



Catalytic hydrogenation of solvent refined coal
by Gary Richard Hass

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:

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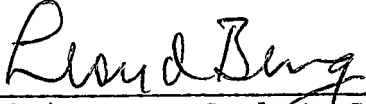
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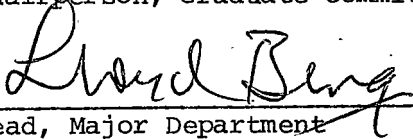
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ABSTRACT

Catalytic hydrogenation of Pittsburg and Midway Coal Mining Company's Solvent Refined Coal was accomplished using commercial hydrotreating catalysts and hydrotreating catalysts fabricated at Montana State University. Forty-four batch autoclave tests and thirty-nine trickle bed reactor tests were performed.

Liquid products from the catalyst tests were analyzed for sulfur content, nitrogen content, and distillate yields.

Harshaw HT-400 E 1/16" (Co-Mo) catalyst gave the best nitrogen removal at 450°C of all commercial catalysts tested in the trickle bed reactor. Cyanamid HDS-20A 1/16" Trilobe (Co-Mo) gave the best sulfur removal at 450°C of all catalysts tested in the trickle bed reactor. MSU STK-5-2-2-1.5E (Ni-Co-Mo) gave the best nitrogen removal at 450°C of all catalysts tested. MSU STK-5-2-6-1.5E (Ni-Co-Mo) gave the best sulfur removal at 450°C of all catalysts tested.

A metal loading study was performed to determine the effects of nickel oxide, cobalt oxide, and molybdenum trioxide concentrations on heteroatom removal. Increased molybdenum trioxide concentration significantly improved nitrogen removal. Increased nickel oxide and cobalt oxide concentrations also improved nitrogen removal.

INTRODUCTION AND BACKGROUND

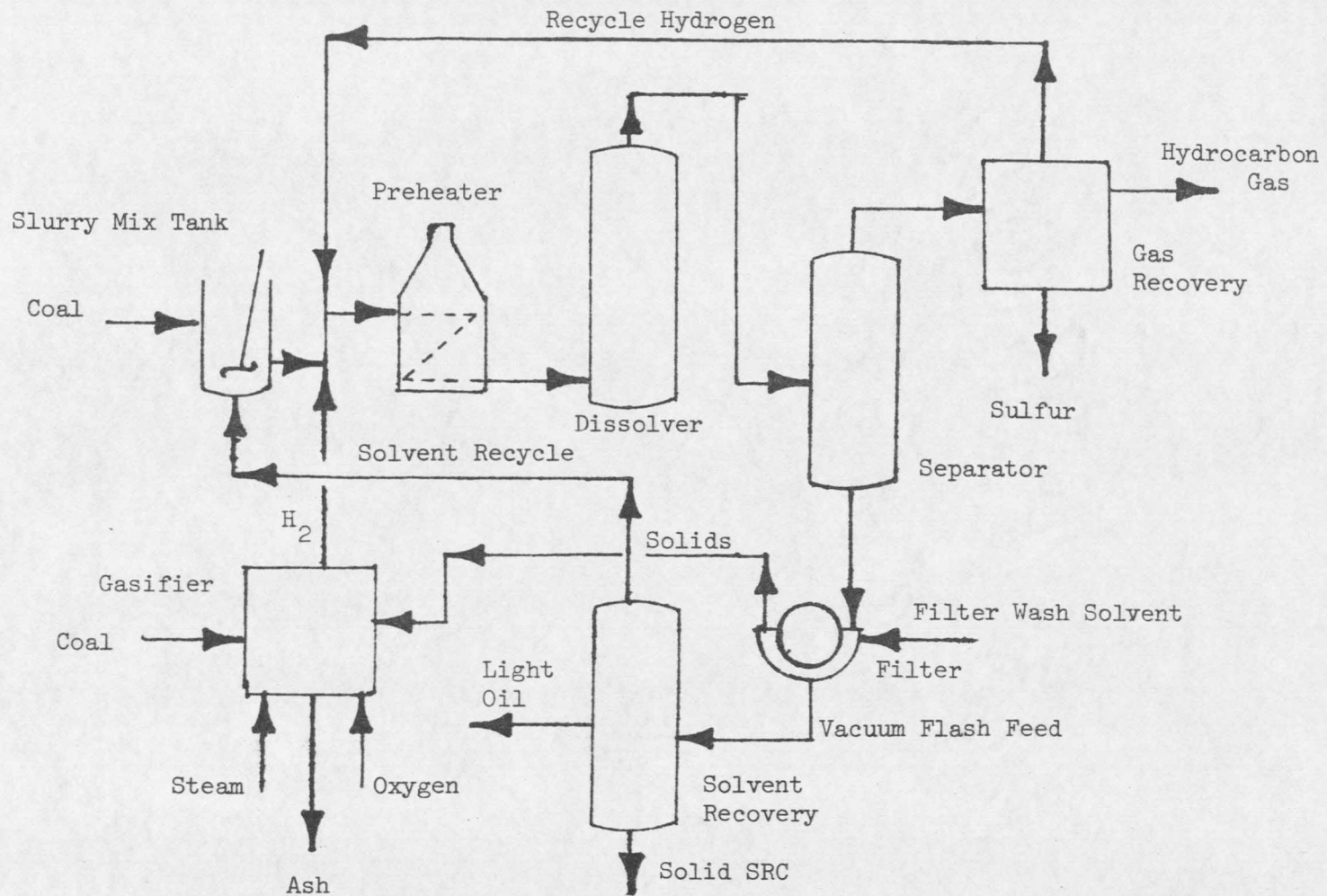
The growing shortage and increased costs of crude oil and natural gas coupled with increased demand for energy in our country has launched an intense effort to find alternative energy sources. Of the many proposed solutions to our energy crisis, coal seems to have the most promising immediate value. Of the 780 billion tons of coal recoverable from reserves determined by mapping and exploration, 226 billion tons are in relatively thick beds and under less than 1000 feet of overburden (1). These deposits are mineable at or near present costs. The American Gas Association reports that there is sufficient coal with available water to support 175 synthetic gas plants of 250 million ft³/day capacity (1,2). A million tons of coal per day could yield 10% of the current daily U.S. needs at 50% conversion to synthetic crude (1).

