



Performance evaluation of catalyst supports used in the hydrotreating of solvent refined coal
by Thomas Irving Insley, Jr

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Chemical Engineering

Montana State University

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Abstract:

A series of commercial catalyst supports impregnated on an equal weight per unit surface area basis were tested for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activity on SRC II, a coal-derived liquid. The surface area distribution in the pore diameter range of 40-200 angstroms (A) was compared to relative catalytic activity of the supports. A correlation was found between relative HDS and/or HDN activity and the surface area attained in the 60-80A pore diameter range. The significance, and supporting evidence, of the correlation between activity and surface area distribution is discussed.

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IN THE HYDROTREATING OF SOLVENT REFINED COAL

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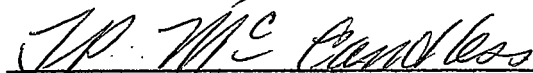
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Chemical Engineering

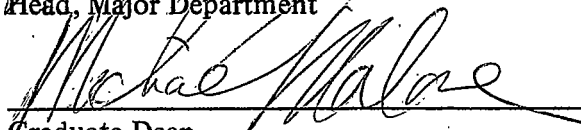
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ABSTRACT

A series of commercial catalyst supports impregnated on an equal weight per unit surface area basis were tested for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activity on SRC II, a coal-derived liquid. The surface area distribution in the pore diameter range of 40-200 angstroms ($\text{\AA}$) was compared to relative catalytic activity of the supports. A correlation was found between relative HDS and/or HDN activity and the surface area attained in the 60-80 $\text{\AA}$ pore diameter range. The significance, and supporting evidence, of the correlation between activity and surface area distribution is discussed.

Chapter I

INTRODUCTION

Late in World War II, pressed by reduced availability of conventional fuels, the German Reich turned to fuels derived from coal, so that they could continue their effort.

The technology they used was developed over many years of intense research in both Europe and America. This research was sparked by the discovery, in the 1800s, of the nature of coal's complex molecular structure, and of the possibilities of rearranging its components into useful products.

Working with hydrogenating catalysts at high temperatures and elevated pressures, Friedrich Bergius succeeded in liquefying coal. In the years after the war, little attention was directed to the development of coal-derived liquids, although, directly after the war a team of more than one hundred scientists was sent into Germany to collect synfuel technology.

In the late 1960s and early 1970s, rekindled by the threat of limited availability of conventional fuels, the United States, like other high energy consumers, turned its interests to synthetic fuels.

One aspect of current research is to reduce nitrogen and sulfur content of coal-derived liquids so that they can be used in either conventional refineries or as a boiler fuel.

The hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of coal-derived liquids, generally performed by supported catalysts, involves the intraparticle mass transport of large molecules inside the catalyst. Since the diameter of reacting molecules is believed to be comparable to the pore size of the supported catalyst, partitioning of the molecules between the bulk liquid and the internal surfaces is a factor in catalyst perfor-

mance. To produce optimum rates of reaction the pore-size distribution of a catalyst should be such that the total of diffusional (pore size dependent) and reaction (surface area dependent) resistances be reduced to a minimum. One way to minimize the combined resistances is to optimize a pore-size and area relationship in terms of performance.

It is the object of this study to ascertain, for a given reaction system, what, if any, optimum pore-size and area relationships do exist.

Chapter II

BACKGROUND

The work presented in this study, that is, the activity of impregnated catalysts towards HDS and HDN of a coal-derived liquid with respect to the physical characteristics of the catalyst support, is based on three basic assumptions:

1. Catalyst support properties, in particular, pore size vs. cumulative surface area, can, in fact, be characterized.
2. Given the proper procedure and conditions, a catalytic component can be uniformly distributed over the entire surface area of the support, with the possible exception of the most minute realms; also, that these dispersions would not significantly alter relative support properties.
3. Diffusion and surface area limitations can both be factors when considering the global rate, and, in turn, degree of HDS and HDN of a coal-derived liquid.

A defense for these assumptions will now be outlined in the following section.

Surface Area Characterization

The relationship between supported catalyst surface area and pore size distribution is a key factor of influence in light of the reaction/transport scheme encountered in the catalytic upgrading of coal-derived liquids. Considering this, any inquiry into the relationship between catalytic performance and the physical nature of the support must include a basis for characterization of the materials' physical structures. Porous materials can be characterized in terms of several quantities; these generally include average pore diameter, pore volume, density, and surface area. Of these methods, surface area characterizations, that is, surface area which is greater than the observable geometric surface area, are of particular

utility. Porous materials differ greatly in their characteristic surface areas; for example, some activated carbons have surface areas 500,000 times the external geometric area, while a porous filter plate's surface area is only 1,000 times its geometric area. Many factors lend to this effect but one of particular interest is that of the pore size distribution within the materials.

Pores in different materials may vary greatly in their absolute dimensions, from those easily seen by the unaided eye, 10^6 angstroms ($\text{\AA}$) in diameter, to those of 4 to 5 $\text{\AA}$ in diameter. Typically the surface area contributed by pores averaging 20 $\text{\AA}$ in diameter is on the order of 1500 sq. meters per gram, while the surface area contributed by a practically equal volume of pores averaging 20,000 $\text{\AA}$ in diameter is only 1.7 sq. meters per gram [1]. While the larger macropores do not contribute significantly to the total surface area they nonetheless play an important role in that they act as arteries to the smaller micropores [2].

In this study, two standard methods were used by the vendors of the carriers in the surface area characterizations of the catalyst supports. While neither of these methods produces a detailed description of the actual size and shape of each void space in the carrier they do give an averaged representation of the carriers' geometric properties. Since the procedures are standardized and widely accepted, the key to their utilization lies not in the ability to accurately determine the actual void volume according to void size, but, in the ability to generate a representative description of structure for a broad range of porous materials.

In 1945 Wheeler [3] proposed a theory, a composite of BET multilayer adsorption and capillary condensation viewpoints, which has been used as the basis for much work involving techniques for estimating the volume and area of porous adsorbents available to

molecules of various sizes. Over the years several refinements were made on Wheeler's original model to the point that today catalysis researchers have available straightforward and reliable methods for characterizations of this type [4].

Pore distribution characterizations founded on Wheeler's model find as their basis an interpretation of the sigmoid-shaped sorption isotherms generated by varying the pressure in a condensable-vapor/carrier system. Experimentally, these isotherms are obtained by measuring the change in volume (relative to an incremental increase in system pressure) of a condensable vapor, generally N_2 at $-196^\circ C$, due to capillary condensation in the porous material. When the system pressure is increased to the point of saturation, 1 atm for N_2 at $-196^\circ C$, the void space of the material is completely filled with condensed vapor and at this point the adsorption branch of the isotherm is complete. By reversing the process, that is, by gradually lowering the system pressure, the desorption branch of the isotherm is obtained.

It is considered that capillary condensation in porous materials occurs as a result of lower vapor pressure over a concave meniscus formed by liquid in the material's void space. The Kelvin equation [5] which gives the relationship between vapor pressure and radius of the concave surface of a meniscus, is used in conjunction with a cylindrical pore model to give a distribution of interior surface area with respect to pore size. When the Kelvin equation (or some form particular to the condensable vapor employed) [6] is used to convert pressure to pore radius the original isotherm can be replotted in terms of volume sorbed (pore volume) vs. radius. Since the pores of the model are considered to be straight and cylindrical (for a given increment of length), the surface area corresponding to a particular volume can be determined through the simple relationship of volume to radius:

$$\text{surface area} = \frac{2 \cdot (\text{pore volume})}{\text{pore radius}}$$

From this information one can formulate a descriptive picture of the distribution of the material's surface area over a wide range of pore sizes.

In an analysis of this type five basic assumptions are made:

1. Pores are cylindrical.
2. Each pore space is connected with at least one larger pore.
3. The meniscus radius is that of the inside tube formed by multilayer adsorption.
4. Liquid nitrogen surface tension is the same regardless of pore size.
5. There exists thermodynamic equilibrium on the desorption branch of the isotherm and that it is this branch to which the Kelvin equation is generally applied. On the adsorption branch of the isotherm there is a question as to the need of a supersaturated state before the pores fill with capillary condensed vapor, and, therefore, the adsorption branch is usually not considered in determinations of this sort.

A direct method for determining the volume and area distributions, in terms of pore size, of porous adsorbents was developed by Ritter and Drake [7]. This method, which utilizes a high pressure mercury porosimeter, is entirely independent of the sorption isotherm method. The idea is based on the phenomenon that mercury does not "wet" most catalyst materials, and, that it will not penetrate the void spaces of the material unless forced in under pressure. Ritter and Drake correlated the force needed to keep mercury out of a pore due to surface tension, to the force applied to the mercury/catalyst system. Using this procedure data can be generated relating the intrusion volume vs. applied pressure, and, from this a volume vs. pore diameter curve can be developed. Pores down to the

40 Å range in diameter can be accessed using modern apparatus which can attain pressures upwards of 50,000 psi. The cylindrical model incorporated in this technique, like that for the isotherm method, allows one to obtain surface area distributions in terms of pore size.

Comparisons between the mercury porosimeter and nitrogen isotherm methods [8] indicate that the two methods give substantially the same distribution curves. When cumulative pore volume vs. pore radius curves are compared, for the same material, the shape of the curves is nearly identical but there is a shift of the porosimeter generated curve towards the higher end of the pore range. Effectively what this shift amounts to is a reduction in surface area vs. pore size in the range of 20%.

In summary, the foregoing experimental methods gives a means of modeling the distribution of void spaces in porous materials over a wide range of void sizes. Even though the pores may be in fact interstices between crystalline building-blocks, and most likely not cylindrical in shape, a useful picture can be developed to give an idea as to what size void a molecule must pass before it can access a given surface area.

Dispersion of Catalytic Components on Alumina-Silica Supports

Typically catalysts are materials that possess high surface areas whether they take the form of fine powders, supported and coprecipitated metals, or films. The focus of this work has been on supported metal catalysts. These catalysts, in which the catalytic component is distributed throughout a porous material's surface area, can be prepared in a number of ways [9]. One procedure for preparation commonly used is the incipient wetness technique. Here, the metallic dispersions are a result of a series of wetting, drying, and

activation steps. The procedure generally consists of saturating a porous support with a solution containing the catalytic component, then after drying and calcination a distribution of small crystallites of the metal oxide are produced in the support.

Optimum composition profiles in supported catalysts are usually dictated by service conditions. For the reaction system encountered in the upgrading of coal derived liquids, which is neither predominately mass-transfer limited nor surface reaction controlled, a uniform impregnation was considered to be desirable from not only the standpoint of performance but also evaluation. The point being that a uniform distribution, throughout the macro- and microsystems of void spaces, gives one the basis by which catalyst performance can be compared to available surface area. (This is a key point of consideration if impregnated catalysts are to be evaluated in terms of the supports' physical properties, as has been done in this work.)

The ability to attain a uniform distribution of the catalytic component throughout, including the fine porous structures of the support material, remains a matter of conjecture, but, several physical phenomena lend credence to the feasibility.

1. Large capillary forces, present in highly porous materials, provide a vehicle by which even the innermost realms of volume can be attained by liquids possessing the proper wetting characteristics. As an example of application of this effect one can consider water adsorption procedures, which are widely used to determine the pore volume of silica alumina supports and similar catalyst carriers [10].

2. When in solution, catalytic components (like those used in this study) maintained at the proper pH remain in the ionic form. These ions possess diameters on the order of angstroms. For example, when solution pH is maintained in the acidic range, the cobalt ion

is generally present in the Co (II) state which has a radius of 0.82 Å [11]. Considering the small ionic size, transport of the catalytic component in solution should only be restricted in the very smallest realms of the support.

3. Adsorption of the catalytic components onto the surface of the support can influence dispersion. If sorption effects during the wetting stage of the impregnation are low, the component in solution would be uniformly distributed in the material's volume [12]. Reason being that if in solution the component has a high affinity for the support material a rapid adsorption will occur, resulting in a drop of its concentration as the liquid front moves throughout the pellet. A low adsorbing component, on the other hand, would remain at a more constant concentration in the pellet.

Depending on the support/impregnating solution combination, the pH of the system can influence the degree of adsorption [13]. For support/solution combinations like those used in this work, it has been found that a lower pH will result in a lower degree of adsorption. For instance, only 5% of a 1.2×10^{-4} M Co (II) ion solution will adsorb onto an SiO₂ surface of 75 square meters per liter of solution when the solution pH is 4.5 [14]. (Solution pH's encountered in this investigation were 4.6 or lower.)

By slowly drying the pellet, impregnated throughout with a constant concentration solution, a finely dispersed phase of the catalytic component uniformly distributed in the volume, will result upon precipitation [15].

It is generally accepted that by manipulating certain aspects of the incipient wetness process of impregnation such as pH (support and solution), concentration of impregnating solution, wetting time, drying speed, and general handling procedures one can attain a good degree of control over the distribution of the catalysts within the support granule.

Diffusion

Liquid-phase diffusivity, in a pore which is of size comparable to that of the diffusing chemical species, may be limited by two independent phenomena. First, the hydrodynamic resistance (drag), above that in the free solution, would hinder the movement of diffusing molecules through the pore. Second, a geometric exclusion factor, which essentially excludes a species from a fraction of the pore volume, leads to equilibrium partitioning; wherein, the species concentration inside the pore is less than the bulk concentration outside the pore. Both of these effects arise as a result of proximity of the species to the pore wall but are also influenced by the degree of adsorption of either the solute or solvent onto the pore surface.

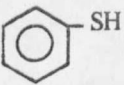
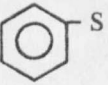
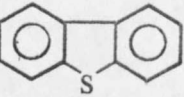
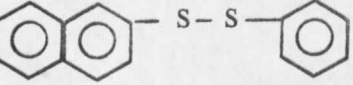
Various models have related these effects to the ratio of the relative size of the diffusing species to pore size [16,17,18,19]. Satterfield demonstrated, using silica-alumina catalysts, that in various solute/solvent combinations of hydrocarbons (saturated and aromatic) the logarithm of the ratio of effective to bulk diffusivity decreases linearly with increasing ratio of solute critical molecular diameter to pore diameter [20]. Another study, which used silica-alumina pellets, involved diffusion of similar solute/solvent systems (for example tetralin-benzene). There, it was shown that with a shift of average pore diameter from 66.4 to 56.9 Å the diffusivity of a component can be reduced by as much as 50% [21].

These and similar works of this nature, that is, the diffusion of a particular species in known solute/solvent systems, can not be directly related to the diffusional phenomena involving coal-derived liquids, which contain a host of components in undetermined concentrations.

There is, though, a general theme that comes forth: the concept that there occurs a rapid decrease in effective diffusivity of a chemical species, manifested with the narrowing of a pore through which the species must pass. Keeping this in mind and recognizing that coal-derived liquids are composed of molecular species with diameters between 25 and 150 Å [22] (comparable to the pore diameters which constitute the majority of surface area of the catalyst in this study) one can almost be assured that diffusional restrictions will play a major role in catalyst performance.

