



Catalysts for hydrotreating COED Pyrolysis Oil
by Stephan Timothy Kujawa

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University
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Abstract:

Commercial and developmental catalysts were screened in their ability to remove sulfur and nitrogen from COED Pyrolysis Oil. The catalysts were tested in both batch autoclaves and in trickle bed reactors operating at 415° C. and 800 psig.

Tests on commercial catalysts showed that nickel-molybdates were best for nitrogen removal. Of the nickel-molybdates tested, Shell 324, Cyanamid HDS 9A, and Harshaw HT 500 performed best. Sulfur removal was best effected by the cobalt-molybdate catalysts, Harshaw HT 400, Shell 344, and Cyanamid HDS-20A. Nickel tungsten catalysts did not perform well at the conditions of the test.

From the tests on commercial catalysts, it was concluded that nitrogen removal was limited by pore diffusion, that molybdenum was more active for nitrogen removal than tungsten, and that sulfur removal was quite possibly being controlled by film diffusion.

Developmental catalysts were prepared at Montana State University to test the effect of supports and of promoters on the heteroatom removal reaction. The larger pore size supports worked best. Of the ten catalysts developed to test promoter effects, the cobalt-nickel-molybdenum combination showed advantages over commercial catalysts in batch tests.

In extending the results from the batch reactor to continuous reactors, eight combinations of the cobalt-nickel-molybdate catalyses were fabricated and tested. The experimental conclusions, from a 24 factorial analysis were: 1. for nitrogen removal a) the more molybdenum and less cobalt on the support, the better, b) nickel was not found to have a significant effect 2. for sulfur removal a) the low cobalt, high molybdenum combination again was best, b) nickel again had no effect.

This seems to suggest that cobalt-molybdate catalysts are sufficient to hydrotreat the feed; however, none of the developmental catalysts worked as well in the continuous tests as the commercial nickel-molybdate catalysts.

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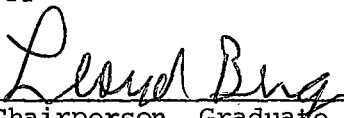
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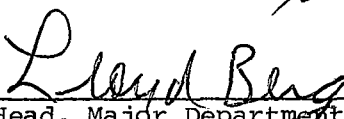
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ABSTRACT

Commercial and developmental catalysts were screened in their ability to remove sulfur and nitrogen from COED Pyrolysis Oil. The catalysts were tested in both batch autoclaves and in trickle bed reactors operating at 415 C. and 800 psig.

Tests on commercial catalysts showed that nickel-molybdates were best for nitrogen removal. Of the nickel-molybdates tested, Shell 324, Cyanamid HDS 9A, and Harshaw HT 500 performed best. Sulfur removal was best effected by the cobalt-molybdate catalysts, Harshaw HT 400, Shell 344, and Cyanamid HDS-20A. Nickel tungsten catalysts did not perform well at the conditions of the test.

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In extending the results from the batch reactor to continuous reactors, eight combinations of the cobalt-nickel-molybdate catalysts were fabricated and tested. The experimental conclusions, from a 2^4 factorial analysis were:

1. for nitrogen removal
 - a) the more molybdenum and less cobalt on the support, the better,
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1. INTRODUCTION

1.1. The Purpose of Coal Research

G. Alex Mills, director of Fossil Energy Materials and Exploratory Research, of what was then called the Energy Research and Development Administration, and now is called the Department of Energy, stated in a recent paper that "In the absence of a national energy policy, present synfuels processes will not be economically competitive before the year 2000" [1]. He further stated in the article that the great need now in the coal to fuels and chemicals route is catalysts that will be able to snip apart the coal molecules at the proper places. Another government report states that for earlier commercialization, a new process will have to be developed that is considerably cheaper than those "first generation" processes now being developed [2]. Therefore, one of the major research needs in coal conversion research is catalyst studies.

