MOLTEN ZINC HALIDE CATALYSTS FOR THE HYDROCRACKING OF COAL EXTRACT AND COAL

C. W. Zielke, R. T. Struck, J. M. Evans, C. P. Costanza, and E. Gorin

Research Division
Consolidation Coal Company
Library, Pennsylvania

INTRODUCTION

The background information leading to the development of fused metal halide catalysts for the hydrocracking of coal extract was discussed in a previous paper.[10] It was shown, therein, that metal halides which are strong Lewis acids are active catalysts for the hydrocracking of polynuclear hydrocarbons and residues from the hydrocracking of coal extract with contact catalysts.

The present paper describes the initial steps in the development of molten zinc chloride catalysts for the hydrocracking of coal extract and even coal itself. An extensive survey of the variables in the hydrocracking of coal extract with massive quantities of zinc chloride melt is presented. Comparative data are also presented with other catalyst systems. All data given here were obtained in batch autoclave experiments.

In addition to the zinc halides, several possible Lewis acid catalysts were considered such as $AlCl_3$, $AlBr_3$, BF_3, etc. These were rejected primarily because they would be completely destroyed by the steam released during the hydrogenation of coal extract. Also, as a consequence of the halogen acids released during hydrolysis of the catalyst, these materials would be much too corrosive to be useful in potential commercial systems.

Zinc bromide was found to be equivalent in activity to zinc chloride. It was rejected from further consideration because of cost.

Zinc chloride has been widely used as a catalyst in experimental work in coal hydrogenation although it has never been employed in commercial plants. No literature data are available on its activity for the hydrocracking of coal extract.

Small amounts of catalyst[9] of the order of 3 wt. % or less of the coal were used and frequently the catalyst was impregnated on the coal before use. There appears to be no record of the use of massive quantities of molten zinc chloride catalyst in the coal hydrogenation literature.

$ZnCl_2$ almost universally has been regarded as being inferior in activity to $SnCl_2$ or halogen-promoted tin compounds[2,5,7,8,9] as a catalyst for coal hydrogenation. One exception to this is found in some Japanese work,[6] on hydrogenating coal to heavy oil at the relatively mild operating conditions of 410°C and 200 atm.

The work was carried out on a fairly large pilot plant scale using 1% of zinc chloride and other catalysts. Zinc chloride was found to be the best catalyst of these tested including tin.

EXPERIMENTAL

The basic unit used in this work was a 300 ml shaking autoclave. This unit and the procedures involved have been described previously.[10] One added feature used in two series of runs at constant hydrogen pressure was the use of a palladium probe. A palladium tube, 1/8-inch I.D., .010" wall and 7 inches long from J. Bishop and Co., was inserted into the autoclave and suitably connected to a gauge to read hydrogen pressure. The ends were silver soldered and the interior of the tube nearly filled with a stainless steel wire for support. At temperatures of 750°F and above, diffusion of hydrogen through the tube was rapid enough to give adequate response to changing pressure. A new tube was used each time to ensure freedom from sulfur poisoning, although burning off between runs was also found to restore activity. The probe was protected from splashing autoclave contents by baffles.

The feedstock for most of this work was "standard" extract prepared by continuous extraction of Pittsburgh Seam coal, Ireland Mine. Tetralin solvent was used with a residence time of 46 minutes at 380°C. Unextracted coal and ash were removed by filtration of the extractor effluent in a pressure filter at 200°C. The final extract represents 53% of the MAF coal. Properties are given in Table I.

The zinc chloride used was Fisher Scientific Co. Certified Reagent, 96-98% pure, dried before use by heating in a vacuum at 110°C. After this treatment, it contained 1-1.5 wt. % water and up to 1.8 wt. % zinc oxide.

The nickel molybdate catalyst is a commercial hydrofining catalyst containing 6.8% molybdenum, 3.8% nickel, and 0.1% cobalt supported on alumina gel. It has a surface area of 200 m^2/g, a porosity of 77%, and an average pore diameter of 200 Å. It was used as 1/16-inch diameter beads, presulfided with 15% H_2S-85% H_2 at 500°F.

The extent of reaction of zinc chloride with nitrogen and sulfur was determined by elementary analyses. The work-up procedure for product analysis was as described previously.[10] All the inorganic nitrogen was found in the water washings and was analyzed as NH_3 by distillation after adding caustic. The NH_3 is assumed to be present as $ZnCl_2 \cdot xNH_3$ or $ZnCl_2 \cdot yNH_4Cl$. The chlorine present in excess of that required for $ZnCl_2$ is assumed to be in the form of the double salt: $ZnCl_2 \cdot yNH_4Cl$. All of the sulfur in the MEK-insoluble fraction is assumed to be ZnS.

The analysis of the gasoline for individual saturated components was carried out by gas chromatography after suitable calibration with pure hydrocarbons. A temperature programmed stainless steel capillary column 0.02" dia. by 300' long coated with squalene was used in conjunction with a hydrogen flame ionization detector.

The analysis for individual aromatic hydrocarbons was carried by first isolating the aromatic fraction of the gasoline by liquid displacement chromatograph using silica gel as the absorbent. The aromatic fraction was then analyzed by gas chromatography in the same capillary column coated with 2,5-xylenol phosphate.

