MASTER

DEVELOPMENT OF NEW CATALYSTS FOR
COAL LIQUIDS REFINING

DOE/ET/12103--T2

FOURTH QUARTERLY REPORT
for the period
1 October 1979 - 31 December 1979

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1 October 1979 - 31 December 1979

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I. ABSTRACT

Base-line catalyst testing conditions for hydrotreating SRC-II fuel Oil Blend have been determined: temperature, 750°F; pressure, 1,000 psig; LHSV, 1 ml/ml-hr; and H₂ flow rate, 5000 SCF/bbl. At these conditions the average values for HDN and HDS after 24 hours on stream are ~85% and 90% respectively with the best series of Ni-Mo on γ -alumina. Nickel and cobalt tungstate are significantly poorer catalysts. They afford 60-40% HDN and 85-75% HDS respectively. Nickel molybdate catalysts show higher activity for HDN than the analogous cobalt molybdate catalysts, however the activity of both types of catalysts is not significantly different for HDS.

Synthesis and characterization of various catalytic components and cation exchange of these materials is essentially complete. Exploratory cracking, hydrocracking, and hydrotreating catalysts are being produced in preparation for activity testing.

II. OBJECTIVE AND SCOPE OF WORK

The objective of this project is to develop catalysts that will be more active and selective and longer-lived under the process conditions necessary for the efficient conversion of coal-derived syncrude to gasoline in current types of catalytic cracking and hydrotreating units. The feedstocks to be processed are: a 350-750°F blend of SRC-II product distillate, and a hydrogenated product from this feed material with a hydrogen content of 11.5-12.0%.

The approach will be to prepare and test catalysts that are likely to be effective with polynuclear aromatics and with high concentration of sulfur and nitrogen compounds. This will entail preparing catalysts with high activity, thermal stability, resistance to poisoning by nitrogen compounds, and large pores to permit diffusion of large molecules. Hydrotreating, hydrocracking, and cracking catalysts will include numerous preparations of catalytic components such as exchanged and impregnated zeolites as well as exchanged and lattice-substituted synthetic montmorillonite micas utilizing catalytically active metals such as cobalt, molybdenum, nickel, chromium, platinum, palladium, iron and manganese, impregnated large pore supports such as aluminas, and combinations of superior catalytic components and support materials. They will be tested to establish their activity as hydrogenation catalysts (for aromatic substitution, heteroatom removal, hydrocracking) and as cracking catalysts (for conversion of high boiling SRC-II feed into low boiling liquid products).

III. SUMMARY OF PROGRESS TO DATE

During the quarter the following tasks have been undertaken and/or completed. These tasks are listed in the Milestone Chart in Figure 1. Detailed discussion of technical progress is found in the next section.

Task I-Modification and Building of Test Units

In the fourth quarter the cutting of the unit frames for the hydrotreating units was completed in our machine shop. Construction of the liquid gas discharge system for one of the units was about 90 percent completed, and this system is being installed in one of the existing hydrotreating units. After check-out the remaining modifications of the unit such as the new pump and reactor will be added and checked out.

Task II-Base-line Data and Test Procedures

During the fourth quarter the two Hewlett-Packard Model 5880A Gas Chromatographs were physically installed. Standard mixed gas samples were obtained and the calibration of response factors was carried out. Standard liquid samples were used to establish conversion and simulated distillation analyses, however, the simulated distillation software was defective and a new copy had to be ordered.

The 3353A computer installation is complete except for the simulated distillation software mentioned above, and the installation of a modem interface to permit transfer of data to a time-sharing computer for further data processing and tabulation.

FIGURE 1. MILESTONE CHART

REMARKS: ☐ * Delay in start of Task due to patent waiver contract negotiations. ☐ ** Delay in start of Task due to failure to receive hydrotreated feed. *** Requested extension to make up for delays.

☐ Progress ☐ Intermediate Event ☐ Major Milestone ☐ Proposed schedule deviation

TASK III-Modification of Catalytic Component

The final series of small crystal size ($\approx 1\mu$) exchanged Na-Y zeolites was produced by slurry milling the exchanged catalysts in a Morehouse Mill. This procedure results in reduction of aggregate particle size distribution without destruction of crystal structure as determined by constancy of line intensities in x-ray diffraction. The average aggregate particle size was reduced from 3.40μ in the unmilled zeolite to 0.94μ in the most highly milled zeolite (Fig. 2, Table I).

The synthesis of ≈ 10 kg of Fe-SMM was completed, but due to a breakdown in the autoclave used to prepare the M-SMM it was not possible to complete the preparation of the last metal substituted SMM, Mn-SMM. However, the autoclave has now been repaired, and a series of tests on a small scale is underway to optimize the preparation of Mn-SMM. After establishing the best method and experimental conditions, the pilot plant scale preps. will be carried out, and should be completed in the next quarter.

