

LOW SULFUR COAL OBTAINED BY CHEMICAL DESULFURIZATION
FOLLOWED BY LIQUEFACTION

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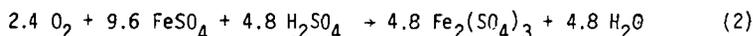
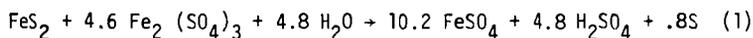
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The sulfur content of coal, nearly all of which is emitted as sulfur oxide during combustion is, on the average, about equally distributed between two chemical forms, inorganic (iron pyrites) and organic sulfur.

An unconventional approach for near total removal of the pyritic sulfur content of coal was recently reported by Meyers *et al* in this journal⁽¹⁾. This new technique involves treatment of coal with a regenerable aqueous ferric solution as outlined in eqs 1 and 2⁽²⁾



followed by a separation of generated elemental sulfur and iron sulfate. Subsequent laboratory investigations demonstrated that the process could reduce the sulfur content of 30-40% of the U.S. Appalachian coal reserves to the 0.7 to 0.8% sulfur level needed to meet the Ambient Air Quality Act⁽³⁾.

Coal liquefaction (Figure 1A), the catalytic or non-catalytic hydrogenation of coal in a coal derived solvent to produce a utility fuel,⁽⁴⁾ has been demonstrated to remove in the range of 40-60% or more of the organic sulfur from coal by conversion to hydrogen sulfide, and to be capable of removing nearly all of the inorganic sulfur and most of the

ash if a suitable means for filtration of the micron-sized inorganic residue from the viscous liquefied coal could be developed. To date, the filtration technology necessary to accomplish the de-ashing of the liquefied coal and limited organic sulfur reduction have been the major problems associated with liquefaction, particularly with the non-catalytic version, known as solvent refined coal.

We have investigated the combination of the Meyers Process with a simplified form of coal liquefaction (Figure 1B) in order to begin to devise a potentially economical, viable combined process. In our approach, the filtration step is eliminated so that desulfurization is effected by a combination of first, ferric ion leaching to remove pyritic sulfur and second, hydrogenation to remove a significant portion of the organic sulfur as hydrogen sulfide. The product coal, however, contains the normal coal ash content less the pyrite which has been removed. This ash, which is also a pollutant when coal is combusted in a power plant, can be removed by available electrostatic precipitation and bag house techniques after combustion but prior to emission into the atmosphere⁽⁵⁾.

We selected two coals, from the Muskingum (Meiggs Creek No. 9 seam) and the Camp (Ky No. 9 seam) mines, for our investigations as representative of the two major coal basins east of the Mississippi River, the Appalachian and Eastern Interior. The two mines are among the largest in the U.S. Samples of run-of-mine coal⁽⁶⁾ were cleaned to remove rock fractions in order to represent the product normally obtained from mines after coal preparation⁽⁷⁾.

The cleaned coals were then chemically desulfurized utilizing the Meyers Process and resulted in 93-98% removal of pyritic sulfur. Two samples of each chemically desulfurized coal and two samples of each untreated coal were subjected to identical and typical batch type coal liquefaction conditions⁽⁸⁾ one hour residence time in 4 to 1 weight ratio of solvent to coal. The filtration step was omitted (Figure 1B) and the solvent was recovered. The results are tabulated in Table 1. Expts. 2 and 4, in which coal containing pyrite was charged to the reactor and Expts. 1 and 3, which had been chemically desulfurized prior to hydrogenation, show very similar organic sulfur reduction and heat content increase. In all cases the small amount of sulfate sulfur present in the coal was destroyed during the hydrogenation process.

We conclude that (i) the presence or absence of pyrite does not materially affect either the hydrogenation of organic sulfur or the uptake of hydrogen by the coal matrix as reflected in the organic sulfur and btu changes, respectively; (ii) nearly all of the pyrite, when present in the coal samples (Expts. 2 and 4), is converted under the hydrogenation conditions to iron sulfide and hydrogen sulfide as in eq 3,



as has been shown for mineral pyrite under similar conditions⁽⁹⁾; and (iii) the two coal samples, although from different coal basins, behaved similarly under hydrogenation conditions.

