The hydrogenation of a Montana sub-bituminous coal using a catalyst-acid system
by David Paul Alzheimer

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:
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The semi—continuous reactor in this study was a two foot length of one inch schedule 80 Inconel Alloy 600 pipe, which was operated between 300°C and 600°C, and a maximum operating pressure of 1500 psi.

The catalysts were impregnated on 16—35 mesh coal in the following concentrations (measured as weight % metal on the coal): 1.9% Nickel, 2.9% Tin (Stannic), 13.2% Tin (Stannous). The analyses which were made included a proximate coal analysis and the conversion of the MAF coal to benzene-soluble material.

The results showed that increasing pressure or temperature increased conversion. At all temperatures and pressures studied, conversions of catalytic coal were better than conversions using non-impregnated coal. Conversions using stannous chloride as a catalyst were superior to both nickel chloride and stannic chloride. The highest conversion reached was 76.2% (MAF) at 600°C, 1000 psi and with the HCl-H2 feed gas.

At lower temperatures, the addition of HCl to the feed gas showed improvements in conversions but had little effect at higher temperatures.

In general, the addition of a vehicle decreased the conversions of catalyst impregnated coal.

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by

DAVID PAUL ALZHEIMER

A thesis submitted in partial fulfillment
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ABSTRACT

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INTRODUCTION

A. CURRENT PETROLEUM RESERVES OF THE UNITED STATES

With the depletion of natural oil reserves, finding a dependable source of liquid fuel becomes a problem of national interest. Research directed towards the conversion of coal to liquid products has received increasing interest in recent years. This has been initiated by a sharp decline in known reserves of petroleum and natural gas in the United States, as measured in terms of the number of years supply which these reserves represent.(5,7)

Increasing difficulty in locating sufficient petroleum reserves has resulted in an appreciable increase in exploration costs. The location of these reserves at greater depths or offshore on the continental shelf will result in high production costs as the reserves are exploited.

The current unease in foreign relations and an unfavorable balance of trade make it undesirable to depend on increased importation of oil. Therefore, it appears necessary to satisfy a significant portion of the growing market for petroleum derived fuels with products derived from coal. (14)

The search for new liquid fuels invariably leads to coal because immense coal reserves are available. Published estimates indicate that the coal reserves of the United States are sufficient to supply all the nation's fuel needs for almost 3000 years. (16)

B. COAL STRUCTURE AND CONVERSION TO USEFUL PRODUCTS

Coal is a high molecular-weight solid with a high ash content. Its structure is very complex and consists of many unsaturated ring compounds with alkyl side chains. (Unsaturated rings are those which contain double bonds, example: ). Petroleum contains three to four times more chemically bound hydrogen (less unsaturation) than coal. Consequently, to convert coal to oil, it is necessary to increase the hydrogen content of coal by a process known as "hydrogenation". Hydrogenation is the addition of hydrogen to unsaturated molecules ($CH_2=CH_2 + H_2 \rightarrow CH_3-CH_3$). This eliminates the double bond, increasing saturation, which is a step closer to the chemical structure of petroleum.

C. GENERAL HYDROGENATION MECHANISM

A lack of information on the chemical constitution and structure of coal handicaps the study of reactions occurring in its hydrogenation. It is currently believed that the hydrogenation process is accompanied by the decomposition (cracking) of high molecular-weight compounds to smaller fragments. (15) Without hydrogen or a catalyst, these fragments will polymerize, forming a solid residue. In the presence of high hydrogen pressure and a catalyst, these fragments are hydrogenated forming benzene soluble components. Of the benzene soluble components, there exist two types of substances:

(1) OILS - the liquid product soluble in benzene and also in hexane or pentane.

(2) ASPHALTENES - the liquid product soluble in benzene but insoluble in hexane or pentane. These compounds are generally of polynuclear aromatic structure.

The production of asphaltenes is undesirable, since further hydrogenation of these aromatics is necessary to reach a desired product. Hydrogenation of asphaltenes is an extremely difficult step, requiring both high temperature and pressure. Any hydrogenation method preventing the production of asphaltenes would be very helpful.

D. EARLY DEVELOPED COAL HYDROGENATION PROCESS

The hydrogenation of coal has been studied for many years. From early studies made by Bergius, and modified by I. G. Farben (a German dye trust), a process was developed to make oil from coal. (1) It is called the Bergius Process and involves two basic steps; the first step is liquid-phase hydrogenation and the second step is vapor-phase hydrogenation.

In liquid-phase hydrogenation, coal and a catalyst are added to a pasting oil, forming a slurry. The slurry passes into a converter where it is contacted with hydrogen for one hour at 450°C and 10,000 psi. The coal is converted mainly to a middle fraction oil, which boils below 325°C. The heavy oil and residue are separated and the heavy oil is recycled as pasting oil. The middle oil is sent to the vapor-phase hydrogenation reactor. It is passed over a fixed catalyst bed (nickel, tungsten) yielding products of gasoline and aviation fuel quality.

During World War II, Germany had twelve similar coal hydrogenation plants in operation. However, after 1953, there was not a single Bergius plant being used. The main reason being that oil and natural gas were meeting all necessary demands at less cost. The high pressure of 10,000 psi and long residence time required were probably the biggest obstacles preventing its use. The extreme conditions demand expensive equipment and material costs, decreasing its economical attractiveness.

In order to compete with the price of petroleum products, the manufacturing costs of producing gasoline from coal must be reduced. Generally, hydrogenation at lower temperatures reduces the formation of gaseous hydrocarbons, but increases asphaltene production. At lower pressures, the cost of power and installation is reduced. If a hydrogenation catalyst active at low temperature and pressure were developed, the cost of gasoline production could be decreased substantially.

An ideal process to produce gasoline from coal would be direct degradation of the high molecular weight components to desired products without producing intermediate asphaltenes. Thus the raw material would be fully utilized, and the waste would be minimal. To approach this ideal degradation, active selective catalysts for cracking functional groups should be developed, and the degradation should be carried out at low pressure. (2) High hydrogen pressure in the primary hydrogenation of coal is not required thermodynamically but is important

because of the kinetics of reaction.

E. RECENT CATALYTIC DEVELOPMENTS

Any new effective coal conversion process will probably involve the use of a highly active catalyst. The following significant developments in the field of catalysis look very encouraging for hydrogenation processes (5):

1. Complexes of transition metals have shown activity at relatively low temperature (200°C). For example, both cobalt carbonyl and a mixture of cobalt, molybdenum, and aluminum oxides ($Co-Mo-Al_2O_3$) have shown to be very active in the hydrogenation of specific aromatic compounds.
2. Alkali metals such as sodium, lithium, and rubidium, can act as direct hydrogenation catalysts with hydrogen or amines and appear to be active in catalytic electrochemical reduction processes.
3. The solution of coal by extraction using organic "hydrogen donor" solvents, has been studied for years. A mixture of tetralin, phenol, and napthalene seems to be the most satisfactory solvent for bituminous coal. Tetralin is a hydroaromatic "donor", capable of transferring hydrogen to the coal. The function of the phenol is apparently to assist in pulling the hydrogenated coal into solution. This area of study needs more investigation to find a mechanism where the coal molecules,

hydrogen donor, and catalyst can all interact together.

4. Finally, the use of halide catalysts, show promise in the production of oil from coal in only one step. Using high concentrations of metal chloride catalysts, almost all of the coal can be converted to benzene solubles, with asphaltene conversion (the most difficult step) nearly complete.

The basis of this investigation utilizes the high activity of metal chloride catalysts in the hydrogenation of coal to obtain products of low asphaltene content. In this study, metal chloride catalysts and gaseous hydrochloric acid are used. The principle catalytic activity for the cracking of high molecular-weight compounds is that of the "acid", which is maintained by the hydrochloric acid. The metal acts as a hydrogenation catalyst, to stabilize the "cracked" components, which were fragmented through catalysis by the acid. It is hypothesized that this type of system will result in high conversion of coal to liquid and gaseous products.

RESEARCH OBJECTIVES

The primary objective of the investigation was to examine the effects of temperature, pressure, types of catalysts and types of vehicles on the conversion of a Montana sub-bituminous coal. Because coal has such a complex structure, there is no one reaction mechanism describing the parameters of conversion to products. The effects of catalysis are also unpredictable and therefore empirical tests are required to determine effective reaction conditions.

MATERIALS, EQUIPMENT & PROCEDURE

A. PREPARATION AND ANALYSIS OF COAL

The coal used in this study was a Rosebud bed sub-bituminous mined near Colstrip, Montana. It was supplied by Western Energy and was shipped in metal drums. To prevent water loss, the inside of the drum was lined with plastic. Upon its receipt, a large sample was drawn randomly from the drums. The sample was crushed to 16-35 mesh using a mortar and pestle. Preliminary research indicated that catalytic conversions showed promise with coal of this size. (8) The coal was then placed into bottles and sealed to prevent any further loss of water or alteration in composition.

Conversions were determined on a moisture-ash-free (MAF) basis, requiring an analysis of the moisture and ash content of the coal. The water analysis was performed using the apparatus shown in Figure 1. Toluene and a weighed amount of coal were added to the boiling flask. The rising toluene and water vapor were condensed and collected into a graduated receiving arm. Since water has a higher density than toluene, it settled to the bottom of the arm. From the volume of water present in the arm, the amount of water per gram of coal was easily determined.

The ash content was determined by heating a weighed sample of coal in a covered procelain crucible with a bunsen burner. After the volatile components were driven off, the lid was removed and the fixed carbon burned off. The ash remaining was weighed and a simple calculation was made.

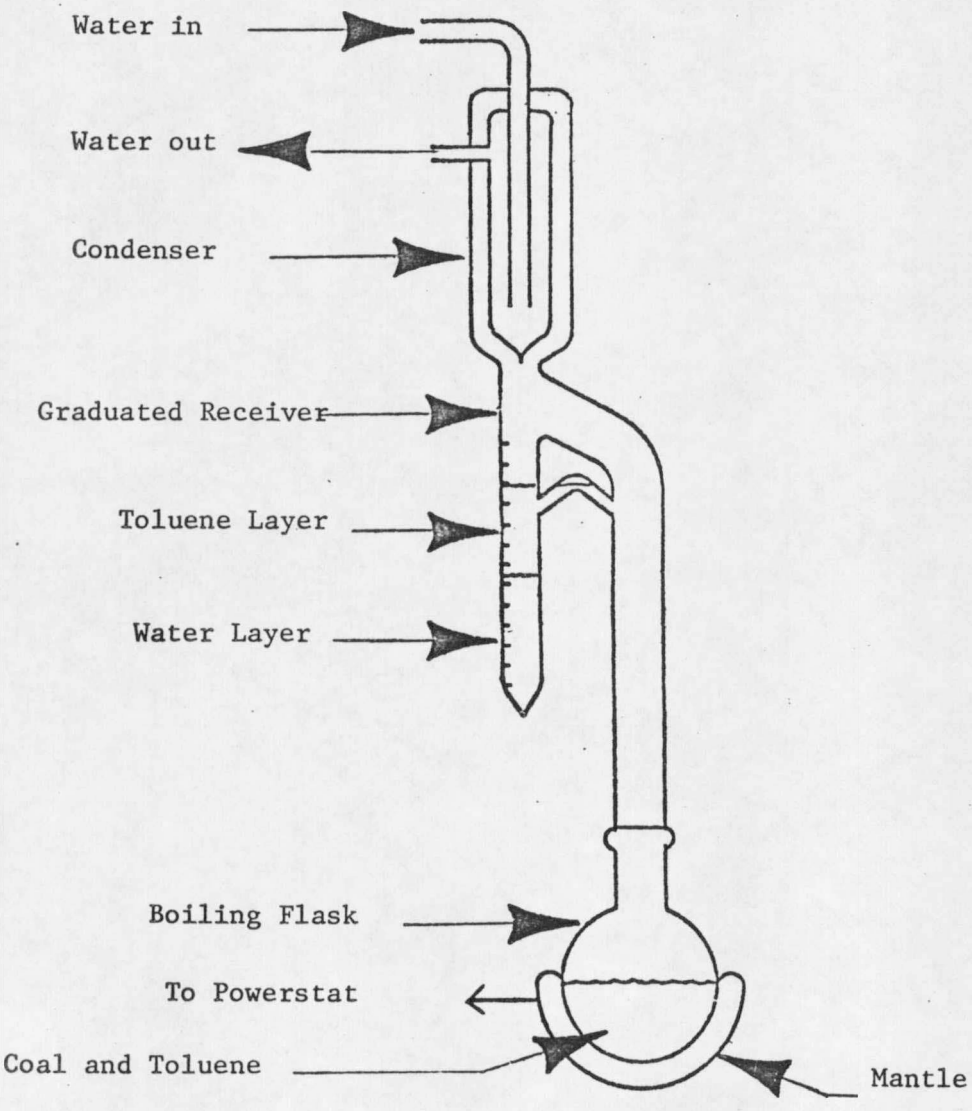

FIGURE 1. Apparatus Used to Determine Water Content of the Coal

B. CATALYST PREPARATION AND COAL IMPREGNATION

The three technical grade catalysts examined were nickel chloride, stannic chloride, and stannous chloride. To compare the activities of the catalysts tested, solutions containing equivalent weights of the respective metals were made. Fifty grams of coal were dried at 100°C for 36 hours and placed into the catalyst-water solution. After soaking for 24 hours, the coal was filtered from the solution, dried and reweighed. The weight gained by the coal was used to determine the percentage of catalyst impregnated on the coal.

