U.S. Department of Energy
Pittsburgh Energy Technology Center

Refining and End Use Study of Coal Liquids

Contract No. DE-AC22-93PC91029

[redacted]

Quarterly Report
April - June 1995

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Section 1

Introduction and Summary

This report is Bechtel's seventh quarterly technical progress report and covers the period of March 27, 1995 through June 30, 1995.

1.1 Introduction

Bechtel, with Southwest Research Institute, Amoco Oil R&D, and the M.W. Kellogg Co. as subcontractors, initiated a study on November 1, 1993, for the U.S. Department of Energy's (DOE's) Pittsburgh Energy Technology Center (PETC) to determine the most cost effective and suitable combination of existing petroleum refinery processes needed to make specification transportation fuels or blending stocks, from direct and indirect coal liquefaction product liquids. This 47-month study, with an approved budget of $4.4 million dollars, is being performed under DOE Contract Number DE-AC22-93PC91029.

A key objective is to determine the most desirable ways of integrating coal liquefaction liquids into existing petroleum refineries to produce transportation fuels meeting current and future, e.g. year 2000, Clean Air Act Amendment (CAAA) standards. An integral part of the above objectives is to test the fuels or blends produced and compare them with established ASTM fuels. The comparison will include engine tests to ascertain compliance of the fuels produced with CAAA and other applicable fuel quality and performance standards.

The final part of the project includes a detailed economic evaluation of the cost of processing the coal liquids to their optimum products. The cost analyses is for the incremental processing cost; in other words, the feed is priced at zero dollars. The study reflects costs for operations using state of the art refinery technology; no capital costs for building new refineries is considered. Some modifications to the existing refinery may be required. Economy of scale dictates the minimum amount of feedstock that should be processed.

To enhance management of the study, the work has been divided into two parts, the Basic Program and Option 1.

The objectives of the Basic Program are to:

- Characterize the coal liquids
- Develop an optimized refinery configuration for processing indirect and direct coal liquids
- Develop a LP refinery model with the Process Industry Modeling System (PIMS) software.

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The work has been divided into six tasks.

Task 1 - Development of a detailed project management plan for the Basic Program
Task 2 - Characterization of four coal liquid feeds supplied by DOE
Task 3 - Optimization of refinery processing configurations by linear programming
Task 4 - Pilot plant analysis of critical refinery process units to determine yield, product quality and cost assumptions. Petroleum cuts, neat coal liquids, and coal liquids/petroleum blends will be processed through the following process units: reforming, naphtha and distillate hydrotreating, catalytic cracking and hydrocracking.
Task 5 - Development of the project management plan for Option 1
Task 6 - Project management of the Basic Program and Option 1

The objectives of Option 1 are to:

- Confirm the validity of the optimization work of the Basic Program
- Produce large quantities of liquid transportation fuel blending stocks
- Conduct engine emission tests
- Determine the value and the processing costs of the coal liquids

This will be done by processing the coal liquids as determined by the optimization work, blending and characterizing the product liquids, and running engine emission tests of the blends. Option 1 has been divided into three tasks.

Task 1 - Based on the pilot plant and linear programming optimization work of the Basic Program, production runs of pilot plants (hydrotreating, reforming, catalytic cracking, and hydrocracking) will be conducted to produce sufficient quantities for blending and engine testing.
Task 2 - The pilot plant products will be blended, characterized, and engine tested
Task 3 - An economic analysis will be conducted to determine the costs of processing the coal liquids through the existing refinery

Table 1-1 shows which organization has the primary responsibility for each task.

1.2 Summary

The major efforts conducted during the second quarter of 1995 were in the areas of:

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- DL1 catalytic cracking - Pilot plant and micro activity tests showed that the DL1 heavy distillate was an excellent catalytic cracking feedstock with good gasoline production properties. Gasoline yield increased with higher hydrotreating severity.
- IL catalytic cracking - Pilot plant tests showed that the indirect liquid (IL) wax was also an excellent catalytic cracker feed.
- IL wax hydrocracking - Pilot plant hydrocracking tests on the IL wax are in progress
- Indirect wax cleanup - Approximately 240 gallons of clean FT wax was produced for future processing tests.

