FEASIBILITY OF PRODUCING JET FUEL FROM GPGP BY-PRODUCTS

Quarterly Technical Progress Report
for the period
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EXECUTIVE SUMMARY

The tar oil stream has the greatest potential to be used as a jet fuel feedstock which warrants its detailed analysis. The oxygenated compounds present comprise about 36 wt% of this stream and are mainly phenolics such as phenol, methoxyphenol, naphthol, and their alkylated derivatives. However, non-polar oxygenated compounds such as dibenzofuran and its alkylated derivatives are also present. Basic compounds present in the tar oil (a minimum of 2.5 wt%) contain nitrogen and include mainly quinolines but pyridines and anilines as well. Aliphatics (a minimum of 8 wt%) are primarily normal alkanes ranging from C11 to C30. The aromatics (at least 48 wt%) are mostly naphthalene and its alkylated derivatives. However, phenanthrenes, fluorenes, and pyrenes are also present.

In the reaction investigation research, a test matrix has been designed for use in first stage data collection. Shell 424 catalyst will be used as the catalyst, and the ranges of temperature and pressure that will be evaluated are 622-728°F and 1500-2500 psig, respectively.

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1.0 GOALS AND OBJECTIVES

It is the goal of the national energy policy to foster an adequate supply of energy at reasonable cost. Domestic production supplies approximately 60% of the United States' petroleum requirements. 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 (DOD) 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 DOD requirements of Grade JP-4 turbine fuel, or 240,000 barrels, are consumed daily by the Air Force for aircraft operations. JP-4 is a naphtha-based fuel used primarily in the United States, while JP-8 is a kerosene-type fuel which is used abroad. Because of the need to assure adequate supplies of both types of turbine fuel at acceptable costs, the Air Force has investigated the characteristics, cost, and yield of these fuels when produced from tar sands, shale oil, and heavy oils, and is seeking similar data for coal-derived liquids.

One producer of coal-derived liquids is the Great Plains Gasification Plant (GPGP) in Beulah, North Dakota. The plant, which is located near several Air Force bases along the northern tier, currently produces over 137 million cubic feet per day of high-Btu synthetic natural gas (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 approximately 4,300 barrels per day, are available as potential sources of aviation jet fuel for the Air Force. Aviation fuels produced from the Great Plains liquids could become an indigenous fuel supply for the northern tier bases. Minot Air Force Base at Minot, North Dakota, is remote from jet fuel supplies and would benefit from this development if the jet fuel produced at Great Plains can meet all specifications and be cost competitive with other suppliers.

The primary 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 chemical and physical characteristics of the resulting turbine fuel products will be compared to petroleum-based fuels to determine their ability to meet 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 intermediates and products will only be characterized to indicate the feasibility of producing such a fuel.

2.0 TASK 1 - FEED STOCK CHARACTERIZATION

The tar oil, phenolic, and naphtha streams of the Great Plains Gasification Plant (GPGP) are being characterized to assess their potential for up-grading to JP4 or 8 or to other valuable by-products. In the February-May Quarterly Report, information concerning the analysis techniques and their results were presented. This report continues that discussion by providing additional information concerning the tar oil stream with an emphasis on oxygen and nitrogen containing compounds.

The oxygenated compounds were successfully concentrated from the total tar oil using short column chromatography (tar polars fraction) or base extraction (tar acids fraction) techniques. Nitrogen-containing compounds were isolated using an acid (HCl) extraction technique (tar base fraction). Analysis of the concentrated samples provide more detailed information on compounds and compound types present in the total tar oil sample, and a method is being developed to improve the accuracy of determination of concentrations in the total sample. The data are being collected in a data base, and a data reduction package has been developed to enable correlations to be made. The use of addition and/or subtraction subroutines on comprehensive gas chromatographic (GC) data of the total sample and its fractions will enable mass balancing and the development of more representative data on the GPGP streams. Results of correlations made with simplified plotting techniques are presented in this report and will be extensively used in the topical report on the characterization work.

