

**HIGH ENERGY DENSITY MILITARY FUELS
BY HYDROPROCESSING OF COAL PYROLYZATES**

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INTRODUCTION

Lummus Crest Inc. (LCI), a subsidiary of Combustion Engineering Inc., successfully responded to a DOE-Morgantown Energy Technology Center (METC) solicitation for development of high energy density fuels from mild gasification coal liquids and other selected synfuels and is currently carrying out a multi-year test program at its Engineering Development Center. With Amoco Oil Company as a major subcontractor, LCI's program is directed towards the determination of the minimum processing requirements to produce high energy density distillate fuels for use in military aircraft and/or diesel-powered vehicles.

The specific objectives of the program are:

- o Conduct a technical and economic assessment of promising processing and upgrading methods to convert raw liquid products from mild coal gasification and other selected synfuel processes into advanced high volumetric energy density test fuels;
- o Conduct screening tests of alternative processing methods; and
- o Generate test quantities, ca., 100 gallons each, of two advanced fuels from mild coal gasification liquids and from Colorado shale oils provided by DOE contractors for a Phase I program and from two additional synfuels to be specified for an optional Phase II program.

BACKGROUND AND STATEMENT OF PROBLEM

METC has recently been reassessing the technologies for best utilizing our domestic coal resources to provide for the future demand for transportation fuels and generation of clean power. Much of the technological strategies has been unidimensional, i.e., development and marketing of coal utilization technologies that produce a main product such as liquid boiler fuel, refinery syncrude, desulfurized clean coal, etc.

As part of its assessment, METC has concluded that there is a technology type, referred to as Mild Coal Gasification (MCG), which has the potential to simultaneously satisfy the transportation and power generation fuel needs in a most cost-effective manner. MCG is based on low temperature pyrolysis, a technique known to the coal conversion 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.

Aviation turbine fuels represent less than 10 percent of the refinery production in the U.S. The growing scarcity of light sweet petroleum crude could impact the future availability of a minor refinery product such as jet fuel. Thus, alternate feedstocks such as coal liquids, shale oils and tar sands bitumen, may eventually be utilized as feedstocks for distillate fuels.

Future aircraft, military as well as commercial, may need to meet certain performance criteria such as extended flying range or need to fly at supersonic or hypersonic speeds. Similarly, future military land vehicles may need to have extended ranges between fuel reloading. With the exception of selected relatively low volume refinery streams (e.g., rerun reformates, pyrolysis gas oils), the bulk of petroleum-derived turbine fuels contains a significant concentration of aliphatic materials. These paraffinic compounds do not possess the desirable specific gravity-calorific value or the endothermic (dehydrogenation ability) characteristics of those of cyclic compounds. These latter cyclic or naphthenic materials, whose precursors can be single or multi-ring aromatics, are the only known and practical hydrocarbons that meet the high energy volumetric density and/or endothermic properties required for the advanced High Energy Density Fuels, hereinafter referred to collectively as HEDF.

Thus, there is a beneficial synergism between the distillable aromatics-rich liquids produced by mild gasification and the production of advanced HEDF.

While the MCG liquids are enriched in the HEDF precursors, namely, 1-, 2-, and 3-ring aromatics, they must be processed in such a manner as to generate a product meeting all environmental and technical specifications for HEDF aviation turbine and diesel fuels. LCI, as a process technology firm, has developed a whole family of hydrogenation processes for hydroprocessing various refinery and petrochemical streams from C₄'s all the way to vacuum residua, utilizing both fixed-bed and expanded-bed hydroprocessing reaction systems. The latter system is of special importance for feedstocks contaminated with trash metals and/or for reactions requiring critical heat removal due to the severe exothermicity of the hydroprocessing reactions. LCI's general approach consists of a combination of mid-distillate hydrotreatment; atmospheric resid or VGO hydrocracking; delayed coking of the atmospheric resid portion of the synfuel liquids. Selection of the optimal processing routes will be identified by use of Amoco's refinery linear programming models.

The MCG liquids contain significant heteroatom content in the form of phenols, aromatic sulfur compounds, pyridines and other organic nitrogen compounds. These materials have to be processed in such a way as to remove the heteroatoms without dearomatizing the ring structure and at conditions that will minimize hydrogen consumption. Although it may be possible to utilize one catalyst having all the required functionalities, i.e., HDN, HDS, HDO and ring saturation, and charged in a single reaction system, an overall loss in selectivity and activity will probably result. It may therefore be more cost effective to segregate the process

functions into separate stages thereby allowing the utilization of more selective and active catalysts for the heteroatom removal and the aromatic ring saturation steps.

