

Liquefaction Study of Several Coals and a Concept  
For Underground Liquefaction

Duane R. Skidmore  
and  
Calvin J. Konya

West Virginia University  
School of Mines  
213 White Hall  
Morgantown, West Virginia

Introduction

In the past, underground coal conversion processes were uneconomical in comparison with cheap energy alternatives or not feasible technically. Some recent changes in technology and economics may have improved the feasibility of underground coal conversion. The selling prices of conventional fossil fuels have been rising because of restricted supply and increasing demand. The price increases should have four effects: (1) the producers of gas and oil are encouraged to find additional sources, (2) the users of these convenient fuels are motivated to restrict their consumption, (3) coal mine operators are inclined toward opening more conventional mines and (4) concepts for alternative energy sources such as underground coal conversion become more attractive for serious engineering evaluation.

The rise of concern for the health and safety of the miners is another factor influencing this renewal of interest in remote coal conversion. Not only have the human costs of conventional mining been large as represented by loss of lives or adverse effects on health but economic costs of industrial accidents have proven considerable. During the summer of 1972 the dreaded pneumoconiosis or "black lung" was the subject of a survivor's benefits bill passed by the U. S. Government in the amount of one billion dollars. The implementation of legislation to protect the health and safety of miners reflects social and economic concern.

The policy alternatives for elimination of energy shortages have been severely restricted by environmental regulations. Surface or strip mining of coal is under severe federal restriction and risks more regulations on the state and federal levels. The spoil banks which result from strip mining, particularly in the eastern United States, have not been reclaimed properly. Siltation of streams has resulted and fish have been killed. Silt has plugged channels and backed up waters to flood areas previously available for recreation and farming. In regions containing high sulfur coal, the streams have become acidic; and additional aquatic life is killed. Public outrage has been predictable.

The need for new technology to extend the coal reserves of the Nation does not and probably should not have a high industrial priority. Domestic coal reserves have been variously estimated but usually are deemed capable of sustaining present total national energy demands for 800 to 4000 years. New technology to utilize coal resources which are presently uneconomical to mine, however, would extend the recoverable energy from a given property and might therefore be worth an intensive research and development effort. The seams of particular interest include those which are low in sulfur and are too deep or too thin for exploitation by presently available methods.

Remote underground coal mines have been developed in northern Europe. As a result, the industry there has become even more increasingly capital intensive. One drawback to this alternative in the United States is that the coal mining industry has had difficulty in borrowing substantial amounts of money for long

time periods at low interest rates. Until the recent shortages of energy became well known and segments of the oil industry entered the coal mining industry, acquisition of equity capital had also been difficult. Some reluctance for stock purchase has been traced to uncertainties over oil import policy and environmental regulations. Furthermore, the European concept requires men underground for equipment maintenance. Finally, some questions have been raised in this country about the acceptability of underground mining for rapid implementation under existing work rules and union contracts.

With the changes in economic and social climate, the United States Bureau of Mines in cooperation with a subsidiary of the Union Pacific Railroad has reopened development work on underground coal gasification.

### History

The first reference to underground coal gasification is dated 1868.<sup>(1)</sup> The most extensive effort occurred in the Soviet Union from the 1930's to about 1960. Premier Stalin had apparently promised the miners some relief from difficult working conditions and had developed underground gasification technology in partial fulfillment of his promise. Some time after Stalin's death, the effort was quietly dropped, probably because extensive oil and natural gas discoveries made underground gasification uneconomical.

The most recent tests in the United States by the Bureau of Mines have defined two main problem areas. The product gas must be confined to the reaction zone and removed under controlled conditions. This implies that an impervious bed of rock must overlay the coal seam. The product gas must be useful for high value energy production. In most circumstances, this would require electrical power generation. Since the gas from underground conversion technology has had low heating value (less than 100 BTU/SCF). The need is obvious for technology to upgrade the product. No previous published work in underground conversion of coal to liquid has been found.