TASK IV -Cation Exchange

This task was completed during the present quarter when the ultra-stable Y zeolite, previously prepared, was exchanged with chromium, manganese, rare-earth, nickel and cobalt.

TASK V -Matrix Modification

This task has been completed. Pilot plant batches of >10 kg each of silica-alumina, silica-alumina-magnesia, and silica-alumina-zirconia gels have been prepared. The chemical composition and physical characterization of these materials has been completed.

TASK VIA -Cracking Catalysts Preparation

Eighteen exchanged Y-zeolites described under Task III have been formulated into cracking catalysts. The catalyst formulation consists of 20% zeolite and 80% matrix binder, which is mixed and spray dried. Physical property analyses are pending on these catalysts.

Five SMM, consisting of different silica-alumina ratio SMM (1,2), are ready to be tested as soon as cracking catalyst testing (Task VIB) begins.

Task VIB-Cracking Catalyst Testing

No exploratory cracking catalysts were tested during the present quarter because the DOE Office of Procurement Operations did not grant final approval of a contract modification, until September 29, 1979, to subcontract the hydrotreating of two drums of SRC-II to UOP to produce a suitable large supply of cracking and hydrocracking feed, and we did not receive this product during the present quarter.

Task VII-Hydrocracking Catalyst Preparation

During the present quarter the exchanged ultra-stable Y-zeolites were compounded with 15% matrix binder and extruded into 1/16" extrudates. During the next quarter these extrudates will be impregnated with hydrogenation components.

Task IX-Hydrotreating Catalysts Preparation

During the present quarter a third series of alumina supported catalysts with different metals ratios, was prepared. Two silica-alumina matrix materials, produced under Task V, were extruded and impregnated with hydrogenation metals.

Task X-New Hydrotreating Catalysts Preparation

The majority of the SMM matrix materials to be used as supports for the new hydrotreating catalysts have been prepared as described under Task III, and exchanged as described under Task IV. We are now producing new hydrotreating catalyst extrudates from nickel and cobalt exchanged SMM, and nickel, cobalt and iron lattice substituted SMM. These materials are also being impregnated with molybdenum, and compounded in various proportions with alumina supports. New hydrotreating catalyst activity testing will be initiated in the next quarter.

Task XI-Hydrotreating Catalyst Testing

Standard conditions were chosen from the base-line studies carried out in the second quarter (2): temperature, 750° F; pressure 1,000 psig; LHSV, 1 ml/ml-hr.; and H₂ flow rate, 5,000 SCF H₂/bbl. Five series of catalysts with different ratios of hydrogenation metals (molybdenum and tungsten), to promoters (nickel and cobalt) impregnated on three different alumina supports, and one series of nickel and cobalt molybdates, at different metals ratios, impregnated on silica-alumina supports, were activity tested. The % HDN and % HDS of the SRC-II Fuel Oil Blend afforded by these catalysts is reported in Tables IV-IX in section IV-J.

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task I - Modification and Building of Test Units

1. Modification of Hydrogenation Units

During the first three quarters (1,2,3) modifications of the two hydrotreating-hydrocracking test units were designed and the components purchased or fabricated. In the fourth quarter the cutting of the unit frames was completed in our machine shop. Construction of the liquid-gas discharge system for one of the units was about 90 percent completed, and this system is being installed in one of the existing hydrotreating units. After check-out the remaining modifications of the unit such as the new pump and reactor will be added and checked out. After the first unit is set up and checked out, the second unit modifications should be constructed and installed in substantially less time. It is expected that the modifications of the two units may be completed in the next quarter.

2. Construction of Microactivity Testing (MAT) Unit

The major components of the MAT unit have been installed in the control panel and on the reactor rack. The interior plumbing inside the control panel unit has been completed. The work still to be completed includes: electrical wiring, external plumbing, and installation of the furnace liners. The construction of the MAT unit is estimated to be 70 percent complete. During the fourth quarter the assembly of the micro-activity reactor unit was deferred to permit completion of the gas chromatographs and lab data system installation and check-out. Work on the micro-activity unit can now resume, and it should be possible to complete it in the first quarter of 1980.

B. Task II-Base-Line Data and Test Procedures

During the fourth quarter the two Hewlett-Packard Model 5880A Gas Chromatographs were physically installed. They are configured as follows:

1. Instrument with two FID detectors
Column 1 -1/8" Diam. stainless steel packed column, 6' long,
containing 10 weight per cent OV-101 on 80/100
mesh Chromosorb W.

Column 2 -25 meter long fused silica capillary column coated
with methyl silicone.

The two detectors are controlled by a level 2 terminal which cannot integrate. The signals are passed on to the H-P 3353A computer for integration and further data processing. Column 1 is intended for a simulated distillation analysis, but the software was not readable by the computer and a new copy is being shipped. Column 2 will be used for detailed analysis of the components of the liquid samples.

2. The second instrument is a three-column solenoid-valve operated thermal conductivity instrument configured for refinery gas analysis. This instrument has a level 4 terminal and is able to complete the analysis by itself. A standard mixed gas sample has been delivered and calibration of the response factors is under way. It will be used for the analysis of the product gas samples.