It is notable to point out that the Ky. No. 9 (Camp) coal was reduced to 0.85% total sulfur (Expt. 3) with a heat content increase to 14156 btu, by the combination of chemical desulfurization and hydrogenation, meeting the requirement of 0.6 lb sulfur/10⁶ btu established by the Federal Ambient Air Quality Act for power plant fuel for new stationary sources. Thus, this coal could meet the federal standard utilizing the combined process.

It therefore appears that a combination of the Meyers Process with a simplified form of coal liquefaction, as described in Figure 1B, is technically feasible for the desulfurization of coal to meet pollution control standards^(10,11).

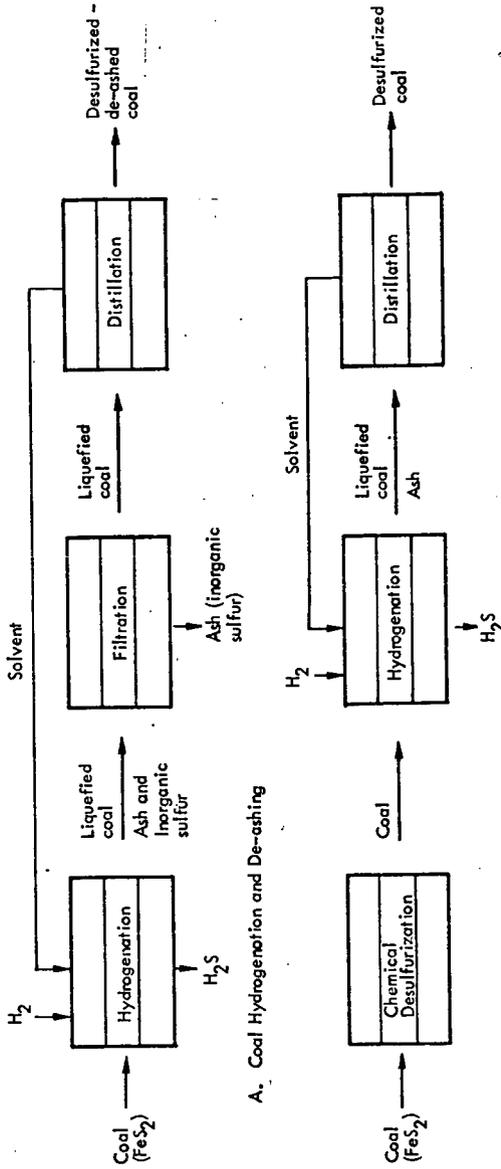


Figure 1. Process flow charts: A. (i) coal containing pyrite is slurried with a coal derived solvent with or without a catalyst, hydrogenated at about 400°C/1000-4000 psig; (ii) undissolved coal, ash and any catalyst is filtered away from the dissolved coal and solvent; (iii) solvent is recovered by distillation to give a desulfurized, de-ashed coal; B. filtration step is omitted to give a desulfurized coal which has most of its iron removed but is not de-ashed.

Table 1. Data on sulfur reduction. Each coal (cleaned) was pulverized to -100 mesh for sampling and processing. Chemical desulfurization was performed at 1020 by treatment with aqueous 1N ferric sulfate solution as described in reference 3. Hydrogenation was performed at 4250/2000 psig in anthracene oil solvent as described in reference 7. Solvent was recovered \pm 3% by multiple repulverization and solvent distillation at 300°C maximum, 3 mm Hg ultimate.

