The University of Utah's Continuous Coal Hydrogenation Process

P. M. Lantz

MASTER

OAK RIDGE NATIONAL LABORATORY

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CHEMICAL TECHNOLOGY DIVISION

THE UNIVERSITY OF UTAH'S CONTINUOUS COAL HYDROGENATION PROCESS

P. M. Lantz*

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On loan from the Health Physics Division

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P. M. Lantz

ABSTRACT

This presentation represents a review of experimentation performed by the University of Utah in cooperation with the U.S. Office of Coal Research (OCR) in the field of flash hydrogenation of Western coals. Monthly and quarterly reports to OCR for the period Oct. 2, 1969 through Jan. 1, 1975 and supplementary additions provided by the investigators were the basis for the review. The development of the current turbulent flow, coal hydrogenation reactor from the initial free-fall reactor concept is traced via bench-scale experimentation. The performance of the coiled-tube reactor is examined under optimum operating conditions of pressure, temperature, gas and coal feed rates, space velocity, residence time, and catalyst loading. Experimental evidence for the exothermic coal hydrogenation reaction is presented with an estimated heat of reaction value. The catalytic properties of ZnCl_2 and other metallic halides are examined in depth.

1. INTRODUCTION

The development of the continuous flash hydrogenation process for the liquefaction and gasification of Western coals is an outgrowth of a joint project initiated in 1962 by the United States Office of Coal Research (OCR) and the State of Utah. This report will concern work accomplished in the second contract period extending from 1969 to 1975.

Various techniques have been investigated for producing stable hydrocarbons by the introduction of hydrogen atoms into the free radicals produced from heated coal. Stabilizing the initial distillate radicals with low molecular weights prior to their polymerization (1) insures a product that is easily converted into gasoline and diesel range products, and (2) minimizes the quantity of tar (much of which ultimately ends up as char or coke).

The treatment technique that has received principal attention during this program in the past five years has been (continuous) flash catalytic hydrogenation of coal. It was demonstrated that a short heating time (less than one second) of coal particles in a system, where hydrogen stabilization of the initial product was accomplished quickly, gave optimum yields of products readily converted to the desired products. A semi-continuous hydrogenation reactor, with a disperse phase and a down-flow free-fall, was built which satisfied the requirements of short residence time in a hydrogen atmosphere. Unfortunately, the operation of this reactor was afflicted with problems of bridging because the coal particles falling through the heated reaction zone attached themselves to the reactor walls, thereby becoming a batch reactor. This problem

was partially alleviated by mixing coke breeze or cornstarch with the pulverized coal feed and by preoxidation of the particle surface to reduce agglomeration.

Since this experimental set-up offered little hope for increased feed throughput (even on a bench-scale level), it was abandoned in favor of a tubular reactor that was dependent on turbulent flow for fast heat transfer to the coal particle.

The information presented in this report, in the interest of conciseness, will address those data derived from the operation of the tubular reactor with reference to where it could be applicable to a scaled-up unit. No attempt will be made to review all of the experiments made during this period. The evolution of the hydrogenation reactor will be covered briefly with an examination of those parameters considered necessary for optimizing the performance of the unit. Two of the areas that are critical in the evaluation of the process will be reviewed in depth: (1) the performance of the chosen catalyst, zinc chloride; and (2) the recovery of this catalyst.

2. COAL LIQUEFACTION IN TURBULENT FLOW REACTORS

The current 50-lb/hr coal hydrogenation bench-scale reactor used by the University of Utah to assess the convertibility of Western coals to liquids and gases under moderate hydrogen pressures has evolved through a series of modifications from the free-fall unit illustrated in Figs. 1 and 2. When it was found that bridging and subsequent plugging could not be prevented in the first unit, a new design was

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Fig. 1. Schematic diagram of O.C.R. free-fall coal hydrogenation unit.

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Fig. 2. Cutaway drawing of O.C.R. reactor and quench tank.
0.1 in. = 1.0 in.

developed incorporating a high-velocity coal feed throughput provided by the hydrogenation medium. To accomplish this, the cross section of the reactor was reduced to a series of replaceable tubes with inside diameters varying from 1/8 to 1/2 in. and lengths in excess of 100 ft. Figures 3 through 5 show successive stages of development of the unit and a schematic diagram of the process. Figure 6 illustrates a schematic of the complete hydrogenation-liquefaction system.

The bench-scale process equipment for high-velocity hydrogenation of a variety of bituminous coals consists of the following: (1) a pressurized dual coal hopper and rotary wheel feeder, (2) a hydrogen-coal particle tubular preheater, (3) a tubular reactor, (4) a solids-liquids receiver, (5) condensers, (6) a filter, and (7) sampling and monitoring devices. The dual coal hopper, permitting continuous operation at 2000 psi, was equipped with a rotating wheel feeder (see Fig. 7) built into the bottom, with provision for hydrogen gas flow to carry the metered coal into the reactor. The variable speed drive on the feeder permits coal feed rates from 3-300 g/m and by changing of the rotating wheel components will permit feed rates from about 5-500 g/m. The preheater, (a later modification) is a 20-ft coiled section of 3/16-in.-ID tubing immersed in a lead bath that is equipped with a 20-kW electrical heater. The preheater heats the gas-coal mixture to about 425°C. The reactor consists of no more than five 20-ft sections of coiled tubing, 3/16-, 1/4-, 5/16-, or 1/2-in.-ID, depending upon the investigation, of which the first two sections are immersed in molten lead and heated. Here the coal-gas mixture is heated to the desired reaction temperature. The subsequent sections, 20 to 60 ft in length, are contained in a

Fig. 3. Proposed systems for high velocity coal reactor.

