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SRC-I NAPHTHA HYDROTREATING STUDY PILOT PLANT AND
OXYGEN ANALYTICAL STUDIES

Final Technical Report

By
M. A. Ulowetz

January 1984

Work Performed Under Contract No. AC05-78OR03054

UOP, Inc.
UOP Process Division
Des Plaines, Illinois

Technical Information Center
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United States Department of Energy

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Author: M. A. Ulowetz

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TABLE OF CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
1.0	Executive Summary	1-1
2.0	Scope of Report	2-1
3.0	Second-Stage Hydrotreating Pilot Plant Nickel-Moly Catalyst Study	3-1
4.0	Oxygen Analytical Study	4-1
5.0	Conclusions and Recommendations	5-1

LIST OF TABLES

<u>Table Number</u>	<u>Title</u>	<u>Page</u>
3.1	SRC-I Naphtha Hydrotreating Second-Stage Pilot Plant Nickel-Moly Catalyst Study Feedstock Analysis	3-6
3.2	SRC-I Naphtha Hydrotreating Second-Stage Pilot Plant Nickel-Moly Catalyst Study Feedstock Analysis UOP 777 Detailed GC Analysis, wt-%	3-7
3.3	SRC-I Naphtha Hydrotreating Second-Stage Pilot Plant Nickel-Moly Catalyst Study Operating Summary	3-10
3.4	SRC-I Naphtha Hydrotreating Second-Stage Pilot Plant Nickel-Moly Catalyst Study Operating Data	3-11
3.5	SRC-I Naphtha Hydrotreating Second-Stage Pilot Plant Nickel-Moly Catalyst Study Product Blend Analyses	3-12
3.6	SRC-I Naphtha Hydrotreating Second-Stage Pilot Plant Nickel-Moly Catalyst Study Product Blend Analyses UOP 777 Detailed GC Analysis, wt-%	3-14
3.7	SRC-I Naphtha Hydrotreating Second-Stage Pilot Plant Used Catalyst Analysis	3-17
4.1	SRC-I Naphtha Hydrotreating Oxygen Analytical Study Sample Container Descriptions	4-9
4.2	SRC-I Naphtha Hydrotreating Oxygen Analytical Study SRC-I Hydrotreated Naphtha Analyses Following Molecular Sieve Drying	4-10
4.3	SRC-I Naphtha Hydrotreating Oxygen Analytical Study Compound Type Analyses, wt-ppm	4-11
4.4	SRC-I Naphtha Hydrotreating Oxygen Analytical Study Benzene Water Content Analyses in Type 1 Container	4-12
4.5	SRC-I Naphtha Hydrotreating Oxygen Analytical Study Benzene Water Content Analyses in Different Sample Containers	4-13

LIST OF FIGURES

<u>Figure Number</u>	<u>Title</u>	<u>Page</u>
3.1	SRC-I Naphtha Hydrotreating Second-Stage Pilot Plant Product Nitrogen Content versus Reactor Average Bed Temperature at Base Pressure and LHSV	3-18
3.2	SRC-I Naphtha Hydrotreating Second-Stage Pilot Plant Product Sulfur Content versus Reactor Average Bed Temperature at Base Pressure and LHSV	3-19
3.3	SRC-I Naphtha Hydrotreating Second-Stage Pilot Plant Product Oxygen Content versus Reactor Average Bed Temperature at Base Pressure and LHSV	3-20

1.0 EXECUTIVE SUMMARY

Following completion of the original Scope of Work covered by the November, 1983 Final Report to ICRC, "SRC-I Naphtha Hydrotreating Pilot Plant and Engineering Process Studies", ICRC authorized UOP to conduct two small additional programs to complete the Hydrotreating Study Task.

The first part of the study covered second-stage pilot plant hydrotreating using a UOP nickel-molybdenum (-moly) catalyst and first-stage product from earlier pilot plant work as feedstock. Results from this study indicate that the nickel-moly catalyst is less active than the cobalt-moly catalyst used during original studies over the lower end of the temperature range tested [250 to 280°C average bed temperature (ABT)], but should produce satisfactory product contaminant levels at the temperature range of commercial interest (335 to 345°C ABT). It should be noted that the catalyst activity comparisons were made at Base pilot plant operating conditions for liquid hourly space velocity (LHSV), reactor pressure and recycle hydrogen rate.

The second part of the study covered oxygen analysis comprising two separate programs. The first was aimed at determining the effect of various molecular sieve drying techniques on SRC-I hydrotreated naphtha. This resulted in the recommendation that 3A molecular sieves be left in contact with the naphtha before analysis to assure that the sample remains relatively dry (approx. 20 wt-ppm water), and therefore minimize water interference during analysis. The second program was conducted to determine if different oxygen compound types give different analytical results for the same oxygen concentrations in the range of 10 to 100 wt-ppm. The results showed that scatter in the analytical data was too large to permit conclusions relative to the type of oxygen compound. Further combustion/GC analytical method development is recommended. It should be noted that none of the laboratories (i.e., UOP, Cintichem, ORNL) employed

during earlier oxygen analysis work were able to produce consistent results in the 10 to 100 wt-ppm range. An associated benefit of the compound type study evolved from testing several types of sample containers to determine to what degree they were moisture-proof. The resulting recommendation was to use a commercially available Teflon valve sample vial closure.

In general, the results from the oxygen analytical study are very beneficial to the ongoing effort to develop an accurate method for total oxygen analysis in the 10 to 100 wt-ppm range.

2.0 SCOPE OF REPORT

This report is being issued as an addendum to the November, 1983 Final Report to ICRC titled "SRC-I Naphtha Hydrotreating Pilot Plant and Engineering Process Studies" (DOE/OR/03054-81). The report covers work authorized by ICRC through their final work order to UOP (84-U-006, Rev. 2) dated November 11, 1983.

This report includes results of additional pilot plant work using a UOP nickel-moly catalyst for activity comparison to UOP cobalt-moly catalyst, which was studied earlier. It also covers an oxygen analytical study conducted to determine the effect of various molecular sieve drying methods on analytical results for SRC-I hydrotreated naphtha, and to determine whether different oxygen compound types typical of coal liquids (e.g., phenols, furans, alcohols) give different analytical responses at the same concentration.

This report represents the last deliverable item associated with the Hydrotreating Study Task conducted by UOP for ICRC.

