

THE DIRECT USE OF NATURAL GAS IN COAL LIQUEFACTION

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The main objective in coal liquefaction is to convert coal into a better fuel that is easier to transport and cleaner to burn. During the liquefaction process, the macromolecular network of coal substance is broken into smaller units and rearranged into lighter products of reduced molecular weight. More specifically, the chemical conversion of coal involves an upgrading in its hydrogen content or in other words, increasing the H/C ratio.

In liquefaction, this is achieved by rapidly heating coal, slurried in a hydrogen donor vehicle, to temperatures of 350-500°C for considerably long residence times. The slurry vehicle serves both as a dispersant as well as the reactant. The commonly employed slurry vehicles contain partly saturated structures such as tetralin. The importance of the vehicle was recognized by Fischer in 1937⁽¹⁾ and the role of hydrogen transfer from vehicles to coal was discussed by Curran et al.⁽²⁾ Recently Neavel studied the hydrogen transfer process in much more detail.^(3,4) In these interesting studies, he found that during initial stages of liquefaction, very little hydrogen is required to stabilize the free radicals generated from coal; however, during the later stages - when more benzene-soluble products are formed - each successive increment of benzene-soluble material required more hydrogen than the previous increment. For example, the incremental conversion from 40 to 50% consumed 0.23 parts by weight of hydrogen, whereas the same 10% conversion increment from 80 to 90% consumed 0.8 parts by weight of hydrogen. Thus, the hydrogen transfer and hence hydrogen requirement is found to increase exponentially with coal conversion.

The hydrogen required has to come either from the coal itself or it must be supplied from an external source, e.g. the slurry vehicle or gaseous hydrogen, or both. A large number of solvents have been used as slurry vehicles. The hydrogen donor capacity of a solvent depends on its molecular structure. Wise found that the hydro-aromatic compounds were more effective hydrogen donors than the aromatic analog; for example, piperidine/pyridine, pyrrolidine/pyrrole, indoline/indole, tetrahydroquinoline/quinoline, tetrahydronaphthalene (tetralin)/naphthalene, perhydroprylene/pyrene, etc.⁽⁵⁾ Tetralin has been used as a hydrogen donor solvent for a long time.⁽⁶⁾ The use of synthetic recycle solvents has increased recently for economic process purposes. However, for laboratory research studies, tetralin is still used extensively where a hydro-aromatic solvent is required.

The hydro-aromatic solvents, rich in donor hydrogen, can meet the hydrogen demand even in the absence of gaseous hydrogen. However, in most of the processes currently under development, solvents with high hydro-aromatic contents are not always practical. For example, in the Exxon donor solvent (EDS) process, in which an externally hydrogenated recycle donor solvent is used, about 50% of the hydrogen requirement is directly

met by the gaseous hydrogen.(7,8) Thus, if the concentration of hydroaromatics is less in the recycle solvent, then the gaseous hydrogen would be anticipated to make up the deficiency. This was the case in which an Illinois No. 6 (Monterey) coal was reacted for 90 minutes under 1000 psi hydrogen pressure in the presence of synthetic recycle solvents of varying tetralin contents.(9)

Vernon(10) studied the role of molecular hydrogen on the pyrolysis of model compounds present in coal. From this study, he concluded that, "...high pressure hydrogen can promote the hydrocracking of some carbon-carbon bonds in the coal structure that are too strong to break thermally, and lead to higher distillable liquid yields." This is also supported by the SRC-I Pilot Plant data.(11) An increase in the partial pressure of hydrogen in the dissolver increased the coal conversion with an attendant increase in the hydrogen consumption. In short-contact-time-liquefaction of several coals of different ranks, the low rank coals consumed greater amounts of hydrogen than the high rank coals and in those cases where the hydrogen consumption was high, substantial quantity of hydrogen was derived from the hydrogen gas.(12) Under long residence times, the hydrogen consumption increased monotonically, both with temperature and pressure.(13)

The deuterium tracer method developed by Heredy and coworkers has revealed that the hydrogen contact opportunity is very important for the production of soluble products. The soluble products increased from 3 to 11 to 23%, as a result of increasing the hydrogen contact opportunity. They concluded that apparently there was a direct route for incorporation of deuterium (presumably hydrogen, too) into the coal matrix without the aid of tetralin.(14,15)

Recent studies by Morita, et al(16) show that the effect of hydrogen pressure on coal hydrogenation was influenced by the type of coal used. The liquefaction conversion of a low volatile, oxygen rich Morwell coal (Australia) was not affected by hydrogen pressure. On the other hand, high oil yields were obtained from a high volatile Taiheiyo coal (Japan) at high hydrogen pressures.

