DOE/MC/25020--3126

DE93 000206

**Development of High Energy Density Fuels
From Mild Gasification of Coal**

Final Report

Work Performed Under Contract No.: DE-AC21-88MC25020

**For
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December 1991

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TABLE OF CONTENTS

	<u>Page No.</u>
List of Figures	
List of Tables	
1.0 <u>EXECUTIVE SUMMARY</u>	1
1.1 Background & DOE Perspective	1
1.2 Contract Objectives	2
1.3 Task Breakdown Structure	2
1.4 Feedstocks	8
1.5 High Energy Density Fuels (HEDF)	9
1.6 Process Screening Alternatives	10
1.7 Experimental Procedures	11
1.8 Summary of Results of COALITE Operations	12
1.9 Summary of Results of Colorado Shale Oil Operations	16
2.0 <u>EXPERIMENTAL PROCEDURES</u>	22
2.1 Overview	22
2.2 Bench-Scale Fixed-Bed Hydrotreating Unit	23
2.3 Bench-Scale Fixed-Bed Hydrocracking Unit	25
2.4 Bench-Scale LC-Fining Unit	28
2.5 Continuous Bench Coking Unit	30
2.6 Laboratory Extraction Unit	32
2.7 4-in Batch Fractionation Unit	32
2.8 Equilibrium Flash Vaporization Pilot Unit	32
2.9 Laboratory Batch Distillation Units	32
2.10 Clay Treating Units	34
2.11 Pilot Plant LC-Fining Unit	34
2.12 Pilot Plant Fixed-Bed Hydroprocessing Unit	36
2.13 Calculation Procedures and Analytical Methods	38

TABLE OF CONTENTS

	<u>Page No</u>
3.0 <u>RAW SYNFUEL FEEDSTOCK ANALYSES</u>	43
3.1 COALITE Feedstock	43
3.2 Colorado Shale Oil Feedstock	51
4.0 <u>SUMMARY OF SCREENING PROGRAM OPERATIONS (TASK 3)</u>	81
4.1 Overview	81
4.2 COALITE Operations	81
4.2.1 Feedstock Preparation	81
4.2.2 Virgin Distillate Hydrotreating Campaigns	82
4.2.3 Virgin Atmospheric Resid Cracking Campaigns	84
4.2.3.1 LC-Fining (Hydrocracking)	94
4.2.3.2 Delayed Coking	94
4.2.4 Cracked Distillate Hydrotreating Campaigns	100
4.2.4.1 Hydrotreating of LC-Finate Distillates	100
4.2.4.2 Hydrotreating of Coker Distillates	100
4.2.5 Two-Step Selective Hydrocracking Campaigns	100
4.3 Colorado Shale Oil Operations	112
4.3.1 Feedstock Preparation	112
4.3.2 Virgin Distillate Hydrotreating Campaigns	112
4.3.3 Virgin Atmospheric Resid Cracking Campaigns	119
4.3.3.1 LC-Fining (Hydrocracking)	119
4.3.3.2 Delayed Coking	119
4.3.4 Cracked Distillate Hydrotreating Campaigns	119
4.3.4.1 Hydrotreating of LC-Finate Distillates	124
4.3.4.2 Hydrotreating of Coker Distillates	124
4.3.5 Two-Step Selective Hydrocracking Campaigns	124
4.3.6 Extraction Studies	134

TABLE OF CONTENTS

	<u>Page No</u>
5.0 <u>SUMMARY OF RESULTS OF COALITE SCREENING OPERATIONS</u>	138
5.1 Overview	138
5.2 Virgin Distillate Hydrotreating	131
5.3 Virgin Atmospheric Resid Cracking	181
5.3.1 LC-Fining	181
5.3.2 Delayed Coking	181
5.4 Cracked Distillate Hydrotreating	187
5.4.1 Hydrotreating of LC-Finate Distillates	187
5.4.2 Hydrotreating of Coker Distillates	187
5.5 Two-Step Selective Hydrocracking of Vacuum Gas Oil (VGO)	200
5.5.1 Overview of Early Results	200
5.5.2 Subtask 3.1/3.2 Scope	203
5.5.3 Subtask 3.1/3.2 Results	205
5.5.3.1 LC-Fining Studies	207
5.5.3.2 Fixed-Bed HDN Studies	208
5.5.3.3 Fixed-Bed Selective Hydrocracking Studies	208
5.5.3.4 Hydrotreating Studies	216
5.5.3.5 HEDF Finishing	216
6.0 <u>SUMMARY OF RESULTS OF COLORADO SHALE OIL SCREENING OPERATIONS</u>	222
6.1 Overview	222
6.2 Virgin Distillate Hydrotreating	222
6.3 Virgin Atmospheric Resid Cracking	252
6.4 Cracked Distillate Hydrotreating	259
6.5 Two-Step Selective Hydrocracking of Vacuum Gas Oil (VGO)	259
6.6 Extraction Studies	262

TABLE OF CONTENTS

	<u>Page No</u>
7.0 <u>SUMMARY OF RESULTS OF PILOT PLANT SAMPLE PREPARATION</u> (Task 5)	267
7.1 Overview	267
7.2 LC-Fining Operations	268
7.3 Fixed-Bed Hydrodenitrogenation Operations	270
7.4 Fixed-Bed Selective Hydrocracking Operations	272
7.5 Post-Hydroprocessing Operations	272
7.6 HEDF Assays	274
8.0 <u>SUMMARY OF REFINERY UPGRADING ECONOMIC ASSESSMENT</u> (Task 4)	281
8.1 Basis Of Linear Programming Model	281
8.2 Results of Linear Programming Model Studies	288
8.3 Economics Sensitivity Studies	300
8.4 Conclusions and Recommendations	311
9.0 <u>REFERENCES</u>	312
10.0 <u>INVENTION DISCLOSURES</u>	313
11.0 <u>ACKNOWLEDGEMENTS</u>	314

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page #</u>
1.8-1	Task 3 Screening Program Results	17
1.8-2	Final COALITE HEDF Test Fuel Properties	19
2.11-1	Formulas for Selected Hydroprocessing Parameters	40
3.1-1	Analyses of Narrow-Boiling COALITE Distillates	46
3.1-2	G.C./M.S. Analysis of 200-550F COALITE	48
3.1-3	NMR Spectroscopy of 390-650F COALITE	58
3.2-1	Analyses of Narrow-Boiling Colorado Shale Oil Distillates	71
4.2.1-1	Hydrotreating Feedstock Analyses of Raw COALITE Mid-Distillate	83
4.2.2-1	Summary of Operating Conditions for Fixed-Bed COALITE Hydrotreating Tests(FB17A1-49)	85
4.2.2-2	Summary of Operating Conditions for Fixed-Bed COALITE Hydrotreating Tests(FB30-36)	89
4.2.2-3	Summary of Operating Conditions for Fixed-Bed COALITE Hydrotreating Tests(FB169-177)	90
4.2.2-4	Summary of Operating Conditions for Fixed-Bed COALITE Hydrotreating Tests(FB94-104)	91
4.2.2-5	Summary of Operating Conditions for Fixed-Bed COALITE Hydrotreating Tests(FB146-147)	92
4.2.2-6	Summary of Operating Conditions for Fixed-Bed COALITE Hydrotreating Tests(FB135-138)	93
4.2.3.1-1	Feedstock Assays for LC-Fining of COALITE Residua	95
4.2.3.1-2	Summary of Operating Conditions for LC-Fining Tests (BLCF86-101)	96
4.2.3.1-3	Summary of Operating Conditions for LC-Fining Tests (BLCF90-95)	97
4.2.3.2-1	Assays of Delayed Coking COALITE Feedstocks	98
4.2.3.2-2	Summary of Operating Conditions for Delayed Coking of COALITE	99
4.2.4.1-1	Assays of COALITE Mid-distillate LC-Finate Feeds to Hydrotreating	101
4.2.4.1-2	Summary of Operating Conditions for Fixed-Bed Hydrotreating of Hydrocracked COALITE Distillate (FB44-105)	102
4.2.4.1-3	Summary of Operating Conditions for Fixed-Bed Hydrotreating of Hydrocracked COALITE Distillate (FB156-158)	103
4.2.4.2-1	Assays of COALITE Coker Mid-distillate Feeds to Hydrotreating	104
4.2.4.2-2	Summary of Operating Conditions for Fixed-Bed Hydrotreating of Thermally Processed COALITE Distillate (FB45-127)	105
4.2.5-1	Assays of COALITE VGO Feedstocks To Fixed- Bed Hydrocracking	108
4.2.5-2	Summary of Operating Conditions for Fixed-Bed Hydrocracking of COALITE(FBHC1-17)	109
4.2.5.-3	Summary of Operating Conditions for Fixed-Bed Hydrocracking of COALITE(FBHC18-27)	110
4.2.5-4	Assays of Selectively Hydrocracked COALITE Mid- Distillate Feed to Hydrotreating	111

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page #</u>
4.3.1-1	Assay of Raw Colorado Shale Oil Mid-Distillate Feedstock to Hydrotreating	113
4.3.2-1	Summary of Operating Conditions for Fixed-Bed Colorado Shale Oil Hydrotreating (FB106-130)	114
4.3.2-2	Summary of Operating Conditions for Fixed-Bed Colorado Shale Oil Hydrotreating (FB148-155)	117
4.3.2-3	Summary of Operating Conditions for Fixed-Bed Colorado Shale Oil Hydrotreating (FB159-164)	118
4.3.3.1-1	Summary of Operating Conditions for LC-Fining of Colorado Shale Oil (BLCF89-1/89-5)	120
4.3.3.1-2	Summary of Operating Conditions for LC-Fining of Colorado Shale Oil (BLCF91-99)	121
4.3.3.2-1	Assay of Delayed Coking Colorado Shale Oil-Derived Feedstock	122
4.3.3.2-2	Summary of Operating Conditions for Delayed Coking of Colorado Shale Oil (CBC65-66)	123
4.3.4.1-1	Assay of Colorado Shale Oil LC-Finate Mid-Distillate to Hydrotreating	125
4.3.4.1-2	Summary of Operating Conditions for Fixed-Bed Hydrotreating of Hydroprocessed Colorado Shale Oil Distillate (FB143-145)	126
4.3.4.2-1	Assay of Colorado Shale Oil Delayed Coker Mid-Distillate to Hydrotreating	127
4.3.4.2-2	Summary of Operating Conditions for Fixed-Bed Hydrotreating of Thermally Processed Colorado Shale Oil Distillate (FB131-134)	128
4.3.5-1	Assay of Colorado Shale Oil VGO Feedstocks To Fixed-Bed Hydrocracking	130
4.3.5-2	Summary of Operating Conditions for Fixed-Bed Colorado Shale Oil Hydrocracking(FBHC5-12)	131
4.3.5-3	Summary of Operating Conditions for Fixed-Bed Colorado Shale Oil Hydrocracking(FBHC28-35)	132
4.3.5-4	Summary of Operating Conditions for Fixed-Bed Hydrotreating of Hydroprocessed Colorado Shale Oil Distillate (FB186-187)	133
4.3.5-5	Summary of Operating Conditions for Fixed-Bed Hydrotreating of Hydrocracked Colorado Shale Oil Distillate (FB188-189)	135
4.3.6-1	Results of Extraction of Hydrotreated Colorado Shale Oils	137
5.2.1-1	Key Specifications for Military Turbine Fuels	141
5.2.1-2	Assays of Distillate Hydrotreating Catalysts	143
5.2.1-3A	Summary of Operating Results for Fixed-Bed COALITE Hydrotreating (FB17A1-49)	145
5.2.1-3B	Summary of Properties of Full-Range Hydrotreated COALITE From Fixed-Bed Hydrotreating (FB17A1-49)	149
5.2.1-4A	Summary of Operating Results for Fixed-Bed COALITE Hydrotreating (FB30/36-2)	153
5.2.1-4B	Summary of Properties of Full-Range Hydrotreated COALITE From Fixed-Bed Hydrotreating (FB30/36-2)	154

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page #</u>
5.2.1-5A	Summary of Operating Results for Fixed-Bed COALITE Hydrotreating (FB169-177)	155
5.2.1-5B	Summary of Properties of Full-Range Hydrotreated COALITE From Fixed-Bed Hydrotreating (FB169-77)	156
5.2.1-6A	Summary of Operating Results for Fixed-Bed COALITE Hydrotreating (FB94-104)	157
5.2.1-6B	Summary of Properties of Full-Range Hydrotreated COALITE From Fixed-Bed Hydrotreating (FB94-104)	158
5.2.1-7A	Summary of Operating Results for Fixed-Bed COALITE Hydrotreating (FB146-47)	159
5.2.1-7B	Summary of Properties of Full-Range Hydrotreated COALITE From Fixed-Bed Hydrotreating (FB146-47)	160
5.2.1-8A	Summary of Operating Results for Fixed-Bed COALITE Hydrotreating (FB135-38)	161
5.2.1-8B	Summary of Properties of Full-Range Hydrotreated COALITE From Fixed-Bed Hydrotreating (FB135-38)	162
5.3.1-1	Summary of Operating Conditions for LC-Fining of COALITE (BLCF86-1/90)	183
5.3.1-2	Summary of Operating Conditions for LC-Fining of COALITE (BLCF92-101)	184
5.3.1-3	Summary of Properties of Full-Range LC-Finates COALITE (BLCF86-90)	185
5.3.1-4	Summary of Properties of Full-Range LC-Finates COALITE (BLCF92-101)	186
5.4.1-1A	Summary of Operating Results for Fixed-Bed Hydrotreating of Hydrocracked COALITE Distillate (FB44-105)	188
5.4.1-1B	Summary of Properties of Full-Range Hydrotreated COALITE From Fixed-Bed Hydrocracking(FB44-105)	189
5.4.1-2A	Summary of Operating Results for Fixed-Bed Hydrotreating of Hydrocracked COALITE Distillate (FB156-158)	190
5.4.1-2B	Summary of Properties of Full-Range Hydrotreated COALITE From Fixed-Bed Hydrocracking(FB156-58)	191
5.4.1-3A	Summary of Operating Results for Fixed-Bed Hydrocracking of COALITE(FBHC1-17)	192
5.4.1-3B	Summary of Properties of Hydrocrackates From Fixed-Bed COALITE Hydrocracking(FBHC1-17)	193
5.4.1-4A	Summary of Operating Results for Fixed-Bed Hydrocracking of COALITE(FBHC18-27)	194
5.4.1-4B	Summary of Properties of Hydrocrackates From Fixed-Bed COALITE Hydrocracking(FBHC18-27)	195
5.4.1-5A	Summary of Operating Results for Fixed-Bed Hydrotreating of Hydrocracked COALITE Distillate (FB165-168)	196
5.4.1-5B	Summary of Properties of Full-Range Hydrotreated COALITE From Fixed-Bed Hydrocracking(FB165-68)	197
5.4.2-1A	Summary of Operating Results for Fixed-Bed Hydrotreating of Thermally Processed COALITE(FB45/126/127)	198

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page #</u>
5.4.2-1B	Summary of Properties of Full-Range Hydrotreated COALITE From Delayed Coking(FB45/126-7)	199
5.5-1	Comparison of COALITE-Derived HEDF Fuels Produced Via Two Hydroprocessing Schemes	202
5.5.3.1-1	Summary Results for LC-Fining Run 6LCF-11	209
5.5.3.2-1	Results of Fixed-Bed Hydrotreating of 975F-COALITE LC-Finate	210
5.5.3.3-1	Summary of Fixed-Bed Hydrocracking Run FBHC-37	213
5.5.3.3-2	Summary of Fixed-Bed Hydrocracking Run FBHC-38	214
5.5.3.3-3	Summary of Fixed-Bed Hydrocracking Run FBHC-39	215
5.5.3.3-4	Summary of Fixed-Bed Hydrocracking Run FBHC-40	217
5.5.3.3-5	Comparison of Run FBHC-40F with FBHC-41	218
5.5.3.4-1	Summary of Fixed-Bed Hydrotreating Run FB-214	219
5.5.3.5-1	COALITE Derived HEDF Fuel Properties for Subtask 3.2 Screening Program	220
6.2-1A	Summary of Operating Results for Fixed-Bed Colorado Shale Oil Hydrotreating(FB148-64)	223
6.2-1B	Summary of Properties of Full-Range Hydrotreated Colorado Shale Oil From Fixed-Bed Hydrotreating (FB148-164)	225
6.2-2A	Summary of Operating Results for Fixed-Bed Colorado Shale Oil Hydrotreating(FB106-130)	227
6.2-2B	Summary of Properties of Full-Range Hydrotreated Colorado Shale Oil From Fixed-Bed Hydrotreating (FB106-130)	230
6.2-3A	Summary of Operating Results for Fixed-Bed Hydrotreating of Hydroprocessed Colorado Shale Oil Distillate(FB186-87)	233
6.2-3B	Summary of Properties of Fixed-Bed Hydrotreated Products from Hydroprocessed Colorado Shale Oil Distillate(FB186-87)	234
6.2-4A	Summary of Operating Results of Fixed-Bed Hydrotreated Products from Hydroprocessed Colorado Shale Oil Distillate(FB143-45)	235
6.2-4B	Summary of Properties of Fixed-Bed Hydrotreated Products from Hydroprocessed Colorado Shale Oil Distillate(FB143-145)	236
6.2-5A	Summary of Operating Results for Fixed-Bed Colorado Shale Oil Hydrocracking(FBHC28-35)	237
6.2-5B	Summary of Properties of Hydrocrackates from Fixed-Bed Colorado Shale Oil Hydrocracking(FBHC28-35)	238
6.2-6A	Summary of Operating Results for Fixed-Bed Colorado Shale Oil Hydrocracking(FBHC5-12)	239
6.2-6B	Summary of Properties of Hydrocrackates from Fixed-Bed Colorado Shale Oil Hydrocracking(FBHC5-12)	240
6.3-1A	Summary of Operating Results for LC-Fining of Colorado Shale Oil (BLCF89-1/89-5)	253
6.3-1B	Summary of Properties of LC-Finates from Colorado Shale Oil(BLCF89-1/89-5)	254

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page #</u>
6.3-2A	Summary of Operating Results for LC-Fining of Colorado Shale Oil (BLCF91-99)	255
6.3-2B	Summary of Properties of LC-Finates from Colorado Shale Oil(BLCF91-99)	256
6.3-3A	Summary of Operating Results for Fixed-Bed Hydrotreating of Thermally Processed Colorado Shale Oil Distillate(FB131-134)	257
6.3-3B	Summary of Properties of Hydrotreated Products from Fixed-Bed Hydrotreating of Thermally Processed Colorado Shale Oil Distillates(FB131-34)	258
6.4-1A	Summary of Operating Results for Fixed-Bed Hydrotreating of Hydrocracked Colorado Shale Oil Distillate(FB188-189)	260
6.4-1B	Summary of Properties of Fixed-Bed Hydrotreated Products from Hydrocracked Colorado Shale Oil Distillate(FB188-189)	261
6.6-1	Results of Solvent Extraction of Hydrotreated Colorado Shale Oils	265
6.6-2	Lab Extraction Study Results	266
7.2-1	Run 6LCF-14 LC-Fining Production Run Summary	269
7.3-1	Run 6LCF-5 Fixed-Bed Hydrodenitrogenation Run Summary	271
7.4-1	Run 6LCF-16 Fixed-Bed Selective Hydrocracking Run Summary	273
7.5-1	Summary of Patch Distillation of Selectively Hydrocracked LC-Finate Gas Oils	275
7.5-2	Summary of Optimum Blending Study of HEDF Test Fuel Cuts From Batch Fractionation	276
7.5-3	Summary of Bentonite Clay Treating of HEDF Test Fuels	277
7.6-1	Summary of Final COALITE HEDF Test Fuel Properties	278
8.1-1	HEDF Specifications Used	282
8.1-2	Process Alternatives Included	283
8.1-3	Feedstock Cost/Co-Product Price Bases	284
8.2-1	Product Comparison with Specifications	291
8.2-2	Investment Summary - Maximum HEDF Jet Fuel	292
8.2-3	Baseline Cases Economic Breakdown Summary	293
8.2-4	Economic Summary	295
8.3-1	Sensitivity Cases Economic Summary	299
8.3-2	Product Comparison with Specifications	308

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page #</u>
1.8-1	Effect of H Content & API Gravity on Energy Density	18
2.2-1	Schematic Flow Diagram of Fixed-Bed Hydroprocessing Pilot Unit	24
2.3-1	Schematic of Bench-Scale Fixed-Bed Hydrocracking Unit	26
2.4-1	Schematic of Autoclave-Based LC-Fining Unit	29
2.5-1	Schematic of Continuous Bench Coking Unit	31
2.7-1	Schematic of Four-in Batch Fractionation Unit	33
3.1-1	Consolidated ASTM D86/D1160 Distillations of Dewatered COALITE	44
3.1-2	ASTM Distillations of Synfuel Feedstocks	45
3.1-3	Wt% Distillate Yield As a Function of VABP of Cut	47
3.1-4	H/C Atomic Ratio of COALITE Distillate Cuts As A Function of VABP of Cut	52
3.1-5	API Gravity of COALITE Distillates As A Function of VABP of Cut	53
3.1-6	Nitrogen Content As A Function of VABP Of Cut	54
3.1-7	Wt% Oxygen Content As A Function of VABP Of Cut	55
3.1-8	Wt% Sulfur Content As A Function of VABP Of Cut	56
3.1-9	PONA Analysis of Selected COALITE Distillates As A Function of VABP Of Cut	57
3.1-10	Hydrogen Distribution by HNMR Spectroscopy As A Function of VABP Of Cut	59
3.1-11	Calculated Carbon Distributions From HNMR As A Function of VABP Of Cut	60
3.1-12	H/C Ratios From HNMR Spectroscopy As A Function of VABP Of Cut	61
3.1-13	Bromine No As A Function of VABP Of Cut	62
3.1-14	Refractive Index @20C As A Function of VABP Of Cut	63
3.1-15	API Gravity As A Function of Refractive Index	64
3.1-16	H/C Atomic Ratio As A Function of Refractive Index	65
3.1-17	Hydrogen Aromaticity As A Function of Refractive Index of Distillate Cuts	66
3.1-18	Carbon Aromaticity As A Function of Refractive Index of Distillate Cuts	67
3.2-1	Consolidated ASTM Distillation of Raw Colorado Shale Oil Feedstock	69
3.2-2	ASTM Distillations of Synfuel Feedstocks	70
3.2-3	H/C Atomic Ratio of Synfuel Distillates As a Function of VABP	72
3.2-4	API Gravity of Synfuel Distillates As a Function of VABP	73
3.2-5	Nitrogen Content of Synfuel Distillates As a Function of VABP	74
3.2-6	Wt% Sulfur of Synfuel Distillates as a Function of VABP	75
3.2-7	PONA Analysis of Synfuel Distillates as a Function of VABP	76
3.2-8	NMR Carbon Distribution for COALITE and Colorado Shale Oil as a Function of Distillate VABP	77
3.2-9	Refractive Index of Synfuel Distillates as a Function of VABP	78

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page #</u>
3.2-10	NMR Carbon Distribution for COALITE & Colorado Shale Oil as a Function of Refractive Index	79
4.2.5-1	Hydrocracking/Hydrogenation Routes To HEDF	107
4.3.5-1	Processing Approaches to Colorado Shale Oil HEDF	129
5.2.1-1	Volumetric Heat Content vs Hydrogen Content of Model Compounds	142
5.2.1-2	Hydrotreating Severity vs VHLV for Hydrotreated COALITE Distillates	163
5.2.1-3	Hydrotreating Severity vs Hydrogen Content For COALITE Distillates Over K-550	164
5.2.1-4	Hydrotreating Severity vs FIA Aromatics For COALITE Distillates Over K-550	165
5.2.1-5	Hydrotreating Severity vs API Gravity For COALITE Distillates Over K-550	166
5.2.1-6	Hydrotreating Severity vs Aniline Pt For COALITE Distillates Over K-550	167
5.2.1-7	Hydrotreating Severity vs Cetane Index For COALITE Distillates Over K-550	168
5.2.1-8	Hydrotreating Severity vs Smoke Pt For COALITE Distillates Over K-550	169
5.2.1-9	Hydrotreating Severity vs Refractive Index For COALITE Distillates Over K-550	170
5.2.1-10	Effect of Aromatics on VLHV of Coal-Derived Diesel/Jet Fuels	171
5.2.1-11	Effect of Aromatics on Cetane Quality of Coal-Derived Diesel Fuels	172
5.2.1-12	Effect of Aromatics on Smoke Point of Coal-Derived Turbine Fuels	173
5.2.1-13	Predicted Net Heat of Combustion of COALITE vs R.I. and API Gravity	174
5.2.1-14	Distillate Hydrogen Content as a Function of R.I. of COALITE Distillates	175
5.2.1-15	Predicted API Gravity as a Function of R.I. of Hydrotreated COALITE	176
5.2.1-16	Watson K Factor As a Function of R.I. of Hydrotreated COALITE	177
5.2.1-17	Smoke Pt and Luminometer No vs R.I. of COALITE	178
5.2.4-1	Relative Hydroprocessing Performance for 350-550F COALITE: Sp. Gr Reduction	179
5.2.4-2	Relative Hydroprocessing Performance for 350-550F COALITE: Aromatics Conversion	180
5.2.4-3	Relative Hydroprocessing Performance for 350-550F COALITE: Hydrogen Uptake	182
6.2-1	Hydrotreating Severity vs VHLV for COALITE & Shale Derived Jet Fuels	241
6.2-2	Hydrotreating Severity vs FIA Aromatics for Coal & Shale Derived Jet Fuels	242
6.2-3	Hydrotreating Severity vs Hydrogen Content for Coal & Shale Derived Jet Fuels	243
6.2-4	Hydrotreating Severity vs API Gravity for Coal & Shale Derived Jet Fuels	244

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page #</u>
6.2-5	Hydrotreating Severity vs Smoke Pt for Coal & Shale Derived Jet Fuels	245
6.2-6	Hydrotreating Severity vs Refractive Index for Coal & Shale Derived Jet Fuels	246
6.2-7	Effect of Aromatics on VLHV of Coal & Shale Derived Jet Fuels	247
6.2-8	Effect of Aromatics on Smoke Pt of Coal & Shale Derived Jet Fuels	248
6.2-9	API Gravity vs Refractive Index of Coal & Shale Derived Distillates	249
6.2-10	Smoke Pt vs Refractive Index of Coal & Shale Derived Jet Fuels	250
6.2-11	Distillate Hydrogen Content vs Refractive Index of Coal & Shale Derived Jet Fuels	251
6.6-1	Extraction/Hydrogenation Route to HEDF From Colorado Shale Oil	263
8.1-1	Effect of Reactor Severity	286
8.1-2	Flash Point Prediction	287
8.2-1	Schematic of Maximum HEDF Jet Fuel	289
8.2-2	Schematic of 40% HEDF Jet Fuel	294
8.2-3	Feedstock Rate Effect on Profit	297
8.2-4	Effect of Feedstock Rate @40% HEDF Yield & \$18/bbl Feed Cost	298
8.3-1	Effect of Heating Value Specification	301
8.3-2	HEDF Cost vs Heating Value	302
8.3-3	HEDF Cost Breakdown	303
8.3-4	Feedstock Rate Effect on Profit	304
8.3-5	Effect of Feedstock Rate @40% HEDF Yield & \$30/bbl Feed Cost	306
8.3-6	Schematic of Maximum HEDF Jet Fuel - No Specifications	307
8.3-7	Effect of HEDF Yield - 40 MBCD Cases	309
8.3-8	Effect of HEDF Yield - 40 & 10 MBCD Cases Compared	310

1.0 EXECUTIVE SUMMARY

1.1 Background and DOE Perspective

In April 1988, the Department of Energy (DOE) Morgantown Energy Technology Center (METC) issued a request for proposal (RFP) soliciting a research effort for the "Development of High Energy Density Fuels from Mild Gasification of Coal". ABB Lummus Crest Inc. (then a subsidiary of Combustion Engineering Inc and currently a subsidiary of Asea Brown Boveri Inc.) and Amoco Oil Company (AOC) as key subcontractor successfully responded to the RFP and entered into a contract (No. DE-AC22-88MC25020) with the DOE on September 30, 1988.

The RFP was predicated on DOE's desire to enhance the development of advanced transportation fuels made from coal via a program to process mild coal gasification (MCG) liquids into high volumetric energy density (HEDF) test fuels. The desired product fuels were to be cost effectively manufactured, have high volumetric energy density, and be hydrocarbon-based for existing and prototype turbine and diesel engines. The sources for these special fuels consist of the abundant and secure indigenous energy resources of coal. Comparison studies were also to be made using other non-petroleum fuels such as shale oil and tar sands bitumen.

METC has concluded that MCG technology has the potential to simultaneously satisfy the transportation and power generation fuel needs in the most cost-effective manner. MCG is based on low temperature pyrolysis, a technique known to the coal community for over a century. Most past pyrolysis developments were aimed at maximizing the liquids yield which results in a low quality tarry product requiring significant and capital intensive upgrading.

By properly tailoring the pyrolysis severity to control the liquid yield-liquid quality relationship, it has been found that a higher quality distillate-boiling liquid can be readily "skimmed" from the coal. The resultant liquids have a much higher H/C ratio than conventional pyrolytic tars and therefore can be hydroprocessed at lower cost. These liquids are also extremely enriched in 1-, 2-, and 3-ring aromatics. The co-product char material can be used in place of coal as a pulverized fuel(pf) for power generation in a coal combustor. In this situation where the original coal has a high sulfur content, the MCG process can be practiced with a coal-lime mixture and the calcium values retained on the char can tie up the unconverted coal sulfur upon pf combustion of the char. Lime has also been shown to improve the yield and quality of the MCG liquids.

The development of advanced fuels will provide increased range of volume-limited aircraft/missiles/vehicles and possibly provide a better heat sink than existing liquid fuels for high-speed aircraft. These special fuels would also provide desired characteristics for aircraft/vehicle operations in extreme conditions. Development of these fuels would have civilian and military applications in turbine and/or diesel engines for extended range and uses in remote areas where fuel supply may be difficult to sustain.

While little R&D has been conducted on the treatment of coal-derived MCG liquids to produce advanced fuels, significant R&D efforts have been carried out to produce specification fuels from shale oil and tar sands bitumen. The major technical challenge in this program is the development of effective methods for treating MCG liquids and in increasing volumetric energy density while still meeting the essential features of the operational fuel specifications.

Processing and upgrading methods are needed to produce good yields of advanced fuels while minimizing overall processing costs. Advanced test fuels of interest must be produced to meet operational requirements reflected in the DOD fuel specifications but may vary in chemical composition so as to increase the volumetric energy density and/or reduce the processing severity.

1.2 Contract Objectives

The overall objective of the research effort is the determination of the minimum processing requirements to produce high energy density fuels (HEDF) having acceptable fuel specifications. The program encompasses assessing current technology capability; selecting acceptable processing and refining schemes; and generating samples of advanced test fuels.

The specific objectives are:

- o Conduct a technical and economic assessment of promising processing and upgrading methods to convert raw products from mild coal gasification into advanced high volumetric energy density test fuels for aviation turbines and diesel engines;
- o Conduct screening tests of alternative processing methods; and
- o Generate and deliver gallon-size test quantities of advanced fuels from mild coal gasification liquids and other sources.

1.3 Task Breakdown Structure

The Phase I Baseline Program is intended to explore the processing alternatives for producing advanced HEDF from two raw synfuel feedstocks, one from Mild Coal Gasification as exemplified by the COALITE process and one from Colorado shale oil. Eight key tasks were initially identified as follows:

<u>Task I.D. No.</u>	<u>Task Definition</u>
1	Planning and Environmental Permitting
2	Transporting and Storage of Raw Fuel Sources and Products
3	Screening of Processing and Upgrading Schemes
4	Proposed Upgrading Schemes for Advanced Fuel
5	Upgrading of Raw Oil into Advanced Fuel
6	Packaging and Shipment of Advanced Fuels
7	Updated Technical and Economic Assessment
8	Final Report of Phase I Efforts

Our overall approach to processing Mild Coal Gasification liquids and shale oils consists of integrated hydrofining technology using catalysts tailored to the heteroatom removal and ring hydrogenation functions. In order to perform the optimization of maximum yield of the desired HEDF products at minimal processing costs, there will have to be a tradeoff of product yield vs. hydrogen consumption requirements. Consideration will have to be given to the handling of the light end and the heavier end of the synfuel feedstocks which can not directly be incorporated into the desired mid-distillate advanced fuel products. Based on in-house hydroprocessing experience with these type of synfuel feedstocks together with Amoco's Refinery LPT model, preliminary flowschemes will be developed to serve as the basis for initiating the screening studies of Task 3.

At this point in the project, one possible route might consist of distilling the volatile fraction from the synfuel feedstock. The purpose of this step is to remove water and certain materials such as pyridinics and light phenolics that are difficult and costly to catalytically upgrade especially with respect to hydrogen consumption requirements. The distillation cut point will have to be determined that will result in the preservation of certain Category II endothermic fuel precursors, e.g., toluene and xylenes.

The heavier end can be hydrocracked under recycle conditions to produce more cyclic (naphthenic or aromatic) material boiling in the required turbine or diesel fuel ranges specified in the MIL specs. The hydrocracking feed will have to be purified of heteroatom content in order to utilize the desirable active hydrocracking catalysts. Thus, there will be a tradeoff in heteroatom removal requirements vs. catalytic hydrocracking catalyst requirements. A goal will be to find hydrogenation/hydrocracking conditions that will result in extinction recycle of the heavier gas oil component of the synfuel feedstocks. The recycle cut point will have to be determined as one that maximizes the yield of the desired two- and single-ring aromatics but still allows for the attainment of the back-end volatility specs for the advanced turbine or diesel fuels.

Task 1: Planning and Environmental Permitting

The objective of this task is to prepare a project management plan for both the Phase I and Phase II tasks in sufficient detail to allow the DOE COTR to understand and ultimately monitor the Contractor's performance. This plan will contain the most current and accurate information and projections available to LCI as Contractor at the time of submission of the work plan.

Of particular importance is the responsibility of the Contractor to obtain all required permits and to comply with all environmental regulations governing the operation of the Contractor's facility and its ability to process the synfuel feedstocks to be provided by DOE.

The project management plan will consist of the following items:

1. A detailed discussion of the technical approach to be used to achieve the contract objectives, specifics about test conditions, equipment configurations, feedstock specifications, calculation procedures, analytical procedures, reporting requirements and milestone/schedule plan;
2. A screening test plan enumerating the currently preferred processing/upgrading schemes; the types of tests planned; and test parameters to be explored for the screening studies of Task 3;
3. Management reports including cumulative estimated costs and cumulative estimated manhours by month and by task as well as for the total contract effort;
4. A project work chart showing key personnel or key groups and their estimated percentage of time to be devoted to each task; and
5. A model subcontract proposed to be negotiated with Amoco Oil Company.

By virtue of the exploratory nature of R&D projects, it is probable that technical redirections might be in order as experimental data are collected during the course of the project. Contractor will submit appropriate work plan revisions, if deemed to be in the best interest of the overall program goals, to the DOE COTR for consideration and approval. Incorporation of such proposed revisions will not be implemented until prior written approval is granted by the DOE COTR.

The deliverables for this task will include:

1. A self-contained written report summarizing all of the work plan items; and
2. A briefing to be made to the DOE COTR on the details of the work plan.

Task 2: Transporting/Storage of Raw Fuel Sources

This task consists of the procurement of the MCG and shale-derived liquids; the storage of feeds and products at Contractor's test facility; and disposal of waste byproducts and unused feedstocks. The details are discussed in more detail below.

Task 3: Screening of Processing/Upgrading Schemes

The objectives of this task are to: 1) characterize the two synfuel feedstocks supplied by DOE with regard to their processability for conversion to advanced HEDF; and 2) perform laboratory screening tests of candidate processing methodologies.

The deliverables for Task 3 will include:

- o Delivery of sample quantities (ca. 1 Liter) of test HEDF to DOE and/or its designated contractors;
- o A draft topical report on the experimental efforts including all analytical results, unit operating reports, material balances and data correlations, to be submitted within 30 days after completion of the screening tests;
- o Briefings on the status of the screening studies outlining the progress and results of the work effort to the DOE COTR at METC;
- o Hot line reports as required to report major breakthroughs or significant events.

Task 4: Proposed Upgrading Schemes For Advanced Fuels

In this task, Amoco as key subcontractor will develop preliminary designs and economic evaluations of commercial processing schemes to make the advanced HEDF from the MCG liquids and the Colorado shale oil based on the use of its Linear Programming Technology (LPT) models of refinery processing units. It is probable that the processes to make these fuels will also produce co-products including motor gasoline and aromatic petrochemicals and thus the economics will include feedstock cost considerations as well as co-product values.

The following deliverables will be provided:

- o A draft topical report on the results of the processing and economics calculations including the economic analyses for producing the three categories of HEDF;
- o Briefings on the status of the processing studies outlining the progress and results of the work effort to the COTR at METC.

Task 5: Upgrading Raw Oil Into Advanced Fuel

The objective of this task is to generate sufficient test quantities (ca. 100 gal) of two advanced fuels, one from Category I and one from either Category II or Category III fuels for the Mild Coal Gasification liquids and the Colorado shale oil. Processes that would minimize the overall cost of production in a full-scale commercial unit will be considered. Thus, approximately 400 gal of advanced HEDF samples will be required.

The Task 4 topical report will identify the specific upgrading schemes and technical approaches to be used for the Task 5 pilot plant sample preparation efforts. Upon approval of this report by the DOE COTR, the Contractor will initiate the required tasks as follows:

1. Contractor will characterize the two candidate feedstocks and prepare them for processing in the bench-scale units. If it is

determined from the Task 4 studies that an initial fixed-bed hydrotreating step will be required, then the feeds will be filtered or centrifuged to remove particulate (e.g., coal char fines or oil shale fines) matter. If it is determined from the Task 4 studies that the initial step will be an expanded-bed (LC-FiningSM) hydroprocessing operation, then the filtration step will not be necessary as the LC-FinerSM can tolerate solids. In either case, the LC-FiningSM Pilot Plant unit will be used, operated either cocurrent downflow for the fixed-bed hydrotreatment or cocurrent upflow for the expanded-bed hydroprocessing operation.

2. If the Task 4 studies indicate that the two-step, heteroatom removal-ring saturation process is the preferred mode, then the initial operation will be to process the first feedstock at the preferred catalytic hydrotreatment severity. The amount of feed to be processed will depend upon the projected ultimate yield of HEDF on feed. This value will be determined from the screening studies of Task 3 and the processing studies of Task 4. Thus, if the ultimate yield of Category I HEDF for example is 60 liquid volume percent on feed, then 166.7-gal of feed would have to be processed. For safety margins related to pilot plant handling efficiencies, we would plan to process at least 250-300 gal. It might also turn out that during the first campaign to produce the required 100 gal of Category I advanced fuel, Category II or Category III fuel might be produced as a co-product. In this event, the second campaign to produce the Category II or Category III fuel could be shortened by the amount of that advanced fuel produced in the first campaign.

3. The unit will be operated on a 24-hour, 7-day per week basis until the total required feed batch has been processed. The upper limit on the throughput of this unit is about 6 gal/hr. Thus, the minimum cycle for a pilot plant campaign will be 250-300 gal divided by 6 gal/hr or about 42 to 50 hours. The upper limit on the catalyst volume is about 1.4 gal per reactor vessel or 2.8 gal total volume which corresponds to a minimum space velocity of about 2.1 to 4.3 hr⁻¹ at the maximum throughput. Thus, if the processing space velocity requirements are lower, then the feed pump rate would have to be lowered and the time for completion of a campaign would be proportionately increased.

4. Two campaigns will be required for each HEDF fuel sample produced, one for the first-step heteroatom removal and one for the second-step ring saturation. Thus, eight pilot plant campaigns could be required for producing two advanced fuels for two synfuel feedstocks, assuming that the same processing scheme will be applicable to both synfuel feeds. The first four campaigns will carry out the catalytic hydrotreatment step with a single charge of preferred heteroatom removal catalyst. The unit would then be disassembled; the spent catalyst removed; the unit thoroughly purged and cleaned with solvent to remove residual heteroatoms; and a fresh charge of the preferred ring saturation catalyst would be installed.

5. The second-step operation may initially consist of a purge period to stabilize the catalyst and to provide a further purging of residual

heteroatoms from the earlier cat hydrotreating campaigns. The unit would then be operated on a 24-hour, 7-day basis until the 100 gal yield of the required advanced fuel sample is achieved. A post-hydrogenation distillation step will be required to fix all of the turbine fuel specs controlled by front-end and back-end volatility.

6. Analytical testing will be grouped into two categories: control analyses for monitoring the heteroatom removal and the ring saturation operations; and product specifications. The control analyses for the heteroatom removal operations will include ultimate analysis, specific gravity, FIA trace sulfur and nitrogen analyses, and simulated distillation. Control analyses for the ring saturation operations will include ultimate analysis, specific gravity, aniline point, diesel index, LHV, smoke point, and simulated distillation. Each of the four HEDF products will be completely analyzed for all of the relevant JP-4, 7, 8 and 10 specifications in addition to calorific value.

The deliverables for this task are:

- o 400 gal(aggregate amount) of advanced fuels, one from Category I and one from Category II or III, for each of the two candidate synfuel feeds;
- o A draft topical report describing the processing techniques, material balances, specification test results, engineering analyses and test reports;
- o Briefings to the DOE COTR at METC to outline the progress and results of the Task 5 work effort;
- o Hot line reports as required to report major breakthroughs or significant events.

Task 6: Package and Shipment of Advanced Fuels

The pilot plant upgrading operations will be structured such that 100 gallons of each of the required HEDF samples will be produced in one month intervals. Once the analytical workup confirms the final targetted specs, the sample will be shipped to DOE's designated site. In order to limit the storage time at the Contractor's site, we propose to ship each 100-gal sample separately. However, it might also be acceptable to await completion of more than one product sample in the event that the samples will be shipped to the same site. The COTR will be notified 30 days in advance of each shipment to allow for sufficient time to transmit the address of the receiving site. A Material Safety Data (MSD) sheet will be completed and sent with the sample shipment to the receiving location specified by the COTR.

The samples will be loaded into sealed, nitrogen-pressurized stainless steel drums using a sampling/valving system installed in the two drum bungs. This system will allow the maintenance of the nitrogen gas

blanket while sampling the drum. This essentially eliminates the infusion of any air into the drum. The drums will be labeled with the proper UN number and appropriate reference sample number. Pressurizing will be maintained at 0.5 to 1 psig nitrogen. Directly after filling and pressurizing, the drums will be stored in a cold box which will be maintained at a temperature of no more than 35 to 40F. The drums will also be connected to a manifold to maintain the nitrogen pressure should there be any small gas leaks. The drums will be transferred to a dedicated refrigerated truck, maintained at or below 35 to 40F, during the loading and transporting.

Task 7: Updated Technical and Economic Assessment

In order to confirm the processing routes developed from the screening studies of Task 3, the pilot plant upgrading efforts of Task 5 were to be used to update the Task 4 results. Consideration was to be given to the scalability of the data between the bench-scale and pilot plant units and the subsequent scaleup to commercial units. The Task 5 data was to be incorporated into the LP model developed in Task 4. The updated LPT model was to be used to generate final optimized processing schemes for the production of Category I, II, and III HEDF fuels. When the contract was modified to reflect the reduced DOE funding availability, this task was eliminated.

Task 8: Final Phase I Report

The objective of this task is to prepare a draft final technical report summarizing the results of all the efforts of the individual tasks in the Phase I program. The report will contain an executive summary highlighting the major project results, conclusions and recommendations and in particular, addressing the issues of alternative processing schemes, anticipated fuel performance characteristics and the conceptual economics of producing HEDF from mild coal gasification liquids. The draft report will be delivered two months prior to the contract completion and a revised final report after receipt of DOE's comments will be issued at contract completion.

1.4 Feedstocks

The two candidate synfuel feedstocks selected for the Phase I program by DOE consisted of a mild coal gasification liquid and a shale oil. The coal liquid consists of a nominal 160-1000F boiling range product from the British COALITE carbonization process. The COALITE process was developed in the early 1900's (1) based on the use of a vertical retort. A COALITE plant built in 1936 at the Bolsover Works of Coalite and Chemical Products Ltd is still in operation and the 1000-gal sample was procured and delivered to Lummus by United Coal Company Research Corporation of Bristol, VA. The COALITE was produced from a medium coking British coal and is expected to have properties similar to those of U.S. Eastern bituminous coals.

The shale oil is derived from Green River oil shale and was produced at the Unocal plant in Colorado. The 1000-gal sample was provided to Lummus by the Western Research Institute of Laramie, WY.

1.5 High Energy Density Fuels (HEDF)

Conventional petroleum-based aviation turbine fuels (e.g., JP-4) generally contain about 20 volume percent aromatics (25% max.) and 30% paraffinics with the balance being naphthenics. If these conventional fuels were severely hydrogenated to convert all the aromatics to naphthenes, the total saturated cyclic content would still only be about 70%. In order to convert the paraffinic compounds, which characteristically have low energy density because of their high H/C ratios and low specific gravities, to cycloparaffins would require complex and expensive processing techniques such as isomerization and aromatization.

Naphthenic hydrocarbons having two or three rings represent the optimal density-calorific value relationship of any hydrocarbon fuel currently produced. The two-ring (and three-ring) saturates can be readily produced by hydrogenation of their unsaturated or aromatic precursors. Coal liquids produced by mild coal gasification are known to have in excess of 90-95% 2-ring and 3-ring polynuclear aromatics content. Thus, by hydroprocessing techniques to insure the integrity of 2- and 3-ring hydrogenated products, these mild gasification products can be converted to advanced high energy density fuels at high yields.

Three advanced HEDF types have been defined for this RFP as discussed below.

Category I - Aviation Turbine Fuel

This advanced fuel is defined as one having a Lower Heating Value (LHV) in excess of 130,000 Btu/gal and preferably on the order of 135,000 Btu/gal and having high thermal stability. For comparison, conventional JP-4 turbine fuel has an LHV of only 119,400 Btu/gal and typical kerosene has a value of about 123,000. Decalin, an unsubstituted 2-ring cycloparaffin, has an LHV of 135,400 Btu/gal and an alkylated decalin has an LHV of 134,950 Btu/gal. This Category I advanced fuel must conform to the operational requirements reflected in the DOD fuel specifications for JP-4 and JP-8 but with necessary chemical composition variations required to achieve the desired higher volumetric energy densities and/or to reduce the required processing severity.

Category II - Endothermic Turbine Fuel

This advanced fuel must have a high energy density value but also must have those properties to make it a satisfactory fuel for use in advanced hypersonic aircraft. At hypersonic speeds, significant thermal problems arise due to the effect of stagnation temperature, the latter being the resultant temperature due to the resistance of the air molecules impeding the motion of the vehicle. Heat can be removed by either a mechanical refrigeration system; a non-combustible coolant; or by the fuel itself, the latter being the most preferred. Three types of endothermic processes can be used depending upon fuel type: a) catalytic dehydrogenation of naphthenes; b) thermal cracking

of various hydrocarbons; and c) depolymerization of polymers. All of these systems have varying heat sink limits and the prior R&D reported in the literature has pinpointed the naphtha dehydrogenation route as a preferred endothermic mechanism. Typical compounds having good heat sinks include methylcyclohexane(MCH), methycyclopentane(MCP), decalin, dicyclohexyl, etc. Compounds of these types or their unsaturated precursors might exist in the Mild Coal Gasification liquids at some appreciable concentrations to result in the production of a reasonable yield of the Category II advanced fuel.

Category III - High Energy Diesel Fuel

This advanced fuel must meet DOD's diesel spec VV-F-800D(this spec supersedes the VV-F-800C spec shown in the RFP) and have an energy density comparable to that of the Category I turbine fuel thus allowing extended driving range for military vehicles such as tanks. This spec has no volumetric energy density limitation per se, but the Cetane No. spec can be effected by hydrocarbon type, in particular, aromatics, and the latter will affect the resultant energy density of the fuel. The three grades of VV-F-800D diesel fuel, namely, DF-A, DF-1 and DF-2 have varying operability characteristics pursuant to the climactic specification. Grade DF-A, Arctic grade, has the lowest viscosity requirement and distillation end point limit. Back-end diesel cut blending to achieve the desired high volumetric energy density will have to be balanced against front-end blending to insure that the Distillation End Point, Viscosity and Carbon Residue specs are not violated.

1.6 Process Screening Alternatives

Our overall approach to processing Mild Coal Gasification liquids and shale oils consists of integrated hydrofining technology using catalysts tailored to the heteroatom removal and ring hydrogenation functions. In order to perform the optimization of maximum yield of the desired HEDF products at minimal processing costs, there will have to be a tradeoff of product yield vs. hydrogen consumption requirements. Consideration will have to be given to the handling of the light end and the heavier end of the synfuel feedstocks which can not completely be incorporated into the desired mid-distillate advanced fuel products. Based on in-house hydroprocessing experience with these type of synfuel feedstocks together with Amoco's Refinery LPT model, preliminary flowschemes were developed to serve as the basis for initiating the screening studies of Task 3.

The initial screening consisted of the catalytic two-step hydrotreatment, i.e., heteroatom removal followed by ring saturation, in a fixed-bed, downflow bench-scale unit. Tests were performed with selected distillate fractions of the feeds. The heavier fraction boiling above the aviation turbine fuel range was cracked either via thermal (e.g., coking); or hydrocracking (e.g., LC-Fining, VGO hydrocracking) technologies.

A contract modification for extending the Task 3 screening studies was approved by DOE. The directive for this modification was to deemphasize the Colorado shale oil feedstock (since the early screening data indicated that it did not have the high energy density potential as that of the MCG liquids) and to concentrate on the production of HEDF components via selective hydrocracking of the gas oil and resid components of the raw COALITE feedstock. An enhanced screening program was implemented to evaluate alternative catalysts for the selective hydrocracking steps and to relate hydroprocessing severities to the thermal stability properties of the finished HEDF test fuels.

1.7 Experimental Procedures

The Task 3 Work Statement called for the screening of processing and upgrading schemes using laboratory-scale screening equipment while the Task 5 sample preparation program required the larger pilot plant-scale equipment. At LCI's Engineering Development Center (EDC), currently referred to as the Bloomfield Research & Development Center (BRDC), process testing including screening and sample preparation activities is carried out in either laboratory-scale, bench-top or pilot plant equipment. The processing and upgrading schemes for producing HEDF from synfuel feedstocks under the subject program include the following unit operations:

- o Fixed-bed Distillate Hydrotreating
- o Fixed-bed Distillate Hydrocracking
- o Expanded-bed Resid Hydrocracking
- o Delayed Coking
- o Fractionation
- o Solvent Extraction
- o Clay Treating

The Task 3 screening of these process operations was carried out in the following test units:

1. Bench-Scale Fixed-Bed Hydrotreating Unit
2. Bench-Scale Fixed-Bed Hydrocracking Unit
3. Bench-Scale Expanded-Bed LC-Fining[™] Unit
4. Continuous Bench Coking Unit
5. Laboratory Extraction Unit
6. 4-in Batch Fractionation Unit
7. Equilibrium Flash Vaporization Pilot Unit
8. Laboratory Batch Distillation Units
9. Laboratory Clay Treating Unit

The Task 5 sample preparation program was carried out in the following test units:

1. Pilot Plant LC-Finingtm Unit
2. Pilot Plant Fixed-Bed Hydroprocessing Unit
3. Pilot Plant Clay Treating Unit

1.8 Summary of Results of COALITE Operations

The raw COALITE feedstock was fractionated in the 4-in Batch Distillation unit in four different campaigns. The initial fractionation, referred to as CC-1, resulted in the collection of sixteen successive distillate cuts and a vacuum resid fraction. The bulk of these materials was used for the analytical characterization tests (described in Section 3), the delayed coking evaluation of the 650F+ resid, and the LC-Fining evaluation of the 650F+ (343C+) resid.

Batch fractionation CC-2 resulted in the collection of 24 distillate fractions and a 670F+ (354C) resid fraction. Two composite blends for distillate hydrotreating were made: a nominal 350-650F (177-343C) blend of distillate fractions 5 through 22 to simulate a Category III boiling-range fuel; and a nominal 350-550F (177-288C) blend of distillate fractions 5 through 14 to simulate a Category I boiling-range fuel. Two additional blends were made with heavier end points (i.e., 750F and 820F) to determine whether the addition of the heavier gas oil components could increase energy densities above and beyond the 130,000 Btu/gal specification.

It should be kept in mind that the final Initial Boiling Point and End Point of the finished HEDF product is set in a post-hydrogenation topping and tailing operation. The nominal ranges of the feeds could not be fine-tuned in advance of and during the screening test work until sufficient information was acquired on the interaction of the process variables on all of the specified HEDF properties. Thus, the approach taken was to use the post-hydrogenation distillation operations to fine tune the critical distillation temperatures controlling the volatility (i.e., flash point spec) and the back-end viscosity/freeze point spec. Of course, in a commercial operation, the design of the fractionation systems would be optimized to reduce the cost of any unnecessary towers.

Six virgin distillate hydrotreating campaigns were made with the COALITE distillates to study the effects of catalyst type, distillate boiling range, single-stage vs two-stage, recycle of first-pass hydrotreated product and severity as controlled by space velocity, hydrogen partial pressure and reactor temperature. A total of 59 material balance tests were made of durations extending from 2-hours to 36-hours. The following table summarizes the salient features of each campaign and the summary table reference number.

<u>CAMPAIGN #</u>	<u># STAGES</u>	<u>CATALYST TYPE</u>	<u>FEED BOILING RANGE</u>	<u>#TESTS</u>
1	1	K-550	350-650F	30
2	1	K-550	350-550F	8
3	2	K-550/K-550	350-750F;350-820F	8
4	2	K-550/K-599	350-650F	7
5	1	K-599	350-650F	2
6	1	Ca-doped K-550	350-650F	4

Campaign 5 was also used for the production of liter-size samples of finished HEDF samples required as a Task 3 deliverable. The specific objectives of each of these six campaigns are summarized below:

- Campaign 1: Initial scans to evaluate the effects of space velocity, reaction temperature, hydrogen partial pressure and single-pass product recycle with a candidate NiWS hydrotreating catalyst in a single-stage reactor using the 350-650F COALITE distillate.
- Campaign 2: Initial scans to evaluate the effects of space velocity, reaction temperature and single-pass product recycle with a candidate NiWS hydrotreating catalyst in a single-stage reactor using the 350-550F COALITE distillate.
- Campaign 3: Initial scans to evaluate the effects of temperature and space velocity with higher end point COALITE distillates using a two-stage NiWS catalyst reaction system.
- Campaign 4: Initial scans to evaluate the effects of temperature and space velocity with the 350-650F COALITE distillate in a two-stage reactor system comprising a NiWS catalyst in the first-stage and a high moly nickel catalyst in the second-stage reactor.
- Campaign 5: Production run to produce liter size samples of HEDF materials in a single-stage reactor with the high moly nickel catalyst using the 350-650F COALITE distillate.
- Campaign 6: Scans of the effects of temperature and space velocity with a calcium-doped NiWS catalyst using the 350-650F COALITE distillate.

There is a considerable yield of atmospheric resid in the raw COALITE. HEDF products are end-point limited because of viscosity and freeze point specifications. Therefore, it is necessary to crack the heavier components to the mid-distillate range comprising the desired HEDF turbine fuel products. Three crackingtm methods were considered: 1) Resid hydrocracking using the LC-Finingtm process; 2) Delayed Coking; and 3) VGO fixed-bed hydrocracking.

LC-Finingtm is a commercial technology for upgrading heavy oils. In the context of the COALITE HEDF application, LC-Finingtm has been used

to hydrotreat long residues (ca., 300F+) and to hydrocrack the 650F+ (343C+) components into the HEDF boiling ranges. Three feedstocks were considered: 1) a virgin or raw 650F+ (343C+) atmospheric resid fraction of the raw COALITE; 2) a virgin 300F+ (148C+) long resid fraction; and 3) a hydrotreated 575F+ (301C+) atmospheric resid fraction. The objectives of these three campaigns were as follows:

- o Evaluate the first-pass reactivity of the virgin 650F+ atmospheric resid fraction towards hydrocracking and the production of hydrocracked HEDF-boiling range materials;
- o Evaluate the hydrocracking reactivity of the first-pass unconverted (575F+) atmospheric resid recovered from the virgin 650F+ LC-Finingtm tests of the above campaigns; and
- o Prepare hydrotreated gas oil (650-975F) for downstream selective fixed-bed hydrocracking campaigns by subjecting the 300F+ long resid to mild LC-Finingtm.

Delayed Coking is another alternative technology for upgrading heavy oils to lighter products, such as HEDF materials. However, Delayed Coking is not as selective as hydrocracking and results in the production of a variety of byproducts, the predominant one being coke. On the other hand, Delayed Coking is much less capital intensive than hydrocracking and the differential HEDF yield losses are modulated by lower capital and operating costs.

Three Delayed Coking tests were made in the Continuous Bench Coker (CBC) unit, two with virgin 650F+ atmospheric residua and one with a hydrotreated resid. Two delayed coking severities were investigated: a) 100 psig coke drum pressure; and b) 25 psig coke drum pressure, all other conditions kept constant.

The above two cracking operations, namely, LC-Finingtm and Delayed Coking, are primarily conversion processes to produce HEDF precursor materials that boil within the HEDF boiling range. They therefore do not result in the production of finished HEDF products and a post-cracking hydrogenation operation is required for upgrading the cracked precursor materials. In a true commercial process, a fractionator would be installed between the cracking unit(s) with the cracked distillate fed continuously to the distillate hydrotreater and the heavier unconverted residuum being recycled back to the cracking unit. In this Task 3 screening program with the COALITE feedstock, the bench-scale cracking and hydrotreating units were not integrated and thus only first-pass crackates, either, delayed coker distillates or hydrocrackates (LC-Finates), were evaluated. Three distillate hydrotreating runs were made with delayed coker distillates and eleven distillate hydrotreating runs were made with LC-Finate (hydrocracked) distillates.

