UOP SLURRY-CATALYZED CO-PROCESSING

by

C. A. Piasecki, J. G. Gatsis, H. E. Fullerton

UOP
Des Plaines, Illinois

INTRODUCTION

UOP is continuing bench-scale research and development of coal and resid co-processing technology under the sponsorship of the DOE. The UOP process uses a single-stage reactor system and a highly active, dispersed slurry catalyst to simultaneously convert coal and petroleum resid to high-quality liquid products. The use of a slurry catalyst has several advantages over alternative ebullating-bed technologies. The finely divided catalyst minimizes diffusion problems that may be associated with a supported catalyst. The catalyst moves with the products rather than staying in the reactor for extended periods. Thus, the catalyst is present to help suppress retrograde reactions in the preheater and downstream fractionation as well as in the reactor. The catalytic metals may be recovered from the waste solids and converted back to the active form of the catalyst. The recovered catalyst is then recycled back to the feed so that the reactants are constantly seeing fresh catalyst rather than an equilibrium catalyst with reduced activity. The recovery of the free metals is also easier than it would be if the metals were impregnated on a support.

Under UOP's first co-processing contract, the concept of single-stage slurry-catalyzed co-processing was successfully demonstrated in batch laboratory autoclave tests [1] and in continuous bench-scale operations [2]. Good long-term operability with the UOP vanadium catalyst was demonstrated for nearly 2,000 hours on-stream [3]. A method of recovering the catalyst was developed and demonstrated on the laboratory scale. Based on the long-term operability and catalyst recovery studies, a conceptual commercial design was completed for a co-processing unit integrated with a 100,000 BPSD conventional refinery [4].

The ongoing effort under the second contract has been devoted to exploring new catalyst systems and improving catalyst activity, dispersion, and recovery techniques. The ultimate goal is to improved the overall profitability of co-processing. Most of the early development work was completed using a vanadium-based slurry catalyst. A newer molybdenum-based catalyst has since been developed. In autoclave testing, a molybdenum catalyst was identified that gave equivalent conversions and yields to the earlier vanadium catalyst at one-tenth of the metal concentration [5]. This molybdenum catalyst is being evaluated in the continuous bench-scale unit. Plant modifications, including the addition of a liquid recycle loop, have made bench-scale operations possible at much higher severities than were previously possible. A study of the effects of catalyst concentration, increased process severity, and the role of the resid on product yields and operability has been completed.

CONTINUOUS BENCH-SCALE OPERATIONS

A simplified block diagram of the UOP bench-scale unit is shown in Figure 1. The unit contains most of the essential features of the commercial flow scheme. The slurry feed (finely ground coal, petroleum vacuum resid, and catalyst) is combined with a hydrogen-rich recycle gas and is preheated before it enters the bottom of an upflow reactor. The products from the reactor are separated into gas and oil streams in the high-pressure separator (HPS). The gas stream from the HPS is combined with makeup hydrogen before being recycled back to the incoming fresh feed. The oil stream from the HPS is sent to a low-pressure stripper (LPS). The lighter hydrocarbon stream from the LPS goes to a debutanizer, where it is stabilized by removing the C_4-light ends. The heavier hydrocarbon stream from the LPS is sent to a vacuum fractionator to recover an overhead stream (light oil and vacuum gas oil) and a bottoms stream containing catalyst, coal minerals, insoluble carbonaceous material, and nondistillable hydrocarbons. An on-line separation unit downstream of the vacuum column can be used to remove the solids from the resid stream.

One modification that has greatly improved plant operability is the recycle of a portion of the HPS liquid back to the fresh feed. A recycle ratio of about 5:1 (based on fresh feed) is typically used. The fresh-feed space velocity is maintained constant so that the recycle results in increased liquid velocities and back-mixing in the reactor but no change in total residence time. The improved mixing may help to eliminate the wall effects associated with a small bench-scale reactor, thus making it more representative of a completely back-mixed commercial reactor. The liquid recycle also has a "fly-wheel" effect that helps the plant better withstand upsets in the rate and composition of the fresh feed.

Prior to the introduction of liquid recycle, the reactor temperature in the bench-scale unit was limited to a maximum of 425°C. Above that temperature, the plant was subject to coking and plugging problems and became increasingly inoperable. Figure 2 shows the results of a temperature study with 1 wt-% vanadium catalyst and reference feedstocks. The asphaltene conversion, measured as the heptane insolubles, is a good indicator of the formation of coke precursors. As the operating temperature was increased beyond 425°C, a rapid decrease in heptane insoluble conversion occurred that paralleled the onset of coking problems.

With the addition of liquid recycle, the bench-scale unit can be run at much higher temperatures than were previously possible without developing coking problems. Figure 3 compares the results of a temperature study with a 5:1 liquid recycle to the temperature study with no liquid recycle using a 1 wt-% vanadium catalyst in both cases. Temperatures of up to 470°C were achieved with an improved heptane insoluble conversion as compared to the no-recycle operations. Only a slight decrease in the heptane insoluble conversion was observed with the recycle operation that did not parallel coking. The increased severity had little effect on the maximum achievable coal conversion of about 92%. The maximum asphaltene conversion (as measured by heptane insolubles) increased about 10%, and the 510°C+ nondistillable conversion increased about 15%.

The mechanism for improved high-temperature operability with liquid recycle is not clear at this time. The increased conversions may be due to better contacting of the reactive coal fragments with hydrogen and catalyst as a result of improved reactor back-mixing or to the decrease in the relative contact between the coke precursors and the hot reactor walls as a result of greater superficial velocities in the reactor. Hydrodynamic differences resulting from the recycle may also affect the flow regime, heat-transfer characteristics, or gas void fraction in the reactor. Further reactor modeling studies are required to thoroughly understand these phenomena.