C. EQUIPMENT AND PROCEDURES FOR PERFORMING TEST RUNS

The reactor used in this study was a one inch, schedule 80, two foot length of Inconel Alloy 600 pipe as shown in Figure 2. The inlet section was fitted with a high pressure Type 316 stainless steel T and appropriate swagelock tubing fittings. The inside upper portion of the reactor was machined slightly to accomodate an alundum thimble, which contained the reactor charge. Since the remaining ridge supports the thimble, its height in the reactor was determined by the length of pipe machined. A thermowell made of 1/4 inch Inconel Alloy 600 tubing extended from the reactor outlet to the bottom of the thimble. Temperature was detected by a chromel-alumel thermocouple and was recorded on a chart recorder. The reactor temperature was regulated by a 110 volt powerstat controlling a 5 ampere, Hoskins furnace. Pressure within the reactor

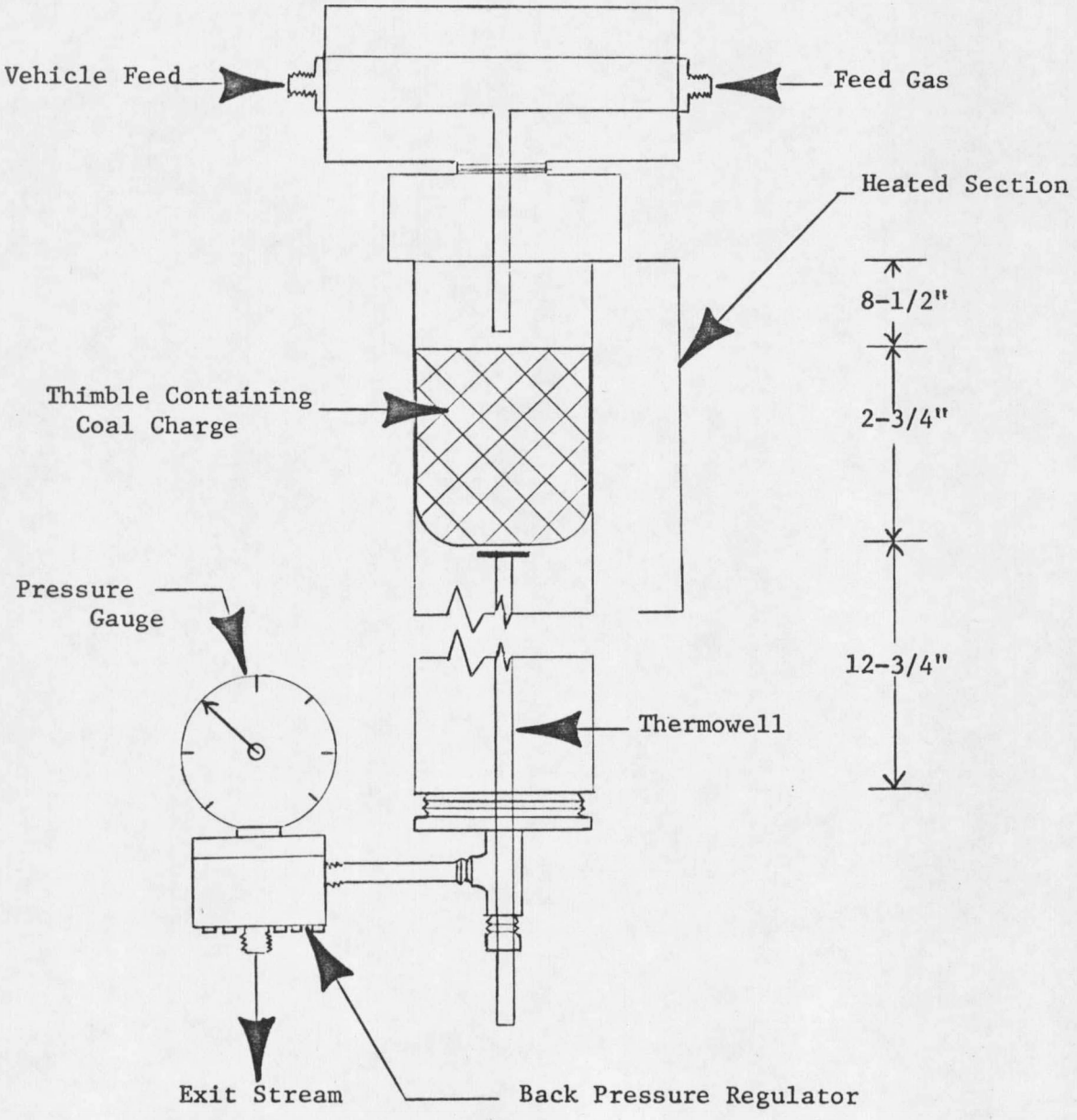

FIGURE 2. Detailed Diagram of Reactor

was maintained by a Grove "Mighty Mite" back pressure regulator.

A variable flow, Milroyal piston pump was used to pump the vehicles into the reactor. The vehicle was fed to the pump through a buret so that vehicle flow rates could easily be determined.

Feed gas was fed to the reactor from high pressure cylinders. A Brooks, high-pressure rotameter was calibrated and used to determine feed gas flow rates.

The feed gas and vehicle entered the reactor passing through the T inlet and into a short piece of Inconel Alloy 600 tubing, leading to the top of the thimble.

To make a test, a five gram sample of coal which had previously been impregnated with catalyst, was mixed with 15 grams of 40 mesh Ottawa sand. The sand prevented coal caking, which would cause diffusional resistance. The mixture was blended and then poured into a 25mm O.D. x 70mm high coarse alundum extraction thimble. After weighing the thimble, it was inserted into the reactor, inlet and outlet fittings were procured, and the reactor was placed into the furnace. The reactor was pressurized to reaction pressure with feed gas from a high pressure cylinder. The powerstat was then turned on and the pumping of the vehicle started.

A flow diagram of the apparatus is shown in Figure 3. The feed gas and solvent entered the reactor, flowed around the coal and through the thimble, and exited with the products through the back pressure regulator.

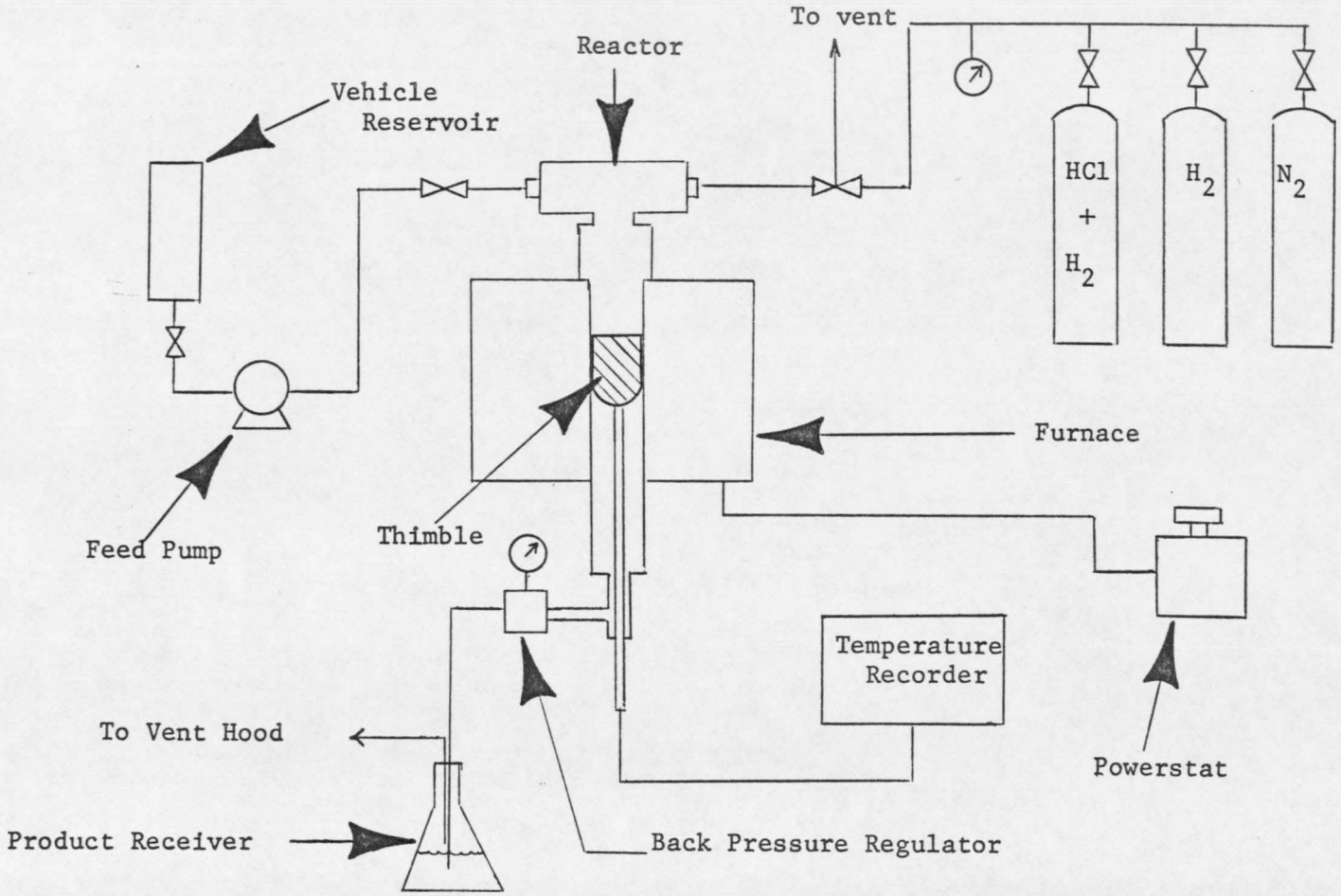

FIGURE 3. Schematic Diagram of Hydrogenation System

The exit stream was bubbled through a water trap (non-vehicle tests were bubbled through benzene) and vented to a hood.

Once the reactor reached reaction temperature, the run continued for thirty minutes. At that time, the feed gas was shut off and the reactor pressure relieved through a bleed value. Nitrogen was purged through the system to cool the reactor and to halt any further reaction. After cooling, the reactor was disassembled and the thimble removed and weighed. The thimble was then extracted with benzene in a Soxhlet Extraction apparatus for 24 hours, dried and reweighed. In preparation for the next run, the thimble was then placed in a flame to burn any residue remaining in its pores.

Note: All fittings, with the exception of swagelock, required teflon tape for sealing.

