

Pressurized Gas Extraction of Coal

By Jerry W. King

The mention of the word coal to non-scientist and scientist alike conjures up a vision of a blackish rock used primarily as a source of fuel for domestic and commercial purposes. In truth, coal is a chemical storehouse, composed of varying amounts of mineral and organic matter, the latter being represented in gaseous, liquid, and solid forms. Coals, in contrast to oil shales, are abundant in decayed organic matter; however, attempts to obtain a definite chemical composition for coal have been thwarted by its relative insolubility and resistance to analysis by all but the most powerful chemical reagents.

Although coal has almost disappeared as a household fuel, its use as the principle source of industrial coke continues to this day. Recently, coals have been examined for the extraction of chemicals which have been traditionally obtained from petroleum feedstocks with the hope that these may be converted into gasoline. Such efforts, although limited until recently in this country, have been successfully employed in countries whose economies have suffered the lack of access to maritime or rail-delivered petroleum, primarily due to war or economically motivated embargo. Prime national examples are Germany, Japan, and Great Britain, although the distinct possibility exists for the United States to join the above list due to any future Arab oil boycott.

The most direct way of isolating chemicals from coal is via solvent extraction (the exposure of coal to selected solvents under various conditions of temperature and pressure) with subsequent separation of the chemically-

laden solvent from the coal matrix. The application of solvent extraction in coal chemistry is not new, the earliest studies being those of DeMarsilly¹ in 1862. Solvent extraction studies initiated prior to World War II were primarily designed to obtain information on the chemical composition and structure of coal and to isolate or upgrade the "coking principle" responsible for the coking properties of coal. Such experiments employed two different types of extraction processes.

The first type of process was characterized by low extraction temperatures (less than 200°C) and the use of solvents whose interaction with coal involved minor physical alteration of the coal extract. In contrast to the above conditions, extractions of a disintegrative nature have also been employed yielding high percentages of recoverable product whose composition bears little resemblance to the parent coal. An example of the latter technique is the Pott-Broche process² employed in Germany during World War II for coke and gasoline production.

The non-destructive solvent extraction processes have used a variety of solvents with varying degrees of success; however, two solvents, pyridine at 118°C and benzene under pressure at 275°C have been extensively investigated³. Non-destructive solvent extraction's primary use besides coal structure elucidation studies has been in the production of an improved coking coal and in the isolation of speciality chemicals, such as the extraction of montan wax from lignite coals.⁴

There are problems associated with the solvent extraction of coal. One such problem is the lack of a suitable theory which could be used to maximize extraction yields. Secondly, it is difficult to remove and recover solvents used in coal extractions. The presence of residual liquid solvent can have an adverse effect on the coking and sintering properties of coal, depending on the end use.

The research that we are now conducting in the chemistry department at the university should overcome some of the above problems. Although our studies have just begun, aided in part by a research grant from the Research Corporation, we should like to describe the theory and experimental methodology that form the basis of our research.

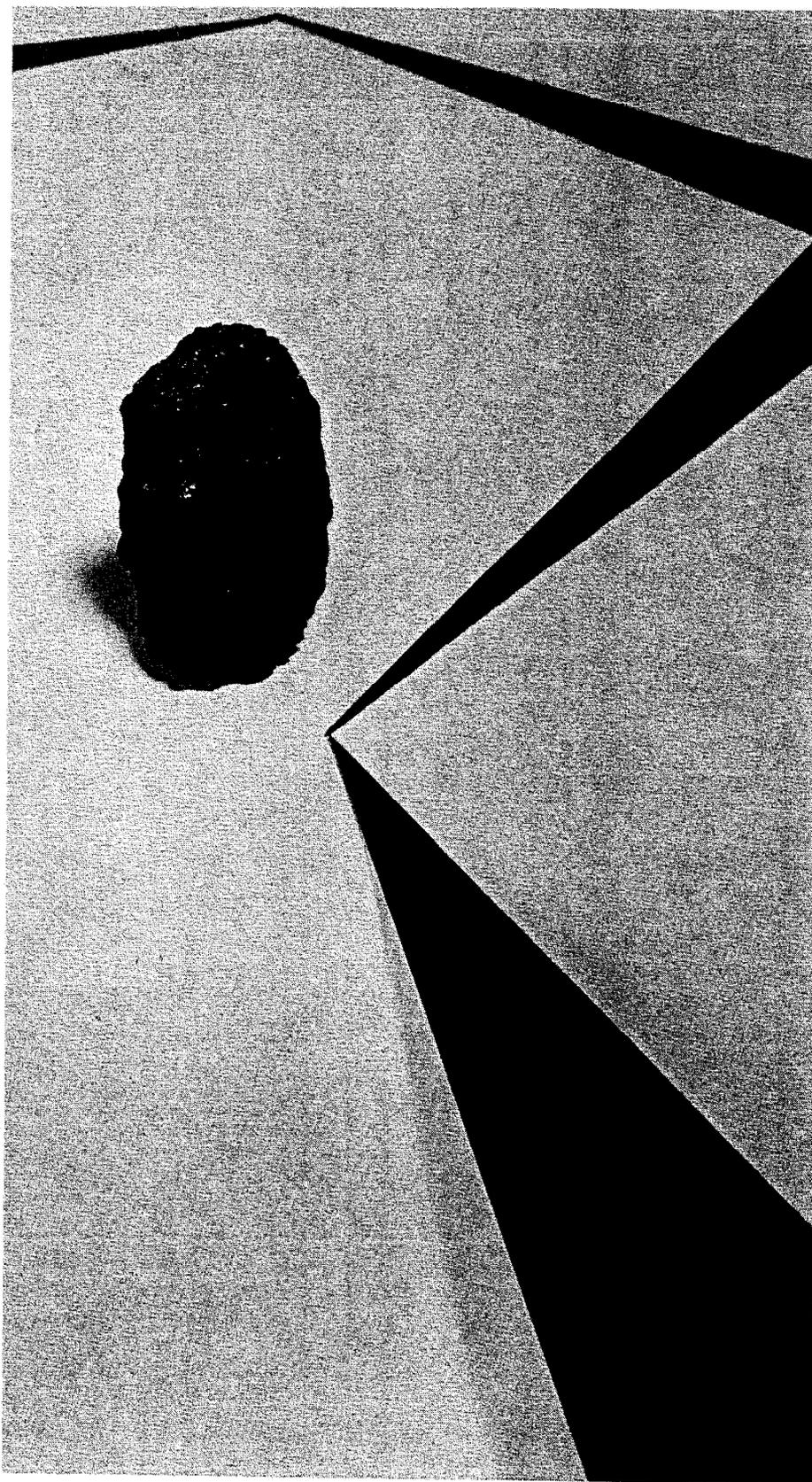
Presently, we are exploiting the solvent properties of highly pressurized gases to extract and purify chemicals from coal. Such a technique uses mechanical compression of the gas to vary the solvent properties of the gaseous fluid as opposed to using a host of liquid solvents of different cohesive energy densities (solvent strengths) to effect fractionation. The selection of the gases is governed by such factors as their critical temperatures, relative acid-base propensities, and commercial availability. In general, one seeks for our research, a gas having a critical temperature between ambient 200°C and solvent properties commensurate with those of liquid solvents which have shown the ability to solvate coal.

