T-3447

LOW SEVERITY COAL/OIL CO-PROCESSING USING MODEL NITROGEN COMPOUNDS

by

Gerald F. Giacomelli

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

T-3447

A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Chemical and Petroleum-Refining Engineering).

Golden, Colorado

Date July 22, 1987

Signed: _____
Gerald F. Giacomelli

Approved: _____
Dr. Ronald L. Miller
Thesis Advisor

Golden, Colorado

Date 7/22/87

_____
Dr. A.J. Kidnay
Head of Chemical and
Petroleum-Refining
Engineering Department

ABSTRACT

Low severity co-processing of Kentucky 9 bituminous and Wyodak subbituminous coals with Cold Lake atmospheric petroleum residuum was studied in a 300 cm^3 batch reactor at 344°C reaction temperature for 30 minutes reaction time. Feed gas consisted of either pure hydrogen or a mixture of carbon monoxide and water. Heterocyclic or aliphatic model nitrogen compounds were added to the petroleum residuum to promote coal dissolution and distillate liquid yield. The model nitrogen compounds studied were 1,2,3,4-tetrahydroquinoline, dipropylamine, diphenylamine, piperidine, 4-piperidinopyridine, 5,6-benzoquinoline and 7,8-benzoquinoline. Dipropylamine was found to be the best reaction promoter resulting in the highest coal conversion levels and least nitrogen incorporation into the insoluble organic matter and mineral matter (IOM & MM) in most instances. Incorporation of the model nitrogen compounds was found to occur primarily into the THF insolubles, rather than the 455°C+ residuum products. At a fixed set of reaction conditions, the relative nitrogen incorporation of different model compounds was monitored by direct measurement of nitrogen content in the THF insoluble product. Finally, the product quality of THF insoluble and 455°C+ residual products after low severity co-processing was essentially

unchanged from the feed coal and petroleum oil quality.

TABLE OF CONTENTS

page

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGMENTS

I wish to express my extreme gratitude to my advisor Dr. Ronald L. Miller for his help and guidance throughout this work, to Dr. Robert Baldwin for his assistance, and to my co-worker Kernan McHugh for his assistance in the experimental runs.

Appreciation is also extended to the United States Department of Energy and the Chemical and Petroleum-Refining Engineering Department for providing financial support for this project and myself. I would not have been able to remain at the Colorado School of Mines without it.

Finally I have to thank my family, Leslie, Lindsay and Nick, for supporting me in mind and body, and enduring the hardships for me and with me. I dedicate this work to them, but especially to Lindsay and Nick who have spent essentially 66% and 100% of their respective lives in Golden, Colorado.

INTRODUCTION

Coal Liquefaction Process Development

The development of coal liquefaction technologies originated in Germany during the early part of this century. The initial concept developed was the Bergius Process, which was a direct liquefaction process designed to hydrogenate the coal directly to distillate products at the severe conditions of 450 - 500°C under a hydrogen gas atmosphere of 25 - 70 MPa (1). The Fischer-Tropsch indirect liquefaction process followed in 1925 (2). It was based on liquid hydrocarbon synthesis from gasified coal products.

Commercial scale plants were developed in Germany during this time to use indigenous coal supplies to meet liquid fuels demand. Production capacity quickly grew and reached a peak during World War II when there were 27 synthetic fuels plants based on direct and indirect liquefaction producing 5 million metric tons/year of liquid fuels (2). Twelve of these plants were based on the Bergius process of direct liquefaction, and accounted for about 4 million metric tons/year of liquid fuels (1,2,3). Following World War II, production of liquid fuels from coal was phased out as cheap petroleum sources became available and the economics of coal liquefaction deteriorated (2). The bulk of the German technology was transferred to the United

States after the war where subsequent developments built upon the original Bergius process. The Bergius technology is not economically competitive in today's markets due to its operating conditions, therefore most of the developments since that time have been directed towards designing processes to operate at milder conditions, thereby improving the economics (1,2).

A number of processes have been developed to convert coal to liquids more efficiently, but only five have been considered for commercial development in the United States:

1. SRC-I and SRC-II (Solvent Refined Coal)
2. EDS (Exxon Donor Solvent Process)
3. H-Coal
4. Dow Coal Liquefaction Process
5. Close Coupled Two Stage Liquefaction (2).

All but the SRC-I process can produce substantial yields of distillate. The SRC-I process produces a clean, low sulfur solid fuel which melts at 177°C (2). All of these processes are similar in that the coal is thermally dissolved in the presence of hydrogen gas and a recycled solvent to produce a spectrum of gaseous, liquid, and solid products. Modifications to this basic process occur in:

1. the EDS process, where the recycle solvent is hydrogenated prior to re-mixing with the coal,

2. the H-Coal process, which incorporates a supported Co-Mo on alumina catalyst within an ebullated bed reactor, and

3. the close coupled two stage process which involves a thermal reactor stage followed by a catalytic reaction stage and a recovery system for the hydrotreated solvent (4).

Coal liquefaction processes can be categorized into three generations of development. The first generation processes involved the liquefaction of coal in the presence of hydrogen and a coal-derived recycled solvent. The second generation processes, as the H-Coal process, use a supported catalyst in the reactor in order to enhance product quality, yields and coal conversion (2,5). Third generation processes generally utilize a 2-stage reactor sequence to further improve quality and product yields. In the close-coupled two stage process the first stage is operated at less severe conditions than those used in direct liquefaction, and is basically designed to dissolve the coal. The second stage uses more severe operating conditions and a catalyst to promote hydrocracking reactions, resulting in higher quality products, as in the close coupled two stage process (4,6).

The next generation of liquefaction processes can be considered coal and petroleum oil co-processing. This type

of process is based on using a non-coal derived solvent such as atmospheric and vacuum tower petroleum residues, fluidized catalytic cracker petroleum oil, heavy petroleum crudes, tar sand bitumen, or shale oil in place of the coal derived solvent (5-15). The coal is liquefied simultaneously as the solvent is upgraded in a synergistic-type reaction. Heavy crudes are a favored feedstock, since conventional refinery processes can only partially convert these feeds to distillate products (12). The advantage of this process is that a relatively hydrogen rich, low grade solvent can be used with a coal, and processed in a once-through flow scheme. This is far more economical than a conventional liquefaction process which requires a recycled solvent stream for best performance (5,6,9).

Reaction Gas Atmosphere

The objective of the coal liquefaction process is to hydrogenate or stabilize the coal free radicals generated during the coal dissolution step, before they can repolymerize and form char (2). Hydrogenation of the primary coal derived materials increases the overall hydrogen to carbon ratio of the products resulting in properties of decreased viscosity and boiling point. The hydrogen feed gas can be provided either as a 100% hydrogen gas atmosphere, or

through a synthesis gas atmosphere which is comprised of a mixture of hydrogen/carbon monoxide/water or carbon monoxide/water. Both of these gas mixtures take advantage of the water-gas shift reaction to form the necessary hydrogen for reaction:

$$CO + H_2O \longrightarrow H_2 + CO_2$$

Since this reaction is mildly exothermic, the maximum conversion is attained at the lowest temperatures. A temperature of 325 to 350°C is necessary for an adequate rate to be achieved. Pressure has no effect on the equilibrium (16), but will likely affect the reaction kinetics.

Moschopedis and Ozum (10) showed that with certain coals a CO/steam atmosphere resulted in significantly higher overall coal conversion compared to a hydrogen atmosphere. However the product quality was better with a hydrogen atmosphere. It was also found that under low severity reaction conditions hydrogen consumption was less with a synthesis gas compared to hydrogen gas (8). The choice of reaction gas also affects product yield distribution. Synthesis gas tends to produce more middle distillate and less naphtha under high severity reaction conditions compared to hydrogen feed gas. However the trend reverses at

low severity conditions (8).

Reaction Severity

The possibility of liquefying coal at low severity reaction conditions (i.e. < 350°C) as opposed to high severity conditions (approximately 440°C) has been investigated since about 1921. At that time Fischer and Schader reported production of an ether-soluble material from coal at 350°C, using carbon monoxide and water as a reducing agent (17).

Not only are the milder conditions conducive to optimal hydrogen production from the water-gas shift reaction, as described previously, but the major advantages in coal liquefaction are:

1. Reduced hydrogen or CO consumption and light gas make,
2. better distillate and residuum product quality since coke and char formation is suppressed to a large extent,
3. production of a less refractory residuum which is more susceptible to second stage hydrogenation reactions as hydrocracking,
4. significant energy savings, hence improved process economics, and

5. lower grade materials requirements which again improves the project economics (17).

Solvents

Coal conversion can be envisioned to occur in three stages: solubilization of the coal, defunctionalization of the coal, and hydrogen transfer and rehydrogenation of the solvent. In each of these stages, the nature of the solvent can affect the rates of reaction and distribution of the products (2). The solvent governs product selectivity by controlling the path taken by generated intermediates of coal dissolution. The availability of hydrogen donors in the solvent will determine the preferred path (2).

There are 4 major properties desired in a solvent:

1. Hydrogen donor capacity of the solvent and the ability to supply hydrogen to the free radicals generated during coal dissolution. The principal sources of hydrogen appear to be partially hydrogenated aromatic hydrocarbons such as tetralin.

2. The ability to dissolve coal. To be effective in dissolution, the solvent must contain polar functionality as do pyridines, phenols, quinolines and their derivatives.

3. Hydrogen transfer capability. This encompasses the ability of the solvent to shuttle hydrogen from one location

within the coal structure to another to cap coal-derived free radicals as they are formed. Compounds which exhibit this ability are naphthalene and its alkyl derivatives, hydrocarbons and their alkyl derivatives, and heterocyclic nitrogen compounds such as quinoline.

4. Chemical structures associated with char formation. With the formation of char, hydrogen will be liberated to react with the hydrogen deficient species (2).

Initial work done to determine the composition of coal derived solvents found the major species present to be:

70% hydrocarbons and condensed aromatics

8% heterocyclic compounds such as ethers

10% monophenols

12% polyphenols and model nitrogen compounds (2).

The solvents analysed were derived from several coals including Wyodak-Anderson, West Kentucky 9 & 14, and Illinois No. 6 coals. The composition of specific solvents will likely vary from coal to coal but remain close to this analysis.

In subsequent research the solvent properties of specific pure components, or mixtures of the pure components were analysed to identify necessary properties for coal dissolution (2). To that end, the bulk of the research seems to have focused on compounds such as tetralin, 1,2,3,4-

tetrahydroquinoline, pyridine and their derivatives (18-24). In particular it was realized that the model nitrogen heterocyclic solvents had the strongest influence on coal dissolution (17-21,23-30), typically resulting in near complete conversion of bituminous coals at approximately 420°C. Most recent work has also focused on nitrogen compounds such as amines for solvents (31,32). The most important observation when using amines as solvents is that it is possible to achieve complete dissolution of low rank coals at temperatures near 275°C (31). However the advantage of high coal dissolution is offset by the fact that the solvent becomes irreversibly incorporated in the various products and cannot be recovered (18,19,24-26,30,33).

As indicated above a large number of studies have demonstrated the effects of using model nitrogen compounds, but the majority have done so at high severity conditions. Distillate yields from these experiments were much lower than expected, and there was significant nitrogen compound incorporation into the non-distillable residue (17). The apparent void in data that exists is the effect of using model nitrogen compounds at low severity conditions. This is precisely the aim of this thesis study.

Project Objective

Preliminary work at the Colorado School of Mines (CSM) showed that the degree of nitrogen compound incorporation in coal liquefaction products may be reduced at low severity reaction conditions. This observation may be explained by the results of Collins et al. (26,33), who showed that physical entrapment of the solvent, as opposed to chemical adduction, may be the likely mode of incorporation at temperatures less than about 400°C. Physical entrapment of the nitrogen compound would allow removal in subsequent solvent extraction processes.

Further results from CSM also indicated that the catalytic effectiveness of the nitrogen compounds increases with decreasing reaction temperature, especially when a CO/H_2O or $CO/H_2O/H_2$ atmosphere is used to supply hydrogen through the water-gas shift reaction (28).

The research objective of this project was to investigate the effect of several model nitrogen compounds on coal conversion, product yield and feed gas consumption for the co-processing of coal and petroleum heavy oil. Co-processing was carried out at both low severity and high severity reaction conditions. Both Wyodak subbituminous and Kentucky 9 bituminous coals were investigated in this study. The model nitrogen compounds used consisted of heterocyclic

compounds which are naturally indigenous to coal derived liquids, and two aliphatic amines.

MODEL NITROGEN SOLVENTS

Basis of Model Nitrogen Compounds' Reactivity

The exact mechanism by which model nitrogen compounds react with coal is unknown, yet it seems certain that the basis for reactivity lies in the substituent nitrogen atom's free pair of electrons (43). The presence of the lone pair of electrons means that such compounds can act as a nucleophile and thus act as a Lewis base. The basicity of a compound is a measure of the availability of the free electrons for reaction. This is generally recorded as a pK_b value of the base, or the pK_a value of the conjugate acid (34-36). Table I lists several representative nitrogen compounds and their respective basicities as measured in aqueous solution The factors which influence availability of the electrons include electrostatic effects, inductive and resonance effects, hydrogen bonding, conformational differences and steric factors (37).

The electrostatic and inductive effects depend on the intrinsic tendency of a substituent to attract electrons to itself, and withdraw them from other locations within the molecule. Most elements likely to be substituted for hydrogen in an organic molecule are more electronegative than hydrogen, so most exert electron withdrawing effects. This effect may lead to an increase in the basic nature of

Table I: Basicity Ranking of Model Nitrogen Compounds in Aqueous Solution

NITROGEN COMPOUND	REFERENCE	pKb
piperidine	39	2.88
dipropylamine	39	3.00
diethylamine	38	3.00
diisobutylamine	39	3.09
triethylamine	38	3.25
dimethylamine	38	3.27
ethylamine	38	3.29
n-butylamine	38	3.32
tri-n-propylamine	38	3.35
n-propylamine	38	3.39
isopropylamine	38	3.40
sec-butylamine	38	3.40
tributylamine	39	4.07
benzylamine	39	4.65
ammonia	38	4.74
4-aminopyridine	39	4.89
morpholine	39	5.67
4-piperidinopyridine	37	8.04
acridine	39	8.42
4-aminophenol	39	8.50
isoquinoline	39	8.58
pyridine	39	8.75
1,2,3,4-tetrahydroquinoline	40	8.97
8-hydroxyquinoline	39	8.98
quinoline	39	9.19
7,8-benzoquinoline	39	9.20
aniline	39	9.40
5,6-benzoquinoline	37	10.05
diphenylamine	38	13.23

the molecule.

The resonance effect refers to electron delocalization. It arises from ¶-bond electron resonance and affects the nitrogen free electron availability, especially in heteroaromatic systems. This effect is prominent in heterocyclic nitrogen compounds in which the free electrons of the nitrogen atom also participate in the ¶-electron resonance. When participating in ¶-bonding, they are occupied and not as free to react with electrophilic compounds.

The conformational differences and steric effects contribute where the structural orientation or size of either the molecule containing the nitrogen or the electrophilic molecule that is reacting with the nitrogen compound, affect the electron availability for reaction. If the free electron availability is reduced, the base is weaker than expected.

Hydrogen bonding with the nitrogen atom also reduces the basic character of the compound because this bonding occupies the free electrons reducing their ability to react.

Nitrogen Atom sp^3 Orbital Configuration

When the nitrogen atom is singly bonded to other constituents, as in aliphatic amines, ammonia or saturated

heterocyclic compounds, the nitrogen atom transforms from its standard electronic structure, with '1s', '2s', and '2p' electron orbitals, to a higher energy hybridized state consisting of '1s' and 'sp^3' electron orbitals. The free pair of electrons on the nitrogen atom resides in the higher energy sp^3 orbital, as shown in Figure 1. In this configuration, the electron orbitals have less 's' orbital character, which imparts a higher energy to the free electrons. These electrons are then not as closely held to the nucleus as in the standard orbital configuration, and as such are more accessible for bonding with an electrophile. These electrons also do not participate in any ¶-bonding.

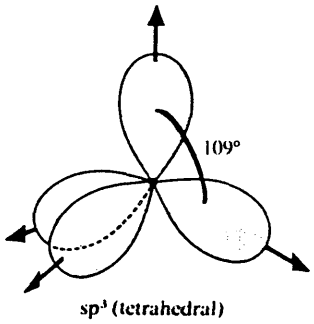


Figure 1: sp^3 Electron Orbital Configuration (41)

Nitrogen Atom sp^2 Orbital Configuration

In unsaturated heterocyclic nitrogen compounds, such as pyridine, (with 1 aromatic ring) or quinoline (with 2 aromatic rings), and variations thereof, the cyclic structure requires a hybridized structure consisting of '1s', 'sp^2' and '2p' electron orbitals for nitrogen, as shown in Figure 2. In this state the free pair of electrons resides in one of the sp^2 orbitals. The sp^2 orbitals have more 's' orbital character than an sp^3 orbital, and as such have a lower energy and are more stable. Thus the electrons in these orbitals are less available for reaction with electrophiles. Also the electrons in the sp^2 orbital resonate with the ¶-electron double bond of the nitrogen atom. This reduces the electrons availability even further. For this reason these heterocyclic compounds are typically not as basic as aliphatic amines.

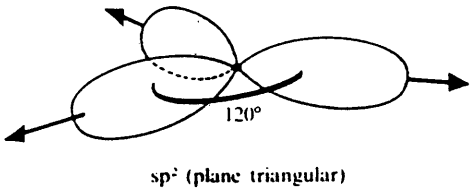


Figure 2: sp^2 Electron Orbital Configuration (41)

Steric Effects of Nitrogen Free Electron Interactions

The other factor which is as important as the electronic effect is the molecular structural effect on any interaction, also known as the steric effect. Aliphatic amines, though more basic than most heterocyclic nitrogen compounds, may be inferior in electrophilic addition reactions in some cases because the nitrogen lone electron pair is more hindered compared to the heterocycle. In the heterocyclic compounds, the substituents bonded on either side of the nitrogen atom are constrained back and away from the nitrogen, thereby presenting the nitrogen and free electrons for better reaction. In this state the outside angle between these adjacent substituents is approximately 240 degrees and approach by an electrophile is rendered easier than in an aliphatic amine. In the aliphatic amine, rotation of the C-N and C-C bonds reduces the angle between the alkyl substituents bonded to the nitrogen, which physically hinders approach. This structural effect on reactivity is known as steric hindrance. In general, heterocyclic nitrogen compounds are likely to have less steric effect than aliphatic amines.

Larsen and Lee (42) used pyridines and anilines substituted in a way which minimized electronic effects on their basicity, so that steric effects involved in the

reaction with coal could be clearly studied. The believed reaction mechanism is through the interaction of the unshared electron pair of the nitrogen with the coal. Alkyl substituents were altered so as to affect the spatial requirements of the base molecule without altering the electron availability. The effect of chain branching was found to be much greater for bituminous coals than in lower rank coals, indicating a much more open structure in the latter.

Halleux and Tschamler (27) studied coal dissolution similarly with alkyl derivatives of pyridine. The overall conclusion was that coal extraction yield depended on both the solvent basicity and the steric effect of interaction between the solvent and the coal. The results indicated that as the alkyl substituents were situated closer to the heterocyclic nitrogen, i.e. in the 2 or 6 position as opposed to the 3 or 5 position in the aromatic ring, coal conversion dropped. The occurrence was attributed to a steric effect which physically hindered the nitrogen substituent in acid-base interactions.

Model Nitrogen Compound Reactivity With Coal

The previous discussion was meant to introduce the reader to some of the more obvious reasons behind the

reactivity of model nitrogen compounds. The possible importance of model nitrogen compounds in the dissolution of coal was first realized and investigated around 1957 (27,43). It was hypothesized that the unpaired electrons present on the bonded nitrogen atom of the solvent complexed with the coal molecules resulting in coal swelling, dissolution, and ultimate incorporation of the solvent into the dissolving coal. The mechanism of reaction is thought to be a function of direct and/or indirect involvement of the nitrogen compound (24,43). In direct involvement, the nitrogen compound acts as a hydrogen transfer agent to shuttle hydrogen from the gaseous atmosphere to the liquid/solid reactants. The indirect mechanism occurs through reaction of the nitrogen compound with oxygen functionalities in the coal, resulting in the cleavage of covalent bonds. The hypothesis of indirect involvement of the nitrogen solvent was substantiated by Atherton et al. (43), who noted that during coal dissolution, much of the coal's oxygen, which is originally present in the form of phenols and ethers, is liberated in the form of water, indicating the breaking of covalent C-O bonds. Some of the more probable reaction mechanisms between coal and nitrogen compounds are those in which the nitrogen compound acts as:

1. a Lewis acid/base complexing agent,

2. a basic tautomerization catalyst, or

3. a hydrogen atom donor.

The Lewis acid-base complexing reaction shown in Figure 3, refers to a reaction in which the nitrogen solvent base hydrogen bonds with a Lewis acid, such as a phenol group, which is itself bonded to the coal. However, evidence exists that this process alone is not sufficient to produce products highly soluble in hexane and benzene (43).

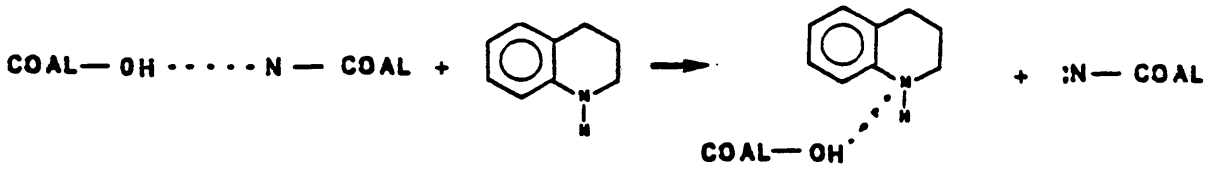


Figure 3: Lewis Acid/Base Reaction of Nitrogen Compound (43)

The tautomerization effect, as shown in Figure 4, is characterized by proton migration within the molecule (37). In this case the nitrogen compound aids in the isomeric transformation of phenolic groups (C-O-) to ketonic groups (C=O), which have a lower overall bond energy. The ketone groups are then more easily attacked and broken down through reduction reactions. Evidence indicates that this mechanism does occur to a large extent (43).

The hydrogen donor reaction mechanism, in which a hydrogen atom is transfered to the coal is the most widely accepted mechanism considered necessary in a good liquefaction solvent. The conventional mechanism is hydrogen transfer to a thermally generated coal radical as shown in Figure 5, followed by rehydrogenation of the nitrogen compound by the reaction gas atmosphere.

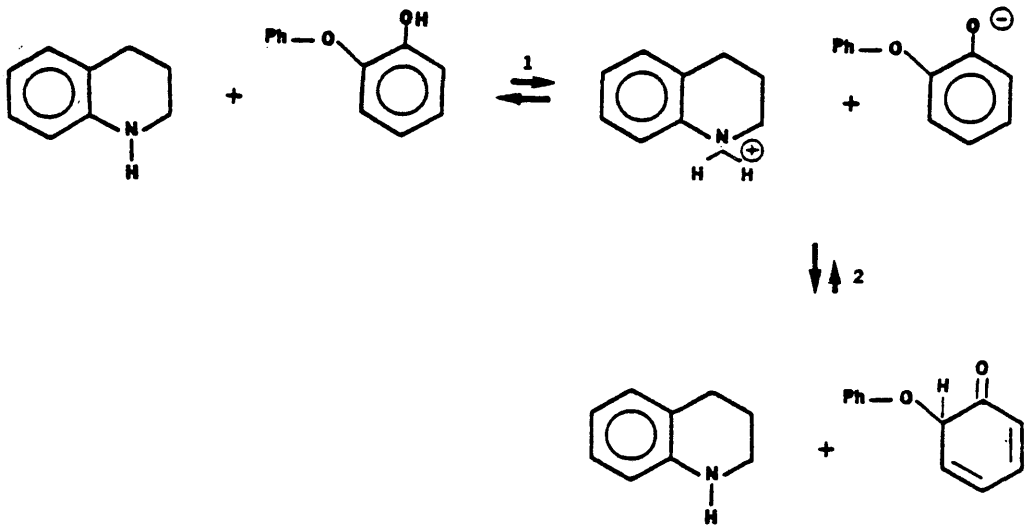


Figure 4: Tautomerization Reaction Mechanism of Nitrogen Compound (43)

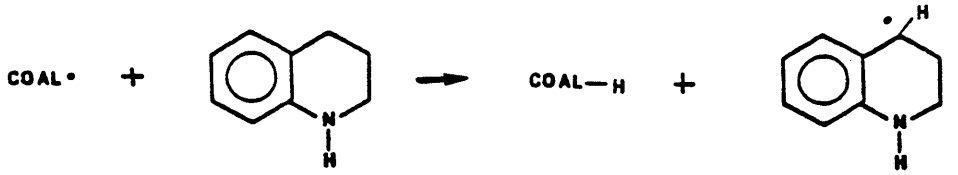


Figure 5: Hydrogen Donor Reaction Mechanism of Nitrogen Compound (43)

Depending on the model nitrogen compound used, the effect of the nitrogen compounds appears to involve several factors:

a) The model nitrogen compound aids in the dissolution of coal through electrophilic addition reactions with oxygen functionalities in the coal,

b) the nitrogen compound is able release weakly bound hydrogen from itself to the coal, and

c) the nitrogen compound acts to shuttle hydrogen from the gaseous reaction atmosphere to the generated coal radicals.

The effect mentioned in (b) is supported by the results of Cronauer et al. (18,19) which indicated that the nitrogen compounds had no effect on product yields when used in conjunction with a good hydrogen donor solvent. When used with a poor solvent, the yields were greatly enhanced. Hirschon and Laine (21) observed that large amounts of THQ (1,2,3,4-tetrahydroquinoline) were not necessary to enhance coal conversion. They found that conversions using 20 weight % THQ were not significantly better than those obtained using 5 weight % THQ, when reacting Wyodak-2 subbituminous coal under a cold charge hydrogen pressure of 8.4 MPa at 400°C for 15 minutes.

The effect described in (c) was concluded to be occurring in the work by Panvelker et al. (29). Since the coal is immersed in the solvent phase, the only way hydrogen from the gas can reach the coal is through transport through the solvent.

Incorporation of Model Nitrogen Solvents into the Coal Conversion Products

Complexing of the nitrogen solvent with the coal can result in solvent incorporation into the dissolving coal and its derived products. This aspect of these compounds is the major drawback to their use.

McNeil et al. (30) found that most incorporation takes place into the asphaltene product fraction (tetrahydrofuran soluble/toluene insoluble material) and the oil product fraction (cyclohexane soluble material).

Atherton (43) concluded that when the solvent consisted of 100% model nitrogen compound which typically resulted in 100% conversion to THF solubles, there was solvent incorporation in the 455°C+ product.

Most recently Silver et al. (23) found that 10-30 weight % of added THQ becomes incorporated into the liquefaction products of Wyodak subbituminous coal at reaction conditions of 418°C, 7.6 MPa cold charge hydrogen pressure, and 30 minute reaction time. The balance was not

incorporated and was present in both the monomer and dimer structure of THQ. Hellgeth et al. (24) similarly found that between 8-15 weight % of the nitrogen solvent, in general, was incorporated into the residium with similar reactants and reaction conditions. The solvents investigated were 2,3-cyclohexenopyridine, 1,2,3,4-tetrahydroisoquinoline, 1-methyl-2,3,4-trihydroquinoline and quinoline. For THQ however, approximately 5.4% was incorporated in the residuum, while 2.6% was lost to light ends and gas products.

Possible Mechanisms of Nitrogen Compound Incorporation

Nitrogen compound incorporation is thought to occur through both physical and chemical means (26,30,33,43). Physical incorporation occurs when the solvent enters the thermally swelled coal and is physically trapped upon coal cooling and subsequent shrinkage. This mechanism was shown to occur at temperatures less than 200°C (26). The chemical adduction is thought to occur through chemical bond attachment and attachment by molecular interactions (22,26,30,43), occurring at higher temperatures of approximately 400°C. The most common bonding mechanism thought to be present is that of hydrogen bonding of the nitrogen solvent to acidic phenolic sites within the coal (26,30,43). However, evidence exists to refute this

hypothesis (43) and was based on subsequent processing of the co-processing product which contained the adducted solvent, at conditions severe enough to disrupt any hydrogen bonding present.

Another possible mechanism is reaction of nitrogen compounds with oxygen functional groups such as carbonyl (C=O), present in the coal (43). Two model systems were studied in an attempt to demonstrate this mechanism. The studies consisted of reacting heterocyclic hydrocarbons containing a carbonyl group (6-methyl-2-pyridone) with a mixture of both piperidine solvent and THQ solvent in tetralin. In both cases the model nitrogen solvent was rapidly adducted to the heterocycle as demonstrated in Figure 6. The apparent reaction is between the carbonyl group carbon and the nitrogen of the model nitrogen solvent. Explanation of this reaction lies in the fact that the carbonyl carbon is electron deficient, hence acidic, and is susceptible to attack by the electron rich model nitrogen solvent. In addition, since the carbonyl group is planar, it is open to relatively unhindered attack from above or below in a direction perpendicular to the plane of the molecule.

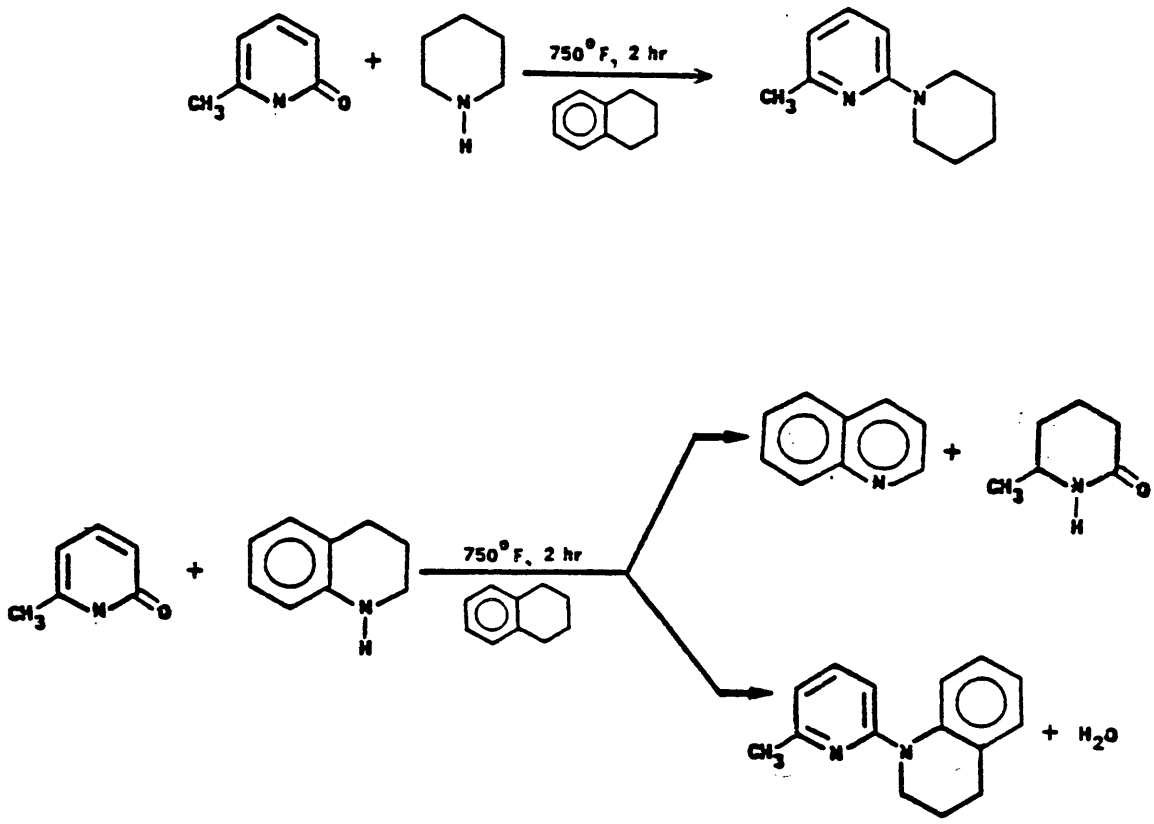


Figure 6: Reaction Mechanism Between Nitrogen Compound and a Heterocyclic Hydrocarbon Containing a Carbonyl Group (43)

Model Nitrogen Compound Reactivity in the Presence of the Water-Gas Shift Reaction

The water-gas shift reaction refers to the reaction of carbon monoxide gas with water under elevated pressure and temperature, to generate carbon dioxide and hydrogen gas:

$$CO + H_2O \longrightarrow CO_2 + H_2.$$

Work by Yoneda et al. (44) first established the concept of using a basic aqueous solution of metal carbonate as a catalyst for the water-gas shift reaction. More recently Elliott et al. (44) completed an extensive study of catalytic agents for the water-gas shift reaction. They investigated the use of alkali metal salts, alkaline earth salts, transition metal salts, ammonia and ammonium compounds. Conclusions of this work indicated that the catalytic effect of the compounds was related to their basic nature, yet a stronger base was not always more reactive than a weaker base. For instance, the alkali metal carbonates generated a pH of 11.5 to 12.0, while the transition metal carbonates exhibited a pH of about 8.5. Both were nearly equal in reactivity (44). The alkali metal carbonates proved to be the most active catalysts. Hodges and Creasy (45) also concluded that alkali metal carbonates promoted both the water-gas shift reaction and coal liquefaction.

Elliott (44) also tested the acid forms of two of the carbonate catalysts, and found that neither exhibited any catalytic activity for the water-gas shift reaction.

Further testing (44) was done with ammonium carbonate and hydroxide, and ammonia gas to demonstrate if the metal cations present in the carbonate solutions were an active

component. The results demonstrated that the ammonium compounds were catalytically active to the same degree as the alkali metal carbonates, indicating that the metal cations present are an inactive part of the reaction.

These results imply that model nitrogen compounds may also promote the water-gas shift reaction, since many model nitrogen compounds are basic, and are similar in structure and composition to the ammonium and ammonia gas.

The proposed reaction sequence would then consist of the nitrogen compound promoting the water-gas shift reaction, thereby generating more hydrogen species that can in turn react with the coal and nitrogen compound to increase coal conversion (45).

EXPERIMENTAL WORK

Materials

Coal

The primary objective of this work was to determine the effect of various model nitrogen compounds on the coal conversion to tetrahydrofuran-soluble product. Two types of coal were analysed to also determine the effect of coal rank on conversion. The coals used were;

(a) Kentucky 9 bituminous coal, and

(b) Wyodak subbituminous coal.

The ultimate analysis of these coals is shown in Table II. Both coals were received stored in air, and as shown by the ultimate analysis, were highly oxidized. They were subsequently crushed to 100% -60 mesh, and were used in this state.

Solvents

Another objective of this work was to determine the effect of a low grade solvent on overall coal conversion. Low grade solvent refers to a hydrocarbon liquid which has a low hydrogen to carbon ratio, is highly viscous, and contains significant quantities of high boiling material. Liquids such as petroleum residuum, heavy oil and the like fall into this category. Only one solvent, a Cold Lake, Alberta atmospheric residuum, was considered in this study.

