FINAL QUARTERLY TECHNICAL PROGRESS REPORT

JANUARY 1 THROUGH MARCH 31, 1995

Contract Number DE-AC22-92PC92149

Deashing of Coal Liquids with Ceramic Membrane
Microfiltration and Diafiltration

Submitted by
CeraMem Corporation
Waltham, Massachusetts

To

U.S. Department of Energy
Pittsburgh Energy Technology Center

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I. SUMMARY

A. Program Objectives

Removal of mineral matter from liquid hydrocarbons derived from the direct liquefaction of coal is required for product acceptability. Current methods include critical solvent de-ashing and filtration, both of which produce an ash reject stream containing up to 15% of the liquid hydrocarbon product.

This program is directed towards development of an improved process for de-ashing and recovery of coal-derived residual oil: the use of ceramic membranes for high-temperature microfiltration and diafiltration. Using laboratory-scale ceramic membrane modules, samples of a coal-derived residual oil containing ash will be processed by crossflow microfiltration, followed by solvent addition and refiltration (diafiltration). Recovery of de-ashed residual oil will be demonstrated.

Data from this program will be used to develop a preliminary engineering design and cost estimate for a demonstration pilot plant incorporating full-scale membrane modules. In addition, estimates for production system capital and operating costs will be developed to assess process economic feasibility.

The five program tasks include (1) ceramic membrane fabrication, (2) membrane test system assembly, (3) testing of the ceramic membranes, (4) design of a demonstration system using full scale membrane modules, and (5) development of estimates for microfiltration capital and operating costs and assessment of process economic feasibility.

B. Summary of Quarterly Progress

The work in this quarter has concentrated on getting process samples analyzed by Consol, Inc. Samples were sent to Consol from Imperial Oil for analysis. The original analytical approach to measuring the percentages of coal liquid and diluent in each of the process permeates and concentrates was not possible due to similarity in distillation characteristics between the coal liquid and diluent. As a result, alternative approaches were explored to evaluate the concentrations of each component in the process streams. Although many routes were explored, no satisfactory approach was identified. Unless an alternate method can be found, process analyses will have to depend on mixture calculations without confirming analytical results.

CeraMem has begun work on the filtration system design and costing. The process evaluations necessary to engineer a conceptual crossflow system design have been started and discussions have been held with several people in the coal liquids field to better define the possible locations for the crossflow filter unit in a direct liquefaction plant.

In addition, a revised scope of work has been incorporated in a revised project contract that better reflects that work to be performed.
II. MEMBRANE PROCESS TESTING

Feed, permeate, and concentrate samples from each of the diafiltration/concentration runs was delivered to Consol, Inc. at the end of 1994. In the first quarter of 1995, CeraMem and Consol attempted to find a route to analyze the samples to determine the quantities of starting coal liquid (O-13 reactor flash drum bottoms) and diluent (HRI's petroleum-based hydrotreated start-up oil) in the process concentrates and permeates. The concentration of coal liquid in the concentrates and permeates is an important factor in analyzing the diafiltration/concentration process used in the project. The data would be used to confirm the calculated amounts of coal liquid and diluent in each of the process streams assuming that the two liquids were miscible. The original approach which was to distill the mixtures thereby driving off the diluent first followed by the coal liquid was not possible because the start-up oil had a distillation curve almost identical to that of the particulate-free coal liquid. An alternative approach was necessary.

Consol and CeraMem, with assistance from HRI, discussed several approaches to making the analytical evaluations. First, the levels of asphaltenes and preasphaltenes in the coal liquid and diluent may be different enough to back calculate the amounts of coal liquid and diluent in each process stream. The measurements are straightforward but the amounts of coal liquid and diluent calculated to be in each of the streams is dependent on the liquids being miscible. Other simple component measurements such as C/H ratios, trace metals, nitrogen, and sulfur were also reviewed but the difference between the coal liquid and diluent was typically less than a factor of two and was deemed to be too small to use as an analytical marker. One other consideration was to use C$^{13}$ isotope measurements as part of an involved analytical procedure. Although the procedure was not discussed much it was clear that it would be expensive and may not provide the desired results. Consequently, it was decided that Consol would start on the asphaltene and preasphaltene analyses in order to determine if the procedure may work.