The gases of particular interest to our research group are carbon dioxide, ammonia, and ethylene. Carbon dioxide has been shown under compression to act as an

acceptor molecule with respect to aromatic compounds⁵ and to possess a cohesive energy density at high compression equal to that of pyridine and phenol, two non-destructive extractants for coal. Ethylene, despite its flammability, can enhance the vapor pressure of naphthalene by a factor of 26,000, hence accelerating its removal from the coal matrix. Naphthalene is but one of the many polynuclear aromatic hydrocarbons which appear associated with coal. For ammonia to be employed, one must operate the extraction device above 132°C, the critical temperature of ammonia, to avoid liquefaction of the gaseous solvent. Despite this requirement, ammonia possesses a lone pair of electrons, an important prerequisite as noted by Dryden⁶ for a coal extractant.

Our experimental apparatus employs commercially available high pressure components. Compression of the solvent gas to pressures exceeding those available in commercially bottled gas is achieved by utilizing a diaphragm compressor. The compressed fluid is then stored in a high pressure ballast tank either as a liquid or gas; however, the former condition requires thermostating at temperatures always above the critical temperature to avoid liquefaction. We favor storage of the solvent gas in the liquid form and employ equilibration coils prior to introduction of the gas to the extraction chamber to effect the transition of the solvent into the gaseous state.

The extraction chamber being used consists of a high pressure bomb into which finely pulverized coal has been placed. Extraction is affected by introducing the compressed gas into the chamber and allowing it to equilibrate with the coal. Subsequently, the gas containing the dissolved chemicals is reduced to atmospheric pressure



through a reducing valve and the material leached from the coal collected.

Two modes of extraction are possible with the above apparatus. The first involves the stepwise increase in pressure of the solvent gas and collection of the extract after each stage. Such a procedure would tend to "cream off" the more volatile components first, leaving behind a coal of potentially high coking value, free of any traces of solvent. The second mode of extraction involves compression to an elevated pressure and subsequent jetting of the pressure to collect various chemical fractions.

Extracts are being characterized by liquid and gas chromatography and the collected fractions analyzed by infrared, ultraviolet, and nuclear magnetic resonance spectroscopy. We are most fortunate in our department to have access to a Waters ALC-202 high pressure liquid chromatograph equipped with four micro-Styrigel columns for rapid molecular weight characterization of the extracts.

Our experiments should provide some insight into the mechanisms of coal processing on the industrial level. The Bureau of Mines' synthane process employs steam or carbon dioxide to lower the caking propensity of coal which if left untreated would otherwise agglomerate in the reactor bed. It is not known what function carbon dioxide plays in altering the coal structure;⁷ however, it is entirely possible

that our experiments will show that the degree of caking is a function of volatiles content of the coal. Hence, poor caking coals should be considerably upgraded through compressed carbon dioxide extraction. In addition, our pressure dependent extracts should involve considerably less molecular complexity than those obtained via conventional liquid extraction methods and allow correlations to be made between the pressure dependent cohesive energy density of the solvent gas and the chemical nature of the extract.



In summary, our research is attempting to ascertain the advantages of compressed gas extractions as applied to coal processing. The ability to perform extractions and isolate solvent-free extracts as well as solvent-free coal overcomes some of the problems associated with liquid diluents. From a more academic point of view, this low temperature extraction technique should allow the extracted products to be related back to the original coal and hopefully improve our understanding of the chemical composition and structure of coal.



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