3.0 SECOND-STAGE HYDROTREATING PILOT PLANT NICKEL-MOLY CATALYST STUDY

3.1 Summary

A second-stage SRC-I naphtha hydrotreating pilot plant study was conducted to determine the relationship between contaminant removal (i.e., nitrogen, sulfur and oxygen) and reactor average bed temperature (ABT) for a UOP nickel-moly (Ni-Mo) catalyst. All original parametric work had been done using UOP's best cobalt-moly (Co-Mo) catalyst. The feedstock was taken from the small remaining quantity of product from earlier first-stage pilot plant hydrotreating work on SRC-I naphtha. Results were obtained for three different ABT's, while other pilot plant conditions were controlled at Base values. These results allowed comparison of the relative activity of the Ni-Mo catalyst for contaminant removal. This comparison showed that the Co-Mo catalyst was more active in removing these species over the lower end of the temperature range (255 to 280°C ABT). However, in the temperature range of interest for producing on-specification hydrotreated naphtha (335 to 345°C ABT), the Ni-Mo catalyst appeared to be as active as the Co-Mo catalyst. Tests to cover this higher temperature range in more detail were not possible due to a lack of feedstock.

3.2 Objective

ICRC requested that UOP propose a second-stage pilot plant test program to evaluate a UOP commercial Ni-Mo hydrotreating catalyst using as feedstock the on-specification first-stage pilot plant product remaining from earlier work in the project. Specifically, the program objective was to determine the relationship between contaminant removal (i.e., nitrogen, sulfur and oxygen) and reactor ABT for the Ni-Mo catalyst system. Since the feedstock quantity was sufficient to run no more than about eight days on stream at feed rates comparable to the original parametric study, it was proposed that the run be made at Base processing conditions of pressure, LHSV and hydrogen recycle, and at least three different reactor ABT's. The results from this study could then be compared to the results

from the original parametric study using UOP Co-Mo catalyst. It should be noted that UOP advised ICRC that its Co-Mo catalyst was the best choice at the time the original tests were planned. It is UOP's understanding that ICRC wanted confirmation of this advice, since other suppliers recommended Ni-Mo catalysts for this application.

3.3 Feedstock Definition

The feedstock used for the Ni-Mo catalyst study was prepared by blending first-stage product Blend Numbers 3802-13, -14 and -15. This material (approximately six gallons) was analyzed to characterize it in a fashion similar to that of the individual blends noted.

Results of the feedstock analyses are presented in Tables 3.1 and 3.2. These results were comparable with those for the original blends with the slight exceptions that oxygen was slightly higher (3.30 vs. 2.98 wt-% max.) and nitrogen was slightly lower (0.10 vs. 0.12 wt-% min.) than was reported in Section 5 of the Final Report. In addition, it was evident that the N₂ jet existent gum contents had increased (59 vs. 32 mg/100 mL max.), since the material had been last analyzed in June, 1983, indicating its inherent storage instability. However, the increased gum content caused no problems during the pilot plant run.

3.4 Pilot Plant Configuration

The pilot plant confirmation used for the Ni-Mo catalyst study was the same as that previously used during the parametric and stability studies for SRC-I Naphtha Hydrotreating. Refer to the Final Report to ICRC (DOE/OR/03054-81) for a detailed description.

3.5 Pilot Plant Processing Procedure

The Ni-Mo catalyst was presulfided and then loaded into the pilot plant reactor. Following normal startup procedure, the operating conditions were lined out at Base, and the reactor inlet and outlet

temperatures were set to produce an ABT below Base. Overall, three ABT's were tested during the study, and processing condition targets were set as shown below (B = Base).

Target Pilot Plant Conditions

Test Number	Reactor Temperature, °C			LHSV, hr ⁻¹	H ₂ Recycle, SCFB	Reactor Pressure, psig
	Inlet	Outlet	Avg. Bed			
1	225	275	255	B	B	B
2	250	300	280	B	B	B
3	300	350	335	B	B	B

Base conditions appear in the proprietary data version of the Final Report to ICRC. The temperature targets were chosen to produce data that would fall within the bounds of those from previous parametric studies.

During the study, pilot plant data were collected, and control product analyses (nitrogen and sulfur content) were made at every 12-hour operating period. Following line-out, products from several operating periods at the same test conditions were blended together for more detailed analysis.

During the study, only minor upsets occurred, and the operation was continuous over the three temperatures tested. A major fault in the hydrogen addition flow meter toward the end of the study was corrected long enough for a spot check (six hours) on the make-up rate; however, the meter was not functioning properly for the last two days on stream, which makes these results less reliable (see Table 3.4 -- Periods 11, 12, 13, 14).

When the feed was exhausted after about eight days on stream, the pilot plant was shut down and the catalyst unloaded for analysis.

3.6 Results and Discussion

Table 3.3 presents pilot plant operating summary results for the 14 operating periods. The pilot plant data show that the target reactor LHSV, ABT, pressure and H₂ recycle rate were met reasonably well.

Analyses for total nitrogen and sulfur in the product show a general decrease with increasing ABT, as expected. It is evident that the < 0.5 wt-ppm target for sulfur in the product was not quite met during the study (1.0 wt-ppm min.). However, if enough feed had been available to raise the reactor ABT to 335 to 345°F, the target probably could have been met, as indicated by extrapolation of the data points in Figure 3.2.

More detailed pilot plant operating data for selected operating periods are presented in Table 3.4. It should be noted that the recycle gas analysis was taken from a previous run using SRC-I naphtha feedstock Blend Number 3802-14 in the same pilot plant at the same operating conditions. The sample connection required for recycle gas analysis had been inadvertently removed before the present study, and reconnection would have required a shutdown and waste of the limited feedstock available. In addition, the hydrogen makeup meter problem discussed earlier resulted in an obviously erroneous consumption result for Period Number 11 (97 SCFB), and the combined result for Period Numbers 13 and 14 is based on a six-hour spot check rather than a preferable 24-hour total. Product oxygen analyses are included that show very little decrease between 255 and 286°C ABT (1.78 and 1.50 wt-%, respectively) and a dramatic drop at 331°C ABT (78 wt-ppm).

A comparison of the five hydrogen consumption values reported in Table 3.4 with values from the previous study shows that the amount of hydrogen consumed to produce equivalent product nitrogen levels may be slightly lower with the Ni-Mo catalyst. More data are needed to confirm this.

Tables 3.5 and 3.6 present results of product blend analyses for the three reactor temperatures tested, and are generally consistent with those of the earlier parametric work. API gravity, hydrogen content, and paraffin plus naphthene content increased directly with reactor temperature, while product contaminants, phenols, aromatics, gum content, octane numbers and viscosities decreased over the increasing temperature range tested. The detailed GC analysis generally shows that cyclohexane derivatives increased as heavier aromatics decreased with increasing reactor temperature.