The 3353A computer installation is complete except for the simulated distillation software mentioned above and the installation of a modem interface to permit transfer of data to a time-sharing computer for further data processing and tabulation.

During the next quarter our analytical data acquisition and processing procedures should be finalized. However, our cracking catalyst testing program will probably not become fully operational until the middle of the next quarter because the DOE Office of Procurement Operation did not grant final approval of a contract modification, until September 29, 1979, to subcontract the hydrotreating of two drums of SRC-II to UOP to produce a suitable large supply of cracking and hydrocracking feed. UOP is scheduled to complete the hydrotreating and fractionation by the middle of January 1980, and it is expected that cracking catalyst testing will begin in February 1980.

C. Task III - Modification of Catalytic Component

1. Faujasite Modification

a. Na-Y Zeolite (normal, 1-8 μ , crystal size)

Na-Y Zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.7$) was obtained from Linde and used after thorough washing for all subsequent exchanges.

b. Na-Y Zeolite (small $\approx 1\mu$ crystal size)

During the first two quarters (1,2) synthesis of small particle size zeolites was unsuccessfully attempted following procedures described in the patent literature such as: synthetic cold mix technique (4), and use of small particle clays as seeds (5). In the third quarter a literature search was carried out to find additional procedures for making the desired small particle size zeolites. A method based on thermally shocking the zeolites by heating at rapid rates to temperatures in excess of about 1000°F was reported to produce refractory oxides with average diameters below 0.1 μ (6). We modified some existing equipment to allow the injection of zeolite slurry as an aerosol into a high temperature rotary calciner. However, the equipment was poorly suited for this purpose and no significant results could be obtained. Previously, in connection with Filtrol proprietary research, it was demonstrated that milling can be effectively used to reduce particle size of zeolite aggregates. Therefore, it was decided to carry out the reduction in average aggregate particle size by slurry milling the exchanged catalysts in a Morehouse Mill. This procedure results in reduction of aggregate particle size distribution without destruction of crystal structure as determined by constancy of line intensities in x-ray diffraction. The average aggregate particle size was reduced from 3.40 μ in the unmilled zeolite to 0.94 μ in the most highly milled zeolite (Fig.2, Table I). In the most highly milled sample 55% by weight of the zeolite particles had an average spherical diameter of less than 1 μ , and 93% less than 2 μ whereas only 14 and 35% by weight of the zeolite particles had similar diameter ranges in the unmilled sample.

c. Ultra Stable Y-Zeolite (US-Y) (without regard to crystal size).

Sixty pounds of ultra stable Y-zeolite was produced by four ammonium exchanges; one at room temperature and three at 100°C, followed by steam calcination at 677° C, and one additional ammonium exchange at 100°C (7). The above described procedures afforded a product with a unit cell size of 24.435 Å, which indicates an increase in the

FIG. 2 PARTICLE SIZE DISTRIBUTION OF MILLED EXCHANGED-Y ZEOLITE (TABLE I)

TABLE I. PARTICLE SIZE OF MILLED EXCHANGED -Y ZEOLITES

<u>SAMPLE NO.</u>	<u>DESCRIPTION</u>	<u>PARTICLE SIZE (50%)^a(μ)</u>
1001-259-1	NH ₄ -R ^b -Y	3.40 ^c
1028-29-2	NH ₄ -R-Y	1.33
1001-231-1	NH ₄ -R-Cr-Y	0.94
1028-29-1	NH ₄ -R-Mn-Y	1.52
1004-71-4	NH ₄ -Y	1.42
1007-65-1	NH ₄ -Ni-Y	1.38
1007-71-1	NH ₄ -Co-Y	1.48

^a 50% by weight lower and higher particle size. Measured with a micromeritics Sedigraph 5000 at Cyprus Labs, Los Angeles, Ca.

^b R-rare earth exchanged.

^c Unmilled zeolite.

$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolite framework from 4.7 to ≈ 10 (8). The soda level was reduced to 0.79%.

2. Synthetic Montmorillonite Mica (SMM) Modification

The background and experimental procedures for synthesizing from 26-37 kg each of SMM with silica-alumina ratios ranging from 2.16 to 2.67 were described in the First Quarterly Report (1).

3. Lattice-Substituted SMM (M-SMM)

The background discussion and synthetic procedures for producing about 10 kg. each of Ni-, Co-, Fe-, and Mn-SMM each at two different metal concentrations were described in the First and Second Quarterly Reports (1,2). At the present time, the syntheses of the Ni-, Co and Fe-SMM have been completed.

The high % Ni-SMM and low % Co-SMM have been homogenized, that is, all of the batches were combined and slurried in water. The water content was lowered either by filtering, decantation, or evaporation to a point where extrusion and further operations could be carried out. The low % Fe-SMM has also been homogenized and it awaits further processing. Chemical analyses are presented in Table II.