RESULTS AND DISCUSSION

Comparison with Other Catalysts and Effect of Catalyst/Extract Ratio

Table II gives a comparison of three types of catalysts at low catalyst concentrations between 1 and 2.5 percent of the extract fed. The literature on coal hydrogenation which states that tin chloride in small concentrations is a superior catalyst is confirmed. In spite of the lower concentration of catalyst used and lower pressure, the tin catalyst gave the highest conversion and highest selectivity for production of liquid products. However, in view of the high cost of tin and its low activity for pyrene hydrocracking when used in massive quantities,[10] no further test work was done with massive quantities of $SnCl_2$ in extract hydrocracking.

The activity of the nickel molybdate hydrofining catalyst increases markedly with increasing catalyst concentrations. Extra conversion tends to level off, however, as the catalyst extract ratio is increased beyond 0.3. These data are illustrated in Figure 1.

Two important features are evident from Figure 1. One is that conversion with the molten zinc chloride catalyst at a comparable catalyst extract ratio is always higher than with the contact catalyst type system and that the conversion reached at high catalyst extract ratios is much greater with the molten zinc chloride catalyst system. Another important feature illustrated in Figure 1 is the high conversion to gasoline boiling distillates obtained with the zinc chloride catalyst system. This especially becomes apparent at high catalyst to extract ratios, i.e., above about 0.3. This again is in distinction to the results obtained with the contact catalyst system where the gasoline range boiling distillates always comprised only a minor fraction of the total distillate oils produced. Thus, an important potential advantage of the molten zinc chloride catalyst system is the possibility of obtaining single-stage direct conversion of coal extract to high octane gasoline.

Figure 2 gives another comparison of results obtained under comparable conditions between the two catalyst systems. Especially interesting here is the rapid increase in the isobutane-to-normal butane ratio with increasing $ZnCl_2$-to-extract ratio. At high catalyst/extract ratios gasoline is produced which contains a very high proportion of isoparaffins quite comparable to what is normally produced by hydrocracking of hydrofined petroleum feedstock with dual function contact catalysts. The isobutane-to-normal butane ratio is always higher than with the hydrofining catalyst system as illustrated at the bottom of the figure. This shows that no acid cracking function exists in the case of the hydrofining catalyst system. The sharp inflection point on the isobutane-to-normal butane ratio occurs at a catalyst ratio of about 0.3.

The data shown in Figure 2 illustrate that a high selectivity in conversion of extract to gasoline is possible with massive quantities of zinc chloride. The selectivity here is measured by the percent by weight of the extract that is converted to C_1 through C_3 hydrocarbon gases. At very high catalyst:extract ratios the gas yield becomes fairly large, but this would be reduced in an actual continuous system by continuous removal of the products to prevent further cracking of the gasoline components. It is also noted that, at catalyst extract ratios up to about .4, the selectivity is better than obtained with the hydrofining catalyst system. The experiments with the hydrofining catalysts were with fresh catalyst not contaminated with ash and carbon such that the activity is substantially greater than one would have in an actual practical system.

Effect of Residence Time, Temperature and Pressure

The influence of these variables with a constant zinc chloride/extract ratio is illustrated in Figures 3, 4, and 5, respectively.

Figure 3 again illustrates the higher conversion rates that can be obtained with molten zinc chloride catalysts as compared with the hydrofining catalyst system. Three hours are required to reach a conversion of 75% with the hydrofining catalyst system, as compared with less than 5 minutes residence time required to reach the same conversion level with the molten zinc chloride catalyst.

Figure 4 gives a very rapid survey of the effects of temperature and pressure on extract conversion with zinc chloride catalyst. It is seen that substantial conversions can be achieved even at low pressures (of the order of 2000 pounds) at quite low temperatures. It also appears that at low temperatures the conversion achieved may not be too sensitive to the actual pressure. Thus, by operating at

very low temperatures of the order of 650°F, substantial conversions can be achieved even at very low pressures perhaps as low as 1500 pounds. This remains to be confirmed by future work.

Figure 5 shows the effect of operating temperature at constant time and pressure on the single stage gasoline yields, i.e., the fraction of the total liquid product which boils within the gasoline range. It also shows the effect of operating temperature on selectivity of the process. It is seen that the gasoline yield increases with operating temperature, but even at temperatures as low as 625°F more than half of the liquid product boils within gasoline range. Thus, in any case, it would appear to be possible to recycle the heavier liquid to obtain ultimate conversion of all distillate products to gasoline. It is seen also that the selectivity of the process becomes better as temperature of operation is reduced, and that accordingly the ultimate gasoline yields, upon recycling of higher boiling liquids to extinction, would be very high at temperatures below about 760°F.

Reactions of Catalyst With Hydrocracked Products

The coal extract is rich in hetero atoms, i.e., N, O, and S, as the analyses of Table I shows. These are released during hydrocracking in the form of NH_3, H_2O and H_2S, respectively.

The following reactions with the catalyst are then possible:

$$ZnCl_2 + H_2S = ZnS + 2\ HCl \qquad (1)$$

$$ZnCl_2 + H_2O = ZnO + 2\ HCl \qquad (2)$$

$$ZnCl_2 + NH_3 = ZnCl_2 \cdot NH_3 \qquad (3)$$

The equilibrium constant for reaction (1) has been determined experimentally by Kapustinsky,[1] and that for (2) may be calculated from available thermodynamic data on zinc compounds[3] with results given below:

$$\log K_2 = \log \frac{P_{HCl}^{\ 2}}{P_{H_2O}} = \frac{-6930}{T} + 8.03 \qquad (4)$$

The dissociation pressure of NH_3 over zinc chloride melts has been measured by Krasnov.[4]

The equilibrium data of Kapustinsky[1] for reaction (1) indicates that nearly quantitative absorption of H_2S to produce ZnS should take place. This was confirmed experimentally, in that no H_2S could be detected in the product gas, and all of the sulfur released was absorbed by the melt.