HIGH-SEVERITY CATALYST-CONCENTRATION STUDIES

The newer molybdenum catalyst was tested in the continuous bench-scale plant. Several temperature surveys were conducted at various catalyst concentrations (0.5 wt.-%, 0.12 wt-%, and 0.05 wt-%) to investigate the catalyst performance at high-severity conditions. The run was conducted at the standard operating conditions of 3,000 psig, 5:1 minimum liquid-recycle ratio, base WHSV, and a 2:1 mixture of resid to coal. The reference feedstocks, Lloydminster Vacuum Resid and Illinois Coal No. 6, were also used. The reactor temperature was increased in a stepwise manner starting from 420°C until evidence of thermal degradation (decreased heptane insoluble conversion) or reactor fouling was observed.

The MAF coal conversions for each catalyst concentration are compared in Figure 4 as a function of reactor temperature. At 425°C, the conversion for the 0.5 wt-% molybdenum case has a noticeable advantage (up to 7 wt-%) over the lower catalyst concentrations. However, as the temperature is increased, this advantage diminishes. Above 450°C, catalyst concentration has little or no effect on the coal conversion. In contrast, the nondistillable conversion is relatively independant of catalyst concentration (Figure 5). As the temperature increased, the nondistillable conversion also increased.

The yields of light ends and the various boiling-range liquid products (Figures 6-10) are all relatively independent of catalyst concentration. As may be expected, the yields of light ends, naphtha, and distillate increase with increasing temperature at the expense of vacumm gas oil and resid. The total C_5+ liquid yield decreases at higher temperatures because the liquefaction of any remaining unconverted coal is exceeded by the cracking of liquids to light gases (Figure 11).

Whereas the product yields appear to be dictated primarily by thermal effects, the properties of the liquid products are strongly influenced by the catalyst concentration. Figures 12 and 13 show the API gravity and sulfur content of the total product as a function of temperature. At 450°C, the product from the run with 0.50 wt-% molybdenum catalyst enjoys about a 5 °API and 0.5 wt-% sulfur advantage over the 0.12 wt-% molybdenum case. The asphaltene content (Figure 14) is also reduced at the higher catalyst concentration but to a smaller degree at higher temperatures.

IMPROVED DISPERSION RUN

In one of the temperature surveys at low catalyst concentration, a modified catalyst addition technique was used. The feedstocks and operating conditions for the run were identical to the previous temperature surveys, but a more highly dispersed molybdenum catalyst at a 0.05 wt-% concentration was used. The effects of the improved catalyst-addition procedure were most evident in the properties of the co-processed liquid product. The reduction of the asphaltene level for the 0.05 wt-% molybdenum case with modified dispersion was equal to or better than those for the 0.12 wt-% molybdenum case with normal dispersion (Figures 15). In fact, the API of the total liquid product was almost as good as the 0.50 wt-% molybdenum case (Figure 16).

INVESTIGATION OF PROCESS SYNERGISM

Others have reported a process synergism between the coal and the petroleum resid during co-processing [7,8,9]. They have experienced an improved overall non-distillable conversion or liquid product yield for co-processing as compared to processing resid by itself. Resid, without the presence of coal, was evaluated in the bench-scale unit to investigate the manner in which the resid is upgraded at the high-severity conditions. The 0.05 wt-% molybdenum catalyst with the improved method of dispersion and the standard co-processing operating conditions was used for this study. The data from this resid-only study are compared to the 0.05 wt-% improved dispersion co-processing study [6] to investigate the synergism in the UOP process.

The conversions and yields for both the resid and the co-processing cases were similar. The 510°C nondistillable conversion was essentially the same for both runs (Figure 17). At 460°C, the nondistillable conversion was just over 80 wt-% in both cases. The heptane insoluble conversion for the co-processing case is slightly higher than the resid-only case (Figure 18). However, the amount of heptane insolubles remaining in the co-processed derived product is slightly greater (Figure 19). The difference in the heptane solubles in the products is probably due to the amount contributed from the coal. The C_5-510°C liquid yield and the resid yield are similar for both the resid and co-processing runs (Figures 20-21), and the light ends yield was slightly higher for the co-processing run (Figure 22). After the initial reaction of the coal, both feeds are upgraded in a similar manner.

The major difference between co-processing and resid upgrading is the liquid product properties. The API of the product derived from co-processing is up to 5° lower (Figure 23), because of the higher aromatic content of the coal derived liquids. The con-carbon (Figure 24) and asphaltene (Figure 18) content in the product derived from co-processing are also slightly higher. As expected, the unconverted coal yield is significantly higher (up to 6.5 wt-%) than the coke yield for the resid run (Figure 25). In contrast, the sulfur content of the product derived from co-processing is slightly lower (Figure 26). The significance of these differences depends mainly on the processing and the upgrading costs for each case.

The co-processing data was used to approximate the contribution from the petroleum resid to the C_5 - 510°C liquid products during co-processing. For this calculation, a linear relationship between the product yields and the weight percent of coal and resid was assumed, and the contributions from the resid were than normalized to 100 percent. The results of this analysis are compared to the resid-only run in Table 1. A small difference was obtained for the average 510°C+ nondistillable conversions. For the resid-only run the conversion was 82.3 wt-%, and for the normalized resid data, the conversion was 85.8 wt-%. However, the C_5+-510°C liquid product yields were 72.0 wt-% and 72.6 wt-% for the resid-only and the normalized co-processing data, respectively. The presence of coal during co-processing did not significantly enhance the conversion of the resid to liquid products as reported by others. [7,8,9]

On this basis, a process synergism was not observed in the UOP process with these feedstocks. The UOP process has the advantage that it can used during possible transition periods where a resid may be more economical to process than co-processing. As the economy dictates, the same plant with the addition of a coal-handling facility can also be used for co-processing.