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Fig. 4. Auger feeder with 1/8-in.-ID reactor.

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Fig. 5. Simplified schematic diagram of 50-lb/hr coal hydrogenation reactor.

Fig. 6. Schematic of University of Utah Fuels Engineering O.C.R. Hydrogenation-Liquefaction System.

Fig. 7. Schematic drawing of rotary wheel feeder for fine coal.

furnace, nominally heated to reaction temperature. Since the char receiver has a capacity of 4 to 5 liters of porous char, the runs are limited to a range of 6500 to 7000 g of coal feed under conditions producing 65-70% conversion of the coal matter. The liquid is trapped in a series of condensers, and the filtered hydrocarbon gases are recycled. No provision has been made to sweep out the accumulating hydrocarbon gases.

The general operating procedure for the bench-scale system provides for the following: (1) the crushing of selected coal to approximately 35 mesh, (2) the impregnating of the particles with 3% (by weight) of Zn from ZnCl_2 water solution, and (3) the drying and charging of the dual-feed hoppers. The system is flushed with an inert gas prior to the pressurizing and beginning of the coal feed and hydrogenating gas flow. The preheater and reactor lead baths and the reactor furnace are brought up to the preselected operating temperatures. The controlled reactor operating temperature ranged from 900 to 1050°F. An operating pressure of 2000 psig was maintained with a cylinder of hydrogen to supplement the recycle gas produced in the process.

The solids and liquids are collected in a quenching receiver, and the condensable gases are collected in a series of water-cooled and dry-ice-acetone condensers with the noncondensable hydrocarbons returning to the reactor.

Analysis of the char for residual volatile matter and zinc catalysts was determined by ASTM and conventional analytical methods, respectively. Lesser quantities of zinc were evaluated by the intensity of the K-alpha X-ray fluorescence line. Liquid products were classified by ASTM

distillation and separation of the aromatic and saturated fractions by adsorption chromatography. Gas analysis was performed by means of gas chromatography that utilized activated alumina, silica gel, and molecular sieve columns.

Figure 8, obtained with tests from the 1/4-in.-ID reactor tube, shows the typical responses to changes in pressure and temperature. An increase in either parameter provides an increase in conversion to liquids and gases to pressures of 2000 psi. At higher pressures, the liquid conversion continues to increase slightly, but the conversion to gases decreases.

Measurements indicated that the residence times for the coal within the hot zone of the 1/2-in.-ID reactor tube were in the range of 2 to 6 sec. Gas residence time (under the same conditions) was found to be about 0.8 sec.

The use of longer reactor tubes has resulted in extension of the residence time. The most obvious consequence of the use of long tubes with small diameters has been that lower operating temperatures are effective. Figure 9 shows the effect of increased reactor length on the conversion of coal samples at two different temperatures in a 3/16-in.-ID reactor tube. Progressing from 20 to 120 ft of reactor length, the conversion increases from 20 to 85% at 538°C and from 10 to 63% at 510°C. These measurements were made at coal feed rates of about 16 lb/hr. Higher temperatures cause reactor plugging, and lower temperatures result in greatly reduced conversion. Reactor operation is very smooth and dependable in the 100-ft length at 530°C or the 120-ft length at 510°C. Conversions of 60 to 70% of the coal matter can be expected in this operating range.

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Fig. 8. Pressure and temperature effects for the 1/8-in. tube reactor.

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Fig. 9. Effect of reactor length in 3/16-in.-ID reactor tube.

Figure 10 shows the effect of increased feed rate; the conversion is plotted in terms of space rate measured in pounds of coal processed per cubic foot of reactor volume. This figure indicates that feed rates of 800 and 500 lb ft⁻³ hr⁻¹ will yield 60 and 70% conversion, respectively. The high space rates reported are the result of the turbulent motion caused by pumping large volumes of hydrogen (6 to 7 vol. of H₂: 1 vol. of coal) through a small tube to push coal and catalyst through the hot zone. This motion makes for intimate contact between coal and hydrogen in the presence of a catalyst, with a minimum of liquid present to act as a diffusion barrier.

Since the goal of the project was to produce synthetic crude oil, one measure of success is the ratio of liquids to gases. Figure 11 shows that, at 60 to 65% conversion, 5 to 7 times as much liquids as gases can be expected.

2.1 Quality of Products

2.1.1 Gases

The recycle hydrogen gas used during the course of a coal hydrogenation test shows a continuous buildup of hydrocarbon gases as well as H₂S, NH₃, and H₂O. Table 1 shows an analysis of samples taken at intervals during a 1-hr test where 15 lb of coal was tested. Results indicate that hydrogen is the major component, with 60% of the hydrocarbon portion as methane and 20% as ethane.

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Fig. 10. Effect of feed rate on coal conversion.

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Fig. 11. Ratio of liquid and gaseous products.

