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FEASIBILITY OF PRODUCING JET FUEL FROM GPGP BY-PRODUCTS

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EXECUTIVE SUMMARY

Stream assessment information indicates that, as expected, the tar oil stream is most suited to jet fuel production. For JP-4 or JP-8 production the preferred feed is the mid 60%-70% (2100-2300 Bbl/D) of the tar oil (430°-600°F distillation cut) and the bottom nominal 30% (280 Bbl/D) of the crude phenols (+430°F fraction). The distillation would remove the phenolics that, upon hydrogenation, would form too much naphtha, which is too light for jet fuels and is more valuable as phenols. Rejection of the tar oil bottoms would remove solids, reduce the nitrogen content, and remove low hydrogen content materials from the resulting feedstock. The addition to the feedstock of phenolic bottoms is less preferred and is needed only to provide additional feedstock since they are relatively high in oxygen and nitrogen. These results are supported by distillation, elemental, NMR, GC-MS, and short-column separation data.

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 Natural Gas 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, of 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%, and the official plant capacity has been recently increased. Additional work is being performed to further increase the output. 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.

For JP-4 or JP-8 production the preferred feed is the mid 60%-70% (2100-2300 Bbl/D) of the tar oil (430°-600°F distillation cut) and the bottom nominal 30% (280 Bbl/D) of the crude phenols (+430°F fraction). The distillation would remove the phenolics that, upon hydrogenation, would form too much naphtha, which is too light for jet fuels and is more valuable as phenols. Rejection of the tar oil bottoms would remove solids, reduce the nitrogen content, and remove low hydrogen content materials from the resulting feedstock. The addition to the feedstock of phenolic bottoms is less preferred and is needed only to provide additional feedstock since they are relatively high in oxygen and nitrogen.

2.2 Feedstock Characterization

In order to evaluate potential uses of the GPGP by-product streams, feedstock characterization work is being performed. The samples being analyzed include total samples of rectisol naphtha, crude phenols, and tar oil, various distillation cuts, and compound-type fractions. Instruments being used include GC, GC-MS, and NMR. This section presents this data emphasizing areas of concern to jet fuel production.

2.2.1 Distillation Data

The distillation specification for successful jet fuel must be met. D86 distillation data for the three streams analyzed by ANG Coal Gasification personnel is depicted in Figure 2-1. The naphtha stream is the lightest, while the tar oil stream is the heaviest. Analysis at UNDERC provided similar distillation results (Table 2.1 and Figure 2-2). The naphtha stream is too light to be used significantly in a jet fuel and will be discussed separately. Estimated true boiling point curves calculated from D1160 ASTM distillation data ($K = 12$) and data from WRI and ANG are compared in Figure 2-3. Figure 2-4 compares the distillation data of commercial aviation jet fuel (AV Jet A) to the phenol and tar oil streams, while Figure 2-5 compares data for tar oil to JP-4 and JP-8 specifications. Both the tar oil and crude phenol streams contain sizable fractions in the correct distillation regions.

Collection and analysis of the D86 distillate fractions adds additional information. In Table 2.2 it can be seen that in the tar oil the oxygen content is maximum in the 194°-207° cut where phenolics distill and is lowest in the residue. The hydrogen content decreases to a minimum in the residue which contains only 4.9 wt%. Nitrogen content is also highest in the residue, and any coal dust (THF insolubles on Table 2.1) would be expected to concentrate in the residue. The hydrogen content of the phenolic stream is also lowest in the residue (see Table 2.3). For the phenolic stream the total sulfur content is only 0.04 wt%, so the difference column represents the oxygen level. Oxygen content is over 15 wt% for all fractions except for the residue. The high oxygen content of the initial 5 vol% over is due to the presence of water in this fraction. As for the tar oil, the nitrogen content is highest in the residue. Comparative data for the analysis of different tar oil samples at different times in the research project are presented in Table 2.1 (D86 and elemental data) and 2.9 (elemental data).

2.2.2 NMR Data

Proton and C-13 NMR data provides information about the hydrogen atoms surrounding carbon and the carbon structure itself. A proton NMR spectrum is a plot of the frequencies at which hydrogen atoms absorb magnetic energy and resonate versus intensity. The resonance frequency can be reported in ppm units from an internal standard, tetramethylsilane (TMS) at zero ppm. The frequency at which a particular hydrogen is observed depends on its position in an organic compound. Table 2.4 indicates where protons of selected carbon compounds would be observed in a spectrum. NMR spectra of pure compounds can be used to obtain absolute structural information, while in complex mixtures more compound type information is obtained. The intensity or area% of a peak is proportional to the number of protons represented by the peak relative to the total number of protons observed by the NMR spectrophotometer. Easily exchanged protons, such as in the tar acid phenolic groups, result in broad peaks or are not observed. The proton NMR spectra were obtained using a Varian XL200 NMR spectrometer at 200 MHz. The pulse width was set for a 90° flip angle. A 3-second acquisition time and a 5-second recycle delay time were used. Spectral width was 2600 Hz and 100 pulses were accumulated for each spectrum. The samples were prepared in deuterated methylene chloride which contained 0.25% TMS. All chemical shift data are presented from TMS at 0 ppm. The residual peak for non-deuterated methylene chloride solvent is observed at about 5.3 ppm.

Figures 2-6 and 2-7 and Table 2.5 present NMR data. The proton NMR spectra in Figure 2-6 compare the three streams. The naphtha and phenol streams contain simple substituted benzene rings, while the tar oil is rich in multiple aromatic ring systems (6.5-8 ppm region). The crude phenol contains relatively small amounts of aliphatics (.1-1.5 ppm region) and contains mainly aliphatic protons on carbon alpha to an aromatic ring (1.9-3.3 ppm region) as in cresols. The tar oil contains more substituted aromatics (see Figure 2-7, 1.5-3.3 ppm region) than AV Jet A and lesser amounts of desirable alkanes. The hydrogenated tar oil contained primarily aliphatics and substituted single ring aromatics and has been described earlier (3,4).

