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HEAVY OIL (RESIDUUM) AND HEAVY OIL/COAL COPROCESSING PROGRAM PROVIDES GOOD ROUTE TO MAKING ACCEPTABLE FUELS FROM HEAVY OIL AND COAL

Final Report

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Heavy Oil (Residuum) and Heavy Oil/Coal Coprocessing Program
Provides Good Route to Making Acceptable Fuels From Heavy Oil and Coal

Overview

In early 1989, SFA Pacific, Inc. developed a comprehensive 5-year research program to carry out fundamental work and explore ideas on processing heavy oil, coal, and coprocessing the two materials together [1]. The program cost was estimated to be \$20.3 million. The program covered work to discover routes to improve process yields and to confirm that high-quality liquids could be made. In particular, the program emphasized the need to define key aspects of potential problems in product quality of the naphthas and middle distillates produced from coal.

SFA Pacific was asked by DOE to review the program in view of the recent trends of using reformulated fuels to reduce emissions from automotive and diesel engines. The rapid developments in reformulated gasolines have set a course to reduce total aromatics in general (and benzene and xylenes particularly), Reid Vapor Pressure (RVP), and olefins. In addition, for diesel various regulatory actions are being proposed:

- Reduce sulfur to less than 0.05 wt%
- Reduce aromatics to the range 10-20 vol%

It is important that a fundamental research program cover the possibility that such restrictions (and more severe) will become law.

The specification on aromatics in diesel requires much more severe hydrotreating than meeting the sulfur specification, even for petroleum fractions. The increasing restriction on aromatics in gasoline and diesel is particularly important when considering coal processing, since the light coal-derived liquids are almost completely aromatic or partially saturated structures. In addition, very little data have been obtained to show the effect of the 2- and 3- ring (saturated or unsaturated) compounds on engine emissions and engine deposits.

There have been recent major developments in catalysts and technologies for heavy oil upgrading. In particular, the "integrated hydrotreater" is an effective technique for adding hydrogen to the products so as to saturate the rings. It can also provide hydrocracking to make single ring structures and paraffins. This technology consists of combining a fixed bed catalytic hydrotreater directly with hydroconversion reactors suitable not only for heavy oil processes but also for coal/heavy oil coprocessing. Both ebullating bed and slurry phase systems can use this technique. Further, new catalysts have been developed that allow control of the degree of hydrogenation and hydrocracking so as to attain very good product quality and a high yield.

Overall, the research program addresses the main thrust of the product specifications:

- Firm data are needed to vary process conditions to attain the required product quality.
- The recommended fund level of approximately \$20 million (1988 \$) is reaffirmed, subject to confirmation through further detailed planning.
- The timing is excellent. Most crucial answers are defined in the first one to three years of the program.

It should be remembered that the research program does not involve toxicity problems. A separate program will likely be needed on toxicity of the various materials in the fuels. This should apply mainly to the liquids from coals. Final fuel products made from petroleum residues are routinely handled by refineries and are set to meet the required EPA regulations. However, since continuing work may identify new materials considered to be toxic, this aspect should be kept in mind.

Regulations Continue to Tighten Specifications on Automotive and Diesel Fuels

The drive to reduce emissions from cars, buses and trucks has continued to gain momentum. California has taken the lead on setting rigid specifications. The U.S. government has begun to consider similar standards. The automobile and oil refining industries have begun a joint program to test "reformulated gasolines" to determine what changes can be made to gasoline composition and engine design to achieve the desired reduction in car emissions.

