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DEVELOPMENT OF NEW CATALYSTS FOR COAL LIQUIDS REFINING

Final Report for January 1979—April 1981

By
I. Schwager
D. N. Stamires

June 1981

Work Performed Under Contract No. AC22-78ET12103

Filtrol Corporation
Los Angeles, California

U. S. DEPARTMENT OF ENERGY

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FINAL REPORT
for the period
January 1979 - April 1981

Report Prepared by: I. Schwager (Project Manager)

Program Manager: D. N. Stamires

June 1981

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U. S. Department of Energy
Under Contract No. DE AC22-78ET12103

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I. ABSTRACT

Cracking, hydrocracking and hydrotreating catalysts, for use in coal liquids refining, were prepared and tested for activity on a 337-700°F SRC-II Fuel Oil Blend and hydrogenated products from this feed material.

Sixty-five cracking catalysts were prepared and activity tested at two different temperatures (900 and 1000°F) on two different feeds (SRC-II Fuel Oil Blend: as is, 8.7 wt.% hydrogen, and hydrogenated, 11.0 wt.% hydrogen). The catalysts were tested in a standard microactivity test at the above temperatures at a catalyst/oil weight ratio of 3, and a WHSV of 16 g oil/g cat.-hr.

With the hydrotreated SRC-II Fuel Oil Blend corrected conversions of 430°F+ feed of 68-75 wt.%, C₅-EP gasoline product distribution of ~ 50 wt.%, and coke makes of 4-9 wt.% were obtained at 900°F with catalysts composed of broad pore volume distribution matrix binder components and active exchanged Y-zeolites.

When the same catalysts were tested on the unhydrotreated SRC-II Fuel Oil Blend, conversion and gasoline in the product were much lower (37-39 wt.%, and 18-20 wt.%, respectively) and coke make was significantly higher (8-14 wt.%).

Thirty hydrocracking catalysts were prepared and activity tested on hydrotreated SRC-II Fuel Oil Blend in 300 ml downflow fixed catalyst bed reactors under the following standard conditions: temperature, 750°F; pressure 1,000 psig; LHSV, 1 ml/ml-hr.; and H₂ flow rate, 5,000 SCF/bbl.

Three series of bi-functional catalysts containing low-sodium cracking bases such as hydrogen and rare earth exchanged ultrastable Y-zeolites (US-Y), and exchanged or metal substituted Synthetic Montmorillonite Micaceous (SMM's) containing Group VIB and/or Group VIII hydrogenating metal components were prepared and tested. Some of the above catalysts exhibited about the same conversion and gasoline make as the commercial baseline prototype catalyst-ultrastable Y-zeolite (85 wt.%), alumina (15 wt.%) and Pd (0.5 wt.%). Corrected conversions of 430°F+ of ~ 50 wt.%, and C₅-430°F gasoline yields of ~ 35 wt.% (after correction for 15 wt.% gasoline in the original feed) were obtained with combinations of rare earth exchanged US-Y/NH₄-US-Y/alumina = 1.9/3.8/1 loaded with MoO₃/CoO or MoO₃/NiO with or without addition of Pd or Pt.

One hundred hydrotreating catalysts were prepared and activity tested continuously under the same conditions used for hydrocracking activity testing.

The activity testing of these catalysts, containing different metals loading and support properties, indicates that none of the exploratory catalysts tested were quite as good as the commercial Filtrol HPC-40 for HDN (85% maximum vs. 88% for HPC-40). The HDS results were similar for the best exploratory and commercial catalysts (94-96%).

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 337-700°F blend of SRC-II product distillate, and hydrogenated products from this feed material with a hydrogen content of 11.0-11.6%.

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 saturation of aromatics and heteroatom removal, and as hydrocracking and cracking catalysts for conversion of high boiling SRC-II feed into low boiling liquid products.

III. INTRODUCTION

ERDA, in PRDA 2595, asked for new approaches to the conversion of syncrudes from coal to gasoline and other distillate fuels.

The reason for preparing distillate fuels from coal is to decrease the reliance on their production from petroleum. Efficient processes for converting syncrudes to distillate fuels might differ markedly from petroleum-refining processes, and such processes should, properly, be sought; however, the closer the processing can be to conventional petroleum-refining processes, the quicker and cheaper it will be to use syncrudes as commercial sources of distillate fuels. With this in mind, Filtrol proposed an experimental program, the goal of which was to develop catalysts that would permit selection of processing conditions that could be carried out, to a great extent, in facilities of the type being used currently.

Current petroleum refinery processes that will probably be adapted to convert coal syncrudes to distillate fuels are hydrotreating of residua, gas oils, and naphtha, hydrocracking of residua and gas oils, catalytic cracking of light and heavy oils, reforming, and alkylation. The latter two, reforming and alkylation, should require no modification to use appropriate feed stocks derived from coal instead of from petroleum, but the other processes are not likely to be useful with syncrudes except with process modifications and with pretreatments of severity not currently used on petroleum-derived feedstocks. Production of gas oils by the cracking of modified syncrudes may be a useful processing step in some refineries.

Processing conditions for syncrudes from coal will be different from those used for petroleum fractions because of the higher content of aromatics and heteroatoms in syncrudes. The low contents of hydrogen, 8% for syncrudes, and their high aromatics content preclude catalytic cracking such as can be done with the heavy oil cracking process, for cracking would yield large amounts of coke and gas (1); that is, if the catalyst were not poisoned by the nitrogen compounds present in these feeds. As a generalization, one can conclude that hydrogen must be added if there is to be a high recovery of carbon as liquid fuel, for if disproportionation were the sole source of hydrogen, polynuclear aromatics would yield only 50% of the carbon as paraffins, the other half would convert to coke. Partial or complete saturation of the components of the feed is but part of the need in converting syncrudes to distillates. There are high contents of sulfur, nitrogen, and oxygen to be removed and large, polycyclic molecules to be cracked to small molecules. The sequence of steps to be followed might be (1) hydrotreating to remove heteroatoms, hydrogenation to break aromatic bonds and saturate some aromatic rings, and catalytic cracking, or (2) hydrotreating to remove heteroatoms, followed by hydrocracking, or (3) hydrotreating, mild hydrocracking and catalytic cracking. Although other methods of treating syncrudes may be developed, the preceding are most likely to be used at first because the basic processing steps and equipment are already being used in petroleum refining.

In the preceeding discussion, it has been pointed out that treatment of syncrudes derived from coal will require more severe processing conditions than similar petroleum fractions, and that syncrudes have a higher content of heteroatoms; hence, the catalysts used need to be more stable on heating, more resistant to aging, and more active in the presence of potential poisons. The need for development of improved catalysts has been shown in experimental programs previously supported by ERDA in which only commercial catalysts were used (2,3). The object of this program is to develop such improved catalysts.

A. Cracking Catalysts

Although FCC feedstocks derived from coal will have been subjected to one or more hydrogenation steps, they are likely to be more aromatic, contain more condensed rings, and have a higher nitrogen content than petroleum-derived feedstocks (2). This means that they may require higher temperature cracking and produce more coke. This, in turn, can require higher temperature regeneration to ensure burning off coke to a sufficiently low level.

The thermal stability of cracking catalyst with faujasite-type zeolite as the active component is enhanced by reducing the soda content to low levels, raising the zeolite silica-alumina ratio, and, to a lesser extent, by having rare earth ions present. The catalytic activity of the zeolite results from the presence of acid sites, which are more acidic but less numerous as the silica-alumina ratio is increased. It is these sites that are poisoned by nitrogen bases; however, because the poisoning may occur through formation of dissociable, substituted ammonium salts of solid acid, one would expect lower adsorption of nitrogen bases at higher temperatures, and thus, greater retention of catalytic activity. To take advantage of this phenomenon, the zeolite must be thermally stable. Consequently, catalysts tested were based on zeolite that is highly stable, consistent with retention of a high degree of catalytic activity.

Zeolites used in commercial catalyst are produced in the sodium form and then ion exchanged, together with suitable ancillary treatments, to give various sodium, hydrogen (via ammonium ion), aluminum (in ultra-stable Y), and rare earth contents. We attempted to optimize the type and contents of these cations to give resistance to poisoning by nitrogen bases.

Although the above-mentioned cations, at suitable levels, have given zeolite catalysts effective for petroleum feedstocks, others may prove to be more useful with feeds contaminated to a great extent with heteroatoms. Transition metal elements such as nickel, cobalt, manganese, and chromium, have coordination characteristics that are significantly different from the rare earth elements and non-transition elements; consequently, they can play a role, through coordination, other than as a source of acid function. The normal coordination energetics of hydrated transition metal ions and the associated ligand fields would be markedly changed, at less than saturation, by the highly polarizing

environment in the cavities of dehydrated zeolites; catalytic activity could occur that would not otherwise be noted. Some transition elements, i.e., iron and nickel are known to carry cracking to an extreme by promoting formation of gas and coke, but judicious doping of the zeolite with transition metal elements and proper selection of the companion cations should mitigate this propensity. It is likely, for example, that chromium, which is not easily reduced and which has a low tendency to form a sulfide, can modify the cracking reaction without causing excessive gas formation.

Another approach that was explored was to use a different solid acid as the catalytic component. Synthetic montmorillonite mica (SMM), produced in the ammonium form, has cracking activity intermediate between that of zeolites and silica-alumina gel, and has excellent thermal stability (4).

Use of feeds with large polycyclic molecules means that cracking can become diffusion limited in the matrix and in the zeolite crystal. This would result in longer residence times within the catalyst and consequent overcracking to coke, which exacerbates the problem by limiting diffusion even more. Two approaches to minimize this are to use a matrix with large pores, and to decrease the diffusion path length in zeolite crystals by compounding the catalyst with finely divided zeolite crystals such as have been described in U.S. Patent No. 3,516,786. Both of these approaches were explored.

B. Hydrotreating and Hydrocracking Catalysts

As has been stated, hydrogenation will be needed as a first step to saturate aromatic rings or to remove sulfur, nitrogen, and oxygen, or to do both. Concurrent with this step could be hydrocracking, but an initial hydrotreating step will probably be needed for effective hydrocracking (5). The first hydrogenation step might be more effective if carried out with a combination of hydrotreating and cracking, or hydrocracking, catalysts but under hydrotreating conditions. The objective will be to obtain hydrotreating and hydrocracking catalysts that are effective with high-nitrogen-content feedstocks containing asphaltenes.

The current preferred catalyst for hydrotreating high-nitrogen feeds is nickel-molybdenum on alumina. Nickel-molybdenum and cobalt-molybdenum catalysts on alumina and other supports with large pore diameters and good strength were prepared and tested. A Filtrol catalyst of this type, HPC-5, has been reported by Amoco to have superior performance as a catalyst in coal liquefaction and to "represent a promising new catalyst for coal liquefaction" (6).

Improved aging resistance has been claimed for residual hydrodesulfurization catalysts based on metals on alumina to which titania has been added. An improved catalyst of this type has been made by Filtrol (7). This approach was

used in this project for the treatment of syncrudes. Among the elements that were added were manganese, tin and zinc.

A type of catalyst that has been tested in the hydrotreating and hydrocracking of petroleum fractions is synthetic montmorillonite mica (SMM) in which catalytically active metals are incorporated into either ion-exchange or framework sites (8). It had not, however, been tested with syncrudes. Filtrol therefore prepared and tested a variety of substituted SMM's using nickel, cobalt, iron, manganese, rare earth, and platinum metals as the active metals.

The commercial reference catalyst chosen for cracking baseline comparison, Filtrol FS-30, is a well established petroleum cracking catalyst with good activity, stability and selectivity. At the beginning of the project in early 1979 it was the best general performance cracking catalyst produced at Filtrol and the best selling catalyst.

The commercial reference hydrotreating catalyst chosen for hydrotreating comparison, Filtrol HPC-40, is a well established, nickel oxide promoted, molybdenum oxide catalyst supported on γ -alumina, which has been shown to afford superior denitrogenation activity in use with vacuum gas oils and resid feeds. It has a relatively large average pore diameter of $\approx 100\text{\AA}$, and a relatively broad range of pores with $\approx 18\%$ pores greater than $200\text{\AA}$ in diameter.

Filtrol does not produce any commercial hydrocracking catalysts, and no hydrocracking catalyst manufacturer would supply us with a commercial sample for use in this project. Therefore, we prepared a baseline catalyst from the patent literature procedure (9) used to prepare the prototype Union Oil Co. catalyst based on commercial zeolites, promoted with noble metals, and compounded with alumina. This type of catalyst is known to be especially useful in hydrocracking heavier, higher-nitrogen containing feedstocks.

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IV. SUMMARY

This is the final report of work performed under U.S. Department of Energy Contract DE AC22-78ET12103, "Development of New Catalysts for Coal Liquids Refining", during the period January, 1979-April, 1981. The objective of the program was to prepare and test cracking, hydrocracking, and hydrotreating catalysts that would be superior to the commercial catalysts in use at the time the program was initiated.

Sixty-five cracking catalysts were prepared and activity tested at two different temperatures (900 and 1000°F) on two different feeds (SRC-II Fuel Oil Blend: as is, 8.7 wt.% hydrogen, and hydrogenated, 11.0 wt.% hydrogen). The catalysts were tested in a standard microactivity test at the above temperatures at a catalyst/oil weight ratio of 3, and a WHSV of 16 g oil/g cat.-hr. Activity was determined by measuring the conversion of the feeds to 430°F-product. Selectivity was determined by measuring the C₁-C₄ light gas composition, the C₅-430°F EP gasoline yields, and the coke make.

With the hydrotreated SRC-II Fuel Oil Blend corrected conversions of 430°F+ feed of 68-75 wt.%, C₅-EP gasoline product distribution of ~ 50 wt.%, and coke makes of 4-9 wt.% were obtained at 900°F with catalysts composed of broad pore volume distribution matrix binder components and active Y-zeolites. Conversion increases linearly as the percent rare earth oxide content of the catalysts is increased; however, gasoline and coke make may deviate somewhat, both positively and negatively, according to the composition of the catalyst and the nature of the exchanged zeolite. Y-zeolites, in the same matrix, which are heavily ammonia exchanged are more selective, but less active than those which are highly rare earth exchanged. When the same catalysts were tested on the unhydrotreated SRC-II Fuel Oil Blend, conversion, and gasoline in the product were much lower (37-39 wt.%, and 18-20 wt.% respectively) and coke make was significantly higher (8-14 wt.%).

Thirty hydrocracking catalysts were prepared and activity tested on hydrotreated SRC-II Fuel Oil Blend in 300 ml downflow fixed catalyst bed reactors under the following standard conditions: temperature, 750°F; pressure, 1,000 psig; LHSV, 1 ml/ml-hr.; and H₂ flow rate, 5,000 SCF/bbl.

Three series of bi-functional catalysts containing low-sodium cracking bases such as hydrogen and rare earth exchanged ultrastable Y-zeolites, and exchanged or metal substituted SMM's containing Group VIB and/or Group VIII hydrogenating metal components were prepared and tested. Some of the above catalysts exhibited about the same conversion and gasoline make as the commercial baseline prototype catalyst-ultrastable Y-zeolite (85 wt.%), alumina (15 wt.%) and Pd (0.5 wt.%). Corrected conversions of 430°F+ of ~ 50 wt.%, and C₅-430°F gasoline yields of ~ 35 wt.% (after correction for 15 wt.% gasoline in the original feed) were obtained with combinations of rare earth exchanged US-Y/NH₄-US-Y/alumina = 1.9/3.8/1 loaded with MoO₃/CoO or MoO₃/NiO

with or without addition of Pd or Pt. It is significant that the expensive noble metals Pd and Pt do not appear to be necessary to impart reasonable activity and selectivity to these catalysts.

One hundred hydrotreating catalysts were prepared and activity tested continuously in downflow with fixed catalyst bed reactors under the following standard conditions: temperature, 750°F; pressure, 1,000 psig; LHSV, 1 ml/ml-hr.; and H₂ flow rate, 5,000 SCF/bbl.

The activity testing of these catalysts, containing different metals loading and support properties, indicates that none of the exploratory catalysts tested were quite as good as the commercial Filtrol HPC-40 for HDN (85% maximum vs. 88% for HPC-40). The HDS results were similar for the best exploratory and commercial catalysts (94-96%). 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 does not differ significantly as a function of either NiO or CoO promoter. Nickel molybdate impregnated Kaiser SA alumina catalysts promoted with ~ 3% P₂O₅ appear to be generally more active for HDN than the unpromoted catalysts. Again, the HDS results are similar.

Catalysts prepared on silica-alumina supports appear to deactivate to a greater extent than similar catalysts prepared on alumina supports.

A series of metal substituted SMM catalysts, impregnated with MoO₃, and compounded with 33 wt.% Kaiser SA alumina to improve their porosity, was also activity tested. The results indicate maximum HDN activity of 60-62% with MoO₃ on Ni-substituted SMM, and maximum HDS of 91-92% with MoO₃ on Co-substituted SMM.

V. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task I - Modification and Building of Test Units

1. Modification of Hydrogenation Units

Two existing hydrogenation units were modified for use in hydrotreating and hydrocracking testing. New reactors, feedstock pumps, liquid-gas discharge systems, and miscellaneous other additional components were incorporated in the existing basic units. The process flow diagram for the final continuous hydrotreating and hydrocracking test units is shown in Fig. 1.

2. Construction of Microactivity Testing (MAT) Unit

A site for the new cracking unit was set aside within the laboratory and cleared of the existing equipment.

The unit has been designed with furnaces and facilities for two catalytic reactors. The feed and product lines are controlled by solenoid valves with the option of manual operation or automatic sequencing of the valves under computer control. The reactor furnaces are three-zone. The temperature of each zone, and the temperature of the feed inlet preheater may be controlled independently.

The major component of the microactivity unit is a glass reactor inserted in a tubular furnace. Feed is injected by a syringe pump through a deadman preheater into the reactor. A thin vycor layer further preheats and disperses the feed before it contacts a fixed catalyst bed, which rests on a pyrex wool support. An automatically actuated four-way valve regulates the on-stream time of the feed. The liquid cracking product, or syncrude, is trapped in calibrated receiver and the gaseous products flow to a collection system. Both liquid and gases are analyzed by gas chromatography (Fig. 2).

To accomplish the objectives of the present project, several improvements were made in the micro unit. In particular, modifications of the feed preheater were needed. Historically the feed preheater in the microactivity unit consisted of a metal block fitted into the reactor body. The block, or "deadman", contained 34 inches of coil in which the feed was vaporized before contacting the catalyst bed. The long residence time of feed vapors in the coil promotes thermal cracking of the heavier components. The use of different feedstocks also leads to problems in maintaining a fixed vapor temperature. Since the metal deadman provides a constant amount of preheat independent of feed composition, lighter feeds are emitted at a higher temperature than heavier ones. Extremely heavy feeds may not even vaporize completely. Data collected from microactivity tests employing identical catalyst and

**FIG. 1 - HYDROTREATING AND HYDROCRACKING
ACTIVITY TEST UNIT^a**

^a SEE P. 12 FOR LEGEND FOR FIG. 1.

LEGEND FOR FIGURE 1

- 1 - 1,000 ml Feed Buret
- 2 - Whitey Diaphragm Feed Pump
- 3 - Hydrogen Feed
- 4 - 1st Stage Grove Regulator
- 5 - 2nd Stage Grove Regulator
- 6 - Tylan Mass Flowmeter
- 7 - 4 Zone Lindberg Electric Furnace
- 8 - 10 μ Filter
- 9 - Bronze Core Block
- 10 - Reactor
- 11 - Product Condenser
- 12 - Liquid Gas Separator
- 13 - Liquid Receiver with Glass Gauge
- 14 - Discharge Control Valve
- 15 - Foxboro Liquid Level Controller
- 16 - Foxboro Differential Cell Transducer
- 17 - Back Pressure Regulator
- 18 - Wet Test Meter
- P - Pressure Gauge

FIG. 2 - MICROACTIVITY TEST UNIT

feedstock (Fig. 3) show that conversion is sensitive to feed temperature. Clearly the metal deadman is inadequate for the present purposes.

A modified design for the deadman was adopted, in which an electrically heated hypodermic needle was combined with the stainless steel housing. The general arrangement is shown in Fig. 4. Near the outlet end of the hypodermic needle three turns were made in the tubing to reduce surging which was noticed in some runs when straight tubing was used.

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

1. Cracking and Hydrocracking

a. Analysis System

The Filtrol MAT and hydrocracking units were coupled with a system which utilizes three gas chromatographs and a laboratory computer to carry out the cracking testing and analysis of the gas and liquid cracking products distribution.

The first G.C. is a Perkin-Elmer Sigma 3B gas chromatograph*, equipped with an automatic sampling system and a temperature programmed boiling point column of OV-101 silicone gum, which is used to determine conversion of liquid product to naphtha (% peak area below where an interpolated 430°F peak would appear).

The second G.C. is a three-column Hewlett-Packard Model 5880A 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 was used to calibrate the response factors. This instrument is connected directly to both the MAT and the hydrocracking units for determination of product gas analysis.

The third G.C. is a Perkin-Elmer Sigma 1 FID gas chromatograph, equipped with thick-film OV-101 capillary pre-column, and analyzer columns, and a valve operated back flush which is not in the sample flow path. It is used to determine the light ends in the liquid product. The columns are maintained at -20°C for 4 minutes after sample injection and are then temperature programmed at 10°/min to a maximum temperature of 250°C. They are held at that temperature for 30 minutes to permit all heavy ends to back-flush from the pre-column. The integrator is set to stop when the C₈ peak has

* Mention of trade name throughout this report does not imply endorsement by the U.S. Department of Energy.

FIG. 3 - CRACKING CONVERSION vs. FEED
TEMPERATURE

FIG. 4 - METAL DEADMAN ASSEMBLY

emerged (22 min) allowing the results to be calculated on the basis of the C₈ content, and related to the C₈ and lighter content of the sample analyzed for naphtha on the previously mentioned P.E. Sigma 3B GC.

b. Standard Cracking Microactivity Test

Baseline testing was carried out with hydrotreated SRC-II Fuel Oil Blend. A commercial catalyst, Filtrol FS-30, was used as the baseline catalyst for cracking. The process conditions were as follows:

Temperatures:	900°F and 1000°F.
Wt. Catalyst:	4 grams
Wt. Feed:	1.333 grams
CAT/Oil:	3
WHSV:	16 goil/g. cat -hr

(1) Procedure

The feed is charged to the MAT unit (Fig. 2), and the liquid syncrude collected in an ice cooled receiver. The gaseous products are collected and measured over water, and then introduced to a Hewlett-Packard refinery gas analyzer (Model 5880A) for analysis. The liquid syncrude is analyzed for cycle oil^a and conversion on a Perkin-Elmer Sigma 3B gas chromatography system. The apparent wt.% 430°F⁺ conversion is calculated as 100-cycle oil. The so-called corrected conversion (1), is the conversion of only that portion of the feedstock boiling above a peak with retention time equal to an interpolated value of 430°F.

Corrected 430°F⁺ Conversion =

$$100 \left(1 - \frac{\%430^{\circ}\text{F}^{+} \text{ in product}}{\%430^{\circ}\text{F}^{+} \text{ in feed}} \right)$$

The wt. percentages of H₂ and the light gases are determined by summing the values obtained from the refinery gas analysis, and the light-ends-in-liquid-analysis described above.

Carbon on catalyst is measured by combustion to CO₂ followed by trapping and weighing of CO₂ on Ascarite.

^a 430°F⁺ material in feed or product.

As a check on the reliability of the G.C. conversion method a sample of CAT A Still Check Oil was obtained from Mobil Research, (Paulsboro, New Jersey) and used to calibrate gas chromatographs for the syncrude analysis. The CAT A syncrude, commonly used throughout the petroleum industry because of its high stability, contains 43.9 wt. percent naphtha based on ASTM distillation. In fourteen checks during a one month interval, Filtrol's gas chromatograph used for syncrude analysis averaged 44.1 percent naphtha with a standard deviation of ± 0.7 percent.

A second check procedure was carried out by distilling blends of petroleum feeds and comparing the yields of 430°F- material obtained with a 15 plate column at a reflux ratio of 5 to 1 with 430°F- yields obtained for the same blends by the gas chromatographic method. An excellent linear correlation was obtained between the 430°F- distillation yields and the 430°F- naphtha found by the gas chromatographic method (Fig. 5).

c. Standard Hydrocracking Test

The hydrocracking testing units were the same units which were used for hydrotreating catalyst testing (Fig. 1).

Because of the relatively high nitrogen content and aromaticity of the SRC-II Fuel Oil Blend, it was decided that a bi-functional catalyst containing a noble metal hydrogenating component such as palladium, and a low-sodium ultrastable hydrogen Y-zeolite cracking base would be most useful as the baseline hydrocracking catalyst. Therefore, a baseline catalyst similar to that described in the Union Oil Company U.S. Patent 3,867,277 was prepared. Extrudates (1/16") were formulated from 85% US-Y and 15% alumina. The dried and calcined extrudates were impregnated with aqueous PdCl_2 in dilute ammonia solution, dried and calcined.

The chemical and physical analyses of the finished catalyst are as follows:

1. SiO_2 , 59.13; Al_2O_3 , 37.49; Na_2O , 0.62; NH_3 , 0.04; Pd, 0.56.
2. Surface area, 552 m^2/g ; Pore volume, 0.44 ml/g ; Pore volume distribution:

FIG. 5 - CORRELATION BETWEEN WT.% 430°F
FOUND BY DISTILLATION AND BY
GAS CHROMATOGRAPHIC PROCEDURE

<u>Pore radius(Å)</u>	<u>Percent</u>
200-300	0.9
150-200	1.4
100-150	6.8
50-100	24.1
25-50	27.3
10-25	39.5

(Measured with Micromeretics Digisorb 2500 SA and PV analyzer in desorption mode.)

The catalyst (100 cc of 1/16" extrudates) was diluted with sand and charged to the reactor in a geometric loading pattern as will be described later in Section IV-B-2. The reactor was flushed with flowing H₂ (3 l/min., 1250 psig). Finally, the reactor was heated to 750°F over 2 hrs., and held 4 hrs. at this temperature with H₂ flowing at the above conditions.

The standard operating conditions used for hydrocracking tests were: temperature, 750°F; H₂ flow rate, 5000 SCF/bbl; LHSV, 1 ml oil/ml cat-hr; H₂ pressure, 1000 psig.

At given times flowing gas samples were injected directly into a refinery gas analyzer gas chromatograph, and liquid samples were collected in cooled receivers for conversion, and light gas analyses. A sample of the analytical work up is shown in Table 1. Although the inlet hydrogen flow and the exit hydrogen plus light gases flow were measured as carefully as possible with calibrated flow meters, determinations of hydrogen consumption, by the hydrogen gas balance method could not be made with meaningful accuracy as experimental errors were apparently too great. Since the Task Schedule did not call for determination of hydrogen balances by the more time consuming and expensive elemental hydrogen balance method no such determinations of hydrogen consumption were carried out.

In Fig. 6, a plot of conversion vs. time shows that the reduced Pd catalyst on US-Y (85%) and alumina (15%) deactivates from ~ 65 to 30 wt.% conversion of 430°F⁺ feed over a period of 24 hours. Because of the screening nature of the catalyst evaluation runs, and the limitation of the available hydrotreated SRC-II feed, it was decided to use 12 hours on stream, after preconditioning, as the standard reaction test time.

TABLE 1. HYDROCRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND¹ WITH Pd (0.56 Wt. %)IMPREGNATED US-Y (85 wt.%) - ALUMINA (15 wt.%) CATALYST²

Run No.	II-159-2	Rxn. Temp.	750°F
Cat. ID.	1029-41-2	Reactor Press.	1000 psig
Feedstock	Hydrotreated SRC II	Sample Time	12 hr.
LHSV	1.0	H ₂ Feed Rate	5000 SCF/bbl

Total Light Hydrocarbons In Product

<u>Component</u>	<u>Wt.% of Feed</u>
Methane	0.11
Ethane	0.34
Ethylene	0.00
Propane	2.14
Propylene	0.00
Isobutane	2.77
n-Butane	3.04
1-Butene + Iso	
Butylene	0.00

Total C ₁ -C ₄	8.42
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H ₂ Consumption ³	1409 SCF/bbl
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Apparent Conversion ⁴	64.4
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Corrected Conversion ⁵	57.9
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Product Distribution, Wt.%

C ₁ -C ₄	8.4
C ₅ -EP Gasoline	51.5
Cycle Oil	35.6

Recovery	95.5
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¹ Elemental Analyses (UOP) %C, 88.27; %H, 11.58; %N, 0.05*; %O, 0.11; %S, 0.03
 Distillation (UOP) IBP/5 10/30 50 70/90 95/FBP
 °F 400/417 424/450 480 520/595 636/696

*Filtrol Kjeldahl N analysis

² See text for catalyst chemical and physical properties.

³ Calculated assuming unanalyzed fraction of vent gas is hydrogen.

⁴ Apparent Conversion: 100-Cycle Oil.

⁵ Corrected Conversion: $100 \left(1 - \frac{\% \text{ 430°F+ in product}}{\% \text{ 430°F+ in feed}} \right) (1).$

**FIG. 6 - HYDROCRACKING CONVERSION OF
HYDROTREATED SRC - II
FUEL OIL BLEND vs TIME**

d. Data Reduction

An H-P 3353D Lab Computer which is equipped with an H-P 2645 Keyboard and CRT terminal, was used to reduce all the analytical data on the gaseous, liquid, and solid products from the cracking and hydrocracking runs. An in-house basic program was used to compute the product distribution and the material balance. Results of the computations were printed out on a Texas Instruments 733 ASR Printer-Terminal. This same unit was alternatively used as a time sharing remote terminal via an Inmac Clear Signal Modem for back-up computation capability whenever the HP3353D computer was out of service.

2. Hydrotreating

a. Introduction

Filtrol hydrotreating units were initially used to develop test procedures for use with the SRC-II Fuel Oil Blend. Base-line data on the effect of unit parameters on catalytic activity were obtained with the commercial hydrotreating catalysts, Filtrol HPC-6^a and HPC-40^b. The hydrotreating testing unit used was similar to the unit described in Fig. 1.

b. Experimental

The catalyst, 100 ml, diluted with 200 ml of sand, was charged to the reactor. Catalysts were presulfided with diesel oil spiked with 1-2 vol. % of CS₂.

A standard presulfiding procedure was developed. The temperature is raised to 400°F in 2 hours at 400 psig, 1500 SCF/bbl H₂, 3 LHSV, with 2% CS₂ spiked diesel oil, and held 3 hours. The temperature is then raised to 600°F at 1 LHSV in 2 hours and held for 8 hours. After presulfiding, the feedstock is introduced at reaction conditions, and the liquid product is collected at suitable times. Initial runs were carried out for 24 hours. Samples were taken every 4 hours, water washed to remove H₂S and NH₃, and dried over 4A molecular sieves. The samples were then analyzed for sulfur on a Tennelec X-ray fluorescence sulfur analyzer. Carbon and hydrogen analyses were carried out by Galbraith Labs, Knoxville, Tenn.

-
- a 15% MoO₃, 4% CoO; on γ-alumina, 1/16";
SA = 230 m²/g, PV = 0.59 ml/g
- b 15% MoO₃, 4% NiO; on γ-alumina, 1/16";
SA = 220 m²/g, PV = 0.50 ml/g

Subsequently, the following changes were made in the standard hydrotreating activity testing units and procedures in an attempt to improve the reproducibility of the test:

- (1) The overall ratio of sand/catalyst volume was increased from 2:1 to 3:1 to increase the catalyst bed length.
- (2) The locations of the catalyst bed and the thermocouples were shifted downward to allow utilization of three furnace zones, and to increase the preheating zone.
- (3) The catalyst and sand were loaded with geometrically different ratios to achieve better temperature control as described below.
- (4) The catalyst and sand were loaded alternately with a teaspoon to achieve uniform distribution of sand and catalyst within the reactor.

Previously, the catalyst bed length was only 11-14 inches long and was located in two furnace zones, with two thermocouples in each zone. The increased bed length permits the use of three furnace zones, and allows better control of the reaction temperature. However, due to the large exothermic heat of reaction, maintaining isothermal conditions is still a difficult task at high LHSV. This is especially critical at the upper portion of the bed where large conversion and heat release occur. Therefore, a geometric loading method was applied by diluting the catalyst with different amounts of sand in each zone. The ratios of 3:1, 3.5:1, 3.5:1, 3:1, 3:1 were maintained from the top to the bottom of the reactor zones for each 20 cc of catalyst. To improve the distribution of catalyst and sand phases uniformly, one-third of a teaspoon of catalyst and the corresponding ratio of sand were loaded alternately, and tapped very gently.

A series of glass tube experiments showed clearly the difference in packing uniformity between the previous loading method^a and the teaspoon method; the latter resulted in a much more uniform distribution. The glass tube experiments also showed that the sand acts as an excellent liquid phase distributor. The liquid feed was spread evenly over the whole catalyst bed.

^a Loading catalyst diluted in a fixed ratio directly as described on p. 23.

Nitrogen analyses were carried out in-house using a Tecator Kjeltac System I high speed macro Kjeldahl nitrogen analyzer. Samples which had lost up to 98 wt.% nitrogen could be routinely analyzed with good reproducibility ($\pm 5\%$).

Simulated distillations, ASTM D2887, were obtained with a proprietary Hewlett-Packard simulated distillation program on the H-P 3353D Computer with an H-P 5880 A Gas Chromatograph. An H-P Sim. Dist. correlation was rewritten, and was used to obtain D-86 or D-1160 correlation distillations from the D2887 simulated distillation data.

Sulfur analyses of N.B.S. petroleum based sulfur standards were carried out in-house with a Tennelec X-ray fluorescence sulfur analyzer, and also by oxygen-bomb combustion followed by chromatographic determination of sulfate by Galbraith Labs. The agreement between the two procedures was good. Similarly, the Sulfur analyses obtained for the initial baseline runs with a Tennelec X-ray fluorescence sulfur analyzer gave results which were in good agreement with results obtained from Galbraith Labs. This occurred because the two commercial catalysts, Filtrol HPC-40 and HPC-6, were highly active and reduced the nitrogen and oxygen content of the SRC-II to levels where they did not cause interference errors in the sulfur analyses. However, it was assumed that many of the exploratory hydrotreating catalysts would not be sufficiently active to reduce the nitrogen and oxygen levels of the products to levels low enough to eliminate such interference error. Therefore, it was decided to have all the subsequent sulfur analyses done at Galbraith Labs.

Most of the catalysts tested appear to still be undergoing some deactivation at 24 hours run time. Nevertheless, due to the screening nature of the testing, the large number of tests (≈ 150) to be carried out, and time and feed limitations, 24 hours was chosen as the standard testing time. Therefore, the final testing procedure calls for 24 hour catalyst testing. The 24 hour product is analyzed for nitrogen, sulfur, carbon and hydrogen. A D-2887 simulated distillation is also carried out for each product sample.

c. Results and Discussion

The SRC-II Fuel Oil Blend was hydrotreated with two Filtrol catalysts (HPC-6 and HPC-40). A wide range of reaction conditions was investigated to establish optimum run conditions. The process variables studied were: temperature (650 -800°F), pressure (500 - 1,500 psig), H₂ flow rate (2,000 -15,000 SCF/bbl) and LHSV (0.5 - 3). When the experiments began we were not in possession of our Kjehldahl nitrogen analyzer; therefore, it was decided that % hydrodesulfurization would be used as the general criterion for determining baseline conditions for the standard hydrotreating test.