To assess the relative effectiveness of the Ni-Mo catalyst system compared with the Co-Mo catalyst used during the original parametric studies, product contaminant level data were plotted against reactor ABT for each study. Figure 3.1 shows product nitrogen content vs. reactor ABT for both catalysts tested. From this plot it is evident that the Ni-Mo catalyst is less active in nitrogen removal over the lower end of the temperature range tested (250 to 280°C). However, at temperatures of interest for producing on-specification product (335 to 345°C ABT), both catalyst systems should be satisfactory.

Product sulfur content is shown to follow a similar trend in Figure 3.2. At 255°C ABT, the Ni-Mo catalyst produced sulfur contents above those expected for Co-Mo catalyst. At 331°C ABT, sulfur content fell within the data scatter (caused by H₂S contamination of the product) from earlier work. It should be noted that the Ni-Mo catalyst results for sulfur content showed no more than 0.1 wt-ppm free sulfur (pilot plant-induced contamination), before and after mercury washing, sample analyses yielded the same total sulfur results.

Finally, Figure 3.3 shows the temperature effect on oxygen content for both catalysts. These results are analogous to those for nitrogen and sulfur.

In general, the Ni-Mo catalyst showed a somewhat lower activity at the lower end of the temperature range tested. However, at the temperature range of interest for commercial operation, the Ni-Mo catalyst is expected to produce on-specification hydrotreated naphtha. Further tests in this temperature range would require additional feedstock.

The results of used catalyst analyses performed following the present study are shown in Table 3.7. However, the length of the run was too short to make any definite conclusions.

TABLE 3.1

SRC-I Naphtha Hydrotreating
Second-Stage Pilot Plant
Nickel-Moly Catalyst Study
Feedstock Analysis

Sample Number	3802-60		
API Gravity at 60°F	41.5	FIA Analysis, vol-%	
Specific Gravity at 60°F	0.8179	Aromatics	23.6
		Olefins	9.6
ASTM D-86 Distillation		Paraffins + Naphthenes	55.8
Temperatures, °F		Polars*	11.0
IBP	175		
5%	210	Air Jet Gum, mg/100 mL	
10%	230	Unwashed	79
20%	248	C7 Washed	78
30%	261		
40%	271	Nitrogen Jet Gum, mg/100 mL	
50%	285	Unwashed	68
60%	299	C7 Washed	59
70%	310		
80%	323		
90%	335		
EP%	367		
Recovered, vol-%	99.0		
Bottoms, vol-%	1.0		
Elemental Analysis, wt-%			
Carbon	84.67		
Hydrogen	12.63		
Oxygen	3.30		
Nitrogen	0.10		
Sulfur	0.59		

* Color band as determined by FIA is attributed to polar compounds present in the feedstock.

TABLE 3.2

SRC-I Naphtha Hydrotreating
Second-Stage Pilot Plant
Nickel-Moly Catalyst Study
Feedstock Analysis

UOP 777 DETAILED GC ANALYSIS, wt-%

<u>Blend Number</u>	<u>3802-60</u>
<u>Aromatics</u>	
Benzene	0.4
Toluene	6.4
Ethylbenzene	1.2
p-Xylene	0.6
m-Xylene	1.5
o-Xylene	1.4
Cg+ Aromatics	14.0
Total Aromatics	25.5
<u>Polars</u> (Total)	12.7
<u>Olefins</u> (Total)	9.4
<u>Paraffins and Naphthenes</u>	
1. Propane	-
2. Isobutane	0.10
3. n-Butane	trace
4. Isopentane	trace
5. n-Pentane	0.20
6. 2,2-Dimethylbutane	-
7. Cyclopentane	trace
8. 2,3-Dimethylbutane	0.01
9. 2-Methylpentane	0.07
10. 3-Methylpentane	0.08
11. n-Hexane	0.49
12. Methylcyclopentane	1.43
13. 2,2-Dimethylpentane	-
14. 2,4-Dimethylpentane	0.02
15. 2,2,3-Trimethylbutane	-
16. Cyclohexane	2.18
17. 3,3-Dimethylpentane	-
18. 1,1-Dimethylcyclopentane	0.03
19. 2-Methylhexane	0.47
20. 2,3-Dimethylpentane	0.20
21. 1-cis-3-Dimethylcyclopentane	0.44
22. 3-Methylhexane	0.81
23. 1-trans-3-Dimethylcyclopentane	0.36
24. 1-trans-2-Dimethylcyclopentane	0.72
25. 3-Ethylpentane	0.08
26. 2,2,4-Trimethylpentane	-
27. n-Heptane	2.40
28. 1-cis-2-Dimethylcyclopentane	0.34
29. Methylcyclohexane	2.95
30. 1,1,3-Trimethylcyclopentane	0.02

TABLE 3.2 (Continued)

SRC-I Naphtha Hydrotreating
Second-Stage Pilot Plant
Nickel-Moly Catalyst Study
Feedstock Analysis

UOP 777 DETAILED GC ANALYSIS, wt-%

<u>Blend Number</u>	<u>3802-60</u>	<u>Multi- Component Number</u>
<u>Paraffins and Naphthenes</u> (Cont.)		
31. 2,2-Dimethylhexane	-	
32. Ethylcyclopentane	1.14	
33. 2,5-Dimethylhexane	0.04	
34. 2,4-Dimethylhexane	0.01	
35. 2,2,3-Trimethylpentane	0.16	35, 36
36. 1-trans-2-cis-4-Trimethylcyclopentane		
37. 1-trans-2-cis-3-Trimethylcyclopentane	0.14	37, 38
38. 3,3-Dimethylhexane		
39. 2,3,4-Trimethylpentane	-	
40. 1,1,2-Trimethylcyclopentane	0.05	
41. 2,3,3-Trimethylpentane	-	
42. 2-Methyl-3-ethylpentane	0.17	42, 43
43. 2,3-Dimethylhexane		
44. 1-cis-2-trans-4-Trimethylcyclopentane	0.03	
45. 1-cis-2-trans-3-Trimethylcyclopentane	0.03	
46. 2-Methylheptane	1.17	46, 47
47. 3-Methyl-3-ethylpentane		
48. 1-cis-2-cis-4-Trimethylcyclopentane		
49. 4-Methylheptane	0.38	48, 49, 50
50. 3,4-Dimethylhexane		
51. 3-Ethylhexane		
52. 3-Methylheptane	0.59	51, 52, 53
53. 1,1-Dimethylcyclohexane		
54. 1-trans-4-Dimethylcyclohexane	0.65	54, 55
55. 1-cis-3-Dimethylcyclohexane		
56. 1-Methyl-cis-3-ethylcyclopentane	0.44	
57. 1-Methyl-trans-3-ethylcyclopentane		
58. 1-Methyl-trans-2-ethylcyclopentane	0.90	57, 58, 59
59. 1-Methyl-1-ethylcyclopentane		
60. 1-cis-2-cis-3-Trimethylcyclopentane	0.22	60, 61
61. 1-trans-2-Dimethylcyclohexane		
62. 1-trans-3-Dimethylcyclohexane	0.31	62, 63
63. 1-cis-4-Dimethylcyclohexane		
64. Isopropylcyclopentane	0.12	
65. n-Octane	2.34	
66. 1-Methyl-cis-2-ethylcyclopentane	0.20	
67. 1-cis-2-Dimethylcyclohexane	0.13	
68. Ethylcyclohexane	1.78	68, 69
69. n-Propylcyclopentane		

