



Effect of successive regenerations on catalysts used for hydrotreating SRC-II  
by Muthuswamy Rameswaran

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:**

Three catalysts were fabricated with supports supplied by NALCO Chemical Company having 90Å, 220Å and 420Å median pore diameter for hydrotreating Solvent Refined Coal (SRC-II, Light End Column Feed) from Pittsburg and Midway Coal Mining Company. These supports were impregnated with 4.0% cobalt oxide (CoO), 8.0% molybdenum oxide (MoO<sub>3</sub>), 1.0% nickel oxide (NiO) and 8.0% tungsten oxide (WO<sub>3</sub>).

Ten runs were made with each catalyst in a batch reactor and regenerated after every one hour at run temperature. The denitrogenation effect and the pore volume after every regeneration were measured. There was no significant difference in the denitrogenation activity of the three catalysts. All three catalysts could be regenerated successively with compressed air without much damage to their pores.

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Date May 11, 1982

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by

**MUTHUSWAMY RAMESWARAN**

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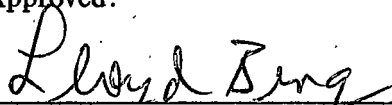
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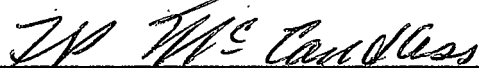
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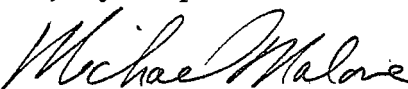
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## ABSTRACT

Three catalysts were fabricated with supports supplied by NALCO Chemical Company having 90Å, 220Å and 420Å median pore diameter for hydrotreating Solvent Refined Coal (SRC-II, Light End Column Feed) from Pittsburg and Midway Coal Mining Company. These supports were impregnated with 4.0% cobalt oxide (CoO), 8.0% molybdenum oxide ( $\text{MoO}_3$ ), 1.0% nickel oxide (NiO) and 8.0% tungsten oxide ( $\text{WO}_3$ ).

Ten runs were made with each catalyst in a batch reactor and regenerated after every one hour at run temperature. The denitrogenation effect and the pore volume after every regeneration were measured. There was no significant difference in the denitrogenation activity of the three catalysts. All three catalysts could be regenerated successively with compressed air without much damage to their pores.

## INTRODUCTION

Conversion of coal to fluid fuels is approaching a time when synthetic gasoline and pipeline gas will be manufactured in the United States of America (U.S.A.) on an enormous scale. Reasons include the growing needs for energy, the large reserves of coal and the limited reserves of petroleum and new technological advances in production of fluid fuels from coal.

There is a critical widening gap between supply and demand for petroleum in the U.S.A., although petroleum reserves are thought to be adequate for some time to come. However, reserves-to-consumption ratios are declining as new discoveries have not kept pace with the demands. Though nuclear power will play an important role in fulfilling the energy shortage, it will not be able to fulfill the growing demand for liquid fuel for the transportation sector of energy demand (1).

Over forty years ago, the concept of complete gasification of coal with oxygen under pressure was put into practice by the pioneering work of Drawe, Danulat and Hubmann (2). Later, during World War II, Germany had converted coal into gasoline in substantial amounts. One plant is currently in operation in South Africa.

There are three major ways to convert coal into liquid fuels. They are pyrolysis, direct hydrogenation and indirect hydrogenation. Of these, the direct hydrogenation process has captured the most attention due to economic considerations.

The United States Department of Energy (DOE) is currently encouraging the development of coal gasification and liquefaction processes. The gasification processes include BiGas, HYGAS and Synthane processes, and liquefaction processes include the Solvent

Refined coal process (SRC), the Exxon Donor Solvent process (EDS) and the Synthoil process. The SRC process is the oldest of these modern processes. The original SRC process is known as SRC-I and the modified version is called SRC-II.

The products of SRC-II cannot be used directly as a transportation fuel or as a feed stock acceptable to a conventional refinery. The nitrogen and sulfur content of the product is higher than the Environmental Protection Agency (EPA) specifications. Therefore, this product should be catalytically hydrorefined to be commercially available to the general public. This research is expected to give the SRC-II process technical advancement to improve the product and have an advantage over the other processes for commercialization.

