FLUIDIZED COMBUSTION PROCESS FOR REGENERATION OF SPENT ZINC CHLORIDE CATALYST FROM DIRECT HYDROCRACKING OF A WESTERN SUBBITUMINOUS COAL

C. W. Zielke

Research Division
Consolidation Coal Company
Library, Pennsylvania 15129

Prior Consol work has been published which shows that molten $ZnCl_2$ is a superior catalyst for making gasoline from coal. It was demonstrated that high yields of high octane gasoline can be obtained directly from the hydrocracking process. Therefore, the use of $ZnCl_2$ is projected in a process for producing gasoline from coal. Coal extract, which is an essentially ash-free feedstock, is used in one process scheme. In another process scheme, raw coal is treated directly in the hydrocracker without first undergoing extraction. It has been demonstrated that, from the point of view of yields and selectivity, coal is equivalent to extract in the hydrocracking process. The relative simplicity of the direct coal hydrogenation scheme makes it attractive in principle, if the added complication of handling the coal ash in the hydrocracking step does not prove too difficult. This is especially true for western subbituminous coals which require a relatively high hydrogen input during the extraction step in order to obtain a high yield of extract.

Large amounts of catalyst relative to feed are used in the hydrocracking process, i.e., as much as one pound or more of catalyst per pound of feed may be used.

During the hydrocracking process, the $ZnCl_2$ catalyst becomes contaminated with ZnS, $ZnCl_2 \cdot NH_3$ and $ZnCl_2 \cdot NH_4Cl$ that are formed by the $ZnCl_2$ catalyst partially reacting with the sulfur and nitrogen liberated from the feed in the hydrocracking step:

$$ZnCl_2 + H_2S \rightarrow ZnS + 2\ HCl$$

$$ZnCl_2 + xNH_3 \rightarrow ZnCl_2 \cdot xNH_3$$

$$ZnCl_2yNH_3 + yHCl \rightarrow ZnCl_2yNH_4Cl$$

The proportions of $ZnCl_2xNH_3$ and $ZnCl_2yNH_4Cl$ depend on the ratio of nitrogen and sulfur in the feed. In addition to these inorganic compounds, the catalyst leaving the hydrocracker also contains residual carbon that cannot be distilled out of the melt. In the case of direct coal hydrocracking, the catalyst also contains the coal ash.

Thus, a commercial process using $ZnCl_2$ requires a viable scheme for regeneration of the catalyst. Regeneration comprises removal of the bulk of the impurities that accumulate in the catalyst during hydrocracking and return of the melt as relatively pure $ZnCl_2$. The regeneration must be accomplished without excessive losses of zinc and chlorine.

Normally the impurities do not settle out of the $ZnCl_2$ melt so that regeneration cannot be accomplished by simple physical means such as settling without adding other materials. One method we have developed for regeneration is combustion of the whole spent melt in a fluidized bed of inert solids. The combustion process removes the N, S and C impurities from the melt and simultaneously vaporizes the $ZnCl_2$. Carbon is removed as CO_2 with some CO and sulfur as SO_2. Ammonia is burned to N_2 and H_2O. The vaporized $ZnCl_2$ out of the combustor is recondensed and is in a suitably pure form for return to hydro.

We have published previously the results of successful demonstration of such combustion regeneration of substantially coal-ash-free spent melts from hydrocracking of coal extracts.

We now have extended this work to a study of regeneration by combustion of spent melts from hydrocracking of coal directly. What makes this work different from the previous work are the relatively large amounts of coal-ash in the spent melt feed to regeneration as compared with the virtually coal-ash-free feedstocks used previously.

Figure 1 gives the composition of the spent melt feedstock. This is a synthetic feedstock simulating spent melt from hydrocracking of a western subbituminous coal. The residue from solvent extraction of Colstrip coal was used in preparing the feedstock. You will note that the feed contains the carbon residue impurities, ZnS, NH_4Cl and NH_3 as well as coal ash. The coal ash composition is typical of many western subbituminous coals, i.e., low potassium, high calcium and magnesium, and relatively low in iron as compared with eastern bituminous coal ashes.

Figure 2 is a diagram of the continuous fluidized bed combustor that was used. The melt is fed via syringe feeders and is dropped from a remote drip tip into a batch bed of fluidized solids that is fluidized by feed air that enters at the apex of the reactor cone. The carbon, nitrogen and sulfur are burned out in the fluidized bed and the $ZnCl_2$ is vaporized. The gas, $ZnCl_2$ vapor and elutriated solids leaving the reactor pass through the cyclone where the solids are collected. The cyclone underflow solids derive solely from the melt since the sizing of the bed solids is such that there is essentially no elutriation of this material. The solids collected at the cyclone then include coal ash, zinc oxide formed by hydrolysis of zinc chloride, and any unburned carbon or zinc sulfide. The gas then passes to the condenser where $ZnCl_2$ is condensed out, then to the electrostatic precipitator to remove $ZnCl_2$ fog and then to sampling and metering.

