This report is the fourth quarterly report for Contract DE-AC22-87PC79818. The objective of this contract is to extend and optimize UOP’s single-stage slurry-catalyzed co-processing scheme developed under previous Contract DE-AC22-84PC70002. Particular emphasis will be given to defining and improving the catalyst utilization and costs, evaluating alternative and disposable slurry-catalyst systems, and improving catalyst recycle and recovery techniques. Pilot plant modification work and several shakedown runs were completed during this quarter. However, complete analytical results are not yet available for these runs, so discussion of the results will be delayed until the next quarterly report. Instead, this report covers the economic implications of the catalyst studies completed to date. Three main issues are discussed with regard to the design of a commercial slurry-catalyst system:

- Which catalyst, molybdenum or vanadium, is more economical?
- What is the optimum catalyst concentration?
- Should the catalyst be used on a once-through basis or recovered and recycled?
RELATIVE CATALYST COSTS FOR VANADIUM AND MOLYBDENUM

Based on autoclave tests reported previously (1), a new molybdenum-based catalyst (K6.2) was observed to have approximately 10 times the activity of the previous vanadium-based reference catalyst (K2.0). The molybdenum (Mo) catalyst had similar conversions, yields, and liquid product properties to the vanadium (V) catalyst but at 10 times lower catalyst concentrations.

At current raw material prices (2), MoO₃ goes for about $3.60/lb ($5.42/lb Mo) or about half as much as V₂O₅, which sells for $6.65/lb ($11.88/lb V). Hence, not only is a lower concentration of catalytic metal required in the Mo case, but the makeup cost per unit metal is also much lower.

To get a fair comparison between the two catalyst systems, the costs of catalyst preparation from the raw material and catalyst recovery should also be included in the analysis. The recovery process for Mo would not be fundamentally different from the V case, for which a plant design and detailed economic analysis has already been completed. Recent recovery experiments have given Mo recoveries of about 85%, and further progress is anticipated as the process is optimized. Assuming that the capital and operating costs for recovering the Mo catalyst are about equal to those (per unit of solid) for recovering the V-based catalyst under the current conceptual commercial design, and that 90% recovery of the Mo can be achieved in practice, then total catalyst costs for a 0.1% Mo catalyst would only be about 30% of costs for the equivalent activity 1.0% V catalyst system.

Cost breakdowns for the two catalyst systems are compared in Figure 1. After including preparation, makeup, and recovery costs, the 10:1 activity advantage of the Mo catalyst over V translates into about a 3.2:1 cost advantage. The V catalyst costs shown here are higher than
those reported in earlier studies (3,4), because the price of V_{2}O_{5} has escalated from about $3.35/lb to $6.65/lb in the year and a half since those studies were completed. The cost of V to a refiner could, however, potentially be a lot less than that assumed here. If the refiner is processing a heavy crude with significant quantities of Ni and V contamination, the by-product metals removed from the crude could be processed through the catalyst recovery unit to extract V for use in preparing the catalyst. The raw material cost for V would then be negligible, and the total catalyst costs for 1.0% V would only be about one and a half times those for 0.1% Mo.

Table I shows the impact that switching from the reference catalyst to the new Mo catalyst would have on the economics of adding a co-processing unit to an existing refinery. A break-even analysis is presented based on the difference in costs and revenues between a conventional refinery processing 90,000 BPSD of mixed Canadian crudes and a conceptual co-processing refinery processing the same crudes plus 2,450 MT/day of Illinois No. 6 Coal. The results are based on a linear programming (LP) refinery economic model (5) that takes into account both the co-processing unit and all the changes that are required in downstream units to upgrade the coal-derived intermediates to meet finished product specifications.

Since the yields and product properties for 1.0% V and 0.1% Mo are so similar, the upgrading schemes for the two cases are essentially identical. Labor, maintenance, and utility costs are assumed to be the same. The only major difference is the cost of the catalyst itself: the cost works out to be about $48 million/year less for the Mo catalyst case. Relative finished-product prices corresponding to a given marker crude price were estimated using EPI projections (6) to allow the analysis to be put in terms of a single well-recognized variable: the average price of Light Arabian crude. The coal price was assumed to be constant at $35/MT. For each catalyst case, the break-even crude price was then calculated at which the product margin was just equal to total operating costs (including catalyst costs and
capital charges). The new Mo catalyst would break even at a $11.61/bbl lower marker crude price than the original V reference catalyst.

