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FEASIBILITY OF PRODUCING JET FUEL FROM GPGP BY-PRODUCTS

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FEASIBILITY OF PRODUCING JET FUEL FROM GPGP BY-PRODUCTS

1.0 GOALS AND OBJECTIVES

The goal of the national energy policy is to foster an adequate supply of energy at reasonable costs. The United States supplies about 60% of its petroleum requirements from domestic production; however, domestic and world supplies have been and will continue to be unreliable in the future. Continued dependence upon foreign suppliers of crude oil could seriously affect our nation's economy as well as jeopardize our national security. As such, synthetic liquid fuels are an essential part of an energy scenario which provides the United States with a means to reduce reliance on imported oil.

The Department of Defense is the largest single consumer of liquid fuels in the United States, accounting for 2.7% of the nation's petroleum demand. Approximately one-half of the Department of Defense's requirements, or 240,000 barrels, of turbine fuel, Grade JP-4, are consumed daily by the Air Force for aircraft operations. JP-4 is a naphtha-based fuel used mainly in the United States, and JP-8 is a kerosene-type fuel used abroad. Because of the need to assure adequate supplies of either turbine fuel at acceptable costs, the Air Force has investigated the characteristics, cost, and yield of these fuels produced from tar sands, shale oil, and heavy oils, and is seeking similar data for coal-derived liquids.

The Great Plains Gasification Plant (GPGP) in Beulah, North Dakota, is in close proximity to several Air Force bases along our northern tier. This plant is producing over 137 million cubic feet per day of high-Btu SNG from North Dakota lignite. In addition, the plant generates three liquid streams, naphtha, crude phenol, and tar oil. The naphtha may be directly marketable because of its low boiling point and high aromatic content. The other two streams, totalling about 4,300 barrels per day, are available as potential sources of aviation jet fuel for the Air Force. If aviation turbine fuels can be made from the Great Plains liquids, an indigenous and nearby supply of fuel could become available. The Air Force base at Minot, North Dakota, is quite remote from jet fuel supplies and would especially benefit from this development if the jet fuel produced at Great Plains can meet all specifications and is cost competitive with other suppliers.

The overall objective of this project is to assess the technical and economic feasibility of producing aviation turbine fuel from the by-product streams of GPGP. These streams, as well as fractions thereof, will be characterized and subsequently processed over a wide range of process conditions. The resulting turbine fuel products will be analyzed to determine their chemical and physical characteristics as compared to petroleum-based fuels to meet the military specification requirements.

A second objective is to assess the conversion of the by-product streams into a new, higher-density aviation fuel. Since no performance specifications currently exist for a high-density jet fuel, reaction products and intermediates will only be characterized to indicate the feasibility of producing such a fuel.

2.0 TASK 1. - FEEDSTOCK ASSESSMENT

2.1 Stream Assessment

The quantity of liquid by-products produced at GPGP is primarily a function of the amount of coal gasified (or SNG produced) and operating conditions and, to a much lesser extent, by the coal feed. This latter effect stems from the fact that the Beulah-Zap lignite mined for use at GPGP actually consists of four laterally continuous lithologic layers (1). Preliminary investigations at UNDERC have shown that the constituents of these distinct layers have different properties, including friability, Btu values, gas/tar yields, and ash chemistry (2). However, since no attempt is made at the mine to segregate layers, but rather the entire seam is mined continuously, these variations will be averaged during normal operation.

Nameplate plant capacity is 137 MM SCF of SNG per day from 14,000 TPD of Beulah-Zap lignite. Recent tests in December illustrated that even with the existing plant bottlenecks, plant capacity can be raised by 10% to 15%. Work is also in progress to eliminate some of these bottlenecks to further increase capacity. The effect of these increased rates will obviously increase the amount of by-products proportionally, and their effect on the by-product quality will be presumed to be minimal.

Thus for purposes of this study, the following average stream rates supplied by ANG will be used.

o	Tar/oil	50,800 lb/hr	3450 Bbl/D
o	Phenolics	14,400 lb/hr	920 Bbl/D
o	Naphtha	10,600 lb/hr	880 Bbl/D

These values were obtained during operation to produce 137 MM SCF/D SNG; at higher production rates these values can be increased accordingly.

2.2 Feedstock Characterization

2.2.1 Rectisol Naphtha

The naphtha stream, as illustrated in the chromatogram in Figure 1a, is already far too light to be used as feed to a hydrotreater and too aromatic to be used for blending with heavier petroleum alkanes. The quantity of single-
[REDACTED] gum-forming stream. One method which merits assessment is [REDACTED], which shows the ability to [REDACTED] (Figure 1b).

2.2.2 Phenolics

Distillation data (Figure 2) illustrate that [REDACTED] For the bottoms, the hydrogen requirements to remove the quantities of oxygen may well negate the consideration of this fraction. Very likely, this entire fraction will have more value as a chemical feedstock (i.e., as cresylic acids).

Figure 1. Components in rectisol naptha before and after acid extraction.

Figure 2. ASTM D86 for commercial aviation fuel and GPGP phenolics

2.2.3 Tar/Oil

The tar/oil stream, at over 3,400 Bbls/D, is by far the largest of the GPGP by-products and thus the prime candidate for upgrading. By virtue of the way the product gases are quenched, heat recovered, and separated, neither the aqueous nor the organic phase (tar/oil) is free from cross contamination (5), and to compound matters, coal, char, and ash fines are ubiquitous in the system. Thus upgrading will be preceded by steps to remove water and light organics, on the order of up to 10% of the tar oil, and particulates. Probably a distillation step will be employed whereby the middle 70% to 80% is used for upgrading.

