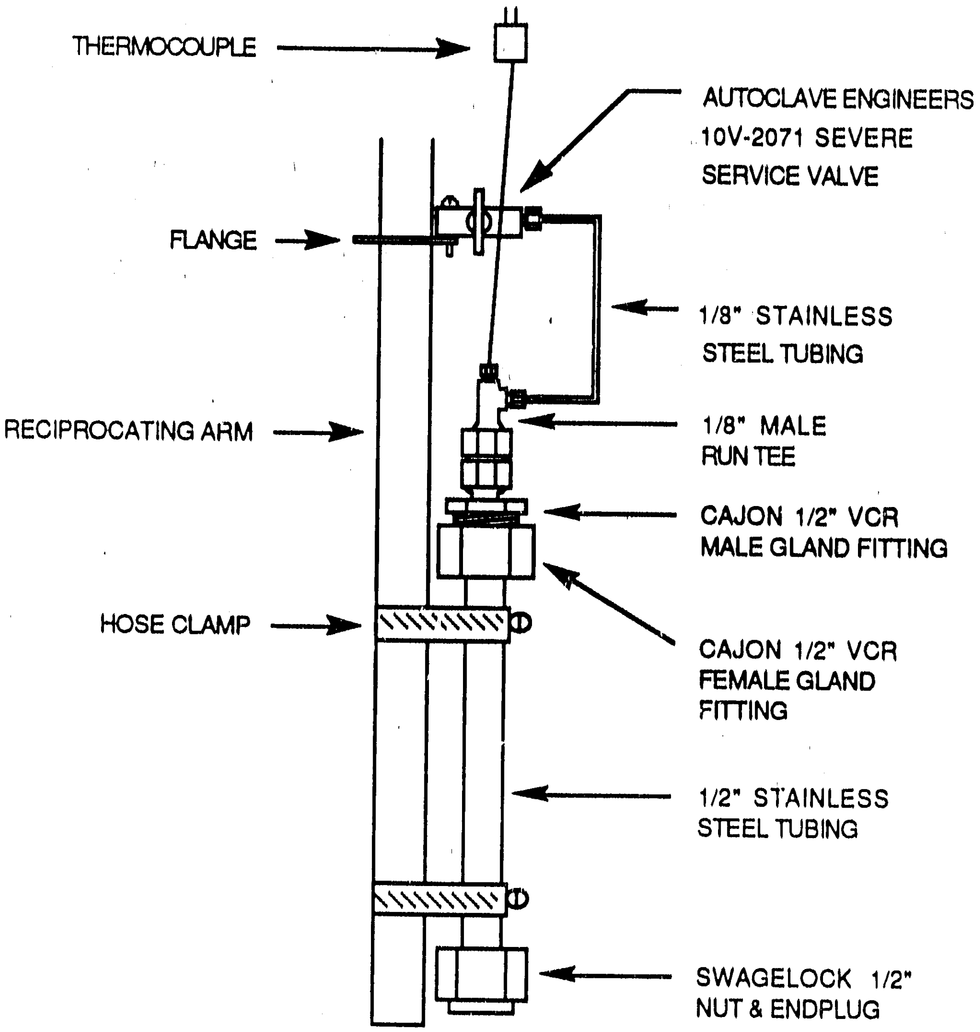
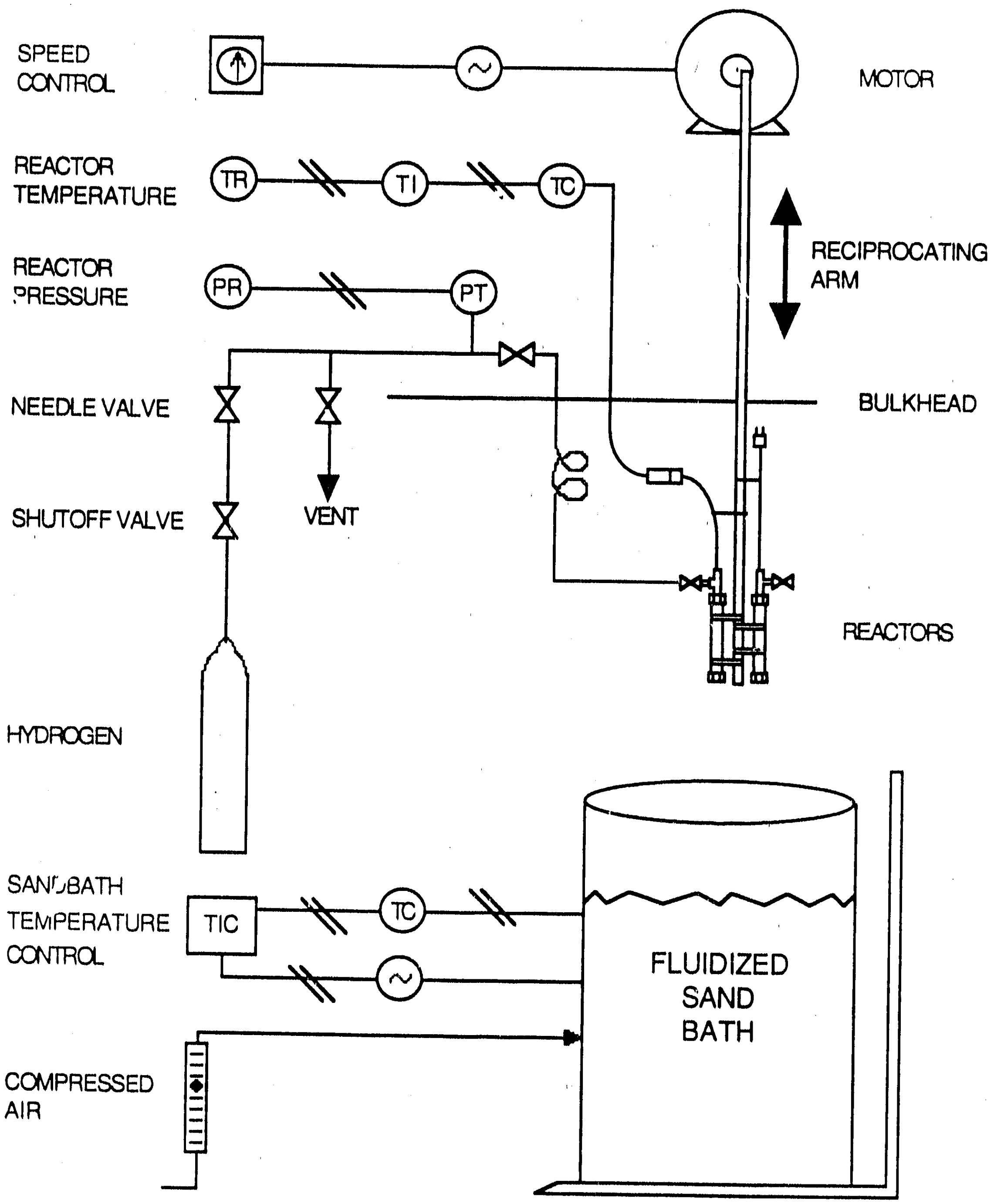


FIGURE 2

Liquefaction Reactor System



gas delivery system.

Heating the two reactors was accomplished with the use of a Tecam model SBL-20 fluidized sand bath which was positioned on an adjustable hoist below the reciprocating arm. The hoist could be raised or lowered as needed, giving good control over the exact amount of time the reactors were immersed in the sand bath. Each reactor's thermocouple was connected to the thermocouple readout, which provided a continuous temperature reading of the reactor contents during the liquefaction run. Initially, both reactor thermocouples were connected during the liquefaction runs. It was soon observed that the temperature between the two reactors never varied by more than 1 ^{o}C, so subsequent runs used a thermocouple readout from only one of the reactors and assumed that this single temperature reading was representative of the internal temperature of both reactors.

During the experimental program, a new pair of reactor heads and ten additional reactor bodies had to be fabricated. A question arose as to whether or not the replacement reactor components would impart a catalytic wall effect to the liquefaction process because of the new stainless steel components. The new reactor components were used in parallel with the old reactor components for three baseline runs where the contents of both reactors were identical.

TABLE V

Liquefaction Conversions for Old and New Reactors

COAL	SOLVENT	REACTION TEMP (C)	REACTION TIME (min)	THF COAL CONVERSION (WEIGHT %) OLD REACTOR	THF COAL CONVERSION (WEIGHT %) NEW REACTOR
WYODAK	DHP	425	5	66.2 %	66.2 %
WYODAK	A - 8	425	5	29.6 %	30.9 %
ILL. #6	DHP	350	30	83.6 %	82.6 %
ILL. #6	DHP	425	5	89.2 %	89.9 %
ILL. #6	A - 8	425	5	45.5 %	43.5 %

properly sealed, and the valve on the reactor assembly was closed. If a continual pressure drop was observed, applying liquid leak detector to the joints of the reactor assembly usually divulged the location of the leak. Once the leak was sealed, the reactor was hooked up again, and repressurized until it was properly sealed. After the reactor valve was closed, the pressurized reactor was removed from the system and reweighed to estimate the mass of hydrogen added to the reactor. The second reactor was then loaded, pressurized and weighed following the same procedure.

Once both reactors were loaded, they were re-attached to the reciprocating arm using adjustable hose clamps. The reactor valves were also secured to the arm by means of a horizontal flange around the arm to which bolts from the valve bodies were attached. The thermocouple was then attached to the reciprocating arm by means of a short length of wire. If any part of either reactor assembly exhibited excessive play, the loose part was reattached and tightened prior to the start of the run.

At this point, the reciprocating motor was started, the sand bath hoist was raised, immersing the reactors in the fluidized bath, and the timer was started. The time required for the reactor contents to rise to reaction temperature was usually less than 2 min. for low severity runs

(350 °C) and less than 3 min. for high severity runs (425 °C). At the end of the desired reaction time, the sand bath was lowered and the reactors were cooled with compressed air followed by immersion into a cold water bath. The reactors were then detached from the reciprocating arm, and blown free of water and fluidizing sand with compressed air. At this point, each reactor was weighed, degassed under a hood, or into an appropriate gas sampling cylinder, and reweighed to estimate the mass of gas removed.

4.3 Liquefaction Product Recovery

In order to calculate the extent of coal liquefaction based upon conversion to tetrahydrofuran soluble products, all reaction products had to be quantitatively recovered from the reactor assembly and washed with tetrahydrofuran (THF). This enabled the use of THF as wash solvent for cleaning the reactor head and body. The reactor body was repeatedly rinsed and agitated with THF, and the THF/product slurry was collected into a pre-weighed centrifuge tube. This process was repeated with both the body and if necessary, the head of the reactor, until any THF removed from the reactor parts remained clear. The centrifuge tubes for each reactor were then filled to equal levels with additional THF, and centrifuged at 2000 rpm for 15 min. Excess

THF was decanted from each of the tubes and fresh THF added. The tubes were then sonically agitated in a water bath for 10 min. to promote complete mixing of the fresh THF with the centrifuge residue. This centrifugation process was repeated until THF decanted from the tubes remained clear. Three washes with THF were usually sufficient to obtain clear THF upon decantation. The centrifuge tubes and each clean reactor body were then placed in a 125 ^{o}C oven overnight, to remove all residual traces of THF.

Once the reactor body and the centrifuge tubes were dried, they were removed from the oven, and were allowed to cool. The centrifuge tubes were weighed in order to determine the mass of THF insoluble products. The reactor body was also weighed, and any gained weight was assumed to be due to traces of THF insoluble material left behind from the reactor cleanout process. For the majority of liquefaction experiments, the weight gain of the reactor body was zero, indicating that the reactor had been thoroughly rinsed. If any weight gain was recorded, it was added to the weight of THF insolubles collected in the centrifuge tubes.

5. MOISTURE FRACTION DETERMINATION

The amount of moisture present in the feed coal was determined by taking a representative sample of the coal charged to the reactor, and performing a weight loss upon drying analysis. Weight lost upon drying was determined by weighing a sample of coal placed in a crucible of known mass. The crucible was placed in a 125 ^{o}C oven overnight, removed, and cooled in a vacuum desiccator. The crucible was reweighed and the loss in weight upon drying was divided by the starting weight of coal, giving a weight fraction loss upon drying which was assumed to be moisture loss. The weight loss analysis was performed in duplicate in order to minimize error in the moisture content calculation; it was found that the two samples always agreed within 2.0 wt%. The moisture content of the THF insoluble material was assumed to be zero due to the drying of the THF insoluble material overnight at 125 ^{o}C.

6. ASH FRACTION DETERMINATION

Coal conversion for all samples liquefied or co-processed is calculated on a moisture and ash free basis, resulting in the need to have an accurate measurement of the ash fraction in each coal. The ash fractions of all coal samples used in the study are listed in Table VI. Ash fractions for the untreated coals were as determined by Argonne National Laboratories, which supplied the coal used in this study (1). Ash fraction of pretreated coal samples were determined by Huffman Laboratories, of Golden, Colorado.

TABLE VI

Ash Fractions Of Untreated and Pretreated Coals On A Moisture Free Basis

	PRETREATMENT METHOD			
COAL	UNTREATED	CC/MAP	LIOTTA	STERNBERG
WYODAK	0.0877	0.0783	0.0656	0.1268
ILLINOIS #6	0.1548	0.1590	0.1434	0.1487

CC/MAP:	Chlorine Catalyst/Mild Alkylation Pretreatment
LIOTTA:	Oxygen Alkylation Pretreatment
STERNBERG:	Reductive Alkylation Pretreatment

TABLE VII

Number Of Alkyl Groups Added To Parent Coal

By Mild Pretreatment

COAL	PRETREATMENT METHOD (alkyl groups/100 C atoms) CC/MAP (1)	STERNBERG (2)	LIOTTA (1)
WYODAK	1.5	5.7	8.0
ILL. #6	---	6.7	4.7

(1) methyl group addition
(2) ethyl group addition

1.1 Oxygen Alkylation

Oxygen alkylation using the Liotta procedure resulted in the addition of 8.0 methyl (CH_3) groups/100 C atoms for the subbituminous coal and 4.7 methyl groups/100 C atoms for the bituminous coal. Subbituminous coal has a higher oxygen content with more oxygen functionalities present within the coal as compared to the bituminous coal. Because O-alkylation is oxygen selective, the coal with more oxygen undergoes a greater extent of alkylation during the Liotta pretreatment process.

1.2 Reductive Alkylation

Reductive alkylation using Sternberg's procedure added 5.7 ethyl groups/100 C atoms to the subbituminous coal and 6.7 ethyl groups/100 C atoms to the bituminous coal. Reductive alkylation is a non-selective alkylation occurring primarily at polar chemical sites within the coal, which is confirmed by the small difference in the extent of alkylation for the coals of different rank. Some oxygen alkylation does occur because of the polar nature of most oxygen functionalities, but its effect is not significant when compared to the reductive alkylation of carbon sites in the coal structure.

1.3 Chlorine Catalyst/Mild Alkylation Pretreatment

1.3.1 Extent Of Alkylation

Selected coals which were pretreated via the chlorine catalyst/mild alkylation pretreatment (CC/MAP) procedure were also subjected to ultimate analysis in order to determine the extent of alkylation during pretreatment. The CC/MAP procedure resulted in the addition of 1.5 methyl groups/100 C atoms to the subbituminous coal. This small extent of alkylation is indicative of the very mild reaction conditions used in this procedure. Although alkylation does take place, the magnitude of alkyl group incorporation is much lower than in the other procedures where alkylation is the sole means of coal pretreatment. The extent of alkylation attained in the bituminous coal using this procedure was not measured.

1.3.2 Extent Of Chlorine Incorporation

Untreated Wyodak coal has a chlorine content of 0.18% by weight, but the chlorine content of the pretreated coal was found to be 2.41% by weight. This shows that pretreatment via the chlorine catalyst/mild alkylation procedure does result in the incorporation of a significant amount of chlorine into the coal structure. During liquefaction, chlorine is possibly converted to hydrochloric acid (HCl) which acts as a strong hydrocracking catalyst. Although the amount of chlorine initially present is small, the subsequent HCl formed may have a significant impact upon coal conversion under liquefaction conditions. The amount of chlorine present in pretreated Illinois #6 coal was not measured, but may be assumed equivalent in proportion to the concentration incorporated into the Wyodak coal samples.

2. INTRINSIC THF SOLUBILITY OF UNTREATED AND TREATED COALS

In order to use coal conversion to THF soluble products as a measure of coal reactivity, the intrinsic THF solubility of both untreated and pretreated coals had to be determined. The intrinsic THF solubility of each coal was determined on a moisture and ash free (MAF) basis (Table VIII). These solubilities were determined by adding a known mass of coal to a centrifuge tube and applying the same THF extraction process used in Section 4.3 of the Experimental Procedure. The fraction of the original coal sample lost to THF extraction represented the intrinsic THF soluble portion of the coal.