Due to a breakdown in the autoclave used to prepare the M-SMM it was not possible to complete the preparation of the last metal substituted SMM, Mn-SMM. However the autoclave has now been repaired and a series of tests on a small scale is underway to optimize the preparation of Mn-SMM. After establishing the best method and experimental conditions, the pilot plant scale preps. will be carried out, and should be completed in the next quarter.

The Fe-, Co-, and Ni-SMM materials have been submitted for SA, PSD, PV analyses, and the results are pending.

TABLE II. CHEMICAL ANALYSES OF M-SMM

-----Wt. % -----				
<u>SAMPLE M-SMM</u>	<u>M</u>	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>NH₃^c</u>
High Ni ^a	15.9	46.6	32.4	1.74
Low Ni ^b	7.8	52.9	36.6	1.95
High Co ^b	15.7	49.1	33.6	2.40
Low Co ^a	9.24	49.5	38.7	4.0
High Fe ^b	14.9	47.0	33.1	3.3
Low Fe ^a	7.0	52.2	37.3	4.0

^a Homogenized total batch.

^b Typical batch.

^c Before calcining.

D. Task IV-Cation Exchange

1. Faujasite Exchange

a. Na-Y Zeolite

In the last quarterly report (3) the details of the ammonium exchanges to produce low soda Na-Y zeolite were described. The further exchanges of this material with nickel, cobalt, rare earth, chromium and manganese were also described. During the present quarter a portion of each of these materials was Morehouse-milled, as described in Section IV-C of this report, to produce small particle, $\approx 1\mu$, exchanged zeolites.

b. Ultra Stable Y-Zeolite (US-Y)

(1) Experimental

Ultra-stable-Y zeolite of framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio ≈ 10 was prepared as described previously (3). Molycorp supplied a mixed rare-earth hydrate. All other materials used were Mallinckrodt's Analytical Reagent grade.

(a) Chromium Exchange (Cr) on US-Y

A 1.5% dose based on Cr_2O_3 per anhydrous weight of US-Y of chromium (III) chloride was slowly added to a 20% solids slurry of US-Y in water. After stirring for 1 1/4 hours the material was filtered and thoroughly washed with deionized water. After analysis showed a low % Cr, the zeolite was reslurried and an additional exchange was performed using a 1.0% dose based on the metal oxide. After four hours, this was washed with deionized water as before.

(b) Manganese Exchanges (Mn) on US-Y

A 2% dose based on MnO per anhydrous weight of US-Y of manganese (II) nitrate was slowly added to a 20% solids slurry of US-Y in water. After stirring for two hours, the material was filtered and washed with deionized water. After analysis showed the Mn was low, the material was reslurried, and the 2% dose exchange was repeated.

(c) Rare-Earth Exchanges (R) on US-Y

The mixed rare-earth hydrate was dissolved in a minimum quantity of HCl to a final pH of ≈ 3.5 . Sufficient quantity of this solution to yield a 10% dose of rare-earth oxide per anhydrous weight of ultra-stable-Y zeolite was added to a US-Y/water slurry to yield a 20% solids by weight slurry. The mixture was stirred for three hours, filtered, and washed with deionized water.

(d) Nickel and Cobalt Exchanges (Ni, Co) on US-Y

After preliminary exchanges showed low efficiency of exchange, large scale exchanges were carried out with 2.57% and 3.98% doses based on CoO and NiO per anhydrous weight of US-Y of cobalt (II) and nickel (II) nitrate as described above.

(2) Results and Discussion

The chemical analyses of the final exchanged materials are given in table III. None of the metal exchanges were quantitative. The most efficient exchanges were with nickel, cobalt and chromium, in which $\approx 2/3$ of the metal dose remained on the zeolite. About one third of the manganese exchanged onto the zeolite and only 1/20 of the 10% dose of rare-earth stayed on the US-Y. The soda content in each case remained the same, the metal replaced only ammonium ion. If a higher level of metal-exchange were needed, some of the cationic aluminum would have to be removed since there is very little ammonium ion left.

TABLE III. CHEMICAL ANALYSES OF EXCHANGED

US-Y ZEOLITE

-----WT. % -----

<u>SAMPLE NO.</u>	<u>DESCRIPTION</u>	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>Na₂O</u>	<u>REO</u>	<u>NH₃</u>	<u>Cr₂O₃</u>	<u>MnO</u>	<u>NiO</u>	<u>CoO</u>
909-97-24	US-Y	73.4	25.4	0.79	---	1.29	---	---	---	---
1007-87-1	Ni-US-Y	70.1	25.0	0.72	---	0.70	---	---	1.82	---
1007-89-1	Co-US-Y	70.8	25.7	0.80	---	0.69	---	---	---	1.41
1025-49-91	R ^a -US-Y	73.1	25.6	0.67	0.46	0.50	---	---	---	---
893-41-71	Cr-US-Y	70.8	26.8	0.62	---	0.39	1.67	---	---	---
1025-45-81	Mn-US-Y	71.0	25.7	0.70	---	0.66	---	1.43	---	---

^a R-rare earth exchange.