There are three major driving forces for the production of synthetic fuels. First, because of the diminishing supply of natural gas, the difficulty in shipping natural gas from abroad, and the large costs invested in existing pipeline systems mean gasified coal could supply much needed pipeline quality gas. Secondly, coal can be used for steam and electricity generation. Thirdly, because of limited supplies of crude oil and the glaring fact that the U.S. is overwhelmingly dependent on gasoline- and diesel-powered vehicles means liquified coal products could help as transportation fuels (3).

Coal liquefaction processes do have their drawbacks, however, including tremendous capital investment requirements, water availability, and social and environmental problems (4). Coal liquefaction processes for the production of synthetic crudes are varied depending upon the quality or rank of the coal to be processed. U.S. coals range in increasing carbon content from lignite, through sub-bituminous and bituminous, to anthracite, each of which has unique chemical and physical properties. Coal liquefaction processes include pyrolysis, indirect hydrogenation, direct hydrogenation, and solvent extraction. Pyrolysis (destructive distillation) consists of heating a pulverized coal at successively higher temperatures for the production of coke, coal gas, liquids, tars, and ammonia. In principle, pyrolysis is one of the simplest methods. Examples of recent pyrolysis processes are the FMC COED Process (5,6), Oil Shale Corporation's TOSCOAL Process (7), and Garret Research's Pyrolysis Process (8). Indirect hydrogenation of coal is exemplified by the Fischer-Tropsch synthesis. In 1933, Franz Fischer and Hans Tropsch showed that in the presence of certain catalysts, carbon monoxide is hydrogenated to aliphatic hydrocarbons. Current indirect hydrogenation processes are operated by the South African Coal, Oil and Gas Corporation (SASOL) (9), and Fluor Corporation (10). The direct hydrogenation process was developed in 1913 by Friedrich Berguis. Direct hydrogenation involves the reaction of coal slurried in a recycle oil with hydrogen gas and a

catalyst either in a fixed bed or ebullating bed configuration. Current processes being operated are Exxon's donor solvent process (11,12), Hydrocarbon Research, Inc.'s H-Coal process (13,14,15) and the Bureau of Mines Synthoil Process (16). Solvent extraction processes are really a modified direct hydrogenation for the production of synthetic fuels. A high boiling donor or non-donor solvent and hydrogen are used to dissolve coal at high temperature and pressure. This solution can then be filtered thus removing large amounts of sulfur and ash. Current solvent extraction processes in operation are Pittsburg and Midway Coal Mining Company's Solvent Refined Coal (SRC) process (11,17,18,19) and Consolidation Coal Company's CSF process (11,20,21,22).