Figure 3 gives the conditions of the runs that I will talk about - essentially atmospheric pressure, superficial residence time of one second, excess air, i.e., 115% of stoichiometric, silica bed solids. Temperatures of 1800 and 1900°F were investigated. No operability problems such as ash agglomeration or defluidization of the bed were encountered at these conditions.

Figure 4 gives the distribution of carbon, sulfur and nitrogen in the products for runs at 1800 and 1900°F. One-hundred fifteen percent of stoichiometric air was used in both runs. The feed gas was pure air. It is apparent that the carbon, nitrogen and sulfur impurities almost completely burned out, i.e., 89% or more burnout was achieved. The effluent melt contains less than 3% of the carbon and sulfur in the feed melt and 11% or less of the nitrogen.

Figure 5 shows the distribution of total coal ash as well as the coal ash components, silica and alumina, in the products in two runs at 1800°F. In Run 3, the feed gas was 100% air while in Run 11, the feed gas was 94.5% air and 5.5% anhydrous HCl. The HCl was added to prevent hydrolysis of the $ZnCl_2$. This will be discussed further later. Eighty-nine percent or more of the total coal ash and silica and alumina were removed from the melt in the regeneration process. The ashes were either trapped in the bed or collected at the cyclone.

Figure 6 shows the distribution of the ash components, iron, calcium, and magnesium in the products of the same two runs as in Figure 5. Again, it is apparent that the large majority of these ash components were removed from the melt and that they were either trapped in the combustor bed solids or collected at the cyclone.

The distribution of sodium and potassium are not given in the figures. Essentially all of the sodium and potassium in the feed appears in the effluent melt. This is likely due to the potassium and sodium being converted into the chlorides which are sufficiently volatile to be vaporized along with the $ZnCl_2$. This chlorine is considered to be irrecoverable. Hence, this method of regeneration is chiefly useful with coals that have relatively low alkali concentrations.

Figure 7 shows the distribution of zinc and chlorine among the products in Runs 3 and 11. The feed gas in Run 3 was pure air. In this run, about 10% of the feed zinc was found in the bed solids and cyclone solids as ZnO while

90% is in the melt as $ZnCl_2$. The large amount of ZnO is formed by hydrolysis of $ZnCl_2$ in the combustor,

$$ZnCl_2 + H_2O = ZnO + 2\ HCl.$$

Because of the hydrolysis, a large amount of the chlorine in the feed melt is found in the gas as HCl. For the process to be economically feasible, $ZnCl_2$ would have to be synthesized from the ZnO and HCl formed by hydrolysis.

To preclude such a step, the HCl can be recycled with the feed air to prevent hydrolysis. Run 11 was made to test this concept where the feed gas contained 5.5% anhydrous HCl. The chlorine in the feed HCl amounted to 14.8% of the chlorine in the $ZnCl_2$ feed. It is apparent that hydrolysis was almost completely suppressed and that the Zn in the feed melt was almost totally converted to and recovered as $ZnCl_2$.

Before starting this work, it was feared that considerable chlorine would be lost as $CaCl_2$ by interaction of the calcium in the coal ash with the $ZnCl_2$, but it appears that essentially no chlorine is lost in this manner. It will be noted in both Runs 3 and 11, that the bed solids contain substantially no chlorine whereas they contained a large percentage of the calcium that was fed. Since $CaCl_2$ is molten but nonvolatile at combustion temperature, it would be expected that any calcium chloride would be retained in the bed solids. Since none was, it is concluded that no calcium chloride was formed. (It also appears that no magnesium chloride was formed.)

Figure 8 shows some pertinent reactions in the regeneration system. We determined the equilibrium constant for reaction (3) and obtained P_{ZnCl_2} of 57 torr whereas P_{ZnCl_2} in the combustor was about 120 torr. Hence, we figured that some $CaCl_2$ would be formed. It is now believed that the reason we didn't get $CaCl_2$ is because of reactions such as (4) and (5) whose equilibria are probably far to the right. Kuxmann and Oder have reported recovering zinc as pure $ZnCl_2$ vapor from impure ores by reaction (4) carried out at about 1650°F.

It appears that some $FeCl_2$ is formed but not in the amount that would be expected if equilibrium had been established in reaction (2). Reactions analagous to (4) and (5) with $FeCl_2$ substituted for $CaCl_2$ may be the reason for this. In any case, the equilibrium constant indicates that the amount of $FeCl_2$ that can be formed is limited to 1 mol per 9 mols of $ZnCl_2$. Further, we have data that indicates that $FeCl_2$ does not affect catalyst activity.