Expts. no.	Coal*	Treatment	Dry forms of sulfur (% by weight) of			Organic sulfur reduction (% by weight)	Heat content btu	Increase in heat content (% by weight)
			Total*	Pyritic	Sulfate			
	Musk		4.37	1.70	0.11	0.00	2.56	11829
	Musk	chem desulfurized	3.14	0.12	0.08	0.00	2.94	12077
1	Musk	chem desulfurized and hydrogenated	1.24	0.01	0.00	0.00	1.20	13180
2	Musk	hydrogenated only	1.95	0.06	0.00	0.76	1.13	12904
	Camp		2.98	0.81	0.30	0.00	1.87	12752
	Camp	chem desulfurized	2.26	0.02	0.28	0.00	1.96	12956
3	Camp	chem desulfurized and hydrogenated	0.85	0.01	0.00	0.00	0.84	14156
4	Camp	hydrogenated only	1.35	0.08	0.00	0.32	0.95	13545

*Total, pyritic, sulfate sulfur and heat content (dry basis) were determined by American Society for Testing Materials techniques at the Commercial Testing and Engineering Laboratories, Chicago, Illinois. The values reported for treated coals are averages for duplicate runs. †Sulfide sulfur was determined by total sulfur analysis of coal after 1 hr extraction with boiling 5N hydrochloric acid, the difference in sulfur content between extracted and unextracted coal, less the sulfate content determined by sulfate analysis of the acid solution being the sulfide sulfur. ‡Organic sulfur is the difference between total sulfur and the sum of pyritic, sulfate and sulfide sulfur.

REFERENCES AND NOTES

1. R.A. Meyers, J.W. Hamersma, J.S. Land and M.L. Kraft, Science **177**, 1187 (1972).
2. J.W. Hamersma, M.L. Kraft, E.P. Koutsoukos and R.A. Meyers, "Pollution Control and Energy Needs", Advances in Chemistry Series, No. 127, American Chemical Society, Washington, D.C., 1973, pp 69-79.
3. J.W. Hamersma, M.L. Kraft, W.P. Kendrick and R.A. Meyers, Am. Chem. Soc., Div. of Fuel Chem., Preprints **19** (2), 33 (1974).
4. H.H. Lowry, "Chemistry of Coal Utilization", Vol. II, John Wiley and Sons, N.Y. (1945).
5. The ash remaining in liquefied coal derived from conventional liquefaction, although usually under 0.5% by weight of coal, is in the form of fine particles which may be environmentally hazardous and might also need to be precipitated prior to emission from a power plant.
6. Detailed analyses of the run-of-mine samples are presented in reference 3.
7. Run-of-mine coal samples crushed to -14 mesh were suspended in a 1.75 specific gravity liquid. The float material, 80-90% by weight was recovered as the "clean" fraction.
8. J.H. Gary, R.M. Baldwin, C.Y. Bao, M. Kirchner and J.O. Golden, "Removal of Sulfur from Coal by Treatment with Hydrogen". Prepared for Office of Coal Research, S/N 2414-00070, U.S. Government Printing Office, Washington D.C. (1973).
9. G.M. Schwab and J. Philinis, J. Am. Chem. Soc. **69**, 2588 (1947)
10. It occurred to us that the filtration step in coal liquefaction could also be eliminated by extraction of iron sulfide with hydrochloric acid following liquefaction. However we have found that hydrochloric acid, in environmentally unsound amounts (about 1% W/W), remains with coal after treatment even after exhaustive washing with boiling water. A matrix of 1-hour sulfuric acid leaches to remove iron sulfide was attempted after it was found that 1N sulfuric acid dissolved pure iron sulfide in near quantitative yields. However we found no decrease in total sulfur for the Camp coal from Expt. 4 and only a slight decrease for the Muskingum coal from Expt. 2, after extraction with either 1N, 3N or 12N sulfuric acid. Thus, it does not appear feasible to chemically remove iron sulfide after liquefaction as a method for production of low sulfur fuel.
11. The finding that residual sulfate is destroyed during hydrogenation, together with the known high reactivity of elemental sulfur with hydrogen, indicates that the elemental sulfur and iron sulfate removal

steps of the Meyers Process could possibly be deferred to the hydrogenation step as a further combined process simplification.

12. Liquefaction studies were supported by Office of Coal Research Contract 14-32-001-1225. Conceptual development and all other experimental work were supported by TRW Inc.