Table 1. Buildup of hydrocarbons in recycle gas during a
1-hr coal-hydrogenation trial

Sample No. Sample Taken	1 Pre Run	2 10 min	3 20 min	4 30 min	5 40 min	6 50 min	7 60 min	8 Post Run
% H ₂	97.8	95.7	94.2	94.4	91.7	87.7	87.8	87.8
% CH ₄	0.28	0.65	1.29	1.30	2.24	3.15	3.02	3.06
% C ₂ H ₆	0.25	0.38	0.59	0.63	0.90	1.10	1.13	1.11
% C ₃ H ₈	0.26	0.32	0.43	0.45	0.57	0.68	0.65	0.65
% N-C ₄ H ₁₀	0.25	0.27	0.30	0.31	0.33	0.35	0.34	0.34
% Other	1.16							7.04

2.1.2 Liquids

The liquid products from the coiled-tube reactor were collected in two fractions: (1) a heavy, viscous product from the first condenser, and (2) a light, low-viscosity material from the combined second and third condensers. The liquid product is filtered to remove char and unconverted coal. The filtered oils are washed with benzene and cyclohexane to yield an asphaltene (cyclohexane insoluble), a benzene insoluble residue and a soluble oil. Table 2 shows the chemical and physical analysis of each of the three samples so treated.

2.1.3 Char

Table 3 gives an analysis of the Hiawatha coal and the three char products resulting from three hydrogenation tests. It can be observed that the carbon, hydrogen, and nitrogen contents are almost unchanged from the original coal, while sulfur is greatly increased in the char. This seems to substantiate the premise that the coal particles are reacted at the outer surface only and that the remaining char is largely unreacted coal. This is supported further by the fact that the char can be recycled through the reactor and converted to more liquids and gases without additional amounts of catalyst. (See Fig. 12.)

3. DEVELOPMENT STAGES OF THE 50-LB/HR CONTINUOUS COAL REACTOR

Many modifications were required in an effort to find the best combination of coal feed rate, hydrogen flow rate, heat transfer medium, reactor cross section, and length and reactor temperature for coal liquefaction in the continuous coal reactor. After the free-fall hydrogenation

Table 2. Chemical and physical analysis of oil products

Filtered oil samples	A	B	C
Flash point °C	29.5	34.5	27.0
Pour point °C	37	35	31.5
Sp. Gr. g/cc	1.078	1.070	1.073
Viscosity	42.1 SFS (58.8°C)	56.8 SFS (50°C)	70.53 SFS (50°C)
Btu/gal	129,179	133,305	136,550
Ash, %	0.54	0.61	0.37
% Sulfur	0.17	0.20	0.17
% Nitrogen	2.2	1.6	1.54
% Carbon	74.7	70.3	74.25
% Hydrogen	7.5	7.5	7.35
% Oxygen (by difference)	(15.2)	(20.6)	(16.3)
<u>Whole Sample (Heavy Liquid)</u>			
Asphaltenes	22.3	15.7	12.62
Residue	16.6	24.2	14.27
Soluble Oils	43.1	36.2	43.32
Water	15.9	18.7	26.33
Loss	<u>2.1</u>	<u>5.2</u>	<u>3.46</u>
	100.0	100.0	100.0
<u>Soluble Oils</u>			
Neutral Oil	87.6	59.8	57.3
Tar acids	11.1	34.2	22.4
Tar bases	1.3	5.5	13.7
Loss	<u>0</u>	<u>0.5</u>	<u>6.6</u>
	100.0	100.0	100.0

Table 3. Proximate and ultimate analyses of starting coal and some selected chars

<u>Proximate analysis (as is basis)</u>					
<u>Sample</u>	<u>% Moisture</u>	<u>% Ash</u>	<u>Volatile matter</u>	<u>Fixed carbon</u>	<u>Btu/lb</u>
Coal (Hiawatha, Utah)	2.43	6.70	44.24	46.63	11,450
Char 1263 85.6% Conversion	0.34	34.40	15.86	49.40	11,020
Char 1271 61.4% Conversion	0.48	17.63	29.90	51.99	12,050
Char 1272 59.6% Conversion	0.24	17.54	29.95	52.27	12,200
<u>Ultimate analysis (dry, ash-free basis)</u>					
<u>Sample</u>	<u>% Carbon</u>	<u>% Hydrogen</u>	<u>% Nitrogen</u>	<u>% Sulfur</u>	
Coal	70.1	5.4	1.6	0.88	
Char 1263	63.3	4.1	1.7	3.63	
Char 1271	70.1	5.6	1.6	1.42	
Char 1272	69.6	5.8	1.5	1.31

Fig. 12. Recycle of reacted char product.

reactor design (with a 2-in. cross section) was abandoned in favor of the high-velocity reactor (1/2-in.-ID tube), it was necessary to increase the reactor tube length and add a coal-hydrogen preheater. By inserting a 3/16-in.-ID, 12-ft-long preheater tube wrapped with three 4000-W electrical heaters in front of the 6-ft-long reactor tube, sufficient heat was provided to heat the coal and hydrogen to any temperature below the softening point of coal.

Tests with the 1/2-in.-ID reactor have covered a gas flow rate ranging from 16 to 30 cubic feet of hydrogen (STP) per minute, coal feed rates of 50 to 250 g/min, and preheater temperatures between 100 and 600°F. Figure 13 shows test data for two coal feed rates and two reactor hot-zone lengths. Although the data indicate a scatter over a wide range in the percent of coal conversion, the indication is that a longer hot reaction zone will provide higher conversion. Also, an increase in coal feed rate will decrease the conversion. Figure 14 shows the effect of coal feed rate on conversion in the range 50 to 250 g/min.