The difference between the intrinsic THF solubility of a raw coal and the same coal after pretreatment reflects the effect of the pretreatment process upon the coal. Untreated Wyodak coal had an intrinsic THF solubility of 1.6 wt. %,

TABLE VIII

Intrinsic THF Solubilities Of Untreated And Pretreated Coals

(wt fraction on a MAF basis)

COAL	UNTREATED	CC/MAP	LIOTTA	STERNBERG
		PRETREATMENT METHOD		
WYODAK	0.0163	0.0586	0.1359	0.0000
ILLINOIS #6	0.1193	0.1172	0.2532	0.0648

CC/MAP:	Chlorine Catalyst/Mild Alkylation Pretreatment
LIOTTA:	Oxygen Alkylation Pretreatment
STERNBERG:	Reductive Alkylation Pretreatment

but after pretreatment using the Liotta procedure, the intrinsic THF solubility was 13.6 wt. %. The difference between these two values represents the effect of Liotta's oxygen alkylation upon Wyodak coal prior to liquefaction. The effect of Sternberg's method upon the treated coal cannot be determined, because Sternberg's procedure involves rinsing the coal with THF during the alkylation procedure. Any increase in THF solubility brought about by the pretreatment is washed away by THF. Table VIII reflects this fact, where the intrinsic THF solubility of both Wyodak and Illinois #6 coal after pretreatment with Sternberg's procedure is lower than the THF solubility of the untreated coal.

3. CALCULATION OF COAL CONVERSION

Coal reactivity was based upon the conversion of THF insoluble coal to THF soluble products on a moisture and ash free basis using the following equation:

$$\text{THF Coal Conversion} = \frac{(I - O)}{I} * 100\%$$

where:

I = (g of coal in)*(1-ash fraction)*(1-moisture fraction) *(1-intrinsic THF soluble fraction of feed coal)

O = (g of THF insoluble material recovered)*(1-fraction ash)

Intrinsic THF soluble matter in the feed coal was estimated using the intrinsic THF solubilities shown in Table VIII. Because intrinsic THF solubilities are accounted for, the conversion equation above estimates the effect of pretreatment upon coal reactivity under liquefaction or co-processing conditions.

4. REACTIVITY PARAMETER MATRIX

Coal conversion results for the reactivity parameter matrix studied are shown in Table IX. The non-alkylated THF coal conversions are for liquefaction/co-processing of the untreated coal samples at each set of reactivity conditions. For each of the pretreatment methods listed (including no pretreatment), the THF coal conversion represents a mean value of repeated reactivity experiments. The percent increase in conversion shown in Table IX was calculated with respect to the corresponding untreated coal conversion.

The raw data used to generate the values listed in the reactivity parameter matrix can be found in Appendix A. Mean values were calculated from repeated trials for each set of reactivity conditions. In situations where repeated trials showed a large difference in the coal conversion values, additional trials at the same conditions were conducted. All trials were then used to calculate an estimate of the mean.

TABLE IX

Completed Reactivity Parameter Matrix

COAL	SOLVENT	TEMP deg C	TIME min	NON-ALKYLATED THF COAL CONVERSION	CC/MAP METHOD		LIOTTA METHOD		STERNBERG METHOD	
					THF CONV.	% INCR. IN CONV.	THF CONV.	% INCR. IN CONV.	THF CONV.	% INCR. IN CONV.
WYODAK	DHP	350	5	14.6	25.6	74.8	32.1	119.2	30.1	105.3
			30	38.7	51.4	33.0	53.6	38.5	64.7	67.2
		425	5	65.4	82.6	26.2	76.8	17.5	79.6	21.6
			30	87.9	89.7	2.0	88.9	1.1	90.0	2.4
	COLD LAKE ATM. RESID	350	5	-0.2	5.4	0.0	-2.4	0.0	10.2	0.0
			30	15.0	20.3	35.7	28.5	90.6	32.8	118.9
		425	5	28.4	39.0	37.2	49.1	72.6	59.5	109.1
			30	69.3	59.1	-14.7	71.6	3.3	63.3	-8.7
ILLINOIS #6	DHP	350	5	37.1	48.2	29.7	46.1	24.0	47.5	27.9
			30	81.3	86.5	6.4	84.6	4.0	83.2	2.3
		425	5	87.7	91.0	3.8	89.0	1.4	86.8	-1.1
			30	89.8	88.0	-2.0	90.9	1.3	84.9	-5.4
	COLD LAKE ATM. RESID	350	5	-1.0	7.0	0.0	-18.5	0.0	11.4	0.0
			30	28.7	34.6	20.5	10.6	-63.3	40.4	40.8
		425	5	38.5	38.5	0.1	32.6	-15.2	65.2	69.5
			30	38.0	56.8	49.4	28.2	-25.9	59.4	56.1

CC/MAP	: Chlorine Catalyst/Mild Alkylation Pretreatment
DHP	: Liquefaction Solvent
Cold Lake atmospheric residuum	: Co-Processing solvent
Reaction Gas	: Hydrogen
Pressure	: 1000 psig cold

Trials which were suspected as outlying data points were subjected to a one tailed t-test. Mean coal conversion was calculated without the suspect point, and the probability of the conversion being less or equal than the suspect point, given the "new" mean conversion, was calculated. If this probability was < 5 wt. %, then the suspect point was not used in the estimate of the mean, and the "new" mean conversion was used.

A five factor analysis of variance (ANOVA) was conducted using reactivity runs for the untreated and the CC/MAP pretreated coals at all combinations of reactivity conditions (Appendix B). It was found that the standard deviation between repeated trials at any one set of conditions was +/- 4.3 wt. %. This means that the amount of random error between trials for any set of conditions is +/- 4.3 wt. %. Although only data from the untreated coal and chlorine catalyst/mild alkylation treated coal samples were used in this analysis, it is assumed that the random error calculated in the analysis of variance also applies to runs made using the Liotta and Sternberg treated coals.

All values used in the subsequent discussion of liquefaction and co-processing reactivity experiments are taken from mean values tabulated in Table IX.

5. LIQUEFACTION REACTIVITY EXPERIMENTS

Prior to performing liquefaction experiments involving pretreated coal samples, the baseline reactivity data for untreated coal using dihydrophenanthrene (DHP) as a liquefaction solvent was determined. In the following discussion, the different combinations of liquefaction reactivity conditions are divided into two groups: low severity parameter combinations (350 °C) and high severity parameter combinations (425 °C). The individual contributions of coal rank and reaction time are more easily observed at each level of severity when this distinction is made.

Baseline reactivity data for both low and high severity liquefaction of untreated coal is shown in Figure 3. At both low and high severity conditions, coal conversion is a function of coal rank, with bituminous coal (Illinois #6) exhibiting a higher conversion to THF solubles than subbituminous coal (Wyodak) for all combinations of time and temperature. These results agree with other coal liquefaction studies where bituminous coal was found to have a higher baseline conversion than subbituminous coal.

At low severity liquefaction conditions reaction time is an important factor, more than doubling the THF conversion of both ranks of coal when the reaction time is increased from 5 to 30 min. Conversion of Wyodak coal increases from

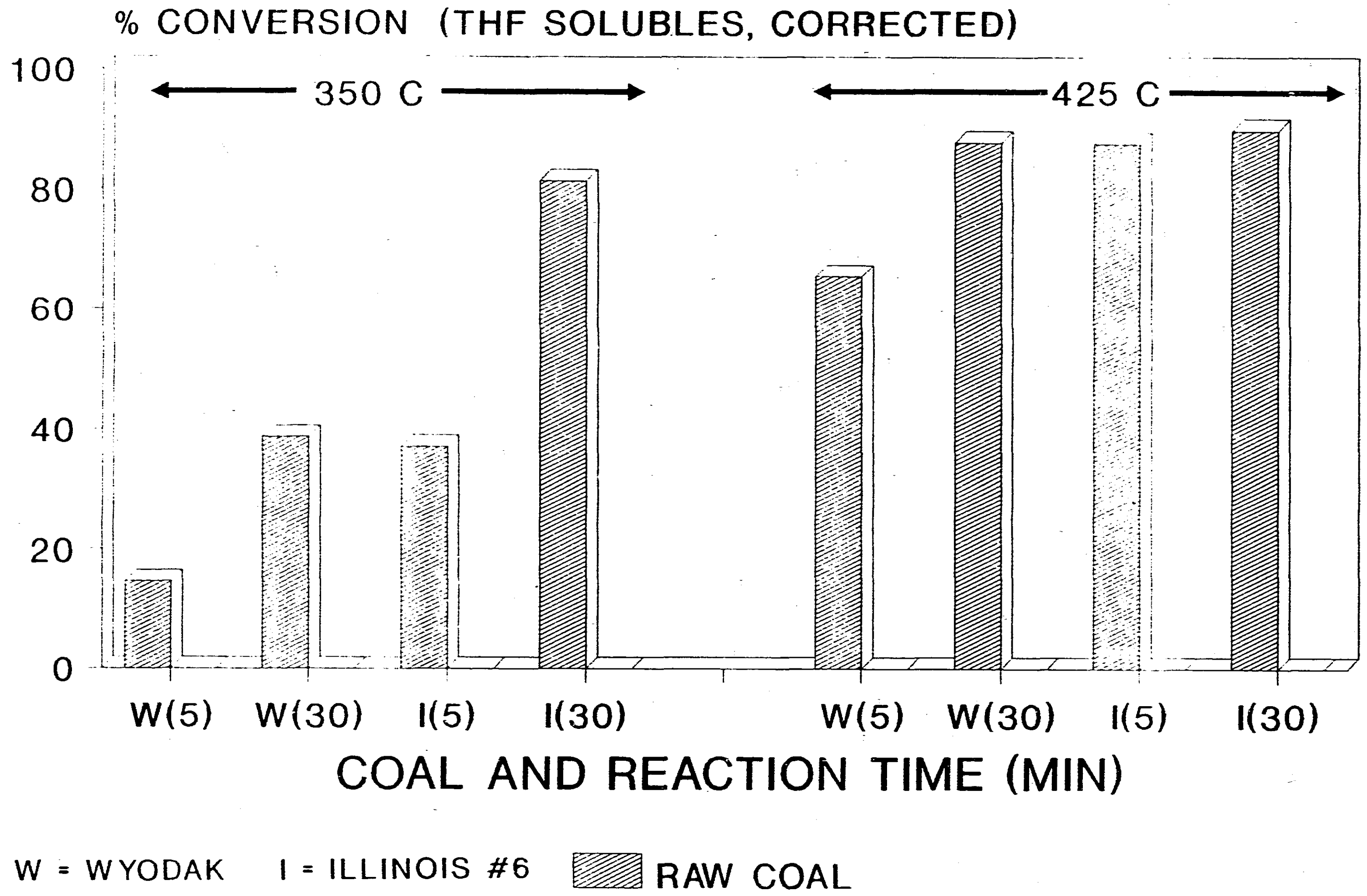


FIGURE 3

Baseline Conversions For Untreated Coal
Under Liquefaction Conditions

14.6 to 38.7 wt. % while conversion of the Illinois #6 coal increases from 37.1 to 81.3 wt. %.

At high severity liquefaction conditions, Figure 3 shows that the baseline coal conversions for the untreated coals are higher for all coal ranks and reaction times when compared to the conversions observed at low severity. The conversion for the Wyodak coal increases from 65.4 to 87.9 wt. % as the reaction time is increased from 5 min to 30 min. The conversion for the Illinois #6 coal increases from 87.7 to 89.8 wt. % for the same corresponding increase in reaction time.

This suggests that for high severity liquefaction using DHP as a solvent, the maximum attainable limit for conversion is close to 90 wt. %. The high rank coal approaches this conversion limit after only 5 min of liquefaction time. Increasing the liquefaction time beyond 5 min results in a negligible increase in coal conversion. For the low rank coal, the conversion attained in 5 min of reaction time is 65.4 wt. %. However, when the reaction time is increased to 30 min, conversion of the low rank coal also approaches this conversion limit of about 90%.

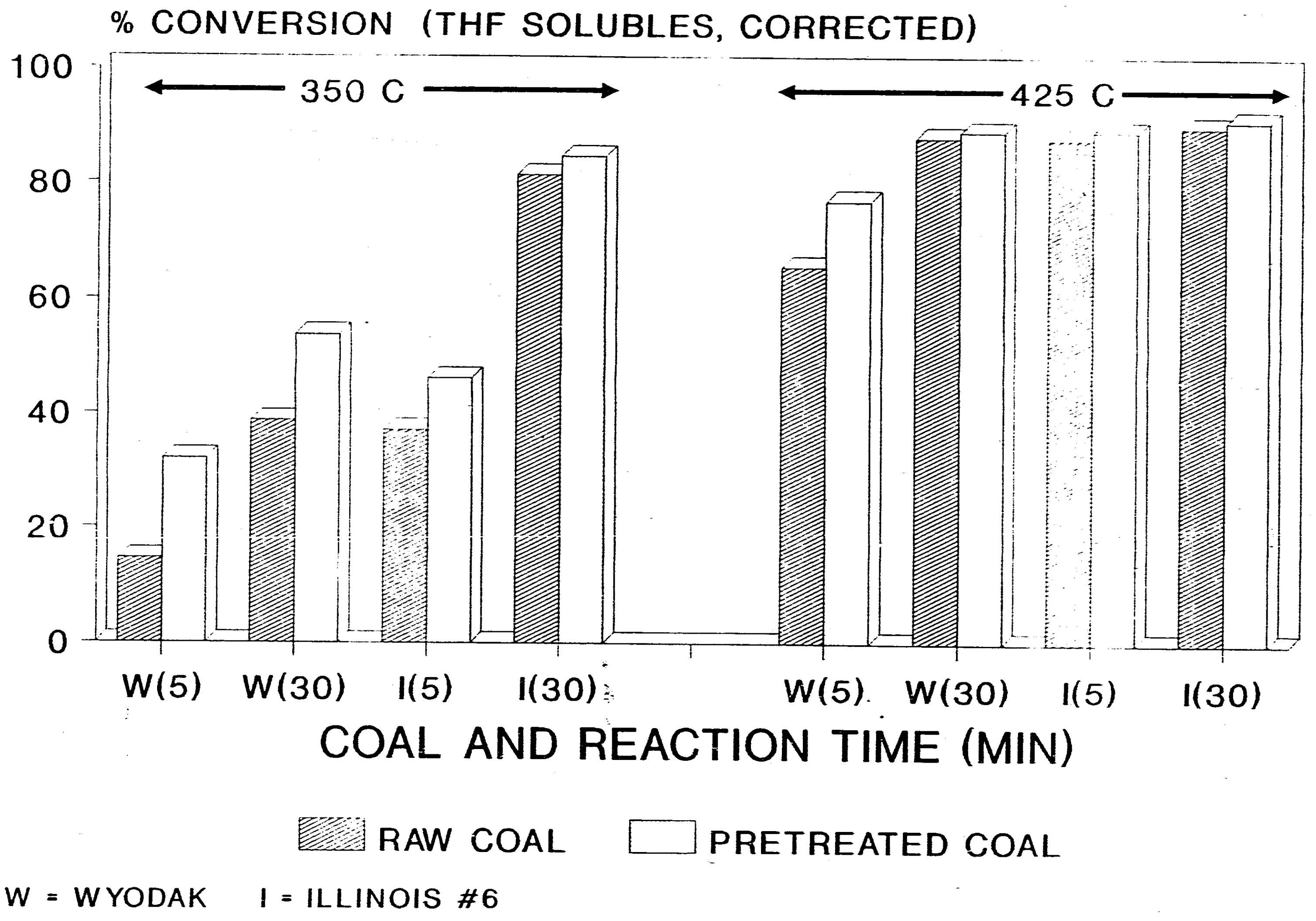


FIGURE 4

Effect Of Pretreatment On Liquefaction, Liotta Procedure oxygen functionalities which are converted to less polar ether linkages, perhaps preventing the phenolic functionalities from participating in retrogressive reactions. In a model compound study, McMillen showed that hydroxyl coupling reactions resulted in peroxide bond formation, hence generating reaction products which were highly refractory (5).

$$R_1\text{-OH} + R_2\text{-OH} \dashrightarrow R_1\text{-O-O-}R_2 + H_2$$

McMillen observed that these coupling reactions were strongly promoted at 400 °C. The formation of these products can be considered representative of the retrogressive reactions observed in low rank coal under certain liquefaction conditions. Even though low severity liquefaction experiments were carried out at a lower temperature (350 °C) than the conditions used by McMillen (400 °C), pretreatment via oxygen alkylation may still result in a greater degree of reactivity enhancement in the low rank coal by chemically altering the coal functionalities which are prone to retrogressive reactions.