The data for reaction (2) indicates that zinc chloride should be quite resistant to hydrolysis but that a small amount of HCl should be present in the gas. Experimentally nothing more than trace quantities of HCl could ever be found. The discrepancy may be due to a high degree of absorption of water by the melt which reduces the partial pressure of steam to a low value.

Krasnov's data[4] indicate that the NH_3 pressure over melts containing less than 25 mole percent of ammonia would be quite small at temperatures in the normal range used for hydrocracking. Quantitative absorption of ammonia by the melts is thus to be expected, which was, in fact, confirmed experimentally. It is usual in the hydrocracking of standard extract to produce at least one mole of NH_3 for each mole of hydrogen chloride formed by reaction (1). The hydrogen chloride so produced is absorbed by the melt by the following reaction:

$$ZnCl_2 \cdot NH_3 + HCl = ZnCl_2 \cdot NH_4Cl \qquad (5)$$

Equilibrium data for reaction (5) will be presented in a subsequent paper.

The melt fed to the autoclave experiments usually contained 2.5 to 3.0 mole percent of ZnO as determined by the ability of the anhydrous melt to chemically react with hydrogen chloride to produce water. The ZnO, of course, reacts with hydrogen chloride released by reaction (1) during hydrocracking by reversal of reaction (2). It is possible to add sufficient ZnO to neutralize all of the HCl produced. In this case no NH_4Cl would be formed in the melt. The ZnO acceptor for HCl can be produced during regeneration of the melt, for example, by oxidation of the ZnS formed by reaction (1).

Effect of NH_3 and NH_4Cl on Melt Activity

It is, therefore, clear that depending upon operating conditions used and whether or not zinc oxide acceptor is employed, both ammonia and ammonium chloride in widely ranged proportions can be present in the melt during hydrogenation. It is therefore of interest to see what effect these materials have on the hydrocracking activity of zinc chloride melt toward extract. The data in Figure 6 illustrate this point.

In these runs, the temperature and pressure were held constant at 750°F and 3000 pounds, respectively, and the amount of ammonia or ammonium chloride added was varied. It is seen that with both ammonia and ammonium chloride there was a decrease in extract conversion, but that the decrease is much more rapid in the case of ammonia than in the case of ammonium chloride.

Another interesting item illustrated in Figure 7 is the effect of ammonia and ammonium chloride addition on selectivity. It is seen that both additives have a favorable effect on this count in that they caused a very dramatic decrease in the gas yield. The effect of other additives was also studied, in particular the effect of the addition of zinc oxide. Zinc oxide prevents the formation of ammonium chloride by absorbing the HCl produced. Zinc oxide was found to have marked inhibiting effect when used in large quantities. The inhibiting effect is quite moderate when only small quantities are used.

The data of Figure 6 were obtained with a zinc chloride/extract weight ratio of 2. Similar data were obtained at other feed ratios of 1 and 3, respectively. Conversions were slightly lower when the feed ratio was lowered, particularly when the amount of NH_3 added was small. The major effect of the zinc chloride/extract ratio at low NH_3 concentrations was that the gas yield decreased rapidly as the feed ratio decreased.

When higher concentrations of NH_3 were used, there was no perceptible effect of feed ratio in the range of 1 to 3.

It is therefore concluded that one controlling factor in determining the amount of melt circulation required in an extract hydrocracking process is the accumulation of nitrogen poisons. It would appear from the prior experience with pyrene,[10] however, that even with a feed low in nitrogen poisons that there is a kinetic advantage in the use of massive quantities of catalyst. The present data indicate, however, that no further advantage is gained by increasing the weight ratio of catalyst to feed beyond 1.

It is abundantly clear, therefore, that a commercial process for hydrocracking with zinc chloride melts would require continuous regeneration to remove the nitrogen poisons. Methods of regeneration will be discussed in a subsequent paper.

Some data on the effect of NH_3 at higher temperatures, i.e., at 800°F were also obtained. They are summarized in Table III. Under these conditions a small amount

of NH_3, i.e., 0.09 mole percent has a favorable effect, in that the conversion is increased, the selectivity is greatly increased because of the lower gas yield and the yield of MEK-Insolubles is decreased. As a matter of fact, the increase in conversion due to NH_3 addition can be ascribed entirely to the decrease in the MEK-Insoluble yield. It appears likely that the favorable effect of small amounts of NH_3 is due to moderation of the cracking activity of the melt which is too high for best results at the conditions used. Even larger quantities of ammonia possibly could be tolerated with favorable results at temperatures above 800°F.

It is noted that at a 1/1 mole ratio of $NH_3/ZnCl_2$ the hydrocracking activity is reduced to about the equivalent to that obtained when only 2 percent of $ZnCl_2$ (with no NH_3 added) is used (cf. Table II).

Further addition of NH_3 decreases the catalytic activity of the melt even further. The data for the melt containing 2 moles NH_3/mole $ZnCl_2$ indicates that at this level the catalytic activity is almost completely poisoned.

The data of Table III also show the effect of increasing amounts of ammonia in decreasing the i C_4/n C_4 ratio. It is thus apparent that the main effect of ammonia is to reduce the acidic cracking properties of the melt by neutralizing the Friedel Crafts acids.

Friedel Crafts acids in the case of extract hydrocracking can be generated by formation of several different zinc chloride complexes such as with phenolic groups in the extract, with water and with HCl formed by reaction (1).

