



Hydrogenation of coal using a metal chloride-HCl catalyst
by David Lee Sire

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

The research presented in this thesis studied the relative activity of different metal chloride catalysts in the hydrogenation of coal.

Since there is no way of analytically determining the optimum catalyst for a reaction, an experimental approach must be used.

In this study, 16—35 mesh prepared coal was impregnated with a metal chloride catalyst, mixed on a 1:3 weight basis with 40 mesh Ottawa sand and placed in a semibatch tube reactor. The coal was then reacted by continuously passing a 5% HCl-95% reactor gas through the reactor at 450°C and 1000 psi for 30 minutes. Conversion of the coal was calculated as the weight loss on the original amount of coal charged. In order to compare the relative activity of the different metal chloride catalysts, this conversion value was reported on a dry, ash-free basis.

Under these operating conditions, nickel chloride and stannic chloride exhibited the highest catalyst activity, converting an average of 67.3% and 67.5%, respectively, of the dry, ash-free coal to hydrogenated products. Stannous chloride was only slightly lower, converting 62.5% of the dry, ash-free coal.

This study also indicated that the alkali metal chlorides exhibited little or no activity or acted as a poison (potassium chloride) in the hydrogenation of coal.

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by

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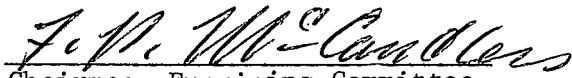
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Chemical Engineering

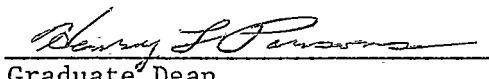
Approved:



Head, Major Department



Chairman, Examining Committee



Graduate Dean

MONTANA STATE UNIVERSITY
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ABSTRACT

The research presented in this thesis studied the relative activity of different metal chloride catalysts in the hydrogenation of coal. Since there is no way of analytically determining the optimum catalyst for a reaction, an experimental approach must be used.

In this study, 16-35 mesh prepared coal was impregnated with a metal chloride catalyst, mixed on a 1:3 weight basis with 40 mesh Ottawa sand and placed in a semibatch tube reactor. The coal was then reacted by continuously passing a 5% HCl-95% H₂ reactor gas through the reactor at 450°C and 1000 psi for 30 minutes. Conversion of the coal was calculated as the weight loss on the original amount of coal charged. In order to compare the relative activity of the different metal chloride catalysts, this conversion value was reported on a dry, ash-free basis.

Under these operating conditions, nickel chloride and stannic chloride exhibited the highest catalyst activity, converting an average of 67.3% and 67.5%, respectively, of the dry, ash-free coal to hydrogenated products. Stannous chloride was only slightly lower, converting 62.5% of the dry, ash-free coal.

This study also indicated that the alkali metal chlorides exhibited little or no activity or acted as a poison (potassium chloride) in the hydrogenation of coal.

INTRODUCTION AND BACKGROUND

Coal is a solid combustible substance formed by the partial decomposition of vegetable matter without free access to air and under the influence of moisture and often increased pressure and temperature. Coal is also a highly unsaturated organic compound with a low BTU value. Coal is found in deposits throughout the world with vast amounts of it being found in the Western United States.

Coal, at one time, was a major source of energy in this country. Its use was pre-empted by the use of petroleum products and natural gas as energy sources. However, the world is now experiencing a shortage of natural gas and petroleum, and interest is again being focused on coal as an energy source. However, coal, in its natural form, is an inefficient source of energy. The purpose of this project was therefore to find a more active catalyst in the hydrogenating and hydrocracking of coal into a more desirable form of energy.

Hydrogenation itself refers to the saturation (with hydrogen) of unsaturated organic compounds in the presence of a metal catalyst. The hydrogen attacks π bonds and forms new C-H σ bonds. Hydrogenation saturates C=C and C=N (also C $\equiv$ C and C $\equiv$ N) groups but generally leaves C=O groups unaffected.(1)

As previously mentioned, coal is a highly unsaturated solid. As a solid, it is bulky and expensive to transport. Being highly unsaturated, it has a low BTU value. When coal is hydrogenated, gaseous and liquid products are formed. This serves two purposes. The coal

is converted into a more efficient, higher BTU source of energy and the coal becomes easier and less expensive to transport.

In converting coal to a liquid or gaseous product, an effective hydrogenation catalyst must accomplish several functions. These include an integral means of separating the catalyst from the ash and product streams, high catalytic ability at relatively low pressure, a high activity-high selectivity ability, and a high hydrocracking activity. Molten metal chloride catalysts have been tried (2), but were abandoned because of the relative high pressures necessary for the operation and the difficulty encountered in regeneration and in the recovery of the catalyst from the product stream.

The basis for this thesis comes from a study done by Dr. F. P. McCandless and Dr. Lloyd Berg of the Department of Chemical Engineering at Montana State University in Bozeman, Montana on hydrodenitrogenation of petroleum.(3). In this study, the hydrodenitrogenation of a heavy California gas oil was investigated using a supported NiCl_2 catalyst. Methylene chloride was used to maintain a high HCl partial pressure in the reactor and to keep the metal in the chloride form. Results from this study indicated that under the proper operating conditions, 90+% of the nitrogen present could be removed from the oil as ammonium chloride (NH_4Cl). The removal of nitrogen in this manner is a single-bond cleavage of hydrogenation known as hydrogenolysis where C-N or C-S groups are hydrogenated to C-H groups. (1)

This system not only exhibited a high hydrogenation ability, but, more important, also showed a high hydrocracking ability. Based on these results, it was proposed to use metal chloride catalysts in the hydrogenation and hydrocracking of coal. The main purpose of this hydrogenation would be to form saturated liquid or gaseous compounds to be used as an energy source. However, it is also possible that the two major pollutants found in coal, nitrogen and sulfur, could also be hydrogenolysized into compounds that could be removed from the product streams.