2.2.3 Component Analysis

GC and GC-MS analysis can provide detailed data concerning components in complex mixtures. A Hewlett-Packard Model 5985B gas chromatograph/mass spectrometer equipped with dual electron impact/chemical ionization sources was used to obtain the mass spectra used for identification of components in the samples. Gas chromatographic separations were performed on a Hewlett-Packard Model 5890 (FID) or a Model 5840 (GC/MS) gas chromatograph equipped with a 60 m x 0.25 mm i.d. DB-5 fused silica capillary column (J&W Scientific, Folsom, California). Tar oil and crude phenols samples were injected at 60°C followed by temperature programming to 320°C at 6°C/min. Tables 2.6 and 2.7 and Figures 2-8 and 2-9 provide detailed information on the crude phenol and tar oil streams. For instance, toluene (methylbenzene) has only one possible structure. However, xylenes (dimethylbenzenes) have three possible structures or isomers: ortho (1,2-dimethylbenzene), meta (1,3-dimethylbenzene), and para (1,4-dimethylbenzene). The xylenes are generically termed C2-benzenes and have elemental formulas of C_8H_{10} . Table 2.8 details some general carbon bonding information as well as names and structures of organic compounds. The phenolics (phenol, cresols, and xylenols) account for about 90 area% of the flame ionization detector (FID) output for the crude phenol stream. FID area% values are within about 12% of actual wt% values depending on individual compounds response factors. The presence of 1.8 area% of methoxyphenol (potentially guaiacol) and as yet unidentified compounds eluting after C2-phenols can be noted (see Table 2.6 and Figure 2-8). However, the previous data (Table 2.3) indicated that even the higher boiling material contained 18 wt% oxygen. The tar oil stream also contains about 13 area% phenolics (summed from Table 2.6). About 13 area% of light boiling toluene and xylenes are present. Aromatic naphthalene and substituted naphthalenes (22 area%) as well phenanthrenes (or anthracenes) (4 area%) are well represented. Small quantities of other aromatics such as biphenyl, acenaphthene, fluorene, and even pyrene are present. Oxygen is also found in various benzofuran structures. A series of various aliphatics is also present. Nitrogen compounds are present at low levels. They have been concentrated by acid extraction and are discussed elsewhere.

2.2.4 Compound-Type Separation and Analysis

Separation of complex mixtures into compound-type fractions followed by analysis of the fractions enables better comparisons. A short column separation technique was used to obtain fractions of compound types. Aldrich grade 12, 28-200 mesh silica gel was activated by heating at 250°C for 15 hours. After cooling, the gel was loosely packed into a 1.5 cm i.d. glass chromatography column to a height of about 47.0 cm. At the bottom of the

column was a fritted glass filter directly above a narrow bore opening which reduced flow through the column. After weighing out an approximately 1.0 g sample, the column was flushed with pentane. When pentane began to flow out the bottom of the column, the sample was placed on the silica gel at the top of the column. The sample was then eluted with 150 ml of pentane, 50 ml of iso-octane, then 50 ml of pentane (aliphatic fraction), 250 ml of methylene chloride (aromatic fraction), and 100 ml of methanol (polar fraction). The three fractions were collected in separate, preweighed flasks. In order to determine quantitative yields, the solvents were evaporated using a Roto-vap vacuum evaporation system. Loss of some light material can occur, decreasing recovery. Crude phenols, tar oil, and AV Jet A have been separated into aliphatics, aromatics, and polars by solvent elution from a silica gel column. Table 2.9 presents yield and elemental data for the samples and fractions. The phenols contain only 0.5 wt% aliphatics and 1.8 wt% of aromatics (light boiling materials were probably lost during solvent removal) with most of the oxygen in the polars. The tar oil is the most complex containing aliphatics (7.9 wt%), aromatics (47.7 wt%) and polars (35.7 wt%). The AV Jet A contains primarily aliphatics (76.7 wt%) and aromatics (18.4 wt%) as expected. Even the aromatics contain over 10 wt% hydrogen.

Figures 2-10, 2-11, and 2-12 depict the NMR data for these samples and fractions. Note that aliphatic fractions are essentially void of aromatics, indicating that the good separations were obtained. Polar fractions contain aromatic protons (5.9-9 ppm region) since most are associated with phenolics. The aromatic regions of tar oil and crude phenol indicate multiple-ring aromatics are present, while in the AV Jet A aromatics they are absent.

2.2.5 Nitrogen Compounds from GPGP Tar Oils

The tar oil stream from the Great Plains Gasification process has the potential to be used as a source for jet fuel, provided it can be upgraded. Hydrogenation, one process of upgrading, is affected by catalytic activity. The catalysts, on the other hand, are affected by the presence of various chemicals including nitrogen bases, which result from the cracking of coal molecules during the gasification process. Earlier work predicted there was a positive correlation between the strength of the nitrogen bases and the loss of catalytic activity (5). Since the hydrogenation of the tar oils will involve the use of nickel-molybdenum catalysts, and these activities will be affected by the presence of nitrogen heterocycles, it is important to know the quantity and types of nitrogen heterocycles present in the oils; hence, the purpose of this work.

Fifteen grams of oil was extracted with 200 ml of n-pentane (some insolubles remained). The pentane layer was then extracted with 3 x 50 ml portions of 2M NaOH. The aqueous layer was extracted with 3 x 50 ml portions of pentane and the pentane layers combined. The pentane layer was extracted with 2M HCl following the same procedure as used with NaOH. The aqueous layer was neutralized to pH 12 with 20% NaOH and extracted with 3 x 75 ml of CH_2Cl_2 to get the base fraction. Evaporation of CH_2Cl_2 gave 0.4 g of nitrogen bases or 2.6% by weight of the tar oil stream. The sample was dissolved in 5 ml of UV grade CH_2Cl_2 and used for GC and GC/Fourier Transform Infra-Red/Ion Trap Detector analysis.