Table II: Properties of Wyodak Subbituminous and Kentucky 9 Bituminous Coals

Ultimate Analysis (wt% dry basis)	Kentucky Bituminous	Wyodak Subbituminous
carbon	69.7	61.5
hydrogen	4.7	4.0
oxygen	9.2*	18.5*
nitrogen	1.4	1.0
sulfur	4.2	0.7
ash	10.8	14.3
Total	100.00	100.00
Solubilities, wt.%		
cyclohexane soluble	0.0	0.0
tetrahydrofuran soluble	9.3	0.3

(*: by difference)

An elemental analysis of this solvent is shown in Table III.

Model Nitrogen Compounds

The model nitrogen compounds used for this study were chosen to provide as wide a range of basicity and steric hindrance effects as possible. The compounds used are shown in Figure 7.

Reaction Gases

Two different reaction gases were used in this study: hydrogen and carbon monoxide. Each gas contained approximately 1% krypton gas to act as a tracer element for accurate gas analysis. When hydrogen was used it was done so with no other gaseous additions; whereas when carbon monoxide was used, approximately 10 grams of distilled water was added to the reactor mixture. This amount of water was equivalent to 50 weight % of the coal charged to the reactor. The water was a necessary reactant to allow the water-gas shift reaction to take place, as described earlier in this text.

Table III: Properties of A-8 Cold Lake Atmospheric Residuum, Petroleum Heavy Oil

Distilled Fraction	Wt. % Distilled
water	0.0
IBP-177°C	0.4
177-260°C	4.1
260-344°C	4.1
344-455°C	10.9
455°C+	80.5

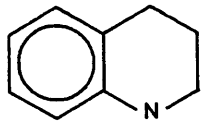
Ultimate Analysis (wt.%)	
carbon	84.2*
hydrogen	12.0*
nitrogen	1.0*
sulfur	1.1
oxygen	1.7
ash	0.0

Solubility (wt.%)	
cyclohexane	100.0
tetrahydrofuran	100.0

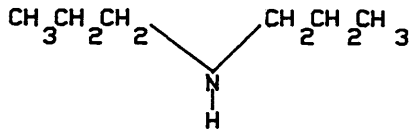
(*: carbon, hydrogen, nitrogen measured in this lab were 89.35, 12.40, and 0.43 respectively. Tabulated values above are from an outside laboratory).

Figure 7: Model Nitrogen Compounds Used in this Thesis

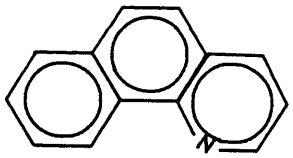
(a) Compound N1
1,2,3,4-tetrahydroquinoline
97% purity, pKb=8.97



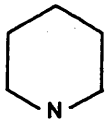
(b) Compound N2
dipropylamine
99% purity, pKb=3.00



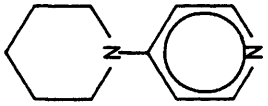
(c) Compound N3
7,8-benzoquinoline
97% purity, pKb=9.20



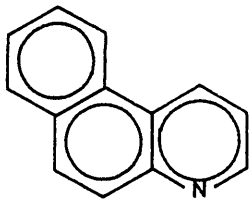
(d) Compound N4
piperidine
98% purity, pKb=2.88



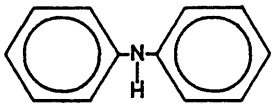
(e) Compound N5
4-piperidinopyridine
98% purity, pKb=8.04



(f) Compound N6
5,6-benzoquinoline
99% purity, pKb=10.05



(g) Compound N7
diphenylamine
99% purity, pKb=13.23



Experimental Procedure

Process Overview

A schematic flow diagram of the experimental steps used in this work is shown in Figure 8. The details of each step are highlighted below.

Reactor Operation

The liquefaction co-processing experiments were carried out in a 300 cm3 Autoclave Engineers Inc. batch reactor equipped with a Magnedrive II rotary type mixer capable of stirring at speeds as high as 2500 rpm. A schematic of the reactor system is shown in Figure 9. The reactor and mixing unit were mounted in a vertical position. Heating was accomplished by an electric heating element which encased the reactor. The element was raised and lowered using an electric jack assembly.

An experimental run was started by charging the reactor with approximately 20g of coal, and 40g of petroleum residuum. If a basic nitrogen compound was used, the feed mixture was changed to 20g of coal, 30g of petroleum residuum and 10g of model nitrogen compound. In each case a coal:solvent weight ratio of 1:2 was maintained. In the carbon monoxide runs, 10g of distilled water was also added to the reactor feed accounting for 50 weight % of coal. The

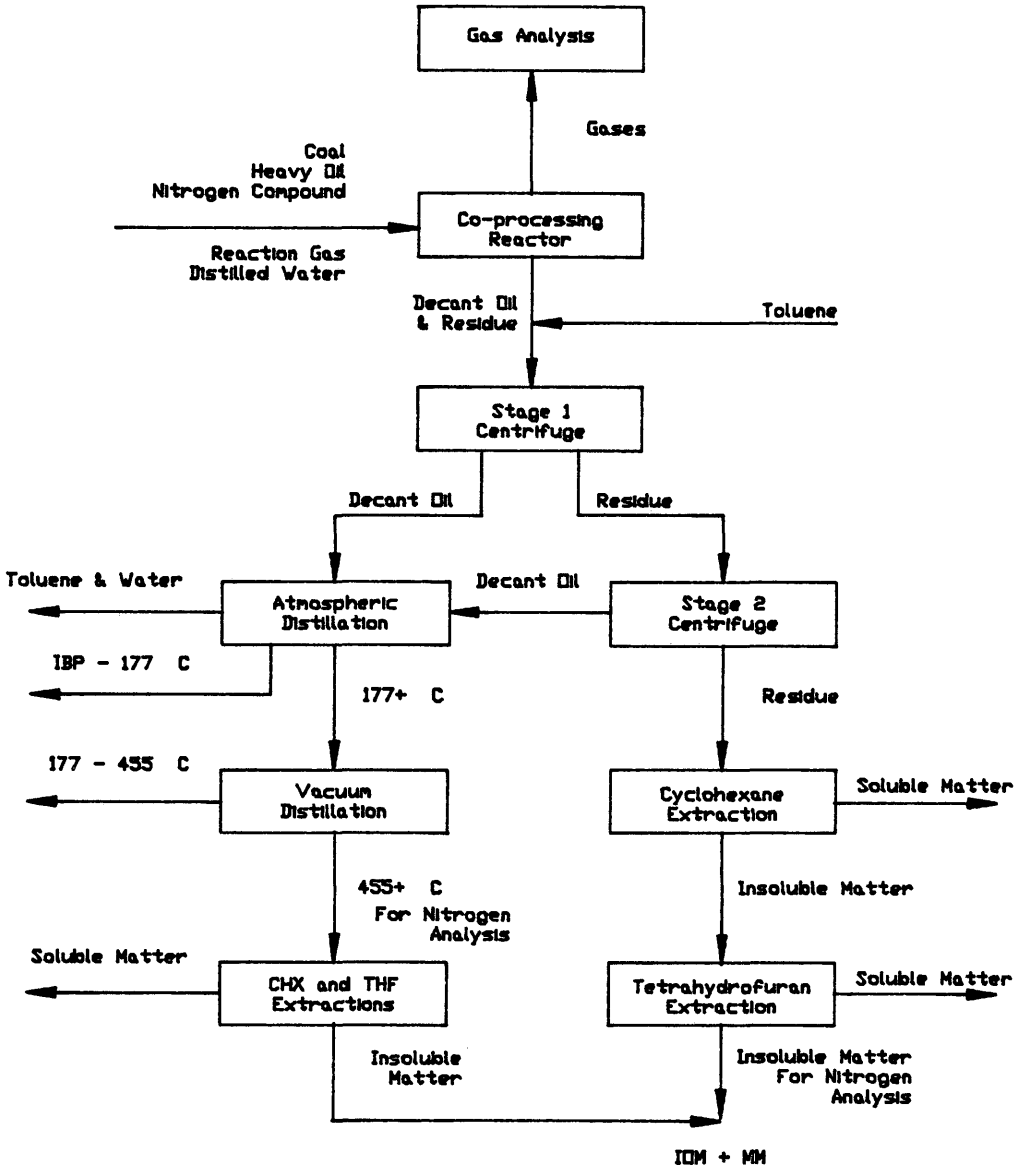


Figure 8: Schematic Flow Diagram of Experimental Co-Processing Runs and Product Separation

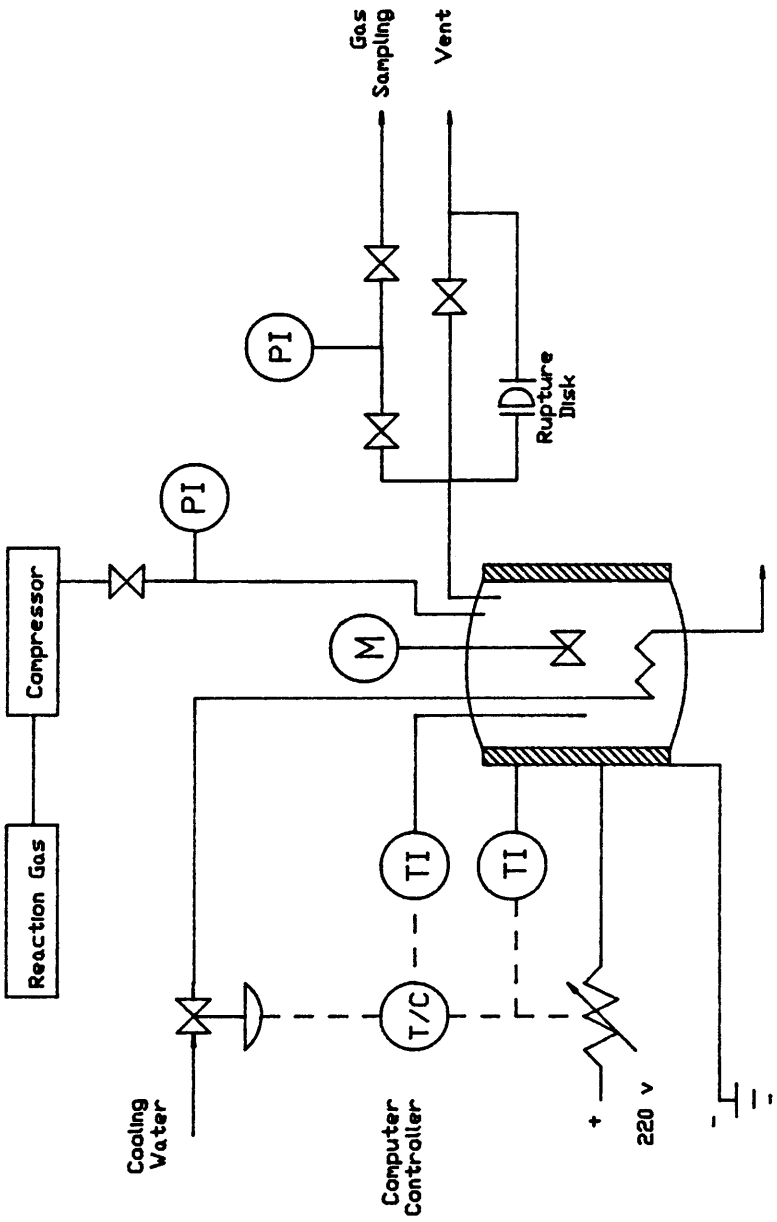


Figure 9: Schematic of Co-Processing Batch Reactor System

reactor system was then sealed and flushed two times with feed gas, to minimize air contamination of the system, and then cold charged with the feed gas to the desired reaction pressure. The system was pressure checked for approximately 30 minutes at the cold charge gas pressure. If a significant pressure drop occurred, the gas was vented, reactor seals were tightened, and the pressurization procedure repeated.

A hydrogen feed gas was cold charged at 8.7 MPa and carbon monoxide was cold charged at 5.7 MPa. Both charge pressures resulted in an operating pressure of 14.5 to 16.6 MPa at an operating temperature of 344°C. The reactor was protected from overpressure by a rupture disk set to vent at 38.6 MPa.

The electric furnace was raised around the reactor and the system was heated to reaction temperature at an average rate of 8 - 11°C/minute. The Magnedrive II stirring mechanism was started when the reactor contents reached 65 - 75°C, and slowly increased to 2500 rpm by the time the reactor contents reached 210°C. This mixing speed was maintained throughout the run and was not decreased until cooling of the reactor contents was started. Experiments were completed at two sets of conditions, as indicated in Table IV. Temperature control of the reactor

Table IV: Liquefaction Co-Processing Reaction Conditions

	High Severity Reaction Conditions	Low Severity Reaction Conditions
Reaction Temperature	427-440°C (800-825°F)	344°C (650°F)
Feed Gas	hydrogen	hydrogen or carbon monoxide/water
Feed Gas Charge Pressure	6.9 MPa	Hydrogen @ 8.7 MPa CO/water @ 5.7 MPa
Maximum Reaction Pressure	14.5-16.6 MPa	14.5-16.6 MPa
Reaction Time	30 minutes	30 minutes
Feed Coal	Bituminous or Subbituminous	Bituminous or Subbituminous
Feed Heavy Oil	Cold Lake Atmospheric resid A-8	Cold Lake Atmospheric Resid A-8

was maintained with an Apple IIe personnal computer, augmented with three additional interface cards from Lawson Labs, Inc. The three interface cards included a Model 14 card for analog/digital translation, a Model 20 card for computer operation as a multi-channel thermometer, and a Model 24 card to allow multi-channel control of external devices. The computer controlled the reactor temperature by varying the power to the electric heater and the flow rate of cooling water through an internal cooling coil within the reactor.

The reactor time-temperature profile, as shown in Figure 10, was typically 30-40 minutes heatup time, 30 minutes at reaction temperature, and 3-5 minutes quenching time from reaction temperature to 100°C.

After turning off and lowering the electric heater from the reactor body, quenching was achieved through a combination of cooling water circulated through the cooling coil present within the reactor and forced air convection on the outside of the reactor.

The reactor and its contents were allowed to cool overnight (12-20 hours) to allow complete cooling and gas evolution from the liquid phase. If less cooling time was allowed, the liquid products would erupt from the reactor wherever a pressure connection was loosened.

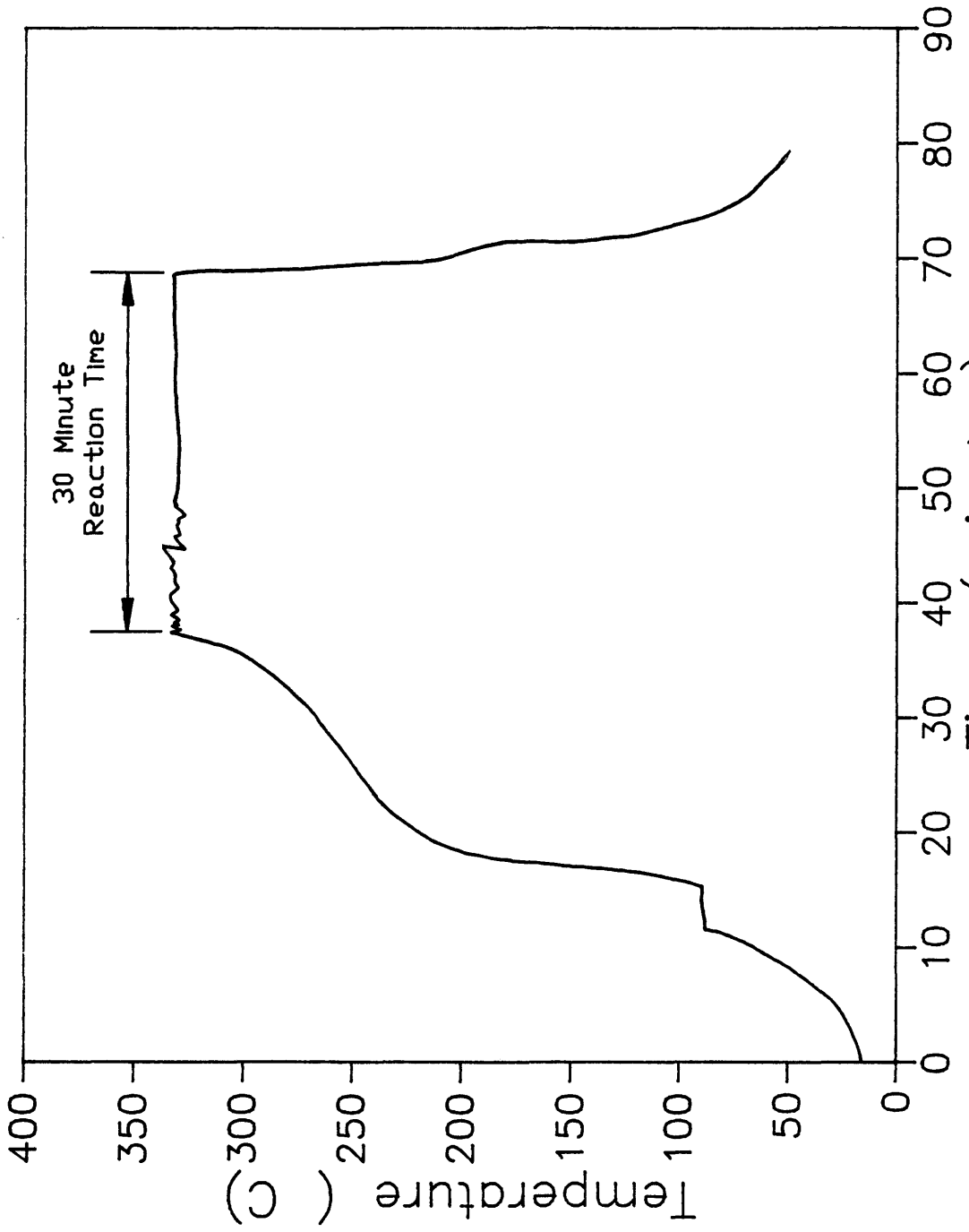


Figure 10: Reactor Time-Temperature Profile for a Typical Low Severity Reactor Run

Once the system was properly cooled, the reaction gases were vented to sample tanks until the reactor pressure was reduced to 0 MPa. The reactor was then removed from the rest of the operating apparatus and the reactor head was removed from the reactor body. The reactor head was placed in a support to allow liquid and solid products to drain into a preweighed container. The contents of the reactor body were also poured into the same preweighed container. To ensure good recovery, a quantitative toluene wash was used to reduce the viscosity of liquid products, and the liquid and solid products were scraped from both the reactor head and the reactor body. Typical mass recovery was in excess of 85 weight % of the charged reactants. After all gaseous, liquid and solid products were removed, the reactor was cleaned in preparation for the next run. The cleaning procedure consisted of loading the reactor with approximately 100 ml of toluene or THF, and taking the reactor through a heat-up cycle up to about 150°C for 10 minutes. Upon cooling the contents were removed and the reactor was dried and made ready for the next run.

Centrifuge

The combined liquid and solid product from the reactor were processed through a centrifuge which operated at 2000

rpm for approximately 45 minutes. The product liquid was separated and collected, and the remaining solids-liquid slurry recentrifuged for an additional 15 minutes. The second centrifuge step usually resulted in an additional 2-4 grams of liquid recovery. The liquid and solid samples were then stored in separate containers for future analysis. The liquid sample was termed 'decant oil', and contained the toluene wash as well as the oil product from the co-processing reaction. The decant oil was essentially solids-free, indicating good solid/liquid separation. The remaining oily solid sample was designated 'residue'. The residue was not in a dry state but was coated by a portion of the liquid product.

Gas Analysis

The product gas samples collected were analysed on a Carle model 111-H gas chromatograph (2100 mm x 3.2 mm column, molecular sieve packing, 13 angstrom pore size, 45/60 mesh particles, 320°C operating temperature) equipped with a Hewlett Packard model 3390A integrator. This system was calibrated for 14 gas components, including C1-C4 alkanes and olefins, hydrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, and krypton. Each sample gas was analysed twice to verify results. The gas chromatograph was

calibrated every 2 - 4 weeks using four standard gas mixtures of the above gas components.

The amount of gas charged to the reactor prior to an experimental run was calculated using the ideal gas law:

$$PV = ZnRT.$$

The gaseous volume of the reactor, the pressure, temperature and gas compressibility factor of the charge gas, were all known or calculated. The reaction gases also contained a known amount of krypton gas to act as an inert tracer element. In this way the moles of product gas were accurately determined in relation to the initial gas charge.

Dean-Stark Analysis of Decant Oil

A 30-40 gram sample of decant oil was used as feed to the Dean-Stark distillation analysis. This sample size ensured that approximately 10 grams of oil was available for further distillation analysis. The remaining 20-30 grams consisted of toluene from the reactor wash procedure and water.

The oil/toluene sample was placed in a 100 ml distillation flask, heated and allowed to boil for approximately 30 minutes in an ASTM D-95 Dean Stark apparatus. The objective of this procedure was to

quantitatively remove any water present in the sample. The Dean-Stark analysis is based on the fact that toluene and water will form an azeotropic mixture at a temperature near 100°C at atmospheric pressure. The procedure results in the vaporization of the toluene/water azeotrope mixture which is condensed and collected. Cooling the mixture to room temperature breaks the toluene/water azeotrope and allows for direct analysis of the water content. The procedure is continued until condensate removal has essentially stopped indicating that all of the water and most of the toluene has been removed. The entire Dean-Stark analysis is generally completed in approximately 30 minutes.

Condensate from the Dean-Stark analysis was quantitatively analysed for water content based on density measurements or qualitatively estimated if a visible water phase was generated.

Dean-Stark Analysis of Centrifuge Residue

The Dean-Stark procedure was also used to measure any residual water trapped in the centrifuge residue for experimental runs which used carbon monoxide and water as reducing agent. It was found in these runs that the majority of water remained trapped in the residue and was not present in the decant oil exclusively. The procedure involved

dissolving approximately 3-4 grams of residue in 20 grams of toluene. This mixture was then refluxed in the Dean-Stark apparatus and the water content was then determined using the procedures described previously. This analysis was not required for runs using a hydrogen gas atmosphere because preliminary Dean-Stark tests showed that essentially no residual water was in the centrifuge residue for these experimental runs.

Atmospheric Distillation

After completing the Dean-Stark analysis of the decant oil, the remaining liquid in the distillation flask was transferred to an ASTM D-86 distillation apparatus. The flask was heated to a 172°C vapor temperature, at Golden, Colorado atmospheric pressure of 620 torr. This temperature corresponds to a 177°C cutpoint temperature at 760 torr (46). Distilled vapors were condensed, collected and weighed directly. The collected liquid sample was designated the 177°C- fraction.

Vacuum Distillation

Following the atmospheric distillation, the remaining decant oil was cooled to approximately 27°C and subjected to an ASTM D-1160 vacuum distillation at a vacuum of 0.1 to

0.35 torr. Based on approximate vapor-pressure correlations previously developed for coal liquids, the actual temperature at the reduced pressure was corrected to a standard pressure of 760 torr. In this manner, product fractions were collected in the ranges of 177-260°C, 260-344°C, and 344-455°C all corresponding to a pressure of 760 torr. These combined fractions all constituted the 177-455°C distillate product. The remaining residual liquid was termed the 455°C+ fraction.

Soxhlet Extraction of the 455°C+ Residuum

In order to quantitatively remove the 455°C+ fraction from the distillation flask, liquid nitrogen was poured into the flask to freeze the residue and enable it to be scraped out of the flask as a solid. A sample of 1-2 grams of the 455°C+ residual fraction was accurately weighed into a ceramic Soxhlet extraction thimble and extracted using cyclohexane (CHX) solvent for approximately 24 hours. After the extraction, the thimble and 455°C+ CHX insoluble material was vacuum-dried for approximately 24 hours. After drying, the thimble was accurately reweighed to determine the extraction weight loss to the solvent. The thimble and 455°C+ CHX insoluble sample were then subjected to a tetrahydrofuran (THF) Soxhlet extraction in a similar

manner. The remaining THF insoluble material consisted of insoluble organic matter (IOM) and mineral matter (MM). These fractions represent the amount of unconverted coal and mineral matter remaining after completion of the co-processing experiment.

Soxhlet Extraction of the Centrifuge Residue

A sample of 1-2 grams of residue was subjected to sequential Soxhlet extractions in cyclohexane and tetrahydrofuran, using the same procedure as described previously.

Elemental Analysis

Elemental analysis was performed for selected experimental runs on the THF insoluble matter from a residue Soxhlet extraction, the 455°C+ residuum and the individual liquid product fractions. The analyses were performed on a Carlo Erba Elemental Analyzer, model 1106, equipped with a Hewlett Packard model 3390A integrator.

Equipment Material Balances

The data collected in each of the procedures previously described were ultimately used to determine the amounts of gaseous, liquid, and solid products from the liquefaction reaction. Mass balances were performed around each process step and any losses were proportionately distributed among the products of the respective steps.

Reactor Material Balance

Losses associated with the reactor occurred in all three phases; gas, liquid and solid. The liquid and solid losses were due to an inability to remove 100% of these product phases from the reactor. Approximately 5 grams of solid and liquid product which amounts to about a 10% loss in material compared to the charged reactants, could not be recovered. Gaseous losses were only noticed in runs in which a carbon monoxide feed gas was used. The detectable loss occurred in the carbon dioxide product. Indications were that a portion of the CO_2 produced remained dissolved in the liquid products. The amount of CO_2 lost to solution was estimated according to the stoichiometry of the water-gas shift reaction. The gaseous losses were added into the total product gas. The liquid and solid losses were added into the total liquid and solid product combined.

Centrifuge Material Balance

Losses occurring in this step were approximately 3 grams or less, and accounted for less than 2% of the total liquid and solid product. These losses occurred as a result of material transfer to the centrifuge container, and back again to storage containers. The loss was added back into the products but split in proportion to the relative amounts of solid and liquid product after the centrifuge. The proportional split of these products was the best choice since the actual product split was not determined.

Dean-Stark and Distillation Material Balances

Losses occurring in the Dean-Stark procedure accounted for less than 1% of the toluene-water mixture extracted. This loss was attributed to uncondensed vapors escaping the apparatus. The loss was added directly to the total fluid extracted by the procedure.

Mass balance discrepancies occurring in the distillation procedure were typically mass gains of approximately 0.1 to 0.4 grams. This gain was attributed to excess glass joint lubricant remaining on the individual glass joints after cleaning. The discrepancy was subsequently detected during weighing of the individual distillation apparatus components. The gain was then

distributed between the first three distillation fractions, accounting for, at most, 1% of the particular fraction added to.

Solvent Extraction Material Balance

Mass balance discrepancies around this unit were rare and if they occurred were attributed to moisture uptake by the ceramic thimble used to contain the sample during the extraction. When these discrepancies occurred they were of the order of .0001 grams, and were thus considered to be negligible.

Elemental Analysis Data

The elemental analyses performed on the Carlo Erba Elemental Analyser have a degree of error inherently present. The operation of the unit requires that a standard compound of known nitrogen, hydrogen and carbon content be analysed to calculate respective 'K' factors. The 'K' factors are used to calculate the elemental contents of unknown samples. The 'K' factor is a strong function of the sample mass analysed, and as a result error with individual readings ranged from about 1 - 6%.

DETERMINATION OF PRODUCT YIELDS

Yield Calculations

The yield of each product species was calculated on the basis of MAF coal feed (moisture and ash free coal), and MAF coal & 455°C+ Resid feed (moisture and ash free coal & the 455°C+ fraction of the feed residuum solvent). The yield was calculated in the following manner:

(a) MAF coal basis:

$$\text{Yield \%} = \frac{100 \times (\text{mass of species out} - \text{mass of species in})}{\text{mass of MAF coal charged}}$$

(b) MAF coal & 455°C+ resid basis:

$$\text{Yield \%} = \frac{100 \times (\text{mass of species out} - \text{mass of species in})}{(\text{mass of MAF coal \& 455°C+ resid charged})} .$$

The amount of MAF coal is determined as:

(mass coal charged) x (1 - fraction ash in coal) x (1 - fraction bulk moisture in coal).

Yields were calculated for the following product species for runs which used a CO gas atmosphere:

(a) carbon dioxide (net total including estimated solubility loss)

(b) hydrogen

(c) water

(d) C_1-C_3 (saturated and unsaturated hydrocarbon gases)

(e) C_4-455°C distillate

(f) 455°C+ (CHX soluble material)

(g) 455°C+ (THF soluble / CHX insoluble material)

(h) IOM & MM (THF insoluble organic matter and mineral matter).

For runs using a hydrogen gas atmosphere, the yield of carbon monoxide gas was calculated in place of the hydrogen yield.

The amount of feed gas consumed in the reaction was calculated in two ways. Both ways resulted in identical values. The first method was based on the species product yields, and the fact that they must sum to 100%. The gas consumed was calculated as:

Feed gas consumption = Sum of individual species product yields - 100.

The second method was calculated as:

$$\text{Feed gas consumption} = \frac{100 \times (\text{mass of gas in} - \text{mass of gas out})}{\text{MAF coal charged}} .$$

Similarly if the MAF coal & 455°C+ basis was used, this term replaced the denominator in the above expression.

The solvent extraction solubility was determined as follows:

(a) $$\%\ \text{Sample CHX soluble} = \frac{(\text{Min} - \text{Mout}) \times 100}{\text{Min}},$$

(b) $$\%\ \text{Sample THF soluble} = \frac{(\text{Min} - \text{M2out}) \times 100}{\text{Min}},$$

where:

Min = mass of wet sample charged to extraction thimble,

Mout = mass of dry sample remaining after CHX extraction,

M2out = mass of dry sample remaining after THF extraction.

EXPERIMENTAL DATA SUMMARY

The experimental data are tabulated in Appendix A. A summary of the experimental runs used in this study, listing reactants and reaction conditions, is shown in Table V. Yield and conversion results for experiments using hydrogen feed gas and carbon monoxide feed gas are summarized in Tables A-1 and A-2 respectively, of Appendix A. Tables A-3 through A-5 tabulate the percent nitrogen, carbon, hydrogen and carbon/hydrogen mass ratio, of the samples analysed on the Elemental Analyser. Tables A-6 and A-7 tabulate the percent of the total nitrogen that resides in the THF insolubles and 455°C+ residuum respectively.

Table V: Summary of Reactants and Conditions Used in Experimental Co-Processing Runs

Run	Coal	Reaction Gas	Nitrogen Compound	Heavy Oil or Solvent	Reaction Conditions
G8	B	H2	----	A8	LS
G9	B	H2	N1	A8	LS
G10	B	CO/H2O	----	A8	LS
G11	B	CO/H2O	----	A8	LS
G12	B	CO/H2O	N4	A8	LS
G13	B	CO/H2O	N5	A8	LS
G14	B	CO/H2O	N1	A8	LS
G15	B	CO/H2O	N6	A8	LS
G16	B	CO/H2O	----	S1	LS
G17	-	CO/H2O	----	A8 & S1	LS
G18	S	CO/H2O	----	S1	LS
G19	B	CO/H2O	N2	A8	LS
G20	B	CO/H2O	N3	A8	LS
G26	B	CO/H2O	N7	A8	LS
G28	B	H2	N2	A8	LS
G29	----------repeat of G9----------				
G30	B	H2	N3	A8	LS
G31	----------repeat of G9----------				
G32	S	H2	N2	A8	LS
G33	S	H2	N1	A8	LS
G34	B	H2	N2	A8	HS
G35	----------repeat of G14----------				
G36	S	CO/H2O	N1	A8	LS
G37	S	CO/H2O	N2	A8	LS
G38	B	CO/H2O	10 wt% N1	A8	LS
G39	B	H2	N1	A8	HS
G40	B	CO/H2O	10 wt% N2	A8	LS
G41	S	CO/H2O	----	A8	LS
G42	S	H2	----	A8	LS

Notes:

B: bituminous coal
S: subbituminous coal
H2: hydrogen gas
CO/H2O: carbon monoxide/water
A8: petroleum heavy oil
S1: 1-methylnaphthalene
LS: low severity
HS: high severity
N1: THQ
N2: dipropylamine
N3: 7,8-benzoquinoline
N4: piperidine
N5: 4-piperidinopyridine
N6: 5,6-benzoquinoline
N7: diphenylamine

DISCUSSION OF RESULTS

Introduction

Approximately 30 co-processing experiments were completed in this study. The low severity reaction conditions (moderate reaction temperature and pressure and short reaction time) were carefully selected for three reasons:

1. to provide a sufficiently lower reaction temperature than used in conventional coal liquefaction processes,
2. to provide optimal conditions for the water-gas shift reaction, and
3. to provide a reasonable reaction time.

The use of a coal:solvent ratio of 1:2 (or 33 weight % coal) was chosen on the basis of previous work by Miller (14). Miller reported that performing the co-processing reaction at 427°C with approximately 40 weight % coal maximized C_4 - 455°C liquid yields. No attempt was made to optimize the reaction conditions further in Miller's previous high severity liquefaction work.

During this study, most reactor runs were not duplicated. For the few runs which were repeated, the results presented in the following discussion are the average of the duplicate runs. The reproducibility of the

THF coal solubility results in the duplicate runs was very good, typically within a 4% variation on a wt% MAF basis.

No runs were replicated enough times to determine if any experimental bias existed, or to determine the statistical significance and confidence intervals for yield and conversion results. For this reason, the relative effects of changing operating variables will be emphasized rather than the absolute values of yields and conversion levels obtained.

Initially, all product distillation and Soxhlet extraction tests were run in duplicate to ensure the accuracy of the analyses. After the first 19 runs were completed, it became evident that the experimental procedure being used was giving the desired reproducibility. Therefore, most of the subsequent run product samples were only distilled and extracted once each.

Finally, the elemental analyses to determine nitrogen, hydrogen and carbon contents of selected products were performed at least in duplicate, but in many instances were repeated 3-4 times. Repeated analyses in most cases resulted in a typical standard deviation of less than 10% of the mean value.

There were some features inherent in the experimental program which resulted in poor repeatability of distillate

and water yields. Most of the major difficulties arose due to the size of the batch reactor used. A small reactant charge was required to ensure that sufficient volume existed for the reaction gas atmosphere, since an insufficient quantity of feed gas could affect the rate and extent of desired coal dissolution and upgrading reactions. A consequence of the small reactant charge is that only small samples of decant oil are available for the Dean-Stark and distillation procedures, giving rise to small product distillation fractions. The small amount of Dean-Stark toluene/water mixture collected resulted in a poor determination of the product water yield. Initially, the amount of water was determined by density measurements of the Dean-Stark toluene/water mixture but this led to tremendous variations in computed water yields. The small amount of decant oil also gave rise to inaccurate product fraction determinations in some runs. This situation was amplified by the fact that typically only one half of the available decant oil could be used for any one distillation to allow sufficient sample for a second distillation, if required. The net result was very poor repeatability on the product water and C_4 - 455°C liquid fractions. Therefore, these results are not included in the following discussion. However, these data are presented for reference in Tables A-

1 and A-2 of Appendix A.

The other experimental difficulty encountered was in obtaining an accurate CO_2 balance for the run. In most experimental runs, there was a net loss of CO_2 gas. Observations of gas evolution from distillate product fractions indicated that the gas remained in solution in the liquid products. The liklihood that a model nitrogen compound will react with CO_2 to form salts is negligible due to the very small equilibrium constant for the reaction.

Two final points to keep in mind are:

1. the implication of coal conversion to measured THF soluble matter, and
2. the implication of model nitrogen compound incorporation in the THF insoluble matter.