D. DETERMINATION OF CONVERSION

In conventional conversion analysis, products are considered to be compounds which are soluble in benzene. The purpose of the benzene extraction after reaction, then, was to remove all benzene soluble components (Figure 4). Benzene vapor from the boiling flask would rise through the side arm and up into the condenser. The benzene condensed and dripped into the residue contained in the extraction thimble. When the benzene level reached a height equivalent to the siphon arm, the benzene was automatically siphoned into the boiling flask, carrying with

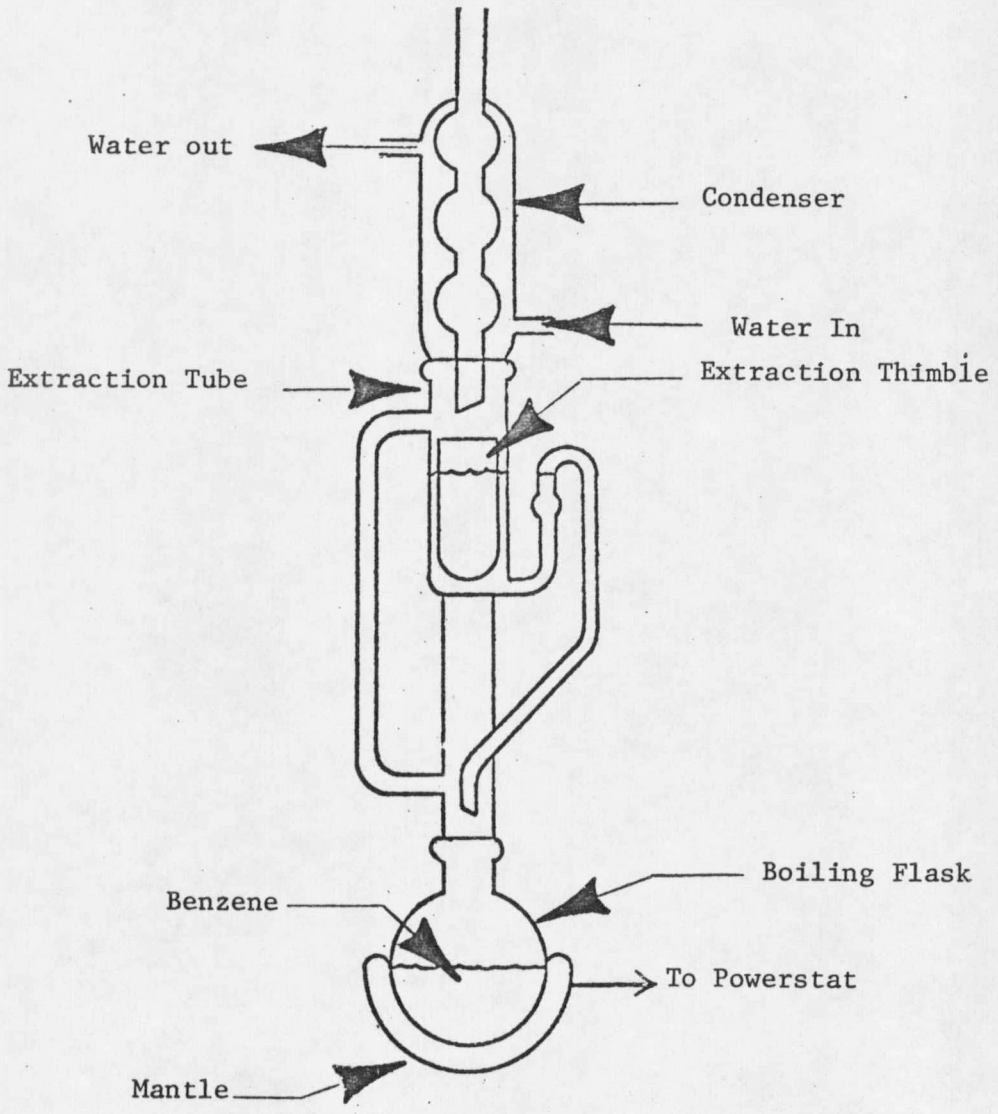

FIGURE 4. Soxhlet Extraction Apparatus Used To Determine Coal Conversion

it benzene soluble components.

The difference in thimble weights before and after the reaction represented the amount of substance lost as products. By knowing the water, ash, and catalyst content of the charge; the moisture, ash, and catalyst free (MACF) content of the coal could be calculated (for non-catalytic charges MAF). The loss in weight minus the amount of initial water and any catalyst loss, yielded the amount of coal converted. Conversions were then calculated by using the following equations:

$$C = ([\ell - m/MAF]) \times 100\% \quad \text{Non-catalytic}$$

$$C = ([\ell - m - c/MACF]) \times 100\% \quad \text{Catalytic}$$

C = % conversion of coal to products

MAF = weight of moisture and ash free material in the initial coal charge

MACF = weight of moisture, ash, and catalyst free material in the initial coal charge

ℓ = weight loss between initial charge and residue

m = weight of moisture in the initial coal charge

c = weight of catalyst lost during reaction

E. ADDITIONAL TESTS

Previous research, performed at Montana State University (4), investigated the hydrodenitrogenation of a heavy California gas oil using

a supported nickel chloride catalyst. Methylene chloride was used to maintain a high HCl partial pressure in the reaction which keeps the metal catalyst in the chloride form. Results indicated that under proper operating conditions, 90% of the nitrogen present could be removed from the oil as ammonium chloride (NH_4Cl). Since metal chloride catalysts and HCl in the hydrogen feed gas were used throughout this investigation, it was speculated that nitrogen contained in the coal could be removed as ammonium chloride. To determine if this hypothesis was accurate, a qualitative experiment testing for ammonia was performed. (9) Residue remaining under the back pressure regulator diaphram was collected. The sample was dissolved in water, added to a solution of sodium hydroxide (NaOH), and gently warmed.

The evolution of ammonia gas (NH_3) would be detected by its odor or by its reaction to a piece of moist red litmus paper held above the solution. Ammonia gas evolves according to the following reaction:

$$NH_4^+ + OH^- \rightleftarrows H_2O + NH_3\uparrow$$

RESULTS & DISCUSSION

A. CATALYST IMPREGNATION AND COAL ANALYSES

Before a coal charge was reacted, it was placed in an oven at 100°C for 36 hours. Therefore in determining conversion, all charges were assumed to have equal moisture contents.

Fifty grams of dried coal were soaked in a solution containing 12.4 grams of the respective catalyst metal in 100 milliliters of water for 24 hours. After drying, the weight gained by the coal was used to determine the amount of catalyst impregnated on the coal. Table I summarizes the coal analysis and catalyst impregnation data which were used for conversion calculations.

TABLE I. MOISTURE, ASH, AND IMPREGNATED CATALYST CONTENT USING COLSTRIP SUB-BITUMINOUS COAL

	Coal as Received	After Drying for 36 hr. at 100°C	Catalytic Coal		
			Nickel Chloride $NiCl_2$	Stannic Chloride $SnCl_4$	Stannous Chloride $SnCl_2$
Moisture	28.6%	.6%	.6%	.6%	.5%
Ash	6.5	9.2	8.9	8.7	7.7
Volatiles & Fixed Carbon	64.9	90.2	86.4	84.7	74.4
Catalyst	-	-	4.1	6.0	17.4
Metal on the Coal	-	-	1.9	2.9	13.2

In determining the percentage of catalyst impregnated on the coal, the assumption that the catalyst impregnates in the chloride form seemed reasonable. From preliminary research by Gerondale (8), it was shown

that analytical determination of catalyst content on the coal, using the same nickel chloride impregnation solution, yielded 2.4% Nickel on the coal. This value compares favorably to the value determined in this investigation of 1.9%.

B. CONTRIBUTION OF BENZENE EXTRACTABLE COMPONENTS TO CONVERSION

It should be noted that the residue-extraction with benzene did not contribute to conversion. In fact, in nearly all extractions, a small gain in weight (∿1%) was observed. A water analysis was performed to determine if the residue had gained water, but no water was detected. A test was performed to investigate the possibility of oxidation. Two identical runs were made and the thimbles weighed. One thimble was left in the air to cool; the other extracted with benzene and dried. The noted gain in weight by each thimble was nearly identical at 1.1% and 1.2%. This indicated that oxidation of the residue was the probable cause for a weight gain.

In the non-vehicle tests, the product stream was bubbled through benzene but no detectable precipitates were observed. Presumably, nearly all the products were benzene soluble. During vehicle tests, the product stream was bubbled through water because it was felt that some solvents would be immiscible with benzene, defeating the intent of the experiment.

C. EFFECT OF FEED GAS FLOW RATE ON CONVERSION

The two feed gases used were pure hydrogen and a mixture of 5 mole %

hydrochloric acid and 95 mole % hydrogen. The purpose of the HCl in the feed gas was to maintain the chloride catalysts in the chloride form and to possibly contribute to the cracking activity of the catalyst system. Hydrogen was received by a commercial supplier at 2000 psi. The $HCl-H_2$ mixture was mixed and pressurized to 1500 psi, using the purchased bottles of hydrogen. Because a compressor was not available to pressurize the gas, once the used gas pressure dropped to the minimum operating pressure (1000 psi) the remaining gas was discarded.

To minimize feed gas usage, the smallest gas flow rate, which did not significantly lower conversion, was determined. Twelve runs with non-catalytic coal were examined at six feed gas flow rates (Figure 5).

It was decided to perform all runs at a gas rate of 31 ml/sec., since doubling that rate resulted in a conversion increase of only .5%. At the chosen flow rate, gas diffusion through the coal was not a controlling resistance to conversion.

D. EFFECT OF TEMPERATURE ON CONVERSION

Two runs were made at each experimental temperature for both feed gases. Tests were not performed above 600°C, since the teflon tape (used as a sealant on the reactor fittings) melted, causing leakage of hot gases. In all conversion calculations, catalyst loss was taken into account (Figures 6 - 11).