2.1 Tar Oil Stream

The tar oil stream has the greatest potential to be used as a feedstock to produce jet fuel. However, it is a thermally unstable material containing a myriad of compounds. The tar oil compounds have been separated into four compound types to provide more information: aliphatics, aromatics or neutrals, polars or acids, and bases. The wt% of each compound type or fraction in the total tar oil has been determined. Nuclear magnetic resonance (NMR), and GC-MS (gas chromatography-mass spectrometry) techniques have been used to provide detail as to what compounds, and at what concentration, are present in the fractions. Elemental analysis on the total sample and each fraction enable mass balancing to be performed.

2.1.1 Thermal Stability and Distillation

Evaluation of simple ASTM D86 distillation data demonstrates the thermal instability of the tar oils. As depicted in Figure 1, the distillation curves and corresponding final boiling point can vary dramatically. The primary factor affecting this variability is the rate of heating of the sample. Figure 2 depicts data from different laboratories (average data from ANG Coal Gasification Company, Western Research Institute, and the UND Energy Research Center) for D86 data.

2.1.2 Short-Column Fractions

Short-column chromatography separation involves the eluting of aliphatics with pentane and isooctane, aromatics with methylene chloride, and polars with methanol from a highly activated silica gel column on which the total sample

Figure 1. Cumulative volume % vs. temperature in °C(°F) for ERC tar oil D-86 distillation data.

Figure 2. Cumulative volume% vs. temperature in °C(°F) for ANG tar oil, WRI tar oil, and ERC tar oil D-86 distillation data.

had been adsorbed (discussed last quarter). Table 1 presents the elemental data for the total tar oil sample and for the column fractions. The overall recovery was 92.4% of the moisture free (mf) organics charged. Water and some organics are irreversibly adsorbed on silica gel, and lighter organics are lost during the removal of eluting solvent under vacuum by rotary evaporation. Carbon and hydrogen recoveries were similar, 89%, and the error is magnified in the oxygen by difference value. Nitrogen values have not been corrected to take into account the high blank value of 0.1 to 0.2 wt% which was obtained during analysis. However, the high nitrogen content in the polars was expected, since many nitrogen compounds are highly polar. The high oxygen content in the polar fractions is due to the presence of phenolics, while in the aromatic fraction the oxygen content is due to dibenzofurans. The aliphatic fraction contains the highest hydrogen content but is also the smallest fraction.

NMR spectra of the various fractions were presented last quarter (Figure 2-11). Table 2 presents the proton distribution data as percent of total hydrogen observed for hydrogen in different structural units, and also indicates that recoveries (or mass balances) are satisfactory (data from Table 1 is included in the calculations). The aliphatic fraction exhibits a high concentration of aliphatic and methyl protons. In the aromatic fraction, the presence of alkyl-aromatic groups is shown by the high H-alpha value of 32.1. A lower H in CH₃ value indicates the average chain length of the alkyl groups is moderate. The H-Beta value of 5.6% indicates the potential presence of tetralin-like hydrogenated aromatics. Hydrocarbon portions of the molecular structure of the polar fraction contain mainly aromatics with methyl side chains.

Figure 3 depicts the difference between the total tar oil sample and the aromatic and polar fractions using GC data. The vertical axis is in cumulative area% of sequentially eluting compounds from a GC column (described last quarter). The horizontal axis is the eluting temperature of the compound. As will be seen, the use of these profiles provides more detail in that compounds that are higher in concentration are readily noticed. The compounds were identified by MS and often more than one isomer or compound with the same elemental composition was present.

In Figure 3 for the polar fraction (36 wt%), the compounds causing the area% increases at about 190°C are C1-phenols (5 and 12 area%). C2-phenols are present at 210°C. Various alkylated naphthols are present around 170°C. In general most of the polar fraction consists of the various isomers of alkylated phenols and naphthols. Small amounts of methoxyphenols are also present.

The aromatic fraction (48 wt%) shows the highest concentration of naphthalene (8 area%) and alkylated naphthalenes. Smaller amounts of indans and indenenes are present. Three ring aromatics such as fluorene (2 area%), phenanthrene (3 area%), pyrene (2 area%) and their alkylated derivatives are eluted at higher temperatures. Dibenzofuran (3 area%), and its alkylated derivatives, are the major oxygenated compounds in the aromatic fraction. In comparison to the total tar oil sample, the polars are found more often at lower temperatures while the aromatics are found in the higher temperature regions.