RESEARCH OBJECTIVES

The purpose of this research was to find a highly active metal chloride catalyst for use in the hydrogenation of coal. This catalyst will have to exhibit a high activity at a relatively low pressure. The process will be carried out in a partial HCl atmosphere. It is felt that this partial HCl atmosphere will help keep the metal in the chloride form and help form active sites for the hydrogenation mechanism.

A second objective of this research was to briefly investigate the amount of metal catalyst consumed during the hydrogenation process.

This research, then, is intended as the initial step in the development of a catalyst that will make hydrogenation of coal economically feasible. It is also intended as a guide for future research in this area.

EXPERIMENTAL APPARATUS

WARNING: When operating this equipment, be careful to wrap all screw thread fittings with Teflon tape. Failure to do so can allow hydrogen to escape into the furnace, causing fire and small explosions to occur.

The reactor design used for this research is shown in Figure 1. The reactor tubing was a 24-inch length of schedule 80 1-inch Inconel Alloy 600 pipe fitted with appropriate inlet and outlet sections. The top 9-3/4 inches was bored out slightly to accommodate a 1 inch outside diameter, 2 inch long porous alumina thimble. Since the inside diameter of the pipe is 0.957 inches, this kept the bottom of the thimble at 9-3/4 inches from the top of the pipe. A 110 volt, 5 ampere electric furnace was used to heat the Inconel pipe reactor.

The feed gas entered through the inlet section at the top of the pipe. The inlet section also had a bleed valve to relieve the internal pressure of the system upon completion of a run. The exit gases passed through a back pressure regulator, into a water trap and then vented through a hood to the atmosphere. A sampling port was located between the back pressure regulator and water trap for sampling of exit gases. A 1/4" tube ran up through the outlet section to the base of the thimble to accommodate an alumel-chromel thermocouple. The temperature inside the reactor tube at the thimble site could then be recorded on a temperature recorder.

The pipe to the inlet section was branched and fitted with appro-

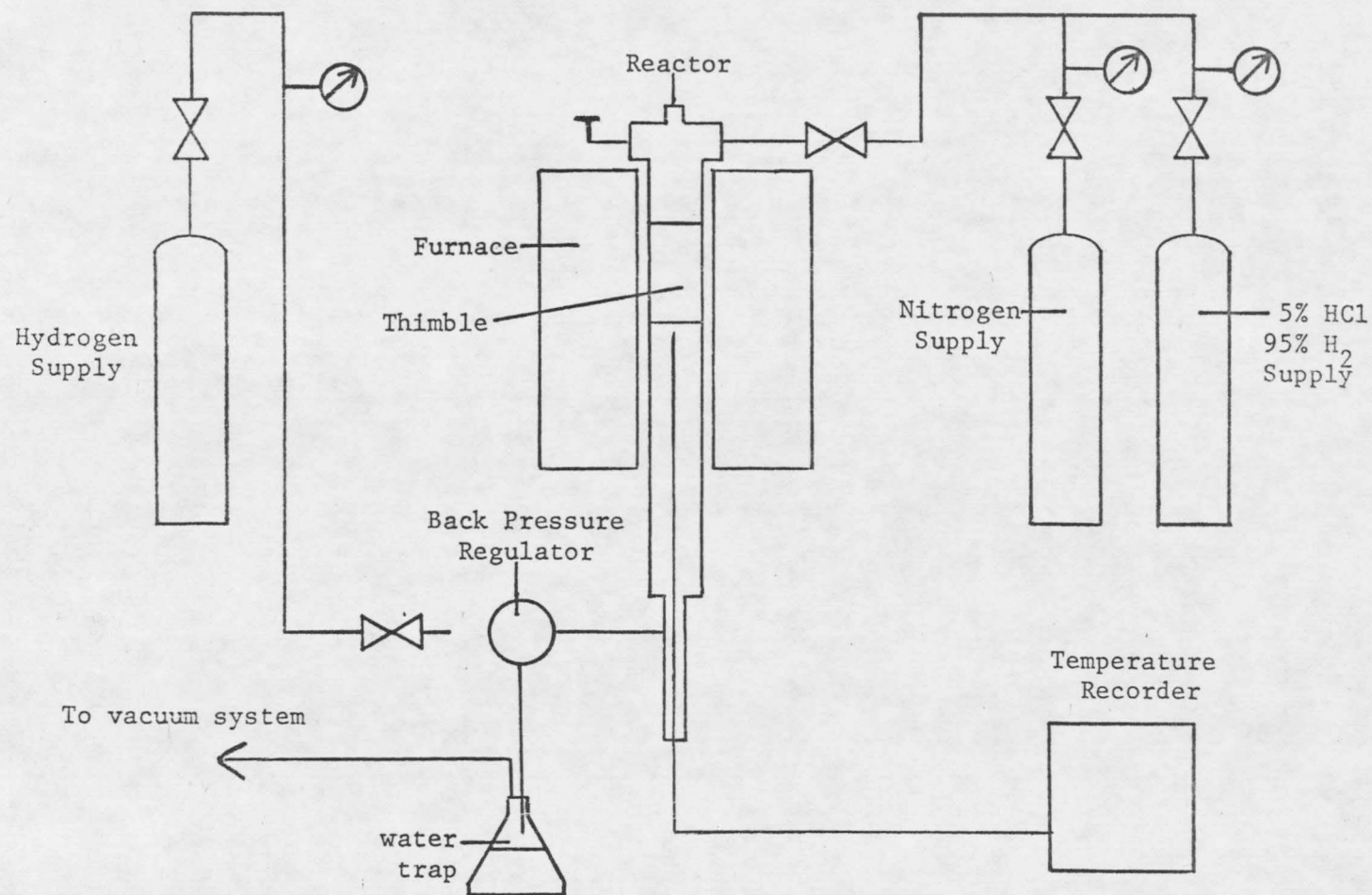


FIGURE 1. Schematic Flow Diagram of Reactor System

priate valves to allow the feed gas to enter the reactor and to allow nitrogen to purge and cool the reactor after the completion of a run.