In all cases, conversion increased with temperature. At lower

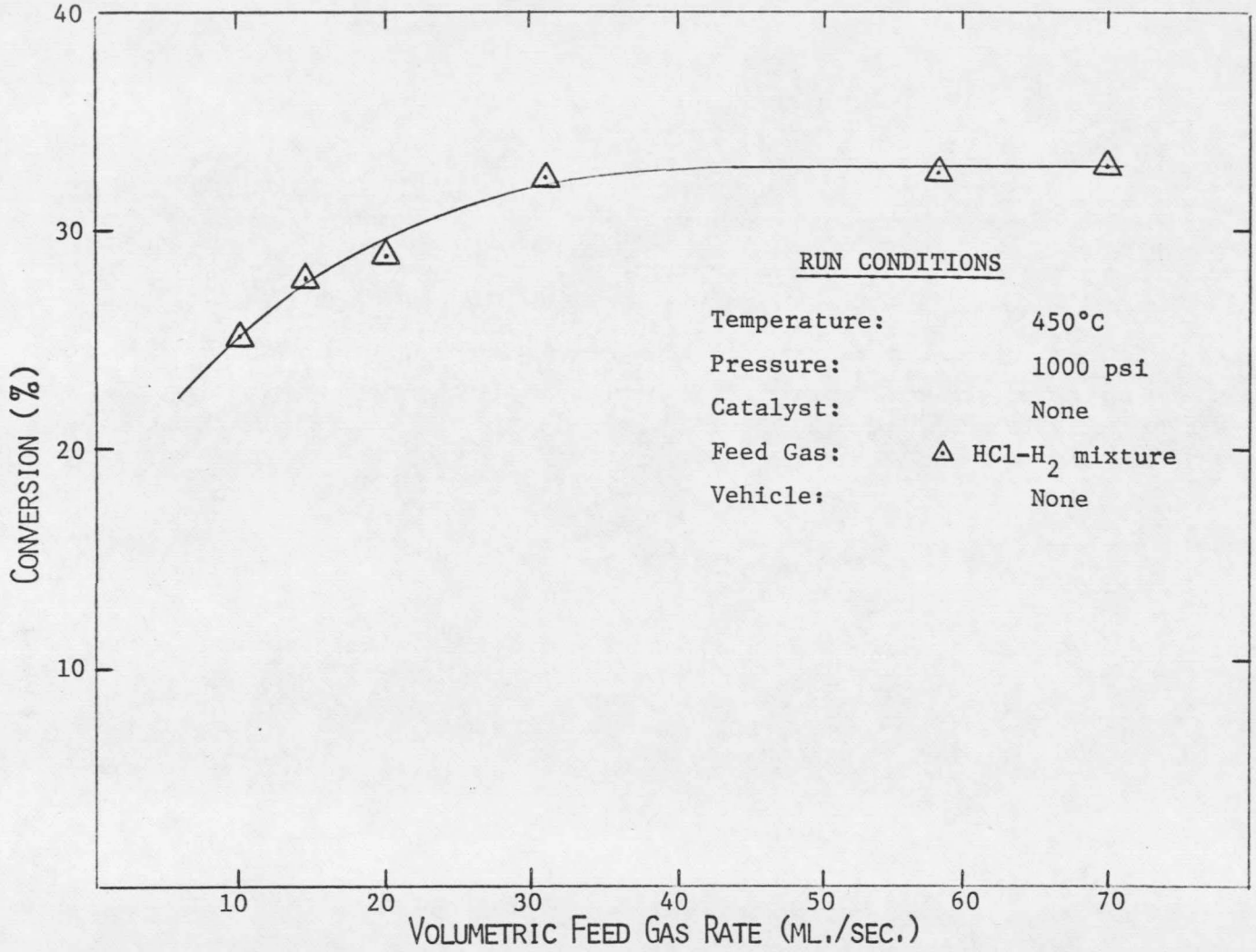

FIGURE 5. Effect of Feed Gas Flow Rate on Conversion

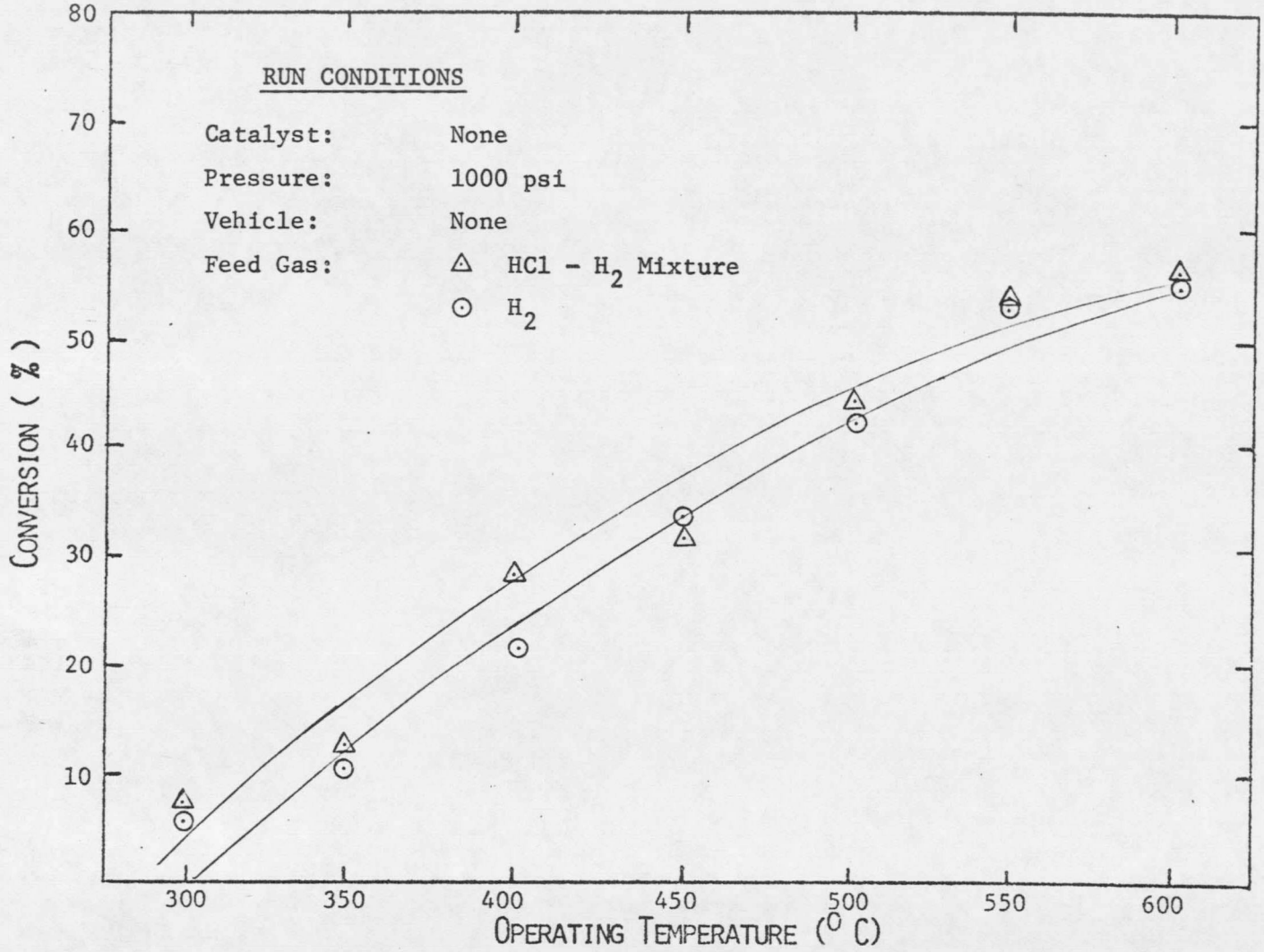

FIGURE 6. Effect of Temperature on Conversion with Non-Catalytic Coal

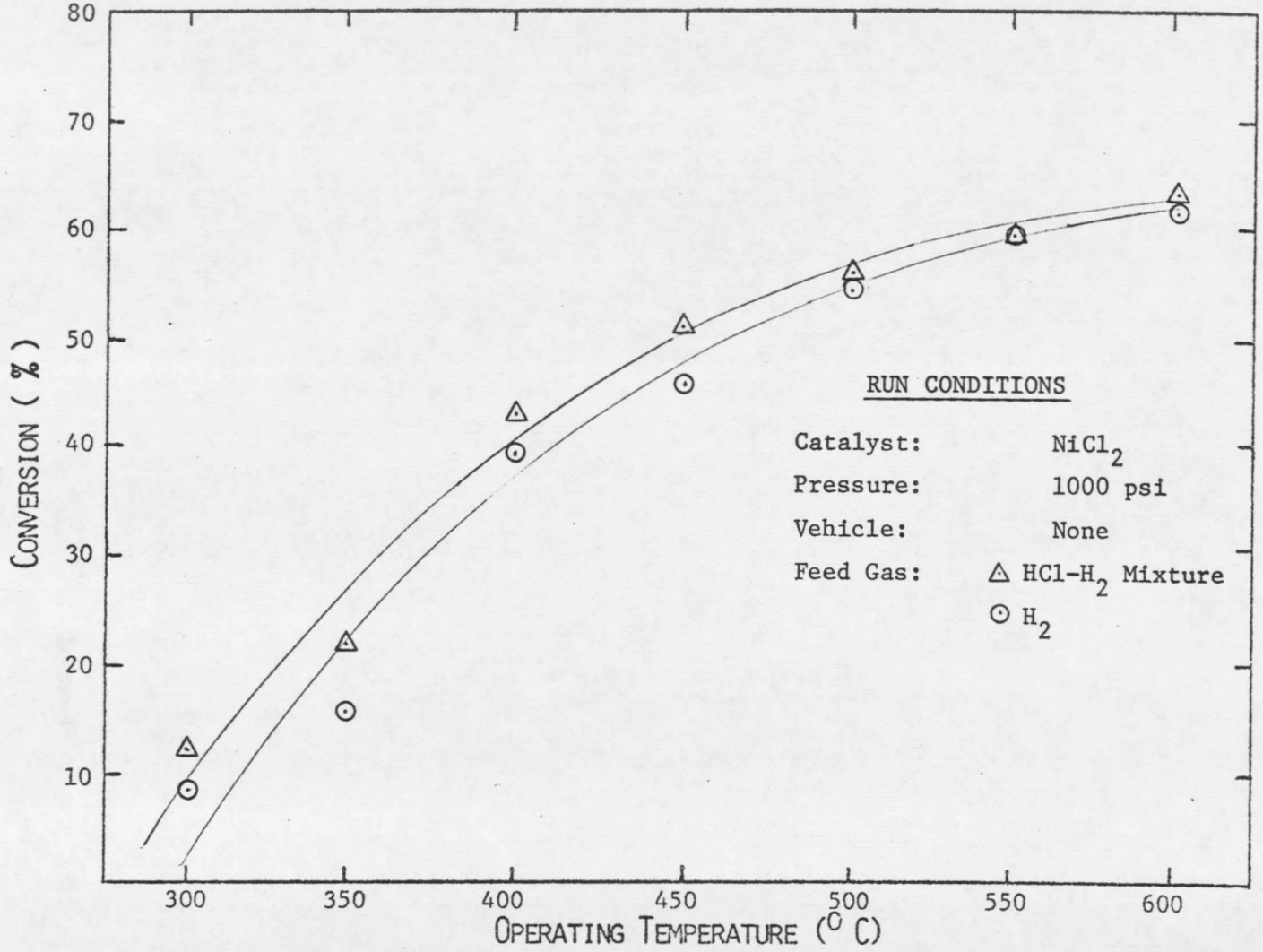

FIGURE 7. Effect of Temperature on Conversion Using a Nickel Chloride Catalyst

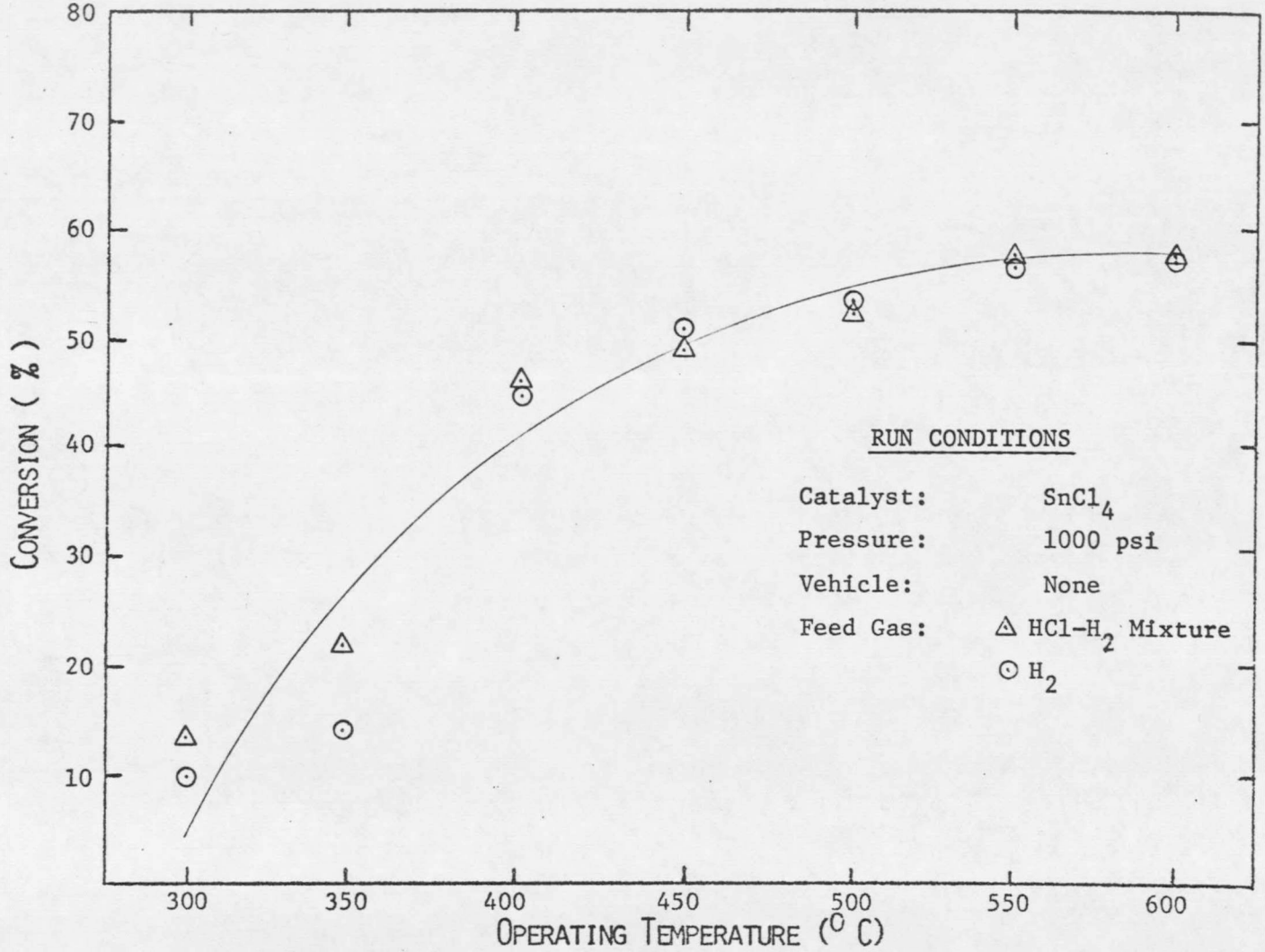

FIGURE 8. Effect of Temperature on Conversion Using a Stannic Chloride Catalyst