Chemistry of Coal-Derived Liquids

As a means of gauging catalytic performance, in terms of the pore size distribution of the carriers, HDN and HDS activity was followed. The kinetics, in particular the reaction sequences, in the hydrotreatment of coal-derived liquids is not well defined. Essentially when one is dealing with the chemistry of coal-derived liquids it must always be kept in mind that specific compounds in known concentrations are not encountered. Rather, models based on representative compounds, Fig. 1, are used to describe reactions that would likely occur. This is the case because, strictly speaking, there is no such thing as a coal molecule, from which these liquids are derived. Coal is a nonhomogeneous, bonded system of molecular groupings, most predominately benzene ring based, such as naphthalene, anthracene and larger-ring compounds. In addition, straight chained hydrocarbon subgroups are believed to be present in the infinitely interlinked system. Not only are large disseminations of chemical subgroups within particular classes of coals present, but, variations in composition between types of coals is notable [23].

<u>Sulfur Containing Structures</u>		<u>Boiling Point of Basic Structure</u>
Mercaptans		169.5° F
Sulfides		---
Thiophenes		183.5° F
Disulfides		---

Generally sulfides are the prevalent structures.

Nitrogen Containing Compounds

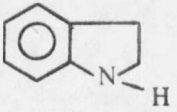
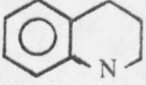
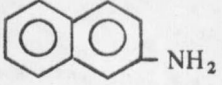
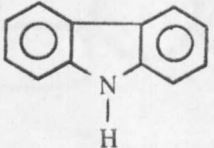
Pyridines		406° F
Indolines		445° F
Pyrroles		226° F
Quinolines		458° F
Amines		306° F
Carbazoles		670° F

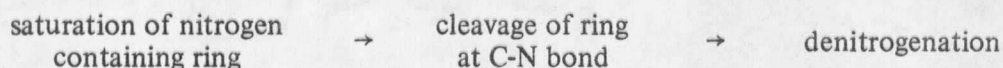
Figure 1. Representative Structures of Coal-Derived Liquids.

In commercial applications the motivation for effecting HDS and HDN is twofold: reduce possible oxide emissions generated through combustion of the final product; and minimize catalyst poisoning in downstream refining steps.

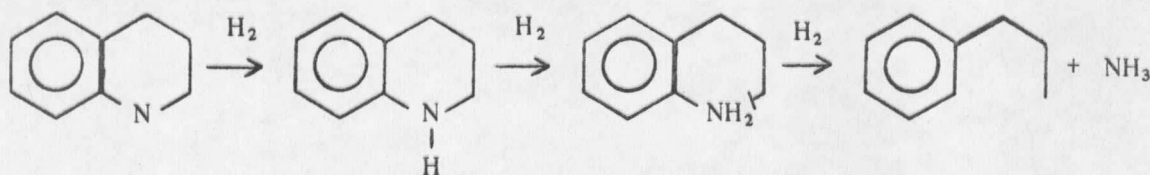
It is generally suggested that bifunctional catalysts play a significant role in HDN and HDS. With respect to nitrogen-containing compounds it is believed that nitrogen interacts with one catalyst site (of particular acid nature) while an adjacent surface site (possibly a transition metal cation) involves a neighboring carbon atom in the nitrogen heterocycle. This would then ultimately lead to the weakening of the C-N bond and facilitate nitrogen removal.

Not unlike nitrogen compounds, sulfur species take advantage of bifunctionality in that they involve the use of catalytic sites of different nature for different steps of the reaction sequence. Since it is believed that HDS involves C-S hydrogenolysis (which occurs on strongly electrophilic sites) and hydrogenation (that occur on weakly electrophilic sites), bifunctionality of the catalyst becomes important.

Generally accepted HDN mechanisms, of representative coal-liquid compounds, involve the following sequence [24]:

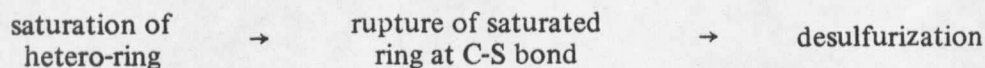


For example:

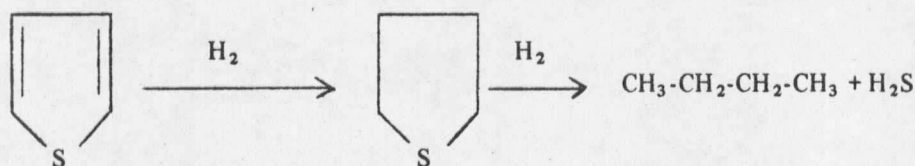


The rate limiting step in a sequence of this type is believed to be that which involves the rupture of the C-N bond [25]. Since the majority of nitrogen in coal-derived compounds is present in the ringed position, the ability to liberate it from these compounds is difficult.

Unlike compounds containing nitrogen, sulfur is generally present outside of the hetero ring in such compounds as mercaptans, sulfides, or disulfides and as a result is more easily removed from the coal-derived liquids. A species that possesses greater difficulty in sulfur removal, thiophene, has been the subject of several HDS studies [26]. A reaction sequence proposed in that study takes in the following steps:



For example:



It has been apparent in several studies involving HDN and HDS [27] that once satisfactory nitrogen removal is attained the sulfur content will also be reduced.

Chapter III

MATERIALS, EQUIPMENT, AND PROCEDURES

Support Characterizations

Supports used in this study were vendor supplied and each support was accompanied with a detailed description of its physical properties. Information available about the physical nature of these supports is generally given on a per unit weight basis; for instance, surface area per gram of pellet. Since procedures used in this work were developed around the use of a constant bulk volume of support it was necessary to adjust the vendor-supplied information, to a per unit volume basis. To do this the bulk density of the support, packed as it would be in the reactor, was determined. By multiplying this value times the given supplied property value one could then determine the property value on a per unit volume basis. For example:

$$\frac{\text{cumulative surface area}}{\text{g support}} \times \frac{\text{g support}}{\text{cm}^3 \text{ (bulk)}} = \frac{\text{cumulative surface area}}{\text{cm}^3 \text{ (bulk)}}$$

This step was absolutely necessary in the analysis, considering the great variance in the bulk densities of the supports.

For comparative purposes unadjusted values of the supports physical properties are given in Table 1. Cumulative surface area vs. pore size information, used in the actual activity analysis, was adjusted to a per volume basis, and is given in Figure 2.

Catalyst Preparation

In order to attain a constant amount of catalytic component per unit area of support, for each of the supports used in this investigation, an incipient wetness procedure was

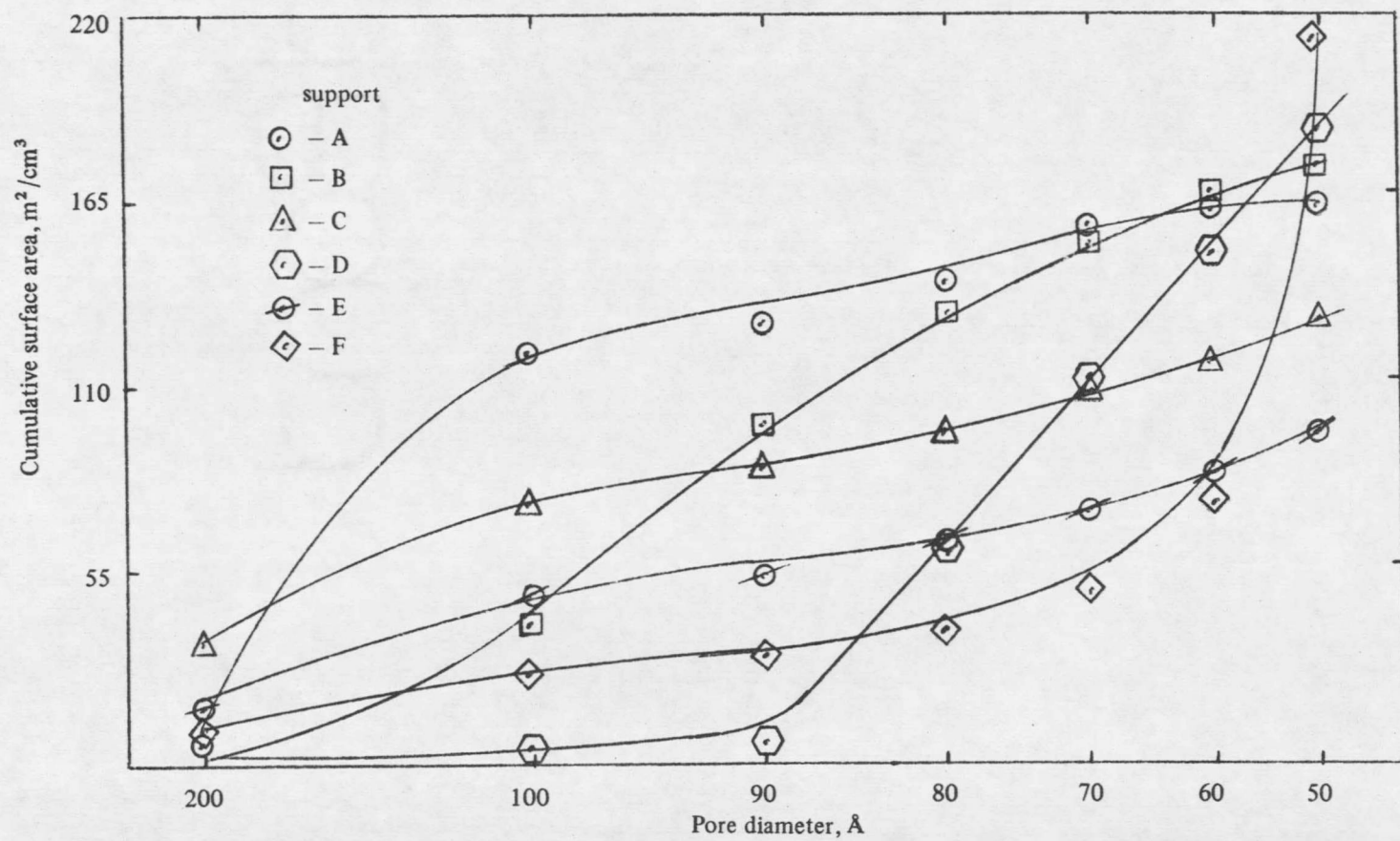


Figure 2. Cumulative Surface Area vs. Pore Diameter.

employed (see Dispersion of Catalytic Components on Alumina-Silica Supports). Since catalyst performance was to be gauged solely on the nature of the supports' physical characteristics (that is, surface area vs. pore size distribution), composition of the catalytic component was considered not to be a critical factor as long as it was such that HDS and HDN were effected. In fact, Yeh [28] has shown, using catalysts of nature similar to this study, that with different compositions of metal loading the physical characteristics of the support is by far the predominant factor in catalyst performance. Nonetheless, in this work careful attention was paid to the impregnation process with respect to consistency of metal loadings.

As a basis for composition of the catalytic component the supports were impregnated in a manner so that a constant amount of the catalytic constituents (from a set weight ratio of cobalt, molybdate, and tungsten salts in solution) would be produced per unit surface area of support. Selection of the weight ratio of salts placed in solution, and of the overall solution concentration was based on one that would produce a resemblance to an ultimate oxide loading previously confirmed to be desirable [29].

This oxide loading corresponded to an oxide weight per unit area of $3.7 \cdot 10^{-4}$ g/m² broken down into a weight percent of 2% MoO₃, 4% CoO, and 2% WO₃ combination on a 161 Å median pore diameter (based on adsorption pore volume) silica-alumina support.

While this exact oxide loading may not have been attained, the impregnation procedures used in this study did provide catalysts with suitable HDS and HDN activity.

To attain the particular impregnation characteristics of each support, so that desired loading could be achieved, a screening procedure that involved varying the impregnating solution's concentration was developed. This screening procedure, necessitated by the

different physical characteristics of the supports (see Table 1) is outlined below in reference to Figure 3.

1. Each support material, as received from the vendor, was oven dried at approximately 110°C for eight hours, and then cooled in a desiccator.

2. Impregnation

- a. Dried supports were then placed in an equal volume of a common solution, of predetermined overall salt concentration, with the weight ratio of the salts always maintained at:

1 gram Ammonium Tungstate $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$

13.3 grams Cobalt(ous) Nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

to

2.3 grams Ammonium Molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$

- b. The supports, each in a sealed container with equal volumes of the impregnating solution, were then gently rolled in a rotating drum. This was done to assure complete wetting of the support over the eight hour contact period. A wetting period of eight hours was selected because it was determined that after this span of time there was little, if any, of the solution's components imparted to the supports. A typical example of this can be seen with support E (Fig. 4).

