

Coal Hydrogenation in Small Tube Reactors

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The office of Coal Research short residence time coal hydrogenation reactor at the University of Utah has been previously discussed in Hydrocarbon Processing¹ and The Quarterly of the Colorado School of Mines².

A schematic diagram of this device is shown in Figure 1. It contains provision for passing dry powdered coal through a heated and pressurized reaction zone. The reactor is mounted vertically and the coal is pushed by means of an auger feeder into the top and the reaction products are collected in a water cooled quench tank at the bottom. This reactor can be pressurized to 5000 PSI and heated to 800°C.

Although conversions to 75 or 80 percent of the coal matter can be realized in this apparatus, it suffers from some rather crippling deficiencies. Of greatest importance in limiting the usefulness of the device is the fact that coal, in falling through the reaction zone becomes plastic and sticky. Some of the liquid-solid product sticks to the reactor walls, becomes devolatilized and the residue remains as a solid char that builds up to eventually block the passage. A second factor is that the limited capacity of the compressor (240 cubic feet per hour maximum) severely restricts the movement of gas through the reaction zone. This essentially stagnant reactor space contributes to the coal and char sticking problem as there is little flow of gas to force the solid material through to the quench vessel.

Calculations of Reynolds numbers for hydrogen at 2000 PSI and 700°C reveals that a flow of 200 cubic feet per hour will not provide turbulent flow in tubes larger than 3/16 inch I.D. Therefore, we restricted the reactor tube size to 1/8 inch and proceeded to work with hydrogen-coal slurries in this type of reactor.

The auger feeder used with the 2 inch I.D. reactor is not adaptable to the 1/8 inch tube because it delivers coal in slugs rather than at a steady rate. The small tube is blocked by each slug of coal delivered by the auger. For this reason a fluidized feeder, where hydrogen gas passing through a coal bed carries the coal into the small tube reactor was developed. The design of this feeder, with the small tube reactor is indicated in Figure 3. This schematic shows the 1/8 inch tube mounted inside the 2 inch tube of the original reactor. This construction adds a further factor in that heat to raise the coal to reaction temperature must be added from outside the 2 inch reactor. Convection and radiation from the inner wall of the larger reactor is insufficient to heat the small tube enough to permit it in turn to properly heat the coal-hydrogen stream passing through it. Therefore, a chamber was constructed around the inner tube such that a molten lead bath could be used to transmit heat from the walls of the outer tube to the inner reactor.

Figure 4 shows the product distribution, in terms of gases and liquids, produced as a function of temperature and pressure for one of the more reactive coal types. This is Orangeville, Utah, coal, a high-volatile bituminous "B" coal from East Central Utah. The production of gases, primarily Methane but with substantial quantities of ethane, propane and higher carbon number hydrocarbon gases; and liquids, a very complicated mixture of aliphatic and aromatic materials is shown at four temperatures and three pressures. Increasing temperature increases the output of both gases and liquids, but the liquids are increased to a greater extent. Increased pressure likewise increases the production of liquids. Above 2000 PSI the gas production is decreased to some extent. The total conversion, equal to the sum of gases

plus liquids is over 60 percent of the original coal material at 675°C and 2000 PSI.

Table I is a compilation of data obtained on several different coals in this small tube reactor. Since these samples were measured over a period of several months, the reaction conditions were not completely uniform. Most were obtained at 1750 PSI hydrogen pressure and 650°C temperature, but some were measured at 675°C and 2000 PSI. The conditions were selected at less than a maximum conversion operation in an effort to spread the data to show coal differences. We have listed the coal, total conversion, feed rate, oxygen content and some observations about the coal. The coals are naturally broken into three categories. The first category contains those coals that are easy to feed and give little or no reactor plugging but which also give very little reaction. These are coals with high oxygen content and are generally of the lignite and subbituminous types. The second group of coals have an intermediate reaction, are not really difficult to feed, give some plugging and have an intermediate oxygen content. The third category of coals is generally the high volatile, non-caking bituminous coals that show good reaction without excessive plugging. Feeding with our hopper arrangement is difficult with these coals because they are sticky and agglomerate readily, particularly when the catalyst is present. This third group of coals is the most interesting because they react most readily. The conversions reported on these coals were obtained with half the catalyst application used with the other types. The lack of conversion numbers on some of these coals was because the higher level of catalyst was used and both feeding and plugging problems were encountered.