Figure 2 shows a detailed sketch of the reactor and the proximate equipment.

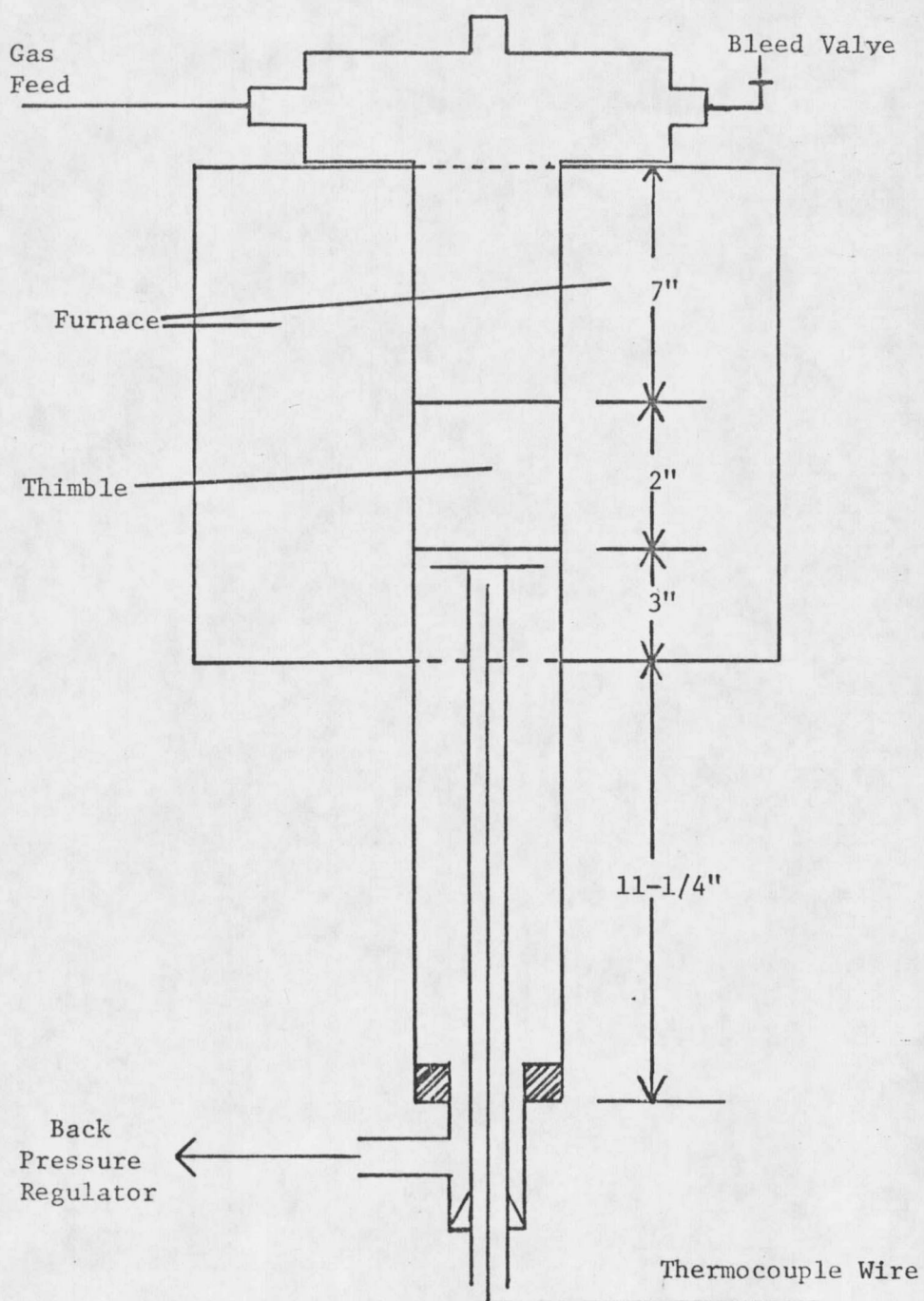


FIGURE 2. Detailed Diagram of Reactor

EXPERIMENTAL PROCEDURE

PRELIMINARY WORK

Initial reaction runs were made with a nickel chloride catalyst and coal ground to minus 100 mesh. A ten gram sample was placed in the thimble for each run and a feed gas of 5% HCl and 95% H₂ was used. Reactor temperature was 450°C and reactor pressure was 1000 psi. In the first runs, methylene chloride was also pumped into the system to help maintain the HCl partial atmosphere. (The equilibrium constant for the reaction $\text{CH}_2\text{Cl}_2 + 2\text{H}_2 \rightarrow 2\text{HCl} + \text{CH}_4$ is approximately 1.4×10^{14} at 425°C). However, the use of methylene chloride had to be discontinued. During these early runs, it was found that some of the methylene chloride was converted to carbon and was laid down in the thimble. Since conversion was based on weight loss, this made the calculation of the conversion impossible.