Table 1-1 Project Task Primary Responsibility Chart

Task	Description	Bechtel	SwRI	Amoco	Kellogg
1	Project Management Plan (PMP) development	x			
2	Feed characterization		x		
3	Linear programming	x			
4	Pilot plant analysis -				
	Cat cracking of DL liquids				x
	Cat cracking of indirect wax			x	
	Hydrocracking of wax			x	
	Fractionation, reforming, hydrotreating, etc.		x		
5	Option 1 PMP development	x			
6	Project management	x			
Option 1 - Task 1	Pilot plant production -				
	Cat cracking of DL liquids and wax				x
	All other production work		x		
Option 1 - Task 2	Fuel blending, characterizing, engine testing		x		
Option 1 - Task 3	Economic analysis	x			

x = key participant

Section 2

SwRI Activities

2.0 Wax Cleanup and Blending

2.1 Background

The LaPorte Alternative Fuels Division Unit (AFDU) produced Fischer-Tropsch indirect coal liquids as three related products: hydrocarbon liquid, light wax (an overhead product), and heavy wax. These materials will be used in future processing experiments on Indirect Coal Liquids (ICL).

The three as-received products required some processing before they could be integrated into the ICL testing scheme. The "light" wax was distilled at an equivalvent separation temperature of 650°F. The 650°F+ material was then combined with clean heavy wax.

The black wax (heavy wax prior to cleaning) was contaminated with catalyst fines during its production. The concentration of iron from the iron oxide fines in this "black" wax was about 5000 ppm. The presence of iron in the wax presents a problem for later processing and analysis. Fines in concentrations above 500 ppm iron may cause catalyst fouling during fixed bed cracking experiments. One hundred and ninety-two (192) gallons of the clean heavy wax are required for testing in the End Use Study.

SwRI was asked to clean the heavy wax to within acceptable limits and then blend it with the heavy portion of the light wax. The objectives of the cleanup effort were to:

1) Remove iron contaminant in the wax down to 500 ppm
2) Produce a finished wax containing a representative sample of the full boiling range of the heavy portion of the original wax
3) Clean and blend sufficient quantities of the waxes to satisfy the needs of the indirect coal liquid testing requirements (a total of 240 gallons) as shown in Table 2-1.

2.2 Wax Cleaning

2.2.1 Approach

A practical and effective means of reducing the iron oxide contaminent to acceptable levels was systematically determined. A simple processing procedure was proposed: 1) the wax would be dissolved in a suitable solvent; 2) the wax/solvent mixture would then be passed through a filter, removing the iron contaminant; and, 3) solvent would be removed from the wax by distillation. The development of the wax cleaning process was conducted in three steps as shown in Figure 2.1. The first step was to conduct laboratory tests to determine if the procedure was feasible on a small scale. The second step was to work out the problems of extending the cleaning technique to a full scale operation capable of treating hundreds of gallons of wax. The final step was to process the quantity of clean heavy wax required.

2.2.2 Laboratory Testing

Wax cleaning was first investigated with laboratory experiments. The primary objective of the experiments was to find a suitable solvent. The solvent to be used had three requirements:

1) It must be capable of dissolving black wax without altering the hydrocarbon distribution as the wax

2) The solvent boiling range must be outside the range of the wax so the mixture could be separated by distillation

3) The solvent/dissolved wax mixture should permit filtering at a temperature safely below the flash point of the solvent

The solubility of ten solvents were examined by placing black wax chips in the solvent, followed by heating and shaking. The solvents tested were: mixed xylenes; methylethylketone; heptane; carbon disulfide; petroleum naphtha; toluene; methylpyrolidone; Isopar M; pyridine; and C14-C16 solvent. The black wax readily dissolved in the carbon disulfide and midboiling range paraffin solvents.

Filtering tests were conducted with mixtures of wax and carbon disulfide, Isopar G, and Isopar M. Paper and gel filters were examined. The paper filter tests gave promising results. Solvent/wax mixtures passed through 1.5 micron porosity Miliport filters (under vacuum), producing a light colored product. This was an indication that the black contaminant content of the wax had been greatly reduced. At this point, no tests were conducted to quantify the iron content in either the black wax (contaminated heavy wax) or the filtered heavy wax.