High severity liquefaction (425 °C) of coal pretreated with Liotta's procedure shows a lesser degree of reactivity enhancement with respect to the untreated coal as compared to low severity liquefaction (Figure 5). Liquefaction of

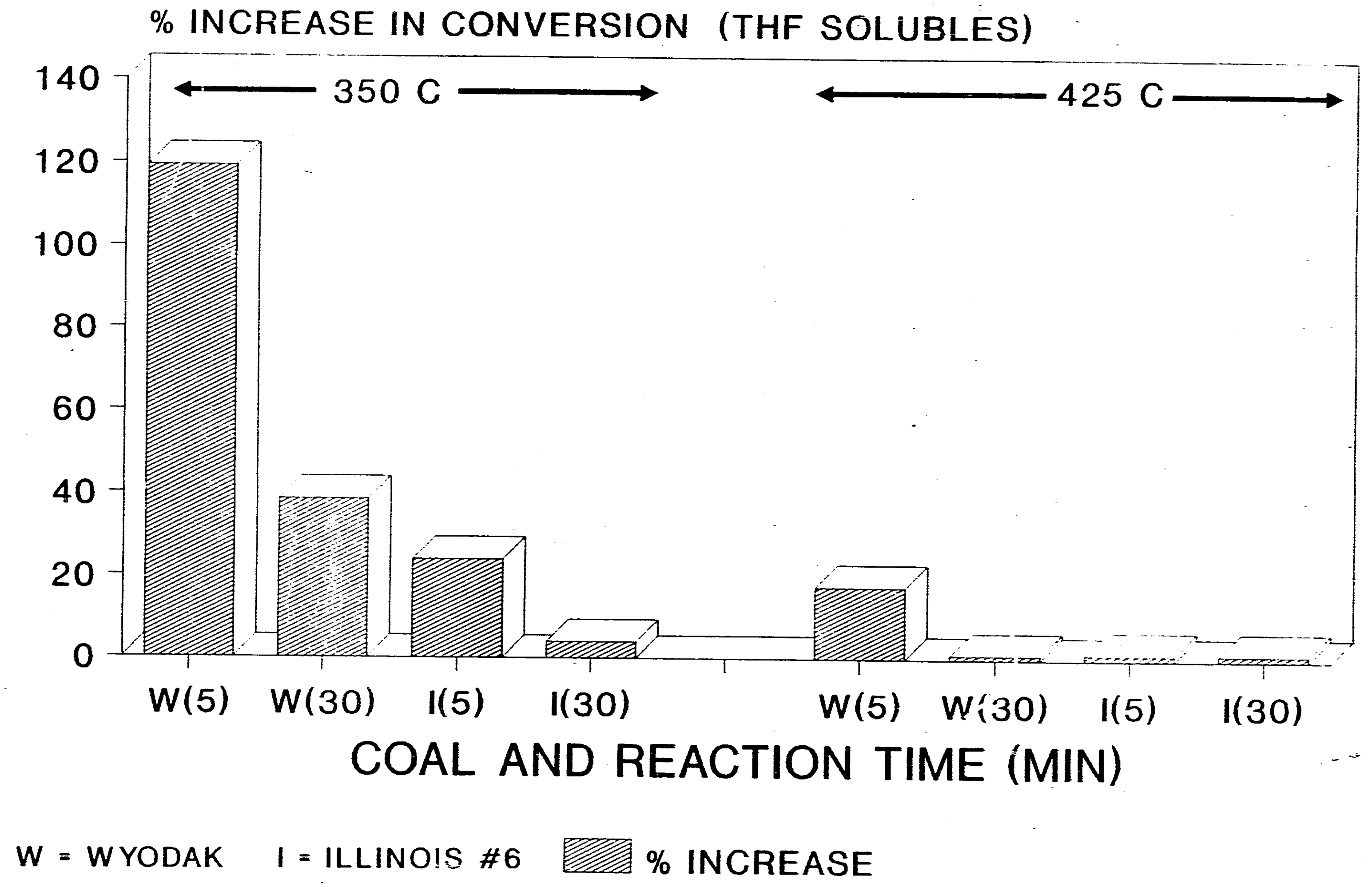


FIGURE 5

Percent Increase In Liquefaction Conversion, Liotta Procedure

Wyodak coal at 5 min reaction time was the only case where a significant increase in reactivity relative to the untreated coal was observed with a 17.1% increase in conversion. Within experimental error, the 30 min liquefaction of Wyodak and both liquefaction times of Illinois #6 coal resulted in no coal reactivity enhancement.

This result can be attributed to the fact that at high severity liquefaction conditions the coal conversion is close to the attainable limit. Pretreatment of the feed coal results in a negligible reactivity enhancement because the maximum coal conversion has already been reached. The 5 min liquefaction of the Wyodak coal did result in a significant reactivity increase because the untreated conversion of 65.4 wt. % was well below the point where the limit of conversion is reached.

5.2 Reductive Alkylation Liquefaction Experiments

Data for reactivity studies of coal pretreated using Sternberg's reductive alkylation procedure are shown in Figure 6 along with the baseline coal conversion for each set of reaction conditions. Figure 7 shows the percent increase in conversion for the pretreated coal with respect to the untreated coal for the same sets of reaction conditions.

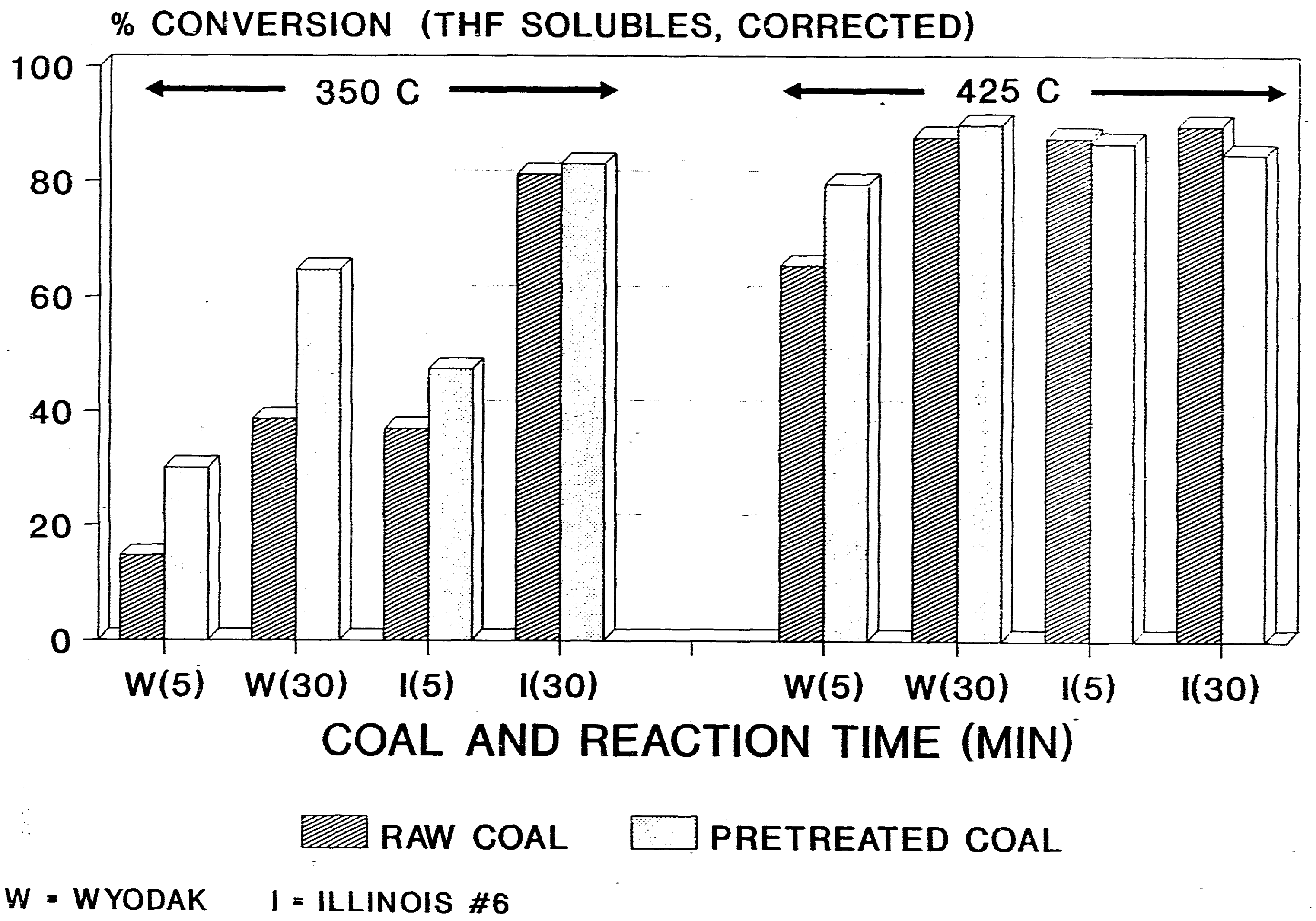


FIGURE 6

Effect Of Pretreatment On Liquefaction, Sternberg Procedure

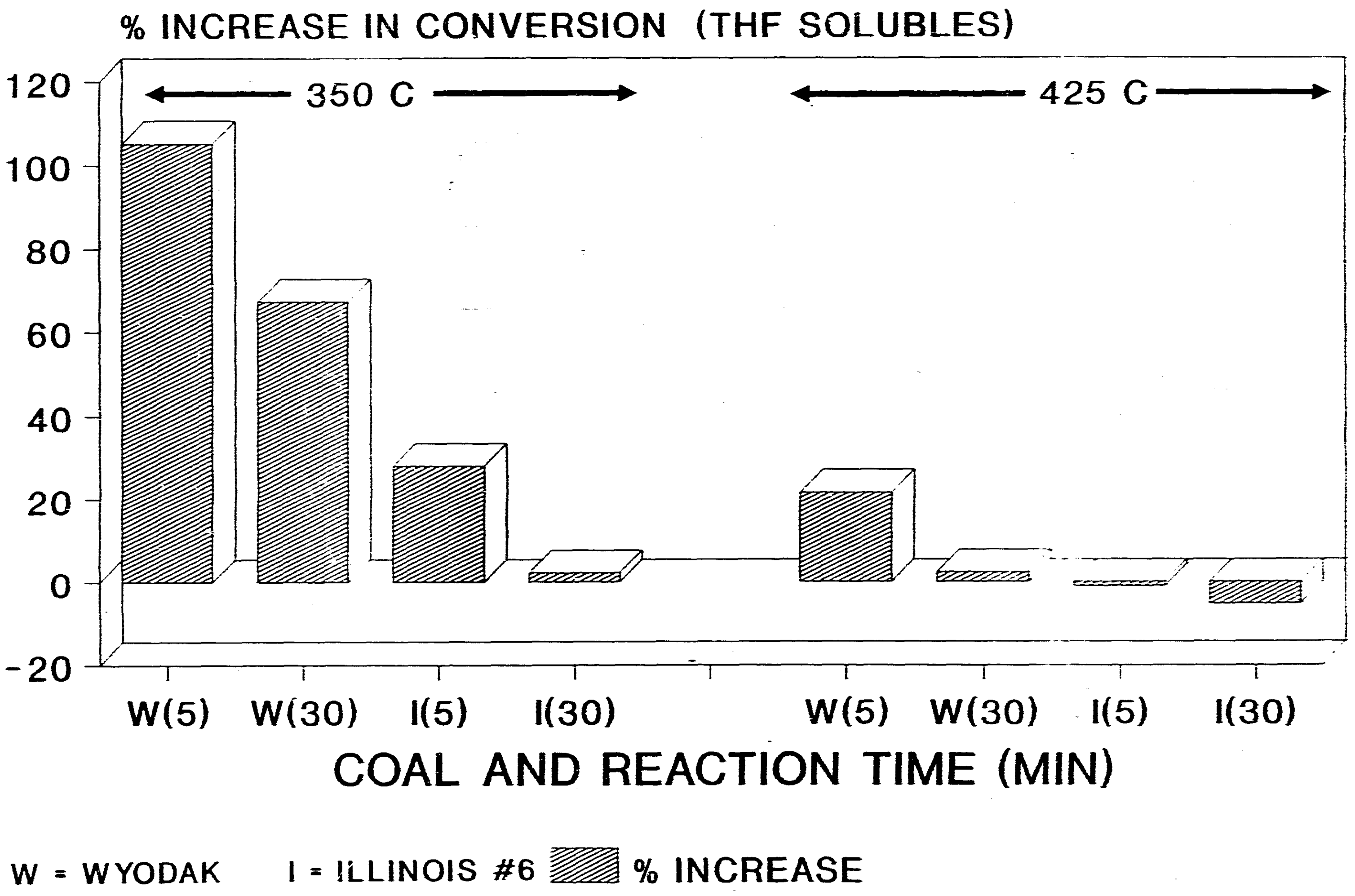


FIGURE 7

Percent Increase In Liquefaction Conversion, Sternberg Procedure

In Figure 7, low severity liquefaction (350 ^{o}C) at a reaction time of 5 min results in a 105.3% increase in conversion for Wyodak coal while Illinois #6 coal shows an increase in conversion of only 27.9%. For a reaction time of 30 min, low severity liquefaction of Wyodak results in a 67.2% increase in conversion while Illinois #6 coal shows only a 2.3% increase in conversion. For both reaction times, Wyodak coal exhibits the greater percent increase in conversion when compared to Illinois #6 coal. The same trend is observed at high severity liquefaction conditions (425 ^{o}C). At a reaction time of 5 min, the percent increase in conversion for Wyodak coal (21.6%) is larger than the percent change for Illinois #6 coal (-1.1%). At a reaction time of 30 min, the percent increase in conversion for Wyodak coal (2.4%) is greater than the percent increase in conversion for Illinois #6 coal (-5.4%).

These trends indicate that Sternberg's reductive alkylation imparts a higher degree of reactivity enhancement to Wyodak coal than to Illinois #6 coal for all combinations of liquefaction reactivity conditions studied. Since reductive alkylation occurs at polar coal sites, resulting in a mild but non-selective alkylation of the coal, the larger concentration of oxygen functionalities in the Wyodak coal doesn't account for the significantly higher degree of reactivity enhancement. Instead, these trends may be due to the fact that the untreated Wyodak coal has a lower inherent reactivity than that seen in the untreated Illinois #6 coal. Because the untreated Wyodak coal has a lower baseline conversion than the untreated Illinois #6 coal, pretreatment of both coals by the same non-selective method may result in a more significant reactivity enhancement in the Wyodak coal.

5.3 Chlorine Catalyst/Mild Alkylation Liquefaction Experiments

Liquefaction conversion data for coal samples pretreated with the chlorine catalyst/mild alkylation pretreatment procedure developed by Armstrong are shown in Figure 8. For each combination of reaction conditions, the baseline conversion for the untreated coal is also displayed. The percent increase in conversion for the pretreated coal compared to the baseline conversion for the untreated coal is shown in Figure 9 for all combinations of reaction conditions.