(1) Effect of Temperature

The effect of temperature on the % hydrodesulfurization (HDS) of the SRC-II Fuel Oil Blend is shown in Fig. 7. The HPC-40 catalyst (Ni/Mo/Al) shows slightly higher HDS activity than the HPC-6 catalyst (Co/Mo/Al). Line-out was observed at temperatures over 700°F with more than 95% HDS.

(2) Effect of Pressure

The effect of pressure on the % HDS at the SRC-II feed is given in Fig. 8. Once again, the HPC-40 catalyst showed slightly greater activity than the HPC-6 catalyst. The slope decreases markedly above 1,000 psig, but higher pressure measurements will be required to determine the line-out condition.

(3) Effect of LHSV

The effect of LHSV on % HDS is presented in Fig. 9. The change in slope appears to be rather small as the LHSV approaches 1 ml/ml-hr.

(4) Effect of H₂ Flow Rate on HDS, HDN, and H/C Ratio

The most detailed results obtained are presented in Fig. 10. All three hydrotreating parameters: % HDS, % HDN, and H/C ratio reach line-out at approximately 10,000 SCF/bbl of H₂. The Ni/Mo/Al catalyst appears to be generally more active than the Co/Mo/Al catalyst.

C. Task III - Modification of Catalytic Component

1. Faujasite Modification

a. Introduction

Although FCC feedstocks derived from coal will have been subjected to one or more hydrogenation steps, they will be more aromatic, contain more condensed rings, and have a higher nitrogen content than petroleum-derived feedstocks. This means that they will require higher temperature cracking and produce more coke. This, in turn, can require longer temperature regeneration to insure burning off coke to a sufficiently low level. The thermal stability of cracking catalysts with faujasite-type zeolite as the active

FIG. 7 - EFFECT OF TEMPERATURE ON % HDS OF SRC-II FUEL OIL BLEND

FIG. 8 - EFFECT OF PRESSURE ON % HDS OF SRC-II FUEL OIL BLEND

FIG.9 - EFFECT OF LHSV ON % HDS OF SRC-II FUEL OIL BLEND

FIG. 10—EFFECT OF H₂ FLOWRATE ON % HDS, % HDN and H/C RATIO

component is enhanced by reducing the soda content to low levels, raising the zeolite silica-alumina ratio, and, to a lesser extent, by having rare earth ions present. The catalytic activity of the zeolite results from the presence of acid sites, which are more acidic but less numerous as the silica-alumina ratio increases. It is these sites that are poisoned by nitrogen bases; however, because the poisoning occurs through formation of dissociable, substituted ammonium salts of solid acid, one would expect lower adsorption of nitrogen base at higher temperatures and, thus, greater retention of catalytic activity. To take advantage of this phenomenon, the zeolite must be thermally stable. Consequently, catalysts to be tested will be based on zeolite that is highly stable, consistent with retention of a high degree of catalytic activity.

Use of feeds with large polycyclic molecules means that cracking can become diffusion limited in the matrix and in the zeolite crystal. This would result in longer residence times within the catalyst and consequent overcracking to coke, which exacerbates the problem by limiting diffusion even more. Two approaches to minimize this are to use a matrix with large pores and to decrease the diffusion path length in zeolite crystals by compounding the catalyst with finely divided zeolite crystals such as have been described in the literature. Both of these approaches will be explored.

b. Experimental

(1) Na-Y Zeolite (normal crystal size)

Normal 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.

(2) Na-Y Zeolite (small $\approx 1\mu$, crystal size)

Synthesis of small particle size zeolites was unsuccessfully attempted following procedures described in the patent literature such as: synthetic cold mix technique (2), and use of small particle clays as seeds (Table 2) (3). However, 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

TABLE 2. PARTICLE SIZE OF SMALL SIZE Na-Y ZEOLITE

<u>Sample No.</u>	<u>Synthetic Procedure</u>	<u>Particle size (50%)^a</u>
850-47-18	Clay: 3.6 μ , Hydrite Flat "D"	6.4 μ
850-47-37	Clay: .0.2 μ , Hydrite "UF"	5.1 μ
1004-1-54	Synthetic, cold mix	1.6 μ
1004-39-73	Synthetic, cold dilute mix	5.0 μ
1004-39-81	Synthetic, control mix	5.0 μ

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

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. 11, Table 3). In the most highly milled sample 55% by weight of the zeolite particles had an average spherical diameter of less than 1μ , and 93% less than 2μ whereas only 14 and 35% by weight of the zeolite particles had similar diameter ranges in the unmilled sample.

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

Sixty pounds of ultra-stable Y-zeolite were 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 (4). The above described procedures afforded a product with a unit cell size of $24.435 \text{ \AA}$, which indicates an increase in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolite framework from 4.7 to ≈ 10 (5). The soda level was reduced to 0.79%.

2. Synthetic Montmorillonite Mica (SMM) Modification

a. Introduction

Synthetic montmorillonite-mica (SMM), a laminar 2:1 layer-lattice aluminosilicate, was first synthesized by Granquist (6). SMM has the general unit cell formula for the ammonium form given below:

where the superscripts "oct" and "tetra" refer to atoms having octahedral and tetrahedral coordination respectively. SMM clays are classified as dioctahedral or trioctahedral, depending upon whether the number of lattice cations per unit cell in the octahedral layer is 4 (dioctahedral) or 6 (trioctahedral; all positions filled), respectively. The formula above refers to a dioctahedral clay.

SMM shows catalytic cracking activity and the available data shows that SMM, although not as active as zeolitic catalysts, is much more active than amorphous silica-alumina (7). SMM would also

FIG. 11 PARTICLE SIZE DISTRIBUTION OF MILLED EXCHANGED-Y ZEOLITE

TABLE 3. PARTICLE SIZE OF MILLED EXCHANGED - Y ZEOLITES

<u>Sample No.</u>	<u>Description</u>	<u>Particle Size (50%)^a(μ)</u>
1C01-259-1	NH ₄ -R ^b -Y	3.40 ^c
1C28-29-2	NH ₄ -R-Y	1.33
1C01-231-1	NH ₄ -R-Cr-Y	0.94
1C28-29-1	NH ₄ -R-Mn-Y	1.52
1C04-71-4	NH ₄ -Y	1.42
1007-55-1	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.

be expected to be an excellent matrix material. The use of SMM as a support for hydrogenation metals has also been patented. Csicsery and co-workers (8,9) demonstrated the activity of Pd-SMM, Pd-SMM-zeolite composites, and Pd-SMM-M (M represents low concentrations of other metals such as Mn, Cr, Fe, W, Mo, Co, etc.) for hydrocracking.

SMM in the ammonium form with a range of silica-alumina ratios was therefore prepared. These materials were tested as cracking catalysts after deammoniation. They were also used as matrix materials, and as components in hydrocracking and hydrotreating catalysts after exchange and impregnation.

b. Experimental

The general procedure for preparing SMM is as follows (6):

Ingredients are thoroughly mixed in a pilot plant Cowles mixer until the resultant slurry is homogeneous and without lumps. The slurry is then charged to a high pressure autoclave equipped with a high speed stirrer (Magne-drive-Autoclave Engineers). The reaction temperature is raised, and autogeneous steam pressure from the slurry is obtained, and maintained for the time indicated. Upon completion of the run, heating is discontinued and the slurry is removed under pressure (temp. ~ 250°F). In most cases the product slurry is sheared with a high speed Cowles mixer and spray dried.

The charge ingredients and run conditions are presented in Table 4, and the charge and product mole ratios, along with the % mica, in Table 5.

c. Results and Discussion

Five large scale pilot plant batches of SMM ranging from 26-37 kg each were produced with silica-alumina ratios from 2.16 to 2.67. These materials were available for testing as cracking catalysts. The most active SMM was also tested in mixtures with zeolites and other matrix modifications for cracking activity. The SMM with a silica-alumina ratio of 2.54 was exchanged with nickel and cobalt to produce hydrocracking and hydrotreating components (Section IV-D-1).

TABLE 4. PREPARATION OF SMM - CHARGE INGREDIENTS AND RUN CONDITIONS

Sample	-----Charge Ingredients (Parts dry wt.)-----						-----Run Conditions-----				
	PSA ^a	Gibb. ^b	m-Kaolin ^c	NH ₄ HF	NH ₄ OH ^d	H ₂ O	Run Time ^e	Pressure	Temp.	pH(in)	pH(out)
2	3.00	1.00	19.95	0.32	1.96	179.0	4 hrs.	1240 psig	572°F	7.8	6.65
3	4.07	1.00	19.11	0.67	1.42	165.1	12 hrs.	1240 psig	600°F	8.3	5.93
4	5.25	1.00	19.11	0.73	1.16	153.2	15 hrs.	1240 psig	675°F	8.1	5.7
1	6.65	1.00	19.88	0.81	0.93	139.6	12 hrs.	1240 psig	575°F	7.2	--
5 ^f	6.42	1.00	19.10	0.78	0.89	138.5	15 hrs.	1240 psig	675°F	7.3	6.0

^a PSA (polysilicic acid) - 5.5 - 6.0 wt.% SiO₂ in water, obtained by passing dilute sodium silicate solution through an acidified (H₂SO₄) ion exchange resin.

^b Gibb. (gibbsite alumina) - Alcoa C-31 (65% solids).

^c m-Kaolin (meta-kaolin) - Freeport Al-Sil-Ate OP (100% solids).

^d NH₄OH (ammonia solution) - 28% NH₃.

^e Does not include heat-up time - usually about 4 hours.

^f Contains "seed" SMM from previous run (~2% on dry basis).

TABLE 5. PREPARATION OF SMM - CHARGE AND PRODUCT MOLE RATIOS

Sample	-----Charge-----			-----Product-----		
	<u>SiO₂/Al₂O₃</u>	<u>NH₄/Al₂O₃</u>	<u>F⁻/SiO₂</u>	<u>SiO₂/Al₂O₃</u>	<u>NH₄/Al₂O₃</u>	<u>% Mica^a</u>
2	2.2	.600	.050	2.16	0.44	70
3	2.4	.532	.100	2.28	0.43	64
4	2.6	.467	.100	2.45	0.41	58
5	2.8	.400	.100	2.58, 2.49 ^b	0.41	52, 44 ^b
1	2.8	.400	.100	2.67	0.39	32, 26 ^b

^a Determined by XRD method similar to that in W. T. Granquist, U.S. Patent 3,252,757.

^b Average values: 2.54, 48, 29.

3. Lattice-Metal-Substituted SMM (M-SMM)

a. Introduction

The charge requirement of SMM may also be met by divalent ions, such as Ni^{2+} , Co^{2+} , and Mn^{2+} , as well as by other trivalent metals such as Fe^{3+} (7). These ions, because of their size and charge, substitute for Al^{3+} in the octahedral coordination position. If all the octahedral positions are filled as a result of complete divalent for trivalent substitution, one then has a tiioctahedral clay. Mixtures of di- and trioctahedral clays can also be obtained if less than stoichiometric substitution occurs.

These lattice-metal-substituted SMM's show a substantial increase in activity relative to SMM in hydrocracking and hydroisomerization studies. In one study (10) involving hexane hydrocracking the data shows an increase in activity with increasing Ni concentration (Ni^{+2} substituted for Al^{+3} in the octahedral layer) with the highest activity corresponding to 5 Ni atoms per unit cell. A study (11) involving hexane hydroisomerization not only shows a dramatic activity increase for Ni-SMM relative to SMM but also increased formation of 2,2-dimethylbutane as the Ni content increases from 0 to 5 Ni atoms per unit cell. Incorporation of cobalt into the SMM lattice also results in increased hydrocracking activity relative to SMM, although not as extensive as for Ni-SMM with the same amount of substitution (12). Generally for the above studies a hydrogenation component such as Pd is placed on the M-SMM prior to use by established ion exchange or impregnation techniques.

M-SMM's with four metals (Ni, Co, Fe, Mn) at different concentrations (7-9% and 13-16% for Ni, Co and Fe; and 6% and 9% for Mn) for testing as components of hydrocracking and hydrotreating catalysts were synthesized.

b. Experimental

According to a previously published procedure (10), which is typical of the general preparative method for SMM and M-SMM minerals, the preparation of high percentage Ni-SMM was carried out in the following manner. To a rapidly stirred solution of 17463.0g ammonium stabilized polysilicic acid (5.12% SiO_2) was added 893.1g $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Alcoa C-31) and 47.1g $\text{NH}_4\text{F} \cdot \text{HF}$. An ammoniacal slurry consisting of 1000g H_2O , 315 g NH_4OH (58.6%) and 1536.3g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was then added to the silica-alumina slurry resulting in the immediate formation of a thick gel. With continued vigorous

stirring an additional 315 g NH_4OH (58.6%) and 600g H_2O were added whereupon the gel became fluid enough to be mixed to homogeneity. The slurry was introduced into the 10 gallon autoclave (Autoclave Engineers) and heated up to 282°C (950 psig) over a period of 3 hr. The temperature was maintained there for 5 hours to insure optimum crystallinity of product. After purging the product from the autoclave, the resultant slurry was diluted with water by approximately 1.5x, filtered to a moist cake, reslurried with approximately 6 gallons of water and again filtered to a moist cake. The product was then dried at 100°C .

The above example is typical of the methods and conditions required to produce M-SMM minerals. Nickel(II), cobalt(II) and iron(III) were introduced as the nitrate salts; manganese(II) as the sulfate salt. The synthesis mix stoichiometric ratios for the preparation of each mineral type are given in Table 6 along with the analytical data for the particular resulting mineral.

c. Results and Discussion

The nature of the M-SMM product is ascertained primarily by X-ray diffraction (XRD) spectra (7). The (06) reflection in the XRD spectrum is particularly diagnostic concerning two mineral characteristics: the amount of transition metal lattice substitution for cases involving divalent-cation-for-trivalent-aluminum replacement in the octahedral layer, and the nature of the bulk mineral in terms of the amount of dioctahedral and/or trioctahedral character.

The high percentage Ni- and Co-SMM minerals exhibit two reflections in the (06) region of the spectrum of approximately equal intensities indicating that the bulk mineral possesses both di- and trioctahedral character and that the transition metal content for both minerals is approximately two metal atoms/unit cell. The low percentage Ni- and Co-SMM minerals exhibit trioctahedral (06) reflections of decreased intensities relative to the dioctahedral (06) reflection consistent with the reduced amount of transition metal in the mineral. For example, the (06) di-to-trioctahedral reflection intensity ratio is approximately two, which is consistent with a transition metal content of about 1 metal atom/unit cell. The Mn-SMM minerals exhibit one (06) reflection with a lower-angle-side shoulder, weak and barely resolvable, indicating some degree of trioctahedral character, although apparently not as much as for the Ni- and Co-SMM minerals possessing

TABLE 6. PREPARATION OF M-SMM-CHARGE RATIOS-pH-PRODUCT ANALYSES

-----Synthesis Mix Formulation-----						-----Chemical Product Analyses (wt.%) ^a -----					
SiO ₂	Al ₂ O ₃	M	NH ₄ F·HF	NH ₄ OH	Reactant Slurry pH	SiO ₂	Al ₂ O ₃	(NH ₄) ₂ O	M ^{II} O or M ₂ ^{III} O ₃	Vm ^b	M
2.60	1	0.90 Ni ^{II}	0.14	2.26	8.1	46.7	32.4	3.1	20.2	13.0	15.9 Ni ^{II}
2.60	1	0.45 Ni ^{II}	0.14	2.25	9.4	52.0	36.3	5.0	10.4	15.5	8.2 Ni ^{II}
2.60	1	0.90 Co ^{II}	0.14	2.25	8.3	46.9	32.4	5.3	19.8	17.4	15.6 Co ^{II}
2.60	1	0.45 Co ^{II}	0.14	2.25	>9.1	49.5	38.7	6.1	11.7	14.4	9.2 Co ^{II}
2.60	1	0.90 Fe ^{III}	0.14	3.25	8.2	47.0	34.7	5.5	19.6	17.3	13.7 Fe ^{III}
2.60	1	0.45 Fe ^{III}	0.14	2.20	9.2	52.2	36.4	7.0	10.4	16.6	7.3 Fe ^{III}
2.60	1	1.00 Mn ^{II,III}	0.14	1.50	8.5	51.8	35.3	4.5	11.4	12.0	8.8 Mn ^{II,c}
2.60	1	0.45 Mn ^{II,III}	0.14	1.20	8.9	54.1	35.8	4.9	7.4	13.0	5.7 Mn ^{II,c}

^a Analyses are carried out on volatiles-free basis (V_f) after calcination of sample to 1750°F.

^b Vm = volatile matter.

^c The Mn-SMM mineral is presumed to consist of a combination of Mn^{II} and Mn^{III} atoms as a result of the air oxidation of Mn^{II}(OH)₂ to Mn^{III}O(OH) (F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd Edition, p. 849). In the reactant slurry pH range of 8.5 to 8.9, however, not all of the manganese is in the hydroxide form some exists as the aquated Mn²⁺ ion. Hence the product mineral is presumed to be a combination of oxidation states II and III. The Mn content is given, however, in terms of Mn^{II}O.

the same transition metal content (~ 8-9%). This observation is consistent with the fact that some of the substituting Mn cations are of oxidation state III which would tend to lessen the amount of the trioctahedral character of the mineral. The Fe-SMM minerals exhibit only the dioctahedral (06) reflection which is expected since one has trivalent aluminum being partially replaced in the octahedral layer only by trivalent iron.

D. Task IV - Cation Exchange

1. Introduction

The faujasite and SMM preparations from Task III were cation exchanged as follows:

a. Faujasite (Silica/Alumina Ratio 4.7 - Crystals Normal Size)

One preparation was partially exchanged with ammonia to produce a low-soda faujasite. A second preparation was partially exchanged with ammonia then further exchanged with nickel to produce an ammonia-nickel low-soda faujasite. A third preparation was partially exchanged with ammonia then further exchanged with cobalt to produce an ammonia-cobalt low-soda faujasite. A fourth preparation was partially exchanged with ammonia then further exchanged with a mixture of rare earth cations to produce a material with rare earth, low soda content. A fifth preparation was partially exchanged with ammonia, then partially exchanged with rare earth cations, then further exchanged with manganese to produce a rare earth-manganese low-soda faujasite. A sixth preparation was partially exchanged with ammonia, then partially exchanged with rare earth cations, and then further exchanged with chromium to produce a rare-earth-chromium low-soda faujasite. Additional high rare earth containing faujasites were produced by carrying out two and three exchanges with rare earth cations.

b. Faujasite (Silica/Alumina Ratio 4.7 - Crystals Milled to Reduce Particle Size)

Same preparations as in Task IV, 1, a.

c. Faujasite (Silica/Alumina Framework Ratio ~ 10, Ultra-stable-Y-zeolite, US-Y)

Same preparations as in Task IV, 1, a. except that the Mn and Cr exchanged US-Y zeolites were not also exchanged with rare earth cations.

d. SMM

Silica/alumina ratio 2.54 - two exchanges were made; one with nickel, the other with cobalt.

e. Metal-Lattice - Substitute SMM

No cation exchanges were performed on these materials.

2. Experimental

Molycorp supplied a mixed rare-earth hydrate. All other materials used were Mallinckrodt's Analytical Reagent grade.

a. Faujasite Exchange (Na-Y-Zeolite)(1) Ammonium Exchanges

Ammonium sulfate (0.7 g per anhydrous gram of zeolite) was added to a zeolite-water slurry to yield a 20% solids by weight slurry. For the first ammonium exchange of Na-Y zeolite, H_2SO_4 was used to adjust the pH to between 5-6. All subsequent ion-exchanges required no pH adjustments. After stirring at room temperature for one hour the mixture was filtered and washed with deionized water until the eluent was sulfate-free. All ammonium exchanges after the first were heated to 100°C while stirring for one hour before the filtration and washing steps. One hundred twenty Vf pounds of ammonium exchanged zeolite was produced. The elemental analyses of the exchanged Na-Y zeolite is given in Table 7.

(2) Nickel and Cobalt Exchanges (Ni or Co)

The ammonium exchanged zeolite was further exchanged with a quantity of nickel or cobalt nitrate sufficient to produce metal exchanged zeolite of ~ 1.5 wt.% reported as metal oxide. The respective slurries were stirred at room temperature for one hour, filtered, and thoroughly washed with deionized water. Twenty Vf pounds each of nickel and cobalt exchanged ammonium exchanged zeolites were produced. Analyses are presented in Table 7.

TABLE 7. CHEMICAL ANALYSES OF EXCHANGED TYPE-Y ZEOLITE

<u>Sample No.</u>	<u>Description</u>	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>Na₂O</u>	<u>REO^b</u>	<u>NH₃</u>	<u>Cr₂O₃</u>	<u>MnO</u>	<u>NiO</u>	<u>CoO</u>
1004-57-4	Na-Y	59.7	25.5	13.64	---	---	---	---	---	---
1004-71-4	NH ₄ -Y	72.7	25.0	1.87	---	6.85	---	---	---	---
1007-65-1	NH ₄ -Ni-Y	71.5	26.6	1.82	---	6.26	---	---	1.54	---
1007-71-1	NH ₄ -Co-Y	70.4	27.1	1.89	---	6.24	---	---	---	1.39
909-65-05	NH ₄ -R ^a -Y	66.5	26.4	1.77	4.92	5.22	---	---	---	---
893-37-61	NH ₄ -R ₂ ^a -Y	62.2	23.7	1.65	9.39	3.06	---	---	---	---
1025-17-6	NH ₄ -R-Cr-Y	67.2	25.6	1.70	4.01	4.24	1.48	---	---	---
1025-21-16	NH ₄ -R-Mn-Y	66.7	25.2	1.72	4.37	4.38	---	1.14	---	---

^a R-rare earth exchange.

^b Rare Earth Oxide.

(3) Partial Rare Earth Exchange (R)

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 5% dose of rare earth oxide per anhydrous weight of zeolite was added to a zeolite-water slurry to yield a 20% solids by weight slurry. The mixture was stirred for one hour, filtered, and washed with deionized water until chloride-free. Sixty pounds of partially rare earth-exchanged zeolite was produced. Additional exchanges were made to produce higher rare earth-exchanged zeolites. Analyses are presented in Table 7.

(4) Chromium and Manganese Exchanges (Cr or Mn)

A sufficient quantity of chromium(III) chloride or manganese(II) nitrate was slowly added to a 20% solids slurry of partially rare earth-exchanged zeolite in water in order to produce metal exchanged zeolite ~ 1.5 wt.% reported as the oxide. The respective slurries were stirred for three hours, filtered, and thoroughly washed with deionized water. Twenty Vt pounds of each exchanged zeolite was produced. Analyses are presented in Table 7.

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

(1) 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.

(2) 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.

(3) 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.

(4) 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.

(5) Results and Discussion

The chemical analyses of the final exchanged materials are given in Table 8. 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 28% 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.

c. SMM Exchange

Following the lab-optimization of the process, pilot plant exchanges were carried out with an NH_4 -SMM, bearing a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.54 ± 0.05 , and a % mica of 48 ± 4 . In each case 10 Vf kg of SMM was treated with 5 kg of salt $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ in 100 liters (total) water at 90°C for one hour. The increase in scale led to substantial difficulties in manipulations, such as filtering and washing. SMM is a very fine material, and passed through all available filter cloth. Attempts to use combinations of filter cloth and filter paper were unsuccessful, since the filter clogged and filtration stopped altogether.

A series of lab tests was designed in order to circumvent this problem. It was determined that a low-solid slurry of SMM in water would settle to a thicker slurry of about 10% solids. Consequently,

TABLE 8. CHEMICAL ANALYSES OF EXCHANGED US-Y ZEOLITE

<u>Sample No.</u>	<u>Description</u>	<u>-----Wt.%-----</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	2.78	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.

the Co-SMM and Ni-SMM were reslurried in water and diluted to about 450 liters total volume. After settling, the supernatant was siphoned off and the procedure repeated two more times, in order to eliminate the excess metal salt.

A portion of the salt-free slurry was further thickened by evaporation in a Patterson mixer and extruded into 1/16" pellets. The Vf residue of the Co-SMM pellets was 82%; that of the Ni-SMM was 86%. The remaining Co-SMM and Ni-SMM were left as wet pastes for loading with Mo.

Analytical data. Co-SMM extrudate...2.01% Co
(Vf basis)

Ni-SMM extrudate...2.57% Ni
(Vf basis)

d. Metal-Lattice-Substituted SMM

No cation exchanges were performed on these materials.

E. Task V - Matrix Modification

1. Alumina

a. Introduction

Hydrogenation catalysts with cobalt-molybdenum and nickel-molybdenum on large pore diameter alumina supports, such as Filtrol's HPC-5 catalyst, have been shown to be active in coal liquefaction and hydrodesulfurization (13). Additional studies have been carried out on the effect of alumina support pore size distribution on the hydrodenitrogenation of heavy coal liquids (14-16). These studies all indicate the importance of support pore size distribution on catalyst activity and deactivation. Therefore, Filtrol prepared a series of relatively large pore size alumina supports with varying pore size distribution, and good strength. Catalysts with improved ageing resistance were produced by adding titania to the alumina (17,18).

b. Experimental

Relatively large pore diameter alumina supports with varying pore size distributions were produced from Kaiser SA, and Condea SB aluminas by varying the proportion of Kaiser to Condea

aluminas from 100% to 0%. In one case, titania was also added to the mixture. The physical properties of these extruded supports are presented below:

<u>Kaiser/Condea</u>	<u>SA^a</u> <u>m²/g</u>	<u>PV^a</u> <u>cc/g</u>	<u>APD^b</u> <u>Å</u>
100/0	224	0.84	150
80/20 ^c	197	0.73	148
80/20 ^{c,d}	196	0.66	135
23/77 ^c	202	0.69	137
0/100	217	0.61	112

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

^b Average pore diameter, $A = 4(PV/SA)10^4$. J. H. deBoer "The Structure and Properties of Porous Materials" (D. H. Everett and F. S. Stone, eds), Butterworth, Lon., 1958.

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

^d +11 wt.% TiO₂.

2. Synthetic Silica-Alumina Gel

a. The general preparation of synthetic silica-alumina gels with varying physical properties and pore size distributions for use as hydrotreating catalyst (Task IX) supports is described below following U.S. Patent 4,142,995:

Sodium silicate (28.7% SiO₂, 8.9% Na₂O by weight) was dissolved in water to a concentration of 5-10% SiO₂. The slurry solution was acidified to a pH of eleven with sulfuric acid. Aluminum sulfate solution was gradually added to the acidified solution with constant agitation. The weight percentages of the SiO₂ and the Al₂O₃ in the mixture should be from about 45% to 52%. The pH at the end of the addition of the aluminum sulfate should be in the range of about 3 to 3.5. The solution was passed through a colloid mill to be well homogenized. The pH of the homogenized solution was raised with ammonium hydroxide with constant and vigorous agitation, and heated with stirring for 1 hour at 180°F. The mixture was then filtered, and the filter cake washed.

The analytical data are listed below (wt.%):

SiO₂ - 47.4
 Al₂O₃ - 52.3
 Na₂O - 0.13
 NH₃ - 1.18

After drying, extruding and calcining the 1/16" extrudate had the following physical properties:

(896-159-1)	896-199-3
SA, m ² /g - 246	354
PV, cc/g - 0.52	0.43
APD, Å - 85	49

b. The following procedure, based on German Patent 1,068,232 (1959), was selected for the preparation of about 5 kg of silica-alumina gel:

- (1) A sodium aluminate solution was prepared by dissolving 41.9 kg of alumina hydrate (Kaiser) in a solution of 29.9 kg of sodium hydroxide flakes in 64.6 liters of water. The solution was stirred at 200-210°F until clarification.
- (2) 7.65 liters of sodium silicate solution (with 28.9% SiO₂) was mixed with 12.6 liters of the sodium aluminate solution diluted with 44.5 gallons D.I. water (pH slurry = 12).
- (3) The resulting gel was stirred for about 30 minutes, then aged without stirring for 2 hours at room temperature.
- (4) The aged gel was filtered and washed, until the pH of the filtrate dropped to 9.
- (5) The gel was spray dried (35% solids).

(6) The spray dried material was reslurried three times with 10% $(\text{NH}_4)_2\text{SO}_4$ solution (ratio solids: solution = 1:10), for one hour each at room temperature.

(7) The material was reslurried twice with a 10% $(\text{NH}_4)_2\text{CO}_3$ solution (ratio solids: solution = 1:1.3), for one hour each at room temperature.

(8) The gel was finally water washed and oven dried at 105°C/3 hours.

The analytical data are listed below (wt.%):

1013-45	-	1
SiO_2	-	61.7
Al_2O_3	-	37.3
Na_2O	-	0.97
SA, m^2/g	-	154
PV, cc/g	-	0.77
APD, A	-	200

3. Synthetic Silica-Alumina, Silica-Alumina-Magnesia, and Silica-Alumina-Zirconia Gels

The gels described in this section were used as matrix components in the preparation of cracking catalysts (Task VI).

a. $\text{SiO}_2\text{-Al}_2\text{O}_3$ Gel (Sample No.'s 896-159-1, 896-199-3 described on page 45).

b. $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ Gels

Following a series of bench scale experiments, two large batches of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ gel (total weight: ~ 10 Vt kg) were prepared in the pilot plant. U.S. Patent No. 2,935,483 was used as a guideline. Solutions of sodium silicate, aluminum sulfate, and magnesium nitrate were used in the preparation.

The gel was filtered and washed with solutions of ammonium sulfate, ammonium carbonate, and water.

The analytical data for Batch #1 and #2 are listed below (wt.%):

<u>Batch #1 (1013-53-2)</u>		<u>Batch #2 (1013-65-1)</u>
SiO_2	- 62.9	69.9
Al_2O_3	- 29.4	22.8
MgO	- 6.63	6.81
Na_2O	- 0.11	0.13
SA, m^2/g	- 320	327
PV, cc/g	- 0.67	0.51
APD, A	- 84	62

c. SiO₂-Al₂O₃-ZrO₂ Gel

Silica-alumina-zirconia gel was prepared by the following procedure: 6503 g Al₂(SO₄)₃·18H₂O (17.3% Al₂O₃) was dissolved in 25 of H₂O. In a separate container 1058 g of ZrO(NO₃)₂·2H₂O (33.2% ZrO₂) was dissolved in 10 l of H₂O. The ZrO(NO₃)₂ solution was added to the Al₂(SO₄)₃ solution with stirring. A slurry of N-Brand sodium silicate (28.9% SiO₂) was added to the above mixture slowly with vigorous stirring, and enough water was added to keep the resulting slurry fluid. The mixture was stirred for 15 minutes and the pH raised to 7 with NH₄OH. After stirring for an additional 15 minutes the gel was filtered, and washed.

The analytical data are listed below (wt.%):

SiO ₂	- 40.2
Al ₂ O ₃	- 40.5
ZrO ₂	- 18.7
Na ₂ O	- 0.13
NH ₃	- 0.30
SA, m ² /g	- 563
PV, cc/g	- 0.4
APD, Å	- 28

F. Task VI - Cracking Catalysts

1. Preparation and Characterization

a. Introduction

A minimum of sixty-four catalyst formulations were prepared from materials described under Tasks III, IV, and V. They were formulated as shown in Table 9. The catalysts were prepared and spray dried as described in U.S. Patent 4,164,483, (Aug. 14, 1979) except that those catalysts not containing hydrated alumina (pseudoboehmite)^a were not peptized.

The chemical analyses, surface areas, pore volumes, and pore size distributions were determined for the most significant catalysts (Tables 13 and 17).

^a Poorly crystallized boehmite (alpha alumina monohydrate).

TABLE 9. CRACKING CATALYSTS FORMULATION

No. Cats.	Catalytic Component	Wt. %	-----Matrix Material Wt.%-----					
			<u>Alumina</u>	<u>Silica/ Alumina</u>	<u>Silica/ Alumina/MgO</u>	<u>Silica/ Alumina/ZrO₂</u>	<u>Clay Kaolinite</u>	<u>Ammonium Polysilicate</u>
5	NH ₄ -SMM, S/A= 2.16 - 2.67	100	--	--	--	--	--	--
5	Best NH ₄ -SMM S/A = 2.16	60	40	40	40	40	40	--
15	Exch. Y-Zeol.	20	80	--	--	--	--	--
6	Exch US-Y-Zeol.	20	80	--	--	--	--	--
10	Best 2 Zeol.	20	80	80	80	30	80	--
10	Best 2 Zeol. Best NH ₄ -SMM	20 40	40	40	40	40	40	--
7	Best 7 Zeol. Best NH ₄ -SMM	20 80	--	--	--	--	--	--
<u>6</u>	Best 6 Zeol.	20	20	--	--	--	54	6

2. Testing with Hydrotreated SRC-II Fuel Oil Blend^a

a. Initial Screening

The first series of 13 exchanged Y-zeolites from Na-Y zeolite (normal crystal size and small, $\approx 1\mu$ crystal size) and ultra stable Y-zeolites (US-Y) (without regard to crystal size) report were formulated into cracking catalysts. The catalyst formulation consisted of 20% zeolite and 80% matrix binder, which was mixed and spray dried. The MAT results are presented in Tables 10 and 11 along with results for an average state of the art, circa 1978, baseline catalyst Filtrol FS-30. It may be seen that none of the catalysts tested afforded conversions or C₅-EP gasoline yields which were as high as those afforded by the standard Filtrol commercial catalyst FS-30. Reducing the particle size of the zeolites did not give any general improvement in activity, but did appear to result in generally lower coke yields.

The US-Y's all afforded better conversions at 900°F than the best exchanged NH₄-Y based catalyst Y-NN₃(100°C)R₂^b, tested in the first series. At 1000°F the US-Y conversions were generally as good or better than those afforded by the catalyst Y-NN₃(100°C)R₂. At 900°F the C₅-EP gasoline yields were generally better also although the US-Y was about the same as the Y-NN₃(100°C)R₂, and the Ni-exchanged US-Y yield was poorer. At 1000°F the C₅-EP gasoline yields were about the same or poorer than those found for Y-NN₃(100°C)R₂. None of the US-Y catalysts afforded either conversions or C₅-EP gasoline yields which were as high as those shown by FS-30 at either 900°F or 1000°F.

The results for the series: NH₄SMM (SiO₂/Al₂O₃ = 2.16 -2.67), are compared with the best results obtained previously for the Filtrol commercial catalyst FS-30, and for the catalyst Y-NN₃(100°C)R₂ ($\approx$ 2% rare earth in the final catalyst) in Table 12. It may be seen that the 100% NH₄SMM's all afforded poorer conversions and C₅-EP gasoline yields than any of the other catalysts. These results were not unexpected since it was shown previously that NH₄SMM has cracking activity intermediate between that of zeolites and silica-alumina gel (7).

The poorer activity of the zeolite based catalysts, compared to the commercial Filtrol catalyst FS-30, may be related to the matrix binder. The exploratory exchanged zeolite catalysts were all formulated with 80%

^a Tables with Cat.-Cracking results are presented in the body of the report. Tables with light gas analyses for all cracking runs are presented in Appendix B.

^b N, NH₃ exchange; R, rare earth exchange.