Wilson, et al(17) have concluded that the large consumption of hydrogen at 400-425°C and 1000 psi hydrogen pressure, in tetralin donor solvent liquefaction of Australian Liddell coal, is not due to the hydrogenation of the aromatic ring, but due to the alkyl bond fission and hydrogenolysis reactions. Thus, high hydrogen pressures can lead to enhanced yield of by-product hydrocarbon gases, C₁-C₄, which result in the unprofitable consumption of expensive hydrogen.

It appears that certain constituents of coal mineral matter may have catalytic effect on the hydrogen transfer. The general agreement is that iron containing minerals, Fe₂O₃ and iron sulfides in particular, are exceptionally good in enhancing the distillable product yield.(18,19)

All existing processes for direct liquefaction of coal by solvent extraction, SRC-I, SRC-II and SRC-SCTL processes, the EDS process and the H-coal process, utilize molecular hydrogen at high pressures (over 1000 psig). The total hydrogen consumption is in the range of 3-5% of the amount of the coal feed of which a significant portion comes from molecular hydrogen depending on the rank of the coal and the quality of the recycle oil. The cost analysis of a typical coal liquefaction process shows that as much as one-third of the overall cost goes towards hydrogen production.(20)

This, naturally, has increased interest in finding cheaper substitutes for expensive hydrogen. The use of CO, CO-H₂O and CO-H₂ in direct coal liquefaction has been explored.(21-24) The beneficial effects of direct addition of H₂S on coal liquefaction has also been reported by several workers.(25,26) More recently, addition of H₂S to the synthesis gas in the liquefaction of a lignite has been found to increase the hydrogen donor capacity of the recycle solvent.(27) The catalytic activity of sulfide minerals in coal liquefaction largely seems to be related to the capacity to generate H₂S via free radical chain reactions.(28,29) However, H₂S might be advantageously recycled only in a process where a high degree of sulfur removal is not required. This is due to the decreased sulfur removal from the product despite the improved conversion of coal. For example, increasing the partial pressure of H₂S, from 6 psi to 40 psi in 1600 psi hydrogen, caused a decrease in the THF insolubles from 10.4 to 5.6%, but at the same time the sulfur in the product liquid rose from 0.45 to 0.61%.(30) This can impose a severe economic penalty.

One of the reasons for the use of CO + H₂, CO + H₂O, CO + H₂ + H₂S, and H₂S in coal hydrogenation is that these gases are produced during the coal liquefaction, and in a real process they could be recycled. It is noted, however, that among the gaseous reaction products, the yield of light hydrocarbon gases (C₁ to C₄), in general, is greater than the combined yield of gases containing hetero-atoms. Roughly, about half of the C₁-C₄ light hydrocarbons is made up of methane alone and the low rank coals produce far greater amounts of methane and C₂-C₄ gases than the higher rank coals.(31)

This leads to an interesting possibility of using methane as a substitute for hydrogen in the direct liquefaction of coal. Though methane gas is homogeneously stable at liquefaction temperatures (methane is thermodynamically stable to temperatures of 750°C), thermally produced free radicals from coal and, the free radicals from the solvent can abstract hydrogen atom from methane, thereby setting the stage for an array of free radical reactions. It should be noted that methane and hydrogen both have the same bond dissociation energy (CH₄ → CH₃ + H, and → H₂ + H.) equal to 104 Kcal/mole.(32) It is possible that during the course of the free radical reactions, the methyl radicals generated from the dissociation of methane could react with radicals from coal thereby causing alkylation of coal. Alkylated coal has been found to produce greater yield of benzene and pyridine soluble products than the untreated coal.(33)

There is, yet, another possible factor to be considered in the interactions of methane with coal in a solvent vehicle. The free radicals produced from the methane will either react with the solvent, the coal, or even the methane itself. This would tend to increase the total liquid and gaseous yield in the system. Thus, it may be expected that not only will the coal be converted to liquid hydrocarbon products, but the makeup feed material also would be converted to valuable higher hydrocarbon products. The economic attractiveness of the entire process should, therefore, improve.

No experimental data on the use of methane in direct liquefaction of coal exist in the literature. In an effort to define the possible role of methane in the conversion of coal to liquid products, experiments were conducted with an Illinois No. 6 coal, designated as PSOC-1098 in Penn State/DOE coal data base. An analysis of the coal employed in this investigation is given in Table 1.