Conversion data for low severity liquefaction conditions (350 ^{o}C) in Figure 9 indicate that, at both 5 and 30 min reaction times, Wyodak coal exhibits a larger percent increase in conversion than Illinois #6 coal. This result again suggests that the lower the baseline conversion of the untreated coal, the more significant the liquefaction

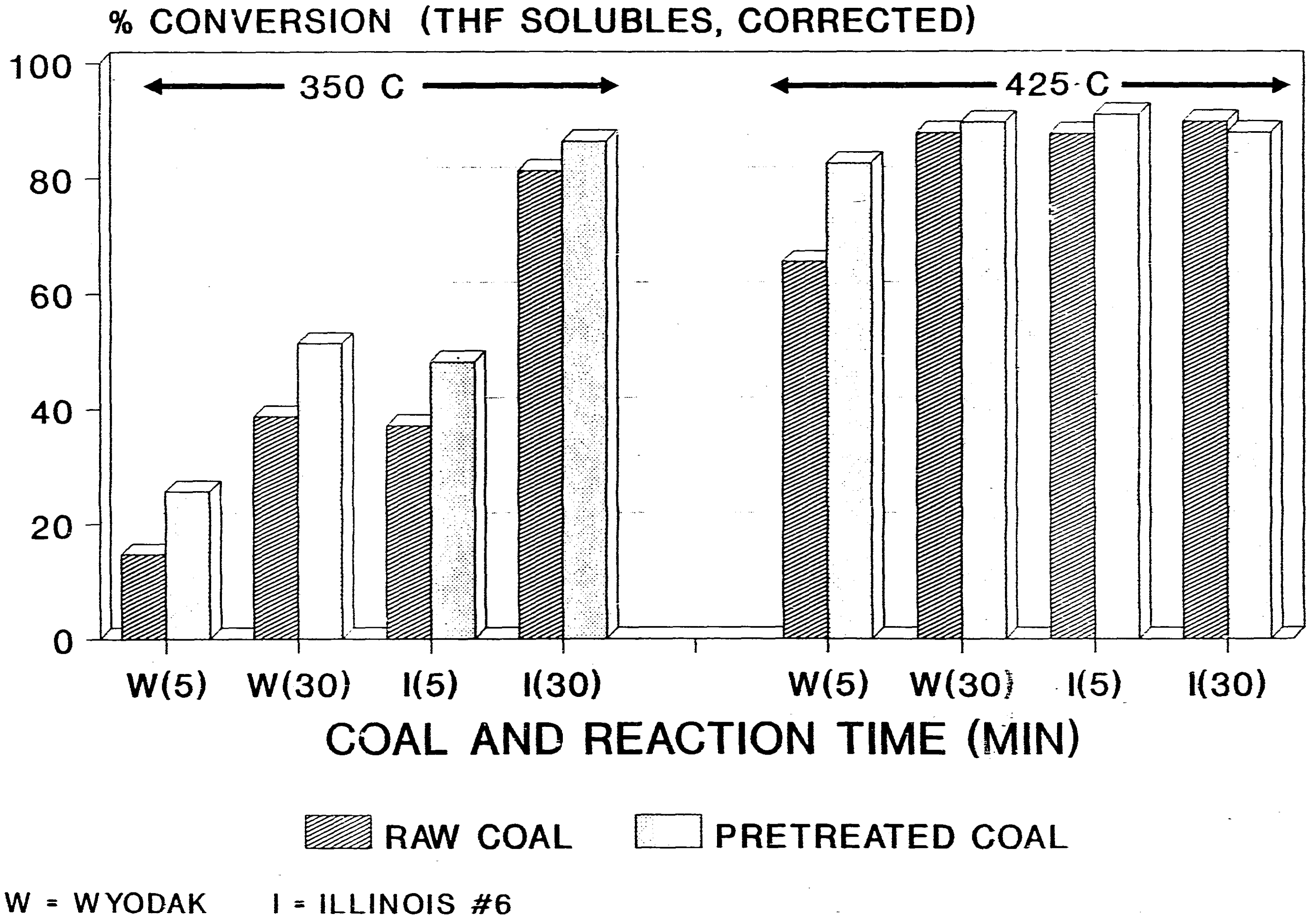


FIGURE 8

Effect Of Pretreatment On Liquefaction, CC/MAP Procedure

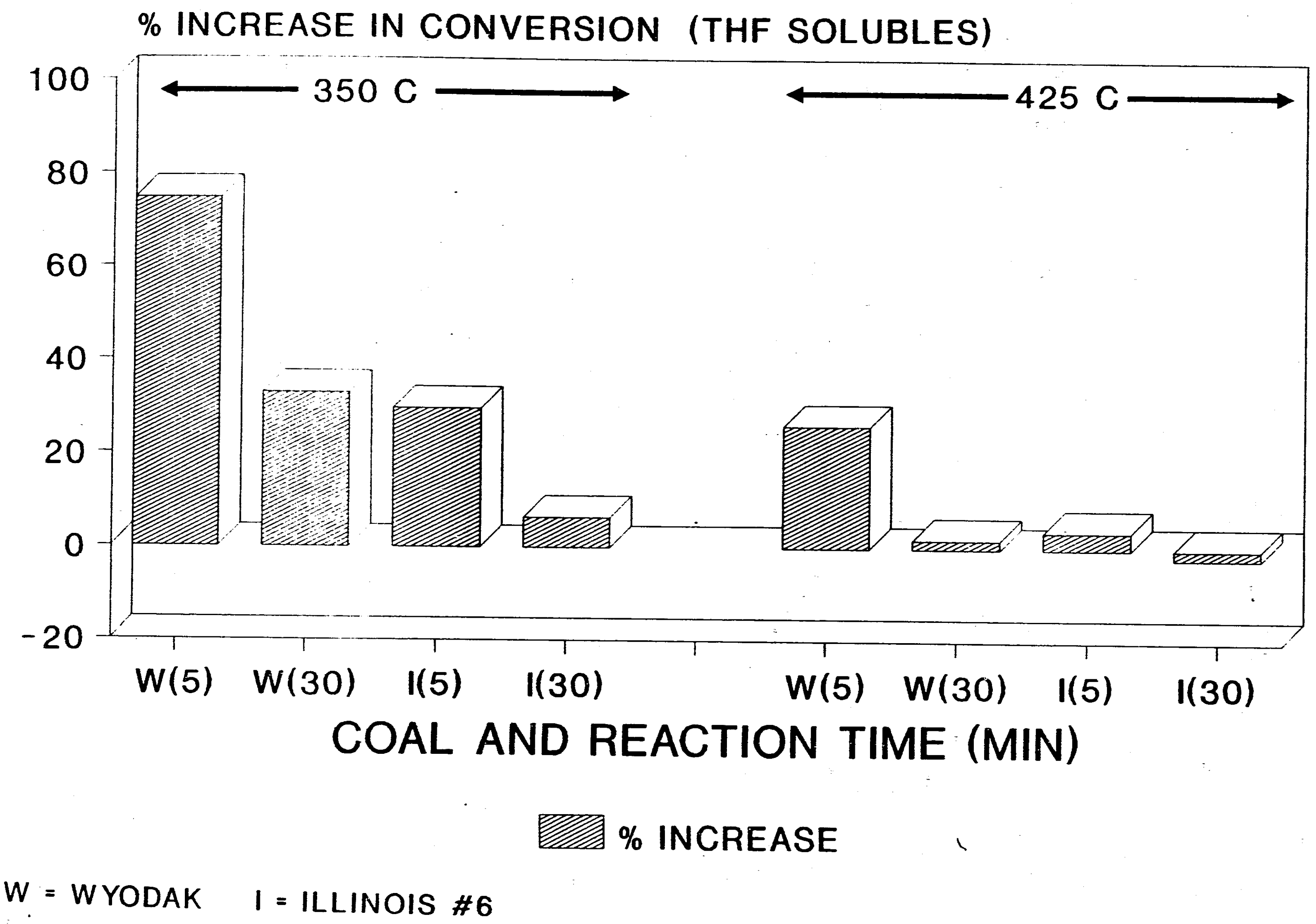


FIGURE 9

Percent Increase In Liquefaction Conversion, CC/MAP Procedure enhancement due to the pretreatment process.

For both Wyodak and Illinois #6 coal, the percent increase in conversion is larger at 5 min reaction time than at 30 min reaction time. This non-linear increase in conversion could be considered a catalytic effect where the activity of HCl catalyst at short reaction times results in an a high degree of initial reactivity enhancement which is obscured at longer reaction times.

Runs at high severity liquefaction conditions (425 ^{o}C) indicate that only Wyodak coal at the 5 min reaction time exhibits a significant increase in reactivity enhancement, with a 26.2% increase in conversion over the untreated baseline conversion. Within experimental error, conversion levels in the other three reaction combinations are identical. This result indicates that under high severity liquefaction conditions, coal pretreatment imparts no reactivity enhancement because coal conversion is already nearly maximized.

6. CO-PROCESSING REACTIVITY EXPERIMENTS

Conversion to THF soluble products was determined for the untreated coal to determine the baseline coal conversion for each combination of co-processing reaction conditions. Mildly hydrotreated Cold Lake atmospheric residuum was used as the co-processing solvent in all experiments. In the following discussion, the different combinations of co-processing reactivity experiments are divided into low and high severity (350 °C and 425 °C) conditions so that the effect of reaction time and coal rank upon reactivity can be more easily appraised at each level of severity.

Figure 10 shows the baseline coal conversion for each combination of low and high severity reaction conditions. For the low severity baseline conversions, the 5 min reaction time resulted in a negative coal conversion for both Wyodak and Illinois #6 coals. These negative conversions may be attributed to adduction of the co-processing solvent into the primary liquefaction products, forming high molecular weight coal/solvent adducts that are insoluble in THF. This results in a mass gain for the THF insoluble products. As the reaction time is increased to 30 min, negative coal conversions are no longer observed. The low rank coal shows a baseline conversion of 15.0 wt. % while the high rank coal shows a baseline conversion of 28.7 wt. %. This trend of increased baseline conversion in the bituminous coal over the subbituminous coal has been observed in numerous liquefaction studies.

At high severity co-processing conditions (425 °C), solvent incorporation does not appear to be a significant

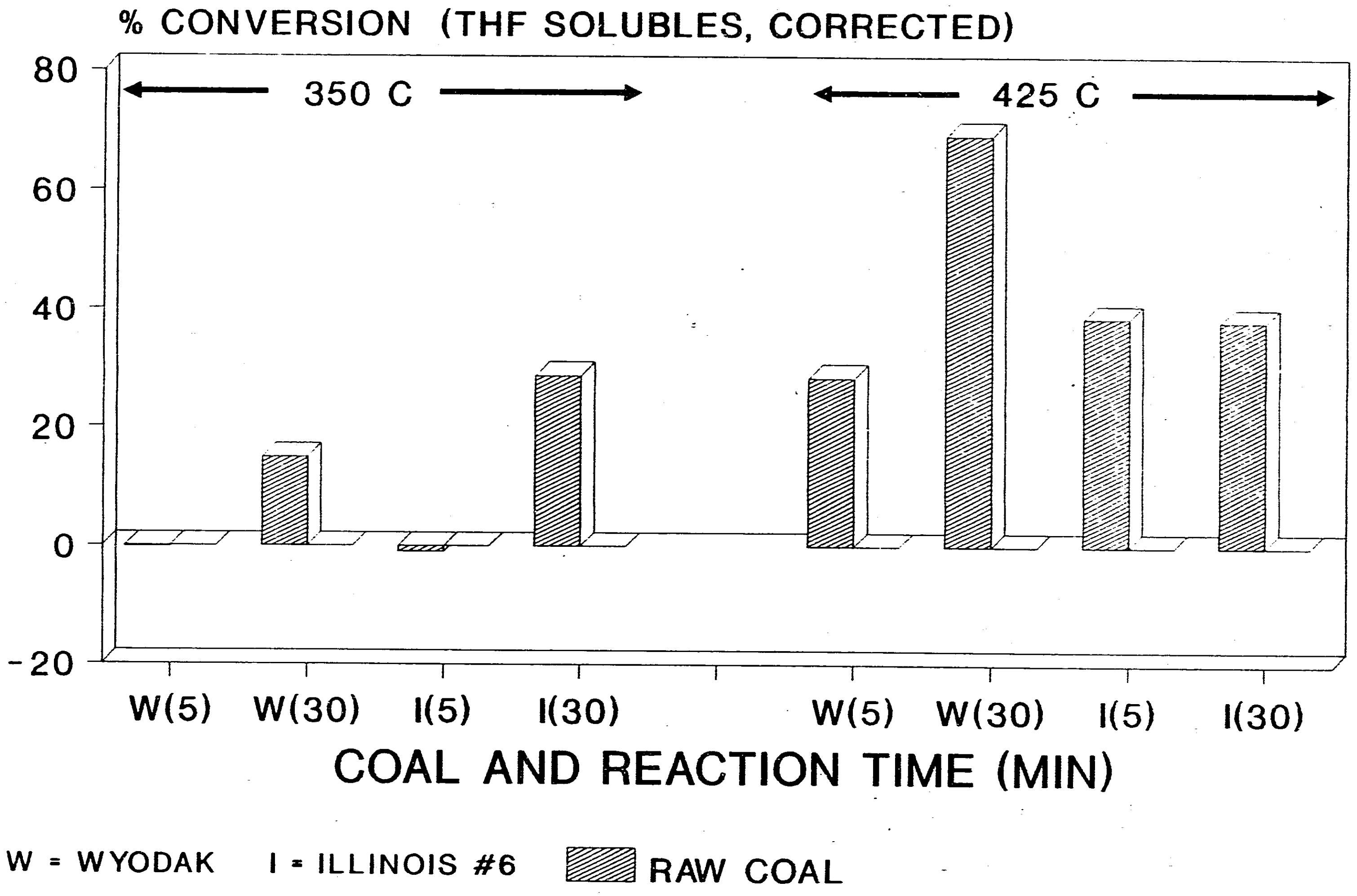


FIGURE 10

Baseline Conversion For Untreated Coal Under Co-Processing Conditions factor. The baseline conversion for untreated Wyodak coal is 28.4 wt. % for a reaction time of 5 min, and 69.3 wt. % for a reaction time of 30 min. This indicates that for low rank coals, reactivity is still significant at longer reaction times, where the conversion increases as a function of time. The baseline conversions for untreated Illinois #6 coal are identical within experimental error for both the 5 and 30 min reaction times (38.5 wt. %, 38.0 wt. %). Although no evidence exists, speculation suggests that coal reactivity at longer reaction times for the high rank coal may be offset by solvent-coal reactions which could be promoted by the higher severity co-processing conditions. The result is that increases in coal conversion due to the higher severity and longer reaction time may be offset by solvent-coal adduction reactions which become more pronounced at longer reaction times, adding mass to the THF insoluble portion of the reaction products.

6.1 Oxygen Alkylation Co-Processing Experiments

Co-processing conversion data for coal pretreated using Liotta's oxygen alkylation method are shown in Figure 11 for each combination of reaction conditions. The percent increase in conversion with respect to the baseline conversion for each combination is shown in Figure 12. At low