TABLE 3.2(Continued)

SRC-I Naphtha Hydrotreating
 Second-Stage Pilot Plant
 Nickel-Moly Catalyst Study
Feedstock Analysis

UOP 777 DETAILED GC ANALYSIS, wt-%

<u>Blend Number</u>	<u>3802-60</u>
<u>Paraffins and Naphthenes</u> (Cont.)	
C ₉ Naphthenes	5.9
C ₉ Paraffins	4.8
C ₁₀ Naphthenes	5.0
C ₁₀ Paraffins	5.0
C ₁₁ Naphthenes	2.0
C ₁₁ Paraffins	5.0
C ₁₂ P + N	0.3
Total Paraffins and Naphthenes	52.4
Grand Total	100.0

TABLE 3.3

SRC-I Naphtha Hydrotreating
Second-Stage Pilot Plant
Nickel-Moly Catalyst Study
Operating Summary

Period Number	Pilot Plant Data				Product Analyses	
	LHSV/ LHSVBase	Rx ABT, °C	Rx Outlet Press./ Base	H ₂ Recycle/ Base	Total Nitrogen wt-ppm	Sulfur wt-ppm
1	1.02	257.0	1.01	0.99	495	-
2	1.03	256.0	1.01	0.98	650	1057
3	1.02	255.9	1.01	0.96	650	867
4	1.02	255.3	1.01	0.98	640	823
5	1.03	255.9	1.00	0.97	590	734
6	1.04	255.9	1.00	0.95	670	823
7	1.01	281.0	1.00	0.99	-	-
8	1.00	278.2	1.00	1.00	230	38.0
9	0.99	274.8	1.00	0.99	196	31.6
10	1.03	275.1	1.00	0.96	200	31.6
11	0.98	286.7	1.00	1.03	174.7	31.0
12	1.03	328.0	1.00	1.03	-	-
13	1.03	331.4	1.00	0.96	0.5	1.4
14	1.00	331.1	1.00	1.00	0.2	1.0

TABLE 3.4

SRC-I Naphtha Hydrotreating
Second-Stage Pilot Plant
Nickel Moly Catalyst Study
Operating Data

Operating Period Number	2	3, 4	6	8	11	13, 14
Catalyst Life, Bbl/lb	0.06	0.17	0.28	0.39	0.55	0.72
LHSV/LHSV _{Base}	1.03	1.02	1.04	1.00	0.98	1.02
Reactor Temperature, °C						
Inlet	224	224.5	226	249	249	301
Outlet	275	275.5	275	300	299	351
Maximum	278	279	278	304	305	355
Average Bed	256.0	255.6	255.9	278.2	286.7	331.3
Reactor Outlet Pressure/Base	1.01	1.01	1.00	1.00	1.00	1.00
Recycle Gas H ₂ Rate/Base	0.98	0.97	0.95	1.00	1.03	0.98
Recycle Gas, mol-%						
H ₂	-----	-----	-----	99.5 (1)	-----	-----
C ₁	-----	-----	-----	-----	-----	-----
C ₂	-----	-----	-----	-----	-----	-----
C ₃	-----	-----	-----	0.1	-----	-----
C ₄	-----	-----	-----	0.1	-----	-----
C ₅	-----	-----	-----	-----	-----	-----
C ₆ ⁺	-----	-----	-----	0.3	-----	-----
H ₂ Consumption, SCFB	110	143	146	175	97 (2)	821 (3)
Total Gas Product, wt-%	2.01	1.18	1.55	2.33	2.90	2.28
Total Liquid Product, wt-%	95.72	95.55	93.96	101.41	96.27	98.07
Weight Recovery, wt-%	97.73	96.73	95.51	103.74	99.17	100.35
Normalized Yields, wt-%						
H ₂ S	0.53	0.56	0.56	0.60	0.63	0.62
NH ₃	0.02	0.03	0.04	0.09	0.10	0.12
H ₂ O	1.75	1.77	1.79	1.95	2.04	3.69
C ₁	0.00	0.00	0.00	0.00	0.00	0.00
C ₂	0.00	0.00	0.00	0.00	0.00	0.00
C ₃	0.08	0.08	0.09	0.17	0.19	0.19
C ₄	0.11	0.21	0.23	0.22	0.26	0.25
C ₅	0.13	0.13	0.14	0.14	0.16	0.15
C ₆ ⁺	97.58	97.49	97.42	97.16	96.80	96.50
Total	100.20	100.27	100.27	100.33	100.18	101.52
Product Contaminants, wt-ppm						
Sulfur	1057	845	823	38	31	1.0
Nitrogen	650	650	670	230	175	0.8
Oxygen (UOP)	-----	17,800 (4)	-----	-- 15,000 (4)	--	78

- (1) Recycle gas analysis taken from previous run on SRC-I naphtha hydrotreating at similar conditions.
- (2) H₂ addition meter fault detected.
- (3) H₂ consumption calculated from six-hour period when addition meter was assumed to be correct.
- (4) Oxygen analyses from product blends made at similar operating conditions.