### Issues

Underground coal liquefaction concepts include several which are adapted from underground coal gasification. In the blind borehole-backfill system for underground gasification, a simple well is drilled vertically to the coal seam and then horizontally for some distance through the coal. The well is then doubly piped by a smaller diameter pipe within a larger one. Reactants are introduced through the central pipe and products are withdrawn through the outer annulus. The piping system is withdrawn as coal is used up. A void is produced by coal removal and the empty volume is filled with a water or solid waste rock fill material. The blind borehole-backfill system has been recommended for thin coal seams by the USBM report on underground coal gasification.

For somewhat thicker seams, the branched borehole-backfill system has been visualized. The borehole is branched after entering the coal seam so that the reactants can be admitted into the bottom of a seam and products withdrawn from the top. Proper downhole baffling arrangements are required.

Very thick seams lend themselves to the vertical blind borehole-fill system during which the concentric feed and product pipes are withdrawn vertically upward as the coal is produced. Fill from the feed pipe or another piping system readily accumulates in the exhausted volume. Each of the single borehole systems has a multiple borehole counterpart.

Use of a single well for feed reactants and for withdrawal of products obviates the need for connecting separately drilled wells. Boreholes can be connected underground by hydraulic fracturing, explosive fracturing and various modifications of

drilling or electro-linking. Some of these techniques have been successful for gas and petroleum field exploitation and underground coal gasification. Their particular disadvantage for use in underground coal conversion systems lies in the relatively rapid exhaustion of the hydrocarbon reservoir and the need for repeated practice of the linking procedure.

In remote mining schemes, the delivery of hot, hydrogen-donor solvent to the coal is a necessity. The solvent is hydrogenated conventionally and introduced while still hot into the reaction zone underground.

One of the principal problems underground is to maintain the solution temperature in the reaction zone. The total heat to be supplied provides (1) the heat of vaporization for the solvent, (2) the energy to pressurize the solvent vapor in the reaction zone in order to prevent excessive volatilization of the liquid solvent and to activate the solvent for the hydrogen transfer reaction, (3) the activation energy for the coal surface so that the reaction may proceed at an adequate rate, (4) losses to the surrounding rock, and finally (5) losses incurred when the reaction zone has passed and filling or flooding occurs.

The reaction itself is considered to proceed through at least two important thermal stages. First, the coal structure is thermally activated so that pyrolytic cracking or chain breaking of hydrocarbons occurs. Later, hydrogen atoms are released from the donor solvent and added to the coal fragments. Between the first and second phase a gel reaction may occur. During gelation ( $\sim 350^{\circ}\text{C}$ ) the coal and solvent form a viscous composite with high resistance to flow. The advantages of maintaining or establishing low slurry viscosities are obvious so that removal of coal is best effected either before or after the gelation step.

#### Further Set of Issues Involved

The design of an underground liquefaction process requires definition of (1) the types of coal seam most likely to be leached or liquefied by the physical arrangements suggested above and (2) the solvent or slurry material which would be most effective. Work was undertaken at West Virginia University to define the behavior of different types of coal monoliths exposed to several solvents under conditions possible for achievement underground.

#### Apparatus and Procedure

The test apparatus was a 750 ml carbon steel autoclave fitted with a Bourdon pressure gauge and a thermocouple well. Closure was effected by a gasket and flange arrangement. Gas inlet and exit lines permitted the autoclave to be flushed with nitrogen. No hydrogen was used. Heat was supplied by a large laboratory Bunsen burner. Reproducibility of heating rate is seen in Figure 1. A final temperature of 270 - 280°C was used for one series of experiments.

Procedure consisted of cutting on a mechanical saw a 1" x 1" x 1 1/4" monolith of the coal type to be tested. Coals included an Oklahoma semi-anthracite, an Illinois #6 sub-bituminous, and an Alabama lignite. Typical chemical analyses are shown in Table 1. After being cut, the coal was carefully placed into the autoclave and 250 ml of solvent was added. Solvents included various cuts of anthracene oil (Table 2), and one commercial motor oil (SAE 30). The autoclave was sealed, flushed with nitrogen, and heated by means of the burner. Figure 2 shows the pressure and temperature for a run with Illinois #6 coal in anthracene oil solvent. Figure 3 shows a similar run with SAE 30 motor oil solvent.