The unfiltered and filtered heavy waxes were examined by TGA (Thermo-gravitational Analysis) and high temperature chromotography. The results of these tests showed that the filtered wax from the Isopar M solution had a boiling range similar to the parent material. Isopar K and carbon disulfide skewed the boiling curve of the filtered wax.

The filtration yield was approximately 30%. That is, about 30% of the wax in the solvent solution was recovered. The remainder was trapped in the filter cake. The experiments showed that the yield increased at higher temperatures and at decreasing concentrations of wax in the solution.

Isopar M was selected as the solvent for the full scale experiments because it produced a relatively clean product and its boiling range falls safely below that of the wax. Isopar M has a boiling range between 401 and 490°F, while the wax begins to boil at about 550°F.

2.2.3 Full Scale Experiments

Full scale experiments, based on scaling up the laboratory filtrations, were conducted. In addition to achieving satisfactory contaminent removal, the full scale separation technique needed to be able to produce filtered wax at a sufficient rate to complete the wax cleanup within the time and budget available. The overall approach was to mix the black wax with hot Isopar M, and filter the mixture to remove the iron oxide contaminant. The wax and solvent were then heated to 220°F, mixed thoroughly, and filtered.

Filtration tests of the black wax suggest that the iron oxide particles were on the order of one micron in size. (A 1.5 micron filter was shown to be able to remove the contaminent in the lab studies). Filter sizes were selected accordingly. Six test series were conducted to explore a number of filtration methods.

Test Series A. Bag Filtration

The first approach was to clean the wax using bag filters. Filters with pore sizes from 10 micron down to 0.1 micron were tested with limited success. Some of the bags simply would not filter out the iron oxide. Others would remove the particulates, but only with a low output (less than one gallon per hour). Attempts to increase the flow tended to breach the filter cake and result in contaminated output.

Test Series B. Paper Filtration

Since preliminary laboratory tests showed the wax could be successfully filtered with paper filters, large scale tests were conducted. Sheets of 24 inch diameter laboratory filter paper were placed over screens set in funnels and the wax was filtered under gravity. The technique produced clean wax, but only at a trickle. A wax/solvent mixture was then forced through the paper at 40 psi with a slightly higher flow rate of clean product but the system would clog within 15 minutes. A 30" x 30" tray of filter press paper filled with a solvent/wax mixture was placed in an oven at 190°F. Relatively clean wax (600 ppm iron) dripped through the paper into a tray below. Unfortunately, the solvent boiled off in the process, creating an unacceptable hazard in the oven, so the method was abandoned.

Test Series C. Cartidge Filters

Several types of cartridge filters were tested including oil filters and fiber filters. None of the cartidges showed any apparent filtering.

Test Series D. Gravity Settling

As the drums of solvent and wax were heated and cooled for the filtration testing, regions of brown wax could be seen in the drum. Analysis of the wax from the lighter areas shown they had distinctly lower iron concentrations (about 200 ppm). A beaker of a 2:1 solvent/wax mixture was placed in an oven at 200°F. Within 12 hours a distinct gravity separation was noticed. Eleven drums of wax at a 2:1 solvent/wax ratio were then placed in an environmental chamber at 176°F (the upper limit of the chamber) for 3 days. The drums were removed and inspected. The first 2 inches of some of the drums were brown (the remainder was black). The test was repeated at a higher temperature for a single drum. Following heating to 200°F for 2 days, the drum developed a brown layer within the top 3 inches. The lower 20 inches were black.

Test Series E. Continuous Centrifuge

In an effort to accelerate the gravity settling, a solvent/wax mixture was passed through a small, continuous centrifuge. There was no observable separation. This was likely due to the short residence time of the mixture in the separation chamber.

Test Series F. Filter Press

A filter press was considered because it provides a high filtering area under high pressure. The plate and frame press allowed the wax mixture to flow through 20" by 20" filters arranged in parallel. As many as 12 filters could be passed through simultaneously. The wax was first successfully filtered using two 4 micron filters and a 20 micron outer layer. The product wax/solvent mix was a tan color (indicating contaminent removal). X-ray analysis of the wax portion of the product showed the iron concentration near 500 ppm. The production rate of filter press was much better than the previous alternatives. Flow rates of about 5 gallons an hour were achieved during the early portion of filtering. The flow rate through the filters would decrease sharply as the filtration progressed, and the contaminent accumulated in the filter.