The next series of runs indicated the need for separating the coal particles. After reacting for a short period of time, the coal in the thimble formed a shell leaving the interior coal unreacted. This indicated that the diffusion rates were both slow and the controlling mechanism. This is briefly illustrated in Table I. Conversion is accomplished quickly until the shell is formed. The extent of conversion is relatively low after this point has been reached. Specifically, approximately 47.5% of the dry, ash-free coal is converted in the first 15 minutes of reaction when the shell is forming. Only an additional 5% is converted in the next 45 minutes.

TABLE I. AVERAGE CONVERSION RATES
(Preliminary Studies)

Length of Run (min)	Average Conversion %	Weight Ratio of Coal to Ottawa Sand
15	47.4	1:0
30	49.8	1:0
60	52.7	1:0
15	46.6	1:1
30	52.8	1:1

The coal was then mixed with 40 mesh Ottawa sand on a 1:1 weight ratio. This improved the conversion only slightly to 52.8% after 30 minutes. This is also shown in Table I.

This led to the final system employed for the remaining test runs. A five gram sample of 16-35 mesh coal was mixed with 40 mesh Ottawa sand on a 1:3 weight ratio (approximately 1:1 volume ratio). Since the purpose of the addition of the Ottawa sand was to help keep the coal particles separated to prevent shell formation, the size of the coal particles had to be increased to 16-35 mesh. Smaller coal particles would settle to the bottom of the reaction thimble and form a shell. It was felt that the use of any larger coal particles would cause too great of an intraparticle diffusion problem.

The associated preliminary work included establishing a weight percent nickel on the coal versus molar concentration $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ plot (Figure 3) and the standard nickel analysis tests used to determine the amount of nickel catalyst consumed during reaction.

The decreased absorbance of nickel on the coal above 4 g.moles $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in Figure 3 seems to result because the coal will no longer be wetted by higher concentrations of nickel chloride. The results of the nickel catalyst consumption tests indicate that all of the nickel stays on the ash and remaining coal during the reaction and is not lost into the product stream.

This was done by first determining the weight of nickel on the

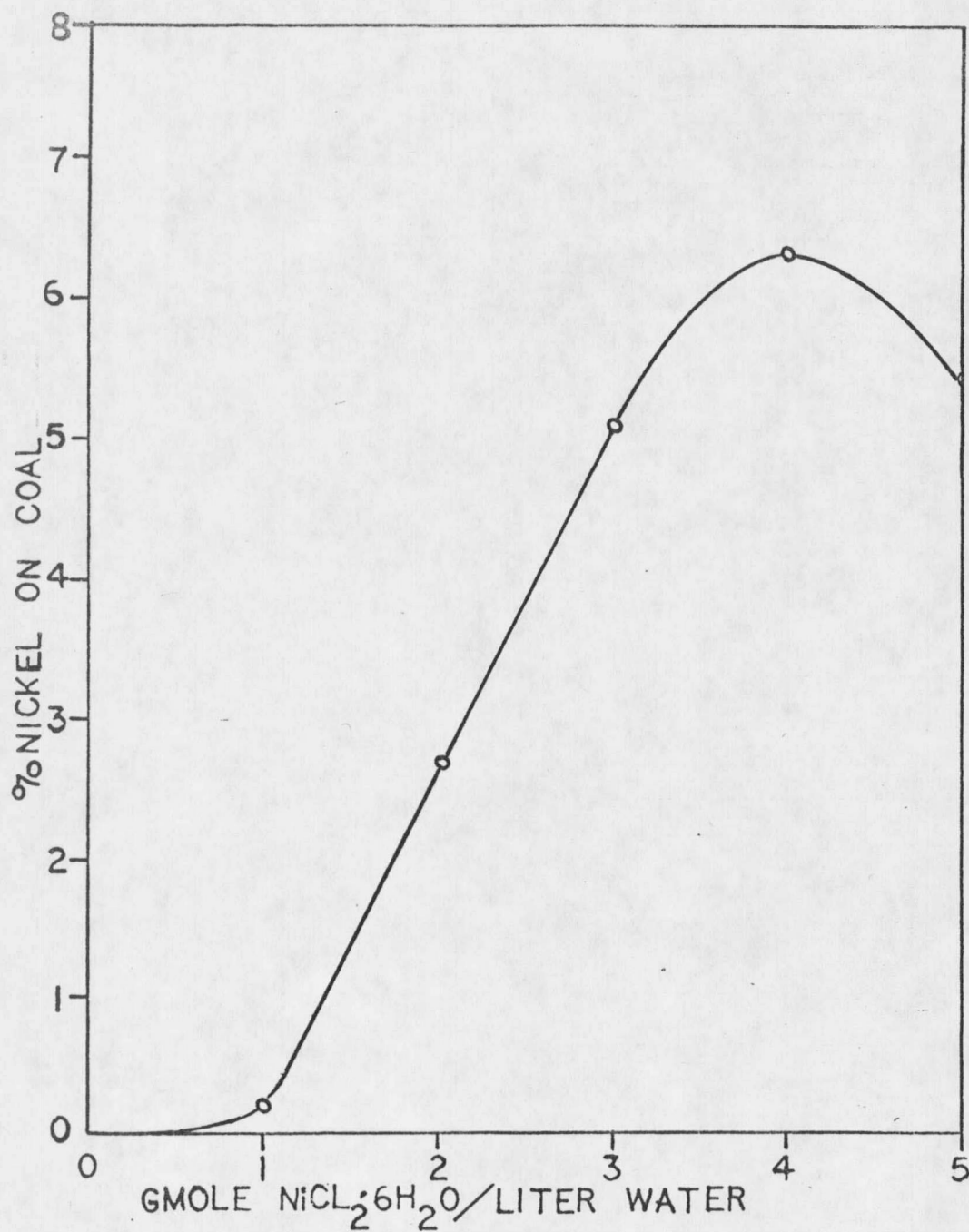


FIGURE 3. Nickel Absorbed on the Coal as a Function of Nickel Chloride Concentration in Impregnating Solution