The objective of the eleven hydrotreating tests made with the LC-Finate mid-distillates produced was to evaluate the effects of hydrocracked distillate end point, catalyst type, space velocity, reactor temperature, and single-stage vs two-stage distillate

hydrotreating. The objective of the hydrotreating tests made with the coker mid-distillates was to evaluate the effects of coker severity, coker distillate end point, reactor temperature, and single-stage vs two-stage distillate hydrotreating.

During the early phases of the screening program, it was determined that the raw atmospheric resid fraction of COALITE was very reactive towards undesirable cracking and condensation reactions. Thus, it was postulated that a pretreatment based on hydrogenation would provide some degree of stabilization of reactive species and thereby allow better performance during subsequent cracking operations. Since the atmospheric COALITE resid contains some coal char particles, it was felt that hydrotreating in a fixed-bed unit would pose significant operability problems. The expanded-bed hydrocracking process of LC-Fining[™] offers the capability to perform the hydrogen addition process in the presence of solids and other contaminants under commercially feasible conditions.

The two-step selective hydrocracking (TSSH) of COALITE consists of a hydrotreating pretreatment step using an LC-Fining[™] reaction system followed by fractionation to recover a hydrotreated vacuum gas oil (HVG0) fraction and a hydrotreated middle distillate fraction, the latter of which can be directed to the HEDF pool. The HVG0 fraction is then catalytically hydrocracked over a fixed-bed hydrocracking catalyst to convert the heavier gas oil-boiling species to HEDF precursors. The thus hydrocracked LC-Finate HVG0, is then subjected to distillate hydrotreating to produce the final HEDF product.

In the screening program, the fixed-bed hydrocracker and the hydrocracked distillate hydrotreater were not integrated and therefore hydrotreating of only the first-pass hydrocracked HVG0 fraction was evaluated. Finally, in order to minimize fractionation equipment costs in a commercial plant, it was decided to perform the initial LC-Fining[™] pretreatment step with a 300F+ atmospheric resid fraction rather than with a 650F+ atmospheric resid fraction. Two hydrocracking campaigns were made: 1) hydrocracking of virgin COALITE VGO; and 2) hydrocracking of hydrotreated LC-Finate VGO. The objective of these tests was to evaluate the effects of space velocity, reactor temperature and VGO feedstock type. All nineteen tests were made with a proprietary fixed-bed hydrocracking catalyst supplied by Amoco Oil Company. The hydrocracked LC-Finate VGO was fractionated to recover a mid-distillate fraction for distillate hydrotreating.

A contract modification was approved by DOE to perform further screening studies of the two-stage selective hydrocracking route with the goal of exceeding the 130,000 Btu/gal energy density target of the finished HEDF test fuels. It was further expanded to also consider the impact of the energy density-JFTOT fuel stability relationships. A proprietary zeolitic hydrocracking catalyst from Zeolyst Enterprises was found to have dual functionality and be able to selectively hydrocrack VGO materials and saturate the cracked aromatic rings in the mid-distillate range simultaneously while generating a HEDF test fuel having a volumetric energy densities on the order of 133 KBtu/gal. Although this did not meet the revised target of 135,000, it

did exceed the original work statement target of 130,000 Btu/gal. Tables 1.8-1 and Figure 1.8-1 summarize the energy density achievements for the four Subtask 3.2 campaigns. Table 1.8-2 summarizes the properties of the gallon-size quantities of test fuels produced during the Task 5 sample preparation campaigns with the proprietary zeolitic selective hydrocracking catalyst. While the energy densities of the two test fuel samples did not achieve the maximum value demonstrated during the Subtask 3.2 screening studies (made with different hydrocracking/hydrotreating catalysts), fuel stability as measured by potential gum, accelerated storage stability and JFTOT tube deposit rating criteria, was excellent.

1.9 Summary of Results of Colorado Shale Oil Operations

Unlike the MCG liquids, the Colorado shale oil distillates are less concentrated in the cyclics and more concentrated in the aliphatic materials as seen in the table below:

	<u>Colo. Shale Oil</u>	<u>COALITE</u>
% Olefins	39.9	11.8
% Saturates (cyclic+aliphatic)	32.9	<13.7
%Aromatics	27.2	>74.5

The COALITE olefins are primarily cyclic in structure, e.g., cyclooctene, cyclodecene, whereas the shale-derived olefins are primarily aliphatic, e.g., n-octene/iso-octene, n-decene/iso-decene. The saturates types, naphthenes vs. paraffins, for these raw synfuels were not readily differentiated by the sulfonation/R.I. procedure of the ASTM FIA analysis.

For the case of the Colorado shale oil, the raw 300-600F distillate had a volumetric heat content of only about 127 KBtu/gal, some 3000 Btu/gal below the target. Upon hydrotreatment, the volumetric energy content decreases significantly away from the target. Thus, the K-550 NiWS and K-599 NiMo catalysts do not appear to have the right functionality to preserve and/or form the desirable cyclic structures. It may be possible to obviate this situation by extending the end point of the distillates beyond 600F and the initial point beyond 300F in order to increase the concentration of the denser 2- and 3-ring cyclics.

Two campaigns of resid hydrocracking via LC-Fining technology were made. One campaign of resid thermal cracking via delayed coking was completed. Only one test campaign was completed for the hydrotreating of cracked distillates. We previously found that volumetric energy densities of 300-600F raw Colorado shale oils after fixed-bed hydrotreating were limited to about 125,000 Btu/gal. While this value is some 5000 Btu/gal below the spec, it still represents a 5000-10,000 Btu/gal energy density premium above that of conventional jet fuels. Nevertheless, a campaign was initiated with the heavy (550F+) Colorado shale oil fraction following parallel processing routes that successfully generated a 132,000+ Btu/gal energy density HEDF from the 550F+ COALITE feedstock.

TABLE 1.8-1
COALITE DERIVED
HEDF FUEL PROPERTIES

TASK 3 SCREENING PROGRAM RESULTS

DESIGNATION	FBHC-41	FB-214D	FB-214E	FB-214F
BOILING RANGE, DEG. F	300-600	300-610	300-620	300-600
GRAVITY, SP. @60	0.8560	0.8745	0.8571	0.8702
GRAVITY, DEG. API	33.8	30.3	33.6	31.1
ELEMENTALS:				
CARBON, WT. %	86.36	86.84	86.55	86.78
HYDROGEN, WT. %	13.64	13.16	13.45	13.22
NITROGEN, ppm	<1	<1	<1	<1
SULFUR, ppm	5	4	1	<1
VISCOSITY @ -4F, cst.	9.1	14.1	9.3	11.0
FLASH POINT, DEG. F	>120	>145	>140	>150
FREEZE POINT, DEG. F	<-50	<-50	<-50	<-50
SMOKE POINT, mm	22	18	20	20
ANILINE POINT, DEG. C	61.9	58.0	62.0	54.9
F.I.A.:				
AROMATICS, VOL. %	4.6	3.7	6.6	15.2
OLEFINS, VOL. %	0.5	0.5	0.5	0.5
SATURATES, VOL. %	94.9	95.8	92.9	84.3
COPPER CORROSION, @ 212F	3A	1A	1A	1A
POTENTIAL GUM, mg/100ml	7.0	NA	7.4	16.4
THERMAL STABILITY (JFTOT):				
TUBE DEPOSIT RATING	0	0	0	2
TUBE DEPOSIT RATING, MAX.	0.5	1.0	1.5	8.0
DIFF. PRESS. MAX., mm Hg	3.0	3.0	3.0	3.0
ENERGY DENSITY, BTU/GAL	130,860	133,992	131,622	132,901

FIGURE 1.8-1

TABLE 1.8-2
FINAL COALITE HEDF TEST FUEL PROPERTIES*

=====	=====	=====	=====	=====	=====	=====
DESIGNATION		FBD-16				FBD-17
GRAVITY, SP. @ 60/60		0.8591				0.8493
GRAVITY, DEG. API		33.2				35.1
ELEMENTALS, WT. %						
CARBON		86.63				86.59
HYDROGEN		13.37				13.41
F.I.A., VOL. %						
AROMATICS		1.2				0.4
OLEFINS		0.3				0.7
SATURATES		98.5				98.9
FLASH POINT, DEG. F		130				125
FREEZE POINT, DEG. F		<-76				<-76
ANILINE POINT, DEG. C		60.8				64.4
SMOKE POINT, mm		25				25
VISCOSITY, cst. @ -4F		7.0				7.5
COPPER CORROSION, @212F		3A				1A
POTENTIAL GUM, mg/100 ml		<1				<1
D2274 ACCEL. STORAGE STABILITY (@95c, 16 Hr, O2), mg/100 ml		<1				<1
THERMAL STABILITY (JFTOT-D3241)						
TUBE DEPOSIT VISUAL RATING(TDR)		0				0
TUBE DEPOSIT RATING MAX SPUN RATIO		4.5				2.5
DIFFERENTIAL PRESSURE MAX., mm Hg		65				57
ENERGY DENSITY, BTU/GALLON		131,740				130,506

* WITHOUT ANTIOXIDANTS, ANTI-DEICING AGENTS, METAL DEACTIVATORS

The selective hydrocracking route, as successfully implemented with the COALITE feedstock, basically consists of mild expanded-bed hydrofining (LC-Fining) of the 300F+ dewatered feed; fractionation to recover the 550-975F LC-Finate vacuum gas oil (VGO); selective hydrocracking of the VGO over the Amoco proprietary fixed-bed hydrocracking catalyst; and fixed-bed hydrogenation of the VGO hydrocrackate.

In the current campaign with the Colorado shale oil feedstock, the selective hydrocracking route followed the steps delineated below:

- o The whole (IBP to end point), undewatered Colorado shale oil was subjected to the mild LC-Fining (test BLCF-102) step. The water collected in the LC-Finate product receivers was phase separated by decanting. The LC-Finate full-range product was fractionated to generate a 575-975F VGO fraction for downstream hydrocracking/hydrogenation.
- o Since the nitrogen content of the LC-Finate VGO was still very high, ca., 15000 ppm, a subsequent fixed-bed hydrotreating (test FB-186/187) step using a NiW/NiMo two-stage catalyst system was used to reduce nitrogen content to 200 ppm.
- o The thus hydrotreated LC-Finate VGO was then subjected to fixed-bed hydrocracking (test FBHC-32/35) over the Amoco proprietary hydrocracking catalyst. The resultant full-range hydrocrackate was then subjected to fixed-bed hydrotreating (FB-188/189) over a NiW/NiMo two-stage catalyst system without fractionating out the unconverted 575-975F gas oil fraction.
- o The hydrogenated hydrocrackate was fractionated to recover a 275-550F HEDF product that met flash point and freeze point specs.

The measured energy density of this latter product was still only about 125,000 Btu/gal, comparable to that generated when hydrotreating the raw 300-600F Colorado shale oil distillate. Thus, the selective hydrocracking of the 575F+ fraction of the Colorado shale oil did not improve energy density quality as was observed with the COALITE feedstock. Furthermore, the per pass conversions during the LC-Fining (BLCF-102) and the fixed-bed hydrocracking (FBHC-32/35) were very low indicating the relative refractory nature of the gas oil fraction of the Colorado shale oils.

The plan for the evaluation of the extraction/hydrogenation route consists of: a) collection of basic equilibrium solvent selectivity data for the two candidate solvents, namely, dimethylformamide (DMF) and tetraethylene glycol (TEG); b) analytical evaluation of the extracts and raffinates with respect to energy density improvements; and c) recommendations for preparation of bench-scale quantities of extracts for demonstration of the potential of fixed-bed hydrotreating (and hydrocracking) to upgrade extracted HEDF precursors to the 130,000 min. Btu/gal energy density spec.

The four feedstocks selected for the initial evaluation include:

- o mildly LC-Fined vac gas oil (BLCF-102 product)
- o severely hydrotreated LC-Finate vac gas oil (FB-186/187)
- o selectively hydrocracked mid-distillate (FB-188/189)
- o hydrotreated raw mid-distillate (FB-130)

The first two feedstocks represent the evaluation of heavier extracts boiling above the HEDF boiling range prior to hydrocracking. The latter two feedstocks to extraction represent HEDF products having nominal 125,000 Btu/gal energy densities.

The test equipment consists of a stirred, externally heated, glass extraction vessel. Testing consisted of three stages of contact using fresh solvent in each stage. Conditions held constant in these initial tests were as follows:

- o Nominal temperature of 195F
- o Atmospheric pressure
- o Stirrer speed of 5 rpm
- o 1 hour extraction contact time per stage
- o Fresh solvent to feed ratio of 1.5 gm/gm

Raffinate and solvent-rich extract phases were separated by decanting in a separatory funnel. The extract was separated from the solvent by introduction of water which dissolved the solvent and freed the hydrocarbon-rich extract. The two solvents selected were premixed on separation from the extract by distillation. The initial testing indicated that the DMF solvent demonstrated a good degree of effectiveness in extracting some species from the heavier feedstock. The TEG solvent appeared to have no specificity for any of the components in the lighter distillate feedstock. Since the DMF solvent is soluble in water, it may be separated from the extract in a commercial-scale application by introduction of a third phase, namely, water or an aqueous-rich recycle stream, instead of distillation.

The DMF extraction of a hydrotreated 300-650F distillate can increase the energy density of the extract by some 2335 Btu/gal over that of the feed but at the expense of a reduction in the energy density of the raffinate.

2.0 EXPERIMENTAL PROCEDURES

2.1 Overview

The Task 3 Work Statement called for the screening of processing and upgrading schemes using laboratory-scale screening equipment while the Task 5 sample preparation program required the larger pilot plant-scale equipment. At LCI's Engineering Development Center (EDC), currently referred to as the Bloomfield Research & Development Center (BRDC), process testing including screening and sample preparation activities is carried out in either laboratory-scale, bench-top or pilot plant equipment. The processing and upgrading schemes for producing HEDF from synfuel feedstocks under the subject program include the following unit operations:

- o Fixed-bed Distillate Hydrotreating
- o Fixed-bed Distillate Hydrocracking
- o Expanded-bed Resid Hydrocracking
- o Delayed Coking
- o Fractionation
- o Solvent Extraction
- o Clay Treating

The Task 3 screening of these process operations was carried out in the following test units:

1. Bench-Scale Fixed-Bed Hydrotreating Unit
2. Bench-Scale Fixed-Bed Hydrocracking Unit
3. Bench-Scale Expanded-Bed LC-Finingtm Unit
4. Continuous Bench Coking Unit
5. Laboratory Extraction Unit
6. 4-in Batch Fractionation Unit
7. Equilibrium Flash Vaporization Pilot Unit
8. Laboratory Batch Distillation Units
9. Laboratory Clay Treating Unit

The Task 5 sample preparation program was carried out in the following test units:

1. Pilot Plant LC-Finingtm Unit
2. Pilot Plant Fixed-Bed Hydroprocessing Unit
3. Pilot Plant Clay Treating Unit

The remainder of this section briefly describes the features of these process test units utilized in this contract.

2.2 Bench-Scale Fixed-Bed Hydrotreating Unit

The Bench-Scale Fixed-Bed Hydrotreating Unit (see Figure 2.2-1) consists of a two-stage, close-coupled, fixed-bed reactor system equipped with high pressure liquid and gaseous (hydrogen) feed systems and a product recovery system. The reactors can be piped in series or in parallel with or without vapor/liquid separation between stages. The following describes each unit operating system.

o Liquid Feed System

The oil feed is charged to a feed tank that is continuously stirred and circulated through a transfer line at about 5-10 psig back into the feed tank using a Tuthill lobe pump. A high pressure piston-type metering pump (Wallace-Tiernan) takes suction from the circulating loop and pumps the oil forward to the first stage reactor preheater. The feed rate is monitored by the rate of weight loss of the feed tank which is installed on a sensitive electronic weigh scale. Changes in the feed rate can be made by adjusting the plunger displacement on the Wallace-Tiernan pump.

o Hydrogen Feed System

A continuous supply of hydrogen is available from high pressure hydrogen trailers. The hydrogen is regulated to a low pressure (ca., 100 psig) and then recompressed to about 2500 psig with a diaphragm compressor. A high pressure piping manifold splits the compressed hydrogen and delivers it to the inlet of the preheater and the inlet of the fixed-bed reactors.

Each hydrogen flow is metered with a high pressure Brooks rotameter. The total hydrogen flow is also continuously metered by use of a precalibrated differential pressure monitor. System pressure is monitored at several locations including the discharge of the Wallace-Tiernan feed pump; inlet and outlet of the fixed-bed reactor; heavy oil product separator and the light oil receiver. System pressure is controlled by a diaphragm type back-pressure regulator.

o Reaction Systems

The preheater consists of a 0.245-in. inside diameter tube electrically heated with Calrod electric heaters providing for two separate controlled heating circuits. A separate transfer line heater controls the temperature of the stage I effluent. The fixed-bed reactors consist of a 1-in. i.d. pipe having an internal volume of about 192-cc. Each reactor is immersed in a sand bath serving as the reactor heater. The bath can be fluidized in the event isothermal operation is desired. Each reactor is equipped with four internal thermocouples. A 25-cc layer of 3-mm glass beads is positioned at the top of each catalyst bed. Each bed contains about 165-cc of catalyst.

o Product Collection System

The recovery system consists of four high pressure separators, each

FIGURE 2.2-1

SCHEMATIC FLOW DIAGRAM OF FIXED-BED HYDROPROCESSING PILOT UNIT

one operated at sequentially lower skin temperatures. In the first vessel, liquid products are separated from the uncondensed hydrocarbons and heteroatoms. This separator is steam traced and operated at system pressure. The resultant product is depressurized to ambient pressure, and then drained into an appropriate storage container.

The overhead vapor stream is further separated in three consecutive high pressure separators, and operated at sequentially lower temperatures. The pressure of the uncondensed vapors from the last separator is reduced to atmospheric, and cooled further in an ambient water-cooled condenser. Light uncondensed gases and hydrogen are then metered by a wet test meter and sampled for subsequent gas chromatographic analysis.

The basic operating procedure is summarized below:

1. The unit is pressurized with hydrogen and brought up to operating temperatures and flow rates using the oil feed. No external startup oil is required.
2. The unit is then lined out with the feed for a period of time to insure at least 95 percent displacement of the existing system inventory. At this point, a material balance period of 6 hour duration is initiated. Gas and liquid product samples are collected.
3. Operating conditions are then changed for the next test and the new line-out period is established prior to initiating a new material balance period.

2.3 Bench-Scale Fixed-Bed Hydrocracking Unit

The Bench-Scale Fixed-Bed Hydrocracking Unit (see Figure 2.3-1) consists of a single-stage, fixed-bed reactor system equipped with high pressure liquid and gaseous (hydrogen) feed systems and a product recovery system. The following describes each unit operating system.

o Liquid Feed System

The liquid feed to the Bench-Scale Fixed-Bed Hydrocracker is generally a vacuum or atmospheric gas oil having a relatively high pour point. The feed system has been designed to provide heating to reduce feed viscosity and to provide circulation/agitation to prevent possible settling of contained solids (e.g., coal char fines as the case for COALITE feedstocks or oil shale fines as the case for Colorado shale oil feedstocks). The feed tank is continuously stirred and circulated through a transfer line at about 5-10 psig back into the feed tank using a Tuthill lobe pump. A high pressure piston-type metering pump (Wallace-Tiernan) takes suction from the circulating heavy oil loop and pumps the feed forward to the high pressure autoclave reaction system. The feed rate is monitored by the rate of weight loss of the feed tank which is installed on a sensitive electronic weigh scale.

FIGURE 2.3-1
SCHEMATIC OF BENCH-SCALE FIXED-BED HYDROCRACKING UNIT

Changes in the feed rate can be made by adjusting the plunger displacement on the Wallace-Tiernan pump.

o Hydrogen Feed System

A continuous supply of hydrogen is available from high pressure hydrogen trailers. The hydrogen is regulated to a low pressure (ca., 100 psig) and then recompressed to about 2500 psig with a diaphragm compressor. A high pressure piping manifold splits the compressed hydrogen and delivers it to the inlet of the preheater, the inlet of the autoclave, and the drive assembly of the autoclave.

Each hydrogen flow is metered with a high pressure Brooks rotameter. The total hydrogen flow is also continuously metered by use of a precalibrated differential pressure monitor. System pressure is monitored at several locations including the discharge of the Wallace-Tiernan feed pump; outlet of the autoclave; heavy oil product separator and the light oil receiver. System pressure is controlled by a diaphragm type back-pressure regulator.

o Reaction System

The preheater consists of a 0.245-in. inside diameter tube electrically heated with Calrod electric heaters providing for two separate controlled heating circuits. The fixed-bed reactor consists of a 1-in. i.d. pipe having an internal volume of about 192-cc. The reactor is wrapped with calrod electric heaters and an insulation laminate to provide some degree of adiabaticity. The reactor is equipped with four internal thermocouples. A 25-cc layer of 3-mm glass beads is positioned at the top of the catalyst bed which contains about 165-cc of catalyst.

o Product Collection System

The recovery system consists of four high pressure separators, each one operated at sequentially lower skin temperatures. In the first vessel, liquid products are separated from the uncondensed hydrocarbons and heteroatoms. This separator is steam traced and operated at system pressure. The resultant product is depressurized to ambient pressure, and then drained into an appropriate storage container.

The overhead vapor stream is further separated in three consecutive high pressure separators, and operated at sequentially lower temperatures. The pressure of the uncondensed vapors from the last separator is reduced to atmospheric, and cooled further in an ambient water-cooled condenser. Light uncondensed gases and hydrogen are then metered by a wet test meter and sampled for subsequent gas chromatographic analysis.

2.4 Bench-Scale LC-Finingtm Unit

As a co-licensor of the proprietary expanded-bed hydrocracking process known as LC-Finingsm, LCI has the responsibility of providing the process design package to LC-Finingsm licensees. In support of this effort, several LC-Finingsm test units are available at the Bloomfield R&D Center. The unit utilized in the Task 3 screening study is a continuous bench-scale system containing an autoclave reactor system to simulate the commercial expanded-bed reactors. Data from this unit can be readily utilized to develop the test conditions of the larger pilot plant reactor system planned for use in Task 5.

Figure 2.4-1 is a schematic of the autoclave-based LC-Finingsm bench-scale unit. The unit consists of a liquid feed system; a hydrogen feed system; a reaction system; and product collection system as described below.

o Liquid Feed System

The liquid feed to the autoclave-based LC-Finersm is generally a vacuum or atmospheric resid having a relatively high pour point. The feed system has been designed to provide heating to reduce feed viscosity and to provide circulation/agitation to prevent possible settling of contained solids (e.g., coal char fines as the case for COALITE feedstocks or oil shale fines as the case for Colorado shale oil feedstocks). The feed tank is continuously stirred and circulated through a transfer line at about 5-10 psig back into the feed tank using a Tuthill lobe pump. A high pressure piston-type metering pump (Wallace-Tiernan) takes suction from the circulating heavy oil loop and pumps the feed forward to the high pressure autoclave reaction system. The feed rate is monitored by the rate of weight loss of the feed tank which is installed on a sensitive electronic weigh scale. Changes in the feed rate can be made by adjusting the plunger displacement on the Wallace-Tiernan pump.

o Hydrogen Feed System

A continuous supply of hydrogen is available from high pressure hydrogen trailers. The hydrogen is regulated to a low pressure (ca., 100 psig) and then recompressed to about 2500 psig with a diaphragm compressor. A high pressure piping manifold splits the compressed hydrogen and delivers it to the inlet of the preheater, the inlet of the autoclave, and the drive assembly of the autoclave.

Each hydrogen flow is metered with a high pressure Brooks rotameter. The total hydrogen flow is also continuously metered by use of a precalibrated differential pressure monitor. System pressure is monitored at several locations including the discharge of the Wallace-Tiernan feed pump; outlet of the autoclave; heavy oil product separator and the light oil receiver. System pressure is controlled by a diaphragm type back-pressure regulator.

FIGURE 2.4-1

SCHEMATIC OF AUTOCLAVE-BASED LC-FINING UNIT

o Reaction System

Two autoclave reaction systems are available: a 300 cc stirred autoclave having a 240 cc internal liquid volume; and a 1000 cc stirred autoclave having an 800-cc volume. Preheated feed is fed directly to the inlet of the autoclave at the bottom and exits at the top of the autoclave. Two impellers each consisting of six-bladed turbines are attached to the stirrer shaft. Typical stirring speeds utilized in the screening program were 175-250 rpm. Use of more violent mixing could possibly result in excessive breakage of the catalyst extrudates. Temperature control was excellent with internal autoclave temperatures not varying by more than 3-4F from set point.

o Product Collection System

The recovery system consists of four high pressure separators, each one operated at sequentially lower skin temperatures. In the first vessel, liquid products are separated from the uncondensed hydrocarbons and heteroatoms. This separator is steam traced and operated at system pressure. The resultant product is depressurized to ambient pressure, and then drained into an appropriate storage container.

The overhead vapor stream is further separated in three consecutive high pressure separators, and operated at sequentially lower temperatures. The pressure of the uncondensed vapors from the last separator is reduced to atmospheric, and cooled further in an ambient water-cooled condenser. Light uncondensed gases and hydrogen are then metered by a wet test meter and sampled for subsequent gas chromatographic analysis.

2.5 Continuous Bench Coking Unit

LCI, as a licensor of commercial delayed coking technology, maintains several delayed coking test units at EDC. The Continuous Bench Coking (CBC) Unit, while somewhat smaller than the Delayed Coking Pilot Plant, matches commercial delayed coking operations with respect to coking time, heavy liquids recycle, coke drum temperature and coke drum pressure.

A schematic flow sheet of the CBC Unit is shown in Figure 2.5-1. The CBC unit can be operated with fresh liquid feed rates from 400 to 1400 gm/hr and with recycle/fresh feed ratios as desired, typically from 0 to 1.5 vol/vol. Coke drum pressures up to 100 psig and coking temperatures from about 800F (426C) to 1000F (538C) can be evaluated. The operating pressure and key temperatures are controlled automatically within a relatively narrow range. The coking cycle is generally conducted up to a 20-24 hour period and depending upon the coke yield for a given feedstock, the coke drum can hold about 1300 to 4500 gm of green coke product.

Fresh feed is pumped from the steam-heated feed tank and is joined with the heavy oil recycle stream. The combined streams flow through the preheater and through the heater coil. From the heater, the fresh

FIGURE 2.5-1
SCHEMATIC OF CONTINUOUS BENCH COKING UNIT

feed/recycle stream is fed to the coke drum. The devolatilized products from the coke drum flow through a pressure control valve and into the heavy oil separator. In this vessel, the recycle portion is condensed and pumped back to the inlet of the preheater. The coker "distillate" product is taken overhead into the light oil separator. The overhead vapor stream from this vessel is subsequently scrubbed in water and caustic scrubbers and then the non-condensibles are metered in a wet test meter.

2.6 Laboratory Extraction Unit

The initial approach to assessing the technical feasibility and amenability of the Colorado shale oil-derived products to HEDF energy density improvement consisted of equilibrium solubility studies in an ambient pressure glass contacting unit. The contactor consisted of a 1-L jacketed flask containing a glass stirring rod. Hot water is circulated through the jacket. Three stages of solvent contact were employed using the raffinate recovered from the preceeding stage in a subsequent extraction with fresh solvent. Contact time was maintained sufficiently to insure equilibrium. Shale oil-derived extracts were recovered from the separated solvents by water extraction.

2.7 4-in Batch Fractionation Unit

The 4-in Batch Fractionation Unit (see Figure 2.7-1) contains a 4-in diameter by 20-ft SS column containing 20 SS decks of bubble caps, 2 bubble caps per deck equivalent to 8-10 theoretical plates; an automatic variable range reflux head; and an 85-gal reboiler. A vacuum system is capable of operation at reflux head pressures of 5-10 mm Hg abs.

2.8 Equilibrium Flash Vaporization Pilot Unit

The Equilibrium Flash Vaporization pilot unit is a continuous system for performing single-stage equilibrium flash operations. The unit consists of an 8-in diameter by 14-in long flash chamber and can process 5-7 gal/hr of liquid feed to a 600F (315C) maximum temperature. At the operating vacuum limits (ca., 3-4 mm Hg abs), this temperature corresponds to a maximum atmospheric equivalent temperature of about 975F (524C). The unit is a true simple flash with essentially no reflux as the flash chamber walls are electrically heated to at or above the flash temperature.

2.9 Laboratory Batch Distillation Units

In the course of the screening work, it is necessary to tailor distillate product boiling ranges to meet certain jet/diesel fuel specs. As a result of the exploratory nature of the screening program, it is not always possible to prepare the hydroprocessing feedstocks to meet the exact boiling ranges of the final HEDF products. Therefore, there is a need for intermediate distillation for tailing front-end and back-end distillation temperatures.

FIGURE 2.7-1
SCHEMATIC OF FOUR-IN BATCH FRACTIONATION UNIT

This work is facilitated in a variety of laboratory glass distillation columns. Two general types of distillation units were used: ASTM distillations and true boiling point distillations. The ASTM distillations were based on the use of either the D-86; D-1130 (Vac Engler); or modified D-1130 (Herzog) units. The true boiling distillation units consisted of either a 2-in diameter by 2-ft long glass column packed with 1/6-in Cannon stainless steel packing, or a 1-in diameter by 18-in long vacuum-jacketed Vigreux column. Both units are equipped with variable reflux heads and a vacuum system capable of 1 mm Hg abs pressure at the reflux head.

2.10 Clay Treating Units

Final purification of finished HEDF products is accomplished by clay treating. A simple laboratory glass column, 1-in diameter by 5-ft long, was charged with adsorbent and feed was allowed to percolate through the column under gravity flow. A second pass can be used to obtain further reduction in trace impurities affecting color, corrosion and other jet fuel specifications. For the pilot plant sample preparation program, the clay treating for the nominal 50-gallons of HEDF product was carried out in a 2.5-in diameter column filled with 7-ft of bentonite packing.

2.11 Pilot Plant LC-Finingtm Unit

The pilot unit, equipped with two reactor stages, has a degree of flexibility and can be operated in alternative hydrogenation modes, fixed-bed upflow or downflow as well as expanded-bed. The following is a description of the major components of the pilot unit.

o Feed Systems

The fresh oil feed is metered into the circulating reactor loop by a positive displacement pump. The oil feed rate is monitored by measuring the weight loss in a feed tank mounted on an electronic scale. The total hydrogen flow is measured using an orifice meter. The individual hydrogen flow rates to the LC-Fining reactor, instrument sensing lines, etc., are measured via high pressure rotameters. All of the "catalytic" hydrogen is introduced at the bottom of the reactor.

o LC-Fining Expanded-Bed Reactor System

The LC-Fining reactor system (see Figure 2.11-1) consists of 1) a two-stage, expanded-bed in series reactor system; 2) a recycle surge bomb for each reactor stage; and 3) a duplex remote head recycle ("ebullating") pump. The liquid hourly space velocity is calculated based on either the total "thermal reactor" volume which includes the reactor, recycle lines and surge bomb, or on the settled-bed catalyst volume. The LC-Fining reactor and reactor loop are electrically heated with nine temperature controlled circuits for each reactor stage which insures essentially isothermal operation.

The internal recycle rate can be set to vary bed expansion from about 10 to 35% of settled bed height. The connecting line to the remote check valve assembly is purged intermittently with a small flow of gas oil from the stripping column.

REACTOR FLOOR
2 REACTORS IN SERIES
TOTAL VOLUME 2 REACTORS - 2.68 GALLONS
PRESSURE 2000 PSIG

HIGH PRESSURE / HIGH TEMPERATURE
SEPARATOR
PRESSURE 2000 PSIG

LOW PRESSURE / HIGH TEMPERATURE
SEPARATOR
PRESSURE 60 PSIG

HIGH PRESSURE / LOW TEMPERATURE
SEPARATOR
PRESSURE 2000 PSIG

FIGURE 2.11-1

LC-FINING PILOT PLANT SCHEMATIC

o Product Recovery System

The net liquid and gas make from the LC-Fining reactor loop are separated in the high temperature/high pressure (HT-HP) separator. The light oil overhead from the HT-HP separator is condensed and collected in the low temperature/high pressure (LT-HP) separator where it is removed under level control. Quench water is introduced periodically upstream of the condenser to prevent the buildup of sulfides in the lines. The quench water is taken off in a decanter following the LT-HP level controller. The vapors from the LT-HP separator pass through the main pressure control valve which reduces the pressure to atmospheric. The low pressure gas is chilled, scrubbed, sampled, metered and vented. The hydrogen is not currently recycled in the pilot plant unit.

The heavy oil from the HT-HP separator is let down through the level control valve to the low pressure/high temperature (LP-HT) separator which is maintained at about 55 psig. The net flow of heavy oil through the recovery section is low. Heavy oil is recycled from the HT-LP separator back to the HT-HP separator to a) eliminate dead spots which may lead to overheating or undesirable phase separations; and b) increase the flow through the level control valve. A small quantity of stripping gas is introduced into the separator to remove a fraction of the gas oil from the heavy oil. The vapors from the HT-LP separator are let down to atmospheric pressure and stripped. The stripped gas oil, removed from the stripper by level control, is combined with stripper overhead product and the liquid from the cold trap to form the light oil product. The heavy oil is removed from the HT-LP separator by level control, collected and weighed on an electronic scale.

o Sampling and Operating Procedure

Daily operations are usually divided into twelve hour material balance test periods. Routine maintenance and changes in operating conditions are usually made during the day shift. The cold trap liquid is blended in with the light oil receiver liquid prior to analysis. The gas analysis is performed on a composite of equal volume hourly samples. The hydrogen consumption is calculated from the normalized feed and product elemental analyses. The yields of H_2S , NH_3 , and H_2O are usually obtained by difference from the elemental balances² for sulfur, nitrogen and oxygen, respectively.

The operation of this hydroprocessing pilot plant can be tailored to the particular objectives of the program and deviations from the above might result when operating the unit under conditions that favor the production of HEDF's from MCG liquids and shale oils.

2.12 Pilot Plant Fixed-Bed Hydroprocessing Unit

The pilot plant fixed-bed hydrotreating unit consists of the pilot plant LC-Fining unit modified to operate in the fixed-bed downflow mode. Two reactors are available and the recycle pumps for expanding the catalyst beds are not energized.

o Feed Systems

The fresh oil feed is metered into the top of the first reactor by a positive displacement pump. The oil feed rate is monitored by measuring the weight loss in a feed tank mounted on an electronic scale. The total hydrogen flow is measured using an orifice meter. The individual hydrogen flow rates to the fixed-bed reactors, instrument sensing lines, etc., are measured via high pressure rotameters. All of the "catalytic" or treat gas hydrogen is introduced at the top of the reactor.

o Reactor System

The reactor system consists of two 2.5 in i.d. fixed-bed reactors in series. The reactor and reactor loop are electrically heated with nine temperature controlled circuits for each reactor stage which insures essentially isothermal operation.

o Product Recovery System

The net liquid and gas make from the fixed-bed reactors are separated in the high temperature/high pressure (HT-HP) separator. The light oil overhead from the HT-HP separator is condensed and collected in the low temperature/high pressure (LT-HP) separator where it is removed under level control. Quench water is introduced periodically upstream of the condenser to prevent the buildup of sulfides in the lines. The quench water is taken off in a decanter following the LT-HP level controller. The vapors from the LT-HP separator pass through the main pressure control valve which reduces the pressure to atmospheric. The low pressure gas is chilled, scrubbed, sampled, metered and vented. The hydrogen is not currently recycled in the pilot plant unit.

The heavy oil from the HT-HP separator is let down through the level control valve to the low pressure/high temperature (LP-HT) separator which is maintained at about 55 psig. The net flow of heavy oil through the recovery section is low. Heavy oil is recycled from the HT-LP separator back to the HT-HP separator to a) eliminate dead spots which may lead to overheating or undesirable phase separations; and b) increase the flow through the level control valve. A small quantity of stripping gas is introduced into the separator to remove a fraction of the gas oil from the heavy oil. The vapors from the HT-LP separator are let down to atmospheric pressure and stripped. The stripped gas oil, removed from the stripper by level control, is combined with stripper overhead product and the liquid from the cold trap to form the light oil product. The heavy oil is removed from the HT-LP separator by level control, collected and weighed on an electronic scale.

o Sampling and Operating Procedure

Daily operations are usually divided into twelve hour material balance test periods. Routine maintenance and changes in operating conditions are usually made during the day shift. The cold trap liquid is blended in with the light oil receiver liquid prior to analysis. The gas

analysis is performed on a composite of equal volume hourly samples. The hydrogen consumption is calculated from the normalized feed and product elemental analyses. The yields of H_2S , NH_3 , and H_2O are usually obtained by difference from the elemental balances² for sulfur, nitrogen and oxygen, respectively.

The operation of this hydroprocessing pilot plant can be tailored to the particular objectives of the program and deviations from the above might result when operating the unit under conditions that favor the production of HEDF's from MCG liquids and shale oils.

2.13 Analytical Methods and Calculation Procedures

The characterization tests consist of performing analytical assays of the COALITE liquids and the Colorado shale oil. Each feedstock was analyzed for the following minimal tests:

1. Elemental Analyses
2. Distillation
3. Specific Gravity
4. Hydrocarbon Type Analyses including % Aromatics
5. Viscosity
6. Aniline Point
7. Bromine Number
8. Heating Value
9. Conradson Carbon Residue (CCR)
10. Solubility in heptane, toluene, quinoline
11. Pour Point
12. Flash Point
13. Diene Number
14. Accelerated Thermal Stability (D-2274)
15. Metals including arsenic
16. Basic Nitrogen

The feeds were also be fractionated into at least three cuts: an IBP-300°F naphtha; a 300-650°F mid-distillate; and a 650°F+ residue. Several mid-distillate cuts were also taken with end-points varying about the nominal 650F value. The naphtha cuts were analyzed for:

1. Ultimate Analysis
2. Specific Gravity
3. Distillation
4. RI
5. Hydrocarbon Type Analysis
6. Flash Point
7. Octane Number
8. Bromine Number
9. Diene Number
10. Basic Nitrogen

The mid-distillate cuts were be analyzed for:

1. Ultimate Analyses
2. Specific Gravity
3. Distillation
4. Hydrocarbon Type Analyses
5. Flash Point
6. Smoke Point
7. Cetane Number
8. Heating Value
9. ASTM D-873 Residue
10. Freeze Point
11. Basic Nitrogen

The resid cuts were analyzed for ultimate analysis, CCR content, specific gravity, solvent solubilities, distillation, viscosity, and metals content.

The finished HEDF materials were analyzed for the following properties:

1. Elemental Analyses
2. Specific Gravity
3. Heating Value
4. Distillation
5. Hydrocarbon Type Analysis
6. Flash Point
7. Smoke Point
8. Pour Point
9. Aniline Point
10. Stability
11. Cetane Number
12. D-873 Residue
13. Luminometer Number
14. Copper Corrosion
15. Viscosity
16. Color
17. Existent Gum
18. JFTOT

Intermediate HEDF products were also analyzed for selected properties, such as, specific gravity, heating value, hydrocarbon type analysis and elemental analysis.

The calculation procedures basically consist of determining performance criteria for hydroprocessing operations. These typically include percent removal of heteroatoms (hydrodesulfurization-HDS, hydrodenitrogenation-HDN, and hydrodeoxygenation-HDO); percent hydrocracking of 650F+ components; light gas yield; advanced HEDF yield; and hydrogen consumption. Other correlating parameters of importance include smoke point improvement; API gravity improvement; cetane number improvement; stability and viscosity improvement; percent aromatics reduction; kinetic activation energy and frequency factors. The formulas for some of these parameters are summarized in Table 2.11-1.

TABLE 2.11-1

FORMULAS FOR SELECTED HYDROPROCESSING PARAMETERS(1.) 650°F+ Conversion

This parameter represents the total conversion of the 650°F+ fraction in the synfuel feedstocks to 650°F minus material (liquid and gaseous products including NH_3 , H_2S , H_2O , CO_x , etc).

650°F+ Conversion =

$$\frac{\left[\frac{(650^\circ\text{F+ in})_{\text{Feed}}}{(650^\circ\text{F+ in})_{\text{Feed}}} - \frac{(650^\circ\text{F+ out})_{\text{TLP}}}{(650^\circ\text{F+ in})_{\text{Feed}}} \right] \times 100}{(650^\circ\text{F+ in})_{\text{Feed}}}$$

(2.) Gas Yield

This is determined from wet gas test meter readings and gas analyses (corrected to a dry and H_2 free basis).

Gas Yield =

$$\left(\frac{\text{SCFH Dry Gas}}{379.5} \right) \times \left(\frac{100 - \text{H}_2 \text{ Conc Dry Gas}}{100} \right) \times \left(\frac{\text{Mol. Wt. H}_2 \text{ Free Dry Gas}}{\text{Feed Rate, lbs/hr}} \right)$$

(3.) Net Distillate Make

Net Distillate Make, $\frac{\text{Net make of C5 - 650}^\circ\text{F in product}}{100 \text{ lbs } 650^\circ\text{F+ in feed}}$

$$= \left[\frac{650^\circ\text{F- out}}{\text{lbs}} - \frac{650^\circ\text{F- in}}{650^\circ\text{F+}} \right] \times 100$$

(4.) Desulfurization

The sulfur removal includes the sulfur converted to H_2S as well as any sulfur absorbed by the catalyst.

$$\text{Percent Desulfurization} = \frac{\left[S_{\text{Feed}} - S_{\text{TLP}} \right] \times \frac{\text{Wt. TLP}}{\text{Wt. Feed}}}{S_{\text{Feed}}} \times 100$$

(5.) Denitrogenation

This parameter represents the percent nitrogen converted to NH_3 during a material balance period.

$$\text{Percent Denitrogenation} = \frac{\left[N_{\text{Feed}} - N_{\text{TLP}} \right] \times \frac{\text{Wt. TLP}}{\text{Wt. Feed}}}{(N)_{\text{Feed}}} \times 100$$

(6.) Deoxygenation

This parameter represents the percent oxygen converted to H_2O and CO_x during a material balance period.

$$\text{Percent Denitrogenation} = \frac{\left[O_{\text{Feed}} - O_{\text{TLP}} \right] \times \frac{\text{Wt. TLP}}{\text{Wt. Feed}}}{(O)_{\text{Feed}}} \times 100$$

Data analysis consists of a combination of approaches. Trendwise correlations of hydroprocessing performance vs. operating conditions were generated from the test data. These are compared to correlations, both in-house as well as in the literature, for similar hydroprocessing operations with other synfuel feedstocks. Where applicable, pseudo-kinetics analyses were performed to help compare hydroprocessing performance for those cases where a constant set of base operating conditions is not readily available.

3.0 RAW SYNFUEL FEEDSTOCK ANALYSES

3.1 COALITE Feedstock

This feedstock consists of a nominal 160-1000F boiling range product from the British COALITE carbonization process. The COALITE process was developed in the early 1900's (1) based on the use of a vertical retort. A COALITE plant built in 1936 at the Bolsover Works of Coalite and Chemical Products Ltd is still in operation and the 1000-gal sample was procured and delivered to LCI in November 1988 by United Coal Company Research Corporation (presently Coal Technology Corporation) of Bristol, VA. The COALITE was produced from a medium coking British coal and is expected to have properties similar to those of U.S. Eastern bituminous coals.

Upon receipt of the 20-drums, 1-quart aliquot samples were taken from each drum and a composite sample of all 20 drums was made. Additionally, grab samples from several of the drums were taken to check the consistency of the liquids from drum to drum. One of the difficulties in analyzing the COALITE is related to its water content and relatively wide boiling range, ca., 160 to about 1000F (71-538C). We found it expedient to first dewater the sample using a rotavap apparatus and then performing the various whole oil and distillate fraction analyses on the dewatered COALITE.

Analytical distillation was accomplished in two steps: atmospheric distillation via the ASTM D-86 procedure followed by vacuum distillation of the atmospheric bottoms using the D-1160 procedure. The consolidated distillation curve for the composite sample is shown on Figure 3.1-1. Figure 3.1-2 shows the quality comparison of the MCG-based COALITE liquids with that of conventional COED pyrolysis (2) oils.

In order to assess the amenability of COALITE distillates to hydroconversion to HEDF materials, it was determined that analytical characterization data on narrow boiling distillate fractions would be of value in formulating a hydroconversion test matrix. One objective of this analytical study was the determination of whether or not there was a sharp break point in cyclic HEDF precursor content with distillate boiling point. The COALITE composite was fractionated in laboratory true boiling point distillation apparatus to recover 16 successive distillate fractions spanning the range of 300-650F (148-343C). The analyses of the individual fractions are shown in Table 3.1-1. Figure 3.1-3 shows the yield curve vs. the volumetric average boiling point (VABP) of the respective distillate fractions. The VABP parameter has also been used as the independent correlating variable in analyzing distillate properties as a function of boiling range.

A heart cut, i.e., 200-550F (93-288C), was also subjected to G.C./M.S. analysis using an SP-1000 column. The sample speciation, as provided by Professor Robert Baldwin of the Colorado School of Mines, is shown on Table 3.1-2.

FIGURE 3.1-1

CONSOLIDATED ASTM D86/D1160 DISTILLATIONS OF DEWATERED COALITE

ASTM DISTILLATIONS OF SYNFUEL FEEDSTOCKS

TABLE 3.1-1
ANALYSES OF NARROW-BOILING COALITE DISTILLATES

CUT #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
CUMULATE WEIGHT % DISTILLED	2.7	4.3	11.6	18.7	27.0	30.9	39.1	41.7	42.9	46.5	46.6	49.5	50.9	54.4	57.8	59.2
SP. GRAVITY	0.835	0.927	0.972	0.972	0.975	0.980	1.005	1.003	1.015	1.023	1.025	1.035	1.035	1.014	1.016	1.028
API GRAVITY	37.96	21.14	14.08	14.08	13.63	12.89	9.30	9.58	7.91	6.82	6.55	5.21	5.21	8.05	7.77	6.15
TBP (B.C.) DISTILLATION, wt %																
1BF	165	307	340	342	366	379	408	407	416	430	431	439	437	454	457	471
10 %	228	345	367	383	401	426	487	484	517	536	536	559	558	589	598	626
30 %	237	354	388	406	442	478	537	533	567	589	590	616	615	646	654	676
50 %	284	375	404	435	482	510	572	568	600	626	627	650	649	678	683	706
70 %	338	388	419	471	516	545	606	602	631	656	657	681	680	709	716	734
90 %	394	414	473	522	575	607	654	653	670	697	698	724	724	755	759	775
99 %	483	450	548	618	704	746	780	785	783	797	795	818	820	846	843	850
FBP	509	460	575	645	743	787	818	824	822	833	830	853	855	882	878	882
VABP	296	375	410	443	483	513	571	568	597	621	622	646	645	675	682	703
ELEMENTAL, wt %																
C	85.18	81.76	80.36	81.80	81.05	83.55	84.34	84.15	84.31	84.65	84.57	85.42	85.05	84.75	84.91	85.04
H	11.34	9.92	9.19	9.41	9.27	9.66	9.33	9.36	9.20	9.10	9.10	8.99	9.00	8.76	8.48	8.52
N	0.30	0.20	0.53	0.63	0.52	0.73	0.92	0.89	0.99	0.94	1.07	1.16	1.12	1.18	1.27	1.33
S	1.27	1.10	0.61	0.46	0.67	1.03	0.90	1.10	1.02	1.02	1.01	1.00	1.03	0.96	0.96	0.90
O (BY DIFF.)	1.91	7.02	9.31	7.70	8.49	5.03	4.51	4.50	4.48	4.29	4.25	3.43	3.80	4.35	4.38	4.21
WT % PARAFFINS	20.60	0.00	0.00	0.00	0.00	0.00	0.00									
WT % OLEFINS	17.50	22.40	20.60	17.60	14.40	15.60	5.50									
WT % NAPHTHENES	8.80	31.60	34.70	22.00	21.40	18.60	7.70									
WT % AROMATICS	53.20	46.10	54.70	60.30	65.50	65.30	87.20									
BROMINE NO.	42	88	83	94	81											
REFRACTIVE INDEX @ 20 C	1.4468	1.4988	1.5224	1.5273	1.5344	1.5400	1.5592	1.5573	1.5657	1.5734	1.5727	1.5815	1.5814	1.5929	1.5955	1.6026

WEIGHT PERCENT DISTILLATE YIELD AS A FUNCTION OF VOLUMETRIC AVERAGE BOILING POINT(VABP) OF CUT

G.C./M.S. ANALYSIS OF 200-550F COALITE

COALITE MID DISTILLATE (200-550 F)
USING SP-1000 COLUMN

RET TIME	AREA%	COMPOUND NAME
2.077	0.11	paraffin or isoparaffin
2.215	0.14	heptane
2.287	0.06	paraffin or isoparaffin
2.387	0.14	paraffin or isoparaffin
2.491	0.13	octane
2.579	0.22	5-methyl-2-hexanone
2.672	0.06	paraffin or isoparaffin
2.742	0.07	paraffin or isoparaffin
2.788	0.10	paraffin or isoparaffin
2.981	0.36	nonane
3.135	0.05	paraffin or isoparaffin
3.237	0.21	paraffin or isoparaffin
3.356	0.16	paraffin or isoparaffin
3.633	0.09	paraffin or isoparaffin
3.772	0.33	decane
3.862	0.11	paraffin or isoparaffin
3.939	0.14	butyl ester of acetic acid
4.120	0.05	paraffin or isoparaffin
4.228	0.15	paraffin or isoparaffin
4.296	0.80	1,3,5-cycloheptatriene
4.489	0.08	paraffin or isoparaffin
4.716	0.10	paraffin or isoparaffin
4.881	0.55	undecane
5.094	0.07	paraffin or isoparaffin
5.246	0.03	paraffin or isoparaffin
5.357	0.02	big 91
5.459	0.38	big 91
5.559	0.60	dimethyl benzene
5.755	0.03	paraffin or isoparaffin
5.819	0.10	paraffin or isoparaffin
5.985	0.03	paraffin or isoparaffin
6.062	0.11	paraffin or isoparaffin
6.214	1.20	dodecane
6.485	0.07	big 91
6.539	0.17	paraffin or isoparaffin
6.724	0.45	ethyl methyl benzene
6.851	0.27	1-dodecene
6.903	0.24	7-methyl-tridecane
7.008	0.52	trimethyl benzene
7.167	0.09	paraffin or isoparaffin
7.256	0.20	ethyl methyl benzene
7.372	0.08	paraffin or isoparaffin
7.568	0.63	ethyl methyl benzene
7.644	0.86	tridecane
7.723	0.15	paraffin or isoparaffin
7.856	0.23	methyl propyl benzene
7.987	0.11	paraffin or isoparaffin
8.090	0.10	paraffin or isoparaffin
8.178	0.21	ethyl dimethyl benzene
8.251	0.18	paraffin or isoparaffin
8.305	0.50	C13 isoparaffin
8.393	0.28	trimethyl benzene

8.446	0.51	C13 isoparaffin
8.609	0.25	methyl phenyl pentadecane
8.710	0.43	trimethyl propyl benzene
8.818	0.20	methyl ethyl benzene
8.918	0.31	dihydro Indene
8.991	0.21	trimethyl pyrridine
9.101	1.14	tetradecane
9.212	0.08	paraffin or isoparaffin
9.275	0.28	dihydro-methyl-1H-Indene
9.413	0.42	benzaldehyde
9.634	0.83	5-methyl-5-ethyl decane
9.761	0.43	paraffin or isoparaffin
9.833	0.23	dimethyl benzene
9.890	0.16	paraffin or isoparaffin
9.961	0.24	paraffin or isoparaffin
10.213	0.18	paraffin or isoparaffin
10.308	0.07	paraffin or isoparaffin
10.422	0.15	paraffin or isoparaffin
10.308	0.15	paraffin or isoparaffin
10.422	0.39	benzene compound
10.521	1.16	2-methyl-heptadecane
10.605	0.28	tetramethyl benzene
10.712	0.34	dihydro-dimethyl-1H-Indene
10.788	1.01	dihydro-methyl-1H-Indene
10.986	0.28	paraffin or isoparaffin
11.088	0.30	dihydro-dimethyl-1H-Indene
11.164	0.51	paraffin or isoparaffin
11.284	0.21	paraffin or isoparaffin
11.342	0.10	paraffin or isoparaffin
11.469	0.31	paraffin or isoparaffin
11.558	0.09	paraffin or isoparaffin
11.632	0.11	paraffin or isoparaffin
11.679	0.21	paraffin or isoparaffin
11.754	0.17	paraffin or isoparaffin
11.825	0.14	Indene or benzene compound
11.881	1.49	hexadecane
12.146	0.60	pyrridine compound
12.239	0.70	dihydro-dimethyl-1H-Indene
12.372	0.11	paraffin or isoparaffin
12.426	0.22	Indene or naphthalene compound
12.518	0.40	paraffin or isoparaffin
12.621	0.28	paraffin or isoparaffin
12.698	0.13	paraffin or isoparaffin
12.765	1.01	5-propyl-tridecane
12.964	0.57	dihydro dimethyl-1H-Indene
13.113	0.22	paraffin or isoparaffin
13.194	0.94	9-octyl-heptadecane
13.359	0.70	paraffin or isoparaffin
13.534	0.50	pyrridine compound
13.607	0.42	dihydro-methyl-naphthalene
13.734	0.35	benzene or naphthalene compound
13.815	0.42	paraffin or isoparaffin
14.002	1.56	naphthalene
14.146	0.57	paraffin or isoparaffin
14.357	0.26	paraffin or isoparaffin
14.437	0.79	hexacosane

14.583	0.47	triethyl-dihydro-Indene
14.673	0.28	paraffin or isoparaffin
14.800	0.33	nitrogen-containing compound
14.942	0.38	ethyl-propyl-benzimidazole
15.069	0.44	ethyl naphthalene
15.176	0.21	paraffin or isoparaffin
15.212	0.22	paraffin or isoparaffin
15.380	2.26	1-ethylidene-1H-Indene
15.702	1.66	dimethyl phenol
15.819	1.52	methyl naphthalene
16.102	0.52	Indenone compound
16.213	0.48	methyl ethyl phenol
16.313	0.54	paraffin or isoparaffin
16.457	0.56	ethyl naphthalene
16.700	9.61	methyl phenol
16.846	0.80	paraffin or isoparaffin
17.013	0.69	dimethyl naphthalene
17.112	1.52	dimethyl naphthalene
17.237	0.63	paraffin or isoparaffin
17.418	1.20	ethyl phenol
17.571	8.49	dimethyl phenol
17.675	5.22	methyl phenol
17.872	0.85	paraffin or isoparaffin
18.042	0.52	paraffin or isoparaffin
18.112	0.37	paraffin or isoparaffin
18.203	1.21	2-ethyl-4-methyl phenol
18.365	2.10	dimethyl phenol
18.548	1.70	2-ethyl-5-methyl phenol
18.696	4.09	ethyl phenol
18.780	2.20	ethyl phenol
18.982	0.64	phenol compound
19.147	1.15	phenol compound
19.323	2.87	dimethyl phenol
19.480	0.37	paraffin or isoparaffin
19.604	0.48	benzene compound
19.701	0.29	paraffin or isoparaffin
19.830	2.73	ethyl methyl phenol
20.163	0.23	paraffin or isoparaffin
20.289	0.61	paraffin or isoparaffin
20.434	0.48	ethyl methyl phenol
20.491	0.16	pyrrolidine or sulfur-containing compound
20.524	0.45	sulfur-containing compound
20.678	0.19	paraffin or isoparaffin
20.818	0.20	paraffin or isoparaffin
20.985	0.52	paraffin or isoparaffin
21.111	0.23	nitrogen- or sulfur-containing compound
21.597	0.77	ar,ar,.alpha.-trimethyl benzenemethanol
21.837	0.19	benzene compound

Figure 3.1-4 shows the H/C atomic ratio of the COALITE distillates as a function of VABP. As expected, the H/C ratio decreases as VABP increases. Also shown on the figure is the H/C ratios required for the HEDF product. The H/C atomic ratio of the raw COALITE distillates has to be improved by approximately 40%.

Figure 3.1-5 shows the API Gravity of the COALITE distillates as a function of VABP. The API of the finished HEDF product should be about 20-40 degrees API higher than that of the raw COALITE 300-650F (148-343C) distillate.

Figures 3.1-6, 7, and 8 show the nitrogen, oxygen and sulfur contents of the COALITE distillates as a function of VABP. Nitrogen content increases linearly with VABP. Oxygen content, as determined by difference, appears to decrease almost linearly with VABP. Sulfur content shows an unusual minima at about 450F (232C) average boiling point and then lines out at a value of about 0.9-1.0 wt percent at higher VABP.

PONA analysis based on the F.I.A./Refractive Index method was used as a measure of hydrocarbon types. The resultant data are presented on Figure 3.1-9. It is to be cautioned that the method may not be accurate for non-petroleum, synfuel-derived distillates such as COALITE. The general trend indicates a continual increase in aromaticity as VABP increases.

Proton NMR spectroscopy was used as an additional analytical tool to assess the hydrogen and carbon distributions in COALITE distillates. Table 3.1-3 shows the NMR parameters for a 390-650F (198-343C) boiling distillate. Figures 3.1-10, 11, and 12 show the NMR hydrogen distributions, carbon distributions and H/C atomic ratios respectively as a function of VABP.

Bromine No., which is a measure of carbon-carbon double bond content, for four lighter COALITE distillates is plotted vs VABP in Figure 3.1-13. There is little effect of VABP on Bromine No. over the range evaluated.

Refractive Index (@ 20C) is a rapid analytical tool and a good measure of distillate quality. Figure 3.1-14 shows the effect of VABP on distillate Refractive Index. Refractive Index can also be used as an independent correlating variable similar to that of the VABP parameter. Figures 3.1-15, 16, 17, and 18 show the dependency of several distillate properties as a function of the Refractive Index. Also shown on the latter four graphs are data published by METC (3) for a variety of full-range coal liquids and shale oils. While the LCI and METC correlations are not completely congruent, the Refractive Index parameter does show to be a widely usable correlating tool.