The research which is the subject of this thesis is an attempt to study and improve a significant step in the overall fossil fuel conversion process. That step consists of the process whereby the heavy, tar-like substances produced in the primary coal liquefaction operation are hydrotreated (reacted in the presence of hydrogen at medium to high pressure and temperature) to remove objectional heteroatomic molecules (N,S,O) and improve the overall product. The reason for removing these compounds is two-fold. The first is to reduce

pollution from any eventual fuels made from the coal liquid. The second is to protect the catalysts in further refining steps.

1.2. Coal Liquefaction Processes

There are four basic processes to make liquids from coal that have received the majority of development in the last decade. The Synthoil process involves running coal, recycle oil, and hydrogen up-flow in an ebullating catalyst bed. Coal ash deactivation of the catalyst seemed to spell an early death for the project. Recently, however, the catalyst has been replaced by inert beads because it was found that either the ash actually catalyzed the conversion reaction or that the conversion reaction occurs mainly through a thermal process.

The Exxon Donor Solvent process and the Gulf Solvent Refined Coal process are similar in many respects. Both processes use a recycle oil to slurry coal which is then pumped into reactors in the presence of hydrogen. In the Exxon process, however, the recycle oil is hydrotreated prior to slurrying. This partially saturates the oil to tetralin type molecules. During the course of the liquefaction reaction, the multi-ring compounds donate this hydrogen to the coal and become more aromatic.

The feedstock used in this research was produced from Pittsburgh Seam bituminous coal in the FMC operated COED process (Char Oil

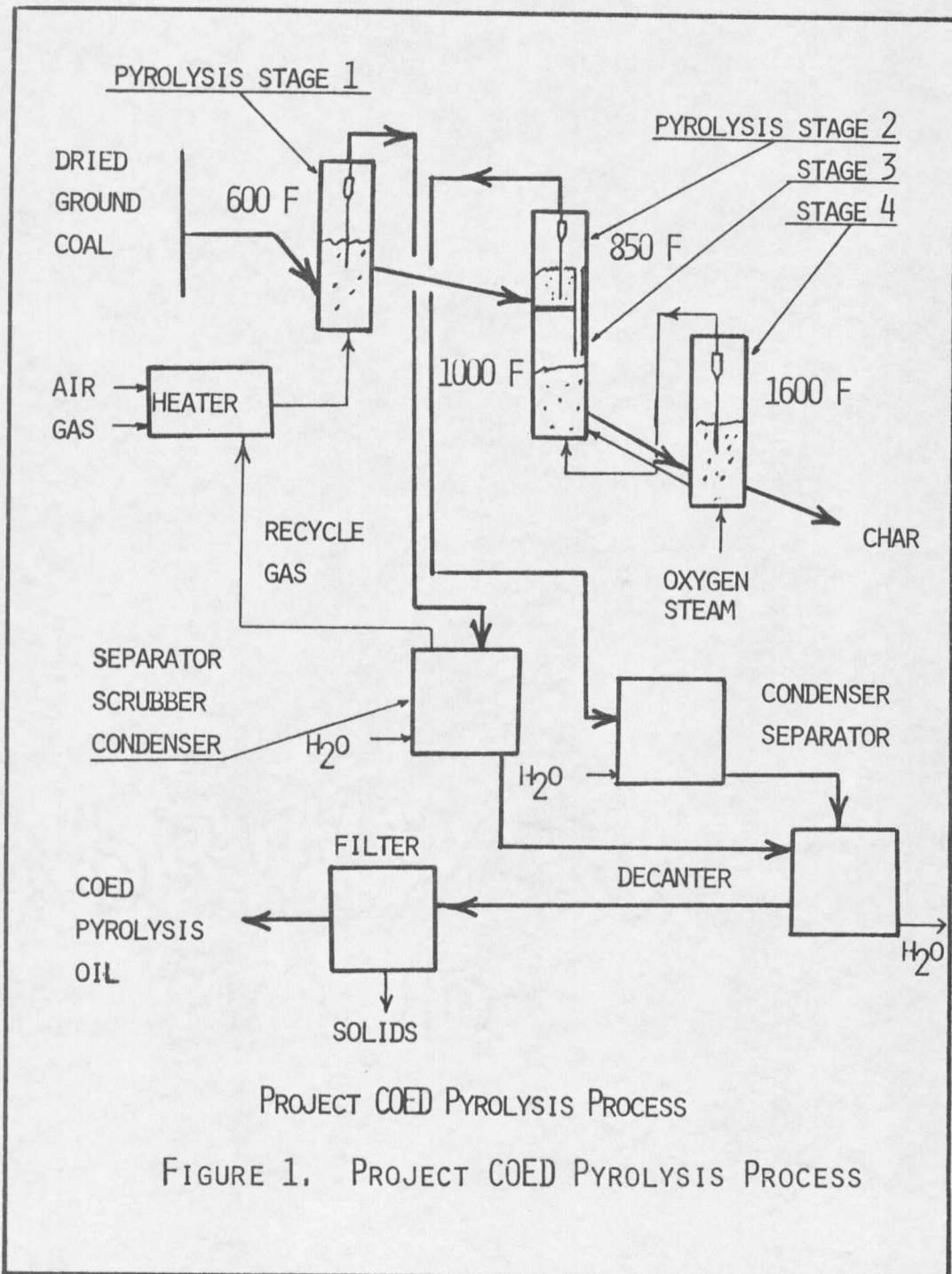
Energy Development process). This is a pyrolysis process where coal is fed into a series of fluidized bed reactors; each operated at a higher temperature. The volatiles are driven off by hot gases which are produced in the final reactor by partial combustion of the char. The process diagram is shown in Figure 1. Table I presents the physical and chemical properties of the feed [3].