It is also noted in Table III, from the catalyst analyses given, that as discussed above a very high percentage of the original nitrogen and sulfur in the feed extract is retained by the catalyst when the extract conversion is high.

Five-Stage Run

The above discussion indicates that if the NH_3 accumulates mostly as NH_4Cl relatively little deactivation of the catalyst occurs. This would be attractive from the practical point of view since it is desirable to reduce the melt circulation rate between regeneration and hydrocracking.

A five-stage run was carried out to demonstrate this. After each stage, the autoclave was cooled to 250°C and depressurized with removal of volatile liquid products and gas. After further cooling, fresh zinc chloride and extract were added (in a weight ratio of 0.23/1) to the catalyst and high-boiling liquid remaining in the autoclave from the previous stage. The autoclave was repressurized with hydrogen and heated back to the operating conditions of 750°F and 3000 psig.

The results after a single-stage are compared with the cumulative results of the five-stage run in Table IV. It is noted that the cumulative results of the five stages are very nearly equivalent to that of the first stage. However, a favorable net reduction in catalyst/extract ratio from 1 to 0.38 is achieved by this technique.

The composition of the catalyst after stages 1 and 5 is also shown in Table IV. It is seen that 82 percent of the nitrogen and 95 percent of the sulfur in the feed accumulate in the melt. The NH_3 is present mostly as NH_4Cl which explains the relatively small loss in catalyst activity.

A chlorine balance around the five-stage run indicates that 85 percent of the HCl released by reaction (1) was retained in the melt. The nature of HCl loss is not clear, however, as none could be found in the off-gas.

Kinetics of the Hydrocracking Process

The maximum extract conversion achieved in 60 minutes residence time in the experiments reported above was 91 percent. It, of course, is desirable to achieve substantially complete conversion. In order to accomplish this it is first of all necessary to substantially reduce the yield of MEK-Insolubles. Secondly, it is necessary to hydrocrack the +400°C MEK-Solubles to distillate oils.

Another characteristic of the previous experiments is that although the total hot pressure was maintained constant, the partial pressure of hydrogen decreased with time due to accumulation of gas and volatile reaction products. The hydrogen pressure is the most important variable in controlling the MEK-Insoluble yield. A series of runs were therefore carried out wherein the hydrogen pressure was maintained constant using a palladium probe to indicate hydrogen partial pressure.

The results of two series of runs at various times carried out at 750°F wherein the hydrogen partial pressures were maintained constant at 2500 psi and 3500 psi, respectively, are shown in Figure 7.

The MEK-Insoluble yield rapidly falls to a nearly constant value after 15 to 30 minutes time after which very little further reduction occurs. The final yield is, of course, lower at the higher hydrogen pressure, i.e., 1.5 percent vs. 3.5 percent.

The rate of total conversion decreases rapidly with time and becomes very slow after one hour. Even after three hours the total conversion only reaches 92.1 percent at 3500 psi and is slightly lower at 2500 psi H_2 pressure.

The cause of the difficulty is shown in Figure 8 where the reaction rate for conversion of the +400°C MEK-Solubles is plotted as a first order reaction, i.e.,

$$k(t - 15) = \ln C_o/C_t$$

where C_o and C_t are the weight percent MEK-Solubles present after 15 minutes and time "t", respectively.

It is seen that the initial rate follows the first order rate law but that the rate falls off rapidly as high conversions are reached. The first order rate increases about 20 percent in going from 2500 to 3500 psi, i.e., less than proportional to increase in pressure.

The higher pressure does not likewise prevent the decrease in rate at high conversions. As a matter of fact at both pressure levels the same yield of MEK-Soluble residue, i.e., 6.2 wt. % remains after three hours.

The decrease in reaction rate is due to formation of a refractory residue and not to decrease in catalytic activity of the melt. That this is so is obvious from the fact that over 95 percent of N and S catalyst poisons have accumulated in the melt after one hour residence time, i.e., long before the rate starts to decrease. It was also confirmed by recovery and separate hydrocracking of the MEK-Soluble residue.

It is clear that to obtain higher conversions a staged hydrogenation system with progressive increase in temperature would be required.

Effect of Feedstock - Direct Hydrogenation of Coal

The use of molten zinc chloride hydrocracking catalyst is not limited, of course, to coal extract but may be applied to a wide range of feedstocks varying from coal itself to middle boiling range petroleum distillates.

A comparison of results with several other coal derived feedstocks is given in Table V. Ireland Mine coal, a Pittsburgh Seam coal from Northern West Virginia, is the coal used for production of the standard extract used in most of this work. It was necessary to use a high ratio of catalyst to coal in this case in order to have sufficient volume of liquid present to produce a handleable coal slurry. As stated above, the use of a catalyst ratio above 1 with extract only increases the conversion slightly but has a relatively marked effect on gas yield. Thus, allowing for the difference in quantity of catalyst used, it is seen that coal and extract behave with remarkable similarity.

Results are also shown for another extract, i.e., "Spencer" extract. This extract was procured from the Spencer Chemical Co., and was prepared by extraction of a West Kentucky No. 11 coal under a pressure of 1000 psig of hydrogen at about 425°C. The depth of extraction was reported by Spencer Chemical to have been over 90%. Inspections of the extract are given in Table I.

Comparison should be made with the 750°F standard extract results of Table IV (Stage 1). Again a remarkable similarity is noted although the yield of middle range distillate is higher and the overall conversion slightly lower.