E. Task V- Matrix Modification

The preparations of the five basic matrix materials (supports): alumina, clay, synthetic silica-alumina, synthetic silica-alumina magnesia, and synthetic silica alumina-zirconia have been completed (1-3). The characterization of these materials in terms of chemical analyses, surface area, pore volume, pore size distribution, and crush strength of extrudates, where applicable, is essentially complete.

These materials are being compounded with the materials of Tasks III and IV, and impregnated with active metals, where necessary, to produce the cracking catalysts of Task VI, the hydrocracking catalysts of Task VII, and the hydrotreating catalysts of Tasks IX and X.

F. Task VIA-Cracking Catalysts Preparation

1. Introduction

A minimum of seventy catalyst formulations will be prepared from materials described under Tasks III, IV, and V. All of these formulations will be activity tested on two coal liquid feed stocks, and at three reactor temperatures giving a minimum of four hundred twenty cracking evaluations. The output data will be in accord with Task IIA.

The nominal chemical composition, surface area, pore volume, and pore size distribution will also be determined.

2. Compounded Zeolite Catalysts

The first series of 18 exchanged Y-zeolites from Na-Y zeolite (normal, 1-8 μ crystal size) (3), (small, $\approx$ 1 μ crystal size), Section IV-C-1 of this report,¹ and ultra stable Y-zeolites (US-Y) (without regard to crystal size), Section IV-D-1 of this report were formulated into cracking catalysts. The catalyst formulation consists of 20% zeolite and 80% matrix binder which is mixed and spray dried. Physical property analyses are still pending on some of these catalysts.

3. SMM Cracking Catalysts

Five SMM catalysts, consisting of different silica-alumina ratios (1,2) are ready to be tested as soon as cracking catalyst testing (Task VIB) begins.

4. Compounded Zeolite -SMM- Clay - Gel Catalysts

All of the above components are ready to be compounded as soon as catalyst activity testing shows which of the exchanged zeolites and SMM materials are most active.

G. Task VII - Hydrocracking Catalyst Preparation

1. Zeolite Based Hydrocracking Catalysts

During the present quarter the exchanged ultra-stable Y-zeolites were compounded with 15% matrix binder and extruded into 1/16" extrudates. During the next quarter these extrudates will be impregnated with hydrogenation components.

2. SMM Based Hydrocracking Catalysts

The Ni-and Co-exchanged SMM and the Ni-and Co-lattice substituted SMM of Task III will be compounded with the ultra-stable Y-zeolite of Task III to produce the desired hydrocracking catalysts during the next quarter.

H. Task IX- Hydrotreating Catalysts Preparation

1. Introduction

Hydrotreating catalysts are to be prepared from matrix materials such as alumina and silica-alumina (Section IV-E). The effects of metals ratios and catalytically active components will be determined by correlating physical and chemical properties versus hydrotreating activity.

2. Alumina Supported Catalysts

Two series of different alumina supported hydrotreating catalysts were prepared and analyzed in the first and second quarters (1,2). A third series of different metal ratios was prepared on a third alumina support during the present quarter, and evaluated in the hydrotreating testing units (Task XI).

3. Silica-Alumina Supported Catalysts

Two silica-alumina matrix materials described in Section IV-E of this report were impregnated with the desired combinations of catalytically active components. Hydrotreating testing on these catalysts was begun under Task XI.

I. Task X- New Hydrotreating Catalysts Preparation

The majority of the SMM matrix materials to be used as supports for the new hydrotreating catalysts have been prepared as described under Task III, and exchanged as described under Task IV. In order to prepare the finished catalysts, it will be necessary to impregnate the SMM with solutions of the catalytically active components, and then extrude and calcine the products obtained. To carry out this task efficiently, a small scale extruder was ordered from the C.W.Brabender Instrument Company. This extruder was received, and we are now producing new hydrotreating catalyst extrudates from nickel and cobalt exchanged SMM, and nickel, cobalt and iron lattice substituted SMM. These materials are also being impregnated with molybdenum, and compounded in various proportions with alumina supports. Catalyst hydrotreating activity testing is underway under Task XI.

J. Task XI - Hydrotreating Catalyst Testing

1. Introduction

The objective of the initial phase of this part of the program is to systematically study the effects of metals ratios and catalytically active components on various alumina and silica-alumina supports of varying physical (surface area, pore volume, and pore size distribution) and chemical properties versus hydrotreating activity. Two series of alumina supported hydrotreating catalysts prepared as described previously (1,2) and a third series prepared during this quarter, were activity tested. Two additional series of silica-alumina supported hydrotreating catalysts were prepared, and are in the process of being activity tested. Activity testing is also about to begin on various new hydrotreating catalysts prepared under Task X (Section IV-I).