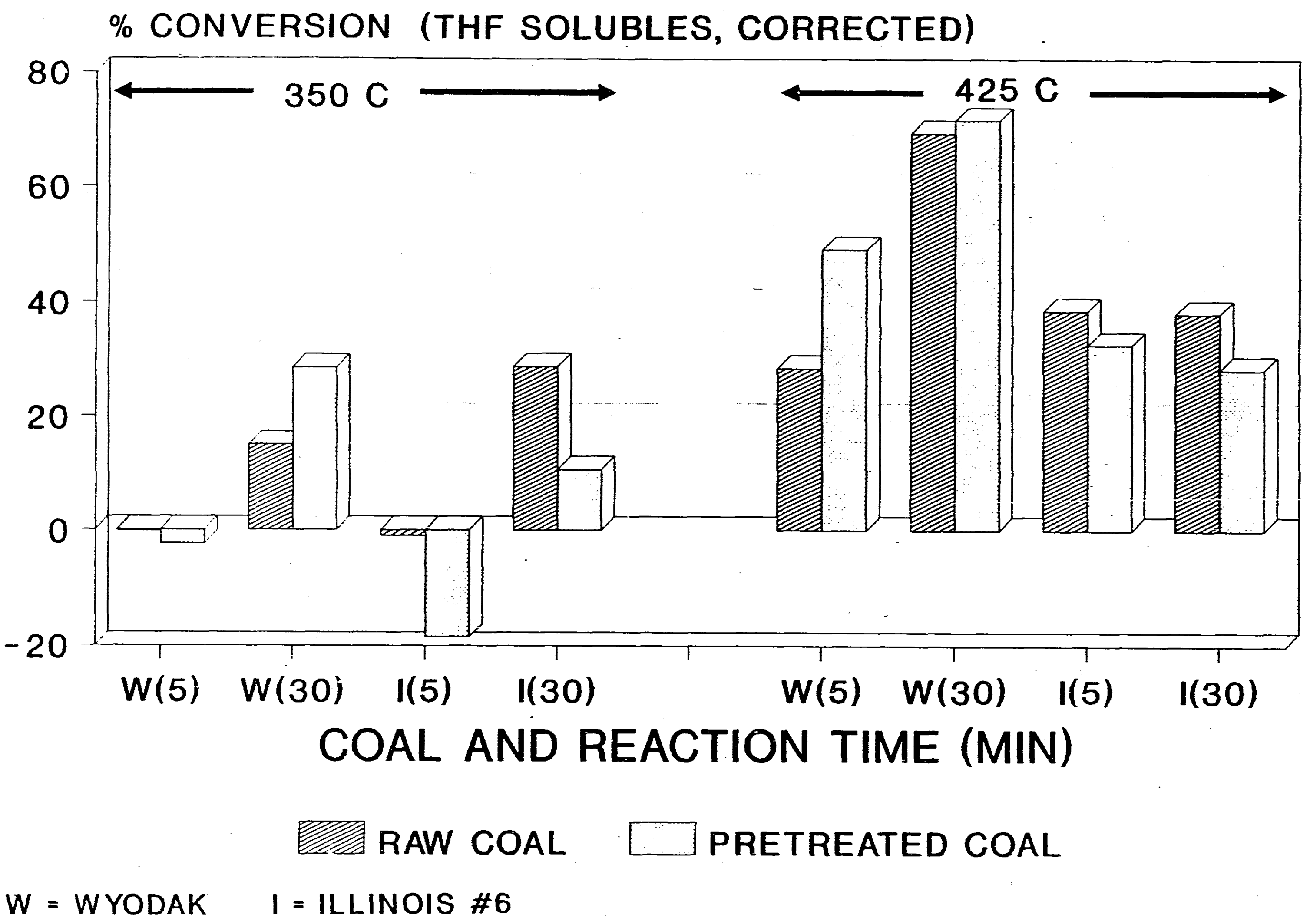


FIGURE 11

Effect Of Pretreatment On Co-Processing, Liotta Procedure

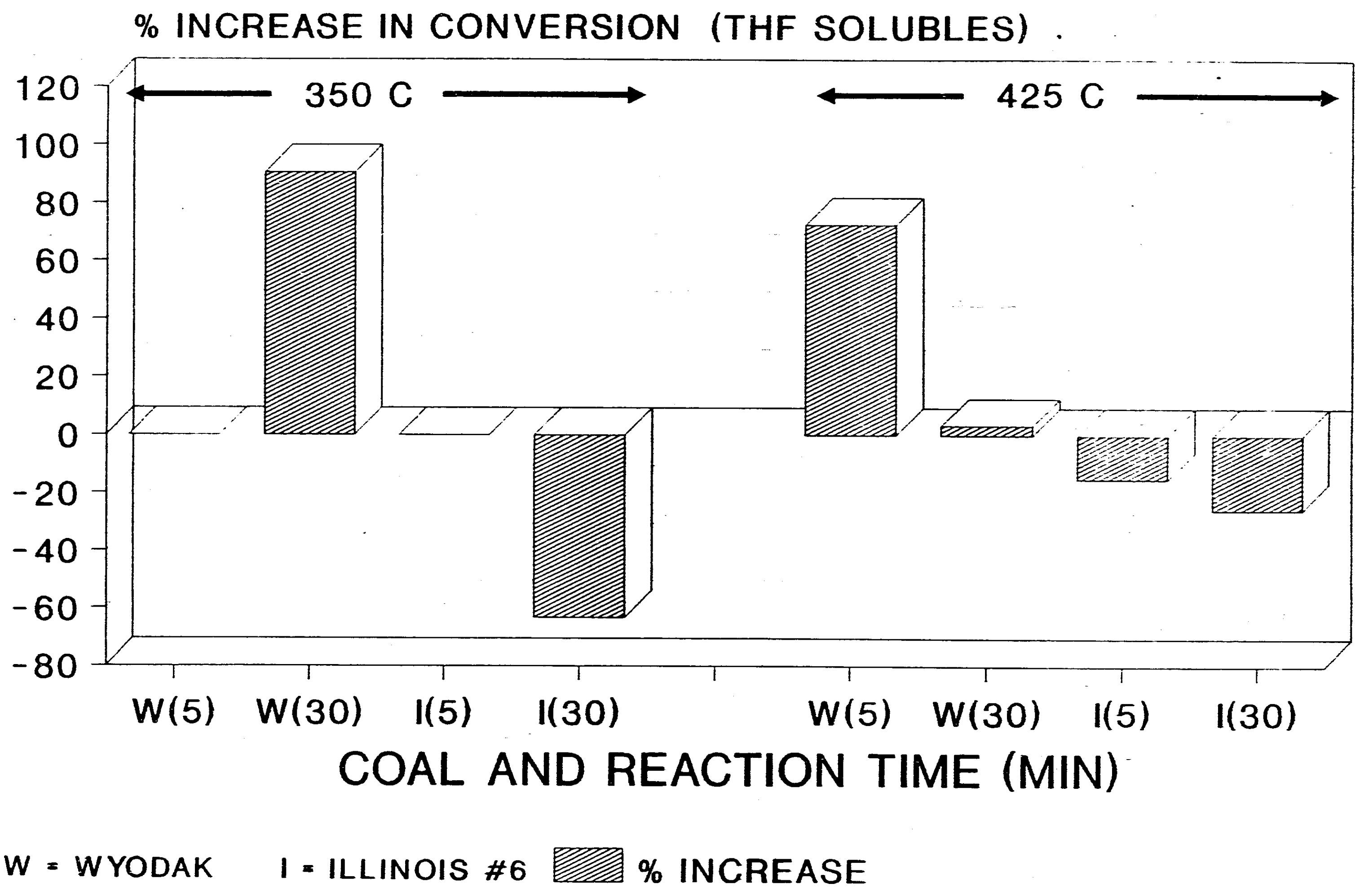


FIGURE 12

Percent Increase In Co-Processing Conversion, Liotta Procedure severity co-processing conditions (350^{o}C) solvent incorporation is significant for both coals at the 5 min reaction time. Coal pretreatment enhances the solvent incorporation effect, further decreasing coal conversion for both Wyodak and Illinois #6 coals. At 30 min reaction time, Wyodak coal exhibits a large conversion increase indicating that pretreatment does result in a significant coal reactivity enhancement. Co-processing of Illinois #6 coal at the 30 min reaction time resulted in a 63.3% decrease in conversion, suggesting that pretreatment enhances the solvent incorporation tendency of the system at longer reaction times.

High severity co-processing (425 ^{o}C) of Wyodak coal resulted in a significant increase in reactivity enhancement at a reaction time of 5 min, but negligible reactivity enhancement at 30 min. This suggests that, at shorter reaction times, coal pretreatment is beneficial to coal conversion, but at longer reaction times the high severity conditions are sufficient to maximize coal conversion, without the aid of the pretreatment. For both 5 and 30 min reaction times, Illinois #6 coal showed a percent decrease in conversion. This indicates that pretreatment of Illinois #6 coal is counterproductive at high severity where retrogressive reactions may be enhanced by the pretreatment process.

6.2 Reductive Alkylation Co-Processing Experiments

Coal conversion data for coal pretreated via Sternberg's reductive alkylation process are shown in Figure 13. Baseline conversion for co-processing of untreated coal is also included in this Figure at each combination of reaction conditions. The percent increase in conversion with respect to the untreated coal at each combination of reaction conditions is shown in Figure 14. At low severity reaction conditions (350 °C), alkylation of Wyodak coal results in an increase in reactivity enhancement at reaction times of both 5 and 30 min (Figure 13). Alkylation of Illinois #6 coal results in a similar increase in reactivity enhancement for both reaction times. Although the Illinois #6 coal achieves a higher ultimate conversion of 40.4 wt. %, Wyodak coal has a lower baseline coal conversion, resulting in a 118.9% increase in conversion while Illinois #6 coal showed only a 40.8% increase in coal conversion (Figure 14).

High severity co-processing (425 °C) of Wyodak coal resulted in a significant increase in reactivity enhancement at 5 min reaction time, but a slight decrease in reactivity enhancement at 30 min reaction time. Once again, the pretreatment process is most beneficial in situations where the baseline coal conversion is low. For 5 and 30 min co-processing experiments using Illinois #6 coal, increases in

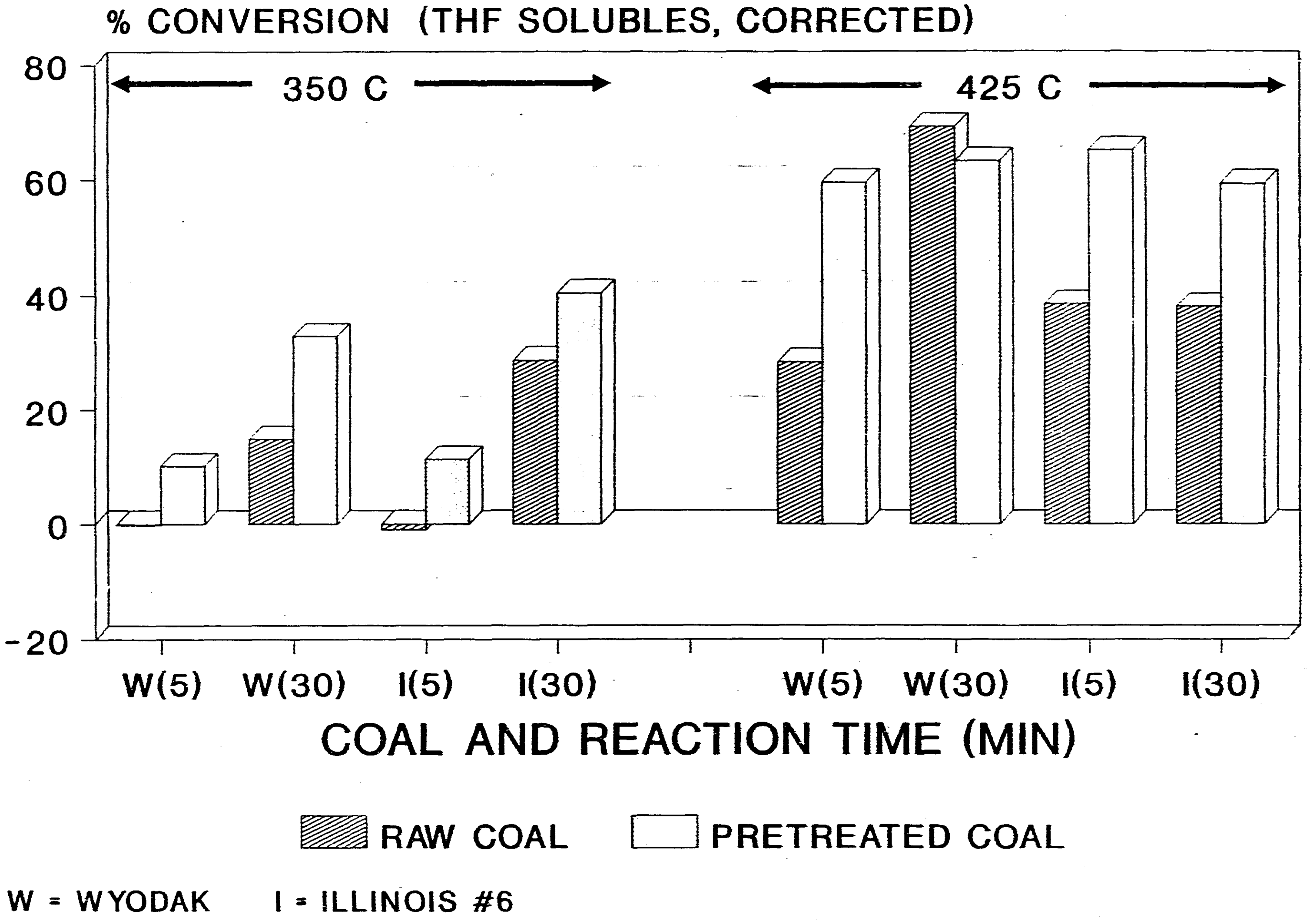


FIGURE 13

Effect Of Pretreatment On Co-Processing, Sternberg Procedure

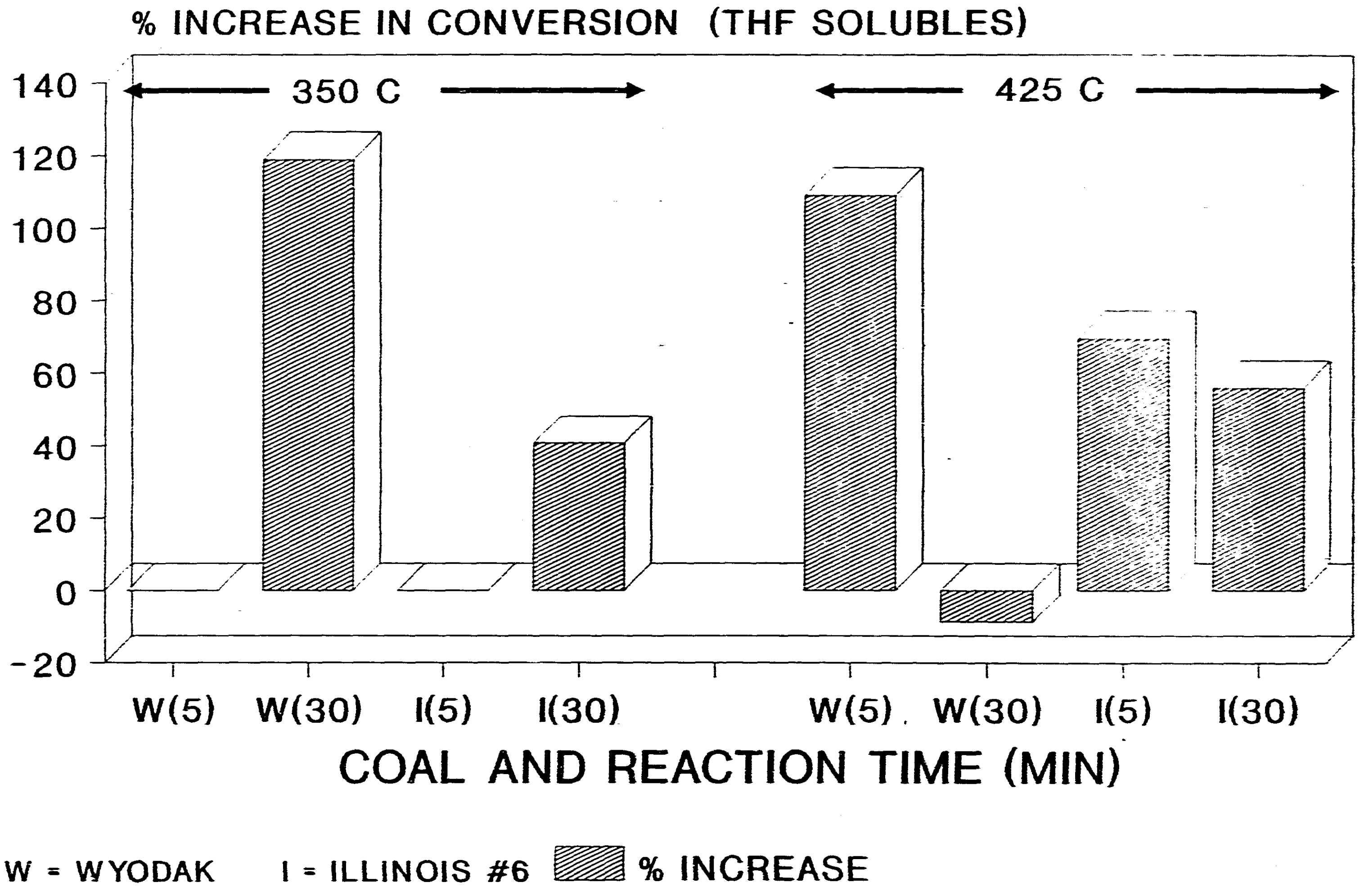


FIGURE 14

Percent Increase In Co-Processing Conversion, Sternberg Procedure conversion of 69.5% and 56.1% were observed. This indicates that for these particular co-processing conditions, reductive alkylation results in a significant increase in reactivity enhancement as reflected in the increase in coal conversion to THF solubles.