TABLE 1
ELEMENTAL ANALYSIS OF TAR OIL TOTAL AND COLUMN FRACTIONS

Fraction	Fraction (wt%)	Elemental Composition (wt%)						Karl Fischer water
		C	H	N	S	O + S ^c		
Total, AR ^a	100.0	83.76	8.83	0.52	0.39	6.89	1.20	
, mf ^b	98.8	84.78	8.80	0.53	0.39	5.89		
Aliphatic	7.9	85.24	14.66	0.11		0.00		
Aromatic	47.7	88.82	8.36	0.20		2.62		
Polar	35.7	75.46	7.62	0.85		16.07		
Recovery	92.4	89.69	89.36	77.41		118.5		

^a as received

^b moisture free

^c O + S by difference

TABLE 2
HYDROGEN DISTRIBUTION NMR ANALYSIS OF TAR OIL COLUMN FRACTIONS

Range (ppm)	Hydrogen Type	Total Sample (wt%)	Aliphatic (wt%)	Aromatic (wt%)	Polar (wt%)	Percent Recovery
9.0-5.9	Aromatic	28.3	1.8	27.6	40.0	99.2
4.4-3.5	Fluoranthene	2.4	0.2	3.2	0.0	68.8
3.5-3.3	Acenaphthene	0.5	0.1	1.1	0.0	114.4
3.3-1.9	H-Alpha	28.4	1.7	32.1	35.1	100.9
1.9-1.5	H-Beta	5.3	4.2	5.6	4.6	95.2
1.5-1.0	H-Aliphatic	23.4	64.2	17.8	14.3	100.1
1.0-.06	H in -CH ₃	11.7	27.8	12.6	6.0	107.3
		100.0	100.0	100.0	100.0	100.0
Normalized Wt% of Fraction		100.0	8.7	52.2	39.1	100.0
Normalized Wt% of H in Fraction		8.83	15.02	8.57	7.80	100.0

Figure 3. Cumulative GC area% vs. temperature in °C(°F) for tar oil, tar oil polar, and tar oil aromatic fractions.

Figure 4 compares the tar oil to the aliphatic fraction (8 wt%). The step increases caused by normal alkanes from C11 at 196°C to C24 at 391°C are readily apparent. Lower boiling alkanes would probably be lost during vacuum evaporation to remove pentane solvent and would be lost during the removal of octane solvent. Higher boiling normal alkanes up to C30 were present in this fraction. The low concentration of the aliphatic fraction in the tar oil obscures observing the alkane steps in the GC area% profile.

A computer subroutine is being prepared to correlate the total and fractional GC data, enabling mass balancing to be made in order to develop a more accurate picture of the tar oil stream. This will enable the prediction of potential end uses.

2.1.3 Acid-Base Neutral Fractions

Acid (28 wt%), base (2.5 wt%), and neutral (48 wt%) fractions were prepared by sequential extraction of a tar oil-pentane solution with aqueous base (NaOH), aqueous acid (HCl), and removing the pentane under vacuum, respectively. The closure was low at 79%. Figure 5 depicts the GC data for comparison to the acid and neutral fractions with each other and with the total tar oil. The plots shown in this figure are virtually identical to those shown in Figure 3, indicating the close similarity of these extraction and column fractions. However, the neutral fraction obtained by extraction does contain normal alkanes which are present in the aromatic fraction obtained by column separation. A fraction of major interest is the base fraction composed of nitrogen-containing compounds found in higher boiling regions, which is also seen in Figure 6. Table 3 presents detailed data on the GC-MS analysis of the base fraction. These data indicate that most individual compounds are present in small amounts even in this concentrated sample. Table 4 presents concentration data in area% of this fraction for pyridine, quinoline, aniline, and their alkylated derivatives.