Table I
Properties of Pittsburgh Filtered Oil

Moisture	0.4 wt%
Quinoline Insolubles	7.0 wt%
API Gravity, 60°F	-7.4
Pour Point, °F	80
Flash Point, °F	240
Viscosity Cp @ 350°F	4.7
ULTIMATE ANALYSIS	
	wt % dry
C	82.9
H	7.3
O	5.9
N	0.9
S	2.3
Ash	0.7
HHV dry	15,900 BTU/lb

1.3. Hydrotreating Studies of COED Pyrolysis Oil

Two bench scale studies have shown the effects of processing conditions in hydrotreating COED Pyrolysis Oil. The first study [4] used a nickel-moly catalyst (American Cyanamid HDS-3A) to hydrotreat the oil at 3000 psig and hydrogen flow rates of 8000 and 12000 scf/bbl. Temperature and space velocity were varied in the study.



The study showed that the activation energies for the removal of oxygen and nitrogen from the feed were not constant and dropped sharply at temperatures of 730°F and 752°F, respectively. This was felt to be an indication of mechanism changes in the reactions and not due to diffusion control.

The product from the reactor was fractionated into naphtha, gas oil, and residual cuts. These were then evaluated for their ability to be processed in a commercial refinery. It was concluded that all of the cuts would have to be further hydrotreated to meet nitrogen specifications. The naphtha would then be a suitable reformer feedstock. The gas oil and residual fractions contain a large amount of refractory polynuclear aromatic molecules that coke cracking catalysts. These molecules would have to be selectively saturated and cracked before further processing. It would then be possible to make high octane gasoline blending stocks from these, but the severity of processes to saturate the feed precludes making diesel or jet fuel from them.

The second bench scale study used essentially the same set up as the first: 100 cc catalyst, 3000 psig, 8000-12000 scf/bbl, 650-800 F, and space velocities of 0.3 to 3 [5]. The temperature in the catalyst bed increased in the first few inches, then dropped again, so to correlate the data, the arithmetic average temperature of one inch increments of bed depth was used.

Two of the results of the study are very important. The first was that the severity of operation of the hydrotreater must be very high compared to conventional petroleum refining. Table II illustrates this.