The degree of coal conversion is a function of the extent of depolymerization and hydrogenation of the coal. As hydrogen content increases, the viscosity and boiling point of liquid fractions decrease, and solid fractions become more soluble in lighter solvents. Therefore, the amount of coal which is THF soluble is an indirect measurement of the upgrading of the coal, and is also a rough indication of how much coal can ultimately be converted to liquid products. In this thesis, the THF coal conversion reported is the gross conversion, including the fraction of unreacted coal which

is soluble in THF as well as the coal that becomes soluble due to processing.

The effects of nitrogen incorporation are important to the long range project objective. This objective is to evaluate the ability of nitrogen compounds to promote low severity coal conversion, followed by separation and recycle of the nitrogen compound or compounds. Nitrogen present in any of the liquid fractions is potentially recoverable, but any present in the THF insoluble matter is likely to be irreversibly lost. Unrecoverable nitrogen compounds represent a direct cost to the process. The obvious desire is to minimize such losses to the THF insoluble matter.

The following subsections discuss the effects of model nitrogen compound addition on coal conversion, the extent of nitrogen incorporation, gas yields, and product quality.

Low Severity Results

Conversion Results of Bituminous and Subbituminous Coals Under CO and Hydrogen Gas Atmospheres

Figure 11 shows the effect of model nitrogen compound addition on Kentucky 9 bituminous coal conversion with CO/H_2O reaction gas. These results were used to prescreen the full slate of nitrogen compounds so as to concentrate further experiments on using the most effective nitrogen

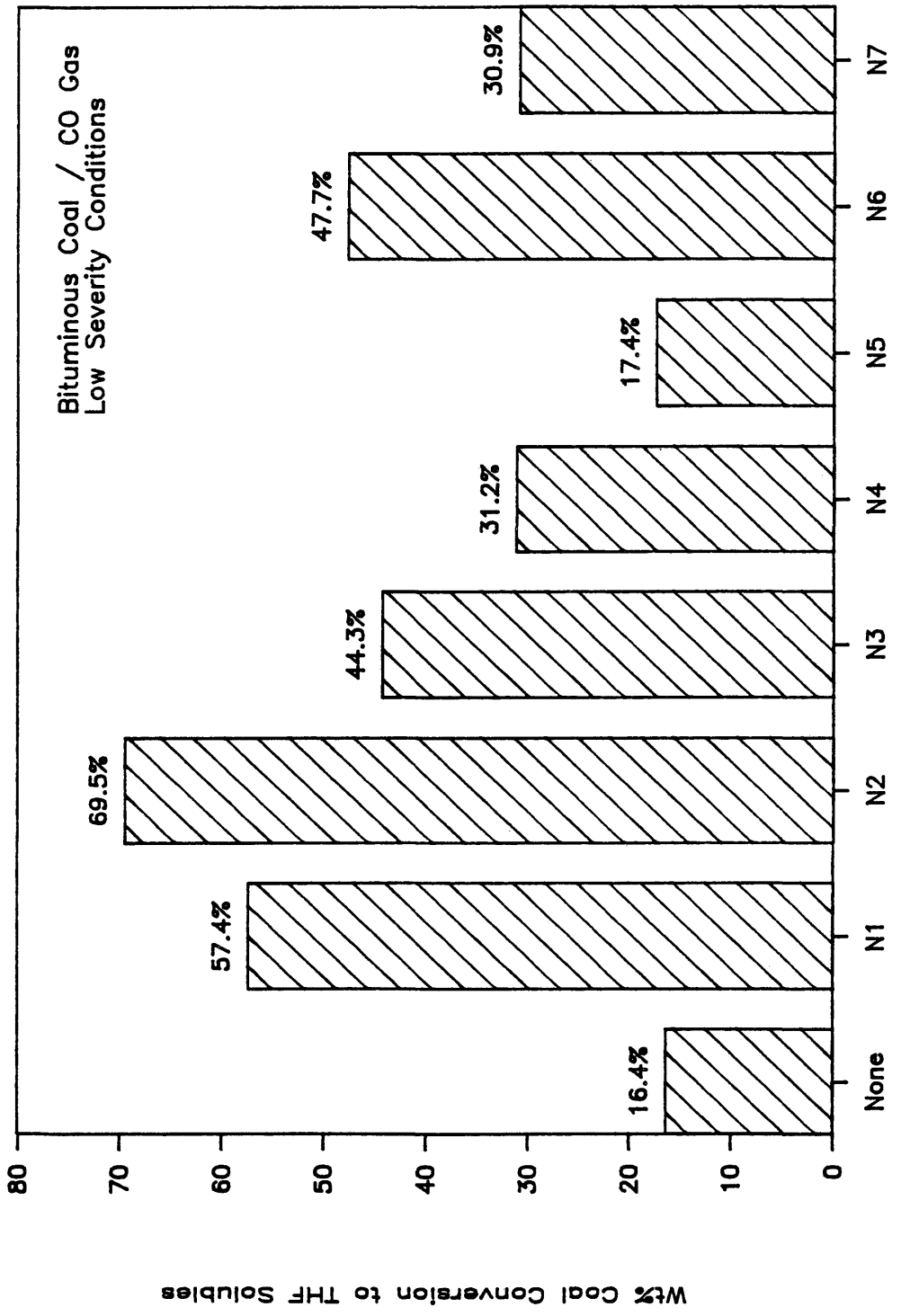


Figure 11: Effect of Model Nitrogen Compound Addition on Conversion of Kentucky 9 Bituminous Coal With CO Feed Gas

compounds. The nitrogen compounds which resulted in the greatest increase in coal conversion were THQ (N1), dipropylamine (N2), 7,8-benzoquinoline (N3) and 5,6-benzoquinoline (N6). The remaining compounds, piperidine (N4), 4-piperidinopyridine (N5), and diphenylamine (N7) all resulted in low coal conversions. With piperidine and 4-piperidinopyridine the low conversions appear to be a consequence of nitrogen compound incorporation into the THF insoluble residue. However, with diphenylamine the low conversion appears to be a consequence of poor reaction promotion since the degree of nitrogen incorporation is lower than with piperidine and 4-piperidinopyridine. This point of nitrogen incorporation is further discussed in the next section. Subsequent experiments primarily concentrated on the use of THQ (N1) and dipropylamine (N2), and their effect on coal conversion since they were by far the best performers.

Figures 12 through 14 summarize additional coal conversion results when using THQ (N1) and dipropylamine (N2) under hydrogen and carbon monoxide atmospheres with both bituminous and subbituminous coals. These data indicate that co-processing performance at low severity conditions is a function of feed coal rank and reaction gas, but is not as dependent on reaction gas. However, Wyodak subbituminous coal

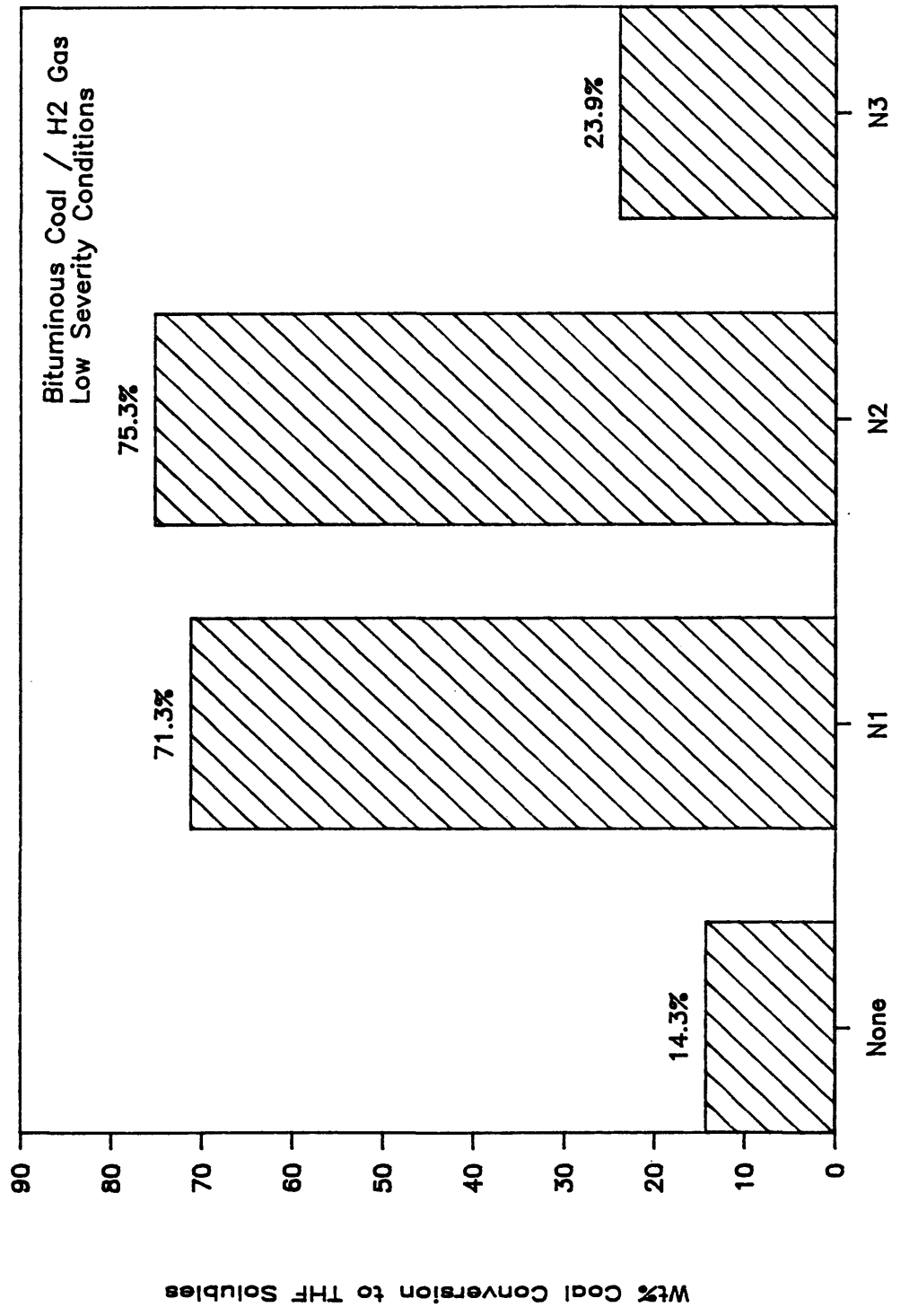


Figure 12: Effect of Model Nitrogen Compound Addition on Conversion of Kentucky 9 Bituminous Coal With a Hydrogen Feed Gas

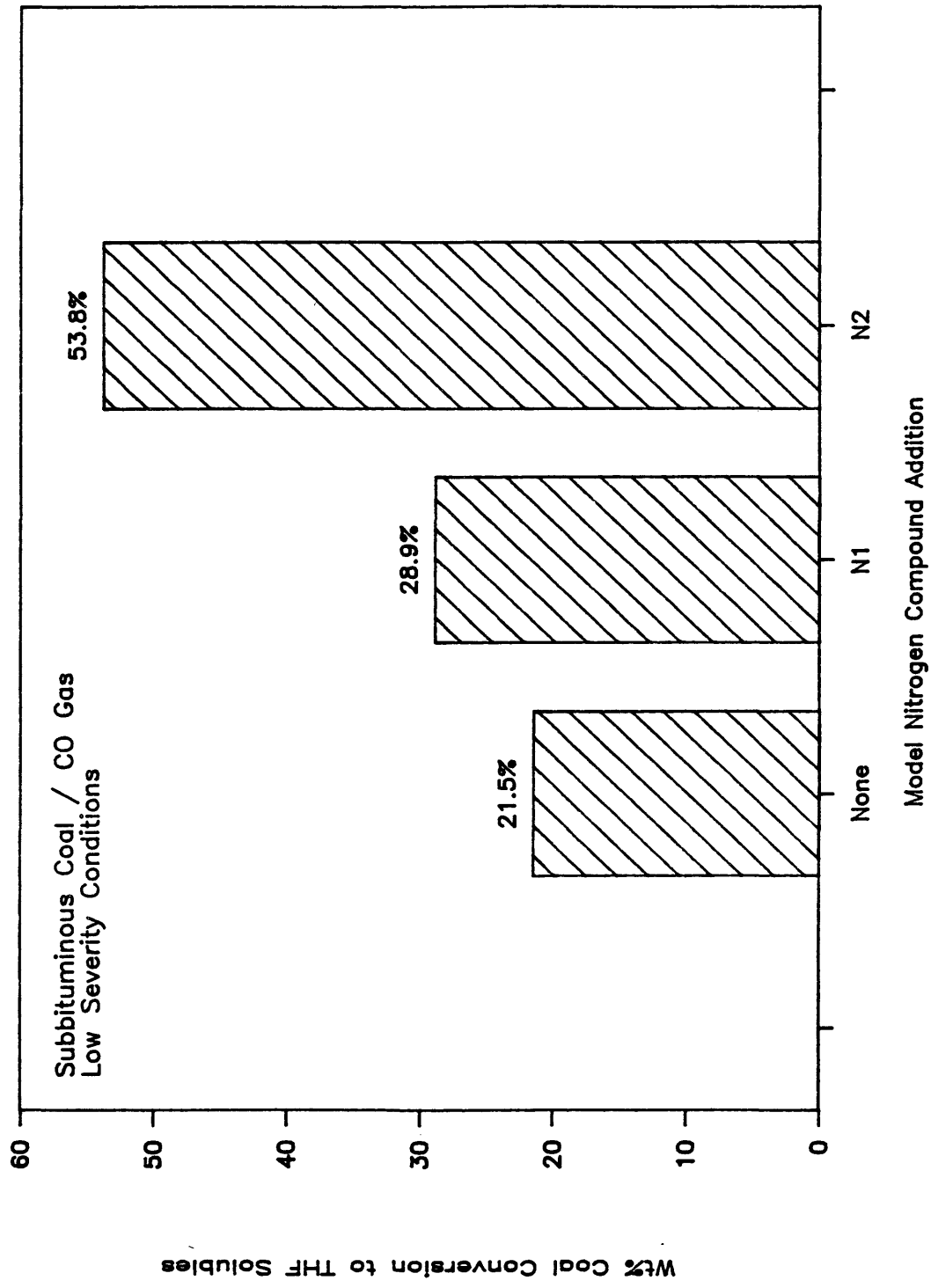


Figure 13: Effect of Model Nitrogen Compound Addition on Conversion of Wyodak Subbituminous Coal With a CO Feed Gas

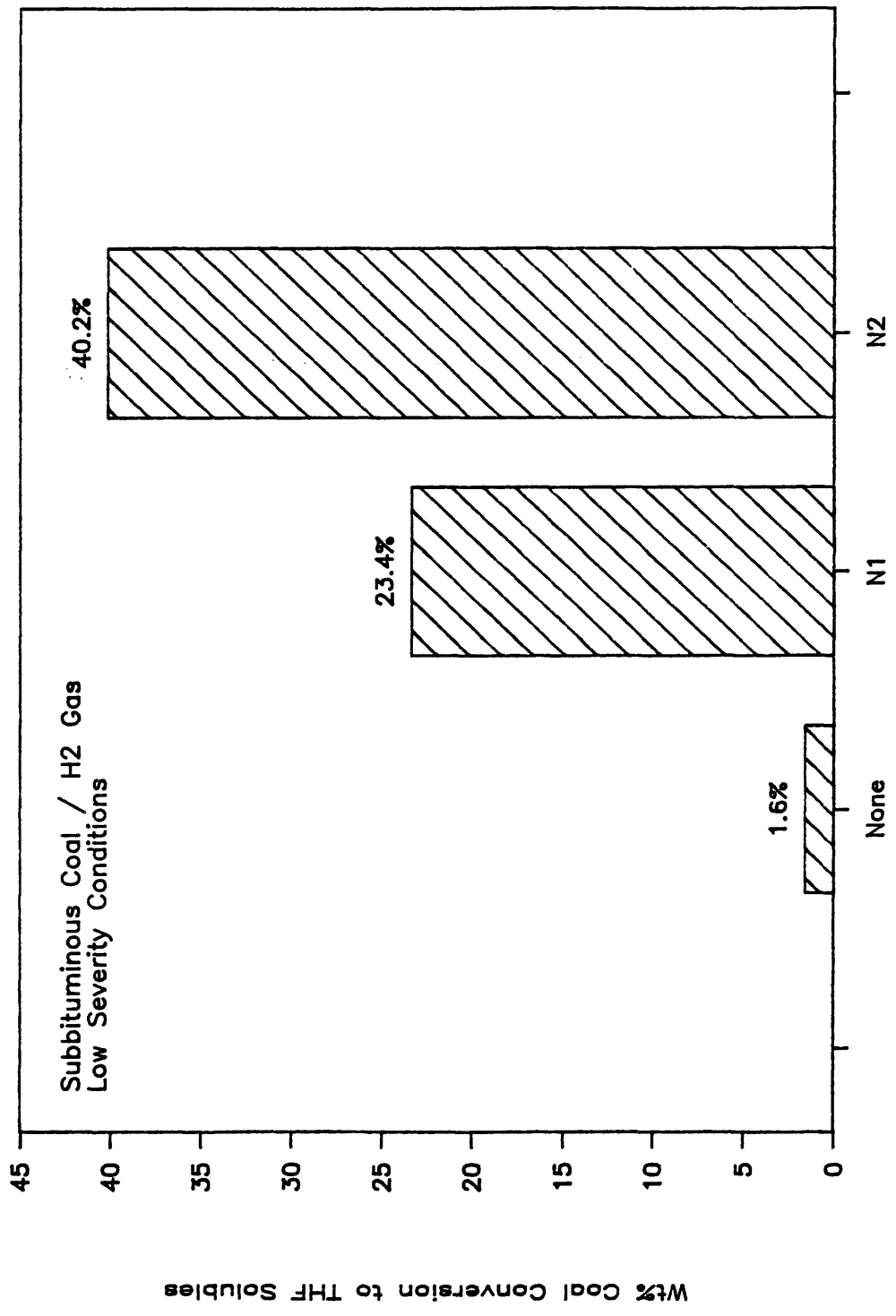


Figure 14: Effect of Model Nitrogen Compound Addition on Conversion of Wyodak Subbituminous Coal With a Hydrogen Feed Gas

performance is more dependent on reaction gas than Kentucky bituminous coal performance. The coal rank dependence however, may be somewhat misleading. Most workers have found that when hydrogen availability is not limited, lower rank coals achieve higher conversion. Since lower rank coals have a higher oxygen content, when the hydrogen is limited, much is used to cleave the weaker bound oxygen-containing side chains such as phenols, rather than on the ester and ether linkages joining coal fragments (47).

At all low severity reaction conditions studied, dipropylamine (N2) was found to be the superior promoter. With Wyodak subbituminous coal, dipropylamine addition resulted in approximately a 16 - 24 wt% increase in coal conversion compared with THQ (N1), while with Kentucky 9 bituminous coal, dipropylamine addition resulted in a 4 - 12 wt% increase in coal conversion compared with THQ (N1). Figure 15 summarizes these results and shows that with bituminous coal, hydrogen marginally increases the coal conversion when dipropylamine (N2) is used, but with THQ (N1) coal conversion is increased by approximately 15 wt%. Figure 16 shows that with subbituminous coal, CO significantly improves coal conversion with both THQ (N1) and dipropylamine (N2). This result would be expected, given the large number of oxygen functionalities available for

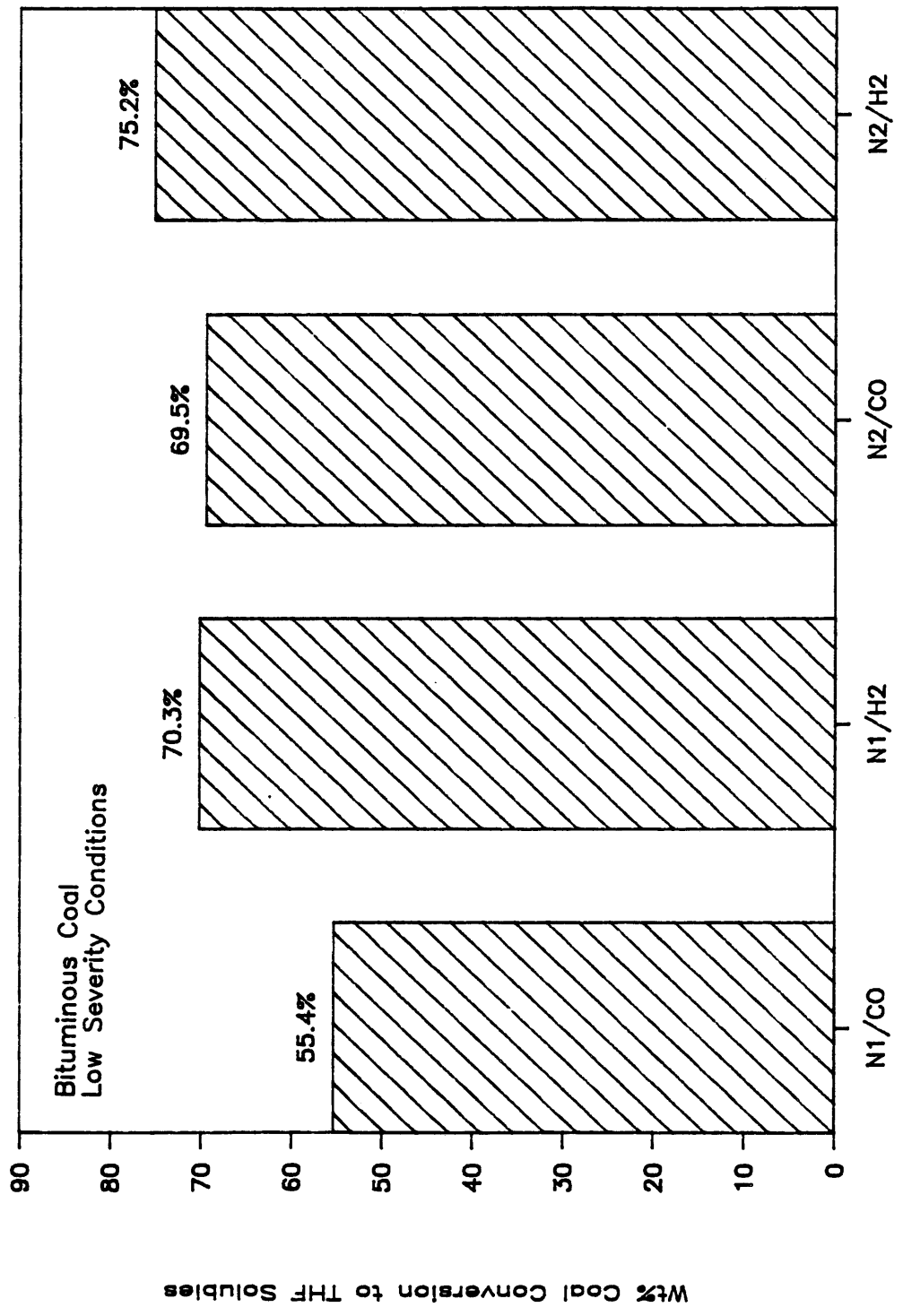


Figure 15: Effect of Model Nitrogen Compound Addition and Feed Gas on Conversion of Kentucky 9 Bituminous Coal

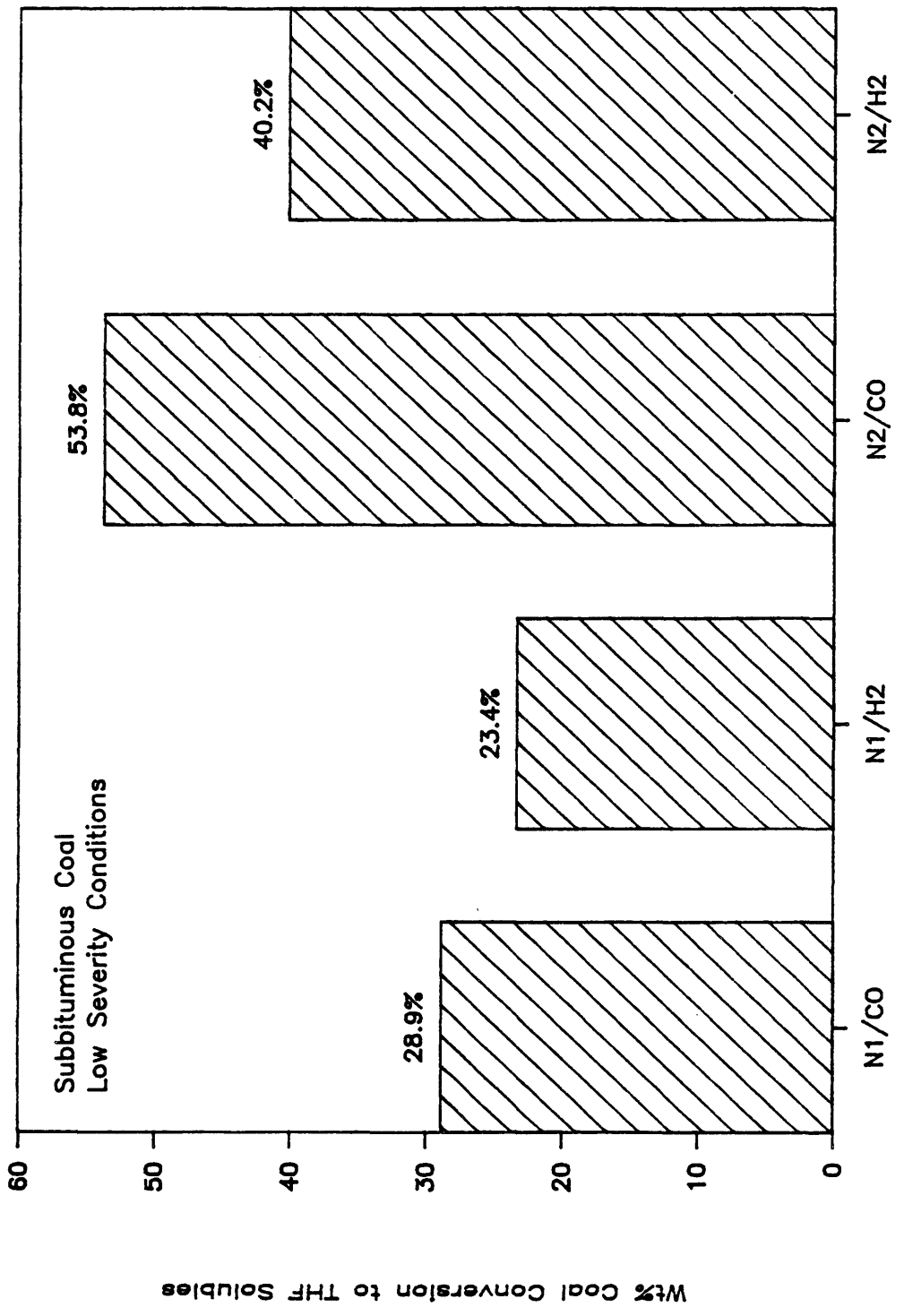


Figure 16: Effect of Model Nitrogen Compound Addition and Feed Gas on Conversion of Wyodak Subbituminous Coal

reaction in subbituminous coal.

Nitrogen Incorporation Results

Figures 17 and 18 show the distribution and amount of elemental nitrogen present in the THF insoluble matter from processing of bituminous coal with carbon monoxide gas at low severity reaction conditions. The nitrogen compounds exhibiting the best promotion of bituminous coal conversion, THQ (N1), and dipropylamine (N2), clearly exhibit the lowest amount of nitrogen present in the THF insoluble matter. Figure 19 summarizes nitrogen incorporation results based on calculations described in Appendix C. This figure shows the estimated amounts of THQ (N1), dipropylamine (N2) and 4-piperidinopyridine (N5) which have been incorporated into the 455°C+ THF soluble and THF insoluble residual products. The manner in which the values in Figure 19 were calculated involves the use of several experimentally-derived numbers, each with respective error. The error in the calculated values is apparent considering that negative incorporation is indicated for THQ (N1) and dipropylamine (N2). As in the instance of no nitrogen compound addition, the lowest amount of incorporation must be zero percent by definition. The important concept presented though is that of low nitrogen incorporation with THQ (N1) and dipropylamine (N2), and high

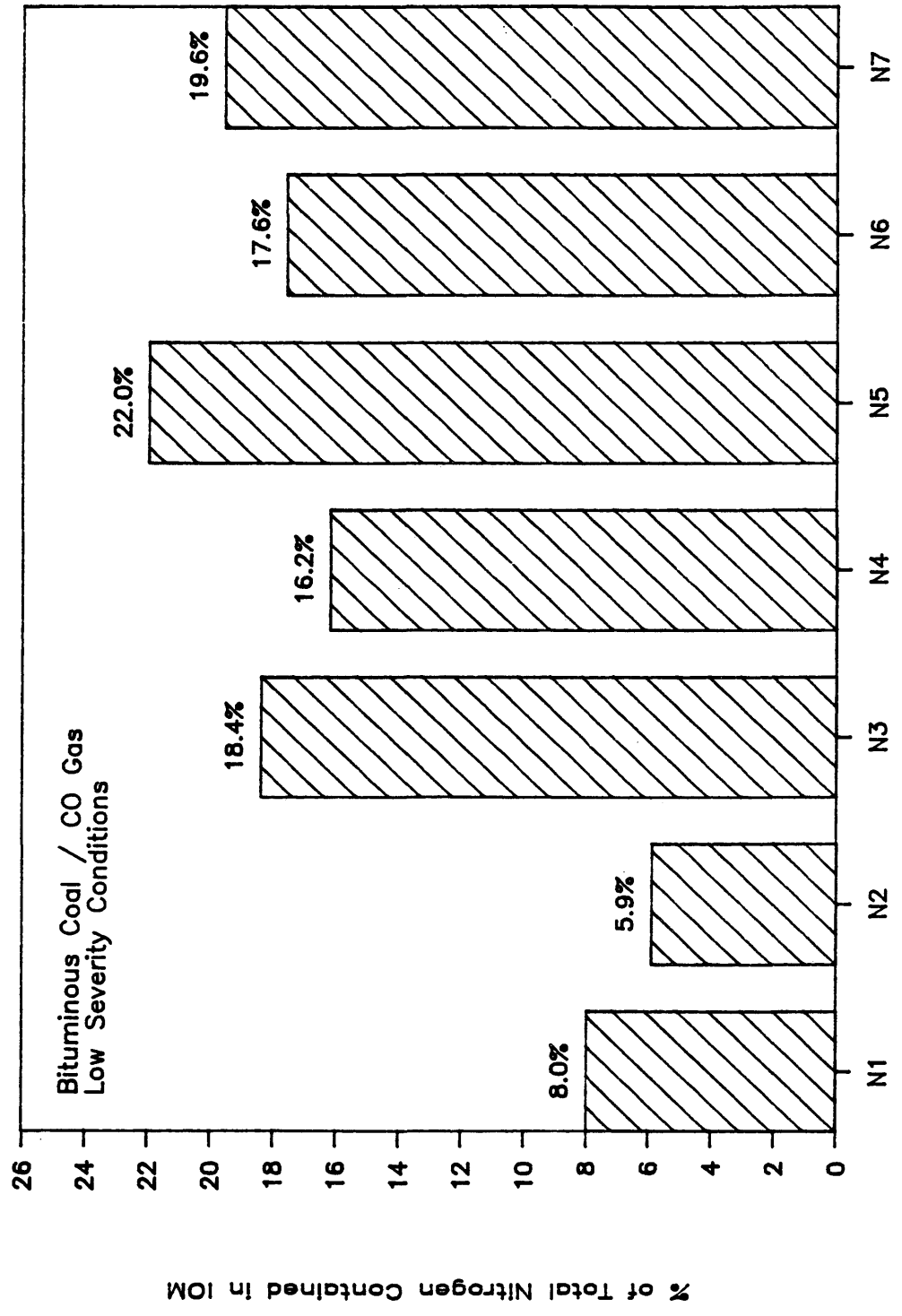


Figure 17: Effect of Model Nitrogen Compound Addition on the Nitrogen Content of the IOM for Kentucky 9 Bituminous Coal With CO Feed Gas

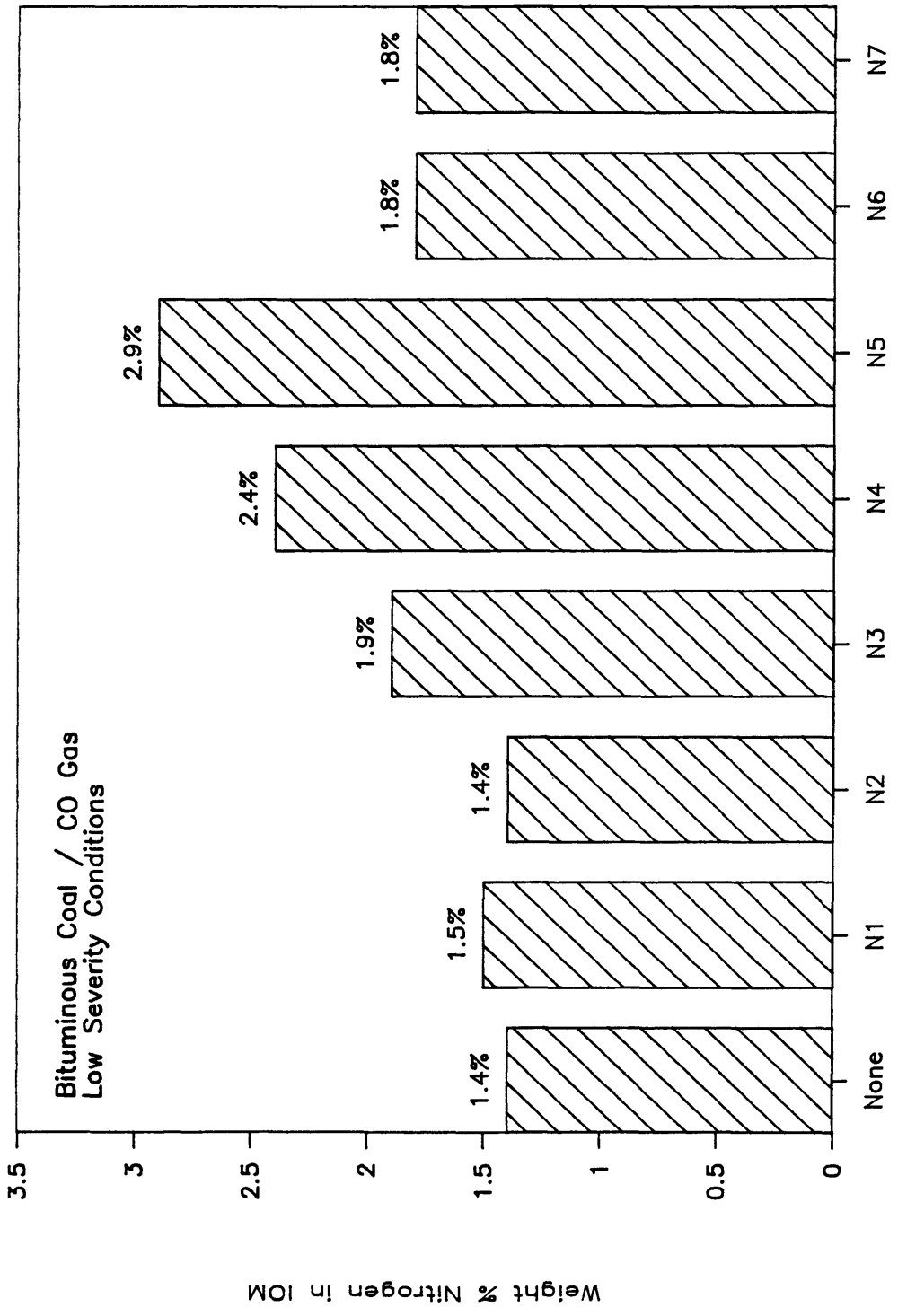


Figure 18: Effect of Model Nitrogen Compound Addition on the Weight % Nitrogen Contained in the IOM

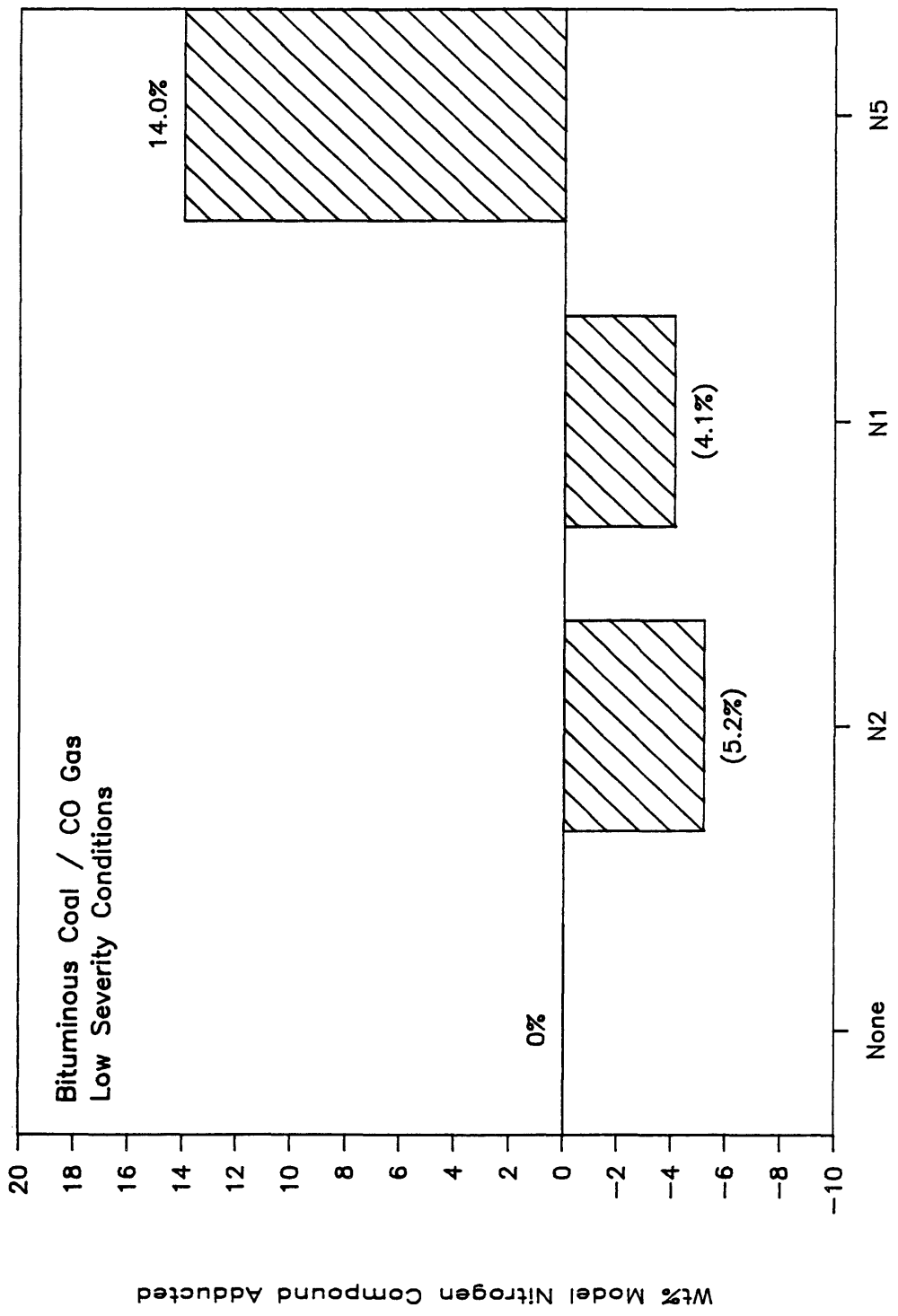


Figure 19: Model Nitrogen Compound Adduction as a Function of Dipropylamine (N2), THQ (N1), and 4-piperidinopyridine (N5) Addition

incorporation with 4-piperidinopyridine (N5). In this sense these results exhibit the same trends indicated in Figures 17 and 18. This demonstrates the possibility that direct measurement of the nitrogen in the THF insoluble matter might be able to be used to monitor the relative nitrogen incorporation of different nitrogen compounds at a fixed set of reaction conditions.