Of major concern to this thesis work is the Solvent Refined Coal (SRC) process operated by Pittsburg and Midway Coal Mining Company. A fifty ton/day pilot plant was operated at Fort Lewis, Washington, in the SRC I mode shown in Figure I. The coal (Kentucky #9) is mixed with a solvent in a slurry tank. This slurry is mixed with hydrogen, preheated and fed to a high pressure dissolver. Dissolver effluent passes to a gas-liquid separator. The off-gas from the separator is hydrotreated and recovered hydrogen is recycled. The liquid from the separator is filtered removing much of the sulfur and ash. The filtrate is fed to the solvent recovery steps producing a solid "solvent refined coal." In principle, filter cake is fed to a gasifier for



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FIGURE 1. SRC I Process Schematic

production of in-plant fuel gas and hydrogen (23,24). More recently, the Pittsburg and Midway pilot plant has been modified to produce a liquid product in the SRC II mode. Major changes include using the dissolver product as the slurry solvent which is mixed with feed coal and the concentrating of mineral ash in the dissolver stream which is believed favorable to the liquefaction (24).

The SRC process should not be defined as a single product process aimed only at producing a clean solid boiler fuel. Table I shows typical product streams on a weight basis. Table II shows that gas and liquid yields are far from insignificant (25).

Table I. Typical SRC Process Yields

Coal Properties, wt%	
Organic sulfur	1.7%
Pyritic sulfur	1.2%
Ash	11.1%
Product wt% MAF coal feed	
Solvent Refined Coal	63*
Undissolved coal	7
C ₁ - C ₄ gas	6
C ₅ - 350°F	6
350-750°F Distillate	10
H ₂ S	2
CO - CO ₂	2
Water	6

*Solvent Refined Coal Properties: Sulfur content < .9 wt%; Ash content < .1%.

Table II. SRC Process Gas and Liquid Yields*

C ₁ - C ₄ gas, scf [†]	3130
CH ₄ gas	2100
C ₅ - 350°F gal	32
bbl	0.762
350-750°F distillate, gal	38
bbl	0.904
Total liquid, gal	70
bbl	1.666

*Per ton solvent refined coal

†Approximate analysis of C₁ - C₄ gas cut:

	<u>Vol %</u>	<u>BTU value/ft³</u>
CH ₄	67.0	680
C ₂ H ₆	19.3	340
C ₃ H ₈	10.0	260
C ₄ H ₁₀	3.7	120
	<u>100.0</u>	<u>1400</u>

The major objective of this thesis research was to catalytically hydrotreat and hydrocrack products from the SRC I process.

Chemistry of Catalytic Hydrotreating

Catalytic hydrotreating of synthetic crudes consists of two main parts: the hydrogenation of unsaturated hydrocarbons, and the hydrogenolysis of heteromolecules. Depending upon the final use of the syncrude products, various degrees of hydrotreating are acceptable.

If liquid SRC products are used as boiler fuels the requirements would be a hydrogen to carbon mole ratio about 1.6; and nitrogen, sulfur, and mineral levels below .5 wt %. The sulfur level is determined from the current EPA standards. Products from SRC can easily meet the sulfur and mineral standard, therefore the major steps in producing a liquid boiler fuel are to reduce nitrogen levels below 0.5 wt % and to increase the hydrogen content of the fuel. Some emphasis must be placed on hydrosulfurization because of possible future changes in EPA standards (26). However, if liquid SRC products are to be used as a catalytic cracker feedstock, the nitrogen requirements are more stringent. Catalysts used in catalytic cracking operations provide acid sites which facilitate cracking of hydrocarbon feeds. These acid sites are neutralized by nitrogen which acts as a poison. Deactivation of the catalysts progresses in direct proportion to the duration of operation and in proportion to the amount of nitrogen in the cat cracker feed. In cat cracking operations it is common practice to maintain activity of the catalyst at desired yield levels by a progressive increase in the severity of the reaction conditions to the extent that this is economically feasible, after which time the catalyst is replaced by fresh or regenerated catalyst. The preferred nitrogen level for catalytic cracker feed is in the range of 100-400 ppm (27). Various hydrocracking processes can tolerate more nitrogen in the feedstock. Examples of these processes are Standard Oil of

Indiana's Ultracracking process and Union Oil's Unicracking process which can tolerate nitrogen concentrations up to .3 wt % (28,29).