Table I. Comparison of Coals Treated in 1/8 inch I.D. reaction tube

	<u>Conversion</u>	<u>Feed Rate g/m</u>	<u>% O₂</u>	<u>Coal Characteristic</u>		
				<u>Feeding</u>	<u>Reacting</u>	<u>Plugging</u>
Sidney, Montana (Lignite)	11.1	19	21.0	GOOD	POOR	NONE
Big Horn, Wyoming	10.3	13	11.2	"	"	"
Navajo, Utah	17.5	14	----	"	"	"
Beluga River, Canada	17.9	10	28.3	"	"	"
Kanab, Utah	6.8	11	13.6	"	"	"
Alton, Utah	7.6	18	24.9	"	"	"
River King, Illinois	30.6	8	8.9	FAIR	FAIR	SOME
Last Chance, Utah	37.2	14	18.6	"	"	"
Kaiparowitz, Utah	45.0	--	18.0	"	"	"
Coalville, Utah	38.8	--	10.3	"	"	"
Powers, Utah	37.2	9	----	"	"	"
Geneva-Somerset, Utah-Colo.	48.4	14	6.4	POOR	GOOD	SOME
Spencer, Utah	44.1	9	12.3	"	"	"
Castle Valley, Utah	56.6	8	5.7	"	"	"
Orangeville, Utah	66.5	2	----	"	"	"
Hiawatha, Utah	76.8	8	----	"	"	"
Cedar City, Utah	----	--	7.5	"	"	"
Castle Gate, Utah	----	--	5.5	"	"	"
Coal Basin, Colorado	----	--	3.0	"	"	"
Bear, Colorado	----	--	8.5	"	"	"

Figure 5 shows the effect of changing catalyst concentration on two types of coal. The catalyst was zinc chloride and the application was measured in terms of weight of zinc metal to MAF coal. For Orangeville, Utah, coal, a good reacting material, the doubling of catalyst concentration accomplished little or nothing. For the Kaiparowitz coal, an intermediate reactor by our other standards, more catalyst gives a marked increase in conversion.

The coal feed rate is a process variable that is difficult to control with a fluidized feeder. It is affected by moisture content, concentration of catalyst, particle size and surface character of the coal particles. Figure 6 is an attempt to show the effect of both feed rate and particle size on the conversion in this process. The length of the horizontal lines indicate the mesh size range of the particles sample. The number by the line indicates the feed rate in grams of coal per minute. Two coals were studied. Kaiparowitz as shown in Figure 5 and Castle Gate, Utah, which is one of the better reacting type coals.

In general, we see that an increase in feed rate results in decreased reaction, presumably because of less efficient heating of larger quantities of coal to the required reaction condition. We see also that a decrease in particle size results in a decreased reaction. This is not to be expected because smaller coal particles should be heated more efficiently. The reason for this decreased reaction lies in the actual residence time of the coal within the heated zone. Because of the small size of the reactor, it has not been possible to insert probes, or even thermocouples to measure residence times. However, we have been able to observe pressure buildup and decay as a small amount of coal is injected. We calculate that the gas is flowing at a rate where its residence in the hot zone is in the range of 0.01 to 0.03 seconds. However, the coal is traveling much less rapidly. Actually, it approaches a plug-flow condition. The pressure difference between top and bottom of the reactor tube increases as coal is injected and decays within 5-10 seconds. The coal residence then is somewhere in the range 1 to 10 seconds. This is somewhat dependent on particle size. The smaller particles tend to be carried with the gas and go through in less than 0.1 second. This is not long enough to heat even the finest particles enough to cause reaction. This, then is the reason for decreased reaction with a smaller particle size sample as indicated by the data of Figure 7.

The catalyst used in this work has been primarily $ZnCl_2$. Its action in the coal hydrogenation reaction is not understood although as a Lewis acid it is expected to act as a cracking catalyst for large organic molecules and the hydrogen reacts with the molecular fragments produced. Some studies have been made in an effort to discover the catalytically active form of the zinc and to devise schemes for recovering the zinc from the char for use on fresh coal. The economic success of the process will certainly depend on the almost complete recovery of this material.