Figure 2-13 shows the GC analysis of the tar oils using a J&W 30 M x 0.25 mm film DB-5 column with H₂ carrier gas at 1 ml/min. The sample was injected into the column at 325°C and detected using FID. The column was programmed from 40° to 50°C at 30 degrees/min and from 50° to 325°C at 2 degrees/min. From the chromatogram one can ascertain that the majority of nitrogen compounds are extremely volatile, as indicated by the mass of material appearing at the beginning of the chromatograph. Although none of the compounds have been identified from the scan, aniline identified by the FTIR and ITD method elutes from the column in about 1.6 minutes and is a potential major compound of the tar oil stream.

Figure 2-14 shows the gas chromatogram with the appropriate molecular ions assigned to specific peaks. The GC conditions used for obtaining the FTIR and mass data were different than those used to obtain Figure 2-13. The column was a J&W 60M x 0.32 mm 1.0 micron film DB-5 with hydrogen carrier gas at 1 ml/min. The sample was injected into the column at 350°C and the column programmed 40° to 50°C at 30 degrees/min and 50° to 350°C at 5 degrees/min. The result was longer retention times for the lower boiling fraction. The most intense peak at mass 93 matched perfectly with the infrared spectrum of aniline from the Aldrich library. The 107 peak of the lowest retention time has been identified as an isomeric dimethylpyridine (Lutidine). In addition, several nitrogen heterocycles containing carboxyl functionality have been tentatively identified as related to pyrrolidinone; these occur at mass 121 or greater.

Aniline and isomeric dimethyl pyridines were identified as constituents in the tar oil stream from the Great Plains Gasification Plant coal gasification process. Nitrogen heterocycles containing carboxyl functionality were also detected. No significant amounts of acridine, carbazole, quinoline, or indole were observed. This could indicate that the carbon content of the nitrogen heterocycles does not contribute significantly to upgrading the tar oils stream after initial hydrogenation.

2.2.6 Rectisol Naphtha Stream

The rectisol naphtha stream is too light for use as a jet fuel. It has a very powerful odor, which makes it commercially unusable and indeed makes it virtually unanalyzable without extreme methods of odor containment. For the latter reason, the deodorization of the naphtha was investigated in order to provide a laboratory sample.

The pH of the as-received naphtha was low (between 2-5 as measured with pH paper). Simply exposing a sample to air and allowing volatile material to escape reduced the odor. A caustic wash also reduced the odor of the naphtha. However, a caustic wash containing a small amount of copper sulfate eliminated the unacceptable odor. To 100 mL rectisol-naphtha, 50 of 0.1 M NaOH and 2 mL .00025 M CuSO₄ was added and stirred vigorously for up to 4 hours. The reaction was greatly facilitated by the addition of ~2 mL of .00150 M quinoline solution to the CuSO₄ before addition to the rectisol-naphtha. This provided a deodorized sample. In order to determine what components had been removed by the caustic-copper wash, as-received and deodorized rectisol naphtha samples were analyzed by GC and GC/MS. Particular emphasis was placed on identifying the odor causing components.

Rectisol naphtha contains a large number of very volatile components that precluded the use of a solvent to dilute the sample, since an added solvent would mask many components. Therefore, a very small sample injection was required to prevent exceeding the sample capacity of the column. A micro-syringe capable of injecting 0.02 ul was used in this analysis. Samples were introduced into the GC and GC/MS via the split/splitless injection port (operating in the split mode). The split ratio was approximately 1:100 with H₂ carrier. The column oven was initially held at -20°C for two minutes and then ramped to 320°C at 6°C/min. Figures 2-15 and 2-16 show the total ion chromatograms (TICs) obtained from the analysis of the two samples. Figure 2-17 is the FID chromatogram from which area% data was obtained. Figure 2-15 is the TIC of the rectisol naphtha before treatment for odor removal, and Figure 2-16 is the TIC of the deodorized rectisol naphtha. It is apparent in comparing these figures that a portion of the material in the untreated rectisol naphtha is removed. Table 2.10 lists the compounds that have been identified. The deodorized sample has fewer "light" components and the low molecular weight sulfur species have been removed. These sulfur compounds along with the thiophenes present probably account for the much of the bad odor of the rectisol naphtha. Ethanethiol has a minimum detectable odor concentration of 1 part in 50 billion parts of air (Merck Index, page 490) so a little goes a long way. It also appears that the deodorization process removes some of the C2 and C3 benzenes.

2.2.7 D86 Distillation and Tar Oil Stability

The initial ASTM D86 distillations of the four stream samples (AV Jet A, crude phenol, tar oil, and rectisol naphtha) did not meet specs for jet fuel analysis; specifically, having a less than 1.5% loss of weight or 98.5% recovery. In order to meet specs, the distillation rate was increased and the condenser temperature lowered, which brought the weight loss down below 1.0%. Table 2.11 shows a comparison between the distillations done at a slow rate to that done at a faster rate. The data shows that the tar oil is thermally unstable to the distillation. As the distillation rate was increased to a point where the weight loss dropped below 1%, the residue increased from less than 10% to greater than 30%, and the final temperature decreased from 303° to 260°C. The final temperature of the distillation is determined by the smoke point of the sample or the thermal decomposition point. At this point, smokey vapors are seen in the flask, and the vapor temperature begins to fall even when more heat is applied. At the higher pot temperatures associated with the faster rate of heating, a polymerization reaction(s) initiated forming a non-distillable material while absorbing heat and affecting the vapor temperature.

The stability of the tar oil was further investigated by performing the distillation at different heating rates. Faster heating rates generally showed an increase in the amount of non-distillables and varied final temperatures. Molecular weight distributions of the THF solubles of these non-distillables were determined by gel permeation chromatography (GPC). GPC analysis showed a larger amount of lower molecular weight material present in resids that reached a lower final temperature. This can be seen in Figure 2-18. This indicates that the decomposition point of the tar oil shifts when different heating rates are applied.