## BACKGROUND

The major problem met in conversion of coal to acceptable fuel is meeting the EPA air quality regulations; this can be resolved by removing the contaminants from coal before using it. The process begins with coal washing and preparation at the mines. The next major step is purifying coal via the solvent refining coal process (SRC process), which has been under development since the early 1970s and for which a 50 ton per day demonstration plant was built in Fort Lewis, Washington, by Pittsburg and Midway Coal Mining Company (P&M Company). This process produces a low sulfur low ash coal liquid.

The SRC process consists of the following major steps:

- (1) Coal preparation and pulverizing to a fine particle size (approximately 200 mesh).
- (2) Blending of fine coal with coalbased hydrocarbon solvent.
- (3) Reaction at high temperature (480°C) and high pressure (about 2400 psig).
- (4) Solvent recovery, utilizing high temperature vacuum flashing, and distillation for the separation of various hydrocarbon oil fractions.
- (5) Removal of a gas containing the evolved sulfur compounds.
- (6) Product collection.

Tests have indicated that coal of almost any quality except possibly anthracite is amenable to refining by the SRC process. A schematic flow sheet of the SRC process is given in Figure 1 (3).

### Chemical and Physical Properties of SRC-II Product

The SRC-II product cannot be considered as single product process. Various products in the SRC-II oil are tabulated in Table 1 (4). Properties of P&M's SRC-II products (Light

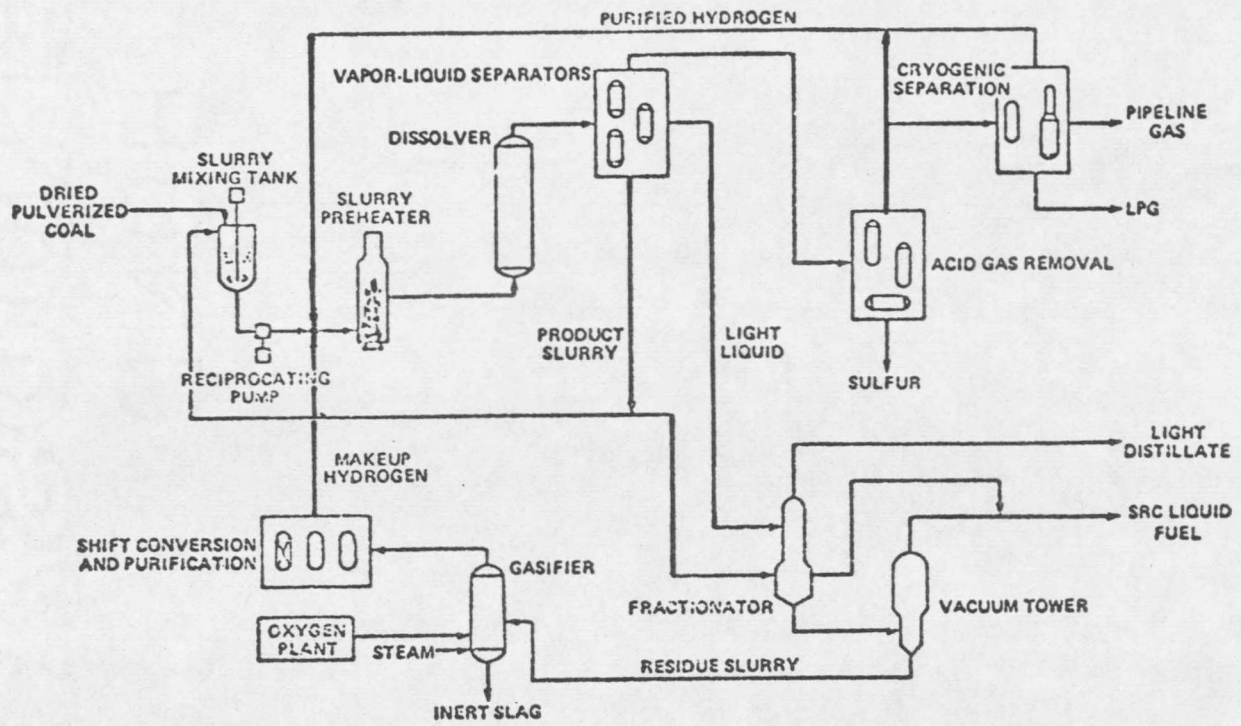


Figure 1. SRC-II Process (P&M's 50 ton pilot plant).