3.0 TASK 2 - REACTION INVESTIGATIONS/PRODUCT ANALYSES

3.1 Staged Processing

To produce quality jet fuel from coal-derived liquids, the content of oxygen-, sulfur-, and nitrogen-containing compounds, also called heteroatoms, must be reduced to virtually nil, while the aromatic rings must be saturated with hydrogen without destroying the ring structures. A survey was undertaken to determine the most promising process, or combination of processes, which would produce these results. Of particular interest was the collection of information regarding suitable catalysts which might be used in this type of processing. The major results of the survey follow.

Currently, two different process approaches are taken. The first is a single-stage process in which heteroatom removal and subsequent hydrocracking and hydrogenation take place under high temperature/high pressure conditions. By varying the severity of the conditions, it is possible to control the composition of the final product. This process is usually performed with a Ni-W catalyst at temperatures of 680-720°F and pressures of 2000-2500 psig. Heteroatom concentration is reduced to less than 100 ppm using this method.

Figure 4. Cumulative GC area% vs. temperature in °C(°F) for tar oil and tar oil aliphatic fraction.

Figure 5. Cumulative GC area% vs. temperature in °C(°F) for tar oil, tar oil acids, and tar oil neutral fractions.

Figure 6. Cumulative GC area% vs. temperature in °C(°F) for tar oil and tar oil base fraction.

TABLE 3
TAR OIL BASES - COMPONENT DATA

GC #	b.p.		Component	Area% Over	Retention Index	Peak Area%	Elemental, atomic				
	°C	°F					C	H	N	O	S
1			C2 Pyridine	0	886	0.28	7	9	1		
2			C2 Pyridine	1	932	0.83	7	9	1		
3			C2 Pyridine	1	947	0.33	7	9	1		
4			C2 Pyridine	2	962	0.15	7	9	1		
5			C2 Pyridine	2	967	0.44	7	9	1		
6			C1 Pyridine	2	981	0.08	6	7	1		
7	184	363	Aniline	3	983	0.42	6	7	1		
8			C3 Pyridine	3	994	0.58	8	11	1		
9			C3 Pyridine	3	998	0.20	8	11	1		
10			C2 Pyridine	4	1006	0.28	7	9	1		
11			C3 Pyridine	4	1010	0.73	8	11	1		
12			C3 Pyridine	5	1018	0.23	8	11	1		
13			C3 Pyridine	5	1020	0.22	8	11	1		
14			C3 Pyridine	5	1026	0.15	8	11	1		
15			C3 Pyridine	5	1028	0.16	8	11	1		
16			C3 Pyridine	5	1031	0.29	8	11	1		
17			C3 Pyridine	6	1038	0.15	8	11	1		
18				6	1045	0.39					
19			C1 Aniline	6	1054	0.16	7	9	1		
20			C3 Pyridine	6	1061	0.27	8	11	1		
21			C4 Pyridine	6	1068	0.12	9	13	1		
22			C3 Pyridine	7	1071	0.32	8	11	1		
23			C4 Pyridine	7	1073	0.36	9	13	1		
24			C2 Aniline	7	1076	0.11	8	11	1		
25			C1 Aniline	8	1079	0.90	7	9	1		
26			C1 Aniline	8	1085	0.31	7	9	1		
27			C4 Pyridine	9	1091	0.87	9	13	1		
28			C4 Pyridine	10	1094	0.18	9	13	1		
29			C4 Pyridine	10	1098	0.32	9	13	1		
30			C2 Aniline	10	1102	0.10	8	11	1		
31			C4 Pyridine	10	1107	0.07	9	13	1		
32			C4 Pyridine	10	1111	0.13	9	13	1		
33			C4 Pyridine	10	1113	0.09	9	13	1		
34				10	1114	0.08					
35	229	444	Dihydroindole	11	1120	0.20	8	9	1		
36			C4 Pyridine	11	1123	0.14	9	13	1		
37			C5 Pyridine	11	1131	0.24	10	15	1		
38			C4 Pyridine	11	1134	0.14	9	13	1		
39			C5 Pyridine	12	1147	0.56	10	15	1		
40				12	1155	0.38					
41				12	1157	0.32					
42			C5 Pyridine	12	1161	0.08	10	15	1		
43			C2 Aniline	13	1164	0.39	8	11	1		
44				13	1166	0.18					
45				13	1171	0.15					

