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BRANDSTOFNAVORSINGSINSTITUUT

VAN SUID-AFRIKA

FUEL RESEARCH INSTITUTE

OF SOUTH AFRICA

NO. 42 OF 1974

TEGNIESE MEMORANDUM
TECHNICAL

HYDROGENATION OF COAL WITH CARBON MONOXIDE AND WATER

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S U M M A R Y

Low-rank coals are hydrogenated and solubilized more effectively and more rapidly by a mixture of carbon monoxide and water than with hydrogen.

The reactivity decreases in the order lignite, sub-bituminous and bituminous coal. The rate of solvation of sub-bituminous coal can be increased by using catalyst solvents. The reaction takes place at 380 - 420°C at pressures of the order of 10 000 kPa and is catalyzed by sodium carbonate. When the char and carbon dioxide produced are utilized to form carbon monoxide, the process, according to an economic evaluation undertaken by the U.S.B.M., is the most economical process proposed for the formation of coal tar oil for refining purposes.

HYDROGENATION OF COAL WITH CARBON MONOXIDE AND WATER

1. INTRODUCTION

In 1921 Fischer¹⁾ found that the yields of ether-soluble material produced by the hydrogenation of coal with carbon monoxide and water were higher than that obtained by the direct utilization of hydrogen at the same temperature and pressure.

The purpose of this memorandum is to present the information presently available on the aforementioned process. The following comparisons²⁾ of the two hydrogenation procedures were found in investigations undertaken with the object of preparing a coal-derived oil which could be converted to more volatile fuels by known hydrocracking techniques.

The hydrogenation of lignite with carbon monoxide and water was much faster than with hydrogen. The reaction with carbon monoxide and water was complete after 10 minutes. During the same reaction period the hydrogen process had not yet reached halfway, and did not eventually hydrogenate to the same extent as with water and carbon monoxide. The advantage of the carbon monoxide and water process was further accentuated³⁾ by the finding that, firstly, higher yields of benzene-soluble material were obtained in the hydrogenolysis of certain coal-related hydrocarbons, and secondly that the hydrogen content of the residual char was increased from 0,73:1 to 1:1.

2. THE EFFECT OF SOLVENTS

When phenanthrene was used as a solvent in conjunction with hydrogenation, the conversion of bituminous coal was increased from 58 to 76%, and about 10% of the solvent was hydrogenated.

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The conversion of lignite was also improved by a solvent, but to a lesser extent. For lignite, a 1:1 mixture of alpha-naphthol and phenanthrene was used as solvent⁵⁾, which was also partially hydrogenated²⁾. This turned out to be the best solvent for lignite. For sub-bituminous coal (from the Elkol mine, U.S.A.) isoquinoline was most effective. This compound acted as a solvent catalyst, and is effective with coals that are hydrogenated less easily. In the absence of solvent the conversion was 45%; the conversion increased to 64% with the addition of lignite tar solvent, while with isoquinoline a conversion of 93% was obtained within fifteen minutes⁴⁾. High conversions of lignite were also obtained using lignite tars and pitches as solvents⁵⁾.

3. THE MECHANISM OF THE HYDROGENATION REACTIONS, AND STRUCTURE OF COAL

The ultimate analysis and physical appearance of the benzene-soluble oil produced by hydrogenation with CO and H₂O were similar to that derived from hydrogen treatment. The greater effectiveness of carbon monoxide and water in the solubilization of low-rank coal was attributed to a number of reasons³⁾, namely,

- (1) the production of activated hydrogen by the water gas shift²⁾,
- (2) the introduction of alkyl groups into the hydrogenated products, and
- (3) a unique ability of carbon monoxide and water (under the conditions of the tests) to cleave certain kinds of bonds and to inhibit condensation reactions leading to higher molecular weight benzene-insoluble materials.

However, alkylation was found to proceed to the same extent with both processes, thereby eliminating possibility (2). As far as the mechanism of alkylation was concerned, the following possibility was given: carbon dioxide can be expected to add to phenolic materials readily via a Kolbe-type carboxylation, with subsequent reduction which was said to occur more readily with carbon monoxide and water³⁾. This was substantiated with experiments undertaken with phenol.

In model investigations undertaken to obtain information on the reaction mechanisms involved, it has been found that pure hydrogen is more effective in the hydrocracking of anisole. Sixty-eight per cent was cracked as opposed to 2.9% with hydrogen generation³⁾. Alpha-naphthol was found to undergo a condensation reaction, which could account for the formation of high molecular weight materials during coal hydrogenation³⁾.

In the hydrogenation of 1 - octane, hydrogen produced by the water gas shift reaction hydrogenated 3 to 4 times faster than pure hydrogen at equivalent partial pressure, indicating that the hydrogen formed is in an activated or nascent state³⁾.