3.2 Colorado Shale Oil Feedstock

The programs being performed under this contract are co-funded by the Coal Projects Management Division/Gasification Branch and by the

FIGURE 3.1-4

H/C ATOMIC RATIO OF COALITE DISTILLATE CUTS
AS A FUNCTION OF VOLUMETRIC
AVERAGE BOILING POINT(VABP) OF CUT

VABP OF DISTILLATE CUT, DEG F

API GRAVITY OF COALITE DISTILLATES AS A FUNCTION OF VOLUMETRIC AVERAGE BOILING POINT(VABP) OF CUT

FIGURE 3.1-6

NITROGEN CONTENT
AS A FUNCTION OF VOLUMETRIC
AVERAGE BOILING POINT(VABP) OF CUT

VABP OF DISTILLATE CUT, DEG F

WEIGHT PERCENT OXYGEN CONTENT AS A FUNCTION OF VOLUMETRIC AVERAGE BOILING POINT(VABP) OF CUT

FIGURE 3.1-8

WEIGHT PERCENT SULFUR CONTENT
AS A FUNCTION OF VOLUMETRIC
AVERAGE BOILING POINT(VABP) OF CUT

FIGURE 3.1-9

PONA ANALYSIS OF SELECTED COALITE DISTILLATES AS A FUNCTION OF VOLUMETRIC AVERAGE BOILING POINT(VABP) OF CUT

TABLE 3.1-3
NMR SPECTROSCOPY OF 390-650°F COALITE

HYDROGEN DISTRIBUTION

ELEMENTAL ANALYSIS %	
H	9.26
C	84.02
(H/C) ELEMENTAL ANALYSIS	1.31
(H/C) NMR	1.34
H AROM/C AROM	0.58
H SAT/C SAT.	2.26

H A POLY, %	12.8
H A MONO	11.3
H F	0
H A1	7.3
H A2	23.7
H B1	9.4
H B2	23.5
H G	12.0

TOTAL H 100.0

H AROM %	24.1
H SAT%	75.9

CARBON DISTRIBUTION

C A POLY	32.8
C A MONO	22.4
C F	0
C A1	4.9
C A2	10.5
C B1	8.4
C B2	15.7
C G	5.3

TOTAL C% 100.0

C AROM %	55.2
C SAT %	44.8

C A SUB %	27.9
C A UNS %	58.4
C A INT %	13.7

C A PER %	86.3
C A INT %	13.7

C NAPHT % 18.8

f AROM	0.552
% AS	32.4
CPER/CINT	6.29
B. I.	0.37
C/H SAT W	5.27
n CHAIN	2.5

HYDROGEN DISTRIBUTION BY HNMR SPECTROSCOPY AS A FUNCTION OF VOLUMETRIC AVERAGE BOILING POINT(VABP) OF CUT

FIGURE 3.1-11

CALCULATED CARBON DISTRIBUTIONS FROM HNM
AS A FUNCTION OF VOLUMETRIC
AVERAGE BOILING POINT(VABP) OF CUT

VABP OF DISTILLATE CUT, DEG F

FIG 3.1-12

H/C RATIOS FROM PROTON NMR SPECTROSCOPY AS A FUNCTION OF VOLUMETRIC AVERAGE BOILING POINT(VABP) OF CUT

FIGURE 3.1-13

BROMINE NUMBER OF DISTILLATE CUT
AS A FUNCTION OF VOLUMETRIC
AVERAGE BOILING POINT(VABP) OF CUT

REFRACTIVE INDEX @ 20C AS A FUNCTION OF VOLUMETRIC AVERAGE BOILING POINT(VABP) OF CUT

FIGURE 3.1-15

API GRAVITY AS A FUNCTION OF REFRACTIVE INDEX OF COALITE DISTILLATE CUTS

FIGURE 3.1-16

H/C ATOMIC RATIO AS A FUNCTION OF REFRACTIVE INDEX OF COALITE DISTILLATE CUTS

FIGURE 3.1-17

HYDROGEN AROMATICITY AS A FUNCTION OF REFRACTIVE INDEX OF COALITE DISTILLATE CUTS

REFRACTIVE INDEX @ 20C

FIGURE 3.1-18

CARBON AROMATICITY AS A FUNCTION OF REFRACTIVE INDEX OF COALITE DISTILLATE CUTS

Extraction Projects Management Division. Thus, there is interest in producing HEDF from both MCG liquids as well as shale oils, tar sands and other liquid synfuels. The Colorado shale oil feedstock is derived from the Unocal retorting facility at Parachute Creek. The 1000-gal sample was provided to LCI by the Western Research Institute in Laramie, WY.

Upon receipt of the 19-drums, 1-quart aliquot samples were taken from each drum and a composite sample of all 19 drums was made. Additionally, grab samples from several of the drums were taken to check the consistency of the liquids from drum to drum.

Analytical distillation was accomplished in two steps: atmospheric distillation via the ASTM D-86 procedure followed by vacuum distillation of the atmospheric bottoms using the D-1160 procedure. The consolidated distillation curve for the composite sample is shown on Figure 3.2-1. As can be seen from the figure, there is a considerable vac resid component in this material approaching about 35% at 975F (524C) as well as a major quantity of atmospheric resid amounting to 63% at 650F+ (343C). The shale oil is somewhat heavier than the COALITE feed but lighter than a COED bituminous coal-derived pyrolysis oil as can be seen in Figure 3.2-2. Thus, considerable cracking, thermal or catalytic hydrocracking, is required to obtain significant yields of HEDF turbine fuels from this Colorado shale oil feedstock.

In order to assess the amenability of the turbine-range boiling distillates to hydroconversion to HEDF materials, it was determined that analytical characterization data on narrow boiling distillate fractions would be of value in formulating a hydroconversion test matrix. One objective of this analytical study was the determination of whether or not there was a sharp break point in cyclic HEDF precursor content with distillate boiling point. Therefore, the Colorado shale oil composite was fractionated in laboratory true boiling point distillation apparatus in a manner similar to that of the COALITE composite to recover 19 successive distillate fractions spanning the range of 300-700F (148-371C). The analyses of the individual fractions are shown in Table 3.2-1.

Figures 3.2-3 through -10 are presented to show the trends of volumetric average boiling point and refractive index with selected distillate properties. For comparative purposes, the analogous data for the COALITE distillates are also included on the figures.

Figure 3.2-3 shows the H/C atomic ratio of the Colorado shale oil distillate and the COALITE distillate as a function of VABP. As expected, the H/C ratios decrease as VABP increases. Also shown on the figure is the H/C ratios required for the HEDF product. The H/C atomic ratio of the raw Colorado shale oil distillates are essentially equal to that of the HEDF product.

Figure 3.2-4 shows the API Gravity of the two synfuel distillates as a function of VABP. The Colorado shale oil has a considerably higher API gravity across the VABP range evaluated but its rate of decline with VABP is about 33% higher than that of the COALITE.

FIGURE 3.2-1
CONSOLIDATED ASTM DISTILLATION OF RAW
COLORADO SHALE OIL FEEDSTOCK

FIGURE 3.2-2
 ASTM DISTILLATIONS OF SYNFUEL FEEDSTOCKS

TABLE 3.2-1

ANALYSES OF NARROW-BOILING COLORADO SHALE OIL DISTILLATES

CUT #	1,2,3,4,5	7	9	11	12	13	15	17	19
WT % YIELD ON WHOLE OIL	5.5	1.9	3.5	3.5	3.6	3.6	3.7	1.9	1.2
SP. GRAV., g/cm ³	0.7905	0.8448	0.8463	0.8729	0.8805	0.8772	0.9052	0.9162	0.9203
A.P.I. GRAVITY	47.5	36.0	35.7	30.6	29.2	29.8	24.8	22.9	22.3
TBF DISTILLATION, wt %									
IBP F	109	331	397	440	449	474	513	514	498
10%	180	365	426	493	518	550	610	641	661
30%	235	383	447	510	540	572	633	663	685
50%	265	389	456	518	550	581	644	675	698
70%	300	395	464	526	564	588	656	685	707
90%	344	408	482	544	580	603	668	694	716
EBP	436	628	662	773	793	816	815	842	829
VABP	265	388	455	518	550	579	642	672	693
ELEMENTAL, wt %									
C	83.50	84.48	84.64	84.75	84.34	84.70	84.32	84.50	84.35
H	12.41	12.92	13.08	12.51	12.26	12.65	11.87	11.75	11.68
N	0.48	0.98	0.84	0.96	1.21	1.31	1.50	1.60	1.70
S	1.14	1.00	0.86	1.08	1.12	0.88	1.00	1.00	0.92
C BY DIFF.	0.46	0.62	0.56	0.70	1.05	0.46	1.31	1.15	1.35
WT % PARAFFINE	31.40	16.10	8.70	0.00	0.00	0.00			
WT % OLEFINE	32.80	33.30	39.10	37.30	40.90	37.50			
WT % NAPHTHENE	0.00	27.50	34.80	41.40	37.70	39.10			
WT % AROMATICS	35.80	23.10	17.40	21.30	21.40	23.40			
REFRACTIVE INDEX @20 C	1.4439	1.4555	1.4667	1.4822	1.4874	1.4840	1.5017	1.5084	1.5122

FIGURE 3.2-3

H/C ATOMIC RATIO OF SYNFUEL DISTILLATES AS A FUNCTION OF VOLUMETRIC AVERAGE BOILING POINT(VABP)

FIGURE 3.2-4

API GRAVITY OF SYNFUEL DISTILLATES AS A FUNCTION OF VOLUMETRIC AVERAGE BOILING POINT(VABP)

FIGURE 3.2-5

NITROGEN CONTENT OF SYN FUEL DISTILLATES AS A FUNCTION OF VOLUMETRIC AVERAGE BOILING POINT(VABP)

FIGURE 3.2-6

WEIGHT PERCENT SULFUR CONTENT OF SYN-FUEL DISTILLATES AS A FUNCTION OF VOLUMETRIC AVERAGE BOILING POINT(VABP)

VABP OF DISTILLATE CUT, DEG F

FIGURE 3.2-7

PONA ANALYSIS OF SYNFUEL DISTILLATES AS A FUNCTION OF VOLUMETRIC AVERAGE BOILING POINT(VABP)

FIGURE 3.2-8

NMR CARBON DISTRIBUTION FOR COALITE AND COLO SHALE OIL AS A FUNCTION OF DISTILLATE VABP

VABP OF DISTILLATE CUT, DEG F

FIGURE 3.2-9

REFRACTIVE INDEX OF SYNFUEL DISTILLATES
AS A FUNCTION OF VOLUMETRIC
AVERAGE BOILING POINT(VABP)

FIGURE 3.2-10

NMR CARBON DISTRIBUTION FOR COALITE AND COLO SHALE OIL AS A FUNCTION OF REFRACTIVE INDEX

Figures 3.2-5 and 6 show the nitrogen and sulfur contents of the two synfuel distillates as a function of VABP. Nitrogen content increases almost linearly with VABP for both distillates with the shale oil having about a 2000 ppmw higher N content than the COALITE. While the sulfur content of the COALITE distillates shows an unusual minima at about 450F (232C) average boiling point, the Colorado shale oil-derived sulfur exhibits a broad maxima at about 325-425F (163-218C). The heavier shale oil and COALITE distillates, ca., 600-700F (315-371C), have essentially the same sulfur content, namely, 0.8-1.0 wt percent.

PONA analysis based on the F.I.A./Refractive Index method was used as a measure of hydrocarbon types. The resultant data are presented on Figure 3.2-7. It is to be cautioned that the method may not be accurate for non-petroleum, synfuel-derived distillates such as shale oil or COALITE. While the COALITE aromatics exhibit an increasing trend with VABP, the shale oil aromatics first decrease and then line out at the higher VABP. As expected, the shale oil aromatics contents are significantly lower than those of the COALITE, especially for the higher boiling distillates.

Proton NMR spectroscopy was used as an additional analytical tool to assess the carbon distributions in the shale oil and COALITE distillates. Figure 3.2-8 shows the NMR carbon distributions as a function of VABP. The shale oil distillates have about a 10-15 mol percent lower cyclic content (naphthenes plus aromatics) than that of the COALITE. However, the desirable naphthenic content, with the latter being key components of HEDF fuels, of the shale oil distillates is some 15-30 mol percent higher than that of the COALITE.

Refractive Index (@ 20C) is a rapid analytical tool and a good measure of distillate quality. Figure 3.2-9 shows the effect of VABP on distillate Refractive Index for the two synfuel distillates. Refractive Index can also be used as an independent correlating variable similar to that of the VABP parameter. Figure 3.2-10 shows the dependency of NMR carbon distribution as a function of the Refractive Index. This type of plot illustrates the major difference in compositional variations between the two feedstocks reflecting a discontinuity at a refractive index level of about 1.520.

4.0 SUMMARY OF SCREENING PROGRAM OPERATIONS

4.1 Overview

The major goals of the screening program were to: a) pinpoint those processing routes that would result in the production of high energy density turbine fuels (HEDF) meeting or exceeding the minimum energy density specification of 130,000 Btu/gal; and b) collect sufficient processing data on the alternative processing routes for use in the subsequent Task 4 economic modelling study. A third goal was the collection of liter size samples of HEDF products for transmittal to DOE-METC.

The methodology chosen was to perform process variable scans in selected existing test units for each of the candidate processing schemes identified in the project management plan. As with any exploratory R&D program, deviations from the original plan are to be expected as emerging test data are acquired. The direction taken during the course of the screening program was always towards the scanning of conditions that would result in achieving the maximum HEDF product energy density. The key processing routes evaluated are as follows:

- o Raw distillate hydrotreating (single and two-stage)
- o Raw atmospheric resid hydrocracking (LC-FiningSM)
- o Vacuum gas oil hydrocracking
- o Raw atmospheric resid delayed coking
- o Cracked distillate hydrotreating
- o Hydrotreated distillate extraction (shale oil only)

These tests were carried out in five different bench-scale facilities. Additionally, test data were collected for the ancillary HEDF manufacturing processes of fractionation and clay treating. In order to maximize the operating efficiency of our pilot plant/analytical staffs and thereby maximize the return on the research investment, the scheduling of the various tests did not follow any predetermined order. Thus, operating campaigns with the COALITE feedstocks were intermingled with the Colorado shale oil feedstock campaigns. By necessity, the cracked distillate hydrotreating campaigns had to follow the hydrocracking and the delayed coking campaigns since these latter operations produced the cracked distillate feedstocks.

4.2 COALITE Operations

4.2.1 Feedstock Preparation

The raw COALITE feedstock was fractionated in the 4-in Batch Distillation unit in four different campaigns. The initial fractionation, referred to as CC-1, resulted in the collection of

sixteen successive distillate cuts and a vacuum resid fraction. The bulk of these materials was used for the analytical characterization tests (described in Section 3), the delayed coking evaluation of the 650F+ resid, and the LC-Fining evaluation of the 650F+ (343C+) resid.

Batch fractionation CC-2 resulted in the collection of 24 distillate fractions and a 670F+ (354C) resid fraction. Two composite blends for distillate hydrotreating were made: a nominal 350-650F (177-343C) blend of distillate fractions 5 through 22 to simulate a Category III boiling-range fuel; and a nominal 350-550F (177-288C) blend of distillate fractions 5 through 14 to simulate a Category I boiling-range fuel. Two additional blends were made with heavier end points (i.e., 750F and 820F) to determine whether the addition of the heavier gas oil components could increase energy densities above and beyond the 130,000 Btu/gal specification.

It should be kept in mind that the final Initial Boiling Point and End Point of the finished HEDF product is set in a post-hydrogenation topping and tailing operation. The nominal ranges of the feeds could not be fine-tuned in advance of and during the screening test work until sufficient information was acquired on the interaction of the process variables on all of the specified HEDF properties. Thus, the approach taken was to use the post-hydrogenation distillation operations to fine tune the critical distillation temperatures controlling the volatility (i.e., flash point spec) and the back-end viscosity/freeze point spec. Of course, in a commercial operation, the design of the fractionation systems would be optimized to reduce the cost of any unnecessary towers.

Batch fractionations CC-3 and CC-4 were used to prepare 300F+ (149C+) dewatered product for use in the selective hydrocracking campaigns and for use in preparing hydrotreated resid for a delayed coking test. Table 4.2.1-1 presents the properties of the raw mid-distillate cuts used as feedstocks in the distillate hydrotreating campaigns.

4.2.2 Virgin Distillate Hydrotreating Campaigns

Six virgin distillate hydrotreating campaigns were made with the COALITE distillates to study the effects of catalyst type, distillate boiling range, single-stage vs two-stage, recycle of first-pass hydrotreated product and severity as controlled by space velocity, hydrogen partial pressure and reactor temperature. A Severity function has been defined as follows:

$$\text{Severity} = 10^4 * \text{H2 Press, psig} * \text{LHSV}^{-1} * \exp\{-35000/[1.987 * T_{\text{avg}}, R]\}$$

A total of 59 material balance tests were made of durations extending from 2-hours to 36-hours. The following table summarizes the salient features of each campaign and the summary table reference number.

HYDROTREATING FEEDSTOCK ANALYSES OF RAW COALITE MID-DISTILLATE

Nominal Boiling Range, °F	350-550°F	350-650°F	300-750°F	300-820°F
R. I. @ 20°C	1.5327	1.5469	1.5445	1.5561
Sp. Grav., g/cc	0.9772	0.9923	0.9902	1.0050
API Gravity	13.3	11.1	11.4	9.3
Distillation, °F				
IBP	D86/TBP-GC	D86/TBP-GC	TBP-GC	
10%	394/345	390/364	335	
30%	416/389	422/409	384	
50%	438/436	460/478	454	
70%	460/478	504/531	522	
90%	488/512	552/588	590	
EBP	518/562	616/658	685	
VABP	550/816	652/851	828	
	465/505	531/572	527	
Watson K, R	9.70/10.04	9.98/10.12	9.89	
Elemental, Wt. %				
C	83.11	84.00	82.55	
H	9.44	9.26	9.62	
N	0.60	0.81	0.81	
S	0.63	0.73	0.88	
O (By Diff.)	6.22	5.20	6.14	
F.I.A./R.I., Liq. Vol %				
Paraffins	0.0	0.0	---	
Olefins	13.4	11.8	---	
Naphthenes	22.5	11.7	---	
Aromatics	64.1	76.5	---	
WLHV, btu/lb	15880	16059	15793	
VLHV, btu/gal	129264	132741	130266	
Viscosity, cs @ -4°F	---	4.0	---	
Pour Pt., °F	<20	5	---	
Aniline Pt., °F	28.0	34.5	---	
Diesel Index	3.7	3.8	---	
Smoke Pt.	9	7	---	
Luminometer No.	32.0	29.0		

<u>CAMPAIGN #</u>	<u># STAGES</u>	<u>CATALYST TYPE</u>	<u>FEED BOILING RANGE</u>	<u>#TESTS</u>	<u>TABLE #</u>
1	1	K-550	350-650F	30	4.2.2-1
2	1	K-550	350-550F	8	4.2.2-2
3	2	K-550/K-550	350-750F;350-820F	8	4.2.2-3
4	2	K-550/K-599	350-650F	7	4.2.2-4
5	1	K-599	350-650F	2	4.2.2-5
6	1	Ca-doped K-550	350-650F	4	4.2.2-6

Campaign 5 was also used for the production of liter-size samples of finished HEDF samples required as a Task 3 deliverable. The specific objectives of each of these six campaigns are summarized below:

- Campaign 1: Initial scans to evaluate the effects of space velocity, reaction temperature, hydrogen partial pressure and single-pass product recycle with a candidate NiWS hydrotreating catalyst in a single-stage reactor using the 350-650F COALITE distillate.
- Campaign 2: Initial scans to evaluate the effects of space velocity, reaction temperature and single-pass product recycle with a candidate NiWS hydrotreating catalyst in a single-stage reactor using the 350-550F COALITE distillate.
- Campaign 3: Initial scans to evaluate the effects of temperature and space velocity with higher end point COALITE distillates using a two-stage NiWS catalyst reaction system.
- Campaign 4: Initial scans to evaluate the effects of temperature and space velocity with the 350-650F COALITE distillate in a two-stage reactor system comprising a NiWS catalyst in the first-stage and a high moly nickel catalyst in the second-stage reactor.
- Campaign 5: Production run to produce liter size samples of HEDF materials in a single-stage reactor with the high moly nickel catalyst using the 350-650F COALITE distillate.
- Campaign 6: Scans of the effects of temperature and space velocity with a calcium-doped NiWS catalyst using the 350-650F COALITE distillate.

4.2.3 Virgin Atmospheric Resid Cracking Campaigns

There is a considerable yield of atmospheric resid in the raw COALITE. HEDF products are end-point limited because of viscosity and freeze point specifications. Therefore, it is necessary to crack the heavier components to the mid-distillate range comprising the desired HEDF turbine fuel products. Three cracking methods were considered: 1) Resid hydrocracking using the LC-Fining[™] process; 2) Delayed Coking; and 3) VGO fixed-bed hydrocracking. The former two are discussed in the next two sections while the latter is discussed in Section 4.2.5.

TABLE 4.2.2-1

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)

FILE ID: REPTB01.WK1

TEST # (FB-)	17A-1	17A-2	18A-1	18A-2	18A-3	19A-1	19A-2	19A-3
DATE (1989)	01-13	01-13	01-16	01-16	01-16	01-17	01-17	01-17
START TIME	14:30	16:30	12:30	14:45	19:00	12:30	15:00	18:20
END TIME	16:30	17:30	13:30	15:45	21:00	13:30	17:00	20:20
FEEDSTOCK	A	A	A	A	A	A	A	A
FEED RATE, cc/hr	1542	590	372	373	167	154	155	135
OPERATING PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H2 PARTIAL PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H2 TREAT RATE, scf/bbl	3000	3000	5000	5000	5000	5000	5000	5000
REACTOR 1 CONDITIONS								
LHSV, cc/hr/cc cat.	9.6	3.7	2.3	2.3	1.0	1.0	1.0	0.8
INLET BED TEMP., F	371	393	499	602	606	609	644	605
UPPER MID BED TEMP., F								
LOWER BED TEMP., F	396	404	507	672	654	628	704	667
AVERAGE BED TEMP., F	384	399	503	637	630	619	674	636
SAND BATH TEMP., F	399	404	579	606	577	606	534	481
REACTOR 2 CONDITIONS								
LHSV, cc/hr/cc cat.								
INLET BED TEMP., F								
UPPER MID BED TEMP., F								
LOWER BED TEMP., F								
AVERAGE BED TEMP., F								
SAND BATH TEMP., F								
SEVERITY STAGE 1	0.0018	0.0067	0.0992	0.9259	1.9210	1.6169	3.5959	2.6233
SEVERITY STAGE 2								
OVERALL SEVERITY	0.0018	0.0067	0.0992	0.9259	1.9210	1.6169	3.5959	2.6233

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

TABLE 4.2.2-1 (continued)

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)

FILE ID: REPT801.WK1

TEST # (FB-)	20A-1	20A-2	21	22	23	24	25	26
DATE (1989)	01-18	01-18	01-19	01-20	01-20	01-23	01-23	01-24
START TIME	16:20	19:00	19:00	16:45	19:30	17:45	20:45	15:20
END TIME	18:20	21:00	21:00	17:45	20:30	18:45	21:45	16:30
FEEDSTOCK	A	A	A	A	A	A	A	A
FEED RATE, cc/hr	152	144	107	109	106	150	151	166
OPERATING PRESSURE, psig	2000	2000	2000	2000	2000	2400	2400	1600
H2 PARTIAL PRESSURE, psig	2000	2000	2000	2000	2000	2400	2400	1600
H2 TREAT RATE, scf/bbl	5000	5000	5000	5000	5000	5000	5000	5000
REACTOR 1 CONDITIONS								
LHSV, cc/hr/cc cat.	1.0	0.9	0.7	0.7	0.7	0.9	0.9	1.0
INLET BED TEMP., F	589	602	612	621	650	601	560	651
UPPER MID BED TEMP., F								
LOWER BED TEMP., F	696	617	660	691	659	602	684	678
AVERAGE BED TEMP., F	643	610	636	656	655	602	622	665
SAND BATH TEMP., F	541	599	559	579	643	601	544	654
REACTOR 2 CONDITIONS								
LHSV, cc/hr/cc cat.								
INLET BED TEMP., F								
UPPER MID BED TEMP., F								
LOWER BED TEMP., F								
AVERAGE BED TEMP., F								
SAND BATH TEMP., F								
SEVERITY STAGE 1	2.3072	1.5659	2.9981	3.9987	3.9146	1.6598	2.2729	2.5230
SEVERITY STAGE 2								
OVERALL SEVERITY	2.3072	1.5659	2.9981	3.9987	3.9146	1.6598	2.2729	2.5230

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)

FILE ID: REPTB02.WK1

TEST # (FB-)	27	28	29	37	38	39	40	41
DATE (1989)	01-24	01-24	01-25	02-02	02-02	02-03	02-03	02-03
START TIME	17:45	20:15	16:40	11:30	20:15	10:35	13:35	17:30
END TIME	18:45	21:15	17:40	19:00	21:45	12:05	15:05	18:45
FEEDSTOCK	A	A	A	A	A	B	B	A
FEED RATE, cc/hr	154	226	164	120	130	109	109	247
OPERATING PRESSURE, psig	1600	1600	2000	2000	2000	2000	2000	2000
H2 PARTIAL PRESSURE, psig	1600	1600	2000	2000	2000	2000	2000	2000
H2 TREAT RATE, scf/bbl	5000	5000	5000	5000	5000	5000	5000	5000
REACTOR 1 CONDITIONS								
LHSV, cc/hr/cc cat.	1.0	1.4	1.0	0.75	0.8	0.68	0.68	1.5
INLET BED TEMP., F	703	653	701	703	739	699	700	692
UPPER MID BED TEMP., F								
LOWER BED TEMP., F	713	699	696	718	743	701	705	753
AVERAGE BED TEMP., F	708	676	699	711	741	700	703	723
SAND BATH TEMP., F	698	657	681	697	724	696	703	714
REACTOR 2 CONDITIONS								
LHSV, cc/hr/cc cat.								
INLET BED TEMP., F								
UPPER MID BED TEMP., F								
LOWER BED TEMP., F								
AVERAGE BED TEMP., F								
SAND BATH TEMP., F								
SEVERITY STAGE 1	4.52	2.11	4.99	7.78	10.69	7.49	7.74	4.53
SEVERITY STAGE 2								
OVERALL SEVERITY	4.52	2.11	4.99	7.78	10.69	15.27	7.74	4.53

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

B: LIQUID PRODUCT FROM FB-37.

TABLE 4.2.2-1 (concluded)

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)

FILE ID: REPT802.WK1

TEST # (FB-)	42	43	46	47	48	49
DATE (1989)	02-06	02-06	02-21/22	02-22	02-23	02-24
START TIME	12:05	18:45	03:45	05:45	02:00	00:00
END TIME	17:35	20:40	04:00	24:00	22:00	20:00
FEEDSTOCK	A	C	A	D	A	A
FEED RATE, cc/hr	104	104	113	114	113	140
OPERATING PRESSURE, psig	2000	2000	2000	2000	2000	2000
H2 PARTIAL PRESSURE, psig	2000	2000	2000	2000	2000	2000
H2 TREAT RATE, scf/bbl	5000	5000	5000	5000	5000	5000
REACTOR 1 CONDITIONS						
LHSV, cc/hr/cc cat.	0.7	0.65	0.7	0.7	0.7	0.88
INLET BED TEMP., F	738	737	702	697	737	623
UPPER MID BED TEMP., F						
LOWER BED TEMP., F	739	735	716	708	741	615
AVERAGE BED TEMP., F	739	736	709	703	739	619
SAND BATH TEMP., F	739	729	695	606	724	602
REACTOR 2 CONDITIONS						
LHSV, cc/hr/cc cat.						
INLET BED TEMP., F						
UPPER MID BED TEMP., F						
LOWER BED TEMP., F						
AVERAGE BED TEMP., F						
SAND BATH TEMP., F						
SEVERITY STAGE 1	11.85	12.38	8.18	7.52	11.92	1.85
SEVERITY STAGE 2						
OVERALL SEVERITY	11.85	24.23	8.18	15.70	11.92	1.85

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

C: LIQUID PRODUCT FROM FB-42.

D: LIQUID PRODUCT FROM FB-46.

TABLE 4.2.2-2

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)

FILE ID: REPTB03.WK1

TEST # (FB-)	30	31	32	33	34	35	36-1	36-2
DATE (1989)	01-25	01-25	01-26	01-26	01-27	01-27	01-30	01-30
START TIME	19:00	20:55	12:55	16:15	13:25	16:45	13:40	14:10
END TIME	20:00	21:55	13:55	22:00	14:10	18:45	14:10	14:40
FEEDSTOCK	A	A	A	A	B	B	C	C
FEED RATE, cc/hr	160	159	157	156	136	104	108	102
OPERATING PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H ₂ PARTIAL PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H ₂ TREAT RATE, scf/bbl	5000	5000	5000	5000	5000	5000	5000	5000
REACTOR 1 CONDITIONS								
LHSV, cc/hr/cc cat.	1.0	1.0	1.0	1.0	0.85	0.65	0.67	0.64
INLET BED TEMP., F	709	659	606	700	701	699	698	698
UPPER MID BED TEMP., F								
LOWER BED TEMP., F	696	668	636	694	693	698	702	700
AVERAGE BED TEMP., F	703	664	621	697	697	699	700	699
SAND BATH TEMP., F	680	649	605	681	679	694	700	696
REACTOR 2 CONDITIONS								
LHSV, cc/hr/cc cat.								
INLET BED TEMP., F								
UPPER MID BED TEMP., F								
LOWER BED TEMP., F								
AVERAGE BED TEMP., F								
SAND BATH TEMP., F								
SEVERITY STAGE 1	5.2623	3.1100	1.6792	4.8966	5.7607	7.6832	7.6018	7.8546
SEVERITY STAGE 2								
OVERALL SEVERITY	5.2623	3.1100	1.6792	4.8966	10.6573	12.5798	20.1700	20.4300

FEEDSTOCK TYPE:

A: 350-550 F VIRGIN COALITE DISTILLATE.

B: LIQUID PRODUCT FROM FB-33.

C: LIQUID PRODUCT FROM FB-34/FB-35.

TABLE 4.2.2-3

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)/K-550 (2ND STAGE)		FILE ID: REPT804.WK1						
TEST # (FB-)	169	172	170	173	174	175	176	177
DATE (1989)	06-27	06-29	06-28	06-29	06-30	06-30	06-30	06-30
START TIME	04:30	09:00	00:00	15:30	22:00	02:00	06:00	10:00
END TIME	20:00	10:00	12:00	20:00	24:00	04:00	08:00	20:00
FEEDSTOCK	A	A	B	B	B	B	B	B
FEED RATE, cc/hr	124	119	118	120	124	118	116	117
OPERATING PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H2 PARTIAL PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H2 TREAT RATE, scf/bbl	8000	8000	8000	8000	8000	8000	8000	8000
REACTOR 1 CONDITIONS								
LHSV, cc/hr/cc cat.	0.75	0.72	0.72	0.73	0.75	0.72	0.70	0.71
INLET BED TEMP., F	720	683	720	662	648	625	600	632
UPPER MID BED TEMP., F	676	662	674	659	646	624	598	639
LOWER BED TEMP., F	660	649	662	643	634	615	593	629
AVERAGE BED TEMP., F	685	665	685	655	643	621	597	633
SAND BATH TEMP., F	651	638	655	630	620	607	586	613
REACTOR 2 CONDITIONS								
LHSV, cc/hr/cc cat.	0.75	0.72	0.72	0.73	0.75	0.72	0.70	0.71
INLET BED TEMP., F	713	695	717	658	644	616	593	627
UPPER MID BED TEMP., F	723	702	721	675	650	624	600	636
LOWER BED TEMP., F	713	720	705	643	655	625	600	621
AVERAGE BED TEMP., F	718	699	719	667	647	620	597	632
SAND BATH TEMP., F	715	693	715	659	643	617	595	629
SEVERITY STAGE 1	5.58	4.38	5.86	3.78	3.08	2.36	1.65	2.85
SEVERITY STAGE 2	8.55	6.92	9.10	4.46	3.28	2.31	1.64	2.77
OVERALL SEVERITY	14.13	11.31	14.96	8.24	6.35	4.67	3.29	5.62

FEEDSTOCK TYPE:

A: 350-750F RAW COALITE DISTILLATE
B: 350-820F RAW COALITE DISTILLATE

TABLE 4.2.2-4

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)/K-599 (2ND STAGE)

FILE ID: REPTB05.WK1

TEST # (FB-)	94-1	94-2	94-3	101	102	103	104
DATE (1989)	04-05	04-06	04-06	04-10	04-10	04-10	04-10
START TIME	21:00	01:00	05:00	05:00	09:30	14:00	18:00
END TIME	01:00	05:00	09:00	06:30	11:00	15:30	20:00
FEEDSTOCK	A	A	A	A	A	A	A
FEED RATE, cc/hr	116	116	115	124	110	118	119
OPERATING PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000
H2 PARTIAL PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000
H2 TREAT RATE, scf/bbl	7000	7000	7000	7000	7000	7000	7000
REACTOR 1 CONDITIONS							
LHSV, cc/hr/cc cat.	0.7	0.7	0.7	0.75	0.7	0.7	0.7
INLET BED TEMP., F	616	621	624	402	400	399	399
UPPER MID BED TEMP., F	671	692	696	402	400	400	399
LOWER BED TEMP., F	617	614	616	403	400	400	400
AVERAGE BED TEMP., F	635	642	645	402	400	400	399
SAND BATH TEMP., F	595	596	598	402	400	400	398
REACTOR 2 CONDITIONS							
LHSV, cc/hr/cc cat.	0.7	0.7	0.7	0.75	0.7	0.7	0.7
INLET BED TEMP., F	628	628	627	632	660	739	772
UPPER MID BED TEMP., F	623	625	624	653	705	704	701
LOWER BED TEMP., F	615	620	620	618	633	663	671
AVERAGE BED TEMP., F	622	624	624	634	666	702	715
SAND BATH TEMP., F	608	618	618	611	626	660	670
SEVERITY STAGE 1	2.9399	3.2880	3.4338	0.0360	0.0364	0.0362	0.0359
SEVERITY STAGE 2	2.4352	2.5220	2.4970	2.7305	4.6003	7.4687	8.7948
OVERALL SEVERITY	5.3752	5.8101	5.9307	2.7665	4.6367	7.5048	8.8307

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

TABLE 4.2.2-5

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-599 (1ST STAGE)

FILE ID: REPTB05.WK1

TEST # (FB-)	146	147
DATE (1989)	05-16/18	05-18/19
START TIME	18:30	08:30
END TIME	06:30	20:30
FEEDSTOCK	A	B
FEED RATE, cc/hr	118	115
OPERATING PRESSURE, psig	2000	2000
H2 PARTIAL PRESSURE, psig	2000	2000
H2 TREAT RATE, scf/bbl	8000	8000
REACTOR 1 CONDITIONS		
LHSV, cc/hr/cc cat.		
INLET BED TEMP., F		
UPPER MID BED TEMP., F		
LOWER BED TEMP., F		
AVERAGE BED TEMP., F		
SAND BATH TEMP., F		
REACTOR 2 CONDITIONS		
LHSV, cc/hr/cc cat.	0.7	1
INLET BED TEMP., F	744	717
UPPER MID BED TEMP., F	684	716
LOWER BED TEMP., F	663	714
AVERAGE BED TEMP., F	697	716
SAND BATH TEMP., F	643	714
SEVERITY STAGE 1	6.8966	8.9077
SEVERITY STAGE 2		
OVERALL SEVERITY	6.8966	8.9077

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

B: LIQUID PRODUCT FROM FB-146.

TABLE 4.2.2-6

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: CACIUM PROMOTED K-550

FILE ID: REPTCA1.WK1

TEST # (FB-)	135	136	137	138
DATE (1989)	04-26/27	04-27/28	04-28	04-28
START TIME	21:00	17:00	13:00	18:30
END TIME	13:00	09:00	15:00	20:30
FEEDSTOCK	A	A	A	A
FEED RATE, cc/hr	120	122	136	161
OPERATING PRESSURE, psig	2000	2000	2000	2000
H2 PARTIAL PRESSURE, psig	2000	2000	2000	2000
H2 TREAT RATE, scf/bbl	7000	7000	7000	7000
REACTOR 1 CONDITIONS				
LHSV, cc/hr/cc cat.	0.7	0.7	0.8	1.0
INLET BED TEMP., F	708	712	641	615
UPPER MID BED TEMP., F	643	707	658	625
LOWER BED TEMP., F	634	691	657	621
AVERAGE BED TEMP., F	662	703	652	620
SAND BATH TEMP., F	623	680	616	591
REACTOR 2 CONDITIONS				
LHSV, cc/hr/cc cat.				
INLET BED TEMP., F				
UPPER MID BED TEMP., F				
LOWER BED TEMP., F				
AVERAGE BED TEMP., F				
SAND BATH TEMP., F				
SEVERITY STAGE 1	4.1526	7.2872	3.2251	1.7138
SEVERITY STAGE 2				
OVERALL SEVERITY	4.1526	7.2872	3.2251	1.7138

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

4.2.3.1 LC-Finingtm (Residue Hydrocracking)

LC-Finingtm, a service mark of Lummus and its co-licensors for engineering, marketing and technical services relating to hydrocracking and hydrosulfurization processes for reduced crude and residual oils, is a commercial technology for upgrading heavy oils. In the context of the COALITE HEDF application, LC-Finingtm has been used to hydrotreat long residues (ca., 300F+) and to hydrocrack the 650F+ (343C+) components into the HEDF boiling ranges. In the screening program, a stirred autoclave simulator of the LC-Finingtm process was used to collect the required data. Three feedstocks were considered: 1) a virgin or raw 650F+ (343C+) atmospheric resid fraction of the raw COALITE; 2) a virgin 300F+ (148C+) long resid fraction; and 3) a hydrotreated 575F+ (301C+) atmospheric resid fraction. The analyses of these three feedstocks are presented in Table 4.2.3.1-1. The objectives of these three campaigns were as follows:

- o Evaluate the first-pass reactivity of the virgin 650F+ atmospheric resid fraction towards hydrocracking and the production of hydrocracked HEDF-boiling range materials;
- o Evaluate the hydrocracking reactivity of the first-pass unconverted (575F+) atmospheric resid recovered from the virgin 650F+ LC-Finingtm tests of the above campaigns; and
- o Prepare hydrotreated gas oil (650-975F) for downstream selective fixed-bed hydrocracking campaigns by subjecting the 300F+ long resid to mild LC-Finingtm.

The summary of the operating conditions for these campaigns is presented in Table 4.2.3.1-2 and -3.

4.2.3.2 Delayed Coking

Delayed Coking is another alternative technology for upgrading heavy oils to lighter products, such as HEDF materials. However, Delayed Coking is not as selective as hydrocracking and results in the production of a variety of byproducts, the predominant one being coke. On the other hand, Delayed Coking is much less capital intensive than hydrocracking and the differential HEDF yield losses are modulated by lower capital and operating costs. The choice of Delayed Coking vs LC-Finingtm (residue hydrocracking) is an economic one and the preferred technology will be based on the results of the subsequent Task 4 economic optimization studies using a refinery linear programming computer model.

Three Delayed Coking tests were made in the Continuous Bench Coker (CBC) unit, two with virgin 650F+ atmospheric residua and one with a hydrotreated resid. Table 4.2.3.2-1 presents a summary of the feedstock properties. Two delayed coking severities were investigated: a) 100 psig coke drum pressure; and b) 25 psig coke drum pressure, all other conditions kept constant. The detailed operating conditions for the three tests are presented in Table 4.2.3.2-2.

TABLE 4.2.3.1-1

FEEDSTOCK ASSAYS FOR LC-FINING OF COALITE RESIDUA

<u>Coalite Type</u> <u>IBP, °F</u>	<u>Virgin</u> <u>300</u>	<u>Virgin</u> <u>650</u>	<u>Hydrotreated</u> <u>575</u>
Sp. Grav., g/cc	1.0513	1.1678	1.0143
A.P.I. Gravity	3.1	-10.3	8.0
Distillation, °F			
IBP	407	294	---
10%	447	703	
30%	512	753	
50%	657	812	
70%	776	946	
90%			
EBP	950 (84.8%)	950 (77%)	
Elemental, Wt.%			
C	85.10	85.47	88.25
H	8.53	7.75	9.18
N	1.06	1.18	0.87
S	0.81	0.75	0.09
Ash	0.01	0.01	0.01
O (By Diff.)	4.50	4.84	1.60

TABLE 4.2.3.1-2

SUMMARY OF OPERATING CONDITIONS FOR LC-FINING TESTS

CATALYST: SHELL 324 M (AGED)

TEST # (BLCF-)	86-1	86-2	87	88-1/2	88-3	88-4	88-5	100	101
DATE (1989)	01-31	02-01	02-08	02-27/28	02-28/03-01	03-1/2	03-2/3	05-17/19	06-13/14
START TIME	19:00	07:00	02:00	15:30	16:30	09:00	07:30	20:00	08:00
END TIME	23:00	15:00	16:00	16:30	09:00	07:30	18:00	19:30	02:30
FEEDSTOCK	A	A	A	A	A	A	A	B	E
FEED RATE, cc/hr	137	73	65	264	273	269	265	697	732
OPERATING PRESSURE, psig	2200	2200	2200	2200	2200	2200	2200	2000	2000
H ₂ PARTIAL PRESSURE, psig	2200	2200	2200	2200	2200	2200	2200	2000	2000
H ₂ TREAT RATE, scf/bbl	10000	10000	10000	10000	10000	10000	10000	7000	7000
LHSV, cc/hr/cc cat.	0.91	0.42	0.43	0.53	0.55	0.54	0.53	1.4	1.5
LHSV, cc/hr/cc react. vol.	0.54	0.27	0.26	0.26	0.27	0.27	0.27	0.70	0.73
INLET SLURRY TEMP., F	650	610	630	730	748	746	743	700	768
UPPER SLURRY TEMP., F	800	800	816	744	779	796	799		
LOWER SLURRY TEMP., F	793	795	809	566	604	616	617	550	530
AVERAGE SLURRY TEMP., F	745	735	752	680	710	719	720	625	650

FEEDSTOCK TYPE:

A: 650 F+ VIRGIN ATMOSPHERIC RESID.

B: 300 F+ VIRGIN ATMOSPHERIC RESID.

TABLE 4.2.3.1-3

SUMMARY OF OPERATING CONDITIONS FOR LC-FINING TESTS

CATALYST: SHELL 324 M (AGED)

TEST # (BLCF-)	90	92	93	94	95
DATE (1989)	04-04	04-10	04-11	04-11	04-12
START TIME	01:00	12:00	24:00	14:00	02:00
END TIME	09:00	20:00	08:00	22:00	10:00
FEEDSTOCK	A	A	A	A	A
FEED RATE, cc/hr					
OPERATING PRESSURE, psig	2200	2250	2250	2250	2250
H2 PARTIAL PRESSURE, psig	2200	2250	2250	2250	2250
H2 TREAT RATE, scf/bbl	7500	10000	10000	10000	10000
STIRRER SPEED, rpm					
LHSV, cc/hr/cc cat.					
LHSV, cc/hr/cc react.vol.					
INLET SLURRY TEMP., F	698	675	681	689	709
UPPER SLURRY TEMP., F	719	760	780	800	798
LOWER SLURRY TEMP., F	699	736	753	770	772
AVERAGE SLURRY TEMP., F	705	724	738	753	760

FEEDSTOCK TYPE:

A: HYDROTREATED 575 F+ PRODUCT FROM BLCF-88.

TABLE 4.2.3.2-1

ASSAYS OF DELAYED COKING COALITE-DERIVED FEEDSTOCKS

<u>Feedstock Type</u>	<u>Virgin</u>	<u>Mildly Hydrotreated</u>
Nominal IBP, °F	650	650
Specific Gravity @ 60°F	1.1678	1.1399
API Gravity	-10.3	-7.4
ASTM Distillation, °F		
5% distilled	650	675
10%	703	732
30%	753	760
50%	812	825
70%	946	928
90%	---	980
Watson K, R	---	9.50
Elementals, Wt%		
C	85.47	87.15
H	7.75	7.99
N	1.18	0.95
S	0.75	0.56
O + Ash (By diff)	4.85	3.35

TABLE 4.2.3.2-2

SUMMARY OF OPERATING CONDITIONS
FOR DELAYED COKING OF COALITE

<u>Test No. (CBC-)</u>	<u>62</u>	<u>63</u>	<u>64</u>	<u>67</u>
Feed Source	----- Virgin 650F+ Resid -----			Mildly Hydrotreated 650F+ Resid
Coke Drum Temp, °F	870	880	880	880
Coke Drum Pressure, psig	100	100	25	25
Coke Drum Preheater Temp, °F	700	700	700	700
Feed Rate, lb/hr	0.85	0.85	0.85	0.85
Run Length, hr.	24	24	24	24
Recycle/Fresh Feed Ratio	0.50	0.50	0.66	0.81

4.2.4 Cracked Distillate Hydrotreating Campaigns

The above two cracking operations, namely, LC-Finingtm and Delayed Coking, are primarily conversion processes to produce HEDF precursor materials that boil within the HEDF boiling range. They therefore do not result in the production of finished HEDF products and a post-cracking hydrogenation operation is required for upgrading the cracked precursor materials. In a true commercial process, a fractionator would be installed between the cracking unit(s) with the cracked distillate fed continuously to the distillate hydrotreater and the heavier unconverted residuum being recycled back to the cracking unit. In this Task 3 screening program with the COALITE feedstock, the bench-scale cracking and hydrotreating units were not integrated and thus only first-pass crackates, either, delayed coker distillates or hydrocrackates (LC-Finates), were evaluated. Three distillate hydrotreating runs were made with delayed coker distillates and eleven distillate hydrotreating runs were made with LC-Finate (hydrocracked) distillates.

4.2.4.1 Hydrotreating of LC-Finate Distillates

Table 4.2.4.1-1 presents the feedstock assays for the three LC-Finate distillates used in the hydrocracked distillate hydrotreating campaigns. Table 4.2.4.1-2 and -3 present the summary of the operating conditions for the eleven hydrotreating tests. The objective of these campaigns was to evaluate the effects of hydrocracked distillate end point, catalyst type, space velocity, reactor temperature, and single-stage vs two-stage distillate hydrotreating.

4.2.4.2 Hydrotreating of Coker Distillates

Table 4.2.4.2-1 presents the feedstock assays for the coker distillates used in the thermally cracked distillate hydrotreating campaigns. Table 4.2.4.2-2 presents the summary of the operating conditions for the three hydrotreating tests. The objective of these campaigns was to evaluate the effects of coker severity, coker distillate end point, reactor temperature, and single-stage vs two-stage distillate hydrotreating.

4.2.5 Two-Step Selective Hydrocracking Campaigns

During the early phases of the screening program, it was determined that the raw atmospheric resid fraction of COALITE was very reactive towards undesirable cracking and condensation reactions. Thus, it was postulated that a pretreatment based on hydrogenation would provide some degree of stabilization of reactive species and thereby allow better performance during subsequent cracking operations. Since the atmospheric COALITE resid contains some coal char particles, it was felt that hydrotreating in a fixed-bed unit would pose significant operability problems. The expanded-bed hydrocracking process of LC-Finingtm offers the capability to perform the hydrogen addition process in the presence of solids and other contaminants under commercially feasible conditions.

TABLE 4.2.4.1-1

ASSAYS OF COALITE MID-DISTILLATE
LC-FINATE (HYDROCRACKATE) FEEDS TO HYDROTREATING

<u>Nominal TBP</u> <u>End Pt., °F</u>	<u>650</u>	<u>600</u>	<u>575</u>
R.I. @ 20°C	1.5493	1.5201	1.5200
Specific Gravity, g/cc	0.9619	0.9396	0.9297
A.P.I. Gravity @ 60°F	15.6	19.1	20.7
Simulated Distillation, °F			
IBP	342	354	247
10%	396	398	363
30%	445	448	411
50%	502	491	453
70%	546	535	493
90%	604	580	546
EBP	680	761	729
VAPB	502	510	463
Watson K, R	10.19	10.35	10.31
Elemental, Wt.%			
C	89.38	86.26	87.97
H	9.60	10.52	10.40
N	0.45	0.57	0.69
S	0.05	0.05	0.03
O (By Diff.)	0.52	2.60	0.91
F.I.A/R.I., 1 Vol%			
Paraffins	N.D.	N.D.	N.D.
Olefins	0.6	2.5	5.3
Naphthenes	18.6	28.3	21.2
Aromatics	80.8	69.2	73.5
WLHV, Btu/lb	16031	---	17142
VLHV, Btu/gal	128451	---	132785
Aniline Pt., °F	-6.9	---	---
Diesel Index	-1.07	---	---
Smoke Pt., mm	7	---	---
Lum. No.	30.1	---	---

TABLE 4.2.4.1-2

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED HYDROTREATING TESTS OF

HYDROCRACKED COALITE DISTILLATE

CATALYST: K-550 (1ST STAGE), K-599 (2ND STAGE)

TEST # (FB-)	44	95	96	97	98	99	100	105
DATE (1989)	02-09	04-06	04-06	04-07	04-07	04-07	04-07	04-11
START TIME	11:35	12:20	18:00	22:30	12:00	17:00	20:00	01:00
END TIME	12:35	14:50	19:30	24:00	13:30	18:00	21:30	12:00
FEEDSTOCK	A	B	B	B	B	B	B	B
FEED RATE, cc/hr	113	108	112	113	110	120	117	111
OPERATING PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H ₂ PARTIAL PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H ₂ TREAT RATE, scf/hr	5000	7000	7000	7000	7000	7000	7000	7000
REACTOR 1 CONDITIONS								
INLET CO. RATE, cc/hr	0.68	0.65	0.68	0.69	0.67	0.73	0.70	0.67
INLET BED TEMP., °F	695	693	630	748	400	395	400	607
UPPER MID BED TEMP., °F		651	702	732	402	400	400	644
LOWER BED TEMP., °F	717	627	650	695	403	401	400	621
AVERAGE BED TEMP., °F	704	634	661	725	401	400	400	624
SAND BATH TEMP., °F	701	605	620	681	402	401	401	601
REACTOR 2 CONDITIONS								
INLET CO. RATE, cc/hr					0.7	0.7	0.7	0.7
INLET BED TEMP., °F					647	713	741	694
UPPER MID BED TEMP., °F					540	667	701	699
LOWER BED TEMP., °F					643	672	699	691
AVERAGE BED TEMP., °F					643	684	714	691
SAND BATH TEMP., °F					617	642	673	684
SEVERITY STAGE 1	7.2912	3.1506	4.3959	10.1685	0.0396	0.0352	0.0364	2.6218
SEVERITY STAGE 2					3.3341	5.8640	8.7202	6.9341
OVERALL SEVERITY	7.8911	3.1506	4.3959	10.1685	3.3756	5.9192	9.7567	9.5559

FEEDSTOCK TYPE:

A: 300-650 °F HYDROCRACKED COALITE DISTILLATE, DERIVED FROM LC-FINING OF VIRGIN 650 °F+
 B: 300-575 °F HYDROCRACKED COALITE DISTILLATE, DERIVED FROM LC-FINING OF VIRGIN 650 °F+

TABLE 4.2.4.1-3

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED HYDROTREATING TESTS OF

HYDROCRACKED COALITE DISTILLATE

CATALYST: K-599 (1ST STAGE)

TEST # (FB-)	156	157	158
DATE (1989)	05-30	05-30	05-31
START TIME	06:00	16:00	00:00
END TIME	10:00	20:00	04:00
FEEDSTOCK	A	A	A
FEED RATE, cc/hr	118	115	116
OPERATING PRESSURE, psia	2000	2000	2000
H ₂ PARTIAL PRESSURE, psia	2000	2000	2000
H ₂ TREAT RATE, scf/bbl	7000	7000	7000
REACTOR 1 CONDITIONS			
LHSV, cc/hr/cc cat.	0.70	0.70	0.70
INLET BED TEMP., °F	625	693	740
UPPER MID BED TEMP., °F	640	709	726
LOWER BED TEMP., °F	649	705	733
AVERAGE BED TEMP., °F	638	701	731
SAND BATH TEMP., °F			
REACTOR 2 CONDITIONS			
LHSV, cc/hr/cc cat.			
INLET BED TEMP., °F			
UPPER MID BED TEMP., °F			
LOWER BED TEMP., °F			
AVERAGE BED TEMP., °F			
SAND BATH TEMP., °F			
SEVERITY STAGE 1	3.0871	7.4363	10.9827
SEVERITY STAGE 2			
OVERALL SEVERITY	3.0871	7.4363	10.9827

FEEDSTOCK TYPE:

A: 300-600 °F HYDROCRACKED COALITE DISTILLATE, DERIVED FROM LO-FINING OF VIRGIN 650 °F.

TABLE 4.2.4.2-1

ASSAYS OF COALITE COKER MID-DISTILLATE
FEEDS TO HYDROTREATING

<u>Feed Type</u>	<u>100 psig Coke Drum Pressure</u>	<u>62 psig Average Coke Drum Pressure</u>
R.I. @ 20°C	1.5406	1.4785
Specific Gravity, g/cc	0.9679	0.8676
API Gravity	14.7	31.6
Simulated Distillation, °F		
IBP	347	300
10%	384	370
30%	436	409
50%	489	454
70%	547	497
90%	609	559
EBP	754	725
VABP	509	473
Watson K, R	10.15	11.17
Elemental, Wt%		
C	84.33	83.88
H	9.50	10.10
N	0.93	0.65
S	0.45	0.46
O (By Diff.)	4.79	4.91
F.I.A./R.I., 1 Vol%		
Paraffins	N.D.	N.D.
Olefins	14.6	25.2
Naphthenes	24.3	22.3
Aromatics	61.1	52.5
WLHV, btu/lb.	15972	16374
VLHV, btu/gal	128775	118337
Aniline Pt., F	37.4	---
Diesel Index	5.50	---
Smoke Pt., mm	5	---
Lum. No.	29.5	---

TABLE 4.2.4.2 - 1

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED HYDROTREATING TESTS OF

THERMALLY PROCESSED COALITE DISTILLATE

CATALYST: K-550 (1ST STAGE) K-599 (2ND STAGE)

TEST # (FB-)	45	126	127
DATE (1989)	02-13	04-19	04-19
START TIME	10:50	07:30	13:30
END TIME	11:50	09:00	14:45
FEEDSTOCK	A	B	B
FEED RATE, cc/hr	106	117	105
OPERATING PRESSURE, psig	2000	2000	2000
H ₂ PARTIAL PRESSURE, psig	2000	2000	2000
H ₂ TREAT RATE, scf/hr	7000	7000	7000
REACTOR 1 CONDITIONS			
INLET COORDINATE, C&I	0.7	0.7	0.7
INLET BED TEMP., °F		610	400
UPPER MID BED TEMP., °F	700	650	400
LOWER BED TEMP., °F	710	600	400
AVERAGE BED TEMP., °F	710	630	400
SAND BATH TEMP., °F			
REACTOR 2 CONDITIONS			
INLET COORDINATE, C&I		0.7	0.7
INLET BED TEMP., °F		620	740
UPPER MID BED TEMP., °F		660	670
LOWER BED TEMP., °F		600	600
AVERAGE BED TEMP., °F		610	640
SAND BATH TEMP., °F			
SEVERITY STAGE 1	8.2311	2.8406	0.0391
SEVERITY STAGE 2		5.2076	6.7534
OVERALL SEVERITY	8.2311	8.0484	6.7925

FEEDSTOCK TYPE:

A: THERMALLY PROCESSED COALITE DISTILLATE, 300-650 °F @ 100 psia COKEDRUM PRESSURE.

B: THERMALLY PROCESSED COALITE DISTILLATE, 300-575 °F @ 62 psia AVERAGE COKEDRUM PRESSURE.

The two-step selective hydrocracking (TSSH) of COALITE consists of a hydrotreating pretreatment step using an LC-Fining[™] reaction system followed by fractionation to recover a hydrotreated vacuum gas oil (HVGO) fraction and a hydrotreated middle distillate fraction, the latter of which can be directed to the HEDF pool. The HVGO fraction is then catalytically hydrocracked over a fixed-bed hydrocracking catalyst to convert the heavier gas oil-boiling species to HEDF precursors. The thus hydrocracked LC-Finate HVGO, is then subjected to distillate hydrotreating to produce the final HEDF product.

In a true commercial process, a fractionator between the fixed-bed hydrocracker and the hydrocracked distillate hydrotreater would allow for near extinction recycle of the heavy gas oil components. In the screening program, the fixed-bed hydrocracker and the hydrocracked distillate hydrotreater were not integrated and therefore hydrotreating of only the first-pass hydrocracked HVGO fraction was evaluated. Finally, in order to minimize fractionation equipment costs in a commercial plant, it was decided to perform the initial LC-Fining[™] pretreatment step with a 300F+ atmospheric resid fraction rather than with a 650F+ atmospheric resid fraction. The residual vacuum resid (975F+) fraction after the initial LC-Fining[™] pretreatment step can be used for power generation by combustion in a steam boiler or be recycled to extinction in the MCG pyrolysis reactor. Figure 4.2.5-1 is a schematic of the processing flow scheme for the TSSH approach.

Table 4.2.5-1 presents the feedstock assays for the two gas oil feeds to the fixed-bed hydrocracking step. Two hydrocracking campaigns were made: 1) hydrocracking of virgin COALITE VGO; and 2) hydrocracking of hydrotreated LC-Finate VGO. Table 4.2.5-2 summarizes the operating conditions for the nine tests made with the virgin VGO and Table 4.2.5-3 summarizes the conditions for the ten tests made with the hydrotreated LC-Finate VGO. The objective of these tests was to evaluate the effects of space velocity, reactor temperature and VGO feedstock type. All nineteen tests were made with a proprietary fixed-bed hydrocracking catalyst supplied by Amoco Oil Company.