6.3 Chlorine Catalyst/Mild Alkylation Co-Processing Experiments

Co-processing reactivity experiments using coal samples pretreated with the chlorine catalyst/mild alkylation pretreatment developed by Armstrong (4) are shown in Figure 15. Baseline conversion of untreated coal at each combination of reaction conditions are also shown for comparison. The percent increase in treated coal conversion with respect to the baseline conversion for each combination of reaction conditions is shown in Figure 16. At low severity co-processing conditions (350 °C) Wyodak coal shows a modest increase in conversion at both 5 and 30 min reaction times. Illinois #6 coal also showed modest increases in conversion at 5 and 30 min reaction times. In Figure 16, the percent increase in conversion for Wyodak at 30 min is higher that the value for Illinois #6 at 30 min because Wyodak has a lower baseline coal conversion. Percent increases for the 5 min reaction times were omitted in Figure 16 because of

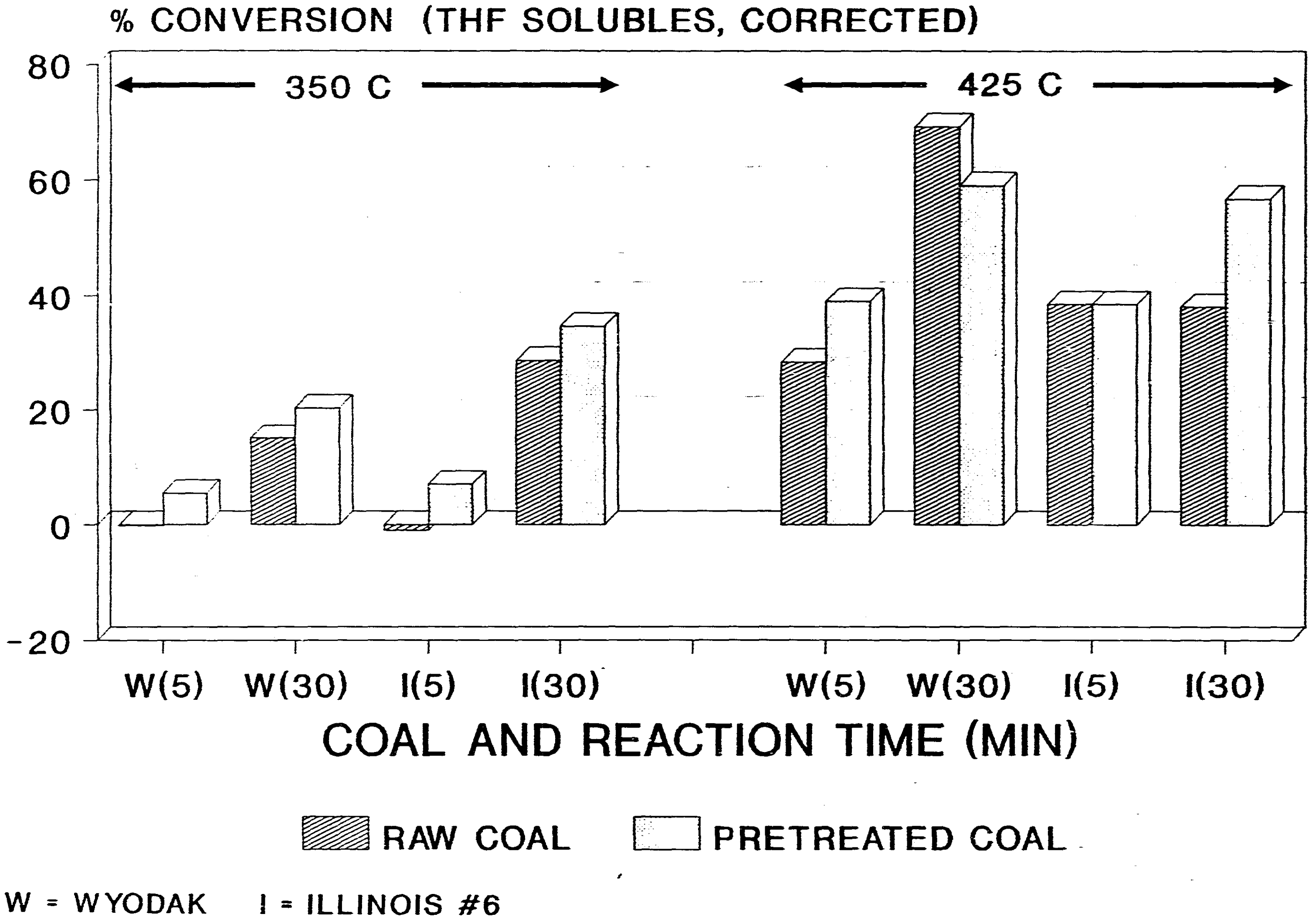


FIGURE 15

Effect Of Pretreatment On Co-Processing, CC/MAP Procedure

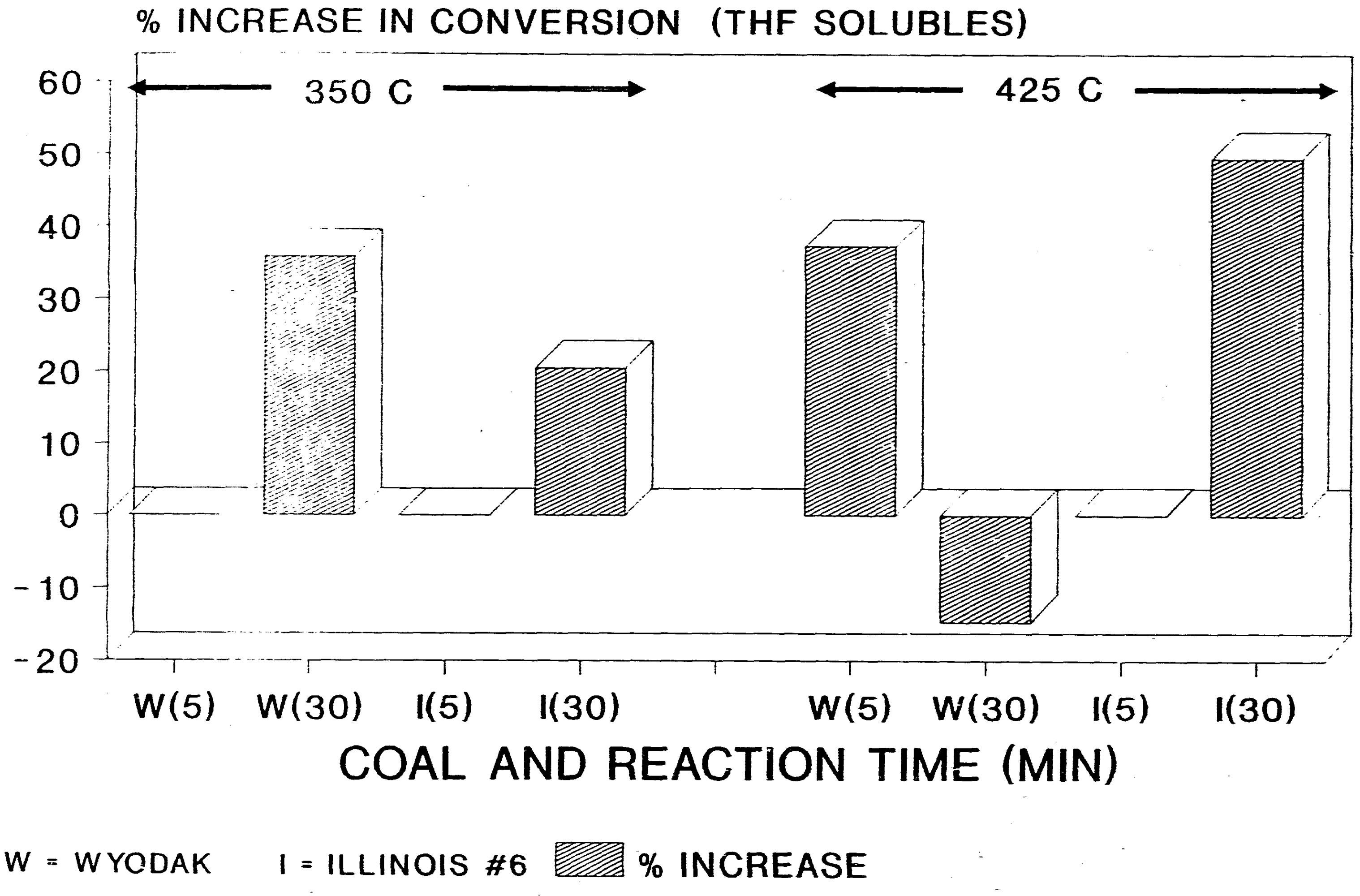


FIGURE 16

Percent Increase In Co-Processing Conversion, CC/MAP Procedure solvent incorporation in baseline conversions.

At high severity co-processing conditions (425 °C) Wyodak coal showed a 37.2% increase in conversion at a reaction time of 5 min, but a 14.7% decrease in conversion at 30 min reaction time. Pretreatment at the shorter reaction time enhances coal reactivity but at longer reaction times, the small amount of alkylation which occurs during pretreatment may promote retrogressive coal-solvent interactions. At the 5 min reaction time, pretreatment of Illinois #6 coal shows no enhancement in coal reactivity, while at 30 min reaction time a 49.4% increase in conversion is observed. This may be due to a lesser tendency for the high rank coal to undergo retrogressive reactions after pretreatment.

7. OPTIMIZATION OF LIQUEFACTION CONDITIONS

High severity conditions are normally utilized in coal liquefaction processes because baseline coal conversion increases with increasing temperature. Low severity liquefaction conditions, coupled with pretreatment for reactivity enhancement, can be beneficial for coal liquefaction processes. This is because the most significant increase in reactivity enhancement due to coal pretreatment occurs at low temperature, as shown in this thesis. This effect however, decreases with increasing temperature. These two opposing trends were observed for all combinations of pretreatment, coal rank, and reaction time, as shown in Figure 17 for Liotta pretreated coal liquefied for 30 min.

Because low temperature favors reactivity enhancement while high temperature favors high ultimate conversion, the most economically effective enhancement in reactivity will occur at some intermediate temperature, where both effects are significant. The determination of this optimal temperature could be made by measuring conversion data at a number of temperature levels between the two extremes utilized in this study. A diagram such as that shown in Figure 18 could then be constructed for each coal and pretreatment combination in order to locate the optimum temperature. Repeated liquefaction experiments where coal, pretreatment method, and reaction time are held constant while reaction temperature is varied would provide the data necessary to construct such a diagram. In the diagram, the intersection of the two curves represents the optimal temperature where the baseline coal conversion is maximized while the percent increase in conversion due to coal pretreatment is still significant for this combination of reactivity parameters. Optimization of the temperature in this manner results in maximization of the reactivity enhancement of the pretreatment process while still maintaining the first stage coal dissolution tempera-

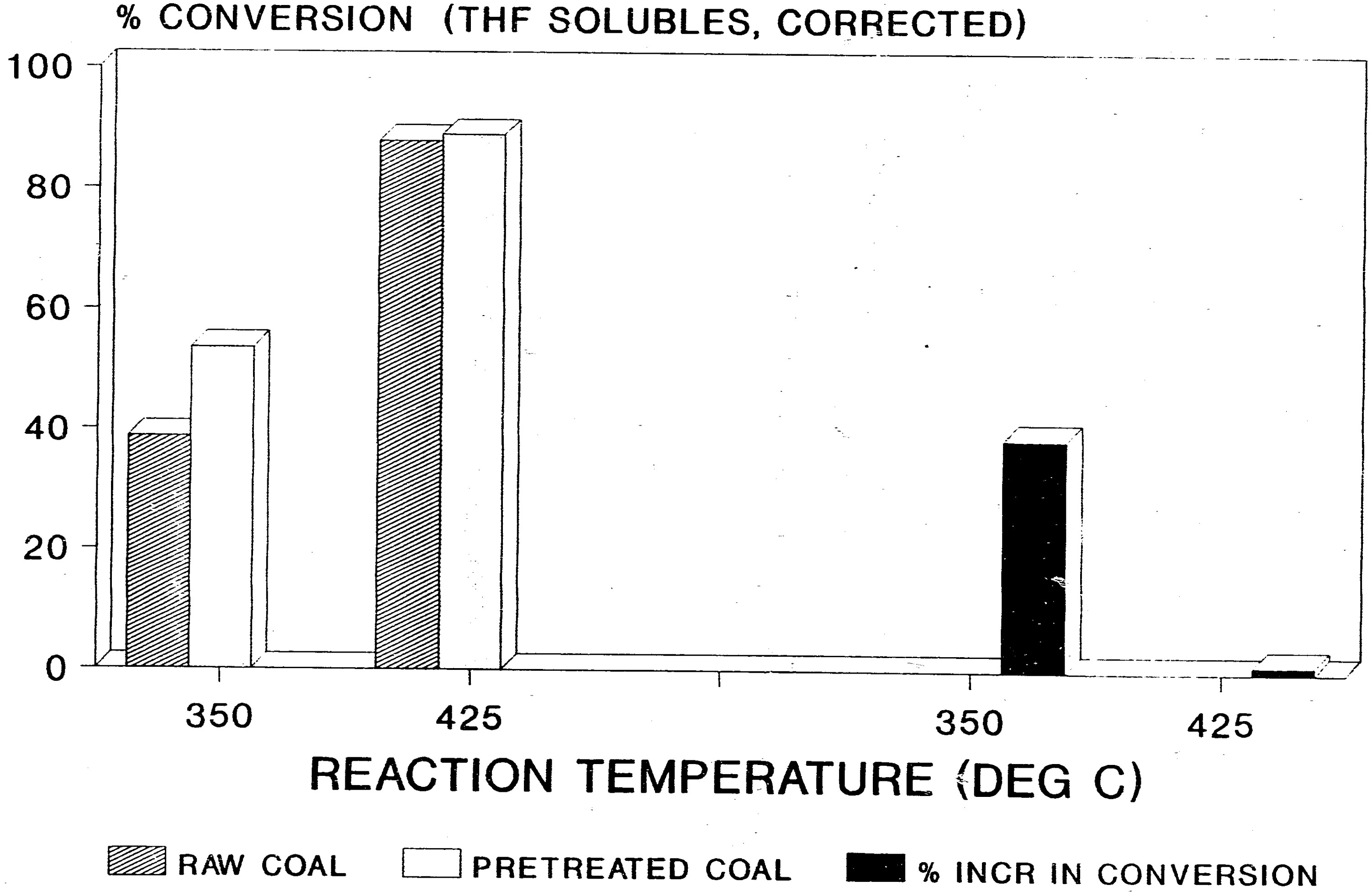


FIGURE 17

Liquefaction Conversions For Wyodak Coal
Liotta Procedure, 30 Min Reaction Time

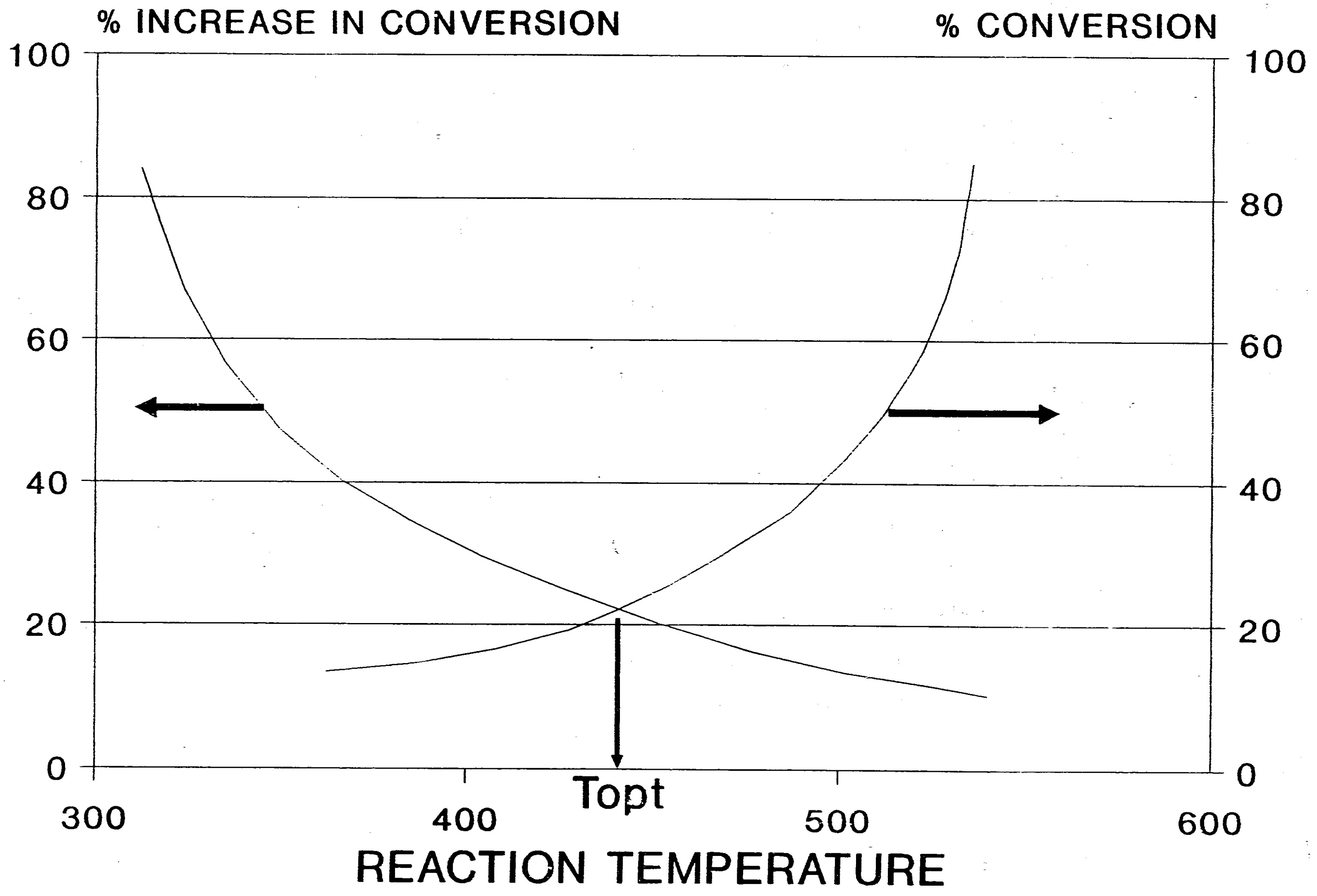


FIGURE 18

Optimization Diagram For Liquefaction Temperature

ture at a sufficiently low value to avoid regressive reactions and excessive hydrocarbon gas make.