Results with a higher quality feedstock, i.e., benzene-soluble component of standard extract, are also shown in Table V. In this case a notable improvement in results is noted. The conversion is substantially increased while the yield of MEK-Insoluble residue is substantially decreased.

Gasoline Composition

The gasoline produced by the zinc chloride process contains a high proportion of branched paraffins and a substantial amount of aromatics. The aromatic content of the gasoline varies with conditions used from about 20 to 50 vol. percent. High aromatic contents are obtained in operations at the higher temperatures around 800°F and with catalyst/extract ratios below one.

A sample of gasoline from a large number of autoclave runs at different conditions was composited for a micro octane number test with results shown in Table VI along with inspections of the gasoline. The gasoline sample tested had substantially all the C_4's and C_6's removed but in spite of this had a clear research octane of 89. It is clear that a motor gasoline with the appropriate C_4's and C_5's added for volatility would have a clear octane number of well over 90.

Another sample of gasoline was obtained by running a number repetitive autoclave runs at Stage 1 conditions shown in Table IV. A more complete analysis of this gasoline is given in Table VI along with a breakdown into individual components.

The ratio of branched-to-normal paraffins is clearly quite large in the C_5 and C_6 fractions.

Potential Commercial Considerations

It is premature to discuss in detail the potential commercial application of the zinc chloride hydrocracking process. Data are required both on continuous hydrocracking and continuous melt regeneration systems. Work is presently in progress on both of these subjects and will be reported in future papers. Some aspects of the regeneration process is discussed in a subsequent paper.

Corrosion control is one of the important aspects of a potential commercial process. Weight loss data over the duration of the autoclave program indicate that the average penetration rate with 316 stainless is less than 80 mpy. Separate

corrosion tests, however, have indicated that pitting may be a problem with 316 stainless when substantial quantities of NH_4Cl are allowed to build up in the melt. In this case more expensive alloys such as Hastelloy B or Inconel 625 may be required.

The formation of NH_4Cl can be eliminated by addition of zinc oxide acceptor. Corrosion test work in this case indicates that 316 stainless may be a satisfactory alloy, i.e., penetration rates below 5 mpy were observed with test specimens.

Therefore, from the corrosion standpoint the zinc-oxide acceptor system is preferred. The disadvantage is the lower catalyst activity for a given nitrogen level. The inhibiting effect of ZnO can be minimized by maintaining at all times a very low concentration of zinc oxide in the hydrocracking zone and by providing for a staged increase in temperature to over 800°F to partially compensate for decrease in catalyst activity by accumulation of NH_3 in the melt. Figure 9 illustrates schematically a continuous operation using the above principles. It should be noted that the zinc chloride melt is miscible with extract, as it was with pyrene.[10]

ACKNOWLEDGMENT

The sponsorship of the U. S. Office of Coal Research for this investigation is gratefully acknowledged.

BIBLIOGRAPHY

(1) Britzke, E. V. Kapustinsky, A. F., and Wesselowsky, B. K. Zeit. Anorg. Chem. 213, 65 (1933).

(2) Kandiner, H. J., Hiteshue, R. W., and Clark, E. L. Chem. Eng. Progress 47, 392-396 (1951).

(3) Kitchener, J. A. and Ignatowicz, S., Trans. Farad. Soc. 47, 1278 (1951).

(4) Krasnov, A. Z., J. Applied Chem. (USSR) 12, 1595-1597 (1939).

(5) Kuo-Chuan Chen and Fuh-Liang Chang, Jan Liso Hsueh Pao 3, 23-34 (1958).

(6) Kurokawa, M., Hirota, W., Takeya, G., and Takenaka, Y. J. Soc. Chem. Ind., Japan 44, 776-779 (1941).

(7) Pelipetz, M., Kuhn, E. M., Freedman, S., and Storch, H. H. Ind. Eng. Chem. 40, 1259-1264 (1948).

(8) Sato, F., Morikawa, K., Morikawa, R., Okamura, T. J. Soc. Chem. Ind., Japan 45, 892-903 (1942).

(9) Weller, S., Pelipetz, M. G., Freedman, S., and Storch, H. H. Ind. Eng. Chem. 42, 330-334 (1950).

(10) Zielke, C. W., Struck, R. T., Evans, J. M., Costanza, C. P., and Gorin, E. "Molten Salt Catalysts for Hydrocracking of Polynuclear Hydrocarbons." Presented Before the Division of Fuel Chemistry, ACS, Atlantic City, N. J., September 12-17, 1965.

TABLE I Analysis of Feedstocks

Feedstock	Ireland Mine Coal	"Standard" Extract	"Spencer" Extract	Benzene Solubles
	MF Basis			
Volatile Matter	40.32			
Fixed Carbon	46.66			
FeS	0.08			
FeS_2	4.19			
Other Ash	10.15			
	MAF Basis			
H	5.73	6.14	5.03	7.04
C	81.90	83.73	87.62	85.30
N	1.58	1.46	1.49	.94
O	8.61	6.87	4.75	5.10
Organic S	2.18	1.80	1.11	1.62
Solvent Fractionation				
Benzene Insolubles		46.9	37.2	.5
Asphaltenes		37.2	31.2	59.6
Oil		15.9	31.5	39.0

TABLE II Comparison of Catalyst Activity at Low Concentration Levels - 1 Hr. Residence Time