Several kinds of inorganic materials have been tested as catalysts for this coal process. Table 2 shows the coal conversion obtained with each of these materials using the same coal and reaction conditions. Zinc halides and stannous chloride are the most effective of those tested. The zinc chloride is by far the cheaper material and therefore is the best selection.

Table 2. Comparison of Inorganic Salt Catalysts

Salt	Percent Conversion	Salt	Percent Conversion
ZnBr ₂	58.5	Sn(powder)	7.9
ZnI ₂	46.3	CuCl ₂ ·2H ₂ O	7.6
ZnCl ₂	41.1	FeCl ₃ ·6H ₂ O	7.2
SnCl ₂ ·2H ₂ O	40.5	Zn(powder)	7.0
SnCl ₄ ·5H ₂ O	25.6	ZnSO ₄ ·7H ₂ O	5.4
LiI	16.6	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	5.4
CrCl ₃	12.8	FeCl ₂	3.3
Pb(C ₂ H ₃ O ₂) ₂ ·3H ₂ O	11.7	CaCl ₂ ·H ₂ O	No Reaction
NH ₄ Cl	11.0	Na ₂ CO ₃ ·H ₂ O	No Reaction
CdCl ₂ ·2 1/2 H ₂ O	7.9		

Conditions

Last Chance, Utah, Coal 40-100 mesh

Feed Rate 10-12 g/m

Pressure 1750 PSI

Reactor, 1/8" I.D. Tube

Temperature 650°C

3 Ft. Heated Section

Catalyst Concentration, 0.06 Weight Metal/Weight Coal (MAF)

Just which form of zinc is catalytically active is not known. We do know that the chloride reacts with aldehydes, ketones and ether oxygen configurations to form complexes. We find that when zinc chloride is impregnated onto coal surfaces, all is not recovered by water extraction. After the coal has been heated even less of the zinc can be extracted by water alone. Table 3 shows the forms of zinc that we have identified in the char product where almost all the zinc is found after reaction. The residual zinc chloride is water soluble but zinc metal, basic zinc chloride and zinc oxide are insoluble in water and require an acid for solution. The basic zinc chloride is formed by reaction with water at elevated temperatures. We have found the zinc metal in char samples and have found zinc oxide in samples subjected to microwave ashing to remove the carbonaceous material. We have not verified the presence of zinc sulfide, but feel that it may be the form of zinc least soluble in hydrochloric acid and therefore a suspect as to the form in which the zinc is most difficultly recoverable.

Table III. Compounds of Zinc in Char

<u>Coal</u>	<u>Char</u>	<u>Solubility</u>
		ZnCl ₂
	Zn	HCl
ZnCl ₂	ZnCl ₂ ·4Zn(OH) ₂ *	HCl
	ZnO**	HCl
	ZnS (not verified)	Slowly soluble in HCl

* Found in H₂O insoluble portion of heated H₂O solution of ZnCl₂

** Found in ash from low temperature ashing of char to remove organic matter and carbon.

Figure 7 shows the recovery from reacted char, using hydrochloric and sulfuric acids, 10 percent in each case. The lower designation is the number of times the same sample was extracted with equal portions of fresh hot acid. About half the zinc, as measured by the intensity of the zinc K alpha x-ray fluorescence line, is readily extracted but the remainder is only slowly extracted. It could be a rather long and involved procedure to recover all the zinc by acid extraction alone.

Because of the fact that zinc sulfide is a potential form of the zinc after the reaction we have considered some methods for dissolving this product. Table 4 shows some solution reactions together with the solubility products involved. Dissolving ZnS in HCl is possible by virtue of the formation of slightly ionized H₂S and the volatilization of H₂S from the solution. Dissolving ZnS in solutions of Pb⁺⁺, Cu⁺⁺ or Hg⁺⁺ ions is possible because these metal ions form sulfides even less soluble than ZnS. Mercury sulfide particularly is very insoluble.

Table IV. Some Reactions for Dissolving ZNS.