TABLE 10. CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND^{1,2} WITH EXCHANGED Y-ZEOLITE-ALUMINA FCC CATALYSTS

FCC Catalyst ³ Steamed 1450°F	Conversion, Wt.% 430°F ⁴		Product Distribution, Wt.%											
	Apparent ⁴ 900°F	Corrected ⁵ 1030°F	H ₂		C ₁ -C ₄		C ₅ -E _{PGAS}		Cycle Oil		Coke		Recovery	
			900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
FS-30 ⁶	61.9/59.1	73.5/71.6	0.08	0.25	8.9	14.4	45.1	46.3	38.1	26.5	3.7	3.7	95.0	90.9
	61.1/59.3	72.2/70.2	0.13	0.11	10.6	12.5	42.5	45.6	38.9	27.8	3.9	3.6	95.0	89.4
Y-NN ₃ (100°C)norm.	36.9/32.3	52.6/49.2	0.06	2.02	4.5	9.5	26.8	34.5	63.1	47.4	1.8	2.2	96.7	95.4
" (≈ 1μ)	39.6/35.3	53.1/49.7	0.11	0.75	5.5	9.4	29.2	36.7	60.4	46.9	1.2	1.7	96.3	95.3
" -Ni normal	36.7/32.1	53.1/49.7	0.12	0.81	5.0	12.7	27.1	36.2	63.3	46.9	1.5	1.5	97.0	98.0
" -Ni (≈ 1μ)	32.7/27.9	54.9/51.6	0.34	0.75	4.3	9.9	24.1	36.5	67.3	45.1	1.3	2.0	97.2	94.2
" -Co normal	38.1/33.7	55.7/52.5	0.13	0.34	6.1	10.6	27.7	37.4	61.9	44.3	1.5	1.9	97.2	94.5
" -Co (≈ 1μ)	43.8/39.7	47.6/43.9	0.11	1.32	6.5	11.4	31.9	26.5	56.2	52.4	1.3	2.3	95.9	93.7
" -R normal	48.6/44.9	56.0/52.8	0.09	0.32	6.2	13.0	36.5	36.2	51.4	44.0	1.8	2.1	95.9	95.5
" -R (≈ 1μ)	45.8/41.9	60 / 57.2	0.11	0.60	6.5	13.3	33.4	40.2	54.2	40.0	1.4	1.7	95.5	95.7
" -R ₂ normal	51.3/47.8	63.5/60.8	0.11	0.35	8.5	13.4	37.8	43.4	48.7	36.5	2.2	2.7	97.1	96.2
" -R-Cr normal	44.2/40.2	51.3/60.1	0.14	0.30	6.3	11.3	32.6	43.1	55.8	37.2	1.5	2.3	96.2	94.1
" -R-Cr (≈ 1μ)	45.3/41.3	60.1/57.2	0.13	0.72	6.5	12.4	33.0	39.7	54.7	39.9	2.0	2.5	96.1	95.1
" -R-Mn normal	45.7/41.8	63.5/60.9	0.11	0.43	5.5	12.1	33.7	44.5	54.3	36.5	1.6	2.2	95.0	95.5
" -R-Mn (≈ 1μ)	44.4/40.4	58.5/55.5	0.12	0.54	6.3	12.7	32.4	38.7	55.6	41.5	1.5	1.7	95.8	95.1

¹Elemental Analyses: %C, 89.12; %H, 10.95; %N, 0.050; %S, 0.026; %O, less than 0.5.

²Sim. Dist. ASTM D2887: IBP/5, 389/415; 10/30, 430/469; 50, 507; 70/90, 551/638; 95/FBP, 682/803.

³Catalyst steamed 2 hrs. at 1450°F; 20% Exchanged zeolite, 80% alumina. Test Cond. 16 WHSV, 3 Cat./Oil.

N, NH₃ exchange; R, rare earth exchange.

⁴Apparent Conversion: 100-Cycle Oil.

⁵Corrected Conversion: $100 \left(\frac{1 - \% \text{ 430°F}^+ \text{ in product}}{\% \text{ 430°F}^+ \text{ in feed}} \right)$

⁶Proprietary formulation. Duplicate runs demonstrate reproducibility of MAT runs.

TABLE 11. CAT. - CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND^{1,2}WITH EXCHANGED US-Y ZEOLITE-ALUMINA FCC CATALYSTS

FCC Catalyst ³	Conversion, Wt.% 430°F ⁺		Product Distribution, Wt.%-----											
	Apparent ⁴ /Corrected ⁵		-----H ₂ -----		---C ₁ -C ₄ ----		-C ₅ -EP Gas-		-Cycle Oil-		-----Coke-----		--Recovery--	
	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
US-Y	55.0/51.7	63.2/60.6	0.23	0.45	9.5	12.2	37.5	43.1	45.0	36.8	2.1	2.4	94.1	94.8
US-Y-Ni	52.8/49.4	61.8/59.1	1.11	2.72	8.5	11.9	34.5	38.7	47.2	38.2	3.6	2.8	94.6	94.1
US-Y-Co	56.0/52.8	63.4/60.7	0.22	1.08	9.7	12.8	39.2	42.8	44.0	36.6	2.0	2.0	94.9	95.2
US-Y-R	54.9/51.7	65.0/62.5	0.19	0.90	10.2	12.5	39.3	43.6	45.1	35.0	1.8	2.5	96.4	94.4
US-Y-Cr	58.0/55.0	67.1/64.7	0.20	1.33	10.9	13.2	41.3	43.7	42.0	32.9	2.0	3.0	96.2	93.9
US-Y-Mn	57.8/50.5	63.6/61.0	0.17	0.43	10.3	13.2	39.4	43.7	42.2	36.4	1.8	2.5	97.7	96.0
FS-30 ⁶	61.9/59.1	73.5/71.6	0.13	0.25	10.6	14.4	42.5	46.3	38.9	26.5	3.9	3.7	95.0	90.9
	61.1/59.3	72.2/70.2	0.08	0.11	8.9	12.5	45.1	45.6	38.1	27.8	3.7	3.6	95.0	89.4
Y-NN ₃ (100°C)-R ₂	51.3/47.8	63.5/60.8	0.11	0.35	8.5	13.4	37.8	43.4	48.7	36.5	2.2	2.7	97.1	96.2

^{1,2} Same as Table 10.³ Catalyst steamed 2 hrs. at 1450°F; 20% Exchanged US-Y zeolite, 80% matrix. Test Cond.: 16 WHSV, 3 Cat/Oil.^{4,5} Same as Table 10.⁶ Proprietary formulation.

TABLE 12. CAT. - CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND^{1,2}WITH NH₄SMM FCC CATALYSTS

FCC Catalyst ³	Conversion, Wt.% 430°F ⁴		-----Product Distribution, Wt.%-----											
	Apparent ⁴ /Corrected ⁵		-----H ₂ -----		---C ₁ -C ₄ ---		-C ₅ -EP Gas-		-Cycle Oil-		-----Coke-----		--Recovery--	
	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
NH ₄ -SMM (S/A=2.16)	46.9/43.1	57.6/54.5	0.25	0.17	6.8	11.7	30.7	36.0	53.1	42.4	0.9	2.1	91.7	92.3
NH ₄ -SMM (S/A=2.28)	40.9/36.6	47.6/43.8	1.01	0.79	3.9	7.6	26.6	28.1	59.1	52.4	3.9	3.1	94.3	91.9
NH ₄ -SMM (S/A=2.45)	43.2/39.1	49.1/46.3	0.27	0.30	5.7	9.6	29.3	36.0	56.8	50.1	2.6	2.3	94.5	98.3
NH ₄ -SMM (S/A=2.53)	39.2/34.8	47.7/44.0	1.01	1.18	5.2	8.6	25.0	27.7	60.8	52.3	3.1	2.9	94.9	92.5
NH ₄ -SMM (S/A=2.67)	36.8/32.2	49.7/46.0	0.41	0.16	5.4	7.6	24.4	34.7	63.2	50.3	1.4	1.2	94.7	94.0
FS-30 ⁶	61.9/59.1	73.5/71.6	0.13	0.25	10.6	14.4	42.5	46.3	38.9	26.5	3.9	3.7	95.0	90.9
	61.1/59.3	72.2/70.2	0.08	0.11	8.9	12.5	45.1	45.6	38.1	27.8	3.7	3.6	95.0	89.4
Y-NN ₃ (100°C)-R ₂ ⁷	51.3/47.8	63.5/60.8	0.11	0.35	8.5	13.4	37.8	43.4	48.7	36.5	2.2	2.7	97.1	96.2

^{1,2} Same as Table 10.³ Catalyst steamed 2 hrs. at 1450°F; 100% NH₄SMM. Test Cond.: 16 WHSV, 3 Cat/Oil.^{4,5} Same as Table 10.⁶ Proprietary Formulation.⁷ 20% Exchanged zeolite, 80% alumina.

acid peptized alumina, whereas the FS-30 catalyst is formulated with a variety of proprietary binder components. The pore size distribution results, shown in Table 13, tend to support this hypothesis. The Filtrol FS-30 catalyst contains a broad pore volume distribution, which extends from radii of 10 to 300 Å. However, the exploratory 20% zeolite, 80% acid peptized alumina catalysts all contain the majority of their pore volume distribution, 89-93%, in the small radius range of 10 to 25 Å.

b. Secondary Screening

After the initial screening, discussed above, was completed the NH_4SMM (silica/alumina = 2.16), which afforded the highest corrected conversion (43.1 wt.% at 900°F), was blended 60 to 40 wt.% with each of a series of matrix materials: alumina, silica-alumina, silica-alumina-magnesia, silica-alumina-zirconia, and kaolinite clay. The cracking test results, shown in Table 14, indicate no improvement in conversion was obtained by formulating NH_4SMM catalysts with a variety of matrix materials.

Another series of cracking catalysts was formulated from the most active exchanged US-Y zeolites and from rare earth exchanged Y-zeolites. These zeolites were formulated (20% zeolite -80% best NH_4SMM) and tested for activity (Table 15). The results indicate that NH_4SMM affords significant improvement over alumina as a binder for rare earth exchanged Y-zeolite FCC catalysts. Both conversion and wt.% C₅-EP gasoline yields are improved.

The best zeolites in each class: (REO-exchanged Y-zeolites, and Cr-exchanged US-Y) zeolite were tested in various matrix formulations (Tables 16 to 20). Table 16 shows the cracking activity results for a series of REO-exchanged Y-zeolites, with different final percentages of rare earth, combined with different matrix materials (20% zeolite -80% matrix material). When these are compared with the chemical and physical properties of the finished catalysts (Tables 17 and 18, Fig. 12) two factors are seen to be important:

When the matrix is held constant at 80% alumina, conversion increases as a function of the rare earth concentration.

When the rare earth concentration is held constant, the conversion is dependent on the pore volume distribution. Those catalysts which have the major portion of their pore volume distribution in the lowest radius range (10-25 Å) show the poorest activity, whereas those catalysts which have a broader pore volume distribution with a substantial amount of pores in the higher radii ranges afford higher activity.

TABLE 13. PHYSICAL PROPERTIES OF FRESH FCC CATALYSTS

Catalyst	SA ¹ m ² /g	PV ¹ ml/g	Pore Volume Distribution (%) ¹					
			-----Radius Range (Å)-----					
			10-25	25-50	50-100	100-150	150-200	200-300
Filtrol FS-30	182	0.35	22.6	28.4	17.0	10.6	8.9	12.5
Y-NN ₃ (100°C) ^{2,3}	468	0.43	88.7	9.2	1.2	0.3	0.3	0.3
" -R ₂ ^{2,3}	434	0.40	92.6	5.7	0.9	0.2	0.2	0.3
" -Ni ^{2,3}	438	0.40	90.3	7.5	1.1	0.6	0.2	0.3
US-Y ^{2,3}	397	0.38	92.3	6.1	0.9	0.4	0.1	0.2
US-Y-Cr ^{2,3}	427	0.40	91.6	6.6	1.2	0.3	0.2	0.2
NH ₄ -SMM ⁴	126	0.81	8.6	11.1	20	22.5	18.4	19.4
	103	0.84	6.5	9.5	18.8	20.9	19.8	24.5

¹Measured with Micromeritics Digisorb 2500 SA and PV analyzer in desorption mode.

²Spray dried with 20% zeolite and 80% acid peptized alumina.

³Normal zeolite particle size-zeolite not milled.

⁴100% NH₄-SMM - spray dried.

TABLE 14. CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND^{1,2} WITH NH₄SMM-MATRIX FCC CATALYSTS

FCC Catalyst ³		Conversion Wt.% 430°F ⁴		Product Distribution, wt.% ⁵											
Sample No.	Matrix	Apparent ⁴ /Corrected ⁵		-----H ₂ -----		---C ₁ -C ₄ ---		-C ₅ -EP Gas-		-Cycle Oil--		----Coke----		-Recovery--	
		900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
1001-11-2	none	46.9/43.1	57.6/54.5	0.25	0.17	6.8	11.7	30.7	36.0	53.1	42.4	0.9	2.1	91.7	92.3
1030-21-4	alumina	45.3/41.4	52.5/49.1	0.21	0.43	7.1	11.0	31.1	32.3	54.7	47.5	2.1	2.7	95.0	93.7
1030-21-3	silica-alumina	44.1/40.1	52.5/49.1	0.13	0.40	6.9	11.5	32.1	31.6	55.9	47.5	1.7	2.5	96.5	93.4
1030-21-2	silica-alumina-magnesia	38.1/33.6	49.1/45.4	0.10	0.19	4.7	8.6	27.6	33.1	61.9	50.9	1.2	1.3	95.4	94.0
1030-21-1	silica-alumina-zirconia	42.2/38.1	50.0/46.4	0.10	0.32	5.1	10.5	30.6	33.1	57.8	50.0	1.4	1.9	94.9	95.7
1030-21-5	kaolinite clay	38.7/34.3	50.9/47.4	0.07	0.20	5.0	9.9	29.7	34.8	61.3	49.1	1.2	1.4	97.1	95.3

^{1,2}Same as Table 10.

³Catalyst steamed 2 hrs. at 1450°F; 60% NH₄SMM 1001-11-2, 40% Matrix. Test Cond.: 16 WHSV, 3 Cat/Oil.

^{4,5}Same as Table 10.

TABLE 15. CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND^{1,2} WITH ZEOLITE-NH₄SMM FCC CATALYSTS

FCC Catalyst ³		Conversion Wt.% 430°F ⁺		Product Distribution, wt.%											
Sample No.	Zeolite	Apparent ⁴ /Corrected ⁵		-----H ₂ -----		---C ₁ -C ₄ ---		-C ₅ -EP Gas-		-Cycle Oil-		-----Coke-----		-Recovery--	
		900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
1030-13-3	US-Y	56.3/53.2	68.3/66.1	0.09	0.30	8.9	15.1	43.8	43.7	43.7	31.7	2.2	3.5	98.6	94.0
1030-13-1	US-Y-Cr	61.2/58.4	69.3/67.1	0.17	0.22	9.7	14.9	44.5	45.1	38.8	30.7	2.5	3.1	95.6	93.8
1030-13-2	US-Y-R	64.5/62.0	70.4/68.2	0.14	0.25	10.1	13.9	46.3	46.7	35.5	29.6	2.5	3.1	94.2	93.4
1030-13-5	Y-NN ₃ ⁶ (100°C)R	63.1/60.5	69.1/66.9	0.11	0.28	9.6	15.4	46.6	44.4	36.9	30.9	3.2	3.0	96.3	93.7
1030-13-4	Y-NN ₃ ⁶ (100°C)R ₂	67.9/65.6	76.5/74.8	0.15	0.20	11.0	16.6	49.4	42.7	32.1	23.5	3.3	4.8	95.8	87.5
1030-17-1	Y-NRCR ⁶	69.5/67.3	75.8/74.1	0.14	0.28	12.8	16.8	48.2	44.0	30.5	24.2	4.2	5.0	95.5	90.0
1030-13-6	Y-RRCR ⁶	71.3/69.3 72.1/70.1	76.8/75.1 76.6/75.0	0.18 0.16	0.32 0.26	12.7 12.5	18.2 17.5	49.8 48.0	44.1 42.3	28.7 27.9	23.2 23.4	5.1 4.6	6.1 5.7	96.1 92.9	91.6 88.8

^{1,2} Same as Table 10.³ Catalyst steamed 2 hrs. at 1450°F; 20% Exchanged zeolite, 80% NH₄SMM. Test Cond.: 16 WHSV, 3 Cat/Oil.^{4,5} Same as Table 10.⁶ See Tables 17 and 18 for Chemical and Physical properties of catalyst, and explanation of abbreviations.

TABLE 16. CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND^{1,2}WITH REO-EXCHANGED Y-ZEOLITE-MATRIX FCC CATALYSTS^a

FCC Catalyst ³		Conversion Wt.% 430°F+		-----Product Distribution, wt.%-----											
Sample No.	Matrix	Apparent ⁴ /Corrected ⁵		-----H ₂ -----		---C ₁ -C ₄ ---		-C ₅ -EP Gas-		-Cycle Oil-		-----Coke-----		-Recovery--	
		900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
1025-25-105	alumina	48.6/44.9	56.0/52.8	0.09	0.32	6.2	13.0	36.5	36.2	51.4	44.0	1.8	2.1	95.9	95.5
1001-205-6	alumina	51.3/47.8	63.5/60.8	0.11	0.35	8.5	13.4	37.8	43.4	48.7	36.5	2.2	2.7	97.1	96.2
1030-17-2	alumina	57.0/53.9	68.6/66.4	0.07	0.24	8.1	10.0	41.6	45.5	43.0	31.4	2.2	2.9	94.9	89.7
1030-49-1	alumina	60.9/58.0	69.5/67.4	0.08	0.21	9.1	14.3	44.1	47.3	39.1	30.5	2.5	2.9	94.7	95.0
1030-51-2	silica- alumina	42.5/38.3	48.4/44.7	0.07	0.25	6.7	11.2	30.1	32.0	57.5	51.6	1.0	3.8	95.3	98.7
1030-51-3	silica- alumina- magnesia	65.6/63.1	73.2/71.2	0.03	0.10	10.1	16.7	47.4	47.5	34.4	26.8	3.3	4.0	95.1	94.8
1030-51-4	silica- alumina- zirconia	62.1/59.4	72.7/70.8	0.05	0.11	9.7	15.0	46.8	47.3	37.9	27.3	2.0	2.3	96.4	91.9

^a Table continued on next page.

TABLE 16. CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND^{1,2}
WITH REO-EXCHANGED Y-ZEOLITE-MATRIX FCC CATALYSTS - Continued

FCC Catalyst ³		Conversion Wt.% 430°F ⁴		Product Distribution, wt.%												
Sample No.	Matrix	Apparent ⁴ /Corrected ⁵		H ₂		C ₁ -C ₄		C ₅ -EP	Gas		Cycle Oil		Coke		Recovery	
		900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	
1030-51-1	kaolinite clay	72.6/70.7	76/74.3	0.11	0.16	13.0	17.8	46.4	45.7	27.4	24.0	5.4	2.4	91.9	90.0	
1030-13-6	NH ₄ SMM	71.3/69.3	76.8/75.1	0.18	0.32	12.7	18.2	49.8	44.1	28.7	23.2	5.1	6.1	96.1	91.6	
		72.1/70.1	76.6/75.0	0.16	0.26	12.5	17.5	48.0	42.3	27.9	23.4	4.6	5.7	92.9	88.8	
1030-49-2	alumina-kaolinite clay-NH ₄ -polysilicate	71.6/69.5	78.1/76.5	0.11	0.28	13.9	17.2	49.7	43.4	28.4	21.9	5.5	7.1	97.2	89.4	
1030-73-1	"	69.6/67.5	75.3/73.5	0.12	0.23	12.4	16.6	48.8	46.0	30.4	24.7	3.5	4.4	95.2	91.8	
1030-81-1	"	70.5/68.4	79.2/77.7	0.09	0.15	11.6	16.3	47.7	45.8	29.5	20.8	4.7	5.7	93.6	88.8	
1030-81-2	"	76.6/74.9	79.3/77.8	0.09	0.13	15.1	17.1	48.4	38.8	23.4	20.7	8.8	9.8	95.9	86.6	
Filtrol FS-30	Proprietary	61.9/59.1	73.5/71.6	0.08	0.25	8.9	14.4	45.1	46.3	38.1	26.5	3.7	3.7	95.0	90.9	
		61.1/59.3	73.2/70.2	0.13	0.11	10.6	12.5	42.5	45.6	38.9	27.8	3.9	3.6	95.0	89.4	

^{1,2} Same as Table 10.

³ Catalyst steamed 2 hrs at 1450°F; 20% REO-Exchanged Y-zeolite, 80% Matrix. See Tables 17 and 18 for Chemical and Physical properties of catalysts. Test Cond.: 16 WHSV, 3 Cat/Oil.

^{4,5} Same as Table 10.

TABLE 17. CHEMICAL ANALYSES OF FCC CATALYSTS

<u>Sample No.</u>	<u>Description (wt%)^a</u>	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>Na₂O</u>	<u>REO</u>	<u>NH₃</u>	<u>MgO</u>	<u>ZrO₂</u>	<u>Fe₂O₃</u>
1025-25-105	Y-NN ₃ (100°C)R(20) + alumina (80)	14.0	84.2	0.70	0.87	0.95	--	--	--
1030-73-1	Y-NN ₃ (100°C)R(20) + 1030-49-2 Matrix (80)	46.4	50.0	0.50	1.18	1.10	--	--	--
1001-205-6	Y-NN ₃ (100°C)R ₂ (20) + alumina (80)	13.4	84.6	0.38	1.90	0.54	--	--	--
1030-81-1	Y-NN ₃ (100°C)R ₂ (20) + 1030-49-2 Matrix (80)	46.8	50.3	0.38	2.82	0.72	--	--	--
FS-30	Filtrol Proprietary Formulation	51.9	44.2	0.72	2.38	0.28	--	--	--
1030-17-2	Y-NRCR (20) + alumina (80)	12.7	83.8	0.40	2.55	0.16	--	--	--
1030-49-1	Y-RRCR (20) + alumina (80)	10.5	83.5	0.27	3.39	0.08	--	--	--
1030-51-2	Y-RRCR (20) + silica-alumina (80)	34.1	60.9	0.33	3.91	1.21	--	--	--
1030-51-3	Y-RRCR (20) + silica-alumina-magnesia (80)	68.9	24.2	0.34	2.01	0.76	3.27	--	--
1030-51-4	Y-RRCR (20) + silica-alumina-zirconia(80)	66.5	21.9	0.22	4.99	1.13	--	5.74	--
1030-51-1	Y-RRCR (20) + kaolinite clay (80)	51.8	42.5	0.24	3.76	0.11	--	--	0.96
1030-13-6	Y-RRCR (20) + NH ₄ SMM (80)	56.6	38.6	0.53	3.94	2.43	--	--	--
1030-49-2	Y-RRCR (20) + alumina (20) + kaolinite clay (54) + NH ₄ - polysilicate (6)	44.8	50.9	0.27	3.71	0.12	--	--	--
1030-81-2	Y-RRCR (30) + alumina (20) + kaolinite clay(45) + NH ₄ -polysilicate (5)	44.7	48.1	0.40	6.91	--	--	--	--

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^a N, NH₃ exchange; R, rare earth exchange; C, calcination.

TABLE 18. CONV. OF HYDROTREATED SRC-II FUEL OIL BLEND vs. PHYSICAL PROPERTIES OF FRESH FCC CATALYSTS

Sample No.	Exch. Y-Zeol. (wt.%) ^a	REO (wt.%)	Corr. Conv. 900°F wt. % ^b	SAC M ² /g	PVC ml/g	Pore Volume Distribution (%) ^c					
						-----Radius Range (Å)-----					
						10-25	25-50	50-100	100-150	150-200	200-300
1025-25-105	Y-NN ₃ (100°C)R(20) ^d	0.87	44.9	439	0.39	92.3	6.0	1.0	0.3	0.1	0.3
1030-73-1	Y-NN ₃ (100°C)R(20) ^f	1.18	67.5	284	0.33	36.7	28.4	11.8	8.9	6.9	7.3
1001-205-6	Y-NN ₃ (100°C)R ₂ (20) ^d	1.90	47.8	434	0.40	92.6	5.7	0.9	0.2	0.2	0.3
1030-81-1	Y-NN ₃ (100°C)R ₂ (20) ^f	2.82	68.4	283	0.36	31.9	29.2	11.6	8.8	8.2	10.3
FS-30	Filtrol Proprietary Formulation	2.38	59.1 59.3	182	0.35	22.6	28.4	17.0	10.6	8.9	12.5
1030-17-2	Y-NRCR (20) ^d	2.55	53.9	415	0.42	88.6	8.0	1.6	0.7	0.4	0.6
1030-49-1	Y-RRCR(20) ^d	3.39	58.0	455	0.42	93.7	5.1	0.7	0.1	0.1	0.2
1030-51-2	Y-RRCR(20) ^g	3.91	38.3	422	0.66	25.3	36.3	33.0	3.7	0.9	0.8
1030-51-3	Y-RRCR(20) ^h	2.01	63.1	436	0.98	18.6	20.3	26.8	13.5	9.0	11.8
1030-51-4	Y-RRCR(20) ⁱ	4.99	59.4	525	0.66	52.2	22.8	10.5	5.9	4.2	4.5
1030-51-1	Y-RRCR(20) ^j	3.76	70.7	138	0.40	16.4	6.5	10.5	13.7	18.5	34.5
1030-13-6	Y-RRCR(20) ^e	3.94	69.3 70.1	223	0.48	18.8	18.2	20.2	14.7	12.6	15.6
1030-49-2	Y-RRCR(20) ^f	3.71	69.5	237	0.31	38.5	23.2	11.0	9.7	8.4	9.1
1030-81-2	Y-RRCR(30) ^k	6.91	74.9	334	0.37	36.8	33.0	10.8	6.2	5.7	7.5

^a N, NH₃ exchange; R, rare earth exchange; C, calcination.^b Catalyst steamed for 2 hours at 1450°F.^c Measured with Micromeritics Digisorb 2500 SA and PV analyzer in desorption mode.^d 80% alumina.^e 80% NH₄-SMM.^f 20% alumina, 54% kaolinite clay, 6% ammonium polysilicate.^g 80% silica-alumina.^h 80% silica-alumina-magnesia.ⁱ 80% silica-alumina-zirconia.^j 80% kaolinite clay.^k 20% alumina, 45% kaolinite clay, 5% ammonium polysilicate.

FIG. 12 - CRACKING CONVERSION OF HYDROTREATED SRC-II FUEL OIL BLEND vs wt.% RARE EARTH OXIDES IN FINISHED CATALYSTS^a

^a SEE TABLE 18.

Fig. 13 shows a correlation between the wt.% coke and the conversion function (1) for various rare earth exchanged Y-zeolite catalysts. The coke yields generally increase linearly as the conversion function increases under identical reactor conditions. However, a few of the catalysts deviate significantly in both a positive and negative direction. Catalyst 1030-81-2, which contains a high percentage of rare earth (6.91 wt.%), produces significantly more coke than would be expected, whereas, catalyst 1030-73-1, which contains a low percentage of rare earth (1.18 wt.%), produces significantly less coke for a relatively active catalyst.

Fig. 14 shows the relationship between wt.% C₅-EP gasoline yields, and the corrected wt.% conversions for catalysts formulated with and without rare earth exchanged zeolites. The figure shows that the maximum C₅-EP gasoline yields obtained from the hydrotreated SRC-II feed stock, which contains 11.0 wt.% hydrogen, are ~ 50 wt.%. These results compare favorably with those obtained by UOP workers who cracked an H-Coal distillate which also contained 11 wt.% hydrogen with equilibrium zeolite catalyst withdrawn from a commercial FCC unit and obtained 50 volume % C₅⁺ gasoline (19).

Table 19 shows the results for blends of the most active rare earth exchanged Y-zeolite RRCR (20%) formulated with the most active NH₄SMM (40%) and various matrices (40%). The results indicate some good activities and good gasoline product yields but no significant improvement in activity is observed by adding a matrix component to the original 20% REO-exchanged Y-zeolite -80% NH₄SMM.

Tables 20 and 21 show activity results for similar sets of Cr-exchanged US-Y zeolite-matrix, and Cr-US-Y-NH₄SMM-matrix catalysts. None of these catalysts afford activity as high as that observed for the REO-exchanged Y-zeolite based catalysts. For these systems the inclusion of NH₄SMM results, in general, in lower conversion.

All catalysts were tested at two different temperatures: 900°F and 1000°F. Conversion, and H₂, C₁-C₄, C₅-EP gasoline, and coke make generally increase in going from 900°F to 1000°F for the low and moderately active catalysts. For the more active catalysts C₅-EP gasoline generally decreases somewhat in going from 900°F to 1000°F, and C₁-C₄ light gas production increases proportionately. The other products increase in the normal manner. This is not unexpected as the more active catalysts would be expected to crack the gasoline range products somewhat further to light gases.

FIG. 13 - CONVERSION FUNCTION vs wt. %
COKE (SEE TABLE 16)

FIG. 14 - GASOLINE YIELD FROM HYDROTREATED SRC-II FUEL
OIL BLEND vs WT. % CONVERSION
 (SEE TABLE 16)

TABLE 19. CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL^{1,2} BLEND WITH REO-EXCH.-Y-ZEOLITE-NH₄SMM-MATRIX FCC CATALYSTS

FCC Catalyst ³		Conversion Wt.% 430°F ⁴		Product Distribution, wt.%											
Sample No.	Matrix	Apparent ⁴ /Corrected ⁵		-----H ₂ -----		---C ₁ -C ₄ ---		-C ₅ -EP Gas-		-Cycle Oil--		----Coke----		-Recovery--	
		900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
1030-13-6	None ⁶	71.3/69.3	76.8/75.1	0.18	0.32	12.7	18.2	49.8	44.1	28.7	23.2	5.1	6.1	96.1	91.6
		72.1/70.1	76.6/75.0	0.16	0.26	12.5	17.5	48.0	42.3	27.9	23.4	4.6	5.7	92.9	88.8
1030-59-3	silica-alumina	64.0/61.4	73.1/71.2	0.09	0.20	12.4	16.7	46.7	44.8	36.0	26.9	4.6	3.6	99.8	91.9
1030-59-4	silica-alumina-magnesia	68.7/66.4	77.0/75.4	0.13	0.21	12.3	21.3	48.8	43.0	31.3	23.0	3.9	6.0	96.3	93.0
1030-59-5	silica-alumina-zirconia	68.7/66.5	74.9/73.1	0.08	0.14	11.5	16.6	48.8	48.6	31.3	25.1	3.0	3.6	94.4	93.8
1030-59-1	alumina	71.1/69.0	77.0/75.4	0.13	0.29	12.7	17.1	50.2	43.9	28.9	23.0	4.8	6.2	96.4	90.0
1030-59-2	kaolinite clay	71.2/69.2	71.5/69.4	0.10	0.17	13.0	17.3	49.3	41.7	28.8	28.5	4.4	5.1	95.3	92.4

^{1,2} Same as Table 10.³ Catalyst steamed 2 hrs. at 1450°F; 20% Y-RRCR, 40% NH₄SMM, 40% Matrix. Test Cond.: 16 WHSV, 3 Cat./Oil.^{4,5} Same as Table 10.⁶ 20% RRCR, 80% NH₄SMM.

TABLE 20. CAT. CRACKING OF HYDROTREATED SRC-II FUEL CIL BLEND^{1,2} WITH Cr-EXCHANGED US-Y ZEOLITE-MATRIX FCC CATALYSTS.

FCC Catalyst ³		Conversion Wt.% 430°F ⁴		Product Distribution, wt.%													
Sample No.	Matrix	Apparent ⁴ /Corrected ⁵		H ₂		C ₁ -C ₄		C ₅ -EP		Gas		Cycle Oil		Coke		Recovery	
		900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
1001-205-7	alumina	59.9/57.0	67.1/64.7	0.15	0.40	9.1	13.2	43.2	43.7	40.1	32.9	2.9	3.0	95.4	93.0		
1030-65-2	silica-alumina	62.7/60.0	67.5/65.2	0.09	0.24	10.1	15.4	44.5	42.9	37.3	32.5	2.0	3.0	93.8	93.8		
1030-65-4	silica-alumina-magnesia	65.9/63.5	72.0/70.0	0.06	0.12	10.9	16.5	48.9	47.8	34.1	28.0	2.3	2.9	96.0	95.1		
1030-65-3	silica-alumina-zirconia	67.4/65.0	68.4/66.2	0.04	0.15	11.5	13.9	48.1	41.8	32.6	31.6	3.9	3.7	95.8	90.9		
1030-65-1	kaolinite-clay	61.1/58.3	71.4/69.3	0.08	0.25	9.5	14.5	44.6	42.6	38.9	28.6	1.5	2.5	94.5	88.3		
1030-23-1	alumina-kaolinite-clay-NH ₄ -polysilicate ⁶	63.3/60.7	70.8/68.7	0.12	0.28	10.5	15.6	45.8	45.3	36.7	29.2	2.2	2.7	95.1	92.9		

^{1,2} Same as Table 10.

³ Catalyst steamed 2 hrs. at 1450°F; 20% Cr-Exchanged US-Y zeolite, 80% matrix. Test Cond.: 16 WHSV, 3 Cat/Oil.

^{4,5} Same as Table 10.

⁶ 20% Cr-Exchanged US-Y zeolite, 20% alumina, 54% kaolinite clay, 6% ammonium polysilicate.

TABLE 21. CAT. CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND^{1,2} WITH Cr-EXCHANGED US-Y ZEOLITE-NH₄SMM-MATRIX FCC CATALYSTS

FCC Catalyst ³		Conversion Wt.% 430°F ⁺		-----Product Distribution, wt.%-----											
Sample No.	Matrix	Apparent ⁴ /Corrected ⁵		-----H ₂ -----		---C ₁ -C ₄ ----		-C ₅ -EP Gas-		-Cycle Oil--		----Coke----		-Recovery--	
		900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
1030-23-2	γ-alumina	61.1/58.3	68.3/66.1	0.17	0.39	10.6	14.6	42.8	40.3	38.9	31.7	2.6	3.5	95.0	90.2
1030-23-4	silica-alumina	59.2/56.3	67.9/65.6	0.12	0.27	10.6	15.3	42.1	42.9	40.8	32.1	2.3	2.9	95.7	93.2
1030-25-1	silica-alumina-magnesia	59.8/56.9	67.5/65.2	0.14	0.19	9.7	14.5	44.5	47.0	40.2	32.5	1.9	2.1	96.3	96.1
1030-25-2	silica-alumina-zirconia	53.7/50.4	65.4/52.9	0.09	0.21	9.2	14.4	41.5	43.7	46.3	34.6	1.6	1.9	98.5	94.6
1030-23-3	kaolinite clay	60.3/57.4	69.0/66.8	0.09	0.18	10.2	15.5	43.0	45.5	39.7	31.0	1.7	2.3	94.5	94.2

^{1,2} Same as Table 10.

³ Catalyst steamed 2 hrs. at 1450°F; 20% Cr-Exchanged US-Y zeolite, 40% NH₄SMM, 40% matrix. Test Cond.: 16 WHSV, 3 Cat/Oil.

^{4,5} Same as Table 10.