CONCLUSIONS

The objective of this research program was to investigate the effect of selective pretreatment methods upon coal reactivity at different liquefaction and co-processing conditions. The conclusions which can be drawn from this thesis are:

1. The chlorine catalyst/mild alkylation pretreatment method developed by Armstrong slightly alkylates the coal and incorporates a small, but significant amount of chlorine into the coal structure. Reactivity enhancement seen for this pretreatment method is a combination of the effect of alkylation with catalysis caused by the added chlorine.

2. Wyodak coal shows the greatest increase in reactivity enhancement as measured by conversion to THF soluble products under liquefaction conditions for all reaction times, reaction temperatures, and pretreatment methods.

3. The effect of coal pretreatment on reactivity is less significant at high severity (425 ^{o}C) liquefaction conditions, where high ultimate coal conversions are observed prior to any pretreatment. Baseline coal conversion to THF

solubles increases with increasing temperature, but the enhancement in reactivity due to pretreatment decreases with increasing temperature. Determination of an optimum reactivity temperature between the two temperature extremes could result in a maximization of reactivity enhancement for the pretreatment process while still maintaining a significant baseline coal conversion.

4. Co-processing of coal in Cold Lake atmospheric residuum at low severity and short reaction times (5 min) results in significant coal-oil adduct formation which prevents the effects of coal pretreatment upon reactivity from being observed.

5. Low severity co-processing of Wyodak coal shows a greater increase in THF coal conversion than Illinois #6 coal for all pretreatment methods at the 30 min reaction time.

6. Reductive alkylation results in the greatest percent increase in reactivity enhancement for both high and low rank coals which are co-processed for 30 min at low severity conditions.

7. For all pretreatment methods, high severity coprocessing of Wyodak coal results in a significant enhancement in THF conversion at a reaction time of 5 min, but no significant enhancement at a reaction time of 30 min.

8. Reductive alkylation was the only pretreatment which showed a significant increase in the high severity coprocessing reactivity of Illinois #6 coal at both 5 and 30 min reaction times.

RECOMMENDATIONS

Based upon the work that has been completed in this thesis, the following areas of liquefaction/co-processing work are recommended for further study:

1. More detailed investigation of coal pretreated with the chlorine catalyst/mild alkylation procedure should be undertaken to determine the relative importance of alkylation and chlorine deposition upon reactivity enhancement.

2. Additional co-processing solvents should be selected for use in reactivity experiments so that potential solvent-pretreatment interactions can be studied.

3. Second stage reactivity experiments under co-processing conditions would indicate the degree to which coal pretreatment enhances the yield of distillable material in two stage processes.

4. Liquefaction experiments at intermediate temperatures would determine the optimal reaction severity in a coal-pretreatment system that shows significant reactivity enhancements.

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Sternberg, H.W., Delle Donne, C.L., Pantages, P., Moroni, E.C. and Markby, R.E., "Solubilization of an lvb Coal by Reductive Alkylation", Fuel, 50, pp 432-437, (1971).

3) The Liotta method for selective O-alkylation and prior references to its application in activation of coals may be found in the following journal articles: Liotta, R., "Selective Alkylation of Acidic Hydroxyl Groups in Coal", Fuel, 58, pp 724-728, (1979); and

Schlosberg, Richard H., Neavel, Richard C., Maa, Peter S. and Gorbarty, Martin L., "Alkylation: A Beneficial Pretreatment for Coal Liquefaction", Fuel, 59, pp 45-47, (1980).

4) Armstrong, M.E., "Enhancement of Coal Liquefaction Reactivity by Mild Alkylation Pretreatment", Master's Thesis, Colorado School of Mines, Golden, (1988).

5) McMillen, D.F., Malholtra, R., Nigenda, S.E., Min, T.C. and Ross, D.S., "Differing Reactivity of Oxygenated Model-Coal Structures in Hydrogen-Donor and COH_2O System", Proceedings: 11th Annual EPRI contractors' Conference on Clean Liquid and Solid Fuels, pp 5-75 to 5-82, (1987).

APPENDIX A

TABLE A-1

Reaction Conditions Reference For Untreated Coals

COAL	SOLVENT	TEMP deg C	TIME min	UNTREATED COAL
				RUN NUMBER OF REACTIVITY EXPERIMENT
WYODAK	DHP	350	5	66 115
			30	68 117
		425	5	70 83 119
			30	85 121
	COLD LAKE ATM. RESID	350	5	56 58 129 132
			30	59 127
		425	5	61 87 123 135
			30	63 125 137 141 142
ILL. #6	DHP	350	5	48 75 96
			30	50 98
		425	5	52 100
			30	54 102
	COLD LAKE ATM. RESID	350	5	39 104
			30	41 107
		425	5	43 77 95 109
			30	47 79 111

TABLE A-2

Reactivity Runs For Untreated Wyodak Coal

WYODAK COAL

RUN #	MF COAL IN (g)	FRACTION ASH IN	GRAMS ASH IN (g)	MAF COAL IN (g)	MF THF INSOL OUT (g)	MAF THF INSOL OUT (g)	FRACTION INTRINSIC THF INSOLS IN FEED COAL	ADJUSTED MAF COAL IN (g)	ADJUSTED THF COAL CONV. (%)	MEAN CONV. (%)
66	0.9956	0.0877	0.0873	0.9083	0.8600	0.7727	0.9837	0.8935	13.5	14.6
115	0.9483	0.0877	0.0832	0.8651	0.8000	0.7168	0.9837	0.8510	15.8	
68	0.9858	0.0877	0.0865	0.8993	0.6200	0.5335	0.9837	0.8847	39.7	38.7
117	0.9579	0.0877	0.0840	0.8739	0.6200	0.5360	0.9837	0.8596	37.6	
70	0.4831	0.0877	0.0424	0.4407	0.2000	0.1576	0.9837	0.4335	63.6	65.4
83	0.9495	0.0877	0.0833	0.8662	0.3700	0.2867	0.9837	0.8521	66.4	
119	0.9483	0.0877	0.0832	0.8651	0.3700	0.2868	0.9837	0.8510	66.3	
85	0.9788	0.0877	0.0858	0.8930	0.1900	0.1042	0.9837	0.8784	88.1	87.9
121	1.0064	0.0877	0.0883	0.9181	0.2000	0.1117	0.9837	0.9032	87.6	
56	0.9759	0.0877	0.0856	0.8903	0.9600	0.8744	0.9837	0.8758	0.2	-0.2
58	0.9858	0.0877	0.0865	0.8993	0.9600	0.8735	0.9837	0.8847	1.3	
129	0.9579	0.0877	0.0840	0.8739	0.8900	0.8060	0.9837	0.8596	6.2	
132	0.9340	0.0877	0.0819	0.8521	0.9900	0.9081	0.9837	0.8382	-8.3	
59	0.9759	0.0877	0.0856	0.8903	0.8300	0.7444	0.9837	0.8758	15.0	15.0
127	0.9870	0.0877	0.0866	0.9004	0.8400	0.7534	0.9837	0.8858	14.9	
61	0.9858	0.0877	0.0865	0.8993	0.7200	0.6335	0.9837	0.8847	28.4	28.4
87	0.9396	0.0877	0.0824	0.8572	0.6700	0.5876	0.9837	0.8432	30.3	
123*	0.9773	0.0877	0.0857	0.8916	0.6500	0.5643	0.9837	0.8771	35.7	
135	0.9247	0.0877	0.0811	0.8436	0.6900	0.6089	0.9837	0.8299	26.6	
137	0.9247	0.0877	0.0811	0.8436	0.3700	0.2889	0.9837	0.8299	65.2	69.3
141	0.7747	0.0877	0.0679	0.7068	0.3300	0.2621	0.9837	0.6952	62.3	
142	0.9587	0.0877	0.0841	0.8746	0.3100	0.2259	0.9837	0.8604	73.7	
125	0.9579	0.0877	0.0840	0.8739	0.2900	0.2060	0.9837	0.8596	76.0	
63*	0.9660	0.0877	0.0847	0.8813	0.4500	0.3653	0.9837	0.8669	57.9	

* INDICATES OUTLYING VALUE NOT USED IN CALCULATION OF MEAN CONVERSION

TABLE A-3

Reactivity Runs For Untreated Illinois #6 Coal

ILLINOIS #6 COAL

RUN #	MF COAL IN (g)	FRACTION ASH IN	GRAMS ASH IN (g)	MAF COAL IN (g)	MF THF INSOL OUT (g)	MAF THF INSOL OUT (g)	FRACTION INTRINSIC THF INSOLS IN FEED COAL	ADJUSTED MAF COAL IN (g)	ADJUSTED THF COAL CONV. (%)	MEAN CONV. (%)
48	0.9500	0.1548	0.1471	0.8029	0.6000	0.4529	0.8807	0.7071	35.9	37.1
75	0.9976	0.1548	0.1544	0.8432	0.6200	0.4656	0.8807	0.7426	37.3	
96	1.0082	0.1548	0.1561	0.8521	0.6200	0.4639	0.8807	0.7505	38.2	
50	0.9400	0.1548	0.1455	0.7945	0.2700	0.1245	0.8807	0.6997	82.2	81.3
98	0.9982	0.1548	0.1545	0.8437	0.3000	0.1455	0.8807	0.7430	80.4	
52	0.9419	0.1548	0.1458	0.7961	0.2300	0.0842	0.8807	0.7011	88.0	87.7
100	1.0082	0.1548	0.1561	0.8521	0.2500	0.0939	0.8807	0.7505	87.5	
54	0.9500	0.1548	0.1471	0.8029	0.2200	0.0729	0.8807	0.7071	89.7	89.8
102	0.9982	0.1548	0.1545	0.8437	0.2300	0.0755	0.8807	0.7430	89.8	
39	1.0200	0.1548	0.1579	0.8621	0.9300	0.7721	0.8807	0.7593	-1.7	-1.0
104	0.9982	0.1548	0.1545	0.8437	0.9000	0.7455	0.8807	0.7430	-0.3	
41	1.0000	0.1548	0.1548	0.8452	0.6900	0.5352	0.8807	0.7444	28.1	28.7
107	1.0282	0.1548	0.1592	0.8690	0.7000	0.5408	0.8807	0.7654	29.3	
43*	0.9600	0.1548	0.1486	0.8114	0.5100	0.3614	0.8807	0.7146	49.4	38.5
77	0.9776	0.1548	0.1513	0.8263	0.5900	0.4387	0.8807	0.7277	39.7	
95	1.0000	0.1548	0.1548	0.8452	0.6100	0.4552	0.8807	0.7444	38.8	
109	1.0082	0.1548	0.1561	0.8521	0.6300	0.4739	0.8807	0.7505	36.8	
47	0.9976	0.1548	0.1544	0.8432	0.6000	0.4456	0.8807	0.7426	40.0	38.0
79	0.9976	0.1548	0.1544	0.8432	0.6300	0.4756	0.8807	0.7426	36.0	
111	1.0082	0.1548	0.1561	0.8521	0.6200	0.4639	0.8807	0.7505	38.2	

* INDICATES OUTLYING VALUE NOT USED IN CALCULATION OF MEAN CONVERSION

TABLE A-4

Reaction Conditions Reference For Liotta Pretreated Coals

COAL	SOLVENT	TEMP deg C	TIME min	LIOTTA METHOD RUN NUMBER OF REACTIVITY EXPERIMENT
WYODAK	DHP	350	5	N1
			30	N2 N3
		425	5	N4
			30	N5
	COLD LAKE ATM. RESID	350	5	N6
			30	N7 N10
		425	5	N8
			30	N9
ILL. #6	DHP	350	5	134
			30	99
		425	5	101
			30	103
	COLD LAKE ATM. RESID	350	5	105 106
			30	108
		425	5	110
			30	112

TABLE A-5

Reactivity Runs For Liotta Pretreated Wyodak Coal

WYODAK COAL

RUN #	MF COAL IN (g)	FRACTION ASH IN	GRAMS ASH IN (g)	MAF COAL IN (g)	MF THF INSOL OUT (g)	MAF THF INSOL OUT (g)	FRACTION INTRINSIC THF INSOLS IN FEED COAL	ADJUSTED MAF COAL IN (g)	ADJUSTED THF COAL CONV. (%)	MEAN CONV. (%)
N1	1.0100	0.0656	0.0663	0.9437	0.6200	0.5537	0.8641	0.8155	32.1	32.1
N2	1.0100	0.0656	0.0663	0.9437	0.4200	0.3537	0.8641	0.8155	56.6	53.6
N3	1.0100	0.0656	0.0663	0.9437	0.4700	0.4037	0.8641	0.8155	50.5	
N4	0.9900	0.0656	0.0649	0.9251	0.2500	0.1851	0.8641	0.7993	76.8	76.8
N5	1.0300	0.0656	0.0676	0.9624	0.1600	0.0924	0.8641	0.8316	88.9	88.9
N6	1.0200	0.0656	0.0669	0.9531	0.9100	0.8431	0.8641	0.8236	-2.4	-2.4
N7	1.0300	0.0656	0.0676	0.9624	0.6900	0.6224	0.8641	0.8316	25.2	28.5
N10	1.0400	0.0656	0.0682	0.9718	0.6400	0.5718	0.8641	0.8397	31.9	
N8	1.0700	0.0656	0.0702	0.9998	0.5100	0.4398	0.8641	0.8639	49.1	49.1
N9	1.1200	0.0656	0.0735	1.0465	0.3300	0.2565	0.8641	0.9043	71.6	71.6

TABLE A-6

Reactivity Runs For Liotta Pretreated Illinois #6 Coal

ILLINOIS #6 COAL

RUN #	MF COAL IN (g)	FRACTION ASH IN	GRAMS ASH IN (g)	MAF COAL IN (g)	MF THF INSOL OUT (g)	MAF THF INSOL OUT (g)	FRACTION INTRINSIC THF INSOLS IN FEED COAL	ADJUSTED MAF COAL IN (g)	ADJUSTED THF COAL CONV. (%)	MEAN CONV. (%)
134	0.9624	0.1434	0.1380	0.8244	0.4700	0.3320	0.7468	0.6157	46.1	46.1
99	0.9922	0.1434	0.1423	0.8499	0.2400	0.0977	0.7468	0.6347	84.6	84.6
101	0.9823	0.1434	0.1409	0.8414	0.2100	0.0691	0.7468	0.6284	89.0	89.0
103	0.9922	0.1434	0.1423	0.8499	0.2000	0.0577	0.7468	0.6347	90.9	90.9
105	0.9823	0.1434	0.1409	0.8414	0.8900	0.7491	0.7468	0.6284	-19.2	-18.5
106	0.9922	0.1434	0.1423	0.8499	0.8900	0.7477	0.7468	0.6347	-17.8	
108	0.9128	0.1434	0.1309	0.7819	0.6700	0.5391	0.7468	0.5839	7.7	10.6
N262	1.0086	0.1434	0.1446	0.8640	0.7300	0.5854	0.7468	0.6452	9.3	
N263	1.0885	0.1434	0.1561	0.9324	0.7500	0.5939	0.7468	0.6963	14.7	
110	0.9922	0.1434	0.1423	0.8499	0.5700	0.4277	0.7468	0.6347	32.6	32.6
112	1.0616	0.1434	0.1522	0.9094	0.6400	0.4878	0.7468	0.6791	28.2	28.2

TABLE A-7

Reaction Conditions Reference For Sternberg Pretreated Coals

COAL	SOLVENT	TEMP deg C	TIME min	STERNBERG METHOD RUN NUMBER OF REACTIVITY EXPERIMENT
WYODAK	DHP	350	5	155 163 183 184 207
			30	153 185 205
		425	5	157 189 208
			30	159 187
	COLD LAKE ATM. RESID	350	5	156 164
			30	154 186 206
		425	5	158 190 209
			30	160 188
ILL. #6	DHP	350	5	154 180
			30	178 184
		425	5	149
			30	151
	COLD LAKE ATM. RESID	350	5	148 181
			30	147 162 174 175 179
		425	5	150 173 183
			30	152 161 176 177 182

