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FEASIBILITY OF PRODUCING JET FUEL FROM GPGP BY-PRODUCTS

Quarterly Technical Progress Report
for the Period May 17, 1988 through August 16, 1988

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EXECUTIVE SUMMARY

The topical report entitled "Production of Jet Fuels from Coal-Derived Liquids, Volume II - Characterization of Liquid By-Products from the Great Plains Gasification Plant," AFWAL-TR-87-2042, was completed and distributed. Laboratory work on the work for Volume VIII dealing with the modeling of heteroatom removal by catalytic hydrogenation was completed, and the topical report is expected by the end of September. Contract modifications have been completed to enable the determinations of oxygenates and the stability of jet fuel products, with a topical report due January 31, 1989. A workshop for this effort was attended by the principal investigator on August 17, 1988, at WPAFB.

1.0 INTRODUCTION

Within the program entitled "Production of Jet Fuels from Coal-Derived Liquids" initiated in November of 1986, UNDEMRC was assigned three tasks which are being published as topical reports.

- Task 1. Market assessment, which resulted in a subcontract to J.E. Sinor Consultants, Inc. and a topical report Volume I - Market Assessment for Liquid By-Products from the Great Plains Gasification Plant, J.E. Sinor, August 1987, AFWAL-TR-87-2042.
- Task 2. Feedstock characterization, which resulted in topical report Volume II - Characterization of Liquid By-Product Streams from the Great Plains Gasification Plant, C.L. Knudson, May 1988, AFWAL-TR-87-2042.
- Task 3. Catalytic upgrading tests will result in topical report Volume VIII - Modeling Heteroatom Removal by Catalytic Hydrogenation, J.R. Rindt, expected September 1988 for review.

Task 4. Oxygenates analysis and thermal stability of fuels studies will result in a topical report by January 31, 1989.

2.0 GOALS AND OBJECTIVES

The goals and objectives for this quarter were to complete the laboratory work for Task 3, to complete the contract modifications in order to implement Task 4, and to attend a workshop concerning the work to be performed under Task 4.

The goals for next quarter are to complete the topical report for Task 3 and to initiate the work in Task 4.

3.0 QUARTERLY ACTIVITIES

During the May 17 to August 16 quarter, the laboratory work for Task 3 was completed, contract modifications to implement Task 4 were completed, and the workshop concerning work to be performed in Task 4 was attended. In addition, the principal investigator was changed from W. Willson, who has left for one year to work in Alaska, to C. Knudson.

A topical report is being prepared which details the catalytic hydrogenation efforts. The report, entitled "Volume VIII - Modeling of Heteroatom Removal by Catalytic Hydrogenation," discusses aviation fuel specifications; feedstock characteristics; methods of upgrading coal liquids to aviation fuel; materials, equipment, and experimental procedures; the statistical experimental design which was followed; the predictive models which were developed as a result of the experiments; material balance results; and the results of verification runs as performed at conditions which were predicted by the mathematical models. It is anticipated that this report will be completed by the end of September.

Contract modifications were completed to implement additional work (Tasks 4a and 4b) on oxygenates analysis and the thermal stability of fuels. This effort is necessary since, prior to upgrading to jet fuel, the coal-derived liquids contain significant quantities of oxygen compounds, some of

which may survive processing and influence fuel stability. The work involves complementary work at UNDEMRC and Western Research Institute (WRI) to develop techniques to determine oxygenates in the fuels prepared by other participants in the overall research effort and work by WRI to determine the thermal stability of the jet fuels. The work statements are as follows:

Task 4.a Evaluation of Oxygenated in Jet Fuels.

Evaluate one petroleum-derived JP-8 fuel and one coal-derived JP-8 fuel for the presence/absence of eight selected target oxygenates representing cyclohexanols, phenolics, decahydro-2-naphthols, naphthols, and benzofurans using, if necessary, class separations (Sep-Pak column) followed by standard electron impact and water chemical ionization GC/MS analysis. Develop detectability and accuracy levels and techniques to determine a minimum of six oxygenates using deuterated internal standards in petroleum-derived (spiked) and a coal-derived JP-8. Analyze four additional samples using techniques developed in Task 2.

Task 4.b Subcontract to WRI, Oxygenates Analysis and Fuel Stability.