Data for this curve was generated, in a process similar to the impregnation process, by placing samples, approximately one gram, of the support in sealed vials containing equal volumes of a common solution. These vials were then placed in a rotating drum, to assure good solution contact, from which samples were selected at various time intervals. After removal of excess solution and drying, the weight of the entrained salts was determined

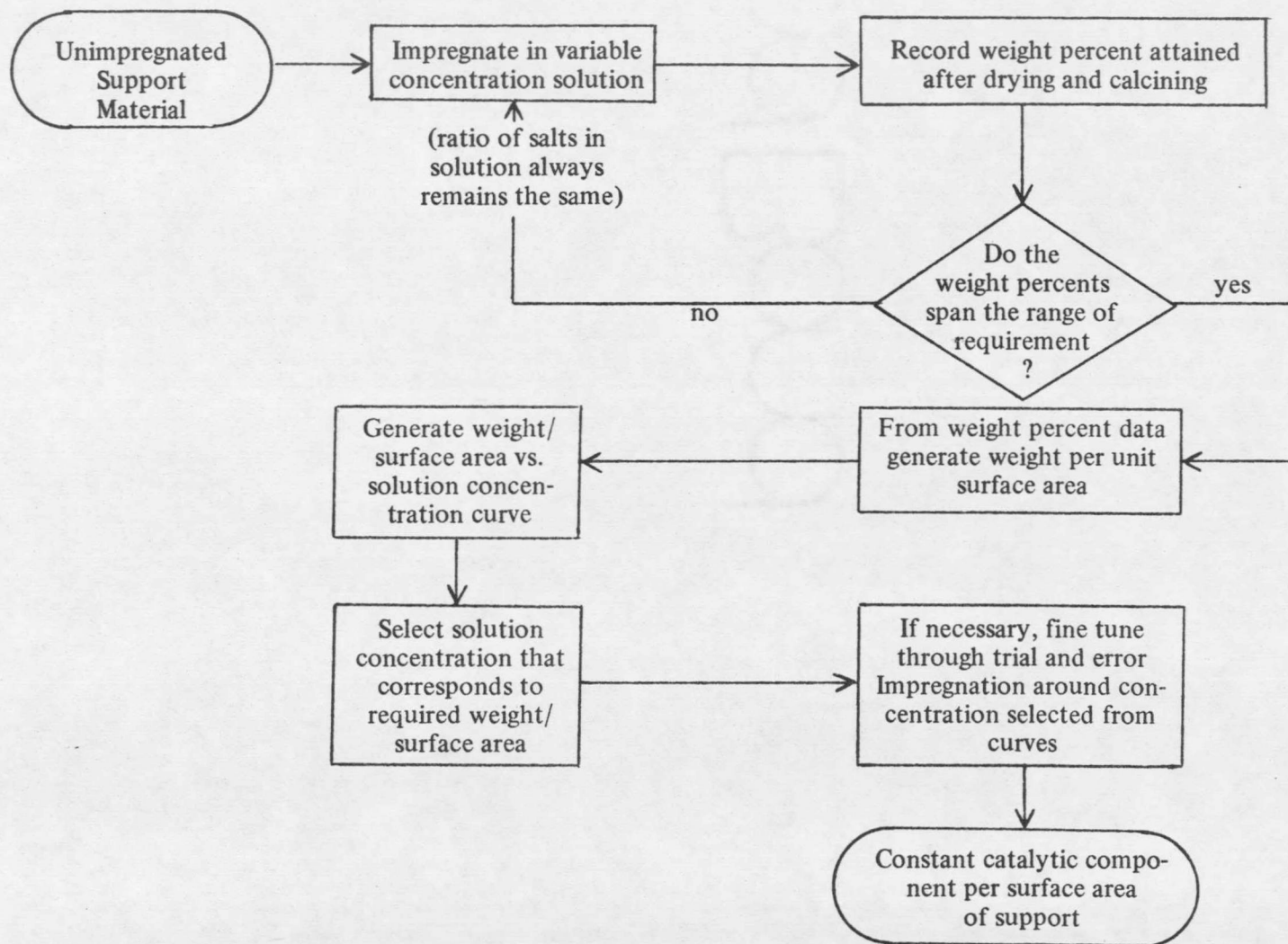


Figure 3. Screening Procedure for Impregnation.

Table 1. Support Properties.

Support	Composition	Size	Desorption Pore Volume Data					Most Frequent Pore Diameter Å	Porosity cm ³ / cm ³ bulk	Bulk Density cm ³ / cm ³ bulk
			1200 PV cm ³ /g	Sat PV cm ³ /g	4 V/A Å	MPD-SA Å	MPD-PV Å			
A	98% Al ₂ O ₃ 2% SiO ₂	1/32" extrudate	0.8702	0.8931	162.2	119.2	126.6	120	0.45	0.51
B	98% Al ₂ O ₃ 2% SiO ₂	1/16" extrudate	0.6918	0.7059	116.2	92.2	93.6	85	0.39	0.55
C	91% Al ₂ O ₃ 9% P ₂ O ₅	1/16" extrudate	0.7848	0.79	148.5	NA	95.0	50	0.48	0.62
D	96% Al ₂ O ₃ 4% SiO ₂	1/32" extrudate	0.7414	0.7648	91.7	73.7	76.1	90	0.35	0.46
E	91% Al ₂ O ₃ 9% P ₂ O ₅	1/16" extrudate	1.0800	1.1005	153.9	93.8	160.4	80	0.35	0.32
F	98% Al ₂ O ₃	pellet	NA	0.90	NA	NA	NA	NA	NA	0.50

PV = Pore volume

SA = Surface area

MPD = Median pore diameter

Sat = Saturated

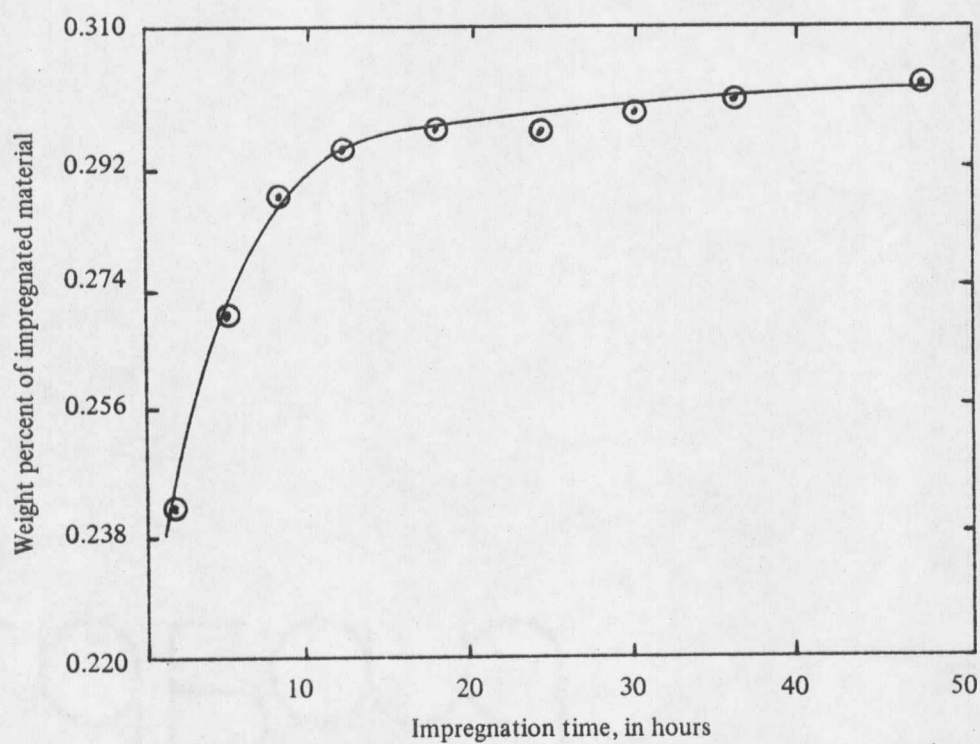


Figure 4. Weight Percent Impregnated Material as a Function of Time, for Support E.

and plotted against the support's time in solution. Information of this nature indicates that the supports are not of the sorption type and that the components in solution are not readily adsorbed onto the surface.

c. After the specified wetting time the support and solution were poured onto a filter plate in a vacuum funnel and the excess solution quickly removed.

d. At this point the catalysts were dried in two stages; forty-eight hours in air at room temperature, then oven dried at 110°C for eight hours. The initial air drying time was done to help facilitate a more uniform distribution of the catalytic components throughout the support (see Dispersion of Catalytic Components on Alumina-Silica Supports).

e. The impregnated catalyst was then, as an activation step, calcined at 450°C for eight hours.

3. After the calcination step the weight percent of the impregnated material was determined where:

$$\text{catalyst weight percent} = \frac{\text{weight of impregnated support} - \text{weight of dried unimpregnated support}}{\text{weight of dried unimpregnated support}} \times 100$$

4. From the weight percent data the weight of the impregnated material per unit surface area was determined for each support, where:

$$\frac{\text{weight}}{\text{unit surface area}} = \frac{\text{weight percent}}{100} \times \text{B.E.T. surface area}$$

5. If at this stage sufficient data points for each support, around the target weight per unit surface area of $3.7 \times 10^{-4} \text{ g/m}^2$, are generated then the initial screening is complete; if

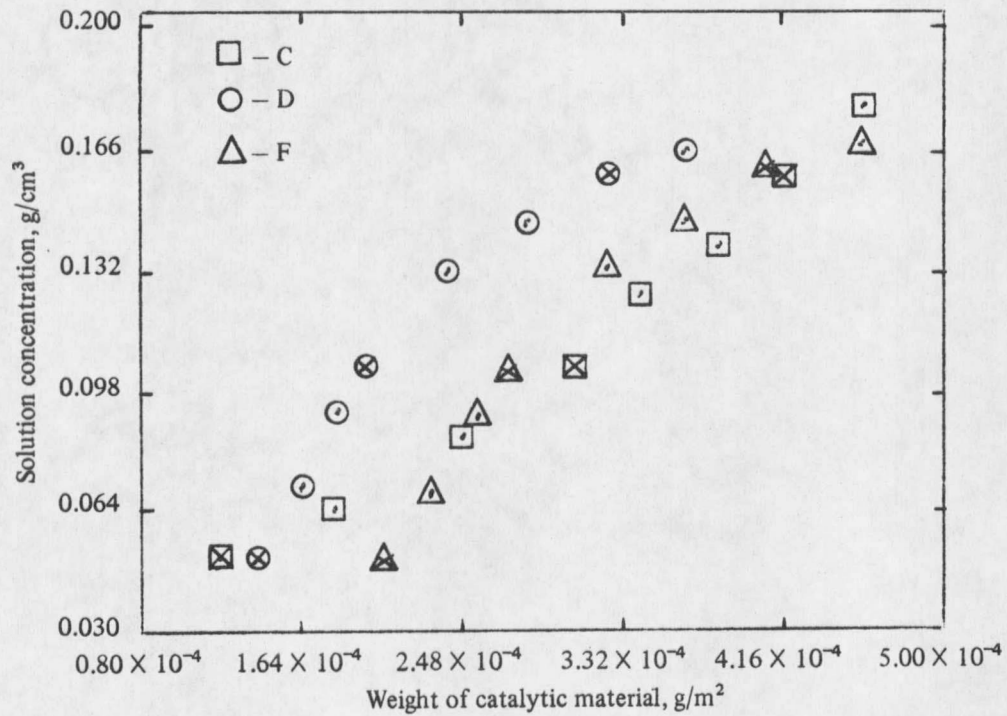


Figure 5. Weight of Catalytic Material Dispersed vs. Concentration of Solution Used in the Impregnation. Crossed points indicate actual data points; the remaining points were generated by polynomial regression equations relating solution concentration, y , and catalytic component weight, x , where:

$$y = \alpha \times 10^{-1} + \beta \times 10^3 (x) + \nu \times 10^7 (x^2) + \delta \times 10^{11} (x^3)$$

with

	α	β	ν	δ
C →	0.4746	-0.0549	0.0896	-0.0030
D →	-1.7937	2.3406	-0.5509	0.0465
F →	-2.5528	2.0760	-0.3117	0.0127

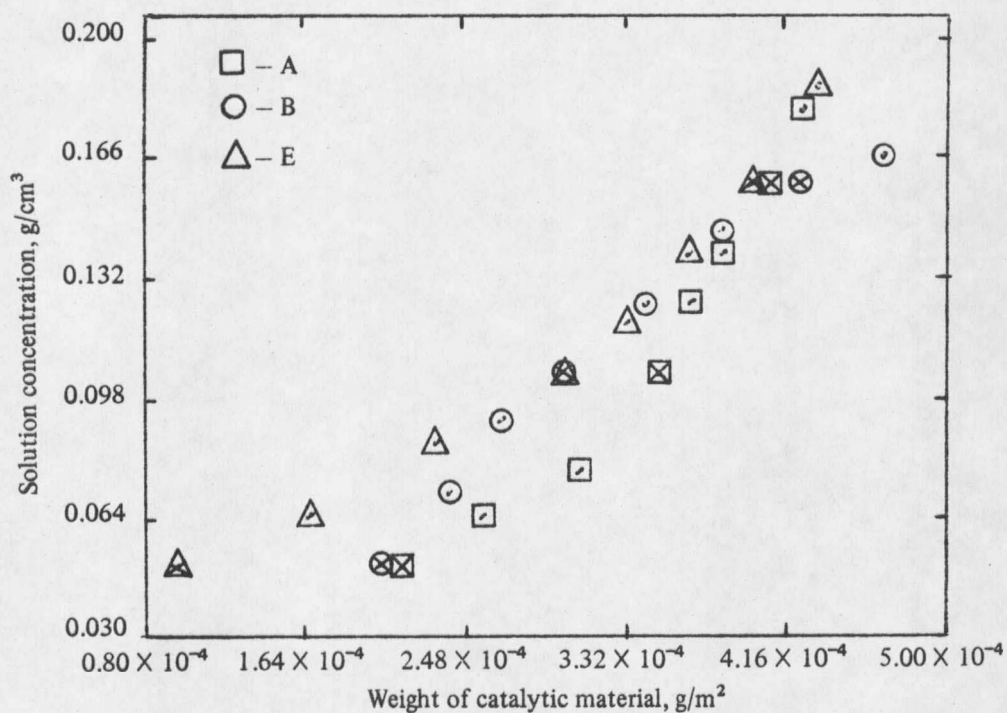


Figure 6. Weight of Catalytic Material Dispersed vs. Concentration of Solution Used in the Impregnation. Crossed points indicate actual data points; the remaining points were generated by polynomial regression equations relating solution concentration, y , and catalytic component weight, x , where:

$$y = \alpha \times 10^{-1} + \beta \times 10^3 (x) + \nu \times 10^7 (x^2) + \delta \times 10^{11} (x^3)$$

with

	α	β	ν	δ
A $\rightarrow$	1.2556	-0.6711	0.1199	0.0166
B $\rightarrow$	-0.6249	0.4333	0.0977	-0.0180
E $\rightarrow$	0.3746	0.1643	-0.0223	0.0144

not, the process (steps 1-4) are repeated with a different concentration salt solution (maintaining the same weight ratio of salts) until sufficient points have been attained.

6. Having attained sufficient data points, those of weight/surface area vs. impregnating solution concentration, numerical analysis can begin. To model this data a polynomial regression routine that generates a polynomial equation of best fit of the data was employed (see Appendix C).

7. Using the polynomial equations generated, solution concentrations that would closely match those needed to produce the target loadings, can be determined, for each individual support (see Figs. 5 and 6).

8. If necessary, slight adjustments can be made on solution concentrations, depending on the degree of consistency required, to fine tune the loading.

Trickle Bed Reactor

Catalysts in this study were evaluated in a continuous trickle bed reactor (Fig. 7). The reactor, made of one-inch inner diameter schedule-80 Inconel pipe, was thirty-six inches in length. At the top of the reactor a quarter-inch stainless steel tee served not only a feed port for hydrogen and SRC, but, was also fitted to accept a thermowell. The bottom of the reactor was threaded inside and accepted a plug that reduced to a one-quarter-inch diameter pipe. This pipe was then connected to a catch pot arrangement which allowed sampling.

The catch pot consisted of a sampling bomb which could be isolated, by cutoff valves, from the reactor system. Between the bomb and reactor was a branch in the connecting pipe leading to a water-cooled condenser. Through this, reactor gases passed, and were condensed, to fall into the reservoir. Those gases not condensed were vented to a hood by way of an NaOH bubbler.