In the hydrogenation of olefins, aromatics, aldehydes and a variety of oxygen- and sulphur-containing compounds, hydrogen consistently gave the highest conversions, while lignin, cellulose, and glucose were liquefied more readily with carbon monoxide and water. The hydrogen process left as much as 40% of insoluble residue, while the carbon monoxide process left only 10% of insoluble residue from crude cellulose, using 10% of sodium carbonate as catalyst. Thus the ease of conversion of lignin and cellulose (the accepted coal precursors) to benzene-soluble products with carbon monoxide and water suggested that structural units derived from those found in carbohydrates exist in low-rank coals³⁾.

In the hydrogenation of lignite, maximum conversion values of 91, 86, and 76% were found after hydrogenation for 10 minutes with carbon monoxide and water with a 1:1 mixture of phenanthrene and alpha-naphthol, phenanthrene, or no solvent, respectively. For bituminous coal, with reaction time of two hours, maximum values were 75% with carbon monoxide and water and phenanthrene as solvent, 73% with hydrogen, and 67% with carbon monoxide and water with no solvent²⁾.

Bituminous coal was thus found to be less reactive than lignite, with little difference between the two methods of hydrogenation.

The sub-bituminous coal was intermediate between the two⁹⁾. Hydrogen was more effective in cleaving side chains of aromatic compounds, whereas carbon monoxide and water gave liquefaction as the major reaction⁹⁾.

The effectiveness of carbon monoxide and water in solubilizing low-rank coal, cellulose, glucose, and presumably other carbohydrates, is also believed to be due, in part, to the inhibition of condensation reactions leading to insoluble chars⁵⁾.

4. TEMPERATURE AND PRESSURE

The conversion of bituminous coal and lignite with carbon monoxide and water increased sharply with up to about 7 000 kPa initial pressure. Above this, increases in solubilization with increase in pressure were smaller²⁾. At 10 000 kPa and 400°C the conversions for bituminous coal and lignite were 75 and 85%, respectively. At 10 000 kPa and 380°C, 90% of lignite was solubilized within 10 minutes²⁾, whereas hydrogen gave a value of 41% which only increased to a maximum value of 80% after another 80 minutes of hydrogenation.

The solubilization of bituminous coal increased constantly with temperature up to 425°C, while with lignite a maximum was reached between 380 and 400°C, with subsequent decline. The decrease in yield is believed to be a result of conversion of part of the soluble product by condensation to high molecular weight insoluble material²⁾.

Results obtained⁸⁾ showed that although increasing temperature and pressure increased conversion, hydrocarbon gas production also increased.

5. THE EFFECT OF AGING

Aged lignites were less reactive than freshly ball-milled lignite²⁾. The conversion of a minus 100 mesh lignite exposed to the atmosphere for four weeks dropped from 90% to 77%.

Drying lignite at 105°C for 24 hours in air caused the conversion to drop to 54%⁵⁾. Drying the lignite at 105°C in vacuum only decreased conversion to 86%, suggesting that oxidization, not drying, was the cause of the deactivation of the lignite²⁾. A higher proportion of methylated aromatic compounds was found in the product from the more reactive lignite⁹⁾. Coal ground in a mortar produced better solubilization than pulverized coal because the coal was less oxidized in the former grinding method⁸⁾.

6. THE EFFECT OF WATER

A small increase in the conversion of a deactivated lignite could be effected by increasing the amount of water used in the reaction. This procedure is generally applicable when a modest increase in the conversion of a low-reactivity coal is desired²⁾. Conversions increase significantly with water content, up to equal parts of water and coal⁵⁾.

7. THE EFFECT OF CATALYSTS

The addition of 10% of sodium carbonate to ash-free cellulose or glucose resulted in an increase in solubilization from 63 to 94%²⁾, and 80 to 92% for lignin. The product was similar to that obtained from lignite, but was less aromatic. In a comparison of U.S.A. lignites, Noonan lignite was found to be more reactive than Stanton lignite, which in turn was more reactive than Savage lignite. The reason for these differences was attributed to the ash content of the coals. Sodium carbonate was found to catalyze the reaction⁸⁾. In experiments using lignite with a range of sodium contents, or where sodium bicarbonate was added, an increase in reaction correlated with an increase in sodium content⁷⁾. The hydrogen gained by reclaimed solvent increased drastically with a total concentration of Na + K + Fe charged (from 0 to 50 millimoles), but at higher concentrations it became independent of Na + K + Fe present. (Figure 7, ref. 7). The catalytic properties of iron, and FeS in particular, have been well established in hydrogenolysis⁷⁾.

8. ECONOMICS OF THE PROCESS

Two processes utilizing the liquefaction of coal using carbon monoxide and water were designed and studied economically⁸⁾. One process produces carbon monoxide from char, water and oxygen, while the other produces carbon monoxide from the interaction of carbon dioxide and char. The first process is competitive with existing liquefaction processes using hydrogen, and the second process is economically more attractive than any liquefaction process that has been proposed for the production of tar products.

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6/12/1974.

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