We believe, based on the results just presented as well as other results, that we have a workable process for regenerating $ZnCl_2$ from direct hydrogenation of western subbituminous coals. Less comprehensive work indicates that the process can be successfully applied to melts from direct hydrogenation of eastern bituminous coals also. The process is restricted to coals having relatively low sodium and potassium contents so that economicially prohibitive amounts of chlorine are not lost to these alkali metals.

CWZielke:rmc
Attachments:
  Figures 1 thru 8

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FIGURE 1

ANALYSES OF THE FEED MELT

MELT COMPOSITION, WT. %

C	5.03
ORGANIC H	0.11
ORGANIC N	0.09
ORGANIC O	0.24
ORGANIC S	0.04
$ZnCl_2$	85.34
ZnS	2.92
NH_4Cl	3.20
NH_3	1.25
ASH	1.78

ASH COMPOSITION, WT. %

Na_2O	0.47
K_2O	0.21
CaO	18.67
MgO	7.07
Fe_2O_3	4.59
TiO_2	1.44
P_2O_5	0.15
SiO_2	42.15
Al_2O_3	25.25

FIGURE 2

FLUIDIZED COMBUSTION UNIT

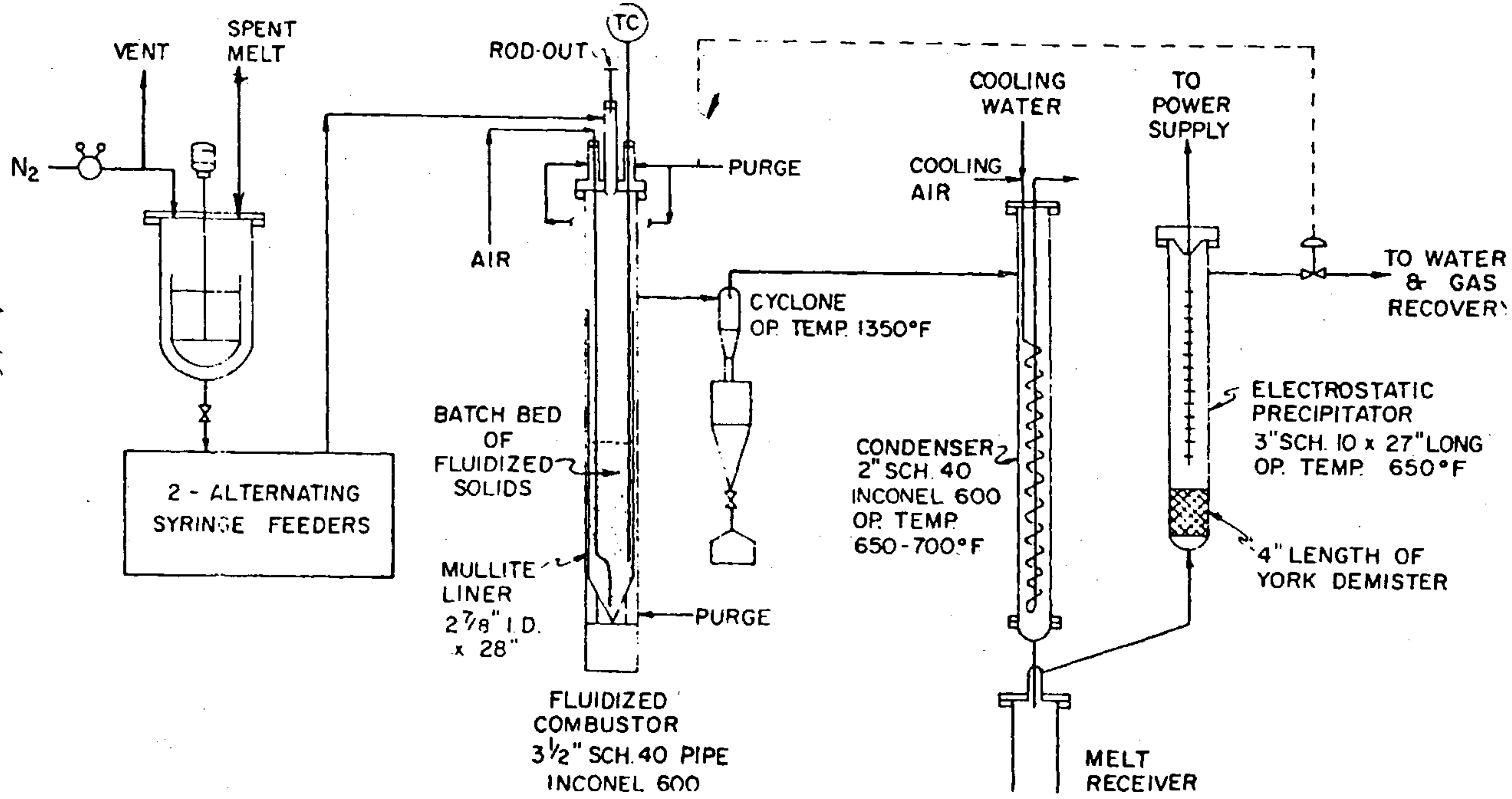

FIGURE 3

GENERAL CONDITIONS

PRESSURE , PSIG	2.0
SUPERFICIAL AIR VELOCITY, FPS	1.0
SUPERFICIAL RESIDENCE TIME , SEC.	1.0
MELT FEED RATE , LB/HR.-FT.^{2}	73
% OF STOICHIOMETERIC AIR	115
FLUIDIZED BED DEPTH, INCHES	12
TYPE OF BED SOLIDS	28 x 48M SILICA

