The design and preliminary optimization of a continuous coal liquefaction system utilizing a coiled tubular reactor
by Michael John Biegalke

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemical Engineering
Montana State University
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Abstract:
A coiled tubular reactor was developed for the rapid hydrogenation of coal. Operational problems of feeding the coal to the system were solved.

The coal studied was a sub-bituminous coal from Colstrip, Montana. The effects of various variables which existed in the equipment, namely temperature, pressure, hydrogen flowrate, reactor length, and catalysts, were studied for their effect on coal conversion.

Three catalysts were studied: nickel chloride, stannous chloride, and stannic chloride. Two methods of catalysis were studied—impregnation of the catalyst and mixing the catalyst with the coal.

The results showed that increasing pressure and temperature increased conversion. Conversion decreased with increasing hydrogen flowrate. Reactor length and coal feedrate did not have any significant effect on coal conversion in the ranges tested. The highest coal conversion (48.0%) was obtained with impregnated stannous chloride (13.9%). Next best conversions were obtained with nickel chloride and stannic chloride, in that order.

Impregnating the catalyst on the coal produced higher conversions (for each respective catalyst) than did mixing the catalyst with the coal. Differences ranged from 5.1% for stannic chloride to 7.0% nickel chloride.

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Date November 30, 1977

THE DESIGN AND PRELIMINARY OPTIMIZATION OF A CONTINUOUS COAL LIQUEFACTION SYSTEM UTILIZING A COILED TUBULAR REACTOR

by

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ABSTRACT

A coiled tubular reactor was developed for the rapid hydrogenation of coal. Operational problems of feeding the coal to the system were solved.

The coal studied was a sub-bituminous coal from Colstrip, Montana. The effects of various variables which existed in the equipment, namely temperature, pressure, hydrogen flowrate, reactor length, and catalysts, were studied for their effect on coal conversion. Three catalysts were studied: nickel chloride, stannous chloride, and stannic chloride. Two methods of catalysis were studied--impregnation of the catalyst and mixing the catalyst with the coal.

The results showed that increasing pressure and temperature increased conversion. Conversion decreased with increasing hydrogen flowrate. Reactor length and coal feedrate did not have any significant effect on coal conversion in the ranges tested. The highest coal conversion (48.0%) was obtained with impregnated stannous chloride (13.9%). Next best conversions were obtained with nickel chloride and stannic chloride, in that order.

Impregnating the catalyst on the coal produced higher conversions (for each respective catalyst) than did mixing the catalyst with the coal. Differences ranged from 5.1% for stannic chloride to 7.0% nickel chloride.

INTRODUCTION

A. Current United States Energy Situation

As the world becomes more dependent upon the Middle Eastern countries for the supply of petroleum, the search for alternative energy sources becomes more and more intense. The United States is also faced with the problem of decreasing national petroleum production. This is a critical matter to this country as it is one of the most energy intensive countries in the world. The supply of petroleum not only affects the standard of living for its citizens, but is also a major factor in determining the position of a country in the world economic picture as well as determining the national economic picture. The disadvantageous position of the United States in terms of both international and national economic situations is shown by the negative balance of trade with foreign countries. A large percentage of this negative balance is a result of the importation of petroleum from the Middle East. Thus, it is seen that in order for the United States to remain a world power, to maintain a high standard of living for its citizens, and to maintain its economic independence, it is necessary for the United States to define alternative energy sources.

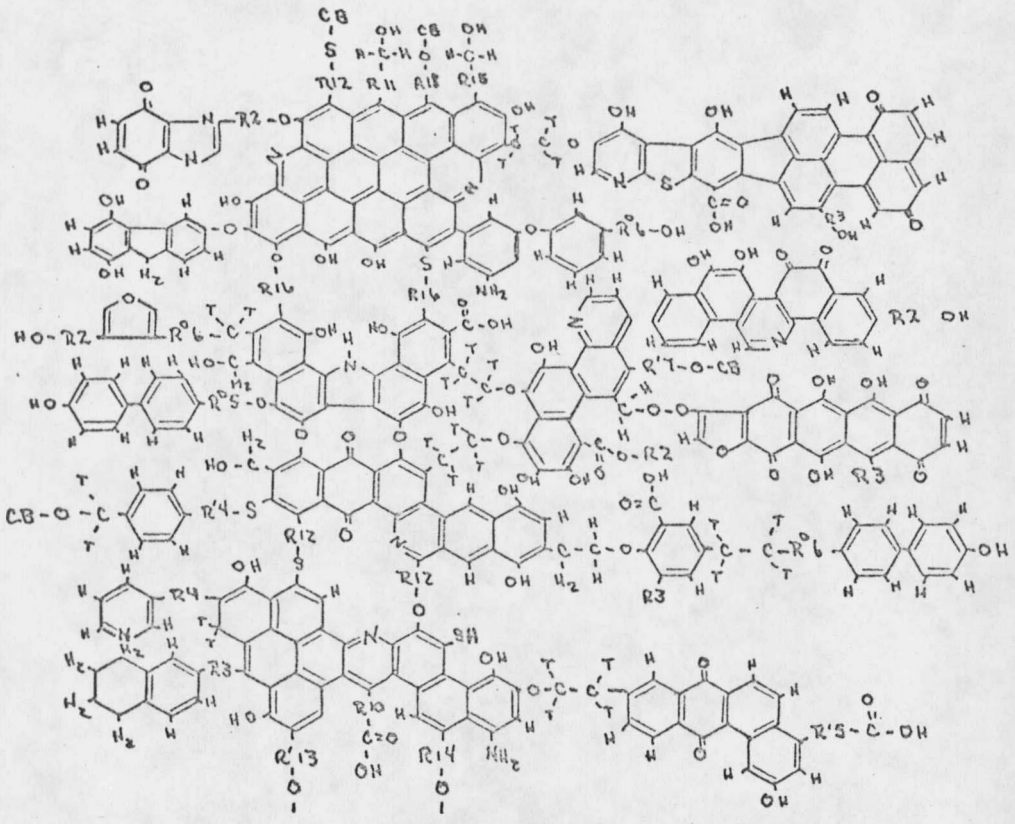
The United States' major source of energy and chemical feedstocks has been petroleum and most of the users are geared to the utilization of this form of energy. Thus, the ideal solution to the petroleum shortage would be to find a substitute source for liquid fuels. The