TABLE 3 CONTINUED

GC #	b.p.		Component	Area% Over	Retention Index	Peak Area%	Elemental, atomic				
	°C	°F					C	H	N	O	S
46			C2 Aniline	13	1175	0.36	8	11	1		
47				14	1178	0.25					
48			C2 Aniline	14	1181	0.43	8	11	1		
49				14	1184	0.16					
50	251	484	Tetrahydro- quino	15	1186	0.53	9	11	1		
51				15	1190	0.09					
52				15	1194	0.21					
53	218	424	Naphthalene	15	1199	0.12	10	8	1		
54				15	1208	0.21					
55				16	1210	0.21					
56				16	1213	0.09					
57			C5 Pyridine	16	1216	0.15	10	15	1		
58			C5 Pyridine	16	1219	0.12	10	15	1		
59			C5 Pyridine	16	1225	0.13	10	15	1		
60				16	1227	0.13					
61				16	1231	0.19					
62	251	484	Tetrahydro- quino	17	1234	0.44	9	11	1		
63				17	1240	0.17					
64				17	1246	0.10					
65	238	460	Quinoline	23	1251	5.68	9	7	1		
66			C5 Pyridine	23	1258	0.31	10	15	1		
67				23	1270	0.24					
68	243	469	Isoquinoline	25	1273	1.70	9	7	1		
69				25	1280	0.08					
70				25	1288	0.24					
71				26	1296	0.14					
72				26	1298	0.21					
73				26	1315	0.16					
74				26	1317	0.14					
75			C1 Quinoline	29	1322	2.97	10	9	1		
76				29	1327	0.09					
77			C1 Quinoline	30	1332	0.96	10	9	1		
78				30	1338	0.08					
79				30	1340	0.15					
80			C1 Quinoline	31	1342	0.84	10	9	1		
81				32	1345	0.35					
82				32	1353	0.15					
83			C1 Quinoline	32	1356	0.41	10	9	1		
84				32	1361	0.09					
85				32	1362	0.17					
86			C1 Quinoline	35	1368	2.21	10	9	1		
87			C1 Quinoline	35	1374	0.92	10	9	1		
88				36	1379	0.17					
89				36	1387	0.13					
90			C1 Quinoline	36	1389	0.55	10	9	1		

TABLE 3 CONTINUED

GC #	b.p.		Area% Over	Retention Index	Peak Area%	Elemental, atomic				
	°C	°F				C	H	N	O	S
91			C2 Quinoline 37	1392	0.90	11	11	1		
92			C1 Quinoline 39	1394	1.62	10	9	1		
93			39	1397	0.57					
94			40	1401	0.18					
95			C1 Quinoline 40	1406	0.45	10	9	1		
96			C2 Quinoline 41	1410	0.83	11	11	1		
97			41	1417	0.18					
98			C2 Quinoline 42	1419	0.60	11	11	1		
99			42	1426	0.08					
100			42	1435	0.12					
101			C2 Quinoline 44	1437	1.72	11	11	1		
102			C2 Quinoline 44	1444	0.39	11	11	1		
103			44	1453	0.11					
104			44	1455	0.32					
105			C2 Quinoline 45	1459	0.59	11	11	1		
106			C2 Quinoline 46	1461	1.19	11	11	1		
107			47	1464	0.37					
108			C2 Quinoline 47	1469	0.66	11	11	1		
109			C2 Quinoline 48	1471	0.81	11	11	1		
110	270	518	Phenyl Pyri- dine 50	1475	1.84	11	9	1		
111			C2 Quinoline 51	1479	0.67	11	11	1		
112			51	1486	0.16					
113			51	1489	0.21					
114			C2 Quinoline 51	1492	0.61	11	11	1		
115			52	1497	0.21					
116			C3 Quinoline 53	1501	0.95	12	13	1		
117			C2 Quinoline 53	1510	0.57	11	11	1		
118			C2 Quinoline 54	1513	0.28	11	11	1		
119			C3 Quinoline 54	1524	0.69	12	13	1		
120			C3 Quinoline 54	1528	0.29	12	13	1		
121			55	1532	0.36					
122	295	563	Diphenyl Am- ine 56	1535	0.76	12	13	1		
123			C3 Quinoline 57	1537	1.15	12	13	1		
124			57	1543	0.26					
125			57	1545	0.40					
126			C3 Quinoline 58	1548	0.21	12	13	1		
127			58	1550	0.18					
128			58	1555	0.38					
129			59		0.72					
130			C3 Quinoline 59	1561	0.24	12	13	1		
131			C3 Quinoline 60	1565	0.36	12	13	1		
132			C3 Quinoline 60	1568	0.82	12	13	1		
133			C3 Quinoline 61	1573	0.36	12	13	1		
134			62		1.09					
135			62		0.36					