Distillation of the tar/oil stream, especially as the heavier ends are approached, will not be straight forward and will require vacuum if a deep cut is used. The main problem is that the [REDACTED] (i.e., distillation rate), tend to polymerize into nondistillable residue. The amount of residue produced in the ASTM D-86 distillation is variable (Table 1a) depending on the heating rates to IBP and the subsequent distillation rates. In no cases were we able to reach the heating rates (ambient to IBP in 10 to 15 minutes) or distillation rates (4 to 5 ml/min) with this material. In tests approaching D-86 rates (3 to 3.5 ml/min) the residue was 30% or greater. However, in cases for slow heating to IBP and distillation rates of 1 to 2 ml/min, distillation residues as low as 11% were achieved. Decomposition (i.e., smoking) was observed at pot temperatures as low as 280°C for slower heating. This also led to difficulties in assessing the end point. An attempt will be made to correlate thermal instability as a function of heating rates, and vacuum distillation D-1160 will be performed.

Elemental data in Table 1b and the NMR spectrum of tar/oil compared to commercial Jet A, shown in Figure 3, are illustrative of what will be necessary to convert tar/oil to jet fuel. Simply put, the hydrogen content must be increased [REDACTED]. These requirements, together with the caveats of economic feasibility, define the research to be performed by the process licensor.

2.3 Market Assessment

A contract was awarded to J.E. Sinor Consultants, Inc., and a meeting was held at GPGP at the end of January to initiate the Market Assessment.

3.0 TASK 2. - REACTION INVESTIGATIONS/PRODUCT ANALYSES

3.1 Single-Stage Processing/Product Characterization

3.1.1 Initial Hydrotreating

A sample of distilled tar oil (Table 2) was hydrotreated over a catalyst in the High-Pressure/Temperature Laboratory at UNDERC. [REDACTED] catalyst was presulfided with

H₂S and hydrogen at 4000 psig and 420°C for 180 minutes. After sulfiding the catalyst, the system pressure was dropped to 1000 psig, and tar oil (1507 g) was charged to the reactor, hydrogen was added, and a constant flow of gas was established. The reaction period was 50 minutes at an average temperature of 410°C, followed by cooling to 240°C, and holding for an additional 60 minutes at 240°C to stabilize aromatics.

TABLE 1
PRELIMINARY TAR/OIL ANALYSES

<u>a. Elemental Analyses (wt%)</u>					
<u>Lab</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>O (diff)</u>
ERC	83.7	8.8	0.7	0.3	6.5*
WRI (5)	83.1	8.7	0.9	0.5	6.8
ANG (5)					
Range	83-89	8-9	0.4-0.6	0.3-0.5	8.3-0.9

*Includes 0.2% Ash

b. ASTM D86 Distillation Data (°C)

<u>Vol. % Dist.</u>	<u>1/2/87</u>	<u>2/4/87</u>
IBD	93	91
5%	167	152
10%	183	186
20%	208	208
30%	223	225
40%	244	245
50%	263	269
60%	294	290
70%	307	315
80%	315	
Max. % Dist	88	78
Residual (wt%)	11	24
T Max. (°C)	318	318

Figure 3. Proton NMR spectrum a) of aviation Jet A; and
b) tar oil

TABLE 2

ELEMENTAL ANALYSES (WT%)

	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>Ash</u>	<u>O (diff)</u>
Tar/Oil Feed*	83.7	8.8	0.7	0.3	0.2	6.3
Hydrotreated Feed	87.5	12.2	.0	.0	.0	0.3

* Distilled to remove 3% light oil and 4% H₂O

The tar oil that was upgraded was distilled to remove nominally 3% light hydrocarbons and 4% water (Table 2). Elemental analysis for the hydrotreated tar oil, also presented in Table 2, shows that the [REDACTED] species were [REDACTED].

Short column separation data of the tar oil and the distillate fraction of the hydrogenated tar oil (Table 3) is indicative of the changes that occurred during hydrogenation. The [REDACTED] GC/MS

analysis of the polar fraction indicates that some unreduced phenolics are still present. GC/MS analysis of the aromatic fraction indicates that single-ring aromatics comprise most of this fraction. Proton NMR data for these fractions indicate less aromatics and CH₂ groups alpha to aromatics in the hydrogenated material, while aliphatics increased. These data also show that while [REDACTED] became [REDACTED].

In general, hydrogenation reduced nitrogen contents to near zero, greatly reduced polar content, and greatly increased the total hydrogen content. The composition was changed from a highly aromatic material to a moderately aromatic material.

TABLE 3

COMPOUND CLASS ANALYSIS (SHORT COLUMN SEPARATION), WT%

	<u>Tar Oil</u>	<u>Hydrotreated Tar/Oil</u>
Alkanes (pentane)	6.8	29.5
Branched Alkanes (iso octane)	1.1	4.4
Aromatics (MeCl ₂)	47.7	57.0
Polars (MeOH)	35.7	5.2
Unrecovered	8.7	3.9

4.0 CONCLUSIONS

This preliminary test did not result in the production of specification-grade jet fuel. It does indicate that hydroaromatics containing a single ring will be present in intermediate and probably final stages of hydrogenation. Thus the most economical route to obtain specification-grade jet fuel may be to blend the more aromatic, hydrogenated tar oil with a highly aliphatic petroleum derivative.

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