unreacted coal. The coal was then reacted and the weight of the nickel on the remaining ash and unreacted coal was determined. The difference in the total weight of nickel before and after the reaction was the amount of nickel catalyst consumed. This was done for initial weight % nickel on the unreacted coal of 4.638%, 2.697%, 5.030%, 5.454%, and 7.086%. In all five cases, the amount of nickel consumed was negligible. These results are shown in Table II.

TABLE II. NICKEL CATALYST CONSUMED DURING REACTION

RUN NO.	% NICKEL ON COAL	GMS NICKEL PER UNREACTED COAL	% NICKEL ON REMAINING ASH & UNREACTED COAL	% ASH AND UNREACTED COAL REMAINING AFTER REACTION	GMS NICKEL PER GM REMAINING ASH & UN-REACTED COAL	% NICKEL CONSUMED IN REACTION
1	4.638	.04638	32.309	14.355	.04638	≈0
2	2.697	.02697	24.356	11.073	.02697	≈0
3	5.454	.05454	39.458	13.822	.05454	≈0
4	7.086	.07086	48.043	14.749	.07086	≈0
5	5.030	.05030	37.186	13.526	.05030	≈0

COAL PREPARATION AND ANALYSIS

Approximately fifty grams of Colstrip sub-bituminous coal was ground to 16-35 mesh for each run by mortar and pestle. This coal was then placed in an oven at 110°C for twelve hours to drive off the water.

After the coal had been dried, it was stirred into the metal chloride catalyst solution and allowed to soak for twenty-four hours. The coal was then filtered and dried in an oven at 110°C again for another twelve hours. At this time, the coal was ready for reacting and for the analysis tests.

The ash content plus the amount of metal chloride catalyst on the coal was found by placing a ten gram sample of the impregnated coal in a porcelain crucible and heating it over a bunsen burner flame. The volatile matter was driven off first, and then a higher heat was used to burn off the fixed carbon. After approximately twenty-four hours, only the original ash and the metal chloride were left. The ash content was found by dividing the weight of the ash by the weight of the original coal charged.

Another ten gram sample of impregnated coal was weighed into a boiling flask and toluene was added. A water analysis tube with graduated sidearm and reflux condenser was then attached to the flask and the toluene allowed to boil.

The toluene vapor carried the water in the coal to the reflux condenser where the two components condensed and dripped into the sidearm. The water in the sidearm separated from the toluene and sank to

the bottom. After twelve hours, all the water had been extracted from the coal and the amount could be read on the graduated sidearm. The fraction of water could then be calculated as the product of the milliliters of water and its density divided by the weight of coal charged to the boiling flask. For the coal used in these experiments, having been dried twice, the water content was virtually constant for all samples at about one percent.

CATALYST PREPARATION AND COAL IMPREGNATION

In order to compare the activities of the metal chloride catalysts tested, the catalysts had to be compared on an equivalent basis. Since all preliminary work had been done with nickel chloride, it was chosen as the reference catalyst. It was decided to use approximately 3 weight % nickel on the coal. (Three percent nickel on the coal was chosen so that enough of the catalyst appeared on the coal to represent the activity of the specific metal chloride catalysts. Any higher relative concentration of the other metal chlorides would cause problems in their wetting the coal. Some of the other metal chlorides would also be limited by their solubility in water.).

From Figure 3, three weight percent nickel on the coal is approximately 2.1 moles $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ per 100 milliliters water. This is equivalent to 50 gms of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ per 100 milliliters water. Since a comparison of the activities of the different metals was needed, all other concentrations of metal chloride solutions were based on equal weights

of the metal per 100 milliliters water and not on equal weights of the metal chloride per 100 milliliters water. The amounts of metal chloride used for impregnating the coal are listed in Table III.

The impregnation of the coal with the metal chloride catalyst was accomplished by soaking predried 16-35 mesh coal in the respective solutions for twenty four hours. A magnetic stirrer was usually used to initially wet the coal. The stirrer was not left running, however, since the stirring rod would grind the coal into minus 35 mesh particles. After the twenty-four hour period, the impregnated coal was filtered from the solution and dried for approximately twelve hours.

REACTOR OPERATION

Five grams of the impregnated coal was mixed with fifteen grams of 40 mesh Ottawa sand. This mixture was then placed in a weighed porous alundum thimble and the thimble placed in the reactor tube. All fittings were then wrapped with Teflon tape and the inlet and outlet sections were put in place and tightened.

The reactor was then positioned in the furnace, and the variac used to heat the furnace turned to full power. The back pressure regulator was then screwed in place and pressured to 1000 psi with hydrogen. The valves were then opened and the 5% HCL-95% H_2 feed gas allowed to flow through the reactor.