A method will be developed for analyzing trace phenols in jet fuels. We propose to use GC/MS as the best and fastest available method. Residual hydroxyaromatics will first be identified in process intermediates from our coal liquids hydrogenation work. After we identify the species of interest, the method can be refined to achieve maximum sensitivity. The aim is to develop a method which will measure trace levels in neat fuel samples.

Five fuel samples produced from coal liquids will be analyzed. Samples for analysis will be selected and provided by the client. Stability tests will be conducted on fuel samples. The fuels will be stressed in borosilicate glass at 60°C in the presence of air. They will then be examined for changes by DTA, TGA, or DSC. The object is to determine if these methods are sufficiently sensitive to detect formation of oxidation products (gum), as well as to evaluate the stability of the coal-derived products.

The workshop held at Wright Patterson AFB on August 17, 1986, was attended, and a presentation was given on the proposed work for Task 4 and related work being performed at UNDEMRC and WRI. Copies of EMRC's slides are attached as Appendix A. No major changes were made in the effort to be conducted at UNDEMRC. However, information was obtained as to the interaction of the various participants, especially on the availability of the samples to be analyzed.

APPENDIX A
SLIDES PRESENTED AT WORKSHOP

JET FUEL FROM COAL

OXYGENATES ANALYSIS

For Presentation at WPAFB
By Curtis L. Knudson, UNDEMRC
August 17, 1988

LIST OF SLIDES

1. Objectives and Approach
2. Samples for Analysis
3. Contracts Background
4. Byproduct Streams
5. Water and Isopropanol
6. Stream Analysis
7. Data Reduction Scheme
8. GC-MS Analysis
9. GC-CI Analysis
10. Gasoline - Volatiles
11. Alcohol - Benzene
12. Gasoline - NMR - Alcohol
13. Gasoline - NMR - Olefins
14. Phenolic Upgrading - Catalytic Hydrogenation
15. Phenolic Upgrading - Alkali Pyrolysis
16. Phenolic Upgrading - Hydropyrolysis

OBJECTIVE and APPROACH

Analysis for Oxygenates
aromatic - aliphatic

GC/FID Analysis
internal standards
external standards

GC/MS for Oxygenates
selected ion current
detection levels, sensitivities

GC/O-FID for Alcohols, Ethers

SAMPLES for ANALYSIS

AF	Petroleum Derived JP8	Aug
WRI	Jet Fuel	
UNDEMRC	Jet Fuel	
AMOCO	JP4	Sep
	JP8	
	JP8X	
	Bulk JP8	Dec
End of Contract		Jan 31

CONTRACTS using GC/FID/MS - HEAD

Jet Fuels

AF/DOE/PETC

Wood Smoke

EPA

PAH Analysis

EPA

Low Severity Liquefaction

DOE/PETC

Mild Gasification

DOE/METC

Heteroatoms in Liq.

DOE/PETC

Gasoline Analysis

Dept. of Ag.

BYPRODUCT STREAMS

CK20/SLD9

TABLE 1

ANALYSES OF AS-RECEIVED DYNAPHEN SAMPLES^a

Sample ID	Isopropanol, wt%		Water, wt%		# GC Peaks		Total ^b A%
	HRI	EMRC	HRI	EMRC	Total	over 0.1 A%	
HRI5511	0.00	0.00	4.92	5.45	124	59	96.9
237-45	35.55	31.84	8.73 ^c	9.23 ^d	46	23	98.7
237-46	41.51	42.22	12.52 ^c	11.98 ^e	44	17	98.6
237-50	33.57	37.29	15.48	13.87	104	31	97.6
237-51	47.23	44.91	10.29	13.37	32	27	99.6
237-61	50.03	49.72	10.34	10.51	80	21	98.5
237-61RC	0.00	0.00	NA ^f	0.178	147	53	95.7
L-731	0.00	0.00	0.18	0.098	168	63	95.7

^aAll values are for the as-received (AR) samples. Samples with a positive isopropanol value were received with the isopropanol present. HRI values were obtained from letters sent with the samples or verbally.

^bThis is the total A% (A% = Area%) in the peaks which were over 0.1 A%.

^cCalculated from data which was not obtained by analysis.

^dThe average of duplicate analyses (9.03 and 9.43) obtained on different days.

^eThe average of duplicate analyses (12.25 and 11.72) obtained on different days.

^fNot analyzed.

^gValues for Karl Fischer water analyses of around 0.1 wt% are within error of zero.