3. Testing With Unhydrotreated SRC-II Fuel Oil Blend^a

After the previously described catalysts were screened for activity on the hydrotreated SRC-II feed, the same catalysts were screened again at 900°F and 1000°F for cracking activity on the "as received" unhydrotreated SRC-II feed. At 900°F the exchanged Y-zeolites (20 wt.%) in an alumina matrix (80 wt.%), Table 22, afforded generally similar corrected conversions of 430°F⁺ feed of between 24-26 wt.%, and C₅-EP gasoline product of around 9-11 wt.%. The C₁-C₄ gas makes generally ranged from 2-3 wt.%, and the coke makes from 8-11 wt.%. These results are considerably poorer than those observed at 900°F for the hydrotreated SRC-II feed (corrected conversions generally between 32-42 wt.%, C₅-EP gasoline product between 27-34 wt.%, C₁-C₄ gas makes between 5-6 wt.%, and coke makes between 1-2 wt.%). With the unhydrotreated feed there was no significant trend observed in reducing the particle size of the zeolites. The best catalyst was Y-NN₃(100°C)-R₂ which afforded higher corrected conversion than FS-30 at 900°F (31.2 vs. 24.8 wt.%) and higher C₅-EP gasoline product (15.9 vs. 14.7 wt.%). It produced more C₁-C₄ (3.7 vs. 2.6 wt.%) and somewhat higher coke yield than FS-30 (7.8 vs. 6.3 wt.%).

The US-Y catalysts, Table 23, afforded similarly poor results for cat.-cracking the unhydrotreated SRC-II at both 900°F and 1000°F.

The 100% NH₄SMM's, Table 24, all afforded poorer results than any of the other catalysts discussed above with the unhydrotreated feed.

The NH₄SMM-matrix material catalysts blended 60-40 wt.%, Table 25, did not show any improvement over pure NH₄SMM, and conversions were generally less than half those observed for the same catalysts when testing was carried out on the hydrotreated SRC-II feed.

When the most active US-Y zeolites and rare earth exchanged Y-zeolites were formulated 20% zeolite-80% best NH₄SMM, Table 26, no significant improvement in activity or selectivity was observed.

The best results were obtained from some catalysts made with different final percentages of rare earth exchanged Y-zeolites combined with various matrix materials (Table 27). The zeolites Y-KKCK and Y-NN₃ (100°C)R₂ afforded the highest corrected conversions at 900°F (37-39 wt.%), and the best C₅-EP gasoline product distributions (18-

^a Tables with cat.-cracking results are presented in the body of the report. Tables with light gas analyses for all cracking runs are presented in Appendix C.

TABLE 22. CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND^{1,2} WITH EXCHANGED Y-ZEOLITE-ALUMINA FCC CATALYSTS

FCC Catalyst ³ Steamed 1450°F	Conversion Wt.% 430°F ⁴ Apparent ⁴ /Corrected ⁵		Product Distribution, Wt.%-----											
	900°F	1000°F	---H ₂ ---	---C ₁ ---	---C ₂ ---	---C ₃ ---	---C ₄ ---	---C ₅ ---	---EPCAS---	---Cycle Oil---	---Coke---	---Recovery---	900°F	1000°F
FS-30 ⁶	29.1/24.8	37.7/33.9	0.09	0.14	2.6	4.8	14.7	14.8	70.9	62.3	6.3	6.1	94.7	88.0
Y-NN ₃ (100°C)norm.	29.3/24.9	40.1/36.4	0.30	0.47	3.0	5.1	8.6	12.6	70.7	59.9	10.7	10.6	92.6	87.9
" (≈ 1μ)	26.0/21.4	33.8/29.7	0.13	0.28	2.7	4.3	9.3	11.7	74.0	66.2	10.4	10.6	96.6	93.1
" -Ni normal	29.9/25.5	34.3/30.3	0.15	0.31	3.1	5.6	9.0	10.7	70.1	65.7	9.7	10.0	91.4	92.2
" -Ni (≈ 1μ)	26.8/22.2	32.2/28.0	0.20	0.42	2.6	5.0	9.3	11.7	73.2	67.8	10.8	11.6	96.1	96.5
" -Co normal	33.5/29.4	35.9/31.9	0.11	0.35	2.3	5.7	12.6	11.3	66.5	64.1	8.1	10.5	89.5	92.0
" -Co (≈ 1μ)	28.0/23.5	33.7/29.6	0.13	0.32	2.5	4.8	8.7	11.1	72.0	66.3	10.2	10.0	93.6	92.6
" -R normal	29.2/26.3	34.8/27.9	0.10	0.25	1.9	4.9	9.0	10.4	69.4	67.9	11.0	9.1	91.4	92.5
" -R (≈ 1μ)	30.3/26.0	33.9/29.9	0.15	0.33	3.3	5.3	12.7	11.7	69.7	66.1	10.7	10.7	96.5	94.1
" -R ₂ normal	35.2/31.2	40.2/36.5	0.19	0.18	3.7	6.0	15.9	17.7	64.8	59.8	7.8	7.8	92.5	91.6
" -R-Cr normal	30.0/25.7	35.9/31.9	0.16	0.37	3.2	5.7	8.6	11.2	70.0	64.1	10.8	10.5	92.7	91.9
" -R-Cr (≈ 1μ)	28.8/24.4	36.4/32.5	0.17	0.34	3.0	5.7	10.6	14.3	71.2	63.6	10.8	10.7	95.8	94.6
" -R-Mn normal	28.4/23.9	36.8/32.9	0.13	0.32	3.1	5.8	8.8	11.3	71.6	63.2	10.1	10.3	93.7	90.9
" -R-Mn (≈ 1μ)	30.4/26.1	39.9/36.2	0.16	0.34	3.3	6.3	10.1	14.7	69.6	60.1	10.4	10.7	93.5	92.1

¹Elemental Analyses: %C, 87.70; %H, 8.74; %N, 0.92; %S, 0.27; %O, 1.91.²Sim. Dist. ASTM D2887: IBP/5, 384/412; 10/30, 429/468; 50, 498; 70/90, 549/667; 95/FBP, 723/856.³Catalyst steamed 2 hrs. at 1450°F; 20% Exchanged zeolite, 80% alumina. Test Cond. 16 WHSV, 3 Cat./Oil.

See Table 17 for explanation of abbreviation nomenclature.

⁴Apparent Conversion: 100 - Cycle Oil.⁵Corrected Conversion: $100 \left(1 - \frac{\% \text{ 430°F}^+ \text{ in Product}}{\% \text{ 430°F}^+ \text{ in Feed}} \right)$.⁶Proprietary formulation.

TABLE 23. CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND^{1,2} WITH EXCHANGED US-Y ZEOLITE-ALUMINA FCC CATALYSTS

FCC Catalyst ³	Conversion Wt.% 430°F ⁺ Apparent ⁴ /Corrected ⁵		-----Product Distribution, Wt.%-----											
	900°F	1000°F	-----H ₂ ----- 900°F 1000°F	-----C ₁ -C ₄ ----- 900°F 1000°F	-----C ₅ -EP Gas----- 900°F 1000°F	-----Cycle Oil----- 900°F 1000°F	-----Coke----- 900°F 1000°F	-----Recovery----- 900°F 1000°F						
US-Y	28.1/23.6	45.8/(42.5)	0.14 0.34	3.5 5.2	9.1 9.1	71.9 54.2	10.3 10.7	94.9 (79.5)						
US-Y-Ni	30.5/26.2	41.1/37.4	0.43 0.77	2.8 5.1	8.6 9.2	69.5 58.9	12.1 12.5	93.4 86.5						
US-Y-Co	31.2/27.0	38.5/34.7	0.20 0.39	3.6 5.8	9.5 11.0	68.8 61.5	10.9 10.7	93.0 89.4						
US-Y-R	33.3/29.2	39.2/35.4	0.17 0.32	3.7 5.7	10.7 12.2	66.7 60.8	10.3 10.0	91.5 89.0						
US-Y-Cr	35.3/31.3	40.1/36.4	0.12 0.34	3.1 5.7	11.7 11.6	64.7 59.9	10.8 10.9	90.5 88.3						
US-Y-Mn	30.7/26.4	40.3/36.6	0.16 0.37	3.5 6.2	9.9 11.6	69.3 59.7	9.9 11.7	92.8 89.5						
FS-30 ⁶	29.1/24.8	37.7/33.9	0.09 0.14	2.5 4.8	14.7 14.8	70.9 62.3	6.3 6.1	94.7 88.0						
Y-NN ₃ (100°C) -R ₂	32.8/28.7	35.8/31.9	0.14 0.32	3.1 5.7	9.2 11.4	67.2 64.2	10.7 10.5	90.3 92.1						

^{1,2} Same as Table 22.

³ Catalyst steamed 2 hrs. at 1450°F;

20% Exchanged US-Y zeolite, 80% alumina. Test Cond.: 16 WHSV, 3 Cat/Oil.

^{4,5} Same as Table 22.

⁶ Proprietary formulation.

TABLE 24. CAT. - CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND^{1,2} WITH NH₄SMM FCC CATALYSTS

FCC Catalyst ³	Conversion Wt.% 430°F ⁺ Apparent ⁴ /Corrected ⁵		-----Product Distribution, Wt.%-----											
	900°F	1000°F	-----H ₂ ----- 900°F 1000°F	---C ₁ -C ₄ --- 900°F 1000°F	-C ₅ -EP Gas- 900°F 1000°F	-Cycle Oil- 900°F 1000°F	-----Coke----- 900°F 1000°F	--Recovery-- 900°F 1000°F						
NH ₄ -SMM (S/A=2.16)	26.3/21.8	31.8/27.6	0.11 0.20	2.0 3.7	13.2 13.5	73.7 68.2	4.6 5.6	93.5 91.1						
NH ₄ -SMM (S/A=2.28)	23.3/18.5	28.1/23.6	0.43 0.59	1.1 2.1	6.6 8.0	76.7 71.9	8.4 (17.7)	93.3 100.3						
NH ₄ -SMM (S/A=2.45)	21.3/16.5	27.8/23.4	0.24 0.26	1.3 3.2	7.4 11.0	78.7 72.2	5.6 6.0	93.2 92.6						
NH ₄ -SMM (S/A=2.53)	21.6/16.7	27.2/22.6	0.29 0.32	1.2 2.9	6.9 9.0	78.4 72.8	5.4 7.2	92.2 92.2						
NH ₄ -SMM (S/A=2.67)	18.4/13.3	21.3/16.5	0.12 0.13	0.9 2.0	6.3 9.2	81.6 78.7	3.1 3.1	92.0 93.1						
FS-30 ⁶	29.1/24.8	37.7/33.9	0.09 0.14	2.6 4.8	14.7 14.8	70.9 62.3	6.3 6.1	94.7 88.0						
Y-NN ₃ (100°C) -R ₂ ⁷	32.8/28.7	35.8/31.9	0.14 0.32	3.1 5.7	9.2 11.4	67.2 64.2	10.7 10.5	90.3 92.1						

^{1,2} Same as Table 22.

³ Catalyst steamed 2 hrs. at 1450°F; 100% NH₄SMM. Test Cond.: 16 WHSV, 3 Cat/Oil.

^{4,5} Same as Table 22.

⁶ Proprietary formulation.

⁷ 20% Exchanged zeolite, 80% alumina.

TABLE 25. CAT.-CRACKING OF UNHYDROTREATED SRC-II FLEL OIL BLEND^{1,2}WITH NH₄SMM-MATRIX FCC CATALYSTS

---FCC Catalyst ³ ---		Conversion Wt.% 430°F+		-----Product Distribution, Wt.%-----											
Sample No.	Matrix	Apparent ⁴ / 900°F	Corrected ⁵ / 1000°F	---H ₂ --- 900°F	---C ₁ -C ₄ --- 1000°F	---C ₅ -E _P Gas--- 900°F	---C ₅ -E _P Gas--- 1000°F	---Cycle Oil--- 900°F	---Cycle Oil--- 1000°F	---Coke--- 900°F	---Coke--- 1000°F	---Recovery--- 900°F	---Recovery--- 1000°F		
1001-11-2	none	26.3/21.8	31.3/27.6	0.11	0.20	2.0	3.7	13.2	13.5	73.7	68.2	4.6	5.6	93.5	91.1
1030-21-4	alumina	24.5/19.9	34.2/30.2	0.00	0.12	1.9	3.3	10.4	12.9	75.4	65.8	7.2	8.1	94.8	90.1
1030-21-3	silica- alumina	25.0/20.4	32.5/28.3	0.03	0.11	1.7	3.6	8.8	12.1	75.0	67.5	7.8	8.1	93.2	91.4
1030-21-2	silica- alumina- magnesia	16.0/10.8	23.4/18.6	0.00	0.08	0.9	1.9	6.9	11.1	84.0	76.6	4.9	5.6	96.8	95.2
1030-21-1	silica- alumina- zirconia	22.5/17.7	29.1/24.7	0.00	0.14	1.4	3.1	7.9	12.1	77.5	70.9	5.9	6.5	92.8	92.7
1030-21-5	kaolinite clay	20.4/15.5	23.7/19.0	0.03	0.12	1.0	3.7	10.8	12.5	79.6	76.3	3.3	3.5	94.7	96.1

^{1,2} Same as Table 22.³ Catalyst steamed 2 hrs. at 1450°F; 60% NH₄SMM 1001-11-2, 40% matrix. Test Cond.: 16 WHSV, 3 Cat./Oil.^{4,5} Same as Table 22.

TABLE 26. CAT. CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND^{1,2} WITH ZEOLITE-NH₄SMM FCC CATALYSTS.

FCC Catalyst ³		Conversion Wt.% 430°F ⁺		Product Distribution, wt.%-----													
Sample No.	Matrix	Apparent ⁴ /Corrected ⁵		-----H ₂ -----		---C ₁ -C ₄ ----		-C ₅ -EP		Gas-		-Cycle Oil--		----Coke----		-Recovery--	
		900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
1030-13-3	US-Y	19.9/14.9	27.5/23.0	0.15	0.14	2.0	4.5	9.3	12.9	80.1	72.5	5.7	5.6	97.2	95.6		
1030-13-1	US-Y-Cr	22.8/18.0	31.3/27.1	0.00	0.04	1.4	4.2	9.0	16.3	77.2	68.7	9.5	5.6	97.1	94.8		
1030-13-2	US-Y-R	20.1/15.2	31.5/27.4	0.06	0.20	2.9	5.4	11.2	14.4	79.9	68.4	5.1	6.7	99.1	95.1		
1030-13-5	Y-NN ₃ (100°C)R ⁶	29.2/24.8	34.3/30.8	0.13	0.18	2.6	5.3	13.1	17.7	70.8	65.2	5.6	6.2	92.3	94.6		
1030-13-4	Y-NN ₃ (100°C) R ₂	35.2/31.2	40.2/36.5	0.19	0.18	3.7	6.0	15.9	17.7	64.8	59.8	7.8	7.8	92.5	91.6		
1030-17-1	Y-NRCR	28.6/24.1	37.3/33.4	0.19	0.25	3.4	5.4	11.6	16.3	71.4	62.7	7.3	8.3	93.9	92.9		
1030-13-6	Y-RRCR	33.1/28.9	49.0/45.9	0.01	0.13	3.9	6.0	16.4	17.8	66.9	51.0	8.0	11.5	95.3	86.4		

^{1,2} Same as Table 22.³ Catalyst Steamed 2 hrs. at 1450°F; 20% Exchanged zeolite, 80% NH₄SMM. Test Cond.: 16 WHSV, 3 Cat./Oil.^{4,5} Same as Table 22.⁶ See Table 17 for explanation of abbreviations.

TABLE 27. CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL^{1,2} BLEND WITH REC-EXCH.-Y-ZEOLITE-MATRIX FCC CATALYSTS^a

FCC Catalyst ³		Conversion Wt.% 430°F ⁴		-----Product Distribution, wt.%-----											
Sample No.	Matrix	Apparent ⁴ /Corrected ⁵		-----H ₂ -----		---C ₁ -C ₄ ---		-C ₅ -EP Gas-		-Cycle Oil--		----Coke----		-Recovery--	
		900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
1025-25-105	alumina	30.6/25.3	32.1/27.9	0.10	0.25	1.9	4.9	9.0	10.4	69.4	67.9	11.0	9.1	91.4	92.5
1001-205-6	alumina	32.8/28.7	34.8/31.9	0.14	0.32	3.1	5.7	9.2	11.4	67.2	65.2	10.7	10.5	90.3	92.1
1030-17-2	alumina	30.9/26.7	38.4/34.6	0.07	0.22	2.6	5.1	10.9	11.3	69.1	61.6	11.6	6.9	94.2	85.1
1030-49-1	alumina	34.2/30.2	38.7/34.9	0.07	0.17	3.5	6.1	11.1	12.5	65.8	61.3	11.2	11.1	91.7	91.1
1030-51-2	silica- alumina	23.5/18.7	28.3/23.8	0.05	0.10	2.3	4.2	8.5	11.1	76.5	71.7	7.2	6.6	94.6	93.7
1030-51-3	silica- alumina- magnesia	38.6/34.8	35.2/31.2	0.03	0.10	3.3	5.3	19.9	16.0	61.4	64.8	6.6	8.4	91.1	94.6
1030-51-4	silica- alumina- zirconia	28.6/24.2	37/33.2	0.03	0.07	3.3	5.5	11.4	14.5	71.4	63.0	8.7	6.8	94.8	89.8

^a Table continued on next page.

TABLE 27. CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL^{1,2}
BLEND WITH REO-EXCH.-Y-ZEOLITE-MATRIX FCC CATALYSTS - Continued

FCC Catalyst ³		Conversion Wt.% 430°F ⁺		-----Product Distribution, wt.%-----											
Sample No.	Matrix	Apparent ⁴ /Corrected ⁵		-----H ₂ -----		---C ₁ -C ₄ ---		-C ₅ -EP Gas-		-Cycle Oil--		----Coke----		-Recovery--	
		900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
1030-51-1	kaolinite clay	34.6/30.6	41.4/37.8	0.08	0.18	4.2	7.1	15.1	17.7	65.4	58.6	6.7	7.9	91.4	91.4
1030-13-6	NH ₄ SMM	33.1/28.9	49.0/45.9	0.01	0.13	3.9	6.0	16.4	17.8	66.9	51.0	8.0	11.5	95.3	86.4
1030-49-2	alumina-kaolinite clay - NH ₄ polysilicate	42.8/39.2	48.7/45.5	0.14	0.33	4.9	9.0	18.2	18.1	57.2	51.3	8.7	11.8	88.6	90.5
1030-73-1	"	30.5/26.1	42.8/39.3	0.18	0.24	3.4	7.2	13.9	16.3	69.5	57.2	7.5	10.5	94.5	91.4
1030-81-1	"	41.2/37.6	49.3/46.2	0.17	0.07	4.7	8.3	19.9	21.3	58.8	50.7	8.4	7.2	92.0	87.5
1030-81-2	"	40.3/36.6	53.2/50.3	0.19	0.13	7.7	10.3	14.4	19.6	59.7	46.8	13.7	13.8	95.7	90.7
Filtrol FS-30	Proprietary	29.1/24.8	37.7/33.9	0.09	0.14	2.6	4.8	14.7	14.8	70.9	62.3	6.3	6.1	94.7	88.0

^{1,2} Same as Table 22.

³ Catalyst steamed 2 hrs. at 1450°F; 20% REO-Exchanged Y-zeolite, 80% Matrix. See Tables 17 and 18 for Chemical and Physical properties of catalysts. Test Cond.: 16 WHSV, 3 Cat/Oil.

^{4,5} Same as Table 22.

20 wt.%). C₁-C₄ gas make ranged from 5-8 wt.%, and coke make from 11-14 wt.%. These relatively high activities and selectivities parallel those obtained for the same catalysts when they were tested with the hydrotreated SRC-II.

Table 28 shows the results for blends of the most active rare earth exchanged Y-zeolite (Y-RRCR) (20%) formulated with the most active NH₄SMM (40%) and various matrices (40%). The results are average with the exception of the Y-RRCR-NH₄SMM-alumina catalyst which afforded a relatively high 900°F corrected conversion of 38.4 wt.%, and a relatively high C₅-EP gasoline product of 15.6 wt.%.

Tables 29 and 30 show activity results for similar sets of Cr-exchanged US-Y zeolite-matrix, and Cr-US-Y-NH₄SMM matrix catalysts. None of these catalysts afford activity or selectivity as good as that observed for the REO-exchanged Y-zeolite based catalysts.

Testing the catalysts at 1000°F on the unhydrotreated feed demonstrated that increased conversion, H₂, C₁-C₄, C₅-EP gasoline and coke make were obtained, but the increases were not dramatic. The maximum corrected conversion obtained at 1000°F for catalyst 1030-81-2 (Table 27) was 50.3 wt.%, while the maximum C₅-EP gasoline product obtained was only 21.3 wt.% for catalyst 1030-81-1 (Table 27).

These results confirm those reported in the literature for FCC cracking of coal derived 400°F⁺ distillates from the H-Coal and EDS processes (19). Low conversions and gasoline yields and high carbon yields are observed, which are consistent with the aromatic and heterocyclic nature of the unhydrotreated coal liquid feed stocks.

G. Task VII - Hydrocracking Catalysts Preparation

Eighteen zeolite based hydrocracking catalysts with various combinations of reducing metals were formulated with acid peptized alumina (15 wt.%) and exchanged zeolites (85 wt.%). The mixtures were milled, extruded and calcined. The 1/16" diameter extrudates were then impregnated with the desired amounts of metals, dried and calcined. The general preparation scheme is shown in Fig. 15. The partial chemical analyses of the finished catalysts are presented in Tables 31 and 32. Two nickel and cobalt exchanged NH₄SMM's, and four metal lattice substituted SMM's: Fe, Co, Ni and Mn (each at two different metal concentrations) were compounded (65 wt.%) with ultrastable-Y zeolite (35 wt.%) to make a total of 10 SMM based hydrocracking catalysts (Fig. 16). The most

TABLE 28. CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL^{1,2} BLEND WITH REO-EXCH.-Y-ZEOLITE-NH₄SMM-MATRIX FCC CATALYSTS

FCC Catalyst ³		Conversion Wt.% 430°F ⁴		Product Distribution, wt.%-----											
Sample No.	Matrix	Apparent ⁴ /Corrected ⁵		-----H ₂ -----		---C ₁ -C ₄ ---		-C ₅ -EP Gas-		-Cycle Oil--		-----Coke-----		-Recovery--	
		900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
1030-13-6	None ⁶	33.1/28.9	49.0/45.9	0.01	0.13	3.9	6.0	16.4	17.8	66.9	51.0	8.0	11.5	95.3	86.4
1030-59-3	silica-alumina	35.1/31.0	37.4/33.6	0.08	0.17	4.1	6.3	12.3	16.3	64.9	62.6	5.2	9.7	86.6	95.0
1030-59-4	silica-alumina-magnesia	35.3/31.3	45.8/42.5	0.17	0.22	4.1	7.5	13.1	17.7	64.7	54.2	9.9	(3.6)	92.0	(83.3)
1030-59-5	silica-alumina-zirconia	33.9/29.8	37.6/33.8	0.06	0.05	3.1	4.6	14.9	15.0	66.1	62.4	8.6	9.4	92.7	91.5
1030-59-1	alumina	42.0/38.4	52.5/47.5	0.11	0.21	4.9	8.3	15.6	18.7	58.0	49.4	10.5	9.2	89.1	85.8
1030-59-2	kaolinite clay	36.1/32.1	47.3/44.1	0.09	0.15	3.8	7.0	14.9	18.7	63.9	52.7	5.7	8.7	88.4	87.1

^{1,2} Same as Table 22.

³ Catalyst steamed 2 hrs. at 1450°F; 20% Y-RRCR, 40% NH₄SMM, 40% Matrix. Test Cond.: 16 WHSV, 3 Cat./Oil.

^{4,5} Same as Table 22.

⁶ 20% Y-RRCR, 80% NH₄-SMM.

TABLE 29. CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND^{1,2}WITH Cr-EXCHANGED US-Y ZEOLITE-MATRIX FCC CATALYSTS

----FCC Catalyst ³ ----		Conversion Wt.% 430°F+		-----Product Distribution, Wt.%-----											
Sample No.	Matrix	Apparent ⁴ /Corrected ⁵		-----H ₂ -----		-----C ₁ -C ₄ -----		-----C ₅ -E _{PG} gas-----		-----Cycle Oil-----		-----Coke-----		-----Recovery-----	
		900°F	1300°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
1001-205-7	alumina	35.3/31.3	40.1/36.4	0.12	0.34	3.1	5.7	11.7	11.5	64.7	59.9	10.8	10.9	90.5	88.3
1030-65-2	silica- alumina	28.2/23.8	37.1/33.2	0.00	0.13	2.6	5.8	11.0	14.1	71.8	62.9	8.2	8.3	93.6	91.2
1030-65-4	silica- alumina- magnesia	32.8/28.6	39.7/36.0	0.00	0.13	2.6	6.3	12.7	16.5	67.2	60.3	7.9	7.9	90.4	91.1
1030-65-3	silica- alumina- zirconia	29.7/25.4	37.3/33.4	0.02	0.05	3.2	5.8	11.7	15.2	70.3	62.7	6.0	8.2	91.1	91.9
1030-65-1	kaolinite clay	15.0/9.7	23.8/18.4	0.02	0.11	0.9	3.2	6.9	12.6	85.0	76.8	2.6	2.9	95.4	95.6
1030-23-1	alumina- kaolinite clay-NH ₄ polysilicate	24.1/19.4	31.8/27.6	0.07	0.15	2.4	4.8	9.9	13.6	75.9	68.2	6.4	6.8	94.6	93.6

^{1,2} Same as Table 22.³ Catalyst steamed 2 hrs. at 1450°F; 20% Cr-exchanged US-Y zeolite, 80% matrix. Test Cond.: 16 WHSV, 3 Cat./Oil.^{4,5} Same as Table 22.⁶ 20% Cr-exchanged US-Y zeolite, 20% alumina, 54% kaolinite clay, 6% ammonium polysilicate.

TABLE 30. CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND^{1,2}WITH Cr-EXCHANGED US-Y ZEOLITE-NH₄SMM-MATRIX FCC CATALYSTS

----FCC Catalyst ³ ----		Conversion wt.% 430°F+		-----Product Distribution, Wt.%-----											
		Apparent ⁴ /Corrected ⁵		-----H ₂ -----	---C ₁ -C ₄ ---	---C ₅ -EPC _{Gas} ---	---Cycle Oil---	---Coke---	---Recovery---						
Sample No.	Matrix	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F	900°F	1000°F
1030-23-2	alumina	28.9/24.5	35.7/31.7	0.09	0.18	2.9	5.0	10.9	13.4	71.1	64.3	8.6	6.4	93.6	89.3
1030-23-4	silica- alumina	26.2/21.6	40.4/36.7	0.08	0.15	2.8	5.1	10.9	12.9	73.8	59.6	7.4	8.2	94.9	86.0
1030-25-1	silica- alumina- magnesia-	24.8/20.2	32.0/27.8	0.17	0.18	2.1	4.2	8.5	11.8	75.2	68.0	6.1	6.9	92.0	91.0
1030-25-2	silica- alumina- zirconia	23.9/19.2	32.7/28.5	0.01	0.11	1.6	4.5	8.6	12.3	76.1	67.3	6.4	6.4	92.7	90.6
1030-23-3	kaolinite clay	20.1/15.1	27.0/22.5	0.04	0.06	1.5	2.8	7.8	11.8	79.9	73.0	3.9	6.5	93.1	94.2

^{1,2} Same as Table 22.³ Catalyst steamed 2 hrs. at 1450°F; 20 wt.% Cr-exchanged US-Y zeolite, 40 wt.% NH₄SMM, 40% Matrix. Test Cond.:
16 WHSV, 3 Cat/Oil.^{4,5} Same as Table 22.

FIG. 15 ZEOLITE BASED HYDROCRACKING CATALYSTS

TABLE 31. CHEMICAL ANALYSES OF NH₄-US-Y + ALUMINA HYDROCRACKING CATALYSTS¹

Sample No.	Description	-----Wt.%-----								
		SiO ₂	Al ₂ O ₃	Na ₂ O	NH ₃	Pt	Pd	NiO	CoO	MoO ₃
1029-41-1	Pt IMP.	59.1	38.0	0.66	0.05	0.53	--	--	--	--
1029-41-2	Pd IMP.	59.1	37.5	0.62	0.04	--	0.56	--	--	--
1028-65-1	Ni Exch., Co-Mo IMP.	--	--	--	--	--	--	1.3	6.5	11.4
1028-67-1	Co Exch., Ni-Mo IMP.	--	--	--	--	--	--	5.5	0.9	11.5
1029-67-1	Ni-Mo IMP.	--	--	--	--	--	--	2.6	--	15.6
1029-67-4	Ni-Mo-Pt IMP.	--	--	--	--	0.42	--	2.5	--	14.8
1029-67-3	Ni-Mo-Pd IMP.	--	--	--	--	--	0.45	2.6	--	15.3
1029-67-2	Co-Mo IMP.	--	--	--	--	--	--	--	2.0	15.0
1029-67-6	Co-Mo-Pt IMP.	--	--	--	--	0.48	--	--	2.1	14.6
1029-67-5	Co-Mo-Pd IMP.	--	--	--	--	--	0.58	--	2.0	14.9

¹ Wt. Ratio Zeolite: Alumina = 5.7:1.

TABLE 32. CHEMICAL ANALYSES OF REO-EXCH. US-Y AND REC-EXCH. US-Y/NH₄-US-Y(1/2) + ALUMINA HYDROCRACKING CATALYSTS¹

<u>Sample No.</u>	<u>Description</u>	<u>-----Wt.%-----</u>									
		<u>SiO₂</u>	<u>Al₂O₃</u>	<u>Na₂O</u>	<u>REO</u>	<u>NH₃</u>	<u>Pt</u>	<u>Pd</u>	<u>NiO</u>	<u>CoO</u>	<u>MoO₃</u>
1029-53-1	REO-EXCH. US-Y Pt IMP.	59.0	36.9	0.60	2.32	0.19	0.50	--	--	--	--
1029-53-2	" Pd IMP.	59.6	36.6	0.40	2.40	0.20	--	0.47	--	--	--
1030-77-1	REO-EXCH. US-Y/NH ₄ -US-Y (1/2) Ni-Mo IMP.	--	--	--	--	--	--	--	5.6	--	15.7
1030-77-3	" Ni-Mo-Pt-IMP.	--	--	--	--	--	0.44	--	5.7	--	13.4
1030-77-4	" Ni-Mo-Pd-IMP.	--	--	--	--	--	--	0.52	6.0	--	13.9
1030-77-2	" Co-Mo IMP.	--	--	--	--	--	--	--	--	5.2	15.9
1030-77-5	" Co-Mo-Pt IMP.	--	--	--	--	--	0.41	--	--	5.8	13.6
1030-77-6	" Co-Mo-Pd IMP.	--	--	--	--	--	--	0.54	--	5.8	13.7

¹ Wt. Ratio Zeolites: Alumina = 5.71:1.

FIG. 16 SMM HYDROCRACKING CATALYSTS

active of these catalysts, a high Ni-SMM was also impregnated with Pt and Pd (Fig. 16). The selected metal analyses of these finished catalysts are presented in Table 36.

The physical properties of selected hydrocracking catalysts are given in Table 33.

H. Task VIII - Hydrocracking Catalysts Testing

1. Introduction

Because of the relatively high nitrogen content and aromaticity of the SRC-II Fuel Oil Blend, it was decided that bi-functional catalysts containing noble metal hydrogenating components and low-sodium cracking bases such as hydrogen and rare earth exchanged ultrastable Y-zeolites, or exchanged and metal substituted SMM's might make active and stable hydrocracking catalysts (4,20,21). In addition to platinum and palladium, other non-noble metal loaded catalysts containing nickel and cobalt molybdates in the sulfided state, and other types of molybdenum loaded metal SMM's appeared to be promising candidates for coal liquids hydrocracking catalysts (7,12).

Three general series of hydrocracking catalysts, prepared as discussed under Task VII, were tested: metal loaded NH_4 -US-Y compounded with alumina; metal loaded combinations of NH_4 -US-Y and rare earth exchanged-US-Y compounded with alumina; and various combinations of metal exchanged and substituted SMM's loaded with reducing metals, and formulated with US-Y.

2. Results and Discussion

a. Metal Loaded NH_4 -US-Y + Alumina Catalysts

The hydrocracking results for this series are presented in Table 34. As discussed previously under Task II, the hydrocracking catalysts undergo significant initial deactivation during the first 24 hours on stream. However, because of the screening nature of the catalyst evaluation runs, and the limitation of the available hydrotreated SRC-II feed, it was decided to use 12 hours on stream, after preconditioning, as the standard reaction test time. Baseline catalysts 1029-41-2 (0.56% Pd), and 1029-41-1 (0.53% Pt) afford average corrected conversions of $\approx 52 \pm 6$ and $\approx 49 \pm 5$ wt.%,

TABLE 33. PHYSICAL PROPERTIES OF HYDROCRACKING CATALYSTS

<u>Catalyst No.</u>	<u>Description</u>	<u>SA¹</u> <u>m²/g</u>	<u>PV¹</u> <u>cc/g</u>	<u>Pore Volume Distribution (%)¹</u> <u>-----Radius Range (Å)-----</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>
1001-225-1	US-Y/Alumina=5.7	505	0.45	38.3	37.2	15.8	3.7	2.0	3.0
1029-41-1	" Pt 0.53 wt.%	474	0.43	28.3	39.9	22.6	4.0	2.0	3.3
1029-41-2	" Pd 0.56 wt.%	552	0.44	39.5	27.3	24.1	6.8	1.4	0.9
1029-67-3	" Pd 0.45 wt.%; MoO ₃ , 15.3 wt.%; NiO, 2.6 wt.%	139	0.16	31.0	41.3	16.5	3.7	2.7	4.7
1030-77-1	[REO-EXCH/NH ₄ -US-Y(1/2)]/ Alumina (5.7) MoO ₃ , 15.7 wt.%; NiO, 5.6 wt.%	289	0.26	33.0	40.1	13.2	3.5	2.9	7.3
1030-77-2	" MoO ₃ , 15.9 wt.%; CoO, 5.2 wt.%	299	0.31	31.3	38.2	14.6	4.0	3.7	8.2
1029-117-1	Ni Subst. SMM (65 wt.%) + US-Y(35 wt.%)	341	0.30	74.7	13.3	4.3	2.4	2.3	3.0

¹ Measured with Micromeritics Digisorb 2500 surface area and pore volume analyzer in desorption mode.

TABLE 34. HYDROCRACKING¹ OF HYDROTREATED SRC-II FUEL OIL BLEND² WITH US-Y + ALUMINA METAL IMPREGNATED CATALYSTS*

Catalyst, Run No. Wt.% Metals ³	Corr. Conv. ⁴ 430°F+, Wt.%	-----Product Distribution, Wt.%-----								
		Gas	Cycle Oil	C1-C4	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	iso-n-C ₄ H ₁₀	Recovery
1029-41-2, II-159	57.9	51.5	35.6	8.4	0.11	0.34	2.14	2.77	3.04	95.5
0.56% Pd ^a , II-196	45.6	49.7	46.0	3.2	0.13	0.29	1.22	0.78	0.76	98.9
1029-41-1, II-154	53.5	53.5	39.3	6.6	0.11	0.47	2.58	2.44	0.89	99.4
0.53% Pt ^a , II-150	44.8	41.8	46.7	3.6	0.04	0.18	1.06	1.07	1.29	92.2
1029-67-1, II-161	31.9	38.5	57.6	3.6	0.15	0.44	0.84	0.73	1.41	99.7
15.0% MoO ₃ , 2.0% NiO ^b										
1029-67-3, II-163	14.2	21.9	72.6	0.6	0.00	0.15	0.22	0.12	0.06	95.1
15.3% MoO ₃ , 2.6% NiO, 0.45% Pd ^c										
1029-67-4, II-154	23.0	28.6	65.2	2.0	0.14	0.21	0.52	0.41	0.67	95.8
14.8% MoO ₃ , 2.5% NiO, 0.42% Pt ^c										
1029-67-2, II-162	39.4	42.0	51.3	5.6	0.12	0.21	1.38	1.59	2.32	98.9
15.0% MoO ₃ , 2.0% CoO ^b										

*Table continued on next page.