LONG-TERM OPERABILITY STUDY

The use of reduced concentrations of the molybdenum catalyst and the ability to operate the co-processing unit at temperatures well above 425°C will have a strong positive impact on the economics of co-processing. To evaluate this impact, a long term-operability study is required to collect enough product sample to complete detailed characterization of the individual naphtha, distillate, and VGO cuts. This study will provide the necessary information to reevaluate the engineering design and product upgrading scheme that were developed under the first contract and to complete a detailed economic analysis of the current co-processing scheme. This long-term operability study is currently being completed.

CONCLUSIONS

Liquid recycle helps to stabilize plant operation and permits higher severity operation without the coking problems that were previously encountered in the bench-scale unit above 425°C. Good plant operation was achieved at temperatures up to 470°C. Nondistillable and asphaltene conversions were significantly enhanced at the higher temperatures. A comparison of the high-severity performance at different catalyst concentrations indicates that the nondistillable conversion and boiling-range distribution of the liquid product are primarily controlled by temperature and are nearly independent of catalyst concentration and type. However, increased catalyst concentration has a strong effect on the properties of the liquid product (improved hydrogenation, increased API, and reduction in heteroatom levels). These beneficial effects are more pronounced at lower temperatures (below about 440°C). The advantages of high catalyst concentration in increasing coal conversion diminish at higher temperatures. An improved method of catalyst dispersion was tested. With this method, the catalyst requirements may be reduced to 0.05 wt-% of MAF feed or less.

The UOP process can be applied to either in co-processing or heavy oil upgrading. The liquified coal and the vacuum resid are upgraded in a similar manner as shown by the conversion and yield data. However, the properties of the two products are different because of the different characteristics of the coal and the resid. To determine the significance of these differences, a comparison of the upgrading economics for the two cases needs to be completed.

REFERENCES

1. C. P. Luebke, et. al., *Coal Liquefaction Co-Processing Topical Report Number 1*, prepared for the United States Department of Energy under Contract No. DE-AC22-84PC70002, June 1, 1987.
2. J. G. Gatsis, et. al., *Coal Liquefaction Co-Processing Topical Report Number 2*, prepared for the United States Department of Energy under Contract No. DE-AC22-84PC70002, Aug. 19, 1988.
3. J. G. Gatsis, et. al., "Continuous Bench-Scale Single-Stage Slurry Catalyzed Co-Processing," *Proceedings of DOE Direct Liquefaction Contractors' Review Meeting*, Oct. 6-8, 1987.
4. D. A. Nafis, et. al., *Coal Liquefaction Co-Processing Final Report*, Prepared for the United States Department of Energy Under Contract No. DE-AC22-84PC70002.
5. D. A. Nafis, et. al., "UOP Co-Processing Developments." *Proceedings of DOE Direct Liquefaction Contractors' Review Meeting*, Oct. 2-4, 1989.
6. D. A. Nafis, et. al., *Bench-Scale Co-Processing Quarterly Report No. 7*, prepared for the United States Department of Energy under Contract No. DE-AC22-87PC79818, Mar. 27, 1990.
7. J. E. Duddy, et. al., *Coal/Oil Co-Processing Program Update*, proceedings from the 12th Annual EPRI Contractors Fuel Science and Conversion Conference, 1987.
8. *Research of Coal Liquefaction Co-Processing Quarterly Technical Progress Summary Report*, prepared for the United States Department of Energy under Contract No. DE-AC22-84PC70042, Oct.-Dec. 1985.
9. A. V. Cugini, *A Review of Coal-Oil Coprocessing Technology*, submitted to the graduate faculty of the University of Pittsburgh in partial fulfillment for a master of science degree. Aug. 1985.

Table 1
Resid Conversion Analysis

	Co-Processing Run 27, wt-%	Normalized Resid Data*, wt-%	Resid-Only Run 30-34, wt-%
Coal Conversion	92.2	No Coal Basis	No Coal
C_7 Insoluble Conversion	87.9	91.3	80.4
510°C+ Nondistillable Conversion	82.6	85.8	82.3
Distillable Conversion	68.2	70.9	67.5
C_5 - 510°C Liquid Product Yield	69.3	72.0	72.6

* Estimated resid conversion based on Run 27 co-processing data.
Resid contribution was normalized to 100% resid.

