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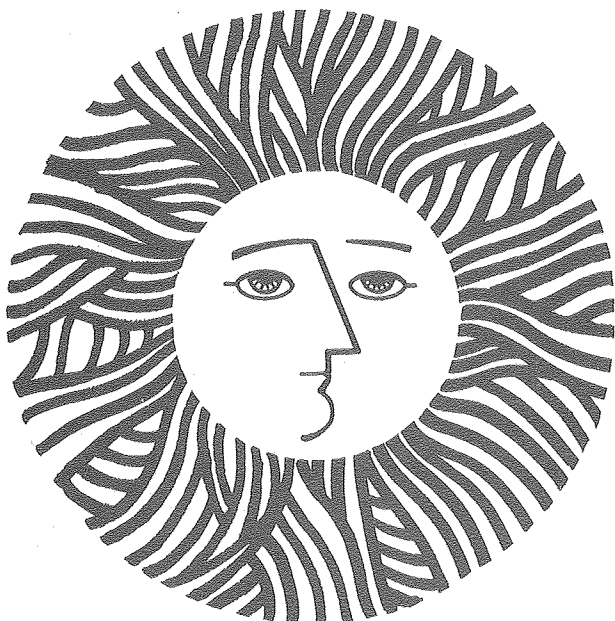
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CATALYTIC LIQUEFACTION BY ZINC CHLORIDE MELTS AT PRE-PYROLYSIS TEMPERATURE

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Liquid-phase catalysts have proved effective for opening chemical linkages in subbituminous coal and capping the reactive segments with hydrogen atoms or other low-molecular-weight groups. The preferred temperature range is 275 to 325°C (530 to 620°F), so that the linkages are opened by controlled catalytic action rather than by thermal pyrolysis which requires appreciably higher temperatures.

The best catalyst "melt" compositions used to date are zinc chloride with 10% water together with tetralin, and zinc chloride with 15% methanol and 3% of zinc metal (1-3). Useful residence times range from 30 minutes, or less, to as high as 90 minutes. The products of the treatment have predominately low (300) to medium (3000) molecular weights, analogous to syncrudes and solvent-refined coal. Conversions to pyridine-soluble products of 95% or better are achieved with Wyodak Roland Seam coal, and to date as much as 70% of that coal has been recovered as toluene-solubles ("oils" and "asphaltenes"). Characteristically, the oils melt between 50 and 80°C, and the asphaltenes between 120 and 200°C.

A major benefit of these conversion conditions is the almost complete absence of by-product char or gas. At these lower temperatures the hydrogen pressure used can be less than in conventional liquefaction; for example, 40 atm rather than 100 atm or more. Hydrogen consumption is significantly lower than in conventional liquefaction, the product yield is higher, and simpler procedures are foreseen for product recovery. Size reduction of the feed coal to minus 30 mesh appears sufficient. Also, moist coal is regularly used as the feed, without pre-drying.

Much more research on this method of catalytic conversion will be required before a liquefaction process can be completely defined. Nevertheless, conceptual design of the entire projected process brings the remaining problems sharply into focus. The research performed so far clearly shows the industrial potential of "homogeneous" (liquid-phase) catalysts in penetrating and interacting with the interior pore surfaces of a solid-phase raw material, otherwise unreactive under the mild temperature and pressure of these studies.

Chemistry and Physics of Zinc Chloride

Zinc chloride has been used previously in coal conversion at higher temperatures. Gorin, Zielke, Struck, and coworkers (4) at Consolidation Coal (now Conoco Coal Development) have developed a well-known process for combined liquefaction and hydrocracking of bituminous coals primarily to gasoline-range products, operating with dry feed streams at conventional temperatures (375 to 450°C, or 700 to 850°F). Wisner, Wood, and coworkers (5) at the University of Utah have explored the short-contact-time liquefaction at 425 to 475°C (800 to 900°F) of finely ground coal dispersed in hydrogen gas, the coal being preimpregnated with 2-4% zinc chloride.

Pure anhydrous zinc chloride melts at or near 315°C (600°F). It complexes reversibly with water or methanol, and its saturated aqueous solution at 25°C contains 82% ZnCl₂. The addition of around 10% water or 15% methanol to anhydrous ZnCl₂ produces a "melt" which remains liquid down to 150°C (300°F). The vapor-pressure behavior of zinc chloride/water mixtures has been charted by Holten (6). Qualitatively, on a mole-for-mole basis, the vapor pressure of methanol in ZnCl₂ is about the same as for water.

Zinc is one of very few metal ions which combine catalytic activity for bond scission with activity for hydrogenation. Halides of less available metals, such as antimony and tin, are also somewhat active.