Temperature, °F	← 800 →		
Total Hot Pressure	4200	4200	3000
Catalyst	Nickel Molybdate on Al_2O_3	$ZnCl_2$	$SnCl_2$
Catalyst/Extract, Wt. Ratio	.025	.02	.01
Yields, Wt. % Feed			
C_1-C_3	5.0	5.1	4.1
C_4	14.9	1.0	1.8
C_5 x 200°C		14.7	13.0
200 x 400°C	14.5	19.8	24.6
MEK-Soluble +400°C Residue	60.3	52.9	53.5
MEK-Insoluble +400°C Residue	0.6	3.0	0.1
Other (NH_3, H_2S, H_2O, etc.)	7.3	7.6	6.7
Total	102.6	104.1	103.8
H_2 Consumption, Wt. % Feed	2.55	4.13	3.71
Conversion, Wt. % Feed	39.0	44.1	46.5
(C_1-C_3) x 100/Conversion	12.8	11.5	8.8

TABLE III

Activity of Zinc Chloride Catalyst as Affected by NH_3 Addition

Temperature = 800°F, Total Pressure = 4200 psig

$ZnCl_2$/Extract Wt. Ratio = 1.0, Time = 60 mins.

$NH_3/ZnCl_2$, Mole Ratio	0	0.091	1.0	2.0
Yields, Wt. % MAF Feed				
CH_4	1.8	1.5	1.6	1.8
C_2H_6	2.6	1.7	1.2	1.4
C_3H_8	8.6	3.0	1.2	1.2
i C_4H_{10}	9.6	2.5	0.4	0.1
n C_4H_{10}	1.6	0.5	0.5	0.5
$(NH_3+H_2S+H_2O+CO+CO_2)$	7.4	7.4	5.5	2.3
C_5 x 200°C Dist.	60.4	68.2	15.8	10.3
200 x 400°C Dist.	3.1	11.4	19.1	9.5
+400°C MEK-Soluble Residue	6.3	6.2	54.5	54.1
+400°C MEK-Insoluble Residue	3.9	2.6	2.4	20.3
N to Catalyst	1.3	1.3	} 1.6	} 1.4
S " "	1.8	1.4		
H " "	0.3	0.3		
Total	108.7	108.0	103.8	102.9
Conversion, Wt. % MAF Feed	89.8	91.2	43.2	25.6
H_2 Consumed, Wt. % MAF Feed	8.7	8.0	3.8	2.9
(C_1-C_3) x 100/Conversion	14.5	6.8	9.3	17.1

TABLE IV

Results of 5-Stage Run

Temperature = 750°F, Total Hot Pressure = 3000 psig

Residence Time/Stage = 60 mins.

Stage No.		1	2 thru 5	Cumulative
Wt. Extract Feed Per Stage/gms		50	50	250
Wt. $ZnCl_2$ Feed Per Stage/gms		50	11.4	95.6
Cumulative $ZnCl_2$/Extract, Wt. Ratio		1	--	0.383
Melt Composition, Mole %	Feed	After Stage 1		After Stage 5
$ZnCl_2$	97.3	81.7		48.5
ZnO	2.7	--		--
$ZnCl_2 \cdot NH_3$		2.3		4.4
$ZnCl_2 \cdot NH_4Cl$		8.9		27.4
ZnS		7.1		19.7
	100.0	100.0		100.0
Yields, Wt. % Total Extract Feed				
C_1-C_3		6.3		6.3
i C_4H_{10}		3.3		3.2
n C_4H_{10}		0.4		0.6
CO		0.1		0.2
H_2O		7.3		5.8
C_5 x 200°C Dist.		59.0		56.0
200 x 400°C Dist.		9.6		14.3
+400°C MEK-Soluble Residue		11.9		12.9
+400°C MEK-Insoluble Residue		6.4		4.5
H to Catalyst		0.3		0.3
N " "		1.1		1.2
S " "		1.6		1.7
Total		107.3		107.0
Conversion, Wt. % MAF Feed		81.8		82.6
H_2 Consumed, Wt. % MAF Feed		7.3		7.0
(C_1-C_3) x 100/Conversion		7.7		7.6

TABLE V

Comparison of Feedstocks in Hydrocracking With Molten Zinc Chloride Catalyst

Residence Time = 60 min.

Feedstock	Ireland Mine Coal	Standard Extract	Spencer Extract	Benzene Solubles from Standard Extract
Temperature, °F	725	725	750	750
$\frac{ZnCl_2}{MAF\ Feed}$ (Wt. Ratio)	3.5	1.0	1.0	1.0
Total Pressure, psig	2000	2000	3000	3000
Yields, Wt. % MAF Feed				
CH_4	0.9	0.6	0.6	.6
C_2H_6	2.3	1.2	0.8	1.2
C_3H_8	7.5	1.7	2.1	5.8
i C_4H_{10}	7.8	1.2	2.1	7.3
n C_4H_{10}	1.3	0.1	0.3	1.0
$(NH_3+H_2S+CO+CO_2+H_2O)$	6.7	6.9	6.8	7.0
C_5 x 200°C Dist.	48.2	49.5	50.4	66.2
200 x 400°C Dist.	2.9	9.4	17.9	6.2
+400°C MEK-Soluble Residue	15.0	17.0	17.9	7.7
+400°C MEK-Insoluble Residue	10.9	14.8	5.7	1.2
N+S+H to Catalyst	5.2	3.5	2.3	3.1
Total	108.7	105.9	106.9	107.3
Conversion, Wt. % MAF Feed	74.2	68.1	76.4	91.1
H_2 Consumption, Wt. % MAF Feed	8.7	5.9	6.9	7.3
(C_1-C_3) x 100/Conversion	14.3	5.1	4.6	8.3