TABLE 3 CONTINUED

GC #	b. p.		Component	Area% Over	Retention Index	Peak Area%	Elemental, atomic				
	C	F					C	H	N	O	S
136	295	563	Diphenyl Am- ine	63	1591	0.84	12	11	1		
137				63		0.24					
138				63		0.23					
139				64		0.45					
140				64		0.43					
141				65		0.30					
142				65		0.14					
143				65		0.16					
144				65		0.21					
145				65		0.08					
146				66		0.58					
147				66		0.27					
148				67		0.46					
149				67		0.24					
150				67		0.31					
151				67		0.22					
152				68		0.22					
153				68		0.22					
154			Indeno- pyridine	69	1665	1.08	12	9	1		
155				69		0.15					
156				69		0.45					
157				70		0.20					
158				70		0.52					
159				70		0.28					
160				71		0.44					
161				71		0.50					
162				71		0.13					
163				72		0.38					
164				72		0.10					
165				72		0.27					
166			C1 Aza- fluorene	73	1730	0.62	13	11	1		
167				73		0.12					
168				73		0.23					
169				74		0.32					
170				74		0.14					
171				74		0.35					
172				74		0.19					
173				74		0.26					
174				75		0.30					
175				75		0.23					
176				75		0.30					
177				76		0.48					
178				76		0.20					
179				76		0.42					
180				77		0.52					

TABLE 3 CONTINUED

GC #	h.p.		Component	Area% Over	Retention Index	Peak Area%	Elemental, atomic				
	°C	°F					C	H	N	O	S
181				77		0.13					
182				77		0.17					
183				77		0.21					
184	338	640	Benzo- quinoline	79	1823	1.93	13	9	1		
185				80		0.44					
186	338	640	Benzo- quinoline	80	1832	0.53	13	9	1		
187				81		0.28					
188				81		0.18					
189	338	640	Benzo- quinoline	83	1858	1.97	13	9	1		
190				83		0.28					
191				83		0.26					
192				84		0.91					
193				85		0.64					
194				85		0.37					
195				85		0.25					
196				86		0.19					
197				86	1929	0.52	14	11	1		
198				87	1938	0.39	14	11	1		
199				87	1943	0.38	14	11	1		
200				87	1946	0.39	14	11	1		
201				88	1955	0.30	14	11	1		
202				88	1959	0.47	14	11	1		
203				88		0.29					
204				89		0.31					
205				89		0.32					
206				89	1980	0.24	14	11	1		
207				90		0.34					
208				90		0.17					
209				90		0.17					
210				90		0.31					
211				90		0.20					
212				91		0.23					
213				91		0.25					
214				91	2042	0.40					
215				92		0.40					
216				92		0.16					
217				92		0.32					
218				92		0.29					
219				93		0.14					
220				93		0.18					
221				93		0.28					
222				93		0.22					
223				94		0.62					
224				94		0.23					
225				94		0.27					