The proposed technical approach for the distillate hydrotreating step is to identify the optimal reaction conditions for each step of the two-step process (heteroatom removal followed by ring saturation). The identification of the preferred catalysts in each stage is a key component of the program. Focus will be placed on determining the minimum processing steps including necessary separation or recycle systems to produce the advanced HEDF.

HIGH ENERGY DENSITY FUELS

Three advanced HEDF types have been defined for the program by the DOE:

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 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 (1) 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 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 affected 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 specifications are not violated.

PROGRAM METHODOLOGY

Eight contract work tasks were defined with the bulk of the experimental testing consolidated into Tasks 3 and 5. Task 3 consists of a screening program to collect process operating data for each of the candidate processes over a relatively wide range of conditions. These data will be used as the input to the Task 4 modeling studies being performed by Amoco for the purpose of identifying the near optimal commercial processing sequences. Based on the latter, the Task 5 pilot plant program will be carried out to produce 100-gal each of two types of advanced HEDF fuel for each candidate synfuel feedstock. Resultant samples as well as liter quantities of test samples produced during the screening task will be delivered to DOE contractors for further evaluation.

Two feedstocks have been identified for the Phase I program: a mild coal gasification liquid and a Colorado shale oil. These liquids were required in 1000-gal quantities and therefore they had to be obtained from relatively large scale pilot or commercial plants. Since MCG technology is currently being scaled up from the laboratory or bench scales, DOE elected to provide a commercially available material having properties comparable to those anticipated for the MCG process. The resultant MCG liquid provided to LCI was derived from the British COALITE Process. The latter is a low temperature carbonization process developed in the early 1900's (2) 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 by United Coal Company Research Corporation under a separate DOE-METC contract. Table 1 is a summary of the properties of the whole range COALITE and the nominal 300-650F mid-distillate fraction which served as the feedstock for fixed-bed hydrotreating. 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 balance of this paper will review the process variables scan testing of the fixed-bed hydrotreatment of the 350-650F COALITE mid-distillates.

The fixed-bed hydrotreating unit 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. Each reactor contains about 100-150 cc of catalyst and both reactors can be operated in series or the second reactor can be bypassed with only the first reactor in use. To date, three catalyst types are being evaluated: a nickel tungsten; a promoted nickel tungsten; and a nickel moly.

The major technical challenge to achieving the minimum energy density specification is the addition of hydrogen to the mid-distillates in such a way that the rate of decrease in specific gravity upon hydrogenation does not exceed the rate of increase of gravimetric heat content. Otherwise, the net volumetric energy density will deviate from the target. Catalysis and operating severity must be controlled to minimize ring opening as well as to minimize hydrogen-consuming gas forming reactions.

In evaluating the process screening data, we found good correlations between the Refractive Index (R.I.) and the other HEDF fuel properties of interest, namely, volumetric energy content, API gravity, hydrogen content, Smoke Point, Cetane Index, Luminometer No., aromatics content, etc. Figure 1 maps the interaction of the API gravity-R.I. relationship vs. the predicted volumetric energy density expressed as lower heating value (LHV). Upon interchanging the API and the R.I. axes (Figure 2), we can see the extent of the hydrogenation on the whole distillate LHV for a series of hydrotreating tests made with the nickel tungsten catalyst. The slope of the regressed data is slightly skewed to the lines of constant LHV. It would appear that at hydrogenation severities resulting in whole distillate product R.I.'s below about 1.49, continued hydrogenation to reduce heteroatoms and smoke-forming aromatics results in excursions away from the LHV target of 130,000 Btu/gal.

However, it is important to appreciate that other jet and diesel properties besides energy density need to be met, such as for example, flash point and freeze (or pour) point, if the HEDF fuel is to be successfully implemented. The original test distillate feedstock was arbitrarily defined as a nominal 350-650F fraction. During hydrotreatment, the heteroatoms, in particular, phenolics and cresylics, are hydrogenated to their cyclic hydrocarbon counterparts and these materials (e.g., cyclohexane, methylcyclohexane). These have boiling points below those in the 350-650F starting material and adversely affect the flash point properties. Furthermore, the selected end point of 650F was apparently too high because it resulted in high freeze points for the whole distillate product. Accordingly, a post-hydrotreating fractionation operation is required to top and tail the material in order to meet the volatility and freeze point properties of HEDF fuels.

Table 2 shows the properties of distillate products recovered from the topping and tailing of the hydrotreated 350-650F COALITE distillates. Even though the whole hydrotreated distillate products from these runs had energy densities some 2.2 to 2.8% below the target, the removal of portions of the front-end and back-end by distillation resulted in a net increase in the LHV to within 0.7 to 1.3% of the 130,000 Btu/gal target. While the removal of the lighter front-end for flash point adjustment increases the LHV to above the target, the simultaneous removal of the heavier back-end for freeze point adjustment reduces the specific gravity with a resultant net LHV fractionally below the target. In tailing the two products shown in Table 2, we apparently removed too much of the back-end causing freeze points (-54 to -57F) better than the -40F spec. Easing off on the tailing operation should increase the LHV to within less than 0.5% of the target. We also are investigating other hydrotreating catalysts that have the potential for further improvements in selectivity towards the desirable 2-ring cyclics in order to meet and/or exceed the 130,000 Btu/gal LHV target.