TABLE VI

Analyses of Product Gasoline

Description	C_5-200°C Gasoline	C_6-190°C Gasoline
FIA, Vol. %(1)		
Aromatics	25.5	30.9
Saturates	74.5	69.1
Olefins	0.0	0.0
Naphthenes	Not Determined	31.7(2)
Research, Clear Octane No.	" "	89
Elemental Analytical, Wt. %		
H	13.42	12.93
C	86.22	87.00
N	0.0	.04
O	.34	.03
S	.02	0.0
Partial Component Breakdown, Vol. %		
Saturates		
i-Pentane	13.4	
n-Pentane	1.2	
Cyclopentane	.8	
2,3-Dimethylbutane	1.1	
2-Methylpentane	4.4	
3-Methylpentane	3.0	
n-Hexane	.5	
Cyclohexane	.6	
Methylcyclopentane	9.3	
Aromatics		
Benzene	2.0	
Toluene	5.9	
Ethyl Benzene	2.4	
Xylenes	3.9	
Cumene	1.1	
n-Propyl Benzene	.5	

(1) Fluorescent Indicator Analysis, A.S.T.M. Method D-1319-61T.

(2) The total saturates are 31.7% naphthenic and 37.4% paraffinic as determined by A.S.T.M. Method D-2159.

Figure 1

EFFECT OF FEED CATALYST-EXTRACT RATIO ON TOTAL CONVERSION AND CONVERSION TO GASOLINE

800°F - 4200 psi Total Pressure.
- 60 min. R.T.

Δ Molten $ZnCl_2$ Catalyst.
⊙ Nickel Molybdate Hydrofining Catalyst.

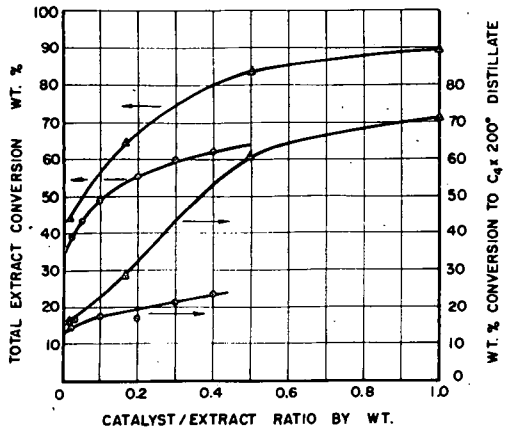


Figure 2.

EFFECT OF CATALYST-EXTRACT RATIO ON iC_4/nC_4 RATIO AND SELECTIVITY

800°F - 4200 psi Total Pressure.
- 60 min. R.T.

Δ Molten $ZnCl_2$ Catalyst.
⊙ Nickel Molybdate Hydrofining Catalyst.

