



Catalytic hydrogenation of PAMCO solvent-refined coal
by Lee Morgan Henton

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:

Catalytic hydrogenation of Pittsburgh and Midway Coal Company's Solvent-Refined Coal was accomplished using commercial and lab-prepared catalysts.

Batch bomb tests indicated the relative activity of twenty-nine catalysts; five catalysts were used in the operation of a continuous reactor.

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Temperature, liquid hourly space velocity, and hydrogen-to-oil flow rates were studied with the continuous reactor; pressure and catalyst amount were held constant at 1000 psig and 70 ml, respectively. As temperature increases, hydrocracking and heteroatom removal increase.

Optimum space velocity varied between 1 and 2, depending on the catalyst. Heteroatom removal decreased as space velocity increased. A hydrogen-to-oil ratio of 10,000 SCF/bbl gave the best hydrocracking and heteroatom removal results at 445° C and liquid hourly space velocity equals 1.

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Signature Lee Morgan Henton

Date May 4, 1978

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by

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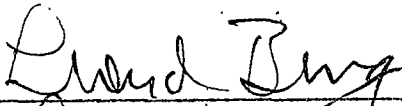
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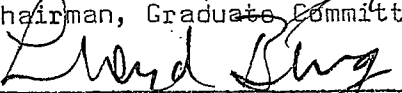
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ABSTRACT

Catalytic hydrogenation of Pittsburgh and Midway Coal Company's Solvent-Refined Coal was accomplished using commercial and lab-prepared catalysts.

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Liquid hydrogenation products were analyzed by ASTM distillation, quartz tube method for sulfur content, and Macro Kjeldahl method for nitrogen content.

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Temperature, liquid hourly space velocity, and hydrogen-to-oil flow rates were studied with the continuous reactor; pressure and catalyst amount were held constant at 1000 psig and 70 ml, respectively.

As temperature increases, hydrocracking and heteroatom removal increase.

Optimum space velocity varied between 1 and 2, depending on the catalyst. Heteroatom removal decreased as space velocity increased.

A hydrogen-to-oil ratio of 10,000 SCF/bbl gave the best hydrocracking and heteroatom removal results at 445°C and liquid hourly space velocity equals 1.

INTRODUCTION

As of 1974, petroleum and natural gas accounted for 75% of the total energy consumed in the United States (1). Since oil is a non-renewable resource and discovery of new reserves are lagging behind consumption, the end of affordable oil is approaching. Since exotic large scale resources like fusion are not expected to be commercial in the next fifty years, an interim source of energy is needed.

Coal is a viable choice. Proven reserves of coal in the United States hold 8 times as much energy as known domestic reserves of crude oil, natural gas, shale oils, and bitumens (2).

The nature of coal makes it unsuitable for many uses. Much transportation fuel must be liquid to fit existing systems; mineral ash accounts for up to 10% of coal. Many coals contain more sulfur and nitrogen than combustion fuels made from crude oil. Processing technology will therefore have to be developed in order to make distillate fuels from coal economically feasible.

Liquefaction of coal is not new. German liquified coal plants operated in the 1920's and 1930's. The Bureau of Mines operated a synthetic fuels demonstration plant from 1949 to 1953; Union Carbide operated a coal hydrogenation plant from 1952 to 1956. But coal-derived liquids were not economically competitive in light of large crude oil discoveries (1, 3).

Coal liquids technology is again being developed to meet anticipated need: FMC COED pyrolysis oil, H-Coal, Synthoil, and Solvent-

Refined Coal are products of current technology. These still do not give large yields of high quality liquid fuel, however.

Therefore, the object of this research is to upgrade Pittsburgh and Midway Coal Company's SRC (Solvent-Refined Coal) into a clean distillate fuel.

RESEARCH OBJECTIVE

The object of this research is catalytic conversion of PAMCO's Solvent-Refined Coal (an upgraded coal product) to clean distillate fuels.

A number of commercial and lab-prepared catalysts were used to hydrotreat a solution of Solvent-Refined Coal (SRC) at high temperature and pressure. The product solution should have more low-boiling fractions than the feed solution; reduced sulfur and nitrogen product content is also desired.

The research plan included autoclave test screening of hydro-treating catalysts. Promising catalysts were employed in the operation of a continuous trickle-bed reactor. Effects of liquid hourly space velocity, hydrogen-to-oil ratio, and temperature were also studied in the continuous reactor.