Detailed description of the construction and operation of the tubing bomb reactor is available.⁽³⁴⁾ The liquefaction conditions were as follows: 2.5gm coal + 7ml tetraline as donor vehicle, 400-425°C, gas pressure (at temperature) 1400 psi, 30 minutes reaction time and agitation at 400 min⁻¹. At the end of the reaction, the contents were cooled by quenching the reactor in cold water and the gases were vented to the atmosphere. The remaining products were rinsed out of the reactor into a soxhlet thimble with ethyl acetate (EtoAc). This was then followed by exhaustive extraction of the products with EtoAc in a soxhlet apparatus for 24 hours. After removal of EtoAc in a vacuum oven, the residue was weighed to determine the total conversion. From a knowledge of the coal mineral matter content of coal, liquefaction conversion on a dry, mineral matter free basis can be calculated.

Table 1

Analysis of PSOC-1098, Illinois No. 6 hvAb Coal

Proximate Analysis:		Ultimate Analysis:		
	daf	dmmf (Parr)		mm: 19.32%
% Volatile matter:	35.15	C	80.20	83.64
% Fixed carbon :	48.99	H	5.73	5.97
% Dry ash :	15.86	N	1.45	1.51
		S	4.73	
		Cl	0.06	0.06
		O (diff)	7.84	8.03

The liquefaction experiments in methane atmosphere were conducted with bottled methane gas at 400, 425, and 450°C. The coal liquefaction conversions to ethyl acetate solubles (oils + asphaltenes) plus gases were 71.3, 73.4 and 75.4% (dmmf) at 400, 425 and 450°C, respectively. These data are plotted as a function of temperature in Figure 1. In comparison, the liquefaction of the same coal at 425°C yielded 74.8% (dmmf) of gases

and liquids in the presence of hydrogen which is only slightly higher than in methane (73.4%) and 68.2% (dmmf) in nitrogen, which is considerably lower than in methane. Thus, the indication is that methane could be a potentially useful hydrogenation agent in direct coal liquefaction. A simplified process block-diagram of the various processing steps are shown in Figure 2.

A comparative assessment of the performance of the coal-methane system with the coal-hydrogen system under nominal liquefaction conditions, in various solvents, will be an important contribution to the emerging coal liquefaction science and technology. This study could lead to the development of alternate, new and economically attractive coal liquefaction processes.

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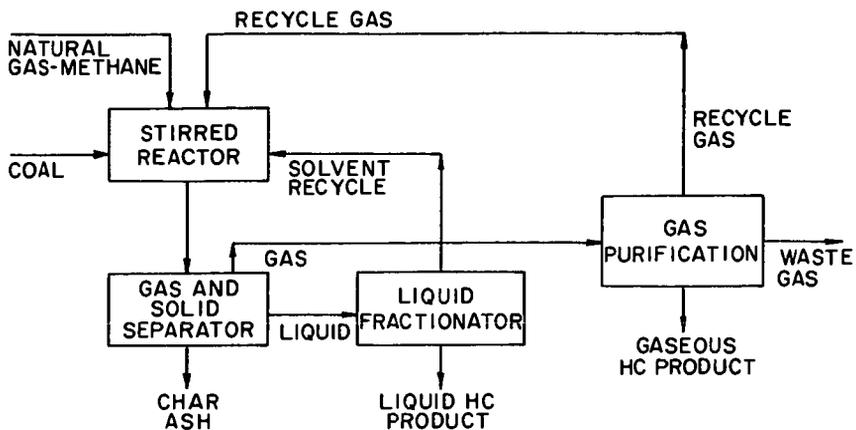


FIGURE 2.

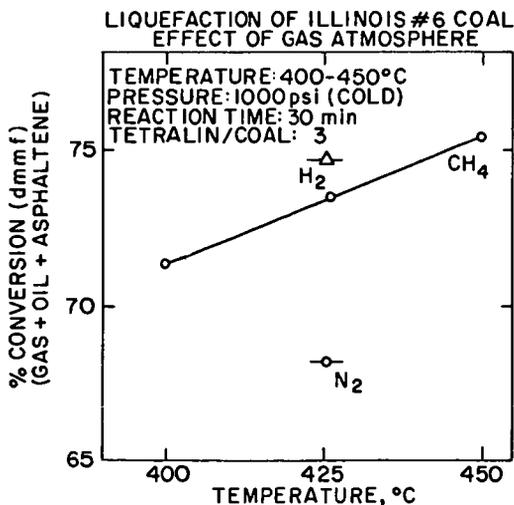


FIGURE 1.