Early filter press trials were plagued by tears in the paper that permitted product contamination. The press would also cake up with wax. Further testing on the filter press was necessary to correct those problems.

Having concluded that the filter press is the most appropriate technique for this application, the challenge was to define the conditions needed for sustained filtration with a high quality product. Four key parameters were then optimized: temperature; dilution; filter pore size; and pressure.

Temperature

The most important factor in developing a sustainable flow is creating a filter press temperature that will prevent the wax from solidifying and suppressing the flow. Modifications were made to the press to increase the heat up rate. A preheater and strip heaters on the plates were added to the filter press. The press was heated by recirculating hot solvent through it for several hours before filtering. The 3000 pound filter press had a high heat capacity and required thorough heating before filtering. It was found that the press needed to be heated to about 200°F for an hour so that the entire machine could be brought up to temperature. Insufficient heating caused the wax to accumulate in the filter paper, which slowed down the flow, reduced yield, and accelerated the cooling by reducing the flow of hot feedstock to the press.

Dilution

The filter press test runs examined solvent/wax mixtures ranging from 2:1 to 10:1. The mixtures with higher wax concentrations generally fouled sooner. In a typical filtration run, the effluent from the press comes out dark (filled with iron oxide) immediately after the solvent/wax mixture is introduced. The flow is initially strong, but begins to decrease with time as the filter cake builds on the filters. The quality of the product then increases, changing to brownish color. The outlet temperature then decreases as the flow gradually slows to a trickle.

Filter Pore Size

A number of sizes of filter paper were used. The wax has been filtered with 4 micron paper, but with inconsistancy and with great difficulty. Multiple (1 to 4) layers of 1.5 micron paper were used with better results.

Pressure

A centrifugal pump was used to maintain a pressure of about 40 psi on the filters. A diaphragm pump was added in series with the centrifugal pump to create pressures up to 80 psi. The increased pressure has significantly increased the flow through the system and helped maintain the temperature. The incidence of filter failure, however, was high with the two-pump system. The production filtering relied on a single gear pump with pressures up to 60 psi.

2.2.4 Production Cleaning and Blending

The processing for the light and heavy waxes is shown in Figure 2.2. Drums of light and heavy waxes were received at SwRI and stored until required for processing. Samples of the waxes were submitted for testing. The light wax was distilled in batches in the DOE Synthetic Fuels Center at SwRI. The material was processed in a batch distillation unit. Seven ten-gallon batches of light wax were distilled, yielding a bottoms portion of 48 gallons of light wax (650°F+). Samples of the light wax were submitted for Thermogravitational Analysis following the distillation.

The heavy wax drums were opened with an air-driven chisel, and the wax was broken into small chunks. The wax was then mixed with Isopar M solvent in a ratio of roughly 7 pounds of Isopar per pound of wax and heated to 220°F.

Filtration

The wax/solvent mixture was passed through a plate and frame filter press to remove the iron oxide contaminent in the wax. A double layer of 1.5 micron filter paper was used. The wax and solvent mixture recovered from the press was inspected for color to assure that an adequate amount of contaminent had been removed. A light brown or tan sample would indicate that the wax contained approximately 500 ppm. This criteria was verified with x-ray testing of the sample products and gravimetrically by ashing. Dark brown samples would be rejected as possibly having too much iron, and returned to the feed drum until a light effluent was obtained.

Filtered wax spanned the sequence of drums from the runs at LaPorte. Wax was drawn from drums 32, 34, 42, 43, 49, 51, and 57. Each of the three batches of finished wax (for Amoco, Kellogg, and SwRI) contains some wax from the 30, 40, and 50 series. SwRI was able to collect an acceptably clean product from the drums, with the exception of the material in drum 55. It is suspected that that drum, produced near the end of the run, had a greater amount of fines than the earlier drums.

Experiments were conducted to estimate the yield of the filtration operation. The experimental setup involved weighing both the feed and product drums as a wax/solvent solution was passed through the filter press. The increase in weight of the product drum was compared to the loss in weight of the feed drum. Approximately 43% of the solvent/wax mixture was recovered. Of the first three drums processed (32, 42, and 57), approximately half of the 150 gallons were recovered. The slightly higher yield of the full scale experiments may be due to the fact that higher temperatures (around 200°F) were used.