While there are no firm answers yet available, there is a general pattern emerging on the nature and composition of the fuels:

- On middle distillate fuels, the short-range goal is to reduce sulfur to 0.05 wt% or less. California has also specified that by October 1993, aromatics in diesel must be less than 20 vol% for small refiners (less than 50,000 barrels per day) and less than 10 vol% for large refiners. Essentially, this would make the future diesel fuel about the same quality as current jet fuel. The California regulations allow for a possible exception: an alternate fuel formulation is satisfactory if it can still meet emission standards.
- The trend in gasoline composition would be:
 - Low in Reid Vapor Pressure (RVP)
 - Low in benzene content (about 1 vol%)
 - Low in xylene content
 - Low in total aromatics (less than 35 vol%)
 - Low in olefins
 - Less heavy ends (to balance the lower RVP)
 - More ethers and alcohols to offset the octane loss due to reduced aromatics and olefin contents

As a result of these events, DOE asked SFA Pacific to review the impact of the changes on the heavy oil (and residuum) and heavy oil/coal coprocessing concepts and what modifications might be needed to the recommended 5-year research program.

Research Recommendations for Heavy Oil and Residue Processing Are Reaffirmed

The research program recognized the general trend to increasing the quality of the light distillate fuels -- both motor gasoline and heavier distillates. The basic framework is set to define and confirm a wide range of qualities for heavy oil conversion processes. This work also sets the basis for comparison for considering any form of coal processing, such as coprocessing with heavy oil or by itself in direct liquefaction.

Gasoline quality testing is set to include engine cleanliness tests, which also generate the data to test emissions. It is expected that the cooperative

industry program will define the appropriate reformulated gasoline compositions to be used as a standard. The recommended program is geared to build on that base to make sure the materials derived from heavy oil conversion are suitable blending components -- or define what process modifications are needed to make them suitable.

The middle distillate program emphasizes severe hydrotreating and other techniques to make ultra-high quality fuels, such as jet fuel and low aromatics diesel, as currently set for California. By its nature, the research program is geared and funded to cover a wider range of qualities than is currently being considered as future regulations.

High Aromaticity and Unusual Compounds in Coal-Derived Liquids Pose Needs for Research

There is much commercial experience in making high-quality products from petroleum residue conversion. The fuels are essentially the same as those made from converting lighter petroleum fractions. The refining industry has been active in developing catalysts and testing product quality on petroleum-derived fuels.

On the other hand, the information on coal liquids processing is more limited. The U.S. Department of Energy has sponsored work on reforming naphthas, which make good reforming stocks, and, in particular, on an extensive program by Chevron on hydrocracking heating oil cuts to make jet fuels [2]. However, more work is needed to show that diesel fuel can achieve the higher qualities demanded by the new Clean Air Act and meet possible future increased restrictions. In addition, more extensive information is needed on treating light and heavy gas oils to make satisfactory fluid catalytic cracking unit (FCCU) feeds, together with the necessary FCCU yields and qualities.

Coal conversion produces nearly all aromatics, which have a different chemical nature from those made from petroleum. The major difference is that the ring structures from coal have few or no paraffinic side chains. As a result, the two-ring structures, such as naphthalene, tetralin, and decalin, are lower boiling than the two-ring structures from petroleum and appear in the naphtha boiling range. For petroleum, the two-ring structures are highly alkylated and

boil within the heating oil range (400/650°F or higher). In addition, the 3- and 4- ring structures from coal can concentrate in the heating oil. For petroleum, such structures would boil in the heavy gas oil range (650/1050°F).

Such two-ring structures in the naphtha increase sludge formation in the lubricating oils, increase engine deposits, and increase hydrocarbon emissions. The 3- and 4- ring structures will make the diesel more difficult to hydrogenate and act as inhibitors for removal of sulfur and nitrogen and for aromatic saturation. As a result, the normal refining hydrotreating conditions used to treat diesel and to prepare fluid catalytic cracking unit (FCCU) feedstocks are not severe enough to meet the desired product quality.

For good cetane number, the diesel material should be low in aromatics and high in paraffins and naphthenes, as illustrated in Figure 1. Even completely saturated aromatic structures would only provide about 40 cetane number. Clearly, some significant amount of paraffins is needed to boost the quality to 45-50 cetane number.