ON-GOING AND FUTURE WORK

Nominal 350-650F distillates derived from the expanded-bed hydrocracking via LC-Finingsm of the 650F+ residual fraction of the COALITE were produced and subjected to fixed-bed hydrotreatment. Noticeable differences in severities to achieve HEDF specs were observed for the LC-Finates in comparison to the raw

(sm) LC-Fining is a service mark of LCI for engineering, marketing and technical services relating to hydrocracking and hydrodesulfurization processes for reduced crudes and residual oils.

hydrotreated distillates, with the LC-Finates being more reactive. Similar testing was carried out with coker distillates derived from delayed coking of the 650F+ COALITE. The process scanning program is also being carried out for the Colorado shale oil sample supplied to LCI by Western Research Institute. The Colorado shale oil is not as aromatic as the MCG liquids and therefore the degree of hydrogen addition is not as severe as for the case of the COALITE. However, tailoring the catalyst functionality to produce the proper mix of cyclics and aliphatics in the hydrotreated shale oil distillates is a technical challenge and is being addressed in this program.

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REFERENCES

- (1) Lander, H. and Nixon, A.C., "Endothermic Fuels for Hypersonic Vehicles", 15th Annual AIAA Meeting, Philadelphia (October 21-24, 1968).
- (2) G.S. Pound, "The Production of Chemicals From Low Temperature Tar", J.Inst. Fuels, Coke & Gas, (October 1952).

Table 1. Summary of Properties of Whole Range and 350-650F COALITE Distillate

	<u>WHOLE DEWATERED COALITE</u>	<u>350-650F DISTILLATE</u>
<u>Elementals, wt%</u>		
Carbon	83.56	84.00
Hydrogen	8.55	9.26
Nitrogen	1.10	0.81
Sulfur	0.85	0.73
Oxygen	5.94	5.20
H/C Atomic Ratio	1.23	1.32
Specific Gravity @ 60F	1.039	0.9923
R.I. @ 20C	-	1.5469
VLHV, Btu/gal	133,100(est.)	132,741
Con Carbon Residue, %	3.52	<0.1
<u>TYPE ANALYSIS, 1vol%</u>		
Saturates	-	24.3
Olefins	-	14.6
Aromatics	-	61.1
<u>Distillation, F</u>		
10% distilled	D-1160	D-86
30% distilled	415	422
50% distilled	543	460
70% distilled	655	504
90% distilled	771	552
End Point	-	616
	958 (87%)	652

Table 2. Summary of Analytical Inspections of Finished COALITE-derived HEDF⁽¹⁾

<u>Source</u>	<u>Test FB-47</u>	<u>Test FB-48</u>
LHV, Btu/gal	129,095 ⁽²⁾	128,295 ⁽³⁾
Aromatics, %	4.3	17.1
Specific Gravity @ 60F	0.8388	0.8504
Refractive Index @ 20C	1.4570	1.4640
Viscosity @ -4F, cs	7.5	7.0
Freeze Point, F	-54	-57
Flash Point, F	115	115
Aniline Point, F	136	116
Diesel Index	50.6	40.5
Smoke Point, mm	30	20
Luminometer No.	82	66
Existent Gum, mg/100 ml	4	10
Accelerated Stability, mg/100 ml	<0.1	2.0
<u>D-86 Distillation, F</u>		
IBP	311	315
10% distilled	347	352
30% distilled	390	393
50% distilled	412	415
70% distilled	448	449
90% distilled	486	486
EP	540	534

- (1) Promoters such as oxidation inhibitors, corrosion inhibitors and deicing agents are not reflected in the analyses of these samples.
- (2) Increases to an estimated 129,775 Btu/gal if Freeze Pt. is relaxed to the equivalent of a -40F max. spec.
- (3) Increases to an estimated 129,275 Btu/gal if Freeze Pt. is relaxed to the equivalent of a -40F max. spec.