The use of the 1/2-in.-ID reactor permitted the insertion of a thermal well for the measurement of reaction temperatures along its entire length (6 ft). Previously, temperatures were measured in the area of the heat transfer medium and, therefore, only indicated the total heat input, without determining the quantity actually adsorbed by the H₂-coal mixture. Figure 15 shows temperatures made with a 1/16-in.-OD thermocouple through the wall of a 1/8-in.-OD thermal well along the full length of the 1/2-in.-ID reactor. Tests were made first with no hydrogen flow to find static temperatures and then with 18, 22, and 26 SCFM hydrogen flow. These flow rates represented apparent gas velocities of 0, 0.79, 0.97 and 1.19 ft/sec

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Fig. 13. Coal conversion in the 1/2-in.-ID reactor.

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Fig. 14. Effect of coal feed rate on coal conversion in the 1/2-in.ID reactor.

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Fig. 15. Static and dynamic temperature profile through length of 1/2-in.-ID reactor tube. All temperature controls set for 660°C.

for the gas. The highest 12 in. was reduced by the incoming gas as much as 300°C, and the next 2 1/2 ft was reduced up to 100°C from the static condition. The lower area of the reactor approached nearly the same temperature regardless of the gas flow rate. Figure 16 shows temperature measurements made with and without the preheater in service. The control set temperature for the upper reaction of the reactor was deliberately set 50°C higher than the lower section to remove the differences in the reactor. It can be seen that with the wide fluctuations encountered both with and without coal present, the reactor attains the same temperature regardless of the presence of coal or of the use of the preheater. However, the preheater does lengthen the hot zone and results in longer residence for particles at the reaction temperature.

The beneficial results indicated by the use of a preheater precipitated the installation of a coiled 40-ft-long x 3/16-in.-ID preheater for use in future tests. Tests were conducted with single and dual pass of 800-g samples of Spencer coal (-40+100 mesh) through the 1/2-in.-ID by 6-ft-long reactor. Reactor conditions include the following: 2000 psi of hydrogen, 120 g per minute of coal, 25 SCFM (hydrogen), 425°C preheater, 510 to 593°C reactor, and Zn/coal ratio of 0.03 ZnCl_2 catalyst. The results in Fig. 12 indicate that the coal is somewhat more reactive after the first treatment (i.e., four samples taken through two cycles averaged 29.8% conversion in the first cycle and 40.2% in the second cycle). Combining the two-cycle conversions results in a 65-70% conversion at rather mild conditions. The fact that the second conversion averages higher than the first may be taken as evidence of an "activation" of the catalyst.

Fig. 16. Dynamic temperature profile through length of 1/2-in.-ID reactor tube. Hydrogen gas flow rate, 22 CFM. Coal feed rate 60 g/min. Upper reactor, 600°C; lower reactor, 540°C.

4. EXOTHERMIC NATURE OF COAL HYDROGENATION

Tests were conducted with two Utah coals, Hiawatha and Kaiparowitz, to examine the exothermic nature of coal hydrogenation. The 1/4-in.-ID reactor tube was used at 60- and 100-ft lengths. The preheater, a 20-ft section with a 3/16-in.-ID was immersed in a lead bath in which 20,000 W of electrical energy could be expended to produce heat. The preheater heated the gas-coal mixture to about 425°C. The first two sections of the reactor (20-ft sections of 1/4-in.-ID tube) were also immersed in molten lead and heated. Here the coal-gas mixture was heated to the desired reaction temperature. The following sections of reactor tube, 20 to 60 ft in length, are contained in an oven, nominally heated to reaction temperature, but the coils are not immersed in lead. This means that the later sections of the reactor show lower temperatures if the process is endothermic and higher temperatures if it is exothermic.

Test No. 1339 (see Table 4), using Hiawatha coal, was the first test where the exothermic nature of the reaction could be shown over a period of time long enough to approach equilibrium. The lines of Fig. 17 show higher temperatures in coils 3, 4, and 5 (toward the outlet of the reactor) than in the sections near the inlet. These five coil temperatures were essentially the same until coal feed was started. The coils that were heated by the reaction returned to the control temperature when coal feed was terminated. An increase of 28°C was noted in coils 4 and 5 during the reaction period. Figure 18, depicting the temperatures during test No. 1341 and using Kaiparowitz coal, indicates an even greater increase (to +38°C) from the control temperature. Figure 19 shows the same increases during the course of a 60-min test (No. 1344)

Table 4. Thirty- to sixty-minute trials with
1/4-in.-ID reactor tubes

Test No.	Duration/ min	Coal feed/g	Feed rate g/m	% Liquids	% Gas	% Conversion
1339	23.0	2095	91.1	61.7	12.9	74.6
1341	31.0	3000	102.0	61.9	12.2	74.1
1344	60.25	6576	109.2	54.9	11.9	66.8
1346	34.0	3215	94.6	Analysis not completed		
1347	48.55	4750	97.8	"	"	"

Fig. 17. Temperature profiles for test No. 1339 (Hiawatha Coal; 482°C; 20 ft- x 3/16-in.-ID preheater; 100 ft- x 1/4-in.-ID reactor).

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Fig. 18. Temperature profiles for test No. 1341 (Kaiparowitz, Utah Coal; 482°C; 20 ft- x 3/16-in.-ID preheater; 100 ft- x 1/4-in.-ID reactor).