The hydrocracked LC-Finate VGO was fractionated to recover a mid-distillate fraction for distillate hydrotreating. The assay of this selectively hydrocracked mid-distillate feedstock is presented in Table 4.2.5-4.

A contract modification was approved by DOE to perform further screening studies of the two-stage selective hydrocracking route with the goal of exceeding the 130,000 Btu/gal energy density target of the finished HEDF test fuels. It was further expanded to also consider the impact of the energy density-JFTOT fuel stability relationships. A new Subtask 3.2 test matrix was formulated and the details of this phase of Task 3 are presented in Section 5.5.3.

HYDROCRACKING/HYDROGENATION ROUTES TO HEDF

TABLE 4.2.5-1

ASSAYS OF COALITE VGO FEEDSTOCKS
TO FIXED-BED HYDROCRACKING

<u>Feed Type</u>	<u>Virgin</u>	<u>Hydrotreated</u>
Specific Gravity, g/cc	1.1159	1.0180
A.P.I. Gravity	-4.7	7.5
Simulated Distillation, °F		
IBP	561	530
10%	695	618
30%	750	663
50%	792	710
70%	835	765
90%	901	849
EBP	1001	965
VABP	791	729
Watson K, R	9.66	10.38
Elemental, Wt%		
C	85.34	88.02
H	7.79	9.29
N	1.28	0.67
S	0.85	0.30
O (By Diff.)	4.74	1.72
Ash	<0.01	---
Conradson Carbon	2.90	0.55
Q.I.	0.018	---

TABLE 4.2.5 - 2

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COALITE HYDROCRACKING TESTS

CATALYST: ANOCO PROPRIETARY

TEST # (FBHC-)	1	2	3	4	13	14	15	16	17
DATE (1989)	04-27	04-28	04-28	04-28	05-03	05-04	05-04	05-04	05-05
START TIME	21:30	03:30	13:00	18:30	15:30	21:30	03:30	11:00	19:00
END TIME	23:30	05:30	15:00	20:30	17:30	23:30	08:30	14:00	08:00
FEEDSTOCK	A	A	A	A	A	A	A	A	A
FEED RATE, cc/hr	175	170	107	125	143	179	103	60	167
OPERATING PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000	2000
H ₂ PARTIAL PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000	2000
H ₂ TREAT RATE, scf/bbl	7000	7000	7000	7000	7000	7000	7000	7000	7000
LHSV, cc/min/cc cat.	1.1	1.0	0.7	0.8	0.9	1.1	0.6	0.4	1.0
INLET BED TEMP., °F	655	682	693	675	714	724	732	739	727
UPPER MID BED TEMP., °F	701	730	758	721	757	801	801	801	801
LOWER BED TEMP., °F	723	755	756	710	782	793	773	765	801
OUTLET BED TEMP., °F									
AVERAGE BED TEMP., °F	694	724	736	701	761	774	767	771	771

FEEDSTOCK TYPE:

A: 650-970 F VIRGIN VCL

TABLE 4.2.5 - 3

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COALITE HYDROCRACKING TESTS

CATALYST: AMOCO PROPRIETARY

TEST # (FBH-)	18	19	20	21	22	23	24	25	26	27
DATE (1989)	05-24	05-25	05-25	05-25	05-26	05-26	05-26	05-26	05-30	06-03/05
START TIME	22:30	04:30	10:30	17:00	23:00	05:00	13:00	20:00	07:00	07:00
END TIME	24:30	06:30	12:30	19:00	01:00	09:00	17:00	21:00	09:00	07:00
FEEDSTOCK	B	B	B	B	B	B	B	B	B	B
FEED RATE, cc/hr	124	122	118	154	147	49	102	107	117	139
OPERATING PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
H ₂ PARTIAL PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
H ₂ TREAT RATE, scf/hr	7000	7000	7000	7000	7000	7000	7000	7000	7000	7000
HSV, cc/hr/cc cat	0.9	0.9	0.8	1.1	1.1	0.4	0.7	0.8	0.8	1.0
INLET BED TEMP., F	683	684	705	707	695	718	690	714	683	701
UPPER MID BED TEMP., F	714	735	772	774	760	770	743	790	763	763
LOWER BED TEMP., F	721	758	751	755	780	765	760	758	720	741
OUTLET BED TEMP., F										
AVERAGE BED TEMP., F	700	727	756	760	746	751	731	771	757	751

FEEDSTOCK TYPE

B: 650-975 F HYDROTREATED LC-FINATE VGO.

TABLE 4.2.5-4

ASSAY OF SELECTIVELY HYDROCRACKED
COALITE MID-DISTILLATE FEED TO HYDROTREATING

TBP Boiling Range °F	300-750
R.I. @ 20°C	1.5406
Specific Gravity, g/cc	0.9619
API Gravity	15.6
Distillation, °F	
IBP	362
10%	552
30%	631
50%	666
70%	697
90%	739
EBP	781
VABP	633
Watson K, R	10.62
Elemental, Wt%	
C	88.26
H	10.97
N	0.35
S	0.05
O (By Diff.)	0.37
F.I.A./R.I., 1 Vol%	
Saturates	6.3
Aromatics	93.7
WLHV, btu/lb	17339
VLHV, btu/gal	138931

4.3 Colorado Shale Oil Operations

4.3.1 Feedstock Preparation

Western Research Institute (WRI) provided nineteen drums of Colorado shale oil produced at the Unocal plant in Parachute Creek. The drums were blanketed with nitrogen prior to and during shipment as well as during the storage time at Lummus. The drums were shipped from WRI's Laramie facility on November 7, 1988.

One drum of the raw Colorado shale oil feedstock was fractionated in the 4-in Batch Distillation unit in distillation campaign referred to as S01. Twenty-three successive distillate cuts were recovered as well as a nominal 650F+ (343C+) vac resid cut. The distillate cuts were consolidated into three composites: IBP-355F raw naphtha; 355-618F mid-distillate; and 618-650F heavy gas oil. The mid-distillate cut was used as the feedstock for the virgin distillate hydrotreating campaigns. The 650F+ bottoms was evaluated as a feedstock to LC-Finingtm and delayed coking. It was also fractionated in the Equilibrium Flash Vaporization (EFV) pilot plant to produce a vacuum gas oil (650-975F) feedstock for fixed-bed hydrocracking. The selective hydrocracking evaluations utilized the raw full-range shale oil in the initial LC-Finingtm hydrotreating campaign. The thus hydrotreated LC-Finate was then fractionated to recover the 575-975F VGO fractions for subsequent fixed-bed distillate hydrotreating evaluations. Table 4.3.1-1 summarizes the properties of the 355-618F mid-distillate feed to the hydrotreating test campaigns.

Based on the processing information and analyses developed during the COALITE campaigns, the test matrix for evaluation of the Colorado shale oil feedstock was readily downsized (relative to that of the COALITE feed) while still allowing the collection of sufficient data for engineering and economic analysis.

4.3.2 Virgin Distillate Hydrotreating Campaigns

Three virgin distillate hydrotreating campaigns were made with the 355-618F mid-distillate fraction to study the effects of catalyst type, single-stage vs two-stage, space velocity, reactor temperature and hydrogen partial pressure. A total of 37 material balance tests were made of durations extending from 2-hours to 15-hours. The specific objective of each campaign is summarized below:

<u>Campaign #</u>	<u>Test # (FB-)</u>	<u>Objective</u>
I	106-125; 128-130 (Table 4.3.2-1)	Initial scans of the effects of space velocity, temperature and number of stages using NiW (K-550) and NiMo (K-599) hydrotreating catalysts
II	148-155 (Table 4.3.2-2)	Initial scans of the dehydroisomerization of raw shale oil distillate using molybdena (Mo-1230) reforming catalyst
III	159-164 (Table 4.3.2-3)	Initial scans of the two-stage dehydroisomerization/distillate hydrotreating using the Mo-1230/K-599 catalyst system

TABLE 4.3.1-1

ASSAY OF RAW COLORADO SHALE OIL MID-DISTILLATE
FEEDSTOCK TO HYDROTREATING

TBP Boiling Range, °F	355-618
R.I. @ 20°C	1.4785
Specific Gravity, g/cc	0.8676
A.P.I. Gravity	31.6
Distillation, °F	
IBP	348
10%	411
30%	467
50%	521
70%	577
90%	630
EBP	787
VABP	521
Watson K, R	11.35
Elemental, Wt%	
C	84.32
H	12.68
N	1.13
S	0.92
O (By Diff.)	0.95
F.I.A./R.I., 1 Vol%	
Paraffins	N.D.
Olefins	39.9
Naphthenes	32.9
Aromatics	27.2
WLHV, btu/lb.	17527
VLHV, btu/gal.	126670

TABLE 4.3.2-1

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COLORADO SHALE OIL

HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)/K-599 (2ND STAGE)

FILE ID: REPTS01.WK1

TEST # (FB-)	106	107	108	109	110	111	112	113
DATE (1989)	04-11	04-11/12	04-12	04-12	04-12	04-13	04-13	04-13
START TIME	17:30	23:30	05:30	11:30	18:30	00:30	06:30	13:00
END TIME	19:30	01:30	07:30	13:30	20:30	02:30	08:30	15:00
FEEDSTOCK	A	A	A	A	A	A	A	A
FEED RATE, cc/hr	115	119	120	115	119	120	119	170
OPERATING PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H ₂ PARTIAL PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H ₂ TREAT RATE, scf/bbl	7000	7000	7000	7000	7000	7000	7000	7000
REACTOR 1 CONDITIONS								
LHSV, cc/hr/cc cat.	0.70	0.72	0.73	0.70	0.72	0.73	0.72	1.03
INLET BED TEMP., F	395	396	396	400	398	397	399	401
UPPER MID BED TEMP., F	395	396	395	400	398	397	399	401
LOWER BED TEMP., F	395	396	396	400	398	397	399	401
AVERAGE BED TEMP., F	395	396	396	400	398	397	399	401
SAND BATH TEMP., F	392	393	393	398	396	394	395	399
REACTOR 2 CONDITIONS								
LHSV, cc/hr/cc cat.	0.70	0.72	0.73	0.70	0.72	0.73	0.72	1.03
INLET BED TEMP., F	596	647	699	742	647	741	744	741
UPPER MID BED TEMP., F	589	635	679	704	732	702	697	720
LOWER BED TEMP., F	587	633	676	699	631	700	692	707
AVERAGE BED TEMP., F	591	638	685	715	670	714	711	723
SAND BATH TEMP., F	584	624	671	696	624	696	690	698
SEVERITY STAGE 1	0.0325	0.0321	0.0316	0.0366	—	—	—	—
SEVERITY STAGE 2	1.5052	3.0109	5.7143	8.8707	4.7192	8.4290	8.1446	6.6131
OVERALL SEVERITY	1.5377	3.0431	5.7459	8.9073	4.7192	8.4290	8.1446	6.6131

FEEDSTOCK TYPE:

A: 355-618 F VIRGIN COLORADO SHALE OIL DISTILLATE.

TABLE 4.3.2-1 (contd)

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COLORADO SHALE OIL

HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)/K-599 (2ND STAGE)

FILE ID: REPTS01.WK1

TEST # (FB-)	114	115	116	117	118	119	120	121
DATE (1989)	04-13	04-14	04-14	04-14	04-17	04-17	04-18	04-18
START TIME	22:00	04:00	10:00	16:00	06:30	12:30	19:30	01:30
END TIME	24:00	06:00	12:00	18:00	08:30	14:30	21:30	03:30
FEEDSTOCK	A	A	A	A	A	A	A	A
FEED RATE, cc/hr	119	115	115	115	118	115	230	116
OPERATING PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H ₂ PARTIAL PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H ₂ TREAT RATE, scf/bbl	7000	7000	7000	7000	7000	7000	7000	7000
REACTOR 1 CONDITIONS								
LHSV, cc/hr/cc cat.	0.72	0.70	0.70	0.70	0.72	0.70	1.39	0.70
INLET BED TEMP., F	599	651	700	738	650	739	724	740
UPPER MID BED TEMP., F	586	640	688	700	640	705	741	708
LOWER BED TEMP., F	578	626	671	691	627	695	707	693
AVERAGE BED TEMP., F	582	639	686	710	639	713	724	714
SAND BATH TEMP., F	574	618	659	688	617	689	679	692
REACTOR 2 CONDITIONS								
LHSV, cc/hr/cc cat.							1.35	0.70
INLET BED TEMP., F							731	738
UPPER MID BED TEMP., F							737	739
LOWER BED TEMP., F							742	740
AVERAGE BED TEMP., F							737	739
SAND BATH TEMP., F							737	740
SEVERITY STAGE 1	1.3864	3.1461	6.0977	8.2846	3.0661	8.6468	4.9706	8.7197
SEVERITY STAGE 2	—	—	—	—	—	—	5.8183	11.8714
OVERALL SEVERITY	1.3864	3.1461	6.0977	8.2846	3.0661	8.6468	10.7889	20.5911

FEEDSTOCK TYPE:

A: 355-618 F VIRGIN COLORADO SHALE OIL DISTILLATE.

TABLE 4.3.2-1 (concl'd)

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COLORADO SHALE OIL

HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)/K-599 (2ND STAGE)

FILE ID: REPT501.WK1

TEST # (FB-)	122	123	124	125	128	129	130
DATE (1989)	04-18	04-18	04-18	04-19	04-19/20	04-20/21	04-21
START TIME	07:30	13:30	19:30	01:30	18:30	12:30	07:30
END TIME	09:30	15:30	21:30	03:30	09:30	03:30	21:00
FEEDSTOCK	A	A	A	A	A	A	A
FEED RATE, cc/hr	118	116	117	117	116	117	115
OPERATING PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000
H ₂ PARTIAL PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000
H ₂ TREAT RATE, scf/bbl	7000	7000	7000	7000	7000	7000	7000
REACTOR 1 CONDITIONS							
LHSV, cc/hr/cc cat.	0.72	0.70	0.71	0.71	0.70	0.71	0.70
INLET BED TEMP., F	599	699	647	600	650	739	700
UPPER MID BED TEMP., F	589	689	637	590	646	709	691
LOWER BED TEMP., F	564	670	625	580	633	693	673
AVERAGE BED TEMP., F	591	686	636	590	643	714	688
SAND BATH TEMP., F	575	662	617	588	623	689	664
REACTOR 2 CONDITIONS							
LHSV, cc/hr/cc cat.	0.72	0.70	0.71	0.71	0.70	0.71	
INLET BED TEMP., F	740	691	643	596	647	736	
UPPER MID BED TEMP., F	728	695	645	600	650	737	
LOWER BED TEMP., F	727	696	647	603	653	739	
AVERAGE BED TEMP., F	732	695	645	600	650	737	
SAND BATH TEMP., F	723	695	645	600	650	742	
SEVERITY STAGE 1	1.4669	6.0181	2.9741	1.4638	3.3056	8.5718	6.2352
SEVERITY STAGE 2	10.6615	6.7540	3.3735	1.7238	3.6559	11.5317	—
OVERALL SEVERITY	12.1285	12.7721	6.3476	3.1876	6.9615	20.1036	6.2352

FEEDSTOCK TYPE:

A: 355-618 F VIRGIN COLORADO SHALE OIL DISTILLATE.

TABLE 4.3.2-2

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COLORADO SHALE OIL

HYDROTREATING TESTS

CATALYST: K-599 (1ST STAGE)/MO-1230 (2ND STAGE)

FILE ID: REPTS02.WK1

TEST # (FB-)	148	149	150	151	152	153	154	155
DATE (1989)	05-24	05-25	05-25	05-25	05-26	05-26	05-26	05-26
START TIME	16:00	00:00	08:00	16:00	00:00	08:00	16:30	20:00
END TIME	20:00	04:00	12:00	20:00	04:00	12:00	17:30	21:00
FEEDSTOCK	A	A	A	A	A	A	A	A
FEED RATE, cc/hr	82	85	83	83	332	333	495	83
OPERATING PRESSURE, psig	500	500	500	500	500	500	500	500
H ₂ PARTIAL PRESSURE, psig	500	500	500	500	500	500	500	500
H ₂ TREAT RATE, scf/bbl	9000	9000	9000	9000	9000	9000	9000	9000
REACTOR 1 CONDITIONS								
LHSV, cc/hr/cc cat.	0.50	0.52	0.50	0.50	2.01	2.02	3.00	0.50
INLET BED TEMP., F	304	306	295	303	293	296	295	298
UPPER MID BED TEMP., F	304	306	294	302	294	299	292	290
LOWER BED TEMP., F	305	308	295	304	296	301	300	296
AVERAGE BED TEMP., F	304	307	295	303	294	299	296	293
SAND BATH TEMP., F	307	307	295	303	298	305	315	284
REACTOR 2 CONDITIONS								
LHSV, cc/hr/cc cat.	0.50	0.52	0.50	0.50	2.01	2.02	3.00	0.50
INLET BED TEMP., F	790	840	891	924	859	794	817	792
UPPER MID BED TEMP., F	778	833	886	922	914	831	880	791
LOWER BED TEMP., F	774	827	882	915	924	841	911	790
AVERAGE BED TEMP., F	781	833	886	920	899	822	869	791
SAND BATH TEMP., F	776	832	883	917	916	835	914	787
SEVERITY STAGE 1	0.0010	0.0011	0.0007	0.0010	0.0002	0.0002	0.0001	0.0006
SEVERITY STAGE 2	6.8760	11.8248	20.6993	28.5693	5.8459	2.6760	2.9361	7.6097
OVERALL SEVERITY	6.8770	11.8259	20.7001	28.5703	5.8461	2.6762	2.9363	7.6104

FEEDSTOCK TYPE:

A: 355-618 F VIRGIN COLORADO SHALE OIL DISTILLATE.

TABLE 4.3.2-3

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED COLORADO SHALE OIL

HYDROTREATING TESTS

CATALYST: K-599 (1ST STAGE)/MO-1230 (2ND STAGE)

FILE ID: REPTS02.WK1

TEST # (FB-)	159	160	161	162	163	164
DATE (1989)	06-05/06	06-06/07	06-08	06-08	06-08	06-09
START TIME	16:00	18:00	00:00	08:00	16:00	00:00
END TIME	16:00	18:00	06:00	14:15	22:00	06:00
FEEDSTOCK	A	A	B	B	C	C
FEED RATE, cc/hr	87	84	80	78	82	82
OPERATING PRESSURE, psig	500	500	2000	2000	2000	2000
H ₂ PARTIAL PRESSURE, psig	500	500	2000	2000	2000	2000
H ₂ TREAT RATE, scf/bbl	9000	9000	7000	7000	7000	7000
REACTOR 1 CONDITIONS						
LHSV, cc/hr/cc cat.	0.53	0.51	0.48	0.47	0.50	0.50
INLET BED TEMP., F	300	300	599	694	699	600
UPPER MID BED TEMP., F	300	300	599	697	698	600
LOWER BED TEMP., F	300	300	600	700	702	602
AVERAGE BED TEMP., F	300	300	599	697	700	601
SAND BATH TEMP., F	302	302	602	698	699	604
REACTOR 2 CONDITIONS						
LHSV, cc/hr/cc cat.	0.53	0.51				
INLET BED TEMP., F	840	790				
UPPER MID BED TEMP., F	837	788				
LOWER BED TEMP., F	836	782				
AVERAGE BED TEMP., F	836	787				
SAND BATH TEMP., F	832	783				
SEVERITY STAGE 1	0.0008	0.0008	2.4818	10.3582	10.2039	2.4724
SEVERITY STAGE 2	11.8398	7.1870				
OVERALL SEVERITY	11.8406	7.1876	2.4818	10.3582	10.2039	2.4724

FEEDSTOCK TYPE:

A: 355-618 F VIRGIN COLORADO SHALE OIL DISTILLATE.

B: LIQUID PRODUCT FROM FB-159.

C: LIQUID PRODUCT FROM FB-160.

4.3.3 Virgin Atmospheric Resid Cracking Campaigns

Like the COALITE, there is also a considerable yield of atmospheric resid in the raw Colorado shale oil. Therefore, it is also necessary to crack the heavier components to the mid-distillate range comprising the desired HEDF turbine fuel products. In a manner similar to that when processing the COALITE, three cracking methods were considered: 1) Resid hydrocracking using the LC-Finingtm process; 2) Delayed Coking; and 3) VGO fixed-bed hydrocracking. The former two are discussed in the next two sections while the latter is discussed in Section 4.3.5.

4.3.3.1 LC-Fining (Residue Hydrocracking)

Two LC-Finingtm campaigns were made with atmospheric residues from the Colorado shale oil feedstock in the stirred autoclave simulator of the LC-Finingtm process. Campaign I included five material balance tests made with a virgin 650F+ atmospheric resid fraction which evaluated the effect of reactor temperature. A NiMo catalyst (Shell 324M) that had previously been aged on coal-oil service was used in the tests. Table 4.3.3.1-1 summarizes the operating conditions evaluated.

Campaign II also included five material balance tests made with a first-pass hydrotreated 575F+ fraction recovered by distillation from the liquids processed in LC-Finingtm Campaign I. This allowed a comparison of the hydrocracking processabilities of virgin and first-pass hydrotreated residua. Table 4.3.3.1-2 summarizes the operating conditions evaluated.

4.3.3.2 Delayed Coking

Two Delayed Coking tests were made in the Continuous Bench Coking unit with the virgin 650F+ atmospheric resid to study the effects of coke drum pressure at constant coke drum temperature. Table 4.3.3.2-1 presents the summary of the feedstock properties. The detailed operating conditions for the two tests are presented in Table 4.3.3.2-2.

4.3.4 Cracked Distillate Hydrotreating Campaigns

The above two cracking operations, namely, LC-Finingtm and Delayed Coking, are primarily conversion processes to produce HEDF precursor materials that boil within the HEDF boiling range. They therefore do not result in the production of finished HEDF products and a post-cracking hydrogenation operation is required for upgrading the cracked precursor materials. In a true commercial process, a fractionator would be installed between the cracking unit(s) with the cracked distillate fed continuously to the distillate hydrotreater and the heavier unconverted residuum being recycled back to the cracking unit.

In this Task 3 screening program with the Colorado shale oil feedstock, the bench-scale cracking and hydrotreating units were not integrated and thus only first-pass crackates, either, delayed coker

TABLE 4.3.3.1 - 1

SUMMARY OF OPERATING CONDITIONS FOR LC-FINING (HYDROCRACKING) TESTS

COLORADO SHALE OIL DISTILLATE

CATALYST: SHELL 324 (AGED)

TEST # VEL-24-	84-1	84-2	84-3	84-4	84-5
DATE (1984)	03-06	03-07	03-07/08	03-08	03-09
START TIME	10:00	11:30	14:00	04:00	10:00
END TIME	20:00	10:00	02:00	10:00	01:30
FEEDRATE	4	4	4	4	4
FEED RATE (g/hr)	387	379	281	280	300
OPERATING PRESSURE (psig)	1150	1150	1150	1150	1150
HYDROGEN PRESSURE (psig)	2000	2000	2000	2000	2000
HYDROGEN FLOW (SCFH)	10.00	10.00	10.00	10.00	10.00
STRAIGHT CHAIN (wt %)					
DATA (wt %)					
DATA (wt %)	0.4	0.3	0.3	0.3	0.3
DATA (wt %)					
DATA (wt %)	7.1	7.1	7.1	7.0	7.1
DATA (wt %)	7.1	7.1	7.1	7.0	7.1
DATA (wt %)	7.1	7.1	7.1	7.0	7.1
DATA (wt %)	7.1	7.1	7.1	7.0	7.1

FEEDRATE (g/hr)

DATA (wt %)

TABLE 4.3.2.1 - 1

SUMMARY OF OPERATING CONDITIONS FOR CO-FINING (HYDROCRACKING) TESTS

COLORADO SHALE OIL DISTILLATE

CATALYST: SHELL 324 - AGED

TEST # BLOCK#	91	96	97	98	99
DATE: 10/1/74	04-09	04-10-11	04-17	04-23-24	04-31
START TIME	18:00	20:00	09:00	20:00	12:00
END TIME	24:00	04:00	18:00	03:00	20:00
FEEDSTOCK	5	8	8	8	8
FEED RATE (cc/hr)	100	90	80	90	100
OPERATING PRESSURE (PSIG)	115	110	105	105	105
HYDROGEN PRESSURE (PSIG)	115	105	105	105	105
HYDROGEN FLOW (SCFH)	700	1000	1000	1000	1000
REACTOR TEMPERATURE (°F)					
INLET REACTOR TEMPERATURE (°F)	100	100	100	100	100
OUTLET REACTOR TEMPERATURE (°F)	600	600	600	600	600
REACTOR TEMPERATURE (°F)	600	600	600	600	600
REACTOR TEMPERATURE (°F)	600	600	600	600	600
REACTOR TEMPERATURE (°F)	600	600	600	600	600

RECORD # 174

B: 500 cc CO-FINATE FEED.

1. USING 500 cc REACTOR FOR BLOCK-91.

USING 250 cc REACTOR FOR BLOCK-96 TO BLOCK-99.

TABLE 4.3.3.2-1

ASSAY OF DELAYED COKING COLORADO SHALE OIL - DERIVED FEEDSTOCK

<u>Feedstock Type</u>	<u>Virgin</u>
Nominal IBP, °F	650
Specific Gravity @ 60°F	0.9680
API Gravity	14.7
ASTM Distillation, °F	
5% Distilled	655
10% Distilled	763
30% Distilled	824
50% Distilled	889
70% Distilled	975
Elementals, Wt%	
C	84.41
H	11.05
N	2.69
S	0.75
O + Ash (By Diff.)	1.10

TABLE 4.3.3.2-2

SUMMARY OF OPERATING CONDITIONS
FOR DELAYED COKING OF COLORADO SHALE OIL

Test No. (CBC-)	<u>65</u>	<u>66</u>
Feed Source	--- Virgin 650F+ Resid ---	
Coke Drum Temp., °F	880	880
Coke Drum Pressure, psig	100	25
Coke Drum Preheater Temp., °F	700	600
Feed Rate, lb/hr	0.85	0.65
Run Length, hr.	24	24
Recycle/Fresh Feed Ratio	0.20	0.75

distillates or hydrocrackates (LC-Finates), were evaluated. Four distillate hydrotreating runs were made with delayed coker distillates and five distillate hydrotreating runs were made with LC-Finate (hydrocracked) distillates.

4.3.4.1 Hydrotreating of LC-Finate Distillates

One fixed-bed hydrotreating campaign was made to evaluate the effects of catalyst type, two-stage vs single-stage, feedstock boiling range, space velocity and reaction temperature. Table 4.3.4.1-1 presents the analyses of the LC-Finate feedstocks to distillate hydrotreating. The campaign included three fixed-bed tests (Table 4.3.4.1-2) made to evaluate the effect of reactor temperature using a 300-575F HEDF precursor-boiling stream.

4.3.4.2 Hydrotreating of Coker Distillates

Table 4.3.4.2-1 presents the feedstock assay for the coker distillate used in the four fixed-bed hydrotreating tests. The summary of the operating conditions for these tests is presented in Table 4.3.4.2-2. The objective of the hydrotreating tests was to evaluate the effects of space velocity, reactor temperature, and two-stage severity.

4.3.5 Two-Step Selective Hydrocracking Campaigns

The two-step selective hydrocracking (TSSH) approach used for the COALITE was also carried out for the Colorado shale oil feedstock. Three feedstocks were considered for the VGO fixed-bed hydrocracking step: 1) a virgin 650-975F VGO; 2) LC-Finate hydrocracked VGO; and 3) LC-Finate hydrocracked and hydrodenitrogenated VGO. The flowscheme with test number denotation for the latter two campaigns is presented in Figure 4.3.5-1. The feedstock assays for all three test campaigns are presented in Table 4.3.5-1. Eight fixed-bed hydrocracking tests were made with the virgin VGO (Table 4.3.5-2) to study the effects of space velocity and reactor temperature using the proprietary Amoco hydrocracking catalyst. Four tests were made with the LC-Finate hydrocrackates to study the effect of space velocity at constant temperature and hydrogen partial pressure. Four tests were made with hydrodenitrogenated LC-Finate VGO to study the effects of space velocity and reactor temperature. Table 4.3.5-3 presents the summary of the operating conditions for both of the latter fixed-bed hydrocracking campaigns. The summary of the operating conditions for the LC-Finate VGO hydrodenitrogenation campaigns is presented in Table 4.3.5-4.

The thus hydrocracked denitrogenated LC-Finate VGO product containing the 300-575F HEDF precursors was subjected to a final hydrogenation step to saturate aromatics to the low levels required for achieving high energy densities. A post-hydrogenation fractionation step was used to recover the final HEDF product meeting the front-end flash point and back-end freeze point specifications. Two distillate hydrotreating campaigns, made at two different space velocities and

TABLE 4.3.4.1-1

ASSAY OF COLORADO SHALE OIL
LC-FINATE MID-DISTILLATE TO HYDROTREATING

T.B.P. Boiling Range, °F	300-575
R.I. @ 20°C	1.4715
Specific Gravity, g/cc	0.8504
API Gravity	34.9

Distillation, °F	
IBP	272
10%	364
30%	425
50%	467
70%	507
90%	570
EBP	767
VABP	467

Watson K, R	11.44
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Elemental, Wt%	
C	84.30
H	13.11
N	1.14
S	0.70
O (By Diff.)	0.75

F.I.A./R.I., 1 Vol%	
Paraffins	N.D.
Olefins	17.8
Naphthenes	53.9
Aromatics	28.3

TABLE 4.3.4.1-2

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED HYDROTREATING TESTS OF

HYDROPROCESSED COLORADO SHALE OIL DISTILLATE

CATALYST: K-599 (2ND STAGE)

FILE ID: REPTSLC1.WK1

TEST # (FB-)	143	144	145
DATE (1989)	05-15/16	05-16	05-16
START TIME	22:30	04:30	10:30
END TIME	00:30	06:30	12:30
FEEDSTOCK	A	A	A
FEED RATE, cc/hr	119	119	112
OPERATING PRESSURE, psig	2000	2000	2000
H ₂ PARTIAL PRESSURE, psig	2000	2000	2000
H ₂ TREAT RATE, scf/bbl	7000	7000	7000
REACTOR 1 CONDITIONS			

LHSV, cc/hr/cc cat			
INLET BED TEMP., F			
UPPER MID BED TEMP., F			
LOWER BED TEMP., F			
AVERAGE BED TEMP., F			
SAND BATH TEMP., F			
REACTOR 2 CONDITIONS			

LHSV, cc/hr/cc cat	0.70	0.72	0.68
INLET BED TEMP., F	701	750	793
UPPER MID BED TEMP., F	682	714	764
LOWER BED TEMP., F	680	713	762
AVERAGE BED TEMP., F	682	726	773
SAND BATH TEMP., F	675	707	760
SEVERITY STAGE 1			
SEVERITY STAGE 2	5.9988	9.8101	18.4357
OVERALL SEVERITY	5.9988	9.8101	18.4357

FEEDSTOCK TYPE:

A: 300-575 F HYDROPROCESSED COLORADO SHALE OIL DISTILLATE.

TABLE 4.3.4.2-1

ASSAY OF COLORADO SHALE OIL (CSO) DELAYED
COKER MID-DISILLATE FEED TO HYDROTREATING

Feed Source	Delayed Coking of 650 ⁰ F+ CSO resid at 62.5 psig average coke drum pressure
R.I. @ 20 ⁰ C	1.4780
Specific Gravity, g/cc	0.8591
A.P.I. Gravity	33.2
Simulated Distillation, ⁰ F	
IBP	245
10%	324
30%	383
50%	427
70%	478
90%	540
EBP	733
VABP	447
Watson K, R	11.26
Elemental, Wt%	
C	84.76
H	12.21
N	1.54
S	0.75
O (By Diff.)	0.74
F.I.A./R.I., Vol%	
Paraffins	N.D.
Olefins	40.4
Naphthenes	26.0
Aromatics	33.6

TABLE 4.3.4.2-2

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED HYDROTREATING TESTS OF

THERMALLY PROCESSED COLORADO SHALE OIL DISTILLATE

CATALYST: K-550 (1ST STAGE) K-599 (2ND STAGE)

FILE ID: REPTSC1.WK1

TEST # (FB-)	131	132	133	134
DATE (1989)	04-24	04-24	04-24	04-25
START TIME	10:00	16:00	21:00	01:30
END TIME	12:00	18:00	22:30	03:00
FEEDSTOCK	A	A	A	A
FEED RATE, cc/hr	116	90	184	157
OPERATING PRESSURE, psig	2000	2000	2000	2000
H2 PARTIAL PRESSURE, psig	2000	2000	2000	2000
H2 TREAT RATE, scf/bbl	7000	7000	7000	7000
REACTOR 1 CONDITIONS				
LHSV, cc/hr/cc cat.	0.70	0.55	1.12	0.95
INLET BED TEMP., F	404	641	415	397
UPPER MID BED TEMP., F	406	638	415	402
LOWER BED TEMP., F	404	620	415	401
AVERAGE BED TEMP., F	405	633	415	400
SAND BATH TEMP., F				
REACTOR 2 CONDITIONS				
LHSV, cc/hr/cc cat.	0.70	0.55	1.12	0.95
INLET BED TEMP., F	743	694	652	651
UPPER MID BED TEMP., F	689	698	634	650
LOWER BED TEMP., F	692	702	630	644
AVERAGE BED TEMP., F	708	698	639	648
SAND BATH TEMP., F				
SEVERITY STAGE 1	0.0405	3.6815	0.0325	0.0268
SEVERITY STAGE 2	8.0386	9.0959	1.9568	2.6375
OVERALL SEVERITY	8.0792	12.7774	1.9893	2.6643

FEEDSTOCK TYPE:

A: THERMALLY PROCESSED COLORADO SHALE OIL DISTILLATE, 300-575 F.

FIGURE 4.3.5-1

PROCESSING APPROCHES
TO COLORADO SHALE OIL HEDF

TABLE 4.3.5-1

ASSAYS OF COLORADO SHALE OIL VGO FEEDS
TO FIXED-BED HYDROCRACKING

<u>Feed Type</u>	<u>Virgin</u>	<u>Mildly Hydrocracked</u> <u>(LC-Finates)</u>
Specific Gravity, g/cc	0.9482	0.9030
A.P.I. Gravity	17.7	25.2
Distillation, °F		
IBP	604	600
10%	738	639
30%	790	688
50%	833	750
70%	879	812
90%	950	881
EBP	1044	1000
VABP	834	754
Watson K, R	11.49	11.71
Elemental, Wt%		
C	84.51	85.68
H	11.64	12.79
N	1.95	1.29
S	0.90	0.07
O (By Diff.)	1.00	0.17
Ash	<0.01	---
Conradson Carbon	0.78	---
Q.I.	0.007	---

TABLE 4.3.5-2

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED

COLORADO SHALE OIL HYDROCRACKING TESTS

CATALYST: AMOCO PROPRIETARY

TEST # (FBHC-)	FILE ID: REPTSHC1.WK1							
	5	6	7	8	9	10	11	12
DATE (1989)	05-01	05-01	05-01	05-01	05-02	05-02	05-02	05-03
START TIME	07:30	13:30	19:30	01:30	07:30	13:30	19:30	04:30
END TIME	09:30	15:30	21:30	03:30	09:30	15:30	24:30	09:30
FEEDSTOCK	A	A	A	A	A	A	A	A
FEED RATE, cc/hr	98	105	211	211	211	190	110	76
OPERATING PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H2 PARTIAL PRESSURE, psig	2000	2000	2000	2000	2000	2000	2000	2000
H2 TREAT RATE, scf/bbl	7000	7000	7000	7000	7000	7000	7000	7000
LHSV, cc/hr/cc cat.	0.59	0.64	1.28	1.28	1.28	1.15	0.67	0.46
INLET BED TEMP., F	680	716	710	675	725	747	738	762
UPPER MID BED TEMP., F	721	763	758	714	779	803	785	804
LOWER BED TEMP., F	717	746	760	721	784	806	771	785
OUTLET BED TEMP., F								
AVERAGE BED TEMP., F	706	742	743	703	763	785	765	784

FEEDSTOCK TYPE:

A: 650-975 F COLORADO SHALE OIL VGO.

TABLE 4.3.5 - 3

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED

COLORADO SHALE OIL HYDROCRACKING TESTS

CATALYST: AMOCO PROPRIETARY

TEST # (FBHC-)	28	29	30	31	32	33	34	35
DATE (1989)	08-16	08-17	08-17/18	08-18/21	08-28/29	08-29/30	08-30/31	08-31/09-01
START TIME	06:00	00:00	12:00	13:00	21:00	20:00	20:00	12:00
END TIME	08:00	08:00	08:00	20:00	18:00	18:00	12:00	21:00
FEEDSTOCK	A	A	A	A	B	B	B	B
FEED RATE, cc/hr	177	144	105	88	111	79	119	139
OPERATING PRESSURE, psig	2000	2000	2000	2000	2400	2400	2400	2400
H ₂ PARTIAL PRESSURE, psig	2000	2000	2000	2000	2400	2400	2400	2400
H ₂ TREAT RATE, scf/hr	7000	7000	7000	7000	6000	6000	6000	6000
LOSS, COAL/OIL, g/g	1.07	0.87	0.65	0.53	0.67	0.48	0.72	0.84
INLET BED TEMP., °F	689	689	689	689	682	685	702	723
UPPER MID BED TEMP., °F	757	760	760	758	724	730	751	766
LOWER BED TEMP., °F	792	800	800	800	750	750	776	790
OUTLET BED TEMP., °F	801	795	793	796	746	740	768	784
AVERAGE BED TEMP., °F	744	750	750	749	719	722	743	760

FEEDSTOCK TYPE:

A. 575-1000 P LC-FINATE.

B. 575-1000 P HYDRODENITROGENATED LC-FINATE.

TABLE 4.3.5 - 4

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED HYDROTREATING TESTS OF

HYDROPROCESSED COLORADO SHALE OIL DISTILLATE

CATALYST: K-550 (1ST STAGE) / K-599 (2ND STAGE)

TEST # (FB-)	186	187
DATE (1989)	08-22/23	08-23/25
START TIME	18:00	18:00
END TIME	18:00	17:00
FEEDSTOCK	A	A
FEED RATE, cc/hr	313	303
OPERATING PRESSURE, psig	2000	2000
H ₂ PARTIAL PRESSURE, psig	2000	2000
H ₂ TREAT RATE, scf/bbl	7000	7000
REACTOR 1 CONDITIONS		
LHSV, cc/hr/cc cat.	1.85	1.84
INLET BED TEMP., °F	748	768
UPPER MID BED TEMP., °F	764	780
LOWER BED TEMP., °F	767	783
AVERAGE BED TEMP., °F	760	776
SAND BATH TEMP., °F	754	751
REACTOR 2 CONDITIONS		
LHSV, cc/hr/cc cat.	1.85	1.84
INLET BED TEMP., °F	760	768
UPPER MID BED TEMP., °F	773	773
LOWER BED TEMP., °F	775	775
AVERAGE BED TEMP., °F	769	768
SAND BATH TEMP., °F	773	774
SEVERITY STAGE 1	5.6639	7.0681
SEVERITY STAGE 2	6.3449	6.3918
OVERALL SEVERITY	12.0088	13.4599

FEEDSTOCK TYPE:

A: 575-1000 F LC-FINATE VGO.

constant temperature/hydrogen partial pressure, were made to produce sufficient sample for detailed analytical evaluation. The summary of the operating conditions for these tests is presented in Table 4.3.5-5.

4.3.6 Extraction Studies

The initial results of the hydroprocessing campaigns summarized above indicated that HEDF volumetric energy densities were practically limited to several thousand Btu/gal below the minimum specification. It was accordingly theorized that this resulted from the relatively high aliphatics content of the shale oils relative to their cyclics content. Thus, it was hypothesized that a hydrocarbon type separation step, such as for example, solvent extraction, could be implemented to generate an extract and a raffinate stream, one being enriched in cyclics and having a significantly higher volumetric energy density than that of either the initial feed or the other reject stream. The disposition of the high energy density cyclics, i.e., in the extract or in the raffinate, would depend upon the choice of solvent and the extraction conditions. The aliphatics-rich stream, albeit in the extract or the raffinate, would represent a high cetane-quality diesel byproduct or alternatively could be further processed catalytically to "reform" the aliphatics to cyclic structures thereby increasing the yield of the desired HEDF.

In applying the solvent extraction approach, there are many parameters that can be considered. Firstly, the HEDF precursor stream (s) for extraction need to be identified. There are several combinations to consider here:

- o Prior to or subsequent to hydroprocessing operations. Prior to hydrogenation, the cyclics in the Colorado shale oil exist as a mixture of aromatics and naphthenics, with the ratios depending upon boiling range of the precursor. Also present prior to hydroprocessing are a considerable quantity of heteroatomic compounds (e.g., organic N, S & O) which could interfere with the solvents.
- o Use of HEDF boiling range precursors vs use of heavier ends. Separation of cyclics from aliphatics might be accomplished with the VGO fraction of the shale oil prior to hydrocracking. Conversely, solvent extraction might be applied after hydrocracking and prior to or after hydrocrackate hydrogenation. In either case, a different solvent would probably be considered from the points of view of solvent effectiveness and method of separation of the solvent from the extract.

In an optimized flowscheme for conversion of the full-range Colorado shale oils to HEDF products, one or more solvent extraction applications may be feasible.

The choice of solvent (s) is also a critical parameter affecting the technical and economic feasibility of the solvent extraction route. If

TABLE 4.3.5 - 5

SUMMARY OF OPERATING CONDITIONS FOR FIXED-BED HYDROTREATING TESTS OF

HYDROCRACKED COLORADO SHALE OIL DISTILLATE

CATALYST: K-550 (1ST STAGE) / K599 (2ND STAGE)

TEST # (FB-)	188	189
DATE (1989)	09-05	09-05/07
START TIME	06:00	19:00
END TIME	15:00	13:00
FEEDSTOCK	A	A
FEED RATE, cc/hr	98	191
OPERATING PRESSURE, psig	2000	2000
H ₂ PARTIAL PRESSURE, psig	2000	2000
H ₂ TREAT RATE, scf/bbl	8000	8000
REACTOR CONDITIONS		
LHSV, cc/hr/cc cat.	0.59	1.16
INLET BED TEMP., °F	679	671
UPPER MID BED TEMP., °F	680	680
LOWER BED TEMP., °F	681	684
AVERAGE BED TEMP., °F	681	676
SAND BATH TEMP., °F	681	684
REACTOR CONDITIONS		
LHSV, cc/hr/cc cat.		1.16
INLET BED TEMP., °F		688
UPPER MID BED TEMP., °F		703
LOWER BED TEMP., °F		705
AVERAGE BED TEMP., °F		699
SAND BATH TEMP., °F		705
SEVERITY STAGE 1	6.6296	3.2956
SEVERITY STAGE 2		4.3237
OVERALL SEVERITY	6.6296	7.6193

FEEDSTOCK TYPE:

A: HYDROCRACKED & HYDROGENITROGENATED LC-FINATE VGO.

the solvent is most effective above ambient temperature, separation would be achieved by decanting and solvent recovery would most likely be achieved by either distillation or water extraction followed by distillation, the latter occurring only if the solvent is totally miscible in water. If the solvent is most effective at sub-ambient conditions, separation would be accomplished by fractional crystallization and the solvent recovery method would be either of the two methods identified above.

One of the most widely used commercial solvent extraction technologies is the dewaxing of petroleum lube oils. In this case, the lube oil feedstocks are heavy boiling fractions, relative to the 300-575F HEDF range. Solvents in use include for example, N-methylpyrrolidone (NMP), N,N-dimethylformamide (DMF), furfural, phenol, etc. These all boil below that of the lube oil feedstocks and are readily separated from the extracts by distillation with the solvent boiling overhead. Other lube oil dewaxing solvents in use include methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), acetone, etc., the latter resulting in the initial paraffin separation via fractional crystallization. When applying solvent extraction to the Colorado shale oil HEDF precursor streams, the solvent should boil either below about 300F or above about 575F if it is to be readily separated by distillation from the extracts. In the initial evaluation studies completed as part of Task 3, two solvent candidates were identified: DMF, a low boiling solvent (B.P. = 307F); and TEG (tetraethylene glycol), a higher boiling solvent (B.P. = 597F).

Four HEDF precursor streams were examined in the initial solvent extraction evaluation campaigns:

1. LC-Finate VGO
2. Hydrodenitrogenated LC-Finate VGO
3. HEDF from selective hydrocracking of VGO
4. HEDF from hydrotreating of virgin mid-distillate

Table 4.3.6-1 summarizes the batch equilibrium extraction test cycles performed with the two candidate solvents at constant temperature, pressure, solvent/feed ratio, extraction time and stirrer speed.

Table 4.3.6-1

RESULTS OF SOLVENT EXTRACTION ON HYDROTREATED COLORADO SHALE OILS

SOLVENT A: TETRAETHYLENE GLYCOL
 SOLVENT B: N,N-DIMETHYLFORMAMIDE

DATE OF OPERATION (1989)	09/06	09/06	09/06	09/07	09/08	09/08	09/08	09/11	09/12	09/15	09/15	09/15	09/19	09/19	09/20
FEEDSTOCK:	FEV 181	FEV 181	FEV 181	FEV 181	FEV 181	FEV 181	FEV 181	FEV 181	FEV 181	FEV 181	FEV 181	FEV 181	FEV 181	FEV 181	FEV 181
	Feed to	Feed to	Feed to	Feed to	Feed to	Feed to	Feed to	Feed to	Feed to	Feed to	Feed to	Feed to	Feed to	Feed to	Feed to
	CYCLE#1	CYCLE#1	CYCLE#1	CYCLE#1	CYCLE#1	CYCLE#1	CYCLE#1	CYCLE#1	CYCLE#1	CYCLE#1	CYCLE#1	CYCLE#1	CYCLE#1	CYCLE#1	CYCLE#1
	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7
AVG. TEMPERATURE, F	191.5	193.5	193.2	193.2	193.3	193.3	193.3	194.8	195.3	195.8	195.0	195.5	195.0	194.7	193.8
MIXING SPEED, rpm	12	5	5	5	5	5	5	5	5	5	5	5	5	5	5
EXTRACTION TIME, hr	1.13	1.08	1.16	1.16	1.50	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
SOLVENT	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
INVENTORY:															
FEED CHARGE, gm	100.4	62.1	44.4	44.4	150.1	129.8	108.5	150.1	150.1	150.0	113.3	83.9	150.0	116.7	75.4
SOLVENT CHARGE, gm	149.7	93.2	88.4	88.4	225.0	194.1	162.9	225.1	225.1	225.1	170.1	188.9	225.0	174.9	113.1

5.0 SUMMARY OF RESULTS OF COALITE SCREENING OPERATIONS

5.1 Overview

The Task 3 screening program consisted of an experimental investigation of thermal and catalytic processing responses of COALITE feedstocks with regard to their conversion to HEDF fuels, namely, Category I high density aviation turbine (jet) fuel; Category II endothermic aviation turbine (jet) fuel; and Category III high density diesel fuel. The overall objectives and technical directions taken in the screening program are as follows:

- o Generate experimental processing data, analyze data and formulate processing strategies aimed at meeting the goal of producing COALITE-derived HEDF fuels meeting a minimum volumetric energy density specification of 130,000 Btu/gal as well as satisfying the other required turbine fuel properties. A secondary goal was the identification of processing strategies that would result in HEDF fuels achieving the energy density target of 135,000 Btu/gal; and
- o Collect sufficient data for use in the refinery LP computer model of Task 5 which is aimed at determining economically optimized process flowschemes for producing HEDF products in a conceptualized refinery processing facility.

The basic technical approach taken consisted of cracking the heavier ends of the COALITE boiling above the HEDF precursor range using thermal (delayed coking) cracking technology and catalytic (LC-Fining[™] and fixed-bed VGO hydrocracking) hydrocracking technology followed by fixed-bed distillate hydrotreating of both the virgin COALITE distillates as well as the cracked COALITE distillates. Since the experimental data are collected in small bench-scale or pilot-scale units, the scaleup interpretation of the resultant data to the HEDF processing requirements must not be underestimated. Although the screening tests could not be comprehensive enough to quantify every commercial processing parameter, including for example, catalyst deactivation, catalyst makeup requirements, extinction recycle requirements, etc., these parameters had to be considered in the execution and resultant analysis of the screening test matrix.

Commercial jet (and diesel) fuel products require a considerable number of detailed specifications that must be met. In this screening program, the major emphasis was on the analytical determination and evaluation of certain key fuel properties in addition to the volumetric energy density specification. These include:

1. Freeze Point
2. Flash Point
3. Viscosity
4. Smoke Point
5. Cetane Number
6. Hydrogen Content
7. Trace sulfur and nitrogen
8. Specific gravity
9. Aromatics

Those properties not investigated for most of the 73 distillate hydrotreating tests made with the COALITE feedstocks included existent gum, JFOT (thermal stability), copper strip corrosion, naphthalenes content, Saybolt color, acid number, mercaptans, particulate matter, water separation index, inhibitor content, carbon residue and ash content. It was assumed that the high degree of hydrogenation required to meet the stringent hydrogen and aromatics content specifications for the finished HEDF products would result in the achievement of the specifications for the above chemical and physical tests.

The following sections sequentially summarize the analyses of the results of the four major processing approaches investigated during the Task 3 screening efforts with the COALITE feedstocks.

5.2 Virgin Distillate Hydrotreating

One of the key advantages of Mild Coal Gasification over those of conventional pyrolysis technologies is the production of coal liquids enriched in distillates having relatively high hydrogen/carbon ratios and leaner in the tarry residue materials. The COALITE sample used in this program contained more than about 50 weight percent boiling in the mid-distillate range. Accordingly, these materials were the first precursors considered for conversion of COALITE to HEDF fuels.

The category I (jet) and III (diesel) fuel specifications differ primarily on the basis of distillation end point, with the diesel allowing a higher end point. It was arbitrarily decided to select two raw mid-distillate fractions for distillate hydrotreating evaluation. The raw jet fraction to hydrotreating was specified as a nominal 350-550F (TBP) cut and the raw diesel fraction was specified as a nominal 350-650F (TBP) cut. In practice, the bulk of the testing was made with the 350-650F fraction, which included the jet precursors as well as the diesel precursors. This allowed for cut point (front-end as well as back-end) control by distillation after hydrotreating. This insured that any heavy materials, i.e., 550F+, boiling above the finished jet fuel range would, upon hydrogenation, be allowed to pass into the jet fuel range. Using model compounds as an example, the hydrogenation of the heteroatomic compound 2-ethylaminonaphthalene (B.P. = 591F) might result in the formation of 2-ethylnaphthalene which boils at 496F and 2-ethyldecahydronaphthalene, a 2-ring naphthene, which also boils within the HEDF range.

The resultant ammonia product of hydrogenation would be a byproduct of the process. There are analogous situations for the hydrotreating of the heavier boiling oxygenates and sulfur-containing compounds present in the 550F+ mid-distillate fractions. These would result in the byproduct formation of H₂O and H₂S. In addition to the heteroatom conversion aspect of hydrotreating, there also exists some degree of hydrocarbon hydrocracking which would convert the heavier 550F+ hydrocarbons to the finished jet fuel range materials.

There is also an analogy to the front-end of the mid-distillate fraction. Front-end cut point is limited in part by the flash point specification. Heteroatom conversion such as hydrogenation of

multi-phenols to alkylated aromatics coupled with ring saturation of the resultant alkylated aromatics would result in a fraction boiling below the 300F nominal HEDF initial boiling point. These materials, which include alkylcyclohexanes for example, represent excellent stocks for the Category II endothermic fuels.

Depending upon the particular aircraft requirements, there are several specifications for jet or aviation turbine fuels as defined by the respective JP- designations (Table 5.2.1-1). With the exception of JP-10, a missile fuel, the other JP fuels have volumetric energy density specifications of about 115 to 121 KBtu/gal. These latter values are ultimately limited by the hydrocarbon structures characteristic of the petroleum stocks used to produce these jet fuels, these being a predominance of aliphatics as opposed to naphthenics. The latter class of hydrocarbons is known to have a unique combination of desirable high specific gravity and high mass heat of combustion which translates to high (net) volumetric energy densities, ca., 130+ KBtu/gal. This is depicted in Figure 5.2.1-1 which shows the volumetric (gross) energy densities as a function of hydrogen content for the cyclics class of hydrocarbons and the conventional petroleum-derived JP- fuels. The difference between gross and net heat of combustion is the latent heat of vaporization of the water product generated during the combustion of the fuel.

Thus, the objective of the hydroprocessing operations with the coal-derived COALITE mid-distillate feedstock is to saturate the existing alkylated single and multi-ring aromatics to alkylated single and multi-ring naphthenics and to hydrotreat the contained heteroatoms sufficiently to achieve a thermally stable fuel product in such a way that the volumetric energy density is maximized. This is accomplished by using active and selective Group 6b and 8 transition metal-based hydrogenation catalysts. In this screening effort, two such commercially available catalysts were utilized: 1) K-550, a nickel-tungsten on alumina catalyst manufactured by Katalco Corporation; and 2) K-599, a nickel-molybdenum on alumina catalyst also manufactured by Katalco. Other competing catalyst vendors also make commercial products similar to the ones utilized in this study. In one series of tests, the K-550 catalyst was specially treated in our laboratories with a calcium promoter in an attempt to improve the catalyst selectivity towards suppression of ring-opening activity. Table 5.2.1-2 summarizes the properties of the fresh catalyst oxides as reported by the manufacturer. Catalyst activation via presulfiding with an H_2S/H_2 mixture was practiced prior to hydrotreating operations.

The results are summarized in a series of spreadsheet tables with the "A" tables presenting the run performance data and the "B" tables presenting the properties of the full-range hydrotreated distillates. The organization of the tabulated results is as follows:

Table 5.2.1-1

KEY SPECIFICATIONS FOR MILITARY TURBINE FUELS

	<u>JP-4</u>	<u>JP-8</u>	<u>JP-7</u>	<u>JP-10</u> 98.5%MIN C ₁₀ H ₁₆
I. VOLATILITY PROPERTIES				
ASTM D-86 Distillation, °F				
IBP	N.L.	N.L.	360	N.L.
10% distilled (MAX)	N.L.	401	385	N.L.
20% distilled (MAX)	293	N.L.	403	N.L.
50% distilled (MAX)	374	N.L.	N.L.	N.L.
90% distilled (MAX)	473	N.L.	500	N.L.
EP (MAX)	518	572	550	N.L.
Flash Point, °F (MIN)	N.L.	100	140	131
Density, API @ 15°C				
MAX	57.0	51.0	50.0	20.0
MIN	45.0	37.0	44.0	18.5
Vapor Pressure @ 100°F, psi				
MIN	2.0	N.L.	N.L.	N.L.
MAX	3.0	N.L.	3.0 @300°F	N.L.
II. FLUIDITY PROPERTIES				
Freezing Point, °F (MAX)	-72	-53	-46	-110
Viscosity @ -4°F (MAX)	N.L.	8.0	8.0	9.0 @0°F
III. COMBUSTION PROPERTIES				
Net Heat of Combustion (MIN)				
Btu/lb	18,400	18,400	18,700	18,100
Btu/gal	115,261	118,944	121,508	141,500
Smoke Point, mm (MIN)	20.0	25.0	N.L.	N.L.
Hydrogen Content, wt % (MIN)	13.6	13.4	14.4	11.6
Aromatics, vol % (MAX)	N.L.	25.0	5.0	1.5
Cetane No. (MIN)	N.L.	N.L.	N.L.	N.L.
IV. CORROSION PROPERTIES				
Copper Strip Corrosion, 2 hr @ 212°F, (MAX)				
	1.0	1.0	1b	N.L.
V. THERMAL STABILITY PROPERTIES				
JFTOT, mm Hg (MAX)				
	25	25	25	10
VI. CONTAMINANTS				
Existent Gum, mg/100 ml (MAX)				
	7.0	7.0	5.0	N.L.
Particulate Matter, mg/L (MAX)				
	1.0	1.0	0.3	1.0
Accelerated Stability, mg/100 ml (MAX)				
	N.L.	N.L.	N.L.	N.L.

Figure 5.2.1.1-1

VOLUMETRIC HEAT CONTENT VS HYDROGEN CONTENT OF MODEL COMPOUNDS

TABLE 5.2.1-2

ASSAYS OF DISTILLATE HYDROTREATING CATALYSTS

Catalyst Designation (Oxided/calced form)	<u>K-550</u>	<u>K-599</u>
B.E.T. Surface Area, m ² /gm	230	220
Crush Strength, lb	15	20
Compacted Bulk Density, lb/ft ³	49.92	57.41
<u>Bulk Chemical Analysis, wt% dry basis</u>		
WO ₃	20.0	0
NiO	5.0	6.7
MoO ₃	0	27.0
Al ₂ O ₃	Balance	Balance
<u>Trace Metals, ppmw on ashed catalyst*</u>		
Vanadium	434	480
Iron	191	100
Arsenic	<2	<2
Calcium	1600	1300
Copper	B.D.L.	B.D.L.
Sodium	633	842
Lead	286	192

* Via Atomic Absorption Spectrophotometry

<u>Table No</u>	<u>Catalyst Type</u>	<u>Feed Boiling Range (F)</u>	<u># Reaction Stages</u>
5.2.1-3A,B	K-550	350-650	1
5.2.1-4A,B	K-550	350-550	1
5.2.1-5A,B	K-550/K-550	350-750(820)	2
5.2.1-6A,B	K-550/K-599	350-650	2
5.2.1-7A,B	K-599	350-650	1
5.2.1-8A,B	K-550/Calcium	350-650	1

Several interesting correlations were developed for the hydrotreating of the raw 350-550F and 350-650F COALITE distillates. Correlations were developed of the HEDF properties vs the kinetic hydrotreating severity parameter (KSF described in Section 4). These are shown graphically in Figures 5.2.1-2 through -9. Cross-correlations of key HEDF properties vs aromatics contents are depicted in Figures 5.2.1-10 through -12. Cross-correlations of key HEDF properties vs Refractive Index are shown in Figures 5.2.1-13 through -17.