Petroleum hydrotreating processes use efficient technologies and are governed by fairly well established kinetics. The most important factor for further progress in this field is the catalyst. The choice of hydrotreating catalyst components depends upon the type of reaction they are meant to activate, i.e., pure hydrogenation, heteromolecule hydrogenolysis, or isomerization. It must be kept in mind that these reactions must be carried out in the presence of large amounts of sulfur containing hydrogen (30).

Specific reactions to be carried out by a hydrotreating catalyst are: (a) Polyaromatic hydrogenation in which polyaromatics are hydrogenated to monoaromatics or saturates which are easier to crack and give less tendency toward coke formation; (b) denitrogenation in which nitrogen compounds are removed thus preventing inhibition of the acid function of cracking catalysts resulting in higher conversion and less severe operating conditions in cracker units; (c) desulfurization providing lower sulfur content in cat cracker gasoline which allows for better lead susceptibility; and (d) heavy metals removal--catalysts act as absorbents for heavy metals which are severe poisons for cracking catalysts and usually limit the end boiling point in cracker feeds (31). Data in the literature show that these reactions can be performed satisfactorily by the use of catalysts made of metallic

sulfides from Group VIB and VIII of the Periodic Table, usually produced by the sulfiding of corresponding metal oxides deposited on a refractory oxide (SiO_2 , Al_2O_3 or $\text{SiO}_2\text{-Al}_2\text{O}_3$) (30).

Solvent Refined Coal has a high asphaltene content (32). In synthetic crude hydrotreating, one of the main problems with catalyst activity is the rapid initial deactivation due to the deposition of carbonaceous materials (33). This is accompanied by the deposition of mineral matter, which continues throughout the reaction. The relationship between the structure of the syncrude and initial carbon deposition is not clear. It is believed to be due to large asphaltene molecules present in syncrude. The average size of these molecules, 40 to 50 Å, is in the range of the diameters of the micropores in conventional alumina supported catalysts. This leads to plugging of small pores which represent a large fraction of the total catalyst surface area. Optimization of the pore size distribution becomes very significant. Similarly, the mineral content of SRC causes problems. The analysis of SRC performed by Mobil Oil Company show high iron (140 ppm), titanium (130 ppm), and sodium (100 ppm) content. Total mineral content can be as high as .25 wt %. This is a large amount of ash. For instance, a pilot plant processes 100 tons of SRC per day would have to handle up to 500 pounds/day ash. This could have considerable effect on catalyst activity. The presence of large molecules causes the additional problem of pore diffusion limitations.

Furthermore, the three phases present lead to film diffusion limitations in the reactor fluid stream (32,34).

Hydrotreating studies performed in microreactors using small concentrations of model compounds such as benzothiophene, acridine, pyridine, and quinoline have given some insight into the mechanism by which sulfur and nitrogen are removed from feedstocks. In studies of the desulfurization of dibenzothiophene and methyl-substituted dibenzothiophenes, data show good fits with first order kinetics with respect to the sulfur containing compound. The mechanism seems to have three steps: (a) Absorption of the reactant molecules on the catalyst surface presumably as the sulfur atom interacts with an anion vacancy; (b) hydrogen donation to the carbon atom contiguous to the sulfur with breaking of the carbon-sulfur bonds (c) desorption of the sulfur by addition of another pair of hydrogen atoms. Methyl substitution near the sulfur atom in dibenzothiophene greatly reduce the reactivity, believed to be caused by steric effects which restrict the interaction of the sulfur atom and the surface of the catalyst (35-42).

In studies involving denitrogenation of acridine, data show that before the nitrogen atom is removed, large amounts of ring hydrogenation takes place. The breaking of the carbon-nitrogen bond has been shown to be the rate determining step (41). This has also been shown to be the case with single ring heterocyclics such as pyridine (42).