The break-even crude price is strongly dependent on some of the economic assumptions made. In Table 1, a 25% capital-recovery factor (CRF) was assumed (i.e., one quarter of the co-processing erected cost is charged off each year as a capital expense). For a lower CRF, the break-even crude price drops, as shown in Table 2. For a 10% CRF, for example, the break-even crude price for the 0.1% Mo case is about $28/bbl. The Mo catalyst maintains its $11.6/bbl advantage over V, independent of the CRF assumed. The price of crude would have to nearly double from current $15/bbl levels before co-processing would be competitive. However, the new Mo catalyst does represent a substantial improvement in the break-even price over previous slurry-catalyst systems.

**OPTIMIZATION OF CATALYST CONCENTRATION**

Figures 2 and 3 show how the yields and quality of the co-processed liquid products increase with increasing Mo concentration. Catalyst and hydrogen costs also increase at higher catalyst concentrations. To determine the optimum catalyst concentration, the relative catalyst costs must be weighed against the value of the improved products.

**Catalyst Costs vs. Concentration**

Catalyst costs have three major components. The first component is the cost of recovering the catalytic metal from the co-processing "waste" solids. The recovery process, illustrated in Figure 4, involves several steps: a crude particle size classification with hydroclones to eliminate larger noncatalytic particles, fluidized-bed calcination to burn off unconverted carbonaceous material and adjust the oxidation state of the catalytic metals, extraction to separate the
metals from the inert ash solids, and crystallization to selectively recover the catalytic metal in purified form. The cost of most of these steps is related to the level of solids loading on the recovery facility. Figure 5 shows catalyst recovery costs as a function of catalyst concentration. The base case uses capital-cost data developed for recovery of V. A commercial design for the Mo system has not yet been completed, but capital costs should be similar. At low concentrations of catalyst, the coal conversion is low, and so more carbonaceous material must be burned off in the calciner. Calcination costs are therefore high. As the catalyst concentration increases in the co-processing unit, conversions improve and calcination costs go down, but extraction and crystallization costs go up to handle the additional metals load. Thus, the recovery cost curve goes through a minimum at about 0.1 wt-% Mo.

The second component of catalyst cost is the makeup cost. Any metal that is not recovered must be made up from purchased raw material (typically the metal oxide). Makeup costs are directly proportional to both the raw material cost and the percentage of metal losses in the recovery facility. In the throwaway slurry-catalyst case, 100% of the catalytic metal requirement is supplied as makeup, and there are no recovery costs.

The final component of the total catalyst cost, the cost to make an active catalyst out of the recovered metal or raw material, is directly proportional to the catalyst concentration and is generally small compared with recovery or makeup costs. Total catalyst costs for recovery, makeup, and preparation are shown as the shaded areas in Figure 6. The minimum total cost of about $10/MT of moisture and ash-free feed (MAFF) is at 0.1 wt-% Mo. Also plotted on the same figure, as a dashed curve, is the throwaway catalyst case (100% makeup and no recovery costs). Catalyst costs in this case are directly proportional to catalyst concentration and show up as an exponentially increasing curve on this log plot. The total catalyst cost curves for the throwaway and catalyst-recovery cases intersect at a Mo concen-
tration of about 0.08 wt-%. At concentrations below this level, once-through catalyst operation is preferable. At higher concentrations, the savings from metals recovery more than offset the capital and operating costs of the recovery facility, and a recycle catalyst operation becomes more economical. The transition point between throw-away and recycle operation is relatively insensitive to other factors. Increasing the recovery efficiency from 90 to 99% has almost no effect at all on the transition point. Changing the capital costs of the recovery facility by a factor of two either way from the V-recovery base-case design would change the transition point from 0.05 to 0.20 wt-%, respectively. Changing the raw material cost by a factor of two affects the absolute catalyst cost but also has little effect on the transition point between once-through and recycle operation.

Product Values vs. Catalyst Concentration

The increased catalyst costs associated with operation at high concentrations of catalyst are at least partly offset by improved yields and product values. Except for makeup hydrogen, feed costs are the same for all of the cases considered. As shown in Figure 7, hydrogen consumption increases at higher concentrations of catalyst. Hydrogen utilization also improves: more of the hydrogen goes into the liquid product, and less ends up in light gases. Thus, the C1-C4 yield (Figure 2) decreases at the same time that hydrogen consumption is increasing.