Figure 20 compares the nitrogen content of the 455°C+ product fractions when THQ (N1), dipropylamine (N2) and 4-piperidinopyridine (N5) have been used with bituminous coal and CO feed gas. These data viewed in conjunction with Figures 17 and 18 indicate that incorporation occurs primarily into the THF insoluble matter rather than the 455°C+ THF soluble fraction.

Figures 21 through 29 summarize nitrogen content data for the THF insoluble matter and the 455°C+ fractions for bituminous and subbituminous coal runs using both reaction gases. Comparing results shown in Figure 21 and Figure 17 presented earlier shows that with bituminous coal under either reaction gas atmosphere, dipropylamine (N2) addition gives a smaller nitrogen content (weight basis) in the THF insolubles compared to THQ (N1) addition. However, Figure 22 indicates a slight increase in the weight percent nitrogen in the THF insolubles when dipropylamine (N2) is used with

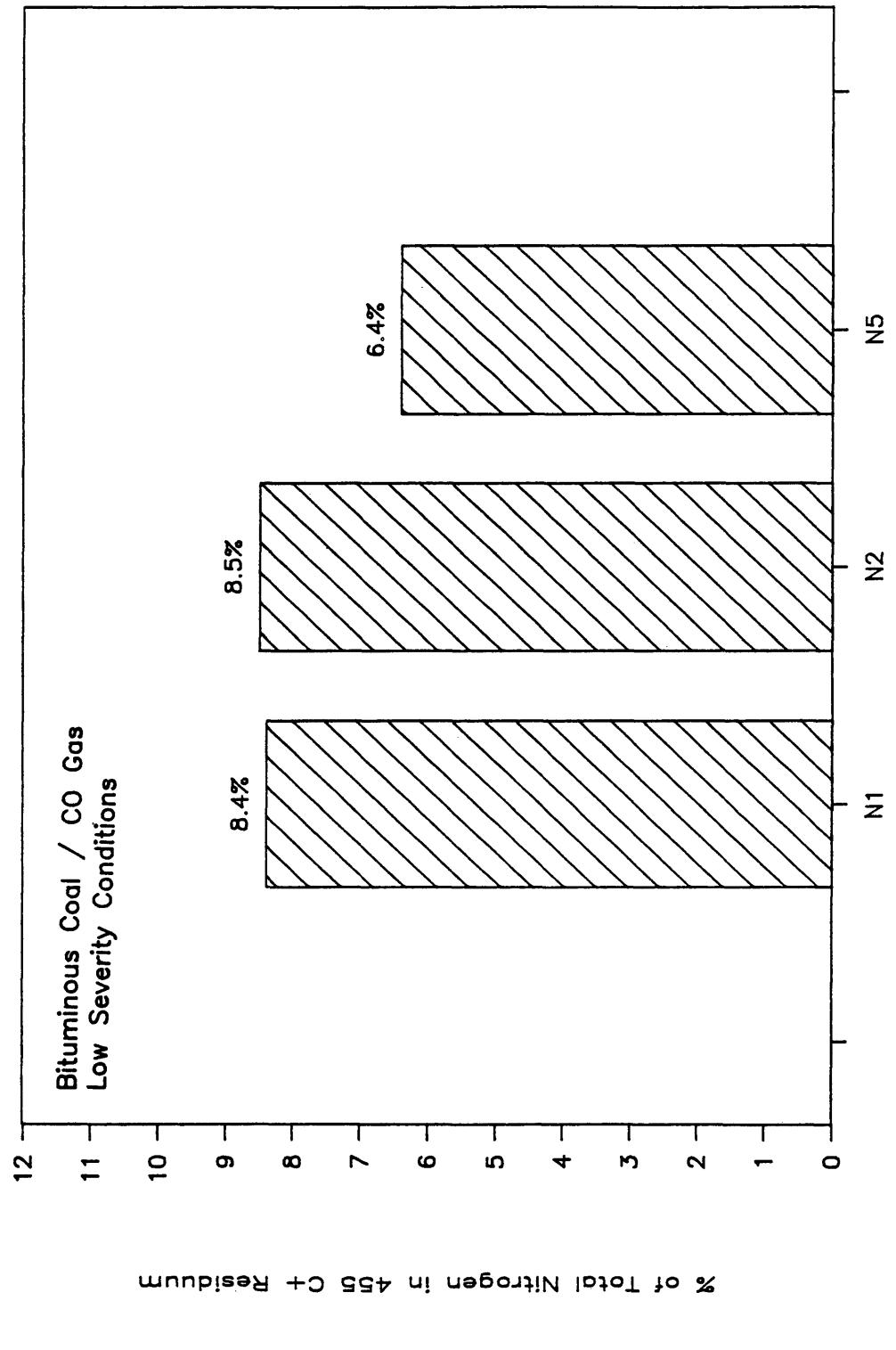


Figure 20: Comparison of the Nitrogen Content of the 455°C+ Residuum With the Use of THQ (N1), Dipropylamine (N2), and 4-Piperdinopyridine (N5)

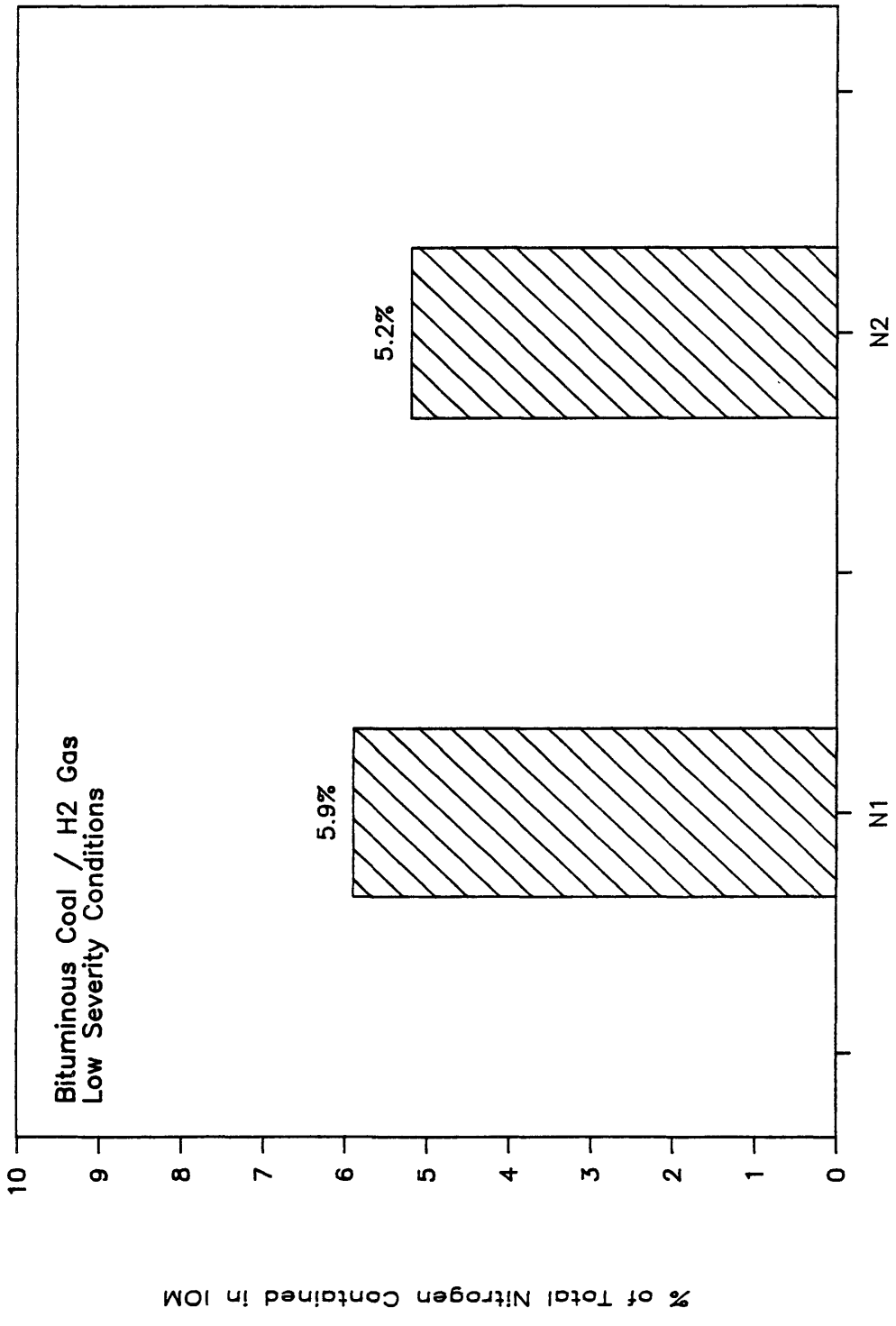


Figure 21: Effect of Model Nitrogen Compound Addition on the Nitrogen Content of the IOM for Kentucky 9 Bituminous Coal With Hydrogen Feed Gas

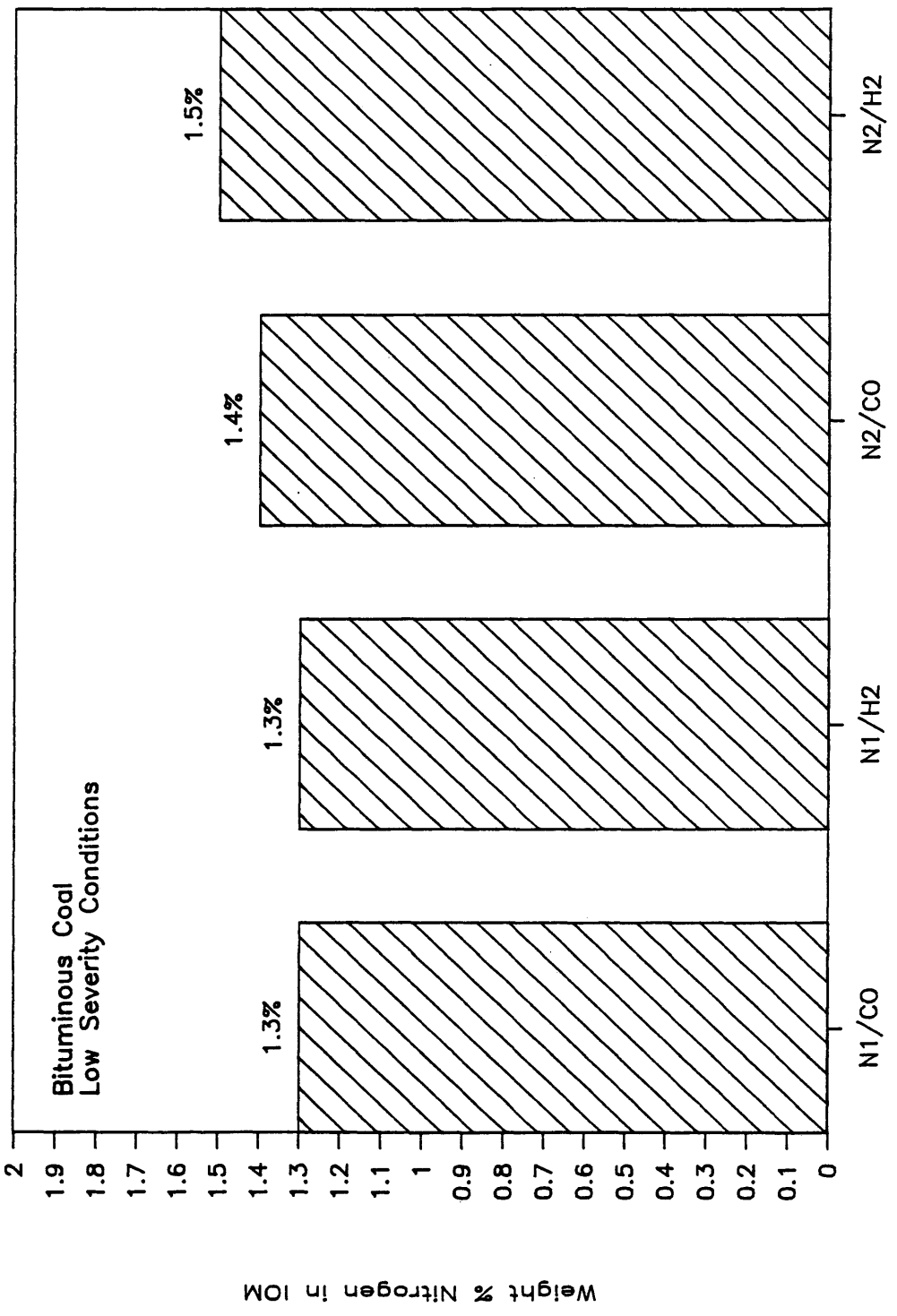


Figure 22: Effect of Model Nitrogen Compound and Feed Gas Addition on the Weight % Nitrogen Contained in the IOM

either reaction gas, implying greater incorporation of the dipropylamine. The conclusion from these data is that under either reaction gas, THQ (N1) adducts approximately the same amount, whereas with dipropylamine (N2) slightly more incorporation occurs when hydrogen gas is used.

Figure 23 indicates that dipropylamine (N2) incorporation into the 455°C+ fraction is essentially the same as THQ (N1) incorporation for bituminous coal liquefaction under a CO atmosphere, and marginally higher than THQ under a hydrogen atmosphere. Figures 24 and 25 indicate that with Wyodak subbituminous coal, THQ (N1) adducts significantly less than dipropylamine (N2) into the THF insoluble matter under a hydrogen atmosphere. Figures 26 and 27 show comparable results for Wyodak subbituminous coal under a CO atmosphere. Figure 27 indicates that incorporation of dipropylamine (N2) is only slightly greater than THQ (N1) incorporation. The large differences shown in Figure 26 arise from the fact that coal conversion with the dipropylamine (N2) addition is almost 25 wt% greater than coal conversion with the THQ (N1) addition, as previously shown in Figure 13. This implies that the high fraction of the total nitrogen present in the THF insoluble matter when THQ (N1) is used is likely due to residual coal nitrogen present as a result of poor coal conversion. Figures 28 and

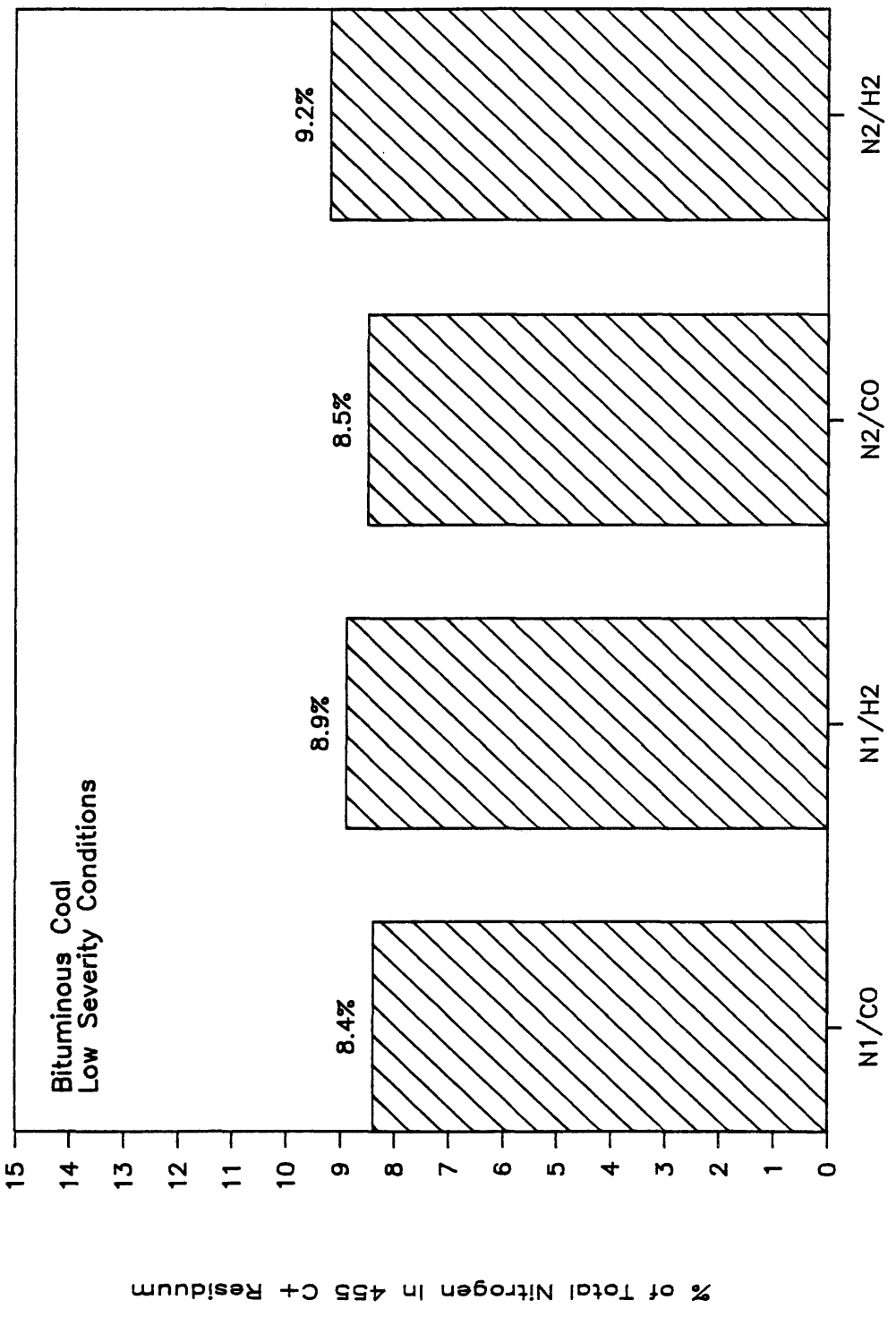


Figure 23:. Effect of Model Nitrogen Compound and Feed Gas Addition on the Nitrogen Content of the 455°C+ Residuum for Kentucky 9 Bituminous Coal

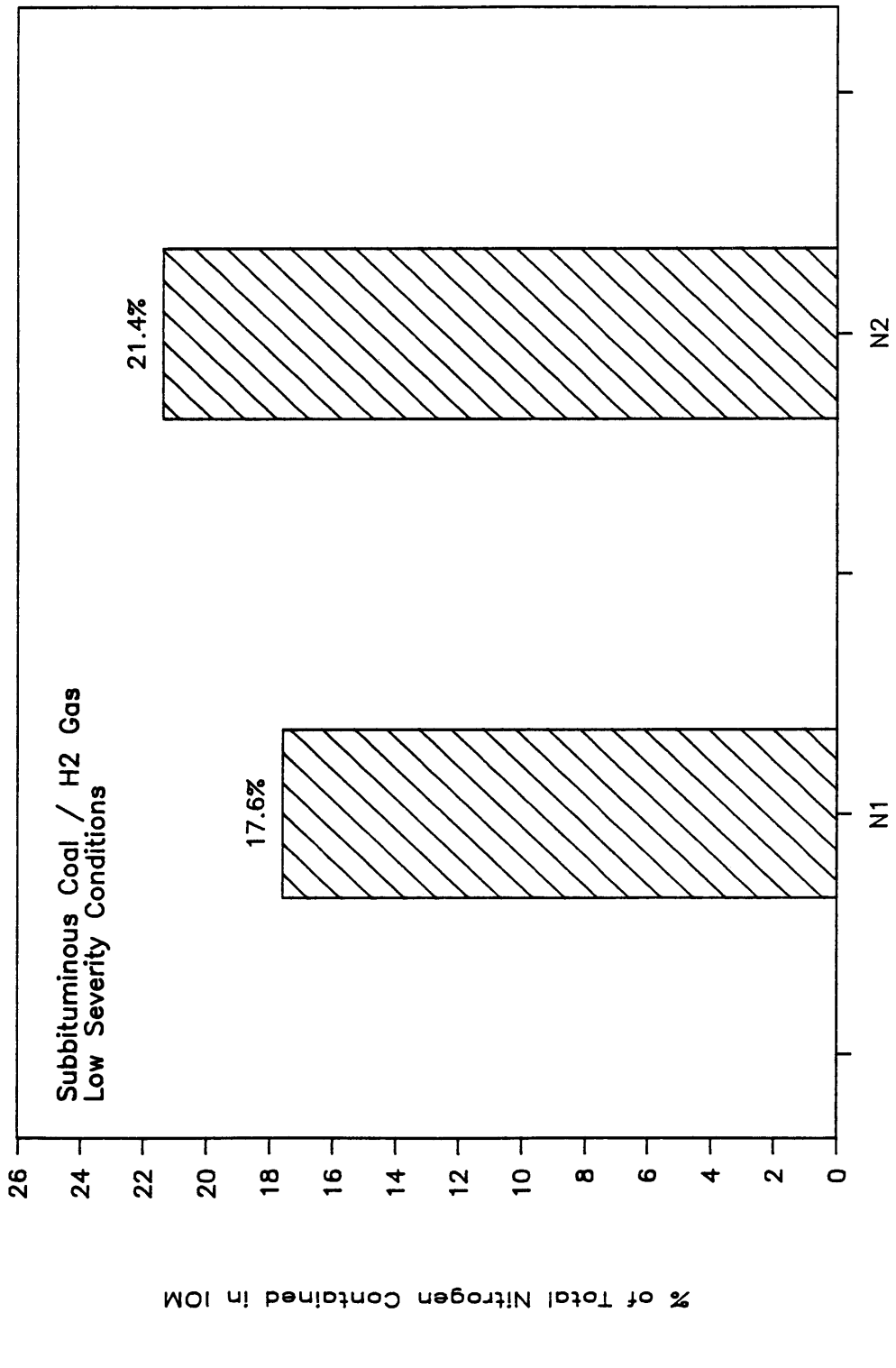


Figure 24: Effect of Model Nitrogen Compound Addition on the Nitrogen Content of the IOM for Wyodak Subbituminous Coal With Hydrogen Feed Gas

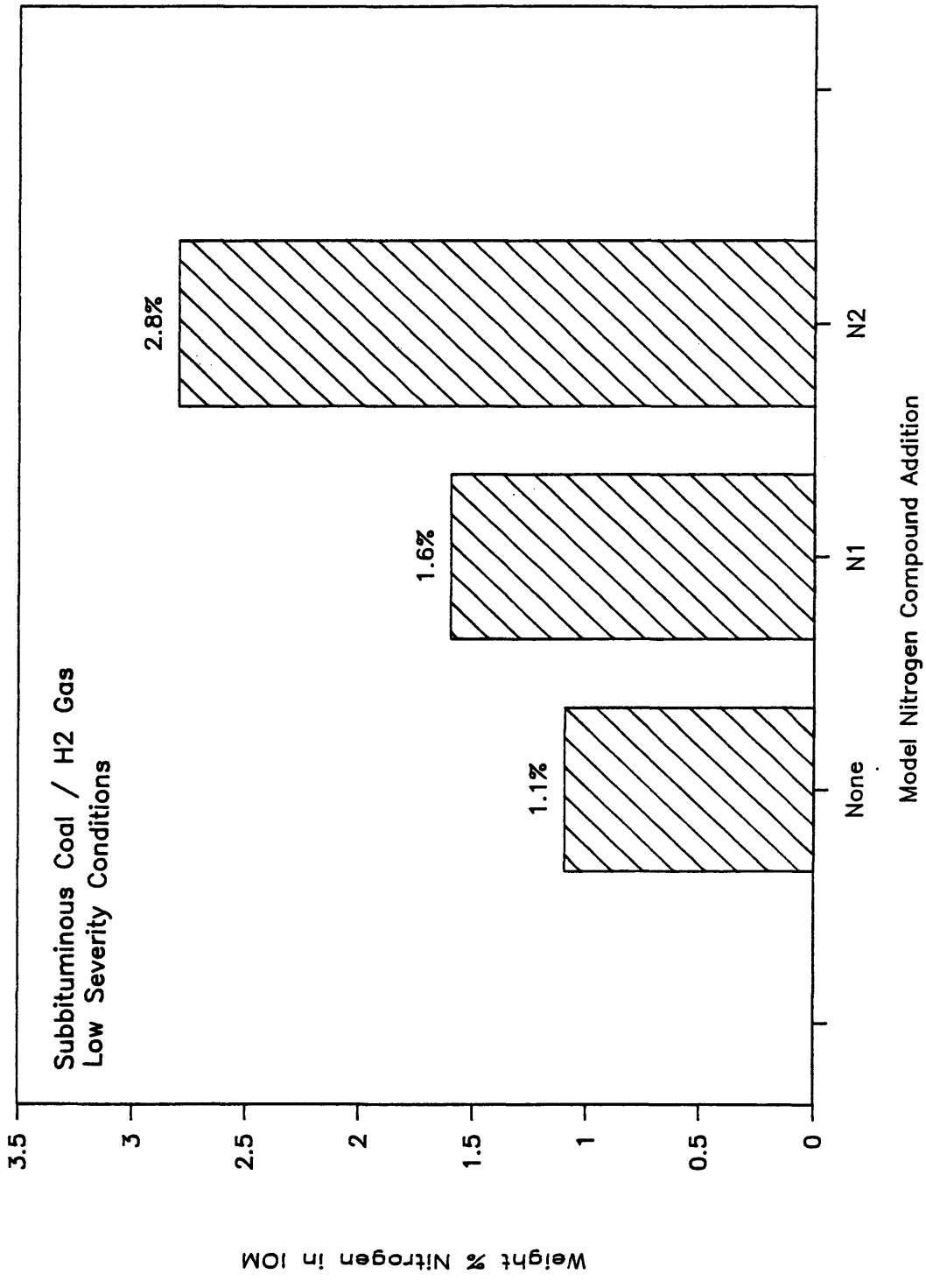


Figure 25: Effect of Model Nitrogen Compound and Feed Gas Addition on the Weight % Nitrogen Contained in the IOM

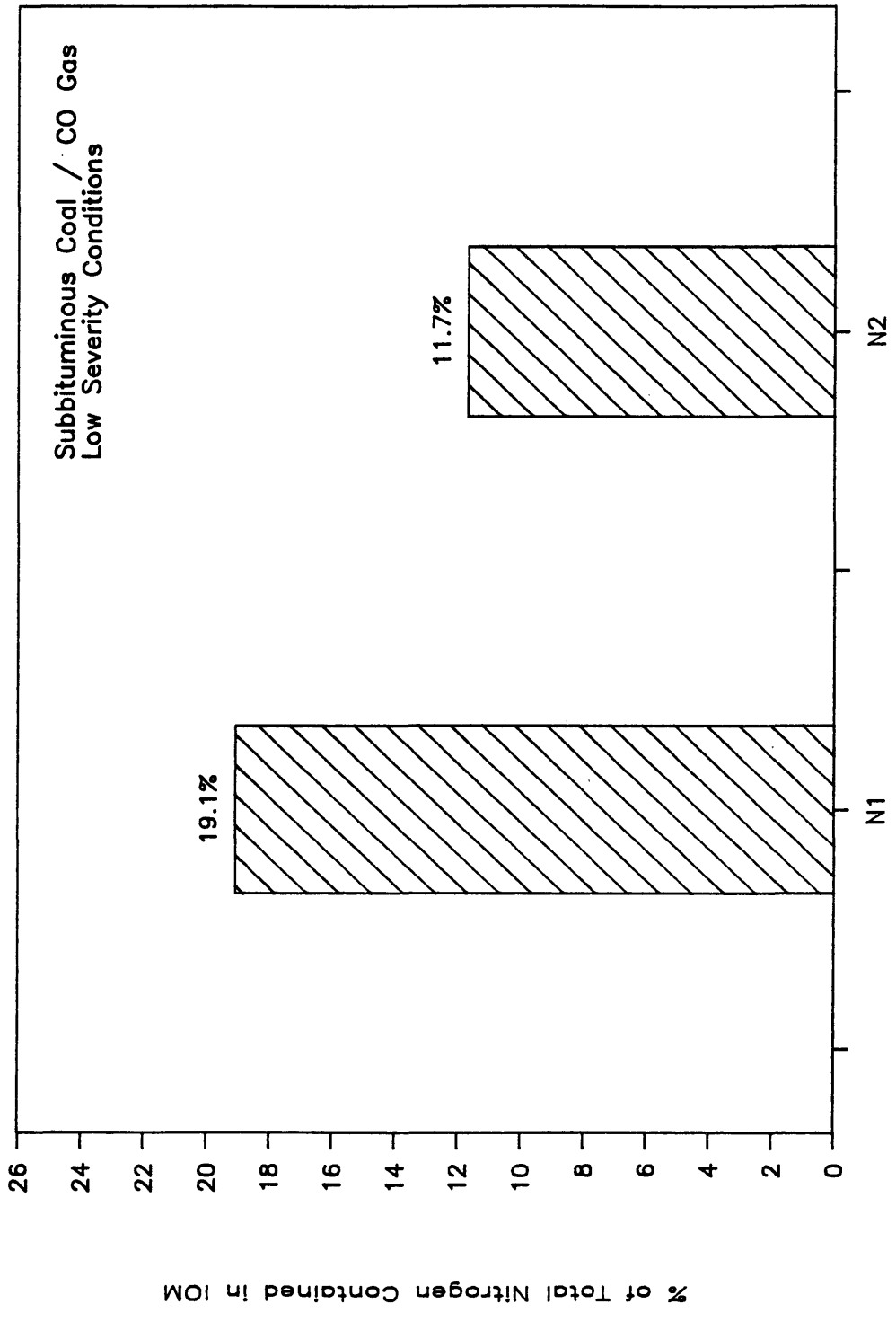


Figure 26: Effect of Model Nitrogen Compound Addition on the Nitrogen Content of the IOM for Wyodak Subbituminous Coal With CO Feed Gas

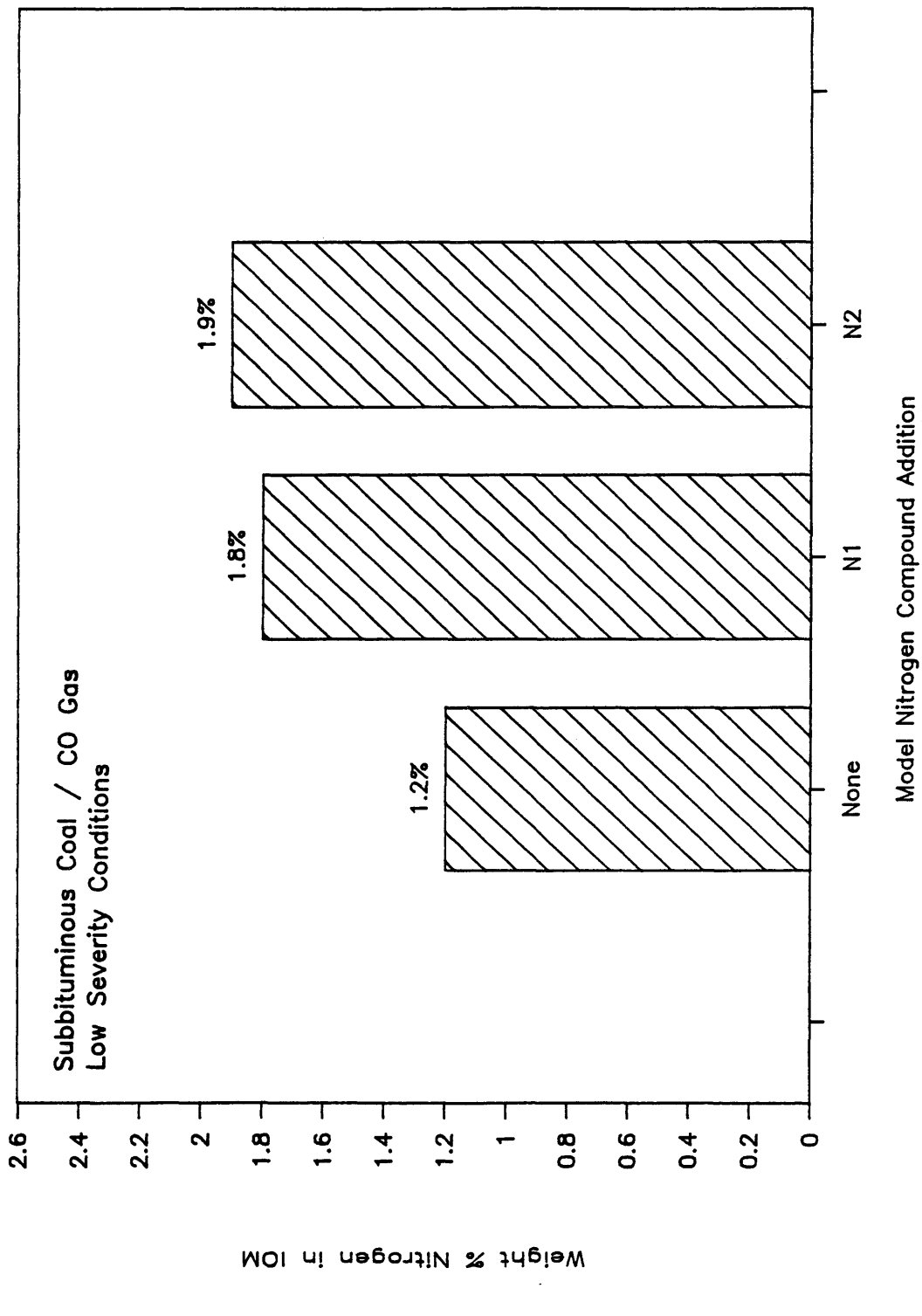


Figure 27: Effect of Model Nitrogen Compound Addition on the Weight % Nitrogen Contained in the IOM for Wyodak Subbituminous Coal With CO Feed Gas

29 summarize the results presented in Figures 24 through 27. Figure 28 indicates that the use of dipropylamine (N2) with subbituminous coal results in greater incorporation than when THQ (N1) is used, regardless of the reaction gas used. Incorporation of dipropylamine (N2) with a hydrogen feed gas is significantly greater than when a CO feed gas is used. As previously stated, when a CO feed gas is used with a dipropylamine (N2) addition, the coal conversion increases by about 25 wt% compared to a CO feed gas with a THQ (N1) addition. This improvement in coal conversion with dipropylamine and a CO feed gas actually reduces the total amount of nitrogen lost to the THF insolubles because there are less insolubles remaining, even though the remaining THF insolubles contain a higher nitrogen content.

