The effects of temperature and space velocity on the catalytic upgrading of solvent refined coal (SRC-II)

by Hemant Bhatia

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemical Engineering
Montana State University

Abstract:
Long run cycle experiments ranging from 30-300 hours were made to determine the effects of temperature and space velocity on the upgrading of SRC-II Light Ends Column Feed (LECF) produced at Pittsburg and Midway Coal Mining Company's SRC-II pilot plant.

MSU's most promising catalyst C-49 with a metal loading of 4% CoO, 8% MoO_3, 1% NiO, and 8% WO_3 was used in all the experiments.

The liquid products were analyzed for their nitrogen and sulfur contents. The ASTM distillation yields were also obtained.

Higher temperature and lower space velocities gave better denitrogenation, while desulfurization was not affected by the temperatures and space velocity in the range of study. A minimum temperature of 425°C is needed to reduce the nitrogen content below the 0.3 Wt% requirement.

Higher temperatures also allowed the use of higher space velocities at the expense of greater coke formation. The best conditions for denitrogenation are an operating temperature of 500°C and a liquid hourly space velocity of 1.25 hr^{-1}.

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Date March 4 1982.

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Approved

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ABSTRACT

Long run cycle experiments ranging from 30-300 hours were made to determine the effects of temperature and space velocity on the upgrading of SRC-II Light Ends Column Feed (LECF) produced at Pittsburg and Midway Coal Mining Company's SRC-II pilot plant.

MSU's most promising catalyst C-49 with a metal loading of 4% CoO, 8% MoO_3, 1% NiO, and 8% WO_3 was used in all the experiments.

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INTRODUCTION

The oil embargo of 1973-74 brought into sharp focus what is known and what is not known about energy flows in the United States. A great deal is known on the supply side - how much oil, gas, coal, and uranium ore are produced, where it comes from, how it is transported, and where it is used. Little is known about interfuel substitutability, and potential for conservation.

The consumption of energy in the United States has been rising rapidly and is expected to increase from 60 quadrillion (10^{15}) BTU in 1969 and 85 in 1980, to a projected 135 in 2000 (1). To supply their needs there are known recoverable resources of fuel amounting to, in the same units of quadrillion BTU, 300 for Petroleum, 300 for gas, 300 for uranium, and 4600 for coal. Overall, coal represents about 80% of known recoverable fossil fuels. (1) About 200 billion metric tons of coal are currently recoverable at today's prices. Presently U.S. coal production is 785 million tons/yr (2) while the petroleum consumption is 2700 million tons/yr (50 million barrels/day) (3). Although coal has only one half the energy value of petroleum, its reserves and production are sufficiently large to supply a part of America's petroleum needs.

Coal has an atomic hydrogen ratio of approximately 0.8 while the ratio for oil is of the order 1.8. Coal liquefaction therefore involves increasing the hydrogen content of coal. Coal liquefaction processes can be grouped into three general categories: pyrolysis, extraction hydrogenation, or indirect liquefaction.

Of major concern to this research is the extraction-hydrogenation process. The Pittsburg and Midway Coal Mining Company has developed the Solvent Refined Coal (SRC-II) as one of the extraction hydrogen processes (4). It converts high sulfur coal to distillate liquids, naphtha and light hydrocarbons. These raw liquid products are not directly interchangeable with comparable products derived from petroleum. The carbon to hydrogen ratio is considerably higher than petroleum crudes, as is the concentration of heteroatoms nitrogen and sulfur. The acceptance of SRC-II products in place of conventional fuels thus requires the development of a secondary catalytic hydrotreatment process.

It is the objective of this research to investigate the proper temperature and space velocity required to optimize the upgrading of SRC-II products into clean distillate fuels.

BACKGROUND

SRC-II Process

The SRC-II process converts high sulfur coal to distillate liquids, naphtha, and light hydrocarbons. A fifty tons per day pilot plant is being operated by Pittsburg and Midway Coal Mining Company at Fort Lewis, Washington. Figure 1 is a flow diagram of the SRC-II demonstration plant. (4)

Raw coal is pulverized and dried, then mixed with hot recycle slurry from the process. The coal and recycle slurry mixture is then pumped together with hydrogen through a fired pre-heater to a reactor maintained at 460°C and 13,780 kPa. The hydrocracking reactions occur primarily in the reactor, and the heat generated by these reactions rapidly raises the temperature of the reactants to the design temperature. The reactor effluent is then separated into process gas, light hydrocarbons and slurry.

The process gas is cooled to 38°C and stripped of H_2S and CO_2. The treated gas is then cryogenically separated to remove hydrocarbons. The pure hydrogen is recycled to the process while the recovered hydrocarbons become by-products of the process.

The C_1 fraction is sold as pipeline gas. The other light hydrocarbon gases are fractionated to produce ethane, propane, and butane. All the light hydrocarbon liquids, and the overhead stream