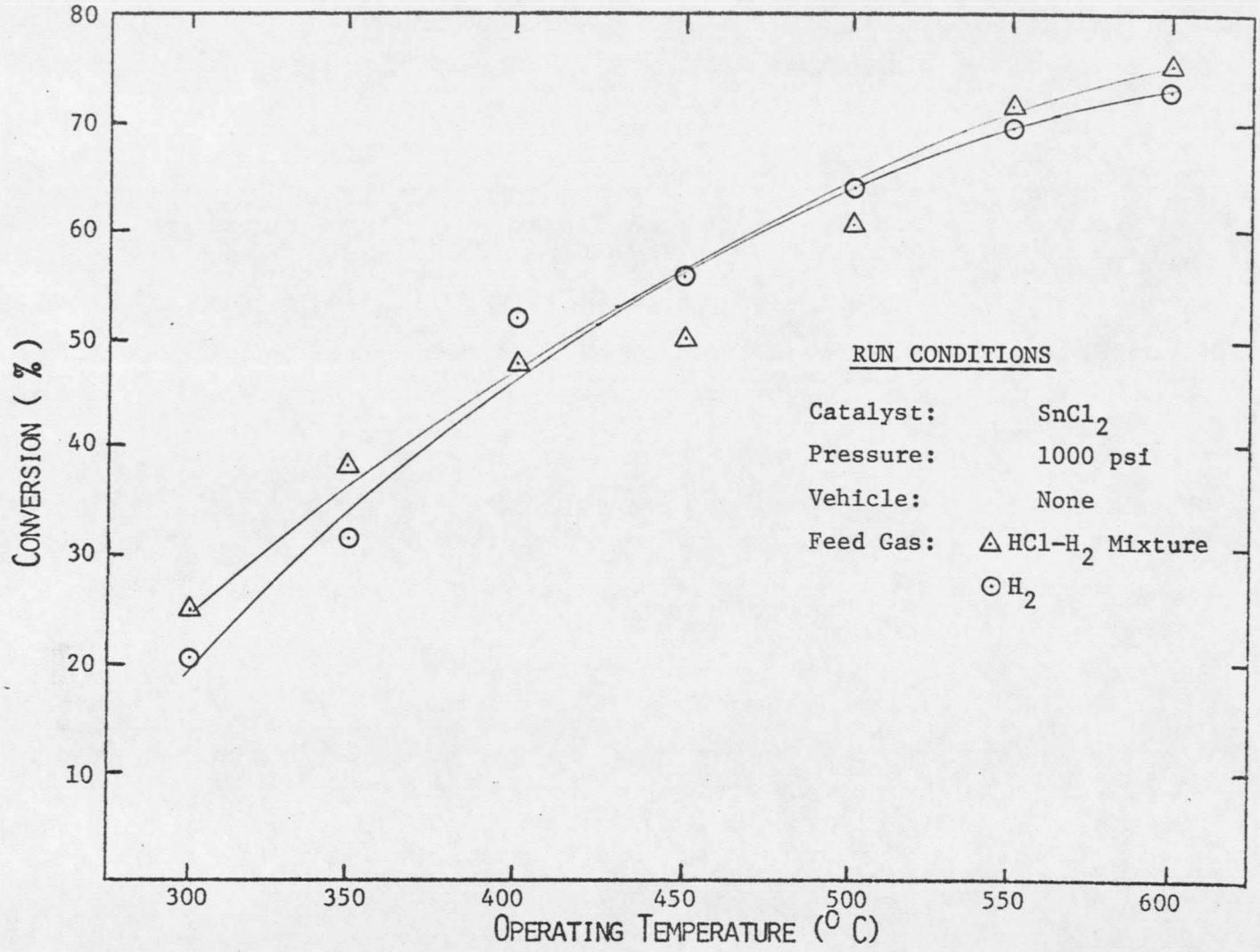

FIGURE 9. Effect of Temperature on Conversion Using a Stannous Chloride Catalyst

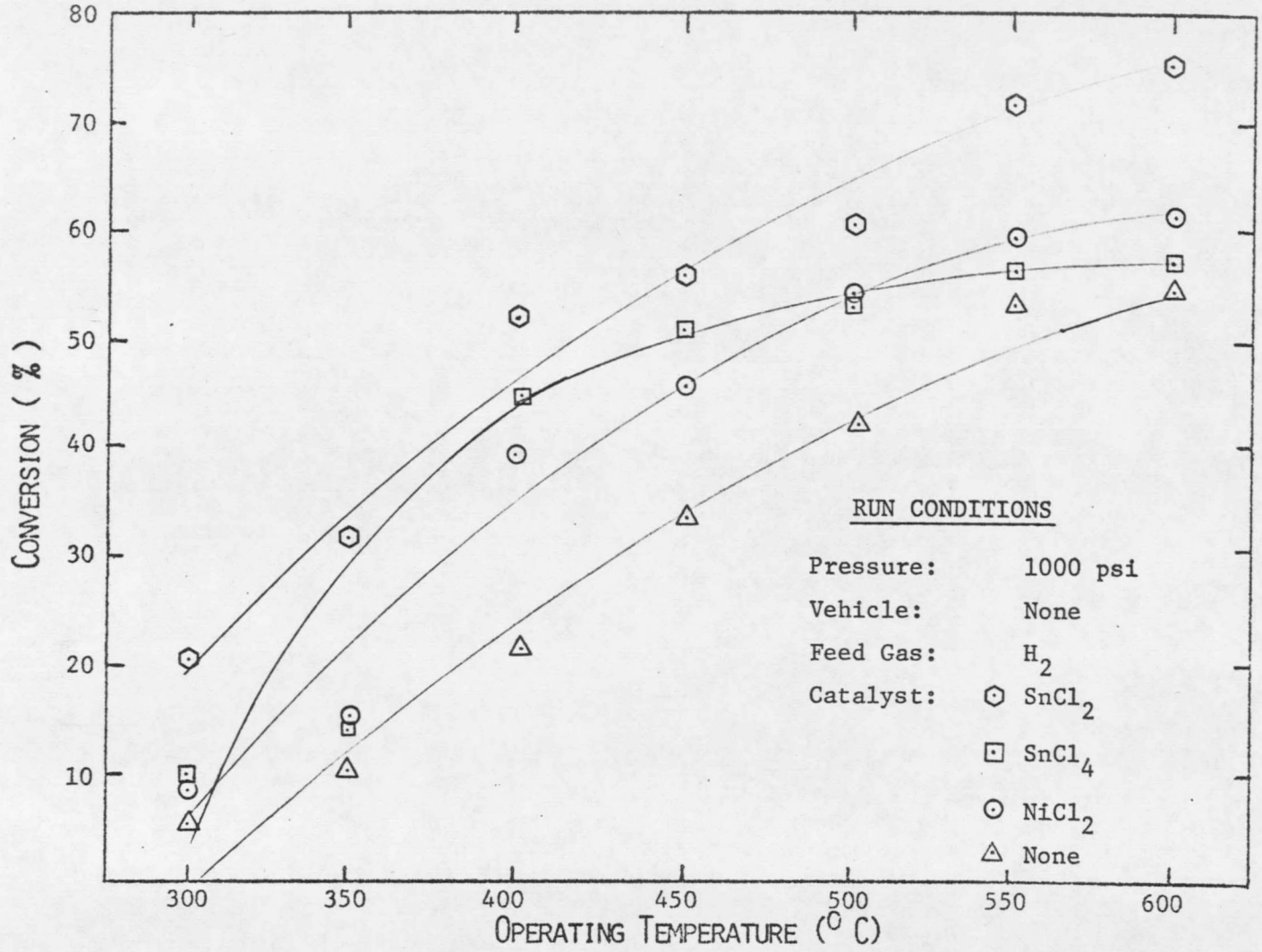

FIGURE 10. Effect of Temperature on Conversion Using H_2 Feed Gas

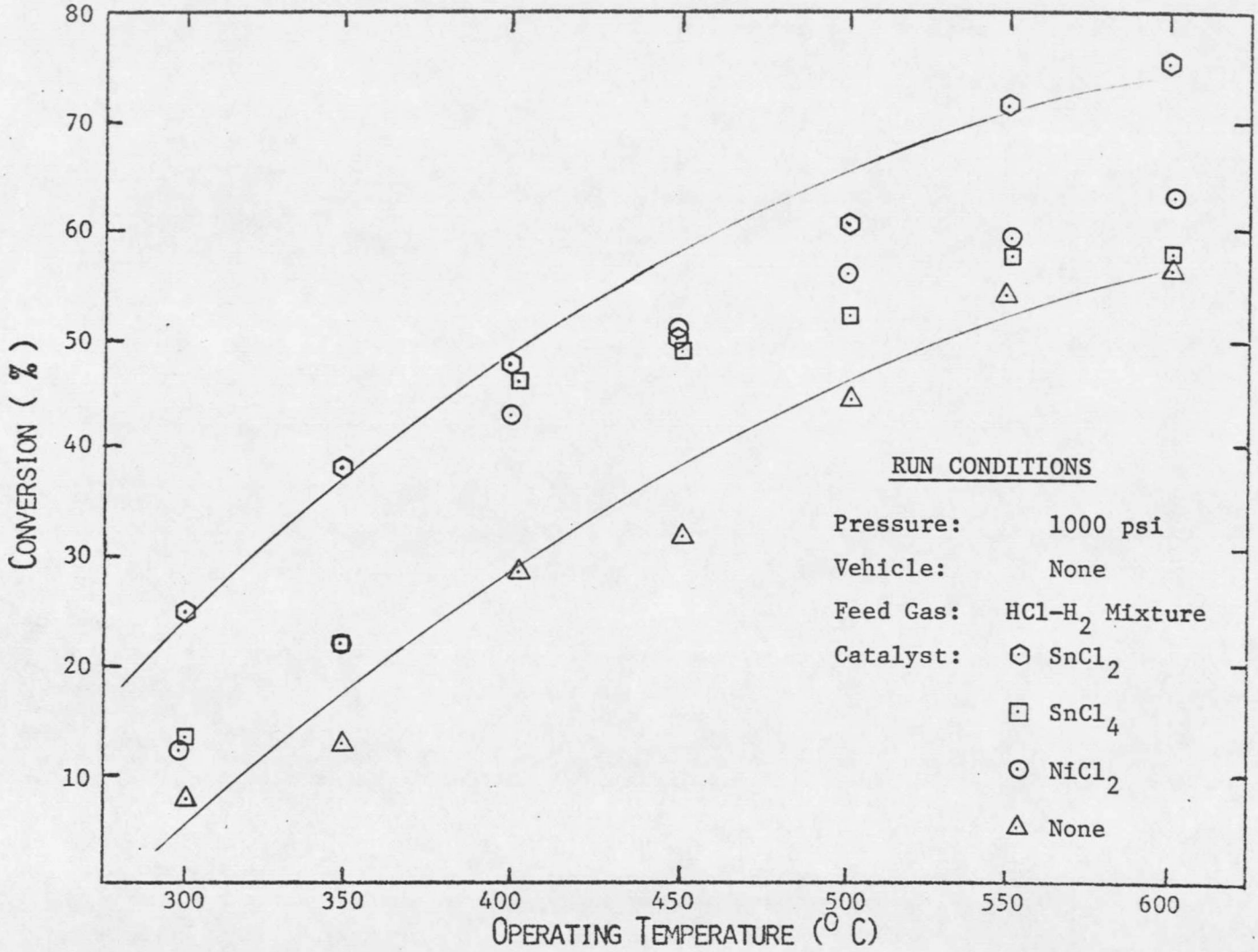

FIGURE 11. Effect of Temperature on Conversion Using A $HCl-H_2$ Feed Gas Mixture

temperatures, higher conversions were obtained by adding HCl to the feed gas. However, at higher temperatures, this effect was not observed.