The approach to evaluating the asphaltene/preasphaltene analytical method was to first determine the asphaltene and preasphaltene concentrations in the coal liquid and diluent and then determine if the feed mixture contained calculated amount of asphaltenes and preasphaltenes based on the amounts in the coal liquid and diluent. If these tests proved that the coal liquid and diluent were significantly different and that the liquids were miscible so that the feed mixture asphaltene and preasphaltene concentrations could be calculated then the approach may be applicable to calculating the concentration of coal liquid and diluent in the process permeates and concentrates from the diafiltration tests.

The particulate-free flash drum bottoms, start-up oil, and initial feed mixture were analyzed in duplicate by Consol for asphaltene and preasphaltene concentrations. The procedures will be reported in the next monthly report in more detail after receipt of the Consol report; but in general, the samples were first subjected to tetrahydrofuran (THF) solubility determination followed by liquid column fractionation of the THF-soluble portions of each sample to determine the concentration of oil, asphaltene, and preasphaltene.

The results of these tests are reported in Table 1. The weight percent of THF-insolubles is slightly higher than that reported by HRI on the coal liquid (15%). The weight percent of THF-insolubles in the mixture is lower than that reported by Imperial Oil (10.6%). It is unclear as
Analyses of the THF-soluble fraction of each sample are reported as a percentage of the soluble fraction, not the whole sample. The concentrations of asphaltenes and preasphaltenes are both less than 5% for all three samples. Within the margin of error, there is no difference between the asphaltene or preasphaltene levels. It appears that due to the very low asphaltene and preasphaltene levels in this coal liquid, it would be very difficult to determine the actual concentrations of coal liquid and start-up oil in the concentrates and permeates through the five diafiltration cycles.

**III. SYSTEM DESIGN AND COSTING**

Based on discussions with several people in the direct liquefaction field, there are three possible places that a crossflow membrane filtration system can be placed in the overall direct liquefaction process. These are 1) after the liquefaction reactors, 2) after the atmospheric still, and 3) after the vacuum still (Rose® unit replacement). Placing the filtration unit after the reactors would provide a hot, low viscosity feed but would require expensive hardware if it was to be at pressure. Placing the unit after the atmospheric still would provide a relatively low viscosity liquid with moderate solids content. The concentrate in this case, without diluent, could be sent to the vacuum still to prepare the material for the Rose® unit. This would decrease the size of the vacuum still and Rose® unit. If diluent recycle was used, as CeraMem originally proposed, the vacuum still and Rose® unit could be replaced because the crossflow unit would produce a dry solids cake and particulate-free permeate that could be easily recycled to make lower boiling point liquids. If the crossflow filtration unit was placed after the vacuum still, diluent would have to be used to dilute the heavy bottoms. But using diluent recycle, dry solids could be produced with clean permeate being recycled for further processing. In this way, the Rose® unit could be directly replaced. There are many possibilities for a crossflow filtration unit either with or without diluent addition and recycle.

**III. FUTURE WORK**

Possible analytical approaches will be reviewed and if practical methods for coal liquid and diluent determination in the concentrates and permeates is found, it will be performed. Otherwise, CeraMem will use mixture calculations to estimate the amount of coal liquid and diluent in the permeates and concentrates.

CeraMem will continue its evaluation of a full size system design and costing. CeraMem will attempt to obtain consultation from Mr. David Grey of Mitre Corporation to help on equipment outside the scope of the membrane unit and the effects of filtration on other processes such as distillation.
Table 1.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>THF Insol.</th>
<th>Oils</th>
<th>Asphaltenes</th>
<th>Preasphaltenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-13 Bottoms</td>
<td>15.78 wt%</td>
<td>92.71 wt%</td>
<td>4.00%</td>
<td>3.79 wt%</td>
</tr>
<tr>
<td>Start-up Oil</td>
<td>-</td>
<td>95.77 wt%</td>
<td>2.35 wt%</td>
<td>1.88 wt%</td>
</tr>
<tr>
<td>Initial Feed</td>
<td>8.72 wt%</td>
<td>92.89 wt%</td>
<td>4.15 wt%</td>
<td>3.00 wt%</td>
</tr>
</tbody>
</table>