Effect of Model Nitrogen Compound Aqueous pK_b

Figure 30 correlates the low severity coal conversion data as a function of model nitrogen compound pK_b for bituminous coal runs using CO feed gas. Each data point in Figure 30 represents the use of 25 wt% model nitrogen compound in A-8 petroleum oil. Since the nitrogen content of each of the model nitrogen compounds is different, these data points represent varying mass concentrations of nitrogen in the solvent mixture. Each point is also

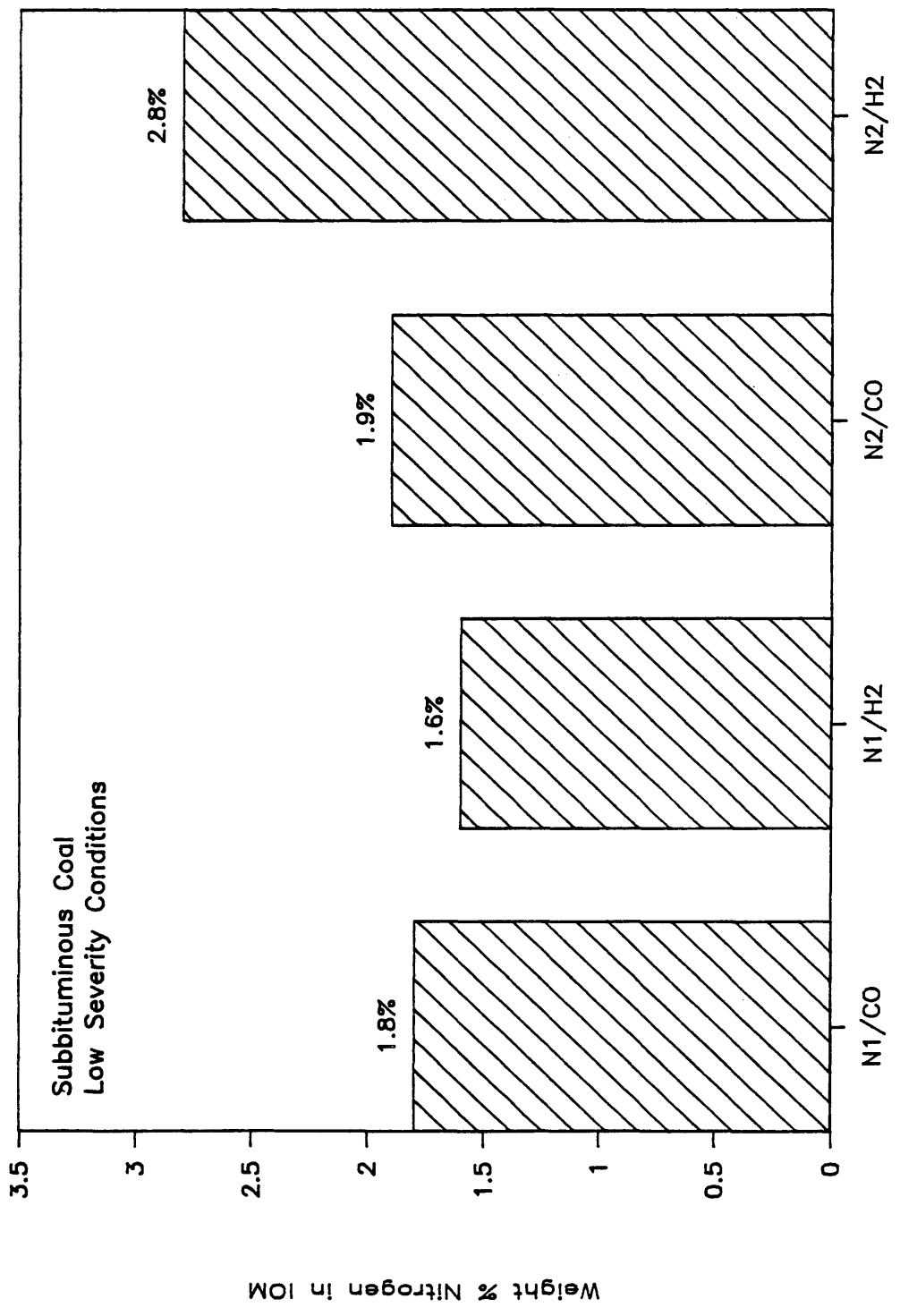


Figure 28: Effect of Model Nitrogen Compound and Feed Gas Addition on the Weight % Nitrogen Contained in the IOM for Wyodak Subbituminous Coal

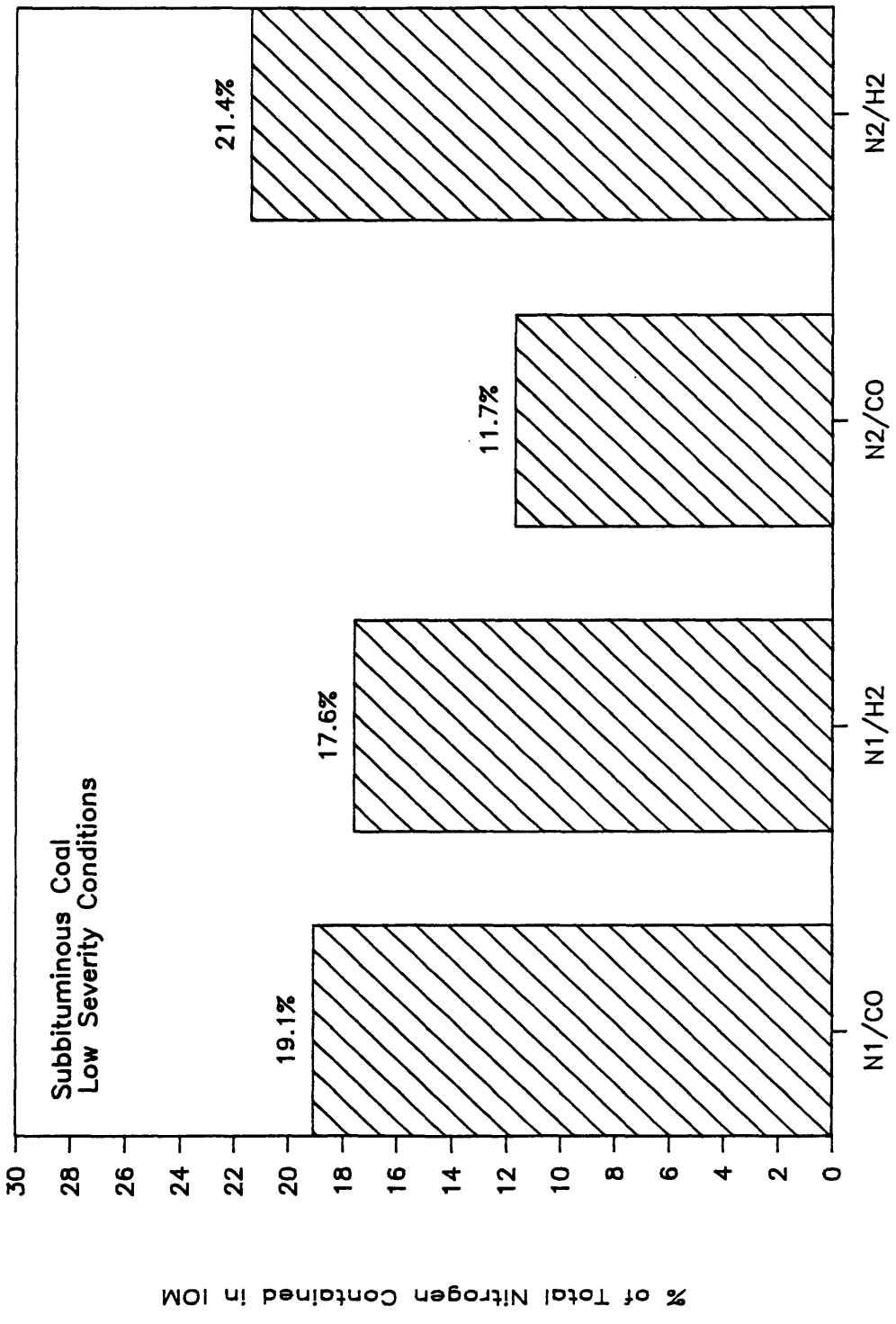


Figure 29: Effect of Model Nitrogen Compound and Feed Gas Addition on the Nitrogen Content of the IOM for Wyodak Subbituminous Coal

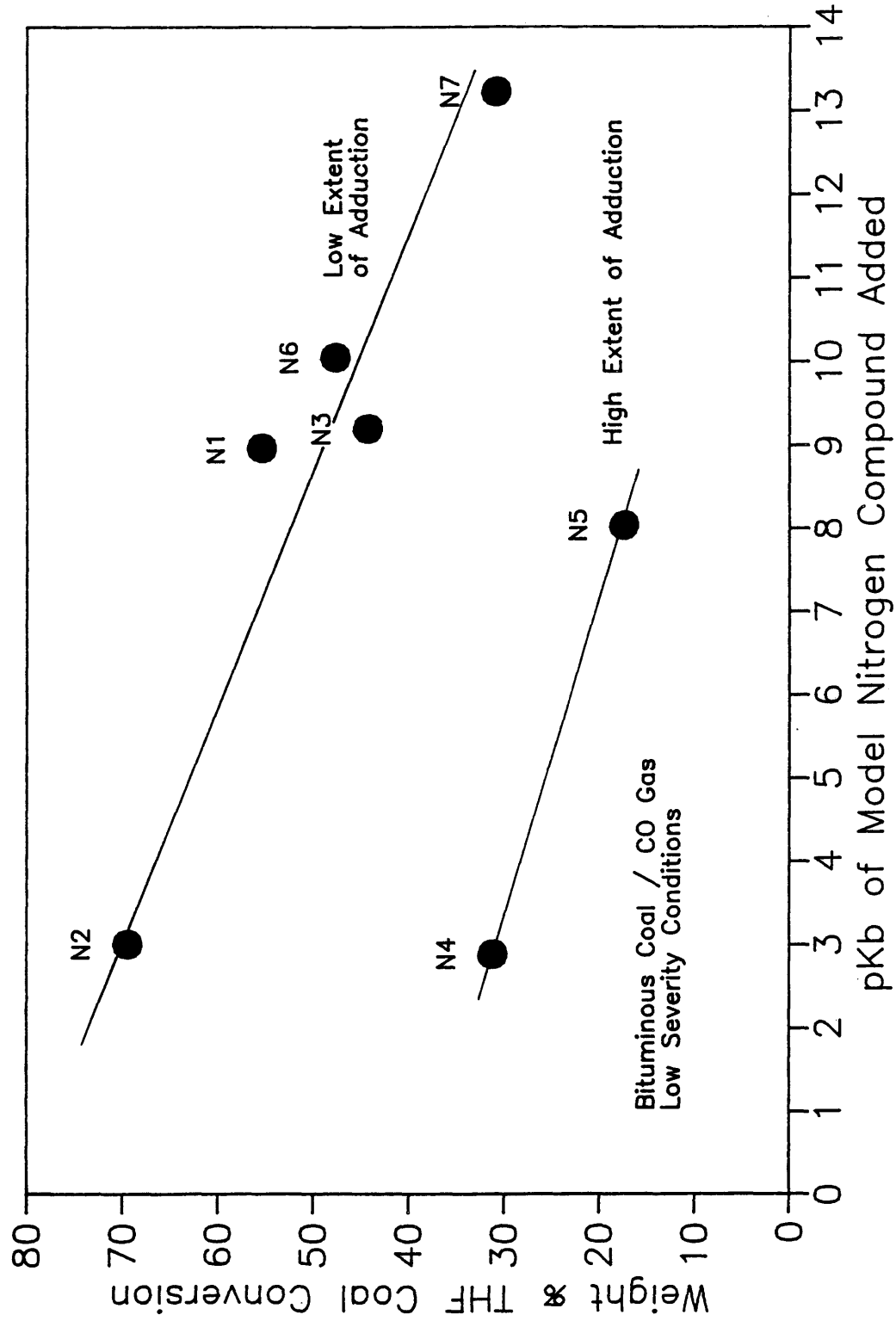


Figure 30: Effect of Model Nitrogen Compound Basicity on Conversion of Kentucky 9 Bituminous Coal With a CO Feed Gas

indicative of a different solvent mixture since a large percentage of the total solvent, 25 wt%, is changed in each case. Different solvents likely have different solvent powers.

The abscissa of Figure 30 represents the pK_b of the respective model nitrogen compound as measured in an aqueous medium. Since an aqueous solution is not used in the co-processing runs, it is reasonable to assume that the true nitrogen compound pK_b values in the system will differ from those plotted.

Keeping in mind that each point represents a variation in the solvent, nitrogen concentration and aqueous pK_b value, the figure does imply a correlation between coal conversion and aqueous pK_b of the model nitrogen compounds. The data appear to lie in two distinct groups. The upper group includes the nitrogen compounds that promoted the best conversion of Kentucky bituminous coal with a CO reaction gas, and showed less propensity for incorporation. The lower group represents the nitrogen compounds which resulted in lower levels of coal conversion and greater extents of incorporation. Since the data does not fall along a single curve it is implied that factors other than aqueous pK_b also govern this relationship.

Effect of Model Nitrogen Compound Concentration

In most experimental runs, 25 wt% of the total liquid solvent used in the run consisted of the model nitrogen compound. Selected experimental runs were completed using only 10 wt% model nitrogen compound to study the effect of nitrogen concentration on process performance.

Figure 31 shows that when either THQ (N1) or dipropylamine (N2) is present at only 10 wt% initial concentration, conversion of Kentucky 9 bituminous coal with a CO feed gas is less than when 25 wt% of each nitrogen compound is used. With THQ (N1) coal conversion drops by 9 wt%, and with dipropylamine (N2) conversion drops by 14 wt%.

Figures 32 through 35 show the nitrogen content of the 455°C+ fraction and the THF insoluble matter when dipropylamine (N2) was added in 10 and 25 wt% concentrations. Figure 32 shows the fraction of the total nitrogen remaining in the THF insoluble matter. The lower dipropylamine addition resulted in a significantly higher fraction of the total nitrogen remaining in the THF insoluble matter. This can be partially explained by the fact that the lower dipropylamine addition also resulted in 14 wt% decreased coal conversion, leaving more of the initial nitrogen present in the coal in the THF insoluble matter. However, Figure 33 indicates that the higher

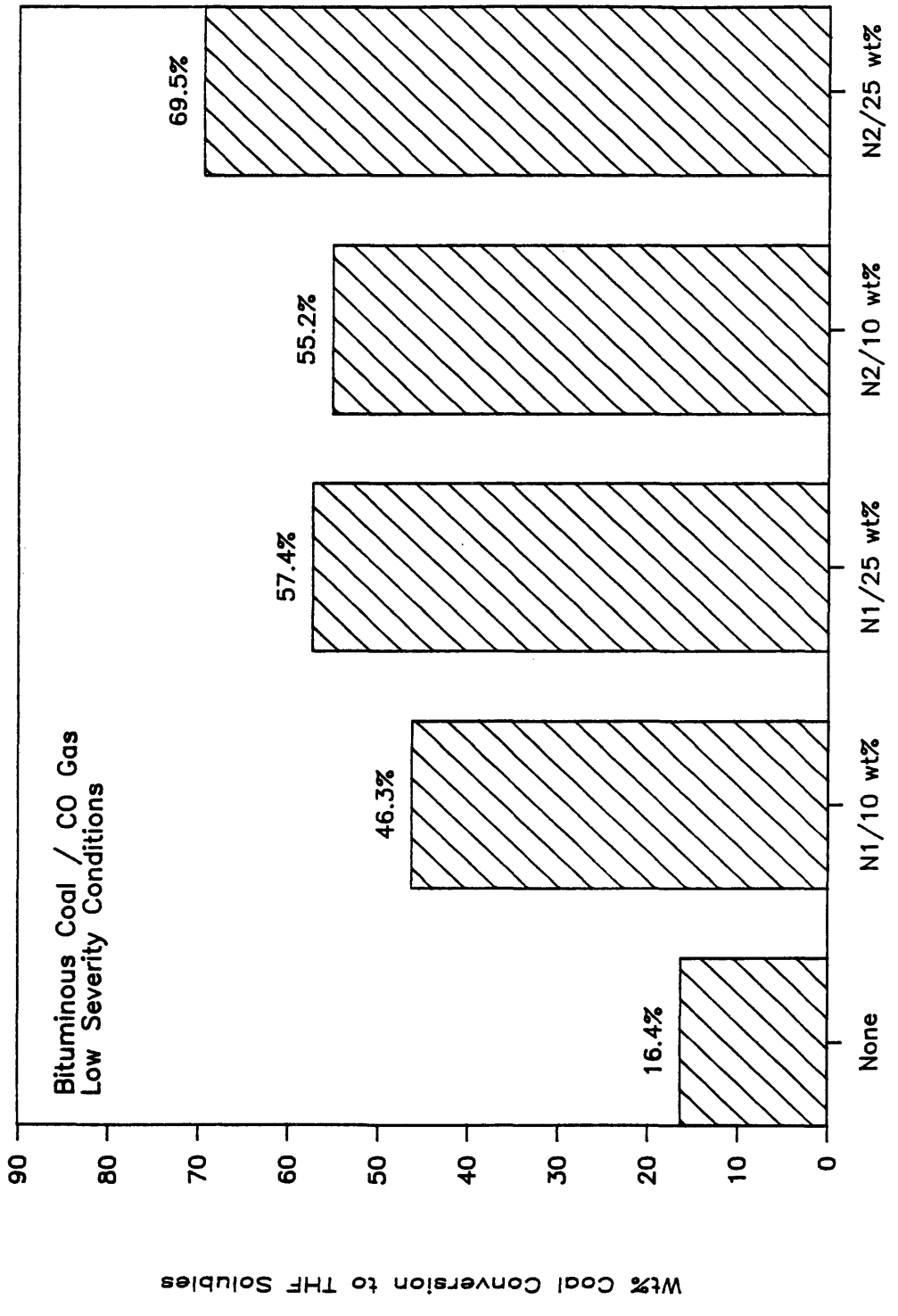


Figure 31: Effect of Model Nitrogen Compound Feed Concentration on Conversion of Kentucky 9 Bituminous Coal With CO Feed Gas

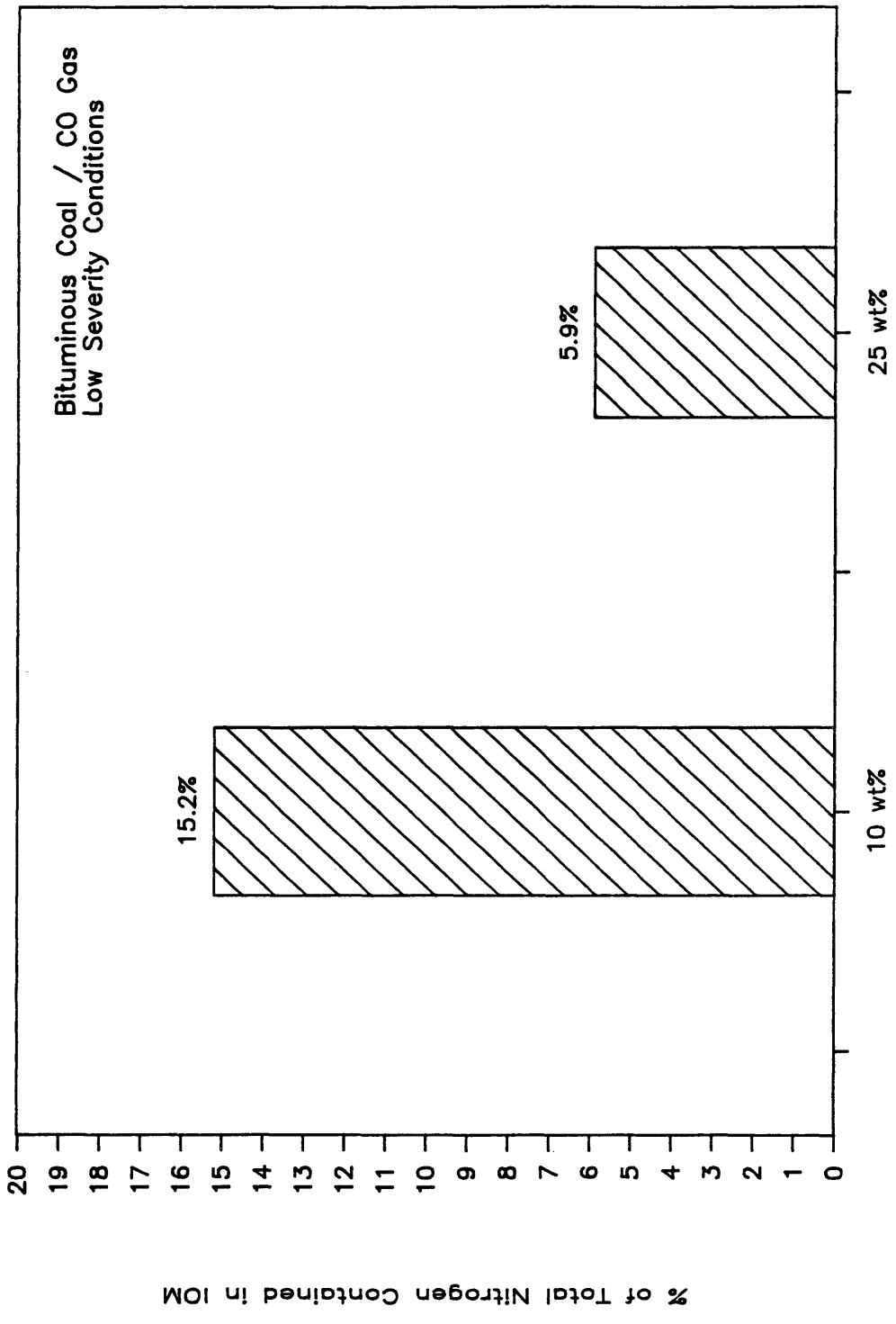


Figure 32: Effect of Dipropylamine (N2) Feed Concentration on the Nitrogen Content of the IOM for Kentucky 9 Bituminous Coal With CO Feed Gas

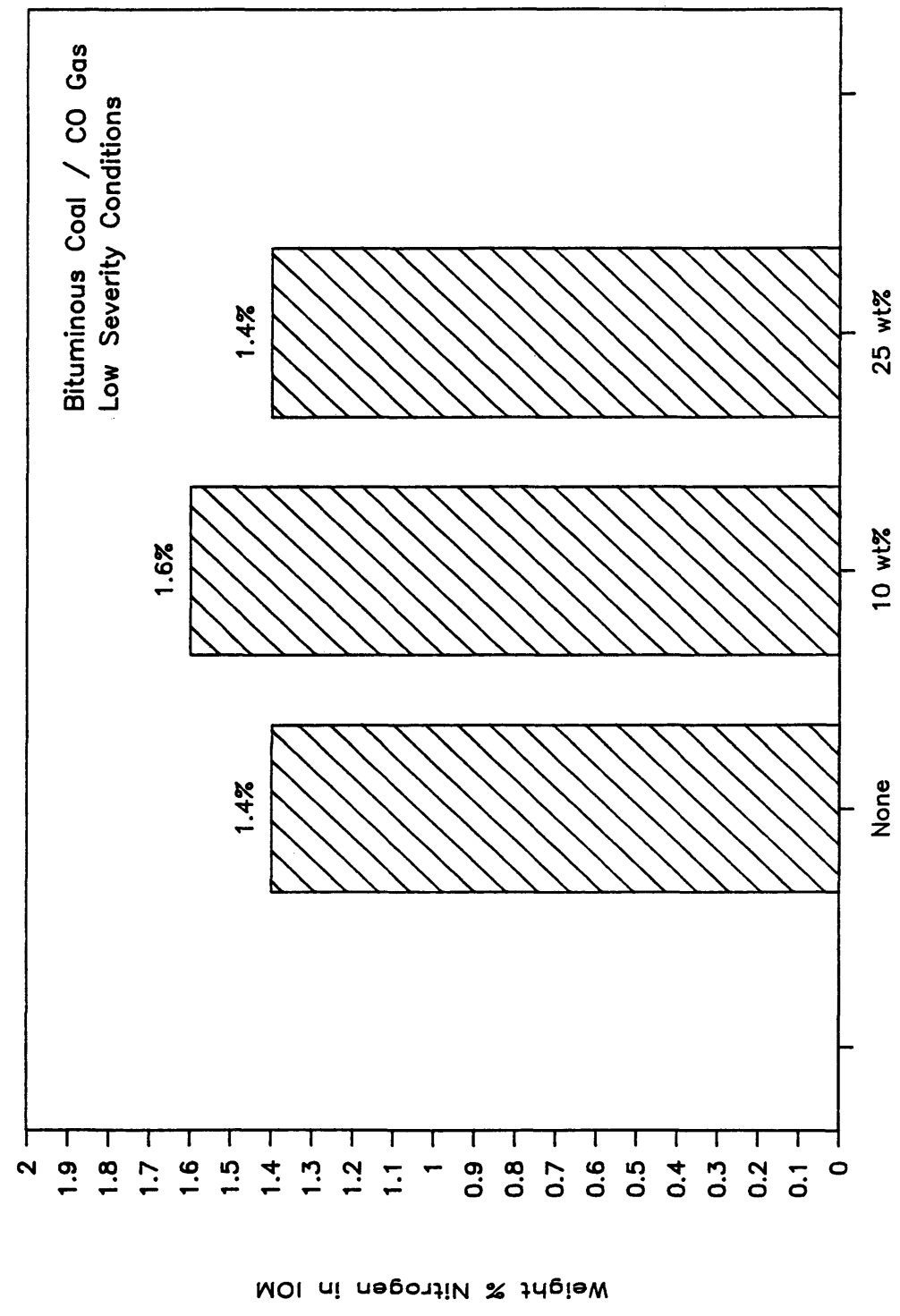


Figure 33: Effect of Dipropylamine (N2) Feed Concentration on the Weight % Nitrogen Contained in the IOM for Kentucky 9 Bituminous Coal With CO Feed Gas

nitrogen content of the THF insoluble matter can also be attributed to a higher degree of adduction with the lower dipropylamine addition. Figures 34 and 35 show a similar comparison for the 455°C+ residuum fraction. Figure 34 shows that a much higher amount of the systems' total nitrogen is present in this product fraction, yet Figure 35 shows that the wt% of elemental nitrogen has actually decreased at the lower dipropylamine addition. The indication is that the lower dipropylamine addition has resulted in a greater degree of product upgrading to the 455°C+ product fraction.

Effect of Initial Carbon Monoxide Pressure

Figure 36 shows the effect of the reactor cold charge feed gas pressure on low severity conversion of Kentucky 9 bituminous coal to THF soluble products. The lower charge pressure of 2.2 MPa results in essentially no net increase in coal conversion, relative to the THF solubility of unreacted coal prior to processing. When the charge pressure is increased to 5.7 MPa, conversion increases by approximately 7 wt%. This increase may indicate that the water-gas shift reaction proceeds as a liquid phase reaction at low severity liquefaction conditions. The CO concentration in the liquid phase then is a function of its partial pressure as described by Henry's Law. Therefore the

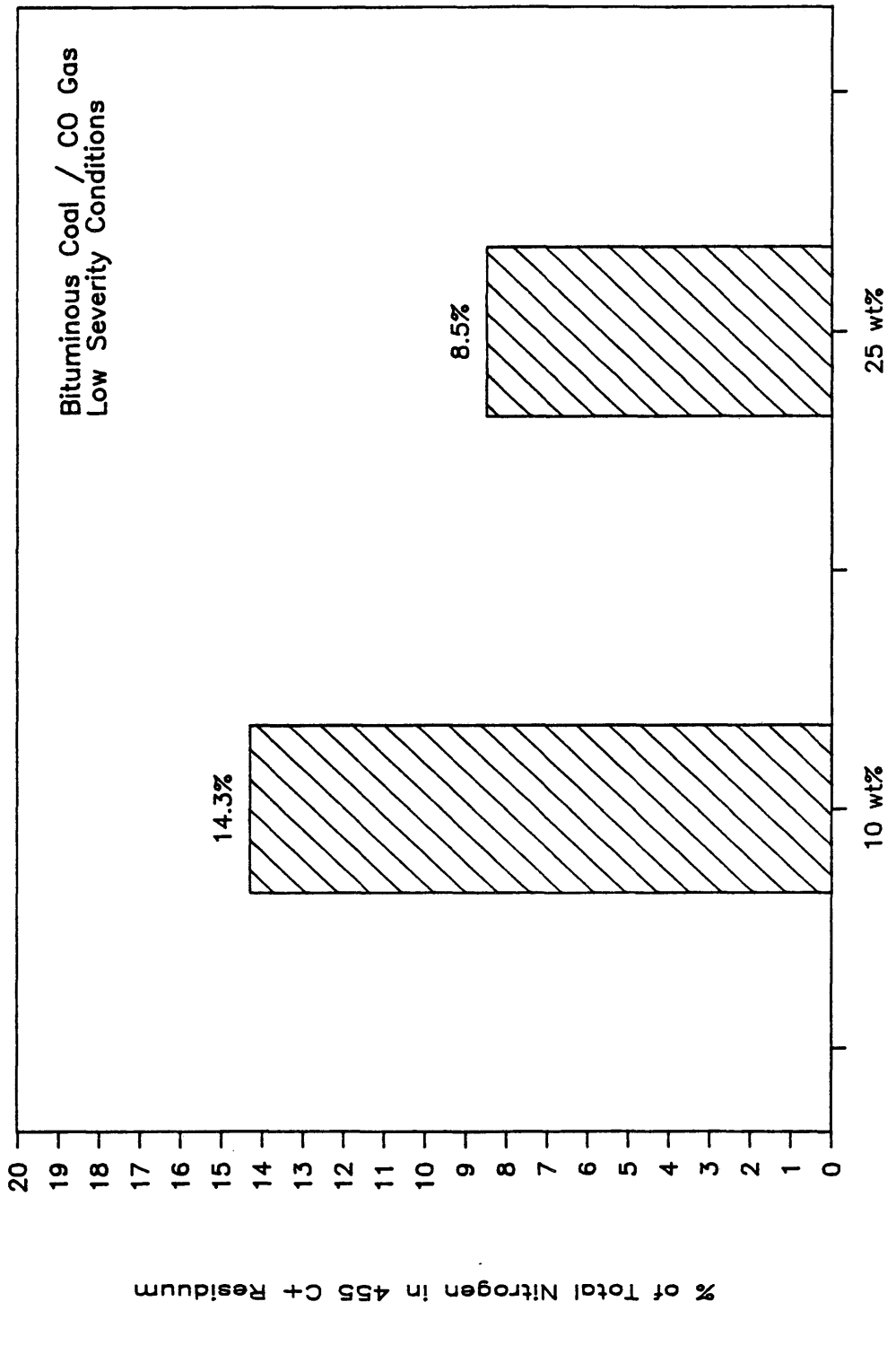


Figure 34: Effect of Dipropylamine (N2) Concentration on the Nitrogen Content of the 455°C+ Residuum for Kentucky 9 Bituminous Coal With CO Feed Gas