Conversion of subbituminous coal to soluble products is accompanied by large reductions of the oxygen content. Recent studies by Hershkowitz and Grens (3) have established that conversion of coal to preasphaltenes involves loss of ether oxygen, and that the slower conversion of preasphaltenes to oils involves removal of hydroxyl (e.g., phenolic) oxygen.

At a low hydrogen pressure of 15 atm, for $ZnCl_2$ with 15% CH_3OH alone, conversion occurs partly by internal hydrogen transfer, and the net hydrogen-to-carbon ratio of the MTC falls to 0.85, compared with 1.00 for the feed coal. Incorporation of methanol or tetralin into the MTC may reach 10-15% of the weight of the feed coal at 250°C and 15 atm, but declines markedly as temperature or hydrogen pressure is increased.

When a low percentage of zinc metal is added, it appears to dissolve in the melt (possibly forming Zn_2^{++} ions). It clearly assists in the conversion of asphaltenes to oils, and raises the usual hydrogen-to-carbon atomic ratio of the melt-treated coal (MTC) from around 0.95 to around 1.12.

Optimum Temperature Sequence

Time-temperature relations have been studied with $ZnCl_2/CH_3OH$ melt to determine the temperature staging that will give the highest production of oils. Runs starting well below 300°C (570°F) give better results than those starting at or above that level. Runs which include a stage at or above 300°C give more complete conversion, but that conversion is reduced if the temperature in this stage is advanced to 340°C (645°F). It appears that the threshold temperatures are different for $ZnCl_2$ -catalyzed scission of different types of bonds in coal, just as they are undoubtedly different (and each one higher) for thermal pyrolysis. (Thus, the pyrolysis temperature of easily broken bonds, such as C-O in ethers, may lie well below the "pre-pyrolysis" temperature for $ZnCl_2$ -catalyzed scission of another type, such as C-O in phenols.)

In Table 1, comparison between run 51 at 275°C and run 77 at 300°C shows almost no advantage for the higher temperature. In contrast to this, run 76 at 275°C and 300°C in succession is clearly superior to run 51 entirely at 275°C (both for 30 minutes). Adding 15 minutes at 325°C (run 69) or 30 minutes at 325°C (run 73) produces highly significant improvement. The result for run 77 suggests that treatment at 300°C or above should be preceded by treatment at 275°C.

Pushing the reaction mixture to 340°C for 15 minutes (run 74) reverses the beneficial effect of 325°C, possibly by fostering coke-forming reactions. Run 78 can be considered kinetically similar to 15 minutes at 275° and 15 minutes at 325°C, and indeed comes out between runs 76 and 69. Thus, while pretreatment at 275° appears beneficial, pretreatment at 250°C imparts no further advantage.

These runs indicate that a sequence of 275°C briefly, and 325°C for a longer period, will give the lowest residual preasphaltene in the shortest total time.

The possibility remains that tetralin added to the methanolic $ZnCl_2$ melt will give still better conversion, and this will be tried. The effect of a third stage of conversion at still higher temperature (350-400°C; or 660-750°F) for converting the preasphaltenes to oils and asphaltenes is now under study. A solvent-extraction step between second- and third-stage treatment may be needed to avoid deterioration of the lighter fractions already formed; this question is also receiving attention.

Conceptual Process Design and Reactor Layout

The questions not yet solved include whether recycled solvent will be used for co-reaction and/or extractive separation of product from the melt. We project that the melt can be recycled repeatedly, and that only a purge stream of melt and mineral residue will undergo an as yet unstudied chemical regeneration. Our existing knowledge, although incomplete, is sufficient to allow the preparation of a tentative flowsheet (Figure 1).

In this flow scheme, raw coal is blended into a slurry with $\text{ZnCl}_2/\text{CH}_3\text{OH}$ melt at 175°C (350°F) and 1 atm, pumped to 25 atm, injected with 5 vol-% H_2 , heated to 275°C (530°F), and fed continuously to the top of a plug-flow reactor where it is contacted countercurrently with a hydrogen-rich gas phase.

Provision is shown for possible extraction of coal liquids from the melt by a recycle fraction of coal-derived solvent. A further reaction stage could be added; it is unlikely that more than one extraction step would be needed.

The mixed slurry then moves to a settler where phase separations take place. A slip stream of ZnCl_2 melt is removed with the ash, purified, and recycled. The main ZnCl_2 layer is recycled. The organic layer will be returned to the extraction step, or perhaps directly to the distillation which separates the recycle solvent from the coal product stream.