This data can be explained by another postulated mechanism for the hydrogenation of coal. (11) Coal is thermally split to form reactive fragments; the splitting being catalyzed by halogen acids. These fragments either polymerize to form benzene insoluble products or are stablizied by the addition of hydrogen to form soluble products. The hydrogenation stabilization is catalyzed by the metal.

It is probable then, that at the lower temperatures, there was insufficient thermal energy to split the coal into fragments. Therefore the effects of the halogen acid (HCl) were more pronounced. But at higher temperatures, there was enough thermal energy to fragment the coal, and the rate of hydrogenation became the controlling mechanism. The hydrogenation was catalyzed by the active metals tin and nickel.

No analytical tests were made to determine what percentage of the products were asphaltenes. If a lower percentage of the products were asphaltenes when the HCl-H_2 gas was used, then the effects of the HCl were positive. The acid would indeed have helped the cracking of aromatic compounds. However, since the conversions using HCl-H_2 were comparable with those using H_2, it is doubtful that the HCl has substantially increased cracking; otherwise a higher product yield would be expected. Another possible mechanism was that the halide catalyst plus the hydrogen feed formed sufficient quantities of HCl to

catalyze cracking.

The conversions of non-catalytic coal and stannic chloride impregnated coal were about the same above 500°C. However, below 500°C, the catalytic conversions were much better. This was explained on a catalyst loss basis. Because of its high volatility, after only ten minutes of reaction at 450°C, all of the stannic chloride catalyst was gone. Then non-catalytic hydrogenation took place, causing the conversion profiles to merge. Conversions with stannous chloride were significantly higher than non-catalytic conversion since catalyst was present at all temperatures.

A similar study on the effectiveness of tin as a catalyst on the hydrogenation of sub-bituminous coal was performed by the U. S. Bureau of Mines.(12) Combinations of powdered tin and aqueous ammonium chloride were added with coal to an autoclave. Table II summarizes the results and compares them with this investigation.

TABLE II. Comparison of Results in This Investigation With Results of Research Performed by The U. S. Bureau of Mines

Catalyst Type	Conversion	Conditions	Run Time
U.S. BUREAU OF MINES			
None	31%	Initial 1000 psi Final 2500 psi 450°C	2-1/2 hours (including warm-up time)
Sn (powdered)	44	"	"
NH_4Cl (aqueous)	33	"	"
NH_4Cl + Sn	88	"	"
THIS INVESTIGATION			
None	35%	1000 psi, 450°C	3/4 hours (including warm-up time)
$SnCl_4$ (impregnated)	52	"	"
$SnCl_2$ (impregnated)	57	"	"
HCl (gaseous)	33	"	"
$SnCl_4$ + HCl	50	"	"
$SnCl_2$ + HCl	51	"	"
$NiCl_2$ + HCl	51	"	"
$SnCl_2$ + HCl	65	1500 psi, 450°C	"
$SnCl_4$ + HCl	59	"	"
$NiCl_2$ + HCl	59	"	"

A remarkable increase in conversion using the combination of ammonium chloride (NH_4Cl) and tin was noted at 2500 psi. (This supports the general mechanism of hydrogenation. In this case, the NH_4Cl probably reacted with the hydrogen to form HCl, which in turn catalyzed cracking.) Highest conversions were also noticed in this investigation using HCl and the tin chlorides at 1500 psi.

E. EFFECT OF PRESSURE ON CONVERSION

Since high pressure equipment is expensive and requires additional maintenance costs, the minimum acceptable operating pressure is desired. Two pressures were examined, 1000 psi and 1500 psi, and in all tests, conversions were significantly higher at the highest pressure (Figure 12). The higher pressure did not seem to influence the relative effectivness of the two feed gases. Equipment limitations prevented the use of pressures higher than 1500 psi.

F. EFFECT OF VEHICLES ON CONVERSION

There has been much speculation as to the function of a vehicle in coal hydrogenation. One theory suggested was that a vehicle, such as tetralin, functions by supplying hydrogen to the coal, and that the high pressure hydrogen present in the system serves to regenerate the tetralin. (6)

In this investigation, twelve vehicles were examined. It was hoped that the vehicle would act as a solvent and help dissolve the coal to

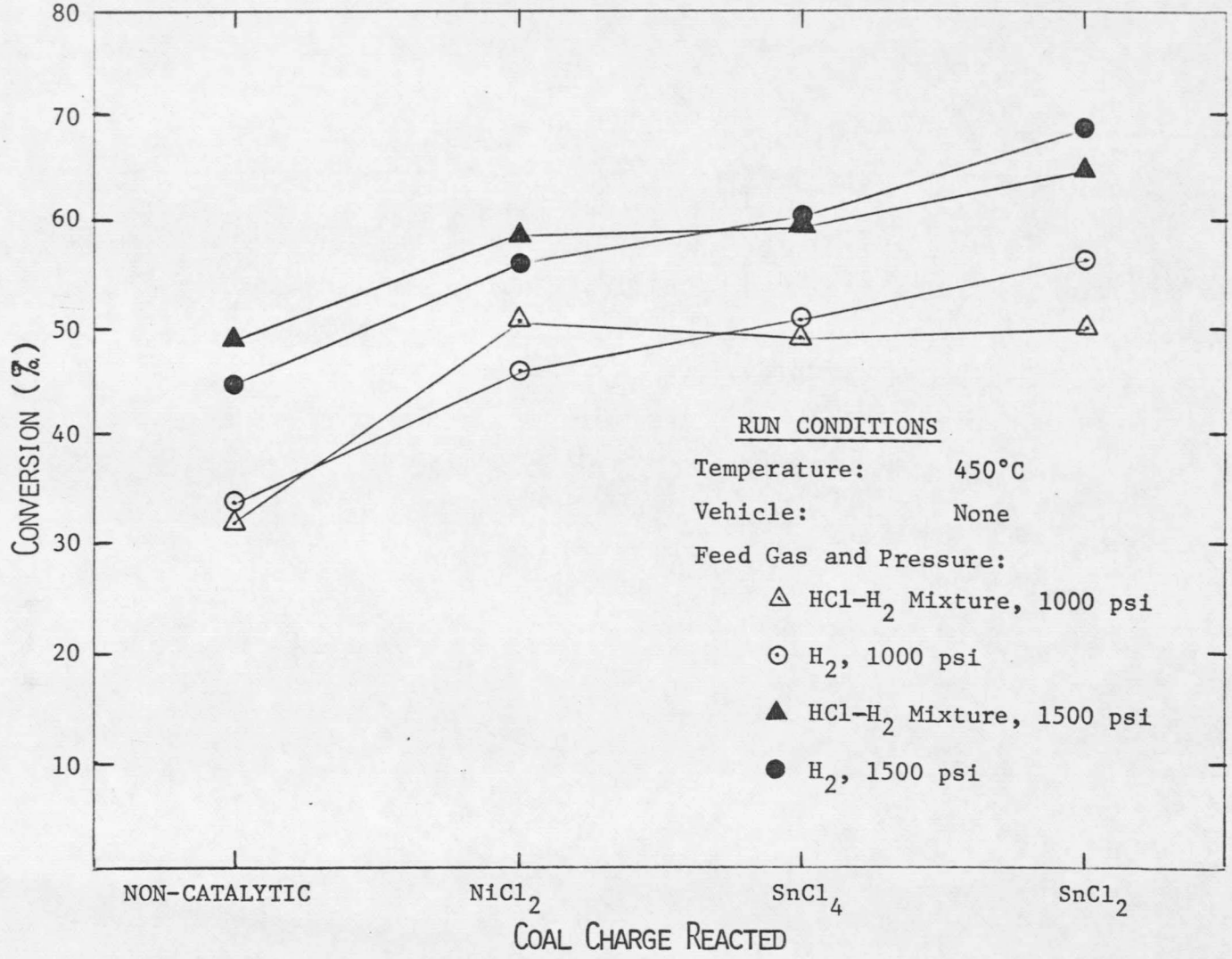

FIGURE 12. Effect of Pressure on Conversion

enhance hydrogenation. For this reason, several solvents exhibiting high coal extractive properties were chosen: toluene, napthalene, m-cresol, biphenyl, and tetralin. The excellent extractive properties have been correlated with compounds possessing high internal pressures.

(3) The middle fraction of a hydrogenated anthracene oil and a 50 weight aviation oil were examined. Peneteck oil, a white mineral oil, supplied by the Penna Refining Company, was also studied. The solvents which were solids at room temperature, were dissolved to their solubility limit (at 20°C) in either benzene or toluene. Each run was performed at 450°C, 1000 psig, with a solvent feed rate of 1 ml/minute, and a HCl-H_2 gas feed rate of 31 ml/sec. At 450°C most of the solvents examined were in the vapor phase. Table III shows the average conversion associated with each solvent and type of coal charge.

TABLE III. CONVERSION OF COAL CHARGES USING DESIGNATED VEHICLES

Vehicle	Coal Charge			
	Non-Catalytic	$NiCl_2$	$SnCl_4$	$SnCl_2$
None	32.6%	51.4%	49.6%	51.0%
Peneteck Oil	53.9	48.8	42.0	50.7
Decaline	34.8	45.4	42.0	47.2
Toluene	40.1	47.4	52.7	51.5
Tetraline	47.7	44.0	42.5	49.1
p-Xylene	45.0	46.3	52.7	54.7
Benzene	47.5	56.2	50.3	49.9
Napthalene in Benzene (.48 grams/ml.)	37.3	53.7	45.3	45.3
m- & p-cresol	39.7	41.6	37.1	49.1
Biphenyl in Toluene (.63 grams/ml.)	39.7	49.1	43.2	47.2
Phenanthrene in Toluene (.24 grams/ml.)	37.0	51.4	44.9	49.9
Hydrogenated Anthracene Oil	-	(gain in wt)	-	-
Shell 50 wt. Aviation Oil	-	28.5	-	-

For non-catalytic coal, all solvents tested improved conversion with Peneteck Oil exhibiting an increase of over 20%. The only conversion improvements for catalytic coal are summarized in Table IV.

TABLE IV. CATALYTIC CONVERSION IMPROVEMENTS USING APPROPRIATE VEHICLES

Catalyst	No. Vehicle	Benzene	Napthalene in Benzene	Toluene	p-xylene
$NiCl_2$	51.4%	56.2%	53.7%	-%	-%
$SnCl_4$	49.6	-	-	52.7	52.7
$SnCl_2$	51.0	-	-	51.5	54.7

Any improvements observed in the conversion of catalytic coal from the addition of a vehicle, were so slight that by taking experimental error into account, the increases in conversion are negligible. However, a 20% increase in conversion using non-catalytic coal and Peneteck Oil did warrant further study. Several runs were made varying the vehicle flow rate (Figure 13). A feed rate of 1 ml/min. was optimum with a decrease in conversion caused by either increasing or decreasing the feed rate.