2. Results and Discussion

Standard testing conditions were chosen from the baseline studies carried out in the second quarter (2): temperature 750° F; pressure, 1,000 psig; LHSV, 1 ml/ml-hr.; and H₂ flow rate, 5,000 SCF H₂/bbl. The results for several series of activity tests are presented in Tables IV-IX.

The most obvious finding in comparing Tables IV-VI with Tables VII and VIII is that nickel and cobalt tungstate impregnated alumina supported catalysts are significantly poorer catalysts for both hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) than their respective nickel and cobalt molybdate analogues.

TABLE IV. HYDROTREATING¹ OF SRC-II FUEL OIL BLEND²
WITH MoO₃/MO KAISER ALUMINA³ SUPPORTED CATALYSTS

<u>% METAL OXIDES</u> <u>MoO₃/NiO</u>	<u>RUN</u>	<u>TIME⁴</u> <u>hr.</u>	<u>%HDN</u>	<u>%HDS⁵</u>
16.5/6.6	I-130	6	92	94
		12	86	92
		18	(69) ⁶	91
		24	84	86
16.5/4.2	I-131	6	94	90
		12	86	86
		18	82	92
		24	78	89
16.1/1.5	II-133	6	91	87
		12	84	84
		18	77	85
		24	73	86
<u>MoO₃/CoO</u>				
16.7/5.5	II-134	6	87	93
		12	77	90
		18	78	94
		24	65	92
16.7/3.7	II-135	6	86	90
		12	78	91
		18	71	94
		24	71	92
15.9/1.3	I-132	6	79	85
		12	70	84
		18	65	84
		24	60	81

¹Standard Test Conditions:

temperature, 750°; pressure, 1000 psig;
LHSV, 1 ml/ml-hr; H₂ flow rate, 5000 SCF/bbl(2).

²Representative Elemental
Analyses:

PAMCO, Ft. Lewis, Washington; %C, 86.59; %H, 8.54;
%N, 0.95; %O, 3.69; %S, 0.26.

³Kaiser SA alumina.

⁴Hours on stream after completion of standard presulfiding procedure with 2% CS₂
spiked diesel oil (2).

⁵Preliminary results obtained with Tennelec x-ray fluorescence sulfur analyzer.

⁶Anomalous result.

TABLE V. ¹ HYDROTREATING OF SRC-II FUEL OIL BLEND ²
WITH MoO₃/MO KAISER/CONDEA ALUMINA ³ SUPPORTED CATALYSTS

% METAL OXIDES <u>MoO₃/NiO</u>	<u>RUN</u>	TIME ⁴ <u>hr.</u>	<u>%HDN</u>	<u>%HDS⁸</u>
12.9/5.9	II-102	6	91	91
		12	85	88
		18	84	87
		24	82	85
12.9/3.7	I-100	6	95	92
		12	84	-- ⁶
		18	--	-- ⁵
		24	80	87
13.0/1.3	I-111	6	94	91
		12	(77) ⁷	88
		18	84	92
		24	80	92
<u>MoO₃/CoO</u>				
13.3/6.0	II-100	6	80	94
		12	76	92
		18	78	97
		24	79	96
13.0/3.7	I-98	6	81	90
		12	74	97
		18	74	95
		24	71	96
12.6/1.2	II-103	6	79	87
		12	74	90
		18	66	85
		24	64	-- ⁶

¹Same as Table IV.

²Same as Table IV.

³Ratio of Kaiser/Condea =80/20

⁴Same as Table IV.

⁵No sample taken.

⁶Sample lost.

⁷Anomalous result.

⁸Same as Table IV.

TABLE VI. ¹HYDROTREATING OF SRC-II FUEL OIL BLEND ²
WITH MoO₃/MO KAISER/CONDEA ALUMINA ³SUPPORTED CATALYSTS

% METAL OXIDES <u>MoO₃/NiO</u>	<u>RUN</u>	TIME ⁴ <u>hr.</u>	<u>% HDN</u>	<u>%HDS⁷</u>
12.9/6.1	I-108	6	91	89
		12	85	91
		18	84	91
		24	83	90
12.1/3.7	II-94	6	95	92
		12	88	92
		18	85	94
		24	82	95
12.2/1.3	II-105	6	95	91
		12	79	90
		18	83	89
		24	80	90
<u>MoO₃/CoO</u>				
12.9/6.3	I-106	6	88	- ⁵
		12	81	96
		18	75	96
		24	69	69
12.4/3.8	II-92	6	77	86
		12	73	97
		18	70	97
		24	72	96
12.2/1.3	I-109	6	78	91
		12	73	90
		18	67	(73) ⁶
		24	62	88

¹Same as Table IV.

²Same as Table IV.

³Ratio of Kaiser/Condea =23/77.

⁴Same as Table IV.

⁵Sample lost.

⁶Anomalous result.

⁷Same as Table IV.