Plug flow of melt/coal slurry is projected, because it should give shorter residence time, fewer secondary reaction products, and fewer mechanical problems than with stirred vessels. The proposal to use a sparged-column reactor, rather than one or several stirred-tank reactors, has been reviewed from the standpoint of adequacy of mass transfer, flow behavior, and holdup.

In a staged-temperature reaction temperature, we have noted that an unusual phenomenon may arise. Almost all the oxygen leaving the coal is removed as water, which tends to dissolve in the zinc chloride melt and reduce its catalytic activity. A rise in temperature will discharge part of this water into the hydrogen stream. If this moist hydrogen then moves to a cooler reaction zone, the moisture will be reabsorbed by the discarding melt, causing excess accumulation within the reactor system. This can be controlled by withdrawing the moist hydrogen from the top of the higher-temperature zone, and replacing it by a fresh dry hydrogen feed at the bottom of the lower-temperature section. Also, in order to maintain a relatively uniform flow of hydrogen all through the reactor, sparging should be used to introduce the hydrogen at at least five separate uniformly spaced levels in the reactor.

To test for any special surface-active behavior of zinc chloride as a liquid-phase component, as well as the effect of varying viscosity, two concentrated solutions of zinc chloride in water-glycerol mixtures were prepared having viscosities of 22 and 84 centipoises. These liquids were measured in comparison with tap water, using air at atmospheric pressure to simulate the mass velocity of hydrogen gas under elevated pressure. For tests in a 6-inch diameter column over a range of gas flow rates and liquid viscosities, the effective average bubble diameter was around 0.25 inch, and holdups of 12 to 16 vol-% were obtained. Mass-transfer tests using helium absorption and desorption suggested that such a system could introduce the needed hydrogen at about ten times the projected rate of hydrogen utilization by the coal.

A slow internal flow of liquid upward at the center and downward at the sides of the column was arrested by inserting pairs of slotted trays with the slots oriented perpendicular in the successive trays, the slot openings being 0.25 to 0.50 inch. From these results it was concluded that the only column intervals required

would be slotted trays in pairs, about 2 inches apart, the assembled pairs of trays being installed with a spacing no less than 12 inches and probably no greater than 30 inches. While our experiments have been run with a 6:1 weight ratio of melt to coal for reasons of stirrer efficiency, it is projected that the column reactor would use a 1.5:1 weight ratio, equivalent to a 1:1 volume ratio. Since the viscosity of the pure melt at blending and reaction conditions would be less than 10 centipoises, the effective viscosity of the melt/coal slurry would always be less than 100 centipoises.

Conclusion

Treatment of subbituminous coal with zinc chloride/methanol melts, containing a low level of metallic or monovalent-ionic zinc, has been shown to give quantitative conversion to solvent-soluble products (including 65% to oils and asphaltenes) in experiments conducted sequentially at 275° and 325°C. Based on related data, similar yields are projected for zinc chloride/water melt with tetralin, or zinc chloride/methanol with tetralin. Although full details are still under study, it is expected that product separation will be facilitated, and that the catalytic melt can be used repeatedly between regenerations.

References

1. E. A. Grens, F. Hershkowitz, R. R. Holten, J. H. Shinn, and T. Vermeulen, "Coal Liquefaction Catalysis by Zinc Chloride Melts in Combination with Organic Solvents", Ind. Eng. Chem. Proc. Dev. Des., in press.
2. J. H. Shinn and T. Vermeulen, "High-Yield Coal Conversion in a Zinc Chloride/Methanol Melt Under Moderate Conditions", Preprints Div. Fuel Chem., Amer. Chem. Soc., 24, no. 2, 80-88 (April 1979).
3. F. Hershkowitz and E. A. Grens, report in preparation.
4. C. W. Zielke, R. T. Struck, J. M. Evans, C. P. Costanza, and E. Gorin, Ind. Eng. Chem. Proc. Des. Dev. 5, 158 (1966).
5. R. E. Wood and W. H. Wiser, Ind. Eng. Chem. Proc. Des. Dev. 15, 144 (1976).
6. R. R. Holten and T. Vermeulen, Univ. of Calif. Lawrence Berkeley Lab. Report LBL-5948 (1977).