The increased non-catalytic conversion with Peneteck Oil was difficult to explain since it appears from its structure that the oil should exhibit little "hydrogen donor" ability. The mineral oil probably consisted of high molecular weight, straight chained hydrocarbons. These hydrocarbons should be relatively inactive (stable) and unable to donate hydrogen atoms. The boiling point of the Peneteck Oil was determined to be

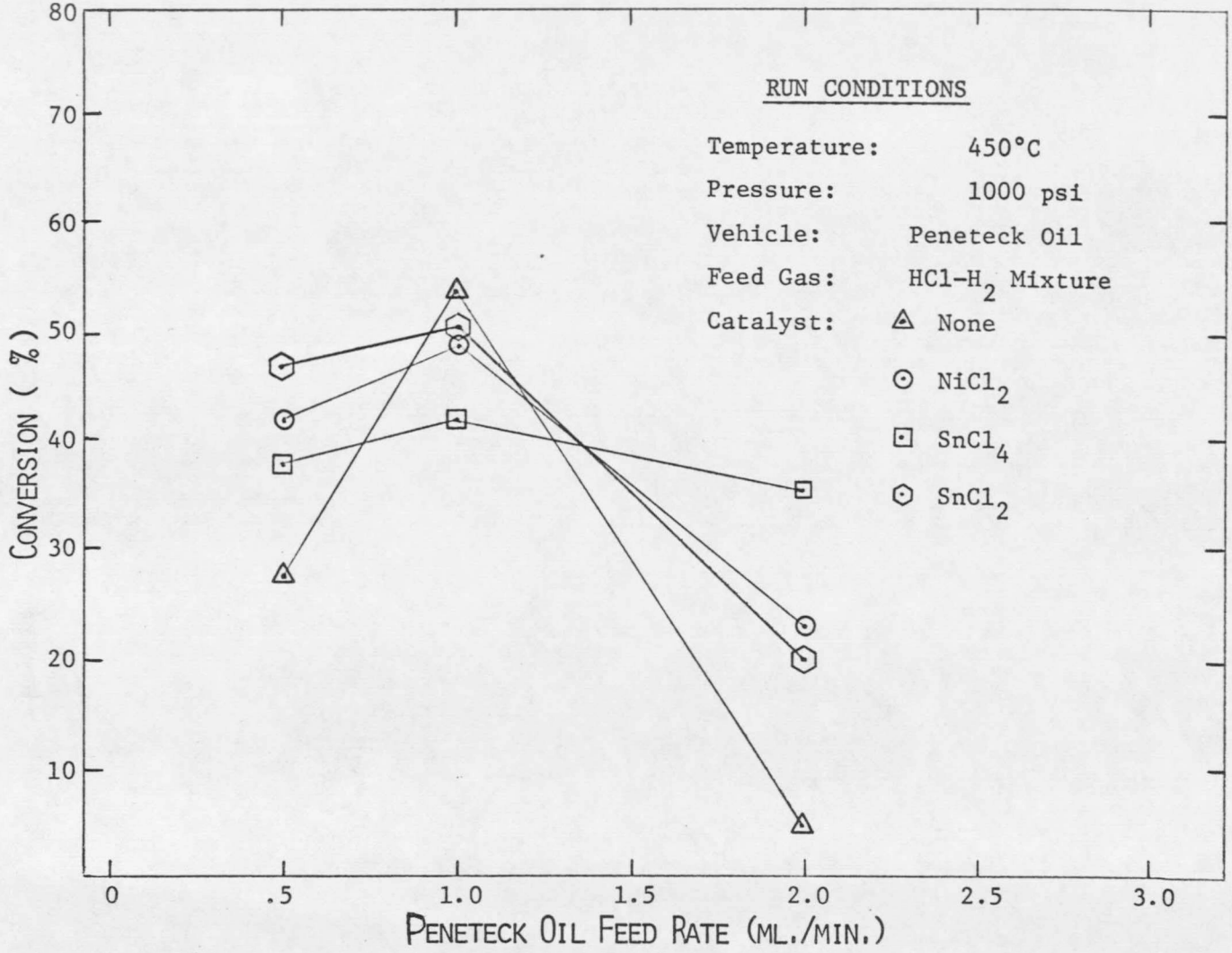

FIGURE 13. Effect of Peneteck Oil Feed Rates on Conversion

460°F (1 atm. pressure), which was the highest boiling point of the vehicles examined. If the oil were in the liquid phase under reaction conditions, it is possible that either solvation of the coal or better hydrogen contact was responsible for the increased conversion.

The hydrogenated anthracene oil caused a negative conversion (gain in weight); probably due to the cracking of the vehicle in the acid atmosphere causing carbon lay-down.

The general decrease in catalytic conversion from the addition of vehicles at 450°C could be explained in either of two ways: (1) the vehicle acted as a poison to the catalyst or (2) the vehicle acted as a resistance to the diffusion of hydrogen into the coal.

G. CATALYST LOSS DUE TO EXTREME REACTION CONDITIONS

Previous analytical work by Gerondale showed that essentially 100% of the nickel was left on the ash and unreacted coal, after reaction at 450°C. (8) Therefore, it was assumed that the nickel chloride catalyst loss was negligible at all temperatures studied. From a comparison of the vapor pressures, the catalysts in order of decreasing volatility are: stannic chloride, stannous chloride, and nickel chloride as shown in Table V. (10)

TABLE V. COMPARISON OF CATALYST VOLATILITY USING CATALYST VAPOR PRESSURE DATA

Catalyst	Volatility	Temperature at Which Catalysts Exhibit The Designated Vapor Pressure				
		1mm Hg	10mm Hg	40mm Hg	100mm Hg	400mm Hg
$NiCl_2$	Low	671°C	759°C	821°C	866°C	945°C
$SnCl_4$	High	-22.7	10	35.2	54.7	92.1
$SnCl_2$	Moderate	316	391	450	493	577

Due to the high volatilities of the tin catalysts, several runs were conducted to determine catalyst loss. An amount of catalyst equivalent to that normally impregnated on the coal was mixed with 20 grams of Ottawa sand. The mixture was placed in the reactor and subjected to normal reaction conditions. Since the sand was non-reactive, any loss in weight was catalyst loss. This test was an approximation of actual catalyst loss, since the catalyst will probably interact quite differently with coal. From experimental data, a calculation was made to determine the fraction of the initial catalyst content remaining on the coal after reaction (Figure 14).

Since essentially all the stannic chloride was lost after one half hour at temperatures above 400°C, a test was made to determine how long the catalyst was present at 450°C. For all practical purposes, 100% of the catalyst was lost after only ten minutes of operation.

At first, a high catalyst loss looked very discouraging; however,

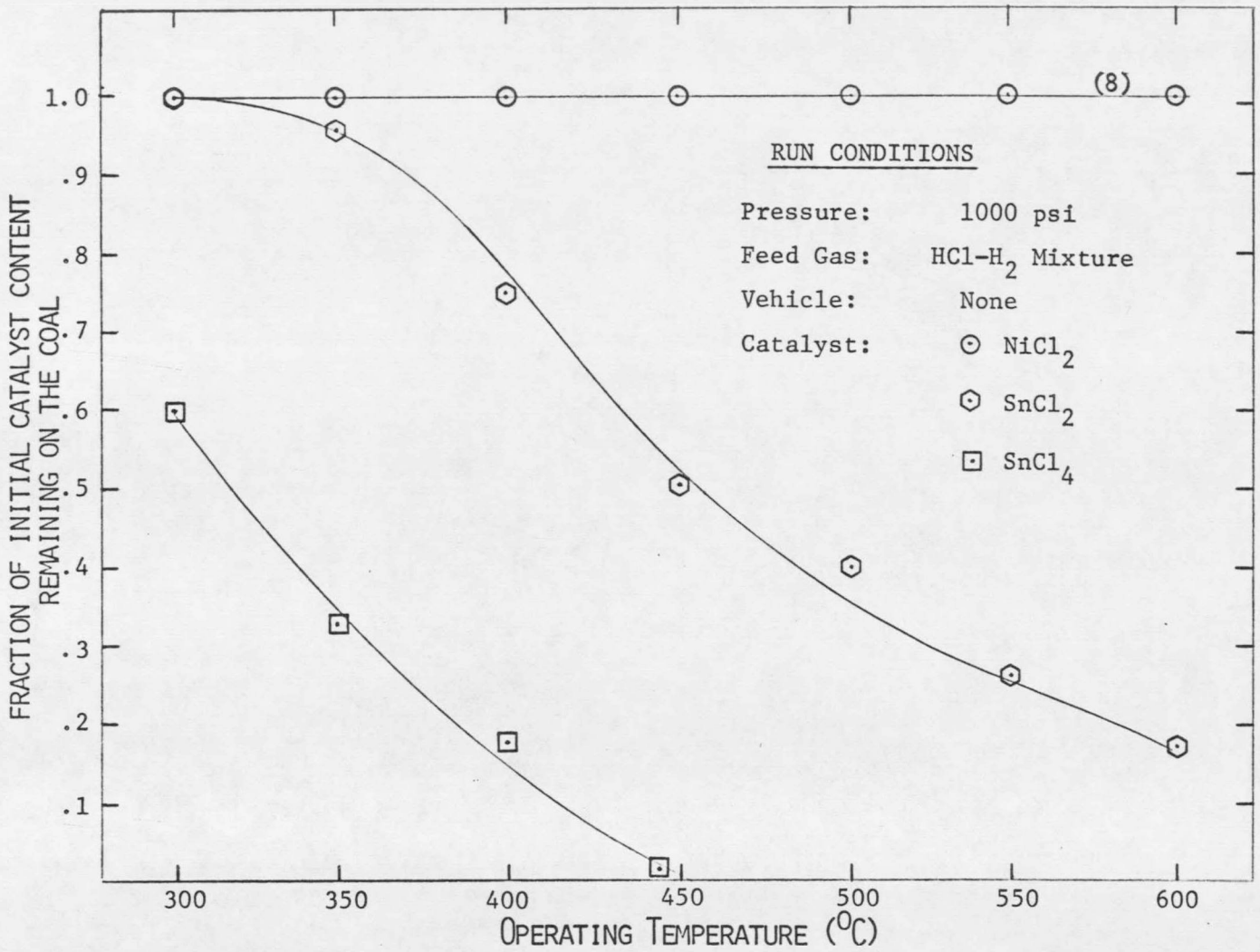

FIGURE 14. Fraction of the Initial Catalyst Content Remaining on the Coal as Simulated by Tests With Ottawa Sand

in a study performed at the University of Utah, catalyst recovery in a continuous system was quite effective. (53) A continuous coal-catalyst feed through a small diameter reactor was used, at 550°C. The catalyst, zinc chloride, melts at 283°C and boils at 732°C at one atmosphere pressure. Under reaction conditions of 550°C and 1750 psi, zinc chloride would be a liquid with a high vapor pressure. Recovery of zinc was 98.5% using a two step process:

(1) the liquid products were washed with water

(2) the char was leached with nitric acid

Consequently, in a semi-continuous reactor such as the one used in this investigation, the catalyst is lost at the reaction site, but could possibly be recovered in the product stream. In a continuous system, catalyst loss at the reaction site would not be critical since it flows with the reactants.

An additional check was performed to determine if the remaining catalyst was in the chloride form. (9) The residue was extracted with water to dissolve any chloride present. After acidifying the extract with nitric acid, silver nitrate was added. If chlorine were present, silver chloride (a white curdy precipitate) would form. Positive results were found on all residues previously shown to contain catalyst. This indicated that the HCl in the feed gas may help to keep at least part of the catalyst in the active chloride form.

H. PRODUCT ANALYSES

It should be noted that no analytical techniques were used to determine what percentage of benzene soluble products were asphaltenes. The hypothesis that the metal chloride catalysts were active in converting coal to oils was assumed to be true. (5)

The only product analyses performed was a qualitative examination of a yellow residuous material thought to be ammonium chloride. The substance was determined not to contain appreciable amounts of ammonium chloride. Since only a small part of coal (~1-1/2%) is nitrogen, it is possible that the small quantity of ammonium chloride formed, if any, would not be detectable by the technique employed.

CONCLUSIONS

The following conclusions can be made:

1. Increasing operating temperature or pressure will increase the hydrogenation of coal.
2. At all temperatures and pressures studied, conversions of catalytic coal were better than conversions using non-catalytic coal.
3. The conversion of non-catalytic coal increased with increasing feed gas flow rates until a rate of 31 ml/sec was reached (space time of 36 seconds). Doubling this flow rate increased conversions only 0.5%.
4. The conversions were generally higher with the addition of 5% HCl to the feed gas at operating temperatures below 400°C. At operating temperatures above 500°C, the addition of HCl had no effect on conversion.
5. Stannic chloride and stannous chloride were volatile at high temperatures and losses were determined to be 100% and 49% respectively at 450°C.
6. Conversions using stannous chloride as a catalyst were superior to both nickel chloride and stannic chloride. The highest conversion reached was 76.2% at 600°C, 1000 psi and with the $HCl-H_2$ feed gas.
7. Each vehicle tested increased the conversion of non-catalytic coal, but generally decreased the conversion of the three catalyst impregnated coals. The vehicle possibly acts as a poison to the

hydrogenation catalyst or as a resistance to the diffusion of hydrogen into the coal.