The filtered wax/solvent was collected in open top, 55 gallon drums and allowed to settle. Solvent was decanted from the upper layer of the drums and returned to the filtering process. The concentrated wax/solvent mixture continued on to the solvent removal step.

Distillation

Solvent was removed from the wax in a Wiped Film Evaporator (WFE). A WFE is a continuous distillation apparatus. Wax/solvent mixture was pumped through a preheater into an evacuated chamber. The mixture was spread along the surface of the chamber by a rotating wiper blade. In this operation, the WFE was maintained at 270 F and 4 Torr, which is an equivalent atmospheric temperature of 550°F. Isopar M boils at temperatures below this point, while the wax requires higher temperatures for distillation. The wax and solvent separate, with the solvent boiling off, recondensed, and then collected in the overhead accumulator. The wax was collected in the bottoms accumulator. Recovered solvent was returned to the filtering step.

Solvent was removed in two passes through the WFE. The first pass, at about 7 gallons per hour was able to remove most of the solvent. The product from the first pass contained approximately 30% solvent. A second pass at roughly 2 gallons per hour reduced the solvent concentration to less than 9%. Samples were drawn from the product wax to measure the iron content by x-ray analysis. Solvent removal was confirmed and boiling point distribution was determined with ASTM D-2887 high temperature simulated distillation. Any residue of solvent was chemically of the same hydrocarbon type as the wax product and made little perturbation of the start of the boiling curve.

Wax Blending

Following filtration and solvent removal, the heavy wax was blended with the light wax heavy fraction. The waxes were mixed in a proportion of 4.97 pounds of heavy wax per pound of light wax heavy fraction. Blended wax batches were prepared for further testing at Amoco, Kellogg, and SwRI.

2.3 Wax Properties Before and After Cleaning

The success of the wax cleanup is measured in three ways: 1) the iron content; 2) the boiling point distribution of the filtered wax (and its similarity to the parent black wax); and 3) the quantity of material produced.

2.3.1 Iron Content

The iron content of the original black wax contained was between 5000 and 7000 ppm, varying from drum to drum. The iron content of the processed heavy wax is shown in Table 2-2 for the batches of wax to be tested at Amoco, Kellogg, and SwRI. Each of the heavy wax samples shows an iron concentration of slightly above 500 ppm. When the heavy wax was blended with the inherently iron-free light wax, the overall iron concentration falls to slightly below the targeted 500 ppm. The exception is the 70 gallon batch prepared for Kellogg which contains 576 ppm. This batch will be blended with the SwRI batch to lower the iron content to just below 500 ppm.

2.3.2 Boiling Point Distribution

The second requirement was for the filtered wax to retain a paraffin distribution similar to the parent material. Samples of the black wax and heavy wax from each of the product batches was analyzed with a high temperature, simulated distillation per ASTM D-2887. The boiling point distribution has been determined for each sample as shown in Table 2-3. Comparing the treated waxes to the black wax shows a close similarity over most of the boiling range. The differences between the values are due mainly to variability in the properties of the black wax from drum to drum and the presence of small amounts of solvent in the wax.

Figure 2.3 shows high temperature gas chromatograms for the black wax (top trace) and the clean heavy wax. The two traces show a similar distribution of paraffins over a wide range of molecular weights. The solvent was not completely removed and is visable as the plateau at the left of the lower trace.

2.3.3 Production Summary

Ample quantities of the wax were filtered and blend as required for the Work Plan. A total of 240 gallons of wax have been processed as denoted in Table 2-4. The three batches were produced from source drums in the 30, 40, and 50 series. These batches will be provided for processing experiments.