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Fig. 19. Temperature profiles for test No. 1344 of 1-hr duration (Kaiparowitz, Utah Coal; 425°C, 20 ft- x 3/16-in.-ID preheater; 482°C; 100 ft- x 1/4-in.-ID reactor).

where 6576 g of coal was fed from two hoppers. The loss of temperature near the middle of the test was caused by buildup of a high pressure differential that required the coal feed to be discontinued for periods of 1 to 2 min. When the coal was fed out of hopper No. 2, the feed motor of hopper No. 1 was again turned on and the remainder of the coal contained in it was fed out. Temperature in coils 3, 4, and 5 decreased during this latter period and returned to the control point as the coal feed was terminated. Figures 20 and 21 show similar temperature profiles for test No. 1346 (a 34-min duration) and No. 1347 (a 48-min duration). The same temperature variations are shown in all tests (i.e., coils 4 and 5 are heated to 35 to 40°C above the control temperature). Coil 3 is heated 15 to 20°C above its control point, and coils 1 and 2 vary only slightly from the set temperature. In the case of test No. 1344, the heat controllers did not turn on any of the heaters after the coal feed was initiated. This indicates that the reaction is sufficiently exothermic to maintain the temperature once the reactor is started. The heat produced in the reaction was estimated to be about 180 Btu per pound of coal treated.

5. CATALYST STUDIES

The thermal properties and reactions of ZnCl_2 , ZnCl_2 impregnated on coal and pure coal samples were studied by Differential Thermal Analysis and Thermogravimetric Analysis. These studies were directed to determining the mechanism of the catalytic action of ZnCl_2 in the reactor system being used for coal hydrogenation. Zinc chloride has

Fig. 20. Temperature profiles for test No. 1346. Of 34-min duration (Kaiparowitz, Utah Coal; 100 ft- x 1/4-in.-ID reactor).

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Fig. 21. Temperature profiles for test No. 1347. Of 48-min duration, (Kaiparowitz, Utah Coal. 100 ft- x 1/4-in.-ID reactor.)

shown catalytic activity in this reactor and in the hydrocracking of coal extracts. This study attempts to correlate the chemical and physical properties of catalysts and coals with hydrocracking behavior in the reactor.

The exact form of the catalyst during the hydrogenation reaction is not known. Since the ZnCl_2 is applied to the coal as an aqueous solution and the coal is then dried, it is possible that hydrolysis and oxidation occur before the sample is reacted. X-ray diffraction patterns taken on dried coal samples confirm that the form is not that of anhydrous ZnCl_2 , but these patterns do not agree with the published patterns of hydroxychlorides. After passage through the reactor, the char samples provide only diffuse patterns. The temperature of the hydrogenation reactions are sufficiently high that ZnCl_2 would melt (M.P. = 262°C), and, in the cases where the temperature rises to 800°C , it would be vaporized (B.P. = 732°C). The coal is in the reaction zone for only a fraction of a second; therefore, it seems logical that the catalyst is actually present as a liquid when its effect is shown.

The study of the thermal behavior of Hiawatha coal and coal- ZnCl_2 catalyst systems was extended to thermogravimetric analysis. Approximately 5 mg of -40 to +60 mesh coal were used in each of the experiments. The heating rate was $10^\circ\text{C}/\text{min}$, and nitrogen gas flowed over the sample at a flow rate of 0.2 liter/min. The differential and integral weight loss for a sample of Hiawatha coal is shown in Fig. 22. The maximum weight loss occurs at 450°C . Figure 23 shows the results for Hiawatha coal with 15 wt % ZnCl_2 impregnated on the coal. The temperature of maximum weight loss was 450°C , but the beginning weight loss occurred at a slightly lower temperature than in the case of the coal. Calorimetric results

Fig. 22. Thermogravimetric analysis of hiawatha coal.

Fig. 23. Thermogravimetric analysis of hiawatha coal with 15% ZnCl_2 .

indicated exotherms at 425 and 490°C. The weight loss at 900°C was 36% for the coal (uncorrected for ash) and 31% for the coal-ZnCl₂ (uncorrected for ash and catalyst). The coal has a volatile matter content of 47%.

Thermogravimetric analysis of alumina and silica-gel (impregnated with ZnCl₂ by the same method as the coals are impregnated with catalyst) indicate that about 8-10% of the initial ZnCl₂ remains as a nonvolatile residue. The ZnCl₂ itself has a nonvolatile residue of 6.5%. Previously reported results corrected for residue from the ZnCl₂ that is not volatilized are indicated below:

<u>Wt % ZnCl₂ on Hiwatha Coal</u>	<u>% Wt Loss at 900°C</u>
0	40.9
2	37.2
5	34.2
12	28.7
20	27.5
25	24.2

The effect of heating rate is shown below.

<u>°C/min, Heating Rate</u>	<u>Wt % ZnCl₂</u>	<u>Wt Loss at 900°C</u>
5	0	40.9
10	0	40.1
20	0	40.7
5	12	28.7
10	12	29.5
20	12	30.1

Thermogravimetric analysis of coal-catalyst systems shows a decrease in the weight loss as the amount of ZnCl_2 catalyst is increased. It can be seen in Fig. 24 that the suppression of the evolution of volatile matter in coal when impregnated with ZnCl_2 depends on the type of coal. The weight loss appears to correspond to the observed reactivity of the coal in the hydrogenation reactor. Hiawatha and Castle Valley coals were found to be highly reactive. The data also appear to correlate with the oxygen content of the coals--Alton having the highest content, while Hiawatha and Castle Valley have the lowest.