## Results

The coal reacted, cracked, crumbled, or dissolved to a greater degree if exposed to reaction conditions for a longer time or at a higher temperature. For a series of runs at the same time and temperature the coals reacted increasingly from semi-anthracite to lignite to sub-bituminous. When different solvents were used the hydrogen donor anthracene oil was more reactive than motor oil. The motor oil was quite unreactive. Recycled anthracene oil lost reactivity.

The coal was observed to fracture at the planes of least resistance which are typified by the joint and bedding planes. The structure of coal which includes bedding and cleavage planes helps in physical breakdown of the sample. As joints and bedding planes open, the fluid is able to penetrate deep into the sample causing rapid disintegrating of the coal.

## Interpretation of Reactions

The effects of different solvents upon the rate of the reaction can be interpreted from the work of Severson et al. (2) Coal solubilization most rapidly proceeds in a solvent which has a high boiling point, the ability to donate hydrogen, a relatively high dipole moment, heterocyclic atoms and ring stability. Apparently during one or two cycles, anthracene oil exhausts its available hydrogen and loses the ability to donate until the hydrogen has been replenished. The lack of effect with the motor oil is somewhat more difficult to evaluate unequivocally. The high vapor pressure exhibited at reaction temperature suggests that the solvent will be present in low concentration within the reaction zone. More significantly, the saturated structure of the hydrocarbon makes the motor oil a poor hydrogen releasing solvent.

The gradation in reactivity which was seen with the different coal ranks may be interpreted in the light of suggestions by Wender. (3) Semi-anthracite structures, represented by Wender as analogous to fused carbon ring systems, were visualized as substantially aromatic but with occasional saturated rings. This system was joined by oxygen bridges to adjacent structural units. These were seen as difficult to thermally crack (300 - 375°C) because of extensive opportunities for resonance and as difficult to hydrogenate rapidly for the same reason. The likelihood of easy dissolution was therefore not considered great.

A similar analysis of chemical structures fails to distinguish the solubility of bituminous coal from that of lignite. Earlier work (4,5) has, however, noted that lignite fails to dissolve as extensively or as rapidly as bituminous coal. The lignitic structures in lignite which comprise up to 50 percent by weight of the structure may form a barrier to prevent access by solvent to the internal grain structure.

Hill et al. (6) analyzed the kinetics and mechanism of solution of a high volatile bituminous coal and presented five ways in which the reaction might proceed. These include: (1) dissolving out of included materials, (2) dissolution of the coal structure in the presence of a large volume of solvent, (3) diffusion out of the micropores, (4) hydrogen transfer reactions and (5) solvent imbibition. Applications were discussed for the order of the reaction with respect to the coal and with respect to the solvent. The discussion proceeded on the assumption that little swelling occurred. This assumption was not verified in the present work where gross volume increases of about three times were observed in the case of the Illinois Seam #6 sub-bituminous coal.

The tentative conclusion based on application of the theories of Wender and of Hill to the present research is that the coal imbibes solvent and swells. The

swelling is accompanied by a close association of coal and solvent and a transfer of hydrogen to the cohesive structures between the micelles or microplatlets of coal. The cohesive structure is weakened; the coal forms fragments, and the action of gravity or fluid turbulence removes the coal fragments from the immediate vicinity of the coal face.

#### Implications for Underground Liquefaction

The implications of this proposed mechanism upon the conceptual design of an underground liquefaction process appear significant. The dissolution of coal need not be completed underground; the reaction may begin underground and be completed at the surface. If the vertical borehole scheme is utilized (Figure 4) the process might be as follows. The borehole is drilled through the thick coal seam and a hot, hydrogen donor solvent is introduced into the bottom of the borehole. The solvent is maintained under pressure to reduce solvent vaporization and to limit the reaction zone as much as possible to the bottom of the coal seam. After some coal has reacted and has fallen from the face of the seam, the recovery step is begun. Solvent, now a slurry medium, under turbulent flow conditions is introduced to suspend coal fragments and carry the fragments to the surface. After significant void volume is produced, the solvent volume would become too great for economy. Water would be introduced to flood the void and to float the solvent upward against the unreacted segment of the coal seam. The loosened coal could be collected periodically in the turbulent stream as before or could be collected continuously with water as the slurry medium. At the surface the coal fragments would be separated by filtration from the water slurry medium or if, in a solvent slurry, would be admitted into the pretreatment step of the complete liquefaction process at the surface.