search for new liquid fuels invariably leads to coal because of the immense coal reserves which the U.S. has available. The United States has 16.5% of the world total recoverable coal resources (mapped and explored) [4]. Coal makes up 94.5% of the U.S. fuel reserves [6].

B. Coal Structure and Hydrogenation and Cracking to Produce Useful Products

Coal is a carbonaceous rock derived from wood and other plant tissues which flourished millions of years ago. Apparently the plants partially decayed and then were covered, preserved, and ultimately compacted by the other sediments that were deposited on them. Coals are actually intricate mixtures of complex compounds of carbon. Coals differ from one another in composition and properties, and even the various constituents of any one coal may be quite unlike [4].

In characterization work done on high volatile bituminous coals it appears that long chain, simple aliphatic and alicyclic hydrocarbon groups predominate in these coals. Multiple polynuclear ring structures are apparently absent. Although coals were once thought to have a chicken-wire structure of 50 to 60 of these ring structures tied together, it now seems more logical to assume that only five or six combine for each aggregate. A model of a high volatile bituminous coal is presented in Figure 1 [7].



CROSS BONDING TO MORE
HETEROCYCLIC GROUPS

R°N - Alicyclic rings of N carbons

RN - Alkyl side chain of N carbons

R'N - Unsaturated alkyl side chain of N carbon

CB - Cross-bonding by O or S to new heterocyclic groups with side chains

T - Tetrahedral 3-dimensional C-C bonds, C-O bonds, and C-S bonds

Figure 1. Typical Cross-bonded Structure for High Volatile Coals

In the coal liquefaction process, it is generally believed that the hydrogenation process is accompanied by the decomposition or cracking of the high molecular weight compounds to smaller fragments [7,8]. If coal is heated in a normal carbonization process, thermal cracking and polymerization-condensation reactions occur, the products being paraffins, olefins, aromatics, tar, coke, char, and polycondensed pitch. If, however, when the coal is heated it is done so in the presence of a catalyst and hydrogen pressure, the amount of polymerization is controlled and more usable products are obtained from the same amount of coal. The typical products obtained in this case are alicyclic alkylated aromatic polycyclic products and gases as well as some coke. The liquid products can be further hydrotreated and hydrocracked to produce isoparaffins, aromatics, paraffins, napthenes, and hydrocarbons [7].

Investigations have shown that an increase in the carbon content and decrease in the hydrogen content of the coal, i.e., with increase in the C:H ratio from 16.0 to 22.4, the conversion of the organic matter and the yield of the liquid products decrease; almost no liquid products are obtained from the hydrogenation of anthracitic coal. Thus, a connection exists between the organic coal matter and the yield of the liquid product; the C:H ratio should ideally not exceed 16. [3,9].

C. Products of Coal Liquefaction

The liquid products obtained from coal liquefaction are generally classified as one of three types. The classifications made are based on the solubility of a portion of the product in an organic solvent. These classifications are:

(1) Oils - the portion of the liquid product which is soluble in hexane.

(2) Asphaltenes - the portion of the liquid product which is soluble in benzene or toluene, but insoluble in hexane.

(3) Aspholtols or pre-asphaltenes - the portion of the liquid product which is soluble in pyridine but insoluble in hexane or benzene and toluene.

The oils are the desired product since these may be directly worked with in typical refinery operations. They are the most highly hydrogenated portion of the overall liquid product.

Asphaltenes are generally of a polynuclear aromatic structure. The production of asphaltenes is not desirable since any further hydrogenation of asphaltenes is a very difficult step [10]. Asphaltenes hydrogenate to oils only slowly. Investigations have shown that asphaltenes are hydrogen-bonded acid-base complexes having components that can be separated. A separated moiety has only an acid or base

character, i.e., amphoteric species are not present. Thus, asphaltenes have a salt-like character [11].