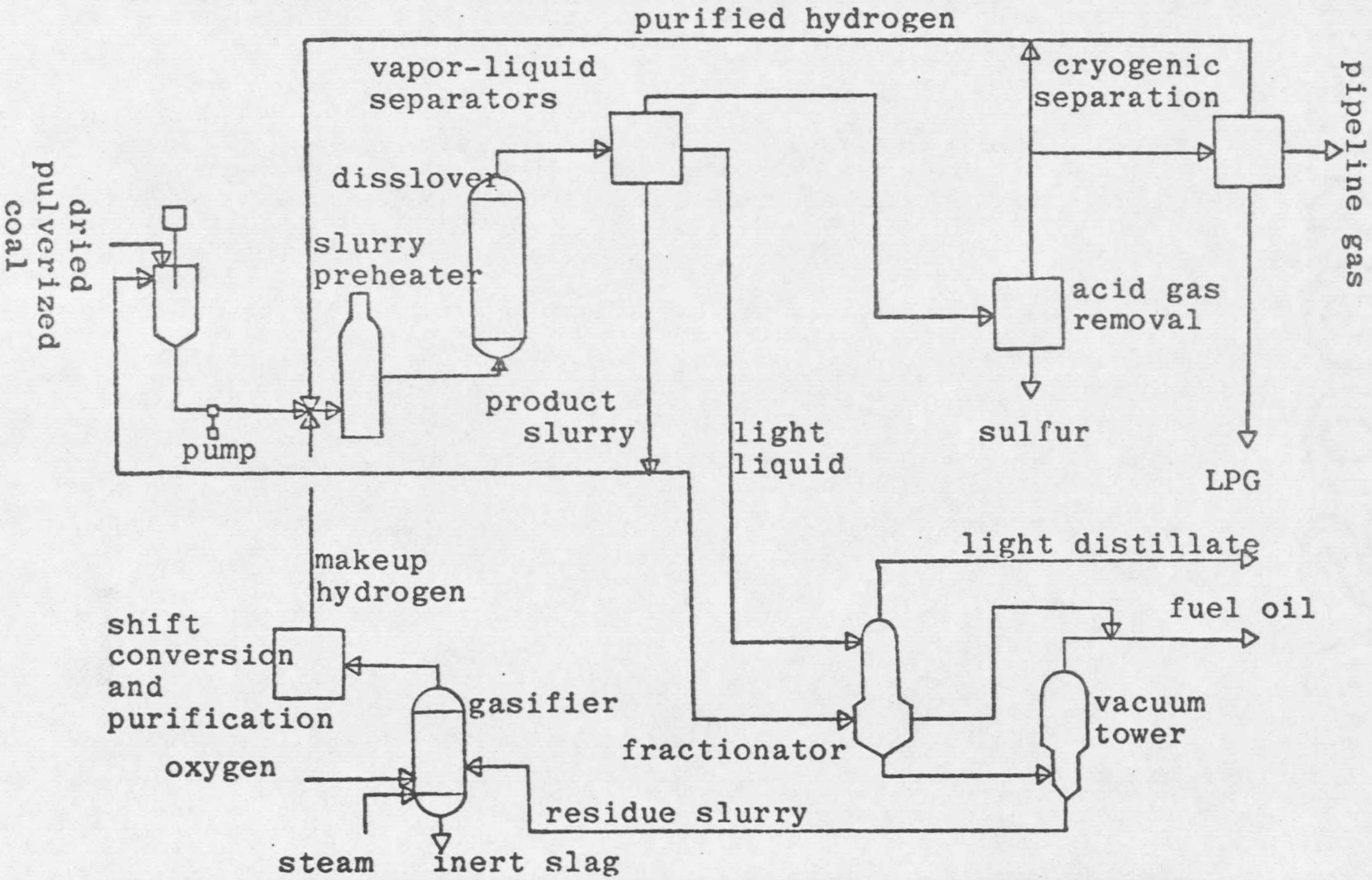

FIGURE 1. SRC-II PROCESS SCHEMATIC

from the vacuum tower are sent to a fractionater (Light Ends Column Feed) where the total liquid is separated into naphtha [C_5-193°C nominal boiling range], a middle distillate [193-316°C], and a heavy distillate [316-482°C]

The product slurry is divided into two parts. One part is recycled to the process, while the other (Vacuum Flash Feed) goes to a vacuum tower where the lighter position of the distillate is removed overhead and sent to the fractionator. A heavy distillate product is removed as the side stream. The residue from the vacuum tower is sent to a slagging gasifier for production of synthesis gas.

Chemical and Physical Properties of SRC-II Product

The SRC-II product cannot be considered as a single product from the process. The various products of SRC-II process are given in Table 1 (5). Properties of P&M's SRC-II product (Light Ends Column Feed are shown in Table 2(6). The SRC-II product used in this research was made from refining Kentucky #9 coal, its analysis is shown in Table 3 (7).

Upgrading SRC-II Liquid Products

The liquid products of SRC-II contain significant amounts of organic nitrogen, and organic sulfur compounds as are commonly found in most petroleum crudes. Akhtar et al (8) have identified a number of sulfur containing compounds liberated from coal during

TABLE 1

SRC PROCESS GAS AND LIQUID YIELDS*

$C_1 - C_4$ gas, Scf**	3130
CH_4 gal	2100
C_5 - 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 $C_1 - C_4$ gas cut:

	Vol %	BTU Value/ft^3 of total gas
CH_4	67.0	680
C_2H_6	19.3	340
C_3H_8	10.0	260
C_4H_{10}	3.7	120
	100.0	1400

* 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
ASTM D-86 DISTILLATION	
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*

Average Raw Coal Analysis (Wt%)	
Ash	9.55
Moisture	6.14
Average Dried Pulverized Coal Analysis, (Wt%)	
Carbon	70.76
Hydrogen	5.18
Nitrogen	1.53
Sulfur	3.57
Oxygen (by difference)	8.60
Ash	9.97
Moisture	6.39
Average Analysis of Forms of Sulfur, (Wt%)	
Pyritic Sulfur	2.03
Sulfate Sulfur	0.27
Organic Sulfur	1.27
Total Sulfur	3.57

*Analyzed in June, 1979.