Table II
Space Velocity for 80% Removal of Heteroatoms @ 720 F,
3000 psig, Pittsburgh Seam

Heteroatom	LHSV
Nitrogen	0.4
Oxygen	0.6
Sulfur	1.1

The second result had to do with the conversion of the feed to gas. The gas forming reaction directly correlates with the amount of coke deposited on the catalyst and thus the catalyst life. Making gas is also an inefficient use of the hydrogen present. The gas make was studied as a function of temperature. It was found that gas conversion was independent of space velocity. The gas yield increased at an enormous rate at bed temperatures above 780°F. It was concluded that it is necessary to keep the bed temperature below 780°F to produce oil and protect the catalyst.

The results from the hydrotreating process development unit at the COED pilot plant were presented to ERDA in 1975 [6]. The pilot hydrotreater processed 30 bbl/day of pyrolysis oil at 1400-1900 psig,

725-765°F, 0.22 to 0.31 LHSV (Liquid Hourly Space Velocity), and a recycle gas rate of 47,000 to 73,000 scf/bbl containing 93 to 96% hydrogen.

The ash in the feed became a problem because it plugged the catalyst pores causing rapid deactivation. This problem was solved by using a guard chamber upstream of the hydrotreaters. A high void volume combination of cobalt moly catalyst and Koch flexirings were used to trap the fines and to initiate demetalization reactions. The hydrotreating runs were terminated when the guard chamber plugged. The guard chamber decreased catalyst usage to 0.2 lb/bbl of oil processed.

Some of the major results of the P.D.U. (Process Development Unit) runs were that, as a function of pressure in the 1300 to 1900 psig range, sulfur removal was close to constant at about 93%; nitrogen removal increased from 45 to 75%; and hydrogen consumption increased from 1800 to 3800 scf/bbl. The projected cost of a barrel of syncrude from the process has recently been estimated to be between \$20 and \$30 [2, p. 143].

The necessary process improvements for syncrude production have been stated to be:

1. Develop selective catalysts to crack polynuclear aromatic molecules with minimum hydrogen production.

2. Reduce the necessary severity of hydrotreating by catalyst optimization thereby reducing equipment requirements which will in turn reduce capital costs.
3. Produce a syncrude refinable by conventional petroleum methods.
4. Be able to operate the entire coal to syncrude process at no less than a 70% overall thermal efficiency.

The above requirements must be met before an early commercialization of coal to fuels can be foreseen [2, p. 14].

1.4. Statement of the Research Problem

From the above discussion, and from the requirements of ERDA contract number E(49-18)-2034, the following topics were addressed in the research presented in this thesis:

1. Commercial hydrotreating catalysts were screened in both batch and continuous trickle bed reactors. The purpose was two-fold:
 - A. determine the best commercial catalyst available.
 - B. determine why the catalysts effected the process as they did.
2. Develop catalysts that are an improvement on the commercial catalysts. Determine what facets of the catalyst make-up cause improvement.

The overall purpose of the project was not to come up with a one-step scheme to produce gasoline or other fuels or feedstocks. The purpose was to see the effect of the catalyst on the process used to upgrade the coal liquids to a point where downstream processes could produce the fuel or feedstock.

The following sections of the Introduction discuss some aspects of the catalyst, the reactions, and the reactor, that must be accounted for when doing a catalyst screening study and interpreting the data produced therein.

2. CATALYSTS

2.1. Introduction

This section will describe what some of the more conventional catalysts are; what they are made of; and what results when certain components are added to them. The section will also go into some of the methods of making catalysts, and some of the processes that use hydrotreating catalysts.

Traditionally, it was supposed that a hydrotreating catalyst consisted of an active component, usually a metal, that was deposited on a high surface area support. The support was considered inert and its only purpose was to disperse the catalyst. However, it has been shown that the support itself is catalytically active, and, in some processes, catalytic cracking, for example, the support is the only catalyst.

The catalysts for hydrotreating and hydrocracking have been found to be bi-functional. Some of the surface sites are active for hydrogenation; and other sites are active for cracking. The metal (actually an oxide or sulfide) promotes the hydrogenation reactions while the cracking activity is due to properties of the support (e.g., Bronsted and Lewis acid sites). The reactions that occur when a feedstock is desulfurized and denitrogenated include hydrogenation and cracking steps. These reactions will be explained in the next section.