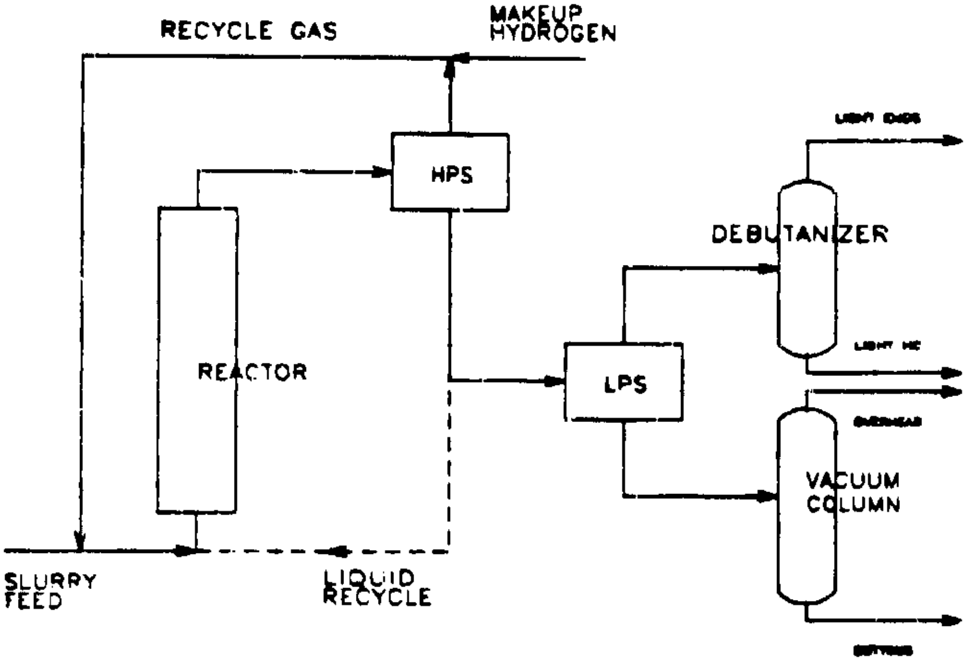
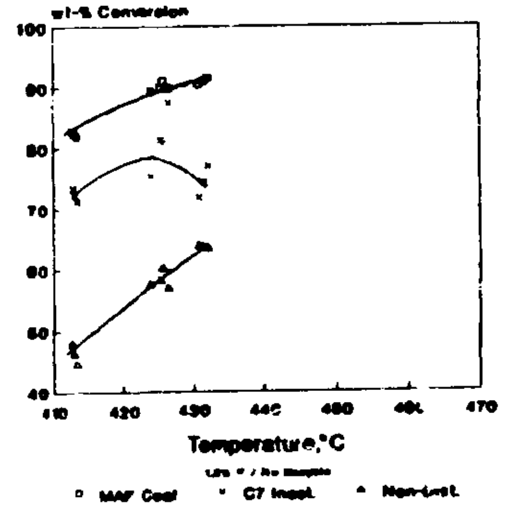


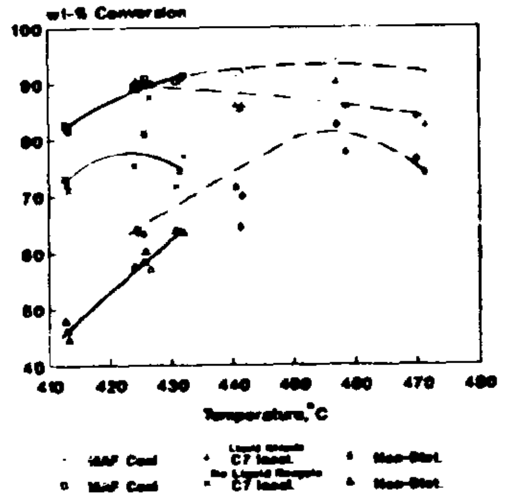
FIGURE 1 – CO–PROCESSING BENCH–SCALE UNIT

Figure 2
Conversions
vs. Temperature



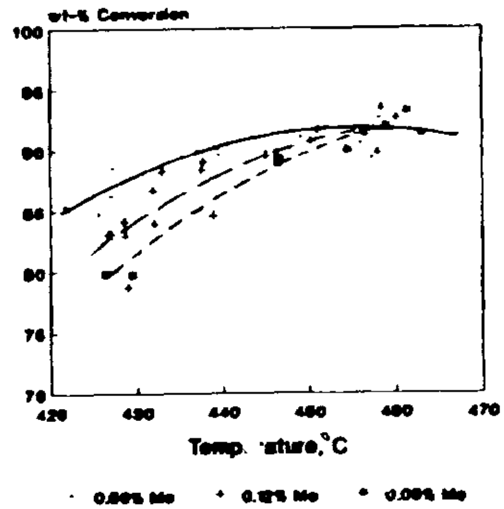
3000 psig, Base WHSV
2:1 Lloydminster Resid/Ill. No. 6 Coal

Figure 3
Conversions
vs. Temperature



% V, 3000 psig, Base WHSV
2:1 Lloydminster Resid/Ill. No. 6 Coal

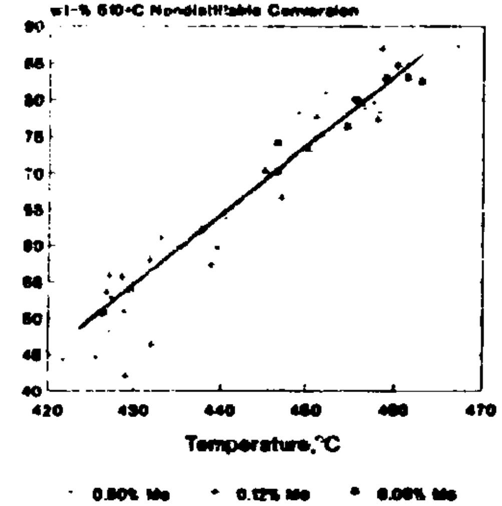
Figure 4
MAF Coal Conversion
vs. Temperature



K8.1 Catalyst, C14 Coal, 2:1 Resid
3000 psig, base WHSV, 2:1 Resid/Coal

Figure 5

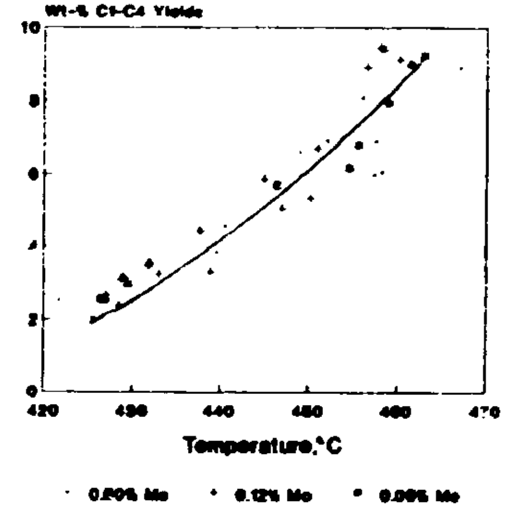
Nondistillable Conversion
vs. Temperature