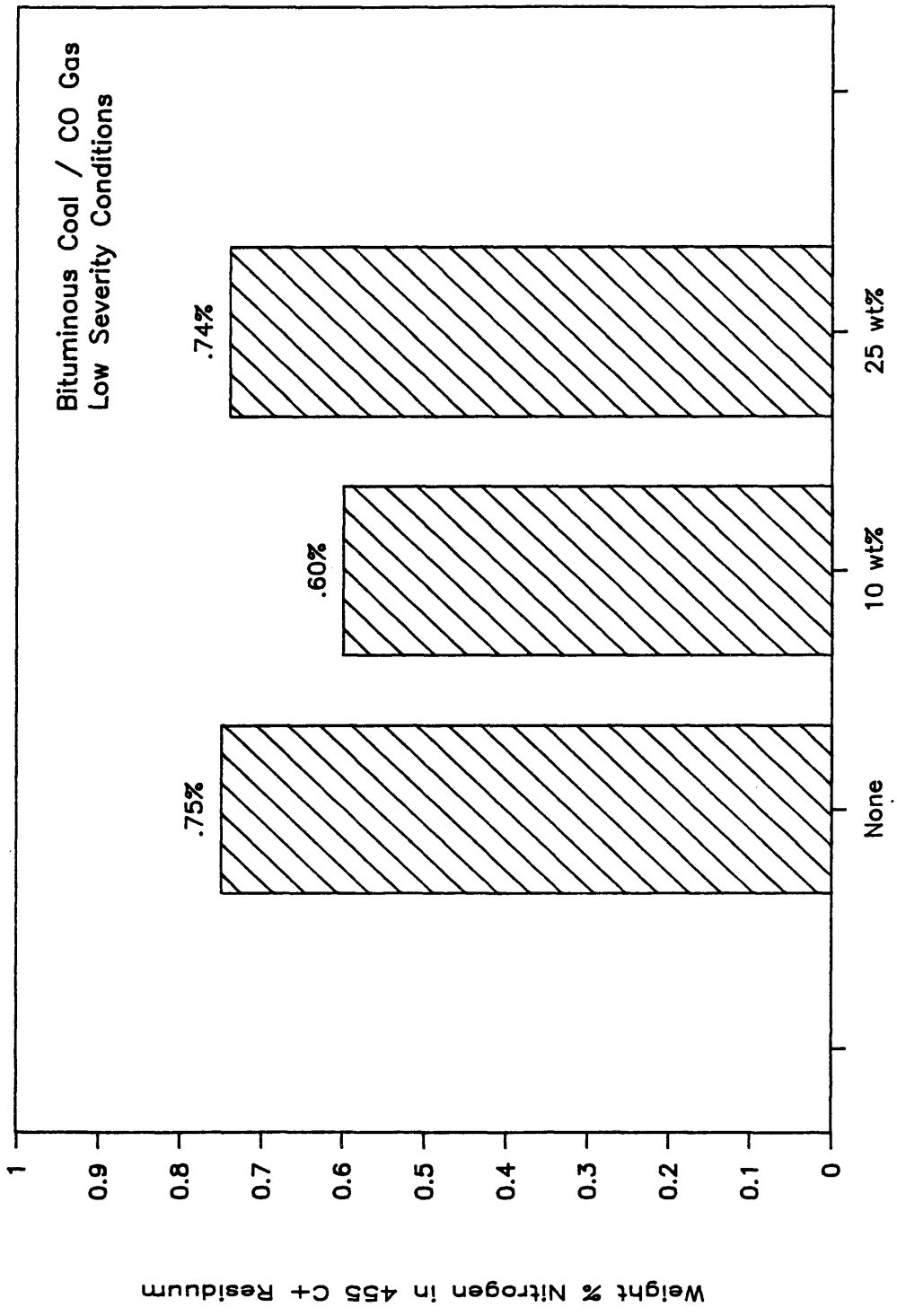


Figure 35: Effect of Dipropylamine (N2) Feed Concentration on the Weight % Nitrogen Contained in the THF Soluble 455°C+ Residuum for Kentucky 9 Bituminous Coal With CO Feed Gas

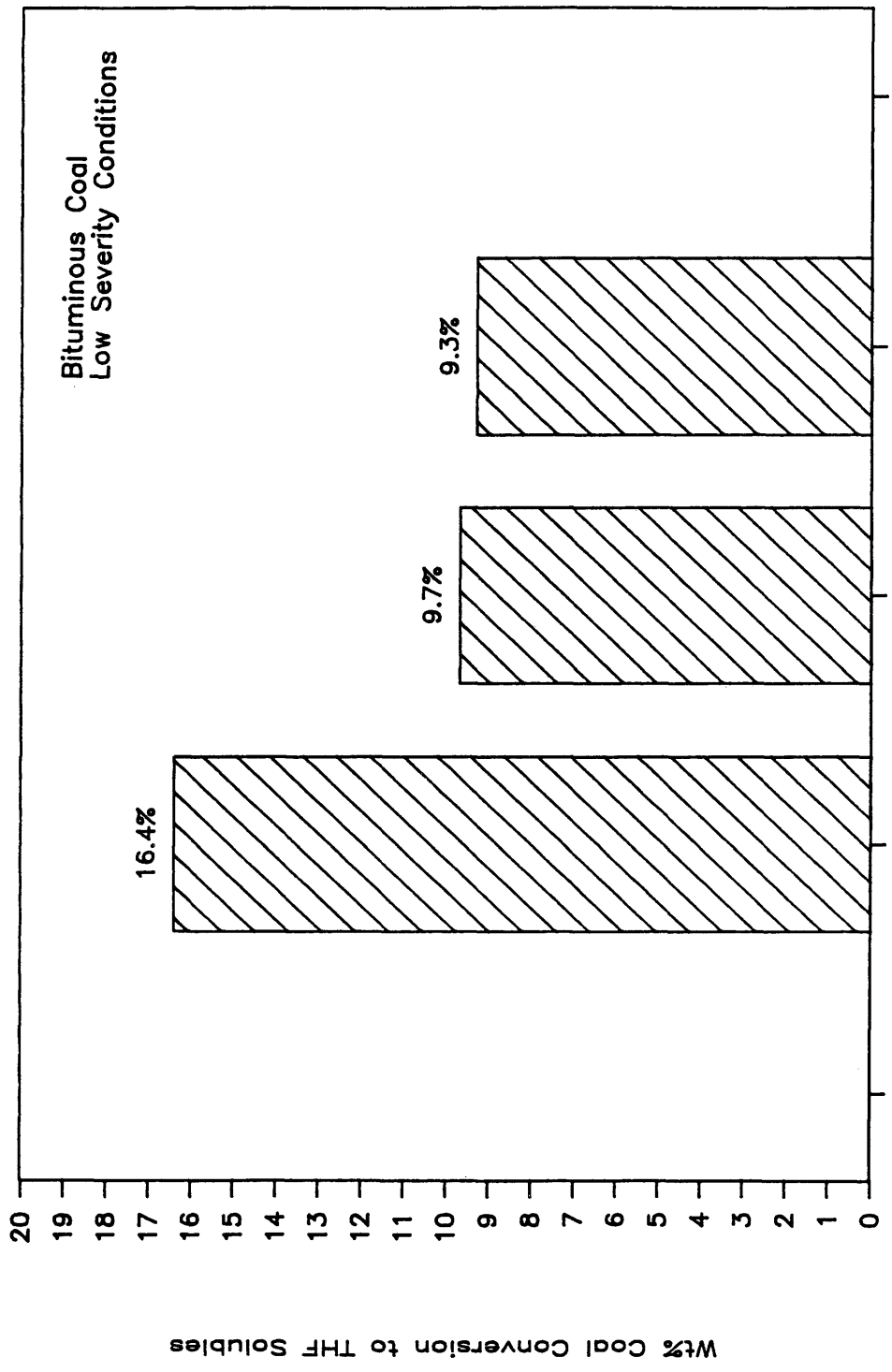


Figure 36: Effect of Initial Carbon Monoxide Pressure on Conversion of Kentucky 9 Bituminous Coal

CO solubility increases with pressure, increasing the extent of the water-gas shift reaction.

Comparison of Low Severity vs. High Severity Liquefaction Co-Processing Performance

Figure 37 compares the effect of low severity and high severity reaction conditions on conversion of bituminous coal with a hydrogen feed gas. Increased reaction severity resulted in a coal conversion increase of about 22 wt% in the THQ (N1) runs, whereas with dipropylamine (N2) addition a marginal increase in conversion of only about 6 wt% occurred.

Figure 38 shows the percent of total nitrogen contained in the THF insoluble product as a function of nitrogen compound addition and reaction severity for bituminous coal conversion with hydrogen feed gas. These data show that as coal conversion increases, the amount of total nitrogen contained in the THF insoluble matter decreases. This is not to imply that nitrogen incorporation has decreased but rather that the amount of THF insolubles that remains to incorporate the nitrogen has decreased.

Figure 39 compares the nitrogen incorporation results based on calculations described in Appendix C. The figure shows the estimated amounts of THQ (N1) which has been incorporated into the 455°C+ THF soluble and the THF

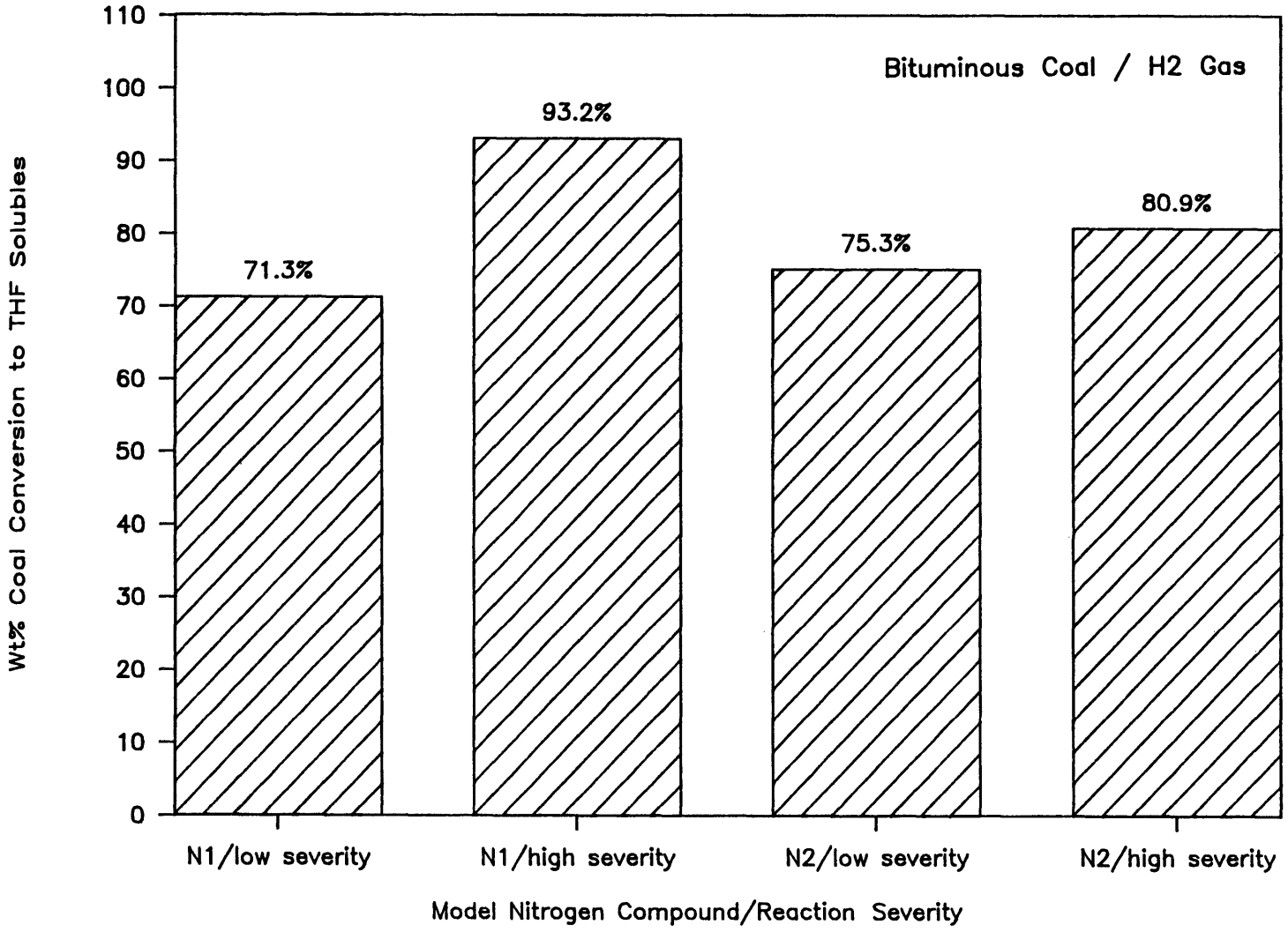


Figure 37: Effect of Model Nitrogen Compound Addition and Reaction Severity on Conversion of Kentucky 9 Bituminous Coal With Hydrogen Feed Gas

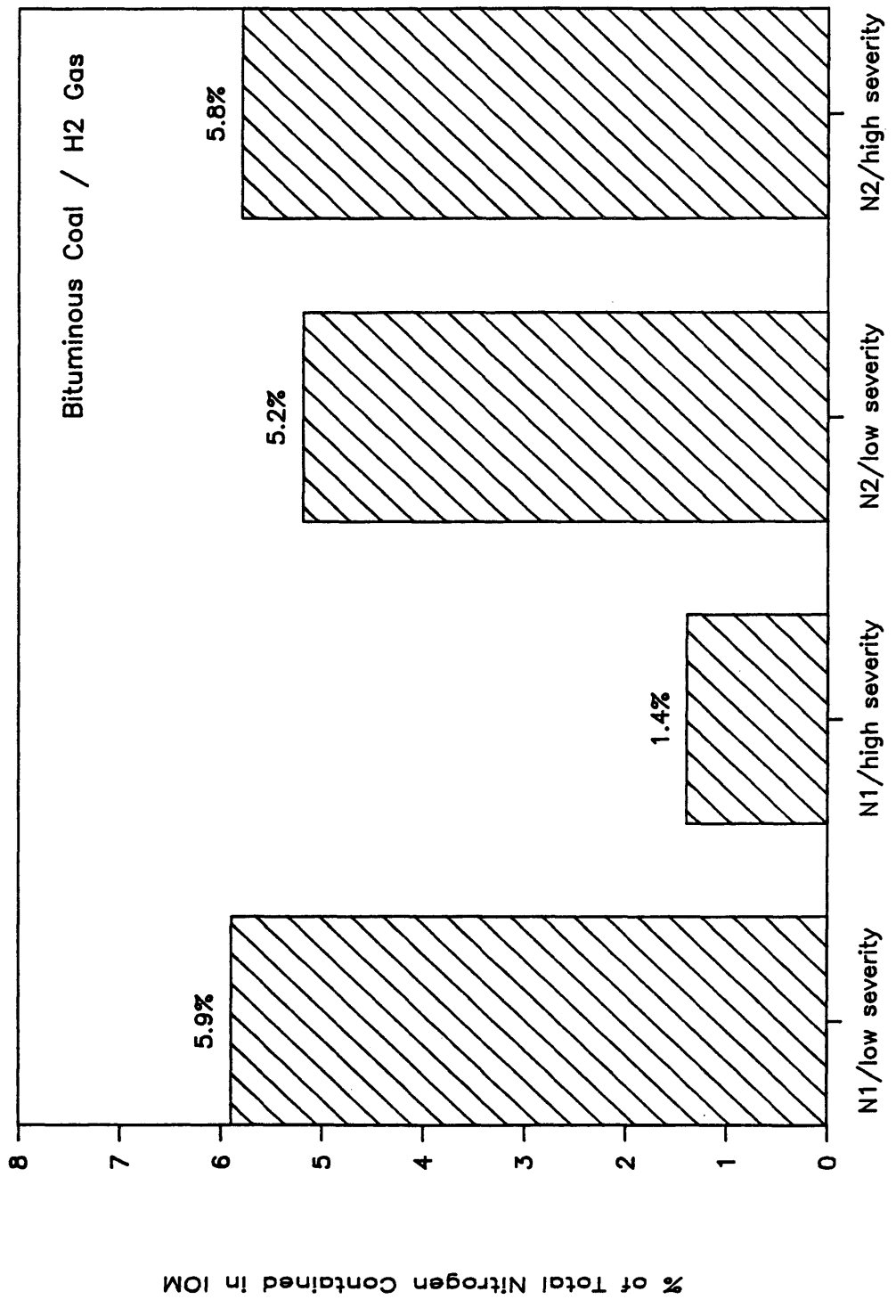


Figure 38: Effect of Model Nitrogen Compound Addition and Reaction Severity on the Nitrogen Content of the IOM for Kentucky 9 Bituminous Coal With Hydrogen Feed Gas

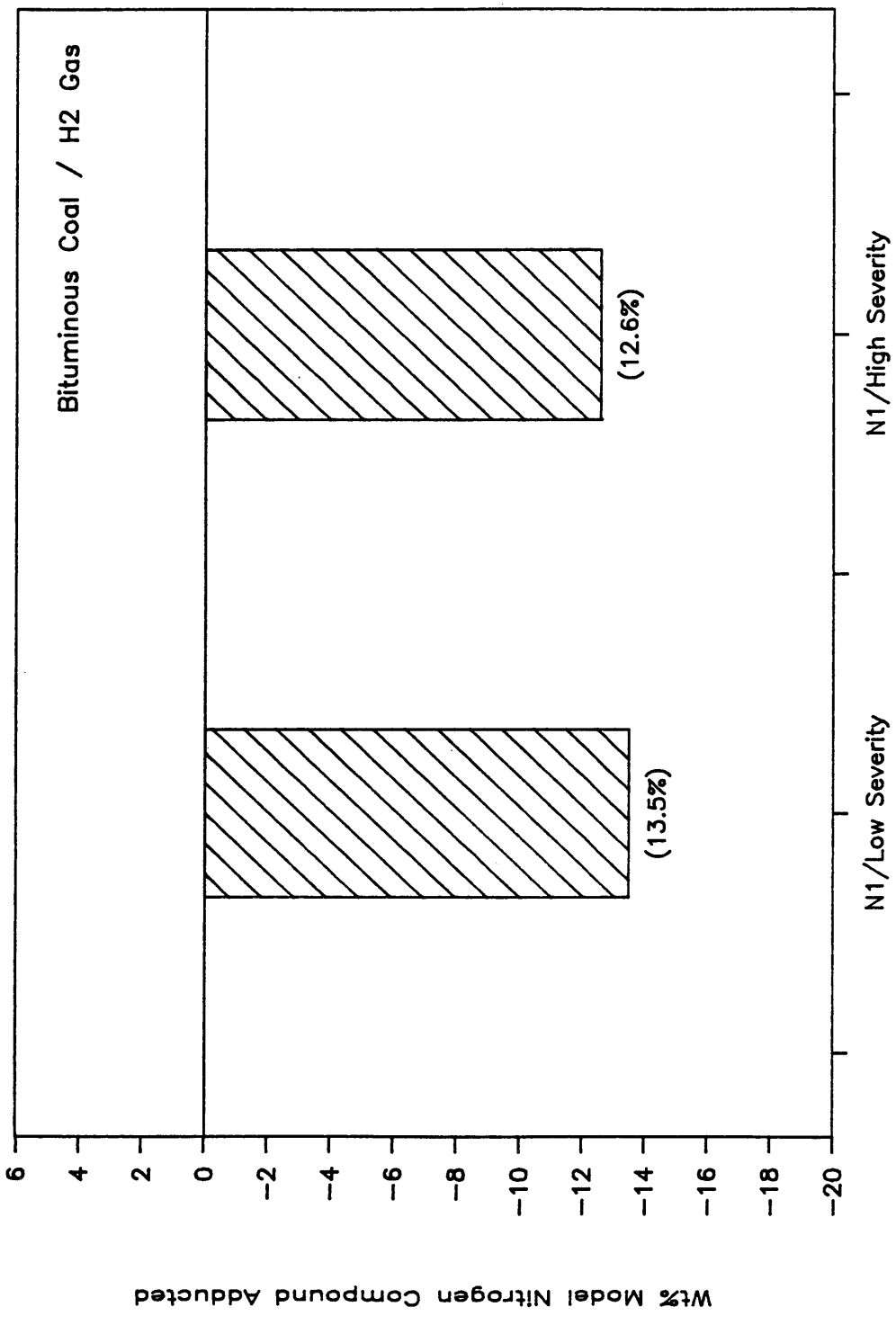


Figure 39: THQ (N1) Adduction as a Function of Reaction Severity for Kentucky 9 Bituminous Coal With Hydrogen Feed Gas

insoluble residual products, as a function of reaction severity. These results indicate that the incorporation increases at higher reaction severity. (The error associated with Figure 39 is similar to that described for Figure 19 on page 69.) Since Figure 38 shows a relatively small amount of nitrogen in the THF insolubles, it is likely that significant nitrogen was lost into the gaseous products as ammonia at the high severity conditions.

Feed Gas Consumption and Light Gas Production

Carbon Monoxide Consumption

Figure 40 shows the effect of THQ (N1) addition, dipropylamine (N2) addition and coal rank on CO consumption. For each coal rank, THQ addition results in lower CO consumption compared with the use of dipropylamine. This observation could be the result of a promotional effect of both the respective nitrogen compounds and the coal rank on promoting the water-gas shift reaction. Figure 40 shows the combined effect of these two variables. Figure 41 demonstrates the effect of THQ (N1) and dipropylamine (N2) concentration on CO consumption. Figure 41 shows that regardless of nitrogen compound concentration, THQ (N1) addition results in a lower CO consumption. Figure 40 demonstrates the same trend, but also includes the factor of

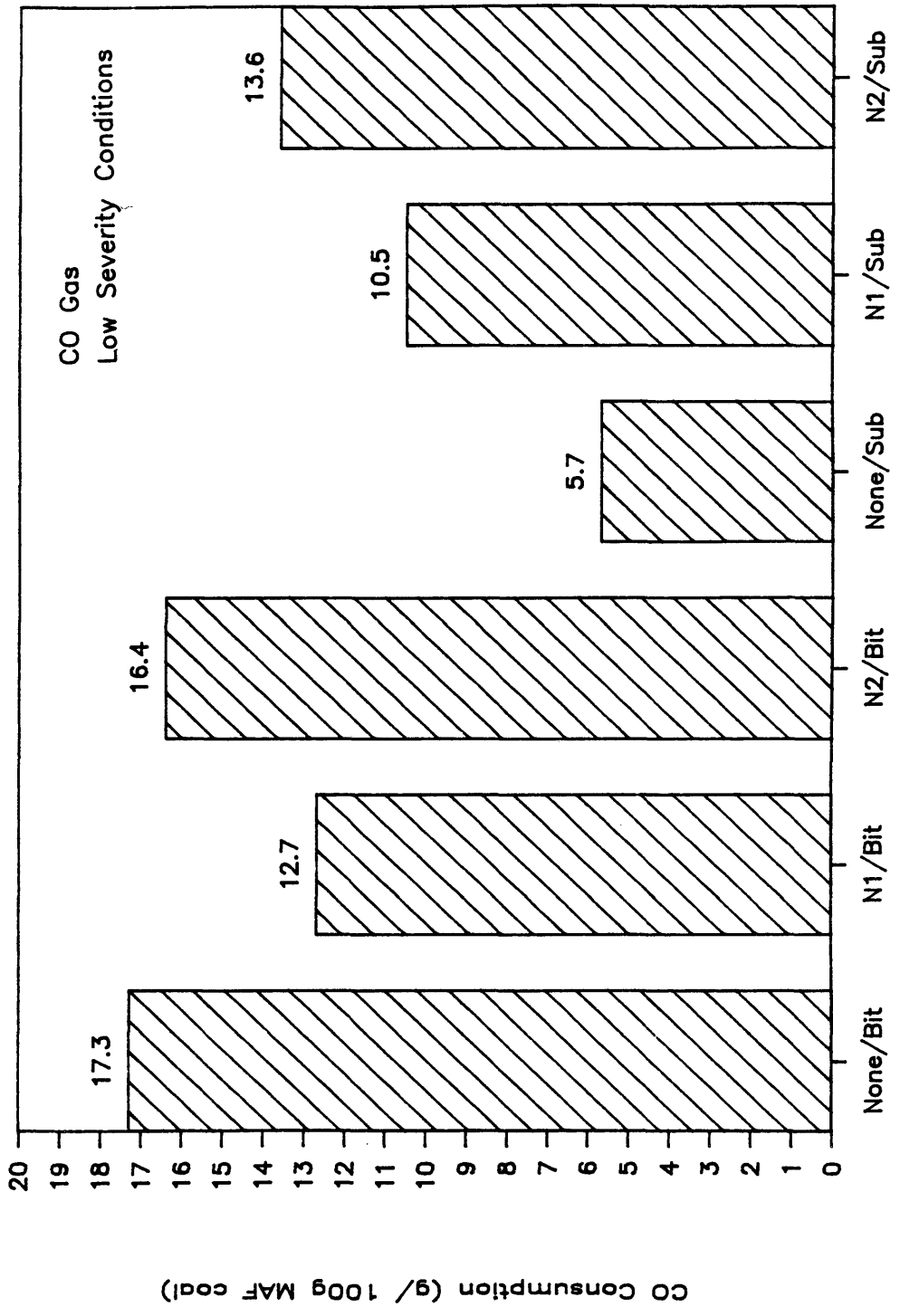


Figure 40: Effect of Model Nitrogen Compound Addition and Coal Rank on CO Consumption

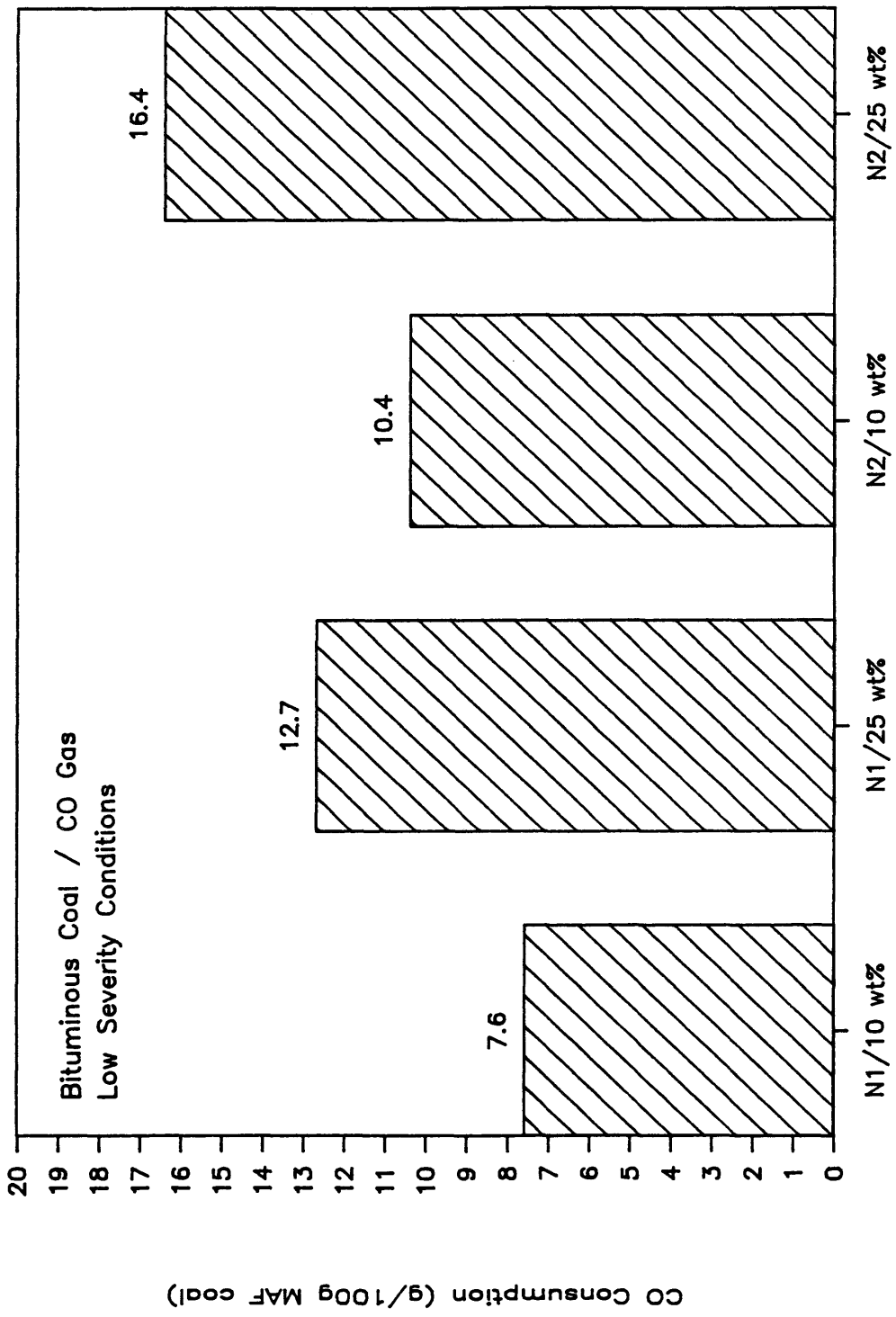


Figure 41: Effect of Model Nitrogen Compound Feed Concentration on CO Consumption for Kentucky 9 Bituminous Coal

coal rank. With both THQ (N1) and dipropylamine (N2), the CO consumption with subbituminous coal is lower than with bituminous coal.

The possibility of CO consumption being related to subsequent hydrogen consumption by the reacting coal and primary liquefaction products is not a consideration. Thermodynamic equilibrium calculations indicate that at the reaction conditions employed, the water-gas shift reaction is only proceeding to approximately 10% of its equilibrium value. Since the reaction is so far from equilibrium the depletion of one of the products (as hydrogen) should not influence the driving force of the reaction with respect to Le Chatelier's principle. Therefore hydrogen concentration should not effect the rate of CO consumption.

Hydrogen Consumption

Figure 42 shows that when THQ (N1) is used with bituminous coal and a hydrogen gas atmosphere, hydrogen consumption increases by about 90% at high severity reaction conditions compared with low severity conditions. However, with dipropylamine (N2) addition, hydrogen consumption increases by nearly 164% at high severity conditions. The reason for this tremendous increase in consumption is probably due to thermal cracking of the free dipropylamine

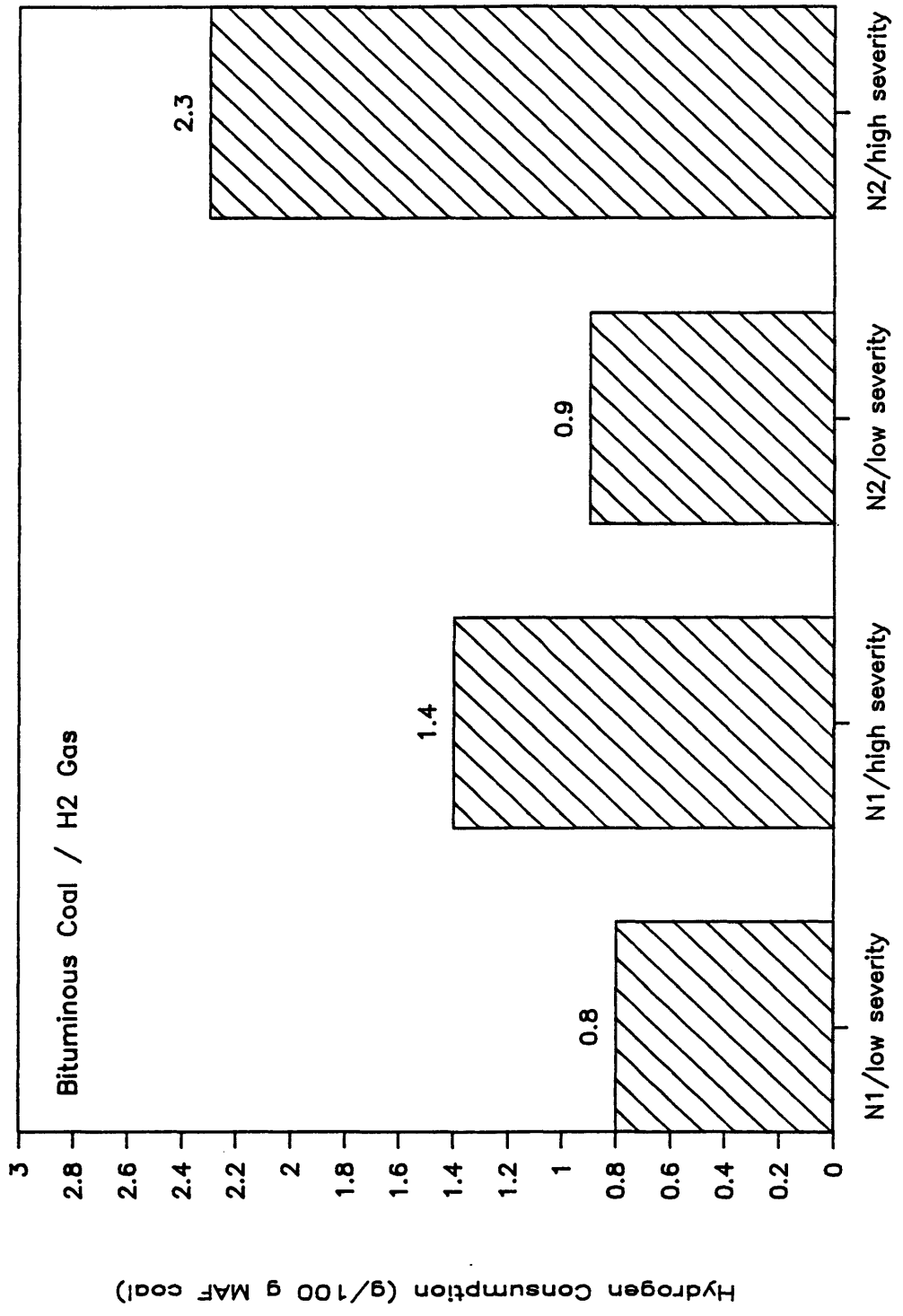


Figure 42: Effect of Model Nitrogen Compound Addition and Reaction Severity on Hydrogen Consumption for Kentucky 9 Bituminous Coal

present and subsequent hydrogenation of the propyl groups and the free NH· radical.

Figure 43 shows the effect of THQ (N1) addition, dipropylamine (N2) addition and coal rank on hydrogen consumption. THQ addition results in a lower hydrogen consumption with bituminous coal, but a higher hydrogen consumption with subbituminous coal, compared to dipropylamine addition. This result can be explained by the fact that with bituminous coal, the increased hydrogen consumption with dipropylamine addition is caused by greater coal conversion and increased light gas make. With subbituminous coal, dipropylamine appears to act more efficiently, in that approximately 60% less hydrogen is consumed than with THQ addition, and yet dipropylamine addition results in greater coal conversion, as shown previously in Figure 14.