Other hydrotreating studies yield data on the interactions of metal sulfides and supports. For a series of tests using pairs of metal sulfides (Co-Mo, Ni-Mo, Co-W, Ni-W) impregnated on alumina and silica supports, maximum hydrogenation activity was obtained using a ratio of Group VIII metal/Group VIB metal in the range of .25 to .33. For the desulfurization of thiophene, which involves simultaneous hydrogenating and hydrogenolysis activity of the metallic sulfides coupled with the acid function of the support, the same metal ratios provided maximum activity. However, the differences in desulfurization activity is less pronounced for metals impregnated on alumina than for those impregnated on silica. This means the acidity of alumina is greater than that of silica. Different deposits of metal on supports also affect the overall acidity of the catalyst. Silica-alumina supports show even more acidity than do pure alumina supports. Nickel oxides deposited on silica alumina reduce the overall acidity of the catalyst. Nickel-tungsten deposits also reduce the overall acidity, whereas molybdenum oxides increase the overall acidity. Metallic sulfides improve the stability of the acid function of the catalyst by improving hydrogenation which eliminates certain unstable compounds which by polymerization on acid sites could cause coke formation. By careful choice of combinations of metals and supports, these catalyst types can lend themselves to varied hydrotreatment processes (30).

Operational Considerations of Trickle Bed Reactors

Trickle bed reactors are fixed bed reactors where the feed consists of both a gas and a liquid. The liquid flows down over the bed of catalyst and the gas either flows concurrent or countercurrent to the liquid. Cocurrent operations allows for better distribution of the liquid over the catalyst and allows for higher liquid flow rates without flooding problems. Commercial trickle bed reactors have been in operation for the last twenty-five years for hydrodesulfurization, hydrocracking, and hydrotreating high boiling petroleum feeds. Reaction conditions allow hydrocarbon feeds to react as a vapor-liquid mixture at liquid hourly space velocities (LHSV - volume of liquid feed/(volume of catalyst x hr)) in the range of .5 to 10. Direct and capital costs of trickle bed reactors are claimed to be twenty percent lower than hydrotreating units that are operated completely in the vapor phase. Also, high boiling feedstocks can be treated in trickle bed reactors that would undergo too excessive cracking if treated entirely in the vapor phase.

The principal alternative to the trickle bed reactor is the fluidized bed reactor in which the catalyst is in motion. Fluidized bed reactors have the advantages of easier temperature control, easy heat recovery, adaptability to either batch or flow processing, easy catalyst removal and regeneration, and ability to operate at high

catalyst effectiveness factors because of the use of finely powdered catalyst. Disadvantages of a fluidized bed reactor include a residence time distribution that approaches that of a continuous stirred tank reactor (CSTR) which makes it difficult to obtain high conversion; the high ratio of liquid to solid which allows homogeneous side reactions to become important, and the high cost of catalyst removal equipment.

In a trickle bed reactor the catalyst bed is fixed, the flow pattern is closer to plug flow, and the liquid to catalyst ratio is much lower thus limiting side reactions. If heat effects are substantial, they can be controlled by recycle of the product liquids or by varying the gas flow rates. Recycle, however, may not be feasible if the product is unstable at reaction conditions or if high conversion is desired, since high recycle rates make the system approach that of a CSTR. When complete vapor phase operation is feasible, trickle bed operation can save energy costs of feedstock vaporization.

Trickle bed reactors in the petroleum industry are operated over a wide variety of conditions depending on the properties of the feedstock and the nature of the reaction. Typically less reactive, higher boiling, viscous feeds are operated at low liquid flow rates. Representative superficial velocities are 10 to 100 ft/hr for heavy gas oils or residual fractions and 100 to 300 ft/hr for naphthas, calculated assuming the feed is all liquid. Hydrogen flow to liquid flow is commonly expressed (at standard conditions) as the volume of