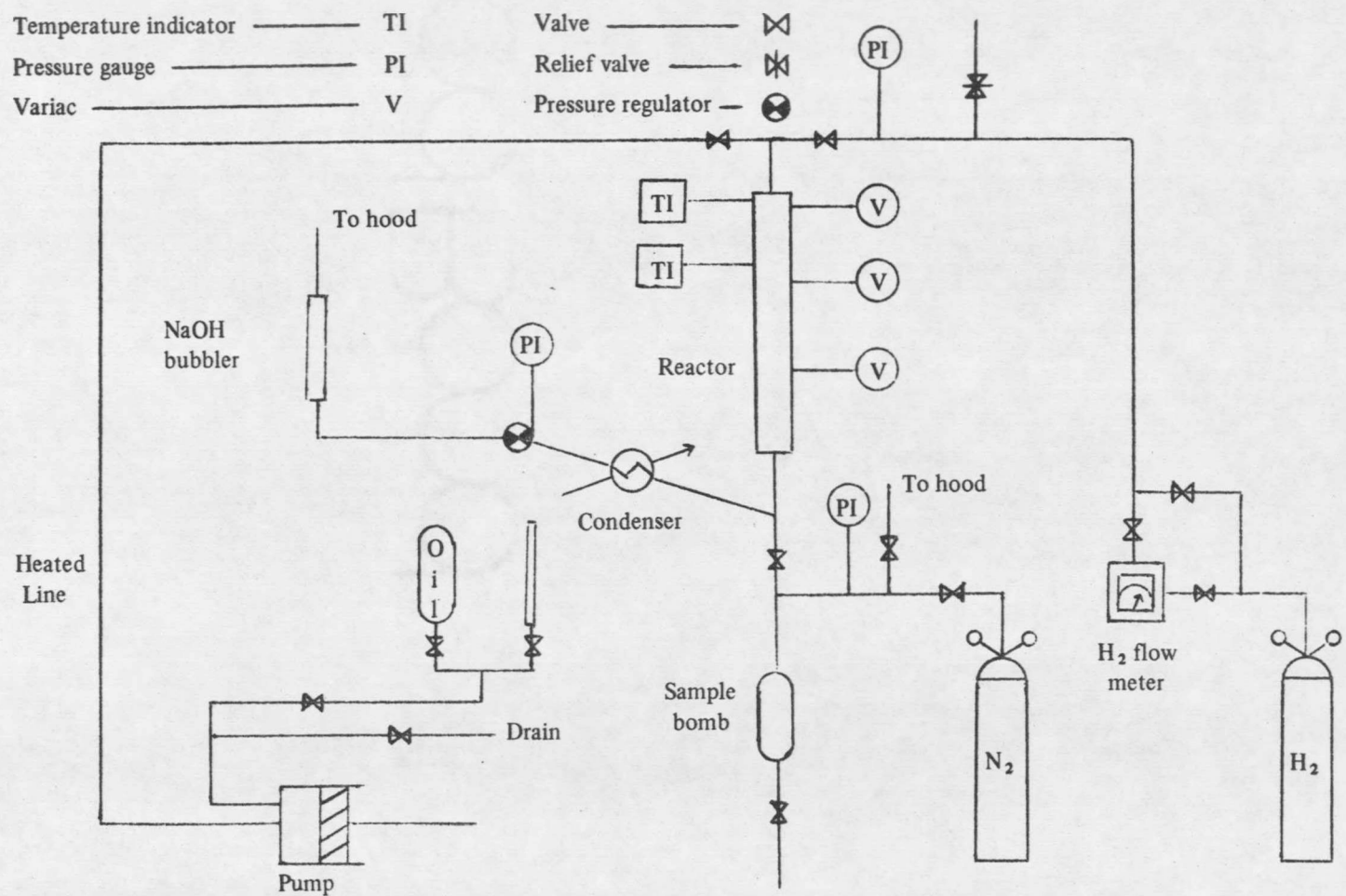


Figure 7. Trickle Bed Reactor System.

To maintain system pressure (and through which reactor exit gases passed), a Grove back pressure regulator fitted with a Teflon diaphragm was used. Gases that passed through the pressure regulator were vented to the atmosphere via a 20% NaOH solution. In order to draw a sample, the sample bomb was isolated from the reactor by closing a valve between the reactor and bomb. The bomb was then slowly depressurized through a vent to the atmosphere. Samples could then be taken by opening a valve at the bottom of the reactor. To bring the bomb back into the system the bottom and vent valves were closed and the bomb pressurized with nitrogen. Once the bomb pressure reached the system pressure the valve between it and the reactor was opened.

A heated aluminum block, in which the reactor was placed, maintained a uniform temperature over the length of the reactor. The block, through which the reactor was passed into from above, was six inches in diameter and wrapped with three sets of Nichrome heating wire enclosed in ceramic beads. The wires were spaced at one quarter inch intervals over the entire length and each of the three leads was connected to a manually controlled Powerstat variable transformer. To ensure that the reactor would be as vertical as possible, in order to allow for proper gravity flow, the aluminum block was carefully leveled.

The reactor temperature was monitored using two iron-constantan thermocouples placed in the thermowell, at preheat and catalyst sections of the reactor. Before the runs were conducted, a temperature profile of the length of the reactor was made. This profile indicated that the temperature over the length of the reactor could be controlled to within $\pm 8^{\circ}\text{F}$, at 425°F .

Feed was delivered to the reactor head, through one-eighth-inch stainless steel tubing, by a Milton Roy Model MR-1-49 Simplex packed, four stage, piston pump. Pumping

speed was varied with a micrometer adjustment on the pump. The feed line to the reactor, in addition to the feed holding reservoir were heated by Cole Parmer flexible heating cords [30].

Technical grade hydrogen was supplied to the tee at the head of the reactor through one-eighth-inch stainless steel tubing via a regulator at the tank head, a micrometer valve, and a thermal mass flowmeter [31].

Trickle Bed Reactor Set-Up and Operation

All catalyst evaluation runs conducted in this study involved the same preparation and operating procedures of the trickle bed reactor. The process, in sequence, went as follows:

1. After having been thoroughly cleaned, using toluene as a solvent, the reactor was then dried and charged with:

- a. 175 cm^3 , $\frac{1}{4}$ in. Denstone support [32]
- b. 25 cm^3 , $\frac{1}{8}$ in. Denstone support
- c. Mixture of 60 cm^3 , $\frac{1}{8}$ in. Denstone support + 60 cm^3 , catalyst
- d. Remaining volume filled with $\frac{1}{8}$ in. Denstone support

The reactor bottom was then capped with a plug that reduced to a $\frac{1}{4}$ in. diameter pipe.

2. Through the charged reactor, with the catalyst zone heated to 325°C , was passed $60 \text{ cm}^3/\text{h}$ of a 10% hydrogen sulfide blend for twelve hours. Sulfiding of the supports was performed as an activation step.

3. After the in situ sulfiding of the catalyst the reactor was placed in the heating block and the Powerstats adjusted to the proper settings. The reactor, after placement of the catch-pot, was also charged with 1000 psi. of nitrogen at this time.

4. If, after an eight hour period, no pressure drop was observed, the reactor was depressurized. Having reached the designated operating temperature, 425°C, the hydrogen and SRC II feed lines were then connected to the head of the reactor.

5. At this time, the reactor was pressurized with hydrogen to 1000 psi., at which point a flow was established past the back pressure regulator. Hydrogen flow was then adjusted, using a micrometer valve attached to the flowmeter, to 1900 standard cubic centimeters per minute (equivalent to 10,000 standard cubic feet per barrel of feed).

6. The SRC II feed was introduced to the reactor for the first five minutes at the rate of 10 cm³ per minute. This was done to help reduce flashing of the feed as it was first introduced into the reactor and in turn help reduce initial carbonization of the catalysts. After five minutes the feed rate was reduced to one cm³ per minute. This corresponded to a liquid hourly space velocity of one.

7. During the run, samples were taken at various time intervals and their volume and weight recorded. The duration of the runs made with unimpregnated catalysts was three hours, whereas those made with the impregnated catalysts were eight hours.

8. At the completion of the run the reactor feeds were shut down and the feed lines disconnected, after depressurization. The catch pot was then removed from the reactor and the reactor pulled from the heating block. The contents of the reactor were immediately dumped to avoid freezing up of the contents.

9. After cooling, all system components that came in contact with the SRC II were cleaned and flushed with toluene.

Feedstock

The SRC II feed stocks used in this study were provided by the Pittsburg and Midway Coal Mining Company's Fort Lewis, Washington, pilot plant. Their process basically consists of solvation of pulverized coal by a process derived slurry, in the presence of hydrogen and at an elevated temperature. Further processing removes the majority of ash and ultimately yields naphtha, boiler fuel, and vacuum residue liquids [33,34,35]. Analysis of the feed coal to the process and products used in this study are given in Table 2.

Table 2. Properties of SRC II and of Coal Used in Its Process.

	Feed Coal Analysis Kentucky #9	SRC II Vacame Flash Feed (used with unimpregnated cat.)	SRC II Light Ends Column Feed (used with impregnated cat.)
Carbon	71.35 ⁽¹⁾	87.43	N.D.
Hydrogen	5.07	7.15	N.D.
Nitrogen	1.44	1.17	0.88
Sulfur	3.50	0.72	0.57 ⁽²⁾
Oxygen	7.55	3.72	N.D.
Ash	10.12	0.249	0.02
API Gravity 60°F	—	1.18	0.98

(1) Unless indicated all values are reported as weight percent.

N.D. — not determined.

(2) As determined in analysis made at M.S.U.

Chemical Analysis

Determination of nitrogen and sulfur content in product oils were made using two standard methods. Sulfur analyses were performed using a Bico-Brown Shell quartz tube

combustion sulfur apparatus [36], whereas nitrogen levels were determined by a Macro-Kjeldahl method [37]. Both of these procedures yield analyses in terms of weight percent of the component being tested for.

Density Measurements

Density measurements of the products from the continuous runs were deemed necessary due to the observation that the products had differing specific gravities, enough so that it was considered to be a factor in the analysis. Chemical analyses of nitrogen and sulfur content are generally reported in weight percent terms, i.e., grams of N_2 /g sample. In order to take into account the variable specific gravity, all nitrogen and sulfur contents reported in this work are those of concentrations generated from:

$$\text{concentration} = \frac{\text{weight percent}}{100} \quad \bigg| \quad \text{density}$$

The determination of density was done using a microsyringe and a highly accurate Mettler balance. The procedure was as follows:

1. Draw 10 μ l of sample into a microsyringe and remove any excess from outside of needle.
2. Weigh syringe and contents using a Mettler balance and record weight.
3. Remove syringe from balance and carefully discharge contents, weigh again, and record weight.
4. From this information sample density can be determined where:

$$\text{density} = \frac{\text{weight of sample}}{\text{volume drawn}}$$

While these procedures generate a density measurement with accuracy comparable to that of a simple pycnometer, $\pm 0.02 \text{ g/cm}^3$ they also facilitate handling of small or volatile samples (see Appendix B for propagation of error analysis).

Characterization of Fractionated Feed and Product Oils

In order to gain an insight as to where nitrogen and sulfur components exist, with respect to their boiling point, both feed and product oils were fractionated into five distillation cuts, and these cuts analyzed for their nitrogen and sulfur content. By comparing the data from the products of runs using catalyst A and E with that of the feed, a determination could be made as to the activity of the respective catalyst toward differing nitrogen and sulfur species.

To generate this data a sample would be fractionated, using an ASTM distillation unit, into five cuts:

1. Initial boiling point to 300°F
2. 300°F to 375°F
3. 375°F to 475°F
4. 475°F to 580°F
5. 580°F to end (including residue)

Then from each of these cuts nitrogen and sulfur weight percent was determined, in addition to density.

When all the pertinent data was compiled it was transformed into a form that would facilitate comparisons of the different samples. Samples were compared in terms of grams of sulfur or nitrogen, present in a given boiling range, per cm^3 of charge, where:

$$\frac{\text{g (N}_2 \text{ or S)}}{\text{cm}^3 \text{ charge}} = \frac{\text{wt \%}}{100} \left| \frac{\text{ASTM Volume fraction}}{\text{density of fraction}} \right|$$

Essentially, what this accomplishes is to break the nitrogen or sulfur content of a sample down into the various boiling point ranges while taking into account the density, volume, and weight percent.

Chapter IV

RESULTS AND DISCUSSION

To gauge catalyst performance of impregnated and unimpregnated supports towards HDN activity, nitrogen concentrations of product oils were monitored as a function of time on the catalyst (see Figures 10-17). In addition, HDS activity of unimpregnated supports based on sulfur concentrations of the product oils were also monitored as a function of time on the catalyst (see Figures 8 and 9).

It is interesting to note the decrease in activity due to poisoning displayed in the increase of nitrogen concentrations over time, on both the impregnated and unimpregnated supports, Figures 10-17, while the product sulfur concentration, Figures 8 and 9, shows little, if any, increase over the length of the runs.

To illustrate the nature of catalytic performance of the various impregnated and unimpregnated supports (see Appendix A), in particular with respect to a support's cumulative surface area attained at a given pore diameter, parameters indicating the degree of HDS and HDN were employed.

HDN performance of the unimpregnated supports was ranked in terms of a percent denitrogenation where:

$$\% \text{ DN} = \frac{\text{wt \% N}_{2\text{-in}} - \text{wt \% N}_{2\text{-out}}}{\text{wt \% N}_{2\text{-in}}} \times 100$$

with:

$\% \text{ DN}$ — percent denitrogenation [=] dimensionless

$\text{wt \% N}_{2\text{-in}}$ — weight percent of nitrogen in the feed [=] g/g

$\text{wt \% N}_{2\text{-out}}$ — average of nitrogen weight percents, for a given catalyst, over the entire run [=] g/g

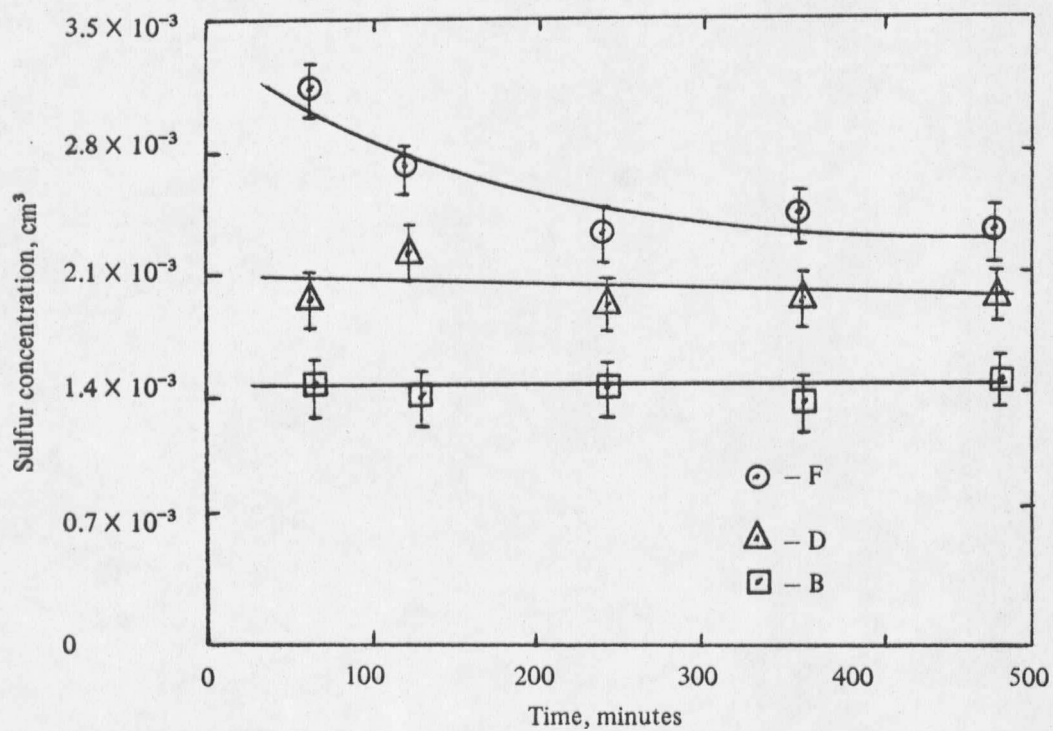


Figure 8. Product Sulfur Concentration as a Function of Time on Impregnated Catalysts. The error bars show the determined limit of error in the concentration measurements. The limit of error in time is less than the size of the point.