TABLE 34. HYDROCRACKING¹ OF HYDROTREATED SRC-II FUEL OIL BLEND² WITH US-Y + ALUMINA METAL IMPREGNATED CATALYSTS - Continued

Catalyst, Run No. Wt.% Metals ³	Corr. Conv. ⁴ 430°F+, Wt.%	-----Product Distribution, Wt.%-----								Recovery
		C5-EP _{Gas}	Cycle Oil	C1-C4	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	iso-n-C ₄ H ₁₀	
1029-67-5, II-165 14.9% MoO ₃ , 2.0% CoO, 0.6% Pd ^c	14.3	22.8	72.5	0.3	0.11	0.04	0.06	0.02	0.06	95.6
1029-67-6, II-166 14.6% MoO ₃ , 2.1% CoO, 0.48% Pt ^c	28.6	25.8	60.4	5.2	0.46	0.18	1.18	1.19	2.17	91.4
1028-65-1, I-183 Ni-Exch. US-Y, 11.4% MoO ₃ , 11.4% NiO, 6.5% CoO ^b	43.4	45.5	47.9	6.0	0.21	0.36	1.71	1.70	2.05	99.4
1028-67-1, I-184 Co-Exch. US-Y 11.5% MoO ₃ , 5.5% NiO, 0.9% CoO ^b	44.5	46.5	47.0	5.4	0.20	0.34	1.54	1.41	1.86	98.8

¹ Standard Test Conditions: temperature, 750°F; pressure, 1,000 psig; LHSV, 1 ml/ml-hr;
H₂ flow rate, 5,000 SCF/bbl; time on line after conditioning and equilibration, 12 hrs.

² Elemental Analyses %C, 88.27; %H, 11.58; %N, 0.056; %O, 0.11; %S, 0.03 .
Sim. Dist., IBP, 15 10/30 50 70/90 95/FBP
ASTM D-2387 °F 340/377 394/442 484 533/624 670/796

³ US-Y/Alumina = 5.7/1. Conditioning: a, hydrogenation; b, presulfiding; c, hydrogenation + presulfiding.

⁴ Corrected Conversion: $100 \left(1 - \frac{\% \text{ 430°F+ in Product}}{\% \text{ 430°F in feed}} \right) (1).$

respectively. C₅-430°F gasoline yields after correction for 15 wt.% gasoline in the original feed are 35.6 ± 1 and 32.7 ± 6 wt.%, respectively. When the Pd impregnated US-Y catalyst was tested on the unhydrotreated SRC-II feed (Table 37) the conversion dropped from 52 wt.% to 24.6 wt.%, and the C₅-430°F gasoline yield, corrected for gasoline in the feed, dropped from 35.6 wt.% to 16.4 wt.%. This is the same type of activity decline which was observed in the cracking testing when the feed was changed from hydrotreated to unhydrotreated SRC-II. This result is not unexpected for the reasons cited in Section IV-F-3. Therefore, no further hydrocracking testing was carried out on the unhydrotreated feed. None of the Mo/Ni or Mo/Co catalysts afforded corrected conversions or C₅-EP_{Gas} yields which were as high as those reported above although a few of these catalysts (1029-65-1, 1028-67-1) gave results which came within experimental uncertainty of the baseline values. Catalyst 1029-67-3, which afforded particularly poor results, also showed significant losses after MoO₃/NiO loading in surface area; 139 m²/g, and pore volume, 0.16 cc/g, compared to catalyst 1029-41-2, 552 m²/g SA and 0.44 cc/g PV (Table 33).

b. Metal Loaded REO-Exch.-US-Y and REO-Exch.-US-Y/NH₄-US-Y (1/2) + Alumina Catalysts

The hydrocracking results for this series are presented in Table 35. The first two catalysts, 1029-53-2 and 1029-53-1, composed of 85 wt.% REO-exch. US-Y and 15 wt.% alumina, impregnated with 0.47 and 0.50 wt.% Pd and Pt respectively, were not as active as the rest of the catalysts although 1029-53-1 was not as inactive as 1029-53-2. The rest of the catalysts which were formulated with a 1/2 mix of REO-Exch.-US-Y and NH₄-US-Y (85 wt.%) + 15 wt.% alumina, and impregnated with various combinations of Mo/Ni, Mo/Ni/Pd, Mo/Ni/Pt, and Mo/Co, Mo/Co/Pd, Mo/Co/Pt afforded corrected conversions and gasoline yields (after correction for 15 wt.% gasoline in the original feed) which were essentially the same as those afforded by the previously discussed baseline catalysts (≈ 50 wt.% corrected conversion, and C₅-EP gas yields of ≈ 32 wt.%). Some representative physical property data for these catalysts (Table 33) indicate reasonable retention of surface area for the finished catalysts (≈ 300 m²/g), and reasonable pore volume distribution in the high pore radius ranges.

The most significant finding in this series is that the expensive noble metals Pd and Pt do not appear to be necessary to impart reasonable activity and selectivity to these catalysts.

TABLE 35. HYDROCRACKING¹ OF HYDROTREATED SRC-II FUEL OIL BLEND² WITH REO-EXCH.US-Y AND REO EXCH. US-Y/NH₄-US-Y + ALUMINA METAL IMPREGNATED CATALYSTS

Catalyst, Run No. Wt.% Metals	Corr. Conv. ⁵ 430°F+, Wt.%	-----Product Distribution, Wt.%-----								Recovery
		C ₅ -EP _{Gas}	Cycle Oil	C ₁ -C ₄	CH ₄	C ₂ H ₆	C ₃ H ₈	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	
1029-53-2 ³ , II-158	26.7	29.5	62.0	3.1	0.12	0.12	0.78	0.88	1.21	94.6
0.47% Pd ^a , I-187	22.9	28.8	65.2	3.1	0.16	0.12	0.84	0.89	1.01	97.1
1029-53-1 ³ , I-186	37.8	38.4	52.6	4.8	0.17	0.28	1.50	1.34	1.50	96.5
0.50% Pt ^a , II-157	43.9	53.0	40.7	6.1	0.12	0.32	1.48	1.89	2.25	99.8
1030-95-1 ⁴ , I-194	49.3	49.8	42.9	6.2	0.20	0.33	1.73	1.90	2.08	98.9
12.5% MoO ₃ , 5.3% NiO ^b , I-189	36.7	38.6	53.6	4.1	0.18	0.24	1.22	1.04	1.34	96.3
1030-77-4 ⁴ , II-172	59.0	47.6	34.7	8.8	0.18	0.40	1.94	3.18	3.14	91.1
13.9% MoO ₃ , 6.0% NiO, 0.50% Pd ^c										
1030-77-3 ⁴ , II-171	47.5	45.5	44.5	4.4	0.13	0.23	1.07	1.30	1.69	94.4
13.4 MoO ₃ , 5.7 NiO, 0.44 Pt ^c										
1030-77-2 ⁴ , II-170	50.0	43.4	42.3	6.1	0.17	0.30	1.53	1.89	2.25	91.8
15.9 MoO ₃ , 5.2 CoO ^b										
1030-95-6 ⁴ , II-179	48.1	45.3	43.9	6.2	0.46	0.36	1.73	1.70	1.97	95.7
12.2 MoO ₃ , 5.0 CoO, 0.55 Pd ^c										
1030-77-5 ⁴ , II-173	51.9	51.9	40.7	5.0	0.00	0.36	1.55	1.51	1.55	97.6
13.6 MoO ₃ , 5.8 CoO, 0.41 Pt ^c										

^{1,2} Same as Table 34.³ REO-Exch. US-Y/Alumina = 5.7/1.⁴ NH₄ US-Y/REO Exch. US-Y/Alumina = 3.8/1.9/1.

Conditioning: a, hydrogenation; b, presulfiding; c, hydrogenation + presulfiding.

⁵ Same as Table 34.

c. Metal Exchanged, Substituted, and Impregnated SMM + US-Y Catalysts

The hydrocracking results for mixtures of metal exchanged and substituted SMM's (65 wt.%) compounded with US-Y (35 wt.%) are given in Table 36. The most active catalyst, a Ni-substituted SMM, was also impregnated with Pd and Pt. The results show that this series of catalysts is the poorest of the three series evaluated. Only the high Ni-substituted SMM (12.7% NiO) afforded moderate activity and gasoline selectivity. A possible explanation for the general lack of activity of the Co, Fe, and Mn substituted SMM's is the poorer hydrogenation activity of these metals as well as their inaccessibility. It is generally assumed that only metal atoms on edge unit cells afford catalytic activity (See Appendix D). It has also been shown that SMM's are not as acidic as zeolites (7), and this factor could also be significant in the poorer hydrocracking activity shown by these catalysts.

I. Task IX - Hydrotreating Catalysts Preparation

1. Introduction

Hydrotreating catalysts were prepared from matrix materials such as alumina and silica-alumina (Task V). The effects of metals ratios and catalytically active components were determined by correlating physical and chemical properties versus hydrotreating activity.

2. Experimental

Three alumina supports with Kaiser SA alumina to Condea SB alumina ratios of 80/20, 23/77, and 80/20 + TiO_2 were produced as 1/16" extrudates after peptizing, mixing, mulling, and drying to proper consistency. The alumina extrudates were dried overnight at 250°F, calcined for 3 hours at 1000°F, and spray impregnated with either $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ or $(\text{NH}_4)_2\text{W}_{12}\text{O}_{42} \cdot x\text{H}_2\text{O}$. The supports were then dried overnight at 250°F and further spray impregnated with either $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The products were then dried at 250°F overnight and calcined at 1000°F for 3 hours. The additional promoters ZnO, MnO and P_2O_5 were formed by calcining extrudates which had been further impregnated with aqueous solutions of $\text{Zn}(\text{SO}_4)$, $\text{Mn}(\text{NO}_3)_2$ and $(\text{NH}_4)_3\text{PO}_4$.

TABLE 36. HYDROCRACKING¹ OF HYDROTREATED SRC-II FUEL OIL BLEND² WITH
METAL EXCHANGED AND SUBSTITUTED SMM + US-Y*

Catalyst, Run No. Wt.% Metals ³	Corr. Conv. ⁴ 430°F+, Wt.%	-----Product Distribution-----								Recovery
		C5-EPGas	Cycle Oil	C1-C4	CH ₄	C ₂ H ₆	C ₃ H ₈	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	
1028-71-2a, II-178 Ni-Exch. SMM, 1.8% NiO	29.4	32.6	59.7	6.5	0.45	0.17	1.79	2.24	1.86	98.9
1028-71-1a, I-175 Co.-Exch. SMM, 1.8% CoO	24.7	25.0	63.7	5.5	0.40	0.72	1.62	1.42	1.18	94.2
----- ⁵ Ni-Subst. SMM, 12.7% NiO	39.9 ± 2.4	36.6 ± 5.0	0.19 ± 0.05	4.3 ± 1.1	0.19 ± 0.05	0.38 ± 0.17	1.27 ± 0.25	1.22 ± 0.28	1.18 ± 0.34	91.7 ± 5.1
1029-95-1a, I-176 Ni-Subst. SMM, 8.9 %NiO	32.8	36.4	56.9	4.4	0.31	0.69	1.03	1.11	0.97	97.6
1030-39-1a, I-177 Co-Subst. SMM, 14.2% Co	20.0	24.5	67.7	1.2	0.20	0.29	0.20	0.34	0.19	93.4
1028-69-2a, I-182 Co-Subst. SMM 8.2% CoO	29.9	35.6	59.3	4.5	0.11	0.70	1.12	1.21	1.08	99.4
1030-41-1a, I-178 Fe-Subst. SMM, 13.9% Fe ₂ O ₃	34.7	35.9	55.2	2.6	0.22	0.17	0.52	0.80	0.73	93.7
1030-43-1a, I-180 Fe-Subst. SMM, 7.8% Fe ₂ O ₃	20.1	21.8	67.6	2.3	0.25	0.11	0.66	0.61	0.49	91.7

*Table continued on next page.

TABLE 36. HYDROCRACKING¹ OF HYDROTREATED SRC-II FUEL OIL BLEND² WITH
METAL EXCHANGED AND SUBSTITUTED SMM + US-Y - Continued

Catalyst Wt.% Metals ³	Corr. Conv. ⁴ 430°F+, Wt.%	-----Product Distribution-----								Recovery
		C5-EP Gas	Cycle Oil	C1-C4	CH ₄	C ₂ H ₆	C ₃ H ₈	iso- C ₄ H ₁₀	n-C ₄ H ₁₀	
1030-45-1a, I-179 Mn-Subst. SMM, 8.3% MnO	30.6	31.3	58.7	2.4	0.25	0.41	0.48	0.42	0.59	92.9
1030-47-1a, I-185 Mn-Subst. SMM 6.0% MnO	30.2	34.3	59.0	2.2	0.18	0.06	0.57	0.70	0.65	95.6
1029-117-2b, II-176 Ni-Subst. SMM, 13.7% NiO, 0.14% Pd	21.6	24.9	66.3	3.7	0.19	0.23	1.14	1.08	1.04	94.9
1029-113-1b, I-191 Ni-Subst. SMM 12.7% NiO, 0.3% Pt	31.3	32.5	58.1	4.7	(0.00)	0.25	1.31	1.60	1.52	95.3

^{1,2} Same as Table 34.

³ Wt. Ratio M-SMM: US-Y = 1.86:1. Conditioning: a, presulfiding; b, hydrogenation + presulfiding.

⁴ Same as Table 34.

⁵ Average of three different catalysts: 1028-69-1, 1029-117-1, 1030-99-1; five different runs, II-167, II-175, I-173, I-190, I-193.

A similar scheme was followed starting with three different silica-alumina matrix materials from Task V to produce silica-alumina matrix catalysts.

Finally a catalyst was produced from the best alumina and the best silica-alumina supports (1:1) impregnated with the most active metals and promoters.

J. Task X - New Hydrotreating Catalysts Preparation

The majority of the SMM matrix materials to be used as supports for the new hydrotreating catalysts were prepared as described under Task III and exchanged as described under Task IV. In order to prepare the finished catalysts, it was 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 obtained from the C. W. Brabender Instrument Company. This extruder was received and used to produce new hydrotreating catalyst extrudates from nickel and cobalt exchanged SMM, and nickel, cobalt, manganese and iron lattice substituted SMM. These materials were also impregnated with molybdenum and compounded in various proportions with alumina supports.

For the metal lattice substituted SMM's it is assumed that only the metal atoms located in the edge unit cells are active for promoting molybdenum. Calculations relating the effective metal concentration to the total metal concentration are presented in Appendix C. The hydrotreating catalysts effective metal/molybdenum atomic ratios are presented in Tables 47, 49.

K. Task XI - Hydrotreating Catalysts Testing

1. Introduction

The objective of the initial phase of this part of the program was 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. Three series of alumina supported hydrotreating catalysts, prepared as described previously, were activity tested. Three additional series of silica-alumina supported hydrotreating catalysts were also activity tested. The most active of the above catalysts, further doped with additional activators, were then tested. Finally, the most active alumina plus silica-alumina supports were combined (1/1) and activity tested with optimum metals and promoter loading.

The various SMM catalysts described previously were also activity tested.

2. Results and Discussion

Standard testing conditions were chosen from the baseline studies carried out: temperature, 750°F; pressure, 1,000 psig; LHSV, 1 ml/ml-hr.; and H₂ flow rate, 5,000 SCF H₂/bbl.

a. Alumina Supported Catalysts

Table 37 shows a comparison between the commercial baseline catalysts Filtrol HPC-40 and HPC-6B, and a series of MoO₃/NiO and MoO₃/CoO catalysts prepared on Kaiser SA alumina. Tables 38 and 39 show two series of catalysts prepared on two different combinations of Kaiser/Condea alumina supports: 80/20 and 23/77.

The most obvious finding in comparing Table 37 with Tables 38 and 39 is that nickel and cobalt tungstate impregnated alumina supported catalysts are significantly poorer catalysts for hydrodenitrogenation (HDN) and somewhat poorer for hydrodesulfurization (HDS) than their respective nickel and cobalt molybdate analogues. Therefore, no additional tungsten impregnated catalysts were prepared for hydrotreating testing. Additional findings from Tables 37 - 39 are:

1. None of the exploratory catalysts are as good as the commercial catalyst Filtrol HPC-40 for HDN (85% maximum vs. 88% for HPC-40). The HDS results, however, are generally similar ($\approx$ 93-96%) for the majority of the MoO₃/NiO and MoO₃/CoO catalysts.
2. With the MoO₃ concentration held within the range of $\approx$ 12-16 weight % the HDN activity generally increases as the NiO and CoO concentrations are increased from $\approx$ 1.3% to $\approx$ 3.7% to $\approx$ 6%. For HDS no significant trends are evident as a function of promoter concentration.
3. Nickel molybdate catalysts show higher activity for HDN than the analogous cobalt molybdate catalysts.
4. The activity of the various MoO₃/Al₂O₃ catalysts for HDS does not differ significantly as a function of either NiO or CoO promoter.

TABLE 37. HYDROTREATING¹ OF SRC-II FUEL OIL BLEND² WITH ALUMINA SUPPORTED CATALYSTS³

Catalyst % Metal Oxides <u>MoO₃/NiO³</u>	Cat No.	SA ⁴ m ² /g	PV ⁴ ml/g	Run	%HDN	%HDS	(HDO) ⁵	%H	%C	-----Wt.% Off at Temp. °F----- (Sim. Dist. ASTM D-2887)				
										IBP/5	10/30	50	70/90	95/FBP
Filtrol HPC-40 15% MoO ₃ /4% NiO on γ-alumina		251	0.64	(Av of 3 runs)	88 ±2	94 ±0.4	91 ±0.03	10.14 ±0.07	89.37 ±0.09	170/217	268/386	436	493/594	654/761
Filtrol HPC-6B 15% MoO ₃ /4% CoO on γ-alumina		230	0.59	II-98	75	94	(75) ⁵	9.90	88.88	261/318	350/412	464	519/624	678/800
<u>% Metal Oxides</u> <u>MoO₃/NiO</u>														
16.5/6.6	1029-63-1	180	0.55	I-130	84	94	(84) ⁵	10.60	88.63	168/211	232/360	429	486/595	661/810
16.5/4.2	1029-63-2	193	0.59	I-131	78	93	(89) ⁵	10.14	89.24	168/213	242/369	432	491/605	666/793
16.1/1.5	1029-63-3	206	0.65	II-133	73	94	(79) ⁵	9.99	88.98	168/213	240/370	433	491/603	666/805
<u>MoO₃/CoO</u>														
16.7/5.5	1029-63-4	181	0.51	II-134	65	95	(88) ⁵	10.06	89.16	168/211	235/371	433	495/610	669/812
16.7/3.7	1029-63-5	188	0.54	II-135	71	95	(--) ⁶	9.99	89.98	168/211	235/369	431	490/598	661/786
15.9/1.3	1029-63-6	200	0.55	I-132	60	96	(89) ⁵	10.16	89.08	168/211	236/375	435	495/607	667/792

¹ Standard Test Conditions: temperature, 750°F; pressure, 1,000 psig; LHSV, 1 ml/ml-hr; H₂ flow rate, 5,000 SCF/bbl; time on line after presulfiding and equilibration, 24 hrs.

² Elemental Analyses PAMCO, Ft. Lewis, Washington: %C, 86.59; %H, 8.54; %N, 0.90; %O, 3.69; %S, 0.26.

Sim Dist., ASTM D 2887, Filtrol: IPB/5 10/30 50 70/90 95/FBP
286/348 366/426 469 513/642 699/844

³ Kaiser SA alumina. Filtrol alumina proprietary.

⁴ Measured with Micromeritics Digisorb 2500 surface area and pore volume analyzer in desorption mode.

⁵ Oxygen calculated by difference.

⁶ %HDO > 100.

TABLE 38. HYDROTREATING¹ OF SRC-II FUEL OIL BLEND² WITH ALUMINA SUPPORTED CATALYSTS³

Catalyst % Metal Oxides		SA ⁴ m ² /g	PV ⁴ ml/g	Run	%HDN	%HDS	(HDO) ⁵	%H	%C	-----Wt.% Off at Temp. °F----- (Sim. Dist. ASTM D-2887)				
MoO ₃ /NiO	Cat. No.									IBP/5	10/30	50	70/90	95/FBP
12.9/5.9	1001-29-4	230	0.63	11-102	82	98	(63)	10.53	87.93	170/214	248/374	437	494/601	664/787
12.9/3.7	1001-29-7	181	0.52	1-100	80	(72)	(100)	10.83	88.90	186/266	309/398	454	516/640	701/859
12.6/1.2	1001-31-1	218	0.59	1-111	80	(92) ⁶	---	---	---	---	---	---	---	---
MoO ₃ /CoO														
13.3/6.0	1001-29-1	208	0.60	11-100	79	(95) ⁶	---	---	---	---	---	---	---	---
13.0/3.7	1001-29-10	191	0.57	1-98	71	92	(99)	10.20	89.45	242/347 ⁸	347/412	464	520/626	680/812
13.0/1.3	1001-31-4	217	0.60	11-103	66	95	(91)	10.09	89.26	169/212	238/377	437	498/607	666/800
WO ₃ /NiO														
12.6/6.2	1001-37-1	222	0.65	11-101	56	93	(100)	10.14	89.48	172/218	272/394	445	500/606	665/785
13.5/3.7	1001-37-7	241	0.67	1-102	60	93	(79)	9.86	88.95	215/290	332/407	461	513/622	679/812
13.4/1.3	1001-37-13	240	0.67	1-112	55	86	(86)	10.13	88.88	172/235	306/402	464	527/661	720/847
WO ₃ /CoO														
13.4/6.6	1001-37-4	210	0.63	11-99	56	93	(100)	10.14	89.48	172/213	272/394	445	500/606	665/785
12.5/3.5	1001-37-10	228	0.64	1-113	50	90	(93)	9.62	89.61	170/234	332/407	449	508/622	680/818
13.9/1.3	1001-37-16	227	0.64	11-104	43	88	(63)	9.28	88.76	172/235	306/402	450	508/622	682/826

^{1,2} Same as Table 37.³ Kaiser/Condea = 80/20.^{4,5} Same as Table 37.⁶ Result obtained with Tennelec X-ray fluorescence sulfur analyzer⁷ 24 hour sample lost.⁸ Anomalous result.

TABLE 39. HYDROTREATING¹ OF SRC-II FUEL OIL BLEND² WITH ALUMINA SUPPORTED CATALYSTS³

Catalyst % Metal Oxides		SA ⁴ m ² /g	PV ⁴ ml/g	Run	%HDN	%HDS	(HDO) ⁵	%H	%C	-----Wt.% Off at Temp. °F----- (Sim. Dist. ASTM D-2887)				
MoO ₃ /NiO	Cat. No.									IBP/5	10/30	50	70/90	95/FBP
12.9/6.1	1001-29-5	205	0.56	I-108	83	79	(70)	10.36	88.31	169/214	247/375	437	496/606	667/803
12.1/3.7	1001-29-8	192	0.56	II-94	82	88	(96)	10.94	88.72	213/284	325/402	455	512/618	673/810
12.2/1.3	1001-31-2	228	0.60	II-105	80	96	(100)	10.60	89.34	169/215	259/383	438	497/604	663/783
<u>MoO₃/CoO</u>														
12.9/6.3	1001-29-2	214	0.61	I-106	75	89	(80)	10.72	88.27	169/212	239/373	435	495/601	665/798
12.4/3.8	1001-29-11	196	0.58	II-92	72	94	(100)	10.16	89.66	272/330	358/419	468	524/628	682/807
12.2/1.3	1001-31-5	222	0.61	I-109	62	96	(96)	10.07	89.40	169/214	255/387	439	500/611	668/797
<u>WO₃/NiO</u>														
14.6/5.9	1001-37-2	195	0.56	I-105	---	---	---	---	---	---	---	---	---	---
15.4/3.9	1001-37-8	201	0.59	II-96	52	91	(84)	9.80	89.14	291/352	387/433	477	530/638	691/814
14.0/1.3	1001-37-14	211	0.61	II-106	52	(68)	(65)	10.14	88.02	170/230	291/400	456	512/623	680/807
<u>WO₃/CoO</u>														
14.6/6.6	1001-37-5	195	0.57	I-107	45	92	(100)	9.82	90.03	170/232	282/397	446	504/612	668/792
13.9/4.1	1001-37-11	199	0.60	II-93	50	84	(83)	9.68	90.03	273/324	357/419	470	525/633	691/828
14.4/1.2	1001-37-17	205	0.61	I-110	45	89	(88)	9.51	89.50	171/234	288/398	450	508/622	680/819

^{1,2} Same as Table 37.³ Kaiser/Condea = 23/77.^{4,5} Same as Table 37.⁶ Pressure dropped during run and no 24 hour point could be obtained.

The next two Tables (40,41) show the results obtained when alumina supported MoO_3/NiO and MoO_3/CoO catalysts are further promoted with P_2O_5 and TiO_2 . The P_2O_5 promoted MoO_3/NiO catalysts show the best HDN and HDS results of any of the exploratory catalysts. The TiO_2 promoted catalysts show relatively poor HDN activity, but satisfactory HDS activity.

The results for the last series of MoO_3/NiO loaded, supported catalysts, with the additional promoters MnO and ZnO are shown in Table 42. This Table also contains the results for a $\text{MoO}_3/\text{NiO}/\text{ZnO}$ catalyst loaded on a Kaiser alumina/silica-alumina (1/1) support. All of these catalysts, with the exception of one $\text{MoO}_3/\text{NiO}/\text{ZnO}$ catalyst, show relatively poor HDN activity and satisfactory HDS activity.

The fact that the most active exploratory catalysts are those supported on 100% Kaiser alumina with $\approx 3\%$ P_2O_5 could be rationalized either in terms of a promotional effect due to phosphorus, or in terms of the physical properties of the two aluminas after metals loading. Both types of alumina catalysts, with or without P_2O_5 , show losses in surface area and pore volume after metals loading, but relatively little change in pore size distribution (see Table 43 for typical examples). Therefore, the increase in HDN activity appears to be related to some sort of promotional effect due to phosphorus.

The activity of the best catalyst, Filtrnl HPC-40, may be related to the relatively high surface area and pore volume of the finished catalyst as well as the pore size distribution, which shows a relatively high % of pore volume distribution in the 100-300 Å radius range.

b. Silica-Alumina Supported Catalysts

Three series of silica-alumina supported catalysts were prepared. Sample 1013-45-1 was difficult to extrude, and the "as is" extrudates had very poor crush strength, so it was compounded with 10% Condea alumina, after metals impregnation; to improve the physical properties of the catalyst extrudates.

The hydrotreating testing results (Tables 44,45) show less HDN and HDS activity for the third series of silica-alumina supported catalysts formulated with 10% Condea alumina. The surface areas and pore volumes of the finished catalysts are lowest in this series. For example (Table 43), the 14.2% $\text{MoO}_3/5.3\%$ NiO impregnated catalyst has SA and PV values of 64 m^2/g and 0.24 ml/g respectively.

TABLE 40. HYDROTREATING¹ OF SRC-II FUEL OIL BLEND² WITH ALUMINA + P₂O₅ SUPPORTED CATALYSTS³

Catalyst		SA ⁴ m ² /g	PV ⁴ ml/g	Run	%HDN	%HDS	(HDO) ⁵	%H	%C	-----Wt.% Off at Temp. °F----- (Sim. Dist. ASTM D-2887)				
% Metal Oxides MoO ₃ /NiO	Cat. No.									IBP/5	10/30	50	70/90	95/FBP
10.3/6.2	1001-257-2	169	0.58	I-114	85	96	(97)	10.72	89.00	169/214	257/383	437	496/604	663/780
10.7/3.9	1001-269-1	188	0.60	I-116	81	95	(91)	9.91	89.56	171/217	270/393	448	513/648	706/843
11.5/1.5	1001-271-1	180	0.60	I-115	85	94	(--) ⁶	10.88	88.98	168/213	244/375	435	493/600	662/785
<u>%MoO₃/%CoO</u>														
10.4/5.8	1001-257-3	157	0.52	II-108	62	96	(84)	10.04	89.01	168/213	257/389	440	502/613	669/805
11.3/3.4	1001-269-2	-- ⁷	-- ⁷	II-109	75	91	(93)	10.07	89.40	169/214	258/380	436	498/612	673/812
11.6/1.2	1001-271-2	168	0.56	I-117	74	94	(85)	10.15	89.03	168/212	242/382	438	499/608	667/795

^{1,2} Same as Table 37.³ 100% Kaiser SA promoted with 3% P₂O₅.^{4,5} Same as Table 37.⁶ HDO > 100.⁷ Sample lost.

TABLE 41. HYDROTREATING¹ OF SRC-II FUEL OIL BLEND² WITH ALUMINA + TITANIA SUPPORTED CATALYSTS³

Catalyst % Metal Oxides		SA ⁴ m ² /g	PV ⁴ ml/g	Run	%FDN	%HCS	(%HDO) ⁵	%H	%C	-----Wt.% Off at Temp.°F----- (Sim. Dist. ASTM D2887)				
<u>MoO₃/NiO</u>	Cat. No.									<u>IBP/5</u>	<u>10/30</u>	<u>50</u>	<u>70/90</u>	<u>95/FBP</u>
12.4/6.4	1001-29-6	197	0.54	I-137	74	93	(65)	10.26	88.21	153/213	238/370	434	493/610	670/813
12.6/3.9	1001-29-9	197	0.58	I-138	82	95	(53)	10.86	87.23	153/212	233/364	430	488/597	658/778
12.1/1.4	1001-31-3	228	0.65	I-139	62	94	(63)	10.35	87.93	153/214	247/379	436	493/604	665/786
<u>MoO₃/CoO</u>														
12.8/6.4	1001-29-3	229	0.65	I-140	59	87	(85)	10.16	88.87	168/211	234/373	434	495/608	667/792
13.0/4.2	1001-31-6	197	0.59	I-141	59	92	(87)	10.48	88.65	168/211	235/374	435	494/606	666/785
12.3/1.4	1001-29-12	221	0.61	II-136	72	88	(89)	10.17	89.14	168/196	231/366	431	492/606	667/805

^{1,2} Same as Table 37.³ Kaiser/Condea Aluminas 80/20 - 11 wt.% TiO₂.^{4,5} Same as Table 37.

TABLE 42. HYDROTREATING¹ OF SRC-II FUEL OIL BLEND² WITH KAISER ALUMINA SUPPORTED CATALYSTS

Catalyst Wt.% Metal Oxide <u>MoO₃/NiO/MnO</u>	Cat. No.	SA ³ m ² /g	PV ⁴ ml/g	Run	%HDN	%HDS	(%HDO) ⁵	%H	%C	-----Wt.% Off at Temp. °F----- (Sim. Dist. ASTM D2887)				
										IBP/5	10/30	50	70/90	95/FBP
13.5/3.2/1.7	1029-99-4	168	0.62	I-156	70	94	(84)	10.42	88.67	170/214	243/381	440	501/600	661/782
13.9/3.2/2.7	1029-99-3	169	0.61	I-152	62	96	(78)	10.63	88.17	134/194	229/364	428	484/598	660/784
<u>MoO₃/NiO/ZnO</u>														
14.1/3.3/3.1	1029-99-2	170	0.60	II-144	83	95	(64)	10.62	87.85	133/192	225/362	426	486/599	661/797
13.7/3.2/4.0	1029-99-1	144	0.56	II-143	76	96	(76)	10.35	88.52	136/196	237/363	425	481/587	650/775
12.2/3.7/3.6 ⁶	1030-69-1	164	0.75	I-160	65	90	(90)	10.01	89.26	176/223	274/394	441	496/606	667/808

^{1,2} Same as Table 37.^{3,4} Same as Table 37.⁵ Oxygen calculated by difference.⁶ Support: Kaiser alumina, 50 wt.%; silica-alumina, 50 wt.%.

TABLE 43. PHYSICAL PROPERTIES OF HYDROTREATING CATALYSTS AND % HYDRODENITROGENATION AND HYDRODESULFURIZATION*

Catalyst	SA ¹ m ² /g	PV ¹ ml/g	Pore Volume Distribution (%) ¹						Wt. %	
			-----Radius Range (Å)-----						HDN	HDS
			0-25	25-50	50-100	100-150	150-200	200-300		
Filtrol HPC-40: 15% MoO ₃ ; 4% NiO on γ-alumina	251	0.64	14.1	29.4	38.9	10.1	3.8	3.7	88 ± 2	94 ± 0.4
Kaiser SA	253	0.83	9.3	41.6	38.1	6.4	1.8	2.3	--	--
Kaiser SA: 16.5% MoO ₃ ; 6.6% NiO	196	0.61	15.5	38.0	35.4	6.3	2.5	2.1	84	94
Kaiser SA: 10.3% MoO ₃ ; 6.2% NiO; 3% P ₂ O ₅	169	0.58	9.6	38.2	39.7	7.6	2.7	2.2	85	96
Kaiser SA/Condea = 80/20	268	0.77	15.2	45.9	31.4	4.4	1.7	1.5	--	--
Kaiser SA/Condea = 80/20: 12.9% MoO ₃ ; 5.9% NiO	230	0.63	16.6	47.3	29.4	3.9	1.5	1.8	82	(98)
Kaiser SA/Condea = 80/20 + 11% TiO ₂	260	0.72	15.5	45.3	31.5	3.7	1.5	1.5	--	--
Kaiser SA/Condea = 80/20 + 11% TiO ₂ ; 12.4% MoO ₃ ; 6.4% NiO	197	0.54	15.9	46	30.2	4.4	1.7	1.8	74	93

*Table continued on the next page.

TABLE 43. PHYSICAL PROPERTIES OF HYDROTREATING CATALYSTS AND % HYDRODENITROGENATION AND HYDRODESULFURIZATION - Continued

Catalyst	SA ¹ m ² /g	PV ¹ ml/g	Pore Volume Distribution (%) ¹						--Wt.%--	
			-----Radius Range (Å)-----						HDN	HDS
Silica-Alumina (896-159-1) ^{2a}	246	0.52	10-25	25-50	50-100	100-150	150-200	200-300	--	--
Silica-Alumina (896-159-1) ³ 10% MoO ₃ ; 6.5% NiO	129	0.27	42.6	44.9	11.5	0.7	0.1	0.2	80	93
Silica-Alumina (896-199-3) ^{2a}	354	0.44	70.3	28.7	0.7	0.2	0.0	0.1	--	--
Silica-Alumina (896-199-3) ³ 11.0% MoO ₃ ; 5.9% NiO	149	0.23	64.6	33.9	0.8	0.0	0.3	0.3	80	96
Silica-Alumina (1013-45-1) ^{2b} + 10% Condea Alumina ⁴	169	0.45	13.3	33.0	45.7	5.4	1.4	1.3	--	--
Silica-Alumina (1013-45-1) ³ + 10% Condea Alumina ⁴ : 14.2% MoO ₃ ; 5.3% NiO	64	0.24	9.5	29.9	49.7	7.2	1.8	1.9	63	89

¹ Measured with Micromeritics Digisorb 2500 SA and PV analyzer in desorption mode.² Catalyst support: a = SiO₂, 52%; Al₂O₃, 47%. b = SiO₂, 61%; Al₂O₃, 39%.³ Finished catalyst.⁴ 10% Condea Alumina added as binder.