Because of time lag, when the temperature recorded indicated a

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

Metal Chloride	Grams Needed	Grams used due to Solubility Limitations
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	50	50
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	23.5	23.5
ZnCl_2	25.75	25.75
NaCl	31.4	31.4
KCl	23.55	23.55
CaCl_2	34.2	34.2
CuCl	19.25	0.1
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	22.0	22.0
$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	63.3	58.0
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	103.3	103.3
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	44.5	44.5
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	59.8	59.8
LiCl	75.45	63.0
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	37.6	37.6
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	49.9	49.9
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	44.0	44.0
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	33.1	33.1
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	36.5	36.5

temperature of 420°C, the variac was turned to half power. At this setting, the temperature rose to 450°C, leveled off and remained fairly constant. Timing of the run began when the temperature recorder reached 440°C.

When 30 minutes had elapsed, the variac was turned off, the feed gas shut off and the internal pressure of the reactor relieved through the bleed valve. The pressure in the back pressure regulator was then reduced to atmospheric and nitrogen allowed to flow through the system to purge any remaining feed gas and to cool the reactor.

After the reactor had cooled, the nitrogen feed was stopped and the reactor disassembled. The thimble was removed from the reactor and placed in a Soxhlet continuous extraction apparatus to extract the benzene soluble products. The extraction lasted for about 24 hours. At this time, the thimble was dried and weighed. The difference in thimble weights before and after reacting represented the amount of coal converted. This value divided by the initial coal charge (five grams) gave the conversion percentage. This value was then converted to a dry ash-free basis by dividing by $[1 - (\text{ash} + \text{water content})]$. The activities of the catalysts could then be compared on an equivalent basis.

It should be noted that the benzene extraction contributed a maximum of only about one percent to the conversion of any run.

The operating conditions used in this research were chosen as

the result of preliminary work. These are temperature, 450°C and pressure, 1000 psi. Although the 5% HCl - 95% H₂ flow rate was not metered, the gas was allowed to flow through the reactor at a rate that made film diffusion negligible. This flow rate was also determined from preliminary work.

RESULTS AND DISCUSSION

One of the objectives of this research was to determine if the catalyst was consumed during the reaction. The results of this testing for nickel were shown as part of the preliminary work, but will be shown here again in Table IV.

The results of Table IV indicate that virtually all of the nickel stays with the ash and unreacted coal during the reaction. This is important for several reasons.

One of these reasons is that the nickel does not have to be separated from the product streams. The presence of the metal and the difficulty in removing it from the product stream is one of the reasons the use of molten metal chlorides as hydrogenation catalysts in coal was abandoned.

Another important feature of the nickel appearing solely in the reactants is in its recovery. Although no tests were run to check this assumption, there is a good possibility that the nickel exists in the chloride form. If this is the case, the reclamation of the nickel should be relatively simple. Leaching the ash with water might possibly work. If the nickel is in another form, some difficulty might be encountered in recovering the nickel. The form that the nickel exists in should be investigated in future work. This future work should also investigate the amount of other metals consumed during a reaction and the form that they exist in after the reaction.

The main objective of this research was to determine the

TABLE IV. AMOUNT OF NICKEL CATALYST CONSUMED DURING REACTION

RUN NO.	% NICKEL ON COAL	GMS NICKEL PER UNREACTED COAL	% NICKEL ON REMAINING ASH & UNREACTED COAL	% ASH AND UNREACTED COAL REMAINING AFTER REACTION	GMS NICKEL PER GM REMAINING ASH & UN-REACTED COAL	% NICKEL CONSUMED IN REACTION
1	4.638	.04638	32.309	14.355	.04638	20
2	2.697	.02697	24.356	11.073	.02697	20
3	5.454	.05454	39.458	13.822	.05454	20
4	7.086	.07086	48.043	14.749	.07086	20
5	5.030	.05030	37.186	13.526	.05030	20

relative activities of the metal catalysts. The average conversion associated with each catalysts are shown in Table V.

Many conclusions can be drawn from this table. The first conclusion is that the most active catalysts are stannic chloride (67.5% conversion dry, ash-free basis) and nickel chloride (67.3% conversion dry, ash-free basis). The least active catalyst is potassium chloride (33.9% conversion dry, ash-free basis).

Table V. can be broken down into four sections: (1) the most active catalysts; stannic chloride, nickel chloride and stannous chlorides, (2) the intermediately active catalysts, (3) the catalysts with little or no effect; barium chloride, lithium chloride, and sodium chloride, and (4) those catalysts with a poisoning effect; potassium chloride.

Several observations can be made from Table V. One concerns the activities of the metals with respect to their position in the periodic table. Of those metal chlorides tested, the ones that exhibited the least activity were exclusively the alkali metals of row one in the periodic chart. These catalysts exhibited virtually no activity in hydrogenating coal. With the inclusion of manganese chloride, the next least active group of catalysts were exclusively the alkaline-earth metals. These catalysts exhibited a low hydrogenation activity. The transition elements and tin exhibited the highest activity. This would indicate that if any other metal chlorides were

TABLE V. COAL CONVERSION WITH METAL CHLORIDE CATALYST

Catalyst	Average Conversion %	% Ash+Catalyst+ Water in Coal	Average Conv. % Dry Ash Free Basis
SnCl_4	55.0	18.5	67.5
NiCl_2	57.2	15.1	67.3
SnCl_2	55.0	12.0	62.5
CuCl_2	46.4	19.2	57.4
CoCl_2	42.7	23.2	55.6
CuCl	45.5	16.3	54.4
FeCl_2	43.3	20.1	54.2
ZnCl_2	45.0	12.9	51.7
CrCl_3	42.9	11.2	48.3
FeCl_3	38.9	18.5	47.7
CaCl_2	38.7	12.8	44.4
MgCl_2	36.1	18.5	44.3
MnCl_2	32.4	22.2	41.7
SrCl_2	31.4	24.5	41.6
BaCl_2	32.0	17.0	38.6
untreated (5% HCl -95% H_2 feed gas)	32.4	15.5	38.4
LiCl	31.9	16.2	38.1
NaCl	32.5	13.8	37.7
KCl	29.1	14.0	33.9
untreated (N_2 feed only)	31.1	8.0	33.8

to be tested, they should be metals found other than in the first two rows of the periodic chart.