At a quarterly project review meeting held in Morgantown in November 1989, WRI presented some data on their efforts to evaluate the hydrotreating of COALITE. Two hydrotreating tests were made with the COALITE mid-distillate fraction at conditions not very dissimilar to tests made at Lummus during the early Task 3 screening operations. While an exact comparison of the operating procedures and analytical methodologies was not able to be made, some interesting relationships and correlations were observed based on a comparison of the major known parameters. These are summarized below:

- o Shell 424, a nickel-molybdenum on alumina catalyst, and Katalco 550, a nickel-tungsten on alumina catalyst, both demonstrated excellent activity for saturating COALITE aromatics in the presence of heteroatomic contaminants.
- o Both catalysts appear to result in comparable specific gravity reductions in the hydrotreated products as a function of the degree of aromatics conversion. Specific gravity reduction is important because it has a direct impact on the desired improvement of the HEDF volumetric energy densities. Approximately 85% of the ultimate specific gravity reduction occurs at aromatics conversions up to about 60-70 percent (Figure 5.2.4-1).
- o Average catalyst bed temperature appears to correlate the extent of aromatics conversion at constant space velocity and hydrogen partial pressure for both catalysts with no discernible differences for the two catalyst types (Figure 5.2.4-2).
- o The experimentally observed hydrogen uptake-average catalyst bed temperature correlation for the two catalysts are nearly parallel suggesting similar activation energies for the two catalyst types. The WRI data obtained with the Shell 424

TABLE 5.2.1-3A 1 of 4

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COALITE HYDROTREATING TESTS

	CATALYST: K-550 (1ST STAGE)									FILE ID: REPTBE1.WK1
TEST # (FB-)	17A-1	17A-2	18A-1	18A-2	18A-3	19A-1	19A-2	19A-3		
DATE (1989)	01-13	01-13	01-16	01-16	01-16	01-17	01-17	01-17		
START TIME	14:30	16:30	12:30	14:45	19:00	12:30	15:00	18:20		
END TIME	16:30	17:30	13:30	15:45	21:00	13:30	17:00	20:20		
FEEDSTOCK	A	A	A	A	A	A	A	A		
% HDS	9.36		22.97	87.25	94.08	91.93	95.68	97.04		
% HDN	25.28		9.03	16.60	50.67	24.82	83.12	60.05		
% HDO	25.51		-9.08	10.08	75.91	21.99	87.86	91.70		
H2 UPTAKE, scf/bbl	3000	3000	5000	5000	5000	5000	5000	5000		
% F.I.A. OLEFINS SATURATION			66.31		91.76		92.87	95.43		
% F.I.A. AROMATICS SATURATION	24.26 *		13.18	31.57 *	50.17	38.88 *	53.25	48.96		
API IMPROVEMENT	0.9	0.2	1.0	9.4	19.4	10.8	23.3	20.6		
R.I. DEPRESSION	0.0015		0.0040	0.0339	0.0601	0.0385	0.0747	0.0657		
EST. HEAT OF REACTION, Btu/lb			83		335		385	363		

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

* ESTIMATED FROM REGRESSION ANALYSIS.

TABLE 5.2.1-3A 2 of 4

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COALITE HYDROTREATING TESTS

TEST # (FB-)	CATALYST: K-550 (1ST STAGE)							
	20A-1	20A-2	21	22	23	24	25	26
DATE (1989)	01-18	01-18	01-19	01-20	01-20	01-23	01-23	01-24
START TIME	16:20	19:00	19:00	16:45	19:30	17:45	20:45	15:20
END TIME	18:20	21:00	21:00	17:45	20:30	18:45	21:45	16:30
FEEDSTOCK	A	A	A	A	A	A	A	A
% HDS	94.48	90.33	91.79					
% HDN	68.89	12.82	48.21					
% HDO	80.03	20.65	55.05					
H ₂ UPTAKE, scf/bbl	5000	5000	5000	5000	5000	5000	5000	5000
% F.I.A. OLEFINS SATURATION	95.73	92.31						
% F.I.A. AROMATICS SATURATION	55.72	38.15	50.25 *	65.73 *	55.96 *	35.45 *	45.90 *	65.40 *
API IMPROVEMENT	21.0	9.6	15.0	22.4	19.8	10.3	15.7	21.0
R.I. DEPRESSION	0.0707	0.0344	0.0530	0.0723	0.0625	0.0361	0.0511	0.0685
EST. HEAT OF REACTION, Btu/lb	389	242						

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

* ESTIMATED FROM REGRESSION ANALYSIS.

TABLE 5.2.1-3A 3 of 4

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)

FILE ID: REPTBE2.WK1

TEST # (FB-)	27	28	29	37	38	39	40	41
DATE (1989)	01-24	01-24	01-25	02-02	02-02	02-03	02-03	02-03
START TIME	17:45	20:15	16:40	11:30	20:15	10:35	13:35	17:30
END TIME	18:45	21:15	17:40	19:00	21:45	12:05	15:05	18:45
FEEDSTOCK	A	A	A	A	A	B	B	A
% HDS								
% HDN								
% HDO								
H ₂ UPTAKE, scf/bbl	5000	5000	5000	5000	5000	5000	5000	5000
% F.I.A. OLEFINS SATURATION				57.97	97.66	100.00	100.00	93.36
% F.I.A. AROMATICS SATURATION	61.96 *	58.57 *	58.75 *	76.40	80.42	94.22	98.59	72.59
API IMPROVEMENT	22.90	19.90	19.90	27.21	27.39	28.01	28.61	26.20
R.I. DEPRESSION	0.0699	0.0625	0.0585	0.0867	0.0903	0.0933	0.0965	0.0853
EST. HEAT OF REACTION, Btu/lb								

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

B: LIQUID PRODUCT FROM FB-37.

* ESTIMATED FROM REGRESSION ANALYSIS.

TABLE 5.2.1-3A 4 of 4

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)

FILE ID: REPTB2.WK1

TEST # (FB-)	42	43	46	47	48	49
DATE (1989)	02-06	02-06	02-21/22	02-22	02-23	02-24
START TIME	12:05	18:45	03:45	05:45	02:00	00:00
END TIME	17:35	20:40	04:00	24:00	22:00	20:00
FEEDSTOCK	A	C	A	D	A	A
% HDS			94.48		98.64	
% HDN			68.9		87.78	
% HDO			100.58		92.01	
H2 UPTAKE, scf/bbl	5000	5000	5000	5000	5000	5000
% F.I.A. OLEFINS SATURATION			96.58		96.65	
% F.I.A. AROMATICS SATURATION			70.63		78.92	
API IMPROVEMENT	8.5	28.5	24.6	28.2	27.2	9.1
R.I. DEPRESSION	0.0357	0.0947	0.0810	0.0943	0.0879	0.0325
EST. HEAT OF REACTION, Btu/lb			478		516	

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

C: LIQUID PRODUCT FROM FB-42.

D: LIQUID PRODUCT FROM FB-46.

* ESTIMATED FROM REGRESSION ANALYSIS.

TABLE 5.2.1-3B 1 of 4

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COALITE PRODUCTS

FROM FIXED-BED HYDROTREATING

CATALYST: K-550 (1ST STAGE)

FILE ID: REPTBP1.WK1

TEST # (FB-)	17A-1	17A-2	18A-1	18A-2	18A-3	19A-1	19A-2	19A-3
DATE (1989)	01-13	01-13	01-16	01-16	01-16	01-17	01-17	01-17
START TIME	14:30	16:30	12:30	14:45	19:00	12:30	15:00	18:20
END TIME	16:30	17:30	13:30	15:45	21:00	13:30	17:00	20:20
FEEDSTOCK	A	A	A	A	A	A	A	A
SPECIFIC GRAVITY, gm/cc	0.9861	0.9909	0.9854	0.9309	0.8735	0.9224	0.8529	0.8670
API GRAVITY @ 60 F	12.0	11.3	12.1	20.5	30.5	21.9	34.4	31.7
REFRACTIVE INDEX @ 20 C	1.5454		1.5429	1.5130	1.4868	1.5084	1.4722	1.4812
ELEMENTALS, wt%								
C	84.30		83.42	84.04	86.17	84.28	86.51	86.89
H	9.33		9.39	10.65	12.26	10.91	12.73	12.39
SIMULATED DISTILLATION, F								
IBP			365		178	183	133	
10% DISTILLED			409		237	314	218	
30%			477		369	429	327	
50%			531		452	487	422	
70%			589		517	549	493	
90%			663		606	632	583	
VOLUM. AVG. BOIL. PT, F			534		436	482	409	
WATSON Y			10.06		10.95	10.55	11.10	
F.I.A. ANALYSIS, 1vol%								
OLEFINS			4.1		0.9		0.8	0.5
SATURATES			27.4		63.8		65.2	63.3
AROMATICS	71.8		68.5	50.6	35.3	47.6	34.0	36.2
WLHV, Btu/lb	16046 *		16087	16820	17869	17021 *	18152	17934 *
VLHV, Btu/gal	131807 *		132048	130429	130019	130781 *	128822	129520 *
FLASH PT., F								
SMOKE PT., °F	3		7	3	7	7	8	5
FREZE PT., F								
ANILINE PT., F	36 *		38 *	61.3 *	81.8 *	64.9 *	93.2 *	86.2 *
CETANE INDEX	4		5	13	25	14	32	27
VISCOSITY, cst @ -4 F					6.5		.3	

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

* ESTIMATED FROM REGRESSION ANALYSIS.

TABLE 5.2.1-3B 2 of 4

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COALITE PRODUCTS

FROM FIXED-BED HYDROTREATING

CATALYST: K-550 (1ST STAGE)

FILE ID: REPTBP1.WK1

TEST # (FB-)	20A-1	20A-2	21	22	23	24	25	26
DATE (1989)	01-18	01-18	01-19	01-20	01-20	01-23	01-23	01-24
START TIME	16:20	19:00	19:00	16:45	19:30	17:45	20:45	15:20
END TIME	18:20	21:00	21:00	17:45	20:30	18:45	21:45	16:30
FEEDSTOCK	A	A	A	A	A	A	A	A
SPECIFIC GRAVITY, gm/cc	0.8616	0.9297	0.8978	0.8576	0.8713	0.9254	0.8939	0.8649
API GRAVITY @ 60 F	32.7	20.7	26.1	33.5	30.9	21.4	26.8	32.1
REFRACTIVE INDEX @ 20 C	1.4762	1.5125	1.4939	1.4746	1.4844	1.5108	1.4958	1.4784
ELEMENTALS, wt%								
C	86.18	84.36	85.59				85.46	
H	12.50	10.78	11.59	12.61 *	12.15 *	10.90 *	11.63	12.43 *
SIMULATED DISTILLATION, F								
IBP	176			178			185	
10% DISTILLED	222			224			272	
30%	357			351			419	
50%	446			442			484	
70%	511			507			547	
90%	602			598			640	
VOLUM. AVG. BOIL. PT. F	428			424			472	
WATSON I.	11.07			11.11			10.85	
F.I.A. ANALYSIS, vol%								
OLEFINS	0.5	0.9						
SATURATES	65.9	52.2						
AROMATICS	33.6	46.9	38.1	25.5	31.9	49.2	39.3	28.0
HLHV, Btu/lb	18051	16868	17440 *	18069 *	17786 *	17015 *	17465 *	17958 *
VLHV, Btu/gal	129554	130633	130430 *	129085 *	129088 *	131159 *	130047 *	129384 *
FLASH PT., F								
SMOKE PT., mm	11	3	4	9	5	9	9	6
FREZE PT., F								
ANILINE PT., F	94.3	61.7 *	76.3 *	91.3 *	83.7 *	66.6	76.3	87.8
CETANE INDEX	31	13	20	31	26	14	20	28
VISCOSITY, cst @ -4 F	7.5				3.5		12.0	4.4

FEEDSTOCK TYPE:

A:350-650 F VIRGIN COALITE DISTILLATE.

* ESTIMATED FROM REGRESSION ANALYSIS.

TABLE 5.2.1-3B 3 of 4

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COALITED PRODUCTS

FROM FIXED-BED HYDROTREATING

CATALYST: K-550 (1ST STAGE)

FILE ID: REPTBP2

TEST # (FB-)	27	28	29	37	38	39	40	41
DATE (1989)	01-24	01-24	01-25	02-02	02-02	02-03	01-03	02-03
START TIME	17:45	20:15	16:40	11:30	20:15	10:35	13:35	17:30
END TIME	18:45	21:15	17:40	19:00	21:45	12:05	15:05	18:45
FEEDSTOCK	A	A	A	A	A	B	B	A
SPECIFIC GRAVITY, gm/cc	0.8550	0.8708	0.8708	0.8333	0.8324	0.8294	0.8265	0.8383
API GRAVITY @ 60 F	34.0	31.0	31.0	38.3	38.5	39.1	39.7	37.3
REFRACTIVE INDEX @ 20 C	1.4770	1.4844	1.4844	1.4602	1.4566	1.4536	1.4504	1.4616
ELEMENTALS, wt%								
C								
H	12.50 *	12.15 *	12.22 *	13.29 *	13.46 *	13.60 *	13.75 *	13.22 *
SIMULATED DISTILLATION, F								
IBF	175.0			166.0	150.0	174.0	177.0	157.0
10% DISTILLED	245.0			219.0	218.0	214.0	215.0	217.0
30%	365.0			325.0	309.0	312.0	321.0	329.0
50%	416.0			412.0	405.0	402.0	402.0	411.0
70%	508.0			482.0	474.0	473.0	472.0	483.0
90%	597.0			558.0	554.0	564.0	562.0	573.0
VOLUM. AVG. BOIL. PT. F	426			399	392	393	407	411
WATSON X	11.15			11.32	11.30	11.34	11.5	11.30
F.I.A. ANALYSIS, lvol%								
OLEFINS				5.0	0.3	0.0	0.0	0.8
SATURATES				81.3	83.3	95.3	98.7	77.8
AROMATICS	27.0 *	31.9 *	31.9 *	18.2	16.3	4.7	1.3	21.4
WLHV, Btu/lb	18002 *	17786 *	17786 *	18489 *	18594 *			18446 *
VLHV, Btu/gal	128210 *	129014 *	129014 *	128339 *	128928 *			128808 *
FLASH PT., F								
SMOKE PT., #	6	5	5	20	20	12	35	25
FREZE PT., F								
ANILINE PT., F	88.2	79.5	78.1	105.4	120.6	132.8	139.3	110.8
CETANE INDEX	30	25	24	40	46	52	55	41
VISCOSITY, cst @ -4 F	4.0	5.0						

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

B: LIQUID PRODUCT FROM FB-37

* ESTIMATED FROM REGRESSION ANALYSIS.

TABLE 5.2.1-3B 4 of 4

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COALITED PRODUCTS

FROM FIXED-BED HYDROTREATING

CATALYST: K-550 (1ST STAGE)

FILE ID: REPTBP2

TEST # (FB-)	42	43	46	47	48	49
DATE (1989)	02-06	02-06	02-21/22	02-22	02-23	02-24
START TIME	12:05	18:45	03:45	05:45	02:00	00:00
END TIME	17:35	20:40	04:00	24:00	22:00	20:00
FEEDSTOCK	A	C	A	D	A	A
SPECIFIC GRAVITY, gm/cc	0.9365	0.8270	0.8462	0.8285	0.8333	0.9328
API GRAVITY @ 60 F	19.6	39.6	35.7	39.3	38.3	20.2
REFRACTIVE INDEX @ 20 C	1.5112	1.4522	1.4659	1.4526	1.4590	1.5144
ELEMENTALS, wt%						
C			86.6	85.8	86.0	83.8
H	10.88 *	13.67 *	13.10	14.0	13.50	10.8
SIMULATED DISTILLATION, F						
18%		171.0	148.0	159.0	104.0	186.0
10% DISTILLED		215.0	219.0	219.0	218.0	354.0
30%		322.0	334.0	315.0	315.0	431.0
50%		402.0	419.0	403.0	405.0	490.0
70%		468.0	490.0	472.0	475.0	553.0
90%		560.0	577.0	561.0	569.0	635.0
VOLUM. AVG. BOIL. PT., F		393	408	394	396	493
WATSON A		11.4	11.2	11.4	11.3	10.5
F.I.A. ANALYSIS, 1vol%						
OLEFINS	5.4	0.0	0.4		0.4	
SATURATES	56.8	96.0	77.3		83.2	
AROMATICS	37.8	4.5	22.3		16.3	
WLHV, Btu/lb	17002 *					
VLHV, Btu/gal	132636 *					
FLASH PT., F			<74	50.0	30.0	70.0
SNOKE PT., °F	3	35	24			
FREZE PT., F						
ANILINE PT., F	135.3	133.5	113.9		103.5 *	60.2 *
CETANE INDEX	27	53	41		40	12
VISCOSITY, cst @ -4 F						

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

C: LIQUID PRODUCT FROM FB-42.

D: LIQUID PRODUCT FROM FB-46.

* ESTIMATED FROM REGRESSION ANALYSIS.

TABLE 5.2.1-4A

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)

FILE ID: REPTBE3.WK1

TEST # (FB-)	30	31	32	33	34	35	36-1	36-2
DATE (1989)	01-25	01-25	01-26	01-26	01-27	01-27	01-30	01-30
START TIME	19:00	20:55	12:55	16:15	13:25	16:45	13:40	14:10
END TIME	20:00	21:55	13:55	22:00	14:10	18:45	14:10	14:40
FEEDSTOCK	A	A	A	A	B	B	C	C
% HDS	98.39		91.90	95.18	98.55	97.94		98.62
% HDN	86.49		-3.72	100.00	78.68	89.18		100.00
% HDO	93.48		22.92	99.02	92.95	89.36		97.20
H ₂ UPTAKE, scf/bbl	5000	5000	5000	5000	5000	5000	5000	5000
% F.I.A. OLEFINS SATURATION	93.94	96.28	93.90			95.73		100.00
% F.I.A. AROMATICS SATURATION	37.48	46.47	33.87	65.90 *	79.07 *	85.13	87.75 *	97.83
API IMPROVEMENT	20.3	20.4	10.7	24.0	26.5	28.9	29.2	29.4
R.I. DEPRESSION	0.0552	0.0551	0.0328	0.0676	0.0778	0.0860	0.0864	0.0887
EST. HEAT OF REACTION, Btu/lb	23.60	26.80	16.00			51.90		57.60

FEEDSTOCK TYPE:

A: 350-550 F VIRGIN COALITE DISTILLATE.

B: LIQUID PRODUCT FROM FB-33.

C: LIQUID PRODUCT FROM FB-34/FB-35.

* ESTIMATED FROM REGRESSION ANALYSIS.

TABLE 5.2.1-4B

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COALITE PRODUCTS

FROM FIXED-BED HYDROTREATING

CATALYST: K-550 (1ST STAGE)

FILE ID: REPTBP3

TEST # (FB-)	30	31	32	33	34	35	36-1	36-2
DATE (1989)	01-25	01-25	01-26	01-26	01-27	01-27	01-30	01-30
START TIME	19:00	20:55	12:55	16:15	13:25	16:45	13:40	14:10
END TIME	20:00	21:55	13:55	22:00	14:10	18:45	14:10	14:40
FEEDSTOCK	A	A	A	A	B	B	C	C
SPECIFIC GRAVITY, gm/cc	0.8571	0.8565	0.9100	0.8383	0.8260	0.8146	0.8132	0.8123
API GRAVITY @ 60 F	33.6	33.7	24.0	37.3	39.8	42.2	42.5	42.7
REFRACTIVE INDEX @ 20 C	1.4775	1.4776	1.4999	1.4651	1.4549	1.4467	1.4463	1.4440
ELEMENTALS, wt%								
C	87.30		83.57	87.13	86.02	85.49		85.55
H	12.21	12.26	11.07	12.78	13.35	13.94	13.91	14.24
SIMULATED DISTILLATION, F								
IBP				173				174
10% DISTILLED				220				219
30%				296				274
50%				392				361
70%				461				419
90%				527				498
VOLUM. AVG. BOIL. PT, F				379				354
WATSON K				11.16				11.40
F.I.A. ANALYSIS, vol%								
OLEFINS	0.8	0.5	0.8			0.4		0.0
SATURATES	59.7	65.0	57.5			92.2		96.4
AROMATICS	39.6	34.5	41.6	21.6 *	14.7 *	7.4	8.9 *	1.6
MLHV, Btu/lb	17995	17605	16645	18072	18251	18600	18582	18512
VLHV, Btu/gal	128478	125609	126174	126197	125575	126211	125874	125261
FLASH PT., F								
SMOKE PT., mm	12	6 *	9	30		30		30
FREZE PT., F								
ANILINE PT., F	74.5	80.2	60.8	101.3 *		125.4		135.7
CETANE INDEX	25	27	15	38		53		58
VISCOSITY, cst @ -4 F								

FEEDSTOCK TYPE:

A: 350-550 F VIRGIN COALITE DISTILLATE.

B: LIQUID PRODUCT FROM FB-33.

C: LIQUID PRODUCT FROM FB-34/FB-35.

* ESTIMATED FROM REGRESSION ANALYSIS.

TABLE 5.2.1-5A

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)/K-550 (2ND STAGE)

TEST # (FB-)	FILE ID: REPTBE4.WK1							
	169	172	170	173	174	175	176	177
DATE (1989)	06-27	06-29	06-28	06-29	06-30	06-30	06-30	06-30
START TIME	04:30	09:00	00:00	15:30	22:00	02:00	06:00	10:00
END TIME	20:00	10:00	12:00	20:00	24:00	04:00	08:00	20:00
FEEDSTOCK	A	A	B	B	B	B	B	B
% HDS								
% HDN	90	75.4						
% HDO								
H ₂ UPTAKE, scf/bbl	8000	8000	8000	8000	8000	8000	8000	8000
%F.I.A. OLEFINS SATURATION								
%F.I.A. AROMATICS SATURATION								
API IMPROVEMENT	34.6	33.6	33.9	30.6	28.1	22.7	18.5	25.4
R.I. DEPRESSION	1.4699	1.4716	1.4703					
EST. HEAT OF REACTION, Btu/lb								

FEEDSTOCK TYPE:

A: 350-750 F VIRGIN COALITE DISTILLATE.

B: 350-820 F VIRGIN COALITE DISTILLATE.

TABLE 5.2.1-5B

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COALITE PRODUCTS

FROM FIXED-BED HYDROTREATING

CATALYST: K-550 (1ST STAGE)/K-550 (2ND STAGE)

FILE ID: REPTBP4.WK1

TEST # (FB-)	169	172	170	173	174	175	176	177
DATE (1989)	06-27	06-29	06-28	06-29	06-30	06-30	06-30	06-30
START TIME	04:30	09:00	00:00	15:30	22:00	02:00	06:00	10:00
END TIME	20:00	10:00	12:00	20:00	24:00	04:00	08:00	20:00
FEEDSTOCK	A	A	B	B	B	B	B	B
SPECIFIC GRAVITY, gm/cc	0.8519	0.8571	0.8555	0.8729	0.8866	0.9176	0.9433	0.9018
API GRAVITY @ 60 F	34.6	33.6	33.9	30.6	28.1	22.7	18.5	25.4
REFRACTIVE INDEX @ 20 C	1.4699	1.4716	1.4703	0.8729	0.8866	0.9176	0.9433	0.9018
ELEMENTALS, wt%								
C	86.49	86.60	86.64					86.27
H	13.49	13.37	13.30					11.86
SIMULATED DISTILLATION, F								
IBP								183
10% DISTILLED								262
30%								411
50%								488
50%								570
70%								676
90%								826
VOLUM. AVG. BOIL. PT. F								539
WATSON K								11.01
F.I.A. ANALYSIS, 1vol%								
OLEFINS	2.0	0.0	1.3					0.8
SATURATES	86.8	83.7	82.6					50.8
AROMATICS	11.3	16.3	16.1					48.4
WLHV, Btu/lb	18195	17876	18116					17563
VLHV, Btu/gal	129118	127564	129100					131933
FLASH PT., F								
SMOKE PT., °F								15
FREZE PT., F	17.6		26.6					10.4
ANILINE PT., F								71.15
CETANE INDEX								
VISCOSITY, cst @ -4 F								13

FEEDSTOCK TYPE:

A: 350-750 F VIRGIN COALITE DISTILLATE.

B: 350-820 F VIRGIN COALITE DISTILLATE.

TABLE 5.2.1-6A

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE)/K-599 (2ND STAGE)

TEST # (FB-)							FILE ID: REPTBES.WK1
	94-1	94-2	94-3	101	102	103	104
DATE (1989)	04-05	04-06	04-06	04-10	04-10	04-10	04-10
START TIME	21:00	01:00	05:00	05:00	09:30	14:00	18:00
END TIME	01:00	05:00	09:00	06:30	11:00	15:30	20:00
FEEDSTOCK	A	A	A	A	A	A	A
% HDS							
% HDN							
% HDO							
H2 UPTAKE, scf/bbl	7000	7000	7000	7000	7000	7000	7000
% F.I.A. OLEFINS SATURATION	94.1	90.1	100	91.4	95.7	95.2	95.2
% F.I.A. AROMATICS SATURATION	94.4	93.9	53.8	59.5	64.2	79.8	80.5
API IMPROVEMENT	34.4	34	20.7	32.4	34.6	37.3	37.5
R.I. DEPRESSION	1.4672	1.4686	1.468	1.4763	1.4696	1.4585	1.4583
EST. HEAT OF REACTION, Btu/lb							

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

TABLE 5.2.1-6B

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COALITE PRODUCTS

FROM FIXED-BED HYDROTREATING

CATALYST: K-550 (1ST STAGE)/K-599 (2ND STAGE)

TEST # (FB-)	94-1	94-2	94-3	101	102	103	104	FILE ID :REPTBPS.WK
DATE (1989)	04-05	04-06	04-06	04-10	4-10	04-10	04-10	
START TIME	21:00	01:00	05:00	05:00	09:30	14:00	18:00	
END TIME	01:00	05:00	09:00	06:30	11:00	15:30	20:00	
FEEDSTOCK	A	A	A	A	A	A	A	
SPECIFIC GRAVITY, gm/cc	0.8529	0.8550	0.8529	0.8633	0.8519	0.8383	0.8373	
A.P.I. GRAVITY @ 60 F	34.4	34.0	34.4	32.4	34.6	37.3	37.5	
REFRACTIVE INDEX @ 20 C	1.4672	1.4686	1.4680	1.4763	1.4696	1.4585	1.4583	
ELEMENTAL, wt. %								
C								
H								
DISTILLATION, F								
IBP								
10% DISTILLED								
30%								
50%								
70%								
90%								
VOLUM. AVG. BOIL. PT. F								
WATSON K								
F.I.A./R.I., vol. %								
OLEFINS	1.0	1.2	0.0	1.0	0.5	0.6	0.6	
SATURATES	92.9	94.0	64.0	68.5	72.4	82.9	83.7	
AROMATICS	6.1	4.8	36.0	30.5	27.1	16.5	15.7	
WLHV, btu/lb.								
VLHV, btu/gal.								
FLASH PT., F								
SMOKE PT., mm				25	15	20	25	
FREZE TP., F								
ANILINE PT., F				98.6				
CETANE INDEX								
VISCOSITY, cst @ -4 F								

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

TABLE 5.2.1-7A

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: K-599 (1ST STAGE)

FILE ID: REPT85.WK1

TEST # (FB-)	146	147
DATE (1989)	05-16/18	05-18/19
START TIME	18:30	08:30
END TIME	06:30	20:30
FEEDSTOCK	A	B
% HDS		
% HDN	89.9	
% HDO		
H ₂ UPTAKE, scf/bbl	8000	8000
% F.I.A. OLEFINS SATURATION	95.7	100
% F.I.A. AROMATICS SATURATION	89.1	97.2
API IMPROVEMENT	25.1	28.8
R.I. DEPRESSION	0.0826	0.0965
EST. HEAT OF REACTION, Btu/lb		

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.
 B: LIQUID PRODUCT FROM FB-146.

TABLE 5.2.1-7B

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COALITE PRODUCTS

FROM FIXED-BED HYDROTREATING

CATALYST: K-599 (1ST STAGE)

FILE ID :REPTBP5.WK

TEST # (FB-)	146	147
DATE (1989)	05-16/18	05-18/19
START TIME	18:30	08:30
END TIME	06:30	20:30

FEEDSTOCK	A	B
SPECIFIC GRAVITY, gm/cc	0.8438	0.8256
A.P.I. GRAVITY @ 60 F	36.2	39.9
REFRACTIVE INDEX @ 20 C	1.4643	1.4504

ELEMENTAL, wt. %

C	86.49	85.08
H	13.33	14.12

DISTILLATION, F

IBP	157	155
10% DISTILLED	217	216
30%	336	314
50%	426	403
70%	492	472
90%	579	563

VOLUM. AVG. BOIL. PT. F	410	394
WATSON K	11.23	11.40

F.I.A./R.I., vol. %

OLEFINS	0.5	0.3
SATURATES	91.4	96.2
AROMATICS	8.1	3.5

WLHV, btu/lb.	18374
VLHV, btu/gal.	126363

FLASH PT., F
 SMOKE PT., °F
 FREEZE TP., F
 ANILINE PT., F
 CETANE INDEX
 VISCOSITY, cst @ -4 F

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.
 B: LIQUID PRODUCT FROM FB-146.

TABLE 5.2.1-8A

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COALITE HYDROTREATING TESTS

CATALYST: CACIUM PROMOTED K-550

FILE ID: REPTCA3.WK1

TEST # (FB-)	135	136	137	138
DATE (1989)	04-26/27	04-27/28	04-28	04-28
START TIME	21:00	17:00	13:00	18:30
END TIME	13:00	09:00	15:00	20:30
FEEDSTOCK	A	A	A	A
% HDS				
% HDN				
% HDG				
H2 UPTAKE, scf/bbl	7000	7000	7000	7000
% F.I.A. OLEFINS SATURATION		96.5	86.3	85.7
% F.I.A. AROMATICS SATURATION		93.5	41.1	39.7
API IMPROVEMENT	20.4	27.1	27.8	12.1
R.I. DEPRESSION	0.0654	0.0926	0.0574	0.0009
EST. HEAT OF REACTION, Btu/lb				

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

TABLE 5.2.1-8B

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COALITE PRODUCTS

CATALYST: CACIUM PROMOTED K-550

FILE ID: REPTCA2

TEST # (FB-)	135	136	137	138
DATE (1989)	04-26/27	04-27/28	04-28	04-28
START TIME	21:00	17:00	13:00	18:30
END TIME	13:00	09:00	15:00	20:30

FEEDSTOCK	A	A	A	A
SPECIFIC GRAVITY, gm/cc	0.8681	0.8338	0.8822	0.9147
API GRAVITY @ 60 F	31.5	38.2	28.9	23.2
REFRACTIVE INDEX @ 20 C	1.4815	1.4543	1.4895	1.5460

ELEMENTALS, wt%

C	86.54	86.36	86.32	84.36
H	12.40	15.53	11.95	11.14

SIMULATED DISTILLATION, F

IBP
10% DISTILLED
30%
50%
70%
90%

VOLUM. AVG. BOIL. PT, F
WATSON F

F.I.A. ANALYSIS, vol%

OLEFINS	0.6	0.5	1.6	1.6
SATURATES	62.1	93.5	53.8	54.6
AROMATICS	37.3	6.0	44.6	43.8

WLHV, Btu/lb	18315	17553	17124
VLHV, Btu/gal	127208	128992	130475

FLASH PT., F
SMOKE PT., mm
FREEZE PT., F
ANILINE PT., F
CETANE INDEX
VISCOSITY, cst @ -4 F

FEEDSTOCK TYPE:

A: 350-650 F VIRGIN COALITE DISTILLATE.

FIGURE 5.2.1-2

HYDROTREATING SEVERITY VS. VLHV FOR HYDROTREATED COALITE DISTILLATES

FIGURE 5.2.1-3

HYDROTREATING SEVERITY VS. HYDROGEN CONTENT
FOR COALITE DISTILLATE OVER K-550 CATALYST

FIGURE 5.2.1-4

HYDROTREATING SEVERITY VS. F.I.A. AROMATICS FOR COALITE DISTILLATE OVER K-550 CATALYST

HYDROTREATING SEVERITY, 10000*P/LHSV *e(-35000/RT)

FIGURE 5.2.1-5

HYDROTREATING SEVERITY VS. API GRAVITY
FOR COALITE DISTILLATE OVER K-550 CATALYST

HYDROTREATING SEVERITY, 10000*P/LHSV * e(-35000/RT)

FIGURE 5.2.1-6

HYDROTREATING SEVERITY VS. ANILINE POINT
FOR COALITE DISTILLATE OVER K-550 CATALYST

HYDROTREATING SEVERITY, $10000 \cdot P / \text{LHSV} \cdot e^{(-35000/RT)}$

FIGURE 5.2.1-7

HYDROTREATING SEVERITY VS. CETANE INDEX
FOR COALITE DISTILLATE OVER K-550 CATALYST

HYDROTREATING SEVERITY, $10000 \cdot P / \text{LHSV} \cdot e^{(-35000/RT)}$

FIGURE 5.2.1-8

HYDROTREATING SEVERITY VS. SMOKE POINT
FOR COALITE DISTILLATE OVER K-550 CATALYST

FIGURE 5.2.1-9

HYDROTREATING SEVERITY VS. REFRACTIVE INDEX
FOR COALITE DISTILLATE OVER K-550 CATALYST

HYDROTREATING SEVERITY, 10000*P/LHSV *e(-35000/RT)

EFFECT OF AROMATICS ON VOLUMETRIC LHV OF COAL-DERIVED DIESEL/JET FUELS

FIGURE 5.2.1-11

EFFECT OF AROMATICS ON CETANE QUALITY OF COAL-DERIVED DIESEL FUELS

FIGURE 5.2.1-12

EFFECT OF AROMATICS ON SMOKE POINT OF COAL-DERIVED TURBINE FUELS

AROMATICS CONTENT, LVOL %

FIGURE 5.2.1-13

PREDICTED NET HEAT OF COMBUSTION (LHV) OF COALITE VS R.I. AND API GRAVITY

DISTILLATE HYDROGEN CONTENT AS A FUNCTION OF REFRACTIVE INDEX OF COALITE DISTILLATES

FIGURE 5.2.1-15

PREDICTED API GRAVITY AS A FUNCTION OF REFRACTIVE INDEX OF HYDROTREATED COALITE

FIGURE 5.2.1-16

WATSON K FACTOR AS A FUNCTION OF REFRACTIVE INDEX OF HYDROTREATED COALITE

FIGURE 5.2.1-17

SMOKE POINT AND LUMINOMETER NO. VS. REFRACTIVE INDEX OF COALITE DISTILLATES

FIGURE 5.2.4-1

RELATIVE HYDROPROCESSING PERFORMANCE FOR 350-550F COALITE

FIGURE 5.2.4-2

RELATIVE HYDROPROCESSING PERFORMANCES OF 350-550F COALITE

catalyst appear to result in significantly higher absolute hydrogen uptake levels. However, this may have resulted from calculational and/or experimental precision differences between the two laboratories in their efforts to quantify the hydrogen uptake values rather than from catalyst type (Figure 5.2.4-3).

5.3 Virgin Atmospheric Resid Cracking

5.3.1 LC-Fining

The LC-Fining process utilizes an expanded-bed of hydrotreating catalyst to provide for backmixing and near isothermal operation during the hydrogenation of heavy oils and residua that contain significant catalyst poisons, e.g., trash metals, organometallics, coke precursors, etc. The process has been widely commercialized, especially for vacuum residua, and the continuous addition and withdrawal of catalysts allows for continuous operation without having to shutdown to replace poison or coked catalysts. While the raw COALITE does not contain much vac resid content, it does contain considerable atmospheric resid (650F+). LC-Fining is a potential technology for upgrading the atmospheric resid fraction of MCG liquids, especially as a means of inputting the high overall hydrogen uptakes required to convert the hydrogen-deficient liquids to hydrogen-rich HEDF.

Four LC-Fining test campaigns were made: two with virgin residua (300F+ and 650F+) and two with hydrotreated resid recovered from the first-pass LC-Fining operation with the 650F+ virgin resid. The performance results for these campaigns are presented in Tables 5.3.1-1 and -2. The summary of the properties of the full-range LC-Finate products from these campaigns is presented in Tables 5.3.1-3 and -4. The main objective of these tests was to produce feedstock for the cracked distillate hydrotreating campaigns in which the jet boiling range aromatics hydrocracked from the VGO material are saturated to high energy density cycloparaffins.

5.3.2 Delayed Coking

With very thermally reactive feedstocks such as pyrolysis oils from the COALITE process, processing in catalytic systems can result in relatively high levels of carbon on the catalysts. This can be ameliorated by operating at low thermal severities which in turn requires high catalyst inventories, i.e., operation at low space velocities, to achieve commercially feasible conversion levels. Another processing approach is based on the use of thermal processing technologies which produce lighter and hydrogen-enriched liquids by rejection of feed carbon as coke. Delayed coking is a mature commercial process for production of distillate fuels from heavy residua. The resultant coke byproduct generated can be upgraded to fuel gas via partial oxidation technology or in the case of MCG can be blended with the MCG char and upgraded to any of the premium solid products being targeted via Mild Coal Gasification.

FIGURE 5.2.4-3

RELATIVE HYDROPROCESSING PERFORMANCE FOR 350-550F COALITE

TABLE 5.3.1-1

SUMMARY OF OPERATING RESULTS FOR LC-FINING (HYDROCRACKING) TESTS

CATALYST: SHELL 324 (AGED)

FILE ID: REPTBLC2.WK1

TEST # (BLCF--)	86-1	86-2	87	88-1/2	88-3	88-4	88-5	90
DATE (1989)	01-31	02-01	02-08	02-27/28	02-28/03-01	03-1/2	03-2/3	04-04
START TIME	19:00	07:00	02:00	15:30	16:30	09:00	07:30	01:00
END TIME	23:00	15:00	16:00	16:30	09:00	07:30	18:00	09:00
FEEDSTOCK	A	A	A	A	A	A	A	B
% NDS								
% HDN								
% NDO								
H2 UPTAKE, scf/bbl				10000	10000	10000	10000	10000
API IMPROVEMENT				21.4	19.6	19.0	18.3	4.0
R.I. REGRESSION								
EST. HEAT OF REACTION, Btu/lb								

FEEDSTOCK TYPE:

A: COALITE ATM RESID, 650+ F.

B: HYDROPROCESSED COALITE DISTILL RESID, 575+ F.

TABLE 5.3.1-2

SUMMARY OF OPERATING RESULTS FOR LC-FINING (HYDROCRACKING) TESTS

CATALYST: SHELL 324 (AGED)

FILE ID: REPTBLC2.WK1

TEST # (BLCF-)	92	93	94	95	100	101
DATE (1989)	04-10	04-11	04-11	04-12	05-17/19	06-13/15
START TIME	12:00	24:00	14:00	02:00	20:00	08:00
END TIME	20:00	08:00	22:00	10:00	19:30	02:30
FEEDSTOCK	B	B	B	B	C	C
% HDS						
% HDN						
% HDO						
H ₂ UPTAKE, scf/bbl	10000	10000	10000	10000	7000	7000
API IMPROVEMENT			8.4	6.7	11.9	1.3
R.I. REGRESSION						
EST. HEAT OF REACTION, Btu/lb						

FEEDSTOCK TYPE:

B: HYDROPROCESSED COALITE DISTILL RESID, 575+ F.
C: COALITE DISTILLATE, 300+ F.

TABLE 5.3.1-3

SUMMARY OF PROPERTIES OF FULL-RANGE LC-FINATE TESTS

CATALYST: SHELL 324 (AGED)

FILE ID: REPTBLC3.WK1

TEST # (BLCF-)	86-1	86-2	87	88-1/2	88-3	88-4	88-5	90
DATE (1989)	01-31	02-01	02-08	02-27/28	02-28/03-01	03-1/2	03-2/3	04-04
START TIME	19:00	07:00	02:00	15:30	16:30	09:00	07:30	01:00
END TIME	23:00	15:00	16:00	16:30	09:00	07:30	18:00	09:00
FEEDSTOCK	A	A	A	A	A	A	A	B
SPECIFIC GRAVITY, gm/cc				0.9923	1.0050	1.0093	1.0143	1.0306
API GRAVITY @ 60F				11.1	9.3	8.7	8.0	5.8
REFRACTIVE INDEX @ 20C								
ELEMENTALS, wt%								
C				87.33	88.24	88.81	87.05	
H				9.35	9.18	9.16	9.15	
SIMULATED DISTILLATION, F								
IBP				184	209	196	194	
10% Distilled				368	399	400	405	
30%				489	539	543	565	
50%				583	628	636	657	
70%				666	697	704	712	
90%				760	783	791	800	
VOLUR. AVG. BOIL. PT., F				573	609	615	628	
WATSON λ				340.4	348.0	348.4	350.9	
WLV, Btu/lb								
VLHV, Btu/gal								

FEEDSTOCK TYPE:

A: COALITE ATM RESID, 650+ F.

B: HYDROPROCESSED COALITE DISTILL RESID, 575+ F.

TABLE 5.3.1-4

SUMMARY OF PROPERTIES OF FULL-RANGE LC-FIMATE TESTS

TEST # (BLCF-)	CATALYST: SHELL 324 (AGED)						FILE ID: REPTBLC3.WK1
	92	93	94	95	100	101	
DATE (1989)	04-10	04-11	04-11	04-12	05-17/19	06-13/15	
START TIME	12:00	24:00	14:00	02:00	20:00	08:00	
END TIME	20:00	08:00	22:00	10:00	19:30	02:30	
FEEDSTOCK	B	B	B	B	C	C	
SPECIFIC GRAVITY, gm/cc			0.9986	1.0107	0.9659	1.0409	
API GRAVITY @ 60F			10.2	8.5	15.0	4.4	
REFRACTIVE INDEX @ 20C							
ELEMENTALS, wt%							
C							
H							
SIMULATED DISTILLATION, F							
IBP					216	393	
10% Distilled					385	453	
30%					479	535	
50%					566	667	
70%					600	791	
90%					787	791	
VOLUM. AVG. BOIL. PT., F					563	647	
WATSON λ					11.1	10.3	
WLMV, Btu/lb							
VLHV, Btu/gal							

FEEDSTOCK TYPE:

B: HYDROPROCESSED COALITE DISTILL RESID, 575+ F.

C: COALITE DISTILLATE, 300+ F.

All four tests made with the two feedstocks (virgin 650F+ and mildly hydrotreated 650F+ residua) gave similar yield structures: 41-49% coke yields, 31-43% liquids yields, and 14-20% gas yields. The mildly hydrotreated resid feed did result in the lowest coke make but the coke suppression did not lead to a concomitant increase in liquids yield. The test made with the virgin resid at 100 psig coke drum pressure had a mid-distillate product with more than 60% aromatics content and an energy density (before hydrogenation) of 128,775 Btu/gal. The mid-distillate product from the coker test made at 62 psig coke drum pressure had a higher olefins content and a lower aromatics content than that for the 100 psig drum pressure. In both cases, coke yields represented a significant loss of potential HEDF yield. However as pointed out previously the capital cost of the coker-derived liquids is relatively lower than that of the higher liquids producing, hydrocracking process-derived route.

5.4 Cracked Distillate Hydrotreating

Products from both the LC-Fining and Delayed Coking tests were fractionated to recover 650F- distillate fractions which served as the feedstocks for the final hydrogenation step necessary to convert aromatics to cycloparaffins, the latter being the high energy density components of the HEDF test fuels. Distillate hydrotreating was carried out in several campaigns to reflect the different sources of the distillate feeds to hydrotreating.

5.4.1 Hydrotreating of LC-Finate Distillates

The results of these campaigns are summarized in a series of spreadsheet tables with the "A" tables presenting the run performance data and the "B" tables presenting the properties of the full-range hydrotreated distillates. The organization of the tabulated results is as follows:

<u>Table No</u>	<u>Catalyst Type</u>	<u>Feed Boiling Range (F)</u>	<u># Reaction Stages</u>
5.4.1-1A,B	K-550/K-599	300-575(650)	2
5.4.1-2A,B	K-599	300-600	1
5.4.1-3A,B	Amoco Propr.	650-975Virgin	1
5.4.1-4A,B	Amoco Propr.	650-975HDT	1
5.4.1-5A,B	K-599/K-599	350-750	2

5.4.2 Hydrotreating of Coker Distillates

The results of the three hydrotreating tests with coker distillates are presented in Table 5.4.2-1A (run performance data) and 5.4.2-1B (properties data).

TABLE 5.4.1-1A

SUMMARY OF OPERATING RESULTS OF FIXED-BED HYDROTREATED PRODUCTS FROM

HYDROCRACKED COALITE DISTILLATE

CATALYST: K-550 (1ST STAGE), K-599 (2ND STAGE)

TEST # (FB-)	44	95	96	97	98	99	100	105
DATE (1989)	02-09	04-06	04-06	04-07	04-07	04-07	04-07	04-11
START TIME	11:45	12:20	16:00	22:30	12:00	17:00	20:00	01:00
END TIME	12:35	14:50	19:30	24:00	13:30	18:00	21:30	12:00
FEEDSTOCK	A	B	B	B	B	B	B	B
% H ₂								
% H ₂	65.80	85.60	95.57	75.56	84.76	84.08	81.17	79.23
% H ₂								
% UPTAKE (SOLVED)	5000	7000	7000	7000	7000	7000	7000	7000
% FUL. A. OLEFINS SATURATION	0.3	1.3	1.2	4.6	1.2		1.0	0.9
% FUL. A. AROMATICS SATURATION	2.5	29.1	11.1	3.3	16.2		4.4	9.8
API IMPROVEMENT	39.1	30	34.2	36.2	32.4	34.4	35.5	35.5
API DEPRESSION	1.4516	1.4744	1.4644	1.4571	1.4727	1.4643	1.4608	1.4590
EST. HEAT OF REACTION BTU/LB								

FEEDSTOCK TYPE:

- A: 300-650 F HYDROCRACKED COALITE DISTILLATE, DERIVED FROM LC-FINING OF VIRGIN 650 F+
- B: 300-575 F HYDROCRACKED COALITE DISTILLATE, DERIVED FROM LC-FINING OF VIRGIN 650 F+

TABLE 5.4.1-1B

SUMMARY OF PROPERTIES OF FIXED-BED HYDROTREATED PRODUCTS FROM

HYDROCRACKED COALITE DISTILLATE

CATALYST: K-550 (1ST STAGE), K-599 (2ND STAGE)

TEST # (FB-)	44	95	96	97	98	99	100	105
DATE (1989)	02-09	04-06	04-06	04-07	04-07	04-07	04-07	04-11
START TIME	11:35	12:20	10:00	20:30	12:00	17:00	20:00	01:00
END TIME	12:35	14:50	15:00	24:00	13:30	18:00	21:30	12:00
FEEDSTOCK	A	B	B	B	B	B	B	B
SPECIFIC GRAVITY, 60/60	0.8270	0.8654	0.8540	0.8468	0.8633	0.8529	0.8473	0.8453
API GRAVITY @ 60 F	39.6	32.0	34.2	35.6	32.4	34.4	35.5	35.9
REFRACTIVE INDEX @ 20 C	1.4515	1.4744	1.4644	1.4572	1.4727	1.4643	1.4608	1.459
ELEMENTALS, Wt%								
C	85.62	87.02	86.35	85.64	86.86	86.34	85.97	86.26
H	13.83	12.89	13.42	13.87	12.84	13.45	13.67	13.84
SIMULATED DISTILLATION, F								
180	176						187	
10+ DISTILLATE	227						294	
30+	330						365	
50+	401						405	
70+	471						457	
90+	554						511	
VOLUME AVE. BOIL. PT., F	397						407	
WATSON	11.41						11.14	
F.I.A. ANALYSIS, Wt%								
OLIFINS	0.3	1.5	1.2	4.6	1.2		1.0	0.5
SATURATES	90.9	69.3	87.7	92.1	82.6		94.6	89.7
AROMATICS	1.9	29.2	11.1	3.3	16.6		4.4	9.8
WLMV, Boiling	18489	18157	17374	18183	17671	18265	18331	18351
WLMV, Boiling	127369	130890	123593	127807	127075	129910	129379	129222
FLASH PT., F								85
SMoke PT., F	35						15	25
FREEZE PT., F								26.1
ANILINE PT., F	128.4	95.1	115	125.1	94.4	115.7	114.6	
CELANE INDEX	55	50	54	46	31	47	41	
VISCOSITY, cSt @ 40 F								

FEEDSTOCK TYPE:

- A. 300-650 F HYDROCRACKED COALITE DISTILLATE DERIVED FROM CO-FINING OF VIRGIL 650 F.
- B. 300-750 F HYDROCRACKED COALITE DISTILLATE DERIVED FROM CO-FINING OF VIRGIL 650 F.

TABLE 5.4.1-2A

SUMMARY OF OPERATING RESULTS OF FIXED-BED HYDROTREATED PRODUCTS FROM

HYDROCRACKED COALITE DISTILLATE

CATALYST: K-599 (1ST STAGE)

TEST # (FEED)	156	157	158
DATE TESTED	05-30	05-30	05-31
START TIME	06:00	16:00	00:00
END TIME	10:00	20:00	04:00
FEEDSTOCK	A	A	A
% H ₂			
% H ₂	84.82	80.00	92.80
% H ₂			
H ₂ UPTAKE, SCF/BBL	2000	2000	2000
% F.I.A. OLEFINE SATURATION	64.8	67.2	779.5
% F.I.A. AROMATICS SATURATION	45.2	74.7	76.3
API IMPROVEMENT	11.9	15.8	17.1
API DEPRESSION	0.0400	0.0545	0.0594
EST. HEAT OF REACTION, BBL/BBL			

FEEDSTOCK TYPE:

A: 300-600 F HYDROCRACKED COALITE DISTILLATE, DERIVED FROM LI-FINING OF 650 F+.

TABLE 5.4.1-2B

SUMMARY OF PROPERTIES OF FIXED-BED HYDROTREATED PRODUCTS FROM

HYDROCRACKED COALITE DISTILLATE

CATALYST: K-599 (1ST STAGE)

TEST # (FE-)	156	157	158
DATE (1989)	05-30	05-30	05-31
START TIME	06:00	16:00	00:00
END TIME	10:00	20:00	04:00
FEEDSTOCK	A	A	A
SPECIFIC GRAVITY, gm/cc	0.8708	0.8504	0.8433
API GRAVITY @ 60 F	31.0	34.9	36.3
REFRACTIVE INDEX @ 20 C	1.4795	1.4653	1.4607
ELEMENTALS, wt%			
C	87.13	85.50	87.46
H	12.76	13.40	13.54
SIMULATED DISTILLATION, %			
10%			18%
10% DISTILLED			26%
30%			38%
50%			43%
70%			45%
90%			54%
VOLUME AVE. BOIL. PT., F			422
WATSON			11.29
P.L.A. ANALYSIS, 1 VOL%			
OLIFINE	0.9	0.8	0.5
SATURATES	60.3	82.1	83.5
AROMATICS	38.8	17.1	16.0
Wt. % Btu/lb			
Wt. % Btu/gal			
FLASH PT., F			
SMOKE PT., F			
FREEZE PT., F			
ANILINE PT., F			
CELANE INDEX			
VISCOSITY, cSt @ 40 F			

FEEDSTOCK TYPE:

At 300-600 F HYDROCRACKED COALITE DISTILLATE, DERIVED FROM C-7 FINEAR OR VIRGIN 650-74

TABLE 5.4.1-3A

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COALITE HYDROCRACKING TESTS

CATALYST: AMOCO PROPRIETARY

TEST # (FBHC-1)	1	2	3	4	13	14	15	16	17
DATE (1984)	04-27	04-28	04-28	04-28	05-03	05-04	05-04	05-04	05-05
START TIME	21:30	03:30	13:00	18:30	15:30	21:30	03:30	11:00	19:00
END TIME	23:30	05:30	15:00	20:30	17:30	23:30	08:30	14:00	08:00
FEEDSTOCK	A	A	A	A	A	A	A	A	A
% HCS							91.2		
% HDN							77.5		
% HDI							92.7		
H2 UPTAKE, scf/dbl	7000	7000	7000	7000	7000	7000	7000	7000	7000
% F.I.A. OLIFINS SATURATION									
% F.I.A. AROMATICS SATURATION									
API IMPROVEMENT	9.1	11.7	14.4	13.7	17.5	17.5	21.0	21.1	17.9
P.L. DEPRESSION									
EST. HEAT OF REACTION, Btu/lb									

FEEDSTOCK TYPE:

A: 650-975 F VIRGIN VGO.

TABLE 5.4.1-3B

SUMMARY OF PROPERTIES OF HYDROCRACKATES FROM FIXED-BED COALITE HYDROCRACKING

CATALYST: AMOCO PROPRIETARY

TEST # (FBHC-)	1	2	3	4	13	14	15	16	17
DATE (1989)	04-27	04-28	04-28	04-28	05-03	05-04	05-04	05-04	05-05
START TIME	21:30	03:30	13:00	18:30	15:30	21:30	03:30	11:00	19:00
END TIME	23:30	05:30	15:00	20:30	17:30	23:30	08:30	14:00	08:00
FEEDSTOCK	A	A	A	A	A	A	A	A	A
SPECIFIC GRAVITY, gm/cc	1.0404	1.0217	1.0021	1.0071	0.9806	0.9806	0.9574	0.9597	0.9797
API GRAVITY @ 60F	4.5	7.0	9.7	9.0	12.8	12.8	16.3	15.9	12.9
REFRACTIVE INDEX @ 20C									
ELEMENTAL, wt %									
C							88.2		
H							11.03		
SIMULATED DISTILLATION, F									
180°	260	254	225	274	220	215	213	217	224
10% DISTILLED	560	507	495	523	465	446	419	418	451
30%	695	671	638	654	611	599	571	554	597
50%	756	744	719	728	695	688	661	639	681
70%	811	805	786	792	768	763	745	717	757
90%	883	880	868	873	857	856	843	829	849
VOLUME, AVG. BOILING PT., F	741	725	701	714	679	670	647	631	667
WATSON	11.60	10.75	10.47	10.56	10.18	10.15	9.65	9.81	10.14
WPM, 500-600									
WPM, 600-800									

FEEDSTOCK TYPE:

A: 650-975 F VIRGIN VGO.

TABLE 5.4.1-4A

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COALITE HYDROCRACKING TESTS

CATALYST: AMOCO PROPRIETARY

TEST # (FBHC-)	18	19	20	21	22	23	24	25	26	27
DATE (1989)	05-24	05-25	05-25	05-25	05-26	05-26	05-26	05-26	05-30	06-05/08
START TIME	22:30	04:30	10:30	17:00	23:00	05:00	13:00	20:00	07:00	07:00
END TIME	24:30	06:30	12:30	19:00	01:00	09:00	17:00	21:00	09:00	07:00
FEEDSTOCK	B	B	B	E	B	B	B	B	B	B
% HDS										
% HDB										93.2
% HDL										
H ₂ UPTAKE, SCF/BDL	7000	7000	7000	7000	7000	7000	7000	7000	7000	7000
% F.I.A. OLIFINS SATURATION										
% F.I.A. AROMATICS SATURATION										
API IMPROVEMENT	5.5									
P.L. DEPRESSION										
EST. HEAT OF REACTION, BTU/LB										

FEEDSTOCK TYPE:

B: 650-975 F HYDROTREATED LC-FINATE VGO.

TABLE 5.4.1-4B

SUMMARY OF PROPERTIES OF HYDROCRACKATES FROM FIXED-BED COALITE HYDROCRACKING

CATALYST: AMOCO PROPRIETARY

TEST # (FBHC-)	18	19	20	21	22	23	24	25	26	27
DATE (1989)	05-24	05-25	05-25	05-25	05-26	05-26	05-26	05-26	05-30	06-05-08
START TIME	22:30	04:30	10:30	17:00	23:00	05:00	13:00	20:00	07:00	07:00
END TIME	24:30	06:30	12:30	19:00	01:00	09:00	17:00	21:00	09:00	07:00
FEEDSTOCK	B	B	B	B	B	B	B	B	B	B
SPECIFIC GRAVITY, gm/cc	0.9792	0.9705	0.9574	0.9613	0.9672	0.9285	0.9765	0.9433	0.9674	0.9705
API GRAVITY @ 60F	13.0	14.3	16.3	15.7	14.8	20.9	13.4	18.5	11.8	14.3
REFRACTIVE INDEX @ 20C										
ELEMENTALS, wt %										
C										86.8
H										10.7
SIMULATED DISTILLATION, F										
16F	310	244	213	217	218	215	251	217	353	234
10% DISTILLED	571	549	498	505	526	445	556	456	596	522
30%	637	631	613	614	624	570	636	583	650	611
50%	690	680	664	668	671	631	687	650	696	672
70%	751	740	727	728	737	690	748	710	753	711
90%	841	834	827	826	832	793	841	811	850	811
VOLUM. FAD. BOLL. FAD. F	700	688	666	669	677	626	693	643	704	671
WATSON	10.23	10.10	9.90	9.95	10.04	9.48	10.18	9.69	10.34	10.07
M.W. BOLL.										
M.W. BOLL.										

FEEDSTOCK TYPE:

B: 650-975 F HYDROTREATED LC-FINATE VGO.

TABLE 5.4.1-5A

SUMMARY OF OPERATING RESULTS FOR FIXED-BED HYDROTREATING TESTS OF

HYDROCRACKED COALITE DISTILLATE

CATALYST: K-599 (1ST STAGE)/K-599 (2ND STAGE)

FILE ID: REPTB6.WK1

TEST # (FB-)	165	166	167	168
DATE (1989)	06-12	06-13/14	06-15	06-15
START TIME	21:00	03:00	10:00	19:00
END TIME	23:00	06:00	15:00	06:00
FEEDSTOCK	A	A	A	A
% HDS				
% HDN				
% HDN				
H ₂ UPTAKE, scf/bbl	7000	7000	7000	7000
% F.I.A. OLEFINS SATURATION				
% F.I.A. AROMATICS SATURATION				
API IMPROVEMENT	18.0	25.5	21.4	17.6
R.I. DEPRESSION	1.5239	1.4909	1.5088	1.5260
EST. HEAT OF REACTION, Btu/lb				

FEEDSTOCK TYPE:

A: 350-750 F CRACKED COALITE DISTILLATE.
FROM TWO-STEPS, 300 F+ COALITE LC-FINING
FOLLOWED BY FIXED-BED HYDROCRACKING OF
575-975 F LC-FINATE VGO.