A cold-charge autoclave run was also made to test the stability of the tar oil. The tar oil was heated to 260°C and held at temperature for two hours, then allowed to cool to room temperature. The autoclave was sampled at various times during the run, and the samples were analyzed to determine molecular weight changes. GPC analysis showed little polymerization taking place at this temperature. Figure 2-19 shows the molecular weight distributions of the original tar oil and that of the tar oil after completion of the run. This indicates that little polymerization took place at this temperature. Stability testing at higher temperatures would be required to observe molecular weight changes. Discussions with clients indicated present industrial schemes do not include a distillation separation of the tar oil stream; therefore, upon their recommendation, work in this area has been discontinued.

2.3 Market Assessment

A draft report on the Market Assessment prepared by J.E. Sinor Consultants, Inc. has been distributed for review, and the major findings will be presented in the next quarterly report. However, to answer some fundamental questions regarding the nature of creosote and the ability of certain GPGP fractions to be used as creosote, the following sections were edited from the Sinor report.

Creosote: Definitions and Specifications

Creosote may be loosely defined as the fraction of coal tar distillate boiling in the range 400°F to 650°F. It is sometimes referred to as "dead oil," indicating that it is the higher boiling fraction of the oil obtained by distilling coal tar. Rather than producing a virgin distillate in this range, creosote is often produced by blending various tar oil fractions.

The oils are blended to give creosotes conforming to certain user specifications. The major outlet for coal-tar creosote is for the preservation of timber. Although other fungicides have been increasingly used, coal-tar creosote has been the most widely used wood preservative. It is particularly effective in prolonging the life of wood that is used outdoors and in contact with the ground, or seawater or freshwater. Examples are telegraph and electricity transmission poles, railway ties, marine piling, fencing, and farm buildings.

To give these structures service lives of 50 years or more, they are impregnated under pressure with creosote so that the vulnerable sapwood cells are either filled with oil (by the Bethell or "full-cell" process generally used for marine piling and railway ties), or coated with a film of creosote (by the Rueping or Lowry "empty-cell" processes more generally used for poles, fencing, and farm buildings).

Other minor uses for creosotes are as horticultural washes to kill overwintering pests on fruit trees, and for making disinfectant emulsions and sheep dips.

Specifications for creosote for timber preservation are published by the American Wood Preservers' Association (AWPA). Standard P1-78 is the most widely used, general-purpose standard (Table 2.12). Standard P7-85 gives the

requirements for a crystal-free product to protect cut surfaces of treated wood, and P13-85 specifies the properties of a marine-grade creosote for pilings and timbers (Table 2.13). Solutions of coal tar in creosote are covered in Standard P2-85 (Table 2.14). These solutions may be used in applications where the surface condition of the treated wood is not important. A marine-grade creosote-coal tar solution, Standard P12-85, gives better protection against marine borers than Standard P2-85. In general, the more severe the service, the higher the required specific gravity (Table 2.15).

As seen in Tables 2.12 through 2.14 the AWWA standards define creosote as a distillate of coal tar produced by the carbonization of bituminous coal. Thus the low-temperature lignite tar produced at the Great Plains Plant is excluded a priori. Also, it probably would not meet the specific gravity specifications. Nevertheless, there is reason to believe that, from a performance standpoint, the Great Plains tar should be satisfactory. Low-temperature lignite tars have been used successfully for wood preservation in the past. The existing specifications are wholly empirical; the requirements evolved through a compromise between the consumers' needs in timber preservation and the producers' processing capabilities and coal tar feedstocks.

3.0 TASK 2 - REACTION INVESTIGATIONS/PRODUCT ANALYSIS

A distillation unit was constructed to enable the production of sufficient quantities of distilled feedstock. It was constructed and successfully operated at its design capacity of two gallons per hour. The unit was used to produce an 84% overhead cut from tar oil and a 16% bottoms cut from crude phenol. These cuts were blended to obtain a feedstock for batch autoclave hydrogenation tests. Figure 3.1 depicts D86 distillation data for the two cuts and the blend. The blend is most like the tar oil distillate. Samples will be analyzed to determine how components are distributed between the distillation cuts.

4.0 REFERENCES

1. Kleesattel, D.R. "Petrology of the Beulah-Zap Lignite Bed." UND Masters Thesis, 1985.
2. Kleesattel, D.R. "Petrology Study of Beulah-Zap Lignite with Respect to Gasifier Performance." Final Report to ANG Coal Gasification Company, January 22, 1987.
3. Knudson, C.L., et al. "Composition of Jet Fuel from Tar Oil." Preprints, National ACS Convention, Denver, CO, April 6-10, 1987.
4. Willson, W.G., Knudson, C.L., and Rindt, J.R. "Feasibility of Producing Jet Fuel from GPGP By-Products." Interim Quarterly Technical Progress Report, November 26, 1986 - February 16, 1987.
5. Stohl, F.V. Sandia National Laboratories, SAND-86-1837C, DOE Contract DE-AC04-76DP00789.

TABLE 2.1
ASTM D86 DISTILLATION DATA

	Tar Oil	Crude Phenol	Rectisol Naphtha	AV Jet A
Barr. Press. (mm Hg)	756	742	731	742
Rm. Temp., °C (°F)	23 (0)	23	24	23
Vol. % Distil.:				
IBP	93 (199.4)	97 (206.6)	43 (109.4)	82 (179.6)
5%	135 (275.0)	98 (208.4)	63 (145.4)	173 (343.4)
10%	170 (338.0)	185 (365)	69 (156.2)	183 (361.4)
20%	195 (383)	190 (374)	76 (168.8)	197 (386.6)
30%	210 (410)	193 (379.4)	79 (174.2)	205 (401.0)
40%	225 (437)	193 (379.4)	83 (181.4)	213 (415.4)
50%	250 (482)	196 (384.8)	86 (186.8)	220 (428)
60%	263 (505.4)	201 (393.8)	89 (192.2)	228 (442.4)
70%	285 (545)	210 (410)	94 (201.2)	235 (455.0)
80%	297 (566.6)	229 (444.2)	102 (215.6)	245 (473)
90%	303 (577.4)	263 (505.4)	119 (246.2)	260 (500)
95%			132 (269.6)	268 (514.4)
Max. Temp., °C	303 (577.4)	265 (509.0)	132 (269.6)	274 (525.2)
Max. Vol., %	92	95	96	98
Res. wt%	9.66	5.75	2.80	2.20
Dist. wt%	87.68	92.45	96.35	96.21
Lost wt%	2.66	1.80	0.85	1.59
Sp. Gr.	1.015	1.060	0.821	0.817
Elemental Analysis, wt%				
Carbon	83.76	72.18	87.65	87.68
Hydrogen	8.83	7.49	10.12	14.30
Nitrogen	0.52	0.28	0.00	0.06
Sulfur	0.39	0.04	0.00	0.17
KF-water	1.20	4.48		0.01
THFI	0.11	0.00		