Light Gas Production

Figure 44 shows the light gas production as a function of nitrogen compound addition and reaction severity for bituminous coal conversion with hydrogen feed gas. For both THQ (N1) and dipropylamine (N2) addition, light gas production increases drastically at high severity conditions. When dipropylamine (N2) is used, hydrocarbon gas

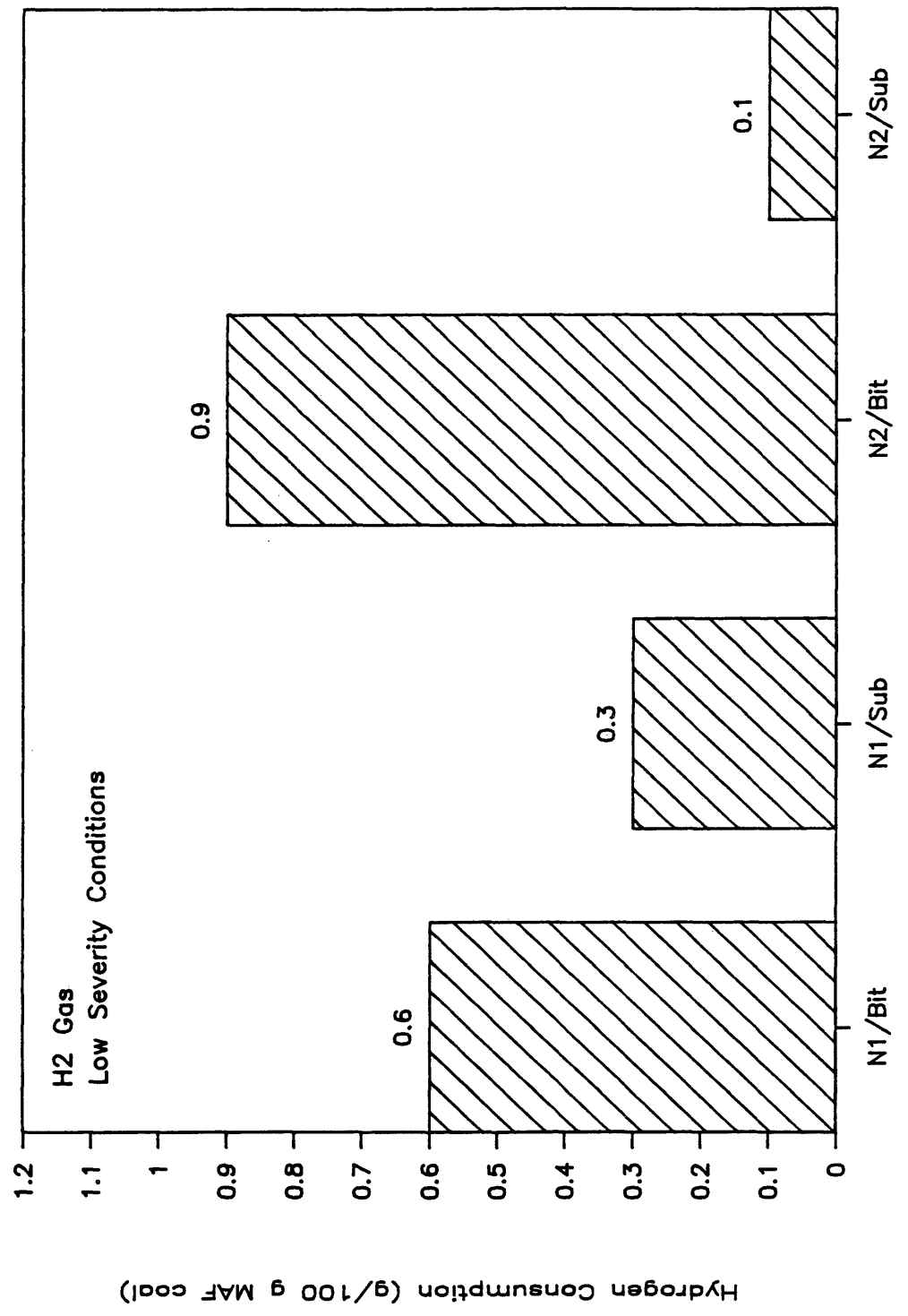


Figure 43: Effect of Model Nitrogen Compound Addition and Coal Rank on Hydrogen Consumption

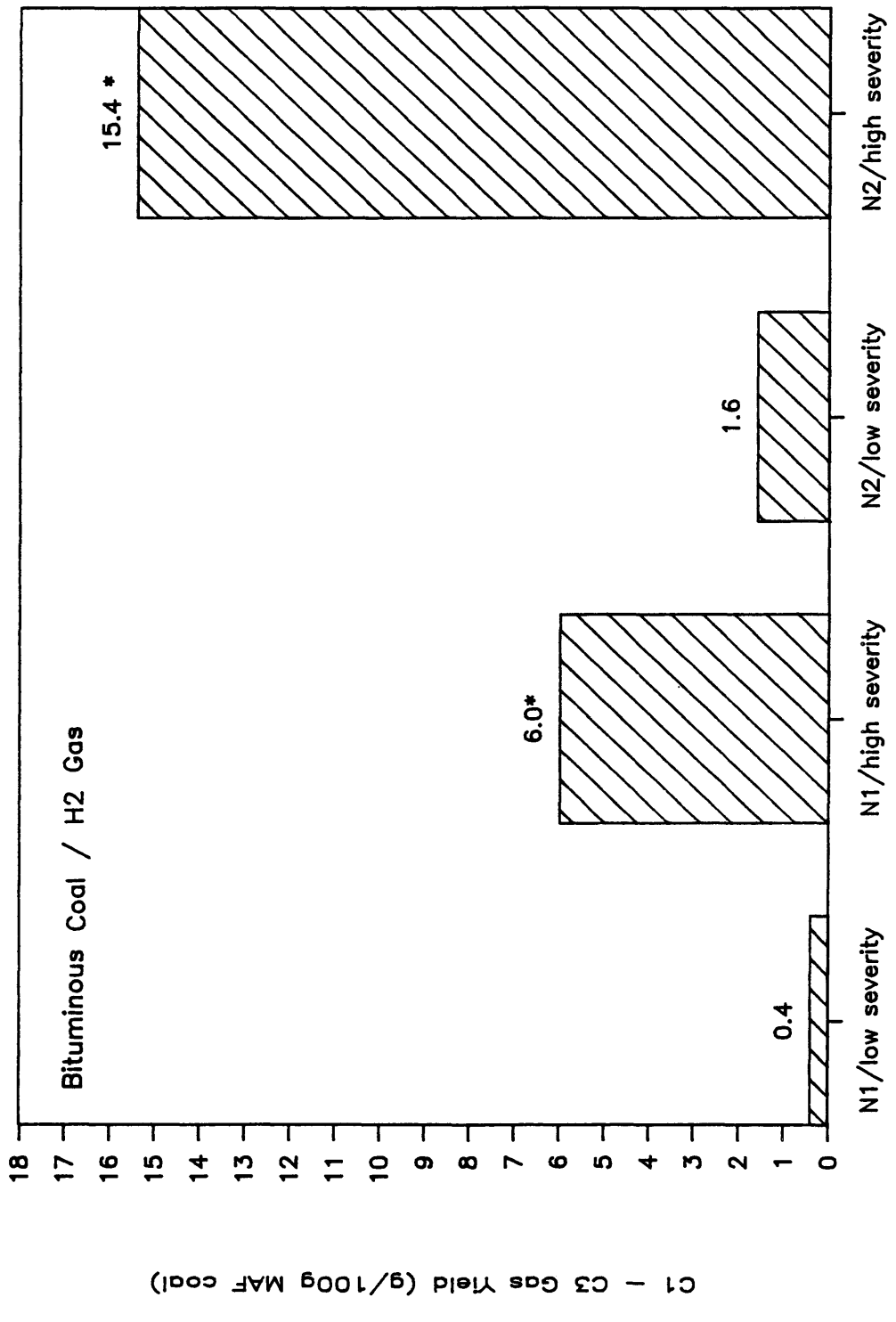


Figure 44: Effect of Model Nitrogen Compound Addition and Reaction Severity on the C1 - C3 (* or C1 - C4) Light Gas Yield for Kentucky 9 Bituminous Coal With Hydrogen Feed Gas

production is tremendous, and is likely the result of thermal cracking of the dipropylamine to produce propylene and propane. This possibility is evident in the product gas analysis where the C_3 components account for 6.6 mole% of the gases at high severity conditions, whereas when THQ (N1) is used at high severity conditions, C_3 components account for only 0.1 mole%.

Figure 45 shows a similar effect when the reaction gas is varied with bituminous coal conversion at low severity conditions. When THQ (N1) is used, the light gas yield is relatively independent of feed gas, whereas with dipropylamine (N2) addition light gas yield increased significantly under a hydrogen atmosphere. This effect is likely the result of increased hydrogen availability to thermally cracked radicals of dipropylamine under a hydrogen atmosphere.

Effect of Reaction Conditions on Product Quality

Tables A-3 and A-4 in Appendix A summarize the measured nitrogen, hydrogen and carbon contents of THF insoluble residues and 455°C+ THF soluble residuum samples. Figures 46 through 50 show the carbon/hydrogen (C/H) mass ratio as a function of THF coal conversion for these products. These results indicate that the C/H ratio for bituminous coal-

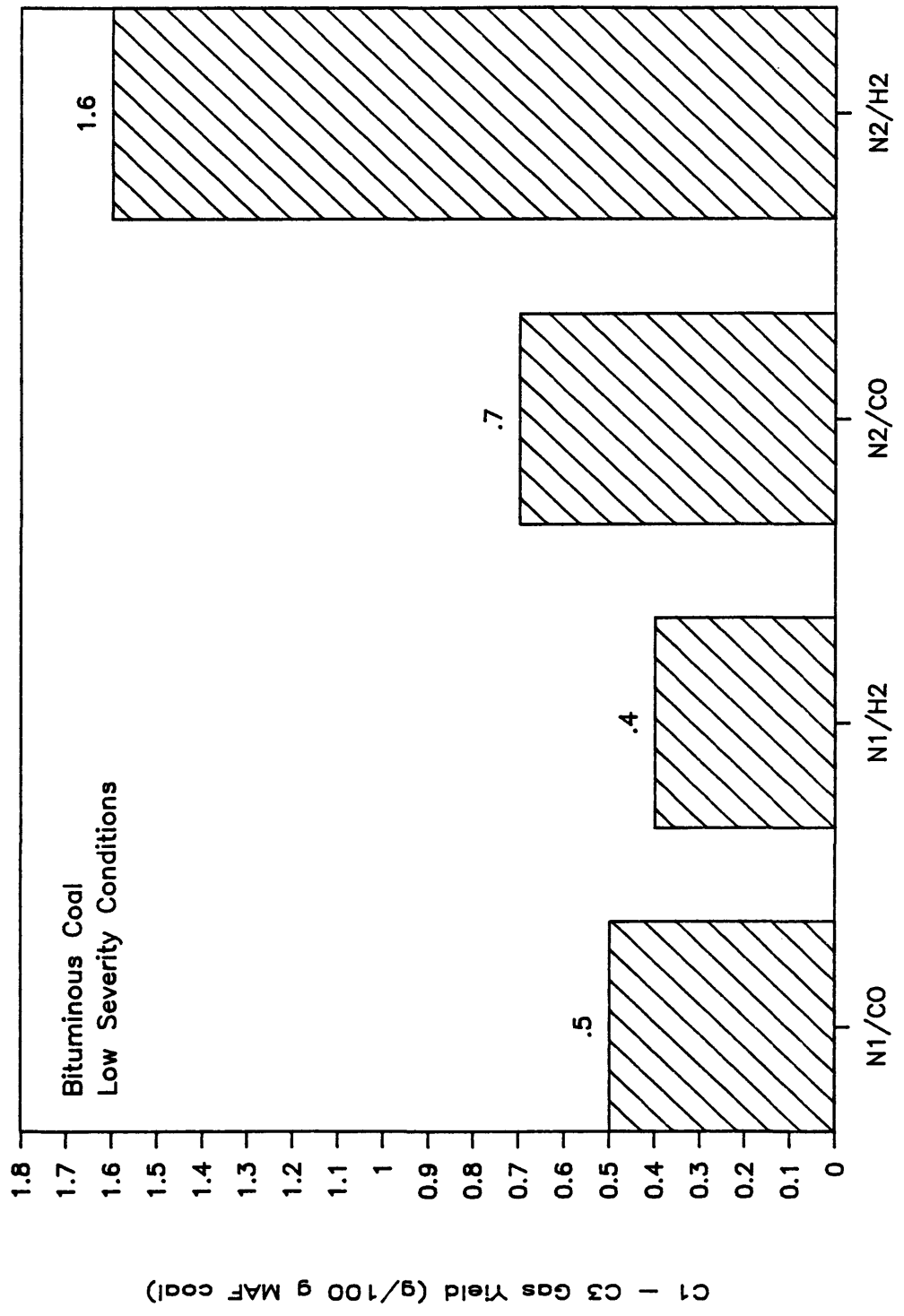


Figure 45: Effect of Model Nitrogen Compound Addition and Feed Gas on the C1 – C3 Light Gas Yield for Kentucky 9 Bituminous Coal

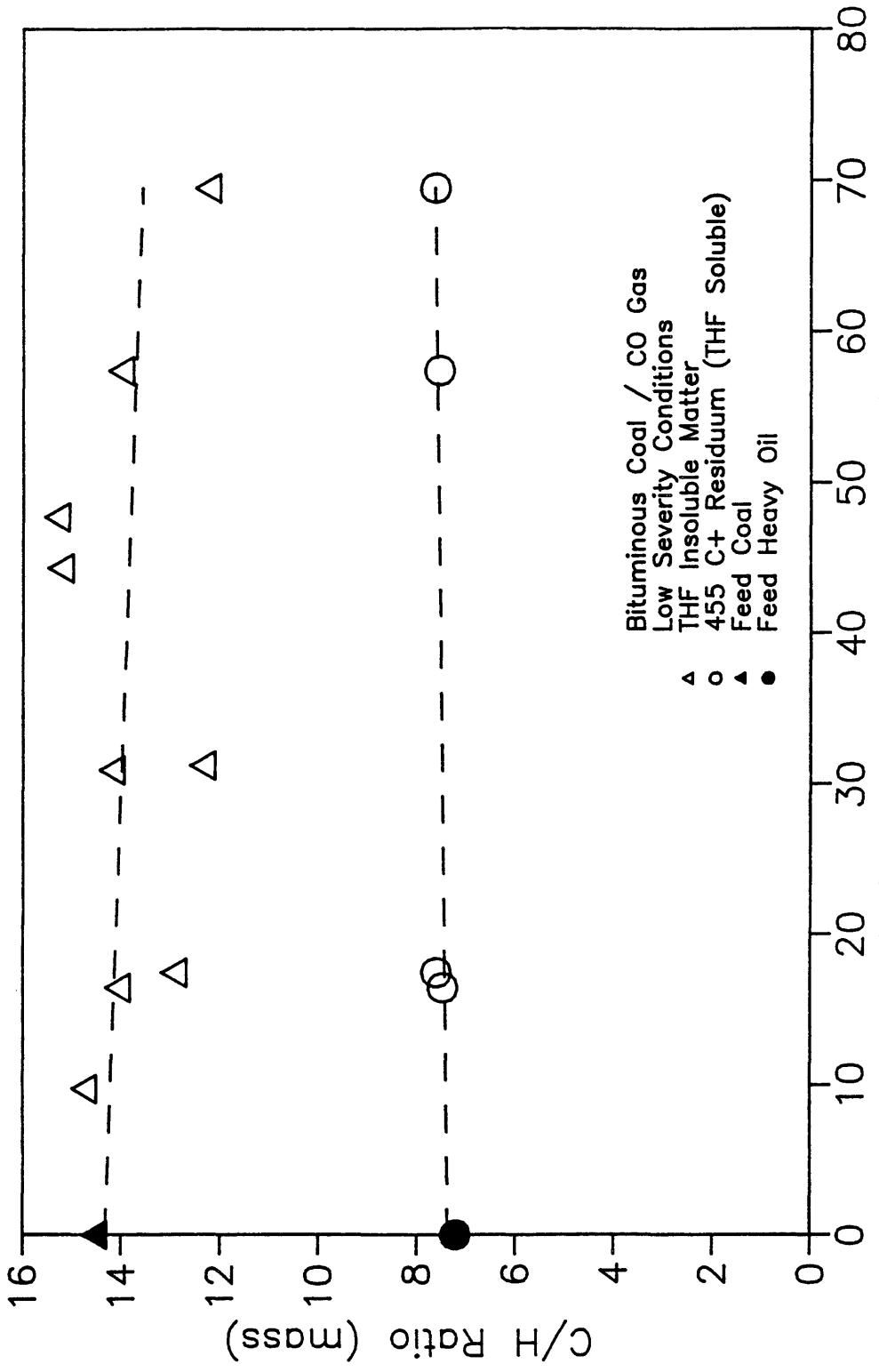


Figure 46: Carbon/Hydrogen Mass Ratio vs. Extent of Conversion of Kentucky 9 Bituminous Coal With CO Feed Gas for THF Insoluble IOM and THF Soluble 455°C+ Product Fractions

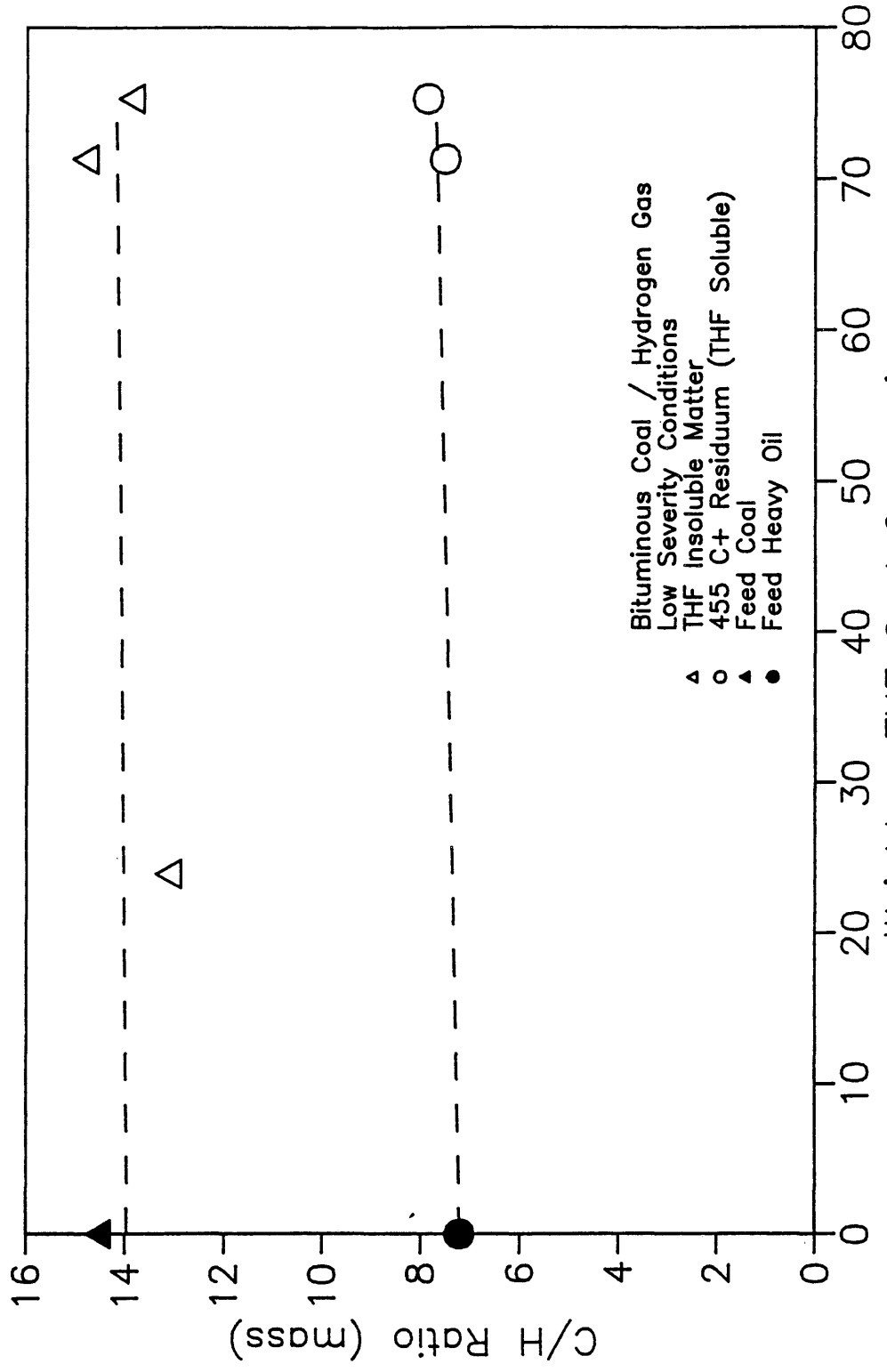


Figure 47: Carbon/Hydrogen Mass Ratio vs. Extent of Conversion of Kentucky 9 Bituminous Coal With Hydrogen Feed Gas, for THF Insoluble IOM and THF Soluble 455°C+ Product Fractions

derived THF insoluble matter is essentially independent of coal conversion extent, reaction gas atmosphere, and concentration of nitrogen compound. This occurrence is due to the small extent of product upgrading at the low severity conditions.

The other observation is that the C/H ratio for the 455°C+ THF soluble samples is also relatively independent of coal conversion, reaction gas atmosphere, and concentration of nitrogen compound. These results suggest that any coal conversion occurring under these reaction conditions is likely being upgraded only to the level that it becomes soluble in THF or, to a much lesser extent, cyclohexane (CHX).

Figures 48 and 49 indicate that a slight degree of hydrogen upgrading of the THF insoluble matter occurs as coal conversion increases when processing Wyodak subbituminous coal under both feed gas atmospheres. However, the 455°C+ product C/H ratio is essentially independent of coal conversion extent and reaction gas atmosphere.

Figure 50 indicates that under high severity conditions, with the bituminous coal under a hydrogen atmosphere, there is a degree of coking occurring which increases the C/H ratio of the THF insoluble matter. Again the 455°C+ product composition is essentially unchanged.

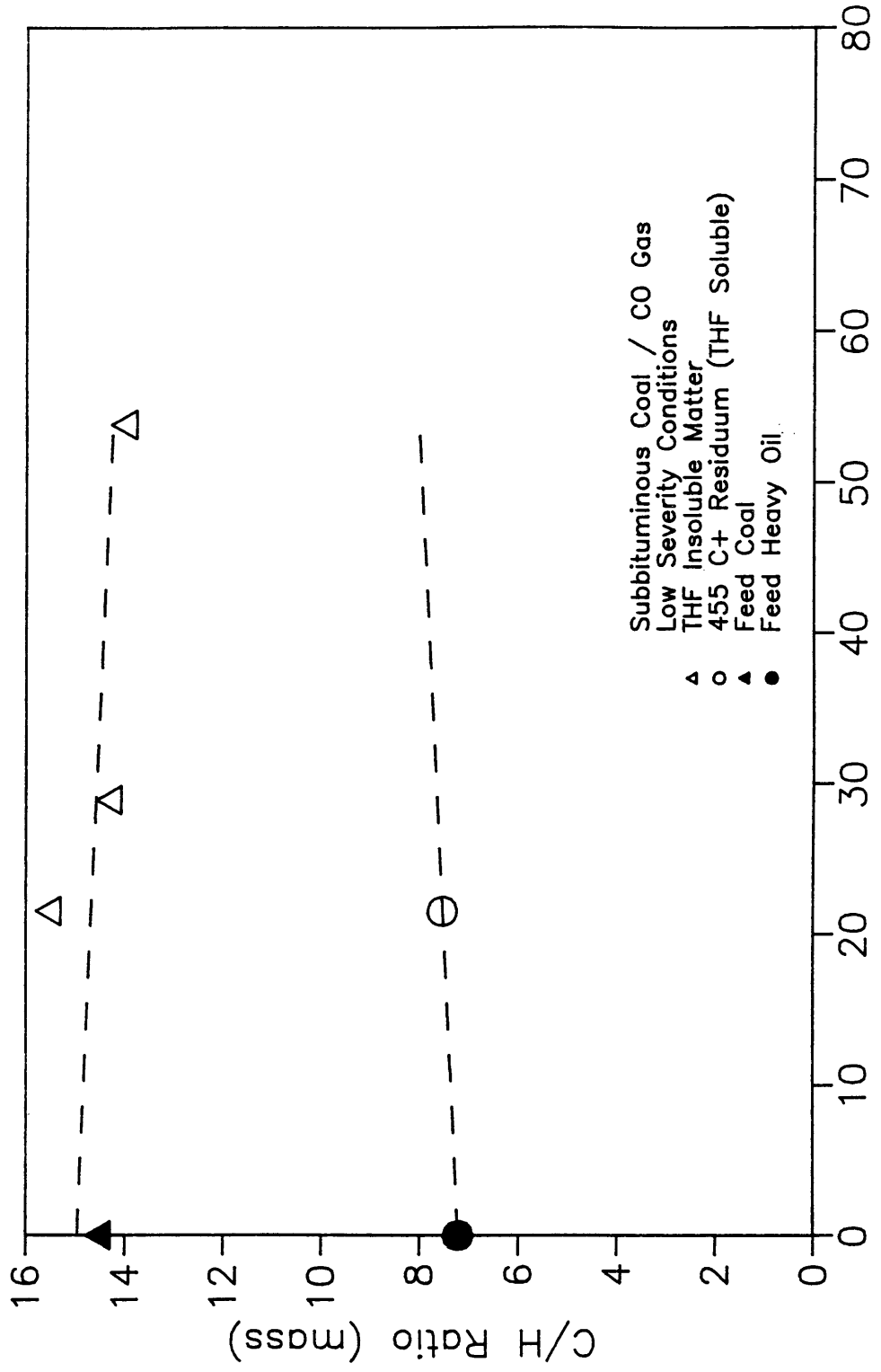


Figure 48: Carbon/Hydrogen Mass Ratio vs. Extent of Conversion of Wyodak Subbituminous Coal With CO Feed Gas, for THF Insoluble IOM and THF Soluble 455°C+ Product Fractions

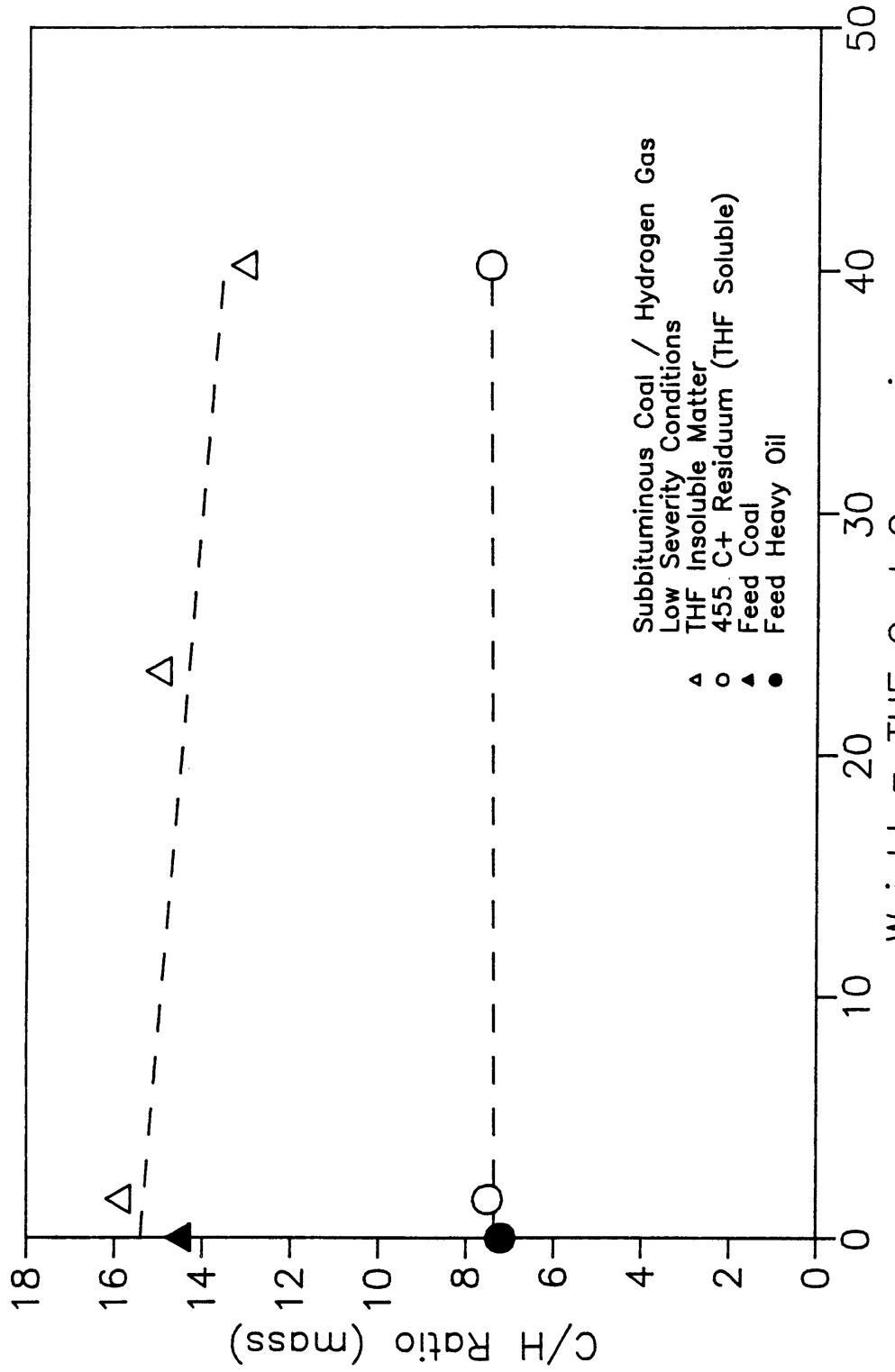


Figure 49: Carbon/Hydrogen Mass Ratio vs. Extent of Conversion of Wyodak Subbituminous Coal With Hydrogen Feed Gas, for THF Insoluble IOM and THF Soluble 455°C+ Product Fractions

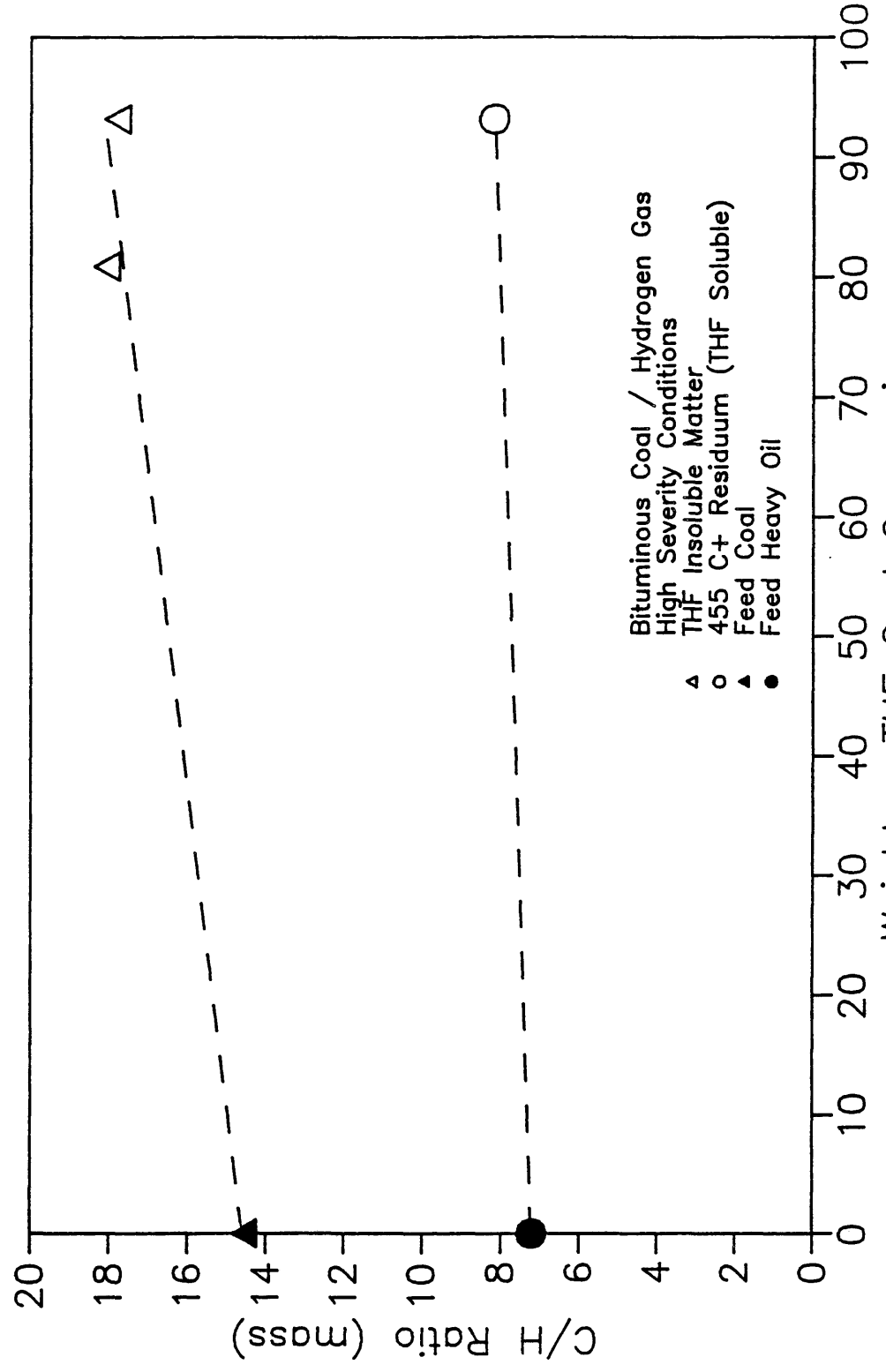


Figure 50: Carbon/Hydrogen Mass Ratio vs. Extent of Conversion of Kentucky 9 Bituminous Coal With Hydrogen Feed Gas at High Severity Conditions, for THF Insoluble IOM and THF Soluble 455°C+ Product Fractions

Nitrogen Balance Results

Table VI presents available nitrogen balance data for selected runs. A comprehensive balance was completed for one experimental run (G-39) in order to determine the precision of the nitrogen balance data. Total recovery of nitrogen in this run totaled approximately 102 wt%. The data in Table VI show the effect of varying reaction severity, reaction gas, and coal rank on nitrogen distribution among various products during THQ (N1) addition. The indication is that depending upon the process variable changed, there is a shift in the nitrogen content of individual product fractions. However, since little data was gathered, no definite conclusions are warranted.

Effect of Model Nitrogen Compound Steric Hindrance

The model nitrogen compounds used in this thesis consisted of a wide cross section of electronic and structural properties. Included were aliphatic amines, heterocyclic amines which behaved as aliphatics, and large polyaromatic heterocycles. Previous work (27,30,42) has indicated that, as the nitrogen compound becomes more bulky with substituents lying in a lateral plane to the nitrogen or in close proximety to the nitrogen, the compound tends to adduct more. This study has demonstrated a complex

Table VI: Nitrogen Content of Selected Product Fractions

Run	Total N Charged To System (g)	N in Centrifuge Residue (g)	N in 177C- (g)	N in 177-260C (g)	N in 260-344C (g)	N in 344-455C (g)	N in 455 C+ (g)	% N Recovery
G39	1.43	0.49 (34.3%)	0.35 (24.5%)	0.22 (15.4%)	0.13 (9.1%)	0.04 (2.8%)	0.23 (16.1%)	102.1
G31	1.53	----	0.34 (22.2%)	0.08 (5.2%)	0.12 (7.8%)	0.07 (4.6%)	0.12 (7.8%)	----
G35	1.52	----	----	0.26 (17.1%)	0.05 (3.3%)	0.03 (2.0%)	0.12 (7.9%)	----
G36	1.46	----	----	0.24 (16.4%)	0.09 (6.2%)	0.17 (11.6%)	0.17 (11.6%)	----

relationship between nitrogen compound basicity, steric factor, and coal conversion.