Hydrotreating catalysts must be sulfur and nitrogen resistant. Traditional metal hydrogenation catalysts (Pt, Pd, Ni) are ruled out because of this [7]. The catalysts that are used for conventional whole crude and residual Oil hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) are usually made up of the oxides of group VIA and VIII metals on silica, alumina, or a combination of these supports. Some of the metal combinations are: Co-Mo, Zn-Mo, Ni-Mo, Cr-Mo, Fe-Co-Mo, Ni-Co-Mo, and Ni-W [8].

In most conventional petroleum refining, cobalt-molybdate catalysts are used for desulfurization; nickel-molybdate catalysts are used for denitrogenation; and nickel tungsten catalysts are used for severe denitrogenations and hydrogenations. The nickel tungsten catalyst is much more expensive, however, and usually its use cannot be economically justified [9].

2.2. Effects of Surface Area and Pore Size

As stated, the physical carrier has two functions:

1. Disperse the hydrogenation component over a large surface area.
2. Provide acid sites for cracking reactions.

The important surface area is not that measured by physical adsorption methods, but is the surface area active for the reaction in question. For the hydrogenation component, it is the area of the

metal crystallite that forms on the surface. The smaller the crystallite, the more surface metal atoms exposed, and the more active the catalyst. For the cracking reaction, the support provides a large number of acid sites of varying types and strengths.

The supports, primarily amorphous solids, are very porous. If the catalyst is intrinsically very active, there is a possibility that the rate of the reaction will be limited by the rate of the molecules diffusing through the pores to the active sites. This is especially true in the case of resid and syncrude desulfurization where very large molecules are reacting. Since, in a catalyst particle, the surface area and pore volume (hence, pore size distribution) are inversely related, there will be a trade off between surface area and pore size. An optimum of the two factors must therefore be found [9, p. 84].

In one study of resid desulfurization, it was found that the activity could be related by [10],

$$\%DS = K + 0.0589A + R(6.6A \times 10^{-4} + .012)$$

K = constant

A = S.A. of catalyst

R = Avg. pore radius

%DS = percent desulfurization

The above shows that both an increase in surface area and pore size would increase activity.

Generally speaking, pure silica supports will be characterized by very high surface area (300-450 m²/gm), and the pore size will be small. Silica aluminas and aluminas will have surface areas of 100 to 250 m²/gm and have correspondingly larger pore sizes. Molecular sieves, which are crystalline supports of silica-alumina, have uniform pore sizes of up to 9 Å and very high surface areas.

There is generally an attempt to characterize catalysts by what is called an average pore size [11]. The calculation assumes that the pore size distribution is mono-disperse; the pores are straight, cylindrical, not interconnected, and have the same radius, \bar{a} , and length, \bar{l} . The average pore size is obtained by writing equations for the surface and volume of the particle, giving finally,

$$\bar{a} = 2 Vg/Sg$$

Vg = cc/gm of catalyst

Sg = surface area per gram

\bar{a} = average pore radius

The major assumption of the above equation is that the pore system has a normal or skewed normal distribution. Aluminas and silica aluminas, however, have pore systems that generally consist of small particles containing micropores ($a < 100 \text{ \AA}$) interconnected by macropores ($a > 100 \text{ \AA}$). Since the pore size distribution will usually have two most common pore sizes, a single value of average size will not describe the catalyst adequately.

2.3. Effects of Metals and Promoters

The most common metals responsible for the hydrogenation-dehydrogenation function of a hydrotreating catalyst are molybdenum and tungsten. Molybdenum has been found to be active for denitrogenation on a support even without additional promoters present [12]. "Metal" is used here, keeping in mind that under reaction conditions the active species is a sulfide or oxy-sulfide.

The metals Ni, Co, Fe, Zn, and Cr are usually described as promoters. The function of the promoter is believed to increase the number of exposed molybdenum or tungsten ions--the active centers for the heteroatom removal reaction [13].