TABLE 8

GC/MS ANALYSIS DATA FOR M237-50

#	Compound	Rf	Rt(min)	A%	wt%	AR, wt%
1.	KF-Water	.	.	.	.	13.87
2.	Isopropanol	0.53	2.030	35.69	43.29	37.29
3.	Benzene	1.12	5.142	8.15	4.68	4.03
4.	Toluene	1.07	8.441	8.08	4.86	4.18
5.	C2-Benzene	1.02	11.596	0.89	0.56	0.48
6.	mp-Xylene	1.02	11.847	1.17	0.74	0.63
7.	o-Xylene	1.02	12.590	0.25	0.16	0.14
8.	Aniline	0.75	15.486	0.23	0.19	0.17
9.	Phenol	0.56	15.784	22.42	25.74	22.17
10.	C3-Benzene	1.00	16.573	0.01	0.01	0.01
11.	Indane	1.00	16.940	0.32	0.21	0.18
12.	Indene	1.00	17.206	0.18	0.11	0.10
13.	o-Cresol	0.69	17.710	2.50	2.33	2.01
14.	mp-Cresol	0.69	18.355	11.81	11.00	9.48
15.	Guaiacol	0.57	18.607	.	.	.
16.	C2-Phenol	0.75	19.056	0.08	0.07	0.06
17.	C2-Phenols	0.75	20.201	0.26	0.23	0.19
18.	C2-Phenol	0.75	20.238	0.32	0.28	0.24
19.	C2-Phenol	0.75	20.697	0.26	0.22	0.19
20.	C2-Phenol	0.75	20.777	1.13	0.97	0.83
21.	Naphthalene	0.90	21.049	1.27	0.91	0.78
22.	C1-Guaiacol	0.60	21.185	0.02	0.02	0.02
23.	Catechol	0.50	21.547	0.16	0.21	0.18
24.	C3-Phenol	0.86	22.343	0.03	0.02	0.02
25.	C3-Phenol	0.86	22.507	0.01	0.01	0.01
26.	Quinoline	0.56	22.595	0.02	0.03	0.02
27.	C1-Catechol	0.63	23.105	0.10	0.10	0.08
28.	C3-Phenol	0.86	23.226	.	.	.
29.	C3-Phenol	0.86	23.340	0.01	0.01	0.01
30.	2-Methylnaphthalene	1.00	23.919	0.19	0.12	0.11
31.	1-Methylnaphthalene	1.00	24.288	0.17	0.11	0.09
32.	C2-Catechol	0.76	25.305	0.02	0.01	0.01
33.	Biphenyl	0.92	25.903	0.12	0.08	0.07
34.	C2-Catechol	0.76	26.028	0.05	0.05	0.04
35.	Acenaphthene	0.90	28.285	0.10	0.07	0.06
36.	Dibenzofuran	0.90	28.969	0.18	0.13	0.11
37.	Naphthol	0.85	29.036	0.35	0.26	0.23
38.	Phenanthrene	0.94	34.300	0.17	0.11	0.10
39.	Fluoranthene	0.93	39.285	0.04	0.03	0.02
40.	Pyrene	0.93	40.159	0.03	0.02	0.02
Total A%, wt%, wt%				96.81	97.95	98.23
# of Peaks, wt counts				37	155.56	

KF-Water = Karl Fischer water; Rf = FID relative response factor; Rt = GC retention time (min); A% = GC area percent; wt% = weight percent; AR = as received; wt counts = sum of A%/Rf;

GC DATA - COMPUTER DATA REDUCTION

Total Ion Current

Selected Ions

Selected Ion Current

Retention Time (min)

(a)

(b)

GAS CHROMATOGRAPHY

GC FINGERPRINT ANALYSIS

-- 2 STATIONS --

VOLATILITIES ARE DIFFERENT

GAS CHROMATOGRAPHY

GC FINGERPRINT ANALYSIS

-- 1 STATION --

BENZENE, ALCOHOL FUELS SIMILAR

NUCLEAR MAGNETIC RESONANCE FINGERPRINT ANALYSIS

IDENTIFIES,
COUNTS HYDROGEN ATOMS

Proton NMR - Olefin Region
(Gasohol)

PHENOLIC UPGRADING

Catalytic Hydrogenation

PHENOLIC UPGRADING

Alkali Pyrolysis

PHENOLIC UPGRADING

Hydropyrolysis

-END-

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