The concept of steric hindrance and coal rank is best shown with the compound 4-piperidinopyridine (N5). In this study the compound was used during bituminous coal co-processing, which resulted in a low coal conversion of 17.4 wt%, and the highest observed level of incorporation into THF insoluble matter. However, Miller (28) used the same compound with a Wyodak subbituminous coal and demonstrated approximately 98 wt% coal conversion with minimal apparent incorporation. The inference is that coal rank and the steric hindrance inherent in the coal structure play an important role in the catalytic effectiveness of the model nitrogen compounds. The indication is that subbituminous coal has a much more open structure than bituminous coal, which is what Larsen and Lee (42) also demonstrated.

CONCLUSIONS

The objective of this work was to investigate the catalytic effect of several representative model nitrogen compounds in a low severity co-processing environment. The conclusions drawn from this work are:

1. Dipropylamine provided the greatest increase in coal conversion for both Kentucky 9 bituminous and Wyodak subbituminous coals with both hydrogen and CO feed gas at all low severity reaction conditions studied. THQ (1,2,3,4-tetrahydroquinoline) provided the next best conversions under similar reaction conditions.

2. Dipropylamine is the best low severity promoter, of those studied, for co-processing, providing the highest coal conversion with the least amount of nitrogen incorporation into the IOM and 455°C+ residual products. However, dipropylamine addition also results in higher CO consumption and higher light gas yield, compared with THQ addition.

3. The direct measurement of the nitrogen content in the THF (Tetrahydrofuran) insoluble matter (IOM) can be used to monitor the relative nitrogen incorporation of different nitrogen compounds at a fixed set of reaction condition.

4. Incorporation of model nitrogen compound occurs primarily into the THF insoluble matter (IOM) rather than the 455°C+ THF soluble residual product.

5. A correlation was developed between the extent of Kentucky 9 bituminous coal low severity conversion and model nitrogen compound aqueous pK_b value.

6. A higher degree of incorporation of THQ was inferred at higher severity reaction conditions.

7. Dipropylamine demonstrates high efficiency in the conversion of Wyodak subbituminous coal with hydrogen feed gas resulting in greater coal conversion and less hydrogen consumption compared with THQ addition. However, at the same reaction conditions dipropylamine also results in very high incorporation of nitrogen into the IOM.

8. At low severity reaction conditions the carbon/hydrogen mass ratio for Kentucky 9 bituminous coal-derived THF insoluble matter and 455°C+ residuum product is essentially independent of coal conversion extent, feed gas, and concentration of model nitrogen compound.

9. The extent of coal upgrading at low severity reaction conditions is only to the degree of producing THF soluble products with very little production of cyclohexane soluble products.

10. The extent of upgrading of A-8 Cold Lake atmospheric residuum at low severity reaction conditions appears to be negligible.

11. Coal conversion is a function of coal rank, feed gas and the concentration of model nitrogen compound addition.

12. Carbon monoxide feed gas significantly improves conversion of Wyodak subbituminous coal compared to using hydrogen feed gas.

13. Coal conversions with Wyodak subbituminous coal were considerably lower than with Kentucky 9 bituminous coal under identical operating conditions. This observation is likely due to the Wyodak coal having a much lower reactivity.

14. Wyodak subbituminous coal conversion is more dependent on the type of feed gas used than Kentucky 9 bituminous coal.

RECOMMENDATIONS

The completion of this work has led to several specific recommendations:

1. In order to obtain accurate liquid yield results, a larger reactor product mass is required. To accomplish this either a larger reactor must be used to allow a larger reactant charge, or the existing reactor must contain a larger amount of reactants and must be modified to provide a sufficiently large gas reservoir for an adequate hydrogen gas supply.

2. Since dipropylamine worked well, other aliphatic amines such as diethylamine, etc. should be investigated.

3. Since the major factor which will enable widespread use of model nitrogen compounds is the ability to separate the compound from the co-processing products and recycle it to the reactor, an increased effort must be placed on devising methods to achieve this result.

REFERENCES

1. Probstein, R.F., Hicks, R.E., 'Synthetic Fuels', McGraw Hill, chapters 1,3,6, (1982).

2. Whitehurst, D.D., Mitchell, T.O., Farcasiu, M., 'Coal Liquefaction, The Chemistry and Technology of Thermal Processes', Academic Press, pp. 1-4, 274-287, 346-359, (1980).

3. Wu, W.R.K., Storch, H.H., 'Hydrogenation of Coal and Tar', Bureau of Mines Bulletin 633, pp. 1-8, (1968).

4. Lamb, C.W., Lee,J.M., Nalitham,R.V., 'Two Stage Coal Liquefaction Process Performance With Close-Coupled Reactors In Wilsonville', Palo Alto, CA, Eleventh Annual EPRI Clean Liquid and Solid Fuels Conf.,(1986).

5. Duddy, J.E., MacArthur, J.B., 'Coal/Oil Co-processing', Philadelphia, Paper 16b presented at AICHE meeting,(1984).

6. MacArthur, J.B., Boehm, F., Liron, A., Shannon, R.H., 'Coal/Oil Co-processing of Canadian Feedstocks', Tenth Annual EPRI Contractors' Conference on Clean Liquid and Solid Fuels, section 15, (1985).

7. Yan, T.Y., Espencheid, W.F., 'Liquefaction of Coal In Petroleum Under Mild Conditions', Miami, Paper presented at AICHE meeting, (1982).

8. Kelly, J.F., Fouda, S.A., Rahimi, P.M., Ikura, M., 'Canmet Co-Processing: A Status Report', Publication of Energy, Mines and Resources, Canada, (1984).

9. Curtis,C.W., Guin, J.A., Pass, M.C., Tsai, K.J., 'Coal Solvolysis in Heavy Petroleum Crudes and Residua', Auburn University, Auburn, Alabama, Chemical Engineering Department, (1985).

10. Moschopedis, S.E., Ozum,B., 'Co-processing of Alberta Subbituminous Coal With Oil Sand Bitumen', Liquid Fuels Technology, 2(2),193, (1984).

11. Moschopedis, S.E., 'Further Investigations on the Use of Bitumen and Heavy Oils to Process Coal', Liquid Fuels Technology, 2(2), 177, (1984).

12. Schindler, H.D., Chen, J.M., Peluso, M., Schiffer, A.N., 'Coal Liquefaction by Coal/Oil Co-processing', Palo Alto, CA., Tenth Annual EPRI Contractors' Conference on Coal Liquefaction, paper No. 23, (1985).

13. Miller, R.L., 'Use of Non Coal-Derived Heavy Solvents in Direct Coal Liquefaction', Palo Alto, CA., Tenth Annual EPRI Contractors' Conference on Coal Liquefaction, paper No. 6, (1985).

14. Miller, R.L., 'Non-coal Derived Heavy Solvents in Direct Coal Liquefaction', Interim report to EPRI, November, (1985).

15. Shinn, J.H., Dahlberg, A.J., Kuehler, C.W., Rosenthal, J.W., 'The Chevron Co-Refining Process', Palo Alto, CA., Ninth Annual EPRI Contactors Conference on Coal Liquefaction, paper No. 33, (1984).

16. Satterfield, C.N., 'Heterogeneous catalysis in practice', McGraw-Hill, pp. 282, 292-294, (1980).

17. Miller, R.L., Baldwin, R.M., 'Low Severity Coal Liquefaction Using Homogeneous Basic Nitrogen Catalysts', DOE Technical Progress Report, October (1986).

18. Cronauer, D.C., Panvelker, S.V., Ge, W., Shah, Y.T., 'Effect of Nitrogen Content of Solvent on Coal Liquefaction',Ind. Eng. Chem. Fundam.,23,202,(1984).

19. Cronauer, D.C., McNeil, R.I., 'The Advantages And Disadvantages Of Nitrogen-Containing Solvents For Coal Liquefaction',Pittsburgh, Proc. Inter. Conf. of Coal Science, 176, (1983).

20. Hirschon, A.S., Sundback, K., Laine, R.M., 'Chemistry of Hydrogen Sulphide Under Coal Liquefaction Conditions, Part 1', Fuel, 64, 772, (1985).

21. Hirschon, A.S., Laine, R.M., 'Chemistry of Hydrogen Sulphide Under Coal Liquefaction Conditions, Part 2', Fuel, 64, 911, (1985).

22. Collins,C.J., Raaen,V.F., Benjamin,B.M., Maupin,P.H., Roark,W.H., 'Coal Chemistry 8. Reactions of Tetralin With Coal and With Some Carbon 14-Containing Model Compounds', J.Am.Chem.Soc., 101, 5009, (1979).

23. Silver, H.F., Frazee, W.S., Broderick, T.E., Hurtubise, R.J., 'Dissolution of Subbituminous Coal in Tetrahydroquinoline', Fuel, 65, 608, (1986).

24. Hellgeth, J.W., Amateis, P.G., Taylor, L.T., 'The Fate of Nitrogenous Model Process Solvents in Coal Liquefaction', Preprint papers Amer. Chem. Soc. Div. Fuel Chem., 29 (5), 99, (1984).

25. Atherton, L.F., Kulik, C.J., 'Coal Liquefaction Chemistry', Anaheim, CA, EPRI Report presented to AICHE meeting, (1984).

26. Narain, N.K., Utz,B.R., Appell,H.R., Blaustein,B.D., 'Incorporation of Quinoline into Coal and Coal-Derived Products', Fuel, 62, 1417, (1983).

27. Halleux, A., Tschameler,H., 'Extraction Experiments on Coal With Various Pyridine Bases', Fuel,38, 291,(1959).

28. Miller, R.L., Baldwin, R.M., 'Low Severity Coal Liquefaction Using Homogeneous Basic Nitrogen Catalysts', Colorado School of Mines,Department of Energy proposal issued, (March, 1986).

29. Panvelker, S.V., Shah, Y.T., 'Hydrogen Transfer Reactions of Model Compounds Typical of Coal', Ind. Eng. Chem. Fundam., 21(3), 236, (1982).

30. McNeil, R.I., Young, D. C., Cronauer, D.C., 'Extents and Models of Adduction of Hydrocarbon and Nitrogen-Containing Solvents in Coal Liquefaction', Fuel, 62, 806, (1983).

31. Kazimi, F., Chen, W.Y., Chen, J.K., Whitney,R.R., Zimny,B., 'Coal Liquefaction in Amine Systems', ACS Fuel Chem Preprints, 30(4),402, (1985).

32. McMillan, D.F., Malhotra,R., Chang,S.J., Ogier, W.C., St. John, G.A., Buttrill,S.E., Fleming,R.H., 'The Effects of Amine Solvents on the Breaking and Making of Strong Bonds in Coal Liquefaction', Palo Alto, CA, Eighth annual EPRI Contractors' Conference on Coal Liquefaction, paper No. 12, (1983).

33. Collins,C.J., Hagaman, E.W., Jones,R.M., Raaen,V.F., 'Retension of Pyridine C-14 and Other C-14 Labelled Amines by Illinois No. 6 Coal', Fuel, 60, 359, (1981).

34. Reid,K.F., 'Properties and Reactions of Bonds in Organic Molecules', American Elsevier Publishing Co., pp. 429-441,483-487, (1968).

35. Badger,G.M., 'The Chemistry of Heterocyclic Compounds', Academic Press, pp. 239-251, (1961).

36. Katritzky,A.R., (editor), 'Advances in Heterocyclic Chemistry, Vol. 6',Academic Press, pp. 230-243,(1966).

37. Perrin, D.D., Dempsey, Boyd, Serjeant, E.P., 'pKa Prediction for Organic Acids and Bases', Chapman and Hall Ltd., (1981).

38. Morrison,R.T., Boyd, R.N., 'Organic Chemistry, 3rd Ed.', Allyn & Bacon, pp. 318,727-749,1016-1018, (1973).

39. Darlage, L.J., Finkbone, H.N., King, S.J., Ghosal, J., Bailey, M.E., 'Nonaqueous Potentiometry of Coal-Derived Asphaltenes and Model Nitrogen Compounds in Acetophenone and Nitrobenzene', Fuel, 57, 479, (1978).

40. Perrin, D.D., 'Dissociation Constants of Organic Bases in Aqueous Solution', Butterworths, (1965).

41. Atkins, P.W., 'Physical Chemistry', W.H. Freeman & Co., pp. 478, (1978).

42. Larsen, J.W., Lee,D., 'Steric Requirements for Coal Swelling by Amine Bases', Fuel, 64, 981, (1985).

43. Atherton,L.F.,Kulik,C.J., 'Advanced Coal Liquefaction', Los Angeles, CA, EPRI Paper presented AICHE meeting, (1982).

44. Elliott, D.C., Sealock,L.J., 'Aqueous Catalyst Systems for the Water-Gas Shift Reaction. 1. Comparative Catalyst Studies', Ind. Eng. Chem. Prod. Res. Dev., 22, 426, (1983).

45. Hodges, S., Creasy, D.E., 'The Effect of Alkali Metal Carbonate Catalysts on the Liquefaction of Victorian Brown Coal Using Carbon Monoxide and Steam', Fuel, 64, 1229, (1985).

46. API Technical Data Book, Procedure 5A1.13, 'Vapor Pressures of Pure Hydrocarbons and Narrow-Boiling Petroleum Fractions, (1964).

47. Kaufman, M., Jamison, W.C.L., Liotta, D., 'Coal Liquefaction in Fluorocarbon Medium. 1. Nitrogen Compounds as Hydrogen Transfer Agents', Fuel, 65, 148, (1986).

APPENDIX A

Experimental Data

Table A-1: Yield and Conversion Results For Experimental Co-Processing Runs Using Hydrogen Gas

Run	G8	G9	G28	G29
Coal	B	B	B	B
Heavy Oil	A8	A8	A8	A8
Nitrogen Compound	--	N1	N2	N1
Solvent	--	--	--	--
Yields (wt% MAF Coal)				
CO, CO2	.84	.71	1.32	5.26
C1 - C3	.22	.24	1.56	.33
H2S	0	.51	0	0
Water	--	--	.62	1.06
C4 - 455°C	13.23	(13.62)	.10	3.79
455°C+	.35	51.36	72.36	60.24
IOM + MM	85.71	61.23	24.90	29.87
Total	100.35	100.43	100.86	100.55
H2 Consumption	0.35	0.43	0.86	0.55
Yields (wt% MAF Coal & 455°C+ Heavy Oil)				
CO, CO2	.30	.30	.56	2.24
C1 - C3	.08	.10	.67	.14
H2S	0	.22	0	0
Water	--	--	.26	.45
C4 - 455°C	4.71	(5.74)	.04	1.62
455°C+	64.53	79.51	88.21	83.03
IOM + MM	30.50	25.79	10.62	12.75
Total	100.12	100.18	100.36	100.23
H2 Consumption	0.12	0.18	0.36	0.23
THF Conversion (MAF Coal Basis)	14.3	38.8	75.3	70.3

Table A-1: Yield and Conversion Results For Experimental Co-Processing Runs Using Hydrogen Gas (cont'd)

Run	G30	G31
Coal	B	B
Heavy Oil	A8	A8
Nitrogen Compound	--	N3
Solvent	--	--
Yields (wt% MAF Coal)		
CO, CO2	4.06	2.03
C1 - C3	.05	.42
H2S	.32	.15
Water	.74	.67
C4 - 455°C	(9.75)	1.08
455°C+	28.77	68.73
IOM + MM	76.21	27.86
Total	100.40	100.94
H2 Consumption	0.40	0.94
Yields (wt% MAF Coal & 455°C+ Heavy Oil)		
CO, CO2	1.73	.86
C1 - C3	.02	.18
H2S	.14	.06
Water	.32	.29
C4 - 455°C	(4.16)	.46
455°C+	69.59	86.71
IOM + MM	32.54	11.84
Total	100.18	100.40
H2 Consumption	0.18	0.40
THF Conversion (MAF Coal Basis)	23.9	72.3

Table A-1: Yield and Conversion Results For Experimental Co-Processing Runs Using Hydrogen Gas (cont'd)

Run	G34	G39
Coal	B	B
Heavy Oil	A8	A8
Nitrogen Compound	N2	N1
Solvent	--	--
Yields (wt% MAF Coal)		
CO, CO2	1.53	2.06
C1 - C3	15.40	5.96
H2S	--	.65
Water	.62	9.49
C4 - 455°C	77.85	47.71
455°C+	(12.33)	28.73
IOM + MM	19.25	6.84
Total	102.32	101.44
H2 Consumption	2.32	1.44
Yields (wt% MAF Coal & 455°C+ Heavy Oil)		
CO, CO2	.65	.88
C1 - C3	6.55	2.55
H2S	0	.28
Water	.26	4.05
C4 - 455°C	33.11	20.36
455°C+	52.23	69.58
IOM + MM	8.19	2.92
Total	100.99	100.62
H2 Consumption	0.99	0.62
THF Conversion (MAF Coal Basis)	80.9	93.2

Table A-1: Yield and Conversion Results For Experimental Co-Processing Runs Using Hydrogen Gas (cont'd)

Run	G32	G33	G42
Coal	S	S	S
Heavy Oil	A8	A8	A8
Nitrogen Compound	N2	N2	--
Solvent	--	--	--
Yields (wt% MAF Coal)			
CO, CO2	1.70	4.39	6.17
C1 - C3	.96	.04	.05
H2S	0	0	0
Water	(1.63)	(1.27)	2.35
C4 - 455°C	5.77	(4.42)	20.17
455°C+	31.22	22.74	(31.21)
IOM + MM	62.10	78.83	102.44
Total	100.12	100.31	99.97
H2 Consumption	0.12	0.31	(0.03)
Yields (wt% MAF Coal & 455°C+ Heavy Oil)			
CO, CO2	.70	1.79	2.12
C1 - C3	.39	.02	.02
H2S	0	0	0
Water	(0.67)	(0.52)	.81
C4 - 455°C	2.37	(1.81)	6.92
455°C+	71.78	68.42	55.00
IOM + MM	25.48	32.22	35.13
Total	100.05	100.12	100.00
H2 Consumption	0.05	0.12	0.0
THF Conversion (MAF Coal Basis)	40.2	23.4	1.6

Table A-2: Yield and Conversion Results For Experimental Co-Processing Runs Using Carbon Monoxide Gas

Run	G10	G11	G12	G13
Coal	B	B	B	B
Heavy Oil	A8	A8	A8	A8
Nitrogen Compound	--	--	N4	N5
Solvent	--	--	--	--
Yields (wt% MAF Coal)				
CO2	27.19	4.28	36.85	28.15
H2	.69	.06	.52	.48
C1 - C3	.04	.08	.05	.14
H2S	.62	.33	0	.59
Water	(16.18)	14.64	10.13	3.92
C4 - 455°C	7.35	11.15	(26.77)	(33.93)
455°C+	14.00	(19.10)	33.88	35.95
IOM + MM	83.59	90.31	68.79	82.61
Total	117.30	101.75	123.45	117.91
CO Consumption	17.30	1.75	23.45	17.91
Yields (wt% MAF Coal & 455°C+ Heavy Oil)				
CO2	9.71	1.52	15.67	11.86
H2	.25	.02	.22	.20
C1 - C3	.01	.03	.02	.06
H2S	.22	.12	0	.25
Water	(5.78)	5.19	4.31	1.65
C4 - 455°C	2.62	3.95	(11.38)	(14.29)
455°C+	69.29	57.82	71.88	73.02
IOM + MM	29.85	31.99	29.25	34.80
Total	106.17	100.64	109.97	107.55
CO Consumption	6.17	0.64	9.97	7.55
THF Conversion (MAF Coal Basis)	16.4	9.7	31.2	17.4

Table A-2: Yield and Conversion Results For Experimental Co-Processing Runs Using Carbon Monoxide Gas (cont'd)

Run	G14	G15	G19	G20
Coal	B	B	B	B
Heavy Oil	A8	A8	A8	A8
Nitrogen Compound	N1	N6	N2	N3
Solvent	--	--	--	--
Yields (wt% MAF Coal)				
CO2	16.51	43.12	25.70	17.40
H2	.30	.13	.23	.14
C1 - C3	.06	.29	.67	.24
H2S	.68	2.07	0	.74
Water	(7.96)	(18.22)	(10.75)	(7.21)
C4 - 455°C	(11.92)	(7.44)	(4.66)	.03
455°C+	67.74	55.21	73.52	42.82
IOM + MM	44.61	52.28	31.64	56.90
Total	110.02	127.44	116.35	111.06
CO Consumption	10.02	27.44	16.35	11.06
Yields (wt% MAF Coal & 455°C+ Heavy Oil)				
CO2	6.80	18.37	10.84	7.37
H2	.12	.06	.10	.06
C1 - C3	.03	.12	.28	.10
H2S	.28	.88	0	.31
Water	(3.28)	(7.76)	(4.54)	(3.05)
C4 - 455°C	(4.91)	(3.17)	(1.97)	.01
455°C+	86.71	80.92	88.83	75.78
IOM + MM	18.38	22.27	13.35	24.10
Total	104.13	111.69	106.89	104.68
CO Consumption	4.13	11.69	6.89	4.68
THF Conversion (MAF Coal Basis)	55.4	47.7	69.5	44.3

Table A-2: Yield and Conversion Results For Experimental Co-Processing Runs Using Carbon Monoxide Gas (cont'd)

Run	G26	G35
Coal	B	B
Heavy Oil	A8	A8
Nitrogen Compound	N7	N1
Solvent	--	--
Yields (wt% MAF Coal)		
CO2	13.71	24.13
H2	.10	.51
C1 - C3	.05	.83
H2S	.52	0
Water	10.36	(5.09)
C4 - 455°C	(35.84)	(2.49)
455°C+	49.55	56.75
IOM + MM	70.28	40.71
Total	108.73	115.35
CO Consumption	8.73	15.35
Yields (wt% MAF Coal & 455°C+ Heavy Oil)		
CO2	5.79	10.31
H2	.04	.22
C1 - C3	.02	.36
H2S	.22	0
Water	4.37	(2.17)
C4 - 455°C	(15.12)	(1.07)
455°C+	78.72	81.52
IOM + MM	29.65	17.40
Total	103.69	106.57
CO Consumption	3.69	6.57
THF Conversion (MAF Coal Basis)	30.9	59.4

Table A-2: Yield and Conversion Results For Experimental Co-Processing Runs Using Carbon Monoxide Gas (cont'd)

Run	G38	G40
Coal	B	B
Heavy Oil	A8	A8
Nitrogen Compound	N1	N2
Solvent	--	--
Yields (wt% MAF Coal)		
CO2	12.36	16.36
H2	.23	.34
C1 - C3	.03	.45
H2S	.25	.16
Water	.88	(14.98)
C4 - 455°C	(1.38)	(1.89)
455°C+	41.61	65.46
IOM + MM	53.66	44.51
Total	107.64	110.41
CO Consumption	7.64	10.41
Yields (wt% MAF Coal & 455°C+ Heavy Oil)		
CO2	4.73	6.28
H2	.09	.13
C1 - C3	.01	.17
H2S	.10	06
Water	.34	(5.75)
C4 - 455°C	(0.53)	(0.72)
455°C+	77.66	86.74
IOM + MM	20.53	17.09
Total	102.93	104.00
CO Consumption	2.93	4.00
THF Conversion (MAF Coal Basis)	46.3	55.2

Table A-2: Yield and Conversion Results For Experimental Co-Processing Runs Using Carbon Monoxide Gas (cont'd)

Run	G36	G37	G41
Coal	S	S	S
Heavy Oil	A8	A8	A8
Nitrogen Compound	N1	N2	--
Solvent	--	--	--
Yields (wt% MAF Coal)			
CO2	16.46	21.39	17.04
H2	.14	.23	.07
C1 - C3	.04	.70	.04
H2S	0	0	0
Water	(9.99)	(0.60)	(24.85)
C4 - 455°C	(13.75)	16.85	81.26
455°C+	44.22	26.57	(18.17)
IOM + MM	73.37	48.47	50.26
Total	110.49	113.61	105.65
CO Consumption	10.49	13.61	5.65
Yields (wt% MAF Coal & 455°C+ Heavy Oil)			
CO2	6.93	8.86	5.87
H2	.06	.09	.02
C1 - C3	.02	.29	.01
H2S	0	0	0
Water	(4.21)	(0.25)	(8.56)
C4 - 455°C	(5.79)	6.98	28.00
455°C+	76.52	69.58	59.28
IOM + MM	30.89	20.08	17.32
Total	104.42	105.63	101.94
CO Consumption	4.42	5.63	1.94
THF Conversion (MAF Coal Basis)	28.9	53.8	21.5

Table A-2: Yield and Conversion Results For Experimental Co-Processing Runs Using Carbon Monoxide Gas (cont'd)

Run	G16	G17	G18
Coal	B	--	S
Heavy Oil	--	A8	--
Nitrogen Compound	--	--	--
Solvent	---1-METHYLNAPHTHALENE---		
Yields (wt% MAF Coal & 455°C+ Heavy Oil)			
CO2	15.18	.67	14.18
H2	.11	.03	.06
C1 - C3	.14	0	.06
H2S	.07	0	0
Water	2.44	(18.89)	(3.01)
C4 - 455°C	(10.82)	12.41	(5.77)
455°C+	46.89	102.65	5.36
IOM + MM	55.66	0	94.86
Total	109.66	96.87	105.74
CO Consumption	9.66	(3.13)	5.74
THF Conversion (MAF Coal Basis)	44.3	----	8.8

Table A-3: Summary of Average Elemental Analyses of THF Insoluble Residues (weight %)

Experimental Run	%N	%C	%H	C/H Ratio
Unprocessed Kentucky 9 Coal	1.70	68.05	4.68	14.54
THF Insoluble Kentucky 9 Coal	1.73	64.02	4.37	14.65
Unprocessed Wyoming Coal	1.21	59.19	3.99	14.83
G-10	1.41	53.48	3.80	14.07
G-11	1.63	64.77	4.39	14.75
G-12	2.42	59.63	4.83	12.35
G-13	2.84	64.10	4.96	12.92
G-14	1.50	50.41	3.66	13.77
G-15	1.76	66.58	4.35	15.31
G-19	1.41	35.29	2.88	12.25
G-20	1.89	63.04	4.14	15.23
G-26	1.77	61.02	4.30	14.19
G-28	1.51	42.61	3.07	13.88
G-29	1.22	48.89	3.32	14.73
G-30	1.73	68.38	5.21	13.12
G-31	1.28	43.47	2.92	14.89
G-32	2.83	58.62	4.47	13.11
G-33	1.56	52.38	3.49	15.01
G-34	1.97	52.93	2.93	18.06
G-35	1.03	33.34	2.34	14.25
G-36	1.76	56.42	3.94	14.32
G-37	1.84	47.53	3.39	14.02
G-38	1.50	58.88	4.30	13.69
G-39	0.77	26.31	1.48	17.78
G-40	1.60	59.38	4.54	13.08
G-41	1.24	65.30	4.20	15.55
G-42	1.14	64.12	4.03	15.91
G-39 (unextracted centrifuge residue)	2.28	72.53	6.71	10.82

Table A-4: Summary of Average Elemental Analyses of 455°C+ Residuum (weight %)

Experimental Run	%N	%C	%H	C/H Ratio
G-10	0.75	81.46	10.90	7.47
G-13	0.70	90.64	11.93	7.60
G-14	0.70	88.60	11.58	7.65
G-19	0.74	87.10	11.41	7.63
G-28	0.77	88.20	11.20	7.88
G-29	0.64	86.20	11.47	7.52
G-31	0.67	88.72	12.04	7.37
G-32	0.92	85.00	11.35	7.49
G-35	0.59	87.03	11.69	7.44
G-36	0.71	84.93	9.56	8.88
G-39	1.05	88.11	10.78	8.18
G-40	0.60	90.41	12.18	7.42
G-41	0.53	88.70	11.76	7.54
G-42	0.44	83.67	11.15	7.50
A8 Unprocessed Heavy Oil	0.43	89.35	12.40	7.21

Table A-5: Summary of Average Elemental Analyses of Selected Liquid Distillates (weight %)

Experimental Run & Distillate Fraction	%N	%C	%H	C/H Ratio
G-31 (177°C-)	0.84	10.25	1.23	8.35
(177-260°C)	3.86	39.13	4.20	9.32
(260-344°C)	4.97	49.78	5.46	9.12
(344-455°C)	1.65	48.43	6.49	7.47
G-35 (177-260°C)	4.12	27.16	2.70	10.06
(260-344°C)	5.41	70.68	9.40	7.52
(344-455°C)	1.03	46.95	5.88	7.98
G-36 (177-260°C)	6.14	60.69	6.34	9.58
(260-344°C)	3.24	33.04	3.38	9.78
(344-455°C)	5.36	84.07	10.06	8.35
G-39 (177°C-)	0.43	19.45	1.83	10.63
(177-260°C)	3.22	43.52	5.15	8.45
(260-344°C)	3.32	69.27	8.87	7.81
(344-455°C)	0.80	29.64	3.88	7.64

Table A-6: % of Total Nitrogen in THF Insoluble Matter

Run	Total Nitrogen Charged (g)	N in THF Insolubles (g)	% of Total N in THF Insolubles
G-10	0.51	0.24	47.1
G-11	0.51	0.29	57.8
G-12	2.15	0.35	16.2
G-13	2.18	0.48	22.0
G-14	1.50	0.14	9.6
G-15	1.14	0.20	17.6
G-19	1.81	0.11	5.9
G-20	1.25	0.23	18.4
G-26	1.31	0.26	19.6
G-28	1.90	0.10	5.2
G-29	1.55	0.09	5.9
G-30	1.23	0.27	22.2
G-31	1.53	0.09	5.9
G-32	1.75	0.37	21.4
G-33	1.42	0.25	17.6
G-34	1.88	0.11	5.8
G-35	1.52	0.10	6.4
G-36	1.46	0.28	19.1
G-37	1.76	0.21	11.7
G-38	0.95	0.18	18.7
G-39	1.43	0.02	1.4
G-40	1.07	0.16	15.2
G-41	0.41	0.20	50.0
G-42	0.41	0.22	54.8

**calculations based on the following:
a) subbituminous coal %N: 1.21
b) bituminous coal %N: 1.70
c) A8 petroleum oil %N: 0.43

Table A-7: % of Total Nitrogen in 455°C+ THF Soluble Residuum

Run	Total Nitrogen Charged (g)	N in 455°C+ Residuum (g)	% of Total N in 455°C+ Residuum
G-10	0.51	0.20	39.0
G-13	2.18	0.14	6.4
G-14	1.50	0.13	8.9
G-19	1.81	0.15	8.5
G-28	1.90	0.17	9.2
G-29	1.55	0.14	8.9
G-32	1.75	0.17	9.9
G-35	1.52	0.12	7.9
G-39	1.43	0.23	16.1
G-40	1.07	0.15	14.3
G-41	0.41	0.13	31.7
G-42	0.41	0.11	26.2

**calculations based on the following:
a) subbituminous coal %N: 1.21
b) bituminous coal %N: 1.70
c) A8 petroleum oil %N: 0.43

APPENDIX B

Material Balances and Coal Conversion Sample Calculations

Material Balances and Coal Conversion

Sample Calculation For Run G-19

a) Reactor Mass Balance

total reactants charged to reactor	84.36	g		
toluene added to reactor	63.92	g		
Total Mass In	148.28	g		
gas recovered			14.10	g
calculated CO2 solubility loss			2.27	g
distillate & residue recovered			125.37	g
Total Mass Out			141.74	g
mass loss (148.28 - 141.74)	6.54	g		
distillate & residue recovered	125.37	g		
Adjusted Reactor Effluent	131.91	g		

b) Centrifuge Mass Balance

adjusted mass charged to centrifuge	131.91	g		
toluene added	16.68	g		
Total Mass In	148.59	g		
recovered residue			41.78	g
recovered distillate			96.10	g
toluene evaporation			0.80	g
Total Mass Out			138.68	g
mass loss (148.59 - 138.68)	9.91	g		
adjusted recovered residue	44.78	g*		
adjusted recovered distillate	103.01	g**		
Adjusted Mass Out	147.79			
plus toluene evaporation	0.80			
Adjusted total	148.59	g		

where: *: $41.78+[(9.91 \times 41.78)/(41.78+96.10)] = 44.78$

**: $96.10+[(9.91 \times 96.10)/(41.78+96.10)] = 103.01$

c) Distillation Fractions

multiply adjusted recovered distillateby the corresponding fraction recovered in the distillation procedure:

water	.0258x103.01	=	2.66 g
(toluene & IBP-177°C)	.7005x103.01	=	72.16 g
177-260°C	.0078x103.01	=	0.80 g
260-344°C	.0109x103.01	=	1.12 g
344-455°C	.0540x103.01	=	5.56 g
455°C+	.2010x103.01	=	20.71 g
Total			103.01 g

Total (IBP-455°C) 79.64 g

d) Soxhlet Extraction of 455°C+

455°C+		20.71 g
CHX soluble:	(1-.043)x20.71 *	19.82 g
THF soluble:	(1-.0004)x(20.71-19.82) **	0.88
THF insoluble (by difference)		0.01 g

where: * CHX insoluble is 4.3%
** THF insoluble is .04%

e) Total CHX Soluble Distillate

IBP-455°C	79.64 g
CHX soluble 455°C+	19.82 g
Total CHX soluble distillate	99.46 g

f) Residue Extractions

Data	
recovered residue	41.78 g
adjusted recovered residue	44.78 g
water in recovered residue	5.17 g
% CHX soluble	54%
% THF soluble	83%
total IBP-455°C	79.64 g

total CHX soluble distillate	99.46 g
455°C+ CHX soluble from distillation	19.82 g

Calculations

water in adjusted residue:
(44.78/41.78)x5.17 = 5.54 g

total CHX soluble (plus water):
44.78x0.54 = 24.18 g

CHX soluble residue:
24.18-5.54 = 18.64 g

CHX soluble(attributed to 455°C-):
18.64x(79.64/99.46) = 14.93 g

CHX soluble (attributed to 455°C+):
18.64x(19.82/99.46) = 3.71 g

THF soluble(CHX insoluble):
.83x(44.78)-(24.18) = 12.99 g

IOM + MM:
44.78-12.99-24.18 = 7.61 g

g) Coal Conversion

Data

MAF coal	17.74 g
coal charged	20.00 g
IOM from distillation extraction	0.01 g
IOM from residue extraction	7.61 g

Calculation

THF coal conversion:
(20.00-.01-7.61)/17.74x100 = 69.8%

APPENDIX C

Calculated Nitrogen Adduction
Sample Calculation

Calculated Nitrogen Adduction

Sample Calculation for Run G-19

Data

grams coal charged	20.0
grams A8 oil charged	30.2
grams dipropylamine charged	9.7
grams 455°C+ THF insolubles	7.67
grams 455°C+ THF solubles	37.35
grams distillate	22.96
wt.% nitrogen in coal	1.70
wt.% nitrogen in A8 oil	0.43
wt.% nitrogen in 455°C+ THF insolubles	1.41
wt.% nitrogen in 455°C+ THF solubles	0.74
wt.% nitrogen in distillate (due to coal & A8 alone)	0.069
molecular weight of dipropylamine	101.19

Calculations

nitrogen in reactants (coal + A8 + dipropylamine)	1.81 g
nitrogen in products (455°C+ THF solubles & insolubles)	0.39 g
nitrogen in distillate (1.81 - 0.39)	1.42 g
nitrogen in distilate due to coal and A8 alone (22.96 x .00069)	0.016 g
nitrogen contribution from dipropylamine (1.42 - 0.016)	1.41 g
basic nitrogen compound in distillate (1.41 x 101.19 / 14)	10.21 g
% adduction of basic nitrogen compound [(9.7 - 10.2)/ 9.7] x 100	(5.23)%