hydrogen per barrel of feed. Representative values are 2000 to 3000 scf/bbl for desulfurization of heavy gas oils, 5000 scf/bbl for desulfurization of resids, and 5000 to 10,000 scf/bbl for a hydrocracker. Mild hydrofinishing reactors may use considerably less hydrogen. Representative operating condition for commercial reactors are a pressure range of 500-2500 psig; temperature range from 345°C to 425°C, and catalyst particle sizes from 1/32 inch to 1/8 inch. Present day units are multiple bed systems three to six meters high and up to two meters in diameter. In multiple bed systems, hydrogen is injected between beds for temperature control. The quantity of hydrogen used far exceeds stoichiometric proportions and is usually determined by requirements of temperature control, better liquid distribution, or to extend catalyst life. Bed height is determined by the need for certain gas or liquid distribution or by the crush strength of the catalyst. In both chemical and petroleum processing, reactors are designed to run essentially adiabatically. Of particular interest to this research is that bench scale reactors can be operated at the same liquid hourly space velocities that are used commercially. The fact that conditions for commercial and bench scale studies operate under different hydrodynamic flow conditions means contacting efficiencies might be somewhat different. Most laboratory studies involving highly exothermic reactions and low liquid flow rates may exhibit significant heat effects which can cause temperature instability and vaporization

which may cause only partial wetting of the catalyst. Another problem encountered with syncrude processing is that the number of compounds of varying reactivities present in coal liquids leads one to be fairly arbitrary in interpreting kinetic data (43,44,45,46,47).

In its physical form the trickle bed reactor is hydrodynamically similar to the absorption tower and much information on matters such as flow patterns, pressure drop, holdup, and liquid distribution can be obtained from studies directed towards absorbers. Absorption occurs entirely between a gas and a liquid and the function of the solid is to provide good contacting. In comparing packed bed absorbers and trickle bed reactors several things should be kept in mind.

1. Absorption towers are operated at higher gas and liquid flow rates, which approach flooding.
2. In order to achieve high flow rates absorption towers use large packing materials such as Berl saddles, whereas trickle bed catalysts are small extrusions, spheres, or pellets.
3. In bench scale absorption towers a considerable portion of the absorption may occur in the liquid trickling down the wall. In a trickle bed reactor the wall contributes nothing to the reaction, but wall flow is a means of bypass channeling.

4. Gas flow is usually cocurrent for trickle bed reaction and countercurrent for absorbers.
5. Catalyst particles are usually highly porous whereas absorber packings are nonporous. Liquid held in catalyst pores may be a major fraction of the holdup which give very different wetting characteristics for trickle bed reactors.

At sufficiently low liquid and gas flow rates liquid trickles over the catalyst in rivulets and the gas flows continuously through the voids. As gas and/or liquid rates are increased one encounters rippling, slugging, or pulsing flow characteristic of commercial trickle bed reactors. At high liquid flow rates and low gas rates, the liquid phase becomes continuous and the gas phase passes in the form of bubbles (43,44,48,49).

One topic that is still under discussion is the effect of the ratios of reactor diameter to catalyst particle diameter. Porter et al. (50,51,52) reports that in bench scale trickle bed reactors, liquid migrates to the wall and that the fraction flowing down the wall increases to a steady state value at about one foot down the bed. The steady state wall fraction corresponds to as much as 30 to 60% of total liquid at ratios of reactor diameter to particle diameter of as high as 10, and drops at higher ratios. This thesis used a ratio between 5.65 (1/8" catalyst particles) and 11.3 (1/16" catalyst particles).

Also important is particle shape. Acres observed that cylindrical catalyst particles tend to pack together end to end causing liquid to channel through the bed and spherical catalyst particles tend to channel liquid to the wall (53).

In all heterogeneous catalytic reactions, the understanding of transport phenomena become important. To insure that data obtained from trickle bed reactors is a true measure of catalyst performance a conscious effort to eliminate mass and heat transfer effects is needed. There are three domains in which concentration and temperature gradients should be minimized. These are intraparticle--within individual catalyst particles; interphase--between the external surface of the catalyst particles and the fluids adjacent to them; and interparticle between local fluid regions (43,44,45,54,55).

For intraparticle effects the general solution is to test catalysts at their highest value of effectiveness factor. Effectiveness factor is defined as the ratio of the actual rate of reaction to that which would occur if the temperature and concentration were constant throughout the catalyst particle. Unfortunately, to calculate the effectiveness factor directly, a knowledge of the reaction kinetics and intrinsic rate constants is required. This becomes difficult with a complex feedstock such as a synthetic crude. Some basic considerations are helpful. Effectiveness factors become inversely proportional to the characteristic dimension of the catalyst. Therefore,