Little seems to be presently known about the character of asphaltols. They appear to have the characteristic of highly functional polyphenols with greater than 10% heteroatoms. They have a higher oxygen content and increased basicity of nitrogen over that of the asphaltenes. Asphaltols are rich in chemical functionalities and may readily cross-link or polymerize. They contain hydrogen at a higher H/C value than 0.5 [11].

Slower reactions convert asphaltenes and asphaltols to oil product which generally occurs with a diminuation of the heteroatom content of the material. Regressive reactions compete with the progressive reactions. For example, an asphaltene might regress to become an asphaltol or semi-coke [11].

Mobile Research and Development Corporation has defined a process for better characterizing the reaction products from coal liquefaction. Reaction products are fractionated using sequential elution with specific solvents through silica gel. The solvents used are:

1. Hexanes (mixed isomers)
2. Hexanes with 15% benzene
3. Chloroform
4. Chloroform with 10% diethyl ether

5. Diethyl ether with 3% ethanol
6. Methanol (absolute)
7. Chloroform with 3% ethanol
8. Tetrahydrofuran
9. Pyridine

The products are separated into fractions which have been identified as follows:

1. Saturates
2. Aromatics
3. Polar aromatics; non-basic nitrogen-, oxygen-, and sulfur-heterocyclics
4. Simple phenols
5. Basic nitrogen heterocyclics
6. Highly functional molecules, with greater than 10% hetero-atoms
7. Polyphenols
8. Increasing oxygen content and increasing basicity of nitrogen
9. Like 8, only more so
10. Non-eluted, unknown materials

Broadly, with some overlap, fractions one and two may be identified as the oil fraction; fractions three, four, and five may be identified

with the asphaltene fraction; and the remaining fractions are the asphaltols [11].

D. Recent Coal Liquefaction Processes

Pilot plant studies can be divided into two classes--coal hydrogenation processes and coal pyrolysis processes, in which the coal is decomposed into liquids by heat. One of each will be discussed here.

The Synthoil process, which has been developed by the U.S. Bureau of Mines, utilizes crushed coal which is then slurried with a coal derived oil. The slurry and turbulently flowing hydrogen are fed to a fixed bed catalytic reactor, in which the coal is liquefied and desulfurized. The yield is about three barrels of low sulfur fuel oil per ton of coal. Other coal hydrogenation processes include the H-coal process developed by Hydrocarbon Research, Inc. [12,16,30].

In the COED process developed by the FMC Corporation, crushed coal is heated to successively higher temperatures in a series of fluidized bed reactors. After further processing, the main products are syncrude, fuel gas, and a residual char. The syncrude yield is about one barrel per ton of coal. Another coal pyrolysis process is the Oil Shale Corporation's Toscoal Process [5,12,16,30].

E. Rapid Coal Liquefaction Through Use of Tubular Reactors

Research studying the rapid hydrogenation of coal in tubular reactors is currently being conducted at two other known locations. Cities Service Research and Development Company has developed a process of this type. In their operation, dry pulverized coal is fed in batches to a hopper, which is then pressurized to reactor pressure with hydrogen. A star-wheel feeder then feeds the coal through a standpipe into the reactor, where it mixes with preheated hydrogen. The coal falls freely through the reactor to a char pot, devolatilizing on the way. A cold quenching medium quickly cools the remaining char. The product gas mixture passes through sequential heat exchangers where the liquid products are withdrawn from the hydrogen stream. Residence time in the reactor varies from 100 to 300 milliseconds. Heat up rate for the coal can be varied from 50,000 to 150,000°F per second. With this continuous bench scale apparatus, Cities Service has processed coal at rates up to 2 lbs per hour with 50 to 80% conversion [13].

Research using coiled tubular reactors is also being carried out at the University of Utah. Their process has been through several bench scale phases which have been directed toward a short contact time and high hydrogen to coal rates under moderate reaction conditions. They also use a hopper with star-wheel feeder to feed the

coal to the reactor. From the hopper, the coal passes through a 20 foot long preheater to bring it to the desired reaction temperature. The coal is then held at the reaction temperature for the desired time (1 to 6 seconds) by the choice of tube length. The reactor configuration is a coiled tube which is operated at temperatures of 500 to 550°C and hydrogen pressures of 1600 to 2000 psi. They have obtained conversions as high as 58.5% for $ZnBr_2$ catalytic coal [14,15].

Recent research has shown that in the rapid heating and hydrogenation process utilized in the coiled tube method of coal liquefaction, the formation of tars and char is partially eliminated. The liquefaction of coal appears to take place in a very short time period. If the coal and liquefaction products are held at an elevated temperature for a longer degree of time, no additional coal conversion is obtained, rather the amount of useful products decreases through polymerization reactions and forms less useful products such as char (see Figure 2)[11]. Cities Service reports that the conversion of coal in their system has been accomplished without the production of high-boiling tars although some char is produced [13]. Work done at Pennsylvania State University indicates that coals generate the greatest amount of volatile matter yield if heated to reaction temperature at very high rates to prevent crosslinking reactions that may reduce yield [1].