ZnS(solid) + HCl	Zn ⁺⁺ + 2Cl ⁻ + H ₂ S	ZnS K _{sp} = 1.2 x 10 ⁻²³ (18°C)
ZnS(solid) + Pb ⁺⁺	Zn ⁺⁺ + PbS(solid)	PbS K _{sp} = 3.4 x 10 ⁻²⁸ (18°C)
ZnS(solid) + Cu ⁺⁺	Zn ⁺⁺ + CuS(solid)	CuS K _{sp} = 8.5 x 10 ⁻⁴⁵ (18°C)
ZnS(solid) + Hg ⁺⁺	Zn ⁺⁺ + HgS(solid)	HgS K _{sp} = 4.0 x 10 ⁻⁵³ (18°C)

Figure 8 shows the extraction of zinc from reacted coal char, first with hot water, then with hot concentrated hydrochloric acid and then with hot dilute solutions of Pb^{++} , Cu^{++} , and Hg^{++} ions. We notice first that the difficulty of removing zinc from the char is directly related to the amount of conversion. For high conversion less zinc is dissolved by the solvent. Longer exposure to the Hg^{++} ion would probably result in essentially complete recovery. This approach is not practical for actual recovery of zinc, but it does illustrate that the zinc is present in the char in a very insoluble form, probably as the sulfide and that some extreme method will be required to recover the catalyst. Tests have indicated that char can be recycled with fresh coal and catalyst without loss of catalytic character. These tests have further indicated that recycled char by itself can be further hydrogenated. The resulting product is higher in gas and lower in liquids than the first cycle but the percent conversion is near to that in the first case. These tests need further study and verification because the difficulty of feeding char alone makes these tests less reliable than when coal alone is fed.

References

1. Qader, S. A., Haddadin, R. A. Anderson, L. L., Hill, G. R., Hydrocarbon Processing 48, No. 9, 147 (1969).
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ZnS(solid) + Cu ⁺⁺	Zn ⁺⁺ + CuS(solid)	CuS K _{SP} = 8.5 x 10 ⁻⁴⁵ (18°C)
ZnS(solid) + Hg ⁺⁺	Zn ⁺⁺ + HgS(solid)	HgS K _{SP} = 4.0 x 10 ⁻⁵³ (18°C)

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References

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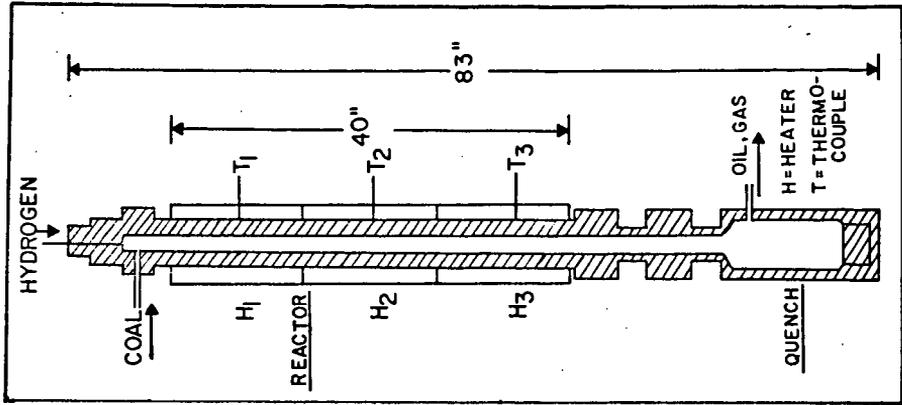


FIGURE 2. O. C. R. REACTOR AND QUENCH TANK.