Although some of the catalysts exhibited no activity for the conversion of coal, all the catalysts tested produced more liquid product than did non-catalyzed coal.

Another notable feature of this table is the comparison of the non-catalyzed runs. The conversion with only a nitrogen feed represents the amount of volatiles being drive off. However, using the 5% HCl - 95% H₂ gas for the runs yields a higher conversion. This would indicate that the HCl is forming some sort of active species with the hydrogen encouraging hydrogenation even in the absence of a catalyst.

Potassium chloride, on the other hand, acted as a poison in the hydrogenation of coal. The amount of conversion with KCl as a catalyst was less than the conversion of coal with no catalyst and the 5% HCl - 95% H₂ feed. The KCl catalyst reduced the conversion of coal to approximately the same level as the non-catalyzed run with nitrogen feed only. This would indicate that the hydrogenation effect of the 5% HCl - 95% H₂ feed gas is negated by using a potassium chloride catalyst.

One other important note should be made here. This is in reference to the activity of cuprous chloride. Although cuprous chloride's activity ranked sixth of the catalysts tested, it has one advantage

over the other catalysts tested. This is in the amount of cuprous chloride used. In order to be on an equivalent metal weight basis with the other catalysts, 19.25 grams were to be dissolved per 100 milliliters of water. However, the solubility of CuCl in water is only about 0.006 grams per 100 milliliters water. In other words, the coal should contain about 3000 times less cuprous chloride than it did relative to the other metal chlorides. However, 0.1 gms of CuCl were added to each 100 milliliters of water. Because of this, some of the undissolved CuCl could have been impregnated directly on the coal. Also, high conversions of the coal might be maintained with just as low of concentrations of the other metal chlorides. Both the effect of the undissolved CuCl in the impregnating solution and the use of lower concentrations of the other metal chlorides should be studied in future work.

Regardless of the results of future work, at least with CuCl , much less catalyst is necessary to affect a relatively high conversion. This could be important for two reasons. Both reasons concern economics. It has been assumed that the metal stays on the ash after the reaction in the chloride form. If this assumption proves invalid, the recovery and regeneration of the metal chloride could be expensive if not virtually impossible. In either case, the use of the cuprous chloride could greatly enhance the economics of the system simply because of its relative lack of quantity used. Even if the metal remains in the chloride form on

the ash, the reclamation and regeneration of a smaller amount of catalyst could make the hydrogenation of coal more economically feasible.

A comparison of the metal chlorides catalysts used in this research and of other published catalyst (2) is shown in Table VI.

Although the conversions were less with the system employed in this research than in the other systems presented, this is not an accurate comparison, since the other systems were not using Colstrip coal. What is important is the comparison of the operating conditions employed and in the success of the published catalysts. The use of the molten SnCl_2 and ZnCl_2 had to be abandoned. These catalysts formed complexes and became trapped in the product streams. This made their recovery and regeneration too costly. The other catalysts compared all used a vehicle in their hydrogenation process. These vehicles included heavy recycle oil, hydrocarbon oil, and tar oil.

The major factor, though, favoring the use of the catalyst and system employed in this research is the operating conditions. Of the catalysts compared in Table VI, the operating temperatures were about the same. With the molten metal chlorides, the reaction time was twice as long as in this research. The operating pressure, however, for this research system was only about one-third or less of the operating pressures employed with the other systems. As mentioned earlier in this thesis, lower operating pressures are one of the requirements for an efficient catalyst.

TABLE VI. COMPARISON OF OPERATING CONDITIONS OF OTHER
HYDROGENATION CATALYSTS WITH OTHER COALS (2)

Catalyst	Coal Conversion	Operating Conditions		Length of run
molten SnCl_2	85	425°C	4000 psi	1 hour
molten ZnCl_2	90	425°C	4000 psi	1 hour
Iron Oxide	80	465°C	200 atms	
Tin	70	450°C	250 atms	
SnS	90	440°C	250 atms	
SnCl_4	67.5	450°C	1000 psi (68 atm)	30 mins.
NiCl_2	67.3	450°C	1000 psi (68 atm)	30 mins.

One last thing should be mentioned. Due to variations in power usage in the building, the operating temperatures varied from 440°C to 460°C during any one run and from run to run. The pressure in the back pressure regulator also varied from about 975 psi to 1025 psi from run to run. These variations had no effect on the amount of conversion. This would indicate that the system is fairly insensitive to pressure and temperature variations, at least near these operating conditions.

CONCLUSIONS

1. The most active metal chlorides for coal hydrogenation in this research were stannic chloride, nickel chloride, and stannous chloride.
2. The alkali metal chlorides showed the least activity in hydrogenating coal.
3. The alkaline-earth metal chlorides exhibited the next least activity.
4. The transition elements, with the inclusion of tin, exhibited the highest activities.
5. Potassium chloride acted as a poison reducing the amount of conversion of coal to less than that of non-catalyzed coal.
6. A feed gas of 5% HCl - 95% H₂ exhibited hydrogenation tendency on non-catalyzed coal indicating that the HCl is probably forming active species sites with the H₂ for hydrogenation.
7. The operating pressure in this research was one-third or less the operating pressure of other published systems presented.
8. All of the nickel was retained on the ash and unreacted coal during the reaction and was not lost into the product streams.
9. All catalysts tested produced more liquid product than non-catalyzed coal.
10. Although cuprous chloride did not exhibit the highest activity, the amount of cuprous chloride used to impregnate the coal was about 200 times less than the respective amounts of the other

catalysts tested in this research.