#### Host Rock

The host rock would be of special importance in this conceptual design. The host rock would necessarily be impervious to loss of vapor from the solvent or to seepage outward of hydrogen donor solvent and water flood. Moreover, the host rock should be unreactive when exposed to the thermal shocks and high thermal gradients. Some shales may react with hot water or solvent. After swelling and spalling the shale particles would be carried away with the coal and contribute to a high level of waste mineral matter in the subsequent process. Considerable disadvantage is apparent in this case since disposal of mineral waste can be inconvenient and expensive. Possibly, the carbon content of the host rock could be extracted to pay for the disposal of the additional mineral matter. More likely initial tests would be performed on coal seams with unreactive host rock.

#### Surface Subsidence and Seismic Effects

Surface subsidence and minor seismic shock effects are experienced with most mining techniques. In the present concept their abatement can be planned. The process would be designed to include access wells so placed as to permit coal pillars to remain and to support the roof. Secondary beneficial effects include the reduction of solvent leakage and restriction of the areas into which coal fragments might fall and from which coal particles could be recovered.

#### Summary

Even in the absence of hydrogen several coal types undergo a swelling and spalling reaction early in their liquefaction reaction with hydrogen donor solvents.

The coals increase their reactivity in the order semi-anthracite, lignite, and sub-bituminous. Increased temperature and reaction time increase the extent of reaction. To utilize these observations a concept is presented which may lead to an underground coal liquefaction process.

TABLE 1  
COAL ANALYSES

Oklahoma (Semi-anthracite)

Moisture %	-	S	0.6
Volatile Matter	17.3	H	4.2
Ash	7.6	C	83.8
Fixed Carbon	-	N	1.2
Heating Value (Btu/ #)	15,570		92.4

Illinois Number 6 (Sub-bituminous)

Moisture %	14.7	S	4.5
Volatile Matter	37.2	H	4.4
Ash	15.7	C	66.1
Fixed Carbon	47.1	N	1.2
Heating Value (Btu/ #)	9980	O	8.1

Alabama (Lignite)

Moisture %	37.8	S	1.1
Volatile Matter	40.8	H	4.3
Ash	11.1	C	64.5
Fixed Carbon	-	N	1.0
Heating Value (Btu/ #)	8,010		18.0

TABLE 2  
 FRACTIONATION OF CRUDE ANTHRACENE OIL IN NITROGEN ATMOSPHERE

	<u>Boiling Range</u> °C	<u>Volume</u> ml	<u>%</u> <u>By Volume</u>
Light Ends	Ambient - 300°C	48	38.7
Middle Fraction	300°C - 400°C	58	46.7
Heavy Ends	400°C+	<u>18</u>	<u>14.6</u>
		124	100.0