BACKGROUND AND THEORY

Coal Liquifaction Processes

Different Types - Four types of liquefaction processes are being developed in the U.S.: pyrolysis, direct hydrogenation, Fischer-Tropsch coal gas-to-liquid synthesis, and solvent hydrogenation.

Examples of the pyrolysis type are: FMC's COED process and Gulf Oil's coker distillate process. Products are a tar oil for hydro-treating and a char product (1).

Direct hydrogenation processes include Hydrocarbon Research Inc.'s H-COAL, Pittsburgh Energy Research Center's Synthoil, Conoco Coal Development Company's Zinc Chloride process and Institute of Gas Technology's Riser Cracking of coal. Types of contacting and catalysts vary widely. Coal slurry and hydrogen gas pass through an ebullating bed of catalyst in the H-COAL process; coal slurry and hydrogen pass turbulently through a fixed catalyst bed for Synthoil. Conoco passes reactants through a molten salt bed; residence time for pulverized coal particles is less than 10 seconds in the Riser Cracking tubular reactor.

Fischer-Tropach synthesis involves reacting steam and coal at high temperature to make CO and H₂ gas. The gas is first purified of sulfur and nitrogen compounds, then it reacts over a catalyst bed to make short chain alcohols and hydrocarbons (1).

Solution hydrogenation processes include PAMCO's Solvent-

Refined Coal (SRC), Consol's Cresap project, Exxon's donor solvent process, Morgantown Energy Research Center's "Two-Step," and the "Clean Fuels West" process sponsored by Southern California Edison, Mobil Oil, EPRI, and Conoco Coal. The method of hydrogen addition to the recycle solvent and/or coal solution varies according to the process (4).

SRC I - The SRC I process is the one of interest in this report. The solvent-refined coal major product is a solid at room temperature, with sulfur and ash content substantially reduced from the original coal. However, the original nitrogen of the coal remains in the product, and the hydrogen-to-coal ratio of the product is slightly less than that of the original coal. The upgrading of the solid solvent-refined coal product from SCR I is the object of this thesis research.

Figure 1 shows a simplified process schematic of Pittsburg and Midway Coal Company's Solvent-Refined Coal I process (5).

The process starts with pulverized coal being slurried with recycle solvent in a mix tank. Hydrogen and slurry are mixed, heated, and pumped to the high pressure dissolver. The product from the dissolver is flashed to separate the raw gases from the coal slurry. The raw gas is treated to remove impurities and hydrogen is recycled.

The coal slurry leaving the separator is at high temperature, as most of the coal matter is still liquid. Filtration separates the undissolved solids (ash and coal residue) from the hot liquid. The