TABLE 3.5

SRC-I Naphtha Hydrotreating
Second-Stage Pilot Plant
Nickel-Moly Catalyst Study
Product Blend Analyses

Sample Number	3802-61		3802-62		3802-63	
Period Numbers	3, 4, 6		8, 9, 10		13, 14	
API Gravity at 60°F	42.5		44.3		49.7	
Specific Gravity at 60°F	0.8132		0.8049		0.7809	
Distillation Type	ASTM		ASTM		ASTM	
	D-86	BRGC	D-86	BRGC	D-86	BRGC
Temperature, °C	(vol-%)	(wt-%)	(vol-%)	(wt-%)	(vol-%)	(wt-%)
at IBP	186	127	182	112	194	112
5%	222	177	212	172	208	171
10%	230	198	228	189	217	176
20%	244	224	244	215	228	200
30%	256	239	256	235	238	215
40%	274	268	268	262	249	234
50%	286	291	282	285	267	260
60%	298	318	296	313	286	284
70%	311	340	310	335	309	310
80%	323	349	323	349	324	334
90%	337	364	338	363	343	356
95%	350	372	353	371	357	370
EP	396	422	400	388	382	408
Recovered, vol-%	99.0		99.0		99.0	
Bottoms, vol-%	1.0		1.0		1.0	
Elemental Analysis, wt-%						
Carbon	85.64		85.57		86.09	
Hydrogen	12.69		13.08		13.66	
Oxygen (UOP)	1.78		1.50		78 (wt-ppm)	
Nitrogen, wt-ppm	650		204		0.8	
Sulfur, wt-ppm	836		33.5		1.0	
Free Sulfur, wt-ppm	-		-		0.1	
Mercaptan Sulfur, wt-ppm	-		-		0.8	
UV Analysis						
Phenols, wt-%	8.40		8.4		-	
Thiophenols, wt-ppm	0.69 (wt-%)		< 5		-	

TABLE 3.5 (Continued)

SRC-I Naphtha Hydrotreating
Second-Stage Pilot Plant
Nickel-Moly Catalyst Study
Product Blend Analyses

Sample Number	3802-61	3802-62	3802-63
Period Numbers	3, 4, 6	8, 9, 10	13, 14
FIA Analysis, vol-%			
Aromatics	23.1	21.7	15.8
Olefins	3.7	0.9	-
Paraffins + Naphthenes	64.3	70.1	84.2
Polars	8.9	7.3	-
Existent Gum (Air Jet), mg/100 mL	13.0	6.7	< 1
Potential Gum, mg/100 mL	61.0	19.0	< 1
Octane Numbers			
Research Clear	74.8	71.2	58.7
Motor Clear	70.4	67.3	57.2
Viscosities at			
60°F, cSt	1.034	1.097	0.974
SUS	26.8	27.3	26.2
100°F, cSt	0.791	0.817	0.752
SUS	24.3	24.6	23.8

TABLE 3.6

SRC-I Naphtha Hydrotreating
Second-Stage Pilot Plant
Nickel-Moly Catalyst Study
Product Blend Analyses

UOP 777 DETAILED GC ANALYSIS, wt-%

<u>Blend Number</u>	<u>3802-61</u>	<u>3802-62</u>	<u>3802-63</u>
<u>Aromatics</u>			
Benzene	0.3	0.4	0.6
Toluene	6.5	6.6	5.7
Ethylbenzene	1.2	1.2	1.0
p-Xylene	0.6	0.6	0.6
m-Xylene	1.5	1.5	1.1
o-Xylene	1.4	1.3	1.0
C ₉ + Aromatics	13.7	12.2	7.9
Total Aromatics	25.2	23.8	17.9
<u>Polars</u> (Total)	10.2	8.5	-
<u>Olefins</u> (Total)	3.7	0.9	-
<u>Paraffins and Naphthenes</u>			
1. Propane	-	-	-
2. Isobutane	-	-	-
3. n-Butane	trace	0.10	0.1
4. Isopentane	trace	0.10	0.1
5. n-Pentane	0.30	0.40	0.4
6. 2,2-Dimethylbutane	-	-	-
7. Cyclopentane	trace	trace	trace
8. 2,3-Dimethylbutane	0.03	0.05	0.04
9. 2-Methylpentane	0.15	0.23	0.23
10. 3-Methylpentane	0.17	0.26	0.27
11. n-Hexane	0.70	0.89	0.90
12. Methylcyclopentane	1.62	1.72	1.85
13. 2,2-Dimethylpentane	-	-	-
14. 2,4-Dimethylpentane	0.02	0.02	0.03
15. 2,2,3-Trimethylbutane	-	-	-
16. Cyclohexane	2.77	4.31	11.42
17. 3,3-Dimethylpentane	-	-	0.03
18. 1,1-Dimethylcyclopentane	0.04	0.05	0.03
19. 2-Methylhexane	0.53	0.57	0.54
20. 2,3-Dimethylpentane	0.29	0.38	0.34
21. 1-cis-3-Dimethylcyclopentane	0.54	0.58	0.58
22. 3-Methylhexane	0.84	0.94	1.07
23. 1-trans-3-Dimethylcyclopentane	0.54	0.67	0.46
24. 1-trans-2-Dimethylcyclopentane	0.81	0.92	1.00
25. 3-Ethylpentane	0.14	0.18	0.18
26. 2,2,4-Trimethylpentane	-	-	-
27. n-Heptane	2.75	2.83	2.83
28. 1-cis-2-Dimethylcyclopentane	0.45	0.53	0.58
29. Methylcyclohexane	3.68	4.00	7.65
30. 1,1,3-Trimethylcyclopentane	0.02	0.03	0.02

TABLE 3.6 (Continued)

SRC-I Naphtha Hydrotreating
Second-Stage Pilot Plant
Nickel-Moly Catalyst Study
Product Blend Analyses

UOP 777 DETAILED GC ANALYSIS, wt-%

<u>Blend Number</u>	<u>3802-61</u>	<u>3802-62</u>	<u>3802-63</u>	<u>Multi- Component Number</u>
<u>Paraffins and Naphthenes</u> (Cont.)				
31. 2,2-Dimethylhexane	-	-	-	
32. Ethylcyclopentane	1.39	1.37	1.63	
33. 2,5-Dimethylhexane	0.08	0.06	0.05	
34. 2,4-Dimethylhexane	0.02	0.04	0.01	
35. 2,2,3-Trimethylpentane	0.29	0.25	0.31	35, 36
36. 1-trans-2-cis-4-Trimethylcyclopentane				
37. 1-trans-2-cis-3-Trimethylcyclopentane	0.18	0.20	0.26	37, 38
38. 3,3-Dimethylhexane				
39. 2,3,4-Trimethylpentane	-	-	-	
40. 1,1,2-Trimethylcyclopentane	0.06	0.07	0.05	
41. 2,3,3-Trimethylpentane	-	-	-	
42. 2-Methyl-3-ethylpentane	0.18	0.20	0.21	42, 43
43. 2,3-Dimethylhexane				
44. 1-cis-2-trans-4-Trimethylcyclopentane	0.03	0.04	0.10	
45. 1-cis-2-trans-3-Trimethylcyclopentane	0.03	0.01	-	
46. 2-Methylheptane	1.29	1.88	1.97	46, 47
47. 3-Methyl-3-ethylpentane				
48. 1-cis-2-cis-4-Trimethylcyclopentane				
49. 4-Methylheptane	0.53	0.77	0.75	48, 49, 50
50. 3,4-Dimethylhexane				
51. 3-Ethylhexane				
52. 3-Methylheptane	0.69	0.82	1.03	51, 52, 53
53. 1,1-Dimethylcyclohexane				
54. 1-trans-4-Dimethylcyclohexane	0.73	0.59	0.50	54, 55
55. 1-cis-3-Dimethylcyclohexane				
56. 1-Methyl-cis-3-ethylcyclopentane	0.46	-	-	
57. 1-Methyl-trans-3-ethylcyclopentane				
58. 1-Methyl-trans-2-ethylcyclopentane	1.02	1.12	1.15	57, 58, 59
59. 1-Methyl-1-ethylcyclopentane				
60. 1-cis-2-cis-3-Trimethylcyclopentane	0.30	0.37	0.54	60, 61
61. 1-trans-2-Dimethylcyclohexane				
62. 1-trans-3-Dimethylcyclohexane	0.40	0.50	0.63	62, 63
63. 1-cis-4-Dimethylcyclohexane				
64. Isopropylcyclopentane	0.10	0.17	-	
65. n-Octane	2.69	2.67	2.74	
66. 1-Methyl-cis-2-ethylcyclopentane	0.23	0.32	0.28	
67. 1-cis-2-Dimethylcyclohexane	0.14	0.24	0.28	
68. Ethylcyclohexane				
69. n-Propylcyclopentane	1.97	1.95	2.16	68, 69