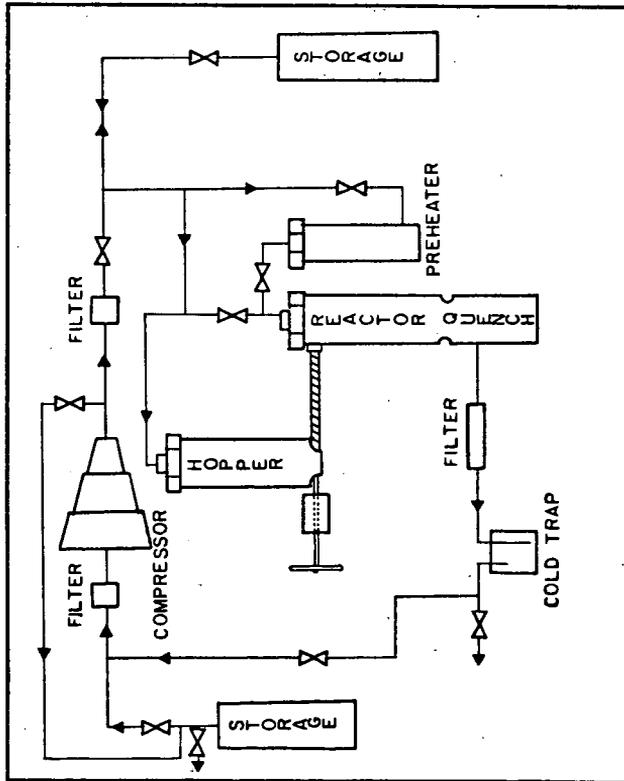


FIGURE 1. SCHEMATIC DIAGRAM OF O. C. R. FREE-FALL COAL HYDROGENATION UNIT.

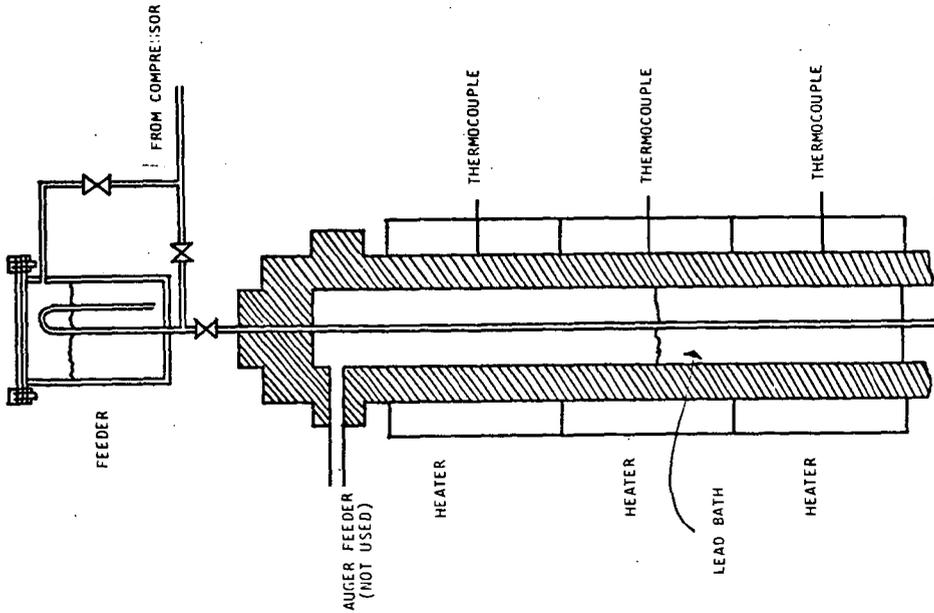


FIGURE 3. FLUIDIZED FEEDER WITH 1/8 INCH REACTOR.

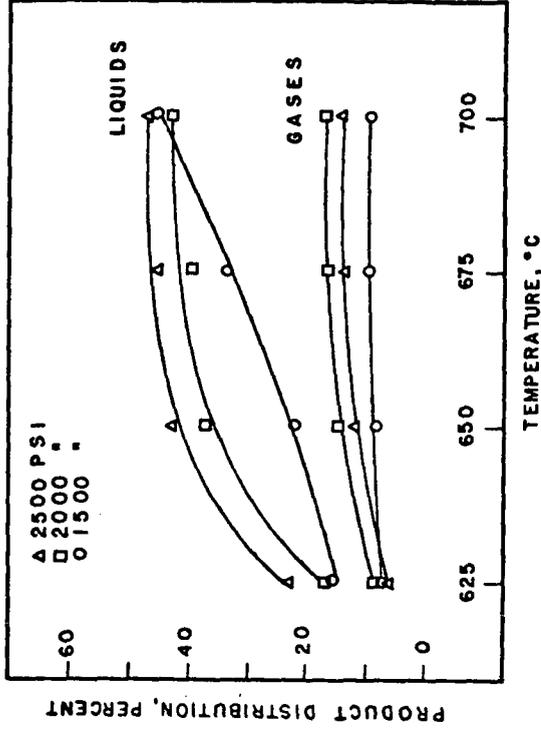


FIGURE 4. PRODUCT DISTRIBUTION FOR A REACTIVE (ORANGEVILLE, UTAH) COAL.