Putting a value on the liquid-product yields at each catalyst concentration is a more difficult task. The autoclave test used did not make large enough quantities of product to allow for complete upgrading studies to be performed on each product fraction. (Continuous pilot plant runs now in progress will provide larger volumes of product for that purpose.) For the initial evaluation, the assumption was made that the total liquid product value could be correlated with its "hydrogen index," which is a measure of how much hydrogen needs to be added in subsequent hydrotreating operations to remove heteroatoms
and improve the H/C ratio of the liquid to meet finished product specifications.

Figure 8 shows a correlation of hydrogen index vs. dollars per pound for a number of heavy crudes and fuel-oil products based on December 1988 prices from Platt's Oilgram.(7) At these price levels, the Lloydminster Vacuum Resid (feed) would be valued at about 2.5¢/lb, and the co-processed total C5+ liquid product from 2.7 to 4.0¢/lb, depending on the catalyst concentration used and the degree of upgrading. Similar correlations can be made for other crude price scenarios.

Figure 9 shows the total product value and feed costs as a function of catalyst concentration for a hypothetical case in which the natural gas and crude prices both double from current levels but the coal prices remain the same. The product margin, which is the area between the total product value and total feed cost curves, is about $40/MT MAFF over a catalyst concentration range from 0.02 to 0.20 wt-% Mo. At low concentrations of catalyst, where significant conversion of coal but little upgrading of the resid occurs, the total product value rapidly increases with increasing concentration. At intermediate concentrations, the added product value is about equally offset by increased hydrogen costs. At higher concentrations, a region of diminishing returns is reached where further upgrading becomes more and more difficult. By-products (sulfur, ammonia, and fuel gas) contribute only about 8% of the total product value.

**Profit vs. Catalyst Concentration**

Figure 10 ties together the product margins from Figure 9 with the catalyst costs from Figure 5 and other operating costs. The dashed product-margin curve is superimposed on a cumulative plot of capital and labor-related expenses, catalyst costs, and utilities. The catalyst-cost portion of the operating expenses has a discontinuity at about 0.08 wt-%, where the transition from once-through to recycle
catalyst operation occurs. The area between the margin curve and the total-operating-cost curve represents operating profit. For the given set of economic assumptions, maximum profit is achieved at a Mo concentration of about 0.02 wt-%, which is in the once-through portion of the operating regime. However, caution must be exercised in interpreting these results. The yields for the catalyst-concentration survey are based on autoclave tests, not continuous plant data. Maintaining stable operation for long at such low catalyst concentrations may not be possible without having coking or plugging problems in the continuous plant. Directionally, however, this analysis shows that the optimum economics may not be at the point of maximum heteroatom removal or non-distillable conversion, but rather at some lower catalyst concentration. The catalyst concentration should be chosen to convert as much coal as possible to liquid, but not necessarily to give maximum conversion of the resid. Further upgrading of the resid may be more economically achieved in conventional refinery units than by running higher catalyst concentrations in the co-processing unit. In practice, the co-processing unit would probably be run to give a liquid product that just meets the minimum feed-quality standards of the refinery conversion units or at the lower operability limit of the co-processing unit, whichever case is limiting. Most of the pilot plant work to date has been with V catalyst at relatively high concentrations of catalyst. Future runs will use the new Mo catalyst and explore lower concentrations of catalyst in the continuous plant.

The location of the operating point for maximum profit is strongly dependent on both the economic assumptions that set product values and on the steepness of the catalyst cost curve. Any move toward higher product margins (i.e., with increasing crude prices) or reduction in the cost of catalyst recovery shifts the optimum toward higher concentrations of catalyst. Figure 11 shows a case with "optimistic" catalyst recovery assumptions (that the capital costs for the Mo recovery facility are only half of those for the initial commercial V recovery design, and that 99% recovery of the metal is possible.) In this case the co-processing unit becomes profitable operating with catalyst recovery at concentrations of catalyst up to about 0.4 wt-%.
CONCLUSIONS

A new Mo-based slurry co-processing catalyst (K6.2) has been tested that is 10 times more active than former reference catalyst K2.0. Switching to the new catalyst is expected to reduce overall catalyst costs by a factor of 3.2 and drop the break-even marker crude price for the addition of slurry co-processing to a refinery by more than $11/bbl. Catalyst cost savings for the conceptual commercial plant design would be on the order of $48 million/year.