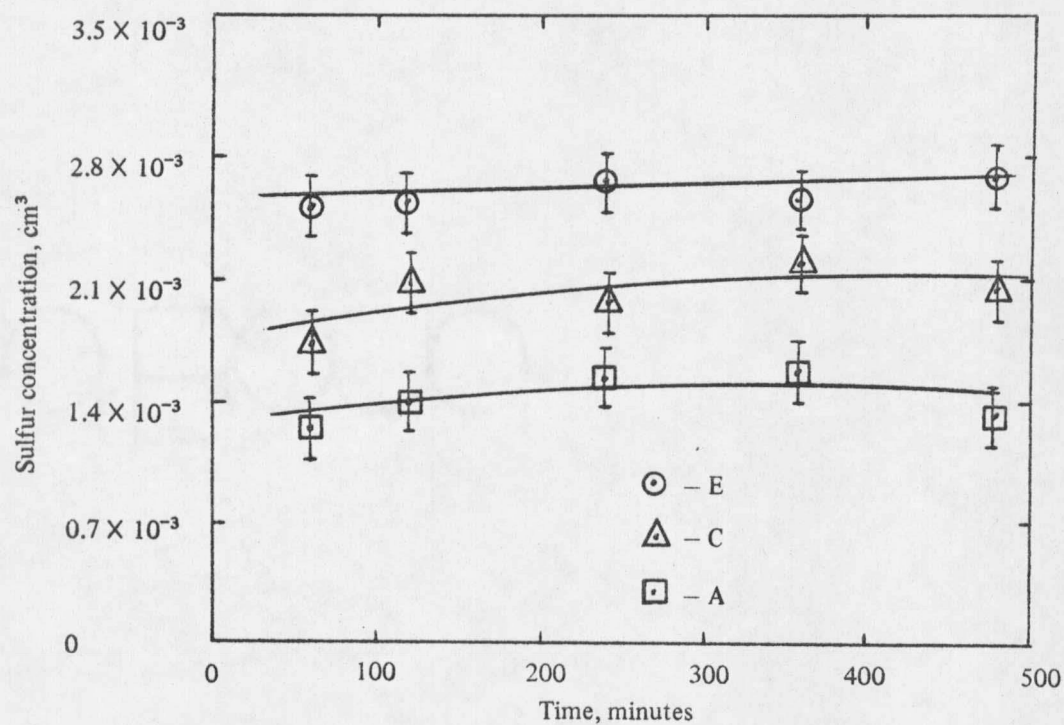


Figure 9. Product Sulfur Concentration as a Function of Time on Impregnated Catalysts. The error bars show the determined limit of error in the concentration of measurements. The limit of error in time is less than the size of the point.

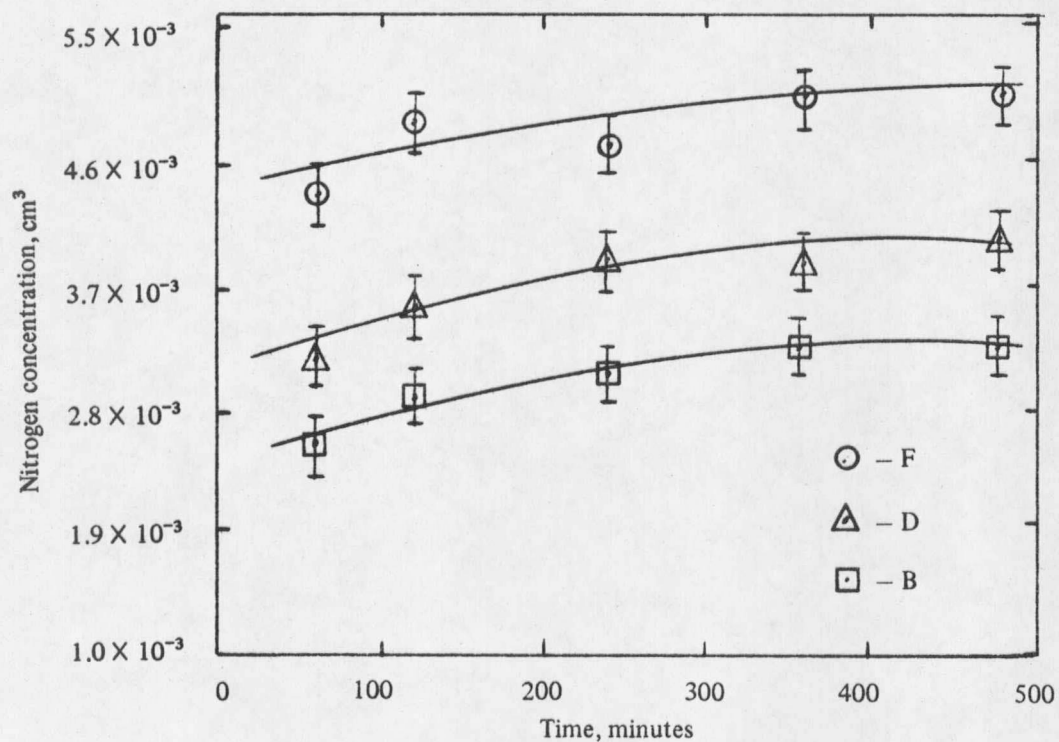


Figure 10. Nitrogen Concentration as a Function of Time on Impregnated Catalysts. The error bars show the determined limit of error in the concentration measurements. The limit of error in time is less than the size of the point.

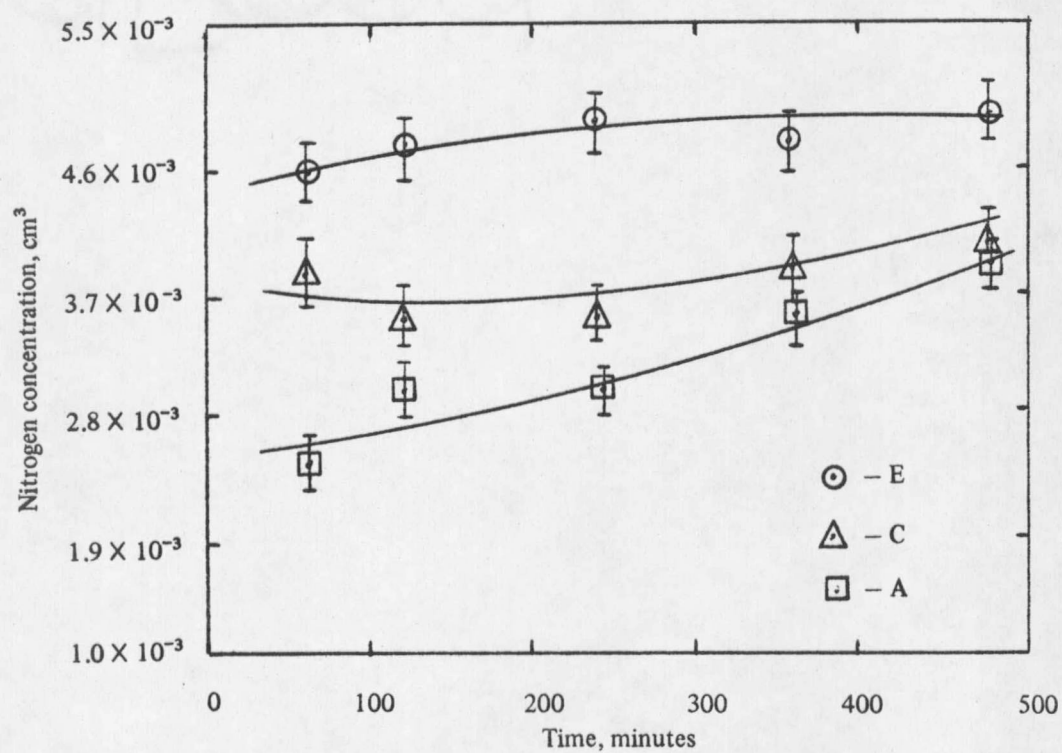


Figure 11. Nitrogen Concentration as a Function of Time on Impregnated Catalysts. The error bars show the determined limit of error in the concentration measurements. The limit of error in time is less than the size of the point.

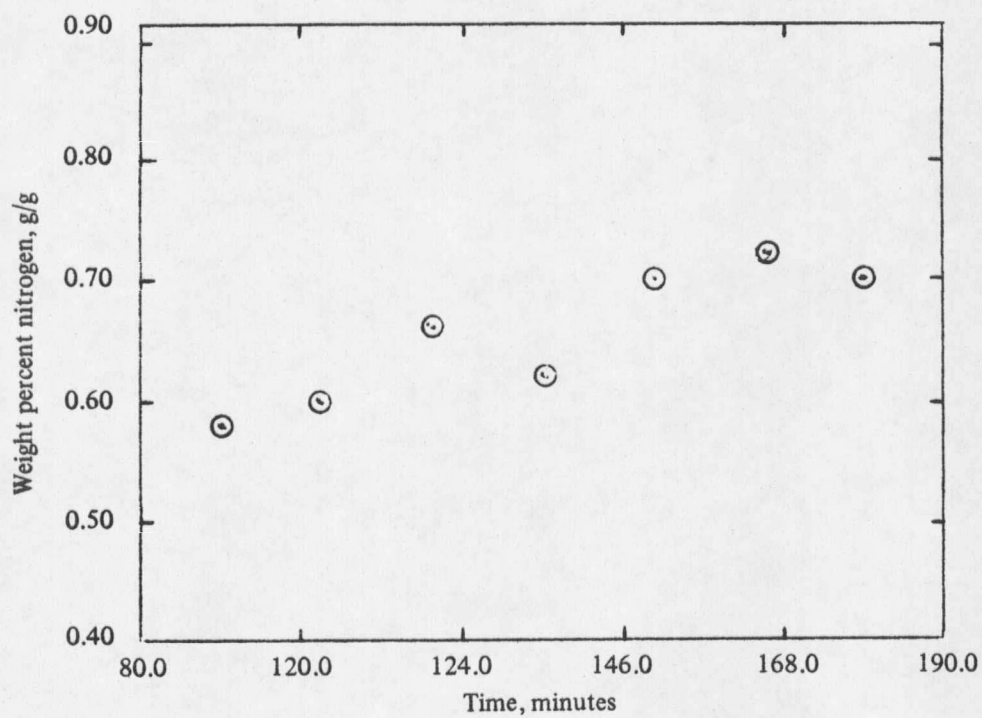


Figure 12. Weight Percent Nitrogen as a Function of Time on Unimpregnated Support A.

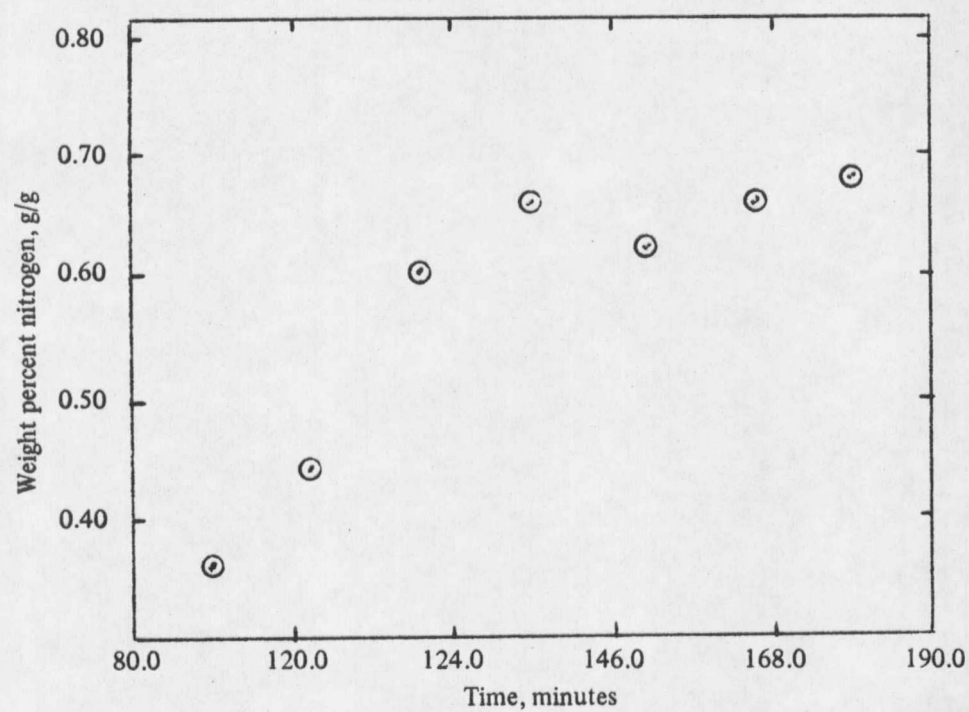


Figure 13. Weight Percent Nitrogen as a Function of Time on Unimpregnated Support B.