Table 2.2

TAR OIL, ASTM D86 DISTILLATE FRACTIONS

SPECIFIC GRAVITY, 1.025:

VOL. %	TEMPERATURE		WT% OF FRAC	WT% C	WT% H	WT% N	WT% O+S (diff)	SUM
	deg.F	deg.C						
IBP	180	82						
5%	275	135	4.49	86.69	10.33	0.56	2.42	100
10%	347	175	4.59	81.62	9.66	0.87	7.85	100
20%	381	194	9.07	80.38	9.59	0.78	9.25	100
30%	405	207	9.37	79.63	9.19	0.67	10.51	100
40%	430	221	9.56	80.88	8.76	0.81	9.55	100
50%	473	245	9.46	83.04	8.86	0.87	7.23	100
60%	511	266	9.27	83.74	8.96	0.85	6.45	100
70%	511	266	9.95	84.64	8.78	0.63	5.95	100
80%	541	283	9.76	85.33	8.91	0.67	5.09	100
90%	565 max	296	10.44	85.32	9.13	0.65	4.90	100
RESIDUE			10.54	90.11	4.90	1.15	3.84	100
TOTAL WT%			96.50	80.90	8.36	0.75	6.49	
ORIGINAL SAMPLE WT%			100.0	82.60	8.63	1.01	7.76	
RECOVERY %			96.5	97.9	96.9	74.4	83.6	

UNDERC/D861B

Table 2.3
CRUDE PHENOL , ASTM D86 DISTILLATE FRACTIONS

SPECIFIC GRAVITY, 1.075:

VOL. %	TEMPERATURE		WT% OF FRAC.	WT% C	WT% H	WT% N	WT% O+S (diff)	SUM
	deg.F	deg.C						
IBP	207	97						
5%	374	190	4.88	73.01	7.47	0.20	19.32	100
10%	374	190	4.87	76.22	7.19	0.00	16.59	100
20%	381	194	9.73	76.78	7.13	0.00	16.09	100
30%	383	195	9.66	76.29	7.10	0.10	16.51	100
40%	387	197	9.64	76.23	7.16	0.17	16.44	100
50%	394	201	9.74	76.57	7.28	0.16	15.99	100
60%	410	210	9.51	77.33	7.38	0.13	15.16	100
70%	433	223	9.73	77.14	7.46	0.19	15.21	100
80%	468	242	9.64	75.31	7.55	0.28	16.86	100
90%	496	258	10.91	73.72	7.55	0.41	18.32	100
94.2%	496	258	4.22	73.22	7.60	0.72	18.46	100
RESIDUE			6.23	83.78	5.73	1.59	8.90	100
TOTAL WT%			98.76	75.39	7.15	0.28	15.93	
ORIGINAL SAMPLE WT%			100.0	76.03	7.34	0.31	16.32	
RECOVERY %			98.8	99.2	97.4	90.3	97.6	

UNDERC/D861A

TABLE 2.4

PROTON NMR ABSORPTION REGIONS

ALIPHATIC PROTONS

AROMATIC PROTONS

POLAR PROTONS

ck7/proton

TABLE 2.5
PROTON AND CARBON-13 NMR DATA

Carbon Type	NMR Region ppm	PROTON NMR		Crude Phenol %Area	Rectisol Naphtha %Area
		AV Jet A %Area	Tar Oil %Area		
Aromatic	9.0 - 5.9	4.8	28.3	50.2	38.9
Phenol	4.4 - 3.5	0.4	2.4	16.9	0.4
Acenaphthene	3.5 - 3.3	0.1	0.5	2.1	1.9
-CH2-alpha	3.3 - 1.9	6.5	28.4	23.5	22.2
-CH2-beta	1.9 - 1.5	7.8	5.3	1.3	10.5
-CH2-	1.5 - 1.0	43.6	23.4	4.8	13.9
-CH3	1.0 - 0.1	36.8	11.7	1.2	12.2
Total Area%		100.0	100.0	100.0	100.0
-CH2-/-CH3		1.2	2.0	4.0	1.1
CARBON-13 NMR					
Aliphatic, C=	240-187	2.5		1.0	2.0
Aromatic, C=O	187-160	2.3		0.1	1.1
Phenolic	160-149	1.0		10.2	0.0
Aromatic, =C=	149-138	2.5		8.3	2.7
Aromatic, =C-	138-95	10.1		65.8	66.7
Methoxy	95-60	0.1		0.2	1.1
Aliph., -CH2-	50-36	23.0		1.4	4.3
+CS	36-27	33.3		2.3	9.7
alpha C	27-17	16.8		5.2	8.0
-CH3	17-0	8.4		5.5	4.4
Total Area%		100.0		100.0	100.0