At current raw material prices, a once-through throwaway catalyst operation is more economical at catalyst concentrations of less than 0.08 wt-%. At higher concentrations of catalyst, catalyst recovery and recycle are preferable. At current crude and product price levels, a low concentration throwaway catalyst appears to be most cost-effective. However, continuous plant operation has yet to be demonstrated at low catalyst concentrations, and operation in this mode would shift a greater upgrading burden to downstream hydrotreaters and conversion units in the refinery. As the margins between crude and product prices increase and further reductions are made in the cost of catalyst recovery, the optimum concentration of catalyst is expected to shift to 0.1 or 0.2 wt-%, where recycle catalyst operation is more attractive.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
References


### TABLE 1 - Break-even Analysis for Adding Co-Processing to a Conventional Refinery

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>1 wt-% V</th>
<th>0.1 wt-% Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Break-even Crude Price, $/bbl</td>
<td>49.94</td>
<td>38.83</td>
</tr>
<tr>
<td>Cash Flows, $MM/year:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Finished Product Sales (a)</td>
<td>216.87</td>
<td>168.24</td>
</tr>
<tr>
<td>Raw Material Costs</td>
<td>43.30</td>
<td>42.93</td>
</tr>
<tr>
<td>Gross Margin</td>
<td>173.56</td>
<td>125.31</td>
</tr>
<tr>
<td>Capital-Related Costs (b)</td>
<td>70.06</td>
<td>70.06</td>
</tr>
<tr>
<td>Labor, Maint. &amp; Ins. Costs</td>
<td>22.72</td>
<td>22.72</td>
</tr>
<tr>
<td>Utility Costs (c)</td>
<td>10.02</td>
<td>10.02</td>
</tr>
<tr>
<td>Catalyst Costs (d)</td>
<td>70.76</td>
<td>22.51</td>
</tr>
<tr>
<td>Total Operating Costs</td>
<td>173.56</td>
<td>125.31</td>
</tr>
<tr>
<td>Operating Profit</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

(a) Feed and finished product prices related to marker crude (MC), fuel gas (FG), or coal (C) prices as follows:

<table>
<thead>
<tr>
<th>Product</th>
<th>$/BBL</th>
<th>$MM/yr</th>
<th>$/BBL</th>
<th>$MM/yr</th>
<th>BPSD (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPL Crude (1.03xMC)</td>
<td>51.50</td>
<td>0</td>
<td>39.53</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Lloydminster Crude (0.878xMC)</td>
<td>43.82</td>
<td>1.60</td>
<td>33.64</td>
<td>1.23</td>
<td>+100</td>
</tr>
<tr>
<td>Isobutane (6.4xFG)</td>
<td>16.80</td>
<td>7.67</td>
<td>16.80</td>
<td>7.67</td>
<td>+1250</td>
</tr>
<tr>
<td>Normal butane (6.72xFG)</td>
<td>16.00</td>
<td>2.78</td>
<td>16.00</td>
<td>2.78</td>
<td>+476</td>
</tr>
<tr>
<td>Premium Gasoline (1.435xMC)</td>
<td>71.66</td>
<td>75.23</td>
<td>55.00</td>
<td>57.74</td>
<td>+2876</td>
</tr>
<tr>
<td>Regular Gasoline (1.325xMC)</td>
<td>66.17</td>
<td>138.92</td>
<td>58.79</td>
<td>106.63</td>
<td>+5752</td>
</tr>
<tr>
<td>Jet Fuel (1.239xMC)</td>
<td>58.07</td>
<td>0.13</td>
<td>44.57</td>
<td>0.10</td>
<td>+6</td>
</tr>
<tr>
<td>Fuel Oil No. 2 (1.15xMC)</td>
<td>57.43</td>
<td>(13.42)</td>
<td>44.08</td>
<td>(10.38)</td>
<td>-640</td>
</tr>
<tr>
<td>Fuel Oil No. 6 (0.90xMC)</td>
<td>44.95</td>
<td>8.30</td>
<td>34.50</td>
<td>6.37</td>
<td>+506</td>
</tr>
<tr>
<td>Ill. No. 6 Coal</td>
<td>35.00</td>
<td>31.26</td>
<td>35.00</td>
<td>31.26</td>
<td>+2447</td>
</tr>
<tr>
<td>High Sulfur Coke (0.85xC)</td>
<td>29.75</td>
<td>(2.22)</td>
<td>29.75</td>
<td>(2.22)</td>
<td>-204</td>
</tr>
<tr>
<td>Sulfur</td>
<td>110.00</td>
<td>9.92</td>
<td>110.00</td>
<td>9.92</td>
<td>+247</td>
</tr>
</tbody>
</table>

(b) Capital charges based on a capital recovery factor of 25%/yr and $280 million erected cost difference between conventional refinery and co-processing refinery.