TABLE 5.4.1-5B

SUMMARY OF PROPERTIES OF FIXED-BED HYDROTREATED PRODUCTS

FROM HYDROCRACKED COALITE DISTILLATE

CATALYST: K-599 (1ST STAGE)/K-599 (2ND STAGE)

FILE ID: REPTBP6

TEST # (FB-)	165	166	167	168
DATE (1989)	06-12	06-13/14	06-14	06-15
START TIME	21:00	03:00	10:00	19:00
END TIME	23:00	06:00	15:00	06:00
FEEDSTOCK	A	A	A	A
SPECIFIC GRAVITY, gm/cc	0.9465	0.9012	0.9254	0.9490
API GRAVITY @ 60 F	18.0	25.5	21.4	17.6
REFRACTIVE INDEX, @ 20 C	1.5239	1.4909	1.5088	1.5260
ELEMENTAL, wt. %				
C	88.44	87.16	88.02	
H	11.59	13.04	12.39	
SIMULATED DISTILLATION, F				
IBP		191		
10% DISTILLED		423		
30%		541		
50%		600		
70%		647		
90%		714		
VOLUM. AVG. BOIL. PT., F		585		
WATSON V		11.19		
F.I.A./R.I., 1vol. %				
OLEFINS				
SATURATES				
AROMATICS				
WLV, btu/lb.		18070		
VLV, btu/gal.		135666		
FLASH PT., F				
SMOKE PT., °F		15		
FREEZ. PT., F		57		
ANILINE PT., F		139		
CETANE INDEX %		35.4		
VISCOSITY, cs @ -4 F		75		

FEEDSTOCK TYPE:

A: 350-750 F CRACKED COALITE DISTILLATE,
FROM TWO-STEPS, 300 F+ COALITE LC-FINING
FOLLOWED BY FIXED-BED HYDROCRACKING OF
575-975 F LC-FINATE VGO.

TABLE 5.4.2-1A

SUMMARY OF OPERATING RESULTS HYDROTREATED PRODUCTS FROM FIXED-BED HYDROTREATING OF

THERMALLY PROCESSED COALITE DISTILLATE

CATALYST: K-550 (1ST STAGE) K-599 (2ND STAGE)

TEST # (FB-)	45	126	127
DATE: 1989	02-03	04-19	04-19
START TIME	10:50	07:30	13:30
END TIME	11:50	09:30	14:45
FEEDSTOCK	A	B	E
% HDS			89.9
% HDN			75.5
% HDI			
HI UPTAKE, BBL/D	7000	7000	7000
% FINAL OLEFIN SATURATION	96.2	98.0	96.2
% FINAL AROMATIC SATURATION	81.8	79.5	81.0
API IMPROVEMENT	34.9	40.6	41.0
R.V. DEPRESSION	1.4635	1.4476	1.4488
EST. HEAT OF REACTION, BBL/D	16230	19107	16478

FEEDSTOCK TYPE:

A: THERMALLY PROCESSED COALITE DISTILLATE, 300-650 F @ 100 psia CONEDOWN PRESSURE.
 B: THERMALLY PROCESSED COALITE DISTILLATE, 300-575 F @ 62 psia AVERAGE CONEDOWN PRESSURE.

TABLE 5.4.2-1B

SUMMARY OF PROPERTIES OF HYDROTREATED PRODUCTS FROM FIXED-BED HYDROTREATING OF

THERMALLY PROCESSED COALITE DISTILLATE

CATALYST: K-550 (1ST STAGE) K-599 (2ND STAGE)

TEST # (FEED)	45	126	127
DATE (1989)	02-03	04-19	04-19
START TIME	10:50	07:30	13:30
END TIME	11:50	09:00	14:45
FEEDSTOCK	A	B	B
SPECIFIC GRAVITY, g/mL	0.8504	0.8222	0.8203
API GRAVITY	34.9	40.6	41.0
REFRACTIVE INDEX @ 20°C	1.4635	1.4490	1.4486
ELEMENTAL ANALYSIS			
C	86.16		86.00
H	13.30		14.13
COMPOSITION, %			
10%	164		188
20%	235		255
30%	360		350
40%	430		400
50%	489		450
60%	544		520
WATER VAPOR, BOIL-UP, %	420		404
PHASE ANALYSIS, INCL. %			
OLEFIN	0.1	0.3	0.3
SATURATED	89.4	88.8	88.8
AROMATIC	10.1	10.7	10.7
WLMV, BOIL-UP	18000 *	18100	18475
WLMV, DISTILL.	129158 *	124027	126262
FLASH, °F			
SMALL, °F			
FREE, °F			
ANILINE, °F			
VISCOSITY, CGS @ 40 °F			

FEEDSTOCK TYPE:

A: THERMALLY PROCESSED COALITE DISTILLATE, 700-650 °F @ 100 psia CONEDRUM PRESSURE

B: THERMALLY PROCESSED COALITE DISTILLATE, 300-375 °F @ 60 psia AVERAGE CONEDRUM PRESSURE.

* EXTRAPOLATED FROM REGRESSION ANALYSIS.

5.5 Two-Step Selective Hydrocracking of Vacuum Gas Oil (VGO)

5.5.1 Overview of Early Results

Early Task 3 screening tests were aimed at investigating the hydrocracking via expanded-bed LC-Fining (using a base metal hydrocracking catalyst) of the 650F+ COALITE feedstock. This was followed by an alternative hydrocracking route consisting of fixed-bed hydrocracking of a VGO fraction (650-975F) of the 650F+ COALITE over a more selective, proprietary, zeolite-based hydrocracking catalyst. The latter operation was somewhat hampered by temperature control/hot spot problems associated with the high hydrogen uptake rates. This problem would be magnified in a true adiabatic commercial unit necessitating multi-bed quenching operations.

As an alternative to the afore-mentioned approach, an initial hydrotreating step prior to the fixed-bed hydrocracking step would input some degree of hydrogen uptake and thus ameliorate the heat removal requirements in the subsequent downstream hydrocracker. In view of the various distillate fractions that will be required to process the raw COALITE, it was decided to hydrotreat a dewatered and essentially full-range (300F+) COALITE stream. This was carried out in the stirred autoclave simulator of the LC-Fining process at nominal conditions of 750F, 1950 psig hydrogen partial pressure and 0.8 liquid hourly space velocity. (The "standard" hydrocracking severity used in the earlier 650F+ COALITE LC-Fining studies included 800-820F temperature, 0.4 space velocity and 2000 psig).

The resultant hydrotreated 300F+ COALITE was then fractionated in the 4-in Batch Still and the Equilibrium Flash Vaporization units to produce a hydrotreated 300-600F distillate; a hydrotreated 600-975F HVGO; and a hydrotreated 975F+ vac resid.

The hydrotreated 600-975F vacuum gas oil (HVGO) was subjected to fixed-bed hydrocracking over the proprietary Amoco hydrocracking catalyst in a series of test scans to evaluate temperature, hydrogen partial pressure and space velocity. The thus hydrotreated hydrocrackates were distilled in a laboratory column to produce a nominal 300-750F distillate for subsequent fixed-bed hydrotreating and upgrading to HEDF product. The higher 750F cut point was selected to allow the continued evaluation of the effect of higher cut points on volumetric energy densities.

The two 300-750F distillates, namely, the raw COALITE and that recovered from the selective fixed-bed hydrocracking of a 650-975F LC-Finate derived from mild LC-Finingsm of the 300F+ COALITE, had similarities in physical properties as per the following:

<u>Feed Source</u>	<u>Raw COALITE</u>	<u>Selectively Hydrocracked LC-Finate-derived HVGO</u>
Refractive Index	1.5445	1.5406
API Gravity	11.4	15.6
Specific Gravity	0.9902	0.9619
Hydrogen Content, wt%	9.62	10.97
VLHV, Btu/gal	133,000	138,931

Of note is the fact that the selectively hydrocracked HVGO has a higher hydrogen content but a lower specific gravity than that of the comparable raw COALITE distillate.

Upon fixed-bed hydrogenation (test FB-166), the selectively hydrocracked LC-Finate HVGO appeared to generate a higher specific gravity product at comparable hydrotreating severity to that achieved with the raw COALITE distillate feedstock (test FB-172). Moreover, the volumetric energy density was significantly higher as can be seen from the following table:

<u>Product Source</u>	<u>HDT COALITE</u> (FB-172)	<u>Hydrotreated Selectively</u> <u>Hydrocracked LC-Finate</u> <u>Derived HVGO (FB-166)</u>
Specific Gravity	0.8571	0.9013
API Gravity	33.6	25.5
Refractive Index	1.4716	1.4909
Hydrogen Content, wt%	13.37	13.04
FIA Aromatics, wt%	16.3	-
VLHV, Btu/gal	130,050	135,666

It would appear that the hydrogenation of the HEDF precursors contained in the selectively hydrocracked LC-Finate derived HVGO retain their desirably higher specific gravity-energy content properties to a greater extent than that of the raw COALITE distillate counterparts.

It should be pointed out that in both cases, the product energy densities are based on the measurement of the total liquid product, unfractionated, recovered from the hydrotreating operations. In order to meet all of the required turbine fuel specifications, a fractionation post-treatment would be required to adjust volatility and viscosity/freeze point properties. In the case of the above two examples, the end points were extended to 750F as per DOE's suggestion in order to maximize product energy densities. Although this was achieved, as noted by the ca. 130,000+ Btu/gal values, the higher end points corresponded to unacceptably high freeze points.

The final distillation operations for adjustment of front-end volatiles (i.e., flash point) and back-end waxes (i.e., freeze point, viscosity) were completed for the HEDF product derived from the selective VGO hydrocracking route. Table 5.5-1 summarizes the properties of the final product. All specifications were met and all identified target properties were exceeded with the exception of smoke point. It appears that the F.I.A. aromatics content of 10% was a little high resulting in the adverse 15 mm smoke point. Thus, FB-166 should have been operated at a slightly higher hydrogenation severity to reduce the aromatics to below 10%, preferably between 5 and 7.5%. From the earlier data on the hydroprocessing of the raw 300-600F COALITE, it would appear that an increase in smoke point of 5 mm would require an aromatics reduction of about 5% suggesting that both the smoke point and the aromatics content specs can be met.

TABLE 5.5-1

COMPARISON OF COALITE-DERIVED HEDF FUELS

PRODUCED VIA TWO HYDROPROCESSING SCHEMES

Property	Specification	Selective HYC	Raw Dist. HD
VLHV, Btu/gal	130,000 (min)	132,915	129,095
FREEZE PT, F	-50	-60	-54
FLASH PT, F	100 (min)	115	115
% HYDROGEN	12.5 (min)	13.2	13.9
% AROMATICS	5 min; 25 max	10.0	5.0
SULFUR, ppmw	500 max	<2	<5
% OLEFINS	5 max	<0.5	<0.5
VISC, cst/-4F	8 min; 12 max	11.0	8.0

This small but finite incremental hydrogenation unfortunately will result in some further reduction in the volumetric energy density. On the positive side, the prior hydroprocessing data with the raw COALITE distillate indicated that at HEDF aromatics levels below about 20%, there was not a great effect of aromatics content on volumetric energy densities.

5.5.2 Subtask 3.1/3.2 Scope

In view of these promising results and DOE's desire to increase the target HEDF energy density from 130,000 Btu/gal to 135,000 Btu/gal, a contract modification was executed. A new Subtask 3.1/3.2 was formulated to concentrate on the selective hydrocracking route by investigating alternative catalysts that will simultaneously produce HEDF test fuels having the targetted high (ca., 135,000 Btu/gal) energy densities and acceptable thermal stability characteristics. The Colorado shale oil studies were to be deemphasized because of their apparent limited cyclics content that prevents the achievement of the 130,000+ Btu/gal energy densities.

It has been hypothesized that there is a set of operating conditions that exists in which a high density jet fuel fraction, derived from hydroprocessing of COALITE heavy distillates, will have an energy density of 135,000 Btu/gal or higher and meet some acceptable thermal stability criterion. Of the many parameters that might affect the achievement of these goals, those that are anticipated to have the greatest influence on energy density and stability include:

- o COALITE feedstock definition
- o Hydroprocessing steps including fractionation between steps to pinpoint preferred distillate compositions
- o Catalyst type
- o Thermal severity as measured by reaction temperature and space velocity

COALITE Feedstock Definition

From the prior Task 3 screening efforts, it was determined that hydrocracked heavy distillates had higher energy densities, by some 3000-4000 Btu/gal, than those of distillates boiling in the jet fuel range by virtue of being thermally cracked during the COALITE MCG process. By tailoring the selective hydrocracking operations to near optimal conditions, it might be possible to increase the energy density advantage over the as-produced jet fuel-range distillates by as much as 5000-6000 Btu/gal.

Assuming the end-point of the finished HEDF product will be 575F, the raw COALITE was fractionated to generate a 575F+ resid, more than 90% of which boils below 975F. The latter vacuum gas oil (VGO) cut, namely, 575-975F, is the candidate feedstock for the selective hydrocracking campaigns of Subtask 3.2.

Hydroprocessing Sequence

The hydroprocessing of the heavy COALITE fractions is carried out in several steps of hydrogen uptake, heteroatom removal, hydrocracking and aromatics saturation. The multi-step operation represents the best approach from the points of view of reactor design, heat removal, and catalyst selectivity/activity. The stepwise process consists of:

1. LC-Fining of 575F+ resid
2. Flash vaporization to recover the 975F- LC-Finates
3. Fixed-bed hydrodenitrogenation of the 975F- LC-Finates
4. Fixed-bed hydrocracking of the hydrodenitrogenated 975F- LC-Finates
5. Fixed-bed hydrogenation (aromatics saturation) of the selectively hydrocracked LC-Finates
6. Fractionation to recover the Category I HEDF product (and Category II and III distillate byproducts)

LC-Fining

The LC-Fining step might commercially be substituted with a fixed-bed resid hydrotreating process. Its primary function is to perform some degree of hydrogen uptake in a manner that can cost effectively remove the corresponding exothermic heats of reaction. Along with HDN, olefins are saturated, some aromatics are saturated and much of the organic oxygen is removed. Additionally, there is some degree of hydrocracking, defined as conversion to 575F-. The LC-Finer also allows the hydroprocessing of the resid portion of the COALITE which contains some coal char fines and coal mineral matter that are normally poisons and deactivators in fixed-bed hydroprocessing units.

The LC-Finer is being used as a unit to prepare feedstock for downstream hydroprocessing technology evaluations and is operated at constant conditions of 2000 psig pressure, 760F reactor temperature, 0.8 LHSV (based on catalyst volume) and 6000 scf/bbl treat gas rate using Criterion 324M catalyst, a nickel-moly catalyst used extensively in coal hydroliquefaction operations.

Flash Vaporization

The LC-Finate product, containing hydrocracked 575F- distillates, hydrotreated 575-975F distillates, and hydrotreated 975F+ resid, is flashed in a continuous equilibrium flash vaporization (EFV) unit operated at 575F and 25 mm Hg absolute. These flashing conditions approximate a 975F atmospheric equivalent end point of the recovered HVGO (hydrotreated VGO). The hydrocracked jet fuel-range distillates co-produced with the HVGO during the LC-Fining operations were not separated from the HVGO and are co-hydroprocessed in the downstream units. Thus, the final HEDF product will have the LC-Finate hydrocrackate and fixed-bed hydrocrackate products co-mingled.

Fixed-Bed Hydrodenitrogenation (HDN)

The primary function of the fixed-bed HDN step is to reduce the nitrogen content of the HVGO sufficiently to protect the downstream

selective hydrocracking catalyst, which is sensitive to N poisons. The catalyst selected for this step is Akzo KF-843, a commercial high moly nickel on alumina, first-stage (HDN) hydrocracking catalyst. The thermal operating severity as measured by reaction temperature and residence time (i.e., space velocity) at constant pressure will be scanned to determine the best conditions for production of hydrodenitrogenated HVG0 for the downstream fixed-bed hydrocracking scans.

Fixed-Bed Hydrocracking

The fixed-bed hydrocracking step represents the key in being able to selectively hydrocrack HVG0 components to the desirable two-ring and three-ring aromatic precursors to HEDF. The key to the selectivity potential resides in the catalyst type. In this program, three catalysts are under consideration: 1) Akzo KF-1015, a commercial nickel-moly Mild Hydrocracking catalyst; 2) a proprietary Amoco nickel-tungsten catalyst previously tested in Task 3; and 3) a new sulfur-resistant, proprietary zeolitic hydrocracking catalyst being offered by Zeolyst Enterprises.

Each catalyst was evaluated in a series of scans to identify that combination of thermal severity and hydrogen partial pressure that results in maximum HEDF precursor yield and maximum precursor quality, the latter being used as a measure of HEDF energy density. From an analytical viewpoint, HEDF precursor quality may be assessed from FIA analysis, HNMR analysis and density-hydrogen content relationships.

Fixed-Bed Hydrogenation (Aromatics Saturation)

A final aromatics saturation step may be required for final hydro-finishing depending upon the selectivity of the hydrocracking catalyst. The proprietary zeolitic catalyst from Zeolyst Enterprises had dual functionality, namely, hydrocracking and ring saturation. In this situation, a final fixed-bed hydrogenation step was not required. For the other hydrocracking catalysts, fixed-bed hydrogenation is required. The key here is to determine the optimal extent of aromatics saturation that will maximize HEDF energy density. This is a function of the hydrogenation severity. Although many nickel-moly or nickel-tungsten hydrogenation catalysts are commercially available, Katalco K-599, a nickel-moly catalyst used extensively in the earlier Task 3 screening program and for which a database exists, was utilized for this hydroprocessing step. A post-hydrogenation finishing step, namely, clay treating, was used to reduce trace polar compounds that might otherwise detrimentally affect the fuel properties of thermal stability and corrosion resistance.

5.5.3 Subtask 3.1/3.2 Results

The purpose of subtask 3.2 was to explore ways to produce a stable high energy density (130,000+ Btu/gal) HEDF test fuel from raw COALITE feed through a selective hydrocracking/hydrotreating approach. The campaign initiated to achieve this goal is summarized below:

- Step 1. The COALITE feed was charged to the 8" batch distillation unit. Run EBD-41 was an atmospheric distillation to produce a 300°F+ material followed by EBD-42 which was a vacuum distillation to produce the 575°F+ material for the LC-Fining™ reactors.
- Step 2. The 575°F+ COALITE was then fed to the LC-Fining™ unit consisted of 2 expanded-bed reactors in series each loaded with 3000cc of Shell 324M catalyst. The operating conditions were 2000 psig pressure, 765°F average reactor temperature and 1.6 LHSV per bed. The product from the LC-Fining™ stage achieved an HDN rate of 84%, HDS of 98%, 575°F+ conversion of 30 vol%, and a 975°F+ conversion of 65 vol%. Enough LC-Finate was generated to conduct the subsequent HDN, hydrocracking and hydrogenation scans.
- Step 3. The LC-Finate from Step 2 was then processed in an Equilibrium Flash Vaporization Unit (EFV) operated at vacuum to remove the 900°F+ material. The resulting IBP-900°F material was then used as feed for the HDN fixed bed scans.
- Step 4. The IBP-900°F distillate then sent to an HDN fixed bed unit where the nitrogen was reduced from 1700 ppm to 43 ppm. The HDN unit was a downflow fixed bed unit with 2 reactors in series. The catalyst charged to each reactor was 165cc Katalco KF-843 extrudates. A total of 18 scanning runs (Runs FB-194-211) were performed at different pressures, liquid hourly space velocities, and reactor temperatures. Production runs were then made to generate HDN material for subsequent fixed bed hydrocracking and hydrotreating operations. The conditions were 2000 psig unit pressure, 1.0 liquid hourly space velocity, and 780°F average reactor temperatures.
- Step 5. Material from the hydrodenitrogenation step was then hydrocracked in a single stage downflow fixed bed reactor. The scanning tests employed AKZO KF-1015 Ni/Mo catalyst for Runs FBHC 37 and 38 and a proprietary zeolitic catalyst for Runs FBHC 39-43.

Run FBHC-37 was a scanning campaign with seven different conditions of space velocity and reactor temperatures at a set pressure of 2000 psig. As a result of the scanning tests, a production run (Run FBHC-38) was made at 2000 psig, 760°F reactor temperature, and a liquid hourly space velocity of 0.5 hr⁻¹ to generate material for the hydrotreating step.

Run FBHC-39 was a scanning test using the proprietary zeolitic catalyst with six different conditions of space velocity and temperature at a set pressure of 2000 psig. The catalyst activity was so high at the conditions that all of the material cracked out of the jet fuel range into the 275°F- naphtha range. Based on the above observations a

second scanning run (FBHC-40) was initiated at lower operating pressures of 1000 psig and reactor temperatures of 550-650°F. Based on the results of the scanning tests, three different production runs (FBHC-41, 42, and 43) were performed with the proprietary zeolitic catalyst. The activity of this catalyst towards hydrocracking and ring saturation was so high that the final hydrotreating step to produce the desirable cycloparaffins was not required. The products from FBHC-41, 42 and 43 were then fractionated and treated with bentonite clay.

- Step 6. A series of hydrotreating runs was performed with a 2 stage fixed bed reactor system using a) hydrodenitrogenated but not hydrocracked LC-Finate distillate from Run FB-213; and b) hydrocracked LC-Finate distillate from Run FBHC-38.

The fixed bed hydrogenation Run FB-214 employed two reactors in series each containing 165cc of Criterion 424 NiMo catalyst. Three scanning tests were performed with the hydrodenitrogenated LC-Finate distillate prior to a production run (Run FB-214D) at 2000 psig unit pressure, 0.5 liquid hourly space velocity, and 715°F average reactor temperature. This run was followed by a production run (FB-214E) at the same conditions except using the hydrocracked (FBHC-38) hydrodenitrogenated LC-Finate distillate as the feed. After the two production runs, one more test was made with the hydrodenitrogenated LC-Finate distillate at 2000 psig unit pressure, 0.25 liquid hourly space velocity and 750°F reactor temperature. This test was made to assess the impact of a 10°F increase in thermal severity on HEDF fuel properties.

5.5.3.1 LC-Fining Studies

The first step in the overall sequence to produce finished HEDF test fuel from the raw COALITE feed is to hydroprocess the atmospheric resid cut via expanded-bed LC-Fining. The throughput to the LC-Fining unit was specified to insure that there would be a minimum quantity of HEDF precursors in the LC-Finate products necessary for the subsequent screening studies. Run 6LCF-11 was carried out using fresh Shell 324M NiMo catalyst. The 6LCF-11 feed was derived from the 575F+ atmospheric resid fraction recovered during the batch fractionation (in an 8-in batch fractionation unit) of the raw COALITE material.

The pilot plant LC-Fining unit was used because of its large size and short operating time needed for production of the Task 3 quantities of materials required. All of the downstream screening tests for the HDN, selective hydrocracking and aromatics saturation were made in bench-scale unit. After the LC-Finer was successfully pressure tested at 2500 psig hydrogen pressure, it was commissioned with a 350-575F raw COALITE distillate until the catalyst bed temperature was 500°F. At this point, the distillate feed was removed and the 575F+ resid was introduced which increasing the heat inputs until the desired catalyst bed temperature was achieved.

The run proceeded for four days without any major operating problems. The reactor operating conditions were 2000 psig operating pressure, 764F average catalyst bed temperature, 6000 scfb treat gas rate and 1.64 LHSV per each of the two catalyst beds.

As indicated in Table 5.5.3.1-1, the products from this LC-Fining step resulted in an HDN rate of 84%, and HDS rate of 98%, a 575F+ conversion of 30 vol% and a 975F+ conversion of 65 vol%. At the end of run 6LCF-11, the composited heavy oil fraction containing unconverted 975F+ COALITE was processed in the Equilibrium Flash Vaporization unit to remove the vac resid material. The entire IBP-900F LC-Finate distillate, which contains HEDF precursor components as well as the vacuum gas oil (VGO) fractions, was composited and drummed for subsequent processing in the bench-scale, fixed-bed hydrotreating unit for deep denitrogenation.

5.5.3.2 Fixed-Bed Hydrodenitrogenation Studies

A total of 165 cc of KF-843 catalyst was charged to each of the two fixed-bed reactors. The catalysts were calcined in situ at 750F for two hours followed by presulfiding with a 2% H₂S/H₂ gas mixture. After the presulfiding operations following the vendor's procedure, the unit was successfully pressure tested at 2500 psig.

The IBP-900F LC-Finate distillate was then subjected to hydrodenitrogenation in a series of 18 brief scanning runs (Table 5.5.3.2-1) to assess the effects of reactor pressure, LHSV and bed temperature at constant hydrogen treat gas rate. From these scans, the conditions of 2000 psig reactor pressure, 1.0 LHSV and 780F average bed temperature were selected as the preferred conditions for an HDN production run. The material thus produced was used for the downstream fixed-bed hydrocracking and aromatics saturation screening tests.

5.5.3.3 Fixed-Bed Selective Hydrocracking Studies

The full-rane hydrodenitrogenated LC-Finate distillate was then subjected to selective hydrocracking in a single-stage fixed-bed reactor. Two candidate hydrocracking catalysts were evaluated: a NiMo catalyst (Akzo KF-1015) in runs FBHC-37 and -38 and a proprietary zeolitic catalyst (Zeolyst Z704A) in runs FBHC 39-41.

Run FBHC-37 consisted of seven process variable scans of space velocity and bed temperature at 2000 psig reactor pressure and 6000 scfb treat gas rate (see Table 5.5.3.3-1). Based on these scans, a production run (FBHC-38 as delineated in Table 5.5.3.3-2) was made at 2000 psig, 6000 scfb treat gas rate, 0.5 LHSV and average bed temperature of 758F to generate enough HEDF precursors for final aromatics saturation prior to HEDF finishing.

Run FBHC-39 consisted of six process variable scans of space velocity and bed temperature at 2000 psig reactor pressure and 6000 scfb treat gas rate. The hydrocracking activity of this zeolitic catalyst was so high at bed temperatures above about 700F that essentially all of the jet fuel range material was cracked into the naphtha range as shown on Table 5.5.3.3-3.

TABLE 3.3.3.1-1
SUMMARY RESULTS FOR LC-FINING RUN 6LCF-11

PERIOD NUMBER	3
DATE	1990 3/31
AVG. CATALYST TEMP. (1st STAGE)	759
AVG. CATALYST TEMP. (2nd STAGE)	769
TOTAL PRESSURE, PSIG	2000
LHSV, HOURS-1	0.82
CATALYST AGE, BBL/LB	0.17
WDSV, BBL/LB/DAY	0.071
CATALYTIC H2, SCF/BBL	5900
CARBON BALANCE, WT.% RECOVERY	101
OVERALL MAT. BAL., WT.% RECOVERY	96
FEED COALITE (575F+) PROPERTIES	
API GRAVITY	-3.7
CARBON, WT.%	85.37
HYDROGEN, WT.%	8.01
SULFUR, ppm	10200
NITROGEN, ppm	14100
OXYGEN, WT.%	4.03
ASH, WT.%	0.16
975F+ RESID, VOL.%	18
LIGHT OIL PRODUCT PROPERTIES	
API GRAVITY	28.2
CARBON, WT.%	87.82
HYDROGEN, WT.%	12.05
SULFUR, ppm	195
NITROGEN, ppm	1118
OXYGEN, WT.% (DIFF.)	0
575F+ RESID, VOL.%	23
HEAVY OIL PRODUCT PROPERTIES	
API GRAVITY	11.6
CARBON, WT.%	89.32
HYDROGEN, WT.%	10.24
SULFUR, ppm	186
NITROGEN, ppm	3121
OXYGEN, WT.% (DIFF.)	0.11
ASH, WT.%	0.02
575F+ RESID, VOL.%	88.8
975F+ RESID, VOL.%	9.0
DAILY PRODUCT YIELDS, WT.% FEED	
OFFGAS H2S	1.07
OFFGAS NH3 + H2O	5.89
OFFGAS C1	0.69
OFFGAS C2	0.66
OFFGAS C3	0.70
OFFGAS C4	1.66
OFFGAS C5+	0.81
LIGHT OIL	29.68
HEAVY OIL	62.30
TOTAL	103.46
H2 CONSUMPTION, SCF/BBL	2700
DENITRIFICATION, WT.%	84
DESULFURIZATION, WT.%	98
VOL.% 575 DEG. F + CONVERSION	30
VOL.% 975 DEG. F + CONVERSION	65

RESULTS OF FIXED-BED HYDROTREATING OF 875 F COALITE LC-FINATE

Re-1: Catalyst Re-93 VOLUME=168 OR WEIGHT=147.7 mm. 1

FR-2: CATALYST, KI-043, VOLUME=165 cc, WEIGHT=148.4 gmm "1

[illegible]

08-Oct-91

RESULTS OF FIRED-BED HYDROTREATING OF 975 F COALITE LC-FINITE

PROJECT NUMBER: 5-272/0002
FILE ID: CCF80321.WK1
PRINTING RANGE: A1-A4108

Re-1: CATALYST: KT-643, VOLUME=165 cc, WEIGHT=147.7 gm

Re-2: CATALYST: KT-643, VOLUME=165 cc, WEIGHT=148.4 gm

DATE OF OPERATION (1000)	FEED #2	04-16	04-17	04-20	04-20	04-20	04-21	04-23	04-24	04-24	04-25	04-25	04-25	04-26	04-26	04-26
RUN #		FB-208 #9 21:00- 23:00	FB-208 #7 05:00- 07:00	FB-210 #8 05:30- 07:30	FB-211 15:00- 21:00	FB-212 #10 08:30- 10:00	FB-212 05:00- 08:00	FB-212 #10 08:30- 10:00	FB-212 05:00- 08:00	FB-212 05:00- 08:00	FB-212 04:00- 06:00	FB-212 04:00- 06:00	FB-212 18:00- 20:00	FB-212 20:00- 24:00	FB-212 08:00- 04:00	FB-212 04:00- 08:00
H2 TREAT RATE, cc/hr		7000	7000	7000	7000	7000	7000	7000	7000	7000	7000	7000	7000	7000	7000	7000
PRESSURE, psig		2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
SPACE VELOCITY, cc/hr/cc cat.		0.46	0.52	1.80	1.00	0.85	0.97	0.97	0.97	0.97	1.00	1.00	1.03	1.02	1.00	1.05
REACTOR #1																
Re-1 TOP TEMP, F		703	738	(697)	(378)	(282)	771	772	771	772	772	772	772	771	773	773
Re-1 MID. TEMP, F		703	745	740	760	774	773	772	773	772	772	772	772	771	773	773
Re-1 BOT. TEMP, F		701	741	742	761	774	773	772	774	773	774	773	773	774	774	774
Re-1 BTM. TEMP, F		699	738	741	763	778	774	776	775	775	776	775	776	776	777	777
AVG. TEMP., F °3		702	741	741	761	775	773	775	775	775	774	774	774	774	775	775
AVG. TEMP., (1/Q)*1000		1.35	1.50	1.36	1.47	1.46	1.46	1.46	1.46	1.46	1.46	1.46	1.46	1.46	1.46	1.46
REACTOR #2																
Re-2 TOP TEMP, F		699	738	741	763	775	774	773	774	773	774	773	774	773	774	774
Re-2 MID. TEMP, F		703	743	740	762	775	774	773	774	773	774	773	774	773	774	774
Re-2 BOT. TEMP, F		700	741	740	761	776	774	775	774	774	775	774	774	775	774	774
Re-2 BTM. TEMP, F		702	742	738	758	772	772	773	773	773	773	773	773	773	773	773
AVG. TEMP., F °3		701	741	740	761	773	771	773	773	773	773	773	773	773	773	773
AVG. TEMP., (1/Q)*1000		1.35	1.50	1.36	1.47	1.46	1.46	1.46	1.46	1.46	1.46	1.46	1.46	1.46	1.46	1.46
AVG. TEMP. Re-1 & Re-2, F		701	741	740	761	773	772	773	774	773	773	773	773	773	774	774
RL @28 C		1.5003	1.5070	1.5182	1.5079	1.5039	1.5038	1.5035	1.5035	1.5035	1.5035	1.5072	1.5079	1.5060	1.5078	1.5079
SP. GRAV., gm/cc		0.9421	0.9003	0.9196	0.9117	0.9033	0.9035	0.9035	0.9035	0.9035	0.9035	0.9108	0.9108	0.9123	0.9108	0.9108
A.P.I. GRAVITY		18.7	24.9	22.3	22.7	24.8	24.1	24.1	24.1	24.1	24.1	24.9	24.9	24.9	24.9	24.9
DISTILLATION, F		SD-P	SD-P	SD-P	SD-P	SD-P	SD-P	SD-P	SD-P	SD-P	SD-P	SD-P	SD-P	SD-P	SD-P	SD-P
18P		182	238	184	184	188	188	188	188	188	188	188	188	188	188	188
10P		371	385	341	341	328	328	328	328	328	328	328	328	328	328	328
10P		371	385	341	341	328	328	328	328	328	328	328	328	328	328	328
30P		516	545	503	480	477	477	477	477	477	477	477	477	477	477	477
50P		611	622	582	574	558	558	558	558	558	558	558	558	558	558	558
70P		702	678	667	654	643	643	643	643	643	643	643	643	643	643	643
80P		811	773	768	768	753	753	753	753	753	753	753	753	753	753	753
EBP		865	829	801	801	816	816	816	816	816	816	816	816	816	816	816
VAEP		891	868	853	853	852	852	852	852	852	852	852	852	852	852	852
SIM. DIS. RESULTS:																
% 575 F+ CONTENT		57.9	63.0	61.3	48.9	48.5	48.5	48.5	48.5	48.5	48.5	48.5	48.5	48.5	48.5	48.5
% 575 F- MAKE				8.7	7.2	10.5	7.2	10.5	7.2	10.5	7.2	10.5	7.2	10.5	7.2	10.5
% 575 F+ CONV.				18.0	12.6	18.4	12.6	18.4	12.6	18.4	12.6	18.4	12.6	18.4	12.6	18.4
ELEMENTAL																
C wt % °4		88														
H wt % °4		11														
ORGANIC N ppm °5		1734		179	177	68	68	32	36	37	45	45	45	45	45	45
ORGANIC S ppm °5		288		18	18	4	4	3	28	28	43	43	43	43	43	43
O (BY DIFF.)																
K (H2O), (1/mcc)*1000				0.31	0.43	0.60	0.60	1.05	0.97	1.05	1.07	1.07	1.07	1.07	1.07	1.07
K (H2O), (1/mcc)*100,000				1.43	3.10	3.75	3.75	5.37	1.85	1.85	1.85	1.85	1.85	1.85	1.85	1.85
CL, %		0.003														

212.

SIM. DIS. RESULTS:
% 575 F+ CONTENT
% 575 F- MAKE
% 575 F+ CONV.

ELEMENTAL
C wt % °4
H wt % °4
ORGANIC N ppm °5
ORGANIC S ppm °5
O (BY DIFF.)
K (H2O), (1/mcc)*1000
K (H2O), (1/mcc)*100,000
CL, %

* Additional 25 cc of
Kalsolva GA-50, 1/16"
aluminum is added to
the BTM of catalyst
KT-643 in Re-1 & Re-2,
weight of 11.9 gm &
12.0 gm respectively.
* Feed source:
Cofine solids -> P. dist.
(300+ F) -> MCF-11,
(H.O. & L.O.) -> EPV, #182,
(H.O. & L.O.) ->
* Asph. wt. of all the 4
bed temps. Temp. measured
at 1/2, 3/4, 7/8, 10/11"
in 1/2" catalyst bed (top
to bottom).
* Tested by LECO, CHN-682,
sample not water washed.
* Tested by ChemLab, temporary
distillation method, sample
was water washed or
H2 stripped before test.
* Repeat run #184
* Repeat run #185
* Repeat run #189
* Tested on ChemLab method
H2 82
H2 stripped 32.4 32.8
H2 stripped & 31.4 38.0
H2O washed
H2 stripped & 3.1
H2 washed
*10 Production run.
Start on stream @ 08:38
04/22/90

FIXED BED
HYDROCRACKING
RUN FBHC-37

CATALYST: 165cc AKZO KF-1015 Ni/Mo

FEED*	37A	37B	37C	37D	37E	37F	37G
-------	-----	-----	-----	-----	-----	-----	-----

OPERATING CONDITIONS:

CATALYTIC H ₂ , SCF/BBL	-	6000	6000	6000	6000	6000	6000	6000
RUN DURATION, HRS.	-	2	2	4	2	4	2	1
AVG. RX. TEMP., DEG. F	-	655	656	703	708	754	751	734
PRESSURE, PSIG	-	2000	2000	2000	2000	2000	2000	2000
AVG. FEED RATE, cc/hr	-	85	188	68	163	61	178	310
LHSV, cc/hr/cc cat.	-	0.52	1.14	0.41	0.98	0.37	1.08	1.88
FEED IN, gms.	-	154	341	245	295	220	322	282
TLP OUT, gms.	-	176	318	235	322	222	297	307
RECOVERY, %	-	114	93	96	109	101	92	109

ANALYTICAL RESULTS:

TLP GRAVITY, gms/cc	0.9082	0.8956	0.9013	0.8789	0.8916	0.8639	0.8762	0.8888
TLP GRAVITY, API	24.3	26.5	25.5	29.5	27.2	32.3	30.0	27.7
DISTILLATION:								
IBP-275 F, WT. %	5.3	5.5	5.1	7.0	6.7	8.7	10.5	6.8
275-575 F, WT. %	49.3	50.4	51.8	58.1	53.9	66.6	59.0	57.5
575 F+, WT. %	45.4	44.1	43.1	34.9	39.4	24.7	30.5	35.7
CONV. 575+, WT. %	-	3	5	23	13	46	33	21

JET FUEL CUT, 275-575 F:

GRAV., gms/cc	0.8860	0.8811	0.8827	0.8713	0.8783	0.8618	0.8729	0.8783
GRAV., API	28.2	29.1	28.8	30.9	29.6	32.7	30.6	29.6
R.I., @ 20 DEG. C	1.4888	1.4817	1.4838	1.4755	1.4819	1.4709	1.4794	1.4840
H/C RATIO	1.65	1.74	1.71	1.78	1.71	1.80	1.70	1.66
ELEMENTALS, WT. %								
CARBON	87.88	87.20	87.38	87.07	87.48	86.84	87.23	87.04
HYDROGEN	12.12	12.67	12.45	12.90	12.50	13.06	12.33	12.03
F.I.A., VOL. %								
AROMATICS	40.7	-	-	-	-	-	-	-
OLEFINS	0.9	-	-	-	-	-	-	-
SATURATES	58.4	-	-	-	-	-	-	-

* THE FEED FOR THE RUN IS COALITE OIL THAT WAS TOPPED TO 300 DEG F+ IN THE 8" BATCH AND PROCESSED IN THE LC-FINING UNIT (RUN 6LCF-11 UPGRADED & REMOVED NITROGEN TO 1000 ppm). THE LC-FINATE WAS THEN RUN THROUGH THE EFV UNIT TO OBTAIN THE 300-975 FRACTION. FINALLY THE FEED WAS HYDROTREATED AND NITROGEN REMOVED (40 ppm) IN FIXED BED RUNS FB-194-199, 202-203, & 211-213. THE SAMPLE # IS 3610.

RUN FBHC-38
HYDROCRACKING COALITE DISTILLATE
MATERIAL BALANCE

PERIOD NUMBER	FEED*	FBHC-38
DATE	1990	8/30
TOTAL PRESSURE, PSIG		2000
LHSV, HOURS-1		0.49
AVERAGE TEMPERATURE, DEG. F		758
CATALYST AGE, BBL/LB		0.947
WDSV, BBL/LB/DAY		0.037
CATALYTIC H ₂ , SCF/BBL		5900
CARBON BALANCE, WT.% RECOVERY		97
OVERALL MAT. BAL., WT.% RECOVERY		98
HYDROGEN CONSUMPTION, SCF/BBL		700
575 DEG F+ CONVERSION, WT.%		61
TLP OIL PRODUCT PROPERTIES		
API GRAVITY	24.3	35.3
CARBON, WT.%	87.99	87.16
HYDROGEN, WT.%	12.00	12.84
SULFUR, ppm	34	9
NITROGEN, ppm	43	0.9
DAILY PRODUCT YIELDS, WT.% FEED		
OFFGAS H ₂ S		0.00
OFFGAS NH ₃ + H ₂ O		0.01
OFFGAS C ₁		0.27
OFFGAS C ₂		0.17
OFFGAS C ₃		0.57
OFFGAS C ₄		0.37
OFFGAS C ₅ +		0.62
IBP-275 DEG. F	5.3	19.42
275-575 DEG. F	49.3	61.83
575 DEG. F +	45.4	17.84
TOTAL	100.00	101.10
JET FUEL CUT (275-575 DEG F) PROPERTIES		
GRAVITY, API	28.2	32.8
GRAVITY, SP. @ 60/60	0.8860	0.8612
ELEMENTALS, WT.%		
CARBON	87.88	87.22
HYDROGEN	12.12	12.57
R.I., @ 20DEG C	1.4888	1.4729
F.I.A., VOL.%		
AROMATICS	42.0	30.5
OLEFINS	0.5	1.0
SATURATES	57.5	68.5

* THE FEED FOR FBHC-38 IS THE SAME AS RUN FBHC-37. REFER TO RUN FBHC-37.

SUMMARY OF FIXED BED HYDROCRACKING RUN
RUN FBHC-39

CATALYST: 165cc ZEOLITE Z-704A

	FEED	39A	39B	39C	39D	39E	39F
	****	----	----	----	----	----	----

OPERATING CONDITIONS:

CATALYTIC H2 RATE, SCF/BBL	-	6000	6000	6000	6000	6000	6000
RUN DURATION, HRS.	-	4	2	4	2	4	2
AVG. RX. TEMP., DEG. F	-	649	653	701	701	751	750
PRESSURE, PSIG	-	2000	2000	2000	2000	2000	2000
AVG. FEED RATE, cc/hr	-	88	166	85	174	86	165
LHSV, cc/hr/cc cat.	-	0.53	1.01	0.52	1.05	0.52	1.00
FEED IN, gms.	-	318	302	310	316	312	300
TLP OUT, gms.	-	309	307	257	268	196	191
RECOVERY, %	-	97	102	83	85	63	64

ANALYTICAL RESULTS:

TLP GRAVITY, gms/cc	0.9082	0.7796	0.8473	0.7286	0.7475	0.6803	0.6879
TLP GRAVITY, DEG. API	24.3	50.0	35.5	62.7	57.8	76.5	74.2
H/C RATIO	1.64	2.05	1.91	2.17	2.13	2.30	2.24
TLP ELEMENTALS: *							
CARBON	88.00	84.90	86.48	83.64	83.95	81.98	83.18
HYDROGEN	12.00	14.50	13.73	15.10	14.92	15.69	15.52

DISTILLATION:

IBP, DEG. F	-	105	190	108	115	81	80
ENDPOINT, DEG. F	-	640	720	480	595	310	346
DISTILLATION RECOVERY, % **		93.8	95.9	77.0	67.3	89.1	86.2
IBP-275 F, WT. %	5.3	49.9	14.9	77.3	70.4	98.8	96.4
275-575 F, WT. %	49.3	42.2	61.3	22.7	27.4	1.2	3.6
575 F+, WT. %	45.4	7.9	23.8	0.0	2.2	0.0	0.0
CONV. 575+, WT. %	-	83	48	100	95	100	100

JET FUEL CUT, 275-575 F:

GRAV., gms/cc	0.8860	0.8222	0.8458	0.7844	0.8090	***	***
GRAV., DEG. API	28.2	40.6	35.8	48.9	43.4	-	-
R.I., @ 20 DEG. C	1.4888	1.4470	1.4585	1.4303	1.4420	1.4168	1.4248
H/C RATIO	1.65	2.00	1.94	2.08	2.03	2.12	2.09
JET FUEL ELEMENTALS, WT. %							
CARBON	87.88	85.33	85.53	84.77	84.62	84.58	85.06
HYDROGEN	12.12	14.20	13.80	14.71	14.34	14.94	14.79

* THE TLP SAMPLES FOR RUNS C THRU F WERE VERY VOLATILE RESULTING IN ERRATIC ELEMENTAL RESULTS.

THE SAMPLES FROM FBHC-39 C-F WERE VERY VOLATILE. THE D-86 DISTILLATION COULD NOT CAPTURE THE VERY LIGHT ENDS WHICH RESULTED IN POOR RECOVERIES.

*** INSUFFICIENT SAMPLE FOR GRAVITY ANALYSIS.

**** THE FEED FOR FBHC-39 IS THE SAME AS FBHC-37. SEE NOTE ON RUN FBHC-37.

A second scanning test (FBHC-40) was made at a lower hydrogen partial pressure by reducing reactor pressure from 2000 psig to 1000 psig and by reducing bed temperatures to the 550-600F range. This resulted in a reduction in the per pass 575F+ conversion but with a significant increase in the selectivity to the HEDF jet precursor range as shown in Table 5.5.3.3-4. Based on these results, a production run (FBHC-41) was made at 1000 psig, 6000 scfb treat gas rate, 0.5 LHSV and 650F average bed temperature as shown on Table 5.5.3.3-5. During the run as the hyperactivity of the freshly activated catalyst declined, the bed temperature was increased a few degrees in order to maintain the gravity and hydrogen content of the jet range product approximately constant. Upon subsequent analysis of the results, it was determined that this catalyst had dual functionality, namely, simultaneous hydrocracking and ring saturation. Accordingly, the hydrocrackate product did not have to be further hydrotreated as was the case for the hydrocracked products generated from the NiMo based catalysts.

5.5.3.4 Hydrotreating Studies

Two series of two-stage, fixed-bed hydrotreating runs using Criterion 424 NiMo catalyst were performed with a) the hydrodenitrogenated LC-Finate distillate from FB-213; and b) the selectively hydrocracked hydrodenitrogenated LC-Finate distillate from run FBHC-38. The data are summarized on Table 5.5.3.4-1. Three scans were performed with the hydrodenitrogenated LC-Finate distillate and an HEDF production run (FB-214D) was then selected at the following conditions: 2000 psig reactor pressure, 4500 scfb treat gas rate, 0.5 LHSV and 715F average bed temperature. Subsequent to this production run, the feed was replaced with the selectively hydrocracked hydrodenitrogenated LC-Finate distillate (FBHC-38 product) and an HEDF production run was made at the same conditions as that of run FB-214D. After the completion of this run, a final hydrogenation scan was made (FB-214F) with the hydrodenitrogenated LC-Finate feedstock at a hydrogenation severity equivalent to higher temperature/lower space velocity in an effort to increase the degree of hydrogenation (as measured by both specific gravity and aromatics reduction) over and above that of the prior tests.

5.5.3.5 HEDF Finishing

All four candidate HEDF products generated during the production campaigns were fractionated in a laboratory TBP distillation column. The front-end distillate cuts were blended to meet the HEDF jet fuel flash point specification and the back-end distillate cuts were blended to meet the freeze point/viscosity specifications. The resultant composites were then clay treated in a laboratory-scale, glass adsorption column packed with bentonite to remove trace polar compounds. The resultant treated HEDF test fuels were subjected to full analytical testing and the results are presented in Table 5.5.3.5-1.

Energy densities of the finished HEDF test fuels varied from a low of 130,860 Btu/gal for FBHC-41 produced during selective hydrocracking with the proprietary zeolitic catalyst to a high of 133,992 Btu/gal

TABLE 5.5.3.3-4
SUMMARY OF FIXED-BED HYDROCRACKING RUN
RUN FBHC-40

CATALYST: 165cc ZEOLITE Z-704A

	FEED*	40A	40B	40C	40D	40E	40F	40G**
OPERATING CONDITIONS:								
CATALYTIC H ₂ , SCF/BBL	-	6000	6000	6000	6000	6000	6000	6000
RUN DURATION, HRS.	-	2	2	2	2	2	4	4
AVG. RX. TEMP., DEG. F	-	550	551	600	600	652	650	650
PRESSURE, PSIG	-	1000	1000	1000	1000	1000	1000	2000
AVG. FEED RATE, cc/hr	-	167	252	168	250	161	83	90
LHSV, cc/hr/cc cat.	-	1.01	1.53	1.02	1.52	0.98	0.50	0.55
FEED IN, gms.	-	302	458	304	454	292	302	328
TLP OUT, gms.	-	310	457	308	456	297	296	333
RECOVERY, %	-	103	100	101	100	102	98	102

ANALYTICAL RESULTS:

TLP GRAVITY, gms/cc	0.9082	0.8794	0.8879	0.8718	0.8756	0.8483	0.8309	0.8468
TLP GRAVITY, API	24.3	29.4	27.9	30.8	30.1	35.3	38.8	35.6
H/C RATIO	1.64	1.80	1.78	1.83	1.80	1.88	1.94	1.90
TLP ELEMENTALS:								
CARBON	88.00	86.75	86.70	86.48	86.87	85.81	85.84	86.04
HYDROGEN	12.00	12.98	12.87	13.17	13.06	13.44	13.89	13.63

DISTILLATION:

IBP, DEG. F	-	205	218	190	188	160	130	143
ENDPOINT, DEG. F	-	736	720	738	724	748	678	706
DISTILLATION RECOVERY, %		100.0	100.0	100.0	99.9	90.4	98.1	98.5
IBP-275 F, WT. %	5.3	7.8	14.5	6.6	7.3	15.7	19.6	14.0
275-575 F, WT. %	49.3	52.6	45.3	57.9	57.2	55.3	60.8	60.8
575 F+, WT. %	45.4	39.6	40.2	35.5	35.5	29.0	19.6	25.2
CONV. 575+, WT. %	-	13	11	22	22	36	57	44

JET FUEL CUT, 275-575 F:

GRAV., gms/cc	0.8860	0.8665	0.8783	0.8545	0.8618	0.8413	0.8403	0.8458
GRAV., API	28.2	31.8	29.6	34.1	32.7	36.7	36.9	35.8
R.I., @ 20 DEG. C	1.4888	1.4707	1.4782	1.4653	1.4685	1.4585	1.4558	1.4575
H/C RATIO	1.65	1.78	1.78	1.87	1.83	1.90	1.92	1.92
JET FUEL ELEMENTALS, WT. %								
CARBON	87.88	86.81	87.10	86.28	86.65	85.70	86.08	86.13
HYDROGEN	12.12	12.89	12.90	13.46	13.23	13.56	13.74	13.76

* THE FEED FOR FBHC-39 IS THE SAME AS FBHC-37. SEE NOTE ON RUN FBHC-37.
** RUN FBHC-40G IS A REPEAT OF RUN FBHC-39A TO CHECK IF THERE IS THE SAME ACTIVITY.

RUN FBHC-41
COMPARISON OF
RUN FBHC-40F WITH RUN FBHC-41

CATALYST: 165cc ZEOLITE Z-704A

DESIGNATION:	FEED*	40F	41	41	41	41	41
DATE, 1990	----	9/20	10/1	10/2	10/3	10/4	10/5
OPERATING CONDITIONS:							
CATALYTIC H2 RATE, SCF/BBL	-	6000	6000	6000	6000	6000	6000
RUN DURATION, HRS.	-	4	2	2	4	4	6
AVG. RX. TEMP., DEG. F	-	650	651	658	657	655	659
PRESSURE, PSIG	-	1000	1000	1000	1000	1200	1200
AVG. FEED RATE, cc/hr	-	83	89	88	86	89	89
LHSV, cc/hr/cc cat.	-	0.50	0.54	0.53	0.52	0.54	0.54
FEED IN, gms.	-	302	161	160	312	324	487
TLP OUT, gms.	-	296	167	147	307	329	492
RECOVERY, %	-	98	104	92	98	101	101

ANALYTICAL RESULTS:

TLP GRAVITY, gms/cc	0.9082	0.8309	0.8423	0.8388	0.8368	0.8468	0.8438
TLP GRAVITY, DEG. API	24.3	38.8	36.5	37.2	37.6	35.6	36.2
H/C RATIO	1.64	1.94	-	-	-	-	-
TLP ELEMENTALS:							
CARBON	88.00	85.84	-	-	-	-	-
HYDROGEN	12.00	13.89	-	-	-	-	-

DISTILLATION:

IBP, DEG. F	-	130	130	130	120	128	125
ENDPOINT, DEG. F	-	678	720	726	702	680	700
DISTILLATION RECOVERY, %		98.1	98.8	99.1	100.0	98.8	99.3
IBP-275 F, WT. %	5.3	19.6	16.0	16.4	18.3	15.1	16.0
275-575 F, WT. %	49.3	60.8	59.9	60.7	58.2	58.2	57.1
575 F+, WT. %	45.4	19.6	24.1	22.9	23.5	26.7	26.9
CONV. 575+, WT. %	-	57	47	50	48	41	41

JET FUEL CUT, 275-575 F:

GRAV., gms/cc	0.8860	0.8403	0.8438	0.8388	0.8393	0.8433	0.8433
GRAV., DEG. API	28.2	36.9	36.2	37.2	37.1	36.3	36.3
R.I., @ 20 DEG. C	1.4888	1.4558	1.4574	1.4566	1.4575	1.4592	1.4580
H/C RATIO	1.65	1.92	1.92	1.93	-	1.91	NA
JET FUEL ELEMENTALS, WT. %							
CARBON	87.88	86.08	85.87	86.18	-	86.08	NA
HYDROGEN	12.12	13.74	13.74	13.85	-	13.73	NA

* THE FEED FOR FBHC-39 IS THE SAME AS FBHC-37. SEE NOTE ON RUN FBHC-37.

FIXED BED
HYDROTREATING
RUN FB-214

CATALYST: USED CRITERION 424
2 REACTORS IN SERIES @ 165 cc CATALYST PER REACTOR

=====	FEED*	214A SPOT	214A	214B	214C	214D	214E **	214F =====
	----	----	----	----	----	----	----	----

OPERATING CONDITIONS:

CATALYTIC H ₂ , SCF/BBL	-	4500	4500	4500	4500	4500	4500	4500
RUN DURATION, HRS.	-	1	3	3	3	48	16	2
DC-101 AVG. TEMP., F		655	655	707	725	718	715	755
DC-201 AVG. TEMP., F	-	651	651	707	724	713	713	752
PRESSURE, PSIG	-	2000	2000	2000	2000	2000	2000	2000
AVG. FEED RATE, cc/hr	-	165	162	162	173	170	167	83
LHSV, cc/hr/cc cat.	-	0.50	0.49	0.49	0.53	0.52	0.51	0.25
FEED IN, gms.	-	150	440	440	472	7425	2274	150
TLP OUT, gms.	-	149	461	466	439	7275	2184	149
RECOVERY, %	-	99	105	106	93	98	96	99

ANALYTICAL RESULTS:

TLP GRAVITY, gms/cc	0.9082	0.8789	0.8778	0.8718	0.8660	0.8724	0.8383	0.8576
TLP GRAVITY, API	24.3	29.5	29.7	30.8	31.9	30.7	37.3	33.5
DISTILLATION:								
IBP-275 F, WT. %	5.3	5.1	5.5	5.8	6.8	6.9	15.0	7.5
275-575 F, WT. %	49.3	53.8	56.2	58.2	60.8	57.5	66.6	70.0
575 F+, WT. %	45.4	41.1	38.3	36.0	32.4	35.6	18.4	22.5
CONV. 575+, WT. %	-	9	16	21	29	22	0	50
JET FUEL CUT, 275-575 F:								
GRAV., gms/cc	0.8860	-	0.8586	0.8618	0.8602	0.8607	0.8428	0.8545
GRAV., API	28.2	-	33.2	32.6	32.9	32.8	36.3	34.0
R.I., @ 20 DEG. C	1.4888	1.4676	1.4674	1.4660	1.4665	1.4686	1.4593	1.4670
H/C RATIO	1.65	-	1.86	1.89	1.87	-	1.92	1.84
ELEMENTALS, WT. %								
CARBON	87.88	-	86.42	86.44	86.13	-	86.14	86.64
HYDROGEN	12.12	-	13.43	13.60	13.40	-	13.78	13.29
F.I.A., VOL. %								
AROMATICS	42.0	-	6.5	5.0	8.5	13.8	5.9	-
OLEFINS	0.5	-	0.5	1.0	0.5	0.5	0.9	-
SATURATES	57.5	-	93.0	94.0	91.0	85.7	93.2	-

* THE FEED FOR THE RUN IS COALITE OIL THAT WAS TOPPED TO 300 DEG F+ IN THE 8" BATCH, AND PROCESSED IN THE LC-FINING UNIT (RUN 6LCF-11 UPGRADED & REMOVED NITROGEN TO 1000 ppm). THE LC-FINATE WAS THEN RUN THROUGH THE EFV UNIT TO OBTAIN THE 300-975 FRACTION. FINALLY THE FEED WAS HYDROTREATED AND NITROGEN REMOVED (40 ppm) IN FIXED BED RUNS FB-194-199, 202-203, & 211-213.

THE SAMPLE # IS 3610.

THE FEED FOR RUN FB-214E IS THE TLP FROM THE FIXED BED HYDROCRACKING RUN 37 (RUN FBHC-37) WHICH HAS 30.5 VOL. % AROMATICS & 18 WT. % 575 F+ MATERIAL.