Figure 1
CETANE NUMBER VERSUS HYDROCARBON TYPE

Source: Criterion Catalyst

New Technology Developments Provide Both High Conversion and Good Product Quality

Several new technologies have been developed which can provide high conversion for petroleum residues and coal [3]. Such processes as H-Oil, LC-Fining, VEBA Combi-Cracking, as well as others, have been well tested on oil (commercial plants) and coal (demonstration plants). In addition, several developers have studied the use of the integrated hydrotreater to obtain further product upgrading. They have carried out experimental and engineering studies on several variations to confirm its process results and investment savings.

One form that is particularly well suited to heavy oil/residues processing and to coprocessing to obtain high cetane numbers is illustrated in Figure 2 for the case of vacuum residues. The concept is also applicable to coprocessing when coal is added to the residue feed and either an ebullating bed or slurry phase reactor is used for the hydrocracking step.

Figure 2

INTEGRATED HYDROTREATER: TWO-STAGE WITH HYDROCRACKING
FOR HIGH CETANE NUMBER

Source: SFA Pacific, Inc.

The effluent from the hydroconversion reactor section flows into a hot separator, where the temperature is about 800 - 850°F. The hot, high pressure vapors, which contain the naphtha and heating oil, go directly to a series of fixed bed reactors. The liquid phase from the hot separator is depressured, cooled and distilled to recover the vacuum gas oil (VGO). The VGO is then fed to the first fixed bed, which contains, typically, a hydrotreating catalyst that removes sulfur and nitrogen and provides substantial aromatic saturation. This hydrogenation is done at the high reaction system pressure, typically 2500 - 3500 psig. This extremely high pressure provides a great increase in hydrotreating reactor severity over that normally used in refineries, where the pressures are typically 800 - 1200 psig. The high pressure range should be adequate to provide a high degree of aromatic saturation and ring cracking for all coal distillates, but needs to be confirmed.

The final product treating is achieved in the second stage, where a hydrocracking catalyst is used. This catalyst can be similar in composition to that used in the first stage but has an acidic component, such as a molecular sieve, added to promote the cracking of the aromatics to naphthenes and paraffins. Shell International has demonstrated this type of operation in its pilot plant over an extended period to convert petroleum vacuum residues to naphtha, jet fuel and high cetane diesel -- with essentially no net yield of VGO and only 10 wt% of the pitch remaining [3].

This approach can also provide a synergism between the petroleum and coal liquids. In setting the severity of the integrated hydrotreater to give a high saturation/conversion of coal products, the more easily cracked paraffins and naphthenes from the petroleum portion will be more severely cracked than would occur processing petroleum liquids alone. This abundance of high-quality materials from petroleum permits the coal products to be treated less severely than if the coal were processed by itself.

One further advantage of this approach is that other aromatic streams from the refinery can be upgraded in the same unit, if desired. For instance, the highly aromatic FCCU heating oil and heavy cycle oils can also be hydrotreated to make good diesel and FCCU feed. Several other variations of the integrated hydrotreater are possible, and can provide a wide flexibility in processing high sulfur and high nitrogen stocks.

Changing Fuel Cut Points Moves Two-Ring Structures Out of Naptha and Balances Products

The trend to less heavy ends in the reformulated fuels ties in well with the research program when using coal in coprocessing. The net effect is to increase the volumetric yield of gasoline and middle distillate due to the extra hydrogen added. In addition, the program specifically investigates how best to handle the two-ring structures from coal processing. SFA Pacific's outlook for the changes in the general boiling range is illustrated in Figure 3.

Figure 3
REFORMULATION IS LEADING TO LIGHTER GASOLINE AND DIESEL

Source: SFA Pacific, Inc.

The current boiling ranges for the various liquids are approximately:

Gasoline	100/380°F
Diesel/Heating Oil	380/600°F
FCCU feed (VGO)	600/1,000°F

The future trend for gasoline is to reduce the light components -- butanes and pentanes/pentylenes -- so as to lower the RVF. This might move the initial

boiling point from 100 to 120°F. To maintain good fuel distribution on startup (as well as for other reasons), some heavy ends will have to be removed. The probable final boiling point will likely be 330 - 350°F.