K8.7 Catalyst, C14 Coal, R19 Resid
3000 psig, base WHSV, 2:1 Resid/Coal

Figure 6

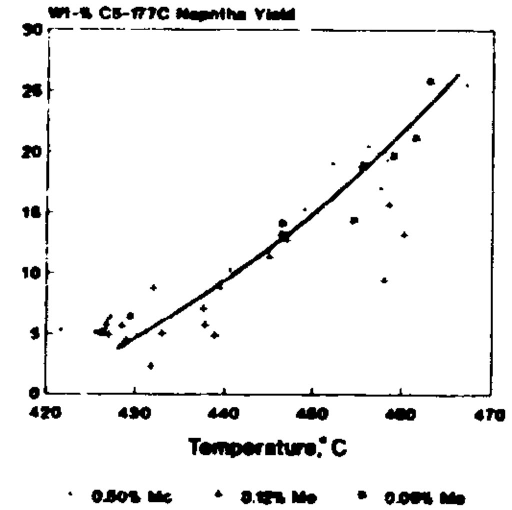
Light Ends Yields
vs. Temperature



K8.7 Catalyst, C14 Coal, R19 Resid
3000 psig, base WHSV, 2:1 Resid/Coal

Figure 7

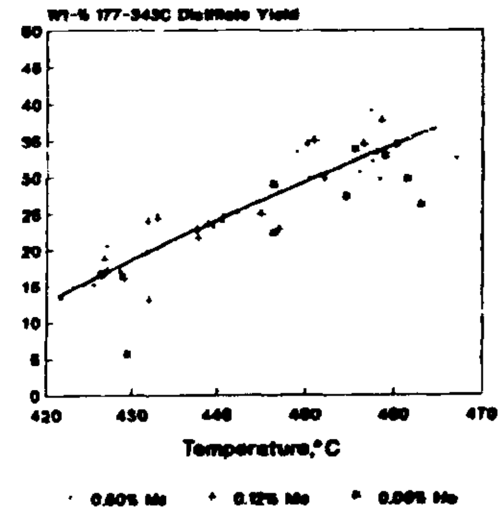
C5-177C Naphtha Yield
vs. Temperature



K8.7 Catalyst, C14 Coal, R19 Resid
3000 psig, base WHSV, 2:1 Resid/Coal

Figure 8

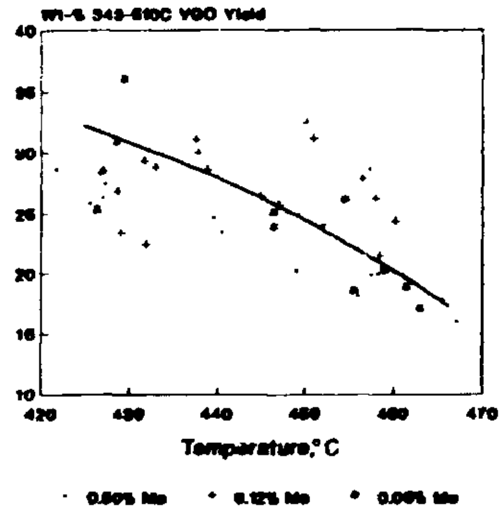
177-343C Dist. Yield
vs. Temperature



K8.7 Catalyst, C14 Coal, R19 Resid
3000 psig, base WHSV, 2/1 Resid/Coal

Figure 9

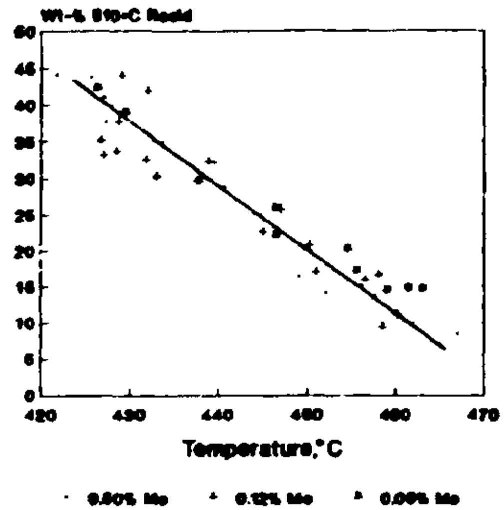
343-510C VGO Yield
vs. Temperature



K8.7 Catalyst, C14 Coal, R19 Resid
3000 psig, base WHSV, 2/1 Resid/Coal

Figure 10

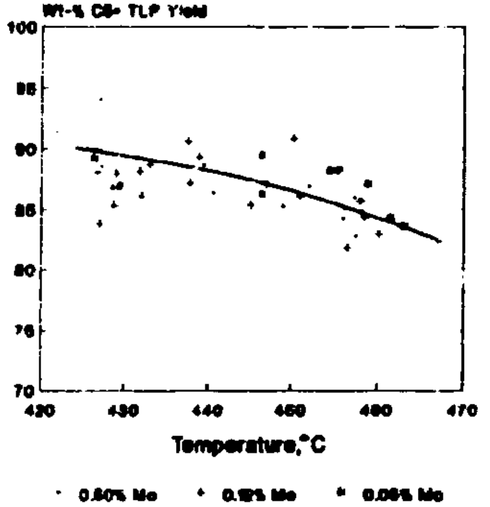
510C+ Resid Yield
vs. Temperature



K8.7 Catalyst, C14 Coal, R19 Resid
3000 psig, base WHSV, 2/1 Resid/Coal

Figure 11