The yield of hydrocarbon gases has been reported for coal in the presence of ZnCl_2 catalyst with nitrogen flowing past the sample. The methane yield at various temperatures is shown in Fig. 25 for coal and for coal impregnated with 12% ZnCl_2 . Figure 26 shows the relative measure of hydrogen evolution from pure coal and zinc chloride impregnated coal under a nitrogen atmosphere. The effect of zinc chloride is to cause the evolution of methane and hydrogen at a lower temperature. Thermogravimetric analysis of zinc chloride impregnated coal was conducted under a hydrogen atmosphere. Hydrogen flowed through the system at a rate of 0.2 liter/min. These results are compared with those for nitrogen flow in Table 5. Zinc chloride does not have the same effect of reducing gas evolution where hydrogen is present in the gas phase. The catalyst appears to act as a transfer agent for hydrogen, promoting hydrogenation in the gas phase when hydrogen is present and dehydrogenation when hydrogen is absent. Dehydrogenation leads to a lower volatile matter in the sample.

Studies were made of the catalysts effective in the short-residence time coal hydrogenation reactor. Acid strength, acidity, and the catalytic

Fig. 24. Weight losses of various coals as a function of catalyst level.

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Fig. 25. Methane evolution during coal pyrolysis.

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Fig. 26. Hydrogen evolution during coal pyrolysis.

Table 5. Effect of ZnCl_2 on evolution of gases under nitrogen and hydrogen atmospheres

% ZnCl_2	% Weight loss (M.A.F.)	
	N_2 Gas	H_2 Gas
0	41.80	54.07
12	29.85	49.86

Table 6. Acid strength of catalysts

	Phonylazo naphthylamine	Dimethyl yellow	Denzeneazo diphenylamine	Dicinnamal acetone	Anthraqui- none
PKa	4.0	3.3	1.5	-3.0	-8.2
Wt % of H_2SO_4 of corresponding acid strength	5×10^{-5}	3×10^{-4}	0.02	48	90
Color Change					
ZnCl_2	Yes	Yes	Yes	No	No
ZnBr_2	Yes	Yes	No	No	No
ZnI_2	Yes	Yes	No	No	No
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	Yes	Yes	No	No	No
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	Yes	Yes	No	No	No
$\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$	Yes	Yes	Yes	Yes	Yes

Table 7. Surface acidity of catalysts

Catalyst	Decrease in n -butylamine concentration, M moles/l	Acidity, M moles/g
ZnCl_2	0.0907	4.54
ZnBr_2	0.0739	3.98
ZnI_2	0.0590	2.90
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	0.0844	4.16
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.0847	4.26
$\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$	0.0216	1.02
$\text{ZnCl}_2/\text{Coal}$ (12.3%)	0.0545	1.36
ZnI_2/Coal (12.4%)	0.0398	1.00
$\text{SnCl}_2/\text{Coal}$ (12.2%)	0.0313	0.78

activity for simple reactions were determined for zinc halides, stannous chloride, and ferric chloride.

The acid strengths of the catalysts were measured with an indicator in various amine bases which are characteristically responsive to different acid strengths. Table 6 shows that the acid strength of the halide is much less than that of the silica-alumina catalyst.

Surface acidities were determined by back titration of n-butyl amine with hydrochloric acid. The surface acidities are shown in Table 7. The acidities of the halide catalysts are greater than the silica-alumina catalyst. Impregnation of the catalyst on the coal decreases the acidity significantly.

The catalytic activity of ZnCl_2 , ZnBr_2 and ZnI_2 was determined for the polymerization of propylene. This reaction is catalyzed by Bronsted acids.³ The catalysts show no activity for this reaction. It is concluded that the halides having a weak Bronsted acidity (if present at all) are not responsible for carbonium-ion reactions. Bronsted and Lewis acids may catalyze the isomerization of butenes. Zinc chloride and bromide show very little activity for the isomerization of 1-butene or trans-2-butene under the conditions of these experiments. The activity was much less than that of other solid acids such as silica-alumina and BF_3 -treated alumina.⁴ Zinc chloride and bromide also show no activity for the hydrogenation of ethylene, although other solid acids show considerable activity at lower temperatures than those employed in these studies.⁵⁻⁷

The metal halide catalysts used in these studies, with the exception of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, demonstrate the following characteristics: (1) strong catalytic activity for the hydrogenation of coal at short reaction times,² (2) high acidity but much lower acid strength than silica-alumina cracking catalysts, and (3) little activity for the acid-catalyzed reactions of this study. Temperature would be expected to be an important factor. In these experiments, the catalysts were in the solid form. In coal hydrogenation reactions, the temperature is about 500°C , and the catalysts are molten.