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 TABLE VII. HYDROTREATING OF SRC-II FUEL OIL BLEND
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With WO₃/MO KAISER/CONDEA ALUMINA SUPPORTED CATALYSTS

<u>% METAL OXIDES</u> <u>WO₃/NiO</u>	<u>RUN</u>	<u>TIME</u> ⁴ <u>hr.</u>	<u>%HDN</u>	<u>%HDS</u> ⁶
12.6/6.2	II-101	6	79	95
		12	65	93
		18	60	89
		24	56	86
13.5/3.7	I-102	6	67	88
		12	60	94
		18	59	(83) ⁵
		24	60	92
13.4/1.3	I-112	6	81	78
		12	67	78
		18	55	78
		24	55	77
<u>WO₃/CoO</u>				
13.4/6.6	II-99	6	51	80
		12	42	78
		18	33	(70) ⁵
		24	28	78
12.5/3.5	I-113	6	53	76
		12	54	86
		18	45	(82) ⁵
		24	50	88
13.9/1.3	II-104	6	44	75
		12	49	75
		18	41	75
		24	44	75

¹ Same as Table IV.

² Same as Table IV.

³ Ratio of Kaiser/Condea=80/20.

⁴ Same as Table IV.

⁵ Anomalous result.

⁶ Same as Table IV.

TABLE VIII. ¹ HYDROTREATING OF SRC II FUEL OIL BLEND ² WITH
³ WO₃/MO KAISER/CONDEA ALUMINA SUPPORTED CATALYSTS

% METAL OXIDES <u>WO₃/NiO</u>	<u>RUN</u>	TIME ⁴ <u>hr.</u>	<u>%HDN</u>	<u>%HDS⁷</u>
14.6/5.9	I-105	6	61	86
		12	50	82
		18	-- ⁵	-- ⁵
		24	-- ⁵	-- ⁵
15.4/3.9	II-96	6	74	85
		12	71	78
		18	64	80
		24	52	78
14.0/1.3	II-106	6	53	73
		12	54	73
		18	53	75
		24	52	76
<u>WO₃/CoO</u>				
14.6/6.6	I-107	6	59	69
		12	52	70
		18	51	78
		24	45	81
13.9/4.1	II-93	6	50	85
		12	45	86
		18	42	(56) ⁶
		24	50	82
14.4/1.2	I-110	6	52	76
		12	53	77
		18	48	76
		24	45	76

¹Same as Table IV.

²Same as Table IV.

³Ratio of Kaiser/Condea = 23/77.

⁴Same as Table IV.

⁵Pressure drop

⁶Anomalous result.

⁷Same as Table IV.

TABLE IX. ¹HYDROTREATING OF SRC II FUEL OIL BLEND ²
WITH MoO₃/MO SILICA/ALUMINA ³SUPPORTED CATALYSTS

METAL OXIDES <u>MoO₃/NiO</u>	<u>RUN</u>	<u>TIME⁴</u> <u>hr</u>	<u>%HDN</u>	<u>%HDS⁵</u>
10.1/6.5	II-119	6	86	91
		12	76	86
		18	65	86
		24	67	86
11.3/3.6	I-121	6	97	94
		12	87	86
		18	75	77
		24	71	81
11.4/1.2	II-114	6	96	92
		12	94	90
		18	88	89
		24	77	89
<u>MoO₃/CoO</u>				
10.2/6.0	II-120	6	94	84
		12	80	79
		18	80	78
		24	79	80
11.3/4.3	I-122	6	91	90
		12	70	85
		18	62	85
		24	62	86
12.1/1.2	II-122	6	91	84
		12	72	79
		18	64	79
		24	63	81

¹Same as Table IV.

²Same as Table IV.

³Ratio of Silica/Alumina = 1.1.

⁴Same as Table IV.

⁵Same as Table IV.

Therefore, no additional tungsten impregnated catalysts will be prepared for hydrotreating testing.

Additional preliminary results determined from Tables IV-VI are:

1. Nickel molybdate catalysts show higher initial (6 hr) and final (24 hr) activity for HDN than the analogous cobalt molybdate catalysts.
2. With the MoO_3 weight % held constant at $\approx 12 \pm 1\%$ the ratios of MoO_3/NiO or MoO_3/CoO had no generally significant effect on either HDN or HDS as the NiO or CoO weight percentages were varied from $\approx 6\%$ to $\approx 3.7\%$ to $\approx 1.3\%$.
3. The activity of the various $\text{MoO}_3\text{-Al}_2\text{O}_3$ catalysts for HDS did not differ significantly as a function of either NiO or CoO promoter.
4. The degree of catalyst deactivation was greater in HDN for the CoO promoted catalysts than for the NiO promoted catalysts.
5. The extent of catalyst deactivation for HDS was significantly less than for HDN for both NiO and CoO promoted catalysts, and neither type of catalyst showed a significantly greater degree of deactivation than the other in HDS.
6. There did not appear to be a clear trend in activity based on variation in the alumina supports (Tables IV-VIII).
7. Catalysts prepared on silica-alumina supports appear to deactivate to a greater extent than similar catalysts prepared on alumina supports (Table IX).