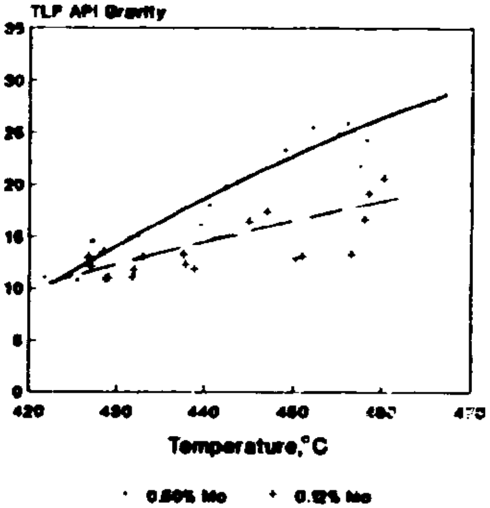
C5+ Total Liquid Yield vs. Temperature



K6.7 Catalyst, C14 Coal, R10 Resid
3000 psig, base WHSV, 2:1 Resid:Coal

Figure 12

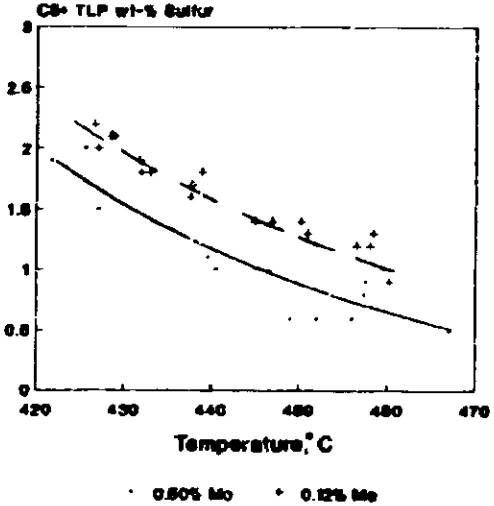
C5+ Liquid Product API vs. Temperature



K6.7 Catalyst, C14 Coal, R10 Resid
3000 psig, base WHSV, 2:1 Resid:Coal

Figure 13

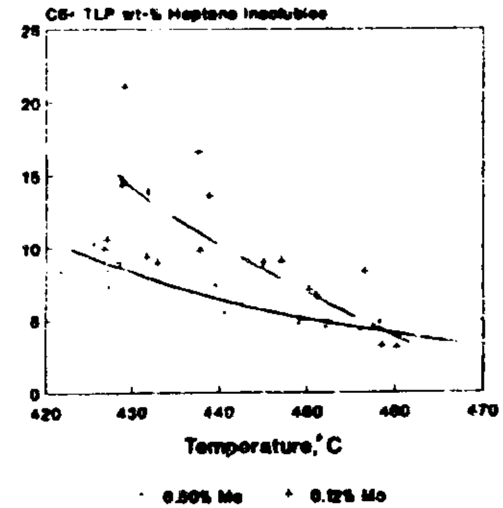
C5+ Product Wt-% S vs. Temperature



K6.7 Catalyst, C14 Coal, R10 Resid
3000 psig, base WHSV, 2:1 Resid:Coal

Figure 14

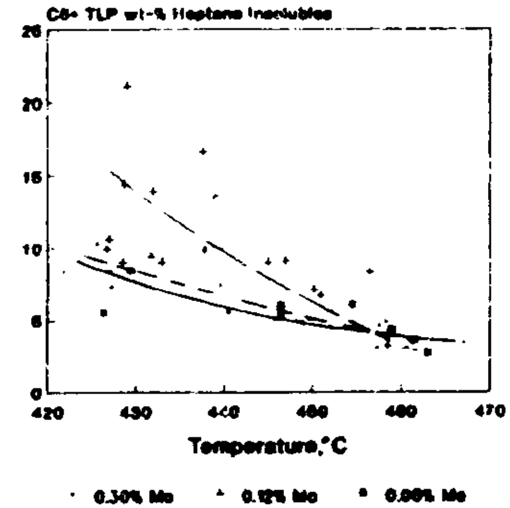
C5+ Product Wt-% HI
vs. Temperature



K9.7 Catalyst, C14 Coal, R19 Resid
3000 psig, base WHSV, 2:1 Resid/Coal

Figure 15

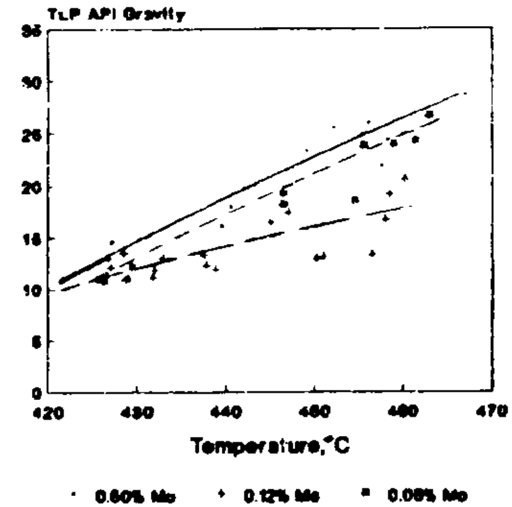
C5+ Product Wt-% HI
vs. Temperature



K9.7 Catalyst, C14 Coal, R19 Resid
3000 psig, base WHSV, 2:1 Resid/Coal

Figure 16

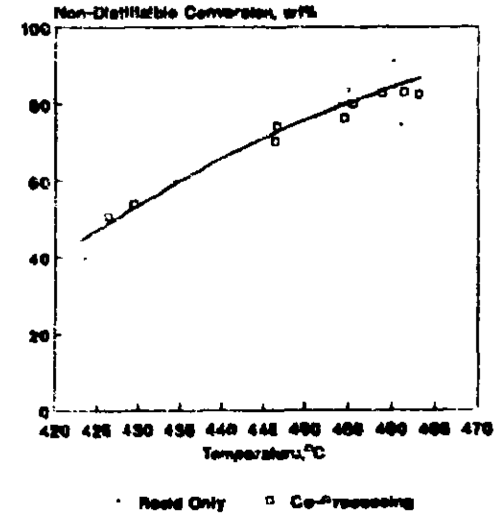
C5+ Liquid Product API
vs. Temperature