CK7/NMR2

TABLE 2.6
TAR OIL COMPONENT DATA

GC #	b.p. -----		Component	Area% Over	Retention Time	Peak Area%	Elemental, atomic				
	deg.C	deg.F					C	H	N	O	S
1	111	231	Toluene	8	3.22	8.34	7	8			
2	138	281	C2 Benzene	9	5.40	0.70	8	10			
3	139	282	C2 Benzene	12	5.52	2.56	8	10			
4	144	292	C2 Benzene	13	5.96	1.39	8	10			
5			C3 Benzene	13	7.16	0.18	9	12			
6			C3 Benzene	14	7.33	0.86	9	12			
7	182	359	Phenol	15	7.36	0.66	6	6			1
8			C3 Benzene	15	7.48	0.32	9	12			
9			C3 Benzene	16	7.75	0.62	9	12			
10			C4 Benzene	17	8.06	1.44	10	14			
11	191	376	C1 Phenol	18	8.76	1.30	7	8			1
12	202	396	C1 Phenol	19	9.10	1.10	7	8			1
13			C2 Phenol	21	9.94	1.65	8	10			1
14			C1 Benzofuran	22	10.78	0.76	9	8			1
15			C2 Phenol	22	10.88	0.55	8	10			1
16			C2 Phenol	24	11.77	1.09	8	10			1
17			C2 Phenol	25	11.94	1.76	8	10			1
18			C2 Phenol	28	12.28	2.29	8	10			1
19			C2 Phenol	28	12.54	0.85	8	10			1
20	218	424	Naphthalene	37	12.88	8.54	10	8			
21			C2 Benzofuran	37	13.38	0.37	10	10			1
22			C3 Phenol	38	13.75	0.79	9	12			1
23			C3 Phenol	39	14.56	1.22	9	12			1
24	240	464	2-Methylnapth.	43	15.62	3.59	11	10			
25	241	466	1-Methylnapth.	45	16.06	1.84	11	10			
26	256	493	Biphenyl	46	17.08	0.90	12	10			
27	254	489	C14H30	47	17.63	1.37	14	30			
28			C2 Naphthalene	48	18.26	0.96	12	12			
29			C2 Naphthalene	49	18.61	1.02	12	12			
30			C2 Naphthalene	50	18.69	1.42	12	12			
31			C2 Naphthalene	51	19.08	0.47	12	12			
32			C2 Naphthalene	52	19.17	0.97	12	12			
33			C2 Naphthalene	52	19.45	0.35	12	12			
34	271	519	C15H32	53	20.02	0.93	15	32			
35	279	534	Acenaphthene	54	20.15	0.95	12	10			
36			C3 Naphthalene	55	20.47	0.66	13	14			
37	287	549	Dibenzofuran	57	20.85	2.00	12	8			1
38			C3 Naphthalene	57	21.11	0.45	13	14			
39	287	549	C16H34	58	22.17	0.44	16	34			
40	294	561	Fluorene	59	22.32	1.44	13	10			
41			C3 Naphthalene	61	22.40	1.63	13	14			
42			C1 Dibenzofuran	61	23.10	0.47	13	10			

TABLE 2.6 (cont.)

TAR OIL COMPONENT DATA

GC #	b.p.		Component	Area% Over	Retention Time	Peak Area%	Elemental, atomic				
	deg.C	deg.F					C	H	N	O	S
43			C1 Fluorene	61	24.73	0.29	14	12			
44	316	601	C18H38	62	26.15	0.64	18	38			
45	340	644	Phenanthrene	64	26.42	2.33	14	10			
46	340	644	Anthracene	65	26.62	0.55	14	10			
47	330	625	C19H40	65	28.00	0.47	19	40			
48			C1 Phenanthrene	65			15	12			
49			C1 Phenanthrene	66	28.56	0.28	15	12			
50			C1 Phenanthrene	66	28.69	0.43	15	12			
51			C1 Phenanthrene	66			15	12			
52			C1 Phenanthrene	67	29.04	0.35	15	12			
53	343	649	C20H42	67	29.77	0.46	20	42			
54	357	674	C21H44	68	31.61	0.63	21	44			
55	375	707	Fluoranthene	69	32.55	1.08	16	10			
56	369	695	C22H46	69	33.07	0.52	22	46			
57	393	739	Pyrene	69			16	10			
58	380	716	C23H48	70	34.63	0.55	23	48			
59	391	736	C24H50	70	36.11	0.45	24	50			
60	402	755	C25H52	71	37.55	0.48	25	52			
61	412	774	C26H54	71	38.93	0.33	26	54			
62	442	828	C27H56	72	40.26	0.61	27	56			
63	432	809	C28H58	72	41.54	0.35	28	58			
64	441	825	C29H60	72	42.78	0.01	29	60			

ck7/dls-tar

TABLE 2.7
CRUDE PHENOL COMPONENT DATA

GC #	b.p. deg.C	----- deg.F	Component	Area% Over	Retention Time	Peak Area%	Elemental, atomic				
							C	H	N	O	S
1	182	359	Phenol	47	75.85	47.08	6	6		1	
2	191	376	C1 Phenol	56	92.77	8.47	7	8		1	
3	202	396	C1 Phenol	79	98.20	23.53	7	8		1	
4			Methoxyphenol	81	102.14	1.88	7	8		2	
5			C2 Phenol	82	113.31	0.82	8	10		1	
6			C2 Phenol	84	116.32	1.96	8	10		1	
7			C2 Phenol	85	120.52	1.54	8	10		1	
8			C2 Phenol	89	121.13	3.51	8	10		1	
9			C2 Phenol	89	123.62	0.70	8	10		1	
10			C2 Phenol	91	127.76	1.04	8	10		1	

ck7/d1 s-ph

TABLE 2.8

MAJOR TYPES OF ORGANIC COMPOUNDS

Type	Example	Symbol
<u>ALKANES</u>	Ethane C_2H_6 or CH_3CH_3
Cycloalkanes	Cyclohexane C_6H_{14}	Chair conformation Boat conformation <i>An energy maximum</i>
Olefins	Ethylene C_2H_4 or $CH_2=CH_2$
<u>AROMATICS</u>	Benzene C_6H_6
Phenolics	Phenol C_6H_5OH
Cresols	m-Cresol $C_6H_4OHCH_3$
<u>HETEROCYCLICS</u>	Furan Pyridine Thiophene