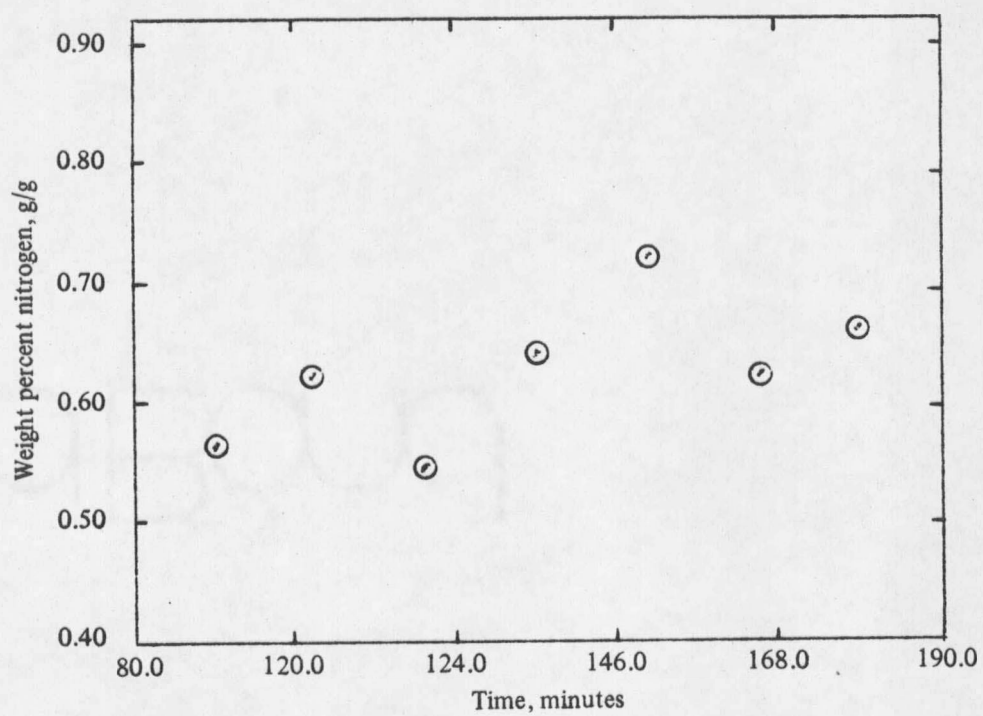


Figure 14. Weight Percent Nitrogen as a Function of Time on Unimpregnated Support C.

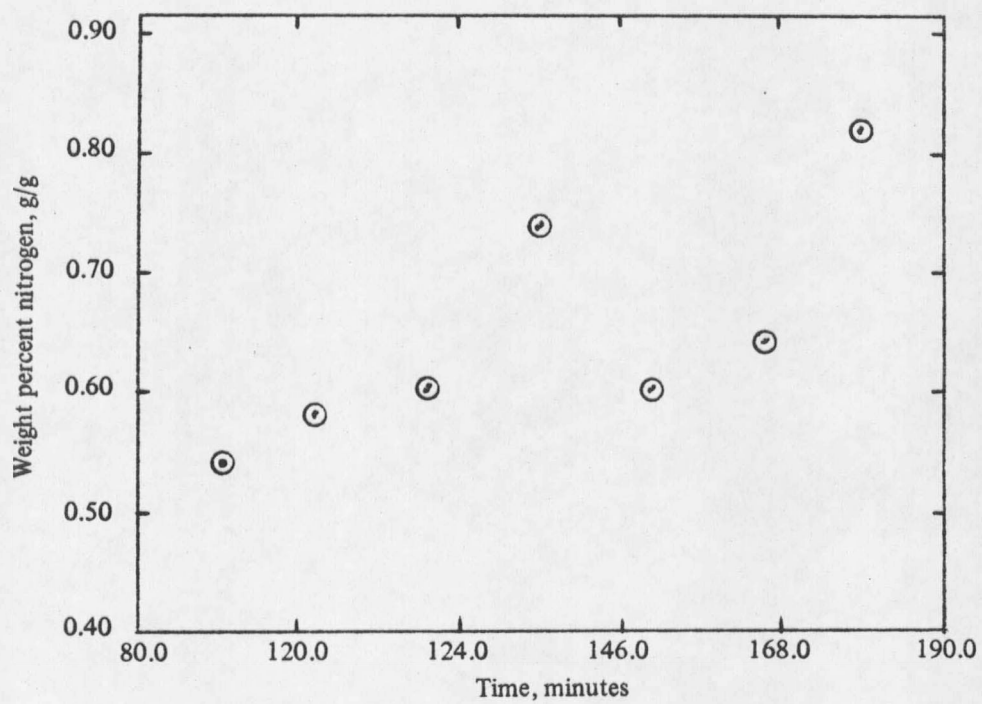


Figure 15. Weight Percent Nitrogen as a Function of Time on Unimpregnated Support D.

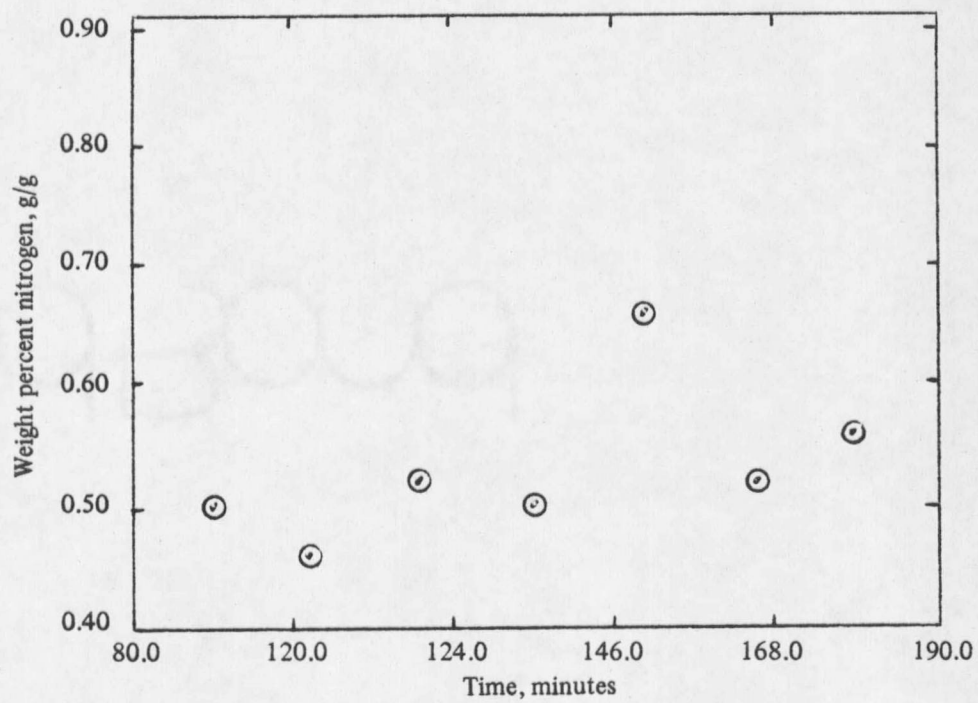


Figure 16. Weight Percent Nitrogen as a Function of Time on Unimpregnated Support E.

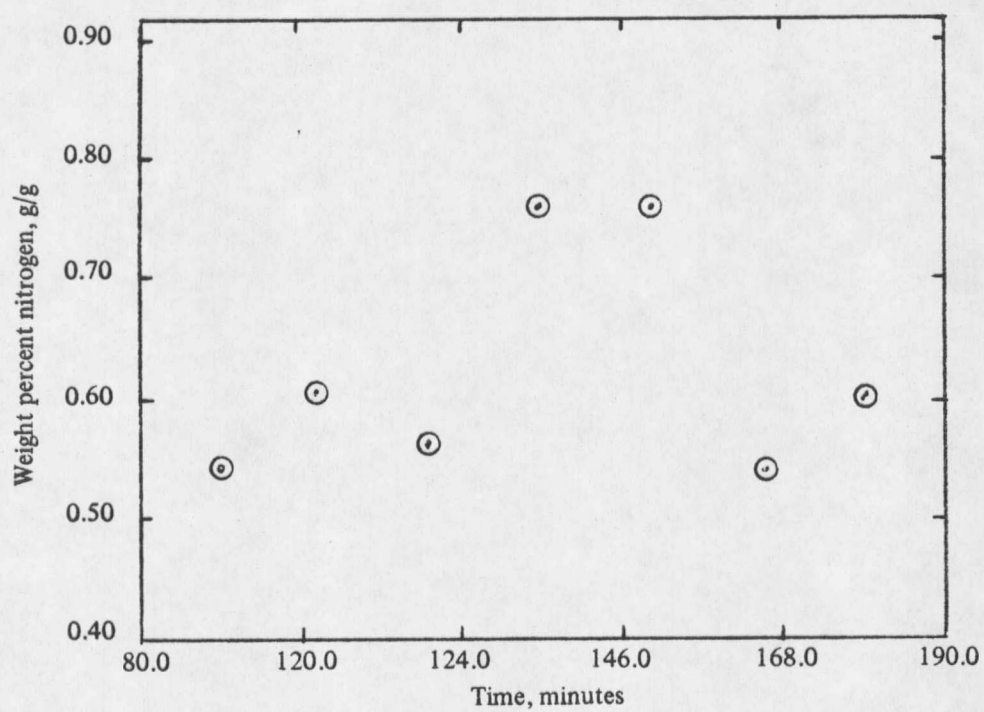


Figure 17. Weight Percent Nitrogen as a Function of Time on Unimpregnated Support F.

Note: weight percent was used rather than concentration because it was found that, unlike the impregnated supports, the variation in density between the feed and products was not significant for the unimpregnated supports.

HDN and HDS performance of impregnated supports were ranked in terms of percent denitrogenation and desulfurization where:

$$\% \text{ DN} = \frac{C_{\text{N}_2\text{-in}} - C_{\text{N}_2\text{-out}}}{C_{\text{N}_2\text{-in}}} \times 100$$

with:

% DN — percent denitrogenation [=] dimensionless

$C_{\text{N}_2\text{-in}}$ — concentration of nitrogen in feed [=] g/cm³

$C_{\text{N}_2\text{-out}}$ — average of nitrogen concentrations, for a given catalyst, over an entire run
[=] g/cm³

and

$$\% \text{ DS} = \frac{C_{\text{S-in}} - C_{\text{S-out}}}{C_{\text{S-in}}} \times 100$$

with:

% DS — percent desulfurization [=] dimensionless

$C_{\text{S-in}}$ — concentration of sulfur in feed [=] g/cm³

$C_{\text{S-out}}$ — average of sulfur concentrations, for a given catalyst, over an entire run [=]
g/cm³

One point particular to these parameters is that they take into account the relative degree of activity over an entire run for the individual supports.

The results of performance ranking and the cumulative surface area (in terms of pore size distribution), for each support are shown in Table 3. Now, if there is, in fact, an optimum pore size vs. surface area relationship, with respect to catalyst performance, it should be evident in this information.

To investigate a possible relationship between activity (in terms of HDS or HDN) and surface area distribution (in terms of pore size vs. cumulative surface area), a product moment correlation coefficient (correlation coefficient) was generated for each level of pore size, with respect to activity. The correlation coefficient gives a measure of the linear covariation of the variables; in other words, a measurement of the linear association between them.

It is a dimensionless quantity that may take any value between -1 and 1 , inclusive. When the value is ± 1 , a correlation is said to be exact; when the value is 0 , the variables are said to be uncorrelated and that there is no linear association between them.

The correlation coefficients generated (for each level of pore size) between HDS and HDN activity and cumulative surface area are given in Table 3.

The work involving unimpregnated supports proved inconclusive as far as discerning a relationship between an increase in activity and an increase of surface area, among the supports. As can be seen in Table 3, there is no positive linear correlation between HDN activity and BET or cumulative surface area at any pore diameter investigated. The small negative linear correlations that do exist indicate, if anything, a slight decrease in activity with an increase in surface area, between the supports. From this information one conclusion would obviously be that greater levels of surface area are not taken advantage of in the unimpregnated state. This was not the case with the impregnated supports.

Table 3. Activity Correlations.

Support	Unimpregnated	Impregnated		Cumulative Surface Area at Given Pore Diameters (m ² /cm ³)							B.E.T. Surface Area
	Percent Denitro- genation (DN)	Percent Desulfur- ization (DS)	Percent Denitro- genation	200Å	100Å	90Å	80Å	70Å	60Å	50Å	m ² /cm ³ _{bulk}
A	44.4	75.0	63.6	3.4	108.63	126.5	139.2	157.0	161.0	163.0	109.4
B	42.7	73.2	64.8	0.4	38.3	97.9	130.8	156.9	170.0	171.0	130.9
C	47.0	64.3	56.8	32.9	75.3	83.9	93.6	103.3	115.4	127.3	131.6
D	45.7	64.3	57.9	0.4	2.0	3.3	58.4	110.8	155.6	184.0	148.7
E	54.7	53.6	45.4	13.9	45.5	52.5	60.8	71.2	82.5	94.7	89.8
F ⁽¹⁾	47.0	51.8	42.0	4.7	23.3	27.4	35.9	48.4	74.7	214.4	140.0

Correlation coefficient⁽²⁾

with respect to:

Unimpregnated supports

% HDN

-0.3849 -0.0948 -0.3320 -0.5614 -0.6282 -0.6005 -0.6697 -0.6387

Impregnated supports

% DN

-0.2216 0.4923 0.7027 0.9249 0.9893 0.9363 0.0712 0.0706

% DS

-0.1783 0.3835 0.6071 0.8729 0.9773 0.9611 0.0323 0.1442

and cumulative
surface area↑
see Figures 18 and 19 for plot of
activity vs. cumulative surface
area at this pore diameter

(1) Cumulative surface area for supports A, B, C, D and E are based on nitrogen desorption determinations, support F's data is based on mercury intrusion determinations.

(2) Values generated by MEGRESS [38].

Once again turning to Table 3 it can be seen that with impregnated supports there exists an excellent positive linear correlation between activity and cumulative surface area in the 80 to 60 Å range, but, that this correlation drops off rapidly at the 50 Å level. Also, the correlation can be seen to progressively approach the zero value as one moves up the pore diameter scale, to the point where at 100 Å, only a small correlation is present. In addition to the cumulative surface area data, BET surface area per unit volume of support is also presented here. As indicated there is almost no correlation between activity and surface area, at what should be close to the total internal area of the support.

One could conclude that the results involving impregnated supports are a manifestation of the effects of diffusion vs. optimum obtainable surface area limitations. This being evident, in that, as one moves down the pore diameter range, attaining more and more surface area at each increment, there exists a point where additional surface area, attained beyond a given pore diameter, is not accessible by the reacting species.

The point of best correlation, with respect to pore diameter, would then give one a landmark for choosing the optimum support in terms of activity, based on which support has the greater surface area in that pore diameter range.

It is interesting to note that both HDS and HDN, while being independently generated parameters, show such good agreement as to the location of optimum pore size with respect to cumulative surface area.

Another point is the distinctness of the band of optimum pore size vs. cumulative surface area that exists; a 20 Å band is very tight, and as such lends to the selection of an optimum support. Figures 18 and 19 illustrate the relationship between activity and surface area in this optimum band of pore sizes.