K9.7 Catalyst, C14 Coal, R19 Resid
3000 psig, base WHSV, 2:1 Resid/Coal

Figure 17

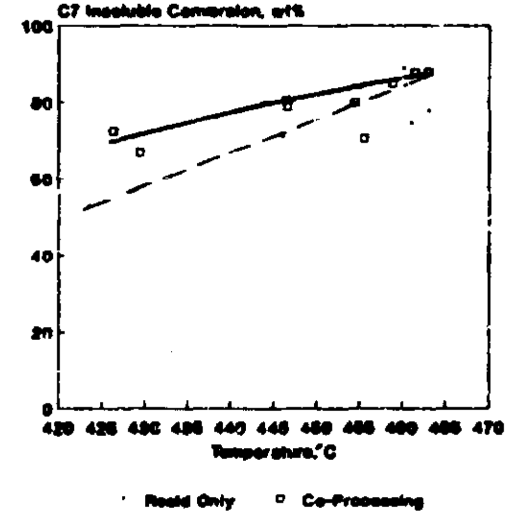
NON-DISTILLABLE CONVERSION
Co-Processing vs. Resid Upgrading



0.06 wt% Mo, 2000 psig, base WHSV
Resid only-Lloyd. resid
Co-Pro.-2:1-Lloyd. resid/Ill. No 6 coal

Figure 18

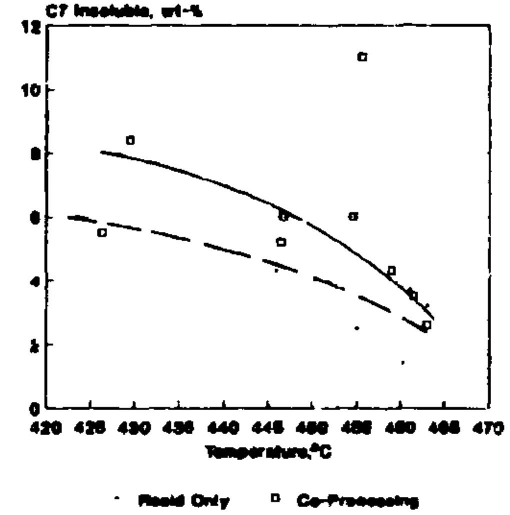
C7 INSOLUBLE CONVERSION
Co-Processing vs. Resid Upgrading



0.06 wt% Mo, 1000 psig, base WHSV
Resid only-Lloyd. resid
Co-Pro.-2:1-Lloyd. resid/Ill. No 6 coal

Figure 19

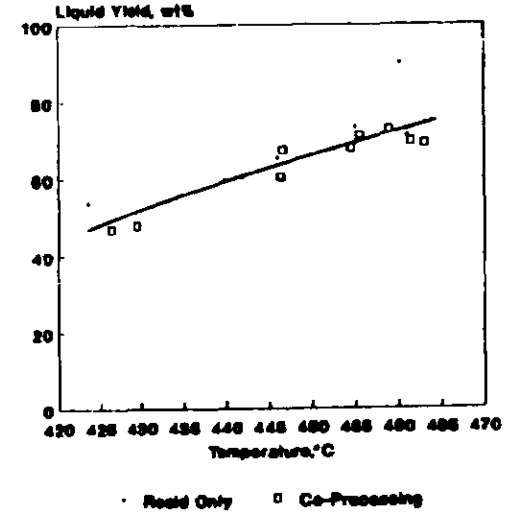
C5+ PRODUCT WT% C7 INSOLUBLE
Co-Processing vs. Resid Upgrading



0.06 wt% Mo, 2000 psig, base WHSV
Resid only-Lloyd. resid
Co-Pro.-2:1-Lloyd. resid/Ill. No 6 Coal

Figure 20

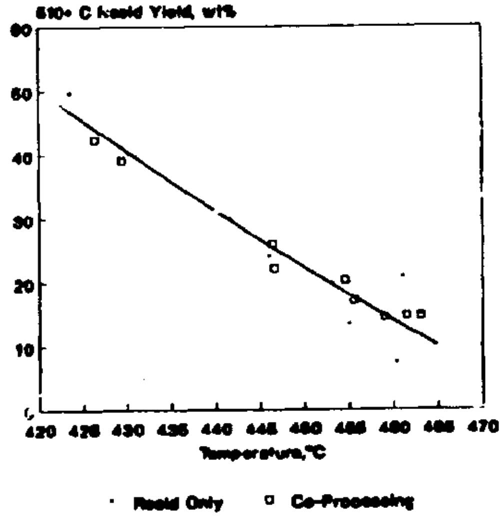
C5--510 C LIQUID YIELD
Co-Processing vs. Resid Upgrading



0.05 wt% Mo, 2000 psig, base WHSV
Resid only-Lloyd. resid
Co-Pro.-2:1-Lloyd. resid/Ill. No 6 coal