The catalytic conversion of 2-pentanol was studied to further determine the catalytic properties of zinc halides and stannous chloride. Lewis acids catalyze the dehydration of 2-pentanol to form pentenes. Semi-conducting materials, such as zinc oxide, catalyze the dehydration of 2-pentanol to form 2-pentanone. Catalysts were impregnated on supports and conditioned at selected temperatures under controlled atmospheres. Conversion was determined by the decrease in 2-pentanol. Selectivity is defined as the molar ratio of 2-pentanone and the moles of 2-pentanol converted multiplied by 100. The results for the catalysts supported on activated charcoal are shown in Table 8. Zinc chloride supported on silica gel gives high conversion but no selectivity. Zinc oxide gives moderate conversion but high selectivity. Zinc halides supported on activated charcoal give high conversion but low selectivity. Results for catalysts impregnated on coal are shown in Table 9. The conversion is decreased slightly relative to the corresponding catalyst impregnated on activated charcoal, but the selectivity increases significantly. Little conversion or selectivity occurs when the concentrations and

Table 8. Catalytic conversion reaction of 2-pentanol over supported molten metal halides (LHSV = 2.48 hr^{-1})

Catalyst ^a	Pretreatment Carrier	Temp. (°C)	Reaction temp. (°C)	Total conv. (mole %)	Selectivity ^b to 2-Pentanone (mole %)
ZnCl ₂	N ₂	404	403	96	29
ZnBr ₂	N ₂	404	403	87	32
ZnI ₂	N ₂	410	410	85	44
SnCl ₂	N ₂	300	300	86	27
ZnO	O ₂	355	299	44	100
NiSO ₄	N ₂	404	301	~99	~0
ZnCl ₂ /SiO ₂	Air	466	369	~99	~0
Activated Charcoal	N ₂	355	307	5	~0
SiO ₂	N ₂	404	302	26	~0

^aCatalyst samples except ZnO, NiSO₄ and SiO₂ were impregnated on activated charcoal from aqueous solutions (0.3 g-sample/g-support).

^bSelectivity to 2-Pentanone was determined as follows:

$$\text{Selectivity (mole \%)} = \frac{\text{Moles of 2-Pentanone produced}}{\text{Moles of 2-Pentanol converted}} \times 100.$$

Table 9. Catalytic conversion of 2-pentanol over some molten metal halides impregnated on coal

(LHSV = 2.48 hr^{-1} , N_2 flow = 100 ml/min)

Catalyst	Pretreatment Carrier	Temp. °C	React. temp. °C	Total conv. mole %	Selectivity mole %
ZnCl_2 (5 wt %)	N_2	452	394	18	0
ZnCl_2 (10 wt %)	N_2	452	399	23	60
ZnCl_2 (23.1 wt %)	N_2	455	405	65	64
ZnCl_2 (33.3 wt %)	N_2	452	399	50	66
ZnCl_2 (50 wt %)	N_2	452	404	54	77
ZnCl_2 (23.1 wt %)	N_2	305	304	5	~0
ZnCl_2 (23.1 wt %)	N_2	455	405	65	64
ZnCl_2 (23.1 wt %)	N_2	459	455	76	53
ZnCl_2 (23.1 wt %)	H_2	455	411	62	50
FeCl_3 (50 wt %)	N_2	395	395	52	~5
SnCl_2 (50 wt %)	N_2	393	387	80	63
Coal	N_2	404	406	~5	~0
ZnO	O_2	355	299	44	100
NiSO_4	N_2	404	301	~99	~0

temperatures of catalysts are low. Coal shows low conversion and no selectivity. The effect of pretreatment with hydrogen sulfide is shown in Table 10. The results of these studies indicate that ZnCl_2 and SnCl_2 are altered when impregnated on coal and lose some of their Lewis acid properties.

Thermogravimetric analysis studies of the coal-zinc chloride system have been extended to include hydrogen atmospheres. The weight loss at 900°C after heating at $10^\circ\text{C}/\text{min}$ is shown in Table 11, along with previous results for nitrogen atmospheres. As previously stated, ZnCl_2 dehydrogenates the coal in a nitrogen atmosphere. The yield of methane as a function of temperature is shown in Fig. 27.

Additional studies were conducted on the evolution of hydrogen from coals impregnated with ZnCl_2 and $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$. Pyrolysis gases were collected at various temperatures and analyzed for hydrogen by gas chromatography. The amount of hydrogen evolved at low temperatures was found to increase with the amount of ZnCl_2 impregnated on the coal, as shown in Fig. 28. Figure 29 indicates the dehydrogenation activity of a number of inorganic salts that are known to be good hydrogenation catalysts.^{1,2} Figure 30 shows the effect of salts which are known to be inferior for coal hydrogenation.^{1,2} Zinc halides and stannous chloride are the most active for coal hydrogenation. Metallic zinc, zinc oxide, and zinc sulfide are inactive for coal hydrogenation, as shown in Fig. 31. The effect of coal rank is noted in Fig. 32. The dehydrogenation activity correlates with the suppression of volatility previously reported.³

In summary, when a coal sample is impregnated with ZnCl_2 and heated, the coal is dehydrogenated, tar evolution is suppressed, the Lewis acidity

Table 10. Effect of pretreatment and catalyst support on selectivity to 2-pentanone over molten halides^a

Catalyst Halide	Support	Pretreatment Carrier	Pretreatment Temp. (°C)	Reaction Temp. (°C)	Total conv. (Mole %)	Selectivity to 2-Pentanone (Mole %)
SnCl ₂ ^b	AC ^c	N ₂	395	388	76	51
SnCl ₂	AC	H ₂ S	398	395	41	12
SnCl ₂	Coal	N ₂	393	387	80	63
ZnCl ₂ ^d	AC	N ₂	404	403	96	29
ZnCl ₂	AC	H ₂ S	397	399	80	42
ZnCl ₂	Coal	N ₂	455	405	65	64
FeCl ₃ ^b	Coal	N ₂	395	395	52	5

^aLHSV = 2.48 hr⁻¹.^bSample wt % is 50.^cActivated charcoal.^dSample wt % is 23.1.