End Column feed) are shown in Table 2 (5). The SRC-II product used in this research was made from refining Kentucky #9 coal from the Colonial mines. The analysis of this coal is shown in Table 3 (6).

### Chemistry of Coal Liquefaction

The term coal is applied to a wide range of substances. It is formed by metamorphosis of vegetable matter under pressure and heat, over a long period of time. According to Francis, coal is (7,8):

... a compact stratified mass of mumified plants which have been modified chemically on varying degree, interspersed with smaller amounts of inorganic matter.

In the strict sense there is no such thing as a coal molecule. Yet scientists have identified many molecular subgroups in a so-called coal molecule. These subgroups are present in all coals, lignites and other similar products. The most prominent of these groupings is the benzene ring and condensed ring varieties such as maphthalene and anthracene. Larger ring compounds are also abundant.

Oxygen is one of the most common elements which is found in any typical representative molecule of coal besides carbon and hydrogen. The percentage of oxygen diminishes from 25% in lignite to almost 0% in anthracite (9). Other than oxygen, sulfur and nitrogen are also found in molecules of coal. These elements are scattered all over the coal molecules, either as part of heterocyclic rings or as a part of functional subgroups. Figure 2 (9) gives a typical representation of coal molecule.

The solvent refined coal process (SRC-II) eliminates almost all mineral matter. The products are practically ash free. Yet the nitrogen and sulfur content is too high to be used as a substitute alternate for refinery feed stock or gasoline. Before it can be used for the

Table 1. SRC Process Gas and Liquid Yields.\*

C <sub>1</sub> -C <sub>4</sub> gas, Scf**	3130
CH <sub>4</sub> gal	2100
C <sub>5</sub> -350°F, gal	32
bbl	0.762
350-750°F distillable, gal	38
bbl	0.094
Total liquid, gal	70
bbl	1.666

\*\*Approximate analysis of C<sub>1</sub>-C<sub>4</sub> gas cut:

	Vol. %	BTU Value/ft <sup>3</sup> of Total Gas
CH <sub>4</sub>	67.0	680
C <sub>2</sub> H <sub>6</sub>	19.3	340
C <sub>3</sub> H <sub>8</sub>	10.0	260
C <sub>4</sub> H <sub>10</sub>	3.7	120
	<u>100.0</u>	<u>1400</u>

\*Per ton of SRC.

Table 2. Properties of SRC-II Light Ends Column Feed.

	Light Ends Column Feed
% Carbon	—*
% Hydrogen	—*
% Nitrogen	0.88
% Sulfur	1.21
% Oxygen	—*
% Ash	0.02
Sp. Gravity 60/60° F	0.983
<b>ASTM D-86 DISTILLATION</b>	
IBP	122
5%	217
10%	288
20%	381
30%	446
40%	488
50%	541
60%	577
70%	611
80%	660
90%	727
95%	795
End Point	956

\*Data not available.



Table 3. Properties of Kentucky #9 Coal.\*

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<i>Average Raw Coal Analysis (Wt %)</i>	
Ash	9.55
Moisture	6.14

<i>Average Dried Pulverized Coal Analysis (Wt %)</i>	
Carbon	70.76
Hydrogen	5.18
Nitrogen	1.53
Sulfur	3.57
Oxygen (by difference)	8.60
Ash	9.97
Moisture	6.39

<i>Average Analysis of Forms of Sulfur (Wt %)</i>	
Pyritic Sulfur	2.03
Sulfate Sulfur	0.27
Organic Sulfur	1.27
Total Sulfur	3.57

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\*Analyzed in June, 1979.











































































































































