TABLE 3.6 (Continued)

SRC-I Naphtha Hydrotreating
 Second-Stage Pilot Plant
 Nickel-Moly Catalyst Study
Product Blend Analyses

UOP 777 DETAILED GC ANALYSIS, wt-%

<u>Blend Number</u>	<u>3802-61</u>	<u>3802-62</u>	<u>3802-63</u>
<u>Paraffins and Naphthenes</u> (Cont.)			
C ₉ Naphthenes	6.8	7.6	9.9
C ₉ Paraffins	5.4	5.4	5.5
C ₁₀ Naphthenes	5.8	6.4	7.3
C ₁₀ Paraffins	5.6	5.6	5.6
C ₁₁ Naphthenes	2.1	2.6	2.7
C ₁₁ Paraffins	5.6	5.4	5.3
C ₁₂ P + N	0.4	0.4	0.5
Total Paraffins and Naphthenes	60.9	66.8	82.1
Grand Total	100.0	100.0	100.0

TABLE 3.7

SRC-I Naphtha Hydrotreating
Second-Stage Pilot Plant
Nickel-Moly Catalyst Study
Used Catalyst Analysis

<u>Analysis</u>	<u>Catalyst Bed Location</u>		
	<u>Top</u>	<u>Middle</u>	<u>Bottom</u>
Sulfur, wt-%	4.74	5.03	5.22
Carbon, wt-%	4.31	2.52	1.43
Nitrogen, wt-%	0.59	0.61	0.58

4.0 OXYGEN ANALYTICAL STUDY

4.1 Summary

UOP conducted two separate analytical test programs during the oxygen analytical study. The first was aimed at determining the effect of various molecular sieve drying techniques on SRC-I hydrotreated naphtha sample water and total oxygen contents. The second covered tests to assess whether different standard oxygen compounds gave different analytical results at the same oxygen concentration in the low (10 to 100 wt-ppm) range of interest for the SRC-I naphtha hydrotreating work. It was determined that 3A molecular sieves left in contact with the naphtha samples provided protection against outside atmospheric moisture contamination. The UOP oxygen analytical method was shown to be inconsistent in determining the difference in oxygen concentrations in the range of 10 to 50 wt-ppm, and further method development is recommended.

Finally, a short study on the benefits of using different sample containers showed that a combination of a screw top vial and a special (commercially available) Teflon valve provided reasonable protection against atmospheric moisture when molecular sieves are not left in contact with the sample.

The removal of water interference from samples containing low oxygenated compound concentrations is an important step in the development of the analytical method.

4.2 Objective

Previous work on total oxygen analysis of hydrotreated SRC-I naphtha by several laboratories (UOP, Cintichem and ORNL) showed that it was difficult to obtain consistent results on samples in the total oxygen region of < 300 wt-ppm (typically < 100 wt-ppm). To aid in improving analytical accuracy in the < 300 wt-ppm range, UOP conducted an oxygen analytical study that included sample drying techniques and oxygen compound type programs.

Atmospheric moisture is a known interference to oxygen analyses in the < 100 wt-ppm range, and the present study addresses this phenomenon. The effect of several means of molecular sieve drying on oxygen analytical results for samples of SRC-I hydrotreated naphtha was proposed to determine if the sieves adsorbed oxygenates and/or provided extra protection against moisture interference in analyses. In addition, UOP conducted analyses of standard total oxygen concentrations (10 to 100 wt-ppm) of specific oxygen compound types (alcohols, furans, phenols) diluted in hydrocarbon solvents based on oxygenates that are expected to be present in coal-derived naphthas. The objective was to determine if different oxygen types produce different total oxygen results using the UOP analytical method for the same total oxygen concentration.

The UOP analytical method is being developed, and it was hoped that the present study would not only give insight into accuracy problems in earlier total oxygen analyses at levels < 300 wt-ppm, but would also determine areas in which the method could be improved. Earlier analyses of SRC-I hydrotreated naphtha showed the UOP, Cintichem and ORNL results were comparable, and none could consistently distinguish differences in the 10 to 100 wt-ppm range.

4.3 Analytical Apparatus

Although all analytical equipment used during the study is not discussed in detail here, special note should be made of several items used to protect samples from atmospheric moisture during this study.

In order to provide very dry conditions for sample transfer during the study, a "dry bag" was used. This bag was constructed of a metal frame covered on all sides but the bottom with polyethylene film. The construction provided access through integrally mounted gloves in the side of the bag, and the open bottom allowed the bag to be fitted over an analytical balance for weighing sample standards. The bag was continuously purged with a stream of chromatographic-grade nitrogen that passed through a high surface area sodium drier before entering the bag.

In addition, several different types of sample vials or containers were employed during part of the study to test their relative effectiveness in keeping moisture out of the samples. These containers are described in detail in Table 4.1. For present discussion purposes they are referred to as:

Container Type	Description
1.	Vial and septum
2.	Teflon valve
3.	Vial and polyseal cap (used in previous SRC-I naphtha hydro-treating studies)
4.	UOP water bottle and rubber septum
5.	Dried sample vial and rubber stopper
6.	Undried sample vial and rubber stopper

4.4 Analytical Procedure

4.4.1 Effect of Molecular Sieves on Oxygen Analysis

In order to determine the effect of molecular sieve drying on oxygen analytical results, samples of SRC-I hydrotreated naphtha were prepared in three separate ways. The three SRC-I naphtha samples used were from previously reported pilot plant stability study Period Numbers 127 and 164 and Blend Number 3802-27. These samples were all expected to have organic oxygen contents of well below 100 wt-ppm based on the very good stability exhibited during the pilot plant work, which consistently produced naphtha with < 0.5 wt-ppm sulfur and nitrogen.