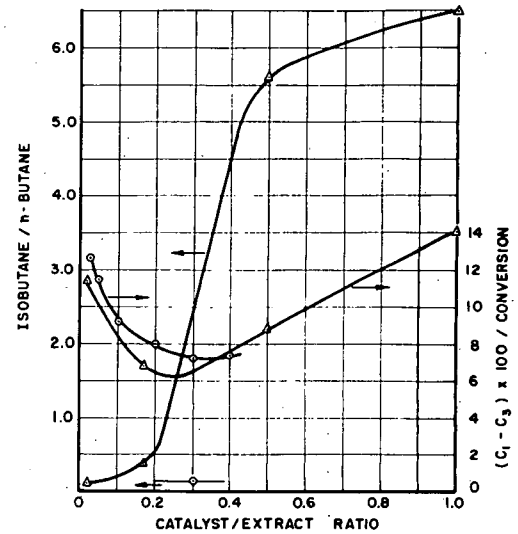


Figure 3

EFFECT OF RESIDENCE TIME ON TOTAL CONVERSION

▲ $ZnCl_2$ / Extract = 1

⊙ Nickel Molybdate / Extract = 0.3

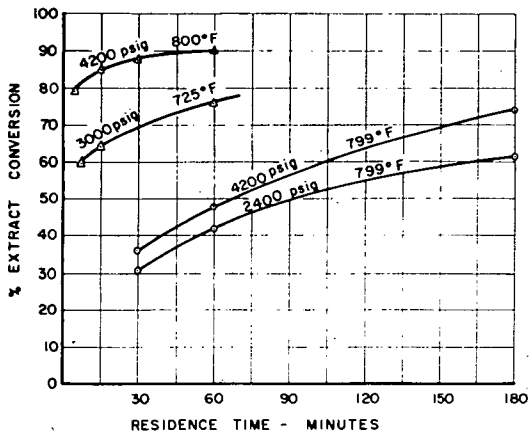


Figure 4

EXTRACT CONVERSION VS TEMPERATURE & PRESSURE

$ZnCl_2$ / Extract = 1.0

Time = 1 Hour

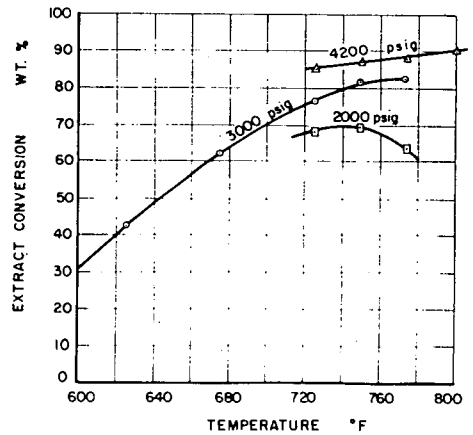


Figure 5

GASOLINE YIELD & SELECTIVITY vs TEMPERATURE

$ZnCl_2$ / Extract = 1.0
Time = 60 Minutes
Pressure = 3000 psig

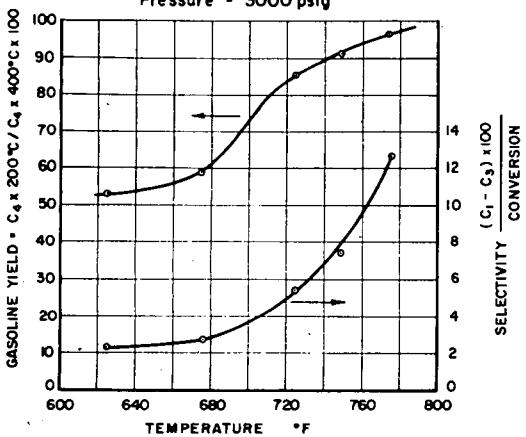


Figure 6

EFFECT OF NH_3 & NH_4Cl ON CONVERSION & SELECTIVITY

$ZnCl_2$ / Extract = 2.0
Temperature = 750 °F
Pressure = 3000 psig

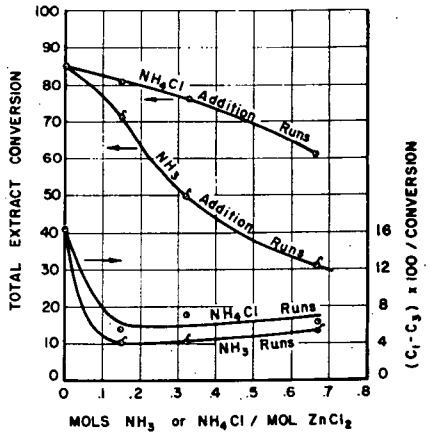


Figure 7

YIELDS vs TIME IN CONSTANT HYDROGEN PRESSURE RUNS AT 750° F

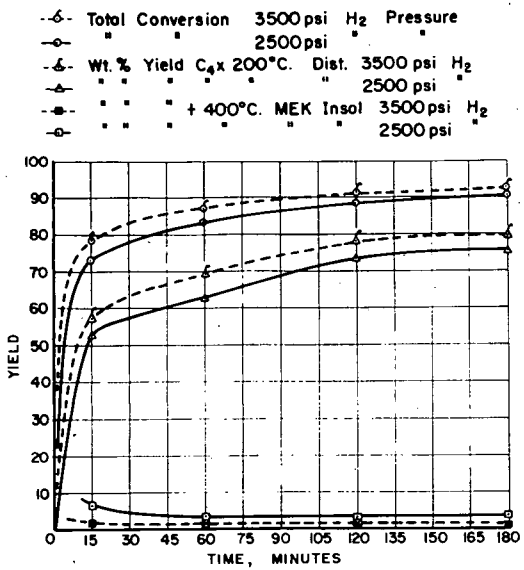


Figure 8

RATE OF HYDROCRACKING OF +400°C MEK SOLUBLE RESIDUE

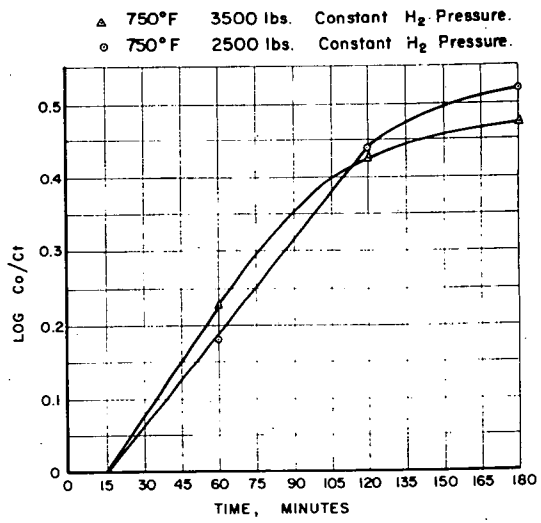
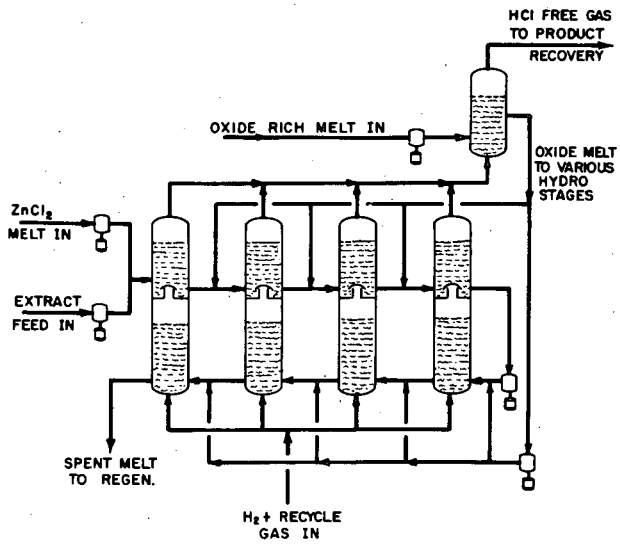


Figure 9

SCHEMATIC HYDRO SYSTEM WITH MASSIVE ZINC CHLORIDE MELT CATALYST ZINC OXIDE ACCEPTOR SYSTEM