TABLE 2.9

ELEMENTAL ANALYSES OF TOTAL AND COLUMN FRACTIONS

	Fraction wt%	C	H	N	S	O&S	KF-water ^a
<u>Crude Phenols</u>							
Total	100.0	72.18	7.49	0.28	0.04	20.05	4.48
Aliphatics ^b	0.5						
Aromatics	1.8	81.41	7.50	0.29	NA ^c	10.80	----
Polars	92.5	73.62	7.32	0.32	NA	18.74	----
Recovery	94.8						
<u>Tar Oil</u>							
Total	100.0	83.76	8.83	0.52	0.39	6.89	1.20
Aliphatics	7.9	86.60	14.89	0.11	NA	-1.60	
Aromatics	47.7	88.82	8.36	0.20	NA	2.62	
Polars	35.7	75.46	7.62	0.85	NA	16.07	
Recovery	91.3						
<u>AV Jet-A</u>							
Total 1)	100.0	87.12	14.19	0.17	----	-1.48	
2)		87.68	14.30	0.06	0.17		
Aliphatics	76.7	86.33	15.03	0.33	NA	-1.69	
Aromatics	18.4	88.99	10.67	0.21	NA	0.13	
Polars ^b	1.9						
Recovery	97.0						
<u>Standards</u>							
Tetralin		90.46	9.28	0.24		0.02	
C ₁₀ H ₁₂ Theory		90.91	9.04	0			
Cyclohexane		86.53	14.97	0.29		-1.79	
C ₆ H ₁₂ Theory		85.71	14.28	0			

^a Karl-Fisher analysis.^b Sample too small.^c NA indicates not analyzed.

TABLE 2.10
RECTISOL NAPHTHA COMPONENT DATA

GC #	b.p. deg.C	deg.F	Component	Area% Over	Retention Time	Peak Area%	Elemental, atomic				
							C	H	N	O	S
1				0	25.79	0.26	4	8			
2				0	26.45	0.22	4	8			
3				1	28.08	0.15	4	8			
4	6.0	43	Methanethiol	1	29.04	0.21	1	4			1
5				1	30.10	0.15	4	8			
6				1	35.46	0.00	5	10			
7	36.0	97	n-Pentane	1	38.65	0.24	5	12			
8				2	43.45	0.31	5	10			
9	52.6	127	Acetone	4	46.39	2.28	3	6		1	
10				4	48.27	0.25	5	8			
11				5	49.13	0.44	5	10			
12				5	51.02	0.25	5	10			
13	37.3	99	Thiobismethane	5	52.17	0.16	2	6			1
14				6	52.71	0.86	5	10			
15	37.0	99	Ethanethiol	6	54.93	0.21	2	6			1
16				6	58.26	0.24	5	6			
17				6	59.13	0.15	5	8			
18				7	63.36	0.55	5	8			
19				7	64.61	0.13	6	12			
20				7	66.27	0.42	5	10			
21				8	68.52	0.47	6	12			
22				8	70.51	0.11	6	14			
23				8	73.59	0.18	6	14			
24				9	77.65	0.91	6	12			
25	68.0	154	n-Hexane	10	80.79	1.24	6	14			
26	79.6	175	2-Butanone	12	82.37	1.45	4	8		1	
27				12	83.22	0.33	6	12			
28				13	84.00	0.33	6	10			
29				13	84.82	0.61	6	12			
30				13	86.00	0.11	6	12			
31				14	90.49	0.81	6	12			
32				14	93.42	0.00	6	12			
33				14	96.44	0.21	6	8			
34				14	98.45	0.17	6	8			
35				16	100.69	1.30	6	10			
36				16	103.07	0.60	6	12			
37	80.1	176	Benzene	63	105.60	46.60	6	6			
38	84.2	184	Thiophene	63	107.13	0.57	4	4			1
39				64	108.27	0.18	6	8			
40	83.0	181	Cyclohexene	64	110.85	0.66	6	10			
41				65	112.31	0.20	7	14			
42				65	113.38	0.13	7	14			

TABLE 2.10 (cont.)

RECTI SOL NAPHTHA COMPONENT DATA

GC #	b.p. deg.C	----- deg.F	Component	Area% Over	Retention Time	Peak Area%	Elemental, atomic				
							C	H	N	O	S
43				65	114.47	0.15	7	14			
44				66	116.70	1.05	7	14			
45				67	119.97	1.51	7	12			
46				68	122.95	0.24	7	14			
47				68	124.13	0.30	7	12			
48				68	125.75	0.21	7	14			
49				69	126.82	0.98	7	14			
50	98.4	209	n-Heptane	69	131.44	0.27	7	14			
51				70	133.58	0.44	7	12			
52				70	139.89	0.47	7	12			
53				70	140.62	0.21	7	12			
54				71	141.05	0.13	8	16			
55	110.6	231	Toluene	88	145.17	17.57	7	8			
56				88							
57				88							
58				88							
59			#56 - 63 total	90		1.61					
60				90							
61				90							
62				90							
63				90							
64	126.0	259	C8H18	91	156.81	0.83	8	18			
65				91							
66				91							
67				91							
68				91							
69			#65 - 73 total	91		0.79					
70				91							
71				91							
72				91							
73				91							
74			C2 Benzene	92	177.95	0.94	8	10			
75				92		0.01					
76			C2 Benzene	95	180.85	2.50	8	10			
77			#77 - 78 total	95		0.18					
78				95							
79			Benzene-C2	96	188.57	0.62	8	10			
80	150.8	303	C9H20	96	190.83	0.27	9	20			
81				96							

ck7/dis-nap

TABLE 2.11
EFFECT OF D-86 DISTILLATION RATES
ON RESIDUE AND LOSS

	Avg. Rate ^a	Condsr. Temp., °C	Min.to IBP., °C	Final Temp., °C	Resid %	Distill %	Loss %
AV Jet A:							
slow	2.96	55	30	274	2.20	96.21	1.59
fast	3.22	30	16	285	3.31	95.83	0.86
Crude Phenol:							
slow	2.35	55	18	265	5.75	92.45	1.79
fast	3.51	20	9	265	5.45	93.71	0.85
Rectisol							
Naphtha:							
slow	----	55	9.5	132	3.53	90.05	6.42
fast	4.67	0	6.6	132	2.80	96.35	0.85
Tar Oil:							
slow	0.99	55	23.5	303	9.66	87.68	2.66
fast	1.89	23	7.8	260	36.93	62.08	0.99

^a Average rate is in ml/min.