TABLE A-8

Reactivity Runs For Sternberg Pretreated Wyodak Coal

WYODAK COAL

RUN #	MF COAL IN (g)	FRACTION ASH IN	GRAMS ASH IN (g)	MAF COAL IN (g)	MF THF INSOL OUT (g)	MAF THF INSOL OUT (g)	FRACTION INTRINSIC THF INSOLS IN FEED COAL	ADJUSTED MAF COAL IN (g)	ADJUSTED THF COAL CONV. (%)	MEAN CONV. (%)
155	0.9362	0.1268	0.1187	0.8175	0.6600	0.5413	1.0000	0.8175	33.8	30.1
163	0.7899	0.1268	0.1002	0.6897	0.6600	0.5598	1.0000	0.6897	18.8	
183*	0.7800	0.1268	0.0989	0.6811	0.3300	0.2311	1.0000	0.6811	66.1	
184	1.0101	0.1268	0.1281	0.8820	0.6200	0.4919	1.0000	0.8820	44.2	
207	0.8796	0.1268	0.1115	0.7681	0.7000	0.5885	1.0000	0.7681	23.4	
153*	0.8874	0.1268	0.1125	0.7749	0.5200	0.4075	1.0000	0.7749	47.4	64.7
185	0.9906	0.1268	0.1256	0.8650	0.4300	0.3044	1.0000	0.8650	64.8	
205	0.8015	0.1268	0.1016	0.6999	0.3500	0.2484	1.0000	0.6999	64.5	
157	0.8777	0.1268	0.1113	0.7664	0.3000	0.1887	1.0000	0.7664	75.4	79.6
189	0.9615	0.1268	0.1219	0.8396	0.2600	0.1381	1.0000	0.8396	83.6	
208	0.8894	0.1268	0.1128	0.7766	0.2700	0.1572	1.0000	0.7766	79.8	
159	0.8679	0.1268	0.1100	0.7579	0.1800	0.0700	1.0000	0.7579	90.8	90.0
187	0.9518	0.1268	0.1207	0.8311	0.2100	0.0893	1.0000	0.8311	89.3	
156	0.8777	0.1268	0.1113	0.7664	0.7900	0.6787	1.0000	0.7664	11.4	10.2
164	0.7704	0.1268	0.0977	0.6727	0.7100	0.6123	1.0000	0.6727	9.0	
154	0.9069	0.1268	0.1150	0.7919	0.7200	0.6050	1.0000	0.7919	23.6	32.8
186	0.9906	0.1268	0.1256	0.8650	0.6300	0.5044	1.0000	0.8650	41.7	
206	0.8992	0.1268	0.1140	0.7852	0.6400	0.5260	1.0000	0.7852	33.0	
158*	0.8972	0.1268	0.1138	0.7834	0.5800	0.4662	1.0000	0.7834	40.5	59.5
190	0.9712	0.1268	0.1231	0.8481	0.4700	0.3469	1.0000	0.8481	59.1	
209	0.8796	0.1268	0.1115	0.7681	0.4200	0.3085	1.0000	0.7681	59.8	
160	0.8972	0.1268	0.1138	0.7834	0.4100	0.2962	1.0000	0.7834	62.2	63.3
188	0.9809	0.1268	0.1244	0.8565	0.4300	0.3056	1.0000	0.8565	64.3	

* INDICATES OUTLYING VALUE NOT USED IN CALCULATION OF MEAN CONVERSION

TABLE A-9

Reactivity Runs For Sternberg Pretreated Illinois #6 Coal

ILLINOIS #6 COAL

RUN #	MF COAL IN (g)	FRACTION ASH IN	GRAMS ASH IN (g)	MAF COAL IN (g)	MF THF INSOL OUT (g)	MAF THF INSOL OUT (g)	FRACTION INTRINSIC THF INSOLS IN FEED COAL	ADJUSTED MAF COAL IN (g)	ADJUSTED THF COAL CONV. (%)	MEAN CONV. (%)
143	0.9746	0.1487	0.1449	0.8297	0.5300	0.3851	0.9352	0.7759	50.4	47.5
180	0.7801	0.1487	0.1160	0.6641	0.4600	0.3440	0.9352	0.6211	44.6	
146	0.9746	0.1487	0.1449	0.8297	0.2700	0.1251	0.9352	0.7759	83.9	83.2
178	0.8000	0.1487	0.1190	0.6810	0.2300	0.1110	0.9352	0.6369	82.6	
149	0.9845	0.1487	0.1464	0.8381	0.2500	0.1036	0.9352	0.7838	86.8	86.8
151	1.0041	0.1487	0.1493	0.8548	0.2700	0.1207	0.9352	0.7994	84.9	84.9
148	0.9647	0.1487	0.1435	0.8212	0.8400	0.6965	0.9352	0.7680	9.3	11.4
181	0.8000	0.1487	0.1190	0.6810	0.6700	0.5510	0.9352	0.6369	13.5	
147	1.0140	0.1487	0.1508	0.8632	0.5500	0.3992	0.9352	0.8073	50.5	40.4
162	0.7875	0.1487	0.1171	0.6704	0.5700	0.4529	0.9352	0.6270	27.8	
174	0.9800	0.1487	0.1457	0.8343	0.6000	0.4543	0.9352	0.7802	41.8	
175	1.0600	0.1487	0.1576	0.9024	0.6300	0.4724	0.9352	0.8439	44.0	
179	0.8100	0.1487	0.1204	0.6896	0.5200	0.3996	0.9352	0.6449	38.0	
150*	0.9844	0.1487	0.1464	0.8380	0.5500	0.4036	0.9352	0.7837	48.5	65.2
173	0.9800	0.1487	0.1457	0.8343	0.4200	0.2743	0.9352	0.7802	64.8	
183	0.7801	0.1487	0.1160	0.6641	0.3300	0.2140	0.9352	0.6211	65.5	
152	0.9647	0.1487	0.1435	0.8212	0.5500	0.4065	0.9352	0.7680	47.1	59.4
161	0.7875	0.1487	0.1171	0.6704	0.2900	0.1729	0.9352	0.6270	72.4	
176	0.9600	0.1487	0.1428	0.8172	0.4200	0.2772	0.9352	0.7643	63.7	
177	1.0101	0.1487	0.1502	0.8599	0.5400	0.3898	0.9352	0.8042	51.5	
182	0.8000	0.1487	0.1190	0.6810	0.3600	0.2410	0.9352	0.6369	62.2	

* INDICATES OUTLYING VALUE NOT USED IN CALCULATION OF MEAN CONVERSION

TABLE A-10

Reaction Conditions Reference For CC/MAP Pretreated Coals

COAL	SOLVENT	TEMP deg C	TIME min	CC/MAP METHOD
				RUN NUMBER OF REACTIVITY EXPERIMENT
WYODAK	DHP	350	5	67 201
			30	69 199
		425	5	71 84 93
			30	86 203
	COLD LAKE ATM. RESID	350	5	57 202
			30	60 200
		425	5	62 65 88 94
			30	64 204
ILL. #6	DHP	350	5	49 76
			30	51 191
		425	5	53 194
			30	55 195
	COLD LAKE ATM. RESID	350	5	40 193 196 197
			30	42 192
		425	5	44 78 113
			30	46 80 114

TABLE A-11

Reactivity Runs for CC/MAP Pretreated Wyodak Coal

WYODAK COAL

RUN #	MF COAL IN (g)	FRACTION ASH IN	GRAMS ASH IN (g)	MAF COAL IN (g)	MF THF INSOL OUT (g)	MAF THF INSOL OUT (g)	FRACTION INTRINSIC THF INSOLS IN FEED COAL	ADJUSTED MAF COAL IN (g)	ADJUSTED THF COAL CONV. (%)	MEAN CONV. (%)
67	0.9758	0.0783	0.0764	0.8994	0.7200	0.6436	0.9414	0.8467	24.0	25.6
201	0.9719	0.0783	0.0761	0.8958	0.6900	0.6139	0.9414	0.8433	27.2	
69	0.4784	0.0783	0.0375	0.4409	0.2500	0.2125	0.9414	0.4151	48.8	51.4
199	0.9435	0.0783	0.0739	0.8696	0.4500	0.3761	0.9414	0.8187	54.1	
71	0.4784	0.0783	0.0375	0.4409	0.1500	0.1125	0.9414	0.4151	72.9	82.6
84	0.9591	0.0783	0.0751	0.8840	0.2000	0.1249	0.9414	0.8322	85.0	
93	0.7844	0.0783	0.0614	0.7230	0.1300	0.0686	0.9414	0.6806	89.9	
86	0.8727	0.0783	0.0683	0.8044	0.1600	0.0917	0.9414	0.7572	87.9	89.7
203	0.9816	0.0783	0.0769	0.9047	0.1500	0.0731	0.9414	0.8517	91.4	
202	0.9341	0.0783	0.0731	0.8610	0.8400	0.7669	0.9414	0.8105	5.4	5.4
57	0.9566	0.0783	0.0749	0.8817	0.8600	0.7851	0.9414	0.8300	5.4	
60	0.9566	0.0783	0.0749	0.8817	0.7500	0.6751	0.9414	0.8300	18.7	20.3
200	0.9531	0.0783	0.0746	0.8785	0.7200	0.6454	0.9414	0.8270	22.0	
62	0.9566	0.0783	0.0749	0.8817	0.4900	0.4151	0.9414	0.8300	50.0	39.0
65	0.9566	0.0783	0.0749	0.8817	0.6700	0.5951	0.9414	0.8300	28.3	
88	0.7768	0.0783	0.0608	0.7160	0.4800	0.4192	0.9414	0.6740	37.8	
94	0.7844	0.0783	0.0614	0.7230	0.4700	0.4086	0.9414	0.6806	40.0	
64	0.9374	0.0783	0.0734	0.8640	0.4200	0.3466	0.9414	0.8134	57.4	59.1
204	0.9814	0.0783	0.0768	0.9046	0.4100	0.3332	0.9414	0.8515	60.9	

TABLE A-12

Reactivity Runs For CC/MAP Pretreated Illinois #6 Coal

ILLINOIS #6 COAL

RUN #	MF COAL IN (g)	FRACTION ASH IN	GRAMS ASH IN (g)	MAF COAL IN (g)	MF THF INSOL OUT (g)	MAF THF INSOL OUT (g)	FRACTION INTRINSIC THF INSOLS IN FEED COAL	ADJUSTED MAF COAL IN (g)	ADJUSTED THF COAL CONV. (%)	MEAN CONV. (%)
49	0.9424	0.1590	0.1498	0.7926	0.5000	0.3502	0.8828	0.6997	50.0	48.2
76	0.9699	0.1590	0.1542	0.8157	0.5400	0.3858	0.8828	0.7201	46.4	
51	0.9225	0.1590	0.1467	0.7758	0.2500	0.1033	0.8828	0.6849	84.9	86.5
191	0.9718	0.1590	0.1545	0.8173	0.2400	0.0855	0.8828	0.7215	88.2	
53	0.9621	0.1590	0.1530	0.8091	0.2300	0.0770	0.8828	0.7143	89.2	91.0
194	0.9912	0.1590	0.1576	0.8336	0.2100	0.0524	0.8828	0.7359	92.9	
55	1.0019	0.1590	0.1593	0.8426	0.2600	0.1007	0.8828	0.7438	86.5	88.0
195	0.9718	0.1590	0.1545	0.8173	0.2300	0.0755	0.8828	0.7215	89.5	
40	0.9423	0.1590	0.1498	0.7925	0.8600	0.7102	0.8828	0.6996	-1.5	7.0
193	0.9718	0.1590	0.1545	0.8173	0.7700	0.6155	0.8828	0.7215	14.7	
196	0.9815	0.1590	0.1561	0.8254	0.8300	0.6739	0.8828	0.7287	7.5	
197	1.0035	0.1590	0.1596	0.8439	0.8500	0.6904	0.8828	0.7450	7.3	
42	0.9225	0.1590	0.1467	0.7758	0.6100	0.4633	0.8828	0.6849	32.4	34.6
192	0.9718	0.1590	0.1545	0.8173	0.6100	0.4555	0.8828	0.7215	36.9	
44	0.9225	0.1590	0.1467	0.7758	0.5700	0.4233	0.8828	0.6849	38.2	38.5
78*	0.9699	0.1590	0.1542	0.8157	0.6800	0.5258	0.8828	0.7201	27.0	
113	0.9455	0.1590	0.1503	0.7952	0.5800	0.4297	0.8828	0.7020	38.8	
46	0.9424	0.1590	0.1498	0.7926	0.4500	0.3002	0.8828	0.6997	57.1	56.8
80	1.0000	0.1590	0.1590	0.8410	0.5000	0.3410	0.8828	0.7424	54.1	
114	0.9552	0.1590	0.1519	0.8033	0.4400	0.2881	0.8828	0.7092	59.4	

* INDICATES OUTLYING VALUE NOT USED IN CALCULATION OF MEAN CONVERSION

APPENDIX B

TABLE B-1

Five Factor Analysis Of Variance

TREATMENT	LOW	HIGH
A = COAL	(1) WYODAK	(A) ILL. #6
B = SOLVENT	(1) COLD LAKE	(B) DHP
C = TEMP	(1) 350 C	(C) 425 C
D = TIME	(1) 5 MIN	(D) 30 MIN
E = TREAT	(1) UNTREATED	(E) CC/MAP

ERROR > 605.2 32 18.91

TOTAL > 57321 58254

STD DEV OF RUNS 4.3 %

COMBO	RUN 1	RUN 2	TOTAL	(1)	(2)	(3)	(4)	(5)	SUM OF SQUARES	DEG OF FR	MEAN SQUARE
(1)	6.2	-8.3	-2.1	-4.1	99.3	538.3	1430.8	3097.0			
A	-1.7	-0.3	-2.0	103.4	439.0	892.5	1666.1	303.3	1437.3	1	1437
B	13.5	15.8	29.3	133.5	327.3	693.4	168.7	1183.0	21865.6	1	21866
AB	35.9	38.2	74.1	305.5	565.2	972.8	134.6	294.0	1350.5	1	1351
C	26.6	30.3	56.9	87.4	171.6	110.0	577.5	1129.0	19916.0	1	19916
AC	39.7	36.8	76.6	240.0	521.8	58.6	605.5	-304.9	1452.5	1	1453
BC	63.6	66.4	130.0	209.9	385.8	44.0	190.1	83.4	108.7	1	109
ABC	88.0	87.5	175.5	355.3	587.0	90.7	103.9	-79.9	99.8	1	100
D	15.0	14.9	29.9	24.0	44.9	279.5	577.5	633.7	6274.3	1	6274
AD	28.1	29.3	57.4	147.6	65.1	298.0	551.5	-4.7	0.3	1	0
BD	39.7	37.6	77.3	164.8	112.8	315.8	-146.7	-7.6	0.9	1	1
ABD	82.2	80.4	162.6	357.0	-54.1	289.7	-158.2	31.2	15.2	1	.15
CD	76.0	57.9	133.9	109.8	47.6	70.6	57.2	-250.8	982.9	1	983
ACD	40.0	36.0	76.0	275.9	-3.6	119.5	26.2	-242.8	921.4	1	921
BCD	88.1	87.6	175.8	231.7	98.8	60.8	-15.0	-182.7	521.8	1	522
ABCD	89.7	89.8	179.5	355.3	-8.1	43.1	-64.9	7.5	0.9	1	1
E	5.4	5.4	10.8	0.1	107.5	339.7	354.3	235.3	865.3	1	865
AE	-1.5	14.7	13.2	44.8	172.0	237.8	279.4	-34.0	18.1	1	18
BE	24.0	27.2	51.2	19.6	152.6	350.2	-51.4	28.0	12.2	1	12
ABE	50.0	46.4	96.4	45.5	145.4	201.2	46.7	-86.2	116.0	1	116
CE	37.8	50.0	87.8	27.5	123.6	20.2	18.5	-26.1	10.6	1	11
ACE	38.2	38.8	77.0	85.3	192.2	-166.9	-26.1	-11.4	2.0	1	2
BCE	85.0	89.9	174.9	-57.9	166.1	-51.2	48.8	-31.0	15.1	1	15
ABCE	89.2	92.9	182.1	3.8	123.6	-106.9	-17.7	-49.8	38.8	1	39
DE	18.7	22.0	40.6	2.4	44.8	64.4	-101.8	-74.8	87.5	1	88
ADE	32.4	36.9	69.2	45.2	25.9	-7.2	-149.0	98.1	150.4	1	150
BDE	48.8	54.1	102.9	-10.8	57.8	68.7	-187.1	-44.6	31.1	1	31
ABDE	84.9	88.2	173.1	7.2	61.7	-42.5	-55.7	-66.5	69.1	1	69
CDE	57.4	60.9	118.3	28.6	42.8	-18.9	-71.6	-47.2	34.7	1	35
ACDE	54.1	59.4	113.4	70.2	18.0	3.9	-111.1	131.4	269.8	1	270
BCDE	87.9	91.4	179.3	-4.8	41.6	-24.8	22.8	-39.5	24.4	1	24
ABCDE	86.5	89.5	176.0	-3.3	1.5	-40.1	-15.3	-38.1	22.7	1	23

END

DATE FILMED

4 / 01 / 92