If the sulfided catalyst, prior to use, is visualized as having a surface monolayer of molybdenum sulfide species, it is believed that, for a cobalt-moly catalyst, the cobalt displaces aluminum into the active monolayer. This stabilizes the monolayer by binding it more strongly with the alumina surface. As the catalyst is used, cobalt ions diffuse back and forth into and out of the monolayer. This causes the molybdenum crystallites to become smaller, thereby exposing more molybdenum ions to the molecules and maintaining activity. Nickel supposedly has a similar effect differentiated slightly by coordination [13, p. 298].

Studies have established the optimum ratio of promoter to hydrogenation component. For cobalt-molybdate catalysts, the ratio is about 1:3. This has been found to be independent of support and material [9].

2.4. Effect of the Support

As stated above, the purpose of the support is not only to disperse the metal component, but also to provide acid sites to initiate the carbonium ion mechanisms of the cracking reactions. The acid sites are of both the Bronsted and Lewis type and are a function of the support preparation temperature [14].

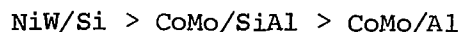
The acid sites are weak or strong and can be manipulated depending on the purpose of the process. Generally, pure silica is less acid than alumina, which is less acid than silica-alumina. The metals on the support also influence acidity. It was found that NiO on alumina reduces the acidity, while MoO₃ increased it [9, p. 276]. This was given as the reason unsulfided HDS catalysts of the cobalt-moly type exhibit uncontrolled cracking when put on stream with feed that is too hot.

The acid sites on a catalyst are subject to nitrogen poisoning. One study found that, when treating a feedstock low in nitrogen, the desulfurizing activity of three catalysts was in the order:



This trend exactly follows acid strength.

When the above catalysts were run on a high nitrogen feed, the order of activity became,



Essentially, the nitrogen had neutralized the strong acid sites of the CoMo catalysts; and the stronger hydrogenation activity of the Ni-W catalyst, which tends to keep the acid sites clean, overcame the support effects.

Hydrocracking occurs along with hydrotreating at the severe conditions usually present in resid and syncrude processes. By varying the relative strengths of the hydrogenation component and the cracking function, the product distribution can be changed [14]. For example, to hydrocrack to middle distillates, moderate acidity with high hydrogenation ability is needed along with high porosity to allow the large molecules to adsorb and desorb. The moderate acidity would allow the larger molecules to desorb sooner; the high hydrogenation ability would reduce aromatics and increase the saturated molecules desired for diesel and jet fuel.

To process to gasoline, strong acid sites are needed to keep the molecule on the support, increasing cracking and isomerization. Low hydrogenation ability is wanted, however, to keep from saturating the high octane alkyl-aromatic molecules.

For polycyclic aromatic cracking, high hydrogenation ability is not wanted, because it would use up hydrogen in saturating the aromatic rings. Selective cracking of the center rings is the desired reaction. Both CoS/SiAl [14] and $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ [7] catalysts have been found to be selective for this reaction.

In any of the hydrocracking processes, the sulfur and nitrogen content of the feed streams must be in the range of 7-100 ppm depending on the process. The sulfur in the feed poisons the hydrogenation function if it is a noble metal; the nitrogen, as stated above, poisons the acid centers.

The effects of pore size must also be accounted for. When heavy feeds are treated, large molecules cannot get into the pores of molecular sieves and high silica catalysts and therefore, silica-alumina and alumina supports must be used for at least the initial hydro-treating step to remove the heteroatoms from the large, aromatic structures.

2.5. Commercial and Conceptual Processes to Hydrotreat and Hydrocrack Heavy Feeds

There are several commercial processes that give clean, lighter products from heavy feeds. Characteristic to almost all is two stage processing. The first stage hydrotreats the high nitrogen containing feeds, while the second stage hydrocracks to the desired products. Examples of operating processes are the U.O.P. - Chevron Isomax, and