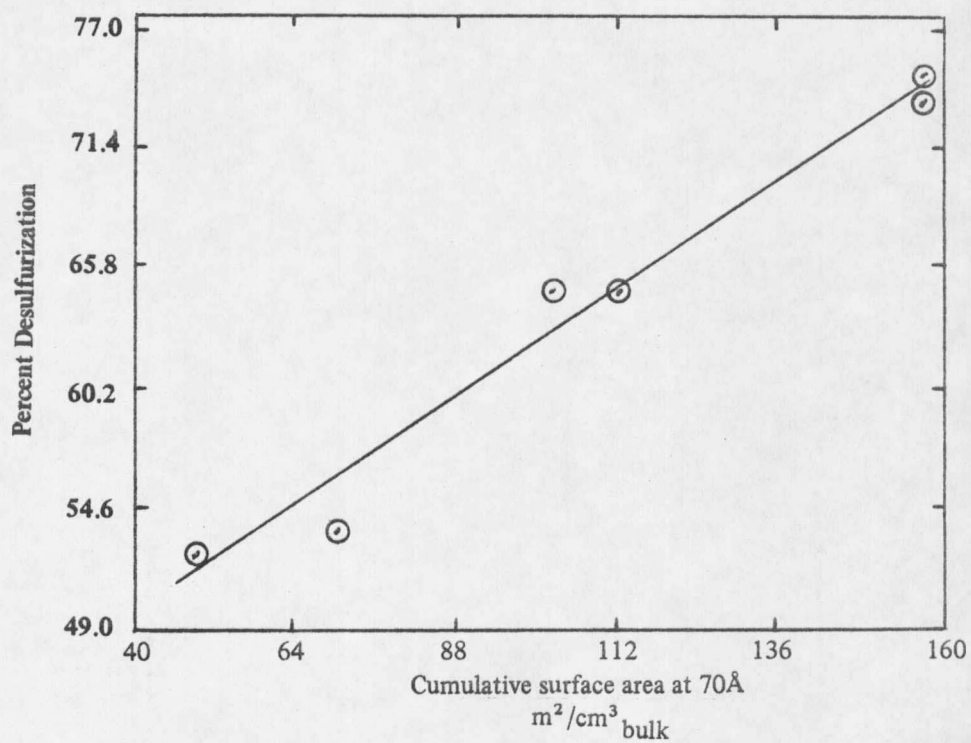


Figure 18. Percent Desulfurization vs. Cumulative Surface Area at a Pore Diameter of 70Å (point of best correlation).

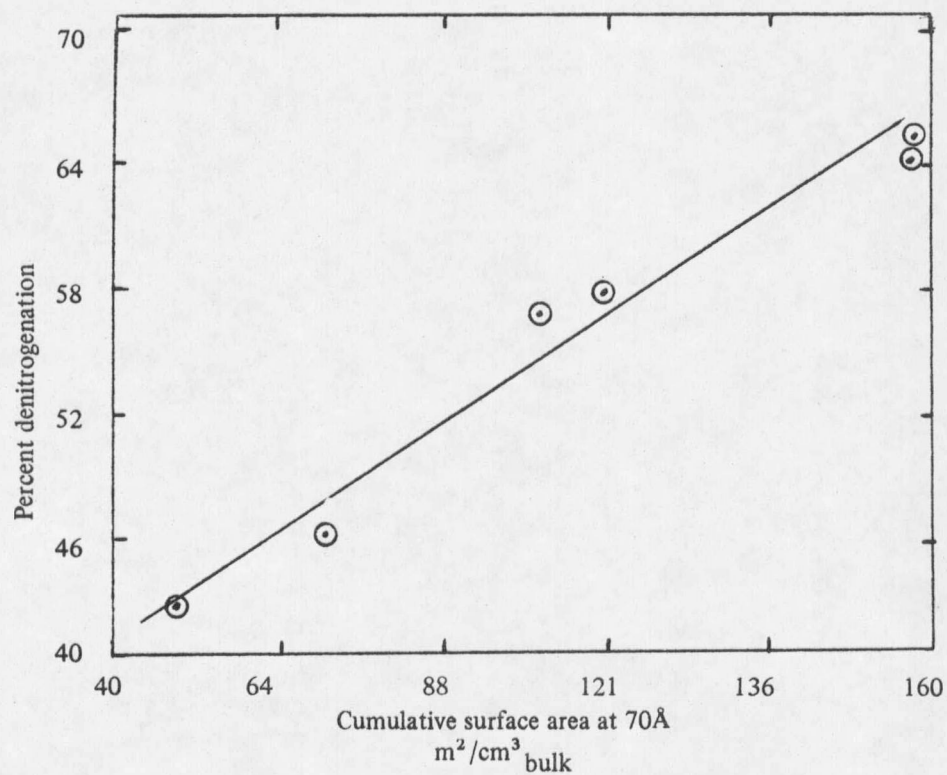


Figure 19. Percent Denitrogenation as a Function of Cumulative Surface Area at a Pore Diameter of 70Å (point of best correlation).

To reinforce the hypothesis that it is the more complex chemical species in coal-derived liquids that present the most difficulty in HDS and HDN, products from runs using catalysts A and E, in addition to the feed, were fractionated into five distillation cuts. From each of these cuts was determined the weight of nitrogen or sulfur per unit volume of charge (see Characteristics of Fractionated Feed and Product Oils). This data is presented in Figures 20 and 21. As can be seen, the catalyst with the better overall performance, catalyst A, gives better denitrogenation and desulfurization in the higher boiling point fractions (i.e., more complex nitrogen-and sulfur-containing molecules). It is also evident, in the lower boiling point fractions, that HDS and HDN of the species is about the same, regardless of the support used. This would lead one to believe that it is the diffusional restrictions of the higher boiling point (more complex) species, that dictate the optimum in surface area vs. pore size characteristics observed in the supports tested in this study.

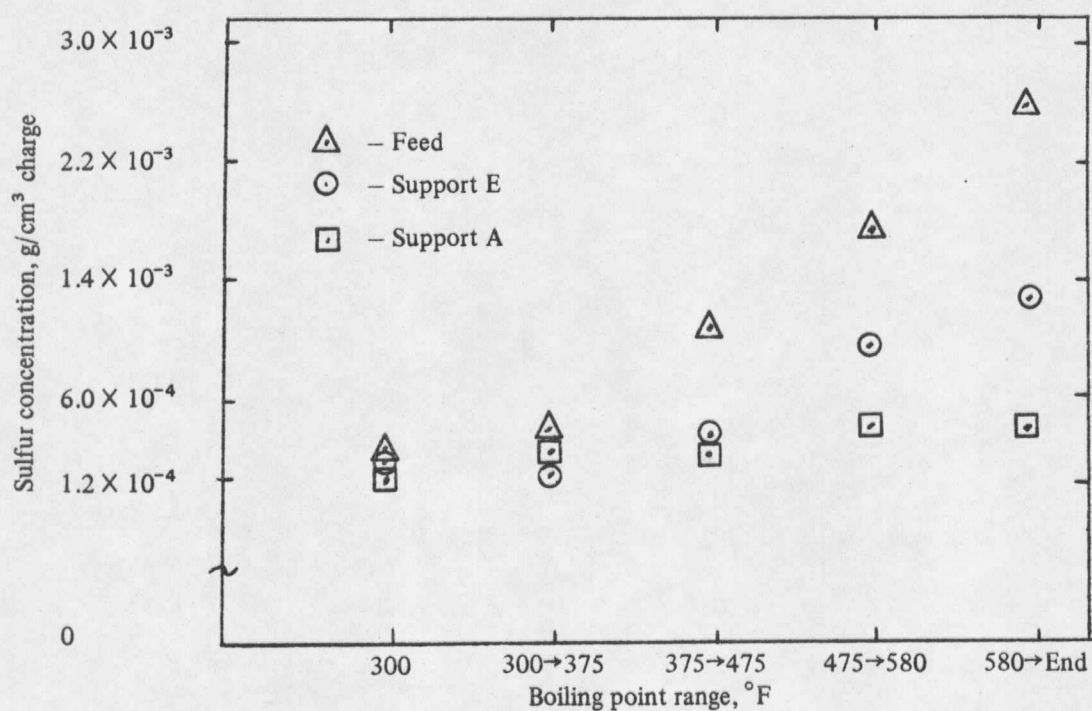


Figure 20. Sulfur Content for Various Boiling Point Ranges of Products From Runs With Impregnated Supports A and E Compared With That of the Feed.

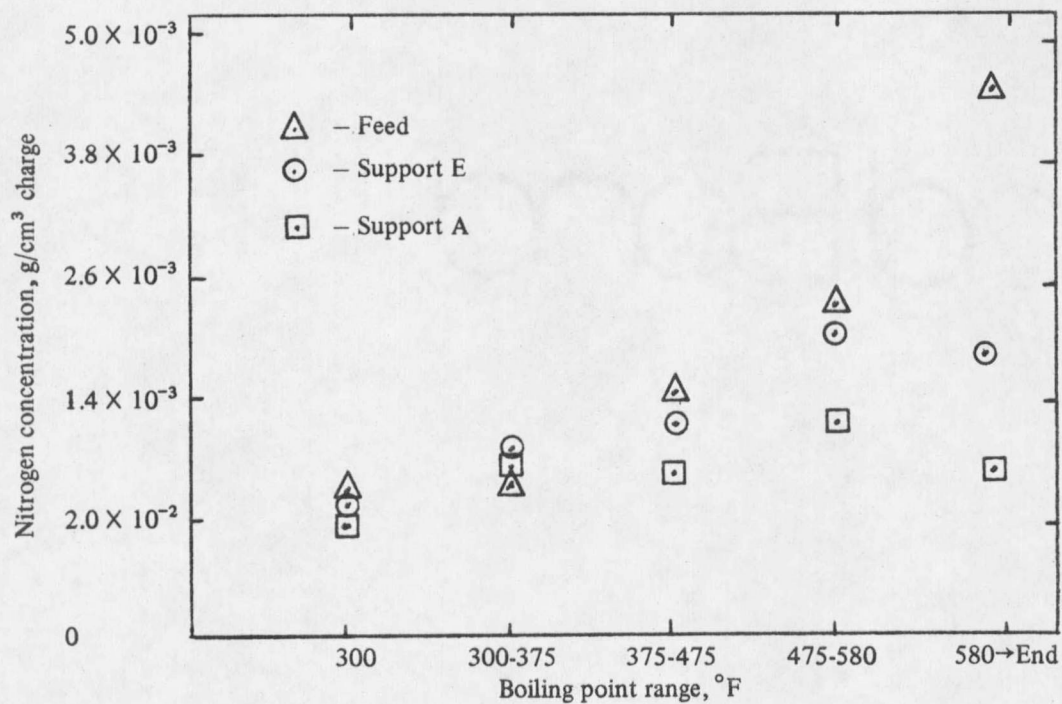


Figure 21. Nitrogen Content for Various Boiling Point Ranges of Products From Runs With Impregnated Supports A and E Compared With That of the Feed.

Chapter V

SUMMARY AND CONCLUSIONS

Performance rating of unimpregnated and impregnated alumina-silica catalysts have been studied with respect to their HDS and HDN activity on an SRC II feedstock. A summary of the results from the trickle bed runs are as follows:

1. Unimpregnated supports do not display an increase in HDN activity with an increase of BET or cumulative surface area at any point on the pore diameter range investigated.

2. Supports, impregnated with a constant weight per unit surface area of catalytic component, and, evaluated on a constant free volume basis (volume in the reactor) do show definite activity characteristics. In particular, analyses based on these catalysts show that there exists an optimum pore size, below which additional surface area can not be attained by the reacting species, due to diffusional limitations; and, above which, limitations in active surface area become an inhibiting factor. A distinct band of pore size, 80 to 60A, was found to be the optimum for the catalyst examined in this study.

3. Higher boiling point species of the SRC II are those that pose the greatest difficulty with respect to HDS and HDN of impregnated supports; also, it is the presence of these species that limit the overall performance of a given catalyst.

While the correlation between HDS and HDN activity and pore size distribution derived in this study is related to the particular operating conditions, feed stock, and support characteristics; the screening procedure, nonetheless, remains general and could be used to characterize other reaction systems.

Chapter VI

RECOMMENDATION FOR FUTURE RESEARCH

Having explored HDS and HDN performance of a considerable range of supports, in terms of cumulative surface area attained at a given pore size, one might ask the question: is there room for appreciable gains in the level of surface area at a given pore diameter, say 70Å? To investigate this query, a hypothetical situation will be posed. Given that the volume of a support (taking support A as an example) is comprised solely of pores of 70Å in diameter, what would be the corresponding surface area of the support (see Table 1)? From the relationship of pore volume to surface area described in Chapter II, under Surface Area Characterizations, we have:

$$SA = \frac{PV}{D} \bigg| \frac{\rho}{2.5 \times 10^{-5}}$$

SA — Surface Area [=] m²/cm³

PV — Pore Volume [=] cm³/g

ρ — Density [=] g/cm³

D — Average Pore Diameter [=] Å

For Support A

$$PV = 0.8931 \text{ cm}^3/\text{g}$$

$$\rho = 0.51 \text{ g/cm}^3$$

$$D = 70\text{Å}$$

which gives

$$SA = \frac{0.8931}{70} \bigg| \frac{0.51}{2.5 \times 10^{-5}} \cong 260 \text{ m}^2/\text{cm}^3$$

This value of surface area is more than 70% greater than the actual established value.

While this represents a maximum level of surface area for support A at the 70Å diameter level, it nonetheless indicates that improvements can be made on supports of this nature, towards the optimization of the pore diameter distribution.

With the ability to alter surface area characteristics of alumina-silica supports through such methods as thermal and steam treatment, further analysis of the type presented in this work would certainly be recommended.

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APPENDICES

APPENDIX A
RUN SUMMARIES

APPENDIX A

Nitrogen Concentration, Sulfur Concentration, and Density of Products for Impregnated Supports.

Support	Time on Catalyst minutes					Metal Loading g/m ²
	60	120	240	360	480	
A						3.68×10^{-4}
wt % N ₂	0.27	0.33	0.33	0.38	0.41	
wt % S	0.14	0.15	0.16	0.16	0.14	
density g/cm ³	0.93	0.93	0.93	0.93	0.93	
B						3.71×10^{-4}
wt % N ₂	0.29	0.32	0.35	0.37	0.37	
wt % S	0.18	0.16	0.17	0.15	0.16	
density g/cm ³	0.90	0.90	0.91	0.93	0.93	
C						3.78×10^{-4}
wt % N ₂	0.42	0.38	0.39	0.42	0.45	
wt % S	0.19	0.23	0.21	0.24	0.20	
density g/cm ³	0.91	0.93	0.93	0.93	0.94	
D						3.67×10^{-4}
wt % N ₂	0.36	0.37	0.41	0.42	0.44	
wt % S	0.21	0.23	0.22	0.21	0.21	
density g/cm ³	0.90	0.94	0.93	0.94	0.94	
E						3.73×10^{-4}
wt % N ₂	0.48	0.49	0.52	0.49	0.52	
wt % S	0.26	0.26	0.28	0.26	0.27	
density g/cm ³	0.96	0.95	0.96	0.96	0.96	
F						3.75×10^{-4}
wt % N ₂	0.47	0.51	0.49	0.53	0.53	
wt % S	0.33	0.28	0.25	0.26	0.25	
density g/cm ³	0.96	0.96	0.96	0.96	0.96	

Nitrogen Weight Percent of Products for Unimpregnated Supports.