TABLE 44. HYDROTREATING¹ OF SRC-II FUEL OIL BLEND² WITH SILICA-ALUMINA SUPPORTED CATALYSTS^{3,4}

Catalyst		SA ⁵ m ² /g	PV ⁶ ml/g	Run	%HDN	%HDS	(HDO) ⁷	%H	%C	-----Wt. % Off at Temp. °F)----- (Sim. Dist. ASTM D2887)				
% Metal Oxides	Cat. No.									IEP/5	10/30	50	70/90	95/FBP
<u>MoO₃/NiO³</u>														
10.1/6.5	1029-39-1	125	0.25	II-119	80	93	(74)	9.87	88.97	169/213	270/394	443	501/608	667/794
11.3/3.6	1029-19-1	113	0.27	I-121	71	94	(86)	10.03	89.17	170/225	283/398	449	503/611	668/796
11.4/1.2	1029-21-1	111	0.30	II-114	77	95	(91)	10.26	89.16	171/222	276/396	447	502/609	667/792
<u>MoO₃/CoO³</u>														
10.2/6.0	1029-39-2	127	0.28	II-120	(79) ⁸	95	(64)	9.82	88.66	168/217	271/389	438	497/599	658/764
11.3/4.3	1029-19-2	104	0.29	I-122	62	94	(73)	9.68	88.96	168/228	276/394	442	504/614	669/798
12.1/1.2	1029-41-1	140	0.33	II-122	63	-- ⁹	-- ⁹	--- ⁹	--- ⁹	--- ⁹	--- ⁹	--- ⁹	--- ⁹	--- ⁹
<u>MoO₃/NiO⁴</u>														
11.0/5.9	1029-23-1	135	0.18	II-118	80	96	(92)	10.13	89.38	169/218	270/394	443	499/605	666/792
10.5/4.1	1029-25-1	134	0.19	II-124	72	90	(86)	10.22	88.99	169/226	281/396	448	503/612	669/791
10.5/1.6	1029-27-1	137	0.20	II-126	77	93	90	9.76	89.64	163/217	271/394	443	501/609	666/775
<u>MoO₃/CoO⁴</u>														
11.0/5.0	1029-31-2	145	0.17	II-116	67	95	(86)	9.89	89.29	168/222	274/392	441	502/608	666/787
10.6/3.5	1029-25-2	139	0.17	II-125	61	92	(99)	9.97	89.63	168/220	275/393	441	502/607	666/783
10.8/1.3	1029-27-2	132	0.17	II-127	71	91	(90)	10.15	89.20	168/216	266/389	439	501/609	667/805

^{1,2} Same as Table 37.³ Support 896-159-1. SiO₂, 52%; Al₂O₃, 47%.⁴ Support 896-199-3. SiO₂, 52%; Al₂O₃, 47%.⁵ B.E.T. single point surface area.⁶ Alcohol pore volume.⁷ Oxygen determined by difference.⁸ 24 hr. point suspect H₂ flow had to be shut during run.⁹ Sample lost.

TABLE 45. HYDROTREATING¹ OF SRC-II FUEL OIL BLEND² WITH SILICA-ALUMINA SUPPORTED CATALYSTS³

% Metal Oxides		SA ⁴ m ² /g	PV ⁵ ml/g	Run	%HDN	%HDS	(%HDO) ⁶	%H	%C	-----Wt. % Off at Temp. °F----- (Sim. Dist. ASTM D 2887)				
MoO ₃ / NiO	Cat. No.									IBP/5	10/30	50	70/90	95/FBP
14.2/5.3	1028-85-1	64	0.24	I-142	63	89	(71)	10.08	88.48	169/220	283/395	443	497/607	665/768
10.5/3.6	1028-79-1	101	0.32	I-133	63	86	(78)	10.22	88.57	171/230	290/397	447	502/616	675/818
11.3/1.0	1028-81-1	120	0.37	I-135	68	92	(66)	10.23	88.22	173/231	289/398	450	508/625	682/825
<u>MoO₃/CoO</u>														
13.5/5.1	1028-85-2	71	0.25	II-137	35	86	(58)	9.49	88.32	171/268	322/401	450	504/616	668/770
10.5/3.7	1028-79-2	121	0.42	I-134	67	89	(62)	10.19	88.06	172/232	292/397	447	502/616	674/818
10.9/1.3	1028-31-2	117	0.40	I-136	53	91	(60)	9.83	88.24	168/227	277/393	441	500/614	672/813

^{1,2} Same as Table 37.³ Support 1013-45-1; SiO₂, 61%, Al₂O₃, 39%. Compounded with 10% Condea alumina as binder.^{4,5} Same as Table 37.⁶ Oxygen determined by difference.

The other two series of silica-alumina catalysts, prepared from supports 896-159-1 and 896-199-3, afford very similar activity results. However, the maximum HDN activity after 24 hours for these catalysts is only 80% compared to 85% for the best alumina supported exploratory catalyst. The HDS results are rather similar (= 95% HDS) for both silica-alumina and alumina types of supported catalysts.

Finally the best silica-alumina support (896-159-1) and metals combination MoO_3/NiO was loaded with a series of additional promoters (MnO , ZnO , P_2O_5) and activity tested (Table 46). The results show no definitive improvement in HDN, and about the same activity for HDS. The relatively poorer activity of the silica-alumina supported catalysts could be caused by the greater acidity of such materials (22). 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 supports tested had the highest percentage of small radii pores (Table 43), coking would be expected to be a significant factor in plugging these pores and deactivating the catalyst.

c. SMM Supported Catalysts

New hydrotreating catalysts prepared from cobalt and nickel exchanged and metal-substituted SMM metal as discussed previously, with or without molybdenum, were evaluated. The results are presented in Tables 47 and 48. The first series of Ni and Co-exchanged and substituted catalysts (Table 47) was evaluated as is, either with or without molybdenum. The activity of the cobalt and nickel exchanged and substituted materials was relatively low, ranging from 11 to 29% HDN, without molybdenum. Impregnation of the nickel exchanged and substituted SMM's with molybdenum increased the HDN to 57 and 43%, respectively. HDS also increased with molybdenum impregnation, and values of 85 and 80%, respectively, for these two most active catalysts were observed.

In order to improve the activity of the best Ni-substituted, molybdenum impregnated catalyst, a second series of Ni-Mo-SMM catalysts was made up with various atomic ratios of Ni/Mo. These catalysts were compounded with various percentages of Kaiser SA alumina to improve their porosity. The results (Table 48) indicate some improvement in both HDN and HDS activity for catalysts with effective atomic Ni/Mo ratios in the range of 0.49 to 0.62 (based on calculations which indicate 16.9% of the total Ni atoms lie in edge unit cells) compounded with 33 wt.% alumina. These catalysts showed 60 and 62% HDN, respectively.

TABLE 46. HYDROTREATING¹ OF SRC-II FUEL OIL BLEND² WITH SILICA-ALUMINA³ SUPPORTED CATALYSTS

Catalyst Wt.% Metal Oxides		SA ⁴ m ² /g	PV ⁵ ml/g	Run	%HDN	%HDS	(%HDO) ⁶	%H	%C	-----Wt. % Off at Temp. °F----- (Sim. Dist. ASTM D2887)				
MoO ₃ /NiO/MnO	Cat. No.									IBP/5	10/30	50	70/90	95/FBP
11.3/3.6/0	1029-19-1	113	C.27	I-121	71	94	(86)	10.03	89.17	170/226	283/398	449	503/611	668/796
9.9/3.5/1.5	1030-61-1	98	C.41	I-149	71	94	(69)	10.39	88.16	136/206	267/388	433	485/592	654/771
9.3/3.4/3.6	1030-53-1	103	C.38	II-141	(24) ⁷	(88) ⁷	(55)	(9.21) ⁷	88.41	159/276	334/406	461	512/648	710/858
<u>MoO₃/NiO/ZnO</u>														
8.4/3.2/2.8	1030-53-3	107	C.41	II-140	69	91	(55)	10.25	87.80	135/203	267/388	435	489/600	660/781
8.9/3.2/6.1	1030-53-4	89	C.31	I-148	68	92	(73)	10.21	88.48	144/211	271/390	438	493/606	664/793
<u>MoO₃/NiO/P₂O₅</u>														
8.9/4.1/3.3	1030-61-3	107	C.43	I-150	48	95	(55)	9.87	87.96	141/249	214/394	443	495/606	662/774
8.8/4.2/6.1	1030-61-2	109	C.37	II-142	65	95	(72)	10.22	88.39	144/217	280/391	438	493/605	663/789

^{1,2} Same as Table 37.³ SiO₂, 52%; Al₂O₃, 47%. Support 896-159-1.^{4,5} Same as Table 37.⁶ Oxygen determined by difference.⁷ Results appear anomalously low.

TABLE 47. HYDROTREATING¹ OF SRC-II FUEL OIL BLEND² WITH SMM EXCHANGED AND SUBSTITUTED SUPPORTED CATALYSTS

Catalyst ³	Cat. No.	SA m ² /g	PV ml/g	Run	%HDN	%HDS	(% HDO) ⁴	%H	%C	-----Wt. % Off at Temp. °F----- (Sim Dist. ASTM D2887)				
										IBP/5	10/30	50	70/90	95/FBP
Co Exch. SMM 2.0% Co	1001-60-2	129	0.12	II-110	11	29	--	8.75	85.70	271/351	369/429	472	513/625	684/813
Co. Subst. SMM 9.3% Co	1026-7-1	172	0.33	II-111	26	57	(24)	8.93	87.46	214/340	365/425	470	514/625	681/798
Co Exch. SMM 1.2% Co, 4.6% Mo	1028-43-1	58	0.12	II-117	37	81	(38)	9.32	87.75	172/283	344/408	461	510/620	677/802
Co Subst. SMM 9.2% Co, 9.3% Mo	1025-7-2	37	0.14	I-119	32	74	(7)	9.04	86.81	174/306	353/416	467	514/628	686/815
Ni Exch. SMM 2.6% Ni	1028-27-3	122	0.12	II-112	15	39	(1)	9.07	86.32	227/347	369/429	473	515/625	681/803
Ni Subst. SMM 14.5% Ni	1028-31-2	217	0.20	I-118	29	73	(7)	8.80	87.05	193/330	364/425	470	514/627	686/820
Ni Exch. SMM 1.6% Ni, 4.5% Mo	1028-27-2	14	0.15	II-128	57	85	(56)	9.88	88.06	174/259	323/406	460	510/625	686/832
Ni Subst. SMM 12.8% Ni, 3.4% Mo	1028-37-1	193	0.19	I-120	43	80	(8)	9.04	86.81	175/292	350/414	464	509/617	672/799
Ni Subst. SMM 12.2% Ni, 6.4% Mo	1028-37-2	103	0.14	II-113	27	71	(46)	9.51	87.71	187/322	361/422	468	512/622	677/792

^{1,2} Same as Table 37.³ Wt.% metal.⁴ Oxygen by difference.

TABLE 48. HYDROTREATING¹ OF SRC-II FUEL OIL BLEND² WITH Mo-IMPREGNATED, Ni-SUBSTITUTEDSMM COMPOUNDED WITH KAISER SA ALUMINA

Catalyst	Cat. No.	SA m ² /g	PV ml/g	Run	%HDN	%HDS	(% HDO) ³	%H	%C	IBP/5	-----Wt. % Off at Temp. °F----- (Sim Dist. ASTM D2887)			
											10/30	50	70/90	95/FBP
13.2 wt.% Ni, 6.3 wt.% Mo Ni/Mo at. eff. 0.58 ⁴	1028-43-2	116	0.13	II-129	35	74	(58)	9.78	88.00	179/311	354/414	464	510/626	687/813
8.9 wt.% Ni, 5.0 wt.% Mo Ni/Mo at. eff. 0.49 ⁴ Comp. with 33% Alumina	1028-47-1	245	0.41	I-125	60	87	(25)	9.66	87.14	169/228	290/398	449	503/616	675/809
4.5 wt.% Ni, 2.8 wt.% Mo Ni/Mo at. eff. 0.45 ⁴ Comp. with 67% Alumina	1028-47-2	295	0.84	I-126	36	85	(53)	9.60	88.04	173/265	325/405	458	509/626	685/815
13.1 wt.% Ni, 5.8 wt.% Mo Ni/Mo at. eff. 0.64 ⁴	1028-49-1	137	0.15	II-130	49	89	(73)	9.82	88.67	178/281	341/409	461	509/624	684/815
8.9 wt.% Ni, 4.1 wt.% Mo Ni/Mo at. eff. 0.62 ⁴ Comp. with 33 wt.% Alumina	1028-51-2	256	0.36	II-131	62	86	(61)	9.78	88.38	183/229	288/398	449	503/617	675/802
4.8 wt.% Ni, 2.3 wt.% Mo Ni/Mo at. eff. 0.58 ⁴ Comp. with 67 wt.% Alumina	1028-51-1	284	0.73	I-127	32	74	(65)	9.26	88.75	189/303	347/412	463	510/622	678/798
13.2 wt.% Ni, 4.0 wt.% Mo Ni/Mo at. eff. 0.92 ⁴	1028-53-1	179	0.15	I-128	47	78	(52)	9.38	88.30	176/286	346/412	463	510/623	681/806
10.0 wt.% Ni, 3.0 wt.% Mo Ni/Mo eff. 0.92 ⁴ Comp. with 33 wt.% Alumina	1028-73-1	260	0.35	II-132	49	89	(65)	9.80	88.40	172/257	320/402	453	507/622	683/815
4.9 wt.% Ni, 1.8 wt.% Mo Ni/Mo at. eff. 0.75 ⁴ Comp. with 67 wt.% Alumina	1028-73-2	293	0.53	I-129	38	74	(35)	9.38	87.57	173/269	330/405	459	510/626	685/815

^{1,2} Same as Table 37.³ Oxygen determined by difference.⁴ Based on calculation showing 16.9% of total Ni atoms lie in edge unit cells.

The relatively poorer activity of the various SMM supported catalysts may be a consequence of the smaller pore volume and generally smaller surface area of these catalysts as well as the larger pore volume distribution in the small 10-25Å pore volume radius range (Table 49). The most active catalyst for HDN (Run II-131, Table 50) had the greatest SA and PV values, and the highest percentage of larger radius range pore volume distribution (Table 49).

The activity data for the complete series of metal substituted SMM catalysts, impregnated with MoO_3 , and compounded with 33 wt.% Kaiser SA alumina to improve their porosity, is shown in Table 50. The results indicate maximum HDN activity of 60-62 % with MoO_3 on Ni-substituted SMM, and maximum HDS of 91-92% with MoO_3 on Co-substituted SMM. The HDN results are significantly poorer than those observed for the best MoO_3/NiO catalysts on γ -alumina (85-88%), but the HDS results are only moderately lower than the best results with the same MoO_3/NiO catalysts on γ -alumina (94-96%).

TABLE 49. PHYSICAL PROPERTIES OF Ni-and-CO SUBSTITUTED and EXCHANGED SMM HYDROTREATING CATALYSTS

<u>Catalyst</u> ¹	<u>SA</u> ² <u>m²/g</u>	<u>PV</u> ² <u>ml/g</u>	<u>Pore Volume Distribution (%)</u> ² <u>-----Radius Range (Å)-----</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>
Ni-Subst. SMM (II-131, 8.9% Ni, 4.1% Mo, 33% γ-Alumina)	253	0.43	41.7	35.4	16.1	3.8	1.5	1.5
Ni-Subst. SMM (I-118, 14.5% Ni)	217	0.20	96.0	3.0	0.7	0.0	0.2	0.0
Ni-Subst. SMM (I-120, 12.8% Ni, 3.4% Mo)	193	0.19	88.4	7.5	2.0	1.0	0.5	0.6
Ni-Subst. SMM (II-113, 12.2% Ni, 6.4% Mo)	103	0.14	72.9	21.3	2.4	1.6	1.0	0.8
Co-Subst. SMM (II-111, 9.2% Co)	172 170	0.33 0.32	(26.1) ³ (24.4)	(61.3) ³ (64.5)	(12.2) ³ (10.7)	0.2 0.3	0.0 0.1	0.1 0.1
Ni-Exch. SMM (II-112, 2.57% Ni)	122	0.12	93.3	2.8	2.3	0.5	0.7	0.3
Co-Exch SMM (II-110, 2.0% Co)	111	0.11	87.6	5.6	4	1.7	0.4	0.7

¹ Wt. %.² Measured with Micromeritics Digisorb 2500 SA and PV analyzer in desorption mode.³ Results seemed anomalous. PSD measurements were repeated.

TABLE 50. HYDROTREATING¹ OF SRC-II FUEL OIL BLEND² WITH METAL SUBSTITUTED SMM- γ -ALUMINA SUPPORTED CATALYSTS³

Catalyst ⁴	Cat. No.	SA M ² /g	PV ml/g	Run	%HDN	%HDS	(%HDO) ⁵	%H	%C	IBP/5	-----Wt.% off at Temp. °F----- (Sim. Dist. ASTM D2287)			
											10/30	50	70/90	95/FBP
3.9 wt.% Ni, 5.0 wt.% Mo Ni/Mo at. eff. 0.49	1028-47-1	245	0.41	I-125	60	87	(25)	9.66	87.14	169/228	290/398	449	503/616	675/809
3.9 wt.% Ni 4.1 wt.% Mo Ni/Mo at. eff. 0.62	1028-51-2	256	0.36	II-131	62	86	(61)	9.78	88.38	183/229	288/398	449	503/617	675/802
8.9 wt.% Co, 7.5 wt.% Mo Co/Mo at. eff. 0.29	1030-19-1	171	0.39	I-144	51	92	(61)	9.82	88.28	134/202	262/385	433	489/597	661/791
5.0 wt.% Co, 3.9 wt.% Mo Co/Mo at. eff. 0.27	1030-27-1	200	0.43	III-146	47	91	(72)	9.56	38.87	135/216	272/391	438	496/611	668/800
3.4 wt.% Fe, 3.6 wt.% Mo Fe/Mo at. eff. 0.28	1030-31-1	186	0.43	I-145	28	76	(35)	9.33	37.55	164/308	342/402	452	502/617	675/797
4.5 wt.% Fe, 1.6 wt.% Mo Fe/Mo at. eff. 0.18	1030-33-1	193	0.52	III-148	27	68	(9)	9.16	36.71	187/320	354/408	457	504/623	689/847
5.7 wt.% Mn, 3.0 wt.% Mo Mn/Mo at. eff. 0.20	1030-35-1	192	0.40	I-147	27	62	(-) ⁶	9.19	86.04	191/321	354/411	460	506/630	689/830
4.5 wt.% Mn, 3.1 wt.% Mo Mn/Mo at. eff. 0.41	1030-37-1	185	0.42	II-139	39	68	(11)	9.20	86.88	163/308	344/404	456	504/617	669/773

^{1,2} Same as Table 37.³ 67 wt.% M-SMM, 33 wt.% alumina.⁴ Only metal atoms on edge unit cells assumed to be effective in activating Mo. See Appendix C.⁵ Oxygen calculated by difference.⁶ Sum of C, H, N, S greater than 100%. Analyses error.

V. CONCLUSIONS

A. Cracking Catalysts

The FCC activity testing of SRC-II Fuel Oil Blend, hydrotreated to 11.0 wt.% hydrogen, with 65 cracking catalysts containing exchanged Y-zeolites, and SMM active components, and varied binder components, indicates that corrected conversion of 430°F+ material and gasoline yield increase as a function of the rare earth concentration of the Y-zeolite when the matrix binder is held constant. A second major factor, which affects conversion and gasoline yield, is related to the matrix binder composition, and pore volume distribution in the final catalyst. With the hydrotreated SRC-II corrected conversions of 430°F+ feed of 68-75 wt.%, C₅-EP gasoline product distribution of ~ 50 wt.%, and coke makes of 4-9 wt.% were obtained at 900°F with catalysts composed of broad pore volume distribution matrix binder components and active Y-zeolites. The conversions increase linearly as the percent rare earth oxide content of the catalysts increases; however, gasoline and coke make may deviate somewhat, both positively and negatively, according to the composition of the catalyst and the nature of the exchanged zeolite. Y-zeolites, in the same matrix, which are heavily ammonia exchanged are more selective but less active than those which are highly rare earth exchanged.

Several of the catalysts developed in this project are as good or better than the best commercially available catalysts in terms of activity and/or selectivity. However, the microactivity test used in this work is primarily a screening test and cannot be expected to simulate catalytic cracking refinery operations closely. Therefore, a logical extension of the present contract would be to scale-up the best of the newly developed FCC catalysts to semi-commercial production in order to obtain large quantities of such catalysts for further testing. Additional testing of these most promising newly developed catalysts should be carried out in a pilot plant unit capable of producing larger quantities of products. This would lead to the production of sufficient quantities of product to establish the quality of motor gasoline, diesel fuel, jet fuel, and burning oils. The present program could not produce enough material to prepare such specification products.

Another area which could be studied more intensively in an extended contract is the effect of process variables such as temperature, pressure, space velocity, etc., on product yields and quality. This experimental data could be organized into a computer model capable of representing all data, and interpolating and extrapolating it effectively into process parameters which could be used to optimize the economics of coal liquid refining to usable products for scaled-up refinery type operations.

When the same catalysts were tested at 900°F on the unhydrotreated SRC-II Fuel Oil Blend (8.7 wt.% H, 0.92 wt.% N), conversion and gasoline in the product were much lower (37-39 wt.% and 18-20 wt.%, respectively) and coke make was significantly higher (8-14 wt.%). Such low conversions and gasoline yields, and high coke makes are consistent with the aromatic and heterocyclic nature of the unhydrotreated SRC-II Fuel Oil Blend. Similar results were observed with commercial catalysts. Therefore, it appears that coal oil distillates will have to be hydrogenated to some extent to produce a reasonable catalytic cracking feed. Another extension of the present program could be a combined hydrogenation-cracking study to determine optimum economics of coal liquids processing to gasoline and distillates.

B. Hydrocracking Catalysts

Hydrocracking activity testing was carried out with the three series of bi-functional catalysts containing low-sodium cracking bases such as hydrogen and rare earth exchanged ultrastable Y-zeolites, and exchanged or metal substituted SMM's containing Group VIb and/or Group VIII hydrogenating metal components. Some of the above catalysts exhibited about the same conversion and gasoline make as the commercial baseline prototype catalyst-ultrastable Y-zeolite (85 wt.%), alumina (15 wt.%) and Pd (0.5 wt.%). Corrected conversions of 430°F+ of $\approx$ 50 wt.%, and C₅-430°F gasoline yields of $\approx$ 35 wt.% (after correction for 15 wt.% gasoline in the original feed) were obtained with combinations of rare earth exchanged US-Y/NH₄-US-Y/alumina = 1.9/3.8/1 loaded with MoO₃/CoO or MoO₃/NiO with or without addition of Pd or Pt. It is significant that the expensive noble metals Pd and Pt do not appear to be necessary to impart reasonable activity and selectivity to these catalysts.

As in cracking testing, the hydrocracking testing was short term screening testing. In order to confirm the results obtained in this work, long-term, larger scale testing should be carried out.

C. Hydrotreating Catalysts

Hydrotreating catalyst testing, carried out on SRC-II Fuel Oil Blend at: 750°F; 1000 psig; LHSV, 1 ml/ml-hr; and H₂ flow rate, 5,000 SCF/bbl, with a series of exploratory catalysts containing different metals loading and support properties, indicates that none of the exploratory catalysts tested are quite as good as the commercial Filtrol HPC-40 for HDN (85% maximum vs. 88% for HPC-40). The HDS results are similar for the best exploratory and commercial catalysts (94-96%). 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 does not differ significantly as a function of either NiO or CoO promoter. Catalysts prepared on silica-alumina supports appear to deactivate to a greater extent than similar catalysts prepared on alumina supports. The apparent relatively rapid deactivation could be 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.

A series of nickel and cobalt molybdate catalysts promoted with P₂O₅ on 100% Kaiser SA alumina was prepared and tested, and the results were compared with those obtained with catalysts prepared on 100% Kaiser SA. The results indicate that the 100% Kaiser SA alumina catalysts promoted with ~ 3% P₂O₅ appear to be generally more active for HDN than the unpromoted catalysts. Again, the HDS results are similar. Since pore size distributions, surface areas, and pore volumes are similar, the increase in HDN activity appears to be related to some sort of promotional effect due to phosphorus.

A series of Kaiser alumina supported catalysts with MoO₃/NiO and the additional known activators ZnO and MnO was tested to determine whether or not an additional promotional effect would be exhibited. The results indicate that these catalysts are not as active for HDN (62-83%) as either the commercial baseline catalyst Filtrol HPC-40 (15% MoO₃/4% NiO on γ-alumina) (88% HDN), or the 100% Kaiser SA catalysts promoted with P₂O₅ reported previously (81-85% HDN) after 24 hours activity testing. The HDS results for the three-component catalysts, 94-96%, were similar to those reported for Filtrol's HPC-40, 95%, and those reported for nickel molybdate catalysts on 100% Kaiser SA, promoted with P₂O₅ (94-96%).

A series of the most active MoO₃/NiO silica-alumina catalysts was impregnated with the additional promoters P₂O₅, ZnO, and MnO and activity tested. The results indicate that these catalysts are not as active for HDN (48-71%) as the best previously tested MoO₃/NiO silica-alumina catalysts (72-80% HDN). HDS results (88-95%) are similar to those obtained previously (90-96%).

A series of metal substituted SMM catalysts, impregnated with MoO_3 , and compounded with 33 wt.% Kaiser SA alumina to improve their porosity, was activity tested. The results indicate maximum HDN activity of 60-62% with MoO_3 on Ni-substituted SMM, and maximum HDS of 91-92% with MoO_3 on Co-substituted SMM. The HDN results are significantly poorer than those observed for the best MoO_3/NiO catalysts on γ -alumina (85-88%), but the HDS results are only moderately lower than the best results with the same MoO_3/NiO catalysts on γ -alumina (94-96%).

The relatively poorer activity of the various SMM supported catalysts may be a consequence of the smaller pore volume and generally smaller surface area of these catalysts as well as the larger pore volume distribution in the small, 10-25 Å, pore volume radius range. The most active catalyst for HDN had the greatest SA and PV values, and the highest percentage of larger radius range pore volume distribution.

Since no improvements over commercial hydrotreating catalysts were observed in this work, we have no recommendations to make concerning avenues of work to be pursued in order to develop such superior catalysts.

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APPENDIX A. Filtrol Catalyst Division Facilities and Procedures

1. Facilities

The proposed work was carried out in Filtrol's Research and Development Laboratory in Vernon, California. This laboratory occupies remodeled space adjacent to the catalyst-manufacturing operation of Filtrol. It shares the analytical services and test facilities with the production organization.

The laboratory employs forty persons with Bachelor of Science degrees or higher and occupies 15,000 square feet of space. It is equipped with the following instruments and test equipment that are necessary to characterize and test catalysts.

a. Pilot Plant and Manufacturing

The Filtrol Research Center has a well-equipped pilot plant containing a variety of mixing/mulling equipment, extrusion equipment, and spray dryers for intermediate scale-up of catalysts developed in the laboratory. In addition, full size manufacturing facilities are available should the need arise to prepare large scale batches of catalysts for major testing purposes.

b. Catalyst Testing Facilities

(1) Hydrotreating Testing Units

Filtrol currently has six operational 100-300 ml downflow fixed catalyst bed reactors (two of which are partially owned by DOE). Several of these units are capable of being run over a wide range of temperatures, space velocities, hydrogen flow rates and pressures up to 3000 psig. These units could be used to hydrotreat coal liquids to varying degrees of HDN, HDS and hydrogenation in order to prepare catalytic cracking feeds.

(2) Microactivity Cracking Units

Filtrol currently possesses six MAT units (two of which are DOE property) coupled with two systems which utilize three gas chromatographs and a laboratory computer (partially DOE owned) to carry out cracking testing, and analysis of the gas and liquid cracking products distribution for screening of FCC catalysts.

(3) FCC Pilot Plant

Filtrol has a fully operational FCC Pilot Plant capable of simulating commercial FCC operations with optimized catalysts under a complete range of process conditions. Such processing would lead to the production of sufficient quantities of product to establish the quality of motor gasoline, diesel fuel, jet fuel, and burning oils.

C. Analyses and Characterization of Catalysts, Intermediates, and Refined Products

(1) Chemical Analysis of Catalysts

Standard procedures are used to determine or verify the chemical composition of catalysts. The procedures in use are atomic absorption, X-ray fluorescence, and wet chemical methods.

(2) Physical Evaluation of Catalysts and Intermediates

Standard procedures are used to measure physical characteristics of materials:

- a. Micro pore size distribution, surface area and pore volume (Micromeritics Digisorb 2500).
- b. Macro pore size distribution, surface area and pore volume (Quantachrome Mercury Intrusion Porosimeter).
- c. Particle size analysis (Micromeritics Sedigraph Particle Size Analyzer).
- d. Thermal Properties (Dupont 500 series Thermogravimetric and Differential Thermal Analyzer).
- e. Crystal Characteristics (X-ray Diffraction Analyzer).
- f. Attrition Index (In-House Test).
- g. Crush Strength (In-House Test).
- h. Misc. Properties (Computerized Infrared Analyzer).

(3) Analysis of Product

- a. Octane Analysis (Foxboro Octane Analyzer).
- b. Micro-distillations (Perkin-Elmer Micro Still).
- c. Nitrogen analysis (High Speed macro Kjehldahl nitrogen analyzer - Property of DOE).
- d. Sulfur Analyzer (Tennelec X-ray Fluorescence Sulfur Analyzer).
- e. ASTM D-2887 simulated distillation (Hewlett-Packard simulated distillation program on H-P 3353D Computer with H-P 5880 A Gas Chromatograph - Property of DOE).

2. Procedures

Standard reactor volumes, catalyst charges, throughput, run duration, sampling procedures, run conditions, etc., are described in great detail in the body of the report (Sections IV A, and IV B). For each type of testing: hydrotreating, hydrocracking, and cracking a single standard test procedure was used. A standard feed (described in detail in Appendix B) was used for each type of testing.

APPENDIX B. SRC-II Fuel Oil Blend Feedstock

The basic coal liquid feed was an SRC-II Fuel Oil Blend from the PAMCO pilot plant at Ft. Lewis, Washington. This material was used as received as feed for the hydrotreating testing. A few gallons of this material was distilled to reduce the content of the lower boiling fraction. This distillation residue was used as feed for cracking testing.

A second basic feed was hydrotreated PAMCO SRC-II Fuel Oil Blend, which was produced for us under a DOE sponsored subcontract to UOP. This material was used as received as feed for the hydrocracking testing program. A few gallons of this hydrotreated material was also distilled to reduce the content of the lower boiling fraction. This distillation residue was used as feed for cracking testing.

The laboratory analyses and boiling point distributions of these various SRC-II Fuel Oil Blend Feeds are presented in Table 1. Additional more detailed analyses of the basic unhydrotreated, as received, PAMCO SRC-II Fuel Oil Blend are shown in Table 2. Additional more detailed distillation data are presented in Table 3. Average molar properties of this blend, calculated from analytical, molecular weight, and proton nuclear magnetic resonance (Figure 1) data, by a modified Brown-Ladner structural characterization procedure (Tables 4, 5), are given in Table 6 (1,2). Infrared functional group analysis (3) indicates that most of the oxygen is present as phenolic OH, and that the nitrogen is present in the ratio of $\approx 60/40$ pyrrolic to pyridine like nitrogen. The ratio of aromatic carbon to total carbon, f_a , is calculated to be 0.63 by the Brown-Ladner ^1H NMR method. Carbon-13 NMR analysis affords a direct f_a measurement of 0.66, and shows the presence of relatively large C-OH adsorption, in the phenolic carbon region (148-158 ppm from TMS) (4).

Mass spectrometric analyses were carried out at 16 eV over the temperature range from 30-200°C. The results for representative scans at low temperature ($\approx 30^\circ\text{C}$) and high temperature (150-200°C) are shown in Table 7. At 30°C about 59% of the total ions may fall into series of possible types such as: phenols, naphthalenes, pyridines, biphenyls and benzenes. At 150 - 200°C $\approx 73\%$ of the ions may fall into the series: phenols, pyridines, biphenyls, anthracenes-phenanthrenes, pyrenes, naphthalenes, tetrahydro-quinolines, and benzenes. In the highest mass scan observed, series

TABLE 1. LABORATORY ANALYSES AND BOILING POINT DISTRIBUTIONS OF VARIOUS SRC-II

<u>Analyses</u>	<u>FUEL OIL BLEND FEEDS</u>			
	<u>As Received from PAMCO^a</u>	<u>As Received From UOP Distillation Residue^b</u>	<u>Hydrotreated by UOP^c</u>	<u>Hydrotreated by UOP Distillation Residue^d</u>
SP Gravity	1.00	1.01	0.93	0.9
° API @ 60°F	10.0	8.7	20.7	19.3
% Carbon	86.59	87.70	88.27	89.12
% Hydrogen	8.54	8.74	11.58	10.95
% Nitrogen	0.90	0.92	0.056	0.046
% Sulfur	0.26	0.27	0.03	0.026
% Oxygen	3.69	1.91	0.11	0.1
% Ash	0.02	0.007	0.001	0.001
B. P. Dist. ASTM D-2887				
<u>% OFF</u>	<u>°F</u>	<u>°F</u>	<u>°F</u>	<u>°F</u>
IDP	286	384	340	389
10	366	429	394	430
30	426	468	442	469
50	469	498	484	507
70	513	549	533	551
90	642	667	624	638
95	699	723	670	682
FBP	844	856	796	803

^a Used as feed for hydrotreating testing

^b Used as feed for cracking testing.

^c Used as feed for hydrocracking testing.

^d Used as feed for cracking testing

TABLE 2. LABORATORY ANALYSES
PAMCO SRC-II FUEL OIL BLEND^a

SP. GRAVITY 60/60°F	1.000	% PYRIDINE INSOLUBLES	0.02
°API @ 60°F	10.0	% CONRADSON CARBON	0.21
VISCOSITY @ 100°F, cSt	4.61	% ASH	0.02
@ 210°F, cSt	1.27	% WATER	TRACE
POUR POINT, °F	-55	% CARBON	86.59
FLASH POINT, °F ASTM D-93	165	% HYDROGEN	8.54
BTU/LB	17,620	% NITROGEN	0.90
COAL TAR ACID, g/100 ml	24.0	% SULFUR	0.26
VPO $\bar{M}_n$ MW in PYRIDINE ^b	160	% OXYGEN	3.69

^a 2.9/1 MID. DIST. HEAVY DIST. - 3/23/79 LOT FROM
POWHATAN No. 5 MINE COAL. Determined for a batch blend by PAMCO.

^b Determined at University of So. Calif. Chemical Eng. Dept.