8. Peneteck Oil increased the conversion of non-catalytic coal as much as 20% at 450°C. The solvent feed rate was critical and was determined to yield optimum conversion at a feed rate of 1 ml/minute.

RECOMMENDATIONS FOR FUTURE STUDY

Future work in the area of coal hydrogenation would be greatly accelerated and more meaningful with the purchase of a high-pressure continuous reactor. A continuous reactor provides more uniform data (no warm up period, etc) and allows more flexibility in testing operating variables. If a continuous reactor were available, the following investigations should be made:

1. The effects of higher pressure (up to 4000 psi) on conversion, using different catalysts.
2. For those catalysts which appear to be active in the hydrogenation of coal, various techniques in catalyst application should be examined - powdered, impregnation, fed as a vapor or liquid, etc. Catalyst concentration should be varied as well as coal size.
3. Space times should be varied so that the effects of time on conversion can be determined. Catalysts can then be compared on a time-conversion basis. Obviously, the highest conversion obtained in the least amount of time is best.
4. Recoverability of the catalyst should be examined.
5. The effects of vehicles on conversion should be examined at higher pressures and lower temperatures. Solid vehicles could be mixed with the coal rather than dissolved in a solvent. Smaller coal size may increase conversion when mixed with a solvent.
6. Complete product analyses should be made. By determining the asphaltene content of the products, a more accurate determination

of catalyst effectiveness is possible. The influence of acid catalysis in the hydrocracking process could also be studied.

APPENDIX

SAMPLE CALCULATION OF CONVERSION

RUN CONDITIONS:

Pressure:	1000 psi
Temperature:	450°C
Catalyst:	$SnCl_2$
Feed Gas:	5% HCl - 95% H_2
Coal Charge:	5 grams

Coal Charge Analysis

Moisture:	.5%
Ash:	7.7
Volatiles & Fixed Carbon:	74.4
$SnCl_2$:	17.4
	100.0%

Weight of Thimble + Charge

Before Reaction:	37.51 grams
After Reaction:	34.16 grams
Weight Lost:	2.35 grams

Determined Catalyst Loss ∿ 49%

Conversion = $[(\ell - m - c)/MACF] \times 100\%$

$$MACF = (1.0 - .174 - .005 - .077) \times (5 \text{ grams}) = 3.72 \text{ grams}$$

(.174 → $SnCl_2$; .005 → Moisture; .077 → ash)

$$\text{Conversion} = \frac{(2.35 - .005(5) - .49\ (.174)(5))\ \text{grams}}{3.72 \text{ grams}} \times 100\%$$

$$= 51.0\%$$

MACF = weight of moisture, ash and catalyst free material in the initial charge

ℓ = weight loss between initial charge and residue

m = weight of moisture in the initial coal charge

c = weight of catalyst lost during reaction

TABLE VI. DATA USED IN THE DETERMINATION OF THE MINIMUM FEED GAS FLOW RATE REQUIRED

Run Conditions: Non-catalytic Coal, 450°C, 1000 psi
no vehicle, HCl-H_2 Feed Gas

Run No.	Gas Flow Rate (ml/sec)	Grams Converted	% Average Conversion
1	10	1.14	25.1
2	10	1.18	
3	15	1.31	27.7
4	15	1.25	
5	20	1.34	29.2
6	20	1.35	
7	31	1.51	32.6
8	31	1.49	
9	58	1.52	33.0
10	58	1.52	
11	70	1.53	33.3
12	70	1.53	

TABLE VII. GRAMS OF METAL CHLORIDE DISSOLVED PER 100 ML. WATER

Metal Chloride	Grams Dissolved (12.4 grams Metal/100 ml H_2O)
$NiCl_2 \cdot 6H_2O$	50 grams
$SnCl_4 \cdot 5H_2O$	36.5 grams
$SnCl_2 \cdot 2H_2O$	23.5 grams

TABLE VIII. DATA USED TO DETERMINE THE EFFECTS OF TEMPERATURE ON CONVERSION

(Two or more runs were made with each feed gas at each temperature. Only average weight losses are shown, based on a 5 gram coal charge.)

RUN CONDITIONS: 1000 psi, no vehicle

Temperature °C	Average Grams Converted with Each Catalyst			
	Non-Catalytic	$NiCl_2$	$SnCl_4$	$SnCl_2$
FEED GAS: $HCl-H_2$				
300	.39 grams	.55 grams	.75 grams	.97 grams
350	.61	1.00	1.17	1.51
400	1.33	1.90	2.24	2.04
450	1.50	2.25	2.43	2.36
500	2.07	2.47	2.58	2.83
550	2.51	2.63	2.81	3.36
600	2.59	2.78	2.83	3.58
FEED GAS: H_2				
300	.33	.40	.56	.80
350	.55	.70	.83	1.25
400	1.05	1.75	2.19	2.21
450	1.62	2.03	2.52	2.57
500	1.97	2.40	2.62	2.96
550	2.50	2.63	2.77	3.29
600	2.57	2.73	2.79	3.50

TABLE IX. DATA USED TO DETERMINE THE EFFECTS OF PRESSURE ON CONVERSION

(Two or more runs were made with each feed gas at both pressures. Only average weight losses are shown, based on a 5 gram coal charge.)

RUN CONDITIONS: 450°C, no vehicle

Catalyst	Average Grams Converted with Each Feed Gas	
Pressure: 1000 psi	$HCl-H_2$	H_2
Non-Catalytic	1.5 grams	1.62 grams
$NiCl_2$	2.25	2.03
$SnCl_4$	2.43	2.52
$SnCl_2$	2.36	2.57
Pressure: 1500 psi	$HCl-H_2$	H_2
Non-Catalytic	2.25	2.1
$NiCl_2$	2.57	2.47
$SnCl_4$	2.83	2.86
$SnCl_2$	2.88	3.02

TABLE X. DATA USED TO DETERMINE THE EFFECTS OF VEHICLES ON CONVERSION

(Two or more runs were made with each type of charge. Only average weight losses are shown, based on a 5 gram coal charge.)

RUN CONDITIONS: 450°C, 1000 psi, HCl-H_2 Feed Gas, 1 ml/min - vehicle rate

VEHICLE	Average Grams Converted with Each Catalyst			
	Non-Catalytic	$NiCl_2$	$SnCL_4$	$SnCl_2$
None	1.5 grams	2.25grams	2.43grams	2.36grams
Peneteck Oil	2.46	2.14	2.11	2.35
Decaline	1.60	1.99	2.11	2.22
Toluene	1.84	2.08	2.56	2.38
Tetraline	2.18	1.93	2.13	2.29
p-Xylene	2.06	2.03	2.56	2.50
Benzene	2.17	2.46	2.46	2.32
Napthalene in Benzene (.48 g/ml)	1.71	2.35	2.25	2.15
m & p-cresol	1.82	1.83	1.90	2.29
Biphenyl in Toluene (.63 g/ml)	1.82	2.15	21.6	2.22
Phenanthrene in Toluene (.24 g/ml)	1.70	2.25	2.23	2.32
Hydrogenated Anthracene Oil	-	(gain)	-	-
50 Wt. Aviation Oil	-	1.26	-	1.15

TABLE XI. DATA USED TO DETERMINE THE EFFECTS OF VARIOUS PENETECK OIL FEED RATES ON CONVERSION

(Two or more runs were made at each vehicle flow rate with each type of charge. Only average weight losses are shown, based on a 5 gram coal charge.)

RUN CONDITIONS: 450°C, 1000 psi, HCl-H_2 Feed Gas

Catalyst	Average Grams Converted at Each Flow Vehicle Rate		
	.5 ml/min	1.0 ml/min	2.0 ml/min
None	1.28 grams	2.46 grams	.24 grams
$NiCl_2$	1.84	2.14	1.01
$SnCl_4$	1.94	2.11	1.83
$SnCl_2$	2.20	2.35	1.21

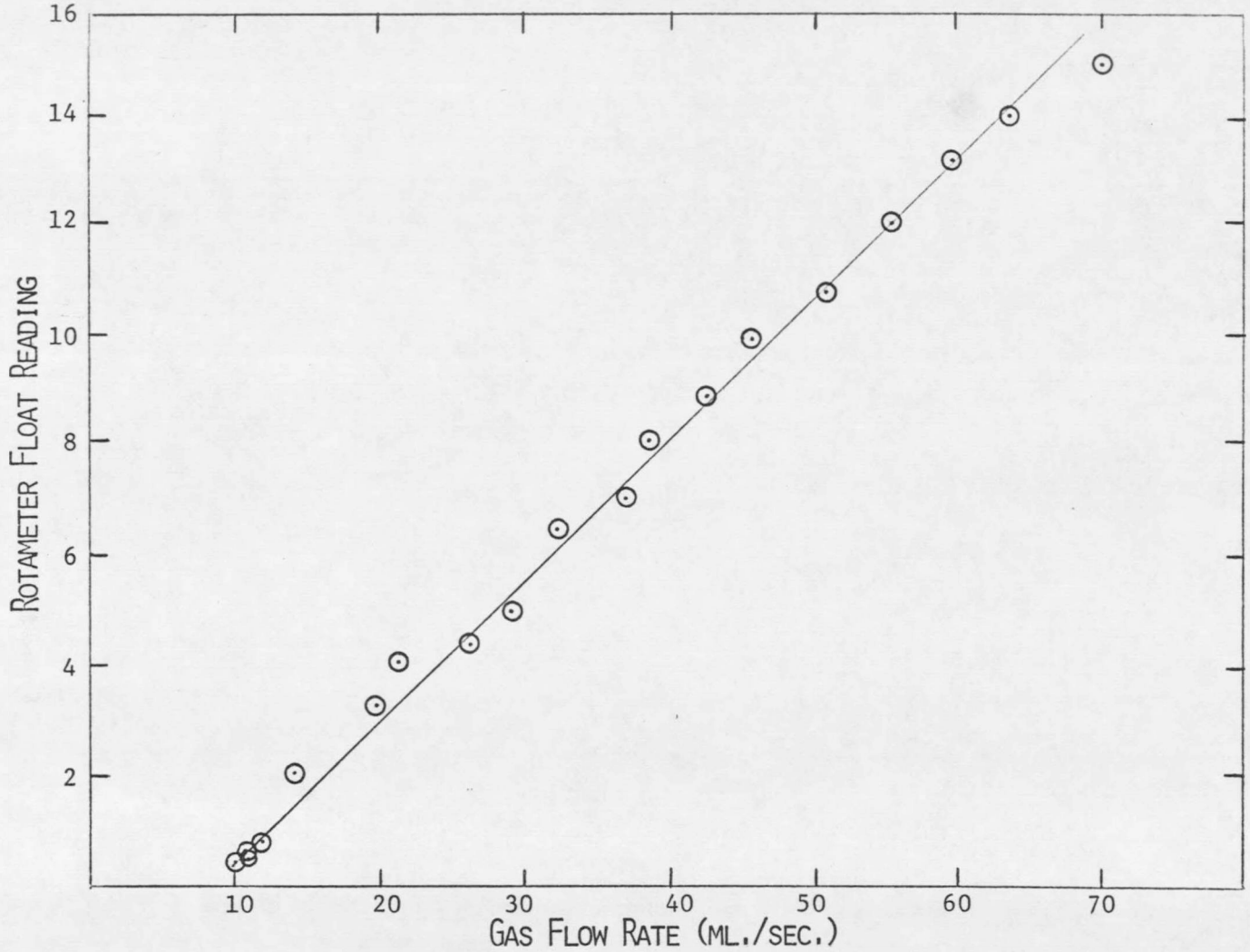

FIGURE 15. Calibration of the Rotameter

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