Table 11. Thermogravimetric analysis of zinc chloride impregnated coal

Percent ZnCl ₂	Percent volatile H ₂ atmosphere	N ₂ atmosphere
0	44.1	41.8
5	44.3	34.9
12	43.4	29.9
20	41.6	26.4
25	43.7	26.3

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Fig. 27. Methane evolution during pyrolysis.

Fig. 28. Effect of ZnCl₂ concentration on dehydrogenation of coal.

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Fig. 29. Dehydrogenation of coal by good hydrogenation catalysts.

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Fig. 30. Dehydrogenation of coal by poor hydrogenation catalysts.

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Fig. 31. Dehydrogenation of coal by zinc compounds.

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Impregnation: 8.806×10^{-2} mole
 ZnCl_2 on coals.

Fig. 32. Effect of rank on coal dehydrogenation.

of the ZnCl_2 is lost, the surface area (see Table 12) is increased, the pore structure is altered, and active sites for hydrogen chemisorption are formed.

6. ZnCl_2 CATALYST RECOVERY

Although ZnCl_2 has been shown to be an effective hydrogenation catalyst for the high conversion of coal to liquids and gases, the economics of the process is dependent upon high recovery of the catalyst. Following hydrogenation of the coal in this process the catalyst is found on the solid char residue, in the filter that removes the particulate matter prior to recirculation of the gas, and dispersed in the liquid product. The amount dispersed in the liquid is less than 2% of the initial amount. After the liquids and solids are separated by a benzene extraction, a water extraction of the char is used to remove soluble zinc compounds. For reactions at 650°C , 50 to 60% of the zinc is recoverable from the char by means of a water extraction. Another 20 to 25% is recoverable from the filter medium used to trap dispersed heavy liquids.

Zinc chloride recovery tests were made with chars from the hydrogenation of three Utah coals, namely, Hiawatha (77% conversion), Castle Valley (54% conversion), and Orangeville (55% conversion). Samples of these chars were extracted with water alone and then with 10% hydrochloric acid. Hot acid extraction resulted in only 50% extraction of the zinc as measured by X-ray spectrographic analysis. This indicates that the zinc chloride was being altered chemically in the hydrogenation process.

Table 12. Surface areas of coal and halide-impregnated coal

Sample	Pretreatment temperature (°C)	Surface Area, m ² /g	
		CO ₂ adsorption at 22°C	N ₂ adsorption at -195°C
Coal	200	170.6	1.3
	300	195.2	-
	400	415.8	25.5
	1000	109.2	25.5
23% ZnCl ₂ /coal	200	108.4	-
	300	332.9	77.4
	400	581.3	432.1
23% SnCl ₂ /coal	400	557.1	317.1
23% FeCl ₃ /coal	400	471.6	206.5
ZnCl ₂ /AC	400	-	487.4
Activated charcoal (AC)	400	-	711.5

In a continuing effort to identify the acid insoluble form of ZnCl_2 , several approaches were made. A water solution of ZnCl_2 passed through the reactor at 675°C and 2000 psi of hydrogen with no coal present precipitates from solution $\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2$, which is not water soluble, but is acid soluble. When coal is present, it is postulated that with high temperature and reducing conditions zinc metal would be produced. This is actually found in the char product. This as well as ZnS which had not been verified is readily acid soluble. Since it was not possible to measure the crystalline form of the zinc compound after reaction, this indicates that the concentration is too low for X-ray diffraction. When samples of the acid-insoluble zinc-bearing char were heated enough to burn off the combustibles, tests showed the presence of ZnO , and acid extraction of the material removed 97 to 99% of the zinc. It appears that the acid insoluble zinc in the char is present in a reduced form and that it is oxidized to a soluble form with low-temperature ashing.

Figure 33 shows the extraction of zinc from reacted coal char by the following methods: (1) with hot water; (2) with hot, concentrated hydrochloric acid; and (3) with hot, dilute solution of Pb^{++} , Cu^{++} , and Hg^{++} ions to remove the sulfur ion. It can be seen that the difficulty of removing zinc from the char is directly related to the amount of conversion of the original char. For high conversion, less zinc is dissolved by the solvent.

Drawing from the previous experiences to recover ZnCl_2 catalyst from the char produced in the continuous coal hydrogenation unit, the recovery was simplified by the use of an oxidizing acid. By leaching hydrogenation char for an hour with cold, concentrated HNO_3 , followed

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Fig. 33. Extraction of zinc from char following coal hydrogenation.

by a single-hour leach with boiling concentrated HNO_3 , 99.3% of the Zn in the 4.0% Zn starting material was recovered. Needless to say, this is an effective but rather drastic recovery approach. This area requires further investigation to make it economically feasible.

A preliminary investigation concerning the recovery of the ZnCl_2 catalyst is included in the Appendix. The study considered the recovery of 99% of the catalyst for a 25,000 TPD plant. Catalyst recovery costs ranged from 8.97 to \$12.07 per ton of coal and are considered to be too high, based on the current value of coal, \$22/ton. Catalyst recovery methods must be practiced since catalyst costs would be 40 to \$50 per ton at the loadings suggested. For the flash hydrogenation process, catalyst recovery presents a challenging problem that must be solved if the process is to become economically viable.

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