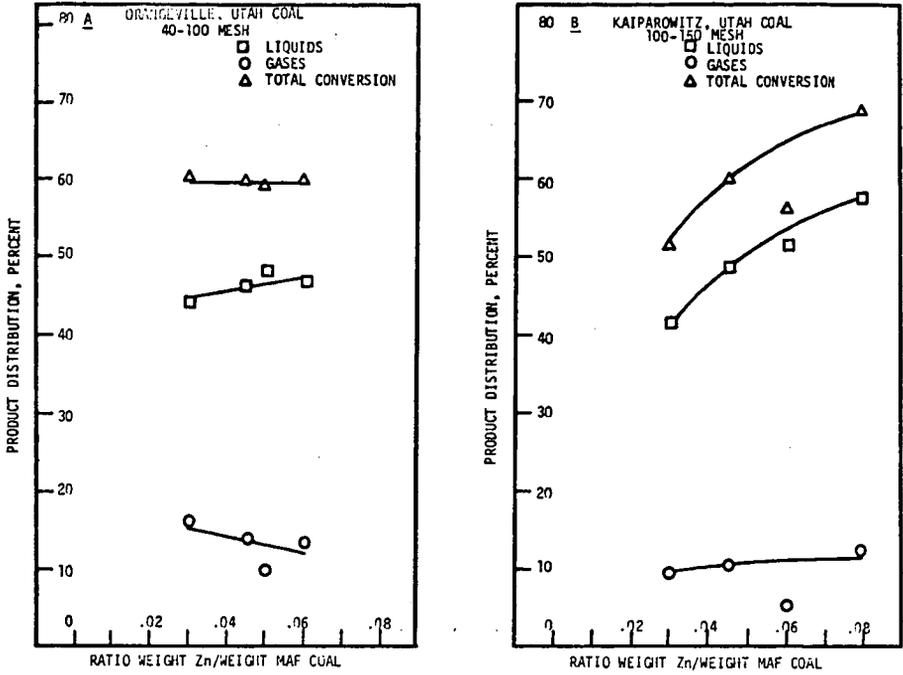


FIGURE 5. EFFECT OF CATALYST CONCENTRATION ON COAL CONVERSION

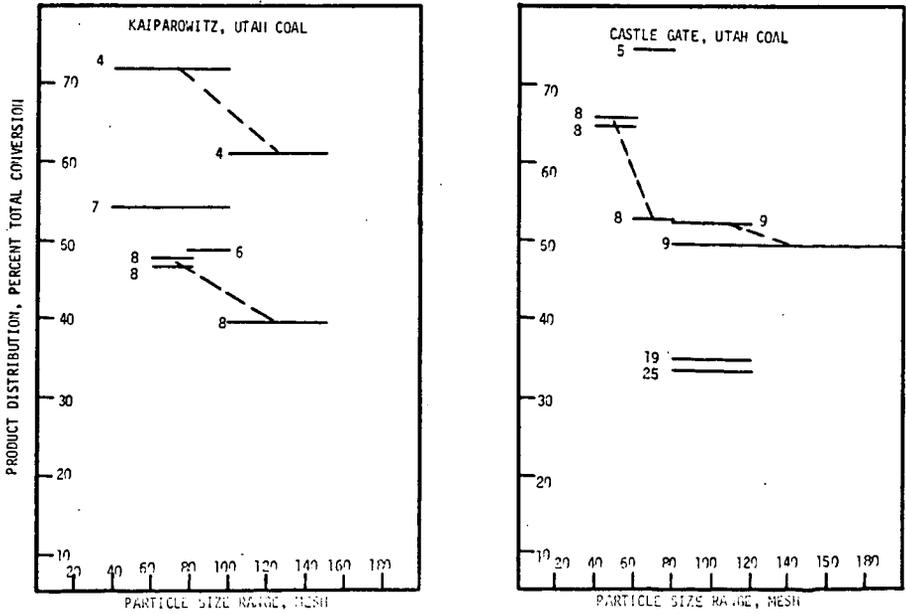


FIGURE 6. EFFECT OF PARTICLE SIZE AND FEED RATE ON CONVERSION OF COAL