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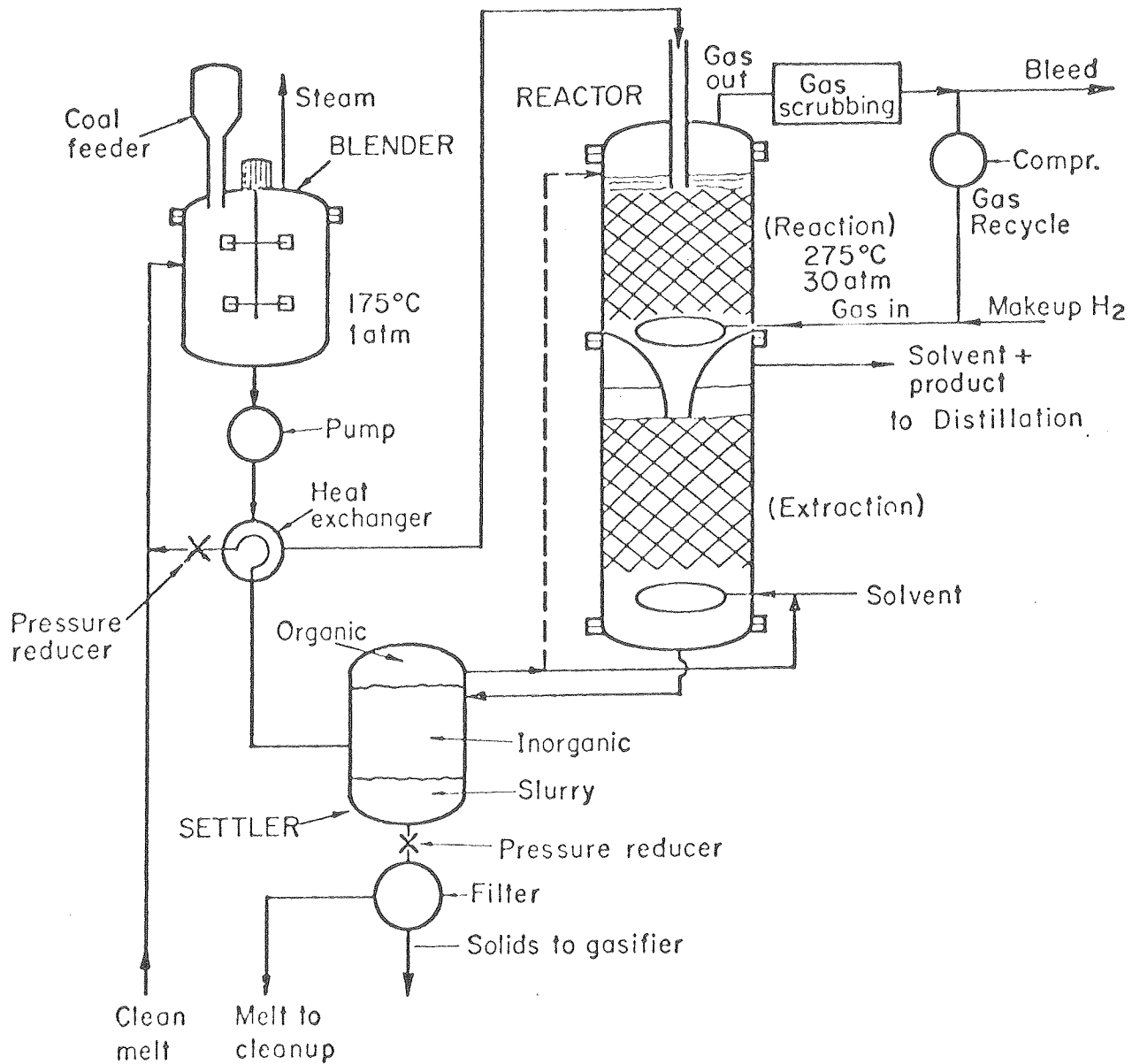


Figure 1. Conceptual flowsheet for liquefaction of subbituminous coal by zinc chloride melt.

Table 1. Effect of Temperature Staging in Treatment of Wyodak Coal at 55 bars Hydrogen, with 3% Zn and 14% CH₃OH (50 g coal, 300 g melt)

Run No.	Temp (°C)	Time (min)	Extractibles, daf basis, %			Atomic H/C
			Oil	Asph.	Preasph.	
70	275	15	31	14	54	1.00
51	275	30	32	15	53	1.05 est
63	275	45	35	15	48	1.09
77	300	30	33	17	50	1.04
76	{ 275 300 }	15	37	18	45	1.10
		15				
69	{ 275 300 325 }	15	46	10	44	1.10
		15				
		15				
73	{ 275 300 325 }	15	54	10	36	1.19
		15				
		30				
74	{ 275 300 325 340 }	15	51	9	40	1.13
		15				
		15				
		15				
79 (without Zn)	{ 250 275 300 325 }	10	27	10	63	1.09
		10				
		10				
		10				
78 (with Zn)	{ 250 275 300 325 }	10	40	15	45	1.06
		10				
		10				
		10				