11. The hydrogenation process appears to be fairly insensitive to pressure and temperature variations, at least near the operating conditions employed in this research.

RECOMMENDATIONS FOR FUTURE STUDY

1. Since a continuous reactor would probably be used in a commercial process, a continuous reactor should be used to test the more active catalysts. This would give better contacting and remove the need for using Ottawa sand. This kind of reactor could also give information on global rate data.
2. A study should be made to determine the form that nickel exists in on the ash and remaining coal after a reaction. This study should also investigate the amount of other metals (notably tin) consumed during the reaction. The form that these other metals exist in should also be determined. After the form of the metal's existence have been determined, methods of recovering and regenerating the catalyst should be explored using lower concentrations of the metal chlorides in the impregnating solution should also be studied to determine their effect on conversion. This study should also investigate the effect on the conversion of the coal of the undissolved CuCl in the impregnating solution.
3. The off gas and product liquid should be analyzed both qualitatively and quantitatively. This includes examining the solid depositions on the outlet section to determine if this substance is NH_4Cl .
4. Tests should be conducted to determine the sensitivity of the system to temperature and pressure variations. Tests should be made to determine how far a combination of lowering the temperature and pressure can go before adversely affecting hydrogenation rates.

5. The use of a vehicle for assisting the hydrogenation process should be investigated.
6. Using lower concentrations of the metal chlorides in the impregnating solution should also be studied to determine their effect on conversion. This study should also investigate the effect on the conversion of the coal of the undissolved CuCl in the impregnating solution.

APPENDIX

TABLE VII SELECTED PRELIMINARY RUN DATA (all runs unless
specified at 1000 psi and 450°C with
5% HCl and 95% H₂ feed gas, nickel chloride catalyst)

Run No.	Time of run (min)	% Conv.	% Ash & water	% Conv. Dry Ash-Free Basis	Comments
1	30	42	14.36	49.9	
2	30	44.7	14.36	52.8	
3	30	41.1	11.02	46.7	
4	60	47.2	11.07	53.7	
5	60	43.5	13.82	50.0	1250 psi
6	60	45.5	14.75	54.0	
7	15	40.5	13.52	47.4	
8	30	31.1	6.94	33.8	no catalyst, N ₂ feed only
9	30	46.5	12.0	53.4	1:1 weight ratio coal to Ottawa sand
10	30	45.5	12.0	52.3	1:1 weight ratio coal to Ottawa sand
11	15	40.5	12.0	46.6	1:1 weight ratio coal to Ottawa sand
12	30	45	12.0	51.7	1:1 weight ratio coal to Ottawa sand

TABLE VIII RUN DATA (all runs at 450°C and 1000 psi
with a 5% HCl and 95% H₂ feed gas)

Run No.	Catalyst	% Conv.	% Ash and Water	% Conversion (dry ash free basis)
1	NiCl ₂ · 6H ₂ O	62	11.7	70.2
2	NiCl ₂ · 6H ₂ O	59	11.7	66.8
3	SnCl ₂ · 2H ₂ O	56	12.0	63.6
4	SnCl ₂ · 2H ₂ O	54	12.0	61.4
5	ZnCl ₂	44	12.9	50.5
6	ZnCl ₂	46	12.9	52.8
7	NaCl	32	13.8	37.1
8	NaCl	33	13.8	38.3
9	KCl	31.4	14.0	36.5
10	KCl	26.8	14.0	31.2
11	CaCl	37.6	12.8	43.1
12	CaCl	39.8	12.8	45.6
13	CuCl	46	16.3	55.0
14	CuCl	45	16.3	53.8
15	BaCl ₂ · 2H ₂ O	30	17.0	36.1
16	BaCl ₂ · 2H ₂ O	34	17.0	41.0
17	CrCl ₂ · 6H ₂ O	43.4	11.2	48.9
18	CrCl ₂ · 6H ₂ O	42.4	11.2	47.7

TABLE VIII (Cont.) RUN DATA

Run No.	Catalyst	% Conv.	% Ash and Water	% Conversion (dry ash free basis)
19	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	35.4	18.5	43.4
20	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	36.8	18.5	45.2
21	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	30.4	22.2	39.1
22	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	34.4	22.2	44.2
23	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	38.4	18.5	47.1
24	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	39.4	18.5	48.3
25	LiCl	31.4	16.2	37.5
26	LiCl	32.4	16.2	38.7
27	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	30.4	24.5	40.3
28	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	32.4	24.5	42.9
29	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	41.0	23.2	53.4
30	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	44.4	23.2	57.8
31	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	46.4	19.2	57.4
32	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	46.4	19.2	57.4
33	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	42.8	20.1	53.6
34	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	43.8	20.1	54.8
35	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	54.0	18.5	66.3
36	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	56	18.5	68.7
37	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	53.6	18.5	65.8
38	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	54.0	18.5	66.3

TABLE VIII (Cont.)

RUN DATA

Run No.	Catalyst	% Conv.	% Ash and Water	% Conversion (dry ash free basis)
39	None	31.4	15.5	37.2
40	None	33.4	15.5	39.5

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