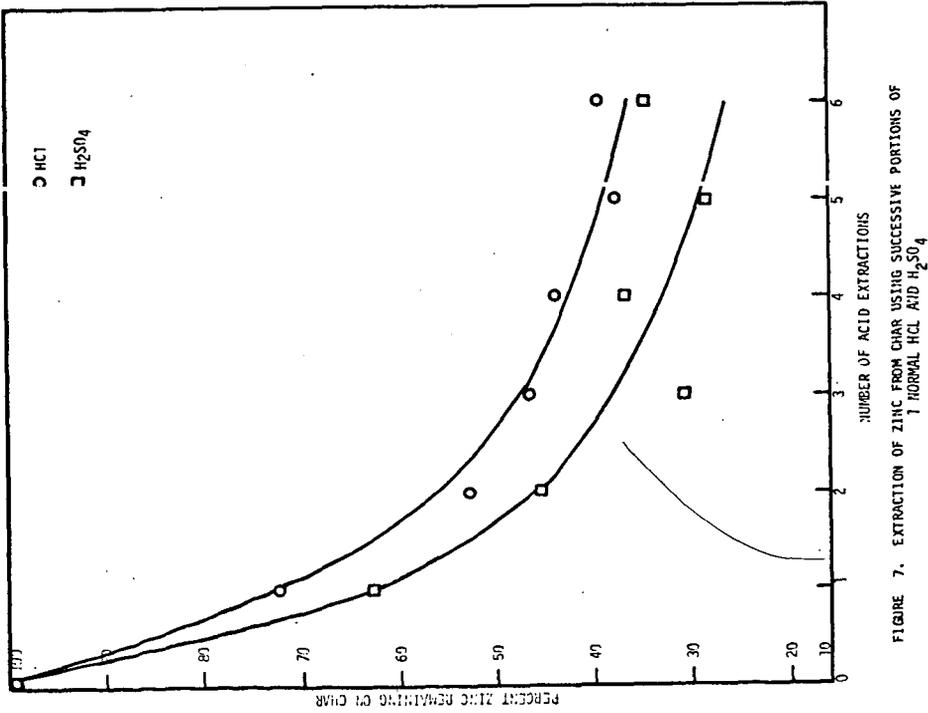


FIGURE 7. EXTRACTION OF ZINC FROM CHAR USING SUCCESSIVE PORTIONS OF NORMAL HCL AND H₂SO₄

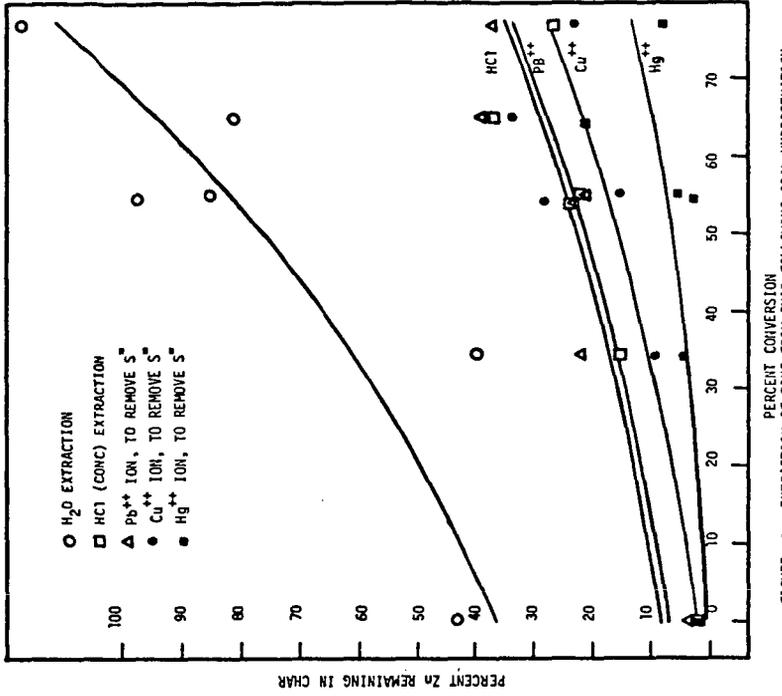


FIGURE 8. EXTRACTION OF ZINC FROM CHAR FOLLOWING COAL HYDROGENATION