Figure 21

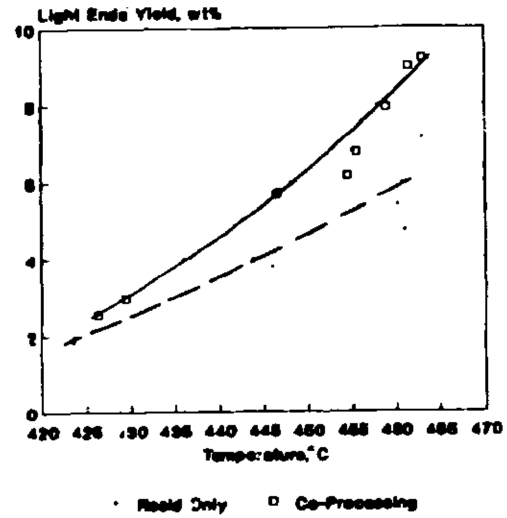
510+ C RESID YIELD
Co-Processing vs. Resid Upgrading



0.05 wt% Mo, 2000 psig, base WHSV
Resid only-Lloyd. resid
Co-Pro -2:1-Lloyd. resid/Ill. No 6 coal

Figure 22

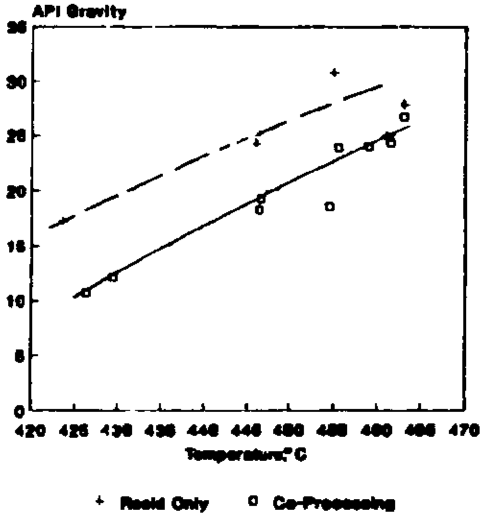
LIGHT ENDS YIELD
Co-Processing vs. Resid Upgrading



0.05 wt% Mo, 2000 psig, base WHSV
Resid only-Lloyd. resid
Co-Pro.-2:1-Lloyd. resid/Ill. No 6 coal

Figure 23

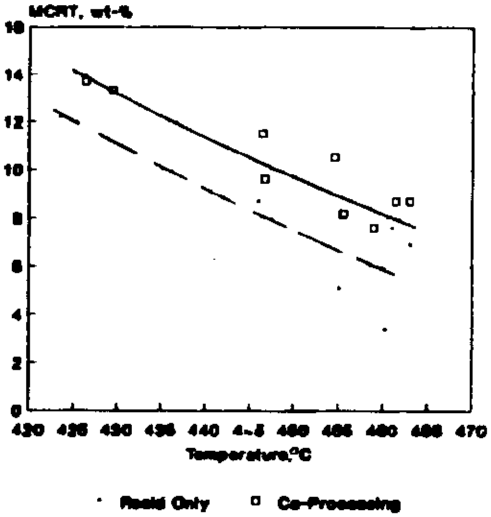
C5+ LIQUID PRODUCT API
Co-Processing vs. Resid Upgrading



0.06 wt% Mo, 2000 psig, base WHSV
Resid only-Lloyd. resid
Co-Pro.-2:1-Lloyd. resid/Ill. No 6 coal

Figure 24

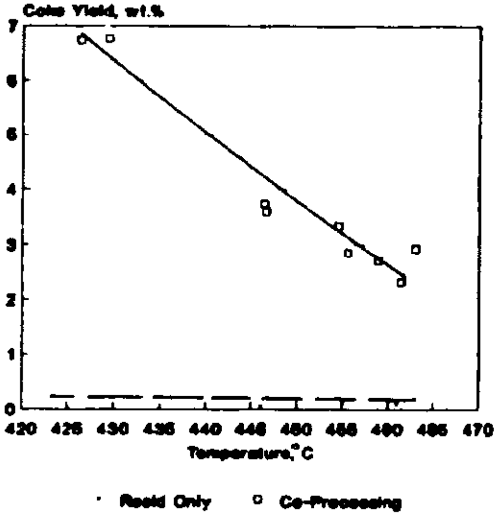
C5+ PRODUCT WT-% MCRT
Co-Processing vs. Resid Upgrading



0.06 wt% Mo, 2000 psig, base WHSV
Resid only-Lloyd. resid
Co-Pro.-2:1-Lloyd. resid/Ill. No 6 coal

Figure 25

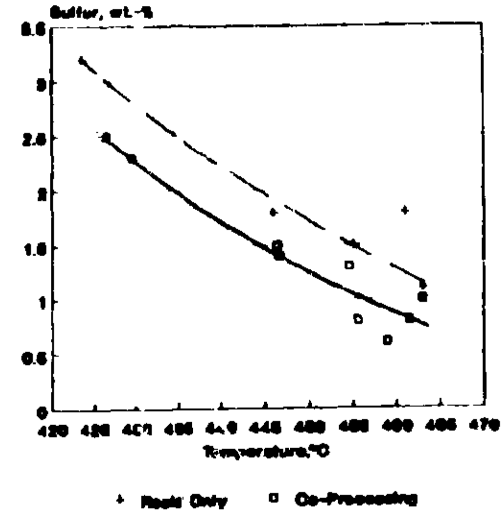
UNCONVERTED COAL/COKE YIELD
Co-Processing vs. Resid Upgrading



0.06 wt% Mo, 2000 psig, base WHSV
Resid only-Lloyd. resid
Co-Pro.-2:1-Lloyd. resid/Ill. No 6 coal

Figure 26

C5+ PRODUCT WT-% S
Co-Processing vs. Resid Upgrading



0.36 wt% Mo, 2000 psi, base WHSV
Resid only-Lloyd. resid
Co-Pro.-[illegible]-Lloyd. resid/Ill. No 6 coal