Support	Time on Catalyst minutes						
	90	105	120	135	150	165	180
A	0.58	0.60	0.65	0.62	0.69	0.71	0.70
B	0.46	0.53	0.69	0.76	0.72	0.76	0.78
C	0.56	0.61	0.53	0.63	0.72	0.61	0.66
D	0.54	0.58	0.60	0.74	0.59	0.63	0.81
E	0.49	0.46	0.52	0.49	0.65	0.51	0.55
F	0.54	0.59	0.55	0.76	0.76	0.53	0.59

APPENDIX B

ERROR ANALYSIS

APPENDIX B

ERROR ANALYSIS

A limit of error, λ , is a quantity chosen sufficiently large so that the error of a measurement will never exceed it for all practical purposes. Limits of error, generally reported for well-tried procedures (such as the sulfur and nitrogen determinations in this study) are based on the standard error of the process but can also be set by judgment and experience [39].

When a physical value is derived from several different measurements, it is useful to estimate the limit of error of the value by a technique known as propagation of errors. The limit of error by an evaluated quantity F is defined as:

$$\lambda(F) = \frac{\partial F}{\partial x_1} \lambda(x_1) + \frac{\partial F}{\partial x_2} \lambda(x_2) + \dots$$

where:

$\lambda(F)$ Limit of error in F

$\lambda(x_1)$ Limit of error in variable x_1

Reported and estimated limits of error for quantities in this work are:

Weight Percent Nitrogen	- $\pm 0.02\%$	Reported
Weight Percent Sulfur	- $\pm 0.02\%$	Reported
Mettler Balance	- ± 0.1 mg	Reported
Micro Syringe	- ± 0.05 μ l	Estimate

Propagation of error for parameters used in this study:

1. Density measurements where:

$$\rho = \frac{A - B}{C - D} = \frac{x}{y}$$

with

A,B - Weight measurements $\lambda(A,B) = \pm 0.1 \text{ mg}$

C,D - Volume measurements $\lambda(C,D) = \pm 0.05 \mu\text{l}$

x - Difference in weight measurements

$$\lambda(x) = \pm 2(0.1 \text{ mg})$$

y - Difference in volume measurement

$$\lambda(y) = \pm 2(0.05 \mu\text{l})$$

$$\lambda(\rho) = \frac{1}{y} \lambda(x) + \frac{x}{y^2} \lambda(y)$$

Typical values for x and y are 9.5 mg and 10.0 μl , respectively.

$$\therefore \lambda(\rho) = \frac{\rho}{10.0 \mu\text{l}} \left| \frac{0.2 \text{ mg}}{10.0 \mu\text{l}} \right| + \frac{9.5 \text{ mg}}{(10.0)^2 \mu\text{l}^2} \left| \frac{0.5 \mu\text{l}}{(10.0)^2 \mu\text{l}^2} \right|$$

$$\lambda(\rho) \cong 0.02 \text{ g/cm}^3$$

2. Concentration measurements, where:

$$C = \frac{\rho}{100} \left| \frac{\text{wt \%}}{100} \right|$$

with ρ - density

wt - weight percent of sulfur or nitrogen

$$\lambda(C) = \frac{\lambda(\rho)}{100} \left| \frac{\text{wt \%}}{100} \right| + \frac{\lambda(\text{wt \%})}{100} \left| \frac{\rho}{100} \right|$$

The median weight percents encountered were 0.25% sulfur or nitrogen, and the highest observed density was 1.0 g/cm^3 .

∴

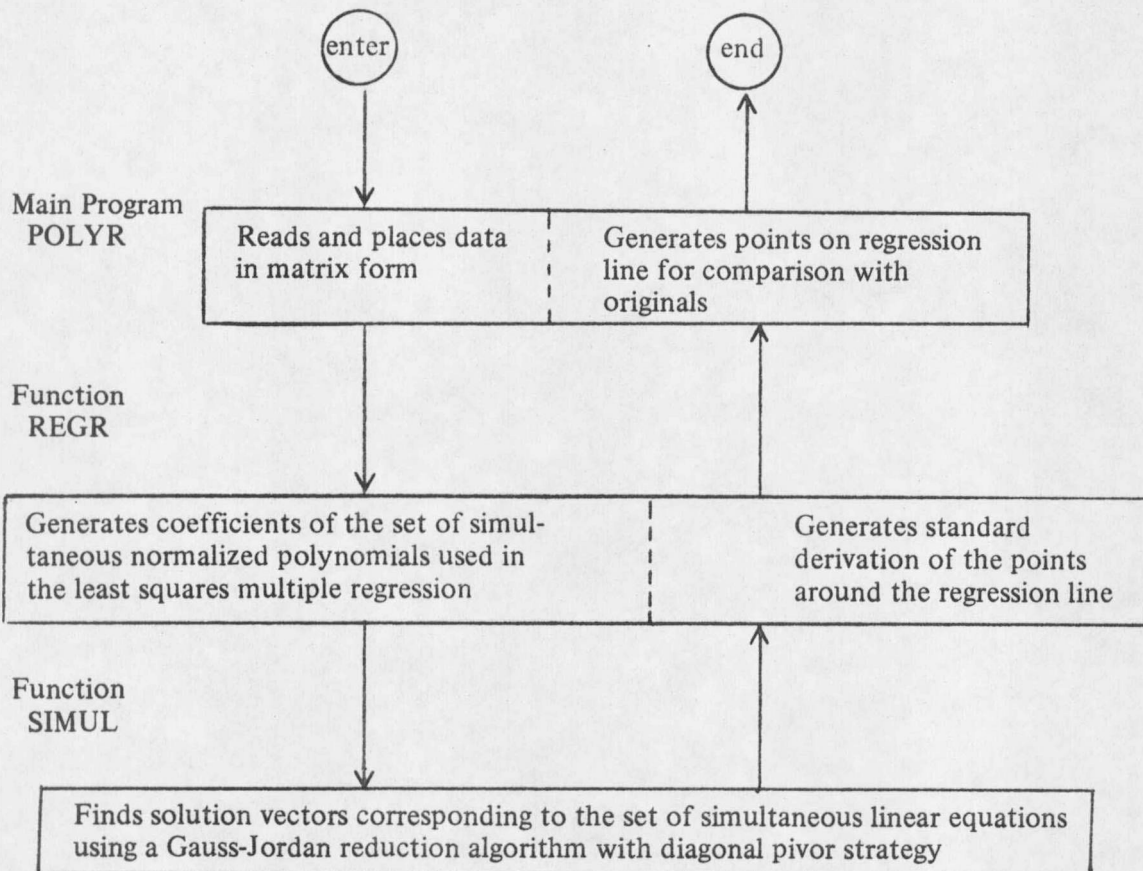
$$\lambda (C) = \frac{0.25 \text{ g}}{\text{g}} \left| \frac{0.02 \text{ g}}{\text{cm}^3} \right| \frac{1}{100} + \frac{1.0 \text{ g}}{\text{cm}^3} \left| \frac{0.02 \text{ g}}{\text{g}} \right| \frac{1}{100}$$

$$\lambda (C) \cong 0.00025 \text{ g/cm}^3$$

APPENDIX C

POLYNOMIAL REGRESSION PROGRAM

Logic of Regression Program Used in the Analysis of Impregnation Data.



Main Program — POLYR

C POLYR - MAIN PROGRAM

```

C
  IMPLICIT REAL*8 (A-H,O-Z)
  DIMENSION X(100),Y(100),YG(100),B(10)
1  CONTINUE
  INPUT M,MIN,MAX
  READ(1,100) (X(I),Y(I),I=1,M)
  WRITE(6,200) M,(X(I),Y(I),I=1,M)
  WRITE(6,201) MIN,MAX
  DO 4 N=MIN,MAX
  WRITE(6,202) N
  S=REGR(M,X,Y,N,A,B)
  IF (S.NE. 0.0) GO TO 2
  WRITE(6,203)
  GO TO 1
2  WRITE(6,204) S,A,(I,B(I),I=1,N)
  DO 3 I=1,M
  YG(I)=A
  DO 3 J=1,N
  YG(I)=YG(I)+B(J)*X(I)**J
3  CONTINUE
  WRITE(6,205) (X(I),Y(I),YG(I),I=1,M)
4  CONTINUE
100  FORMAT(2F13.3)
200  FORMAT(34H1 POLYNOMIAL REGRESSION, WITH M = ,I2,12H DATA POINTS
1 //8X, 5H X(I),8X, 5H Y(I)//(2F13.3))
201  FORMAT(59H0 THE LOWEST AND HIGHEST ORDER POLYNOMIALS TO BE TRIED
1ARE//6X, 7H MIN = ,I3,5X, 7H MAX = ,I3)
202  FORMAT(32H0 POLYNOMIAL REGRESSION OF ORDER/1H0, 5X, 7H N = , I3)
203  FORMAT (69H0 MATRIX C IS NEAR SINGULAR.  REGRESSION COEFFICIENTS
1 NOT DETERMINED)
204  FORMAT(1H0, 5X,5H S = ,F10.6/6X,5H A = ,F10.6//
1 (6X,3H B(,I2,4H) = ,F11.6))
205  FORMAT(48H0 GENERATED REGRESSION POINTS VS ORIGINAL POINTS //
1 8X,5H X(I),8X,5H Y(I),8X,6H YG(I)//(3F13.3))
  END

```

Function — REGR

```

FUNCTION REGR(M,X,Y,N,A,B)
IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 A,B,REGR,X,Y
DATA EPS/1.0E-20/
DIMENSION C(11,11),SX(20),SYX(10),CYX(10),
1 X(100),Y(100),B(10)
NTWO=2*N
NP1=N+1
SY=0.0
SYY=0.0
DO 1 I=1,N
  NP1=N+1
  SX(I)=0.0
  SYX(I)=0.0
1 CONTINUE
DO 3 I=1,M
  SY=SY+Y(I)
  SYY=SYY+Y(I)**2
  DUM=1.0
  DO 2 J=1,N
    DUM=DUM*X(I)
    SX(J)=SX(J)+DUM
    SYX(J)=SYX(J)+Y(I)*DUM
2 CONTINUE
DO 3 J=NP1,NTWO
  DUM=DUM*X(I)
  SX(J)=SX(J)+DUM
3 CONTINUE
FM=M
CYY=SYY-SY*SY/FM
DO 4 I=1,N
  CYX(I)=SYX(I)-SY*SX(I)/FM
  C(I,NP1)=CYX(I)
DO 4 J=1,N
  IPJ=I+J
  C(I,J)=SX(IPJ)-SX(I)*SX(J)/FM
4 CONTINUE
DET=SIMUL(N,C,B,EPS,1,11)
WRITE(6,200) DET
200 FORMAT(13H0 DET = ,E14.8)
IF(DET.NE. 0.0) GO TO 6
REGR=0.0
RETURN
6 CONTINUE
DUM=SY
TEMP=CYY
DO 7 I=1,N
  DUM=DUM-B(I)*SX(I)
  TEMP=TEMP-B(I)*CYX(I)
7 CONTINUE
A=DUM/FM
DENOM=M-N-1
S=DSQRT(TEMP/DENOM)
REGR=S
RETURN
END

```

Function — SIMUL

```

FUNCTION SIMUL(N,A,X,EPS,INDIC,NCR)
IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 A,X,EPS,SIMUL
DIMENSION IROW(50),JCOL(50),JORD(50),Y(50),A(NCR,NCR),X(N)
MAX=N
IF(INDIC .GE. 0) MAX=N+1
IF(N .LE. 50) GO TO 1
WRITE(6,200)
SIMUL=0.0
RETURN
1 CONTINUE
DETER=1.0
DO 8 K=1,N
  KM1=K-1
  PIVOT=0.0
  DO 4 I=1,N
    DO 4 J=1,N
      IF(K .EQ. 1) GO TO 3
      DO 2 ISCAN=1,KM1
        DO 2 JSCAN=1,KM1
          IF(I .EQ. IROW(ISCAN)) GO TO 4
          IF(J .EQ. JCOL(JSCAN)) GO TO 4
2 CONTINUE
3 IF(DABS(A(I,J)) .LE. DABS(PIVOT)) GO TO 4
  PIVOT=A(I,J)
  IROW(K)=I
  JCOL(K)=J
4 CONTINUE
  IF(DABS(PIVOT) .GT. EPS) GO TO 5
  SIMUL=0.0
  RETURN
5 CONTINUE
  IROWK=IROW(K)
  JCOLK=JCOL(K)
  DETER=DETER*PIVOT
  DO 6 J=1,MAX
    A(IROWK,J)=A(IROWK,J)/PIVOT
6 CONTINUE
  A(IROWK,JCOLK)=1.0/PIVOT
  DO 8 I=1,N
    AIJCK=A(I,JCOLK)
    IF(I .EQ. IROWK) GO TO 8

```

Function - SIMUL

```

      A(I,JCOLK)=-AIJCK/PIVOT
      DO 7 J=1,MAX
7      IF(J.NE. JCOLK) A(I,J)=A(I,J)-AIJCK*A(IROWK,J)
8      CONTINUE
      DO 9 I=1,N
      IROWI=IROW(I)
      JCOLI=JCOL(I)
      JORD(IROWI)=JCOLI
      IF(INDIC .GE. 0) X(JCOLI)=A(IROWI,MAX)
9      CONTINUE
      INTCH=0
      NM1=N-1
      DO 10 I=1,NM1
      IF1=I+1
      DO 10 J=IF1,N
      IF(JORD(J) .GE. JORD(I)) GO TO 10
      JTEMP=JORD(J)
      JORD(J)=JORD(I)
      JORD(I)=JTEMP
      INTCH=INTCH+1
10     CONTINUE
      IF(INTCH/2*2 .NE. INTCH) DETER=-DETER
      IF(INDIC .LE. 0) GO TO 11
      SIMUL=DETER
      RETURN
11     CONTINUE
      DO 13 J=1,N
      DO 12 I=1,N
      IROWI=IROW(I)
      JCOLI=JCOL(I)
12     Y(JCOLI)=A(IROWI,I)
      DO 13 I=1,N
13     A(I,J)=Y(I)
      DO 15 I=1,N
      DO 14 J=1,N
      IROWJ=IROW(J)
      JCOLJ=JCOL(J)
14     Y(IROWJ)=A(I,JCOLJ)
      DO 15 J=1,N
15     A(I,J)=Y(J)
      SIMUL=DETER
      RETURN
200    FORMAT(10HON TOO BIG)
      END

```