TABLE 3. DISTILLATION PAMCO SRC-II FUEL OIL BLEND^a

<u>DISTILLATION:</u>	<u>ASTM D-1160</u>	<u>ASTM D-86</u>
Effective Pressure	3 mm Hg	ATM. mm Hg
	°F	°F
I.B.P.	---	336
5%	133	401
10%	142	413
20%	153	431
30%	163	448
40%	175	464
50%	187	483
60%	206	503
70%	225	527
80%	262	565
90%	348	657
95%	413	---
E.P.	462	700
RECOVERY, %	98	94
RESIDUE, %	2	5
LOST, %	0	1

(550°F
@ 76%)^a Determined for a batch blend at PAMCO.

FIGURE 1. ^1H NMR PAMCO SRC-II
FUEL OIL BLEND

TABLE 4. MODIFIED BROWN-LADNER EQUATIONS

$$f_a = \frac{\frac{C}{H} - \frac{H_{\alpha}^*}{x} - \frac{H_o^*}{y}}{\frac{C}{H}} = \text{FRACTION OF TOTAL CARBON WHICH IS AROMATIC CARBON}$$

$$\frac{H_{aru}}{C_{ar}} = \frac{\frac{H_{\alpha}^*}{x} + H_{ar}^* + \frac{O-OH}{H}}{\frac{C}{H} - \frac{H_{\alpha}^*}{x} - \frac{H_o^*}{y}} = \text{RATIO OF SUBSTITUTABLE AROMATIC EDGE ATOMS TO TOTAL AROMATIC ATOMS}$$

$$\sigma = \frac{\frac{H_{\alpha}^*}{x} + \frac{O}{H}}{H_{ar}^* + \frac{H_{\alpha}^*}{x} + \frac{O-OH}{H}} = \text{FRACTION OF THE AVAILABLE AROMATIC EDGE ATOMS OCCUPIED BY SUBSTITUENTS}$$

$$R_S = \sigma C_A \frac{H_{aru}}{C_{ar}} = \text{NUMBER OF SUBSTITUTED AROMATIC RING CARBONS}$$

$$n = \frac{H_o^*}{H_{\alpha}^*} + 1 = \text{NUMBER OF CARBON ATOMS PER SATURATED SUBSTITUENT}$$

$$C_A = \frac{f_a (C) (M)}{100} = \text{TOTAL NUMBER OF AROMATIC CARBON ATOMS}$$

$$R_A = C_A \left(\frac{1 - H_{aru}/C_{ar}}{2} \right) + 1 = \text{NUMBER OF AROMATIC RINGS}$$

TABLE 5. DEFINITIONS BROWN-LADNER EQUATIONS

C	=	MOLE % CARBON
H	=	MOLE % HYDROGEN
O	=	MOLE % OXYGEN
O _{OH}	=	MOLE % PHENOLIC OXYGEN
H _{ar} [*]	=	MOLE FRACTION AROMATIC HYDROGEN
H _α [*]	=	MOLE FRACTION HYDROGEN α TO AROMATIC RING
H _O [*]	=	MOLE FRACTION OF ALIPHATIC HYDROGEN NOT α RING
x	=	AVERAGE RATIO OF HYDROGEN TO CARBON ON CARBONS α TO ARYL RING
y	=	AVERAGE RATIO OF HYDROGEN TO CARBON ON ALIPHATIC CARBONS NOT α TO ARYL RING

ASSUMPTIONS: ALL OXYGEN IS ATTACHED TO ARYL RINGS IN EITHER PHENOL OR ARYL ETHER GROUPS. ALL PHENOLIC HYDROGENS FOUND BY THE TMS DERIVATIVE METHOD ARE UNDER THE ARYL ABSORPTION: $x = y = 2$.

TABLE 6. AVERAGE MOLAR PROPERTIES OF PAMCO
SRC-II FUEL OIL BLEND

MOLECULAR FORMULA $C_{11.54} H_{13.56} N_{0.1} O_{0.37} S_{0.01}$

MOLECULAR WEIGHT 160

H_{ar}^* 0.343

H_{α}^* 0.365

H_O^* 0.265

H_{OH}^* 0.027

f_a 0.630

H_{aru}/C_{ar} 1.03

σ 0.38

C_A 7.3

R_S 2.8

R_A 0.9

n 1.7

H/C 1.18

TABLE 7. LOW VOLTAGE (16 ev) MASS SPECTROMETRIC ANALYSIS OF SRC-II FUEL OIL BLEND

		30°C	150-200°C
<u>Series</u>	<u>Possible Types</u>	<u>Ion %</u>	<u>Ion %</u>
	<u>Aromatic Hydrocarbons</u>		
C_nH_{2n-6}	Benzenes	3.4	6.0
C_nH_{2n-12}	Naphthalenes	17.3	6.0
C_nH_{2n-14}	Biphenyls-Acenaphthenes	8.7	10.8
C_nH_{2n-18}	Anthracenes-Phenanthrenes	--	9.5
C_nH_{2n-22}	Pyrenes	--	7.5
	<u>Oxygenated Aromatics</u>		
$C_nH_{2n-6}O$	Phenols	17.8	15.7
	<u>Nitrogenated Aromatics</u>		
$C_nH_{2n-5}N$	Pyridines	11.6	12.1
C_nH_{2n-7}	Tetrahydroquinolines	--	5.6

FIG. 2 - HPLC OF SRC-II FUEL OIL BLEND AND HYDROTREATED SRC-II FUEL OIL BLEND

COLUMNS: 2- μ - Porasil
4 mm x 30 cm

SOLVENT: n-Hexane

FLOW RATE: 1.0 ml/min.

FIG. 3 - HPLC OF SRC-II FUEL OIL BLEND AND HYDRO-TREATED SRC-II FUEL OIL BLEND WITH BACKFLUSH

of possible aromatic types such as benzantracenes, and benzopyrenes may have been present.

Liquid chromatography was carried out with a Waters Associates high pressure liquid chromatograph (HPLC) system. Hexane was used as eluent, and two μ -Porasil columns (30 cm x 4 mm) were used to separate the SRC-II Fuel Oil Blend into saturates, alkylbenzenes, aromatics, and polars (Figure 2). Polar materials such as phenols and pyridines are retained on the column. Crude refractive index peak area data for the eluted fraction, not corrected for refractive index sensitivities, show roughly: 7% saturates, 22% alkylbenzenes, 32% naphthalene derivatives, and 10% anthracene-phenanthrene and larger aromatic derivatives. Similar results obtained by use of a μ -Bondapak-NH₂ column, from which the polars can be eluted by backflushing, (Figure 3) indicate ~ 32% polars in the starting SRC-II, and < 4% polars in the hydrotreated product.

References to Appendix B.

1. J. K. Brown and W. R. Ladner, Fuel, 39, 87 (1960).
2. I. Schwager, P. A. Farmanian, and T. F. Yen in "Analytical Chemistry of Liquid Fuel Sources", P. C. Uden, S. Siggia, and H. B. Jensen, eds., Adv. Chem. Ser., 170, Am Chem. Soc., Wash., D.C., Chapt. 5 (1978).
3. I. Schwager and T. F. Yen, Anal. Chem., 51, 569 (1979).
4. K. D. Bartle, T. G. Martin, and D. F. Williams, Chem. & Ind., 1975, 313.

APPENDIX C. Light Gas Analysis - Cat.-Cracking
of Hydrotreated and Unhydrotreated SRC-II Fuel Oil Blend

The results of the light gas analyses for the cracking runs reported under Task VI in Tables 10-12, 14-16, 19-21, and 22-30 are reported in this Appendix in Tables 10B-12B, 14B-16B, 19B-21B, and 22B-30B.

TABLE 10B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLENDWITH EXCHANGED Y-ZEOLITE-ALUMINA FCC CATALYSTS^a

FCC Catalyst	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
FS-30	900	8.8	0.08	0.08	0.12	0.28	1.06	1.79	2.76	1.14	0.53	0.62	0.47
	1000	14.4	0.25	0.47	0.40	0.72	1.74	3.20	3.88	1.65	0.88	0.85	0.63
Y-NH ₃ (100°C)(normal)	900	4.5	0.68	0.06	0.06	0.11	0.22	1.20	1.04	0.45	0.68	0.39	0.27
	1000	0.95	2.02	0.33	0.20	0.42	0.44	2.64	1.87	0.72	1.38	0.87	0.61
" (≈ 1μ)	900	5.5	0.11	0.04	0.06	0.11	0.28	1.30	1.37	0.63	0.87	0.49	0.35
	1000	9.4	0.75	0.28	0.21	0.36	0.45	2.70	1.95	0.46	1.22	1.02	0.76
" -Ni (normal)	900	5.0	0.12	0.05	0.06	0.10	0.25	1.24	1.22	0.61	0.83	0.42	0.28
	1000	12.7	0.81	0.35	0.25	0.47	0.60	3.59	2.68	0.91	1.82	1.19	0.83
" -Ni (≈ 1μ)	900	4.3	0.34	0.04	0.05	0.10	0.16	1.12	0.93	0.47	0.78	0.39	0.26
	1000	9.9	0.75	0.30	0.21	0.40	0.43	2.90	1.97	0.79	1.42	0.89	0.63
" -Co (normal)	900	6.1	0.13	0.05	0.06	0.13	0.29	1.41	1.52	0.73	1.02	0.54	0.36
	1000	10.6	0.34	0.28	0.21	0.35	0.47	2.82	2.20	0.93	1.62	0.99	0.72
" -Co (≈ 1μ)	900	6.5	0.11	0.05	0.07	0.15	0.34	1.47	1.65	0.79	1.00	0.57	0.40
	1000	11.4	1.32	0.25	0.19	0.38	0.57	3.10	2.46	1.05	1.67	1.05	0.73

^a Table continued next page.

TABLE 10B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF HYDROTREATED SFC-II FUEL OIL BLENDWITH EXCHANGED Y-ZEOLITE-ALUMINA FCC CATALYSTS - Continued

FCC Catalyst	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
" -R (normal)	900	6.2	0.09	0.06	0.07	0.18	0.47	1.60	1.67	0.65	0.72	0.47	0.32
	1000	13.0	0.32	0.34	0.25	0.47	0.78	3.37	3.05	1.17	1.72	1.07	0.77
" -R ($\approx 1\mu$)	900	6.5	0.11	0.05	0.07	0.13	0.38	1.60	1.72	0.77	0.96	0.52	0.35
	1000	13.3	0.60	0.30	0.23	0.43	0.73	3.35	3.05	1.31	1.90	1.17	0.85
" -R ₂ (normal)	900	8.5	0.11	0.13	0.11	0.20	0.58	1.84	2.24	1.02	1.25	0.68	0.46
	1000	13.4	0.35	0.34	0.27	0.47	0.91	3.40	3.14	1.33	1.75	1.06	0.77
" -R-Cr (normal)	900	6.3	0.14	0.06	0.07	0.14	0.34	1.46	1.64	0.74	0.93	0.53	0.36
	1000	11.3	0.30	0.28	0.23	0.42	0.78	3.07	2.74	0.82	1.14	1.06	0.80
" -R-Cr ($\approx 1\mu$)	900	6.4	0.13	0.11	0.09	0.16	0.46	1.48	1.75	0.74	0.86	0.48	0.32
	1000	12.4	0.72	0.34	0.24	0.42	0.72	3.25	2.85	1.13	1.70	1.06	0.74
" -R-Mn (normal)	900	5.5	0.11	0.06	0.72	0.14	0.39	1.39	1.50	0.57	0.67	0.42	0.28
	1000	12.1	0.43	0.34	0.27	0.44	0.80	3.24	2.90	0.84	1.23	1.17	0.86
" -R-Mn ($\approx 1\mu$)	900	6.3	0.12	0.06	0.72	0.13	0.39	1.51	1.64	0.75	0.93	0.51	0.34
	1000	12.7	0.54	0.28	0.21	0.39	0.66	3.28	2.86	1.22	1.84	1.12	0.81

TABLE 11B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND WITH
EXCHANGED US-Y-ZEOLITE-ALUMINA AND FCC CATALYSTS

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
US-Y	900	9.5	0.23	0.06	0.08	0.21	0.67	2.07	2.64	1.13	1.37	0.74	0.49
	1000	12.2	0.45	0.35	0.25	0.51	0.85	3.21	2.99	0.91	1.19	1.08	0.89
US-Y-Ni	900	8.5	1.11	0.07	0.07	0.22	0.53	1.92	2.37	0.95	1.16	0.71	0.48
	1000	11.9	2.72	0.37	0.23	0.55	0.79	2.78	2.97	1.01	1.51	0.97	0.68
US-Y-Co	900	9.7	0.22	0.06	0.09	0.24	0.77	2.00	2.82	1.16	1.34	0.71	0.50
	1000	12.8	1.08	0.36	0.27	0.57	1.08	3.29	3.30	1.08	1.10	1.03	0.75
US-Y-R	900	10.2	0.19	0.04	0.09	0.21	0.76	2.13	2.91	1.21	1.47	0.78	0.55
	1000	12.5	0.90	0.35	0.27	0.53	1.02	3.25	3.22	1.04	1.05	0.99	0.73
US-Y-Cr	900	10.9	0.20	0.12	0.10	0.27	0.91	2.22	3.26	1.27	1.50	0.78	0.52
	1000	12.5	0.40	0.55	0.33	0.63	1.24	2.99	3.13	1.11	0.92	0.80	0.60
US-Y-Mn	900	10.3	0.17	0.07	0.09	0.24	0.78	2.18	2.99	1.18	1.43	0.78	0.52
	1000	13.2	0.43	0.37	0.27	0.56	1.00	3.32	3.35	1.08	1.21	1.15	0.93
FS-30	900	8.8	0.08	0.08	0.12	0.28	1.06	1.79	2.76	1.14	0.53	0.62	0.47
	1000	14.4	0.25	0.47	0.40	0.72	1.74	3.20	3.88	1.65	0.88	0.85	0.63
Y-NN ₃ (100°C)-R ₂	900	8.5	0.11	0.13	0.11	0.20	0.58	1.84	2.24	1.02	1.25	0.68	0.46
	1000	13.4	0.35	0.34	0.27	0.47	0.91	3.40	3.14	1.33	1.75	1.06	0.77

TABLE 12B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND WITHNH₄SMM FCC CATALYSTS

Sample No:	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
NH ₄ SMM (S/A = 2.16)	900	5.8	0.25	0.03	0.11	0.16	0.36	1.59	1.76	0.73	1.13	0.58	0.39
	1000	11.7	0.17	0.45	0.34	0.48	0.68	3.21	2.33	0.54	1.69	1.13	0.84
NH ₄ SMM (S/A = 2.28)	900	3.9	1.01	0.03	0.07	0.11	0.19	1.13	0.94	0.18	0.51	0.43	0.31
	1000	7.6	0.79	0.31	0.24	0.35	0.32	2.20	1.18	0.27	1.31	0.81	0.61
NH ₄ SMM (S/A = 2.45)	900	5.7	0.27	0.02	0.08	0.11	0.28	1.32	1.44	0.66	0.95	0.49	0.33
	1000	9.7	0.30	0.28	0.23	0.31	0.45	2.32	1.63	0.37	1.26	0.88	0.68
NH ₄ SMM (S/A = 2.53)	900	5.2	1.01	0.03	0.10	0.13	0.23	1.38	1.13	0.43	0.94	0.49	0.36
	1000	8.6	1.18	0.36	0.30	0.38	0.35	2.41	1.26	0.52	1.67	0.77	0.55
NH ₄ SMM (S/A = 2.67)	900	5.4	0.41	0.04	0.07	0.10	0.19	1.24	1.17	0.65	1.05	0.51	0.34
	1000	7.6	0.16	0.28	0.23	0.36	0.36	2.50	0.35	0.34	1.49	0.99	0.75
FS-30	900	8.8	0.08	0.08	0.12	0.28	1.06	1.79	2.76	1.14	0.53	0.62	0.47
	1000	14.4	0.25	0.47	0.40	0.72	1.74	3.20	3.88	1.65	0.88	0.85	0.63
Y-NN ₃ (100°C)-R ₂	900	8.5	0.11	0.13	0.11	0.20	0.58	1.84	2.24	1.02	1.25	0.68	0.46
	1000	13.4	0.35	0.34	0.27	0.47	0.91	3.40	3.14	1.33	1.75	1.06	0.77

TABLE 14B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND WITHNH₄SMM-MATRIX FCC CATALYSTS

Sample No.	Temp. °F	-----Weight %-----											
		<u>C₁-C₄</u>	<u>H₂</u>	<u>CH₄</u>	<u>C₂H₆</u>	<u>C₂H₄</u>	<u>C₃H₈</u>	<u>C₃H₆</u>	<u>iso-C₄H₁₀</u>	<u>n-C₄H₁₀</u>	<u>1-C₄H₈+ iso-C₄H₈</u>	<u>tr-C₄H₈</u>	<u>cis-C₄H₈</u>
1001-11-2	900	6.8	0.25	0.03	0.11	0.16	0.36	1.59	1.76	0.73	1.13	0.58	0.39
	1000	11.7	0.17	0.45	0.34	0.48	0.68	3.21	2.33	0.54	1.69	1.13	0.84
1030-21-4	900	7.1	0.21	0.15	0.12	0.21	0.38	1.81	1.88	0.39	0.85	0.74	0.55
	1000	11.0	0.43	0.48	0.33	0.48	0.58	3.13	2.06	0.45	1.64	1.07	0.79
1030-21-3	900	6.9	0.13	0.03	0.10	0.16	0.41	1.68	1.89	0.37	0.92	0.77	0.57
	1000	11.5	0.40	0.41	0.30	0.49	0.53	3.41	2.06	0.41	1.87	1.16	0.87
1030-21-2	900	4.7	0.10	0.05	0.07	0.10	0.15	1.25	1.05	0.21	0.74	0.60	0.46
	1000	8.6	0.19	0.27	0.23	0.31	0.33	2.44	1.46	0.29	1.58	0.97	0.72
1030-21-1	900	5.1	0.10	0.07	0.09	0.15	0.33	1.51	0.57	0.30	0.87	0.71	0.53
	1000	10.5	0.32	0.36	0.28	0.45	0.45	3.13	1.78	0.36	1.80	1.10	0.83
1030-21-5	900	5.0	0.07	0.05	0.07	0.11	0.19	1.32	1.20	0.24	0.73	0.61	0.46
	1000	9.9	0.20	0.31	0.26	0.38	0.38	2.85	1.79	0.37	1.66	1.09	0.84

TABLE 15B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND WITH
ZEOLITE-NH₄SMM FCC CATALYSTS

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
1030-13-3	900	8.9	0.09	0.07	0.13	0.27	0.75	1.96	2.81	0.81	0.75	0.80	0.59
	1000	15.1	0.30	0.55	0.36	0.75	1.28	3.83	3.95	1.11	1.35	1.12	0.83
1030-13-1	900	9.7	0.17	0.16	0.13	0.31	0.80	2.00	2.92	0.90	0.80	0.89	0.76
	1000	14.9	0.22	0.47	0.36	0.75	1.34	3.64	4.17	1.22	1.21	1.03	0.74
1030-13-2	900	10.1	0.14	0.13	0.14	0.32	0.95	2.16	3.16	1.05	0.73	0.82	0.60
	1000	13.9	0.25	0.41	0.32	0.64	1.23	3.46	3.81	1.18	1.14	1.01	0.74
1030-13-5	900	9.5	0.11	0.15	0.15	0.33	1.16	1.90	3.16	1.14	0.54	0.60	0.44
	1000	15.4	0.28	0.40	0.32	0.70	1.33	3.88	4.10	1.32	1.28	1.20	0.90
1030-13-4	900	11.0	0.15	0.15	0.18	0.38	1.42	2.16	3.46	1.45	0.60	0.71	0.52
	1000	16.6	0.20	0.67	0.56	0.90	2.39	3.28	4.71	2.01	0.80	0.72	0.53
1030-17-1	900	12.8	0.14	0.20	0.22	0.48	1.95	2.20	4.14	1.86	0.56	0.66	0.49
	1000	16.8	0.28	0.64	0.54	0.93	2.34	3.45	4.67	1.98	0.88	0.79	0.59
1030-13-6	900	12.7	0.18	0.23	0.25	0.49	1.90	2.17	4.05	1.85	0.58	0.68	0.53
	1000	18.2	0.32	0.78	0.65	1.02	2.76	3.50	5.08	2.31	0.83	0.74	0.53

TABLE 16B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND WITH
REO.-EXCH.-Y-ZEOLITE-MATRIX FCC CATALYSTS^a

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso- C ₄ H ₁₀	n- C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr- C ₄ H ₈	cis- C ₄ H ₈
1025-25-105	900	6.2	0.09	0.06	0.07	0.18	0.47	1.60	1.67	0.65	0.72	0.47	0.32
	1000	13.0	0.32	0.34	0.25	0.47	0.78	3.37	3.05	1.17	1.72	1.07	0.77
1001-205-6	900	8.5	0.11	0.13	0.11	0.20	0.58	1.84	2.24	1.02	1.25	0.68	0.46
	1000	13.4	0.35	0.34	0.27	0.47	0.91	3.40	3.14	1.33	1.75	1.06	0.77
1030-17-2	900	8.1	0.07	0.12	0.11	0.23	0.72	1.84	2.30	0.81	0.65	0.78	0.58
	1000	10.0	0.24	0.40	0.33	0.54	1.11	3.12	0.56	1.12	1.01	1.02	0.76
1030-49-1	900	9.1	0.08	0.13	0.13	0.27	0.94	1.99	2.63	1.01	0.65	0.79	0.58
	1000	14.3	0.21	0.53	0.38	0.63	1.43	3.47	3.57	1.42	1.05	1.05	0.78
1030-51-2	900	6.7	0.07	0.03	0.08	0.18	0.44	1.66	1.84	0.38	0.81	0.71	0.53
	1000	11.2	0.25	0.38	0.29	0.48	0.52	3.38	1.89	0.42	1.85	1.16	0.88
1030-51-3	900	10.1	0.03	0.18	0.17	0.33	1.31	1.99	2.96	1.35	0.57	0.70	0.52
	1000	16.7	0.10	0.69	0.56	0.82	2.14	3.65	4.26	1.96	0.97	0.93	0.69
1030-51-4	900	9.7	0.05	0.15	0.13	0.32	1.21	1.95	2.94	1.23	0.56	0.71	0.52
	1000	15.0	0.11	0.40	0.36	0.74	1.87	3.34	4.1	1.73	0.90	0.89	0.66

^a Table continued on next page.

TABLE 168. LIGHT GAS ANALYSIS-CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND WITH
REO.-EXCH.-Y-ZEOLITE-MATRIX FCC CATALYSTS - Continued

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
1030-51-1	900	12.9	0.11	0.24	0.27	0.53	2.31	2.03	4.02	2.06	0.48	0.58	0.42
	1000	17.8	0.16	0.71	0.62	1.04	3.13	3.01	4.95	2.51	0.70	0.63	0.46
1030-13-6	900	12.7	0.18	0.23	0.25	0.49	1.90	2.17	4.05	1.85	0.58	0.68	0.53
	1000	18.2	0.32	0.78	0.65	1.02	2.76	3.50	5.08	2.31	0.83	0.74	0.53
1030-49-2	900	13.9	0.11	0.28	0.29	0.54	2.38	2.20	4.40	2.16	0.54	0.62	0.45
	1000	17.2	0.28	0.99	0.74	0.96	3.06	2.78	4.65	2.35	0.67	0.58	0.43
Filtrol FS-30	900	8.8	0.08	0.08	0.12	0.28	1.06	1.79	2.76	1.14	0.53	0.62	0.47
	1000	14.4	0.25	0.47	0.40	0.72	1.74	3.20	3.88	1.65	0.88	0.85	0.63
1030-73-1	900	12.4	0.12	0.22	0.21	0.46	1.77	2.26	3.93	1.71	0.61	0.70	0.51
	1000	16.6	0.23	0.65	0.51	0.91	2.43	3.31	4.70	2.02	0.82	0.71	0.53
1030-81-1	900	11.6	0.09	0.25	0.19	0.51	1.87	2.10	3.80	1.88	0.42	0.33	0.21
	1000	16.0	0.15	0.76	1.05	1.17	2.79	2.85	4.15	1.94	0.63	0.42	0.27
1030-81-2	900	15.1	0.09	0.55	0.26	0.61	2.74	2.06	4.62	2.50	0.72	0.59	0.47
	1000	17.1	0.13	1.14	0.53	1.05	3.80	2.58	4.66	2.35	0.50	0.29	0.24

TABLE 19B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND WITH
REO.-EXCH.-Y-ZEOLITE-NH₄SMM-MATRIX FCC CATALYSTS

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
1030-13-6	900	12.7	0.18	0.23	0.25	0.49	1.90	2.17	4.05	1.85	0.58	0.68	0.53
	1000	18.2	0.32	0.78	0.65	1.02	2.76	3.50	5.08	2.31	0.83	0.76	0.53
1030-59-3	900	12.4	0.09	0.20	0.19	0.51	2.14	1.91	4.17	1.81	0.51	0.56	0.41
	1000	16.7	0.20	0.52	0.45	0.93	2.33	3.55	4.68	1.93	0.91	0.83	0.62
1030-59-4	900	12.3	0.13	0.20	0.23	0.46	1.97	2.21	3.71	1.85	0.54	0.67	0.48
	1000	21.3	0.21	0.90	2.03	1.53	3.34	3.50	5.31	2.68	0.78	0.70	0.51
1030-59-5	900	11.5	0.07	0.13	0.16	0.41	1.62	2.17	3.55	1.59	0.58	0.73	0.53
	1000	16.6	0.14	0.48	0.43	0.86	2.24	3.56	4.52	2.01	0.91	0.90	0.66
1030-51-1	900	12.7	0.13	0.26	0.26	0.48	1.98	2.11	4.16	1.85	0.54	0.62	0.45
	1000	17.1	0.29	0.78	0.61	0.99	2.68	3.14	4.82	2.17	0.74	0.65	0.48
1030-59-2	900	13.0	0.10	0.21	0.24	0.50	2.13	2.15	4.18	2.01	0.53	0.63	0.46
	1000	17.3	0.17	0.69	0.58	0.97	2.81	3.16	4.83	2.33	0.73	0.65	0.48

TABLE 20B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND WITH
Cr-EXCHANGED US-Y ZEOLITE-MATRIX FCC CATALYSTS

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
1001-205-7	900	9.1	0.15	0.17	0.14	0.33	1.03	1.90	2.87	1.00	0.56	0.62	0.46
	1000	13.2	1.32	0.45	0.32	0.61	1.22	3.25	3.40	1.19	1.03	0.96	0.73
1030-65-2	900	10.1	0.09	0.10	0.11	0.32	1.00	2.16	3.30	0.98	0.71	0.79	0.57
	1000	15.4	0.24	0.40	0.31	0.75	1.42	3.93	4.20	1.21	1.26	1.09	0.80
1030-65-4	900	10.8	0.05	0.13	0.15	0.35	1.29	2.23	3.34	1.38	0.62	0.76	0.55
	1000	16.5	0.12	0.54	0.45	0.84	2.03	3.67	4.47	1.93	0.95	0.92	0.68
1030-65-3	900	11.5	0.03	0.15	0.19	0.38	1.55	2.22	3.44	1.58	0.60	0.75	0.55
	1000	13.9	0.14	0.27	0.23	0.57	1.05	3.71	3.63	1.00	1.31	1.18	0.87
1030-65-1	900	9.5	0.07	0.02	0.09	0.30	1.03	2.01	2.97	1.05	0.64	0.78	0.57
	1000	14.5	0.25	0.40	0.30	0.75	1.44	3.56	3.82	1.32	1.13	1.01	0.75
1030-23-1	900	10.5	0.11	0.16	0.12	0.34	1.13	2.17	3.32	1.16	0.67	0.78	0.57
	1000	15.6	0.27	0.48	0.37	0.81	1.65	3.65	4.35	1.51	1.08	0.96	0.71

TABLE 21B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF HYDROTREATED SRC-II FUEL OIL BLEND WITH
Cr-EXCHANGED US-Y ZEOLITE-NH₄SMM-MATRIX FCC CATALYSTS

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
1030-23-2	900	10.6	0.17	0.17	0.16	0.36	1.03	2.26	3.44	0.99	0.78	0.82	0.60
	1000	14.6	0.39	0.51	0.35	0.74	1.23	3.71	3.90	1.05	1.29	1.04	0.77
1030-23-4	900	10.6	0.12	0.18	0.13	0.35	0.98	2.30	3.42	0.97	0.81	0.85	0.62
	1000	15.3	0.27	0.42	0.31	0.75	1.27	3.93	4.15	1.12	1.36	1.12	0.83
1030-25-1	900	9.7	0.14	0.12	0.12	0.30	0.89	2.13	2.97	0.97	0.73	0.84	0.62
	1000	14.5	0.19	0.41	0.31	0.73	1.28	3.68	3.87	1.22	1.16	1.06	0.79
1030-25-2	900	9.2	0.09	0.12	0.10	0.27	0.74	2.11	2.85	0.76	0.80	0.85	0.63
	1000	14.4	0.21	0.36	0.27	0.65	1.04	3.85	3.72	0.56	1.44	1.20	0.90
1030-23-3	900	10.2	0.09	0.15	0.12	0.32	0.94	2.19	3.20	0.99	0.77	0.86	0.63
	1000	15.5	0.18	0.48	0.32	0.77	1.40	3.84	4.21	1.27	1.27	1.09	0.81

TABLE 22B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND
WITH EXCHANGED Y-ZEOLITE-ALUMINA FCC CATALYSTS^a

FCC Catalyst	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
FS-30	900	2.6	0.09	0.18	0.15	0.19	0.30	0.83	0.31	0.13	0.22	0.18	0.16
	1000	4.8	0.14	0.67	0.50	0.54	0.48	1.47	0.36	0.19	0.06	0.28	0.22
Y-NN ₃ (100°C)(normal)	900	3.0	0.30	0.27	0.21	0.26	0.13	1.13	0.15	0.09	0.31	0.26	0.21
	1000	5.1	0.47	0.90	0.56	0.62	0.29	1.54	0.15	0.11	0.40	0.29	0.23
" (≈ 1μ)	900	2.7	0.13	0.22	0.17	0.27	0.14	1.04	0.17	0.08	0.24	0.19	0.15
	1000	4.3	0.23	0.73	0.43	0.52	0.25	1.37	0.16	0.10	0.34	0.24	0.19
" -Ni (normal)	900	3.1	0.15	0.27	0.22	0.35	0.12	1.22	0.11	0.07	0.31	0.25	0.21
	1000	5.6	0.31	0.91	0.63	0.80	0.27	1.77	0.16	0.10	0.43	0.30	0.23
" -Ni (≈ 1μ)	900	2.6	0.20	0.28	0.21	0.27	0.14	1.01	0.14	0.07	0.07	0.20	0.17
	1000	5.0	0.42	0.89	0.53	0.62	0.29	1.57	0.17	0.10	0.38	0.26	0.20
" -Co (normal)	900	3.0	0.17	0.26	0.22	0.30	0.13	1.15	0.15	0.09	0.29	0.25	0.20
	1000	5.7	0.35	0.92	0.65	0.78	0.30	1.81	0.13	0.11	0.44	0.31	0.23
" -Co (≈ 1μ)	900	2.5	0.13	0.24	0.19	0.29	0.25	0.94	0.11	0.05	0.09	0.20	0.16
	1000	4.8	0.32	0.81	0.50	0.60	0.26	1.56	0.15	0.10	0.39	0.27	0.20

^a Table continued next page.