TABLE 5.5.3.5-1
COALITE DERIVED
HEDF FUEL PROPERTIES

TASK 3.2 SCREENING PROGRAM RESULTS

DESIGNATION	FBHC-41	FB-214D	FB-214E	FB-214F
BOILING RANGE, DEG. F	300-600	300-610	300-620	300-600
GRAVITY, SP. @60	0.8560	0.8745	0.8571	0.8702
GRAVITY, DEG. API	33.8	30.3	33.6	31.1
ELEMENTALS:				
CARBON, WT. %	86.36	86.84	86.55	86.78
HYDROGEN, WT. %	13.64	13.16	13.45	13.22
NITROGEN, ppm	<1	<1	<1	<1
SULFUR, ppm	5	4	1	<1
VISCOSITY @ -4F, cst.	9.1	14.1	9.3	11.0
FLASH POINT, DEG. F	>120	>145	>140	>150
FREEZE POINT, DEG. F	<-50	<-50	<-50	<-50
SMOKE POINT, mm	22	18	20	20
ANILINE POINT, DEG. C	61.9	58.0	62.0	54.9
F.I.A.:				
AROMATICS, VOL. %	4.6	3.7	6.6	15.2
OLEFINS, VOL. %	0.5	0.5	0.5	0.5
SATURATES, VOL. %	94.9	95.8	92.9	84.3
COPPER CORROSION, @ 212F	3A	1A	1A	1A
POTENTIAL GUM, mg/100ml	7.0	-	7.4	16.4
THERMAL STABILITY (JFTOT):				
TUBE DEPOSIT RATING	0	0	0	2
TUBE DEPOSIT RATING, MAX.	0.5	1.0	1.5	8.0
DIFF. PRESS. MAX., mm Hg	3.0	3.0	3.0	3.0
ENERGY DENSITY, BTU/GAL	130,860	133,992	131,622	132,901

for FB-214D produced for the scheme comprised of hydrodenitrogenation of LC-Finate followed by aromatics saturation with Criterion C-424 catalyst.

Although the highest volumetric energy density is desired, there are two other criteria to consider. The first is a function of economics and the resultant tradeoffs between the additional cost of the incremental energy density improvement vs the value of the higher density fuel to the end user. The other criteria concerns the storage stability and thermal stability of the fuel for use in high speed aircraft. One analytical device for assessing stability performance is the Standard Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure, ASTM D3241-85). JFTOT subjects the test fuel to conditions that are relatable to those occurring in gas turbine engine fuel systems. The fuel is pumped at a fixed volumetric flow rate through a heater after which it enters a precision stainless steel filter where fuel degradation products become trapped. The essential data derived are the amount of deposits on an aluminum heater tube and the rate of plugging of a 17 micron nominal porosity filter located just downstream of the heater tube. This test has long been used by petroleum refiners to meet process specifications for shipment of aviation fuel products to the end users, namely, the commercial airline industry and the U.S. Air Force. With the advent of new aircraft engines and new fuel compositions, the JFTOT test is not always an accurate gauge for assessing on-board fuel stability performance. The Air Force is continually improving technology for on-ground determination of thermal stability of aviation turbine fuels. With regard to the new fuel type, High Energy Density (Category I) fuel, it is not known how applicable the JFTOT test will be for assessing thermal stability.

6.0 SUMMARY OF RESULTS OF COLORADO SHALE OIL SCREENING OPERATIONS

6.1 Overview

The Work Statement for this contract, which was co-funded by METC's Coal Gasification group and by the Extraction Projects division which is responsible for non-coal resources such as oil shale, tar sands and gases, called for assessment of HEDF test fuel production from several fossil fuel sources. In addition to the MCG liquids generated in the COALITE process, a sample of Colorado shale oil derived from the UNOCAL plant at Parachute Creek. This feedstock is of importance because of its commercial availability and its demonstrated conversion to conventional jet fuel and subsequent on-board testing under past DOE contracts.

6.2 Virgin Distillate Hydrotreating

The results of the several campaigns are summarized in a series of spreadsheet tables with the "A" tables presenting the run performance data and the "B" tables presenting the properties of the full-range hydrotreated distillates. The organization of the tabulated results is as follows:

<u>Table No</u>	<u>Catalyst Type</u>	<u>Feed Boiling Range (F)</u>	<u># Reaction Stages</u>
6.2-1A,B	K-599/MO-1230	350-600	2
6.2-2A,B	K-550/K-599	350-600	2
6.2-3A,B	K-550/K-599	575-1000HDT	2
6.2-4A,B	K-599	300-575HDT	1
6.2-5A,B	Amoco Propr.	575-1000HDT	1
6.2-6A,B	Amoco Propr.	650-975Virgin	1

Several interesting correlations were developed for the hydrotreating of the raw 350-550F and 350-650F COALITE distillates. Correlations were developed of the HEDF properties vs the kinetic hydrotreating severity parameter (KSF described in Section 4). These are shown graphically in Figures 6.2-1 through -6. The data for the COALITE correlations are shown on the figures for reference purposes. Cross-correlations of key HEDF properties vs aromatics contents are depicted in Figures 6.2-7 and -8. Cross-correlations of key HEDF properties vs Refractive Index are shown in Figures 6.2-9 through -11.

Unlike the MCG liquids, the Colorado shale oil distillates are less concentrated in the cyclics and more concentrated in the aliphatic materials as seen in the table below:

	<u>Colo. Shale Oil</u>	<u>COALITE</u>
% Olefins	39.9	11.8
% Saturates (cyclic+aliphatic)	32.9	<13.7
%Aromatics	27.2	>74.5

The COALITE olefins are primarily cyclic in structure, e.g., cyclooctene, cyclodecene, whereas the shale-derived olefins are

TABLE 6.2-1A 1 of 2

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COLORADO SHALE OIL

HYDROTREATING TESTS

CATALYST: K-599 (1ST STAGE) / MO-1230 (2ND STAGE)

FILE ID: REPTSE2.WK1

TEST # (FB-)	148	149	150	151	152	153	154	155
DATE (1989)	05-24	05-25	05-25	05-25	05-26	05-26	05-26	05-26
START TIME	16:00	00:00	08:00	16:00	00:00	08:00	16:30	20:00
END TIME	20:00	04:00	12:00	20:00	04:00	12:00	17:30	21:00
FEEDSTOCK	A	A	A	A	A	A	A	A
% HDS								
% HDN								
% HDI								
HC UPTAKE, scf/bbl	9000	9000	9000	9000	9000	9000	9000	9000
% F.I.A. OLEFINS SATURATION								
% F.I.A. AROMATICS SATURATION								
API IMPROVEMENT	7.3	8.3	10.1	11.5	7.0	5.3	5.6	5.6
R.I. DEPRESSION	0.0167	0.0161	0.0176	0.0194	0.0115	0.0109	0.0097	0.0131
EST. HEAT OF REACTION, Btu/lb								

FEEDSTOCK TYPE:

A: 355-618 F VIRGIN COLORADO SHALE OIL DISTILLATE.

TABLE 6.2-1A 2 of 2

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COLORADO SHALE OIL

HYDROTREATING TESTS

CATALYST: K-599 (1ST STAGE) / MO-1230 (2ND STAGE)

FILE ID: REPTSE2.WK1

TEST # (FB-)	159	160	161	162	163	164
DATE (1989)	06-05/06	06-06/07	06-08	06-08	06-08	06-09
START TIME	16:00	18:00	00:00	08:00	16:00	00:00
END TIME	16:00	18:00	06:00	14:15	22:00	06:00
FEEDSTOCK	A	A	B	B	C	C
% HDS						
% HDN						
% POC						
CO UPTAKE, scf/bbl	9000	9000	7000	7000	7000	7000
% F.I.A. OLEFINS SATURATION						
% F.I.A. AROMATICS SATURATION						
API IMPROVEMENT	7.3	6.5	9.5	12.6	12.5	9.0
F.I. DEPRESSION	0.0145	0.0143	0.0249	0.0355	0.0349	0.0241
EST. HEAT OF REACTION, Btu/lb						

FEEDSTOCK TYPE:

A: 355-618 F VIRGIN COLORADO SHALE OIL DISTILLATE.

E: LIQUID PRODUCT FROM FE-159.

C: LIQUID PRODUCT FROM FB-160.

TABLE 6.2-1B 1 of 2

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COLORADO SHALE OIL PRODUCTS

FROM FIXED-BED HYDROTREATING

CATALYST: K-550 (1ST STAGE) / MO-1230 (2ND STAGE)

TEST # (FB-)	FILE ID: REPTSP2.WK1							
	148	149	150	151	152	153	154	155
DATE (1989)	05-24	05-25	05-25	05-25	05-26	05-26	05-26	05-26
START TIME	16:00	00:00	08:00	16:00	00:00	08:00	16:30	20:00
END TIME	20:00	04:00	12:00	20:00	04:00	12:00	17:30	21:00
FEEDSTOCK	A	A	A	A	A	A	A	A
SPECIFIC GRAVITY, gm/cc	0.8304	0.8256	0.8170	0.8104	0.8319	0.8403	0.8388	0.8378
API GRAVITY @ 60 F	38.9	39.9	41.7	43.1	38.6	36.9	37.2	37.4
REFRACTIVE INDEX @ 20 C	1.4618	1.4624	1.4609	1.4591	1.4670	1.4676	1.4688	1.4654
ELEMENTALS, wt%								
C	86.04	86.10	86.41	86.43	85.95	85.68	85.71	86.17
H	13.75	13.66	13.52	13.26	13.29	13.38	13.28	13.63
SIMULATED DISTILLATION, F								
100								
100 DISTILLED								
300								
500								
700								
900								
VOLUM. AVG. BOIL. PT., F								
WATSON K								
F.I.A. ANALYSIS, vol%								
OLEFINS	0.6	0.5	0.7	0.6	1.7	3.9	10.1	3.7
SATURATES	75.6	73.2	71.1	68.3	71.3	68.2	62.4	75.3
AROMATICS	23.8	26.3	28.2	30.9	27	27.9	27.5	20.9
WCHN, Btu/lb	15433		18129	18201	18090			
VLHV, Btu/gal	106767		123379	122868	125359			
FLASH PT., F								
SMOKE PT., mm								
FREZE PT., F								
ANILINE PT., F								
CETANE INDEX								
VISCOSITY, cSt @ 100 F								

FEEDSTOCK TYPE:

A: 355-618 F VIRGIN COLORADO SHALE OIL DISTILLATE.

TABLE 6.2-1B 2 of 2

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COLORADO SHALE OIL PRODUCTS

FROM FIXED-BED HYDROTREATING

CATALYST: CATALYST: K-550 (1ST STAGE) / MO-1230 (2ND STAGE)

FILE ID: REPTSP2.WK1

TEST # (FB-)	159	160	161	162	163	164
DATE (1989)	06-05/06	06-06/07	06-08	06-08	06-08	06-09
START TIME	16:00	18:00	00:00	08:00	16:00	00:00
END TIME	16:00	18:00	06:00	14:15	22:00	06:00

FEEDSTOCK	A	A	B	B	C	C
SPECIFIC GRAVITY, gm/cc	0.8304	0.8343	0.8198	0.8054	0.8058	0.8222
API GRAVITY @ 60 F	38.9	38.1	41.1	44.2	44.1	40.6
REFRACTIVE INDEX @ 20 C	1.4640	1.4642	1.4536	1.4430	1.4436	1.4544

ELEMENTAL, WT%

C	86.36	86.05	86.32	85.72	86.00	85.87
H	13.64	13.70	14.32	14.57	14.80	14.87

SIMULATED DISTILLATION, F

18%
10% DISTILLED
30%
50
70%
90%

VOL. AVG. BOIL. PT. F
WATSON X

P.L.A. ANALYSIS, VOL%

OLEFINS	1.9	3.0	0.0	1.2	2.3	2.3
SATURATES	74.9	75.1	91.7	90.0	74.4	82.8
AROMATICS	23.2	21.9	8.3	7.9	23.3	14.9

WLV, Btu/lb
VLHV, Btu/gal

FLASH PT., F
SMOKE PT., °R
FREEZE PT., F
ANILINE PT., F
CETANE INDEX
VISCOSITY, cst @ -4 F

FEEDSTOCK TYPE:

A: 355-618 F VIRGIN COLORADO SHALE OIL DISTILLATE.
B: LIQUID PRODUCT FROM FB-159.
C: LIQUID PRODUCT FROM FB-160.

TABLE 6.2-2A 1 of 3

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COLORADO SHALE OIL

HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE) / K-599 (2nd STAGE)

FILE ID: REPTSE1.WK1

TEST # (FB-)	106	107	108	109	110	111	112	113
DATE (1989)	04-11	04-11/12	04-12	04-12	04-12	04-13	04-13	04-13
START TIME	17:30	23:30	05:30	11:30	18:30	00:30	06:30	13:00
END TIME	19:30	01:30	07:30	13:30	20:30	02:30	08:30	15:00
FEEDSTOCK	A	A	A	A	A	A	A	A
% HDS								
% HDN								
% HDC								
H ₂ UPTAKE, scf/bbl	7000	7000	7000	7000	7000	7000	7000	7000
% F.I.A. OLEFINS SATURATION								
% F.I.A. AROMATICS SATURATION								
API IMPROVEMENT	6.0	8.8	10.6	11.7	9.2	11.8	11.2	11.5
F.I. DEPRESSION	0.0169	0.0242	0.0303	0.0333	0.0256	0.0340	0.0321	0.0322
EST. HEAT OF REACTION, Btu/lb								

FEEDSTOCK TYPE:

A: 355-618 F VIRGIN COLORADO SHALE OIL DISTILLATE.

TABLE 6.2-2A 2 of 3

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COLORADO SHALE OIL

HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE) / K-599 (2nd STAGE)

FILE ID: REPTSE1.WK1

TEST # (FB-)	114	115	116	117	118	119	120	121
DATE (1989)	04-13	04-14	04-14	04-14	04-17	04-17	04-18	04-18
START TIME	22:00	04:00	10:00	16:00	06:30	12:30	19:30	01:30
END TIME	24:00	06:00	12:00	18:00	08:30	14:30	21:30	03:30
FEEDSTOCK	A	A	A	A	A	A	A	A
% HDS								
% HDN								
% HDI								
HC UPTAKE, scf/bbl	7000	7000	7000	7000	7000	7000	7000	7000
% F.I.A. OLEFINS SATURATION								
% F.I.A. AROMATICS SATURATION								
API IMPROVEMENT	5.6	7.8	9.6	10.4	8.4	10.5	13.0	14.3
F.I. DEPRESSION	0.0163	0.0223	0.0269	0.0292	0.0228	0.0298	0.0359	0.0395
EST. HEAT OF REACTION, Btu/lb								

FEEDSTOCK TYPE:

K-550-610 F VIRGIN COLORADO SHALE OIL DISTILLATE.

TABLE 6.2-2A 3 of 3

SUMMARY OF OPERATING RESULTS FOR FIXED-BED COLORADO SHALE OIL

HYDROTREATING TESTS

CATALYST: K-550 (1ST STAGE) / K-599 (2nd STAGE)

FILE ID: REPTSE1.WK1

TEST # (FE-1)	122	123	124	125	128	129	130
DATE (1989)	04-18	04-18	04-16	04-19	04-19/20	04-20/21	04-21
START TIME	07:30	13:30	19:30	01:30	18:30	12:30	07:30
END TIME	09:30	15:30	21:30	03:30	09:30	03:30	21:00
FEEDSTOCK	A	A	A	A	A	A	A
% HDS							
% HDN							
% HDI							
H ₂ UPTAKE, scf/bbl	7000	7000	7000	7000	7000	7000	7000
% F.I.L. OLEFINS SATURATION							
% F.I.L. AROMATICS SATURATION							
API IMPROVEMENT	13.1	9.3	10.3	8.3	10.3	13.6	9.7
F.I. DEPRESSION	0.0370	0.0345	0.0285	0.0225	0.0286	0.0381	0.0269
EST. HEAT OF REACTION, Btu/lb							

FEEDSTOCK TYPE:

A: 355-618 ° VIRGIN COLORADO SHALE OIL DISTILLATE.

TABLE 6.2-2B 1 of 3

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COLORADO SHALE OIL PRODUCTS

FROM FIXED-BED HYDROTREATING

CATALYST: K-550 (1ST STAGE) / K-599 (2ND STAGE)

FILE ID: REPTSP1.WK1

TEST # (FB-)	106	107	108	109	110	111	112	113
DATE (1989)	04-11	04-11/12	04-12	04-12	04-12	04-13	04-13	04-13
START TIME	17:30	23:30	05:30	11:30	18:30	00:00	06:30	13:00
END TIME	19:30	01:30	07:30	13:30	20:30	02:30	08:30	15:00
FEEDSTOCK	A	A	A	A	A	A	A	A
SPECIFIC GRAVITY, gm/cc	0.8368	0.8232	0.8146	0.8095	0.8212	0.8090	0.8118	0.8104
API GRAVITY @ 60 F	37.6	40.4	42.2	43.3	40.8	43.4	42.8	43.1
REFRACTIVE INDEX @ 20 C	1.4616	1.4543	1.4482	1.4452	1.4529	1.4445	1.4464	1.4463
ELEMENTALS, wt%								
C	85.70	85.80	85.60	85.43	85.80	85.42	84.86	85.08
H	13.62	14.21	14.47	14.62	14.26	14.62	14.50	14.50
SIMULATED DISTILLATION, F								
10%								
10% DISTILLED								
30%								
50%								
70%								
90%								
VOLUM. AVG. BOIL. PT., F								
WATSON								
F.I.A. ANALYSIS, vol%								
OLEFINS	1.8	1.0	1.1	0.8	0.9	0.6	0.6	0.5
SATURATES	76.8	84.7	90.8	93.0	83.7	94.6	89.9	93.6
AROMATICS	21.4	14.3	8.1	6.2	15.4	4.8	9.3	7.9
Wt.%, Btu/lb	18358	18471	18169	18639				
Wt.%, Btu/gal	127965	126660	123288	125685				
FLASH PT., F								
SMOKE PT., F	25	25	35	35	30	35	35	30
FREZE PT., F								
ANILINE PT., F								
CETANE INDEX								
VISCOSITY, cSt @ 100 F								

FEEDSTOCK TYPE:

A: 355-618 F VIRGIN COLORADO SHALE OIL DISTILLATE.

TABLE 6.2-2B 2 of 3

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COLORADO SHALE OIL PRODUCTS

FROM FIXED-BED HYDROTREATING

CATALYST: K-550 (1ST STAGE) / K-599 (2ND STAGE)

	FILE ID: REPTSP1.WK1							
	114	115	116	117	118	119	120	121
DATE (1989)	04-13	04-14	04-14	04-14	04-17	04-17	04-18	04-18
START TIME	22:00	04:00	10:00	16:00	06:30	12:30	19:30	01:30
END TIME	24:00	06:00	12:00	18:00	08:30	14:30	21:30	03:30
FEEDSTOCK	A	A	A	A	A	A	A	A
SPECIFIC GRAVITY, gm/cc	0.8388	0.8280	0.8193	0.8156	0.8251	0.8151	0.8035	0.7976
API GRAVITY @ 60 F	37.2	39.4	41.2	42.0	40.0	42.1	44.6	45.9
REFRACTIVE INDEX @ 20 C	1.4622	1.4567	1.4516	1.4452	1.4557	1.4487	1.4426	1.439
ELEMENTALS, wt%								
C	84.81	85.29	85.41	85.04	85.61	85.37	85.03	8.95
H	13.61	13.96	14.15	14.42	13.96	14.31	14.62	14.87
SIMULATED DISTILLATION, %								
18%	242							
10% DISTILLATE	391							
50%	448							
50%	503							
70%	563							
90%	626							
VOLUM. AVG. BOIL. PT., F	507							
WATSON K	10.71							
ANAL. ANALYSIS, %vol								
OLEFINS	1.1	0.6	0.8	0.6	0.6	0.5	0.3	0.3
SATURATES	79.6	82.0	84.7	89.1	82.4	89.6	93.6	96.7
AROMATICS	19.0	17.4	14.5	10.3	17.0	9.9	5.9	3.0
WLV, Btu/lb	18320	16431	18497	18587				
VLHV, Btu/gal	128006	127123	126238	126279				
FLASH PT., F	110							
SMOKE PT., °F	30	30	40	40	35			
FREZE PT., F	-0.4							
ANILINE PT., F								
CETANE INDEX								
VISCOSITY, cSt @ 40 F								

FEEDSTOCK TYPE:

A: 355-618 F VIRGIN COLORADO SHALE OIL DISTILLATE.

TABLE 6.2-2B 3 of 3

SUMMARY OF PROPERTIES OF FULL-RANGE HYDROTREATED COLORADO SHALE OIL PRODUCTS

FROM FIXED-BED HYDROTREATING

CATALYST: K-550 (1ST STAGE) / K-599 (2ND STAGE)

FILE ID: REPTSP1.WK1

TEST # (FB-)	122	123	124	125	128	129	130
DATE (1989)	04-18	04-18	04-18	04-19	04-19/20	04-20/21	04-21
START TIME	07:30	13:30	19:30	01:30	18:30	12:30	07:30
END TIME	09:30	15:30	21:30	03:30	09:30	03:30	21:00
FEEDSTOCK	A	A	A	A	A	A	A
SPECIFIC GRAVITY, gm/cc	0.8026	0.8207	0.8160	0.8256	0.8160	0.8008	0.8189
API GRAVITY @ 60 F	44.8	40.9	41.9	39.9	41.9	45.2	41.3
REFRACTIVE INDEX @ 20 C	1.4415	1.4440	1.4500	1.4560	1.4497	1.4404	1.4516
ELEMENTAL, wt%							
C	85.07				85.89	85.55	85.25
H	14.77				14.35	14.76	14.31
SIMULATED DISTILLATION, F							
IBP							197
10% DISTILLED							371
30%							431
50%							484
70%							541
90%							606
VOLUM. AVE. BOIL. PT., F							467
WATSON K							11.91
P.L.A. ANALYSIS, 1vol%							
OLEFINS	0.3	0.5	0.7	0.9	0.7	0.5	0.7
SATURATES	96.1	95.1	88.4	78.6	86.0	95.7	83.5
AROMATICS	3.6	4.4	10.9	20.5	13.3	3.8	15.8
WLMV, Btu/lb					18516	18430	18200
WLMV, Btu/gal					125872	122940	124150
FLASH PT., F							90
SMOKE PT., mm							
FREZE PT., F							6.8
ANILINE PT., F							
CETANE INDEX							
VISCOSITY, cst @ -4 F							

FEEDSTOCK TYPE:

A: 355-618 F VIRGIN COLORADO SHALE OIL DISTILLATE.

TABLE 6.2-3A

SUMMARY OF OPERATING RESULTS OF FIXED-BED HYDROTREATED PRODUCTS FROM

HYDROPROCESSED COLORADO SHALE OIL DISTILLATE

CATALYST: K-550 (1ST STAGE), K-599 (2ND STAGE)

FILE ID: REPTSLC2.MK1

TEST # (FB-)	186	187
DATE (1989)	08-22/23	08-23/25
START TIME	18:00	18:00
END TIME	18:00	17:00
FEEDSTOCK	A	A
% HDS		
% HDN		
% HDC		
H2 UPTAKE, scf/bbl	7000	7000
% F.I.A. OLEFINS SATURATION		
% F.I.A. AROMATICS SATURATION		
API IMPROVEMENT	7.0	7.7
R.I. DEPRESSION		
EST. HEAT OF REACTION, Btu/lb		

FEEDSTOCK TYPE:

A: 575-1000 F HYDROPROCESSED COLORADO SHALE OIL DISTILLATE.

TABLE 6.2-3B

SUMMARY OF PROPERTIES OF FIXED-BED HYDROTREATED PRODUCTS FROM

HYDROPROCESSED COLORADO SHALE OIL DISTILLATE

CATALYST: K-550 (1ST STAGE), K-599 (2ND STAGE)

FILE ID: REPTSLC3.WK1

TEST # (FB-)	186	187
DATE (1989)	08-22/23	08-23/25
START TIME	18:00	18:00
END TIME	18:00	17:00
FEEDSTOCK	A	A
SPECIFIC GRAVITY, gm/cc	0.8644	0.8612
API GRAVITY @ 60 F	32.2	32.8
REFRACTIVE INDEX @ 20 C		
ELEMENTALS, wt%		
C	86.47	86.41
H	14.04	13.65
SIMULATED DISTILLATION, F		
IBP		
10% DISTILLED		
30%		
50%		
70%		
90%		
VOLUM. AVG. BOIL. PT., F		
WATSON K		
S.I.A. ANALYSIS, 1vol%		
OLIFINS		
SATURATES		
AROMATICS		
WLHV, Btu/lb		
VLHV, Btu/gal		
FLASH PT., F		
SMOKE PT., °		
FREEZE PT., F		
ANILINE PT., F		
CETANE INDEX		
VISCOSITY, cst @ -4 F		

FEEDSTOCK TYPE:

A: 575-1000 F HYDROPROCESSED COLORADO SHALE OIL DISTILLATE.

TABLE 6.2-4A

SUMMARY OF OPERATING RESULTS OF FIXED-BED HYDROTREATED PRODUCTS FROM

HYDROPROCESSED COLORADO SHALE OIL DISTILLATE

CATALYST: K-599 (2ND STAGE)

FILE ID: REPTSLC2.WK1

TEST # (FB-)	143	144	145
DATE (1989)	05-15/16	05-16	05-16
START TIME	22:30	04:30	10:30
END TIME	00:30	06:30	12:30
FEEDSTOCK	A	A	A
% HDS			
% HDN			
% HDO			
H ₂ UPTAKE, scf/bbl	7000	7000	7000
% F.I.A. OLEFINS SATURATION			
% F.I.A. AROMATICS SATURATION			
API IMPROVEMENT	8.0	9.0	8.7
R.I. DEPRESSION	0.0250	0.0267	0.0235
EST. HEAT OF REACTION, Btu/lb			

FEEDSTOCK TYPE:

A: 300-575 F HYDROPROCESSED COLORADO SHALE OIL DISTILLATE.

TABLE 6.2-4B

SUMMARY OF PROPERTIES OF FIXED-BED HYDROTREATED PRODUCTS FROM

HYDROPROCESSED COLORADO SHALE OIL DISTILLATE

CATALYST: K-599 (2ND STAGE)

FILE ID: REPTSLC3.WK1

TEST # (FB-)	143	144	145
DATE (1989)	05-15/16	05-16	05-16
START TIME	22:30	04:30	10:30
END TIME	00:30	06:30	12:30
FEEDSTOCK	A	A	A
SPECIFIC GRAVITY, gm/cc	0.8114	0.8067	0.8081
API GRAVITY @ 60 F	42.9	43.9	43.6
REFRACTIVE INDEX @ 20 C	1.4465	1.4448	1.4480
ELEMENTALS, wt%			
C	85.61	85.59	86.06
H	14.44	14.49	14.13
SIMULATED DISTILLATION, F			
IBP			
10% DISTILLED			
30%			
50%			
70%			
90%			
VOLUM. AVG. BOIL. PT., F			
WATSON K			
F.I.A. ANALYSIS, 1vol%			
OLIFINS	0.5	0.4	0.3
SATURATES	91.9	91.6	81.3
AROMATICS	7.6	8.0	18.4
WLHV, Btu/lb	18401	18552	18400
VLHV, Btu/gal	124372	124666	123859
FLASH PT., F			
SMOKE PT., °F			
FREEZE PT., F			
ANILINE PT., F			
CETANE INDEX			
VISCOSITY, cst @ -4 F			

FEEDSTOCK TYPE:

A: 575-1000 F HYDROPROCESSED COLORADO SHALE OIL DISTILLATE.

TABLE 6.2-5A

SUMMARY OF OPERATING RESULTS FOR FIXED-BED

COLORADO SHALE OIL HYDROCRACKING TESTS

CATALYST: AMOCO PROPRIETARY

TEST # (FBHC-)	FILE ID: REPTSHCS.WK1							
	28	29	30	31	32	33	34	35
DATE (1989)	08-16	08-17	08-17/18	08-18/21	08-28/29	08-29/30	08-30/31	08-31/09-01
START TIME	06:00	00:00	12:00	13:00	21:00	20:00	20:00	12:00
END TIME	08:00	08:00	08:00	20:00	18:00	18:00	12:00	21:00
FEEDSTOCK	A	A	A	A	B	B	B	B
% HDS								
% HDN	73		84	90				
% HDI								
H ₂ UPTAKE, scf/bbl	7000	7000	7000	7000	7000	6000	6000	6000
% F.I.A. OLIFINS SATURATION								
% F.I.A. AROMATICS SATURATION								
API IMPROVEMENT	6.2	5.6	6.6	9.8	3.9	3.1	1.9	4.4
P.I. DEPRESSION								
EST. HEAT OF REACTION, Btu/lb								

FEEDSTOCK TYPE:

A: 575-1000 F HYDROPROCESSED COLORADO SHALE OIL DISTILLATE .
 B: 575-1000 F, HYDROPROCESSED COLORADO SHALE OIL DISTILLATE
 FOLLOWED BY FIXED-BED HYDROTREATING.

TABLE 6.2-5B

SUMMARY OF PROPERTIES OF HYDROCRACKATES FROM FIXED-BED

COLORADO SHALE OIL HYDROCRACKING

CATALYST: AMOCO PROPRIETARY

TEST # (FBHC-)	FILE ID: REPTSHC6.WK1							
	28	29	30	31	32	33	34	35
DATE (1989)	08-16	08-17	08-17/18	08-18/21	08-28/29	08-29/30	08-30/31	08-31/09-01
START TIME	06:00	00:00	12:00	13:00	21:00	20:00	20:00	12:00
END TIME	08:00	08:00	08:00	20:00	18:00	18:00	12:00	21:00
FEEDSTOCK	A	A	A	A	B	B	B	B
SPECIFIC GRAVITY, gm/cc	0.8686	0.8718	0.8665	0.8499	0.8424	0.8461	0.8523	0.8398
API GRAVITY @ 60 F	31.4	30.8	31.8	35.0	36.5	35.7	34.5	37.0
REFRACTIVE INDEX @ 20 C								
ELEMENTALS, wt %								
C	86.23		86.36	86.07	85.38	85.41	85.43	85.37
H	13.42		13.87	14.21	14.38	14.56	14.30	14.42
DISTILLATION (ASTM D-1160), F								
IBP	319		316	311	275	311	315	304
10% DISTILLED	572		532	456	449	478	520	447
30%	646		630	573	622	615	624	602
50%	710		690	659	694	684	686	670
70%	783		762	737	778	766	763	763
90%	805		858	838	893		858	
VOLUM. AVG. BOIL. PT. F	719		694	653	687	636	690	621
WATSON A	12.05		12.04	12.12	12.35	12.11	12.22	12.14
WLMV, BTU/lb								
VLHV, BTU/gal								

FEEDSTOCK TYPE:

A: 575-1000 F, HYDROPROCESSED COLORADO SHALE OIL DISTILLATE.

B: 575-1000 F, HYDROPROCESSED COLORADO SHALE OIL DISTILLATE
FOLLOWED BY FIXED-BED HYDROTREATING.

TABLE 6.2-6A

SUMMARY OF OPERATING RESULTS FOR FIXED-BED

COLORADO SHALE OIL HYDROCRACKING TESTS

CATALYST: ANOCO PROPRIETARY

FILE ID: REPTSHC2.WK1

TEST # (FBHC-)	5	6	7	8	9	10	11	12
DATE (1989)	05-01	05-01	05-01	05-01	05-02	05-02	05-02	05-03
START TIME	07:30	13:30	19:30	01:30	07:30	13:30	19:30	04:30
END TIME	09:30	15:30	21:30	03:30	09:30	15:30	24:30	09:30
FEEDSTOCK	A	A	A	A	A	A	A	A
% HDS								
% HDN								
% HDG								
H ₂ UPTAKE, scf/bbl	7000	7000	7000	7000	7000	7000	7000	7000
% F.I.A. OLIFINS SATURATION								
% F.I.A. AROMATICS SATURATION								
API IMPROVEMENT	5.6	9.4	7.1	4.6	8.5	11.2	11.4	14.5
R.I. DEPRESSION								
EST. HEAT OF REACTION, Btu/lb								

FEEDSTOCK TYPE:

A: 650-975 F COLORADO SHALE OIL VGO.

TABLE 6.2-6B

SUMMARY OF PROPERTIES OF HYDROCRACKATES FROM FIXED-BED

COLORADO SHALE OIL HYDROCRACKING

CATALYST: AMOCO PROPRIETARY

FILE ID: REPTSHC3.WK1

TEST # (FBHC-)	5	6	7	8	9	10	11	12
DATE (1989)	05-01	05-01	05-01	05-01	05-02	05-02	05-02	05-03
START TIME	07:30	13:30	19:30	01:30	07:30	13:30	19:30	05:30
END TIME	09:30	15:30	21:30	03:30	09:30	15:30	24:30	09:30
FEEDSTOCK	A	A	A	A	A	A	A	A
SPECIFIC GRAVITY, gm/cc	0.9141	0.8922	0.9053	0.9200	0.8973	0.8822	0.8811	0.8644
API GRAVITY @ 60 F	23.3	27.1	24.8	22.3	26.2	28.9	29.1	32.2
REFRACTIVE INDEX @ 20 C								
ELEMENTALS, wt %								
C								86.4
H								13.75
SIMULATED DISTILLATION, F								
IBP	273	249	263	321	249	269	242	
10% DISTILLED	581	516	578	654	522	466	483	
30%	729	701	736	757	709	657	673	
50%	788	773	796	811	778	753	759	
70%	843	832	851	862	838	817	825	
90%	918	911	932	943	921	903	910	
VOLUM. AVG. BOIL. PT. F	772	747	779	805	754	719	730	
WATSON F	11.66	11.87	11.80	11.69	11.82	11.91	11.96	
WLV, Btu/lb								
VLHV, Btu/gal								

FEEDSTOCK TYPE:

A: 650-975 F COLORADO SHALE OIL VGO.

FIGURE 6.2-1

HYDROTREATING SEVERITY VS. VLHV FOR COAL & SHALE-DERIVED JET FUELS

FIGURE 6.2-2

HYDROTREATING SEVERITY VS. FIA AROMATICS ANALYSIS FOR COAL & SHALE-DERIVED JET FUELS

HYDROTREATING SEVERITY, $10000 \cdot P / LHSV \cdot e(-35000/RT)$

FIGURE 6.2-3

HYDROTREATING SEVERITY VS. HYDROGEN CONTENT FOR COAL & SHALE-DERIVED JET FUELS

FIGURE 6.2-4

HYDROTREATING SEVERITY VS. API GRAVITY FOR COAL AND SHALE-DERIVED JET FUELS

HYDROTREATING SEVERITY, $10000 \cdot P / LHSV \cdot e(-35000/RT)$

FIGURE 6.2-5

HYDROTREATING SEVERITY VS. SMOKE POINT FOR COAL & SHALE-DERIVED JET FUELS

HYDROTREATING SEVERITY, $10000 \cdot P / LHSV \cdot e(-35000/RT)$

FIGURE 6.2-6

HYDROTREATING SEVERITY VS. REFRACTIVE INDEX FOR COAL & SHALE-DERIVED JET FUELS

HYDROTREATING SEVERITY, $10000 \cdot P / \text{LHSV} \cdot e^{(-35000/RT)}$

FIGURE 6.2-7

EFFECT OF AROMATICS ON VOLUMETRIC LHV OF COAL & SHALE-DERIVED JET FUELS

F.I.A. AROMATICS CONTENT, Vol%

FIGURE 6.2-8

EFFECT OF AROMATICS ON SMOKE POINT OF COAL & SHALE-DERIVED TURBINE FUELS

F.I.A. AROMATICS CONTENT, |vol|%

FIGURE 6.2-9

API GRAVITY VS REFRACTIVE INDEX FOR COAL & SHALE-DERIVED DISTILLATES

FIGURE 6.2-10

SMOKE POINT VS REFRACTIVE INDEX OF COAL & SHALE-DERIVED JET FUELS

REFRACTIVE INDEX @ 20C

FIGURE 6.2-11

DISTILLATE HYDROGEN CONTENT VS REFRACTIVE INDEX FOR COAL & SHALE-DERIVED JET FUELS

primarily aliphatic, e.g., n-octene/iso-octene, n-decene/iso-decene. The saturates types, naphthenes vs. paraffins, for these raw synfuels were not readily differentiated by the sulfonation/R.I. technique.

For the case of the Colorado shale oil, the raw 300-600F distillate had a volumetric heat content of only about 127 KBtu/gal, some 3000 Btu/gal below the target. Upon hydrotreatment as seen in Figure 6.2-7, the volumetric energy content decreases significantly away from the target. Thus, the K-550 NiWS and K-599 NiMo catalysts do not appear to have the right functionality to preserve and/or form the desirable cyclic structures. It may be possible to obviate this situation by extending the end point of the distillates beyond 600F and the initial point beyond 300F in order to increase the concentration of the denser 2- and 3-ring cyclics.

One possible alternative to nickel-based aromatics saturation is the use of selective hydroisomerization (or aromatization or reforming) catalysts to reform aliphatics into the desirable aromatic precursor structures. The product of this operation would then be subjected to the nickel-based aromatics saturation catalysts thereby generating the naphthenic-rich HEDF fuels. Current state-of-the-art reforming catalysts are based on noble metals such as platinum, rhenium, palladium, etc. However, these catalysts are extremely sensitive to poisons, e.g., sulfur and nitrogen, and therefore cannot be used without a high severity pretreatment.

Prior to the advent of the noble metal catalysts, there was another family of reforming catalysts that was resistant to heteroatom contamination. These included chromia-alumina and molybdena-alumina catalysts. These catalysts are not as active as the noble metal catalysts and require higher operating severities to achieve comparable performance. A sample of a Harshaw Mo-1230 molybdena catalyst was obtained and used to evaluate the feasibility of this approach. A series of tests was made in the fixed-bed unit to screen the molybdena-based hydroisomerization of the 300-600F Colorado shale oil distillates. The hydroisomerizates were recovered and separately hydroprocessed over the K-599 nickel-moly catalyst to saturate aromatics, those originally present in the raw shale oil distillate as well as any produced during the molybdena reforming step. The data from the tests made did not however achieve the desired improvement. In fact, the highest volumetric energy density (125,359 Btu/gal) achieved was still lower than that achievable with the two-stage NiMo hydrotreating catalysts. Further improvements might be achieved by extending the distillate initial and end points to increase the content of the aromatics as well as the straight or branched chain aliphatics that might be more amenable to hydroisomerization.

6.3 Virgin Atmospheric Resid Cracking

Two campaigns of resid hydrocracking via LC-Fining technology were made and the results are summarized in Tables 6.3-1A,B for the virgin resid feedstock and Tables 6.3-2A,B for the hydroprocessed resid feedstock. One campaign of resid thermal cracking via delayed coking was completed and the results are summarized in Table 6.3-3A (operating results) and 6.3-3B (properties of coker distillate products).

TABLE 6.3-1A

SUMMARY OF OPERATING RESULTS FOR LC-FINING (HYDROCRACKING) TESTS

COLORADO SHALE OIL DISTILLATE

CATALYST: SHELL 324 (AGED)

FILE ID: REPTSBL2.WK1

TEST # (BLCF-)	89-1	89-2	89-3	89-4	89-5
DATE (1989)	03-06	03-07	03-07/08	03-08	03-09
START TIME	11:30	21:30	14:00	04:00	13:00
END TIME	26:30	12:00	02:00	13:00	01:30
FEEDSTOCK	A	A	A	A	A
% HD3					
% HD4					
% HD6					
H2 UPTAKE, scf/bbl	10000	10000	10000	10000	10000
API IMPROVEMENT					
R.I. REGRESSION					
EST. HEAT OF REACTION, Btu/lb					

FEEDSTOCK TYPE:

A: COLORADO SHALE OIL ATM RESID 650+ F.

TABLE 6.3-1B

SUMMARY OF PROPERTIES OF FULL-RANGE LC-FINATE TESTS

COLORADO SHALE OIL DISTILLATE

CATALYST: SHELL 324 (AGED)

FILE ID: REPTSBL3.WK1

TEST # (BLCF-)	89-1	89-2	89-3	89-4	89-5
DATE (1989)	03-06	03-07	03-07/08	03-08	03-09
START TIME	11:30	21:30	14:00	04:00	13:00
END TIME	20:30	12:30	02:00	13:00	01:30
FEEDSTOCK	A	A	A	A	A
SPECIFIC GRAVITY, gm/cc	0.9934	0.9911	0.8959	0.9094	0.9123
API GRAVITY @ 60F	10.9	11.3	26.4	24.1	23.6
REFRACTIVE INDEX @ 20C					
ELEMENTALS, wt%					
C	85.11	85.63	85.56	85.74	85.72
H	11.6	11.92	12.0	11.86	11.77
SIMULATED DISTILLATION, F					
IBP	196	175	157	160	168
10% Distilled	436	391	344	351	376
30%	665	574	510	517	540
50%	765	716	642	653	677
70%	836	796	748	754	771
90%	929	899	855	858	875
VOLUP. AVG. BOIL. PT., F	727	675	620	627	648
WATSON	10.6	10.5	11.4	11.2	11.3
WLHV, Btu/lb					
VLHV, Btu/gal					

FEEDSTOCK TYPE:

A: COLORADO SHALE OIL ATM RESID 650+ F.

TABLE 6.3-2A

SUMMARY OF OPERATING RESULTS FOR LC-FINING (HYDROCRACKING) TESTS

COLORADO SHALE OIL DISTILLATE

CATALYST: SHELL 324 (AGED)

FILE ID: REPTSBL2.WK1

TEST # (BLCF-)	91	96	97	98	99
DATE (1989)	04-05	04-12/13	04-13	04-13/14	04-14
START TIME	18:00	20:00	08:00	20:00	12:00
END TIME	24:00	04:00	16:00	08:00	20:00
FEEDSTOCK	B	B	B	B	B
% HDS					
% HDN					
% HDG					
H ₂ UPTAKE, scf/bbl	7500	10000	10000	10000	10000
API IMPROVEMENT					
F.I. REGRESSION					
EST HEAT OF REACTION, Btu/lb					

FEEDSTOCK TYPE:

B: HYDROPROCESSED COLORADO SHALE OIL DISTILL RESID, 575+ F.

TABLE 6.3-2B

SUMMARY OF PROPERTIES OF FULL-RANGE LC-FINATE TESTS

COLORADO SHALE OIL DISTILLATE

CATALYST: SHELL 324 (AGED)

FILE ID: REPTSBL3.WK1

TEST # (BLCF-)	91	96	97	98	99
DATE (1989)	04-05	04-12/13	04-13	04-13/14	04-14
START TIME	18:00	20:00	08:00	20:00	12:00
END TIME	24:00	04:00	16:00	08:00	20:00
FEEDSTOCK	B	B	B	B	B
SPECIFIC GRAVITY, gm/cc	0.9123	0.9267	0.9188	0.9170	0.9371
API GRAVITY @ 60F	23.6	21.2	22.5	22.8	19.5
REFRACTIVE INDEX @ 20C					

ELEMENTALS, wt%

C

H

SIMULATED DISTILLATION, F

16P

10% Distilled

30%

50%

70%

90%

VOLUM. AVG. BOIL. PT., F

WATSON

Wt.%, Btu/lb

Vt.%, Btu/gal

FEEDSTOCK TYPE:

B: HYDROPROCESSED COLORADO SHALE OIL DISTILL RESID, 575+ F.

C: COALITE DISTILLATE, 300+ F.

TABLE 6.3-3A

SUMMARY OF OPERATING RESULTS ON HYDROTREATED PRODUCTS FROM FIXED-BED HYDROTREATING OF

THERMALLY PROCESSED COLORADO SHALE OIL DISTILLATE

CATALYST: K-550 (1ST STAGE) K-599 (2ND STAGE)

FILE ID: REPTSC3.WK1

TEST # (FB-)	131	132	133	134
DATE(1989)	04-24	04-24	04-24	04-25
START TIME	10:00	16:00	21:00	01:30
END TIME	12:00	18:00	22:30	03:00
FEEDSTOCK	A	A	A	A
% HDS				
% HDN				
% HDC				
H ₂ UPTAKE, scf/bbl	7000	7000	7000	7000
% F.I.A. OLEFINS SATURATION				
% F.I.A. AROMATICS SATURATION				
API IMPROVEMENT	11.9	12.4	8.9	9.60
R.I. DEPRESSION	0.0364	0.0374	0.0260	0.03
EST. HEAT OF REACTION, Btu/lb				

FEEDSTOCK TYPE:

A: THERMALLY PROCESSED COLORADO SHALE OIL DISTILLATE, 300-575 F.

TABLE 6.3-3B

SUMMARY OF PROPERTIES OF HYDROTREATED PRODUCTS FROM FIXED-BED HYDROTREATING OF

THERMALLY PROCESSED COLORADO SHALE OIL DISTILLATE

CATALYST: K-550 (1ST STAGE) K-599 (2ND STAGE)

FILE ID:REPTSC2.WK1

TEST # (FB-)	131	132	133	134
DATE(1989)	04-24	04-24	04-24	04-25
START TIME	10:00	16:00	21:00	01:30
END TIME	12:00	18:00	22:30	03:00
FEEDSTOCK	A	A	A	A
SPECIFIC GRAVITY, gm/cc	0.8012	0.7990	0.8151	0.8118
API GRAVITY	45.1	45.6	42.1	42.8
REFRACTIVE INDEX @ 20 C	1.4416	1.4406	1.4520	1.4529
ELEMENTAL, wt. %				
C	85.47	85.54	86.04	85.61
H	14.50	14.53	13.89	13.65
DISTILLATION, F				
IBP				
10%				
50%				
50%				
70%				
90%				
VOLUM. VAC. BOIL. PT. F				
RATSON				
F.T.A. ANALYSIS, 1vol. %				
OLEFINS	0.5	0.3	0.5	0.30
SATURATES	91.1	91.7	76.4	75.50
AROMATICS	8.4	8.0	23.1	24.20
WLHV, btu/lb.		18283		18200
VLHV, btu/gal.		121686		123074
FLASH PT., F				
SMOKE PT., °F				
FREEZ. PT., F				
ANILINE PT., F				
VISCOSITY, cs @ -4 F				

FEEDSTOCK TYPE:

A: THERMALLY PROCESSED COLORADO SHALE OIL DISTILLATE, 300-575 F.

6.4 Cracked Distillate Hydrotreating

Only one test campaign was completed for the hydrotreating of cracked distillates. Tables 6.4-1A,B summarize the results for the tests made with a hydroprocessed distillate derived from fixed-bed hydrocracking of LC-Finate VGO.

6.5 Two-Stage Selective Hydrocracking of Vacuum Gas Oil (VGO)

Early Task studies demonstrated that volumetric energy densities for 300-600F raw Colorado shale oils after fixed-bed hydrotreating were limited to about 125,000 Btu/gal. While this value is some 5000 Btu/gal below the spec, it still represents a 5000-10,000 Btu/gal energy density premium above that of conventional jet fuels. Nevertheless, a campaign was initiated with the heavy (550F+) Colorado shale oil fraction following parallel processing routes that successfully generated a 132,000+ Btu/gal energy density HEDF from the 550F+ COALITE feedstock.

The selective hydrocracking route, as successfully implemented with the COALITE feedstock, basically consists of mild expanded-bed hydrofining (LC-Fining) of the 300F+ dewatered feed; fractionation to recover the 550-975F LC-Finate vacuum gas oil (VGO); selective hydrocracking of the VGO over the Amoco proprietary fixed-bed hydrocracking catalyst; and fixed-bed hydrogenation of the VGO hydrocrackate.

In the current campaign with the Colorado shale oil feedstock, the selective hydrocracking route followed the steps delineated below:

- o The whole (IBP to end point), undewatered Colorado shale oil was subjected to the mild LC-Fining (test BLCF-102) step. The water collected in the LC-Finate product receivers was phase separated by decanting. The LC-Finate full-range product was fractionated to generate a 575-975F VGO fraction for downstream hydrocracking/hydrogenation.
- o Since the nitrogen content of the LC-Finate VGO was still very high, ca., 15000 ppm, a subsequent fixed-bed hydrotreating (test FB-186/187) step using a NiW/NiMo two-stage catalyst system was used to reduce nitrogen content to 200 ppm.
- o The thus hydrotreated LC-Finate VGO was then subjected to fixed-bed hydrocracking (test FBHC-32/35) over the Amoco proprietary hydrocracking catalyst. The resultant full-range hydrocrackate was then subjected to fixed-bed hydrotreating (FB-188/189) over a NiW/NiMo two-stage catalyst system without fractionating out the unconverted 575-975F gas oil fraction.
- o The hydrogenated hydrocrackate was fractionated to recover a 275-550F HEDF product that met flash point and freeze point specs.

TABLE 6.4-1A

SUMMARY OF OPERATING RESULTS FOR FIXED-BED HYDROTREATING TESTS OF

HYDROCRACKED COLORADO SHALE OIL DISTILLATE

CATALYST: K-550 (1ST STAGE)/K-599 (2ND STAGE)

FILE ID: REPTSE3.WK1

TEST # (FE-)	188	189
DATE (1989)	09-05	09-05/07
START TIME	06:00	19:00
END TIME	15:00	13:00
FEEDSTOCK	A	A
% H ₂		
% H ₂ N		
% H ₂ O		
H ₂ UPTAKE, scf/dbl	8000	8000
% F.I.A. OLEFINS SATURATION		
% F.I.A. AROMATICS SATURATION		
API IMPROVEMENT		3.0
K.I. DEPRESSION		
EST HEAT OF REACTION, Btu/lb		

FEEDSTOCK TYPE:

A: CRACKED VIRGIN COLORADO SHALE OIL.
FROM THREE-STEPS, HYDROPROCESSED VIRGIN
COLORADO SHALE OIL FOLLOWED BY FIXED-BED
HYDROTREATING AND HYDROCRACKING.

TABLE 6.4-1B

SUMMARY OF PROPERTIES OF FIXED-BED HYDROTREATED PRODUCTS

FROM HYDROCRACKED COLORADO SHALE OIL DISTILLATE

CATALYST: K-550 (1ST STAGE)/K-599 (2ND STAGE)

FILE ID: REPTSP3

TEST # (FB-)	186	189
DATE (1989)	09-05	09-05/07
START TIME	06:00	19:00
END TIME	15:00	13:00

FEEDSTOCK	A	A
SPECIFIC GRAVITY, gm/cc		0.83
API GRAVITY @ 60 F		38.9
REFRACTIVE INDEX @ 20 C		

ELEMENTAL, wt. %

C
H

SIMULATED DISTILLATION, F

16%	19%
10% DISTILLED	41%
30%	58%
50%	66%
70%	74%
90%	84%

VOLUM. AVG. BOIL. PT., F	656
WATSON	0.26

F.I.A./F.I.L. 1 vol. %

OLEFINS
SATURATES
AROMATICS

W.P.V. BTU/lb.

V.P.V. BTU/lb.

FLASH PT., F

SMOKE PT., °F

FREEZ. PT., F

ANILINE PT., F

CETANE INDEX %

VISCOSITY, cP @ 100 F

FEEDSTOCK TYPE:

A: CRACKED COLORADO SHALE OIL DISTILLATE,
FROM THREE-STEPS, HYDROPROCESSED VIRGIN
COLORADO SHALE OIL FOLLOWED BY FIXED-BED
HYDROTREATING AND HYDROCRACKING.

The measured energy density of this latter product was still only about 125,000 Btu/gal, comparable to that generated when hydrotreating the raw 300-600F Colorado shale oil distillate. Thus, the selective hydrocracking of the 575F+ fraction of the Colorado shale oil did not improve energy density quality as was observed with the COALITE feedstock. Furthermore, the per pass conversions during the LC-Fining (BLCF-102) and the fixed-bed hydrocracking (FBHC-32/35) were very low indicating the relative refractory nature of the gas oil fraction of the Colorado shale oils.

This campaign did generate samples of Colorado shale oil-derived HEDF and HEDF precursor streams for testing in the extraction evaluation screening program.

6.6 Extraction Studies

The plan for the evaluation of the extraction/hydrogenation route (schematic diagram shown in Figure 6.6-1) consists of: a) collection of basic equilibrium solvent selectivity data for the two candidate solvents, namely, dimethylformamide (DMF) and tetraethylene glycol (TEG); b) analytical evaluation of the extracts and raffinates with respect to energy density improvements; and c) recommendations for preparation of bench-scale quantities of extracts for demonstration of the potential of fixed-bed hydrotreating (and hydrocracking) to upgrade extracted HEDF precursors to the 130,000 min. Btu/gal energy density spec.

The four feedstocks selected for the initial evaluation include:

- o mildly LC-Fined vac gas oil (BLCF-102 product)
- o severely hydrotreated LC-Finate vac gas oil (FB-186/187)
- o selectively hydrocracked mid-distillate (FB-188/189)
- o hydrotreated raw mid-distillate (FB-130)

The first two feedstocks represent the evaluation of heavier extracts boiling above the HEDF boiling range prior to hydrocracking. The latter two feedstocks to extraction represent HEDF products having nominal 125,000 Btu/gal energy densities.

The test equipment consists of a stirred, externally heated, glass extraction vessel. Testing consisted of three stages of contact using fresh solvent in each stage. Conditions held constant in these initial tests were as follows:

- o Nominal temperature of 195F
- o Atmospheric pressure
- o Stirrer speed of 5 rpm
- o 1 hour extraction contact time per stage
- o Fresh solvent to feed ratio of 1.5 gm/gm

Raffinate and solvent-rich extract phases were separated by decanting in a separatory funnel. The extract was separated from the solvent by introduction of water which dissolved the solvent and freed the hydrocarbon-rich extract. The two solvents selected were premised on

FIGURE 6.6-1

EXTRACTION/HYDROGENATION ROUTES TO HEDF FROM COLORADO SHALE OILS (CSO)

separation from the extract by distillation. The TEG, the heavier boiling solvent (B.P. = 622F), was to have been used for the lighter (275-575F) boiling mid-distillate stream. The DMF, the lighter boiling solvent (B.P. = 307F), was to have been used for the heavier (575-975F) boiling gas oil stream.

The summary of the operating conditions and raffinate properties is presented on the spreadsheet of Table 6.6-1. The initial testing indicated that the DMF solvent demonstrated a good degree of effectiveness in extracting some species from the heavier feedstock. The TEG solvent appeared to have no specificity for any of the components in the lighter distillate feedstock. Since the DMF solvent is soluble in water, it may be separated from the extract in a commercial-scale application by introduction of a third phase, namely, water or an aqueous-rich recycle stream, instead of distillation.

The results are summarized on Table 6.6-2 which shows that DMF extraction of a hydrotreated 300-650F distillate can increase the energy density of the extract by some 2335 Btu/gal over that of the feed but at the expense of a reduction in the energy density of the raffinate.

RESIN IS OF SOLVENT EXTRACTION ON HYDROTREATED COLORADO SHALE OILS

SOLVENT A: TETRAETHYLENE GLYCOL
SOLVENT B: N,N-DIMETHYLFORMAMIDE

265.

TABLE 6.6-2

LAB EXTRACTION STUDY RESULTS

FEED: HYDROTREATED 300-650F COLO SHALE OIL DISTILLATE
SOLVENT: DIMETHYLFORMAMIDE (DMF)

	<u>3-STAGE PERFORMANCE RESULTS</u>		
	<u>FEED</u>	<u>EXTRACT</u>	<u>RAFFINATE</u>
MATERIAL BALANCE	100	26.22	73.78
SPECIFIC GRAVITY	0.8189	0.8285	0.8130
Δ API IMPROVEMENT	—	2.0	(1.25)
% HYDROGEN CONTENT	14.31	13.88	14.46
Δ H REDUCTION, scf/bbl	—	232	(80)
VLHV, Btu/gal	124,150	126,485	122,951
Δ VLHV, Btu/gal	—	2335	(1199)

7.0 SUMMARY OF RESULTS OF PILOT PLANT SAMPLE PREPARATION (Task 5)

7.1 Overview

The specific objectives of Task 5 (in addition to the preparation of this topical report) were to:

- o Perform laboratory characterization tests on the raw COALITE feed, the intermediate liquids to the required hydroprocessing units and final advanced fuels and byproducts; and
- o Produce a minimum of 25-gal of Category I test fuel for evaluation by DOE and its contractors.

While sample preparation for the purpose of end user assessment is a very important component of process development. The end user assessment can provide good feedback to the process developer on the properties of the test fuels under static and dynamic engine test evaluations. However, the structure of this project allowed for only a single interface between the process developer and the end user of the HEDF test fuel and this interface will occur after the termination of the project. Accordingly, the decision on what fuel samples of the many options available to the process developer is a critical one. In selecting processing conditions, it was necessary to consider the tradeoffs in ultimate HEDF yield with fuel cut points, the latter having great effects on the energy density and thermal stability properties of the candidate HEDF fuels. It was also necessary to consider the severities of the various hydroprocessing steps and their impacts on capital and operating costs. Finally, good judgment had to be applied in selection of screening conditions since the project, and especially the Task 5 pilot plant sample preparation program, had definitive cost and schedule limitations.

The original work statement called for production of test samples from both the COALITE MCG liquids as well as from UNOCAL Process-derived Colorado shale oils. Since the Colorado shale oils were shown during the Task 3 screening studies to be less responsive to hydroprocessing with regards to achieving 130,000+ Btu/gal energy densities, the work statement was modified to concentrate on the COALITE liquids and to produce two different quality HEDF test fuel samples based on COALITE processing. The particular processing methodology selected for the sample preparation efforts was based on a target of optimizing the volumetric energy density-thermal stability relationships for the HEDF fraction. The processing steps consisted of:

- o Fractionating the raw full-range COALITE to generate a 575F+ atmospheric resid fraction;
- o LC-Fining of the 575F+ COALITE to hydrocrack some of the vac resid components as well as to impart part of the hydrogen uptake requirements in a backmixed, near isothermal reaction system;

- o Flash vaporizing the full-range LC-Finates to remove the unconverted 900F+ vac resid;
- o Hydrodenitrogenating in a fixed-bed hydrotreater the thus prepared IBP-900F LC-Finate gas oils using a NiMo catalyst selective to deep denitrogenation removal;
- o Selectively hydrocracking the hydrodenitrogenated LC-Finate gas oils using a proprietary zeolitic-based hydrocracking catalyst in a fixed-bed hydrotreater at two operating severities;
- o Fractionating the hydrocrackate products to recover the nominal 280-580F HEDF precursors;
- o Clay treating the 280-580F materials over bentonite to remove trace polar impurities; and
- o Treating the HEDF test fuels with anti-oxidant and corrosion inhibitor.