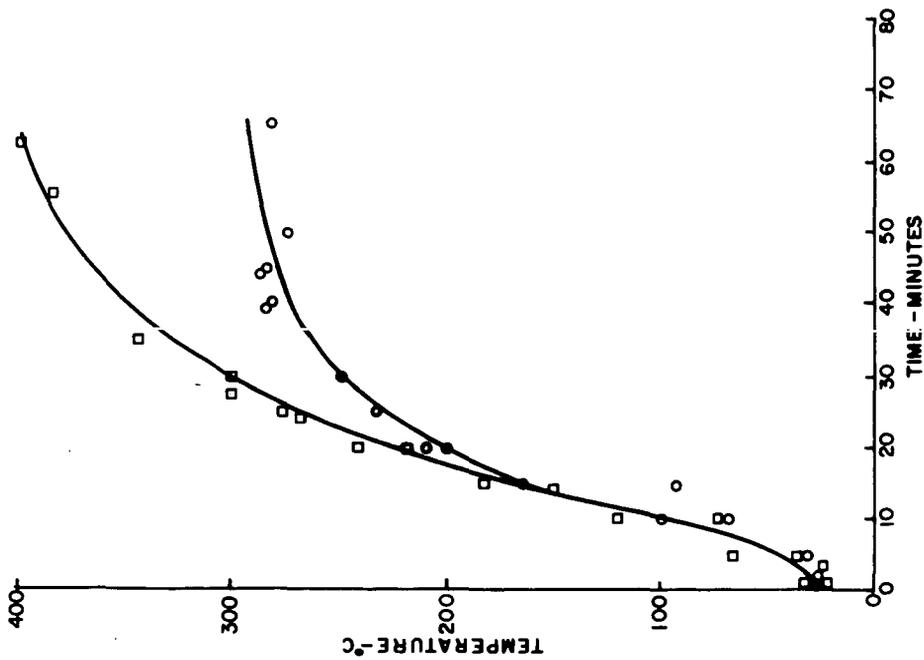


FIG. 1 - THE RELATIONSHIP OF TEMPERATURE AND TIME FOR SIX RUNS.

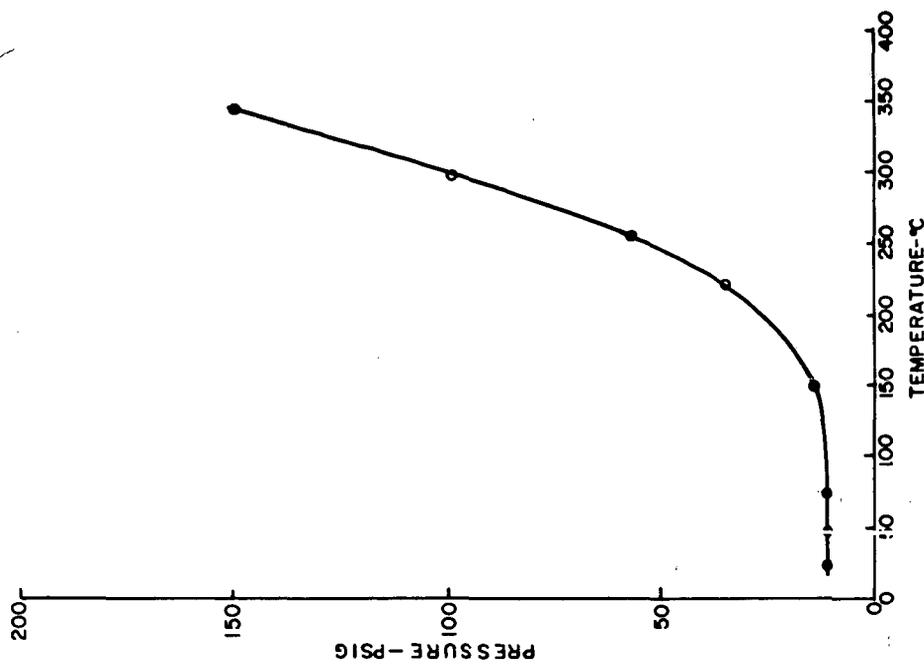


FIG. 2 - THE RELATIONSHIP OF PRESSURE AND TEMPERATURE FOR ANTHRACENE OIL SOLVENT AND ILLINOIS NO. 6 COAL.