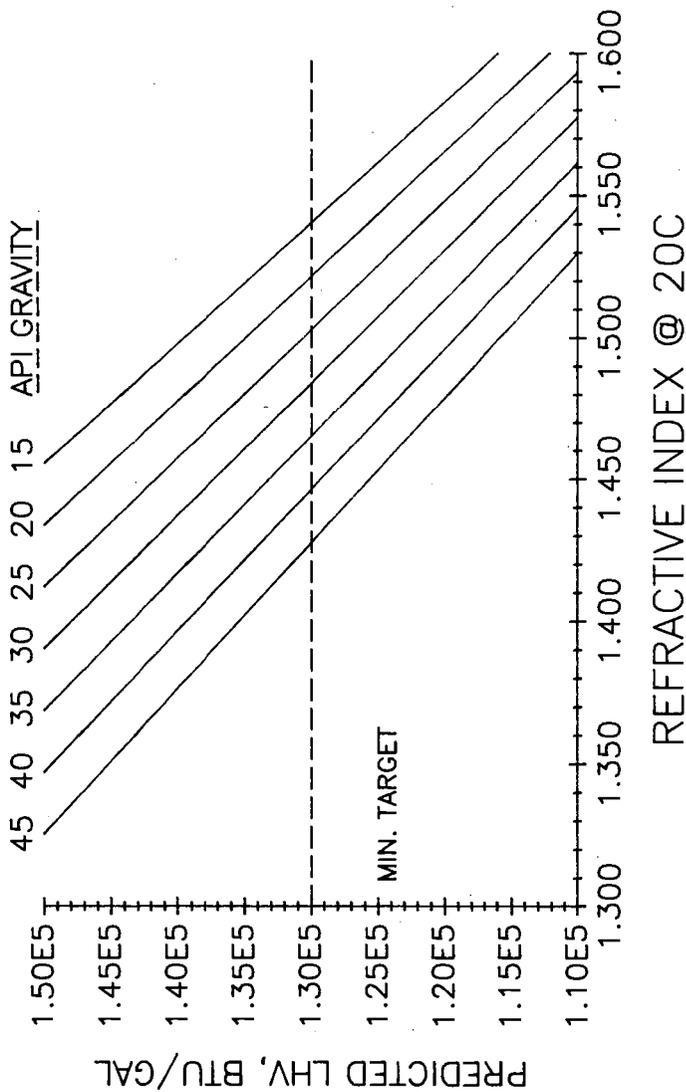


Figure 1. Predicted LHV of Hydrotreated 350-650F COALITE Distillates

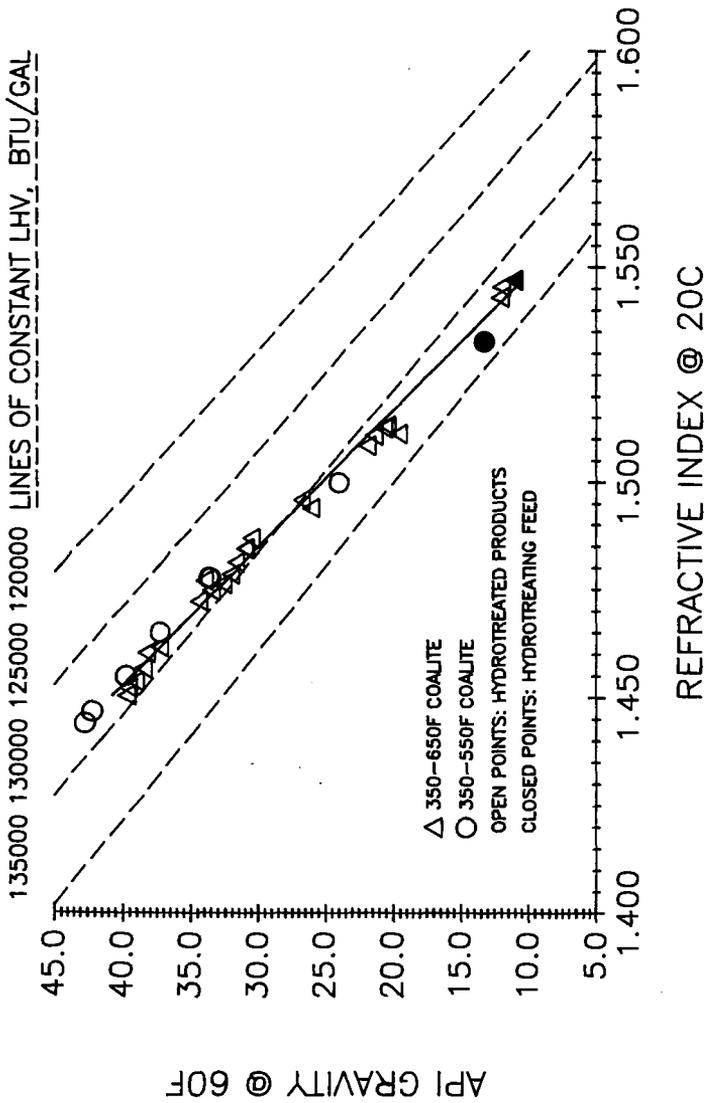


Figure 2. LHV-R.I.-API Relationships For Whole Hydrotreated COALITE Distillates