FIGURE 4

DISTRIBUTION OF C, S AND N IN THE PRODUCTS

RUN NUMBER	3	4
TEMP. , °F	1800	1900
% of STOICH. AIR	115	115
DISTRIBUTION of C, %		
BURNED to CO_2 (+ LOSS)	92.7	92.9
BURNED to CO	5.9	4.2
IN CYCLONE SOLIDS	0.4	0.5
IN MELT	1.0	2.4
DISTRIBUTION of S, %		
BURNED to SO_2 (+LOSS)	91.3	96.4
IN BED	1.8	0.4
IN CYCLONE SOLIDS	3.8	1.4
IN MELT	3.1	1.8
DISTRIBUTION of N, %		
NH_3 BURNED to $N_2 + H_2O$ (+LOSS)	89.3	100.0
N IN MELT	10.7	0.0

FIGURE 5

DISTRIBUTION OF TOTAL COAL ASH, Si, Al, AMONG THE PRODUCTS

RUN NUMBER	3	11
TEMP., °F	1800	1800
FEED GAS COMP., MOL %		
AIR	100	94.5
ANHYDROUS HCl	-	5.5
DIST. OF TOTAL ASH, %		
BED SOLIDS (+ LOSS)	19	34
CYCLONE SOLIDS	70	59
MELT	11	7
DIST. OF Si, %		
BED SOLIDS (+ LOSS)	29	28
CYCLONE SOLIDS	67	68
MELT	4	4
DIST. OF Al, %		
BED SOLIDS (+ LOSS)	94	31
CYCLONE SOLIDS		64
MELT	6	5

FIGURE 6

DISTRIBUTION OF Fe, Ca, Mg AMONG THE PRODUCTS

RUN NUMBER	3	11
TEMP., °F	1800	1800
FEED GAS COMP., MOL %		
AIR	100	94.5
ANHYDROUS HCl	–	5.5
DIST. OF Fe, %		
BED SOLIDS (+ LOSS)	73	0
CYCLONE SOLIDS		61
MELT	27	39
DIST. OF Ca, %		
BED SOLIDS (+ LOSS)	29	53
CYCLONE SOLIDS	48	42
MELT	23	5
DIST. OF Mg, %		
BED SOLIDS (+ LOSS)	44	57
CYCLONE SOLIDS	43	41
MELT	13	2

FIGURE 7

DISTRIBUTION OF ZINC AND CHLORINE IN THE PRODUCTS

RUN NUMBER	3	11
TEMP., °F	1800	1800
FEED GAS COMP., MOL %		
AIR	100	94.5
ANHYDROUS HCl	-	5.5
Cl DIST., % OF Cl IN FEED MELT		
BED SOLIDS	.02	.01
CYCLONE SOLIDS	.44	.30
GAS	9.10	14.50
MELT (+ LOSS)	90.40	100.00
TOTAL	100.00	114.80
Zn DIST., % OF Zn IN FEED MELT		
BED SOLIDS	5.5	.40
CYCLONE SOLIDS	4.4	.74
MELT (+ LOSS)	90.1	98.90

FIGURE 8

SOME PERTINENT REACTIONS

K at 1800°

1) $ZnCl_{2(v)} + H_2O_{(g)} = ZnO_{(s)} + 2HCl_{(g)} \quad K_1 = \frac{(P_{HCl})^2}{(P_{ZnCl_2})(P_{H_2O})}$; .28

2) $ZnCl_{2(v)} + FeO_{(s)} = FeCl_{2(v)} + ZnO_{(s)} \quad K_2 = \frac{P_{FeCl_2}}{P_{ZnCl_2}}$; .11

3) $CaCl_{2(l)} + ZnO_{(s)} = CaO_{(s)} + ZnCl_{2(v)} \quad K_3 = P_{ZnCl_2}$ 57 Torr

4) $CaCl_{2(l)} + SiO_{2(s)} + ZnO_{(s)} = CaSiO_{3(s)} + ZnCl_{2(v)}$

5) $CaCl_{2(l)} + SiO_{2(s)} + H_2O_{(g)} = CaSiO_{3(s)} + 2HCl_{(g)}$

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