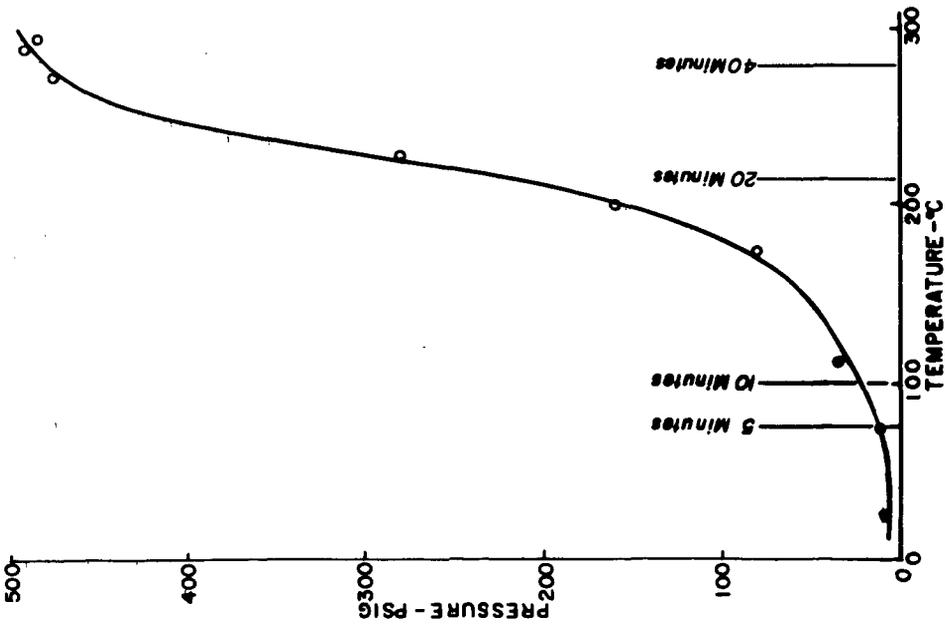


FIG. 3- THE RELATIONSHIP OF PRESSURE AND TEMPERATURE FOR SAE 30 MOTOR OIL SOLVENT AND ILLINOIS NO. 6 COAL.

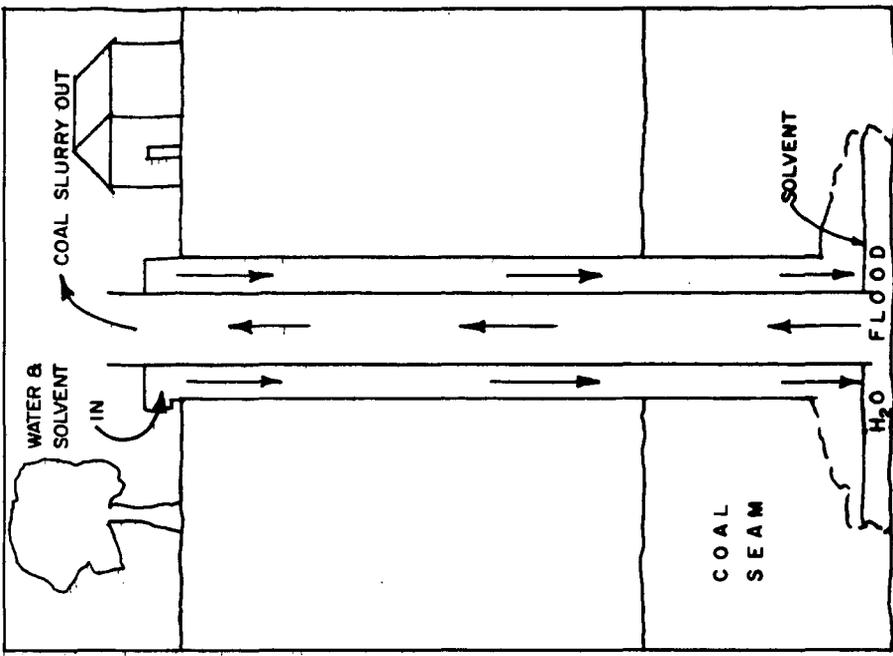


FIG. 4- VERTICAL BLIND BOREHOLE SYSTEM FOR UNDERGROUND COAL MINING AND LIQUEFACTION.

## Bibliography

1. A Current Appraisal of Underground Coal Gasification. Report to the United States Bureau of Mines, C-73671, December, 1971.
2. Severson, D. E., Skidmore, D. R., and Gleason, D. S. Solution - Hydrogenation of Lignite in Coal-Derived Solvents. Transactions of the AIME, SME, 247, No. 2, 133-136, 1970.
3. Wender, I., Characteristics of Coal Behavior in Chemical Reactions. Unpublished report.
4. Bull, Willard C., Summary Report of O.C.R. Contract. Pittsburgh and Midway Coal Mining Company, 1965.
5. Appell, H. R., Wender, I. and Miller, R. D. Solubilization of Low Rank Coal With Carbon Monoxide and Water, Chemistry and Industry (London), 1703, 1969.
6. Hill, George R., Hariri, Hassan, Reed, R. I. and Anderson, Larry L., Kinetics and Mechanism of Solution of High Volatile Coal, "Coal Science", ACS Advances in Chemistry Series, No. 55, 1966.