A portion of each original sample was dried over equilibrated (previously washed with SRC-I naphtha) molecular sieves, remaining in

contact with them for 16 hours. A part of the dried sample was then decanted into a previously dried sample vial with a septum top, leaving part of the sample in contact with the equilibrated sieves. Another part of each of the three original samples was allowed to stand in contact with unequilibrated sieves for 16 hours before oxygen analysis. The result of this procedure was three groups of three samples, comprising an equilibrated sieve sample in contact with naphtha (ES), a decanted sample from the equilibrated sieves (E) and an unequilibrated sieve sample in contact with the naphtha (US). All samples of naphtha were summarily analyzed for water (Karl Fischer) and total oxygen (UOP Method) to compare any variations produced by the different sample drying techniques.

4.4.2 Oxygen Compound Type Analysis

To determine if different oxygenated compounds gave different analytical results at the same total oxygen concentration, sample standards of four different compounds in benzene solvent were prepared. The sample compounds used were phenol, 2,6-dimethylphenol, 2,3-benzofuran and 2-hexanol. Each of these compounds was diluted in benzene (previously dried over high surface area sodium) to three total oxygen concentrations of 10, 50 and 100 nanograms (10^{-9} grams) per microliter (10^{-6} liter), corresponding to 11.4, 57 and 114 wt-ppm, respectively. Originally, all samples were analyzed against a standard of 9-fluorenone diluted to 50 nanograms of oxygen per microliter (64 wt-ppm) in a 75/25 vol-% mixture of tetradecane/benzene solvent. This standard was also used as the basis for calculating absolute oxygen values for earlier SRC-I naphtha analyses.

Several problems arose during the analysis of the compound type standards for total oxygen. The major one was that the tetradecane/benzene solvent gave a greater analytical output response (GC detector) without any oxygen compound present than did any of the sample compound mixtures. This required the use of one of the sample compound mixtures as a standard on any given day. Daily variations in output response for the same sample, even when corrected for water analysis, made it difficult to compare results from different days. Finally, the sample container configuration proved to have a marked effect on water contamination over the

duration of the study. This led to a separate small study using the five types of containers outlined in Section 4.3 over a three-day period, with water analysis before and after to determine the integrity of each type against sample contamination from the outside atmosphere.

Considering that sample handling was known to be a questionable area in the earlier SRC-I naphtha oxygen analyses, the present procedure was designed to be as methodical as possible to aid in future development of these methods.

4.5 Results and Discussion

4.5.1 Effect of Molecular Sieves on Oxygen Analysis

The results of various molecular sieve drying techniques are presented in Table 4.2. These results show both the water content and the total oxygen content (without water) for each sample. The most important result is the effect of the constant contact of the sieves with the samples before analysis. It is evident that all of these samples (ES and US designation) contained much less water than the samples without sieves (E designation), with an average of < 20 wt-ppm vs. 50 to 60 wt-ppm, respectively. This result is important since the more water present in a sample of low oxygenated hydrocarbon content, the more masked the low oxygenate concentration becomes.

The total oxygen contents (without water) do not indicate that any consistent effect on measured oxygen is caused by having sieves in continuous contact with the sample. To determine if there is some effect, it would be beneficial to test samples with higher total oxygen concentrations (300 to 1,000 wt-ppm). However, higher concentrations were outside the scope of the present study, considering that ICRC's original target for SRC-I hydrotreated naphtha was < 10 wt-ppm total oxygen.

4.5.2 Oxygen Compound Type Analysis

Results of analyzing the three concentrations of each of the four oxygen compound types in benzene against the 9-flourenone standard in tetradecane/benzene immediately showed that no information on relative oxygen content vs. sample response in the GC could be obtained. The background response from the tetradecane/benzene solvent was higher than any of the sample compound mixtures.

To determine if different compound types gave different responses, it was necessary to treat one of the weighed mixtures as a standard on a given day and compare the response for other samples tested that day. As noted earlier, the response for the same sample could vary from day to day, and this required a standardization of the GC detector each day with a concentration close to those of the unknowns tested.

The results of running the four hydrocarbon types in benzene are reported in Table 4.3 on a chronological basis. The samples were given to the analyst unmarked in a random order to avoid problems with advance knowledge of sample oxygen content.

These results show that using the present method, there is no way to consistently distinguish between oxygen contents of 50, 10 or < 1 wt-ppm, or determine if different compound types respond differently at the same oxygen concentration. The best example of the fact that the data cannot be correlated on either of these bases is demonstrated by the results from November 14 and 15, 1983. Here the lower weighed concentration of 2-hexanol-based oxygen (11.4 wt-ppm) gave a higher response (71 wt-ppm) than both of the higher weighed concentrations of phenol (57 wt-ppm) and 2-hexanol (57 wt-ppm); in one case, the benzene blank (< 1 wt-ppm) gave a higher response (75 wt-ppm) than a 57 wt-ppm oxygen concentration of 2,3-benzofuran. Based on the inconsistency of these data, UOP is exploring options for GC detector improvement to produce more accurate results in the 10 to 100 wt-ppm oxygen range.

The chronological data presented do reveal a general increase in sample water content from < 100 wt-ppm on November 10 to the region of 110 to 170 wt-ppm by November 16. Table 4.4 shows the chronological analyses of the benzene solvent used during the oxygen compound type analytical study. As indicated by the increase in water content from November 3 to 14 (33 to 133 wt-ppm) water from the outside atmosphere was contaminating the samples. Starting with freshly dried benzene on November 15 (14 wt-ppm) resulted in an increase to 40 wt-ppm by November 16. This evidence led to the separate test of different types of sample containers to determine if any provided better protection against water from the outside atmosphere. It should be noted that none of the compound-type samples tested contained molecular sieves due to concern at the beginning of the study that the sieves might adsorb oxygenates other than water.

The five types of sample containers described in Section 4.3 were dried and filled with a sample of freshly dried benzene. In addition, sample container Type 5 was not dried before filling it with benzene. These six samples were analyzed for water content immediately following preparation and then after three days in the containers.

The results of both analyses are reported in Table 4.5. Only container Types 2 and 4 provided protection sufficient to maintain water contents at near original values. Of these, only Type 2 is acceptable, since the rubber septum of Type 4 was attacked by the benzene sample.