(c) Utility costs include power at $0.05/kWh plus the internal refinery conversion costs for the production of cooling water, steam, and hydrogen from other internal streams.

(d) Catalyst costs based on makeup costs of $6.65/lb V_2O_5 (with 92.9% V recovery) and $3.60/lb MoO_3 (with 90% Mo recovery).

(e) Difference between net flows for co-processing refinery and conventional refinery based on LP optimum unit configurations.

See reference 5 for other LP assumptions, including product specifications. Products are priced relative to Light Arabian Crude based on EPI projections from reference 6.
TABLE 2 - Break-even Crude Price vs. Capital Recovery Factor

<table>
<thead>
<tr>
<th>CRF</th>
<th>1 wt-% V</th>
<th>0.1 wt-% Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>39.83</td>
<td>28.22</td>
</tr>
<tr>
<td>15%</td>
<td>43.20</td>
<td>31.59</td>
</tr>
<tr>
<td>20%</td>
<td>46.57</td>
<td>34.96</td>
</tr>
<tr>
<td>25%</td>
<td>49.94</td>
<td>38.33</td>
</tr>
</tbody>
</table>

Figure 1

Relative Catalyst Costs
K6.2 (Mo) vs. K2.0 (V)
Figure 2

Yields vs. Catalyst Concentration

![Graph showing yields vs. catalyst concentration.](image)

Figure 3

Liquid Product Properties vs. Catalyst Concentration

![Graph showing liquid product properties vs. catalyst concentration.](image)

Properties are for debutanized C5+ total liquid product.
Figure 4

CATALYST RECOVERY

[Diagram showing the process of catalyst recovery with labeled steps: Catalyst, Coal Solids, Physical Separation, Fine Solids, Calcination, Flue Gas, NH₃, Unleached Solids, Leaching, Crystallization, Other Salts, Air, Coarse Solids.]
Figure 5

Catalyst Recovery Costs vs. Catalyst Concentration

Figure 6

Catalyst Costs vs. Concentration

Capital costs are scaled from a base case recovery design.

Assumes 90% recovery and base capital costs for recovery section.
**Figure 7**

Hydrogen Consumption vs. Catalyst Concentration

<table>
<thead>
<tr>
<th>wt-% of MAFF</th>
<th>$/MT MAFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.08</td>
</tr>
<tr>
<td>0.01</td>
<td>0.07</td>
</tr>
<tr>
<td>0.1</td>
<td>0.06</td>
</tr>
<tr>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>4</td>
<td>0.04</td>
</tr>
<tr>
<td>16</td>
<td>0.03</td>
</tr>
</tbody>
</table>

K2.0 Catalyst (V)  ▲  K6.2 Catalyst (Mo)

Average

Assumes H2 Cost = $800/MT

**Figure 8**

Crude & Fuel Oil Prices vs. Hydrogen Index

$/lb (12/88)

Hydrogen Index

H Index = (H-2/32+B-3/14+N-2/10+O)/C.
Figure 9

Feed & Product Values vs. Catalyst Concentration

Figure 10


Assumes Marker Crude = $34/barrel; Fuel Gas = $5.00/MMBTU; H2 = $1214/MT; Coal = $35/MT; S = $110/MT; NH3 = $180/MT;

Assumes Crude = $34/barrel; Power = $0.05/kWh; Fuel Gas = $5.00/MMBTU; Coal = $35/MT; Base Catalyst Costs (ass. 90% recovery).
Figure 11


$/MT MAF Feed

- Cap. Costs
- Labor Costs
- Utility Costs
- Cat. Costs
- Prod. Margin

Assumes Crude=$34/bbl; Power=$0.05/kWh; Optimistic Catalyst Costs (assumes 50% of base capital & 99% recovery).