Table 2-1. Wax Production Requirements

Testing by:	Total Wax, gal	Heavy Wax, gal	Light Wax, gal
Amoco	10	8	2
Kellogg	70	56	14
SwRI	160	128	32
TOTAL	240	192	48

Table 2-2 Iron Content of Wax Samples

	Amoco	Kellogg	SwRI
Sample ID Number	FL-2442	LN 772	LN 773
Heavy Wax Iron Conc, ppm	579	721	530
Blended Wax Conc, ppm	463	576	424

Table 2-3 Boiling Point Distributions per ASTM D-2887

		Heavy Wax (°F)		
	Black Wax (°F)	Amoco	Kellogg	SwRI
IBP	517	369	443	437
10	792	523	502	488
20	875	878	695	510
50	1101	1113	882	984
70	1217	1228	1066	1154
80	1271	1272	1165	1226
90	1310	1302	1253	1286
FBP	1340	1326	1304	1325

Table 2-4 Wax Production Summary

Source Drum Numbers	Testing by:	Total Wax, gal	Heavy Wax, gal	Light Wax, gal
32,42,57	Amoco	10	8	2
32,42,57	Kellogg	70	56	14
34,43,49,51	SwRI	160	128	32
	TOTAL	240	192	48

Figure 2-1 Wax Cleaning Process Development

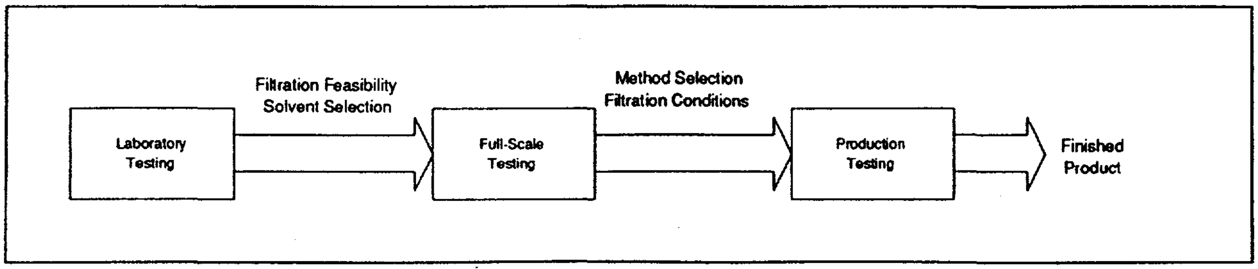


Figure 2-2 Wax Cleanup and Blending

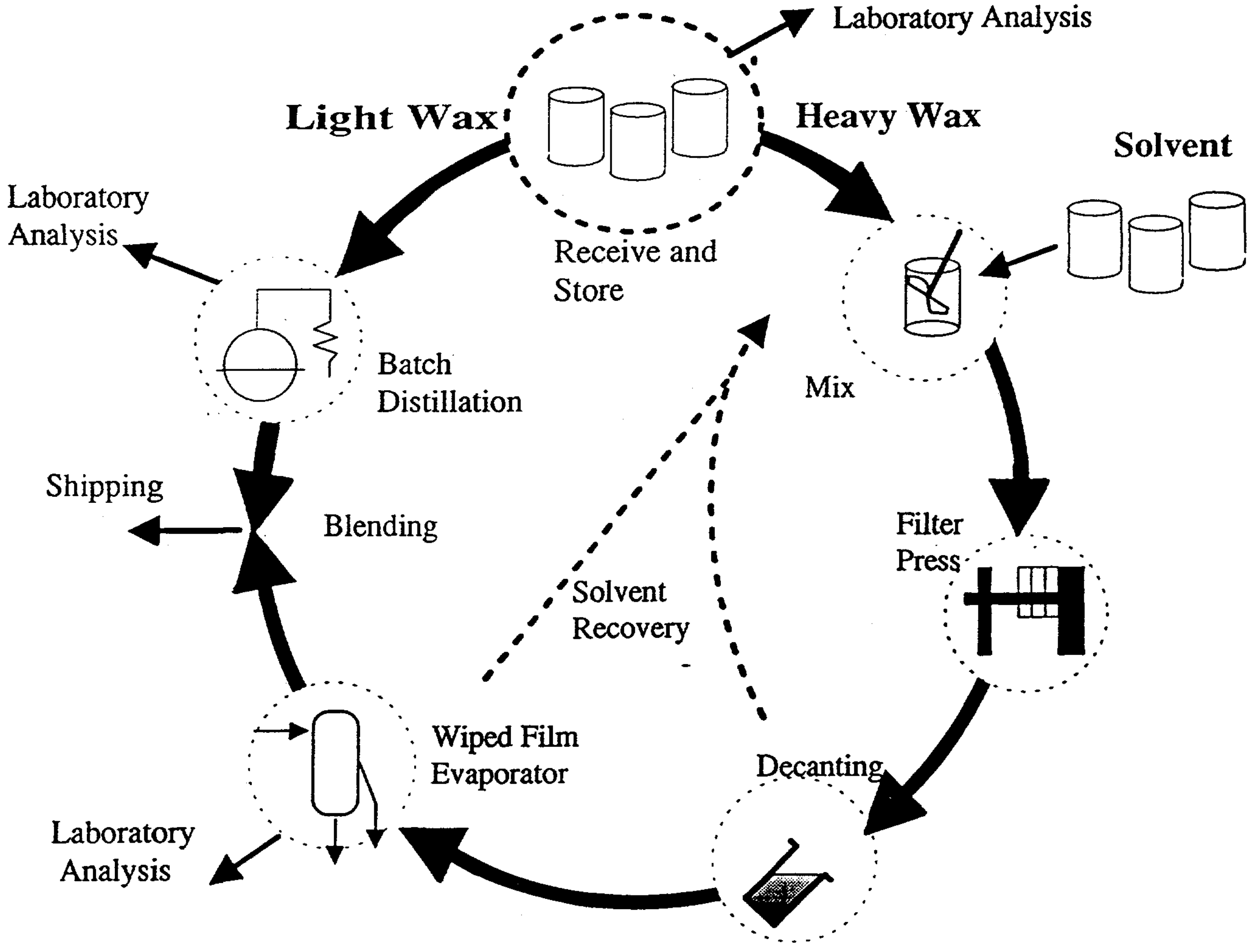
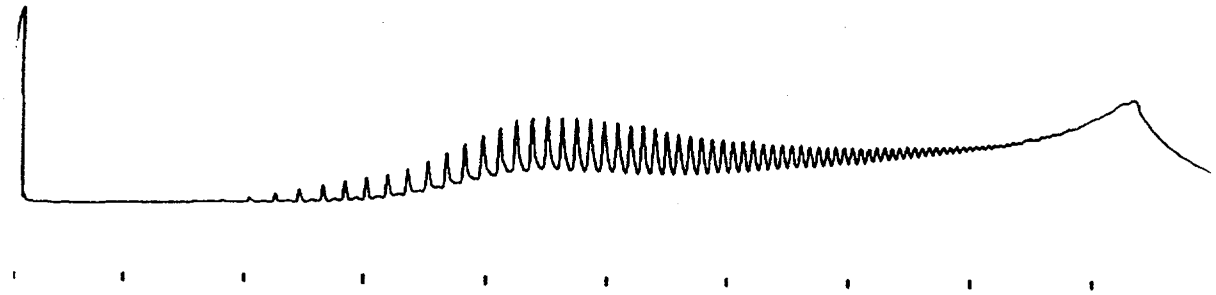
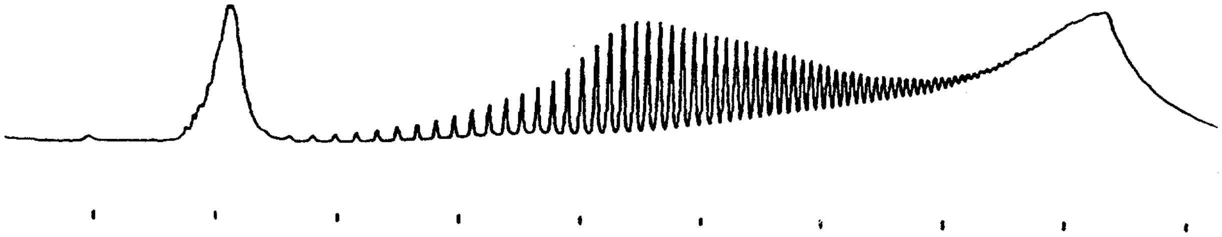


Figure 2-3 High Temperature Chromatograms of Black Wax (top) and Heavy Wax (below)



Black Wax



Heavy Wax

Section 3

Bechtel Activities

3.1 Linear Programming Model - Task 3

A report on the design basis of the linear programming model for direct coal liquids is being developed.

Section 4

Amoco Activities

4.1 Indirect wax catalytic cracking

A report summarizing the bench scale wax catalytic cracking tests is being developed and will be issued in the next quarterly report.