The fact that the NiO promoted catalysts are more active in HDN, and maintain about the same activity in HDS as CoO promoted catalysts can be used to great advantage since nickel compounds are considerably less expensive than the analogous cobalt compounds. If long term testing confirms that no significant difference in activity is obtained with low percentage nickel oxide promoted catalysts, this finding is of obvious economic importance.

Preliminary data indicates that loading the various alumina supports with ~ 12% MoO_3 on WO_3 , and from 1.3-6% NiO or CoO reduces both the surface area and pore volume, but does not seem to significantly change the pore size distribution (Table X).

The apparent relatively rapid deactivation of the silica-alumina supported catalysts could be caused by the greater acidity of such materials (9). Greater acidity would be expected to promote hydrocracking relative to hydrogenation, and coke formation would therefore be expected to be increased. Since the silica-alumina support tested had the highest percentage of small radii pores (Table X), coking would be expected to be a significant factor in plugging these pores, and deactivating the catalyst.

3. Future Work

Additional silica-alumina supported catalysts with different pore size distributions have been prepared, and will be tested in the next quarter. Carbon deposition will be determined, and compared with alumina supported catalysts to check the effect of support properties on coking. New hydrotreating catalysts, Task X, will be activity tested and compared with the previously tested conventional hydrotreating catalysts of Task IX.

TABLE X. PHYSICAL PROPERTIES OF HYDROTREATING CATALYST SUPPORTS

	B.D. ¹	SA ²	PV ²	Pore Volume Distribution (%) ²					
				Radius Range (μ)					
<u>Kaiser/Condea</u>	<u>g/cc</u>	<u>M²/g</u>	<u>cc/g</u>	<u>10-25</u>	<u>25-50</u>	<u>50-100</u>	<u>100-150</u>	<u>150-200</u>	<u>200-300</u>
100/0 ³	0.46	253	0.83	9.8	41.6	38.1	6.4	1.8	2.3
80/20 ³	0.46	268	0.77	15.2	45.9	31.4	4.4	1.7	1.5
80/20 ^{3, 4}	0.66	218	0.59	18.2	43.1	31.7	4	1.6	1.4
80/20 ^{3, 5}	0.62	230	0.63	16.2	47.3	29.4	3.9	1.5	1.8
23/77 ^{3, 6}	0.64	200	0.60	17.5	43.8	31.3	4	1.7	1.7
23/77 ^{3, 7}	0.62	205	0.56	15.8	46.6	30.1	4.2	1.6	1.6
Silica-Alumina ⁸	0.57	246	0.52	17.6	56.0	25.6	0.6	0.1	0.1

¹Bulk Density, 1/16" extrudates.

²Measured with Micromeritics Digisorb 2500 surface area and pore volume analyzer in desorption mode.

³Mixed mull supports using volatile free wt. ratios of aluminas shown. Prepared by peptizing mulling, extruding, and calcining as 1/16" extrudates.

⁴Finished Catalyst: MoO₃, 12.9%; NiO, 1.2%.

⁵Finished Catalyst: MoO₃, 12.9%; NiO, 5.9%.

⁶Finished Catalyst: MoO₃, 12.2%; NiO, 1.3%

⁷Finished Catalyst: MoO₃, 12.9%; NiO, 6.1%

⁸Wt. %: SiO₂, 51.8; Al₂O₃, 46.9; Na₂O, 0.07; NH₃ prior to calcining 0.87.

V. CONCLUSIONS

Preliminary hydrotreating catalyst testing on SRC-II Fuel Oil Blend with a series of exploratory catalysts containing different metals loadings and support properties, indicates that nickel and cobalt tungstate impregnated alumina supported catalysts are significantly poorer catalysts for both hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) than their respective nickel and cobalt molybdate analogues. Nickel molybdate catalysts show higher activity for HDN than the analogous cobalt molybdate catalysts, however, for HDS, the activity of both types of catalysts did not differ significantly as a function of either NiO or CoO promoter. Catalysts prepared on silica-alumina supports appeared to deactivate to a greater extent than similar catalysts prepared on alumina supports. The apparent relatively rapid deactivation could have been caused by the greater acidity of such materials, which would be expected to promote hydrocracking relative to hydrogenation, and the formation of pore-plugging coke deposits.

Numerous cracking catalysts have been prepared, and the baseline testing procedures have been worked out for carrying out the microactivity cracking testing. However, no testing of exploratory cracking catalysts can begin until we receive a suitable large supply of cracking and hydrocracking hydrotreated SRC-II feed. Receipt of this feed has been delayed for six months due to the failure of the DOE Office of Procurement Operations to approve a contract modification order to subcontract this large scale hydrotreatment to UOP. This hydrotreated feed is now expected to be received by the middle of February 1980.

VI. REFERENCES

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