TABLE 3 CONTINUED

GC #	b.p.		Component	Area% Over	Retention Index	Peak Area%	Elemental, atomic				
	°C	°F					C	H	N	O	S
226				95		0.16					
227				95		0.38					
228				95		0.10					
229				95		0.39					
230				96		0.15					
231				96		0.17					
232				96		0.14					
233				96		0.12					
234				96		0.13					
235				97	2209	0.37					
236				97		0.12					
237				97		0.11					
238				97	2273	0.25					
239				97		0.14					
240				98	2289	0.39					
241				98		0.09					
242				98		0.14					
243				98		0.08					
244				98		0.34					
245				98		0.11					
246				98		0.12					
247				99		0.16					
248				99		0.10					
249				99		0.10					
250				99		0.15					
251				99		0.13					

TABLE 4
TAP OIL BASES - ISOMER DATA

Component	No. of Isomers	Area Percent
Pyridine	0	0.00
C1 Pyridine	1	0.08
C2 Pyridine	6	2.31
C3 Pyridine	11	3.30
C4 Pyridine	10	2.42
C5 Pyridine	<u>7</u>	<u>1.59</u>
TOTAL	35	9.70
Quinoline	1	5.68
C1 Quinoline	9	10.93
C2 Quinoline	13	8.97
C3 Quinoline	9	5.07
Benzoquinoline	<u>3</u>	<u>4.43</u>
TOTAL	35	35.08
Aniline	1	0.42
C1 Aniline	3	1.37
C2 Aniline	<u>5</u>	<u>1.39</u>
TOTAL	9	3.18

The second method employs a two-stage process. In the first, high-severity, stage, the heteroatoms are removed using commercially-available catalysts. During this stage, nitrogen must be removed to concentrations of less than 10 ppm in order not to poison the second-stage catalyst. The second stage is a low-severity stage in which a noble metal catalyst is employed to saturate the aromatic ring structure without destroying it. With this system, it is possible to obtain products which contain less than 5% aromatics.

At the University of North Dakota Energy Research Center (UNDERC), processing of the GPGP by-product streams is being performed using a two-stage process in which removal of the heteroatoms takes place in the first stage and hydrogenation of the ring structures takes place in the second stage. To efficiently obtain the information required for determination of the "optimum" conditions necessary for heteroatom removal in the first stage processing, a statistical experimental design will be used. It is not expected that the heteroatom content of the product of the first stage will be a linear function of the temperature and pressure of the process. Therefore, a central

composite design for two factors will be used to collect the experimental data. This will allow the fitting of a general quadratic equation for smoothing and prediction. This class of design allows the experimenter to build upon a two-level factorial design and adds a set of axial points, which, together with a center point, allow the estimation of all pure quadratic terms.

Table 5 shows the matrix which has been designed for use in first-stage data collection. For these experiments, Shell 424 will be used as the catalyst, and the ranges of temperature and pressure that will be evaluated will be 622-728°F and 1500-2500 psig, respectively. Usually, five center point replications are performed with this type of analysis. Because the variability of the equipment is known and can be factored in, only two center point replications will be performed. The matrix will be randomized to ensure that all results are independent.

Following collection of the data, each response will be analyzed via computer regression analysis. The full model will be fit, and a check made for outlying data points. After a check is made for lack of fit of the quadratic equation, any unnecessary terms will be eliminated from the quadratic equation, and another check will be performed for lack of fit. Predictions made from the resulting equations will be displayed via contour plots, and the predicted "best" run conditions will be determined. A final run will be made at these conditions to verify the results.

When the first-stage testing has been completed, second-stage testing will begin. It has not been decided which particular catalyst will be used in the second stage. One to two runs will be performed at catalyst-specific conditions to determine the effectiveness of the catalyst/conditions at hydrogenation without hydrocracking.

TABLE 5
MATRIX FOR STUDYING EFFECTS OF TEMPERATURE & PRESSURE
IN FIRST-STAGE PROCESSING TO REMOVE HETEROATOMS

<u>Run</u>	<u>Temperature</u> (°F)	<u>Pressure</u> (psig)	
1	728	2500	} factorial points
2	728	1500	
3	622	2500	
4	622	1500	
5	675	2710	} star points
6	675	1300	
7	750	2000	
8	600	2000	
9	675	2000	} center points
10	675	2000	

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