TABLE 2.12

AWPA P1-78 (REVISED) STANDARD
FOR COAL TAR CREOSOTE

The Creosote shall be a distillate derived
entirely from tar produced by the
carbonization of bituminous coal.

	<u>Not Less Than</u>	<u>Not More Than</u>
Water, Percent by Volume	-----	1.5
Matter Insoluble in Xylene Percent by Wt	-----	0.5
Specific Gravity		
Whole Creosote	1.050	-----
Fraction 235-315°C	1.027	-----
Fraction 315-355°C	1.095	-----
Distillation: Percent By Wt On a Water-Free Basis:		
Up To 210°C	-----	2.0
Up To 235°C	-----	12.0
Up To 270°C	10.0	35.0
Up To 315°C	40.0	65.0
Up To 355°C	60.0	77.0

TABLE 2.13

AWPA P13-85 STANDARD FOR COAL TAR CREOSOTE TO BE USED IN
THE TREATMENT OF MARINE PILES AND TIMBERS

The creosote shall be a distillate derived entirely from
tar produced by the carbonization of bituminous coal.

	<u>Not Less Than</u>	<u>Not More Than</u>
Water, Percent by Volume	----	1.5
Matter Insoluble in Xylene, Percent by Weight	----	0.15
Specific Gravity:		
Whole Creosote	1.080	----
Fraction 235-315°C	1.090	----
Fraction 315-355°C	1.105	----
Residue Above 355°C	1.160	----
Distillation: Percent By		
Wt on a Water-Free Basis		
Up to 210°C	----	2.0
Up to 235°C	----	12.0
Up to 270°C	20.0	40.0
Up to 315°C	45.0	65.0
Up to 355°C	65.0	75.0

TABLE 2.14

AWPA P2-85 STANDARD FOR CREOSOTE SOLUTIONS

The material shall be a pure coal tar product, derived from tar produced by the carbonization of bituminous coal. It may be either a coal tar distillate or a solution of coal tar in coal tar distillate.

	Grade A			Grade B			Grade C			Grade D		
	Not Less Than	More Than	Not	Not Less Than	More Than	Not	Not Less Than	More Than	Not	Not Less Than	More Than	Not
Composition: Coal Tar												
Distillate Percent By Volume	80			70			60			50		
Water: Percent By Volume		3.0			3.0			3.0			3.0	
Material Insoluble In Xylene: Percent By Weight		2.0			3.0			3.5			4.0	
Coke Residue: Percent By Weight		5.0			7.0			9.0			11.0	
Specific Gravity												
Whole Material	1.06	1.11		1.07	1.12		1.08	1.13		1.09	1.14	
Fraction 235/315°C	1.025			1.025			1.025			1.025		
Fraction 315/355°C	1.085			1.085			1.085			1.085		
Distillation By Weight On A Water Free Basis:												
Up to 210°C	5			5				5			5	
Up to 235°C	25			25				25			25	
Up to 315°C	36			34			32			30		
Up to 355°C	60			56			52			48		

TABLE 2.15

SPECIFIC GRAVITY OF AWPA CREOSOTE GRADES

<u>Standard</u>	<u>Specific Gravity</u>
P1 Coal Tar Creosote	1.05
P2 Creosote Solutions	1.06
P7 Creosote for Field Cuts	1.06
P13 Creosote for Marine Piles	1.08
P12 Creosote Solution for Marine Piles	1.09

Figure 2-1. ASTM D86 distillation profiles of rectisol naphtha, crude phenol, and tar oil as determined by ANG personnel.

Figure 2-2. D86 distillation profiles of tar oil, crude phenol, rectisol naphtha, and AV Jet A.

Figure 2-3. True boiling point distributions of tar oil for data from left-to-right from WRI, ANG (no symbols) and ERC (K=12).

Figure 2-4. ASTM D86 distillation profiles of AV Jet A, crude phenol, and tar oil.

Figure 2-5. ASTM D86 distillation profiles of specification JP-4, tar oil, and specification JP-8.

2-6. Proton NMR spectra of tar oil, crude phenol, and rectisol naphtha.

Figure 2-7. Proton NMR spectra of aviation Jet A, hydrogenation tar oil, and tar oil.

Figure 2-8. FID output for the crude phenol stream.

Figure 2-9. GC-FID output for the tar oil stream.

Figure 2-10. Crude phenol NMR spectrum and of each short column fraction.

Figure 2-11. Tar oil proton NMR spectrum and of each short column fraction.

Figure 2-12. Commercial aviation Jet A proton NMR spectrum and of each short column fraction.

Figure 2-13. Capillary gas chromatogram of nitrogen bases extracted from GPGA tar oils stream.

Figure 2-14. Capillary gas chromatogram of nitrogen compounds from GPGA tar oil stream from which FTIR and ITD data was obtained.

Figure 2-15. GC/MS analysis of rectisol naphtha.

Figure 2-16. GC/MS analysis of deodorized rectisol naphtha.

Figure 2-17. GC-FID output for the rectisol naphtha stream.

Figure 2-18. Molecular weight distributions of ASTM D86 distillation pot residues of tar oil. Pot resid C: 36.44% residue, final temp. 305C, 0% THF insoluble. Pot resid D: 23.96% residue, final temp. 318C, 0.24% THF insoluble.

Figure 2-19. Molecular weight distributions of tar oil before and after autoclave stability test.

Figure 3-1. D86 distillation profiles of blend, crude phenol bottoms, and tar oil overhead.

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