This heavy end of naphtha can be placed in the diesel fraction. This move will substantially increase the size of diesel production. Since diesel consumption is only about one-half that for gasoline, the diesel boiling range must also be lowered to about 550°F. This can be done by removing the heavy end of the diesel, e.g., the 550/600°F material.

The heavy diesel end can be disposed of in two ways: it can be hydrocracked to gasoline, with an accompanying large volumetric expansion of yield, or it can be used as a portion of the FCCU feed. The exact rebalancing of cut points must await the results of the automotive/refiner cooperative program.

The 5-year research program provides for the testing of the product qualities and for the conversion of heavy cuts of naphtha and diesel.

Additional Costs Are Modest For Making Higher Quality Coal Liquids

In our prior evaluation of the economics of coprocessing, SFA Pacific's design was set to produce about 20 vol% aromatics in the liquid products, which was judged to be satisfactory for refinery processing. This was suitable for that time frame.

SFA Pacific re-estimated the costs of hydrogenating the liquids to essentially full saturation. The cost for the additional hydrogen and increased reactor severity were relatively modest: about \$1 - 2 per barrel for the petroleum case and \$3 - 5 per barrel for the coal case.

This cost for coal assumes that there is no synergism with the petroleum portion, as described above. The possible synergism requires experimental data to confirm or refute. For the time being, we would regard this extra cost as being tolerable, and not require any special additions to the recommended research program.

The Main Message . . . Data Are Needed Rather Than Speculations

We judge that the recommended 5-year research program provides adequate scope and funding to answer the questions raised above. The program had anticipated many of the questions.

The recommended funding for product quality questions (including product testing and treatment by hydrogenation and adsorption) was substantial for all the distillate liquids, and we judge it still adequate:

Total Level: \$M

Naphtha	1,200
Middle Distillate	1,000
VGO for FCCU feed	1,000

Most of this data is obtained in the first one-to-three years. We would recommend no change in the amounts until the data are analyzed and the main conclusions drawn. Since the total program is \$20.3 million and emphasizes heavy oil conversion, as shown in Table 1 below, we believe there is ample funding and time to rebalance the effort, as judged advisable.

Table 1

SUMMARY OF RESEARCH PROGRAM COSTS

	<u>Program Costs: \$M</u>	
	<u>Heavy Oil</u>	<u>Coprocessing</u>
Naphtha Quality and Processing	800	400
Middle Distillate Fuels	600	400
Gas Oil Conversion	600	400
Heavy Residue Product Analysis	2,500	1,600
Coking of Residual Products	800	400
Feed Characterization	1,500	1,500
Roles of Solids in Processing	2,000	1,000
Alternate Catalyst Studies	3,000	1,400
Hydrogen Manufacture	<u>1,000</u>	<u>400</u>
Total	12,700	7,600

Source: SFA Pacific, Inc.

Summing Up

The tightening regulations on automobile and diesel fuel product qualities emphasize the need for obtaining good basic data on product quality, which is an integral part of the 5-year recommended fundamental research program on heavy oil/residuum conversion and coprocessing:

- There is a definite need to extend the data base on product quality of naphtha and diesel into the range of ultra-high quality, reflecting the new and future regulations, and covering products from heavy oil conversion and coal.
- The program covers this new range and addresses the fundamental, critical issues.
- The main route of achieving higher quality is to use a larger amount of hydrogen and much more severe hydrotreating conditions.
- The development of new catalysts and the use of the high-pressure integrated hydrotreater provide an excellent, versatile technique for achieving this goal. The correct combination can produce highly saturated naphthenic structures, as well as isoparaffins. It applies equally well to the case of heavy oil conversion and coal processing.
- The cost for additional hydrogenation over that used in our prior study, to meet ultra-high quality fuels from petroleum, is about \$1 - 2 per barrel.
- For coal, with its higher hydrogen consumption, the additional cost is about \$3 - 5 per barrel.
- The scope, schedule, and level of funding of the program are sufficiently broad that we would judge it to be still valid today. As with all programs, once the data are obtained and analyzed, some revisions may be desired. The program is versatile enough to be changed as the experimental results indicate.

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