7.2 LC-FiningSM Operations

The first step in the overall sequence to produce finished HEDF test fuel from the raw COALITE feed is to hydroprocess the atmospheric resid cut via expanded-bed LC-Fining. The throughput to the LC-Fining unit was specified to insure that there would be a minimum quantity of HEDF precursors in the LC-Finate products necessary for the achievement of at least 25-gal of HEDF test fuels. Run 6LCF-14 was carried out using Shell 324M NiMo catalyst recovered from a prior campaign in the LC-Fining pilot unit made during Subtask 3.2 to recover LC-Finates for the screening studies. The 6LCF-14 feed was derived from the 575F+ atmospheric resid fraction recovered during the batch fractionation (in an 8-in batch fractionation unit) of the raw COALITE material.

The LC-Fining unit was successfully pressure tested at 2500 psig hydrogen pressure and commissioned with a 350-575F raw COALITE distillate until the catalyst bed temperature was 500F. At this point, the distillate feed was removed and the 575F+ resid was introduced which increasing the heat inputs until the desired catalyst bed temperature was achieved.

The run proceeded for four days without any major operating problems and a total of 105 gallons of LC-Finate were recovered. The reactor operating conditions were 2000 psig operating pressure, 773F average catalyst bed temperature, 6000 scfb treat gas rate and 1.5 LHSV per each of the two catalyst beds.

As indicated in Table 7.2-1, the conditions for run 6LCF-14 were more severe than those of the prior Subtask 3.2 screening test of run 6LCF-11. The bed temperatures were about 9F higher and space velocity per bed was about 0.1 hr⁻¹ lower. The incremental increase in severity was an attempt to match the possible catalyst activity loss

TABLE 7.2-1
RUN 6LCF-14 LC-FINING PRODUCTION RUN

=====	=====	=====
RUN NUMBER	6LCF-11	6LCF-14
PERIOD NUMBER	3	2
-----	-----	-----
DATE (1990)	3/31	12/12
AVG. CATALYST TEMP. (1st BED)	759	774
AVG. CATALYST TEMP. (2nd BED)	769	772
TOTAL PRESSURE, PSIG	2000	2000
LHSV PER BED, HOURS-1	1.63	1.49
SHELL 324M CATALYST AGE, BBL/LB	0.17	0.272
TWO-STAGE WDSV, BBL/LB/DAY	0.071	0.064
TREAT GAS (HZ), SCF/BBL	5900	6000
CARBON BALANCE, WT.% RECOVERY	101	99
OVERALL MAT. BAL., WT.% RECOVERY	100	100
-----	-----	-----
FEED COALITE (575F+) PROPERTIES		
API GRAVITY	-3.7	-3.7
CARBON, WT.%	85.37	84.72
HYDROGEN, WT.%	8.01	7.86
SULFUR, ppm	10200	9340
NITROGEN, ppm	14100	8500
OXYGEN, WT.%	4.03	5.48
ASH, WT.%	0.16	0.16
975F+ RESID, VOL.%	18	12.3
-----	-----	-----
LC-FINATE LIGHT OIL PRODUCT PROPERTIES		
API GRAVITY	28.2	24.8
CARBON, WT.%	87.82	88.33
HYDROGEN, WT.%	12.05	11.52
SULFUR, ppm	195	167
NITROGEN, ppm	1118	1253
575F+ RESID, VOL.%	23	31
-----	-----	-----
LC-FINATE HEAVY OIL PRODUCT PROPERTIES		
API GRAVITY	11.6	10.3
CARBON, WT.%	89.32	89.39
HYDROGEN, WT.%	10.24	9.99
SULFUR, ppm	186	222
NITROGEN, ppm	3121	3106
OXYGEN, WT.% (DIFF.)	0.11	0.29
ASH, WT.%	0.02	0.02
575F+ RESID, VOL.%	88.8	93.9
975F+ RESID, VOL.%	9.0	9.8
-----	-----	-----
PRODUCT YIELDS, WT.% FEED		
OFFGAS H2S	1.07	0.97
OFFGAS NH3 + H2O	5.89	6.83
OFFGAS C1	0.69	0.86
OFFGAS C2	0.66	0.82
OFFGAS C3	0.70	0.86
OFFGAS C4	1.66	2.05
OFFGAS C5+	0.81	1.00
LIGHT OIL	29.68	49.26
HEAVY OIL	62.30	41.02
TOTAL	103.46	103.67
-----	-----	-----
H2 CONSUMPTION, SCF/BBL	2700	2800
DENITROGENATION, WT.%	84	78
DESULFURIZATION, WT.%	98	98
VOL.% 575 DEG. F + CONVERSION	30	38
VOL.% 975 DEG. F + CONVERSION	65	64
-----	-----	-----
	269	

attributable to the use of the spent catalyst. The LC-Finate product characteristics did indicate that the catalytic activity was less than that of run 6LCF-11 based on the HDS and HDN removal efficiencies. However, thermal conversion activity was greater as indicated by the 575F+ conversion. Chemical hydrogen consumptions were approximately equivalent for both tests (2700-2800 scfb).

At the end of run 6LCF-14, the composited heavy oil fraction containing unconverted 975F+ COALITE was processed in the Equilibrium Flash Vaporization unit to remove the vac resid material. The entire 110 gallons of IBP-900F distillate, which contains HEDF precursor components as well as the vacuum gas oil (VGO) fractions, was composited and drummed for subsequent processing in the pilot plant fixed-bed hydrotreating unit for deep denitrogenation.

7.3 Fixed-Bed Hydrodenitrogenation Operations

The LC-Fining pilot plant unit was modified to be able to operate in the two-stage, downflow fixed-bed mode of hydroprocessing. The SHELL 324M catalysts from the LC-Fining campaign were removed and replaced with Akzo Chemicals KF-843 NiMo catalyst designed for deep denitrogenation removal. Deep denitrogenation is required to protect the downstream zeolite-based VGO hydrocracking catalysts from poisoning by basic nitrogen compounds.

A total of 4000 cc of KF-843 catalyst was charged to each of the two fixed-bed reactors. The catalysts were calcined in situ at 750F for two hours followed by presulfiding with a 2% H₂S/H₂ gas mixture. After the presulfiding operations following the vendor's procedure, the unit was successfully pressure tested at 2500 psig.

The conditions selected for the HDN campaign were based on the screening test results of Subtask 3.2. These consisted of 2000 psig operating pressure, 785F average bed temperature, 2.0 LHSV per each of the two reactors and 3400 scfb treat gas rate. The latter treat gas rate had to be reduced from the previously used 6000 scfb because at the higher space velocity, the absolute flow rate limitations of the unit. Treat gas rate has been specified at a considerable excess over stoichiometry and it was not deemed detrimental to operate at the 3400 scfb rate. In both cases, hydrogen partial pressures are high and close to that of the system operating pressure. Table 7.3-1 summarizes the operating conditions and results.

The nitrogen content of the full-range hydrodenitrogenated VGO product was 31 ppm vs 2185 ppm for the feed representing an HDN rate of about 98.6%. Sulfur content was reduced from 295 ppm to 1 ppm. At the 785F bed temperatures, there was a modest conversion of 575F+ equivalent to 23 wt% with a corresponding chemical hydrogen consumption rate of 600 scfb. This hydrocracking achieved over the HDN catalyst represents a reduction in the severity of hydrocracking required in the downstream selective hydrocracking step for conversion of additional VGO components to HEDF precursors.

TABLE 7.3-1
 RUN 6LCF-15 PRODUCTION RUN
 FIXED BED HYDRODENITROGENATION
 OF 900F- COALITE-DERIVED LC-FINATE

=====	=====	=====	=====	=====
PERIOD NUMBER			6LCF-15	
DATE	1991		1/17	
TOTAL PRESSURE, PSIG			2000	
LHSV PER BED, 1/HOURS			2.03	
1st STAGE AVG. BED TEMP., DEG. F			781	
2nd STAGE AVG. BED TEMP., DEG. F			788	
AKZO KF-843 CATALYST AGE,			0.179	
TWO-STAGE WDSV, BBL/LB/DAY			0.076	
TREAT GAS (H2), SCF/BBL			3400	
CARBON BALANCE, WT.% RECOVERY			99	
OVERALL MAT. BAL., WT.% RECOVER			98	

FEED PROPERTIES:				
API GRAVITY			19.2	
CARBON, WT.%			88.55	
HYDROGEN, WT.%			11.06	
SULFUR, ppm			295	
NITROGEN, ppm			2185	
OXYGEN, WT.% (BY DIFFERENCE)			0.14	

FULL-RANGE HDN PRODUCT PROPERTIES:				
API GRAVITY			24.0	
CARBON, WT.%			88.37	
HYDROGEN, WT.%			11.63	
SULFUR, ppm			1	
NITROGEN, ppm			31	

PRODUCT YIELDS, WT.% FEED				
OFFGAS H2S			0.03	
OFFGAS NH3 + H2O			0.42	
OFFGAS C1			0.44	
OFFGAS C2			0.44	
OFFGAS C3			0.37	
OFFGAS C4	FEED		0.47	
OFFGAS C5+	----		1.27	
IBP-275 DEG. F	2.8		2.83	
275-575 DEG. F	41.7		52.13	
575 DEG. F +	55.5		42.48	
TOTAL	100.00		100.88	

HYDROGEN CONSUMPTION, SCF/BBL			600	
575 DEG F + CONVERSION, WT.%			23	
HYDRODENITROGENATION, % REMOV			99	
HYDRODESULFURIZATION, % REMOV			100	

The net recovery of hydrotreated product at the completion of the HDN step was 118 gallons (approximately half of which was in the HEDF precursor boiling range). This material serves as the feedstock supply to the subsequent selective hydrocracking operations.

7.4 Fixed-Bed Selective Hydrocracking Operations

The same reactor configuration as that used for the hydrodenitrogenation campaign was used for the selective hydrocracking operations. The objective of this campaign is to maximize the selective hydrocracking of 575F+ in the hydrodenitrogenated VGO material to high energy density, jet range components. During the Subtask 3.2 screening studies, three catalysts were evaluated and a proprietary zeolitic-based catalyst (manufactured by Zeolyst Enterprises, a joint venture of PQ Corporation, Shell Polymers and Catalysts Enterprises), was selected as the preferred candidate on the basis of its simultaneous hydrocracking-hydrotreating performance. Thus, an additional hydrotreating step to saturate hydrocracked aromatics is avoided.

A total of 4000 cc of Z-704A catalyst was charged to each reactor. The unit was then successfully pressure tested at 1500 psig. The catalyst was dried in situ at 550F for 2 hours followed by reduction with hydrogen at 500 psig and 750F for 8 hours. Two operating severities were employed to allow production of two samples of HEDF test fuels.

The low severity condition was carried out at 500 psig hydrogen pressure, 1.16 LHSV per catalyst bed, 525F average bed temperature and treat gas rate of 5700 scfb. The high severity condition was carried out at 1000 psig hydrogen pressure and 650F average bed temperature. When excessive light ends make was observed, the bed temperatures were reduced to an average of 550F. Table 7.4-1 summarizes the operating conditions and results for both selective hydrocracking campaigns.

Performance as measured by extent of HDN, 575F+ conversion and chemical hydrogen consumption rates was approximately equal. The major differences in the full-range hydrocracked products were the API Gravities and elemental hydrogen contents. While these differed only by a couple of API degrees and two-tenths of a percent hydrogen contents, respectively, these latter parameters can have significant effects on volumetric energy density and JFTOT stability.

7.5 Post-Hydrotreatment Operations

The products from each campaign of the selective hydrocracking operations were fractionated in the pilot plant 4-in Batch Fractionation Unit as runs FBD-16 and FBD-17, respectively. The batch fractionation was operated to collect multiple narrow boiling fractions in the vicinity of the key cut points, namely, 280F representing the front end volatility affecting the HEDF flash point specification, and 550F representing the back end volatility affecting the viscosity and freeze point specifications.

TABLE 7.4-1
 RUN 6LCF-16 PRODUCTION RUN
 FIXED BED SELECTIVE HYDROCRACKING
 OF HYDRODENITROGENATED LC-FINATE GAS

=====			
RUN NUMBER		6LCF-16	6LCF-16
PERIOD NUMBER		1&2	3&4

DATE	1991	4/23-24	4/24-25
TOTAL PRESSURE, PSIG		500	1000
LHSV PER BED, 1/HOURS		1.15	1.24
1st STAGE AVG. BED TEMP., DEG. F		525	650-550
2nd STAGE AVG. BED TEMP., DEG. F		525	650-550
Z-704A CATALYST AGE, BBL		0.112	0.226
TWO-STAGE WDSV, BBL/LB/DAY		0.067	0.072
TREAT GAS (H2), SCF/BBL		5700	5300
CARBON BALANCE, WT.% RECOVER		99	98
OVERALL MAT. BAL., WT.% RECOVER		99	98

FEED PROPERTIES:			
API GRAVITY		24.0	24.0
CARBON, WT.%		88.37	88.37
HYDROGEN, WT.%		11.63	11.63
SULFUR, ppm		1	1
NITROGEN, ppm		31	31
OXYGEN, WT.% (BY DIFFERENCE)		0	0

FULL-RANGE HYDROCRACKATE PRODUCT PROPERTIES:			
API GRAVITY		36.3	38.5
CARBON, WT.%		86.45	86.28
HYDROGEN, WT.%		13.55	13.72
SULFUR, ppm		<1	<1
NITROGEN, ppm		<1	<1

PRODUCT YIELDS, WT.% FEED			
OFFGAS H2S		0.00	0.00
OFFGAS NH3 + H2O		0.00	0.00
OFFGAS C1		0.68	0.63
OFFGAS C2		0.68	0.62
OFFGAS C3		0.58	0.53
OFFGAS C4	FEED	0.73	0.67
OFFGAS C5+	----	1.96	1.80
IBP-275 DEG. F	2.9	12.82	19.49
275-575 DEG. F	53.5	73.30	68.10
575 DEG. F +	43.6	11.74	10.83
TOTAL	100.00	102.49	102.66

HYDROGEN CONSUMPTION, SCF/BBL		1500	1600
575 DEG F+ CONVERSION, WT.%		73	75
HYDRODENITROGENATION, % REM		100	100
HYDRODESULFURIZATION, % REMO	273.100		100

The batch distillations were each carried out in two discrete operations: an atmospheric distillation from the initial boiling point up to 450F distillate temperature followed by a 100 mm Hg vacuum distillation up to 610F atmospheric equivalent distillate temperature. Table 7.5-1 presents the summary of the distillate fractions and corresponding yields. As expected, the product from the low severity hydrocracking operation contained the highest yield of 610F+ (unconverted) material.

The distillate cuts from each batch fractionation run were blended in proportion to their overall batch fractionation yields to generate small samples for analytical testing of flash point, freeze point and energy density. As shown in Table 7.5-2, the heart cut HEDF blend (280-550F) met the flash point specification. Subsequent aliquot blends were made by adding the narrow boiling cuts above the 550F point and checking freeze point. Volumetric energy density increases with end point while freeze point also increases. The hydrogen content however decreases which is directionally adverse to good JFTOT stability. Because of the large sample quantity and cost of the JFTOT test, only selected blends were subjected to JFTOT testing.

Based on these results, it was decided that the preferred HEDF boiling range is 280-580F for both the low severity and high severity hydrocrackates. The full quantity distillate blends having the 280-580F boiling range were made from all the materials fractionated in the four-in batch fractionation unit.

Clay treating is a process aimed at removing trace polar compounds that could have an adverse effect on fuel stability. It is practiced commercially in refineries for petroleum-based aviation turbine fuels. Many types of clays can be used and we selected bentonite for this program. A total of 4500 cc of bentonite clay was charged to the pilot plant clay treating column.

Both the low severity and high severity materials were treated by clay treating. The conditions selected for the pilot plant clay treating unit were based on some laboratory screening studies of clay treating using a small diameter glass column. These conditions consisted of operation at ambient temperature, 4 psig pressure with a liquid percolation rate of 1.3 gph equivalent to a bentonite space velocity of 1.2 gal/hr/gal. The results of the batch-continuous clay treating operations are presented in Table 7.5-3. The loss of material of about 1% was primary a result of liquid holdup in the packed bed as well as physical adsorption of polar compounds in the HEDF test fuel. In a true continuous process, the holdup component, which represents the bulk of the apparent loss of material, would be a very small fraction of the total liquid processed.

7.6 HEDF Assays

The bentonite-treated HEDF products were stored in clean 30-gallon drums with about 25-gal of each sample type (low severity hydrocracking and high severity hydrocracking) available for delivery to DOE-METC and/or its contractors. Representative samples were taken for assay. The results are summarized in Table 7.6-1.

TABLE 7.5-1
BATCH DISTILLATION OF
HYDROTREATED COALITE PRODUCTS FROM
SELECTIVE HYDROCRACKING RUN 6LCF-16

BATCH DIST. RUN #	FBD-16	FBD-17
HYDROCRACKING RUN #	6LCF-16	6LCF-16
HYDROCRACKING SEVERITY	'LOW'	'HIGH'
AVG. HYDROCRACKING BED TEMP, DEG. F	550	650-550
HYDROCRACKING PRESSURE, PSIG	500	1000
TWO-STAGE HYDROCRACKING LHSV, HR-1	0.5	0.7
DISTILLATION YIELDS, WT.% on FEED		
IBP-260 DEG F (CUT #1)	6.1	12.0
260-270 DEG F (CUT #2)	1.2	1.5
270-280 DEG F (CUT #3)	1.0	1.4
280-290 DEG F (CUT #4)	0.8	1.3
290-300 DEG F (CUT #5)	1.0	1.7
300-310 DEG F (CUT #6)	1.0	1.3
310-450 DEG F (CUT #7)	25.0	31.5
450-550 DEG F (CUT #8)	27.9	27.2
550-560 DEG F (CUT #9)	2.9	1.4
560-570 DEG F (CUT #10)	1.6	1.2
570-580 DEG F (CUT #11)	1.7	0.9
580-590 DEG F (CUT #12)	2.1	3.2
590-600 DEG F (CUT #13)	1.9	0.7
600-610 DEG F (CUT #14)	2.1	2.0
610 DEG F + BTMS. (CUT #15)	23.7	12.7
TOTAL	100.0	100.0

TABLE 7.5-2
OPTIMUM BLENDING STUDY OF
FINISHED COALITE JET FUEL CUTS
FROM FBD-16 & FBD-17

HEDF BOILING RANGE	FLASH POINT DEG. F	FREEZE POINT DEG. F	GRAVITY @60/60 gm/cc	CARBON WT. %	HYDROGE WT. %	ENERGY DENSITY BTU/Gal
FBD-16: LOW SEVERITY HYDROCRACKATES						
280-550 F	130	< -85	0.8565	86.29	13.37	131,460
280-560 F	-	< -85	0.8581	86.25	13.35	131,962
280-570 F	-	< -85	0.8591	86.57	13.36	131,766
280-580 F	-	-76	0.8602	86.20	13.30	132,140
280-590 F	-	-72	0.8607	86.31	13.29	132,036
280-600 F	-	-67	0.8623	86.36	13.23	132,525
280-610 F	-	-63	0.8633	86.26	13.18	132,523
FBD-17: HIGH SEVERITY HYDROCRACKATES						
280-550 F	125	< -85	0.8473	86.24	13.55	127,677
280-560 F	-	< -85	0.8473	85.83	13.49	130,350
280-570 F	-	-85	0.8488	86.22	13.51	130,625
280-580 F	-	-72	0.8493	86.25	13.51	130,858
280-590 F	-	-63	0.8514	85.95	13.51	131,011
280-600 F	-	-58	0.8514	85.87	13.53	130,927
280-610 F	-	-49	0.8524	86.00	13.45	130,863

TABLE 7.5-3
BENTONITE CLAY TREATING
OF HEDF FUEL BLENDS

TEST FUEL DESIGNATION	FBD-16	FBD-17
COLUMN I.D., in.	2.3	2.3
COLUMN SURFACE AREA, in ²	4.15	4.15
COLUMN SURFACE AREA, ft ²	0.029	0.029
BENTONITE CLAY :		
VOLUME, cc	4500	4000
VOLUME, gal	1.19	1.06
WEIGHT, lbs. START	8.28	7.31
WEIGHT, lbs. END	10.47	10.77
PICKUP WEIGHT, lbs.	2.19	3.46
TREATMENT PRESSURE, psig	4	4
PACKED BED FLOW DIRECTION	DOWN	DOWN
FEED RATE, GPH	1.33	1.30
FEED RATE, lb/hr	9.53	9.45
LHSV, 1/HR	1.12	1.23
FEED IN, lbs.	207.50	208.00
PRODUCT OUT, lbs.	205.21	205.50
APPARENT LOSS, lbs*	2.29	2.50
APPARENT % LOSS*	1.1	1.2

* Apparent Loss Consists of Liquid Holdup in Interstices of Clay Bed
Plus Adsorbed Trace Polar Compounds

TABLE 7.6-1
FINAL COALITE HEDF TEST FUEL PROPERTIES*

DESIGNATION	FBD-16	FBD-17
GRAVITY, SP. @ 60/60	0.8591	0.8493
GRAVITY, DEG. API	33.2	35.1
ELEMENTALS, WT. %		
CARBON	86.63	86.59
HYDROGEN	13.37	13.41
F.I.A., VOL %		
AROMATICS	1.2	0.4
OLEFINS	0.3	0.7
SATURATES	98.5	98.9
FLASH POINT, DEG. F	130	125
FREEZE POINT, DEG. F	<-76	<-76
ANILINE POINT, DEG. C	60.8	64.4
SMOKE POINT, mm	25	25
VISCOSITY, cst. @ -4F	7.0	7.5
COPPER CORROSION, @212F	3A	1A
POTENTIAL GUM, mg/100 ml	<1	<1
D2274 ACCEL STORAGE STABILITY (@95c, 16 Hr, O2), mg/100 ml	<1	<1
THERMAL STABILITY (JFTOT-D3241)		
TUBE DEPOSIT VISUAL RATING(TDR)	0	0
TUBE DEPOSIT RATING MAX SPUN RATIO	4.5	2.5
DIFFERENTIAL PRESSURE MAX., mm Hg	65	57
ENERGY DENSITY, BTU/GALLON	131,740	130,508

* WITHOUT ANTIOXIDANTS, ANTI-DEICING AGENTS, METAL DEACTIVATORS

The volumetric energy densities for the two samples were 130,506 Btu/gal for the high severity hydrocracking route and 131,740 for the low severity route, both meeting the original Work Statement energy density target of 130,000 Btu/Gal min. Subsequent to the original Statement of Work, DOE set a new technical goal of achieving an energy density target of 135,000 Btu/gal. As shown previously, energy densities for the low severity hydrocracking sample increased with distillate end point to a high value of 132,523 Btu/gal @610F end point vs the 580F value for the test fuel sample. Even higher values can be achieved depending upon hydroprocessing reaction conditions. During the Subtask 3.2 screening program, four tests were made in bench-scale equipment and energy densities as high as 133,992 Btu/gal were achieved).

Although the highest volumetric energy density is desired, there are two other criteria to consider. The first is a function of economics and the resultant tradeoffs between the additional cost of the incremental energy density improvement vs the value of the higher density fuel to the end user. The other criteria concerns the storage stability and thermal stability of the fuel for use in high speed aircraft. One analytical device for assessing stability performance is the Standard Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure, ASTM D3241-85). JFTOT subjects the test fuel to conditions that are relatable to those occurring in gas turbine engine fuel systems. The fuel is pumped at a fixed volumetric flow rate through a heater after which it enters a precision stainless steel filter where fuel degradation products become trapped. The essential data derived are the amount of deposits on an aluminum heater tube and the rate of plugging of a 17 micron nominal porosity filter located just downstream of the heater tube. This test has long been used by petroleum refiners to meet process specifications for shipment of aviation fuel products to the end users, namely, the commercial airline industry and the U.S. Air Force. With the advent of new aircraft engines and new fuel compositions, the JFTOT test is not always an accurate gauge for assessing on-board fuel stability performance. The Air Force is continually improving technology for on-ground determination of thermal stability of aviation turbine fuels. With regard to the new fuel type, High Energy Density (Category I) fuel, it is not known how applicable the JFTOT test will be for assessing thermal stability.

In any event, JFTOT testing (as well as Potential Gum and Accelerated Storage Stability) was used to assess fuel stability. Directionally, increasing fuel end point to increase specific gravity and volumetric energy density is inversely proportional to stability. The JFTOT stability criterion, Maximum Heater Tube Deposit/Visual Rating (TDR), was 0 for both the high severity and the low severity hydrocracking routes, both meeting the spec for conventional JP-3 turbine fuel. The specs for the JFTOT stability criterion of Change in Pressure Drop were not met. However, the specs for both Accelerated Storage Stability and Potential Gum were met.

In view of the JFTOT pressure drop results, aliquots of the test fuel samples were rerun through the laboratory clay treating column and the

resultant samples were analyzed for JFTOT. These samples passed both the TDR criterion and the pressure drop criterion. It was concluded that there were some trace polar compounds in the HEDF test fuels that were not removed in the pilot plant clay treating unit as a result of a hydrodynamic bypassing of material in the column. Probably optimization of the liquid contacting efficiency in the pilot plant clay treating unit, such as by operating at higher Reynolds Numbers or by recycling material through multiple passes, would result in the clay-treated material passing both JFTOT criteria. Unfortunately, the 50 gallons of test fuel could not be scheduled to be rerun.

The finished HEDf test fuels after the clay treating operations were dosed with the following additives while in storage awaiting shipment to DOE-METC:

- o BHT (anti-oxidant) 24 mg/L
- o DCI-4A (DuPont corrosion inhibitor) 20 mg/L

8.0 SUMMARY OF REFINERY UPGRADING ECONOMIC ASSESSMENT (Task 4)

8.1 Basis of LP Model

Several processes for treating raw COALITE liquid, or some substituent boiling fractions thereof, were experimentally tested in the initial Task 3 campaigns. These processes were selected because of their potential ability to change some of the properties of the feed stream towards those required of the finished HEDF products. The desired properties for HEDF are discussed in the Task 3 (4) and Task 4 (5) topical reports and are summarized in Table 8.1-1. The selected processes performed generally as expected in the Task 3 studies. However, no one process was able to provide all the properties needed for the production of HEDF. For instance, hydrotreating reduced aromatics and heteroatom levels, but also reduced energy density. To meet all the specifications for HEDF, it was expected that several processing steps would need to be combined. This may have involved combining processes in ways that could not have been either predicted at the start of this program or studied experimentally in the limited time available.

A linear program (LP) model was built which incorporated the most promising test periods from the experimental program in Task 3. In addition, there were a number of other conventional hydrocarbon processes that might also move stream properties towards the specifications for HEDF. These were also included in the linear program model. Table 8.1-2 lists all the process alternatives incorporated in the model developed for this study. Sometimes, each process alternative included more than one process condition. For example, the hydrotreating alternatives included several reactor severities. When process data were not available from the Task 3 program, process performance and costs were estimated from correlations based on either literature studies with coal-based stocks or AOC's in-house experience with petroleum-based stocks. An example of a process option that was included in the LP model but could not be studied in Task 3 is the recycle of hydrocracker bottoms product to the extinction of that stream. Investigators are continuing to find other ways to produce high quality liquid products from coal-derived liquids.

The linear program model was able to combine any or all of these process alternatives and to blend various streams from these alternatives to make finished products, preferably HEDF. When the streams could not be used to make HEDF, they were allowed to be blended into some conventional co-products. Sales of these co-products could help subsidize the cost of HEDF production and make sure the plant did not produce any waste streams that might be an environmental disposal problem. Table 8.1-3 lists the co-products that were included in the LP model for this study. The LP model included technology to blend process streams to meet the product specifications for all the products listed in Table 8.1-3. Proprietary AOC technology was used to describe properties, such as viscosity and flash point, that do not blend linearly. Typical ASTM specifications were used for the

TABLE 8.1-1
HEDF SPECIFICATIONS USED

<u>Property</u>	<u>HED Jet Fuel</u>	<u>HED Diesel</u>
Specific Gravity	.850 min	
Sulfur, Wt %	.05 max	.05 max
Cetane Number		40 min
Heating Value, MBtu/gal	130 min	130 min
Freeze Point, °F	-50 max	-50 max
Hydrogen Content, Wt %	12.5 min	
Flash Point, °F	100 min	133 min
Aromatics Content, Wt %	25 max	25 max
	5 min	
Viscosity, cs at -4°F	12 max	
	8 min	
		12 max
		8 min
Distillation, % off		
at 400°F	10 min	
at 465°F	95 max	
at 540°F	96 min	
at 640°F		80 min
Paraffins Content, Wt %	50 max	

TABLE 8.1-2
PROCESS ALTERNATIVES INCLUDED

Alkylation
Aromatics Recovery
Catalytic Cracking
Coking
Diolefin Saturation
Distillate Extraction
Distillation
Dynaphen
Ebullated Bed Hydrotreating (LC-Fining)
Fixed Bed Naphtha Hydrotreating
Fixed Bed Distillate Hydrotreating
Fixed Bed Gas Oil Hydrotreating
Hydrocracking
Hydrogen Production (Steam Reforming)
Hydrogen Purification (PSA)
Isomerization
Naphtha Reforming for Aromatics
Naphtha Sweetening
Polygasoline Production
Sulfur Production
Utilities Generation

TABLE 8.1-3
FEEDSTOCK COST/CO-PRODUCT PRICE BASES

<u>Stock</u>	<u>Price</u>	<u>Volume</u>	<u>Unit</u>
Natural gas	12.61		FOE Barrel
LPG/ Propane	7.60		Barrel
Mixed/ n-Butanes	11.76		Barrel
Isobutane	19.11		Barrel
Coalite/ HS Crude	18.00	10M, 40M	Barrel
Toluene	38.00		Barrel
Unleaded Regular	23.35		Barrel
Unleaded Premium	26.29		Barrel
Unleaded Mid-Grade	24.61		Barrel
Hydtrt Sweet Naphtha	25.40		Barrel
Reformer Feed	24.61		Barrel
Naphtha Jet Fuel(JP-4)	24.20		Barrel
Jet Fuel(JP-8)/Kerosene	21.84		Barrel
HED Jet Fuel	21.84	4M, 16M, max	Barrel
HED Diesel	21.84	4M, 16M, max	Barrel
Diesel Fuel	21.60		Barrel
Furnace Oil/ No. 2	21.00		Barrel
Coke	16.00		Ton
Sulfur	63.00		Ton
Fuel	2.00		MM Btu
Cooling Water	0.20		M gal
Power	0.05		KWH
Steam- High Pressure	5.00		M pound
Steam- Medium Pressure	4.40		M pound
Steam- Low Pressure	4.25		M pound

Note: M = thousand

conventional fungible coproducts and are not repeated here. Two different high energy density fuels were targeted - one in the jet fuel boiling range (Category I) and the other in the diesel fuel boiling range (Category III). Category II endothermic HEDF fuel was not considered in this study. The specifications used in the LP model for these high energy density fuels which were developed in consultation with DOE, are shown in Table 8.1-1. These are expected to result in compatibility with current jet fuel engine hardware components and mission requirements.

Because it was not always possible to measure each of the qualities needed for these specifications with each stock in the experimental program (usually because of limited sample size), the needed quality parameters were sometimes estimated from correlations with those properties that were measured. For example, Figure 8.1-1 shows how the hydrogen content and the heating value of the total liquid product (TLP) from hydrotreating 350-650F COALITE vary with hydrotreating reactor severity, while Figure 8.1-2 shows how stream flash point varies with simulated distillation (SD) initial boiling point. Other correlations were used that were developed from the extensive Task 3 experimental data set.

The linear program model contained almost 600 balance constraints (rows) and over 1200 process, blending, and economics options (columns). Each of the cases and sensitivities reported later considered each of these large numbers of process alternatives.

Since it is not possible to produce HEDF without consuming some feedstocks and utilities or without producing some co-products, the economics require a pricing scenario for the feed, products, and utilities. Table 8.1-3 shows the price and volume bases used. For this study, it was assumed that the mild gasification coal liquids exemplified by COALITE, was available for about the same price as current crude oil, namely \$18 per barrel. A crude oil price of \$30/Bbl was studied later in a sensitivity case. The relative prices of the other feeds and products come from an average of AOC's in-house historical data.

Another component of the economics requires return on the capital that is employed to build the necessary processing units. The capital investment costs for these units were scaled to represent the size of the units required in each case using a power law factor. The investment costs were then escalated to be equivalent to mid-1988 construction completion. The calculated investment requirement for a process plant included a prorated portion for typical utilities and OSBL support facilities. It was assumed that 65% of the capital was financed at an annual cost of 12%, while the remaining 35% was financed internally at a required 15% annual DCF rate of return. Other economic parameters include a generic U.S. Gulf Coast location, three year plant construction period, no investment tax credit, a 20 year project life, a 90% on-stream operating factor, and no net plant salvage value at the end of the project life. Using the ten-year plant depreciation schedule from the Tax Recovery Act of 1986 and a 38% tax

Figure 8.1-1
Effect of Reactor Severity
Coalite 350-650 F Feedstock

Rx Severity = 100,000 P/SV E(-35,000/RT)

Figure 8.1-2
Flash Point Prediction
Effect of Product SD IBP

SD = simulated distillation

rate, a capital recovery factor of about 21% per year was found to represent these parameters. Another 4% per year was added to account for the cost of maintenance, local taxes, insurance, and overhead.

8.2 Results of Linear Programming Model Study

The LP model was not able to produce HEDF in the diesel boiling range from COALITE liquid when using the specifications listed in Table 8.1-1. There were indications that HEDF diesel could be produced if the viscosity specification was changed. However, the linear program computer modeling effort was halted due to budget limitations before additional studies could be done on this fuel target. However, HEDF jet fuel was produced in many case studies as discussed in the following section. A sensitivity case described below for waiving the HEDF jet fuel distillation specifications resulted in producing a heavier diesel-like HEDF fuel.

Several case studies were done on the LP model which produced various quantities of HEDF jet fuel from two alternative commercial feedrates, 40 MBCD (thousands of barrels per calendar day) and 10 MBCD. Interpolation and extrapolation of these cases can be used to project the economics at other feedrates. The case studies completed are discussed individually below. The first two cases are documented in detail to explain the implementation of the bases used in the model. Only the important economic parameters are given for the other cases, since all the economic and process conclusions can be drawn from these values.

Figure 8.2-1 shows the liquid stream process units selected when the linear program model produced the maximum amount of HEDF jet fuel from 40 MBCD of COALITE liquids. The processing system first fractionated the COALITE liquids at 300F and at 650F to produce three streams for optimum processing. The 0.8 MBCD of raw 300F- naphtha was sweetened and had its diolefin content saturated to make it into an acceptable gasoline blending stock. This stock was sold as a co-product. The 20 MBCD of 300-650F raw COALITE distillate was hydrotreated using fixed bed hydrotreating technology. Most of the product from this step was redistilled, although 0.8 MBCD was directly blended to HEDF. The 400F minus naphtha from the redistillation was either blended to JP-4 jet fuel or sold as reformer charge stock. The 400-575F distillate from the redistillation was blended to HEDF jet fuel. The 575F+ from redistillation was routed to hydrocracking.

The 19.2 MBCD of raw 650F+ COALITE was first hydrotreated using expanded-bed technology (LC-Fining). The naphtha from this step was blended to JP-4 jet fuel while the distillate was split between HEDF blending, redistillation, and further upgrading by hydrotreating in the fixed bed distillate hydrotreater, as shown in Figure 8.2-1. The 575F+ stream from the LC-Finer was hydrocracked along with the bottoms stream from the redistillation step. The naphtha produced in the hydrocracking step was blended to JP-4, while the distillate was split between direct blending to HEDF and redistillation. The recycle of the heavy stock to hydrocracking through redistillation resulted in extinction of this stream and in the sales of no products heavier than

FIGURE 8.2-1
MAXIMUM HED JET FUEL

HEDF jet fuel. In total, almost 30 MBCD of HEDF jet fuel could be produced from 40 MBCD COALITE, for a 75% yield. Table 8.2-1 gives the properties of the HEDF jet fuel produced in the maximum HEDF case column, and compares those properties with the specifications. The product slightly exceeded the desired minimum volumetric energy density. The limiting specifications were maximum aromatics content, minimum viscosity, and distillation endpoint.

Table 8.2-2 shows the process unit sizes that had to be constructed for this case, along with the corresponding investment costs. The capital total of 439 MM\$ includes 12.7 MM\$ for initial catalyst fills and 46 MM\$ for allocated costs of utilities and OSBL.

Table 8.2-3 summarizes the economics for the maximum HEDF jet fuel case, as well as the volume of feed, product, and utilities required. The sum of raw material and utilities costs is about equal to the profit from sales of HEDF jet fuel and co-products. The added costs for fixed items and capital recovery leave a net cost (loss) of 315 M\$/CD. This is equivalent to a loss of \$10.53 per barrel of HEDF above its assumed \$21.84 selling price. Thus, the HEDF jet fuel must sell for about \$32.37/B in order to break-even with all the costs necessary for its production.

Because the maximum HEDF jet fuel processing scheme had so many branches and recycles, another case was investigated that produced about half of this maximum production of HEDF jet fuel. Figure 8.2-2 shows that the same process units are required but the processing scheme is indeed simpler, as many of the branches and recycles have zero flow rates. Much of the raw 650F+ COALITE liquid and the heavy LC-Finer bottoms is diverted to plant fuel needs instead of finished product sales. These high boiling streams are obviously the most expensive to convert to HEDF or any other salable product, although they provide some of the desirable properties for HEDF. Table 8.2-1 shows that the 40% HEDF yield jet fuel product is lower in specific gravity and volumetric heating value than the maximum HEDF product. The viscosity and distillation specifications are still limiting, but the aromatics content has been reduced to 12%.

Although Figures 8.2-1 and 8.2-2 do not show by-product gas streams (because gases are treated as fuel gas utilities), the high production of liquid plant fuel in the 40% yield HEDF case allows the plant to sell some by-product gases for fuel. Thus this case is a net exporter rather than importer of fuel gas as indicated in Table 8.2-3.

Table 8.2-4 shows that the capital requirement has been reduced to 305 MM\$, or about 70% of that of the maximum HEDF yield case requirement. Since it produces only about 55% of the amount of HEDF, the capital and fixed costs per barrel of HEDF are higher. Since the feed is the same amount of COALITE liquid, the cost of raw material per barrel of HEDF has also increased as indicated in Table 8.2-3. On the other hand, relatively more of the COALITE is sold as co-product and as by-product fuel, so these cost elements are more favorable than in the maximum HEDF yield case. Overall, the losses are reduced to 274 M\$/CD, although the loss per barrel of HEDF is increased to \$17.11 per barrel.

TABLE 8.2-1
PRODUCT COMPARISON WITH SPECIFICATIONS
40 MBCD \$18/B Coalite

<u>Property</u>	<u>HED Jet Specif.</u>	<u>Max HEDF Product</u>	<u>40% HEDF Product</u>
Specific Gravity	.850 min	.868	.857
Sulfur, Wt %	.05 max	.032	.021
Heating Value, MBtu/gal	130 min	130.9	130.3
Freeze Point, °F	-50 max	-70	-70
Hydrogen Content, Wt %	12.5 min	13.2	13.9
Flash Point, °F	100 min	210	205
Aromatics Content, Wt %	25 max	25	12
	5 min		
Viscosity, cs at -4°F	12 max	8	8
	8 min		
Distillation, % off			
at 400°F	10 min	22	20
at 465°F	95 max	68	69
at 540°F	96 min	96	96
Paraffins Content, Wt %	50 max	49	40

TABLE 8.2-2
INVESTMENT SUMMARY - MAXIMUM HEDF JET FUEL
40 MBCD \$18/B Coalite

<u>Process Unit</u>	<u>Size BSD</u>	<u>Investment MMS (1988)</u>
Naphtha Diolefin Hydrotreater	870	4.5
Hydrogen Manufacture	216*	113.3
Hydrocracker	34,300	33.2
Fixed Bed Hydrotreater	23,100	115.3
Power Distribution		8.6
Ebullated Bed Hydrotreater	21,300	122.5
Oil Distillation	44,000	29.9
Sulfur Plant	61**	10.4
Naphtha Sweetening	880	<u>0.8</u>
Total		438.7

Investment Includes Allocated Utilities and OSBL.

* Based on MMSCFSD instead of BSD.

** Based on LTSD instead of BSD.

TABLE 8.2-3
 BASELINE CASES ECONOMIC BREAKDOWN SUMMARY
 40 MBCD \$18/B Coalite

<u>Cost Component</u>	<u>Maximum HEDF Jet</u>		<u>40% Yield HEDF Jet</u>	
	<u>Costs,</u> <u>M\$/CD</u>	<u>HEDF Cost</u> <u>\$/Bbl</u>	<u>Costs,</u> <u>M\$/CD</u>	<u>HEDF Cost</u> <u>\$/Bbl</u>
Raw Materials Cost	794.2	26.56	762.2	47.64
HEDF Sales	-652.9	-21.84	-349.4	-21.83
Co-Product Sales	-388.0	-12.97	-265.0	-16.56
Utilities	250.8	8.39	-92.1	-5.76
Fixed Costs	54.0	1.81	39.4	2.46
Capital Recovery	256.6	8.58	178.6	11.16
Total Costs	314.7	10.53	273.7	17.11

<u>Purchases</u>	<u>Quantity</u>	<u>Unit</u>	<u>Quantity</u>	<u>Unit</u>
Coalite	40.0	MBCD	40.0	MBCD
Natural Gas	12.4	MFOEB CD	0	MFOEB CD
Catalyst & Chemical	72.2	M\$/CD	27.7	M\$/CD
Cooling Water	105.7	Mgal/CD	41.2	Mgal/CD
Process Water	3.7	Mgal/CD	1.7	Mgal/CD
Power	50.9	MW	21.3	MW

<u>Sales</u>				
HEDF Jet Fuel	29.9	MBCD	16.0	MBCD
Sweetened Naphtha	0.8	MBCD	0.8	MBCD
Reformer Feed	2.3	MBCD	1.0	MBCD
JP-4 Jet Fuel	12.2	MBCD	8.9	MBCD
Fuel Gas	0	MFOEB CD	9.3	MFOEB CD
Propane	1.7	MBCD	0.5	MBCD
Sulfur	58.	LTCD	31.	LTCD

FIGURE 8.2-2
40% HED JET FUEL

TABLE 8.2-4
ECONOMIC SUMMARY
\$18/B Feedstock Price Basis

<u>Coalite</u> <u>MBCD</u>	<u>HS Crude</u> <u>MBCD</u>	<u>HED Jet</u> <u>MBCD</u>	<u>Profit</u> <u>MS/CD</u>	<u>Invest</u> <u>MMS</u>	<u>Equivalent S/B</u> <u>Feed Cost Basis</u> <u>\$18/B Breakeven</u>	
40	0	29.9	-315.	439	32.40	24.70
40	0	16	-274.	305	38.90	24.70
40	0	8	-244.	211	52.40	23.80
40	0	0	-229.	206	-	12.30*
10	0	7.5	-157.	217	42.90	28.90
10	0	4	-134.	147	55.30	29.20
10	0	0	-104.	55	-	7.60*
0	50	0	-97.	300	-	16.10*
0	40	0	-100.	265	-	15.50*
40	0	38.6	-264.	295	35.00	23.60**
40	0	20	-252.	318	28.40	22.50**
40	0	0	-229.	206	-	12.30*

* Based on feed rather than jet fuel.
 ** All HEDF specs waived, see Figure 12 and Table IX.

TABLE 8.2-4
ECONOMIC SUMMARY
\$18/B Feedstock Price Basis

<u>Coalite</u> <u>MBCD</u>	<u>HS Crude</u> <u>MBCD</u>	<u>HED Jet</u> <u>MBCD</u>	<u>Profit</u> <u>M\$/CD</u>	<u>Invest</u> <u>MMS</u>	<u>Equivalent \$/B</u> <u>Feed Cost Basis</u> <u>\$18/B Breakeven</u>	
		29.9	-315.	439	32.40	24.70
40	0	16	-274.	305	38.90	24.70
40	0	8	-244.	211	52.40	23.80
40	0	0	-229.	206	-	12.30*
40	0					
		7.5	-157.	217	42.90	28.90
10	0	4	-134.	147	55.30	29.20
10	0	0	-104.	55	-	7.60*
10	0					
	50	0	-97.	300	-	16.10*
0	40	0	-100.	265	-	15.50*
0						
		38.6	-264.	295	35.00	23.60**
40	0	20	-252.	318	28.40	22.50**
40	0	0	-229.	206	-	12.30*
40	0					

* Based on feed rather than jet fuel.
** All HEDF specs waived, see Figure 12 and Table IX.

Table 8.2-4 summarizes the investment costs, net losses of cash flow (negative profit), and break-even HEDF costs when feeding 10 MBCD of COALITE instead of 40 MBCD. Similar processing routes were chosen as for the 40 MBCD cases, but the economics are less favorable because of decreased economies of scale.

Table 8.2-4 and Figure 8.2-3 show the economics when no HEDF jet fuel is produced, and only co-products (chiefly JP-4 and normal diesel fuel) and by-products are sold. Obviously, the economic parameters per barrel of HEDF are undefined in these cases. Figure 8.2-3 shows that, in all cases studied, increased HEDF production for sale at \$21.84 per barrel results in lowered profits. The break-even cost calculations already discussed confirm that the cost of HEDF from COALITE is higher than this current jet fuel price.

To provide an alternative way to evaluate these economics, the linear program model was run feeding petroleum crude oil and no COALITE, at rates of 40 and 50 MBCD, respectively. The LP model chose typical refinery process units and produced no HEDF. Table 8.2-4 and Figure 8.2-3 show the economics of these cases. The small refineries produced in these crude oil cases lost money, confirming the industry-wide lack of current and scheduled refinery construction plans. Since even crude oil processing loses money with the economic bases assumed here, the small economies of scale and pricing assumptions used in this study also bias the above HEDF cases. Another way to state this is that the above HEDF costs include the losses that any small grass-roots processing plant would incur, and are not related to the true inherent or incremental HEDF costs.

To look at the economics without these small plant inefficiency costs, we will price the feedstock at its break-even cost, and determine true product costs from that base point. The break-even costs per barrel of feedstock for these crude oil cases, and also the no HEDF cases, are shown in Table 8.2-4 and as the lower points in Figure 8.2-4. The difference between the crude oil and COALITE lines implies that COALITE liquid is worth only about \$3/B less than crude oil for making conventional products. This might be expected from the lower hydrogen and higher aromatics content of COALITE and its more severe refining processing requirements compared with crude oil.

If COALITE were priced at this break-even cost (\$7.60/B at 10 MBCD and \$12.30/B @ 40 MBCD), we get a different picture of the incremental cost of producing HEDF. The costs for the 40% HEDF yield case are shown in Table 8.2-4 under the break-even feedstock cost column and as the center points in Figure 8.2-4. These HEDF costs are in the mid- to high- twenty dollar per barrel range, and are not that far from the current jet fuel price (\$21.84/B). Table 8.3-1 shows that the trends in the \$/B costs for the maximum HEDF yield cases are very similar to the 40% HEDF yield cases. Thus, if processing units were available that could process COALITE to conventional products, the incremental costs for making high energy density analogs would not be very much higher.

Figure 8.2-3
Feedstock Rate Effect on Profit
\$18/B Feedstock Cost

Figure 3.2-4
Effect of Feedstock Rate
40% HEDF Yield - \$18/B Feedstock Cost

TABLE 8.3-1
SENSITIVITY CASES ECONOMIC SUMMARY
\$30/B Feedstock Price Basis

<u>Coalite</u> <u>MBCD</u>	<u>HS Crude</u> <u>MBCD</u>	<u>HED Jet</u> <u>MBCD</u>	<u>Profit</u> <u>MS/CD</u>	<u>Invest</u> <u>MMS</u>	<u>Equivalent \$/B</u> <u>Feed Cost Basis</u> <u>\$30/B Breakeven</u>	
40	0	30.0	-216.	443	43.60	37.10
40	0	16.0	-173.	420	47.20	35.00
40	0	13.1	-195.	387	51.20	36.30
40	0	0	-196.	398	-	25.10*
10	0	7.5	-130.	217	53.80	39.00
10	0	4.0	-122.	150	66.80	39.00
10	0	0	-111.	120	-	11.10*
0	40	0	7.	310	-	30.20*
40	0	22.3	-326.	499	51.10	42.30**
40	0	0	-196.	398	-	25.10*

* Based on feed rather than jet fuel.

** Based on 132,500 Btu/gallon specification.

8.3 Economics Sensitivity Studies

Since Table 8.2-1 shows that the HEDF jet fuels produced in the cases discussed above slightly exceeded the 130,000 Btu/gallon specification, a question might be asked of how high an energy density could be produced with the technologies currently known as a result of this project. To answer that question, the energy density specification was incrementally increased and the volume and cost of the resultant HEDF was calculated. Figure 8.3-1 shows that the volume of HEDF that can be produced at 132,500 Btu/gallon is about half of the baseline volume. The fully loaded cost for this higher heating value product is about \$6/B higher with \$18/B feedstock costs, while the cost using the break-even feedstock cost is only about \$3/B higher. It was not possible to produce a HEDF with a heating value of 133,000 Btu/gallon using the current database generated from the Task 3 screening program. Figure 8.3-2 shows how these higher energy density costs compare to the current jet fuel cost as a function of feedstock price. Further \$30/B feedstock cost cases are discussed in the following sections.

Figure 8.3-3 shows the componential break down of HEDF dollar per barrel transfer costs for the \$18/B feedstock cost, 40 MBCD cases into component areas. Figure 8.3-3 shows that net raw material cost (feedstock minus by- and co-products) is the major cost component. Capital costs account for about a quarter of the total HEDF costs. Hydrogen costs, taken as the sum of hydrogen plant capital, fixed, and operating costs, amount to just over \$8/B, so improvements in the costs of hydrogen generation might lead to reductions in the cost of HEDF manufacture. Not much improvement could be expected from reduction of the fixed expense components since these represent a small fraction of the total HEDF costs. The net variable operating costs for catalyst, chemicals, and utilities are the next smallest component over fixed expenses.

To provide a sensitivity to feedstock and product prices, the crude oil and COALITE price was increased to \$30/B from \$18/B. The by-product, co-product, and utility prices in Table 8.1-3 were also increased by the same proportion. Since hydrogen is made from either natural gas or a fuel gas which is a byproduct of these feedstocks, the hydrogen cost will roughly escalate with these prices also. Capital related costs remained constant in these sensitivity studies.

Table 8.3-1 and Figure 8.3-4 show the economic trends for the cases with these higher feed and product prices. These data can be compared with Table 8.2-4 and Figure 8.2-3 that use the \$18/B price basis. The LP model predicts a small profit for the crude oil only case. Table 8.3-1 shows that the profit for the 40 MBCD COALITE feedstock cases shows an optimum in the intermediate range of Jet fuel production, although the overall profit for the plant is still in the negative range. This optimum is confirmed by a break-even cost in that range that falls below the \$36.40/B base jet fuel price that is consistent with the \$30/B feedstock cost. Since it is known that the hydroprocessing routes selected by the LP are capital intensive,

Figure 8.3-1
 Effect of Heating Value Specification
 \$18/B Feedstock Cost

Figure 8.3-2
 HEDF Cost vs Heating Value

Figure 8.3-3
HEDF Cost Breakdown
 \$18/B Feedstock Cost

Figure 8.3-4
Feedstock Rate Effect on Profit
 \$30/B Feedstock Cost

raising product prices helps to encourage the more severe processing needed to produce HEDF by providing more net sales margin to cover capital recovery costs. However, as more HEDF production is required with a fixed COALITE feedrate, costs eventually rise because ultimately stocks are selected for which the incremental processing costs are higher than the let fuel selling price.

The \$/B analysis of these cases is shown in Table 8.3-1 and Figure 8.3-5 for comparison with Table 8.2-4 and Figure 8.2-4. Because the crude oil only case shows a slight profit, the breakeven \$/B for this case is above, rather than below, the \$30/B starting basis. COALITE is worth about \$5/B less than crude oil at this price level. This is about 17% below the crude oil price, as in the \$18/B cases.

It was recognized that the HEDF specifications listed in Table 8.1-1 were somewhat arbitrary. Experience with petroleum based fuels and current fuel delivery systems was used to set their levels. If a HEDF was needed for some specialized application, a hardware solution could be found for most cases of non-compliance with the specifications listed. For example, if the new HEDF was produced that was more viscous than current specifications, a higher power fuel pump might be specified in the target engine instead. A case was run to see what HEDF would be produced if all specifications in Table 8.1-1 were waived except energy density.

Figure 8.3-6 shows that over 95% Yield of HEDF could be obtained from the COALITE starting material. The processing options selected include the same sweetening and diolefin hydrotreating for the COALITE naphtha as in the baseline cases. The whole 300F+ COALITE stream is treated in an expanded-bed LC-Finer. The light LC-Finer naphtha is blended to gasoline, while the heavy LC-Finer naphtha is sold as reformer feed. The LC-Finer distillate is blended directly to HEDF. The LC-Finer bottoms stream is hydrocracked, and the hydrocracked products are blended in the same manner as the corresponding LC-Finer streams.

The properties of the HEDF produced are shown in Table 8.3-2. This HEDF exceeds the energy density specification and is much heavier than conventional jet fuel as the high viscosity and the 50% off at 540F shows. The viscosity is probably equivalent to around 5 cs at 68F, and would be slightly lower than diesel fuel. The high aromatics and low hydrogen contents suggest a fuel that would require major jet engine modifications. However, some intermediate processing between this case and those previously discussed may be worth pursuing to improve yields and energy density.

Figure 8.3-7 shows how the HEDF jet fuel cost from the 40 MBCD plant size varies as a function of HEDF yield for both feedstock costs. The HEDF cost falls as the yield increases. However, at best, the HEDF cost remains some \$8-10/B above the conventional jet fuel cost when the feedstock is priced at \$18/B. Figure 8.3-8 shows the same trends for the 10 MBCD size plant with some of the 40 MBCD points shown for reference as dashed lines. The smaller scale of the 10 MBCD plant always leads to higher HEDF costs.

Figure 3.3-5
Effect of Feedstock Rate
40% HEDF Yield - \$30/B Feedstock Cost

FIGURE 8.3-6
MAXIMUM HED JET FUEL - NO SPECS

TABLE 8.3-2
PRODUCT COMPARISON WITH SPECIFICATIONS
40 MBCD \$18/B Coalite

<u>Property</u>	<u>HED Jet Specif.</u>	<u>Max HEDF Product</u>	<u>All Specs Waived</u>
Specific Gravity	.850 min	.868	.949
Sulfur, Wt %	.05 max	.032	.033
Heating Value, MBtu/gal	130 min	130.9	134.5
Freeze Point, °F	-50 max	-70	-45
Hydrogen Content, Wt %	12.5 min	13.2	10.7
Flash Point, °F	100 min	210	200
Aromatics Content, Wt %	25 max	25	79
	5 min		
Viscosity, cs at -4°F	12 max	8	24
	8 min		
Distillation, % off			
at 400°F	10 min	22	11
at 465°F	95 max	68	29
at 540°F	96 min	96	50
Paraffins Content, Wt %	50 max	49	21

Figure 8.3-7
Effect of HEDF Yield

Figure 8.3-8

Effect of HEDF Yield

8.4 Conclusions/Recommendations

The major conclusions of the LP study when applied to refining COALITE fluids utilizing the current database obtained during the Task 3 screening efforts are as follows:

- o The COALITE (MCG) liquid feedstock cost is a major component of the HEDF transfer price. For a 40,000 bpcd refinery operated under the constraints of an \$18/bbl petroleum crude-based economy, the allowable COALITE cost with conventional products is estimated at \$12.30 per barrel. This represents only a \$3 per barrel disadvantage relative to high sulfur petroleum crude. When the refinery is allowed to produce HEDF products, the allowable COALITE cost decreases only to about \$10-11 per barrel.
- o Refining of COALITE to HEDF products is capital intensive and capital recovery costs can amount up to 25% of the HEDF transfer price.
- o Hydrogen-related costs, operating as well as capital costs, can represent up to 15-25% of the HEDF transfer costs suggesting the importance for development of catalysts to improve hydrogen utilization.
- o The economy of scale also has a great effect on HEDF transfer prices and refining capacities on the order of a hundred thousand barrels per day or greater should significantly reduce the per barrel cost of upgrading COALITE.
- o Determining the use value of a high density iet fuel could have a great impact on the processing alternatives and the allowable production costs of MCG liquids via Mild Coal Gasification. In this study, the baseline case assumed the HEDF product would have a value equivalent to that of conventional JP-8 fuel, namely, \$21.84/bbl. Raising product prices helps to encourage the more severe processing needed to produce HEDF by providing more net sales margin to cover capital recovery costs.
- o While Task 3 and 5 efforts did not achieve the 135,000 Btu/gal energy density target, values in the vicinity of 133,000 were achieved. If the proper premium is placed on this type of fuel, when used either for military or commercial applications, and assuming the MCG char can be sold at some premium value over that of the feed coal (on an energy value basis), an LP model study would probably indicate that the MCG to HEDF route would be economically viable for a petroleum pricing scenario of \$20-25/bbl.

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10.0 INVENTION DISCLOSURES

No invention disclosures were filed as a result of performance of work under this contract.

11.0 ACKNOWLEDGEMENTS

Lummus would like to acknowledge the following individuals for their guidance and assistance in facilitating the efforts on this HEDF technology screening program:

Charles Byrer	DOE-METC COTR
Jim Burchfield	DOE-METC Extraction Projects
(retired)	Management Division
Joe Masin	AOC Subcontractor, Lead LP Modeling
	Process Engineer

We would also like to acknowledge the following Lummus personnel for their contributions on the screening program:

Marvin Greene	Project Manager/Principal
	Investigator
Steven Huang	Pilot Plant Engineer
Sam Mikhail	Analytical Chemistry Supervisor
Louis Senario	Pilot Plant Operations Supervisor
Vincent Strangio	Pilot Plant Operations Manager
Robert Valente	Pilot Plant Engineer

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