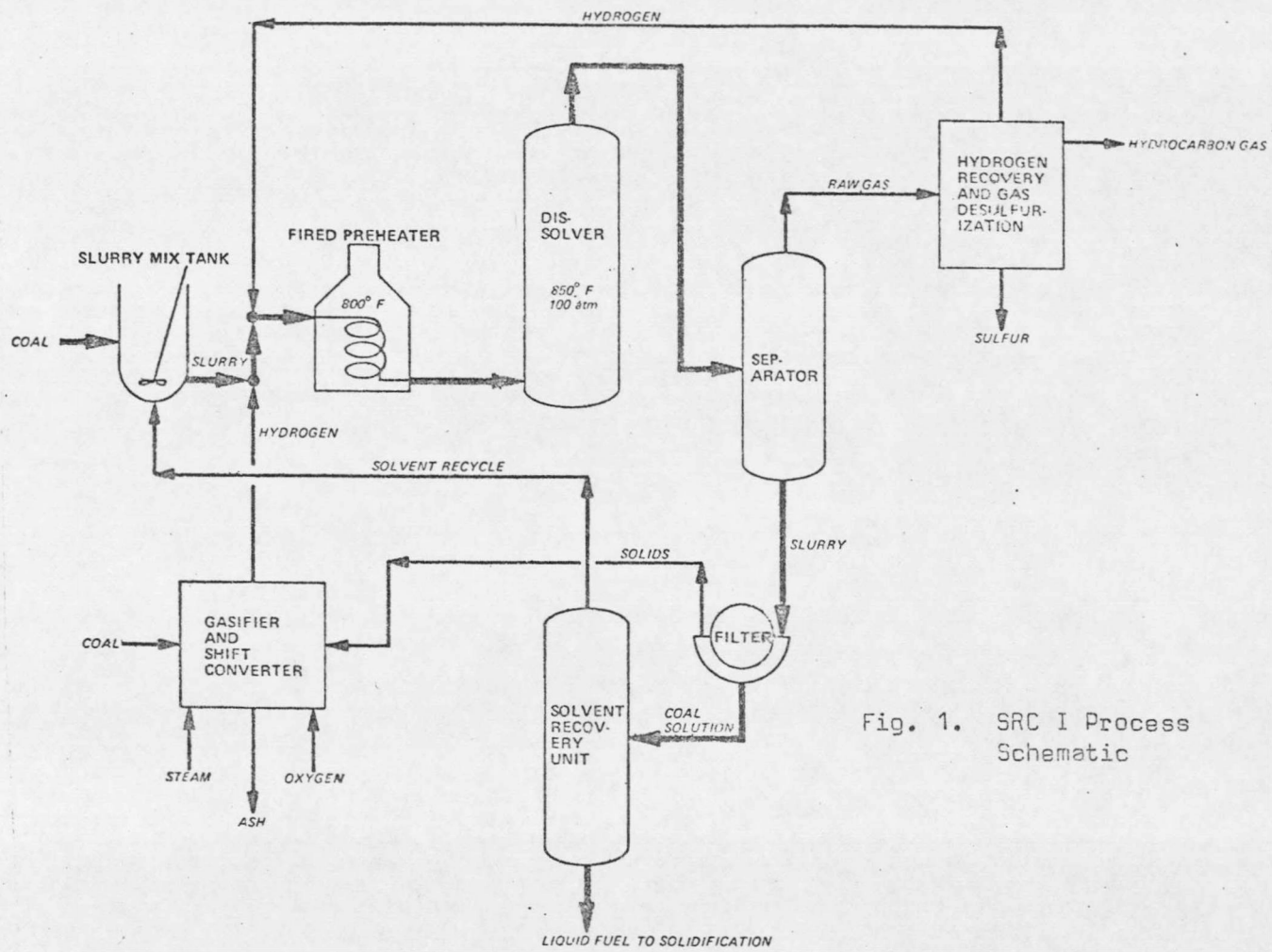


Fig. 1. SRC I Process Schematic

solid coal residue is reacted with steam and air to yield make-up hydrogen for the process.

The hot liquid from the filter enters a solvent recovery unit. The lower boiling material is separated from the recycle solvent. This lower boiling material yields a small amount of liquid product and a large amount of solid material at room temperature. The solid is "solvent-refined coal" (5, 6).

SRC II - More liquids and gases, with less solid product, can be made by a modified solvent-refined coal process called SRC II. The two main changes from the SRC I process are that: a) ash is not removed, but retained in the final solid product; b) it does not use a light "recycle solvent." Instead, some of the hot product stream is diverted for use as the process solvent (6).

If the SRC II liquid yields are high enough, upgrading the SRC II liquids may be more feasible than upgrading the ash-free solid from SRC I.

Factors in Liquefaction

A good many factors influence coal-to-liquid conversion. The rank of coal influences what products are possible. Coals vary in sulfur, nitrogen, oxygen, ash, and trace metal content. Some of those contaminants may be catalytic, but some inhibit catalysis by reacting with the catalyst or plugging heterogeneous catalyst pores.

A myriad of other factors influence coal conversion and types

of products. Length of processing time and type of process appear to be very important. The influence of solvent chemical and physical nature, solvent ratio, amount and type of reducing agents, pressure and temperature of solution and reaction, catalyst nature, and reactor configuration varies, depending on the time and type of processing.

Coal Structure and Composition - Figure 2 shows a representative structure for bituminous coal (7). Coal structure "consists of aromatic ring clusters of no larger than 6 or 7 rings tied together by bridge linkage"(8). Coal's H/C ratio is lower than most fuel materials derived from petroleum. The H/C ratio of Illinois No. 6 is 0.86, while residual heating oil No. 6's ratio is 1.55 and a refining naphtha fraction is 2.20 (9). Coal's low H/C ratio is another indication of the aromaticity of coal compared to petroleum.

Coal contains significant amounts of oxygen, sulfur and nitrogen. Compounds containing these impart undesirable qualities to fuel products, poison catalysts, or become combustion pollutants.

Removal of oxygen is least difficult because oxygen atoms are usually in phenol structures and not heterocyclic.

In uses of upgraded coal when the presence of oxygen is acceptable (low grade fuels), "it is desirable to remove only sulfur and nitrogen to minimize hydrogen consumption" (10).

Sulfur is less difficult than nitrogen to remove (10). Organic and inorganic sulfur are found in coal. Most inorganic sulfur is iron sulfide, FeS_2 , and a small amount is present as sulfate ion.