The results of sieve drying and container type studies provide a good basis for recommendations concerning future sample handling techniques for oxygen analysis. The sieves' effect on the oxygenated compounds in SRC-I naphtha is expected to be minimal, and maintaining a small amount of 3A sieves (2 to 4 cm³) in contact with the sample (10 to 30 cm³) is recommended before analysis. Type 2 containers are recommended in situations in which concern over adsorption of specific compounds is warranted by any future study.

UOP is continuing the development of the oxygen analytical method in an attempt to improve its accuracy in the 10 to 100 wt-ppm range. Removal of extraneous water interference from samples tested is an important part of this development.

TABLE 4.1

SRC-I Naphtha Hydrotreating
Oxygen Analytical Study
Sample Container Descriptions

<u>Container Type</u>	<u>Description</u>
1	Vials, screw cap, 25 mL, Pierce Cat. No. 13074 or equivalent. Teflon/silicone discs, Pierce Cat. No. 12722 or equivalent. Open top screw caps, Pierce Cat. No. 13219 or equivalent.
2	Vials, screw cap, 25 mL, Pierce Cat. No. 13074 or equivalent. Mininert valves, Pierce Cat. No. 10130.
3	Vials, capsule screw cap, No. 1, 2 1/4", Kimble Cat. No. 60957. Bottle caps, black phenol resin, polycone liner, Sargent-Welch Cat. No. A1855D or equivalent.
4	Bottles, serum, 100 mL, Clearglass, Wheaton "400", Sargent-Welch Scientific or equivalent. Septa, rubber to fit bottles, Sargent-Welch Cat. No. S-9075 or equivalent.
5	Vials, capsule, No. 1, 2 1/4", Kimble Cat. No. 60957. 15 x 30 mm Redrubber Stopper, Wheaton, American Scientific Cat. No. 80-4100.

TABLE 4.2
 SRC-I Naphtha Hydrotreating
 Oxygen Analytical Study
 SRC-I Hydrotreated Naphtha Analyses
Following Molecular Sieve Drying

<u>Identification</u>	<u>Total Oxygen Without Water, wt-ppm</u>	<u>Water Content, wt-ppm</u>
<u>Blend Number 3802-27</u>		
E (1)	58	81
ES (2)	20	24
US (3)	22	19
<u>Period Number 164</u>		
E	15	44
ES	45	17
US	71	18
<u>Period Number 127</u>		
E	95	41
ES	92	18
US	66	20

- (1) E denotes sample without sieve following equilibrated sieve drying.
 (2) ES denotes sample with equilibrated sieve left in before analysis.
 (3) US denotes sample with unequilibrated sieve left in before analysis.

TABLE 4.3

SRC-I Naphtha Hydrotreating
Oxygen Analytical Study
Compound Type Analyses, wt-ppm

<u>Analysis Dated</u>	<u>Compound Type</u>	<u>Weighed Oxygen Concentration</u>	<u>Analyzed Oxygen Concentration</u>	<u>Water Content</u>
11-10-83	2,3-Benzofuran	114	162	75
11-10-83	2-Hexanol	114	114*	74
11-10-83	Benzene	< 1	< 1	90
11-11-83	2,6-Dimethylphenol	114	114*	75
11-11-83	Benzene	< 1	< 1	90
11-14-83	Phenol	57	57*	89
11-14-83	2-Hexanol	11.4	71	87
11-14-83	2-Hexanol	57	20	77
11-14-83	Benzene	< 1	< 1	133
11-14-83	Benzene	< 1	< 1	133
11-15-83	Benzene	< 1	75	168
11-15-83	2,3-Benzofuran	57	57*	138
11-15-83	Benzene	< 1	< 1	14
11-16-83	2,6-Dimethylphenol	11.4	< 1	169
11-16-83	2,6-Dimethylphenol	57	< 1	110
11-16-83	2,3-Benzofuran	11.4	< 1	120
11-16-83	Phenol	11.4	49	179
11-16-83	Phenol	114	114*	111
11-16-83	Benzene	< 1	< 1	40
11-16-83	Benzene	< 1	< 1	40

* Sample chosen as standard for comparison to other results on same day.

TABLE 4.4

SRC-I Naphtha Hydrotreating
Oxygen Analytical Study
Benzene Water Content Analyses
in Type I Sample Container

<u>Analysis Date</u>	<u>Description</u>	<u>Water Content, wt-ppm</u>
11-03-83	Original Solvent Sample	33
11-11-83	Original Solvent Sample	90
11-14-83	Original Solvent Sample	133
11-15-83	Fresh Solvent Sample	14
11-16-83	Reanalysis of Fresh Solvent Sample	40

TABLE 4.5
 SRC-I Naphtha Hydrotreating
 Oxygen Analytical Study
Benzene Water Content Analyses
 in Different Sample Containers

<u>Container Type*</u>	<u>Water Content, wt-ppm on</u>	
	<u>11-18-83</u>	<u>11-21-83</u>
1	32	100
2	36	25
3	24	51
4	35	41
5 (dried)	49	105
6 (undried)	91	182

* See Table 4.1 for container type descriptions.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations address only the scope of the Final Report Addendum to ICRC.

5.1 Conclusions

- UOP nickel-moly catalyst activity for SRC-I naphtha feedstock contaminant removal is inferior to cobalt-moly catalyst at lower temperatures (250 to 280°C ABT), but is of approximately equal activity at the reactor temperatures of 335 to 345°C required to meet the product quality requirements.

- Leaving 3A molecular sieves in SRC-I hydrotreated naphtha samples of low oxygen concentration (< 100 wt-ppm) provides reasonable protection when atmospheric moisture is known to leak into the sample container.

- The 3A sieves do not appear to affect the hydrocarbon oxygenate content of the SRC-I hydrotreated naphtha samples.

- Sample container configuration has a marked effect on water ingress from the atmosphere during storage periods of several days. A Teflon valve closure provides reasonable protection from atmospheric contamination.

5.2 Recommendations

- Further work is needed to confirm the activity, stability and hydrogen requirement of UOP nickel-moly catalyst at the 335 to 345°C ABT range of commercial interest.

- Further development work is needed to improve the capability of the combustion/GC analytical method for the determination of oxygen in the range of 10-100 ppm.

- In order to control water ingress and interference during oxygen analysis of SRC-I naphtha in the low (10 to 100) wt-ppm range, UOP recommends leaving several cubic centimeters of 3A molecular sieves in the 10 to 30 cm³ sample before analysis. Alternatively, or in conjunction, a Teflon valve sample container closure may be used for samples that may adsorb onto the 3A sieves, or for added protection against atmospheric moisture contamination.

- It is evident that further development is necessary to improve analytical methods for the consistent detection of oxygen in the 10 to 100 wt-ppm range.