TABLE 22B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND
WITH EXCHANGED Y-ZEOLITE-ALUMINA FCC CATALYSTS - Continued

		-----Weight %-----												
FCC Catalyst		Temp. °F	C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
Y-NN ₃ -R	(normal)	900	1.9	0.10	0.20	0.21	0.28	0.07	0.64	0.07	0.05	0.17	0.12	0.10
		1000	4.9	0.25	0.79	0.47	0.65	0.25	1.61	0.18	0.10	0.39	0.27	0.21
" -R	(≈ 1μ)	900	3.3	0.15	0.28	0.22	0.33	0.35	1.09	0.18	0.09	0.31	0.25	0.19
		1000	5.3	0.33	0.92	0.65	0.72	0.34	1.70	0.24	0.15	0.07	0.29	0.22
" -R ₂	(normal)	900	3.1	0.14	0.24	0.20	0.36	0.12	1.26	0.15	0.07	0.29	0.23	0.18
		1000	5.7	0.32	0.87	0.60	0.82	0.30	1.85	0.23	0.13	0.38	0.33	0.25
" -R-Cr	(normal)	900	3.2	0.16	0.26	0.27	0.39	0.13	1.24	0.15	0.06	0.28	0.22	0.17
		1000	5.7	0.37	0.92	0.56	0.75	0.30	1.86	0.21	0.12	0.45	0.32	0.24
" -R-Cr	(≈ 1μ)	900	3.0	0.17	0.29	0.24	0.35	0.13	1.29	0.13	0.06	0.11	0.25	0.19
		1000	5.7	0.34	0.94	0.67	0.75	0.31	1.91	0.20	0.13	0.14	0.37	0.29
" -R-Mn	(normal)	900	3.1	0.13	0.29	0.20	0.32	0.13	1.18	0.18	0.08	0.29	0.23	0.18
		1000	5.8	0.32	0.93	0.65	0.79	0.31	1.80	0.21	0.12	0.44	0.31	0.24
" -R-Mn	(≈ 1μ)	900	3.3	0.16	0.28	0.29	0.38	0.15	1.26	0.16	0.08	0.30	0.24	0.19
		1000	5.3	0.34	1.01	0.71	0.80	0.34	1.94	0.24	0.14	0.50	0.35	0.28

TABLE 23B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND WITH
EXCHANGED US-Y-ZEO-ITE-ALUMINA FCC CATALYSTS

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
US-Y	900	3.5	0.14	0.30	0.32	0.47	0.17	1.30	0.19	0.08	0.28	0.22	0.17
	1000	5.2	0.34	0.89	0.53	0.69	0.31	1.58	0.22	0.12	0.39	0.26	0.20
US-Y-Ni	900	2.8	0.43	0.30	0.27	0.31	0.19	0.81	0.15	0.09	0.28	0.23	0.19
	1000	5.1	0.77	1.00	0.65	0.68	0.29	1.47	0.15	0.10	0.36	0.24	0.18
US-Y-Co	900	3.6	0.20	0.32	0.26	0.43	0.21	1.35	0.26	0.11	0.28	0.23	0.17
	1000	5.8	0.39	0.95	0.57	0.75	0.38	1.78	0.30	0.15	0.43	0.30	0.23
US-Y-R	900	3.7	0.17	0.35	0.32	0.46	0.21	1.32	0.25	0.11	0.29	0.24	0.19
	1000	5.7	0.32	1.12	0.59	0.76	0.40	1.80	0.31	0.16	0.05	0.29	0.22
US-Y-Cr	900	3.1	0.12	0.36	0.21	0.36	0.23	1.13	0.26	0.11	(0.06)	0.21	0.18
	1000	5.7	0.34	1.14	0.61	0.76	0.48	1.65	0.31	0.17	(0.05)	0.28	0.22
US-Y-Mn	900	3.5	0.16	0.34	0.32	0.41	0.28	1.13	0.24	0.11	0.26	0.20	0.16
	1000	6.2	0.37	1.17	0.72	0.82	0.48	1.84	0.32	0.18	(0.09)	0.33	0.25
FS-30	900	2.6	0.09	0.18	0.15	0.19	0.30	0.83	0.31	0.13	0.22	0.18	0.16
	1000	4.8	0.14	0.67	0.50	0.54	0.48	1.47	0.36	0.19	0.06	0.28	0.22
Y-NN ₃ (100°C)R ₂	900	3.1	0.14	0.24	0.20	0.36	0.12	1.26	0.15	0.07	0.29	0.23	0.18
	1000	5.7	0.32	0.87	0.60	0.82	0.30	1.85	0.23	0.13	0.38	0.33	0.25

TABLE 24B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND WITHNH₄SMM FCC CATALYSTS

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
NH ₄ SMM	900	2.0	0.11	0.14	0.13	0.11	0.11	0.70	0.12	0.07	0.24	0.19	0.16
S/A = 2.16	1000	3.7	0.20	0.60	0.49	0.41	0.25	1.24	0.12	0.08	(0.08)	0.24	0.19
NH ₄ SMM	900	1.1	0.43	0.26	0.07	0.07	0.06	0.35	0.04	0.02	0.10	0.07	0.06
S/A = 2.28	1000	2.1	0.59	0.41	0.29	0.22	0.10	0.63	0.03	0.05	0.17	0.12	0.10
NH ₄ SMM	900	1.3	0.24	0.15	0.09	0.09	0.07	0.47	0.08	0.04	0.13	0.09	0.08
S/A = 2.45	1000	3.2	0.26	0.50	0.36	0.32	0.24	0.95	0.10	0.07	0.28	0.18	0.15
NH ₄ SMM	900	1.2	0.29	0.14	0.11	0.09	0.10	0.41	0.06	0.02	0.12	0.08	0.07
S/A = 2.53	1000	2.9	0.32	0.52	0.37	0.30	0.19	0.85	0.09	0.05	0.24	0.14	0.11
NH ₄ SMM	900	0.9	0.12	0.11	0.13	0.08	0.04	0.31	0.04	0.02	0.03	0.07	0.06
S/A = 2.67	1000	2.0	0.13	0.38	0.25	0.20	0.12	0.67	0.04	0.04	0.04	0.12	0.11
FS-30	900	2.6	0.09	0.18	0.15	0.19	0.30	0.83	0.31	0.13	0.22	0.18	0.16
	1000	4.8	0.14	0.67	0.50	0.54	0.48	1.47	0.36	0.19	0.06	0.28	0.22
Y-NN ₃	900	3.1	0.14	0.24	0.20	0.36	0.12	1.26	0.15	0.07	0.29	0.23	0.18
(100°C)R ₂	1000	5.7	0.32	0.87	0.60	0.82	0.30	1.85	0.23	0.13	0.38	0.33	0.25

TABLE 25B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND WITHNH₄SMM-MATRIX FCC CATALYSTS

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
1001-11-2	900	2.0	0.11	0.14	0.13	0.11	0.11	0.70	0.12	0.07	0.24	0.19	0.16
	1000	3.7	0.20	0.60	0.49	0.41	0.25	1.24	0.12	0.05	0.08	0.24	0.19
1030-21-4	900	1.9	0.00	0.00	0.00	0.00	0.23	0.91	0.18	0.05	0.22	0.13	0.09
	1000	3.3	0.12	0.00	0.01	0.00	0.33	1.73	0.20	0.12	0.44	0.27	0.22
1030-21-3	900	1.7	0.03	0.00	0.00	0.00	0.13	0.89	0.12	0.05	0.21	0.15	0.12
	1000	3.6	0.11	0.11	0.52	0.00	0.28	1.64	0.16	0.05	0.16	0.26	0.21
1030-21-2	900	0.9	0.00	0.00	0.00	0.00	0.06	0.49	0.05	0.02	0.14	0.10	0.08
	1000	1.9	0.08	0.00	0.00	0.00	0.20	0.99	0.06	0.05	0.27	0.16	0.14
1030-21-1	900	1.4	0.00	0.00	0.00	0.00	0.10	0.76	0.10	0.05	0.19	0.13	0.11
	1000	3.1	0.14	0.00	0.51	0.00	0.23	1.38	0.11	0.05	0.35	0.22	0.18
1030-21-5	900	1.0	0.00	0.12	0.08	0.00	0.06	0.41	0.06	0.03	0.11	0.08	0.07
	1000	3.7	0.12	0.42	0.34	0.36	0.23	1.21	0.22	0.15	0.39	0.25	0.22

TABLE 26B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND WITHZEOLITE-NH₄SMM FCC CATALYSTS

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
1030-13-3	900	2.0	0.15	0.17	0.15	0.14	0.21	0.63	0.17	0.08	0.17	0.13	0.11
	1000	4.5	0.14	0.64	0.46	0.44	0.41	1.30	0.25	0.14	0.37	0.24	0.20
1030-13-1	900	1.4	0.00	0.00	0.00	0.00	0.16	0.68	0.17	0.08	0.15	0.11	0.08
	1000	4.2	0.04	0.65	0.51	0.00	0.35	1.46	0.26	0.15	0.37	0.25	0.20
1030-13-2	900	2.9	0.06	0.47	0.19	0.20	0.25	0.88	0.29	0.13	0.20	0.16	0.13
	1000	5.4	0.20	0.72	0.60	0.57	0.51	1.50	0.33	0.20	0.40	0.28	0.24
1030-13-5	900	2.6	0.13	0.30	0.20	0.20	0.27	0.77	0.29	0.13	0.18	0.14	0.12
	1000	5.3	0.18	0.70	0.52	0.52	0.43	1.52	0.41	0.24	0.44	0.31	0.25
1030-13-4	900	3.7	0.19	0.42	0.24	0.27	0.44	1.06	0.51	0.22	0.23	0.20	0.16
	1000	6.0	0.18	0.00	0.73	0.71	0.80	1.88	0.60	0.32	0.44	0.32	0.25
1030-17-1	900	3.4	0.19	0.40	0.22	0.22	0.44	0.90	0.49	0.22	0.21	0.18	0.14
	1000	5.4	0.25	0.00	0.65	0.60	0.73	1.67	0.52	0.29	0.42	0.30	0.23
1030-13-6	900	3.9	0.01	0.00	0.36	0.00	0.74	1.16	0.73	0.34	0.24	0.20	0.16
	1000	6.0	0.13	0.00	0.96	0.00	1.17	1.74	0.82	0.45	0.39	0.28	0.22

TABLE 27B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND WITH
REC.-EXCH.-Y-ZEOLITE-MATRIX FCC CATALYSTS^a

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
1025-25-105	900	1.9	0.10	0.20	0.21	0.28	0.07	0.64	0.07	0.05	0.17	0.12	0.10
	1000	4.9	0.25	0.79	0.47	0.65	0.25	1.61	0.18	0.10	0.39	0.27	0.21
1001-205-6	900	3.1	0.14	0.24	0.20	0.36	0.12	1.26	0.15	0.07	0.29	0.23	0.18
	1000	5.7	0.32	0.87	0.60	0.82	0.30	1.85	0.23	0.13	0.38	0.33	0.25
1030-17-2	900	2.6	0.07	0.33	0.15	0.26	0.19	0.95	0.16	0.06	0.08	0.20	0.17
	1000	5.1	0.22	0.85	0.58	0.73	0.36	1.67	0.20	0.11	0.07	0.32	0.25
1030-49-1	900	3.5	0.07	0.29	0.26	0.39	0.26	1.23	0.26	0.12	0.29	0.22	0.22
	1000	6.1	0.17	0.94	0.64	0.82	0.43	1.82	0.31	0.17	0.43	0.30	0.25
1030-51-2	900	2.3	0.05	0.21	0.21	0.22	0.12	0.89	0.13	0.06	0.22	0.15	0.14
	1000	4.2	0.10	0.66	0.42	0.47	0.23	1.43	0.13	0.08	0.38	0.24	0.19
1030-51-3	900	3.3	0.03	0.30	0.20	0.25	0.29	1.05	0.40	0.18	0.23	0.21	0.19
	1000	5.3	0.10	0.77	0.49	0.56	0.49	1.50	0.41	0.22	0.36	0.26	0.21
1030-51-4	900	3.3	0.03	0.50	0.19	0.26	0.36	0.95	0.38	0.17	0.20	0.16	0.15
	1000	5.5	0.07	0.83	0.52	0.63	0.57	1.56	0.43	0.23	0.34	0.23	0.20

^a Table continued next page.

TABLE 27B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND WITH
REO.-EXCH.-Y-ZEOLITE-MATRIX FCC CATALYSTS - Continued

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
1030-51-1	900	4.2	0.08	0.30	0.27	0.31	0.72	1.02	0.69	0.33	0.21	0.17	0.16
	1000	7.1	0.18	0.97	0.73	0.70	0.99	1.70	0.70	0.39	0.39	0.29	0.23
1030-39-2	900	3.9	0.01	0.00	0.36	0.00	0.74	1.16	0.73	0.34	0.24	0.20	0.16
	1000	6.0	0.13	0.00	0.96	0.00	1.17	1.74	0.82	0.45	0.39	0.28	0.22
1030-49-2	900	4.9	0.14	0.31	0.38	0.34	0.69	1.29	0.76	0.36	0.30	0.30	0.23
	1000	9.0	0.33	1.35	0.96	0.85	1.16	2.12	0.85	0.48	0.52	0.41	0.32
1030-73-1	900	3.4	0.18	0.64	0.36	0.34	0.45	0.69	0.32	0.16	0.19	0.14	0.14
	1000	7.2	0.24	0.83	1.27	0.73	0.69	1.54	0.69	0.38	0.46	0.31	0.25
1030-81-1	900	4.7	0.17	0.33	0.3	0.38	0.65	1.28	0.77	0.41	0.24	0.20	0.14
	1000	8.3	0.07	1.08	0.90	0.86	1.01	2.14	0.81	0.54	0.43	0.31	0.23
1030-81-2	900	7.7	0.19	0.58	0.62	0.65	1.25	1.85	1.31	0.61	0.32	0.31	0.24
	1000	10.3	0.13	1.57	1.23	1.02	1.66	1.97	1.22	0.71	0.39	0.29	0.21
Filtrol FS-30	900	2.6	0.09	0.18	0.15	0.19	0.30	0.83	0.31	0.13	0.22	0.18	0.16
	1000	4.8	0.14	0.67	0.50	0.54	0.48	1.47	0.36	0.19	(0.06)	0.28	0.22

TABLE 288. LIGHT GAS ANALYSIS-CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND WITH
REO-EXCH.-Y-ZEOLITE-NH₄SMM-MATRIX FCC CATALYSTS.

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr-C ₄ H ₈	cis-C ₄ H ₈
1030-13-6	900	3.9	0.01	0.00	0.36	0.00	0.74	1.16	0.73	0.34	0.24	0.20	0.16
	1000	6.0	0.13	0.00	0.96	0.00	1.17	1.74	0.82	0.45	0.39	0.28	0.22
1030-59-3	900	4.1	0.08	0.31	0.27	0.37	0.56	1.13	0.58	0.25	0.24	0.19	0.16
	1000	6.3	0.17	0.85	0.59	0.69	0.65	1.76	0.55	0.26	0.40	0.29	0.23
1030-59-4	900	4.1	0.17	0.29	0.28	0.31	0.65	1.04	0.67	0.30	0.22	0.18	0.16
	1000	7.5	0.22	1.15	0.84	0.78	0.90	1.83	0.69	0.36	0.42	0.31	0.24
1030-59-5	900	3.1	0.06	0.24	0.22	0.21	0.30	1.00	0.39	0.18	0.22	0.19	0.17
	1000	4.6	0.05	0.00	0.60	0.00	0.59	1.68	0.47	0.25	0.41	0.30	0.25
1030-59-1	900	4.9	0.11	0.36	0.36	0.40	0.61	1.38	0.72	0.28	0.25	0.29	0.20
	1000	8.3	0.21	1.26	0.93	0.83	1.01	1.93	0.79	0.42	0.46	0.35	0.29
1030-59-2	900	3.8	0.09	0.27	0.26	0.27	0.51	1.07	0.58	0.26	0.23	0.20	0.16
	1000	7.0	0.15	0.97	0.74	0.69	0.85	1.79	0.67	0.36	0.41	0.31	0.24

TABLE 29B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND WITHCr-EXCHANGED US-Y ZEOLITE-MATRIX FCC CATALYSTS

<u>Sample No.</u>	<u>Temp. °F</u>	-----Weight %-----											
		<u>C₁-C₄</u>	<u>H₂</u>	<u>CH₄</u>	<u>C₂H₆</u>	<u>C₂H₄</u>	<u>C₃H₈</u>	<u>C₃H₆</u>	<u>iso-C₄H₁₀</u>	<u>n-C₄H₁₀</u>	<u>1-C₄H₈+ iso-C₄H₈</u>	<u>tr-C₄H₈</u>	<u>cis-C₄H₈</u>
1001-205-7	900	3.1	0.12	0.36	0.21	0.36	0.23	1.13	0.26	0.11	0.06	0.21	0.18
	1000	5.7	0.34	1.14	0.61	0.76	0.48	1.65	0.31	0.17	0.05	0.28	0.22
1030-65-2	900	2.6	0.00	0.00	0.22	0.00	0.22	1.13	0.28	0.11	0.25	0.18	0.16
	1000	5.8	0.13	0.89	0.57	0.73	0.43	1.74	0.31	0.15	0.43	0.27	0.22
1030-65-4	900	2.6	0.00	0.00	0.19	0.00	0.35	0.92	0.41	0.18	0.21	0.17	0.15
	1000	6.3	0.13	0.91	0.65	0.72	0.65	1.68	0.49	0.28	0.41	0.30	0.23
1030-65-3	900	3.2	0.02	0.22	0.19	0.26	0.42	0.94	0.40	0.18	0.23	0.18	0.18
	1000	5.8	0.06	0.93	0.58	0.66	0.55	1.55	0.42	0.23	0.37	0.26	0.22
1030-65-1	900	0.9	0.02	0.10	0.07	0.07	0.08	0.29	0.07	0.03	0.07	0.05	0.04
	1000	3.2	0.11	0.35	0.29	0.33	0.28	0.96	0.16	0.12	0.31	0.20	0.18
1030-23-1	900	2.4	0.07	0.18	0.15	0.20	0.19	0.84	0.25	0.11	0.19	0.14	0.13
	1000	4.8	0.15	0.74	0.49	0.56	0.37	1.48	0.29	0.15	0.34	0.24	0.18

TABLE 30B. LIGHT GAS ANALYSIS-CAT.-CRACKING OF UNHYDROTREATED SRC-II FUEL OIL BLEND WITH
Cr-EXCHANGED US-Y ZEOLITE-NH₄SMM-MATRIX FCC CATALYSTS

Sample No.	Temp. °F	-----Weight %-----											
		C ₁ -C ₄	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso C ₄ H ₁₀	n- C ₄ H ₁₀	1-C ₄ H ₈ + iso-C ₄ H ₈	tr- C ₄ H ₈	Cis- C ₄ H ₈
1030-23-2	900	2.92	0.09	0.23	0.25	0.32	0.21	1.03	0.28	0.13	0.20	0.15	0.11
	1000	4.98	0.18	0.00	0.59	0.73	0.41	1.83	0.33	0.16	0.43	0.28	0.22
1030-23-4	900	2.78	0.08	0.32	0.20	0.27	0.22	0.94	0.26	0.10	0.20	0.15	0.12
	1000	5.14	0.15	0.83	0.48	0.64	0.38	1.60	0.30	0.14	0.36	0.23	0.18
1030-25-1	900	2.05	0.17	0.17	0.14	0.17	0.15	0.74	0.19	0.08	0.17	0.13	0.11
	1000	4.18	0.18	0.58	0.38	0.49	0.29	1.36	0.23	0.13	0.33	0.21	0.18
1030-25-2	900	1.59	0.01	0.00	0.14	0.16	0.12	0.65	0.12	0.06	0.15	0.11	0.09
	1000	4.52	0.11	0.92	0.45	0.74	0.22	1.24	0.16	0.10	0.31	0.20	0.17
1030-23-3	900	1.55	0.04	0.12	0.11	0.13	0.16	0.53	0.13	0.06	0.13	0.09	0.08
	1000	2.81	0.06	0.00	0.36	0.00	0.25	1.22	0.19	0.11	0.30	0.19	0.17

APPENDIX D. Calculation of $M_{\text{effective}}$ for M_{SMM} 's Assuming

Only Edge Sites Are Active

A sample calculation is illustrated for the High % NiSMM; 15.9 wt.% Ni, Table 6.

From particle size analysis the estimated average spherical diameter for high % Ni-SMM has been found to be 130 ± 20 Å. This value is not the average platelet diameter.

As the x-ray beam looks at the particles there are two extreme views:

1. the platelet diameter appears to be the spherical diameter.
face on
2. the average of the platelet diameter and platelet thickness appear to be the average spherical diameter.
edge on

So the average spherical diameter as measured =

$$\frac{\text{platelet diameter} + \frac{\text{platelet diameter} + \text{platelet thickness}}{2}}{2}$$

Taking the platelet thickness to be 50 Å, which is the reported value, and the average spherical diameter to be 130 Å one obtains a platelet diameter of 160 Å.

Now:

1. Assume only edge sites are active to loading.
2. Assume all metal atoms in edge unit cells are active to loading.

Therefore, the relative amount of M atoms in edge unit cells =

$$\frac{\text{number of edge unit cells/platelet layer}}{\text{number of total unit cells/platelet layer}} =$$

$$\frac{\text{area of edge unit cells}}{\text{total platelet area}}$$

Total platelet area =

$$\pi r^2 = \pi (80 \text{ \AA})^2 = 20,105 \text{ \AA}^2$$

Area of edge unit cells =

(Total platelet area -
area encompassed by all unit cells except those on edge) =

$$\pi (80 \text{ \AA})^2 - \pi \left[80 \text{ \AA} - \frac{(a+b)}{2} \right]^2 = 3,400 \text{ \AA}^2$$

where $a = 5.2 \text{ \AA}$ (a & b are unit cell dimensions in diameter plane)
 $b = 9.0 \text{ \AA}$

Therefore, $M_{\text{effective}} =$

$$\frac{3400 \text{ \AA}^2}{20,105 \text{ \AA}^2} = 16.9\% \text{ of total metal atoms.}$$

For 5 out of the 8 SMM's in Table 6 the avg. spherical diameter was estimated using "reasonable" curve shapes since their size distribution analysis curves did not continue, or were not plotted down to the 50% line from which one can measure an average diameter.

High % NiSMM (15.9 wt.%)

avg. spherical diam. est. $130 \pm 20 \text{ \AA}$ (avg. platelet diam. of $160 \text{ \AA}$)

$$Ni_{\text{eff}} = 16.9\% \text{ of } Ni_{\text{total}}$$

Low % NiSMM (8.2 wt.%)

avg spherical diam est. $170 \pm 20 \text{ \AA}$ (avg. platelet diam. $210 \text{ \AA}$)

$$Ni_{\text{eff}} = 12.8\% \text{ of } Ni_{\text{total}}$$

High % Co SMM (15.6 wt.%)

avg. spherical diam est. $150 \pm 25 \text{ \AA}$ (avg. platelet diam. $183 \text{ \AA}$)

$$Co_{\text{eff}} = 14.9\% \text{ of } Co_{\text{total}}$$

Low % Co-SMM (9.2 wt.%)

avg. spherical diam. est. $170 \pm 25 \text{ \AA}$ (avg. platelet diam. $210 \text{ \AA}$)

$$Co_{\text{eff}} = 12.8\% \text{ of } Co_{\text{total}}$$

High % FeSMM (13.7 wt.%)

avg. spherical diam. est. 350 Å (avg. platelet diam. 450 Å)

$$\text{Fe}_{\text{eff}} = 7.1\% \text{ Fe}_{\text{total}}$$

Low % FeSMM (7.3 wt.%)

avg. spherical diam. 560 Å (avg. platelet diam. 730 Å)

$$\text{Fe}_{\text{eff}} = 3.8\% \text{ of Fe}_{\text{total}}$$

High % MnSMM (8.8 wt.%)

avg. spherical diam. 370 Å (avg. platelet diam. 477 Å)

$$\text{Mn}_{\text{eff}} = 5.9\% \text{ of Mn}_{\text{total}}$$

Low % Mn-SMM (5.7 wt.%)

avg. spherical diam. 140 ± 20 Å (avg. platelet diam 170Å)

$$\text{Mn}_{\text{eff}} = 16.0\% \text{ of Mn total}$$

APPENDIX E. Description of All Runs

Appendix E shows where tabular descriptions of all runs and catalysts may be found. It locates the three types of experiments: Cat.-cracking, hydrocracking and hydrotreating. The cat.-cracking section includes run numbers, catalyst identifications, catalyst descriptions, and table numbers where run conditions and experimental results may be found for the 254 cracking runs and the 65 cracking catalysts.

The descriptions of the 39 hydrocracking runs, and the 30 hydrocracking catalysts are already adequately presented in Tables 34, 35, 36.

The descriptions of the 103 hydrotreating runs, and the 100 hydrotreating catalysts are already adequately presented in Tables 37-42, 44-48, and 50.

TABLE 1. DESCRIPTION OF CAT.-CRACKING EXPERIMENTS

<u>Run No.</u>	<u>Catalyst ID</u>	<u>Catalyst Description</u>	<u>Feed^a</u>	<u>Temp. °F.</u>	<u>Table No.</u>
57105	Filtrol FS-30	Proprietary Formulation	H	900	10
58304	"	"	H	1000	10
57304	"	"	H	900	11
57904	"	"	H	1000	10
60508	"	"	U	900	22
60601	"	"	U	1000	22
57204	1001-205-1	20% Y-NN ₃ (100°C)normal, 80% alumina	H	900	10
57403	"	"	H	1000	10
59001	"	"	U	900	22
59007	"	"	U	1000	22
57205	1028-29-3	milled	H	900	10
57506	"	"	H	1000	10
59909	"	"	U	900	22
60001	"	"	U	1000	22
57106	1001-205-2	20% Y-NN ₃ (100°C)-Ni normal, 80% alumina	H	900	10
57306	"	"	H	1000	10
59002	"	"	U	900	22
50104	"	"	U	1000	22
57107	1028-29-4	milled	H	900	10
57707	"	"	H	1000	10
60003	"	"	U	900	22
60002	"	"	U	1000	22

^a H, U = Hydrotreated, unhydrotreated.

TABLE 1. DESCRIPTION OF CAT.-CRACKING EXPERIMENTS

<u>Run No.</u>	<u>Catalyst ID</u>	<u>Catalyst Description</u>	<u>Feed^a</u>	<u>Temp. °F</u>	<u>Table No.</u>
57108	1001-205-3	20% Y-NN ₃ (100°C)-Co normal, 80% alumina	H	900	10
57706	"	"	H	1000	10
60605	"	"	U	900	22
60105	"	"	U	1000	22
57201	1028-29-5	milled	H	900	10
57307	"	"	H	1000	10
60004	"	"	U	900	22
60005	"	"	U	1000	22
57206	1025-25-105	20% Y-MN ₃ (100°C)-R normal, 80% alumina	H	900	10
57606	"	"	H	1000	10
60108	"	"	U	900	22
60201	"	"	U	1000	22
57207	1028-29-2	milled	H	900	10
57406	"	"	H	1000	10
60006	"	"	U	900	22
60007	"	"	U	1000	22
57708	1001-235-6	20% Y-VN ₃ (100°C)R ₂ normal, 80% alumina	H	900	10
57801	"	"	H	1000	10
60106	"	"	U	900	22
60107	"	"	U	1000	22

TABLE 1. DESCRIPTION OF CAT.-CRACKING EXPERIMENTS

<u>Run No.</u>	<u>Catalyst ID</u>	<u>Catalyst Description</u>	<u>Feed^a</u>	<u>Temp. °F</u>	<u>Table No.</u>
57202	1025-25-106	20% Y-NN ₃ (100°C)-R-Cr normal, 80% alumina	H	900	10
58303	"	"	H	1000	10
60202	"	"	U	900	22
60203	"	"	U	1000	22
57203	1001-231-1	milled, 80% alumina	H	900	10
57504	"	"	H	1000	10
60101	"	"	U	900	22
60008	"	"	U	1000	22
57305	1025-25-116	20% Y-NN ₃ (100°C)-R-Mn normal, 80% alumina	H	900	10
57908	"	"	H	1000	10
60301	"	"	U	900	22
60302	"	"	U	1000	22
57208	1028-29-1	milled	H	900	10
57405	"	"	H	1000	10
60102	"	"	U	900	22
60103	"	"	U	1000	22
57407	1001-206-1	20% US-Y, 80% alumina	H	900	11
57602	"	"	H	1000	11
60303	"	"	U	900	23
60304	"	"	U	1000	23

TABLE 1. DESCRIPTION OF CAT.-CRACKING EXPERIMENTS

Run No.	Catalyst ID	Catalyst Description	Feed ^a	Temp. °F	Table No.
57401	1001-205-4	20% US-Y-Ni, 80% alumina	H	900	11
57402	"	"	H	1000	11
60305	"	"	U	900	23
60306	"	"	U	1000	23
57502	1001-205-5	20% US-Y-Co, 80% alumina	H	900	11
57507	"	"	H	1000	11
60307	"	"	U	900	23
60308	"	"	U	1000	23
57503	1025-49-91	20% US-Y-R, 80% alumina	H	900	11
57508	"	"	H	1000	11
60401	"	"	U	900	23
60402	"	"	U	1000	23
57408	1001-205-7	20% US-Y-Cr, 80% alumina	H	900	11
59905	"	"	H	1000	11
60602	"	"	U	900	23
60603	"	"	U	1000	23
57501	1001-206-2	20% US-Y-Mn, 80% alumina	H	900	11
57603	"	"	H	1000	11
60403	"	"	U	900	23
60404	"	"	U	1000	23
57802	1001-11-2	100% NH ₄ -SMM (S/A = 2.16)	H	900	12
57803	"	"	H	1000	12

TABLE 1. DESCRIPTION OF CAT.-CRACKING EXPERIMENTS

<u>Run No.</u>	<u>Catalyst ID</u>	<u>Catalyst Description</u>	<u>Feed^a</u>	<u>Temp. °F</u>	<u>Table No.</u>
60502	1001-11-2	100% NH ₄ -SMM (S/A = 2.16)	U	900	24
60501	"	"	U	1000	24
57808	1001-13-3	" (S/A = 2.28)	H	900	12
58307	"	"	H	1000	12
60503	"	"	U	900	24
60504	"	"	U	1000	24
57902	1001-13-4	" (S/A = 2.45)	H	900	12
57903	"	"	H	1000	12
50505	"	"	U	900	24
50506	"	"	U	1000	24
57608	1001-15-5	" (S/A = 2.53)	H	900	12
57705	"	"	H	1000	12
60507	"	"	U	900	24
61402	"	"	U	1000	24
57404	1001-11-1	" (S/A = 2.67)	H	900	12
58406	"	"	H	1000	12
60407	"	"	U	900	24
60408	"	"	U	1000	24
58903	1030-21-4	60% NH ₄ -SMM (S/A = 2.16), 40% alumina	H	900	14
58906	"	"	H	1000	14
60807	"	"	U	900	25
60808	"	"	U	1000	25

TABLE 1. DESCRIPTION OF CAT.-CRACKING EXPERIMENTS

<u>Run No.</u>	<u>Catalyst ID</u>	<u>Catalyst Description</u>	<u>Feed^a</u>	<u>Temp. °F</u>	<u>Table No.</u>
58303	103C-21-3	50% NH ₄ -SMM (S/A = 2.16), 40% silica-alumina	H	900	14
58507	"	"	H	1000	14
60902	"	"	U	900	25
60901	"	"	U	1000	25
58502	1030-21-2	" , 40% silica-alumina- magnesia.	H	900	14
58506	"	"	H	1000	14
60903	"	"	U	900	25
60904	"	"	U	1000	25
58501	1030-21-1	" , 40% silica-alumina- zirconia	H	900	14
58508	"	"	H	1000	14
60906	"	"	U	900	25
60905	"	"	U	1000	25
58504	1030-21-5	" , 40% kaolinite clay	H	900	14
58601	"	"	H	1000	14
60806	"	"	U	900	25
60805	"	"	U	1000	25
58402	1030-13-3	80% NH ₄ -SMM (S/A = 2.16), 20% US-Y	H	900	15
58602	"	"	H	1000	15
60707	"	"	U	900	26
60708	"	"	U	1000	26

TABLE 1. DESCRIPTION OF CAT.-CRACKING EXPERIMENTS

<u>Run No.</u>	<u>Catalyst ID</u>	<u>Catalyst Description</u>	<u>Feed^a</u>	<u>Temp. °F</u>	<u>Table No.</u>
58403	1030-13-1	80% NH ₄ -SMM (S/A = 2.16), 20% US-Y-Cr	H	900	15
58405	"	"	H	1000	15
60803	"	"	U	900	26
60804	"	"	U	1000	26
58401	1030-13-2	" , 20% US-Y-R	H	900	15
58505	"	"	H	1000	15
60802	"	"	U	900	26
60801	"	"	U	1000	26
59807	1030-13-5	" , 20% Y-NN ₃ (100°C)R	H	900	15
59507	"	"	H	1000	15
60701	"	"	U	900	26
60702	"	"	U	1000	26
58603	1030-13-4	" , 20% Y-NN ₃ (100°C)R ₂	H	900	15
58707	"	"	H	1000	15
60703	"	"	U	900	26
60704	"	"	U	1000	26
58604	1030-17-1	" , 20% Y-NRCR	H	900	15
58704	"	"	H	1000	15
60706	"	"	U	900	26
60705	"	"	U	1000	26
58306	1030-13-6	" , 20% Y-RRCR	H	900	15
58702	"	"	H	1000	15

TABLE 1. DESCRIPTION OF CAT.-CRACKING EXPERIMENTS

Run No.	Catalyst ID	Catalyst Description	Feed ^a	Temp. °F	Table No.
58607	1030-29-2	80% NH ₄ -SMM (S/A = 2.16), 20% Y-RRCR	H	900	26
59506	"	"	H	1000	26
60907	"	"	U	900	15
60908	"	"	U	1000	15
58305	1030-17-2	20% Y-NRCR, 80% alumina	H	900	16
58404	"	"	H	1000	16
60606	"	"	U	900	27
60607	"	"	U	1000	27
58807	1030-49-1	20% Y-RRCR, 80% alumina	H	900	16
58901	"	"	H	1000	16
61106	"	"	U	900	27
61105	"	"	U	1000	27
59207	1030-51-2	" , 80% silica-alumina	H	900	16
59201	"	"	H	1000	16
61403	"	"	U	900	27
61401	"	"	U	1000	27
58905	1030-51-3	" , 80% silica-alumina-magnesia	H	900	16
58908	"	"	H	1000	16
61102	"	"	U	900	27
61101	"	"	U	1000	27

TABLE 1. DESCRIPTION OF CAT.-CRACKING EXPERIMENTS

Run No.	Catalyst ID	Catalyst Description	Feed ^a	Temp. °F	Table No.
59203	1030-51-4	20% Y-RRCR, 80% silica-alumina zirconia	H	900	16
59205	"	"	H	1000	16
61103	"	"	U	900	27
61104	"	"	U	1000	27
59402	1030-51-1	, 80% kaolinite clay	H	900	16
59108	"	"	H	1000	16
61001	"	"	U	900	27
61002	"	"	U	1000	27
58904	1030-49-2	20% Y-RRCR, 20% alumina, 54% clay, 6% NH ₄ PSA ^b	H	900	16
58907	"	"	H	1000	16
59008	"	"	U	900	27
60204	"	"	U	1000	27
60205	1030-73-1	20% Y-NN ₃ (100°C)R, "	H	900	16
60206	"	"	H	1000	16
61604	"	"	U	900	27
61605	"	"	U	1000	27

^b NH₄-polysilicate

TABLE 1. DESCRIPTION OF CAT.-CRACKING EXPERIMENTS

<u>Run No.</u>	<u>Catalyst ID</u>	<u>Catalyst Description</u>	<u>Feed^a</u>	<u>Temp. °F</u>	<u>Table No.</u>
61902	1030-81-1	20% Y-NN ₃ (100°C)R ₂ , 20% alumina, 54% clay 6% NH ₄ PSA	H	900	16
61903	"	"	H	1000	16
62102	"	"	U	900	27
62103	"	"	U	1000	27
61906	1030-81-2	30% Y-RRCP, 20% alumina, 45% clay, 5% NH ₄ PSA	H	900	16
61907	"	"	H	1000	16
62204	"	"	U	900	27
62107	"	"	U	1000	27
59903	1030-59-3	20% Y-RRCP, 40% NH ₄ -SMM (S/A = 2.16), 40% silica-alumina	H	900	19
59304	"	"	H	1000	19
61203	"	"	U	900	28
61204	"	"	U	1000	28
59303	1030-59-4	" , 40% silica-alumina- magnesia	H	900	19
59305	"	"	H	1000	19
61206	"	"	U	900	28
61205	"	"	U	1000	28
59401	1030-59-5	" , 40% silica-alumina- zirconia	H	900	19
59306	"	"	H	1000	19

TABLE 1. DESCRIPTION OF CAT.-CRACKING EXPERIMENTS

<u>Run No.</u>	<u>Catalyst ID</u>	<u>Catalyst Description</u>	<u>Feed^a</u>	<u>Temp. °F</u>	<u>Table No.</u>
61302	1030-59-5	20% Y-RRCR, 40% NH ₄ -SMM (S/A = 2.16), 40% silica-alumina-zirconia	U	900	28
61301	"	"	U	1000	28
59102	1030-59-1	"			
		40% alumina	H	900	19
59206	"	"	H	1000	19
61107	"	"	U	900	28
61108	"	"	U	1000	28
59208	1030-59-2	"			
		40% clay	H	900	19
59301	"	"	H	1000	19
61201	"	"	U	900	28
61202	"	"	U	1000	28
59404	1030-65-2	20% US-Y-Cr, 80% silica-alumina	H	900	20
59308	"	"	H	1000	20
61503	"	"	U	900	29
61502	"	"	U	1000	29
59406	1030-65-4	, 80% silica-alumina-magnesia	H	900	20
59408	"	"	H	1000	20
61507	"	"	U	900	29
61506	"	"	U	1000	29

TABLE 1. DESCRIPTION OF CAT.-CRACKING EXPERIMENTS

<u>Run No.</u>	<u>Catalyst ID</u>	<u>Catalyst Description</u>	<u>Feed^a</u>	<u>Temp. °F</u>	<u>Table No.</u>
59405	1030-65-3	20% US-Y-Cr, 80% silica-alumina-zirconia	H	900	20
59407	"	"	H	1000	20
61504	"	"	U	900	29
61505	"	"	U	1000	29
59403	1030-65-1	, 80% clay	H	900	20
59307	"	"	H	1000	20
61408	"	"	U	900	29
62408	"	"	U	1000	29
59505	1030-23-1	20% US-Y-Cr, 20% alumina, 54% clay, 6% NH ₄ PSA	H	900	20
58804	"	"	H	1000	20
61207	"	"	U	900	29
61208	"	"	U	1000	29
58605	1030-23-2	20% US-Y-Cr, 40% NH ₄ -SMM (S/A = 2.16), 40% alumina	H	900	21
58608	"	"	H	1000	21
61303	"	"	U	900	30
61304	"	"	U	1000	30
58805	1030-23-4	40% silica-alumina,"	H	900	21
58808	"	"	H	1000	21
61307	"	"	U	900	30
61308	"	"	U	1000	30

TABLE 1. DESCRIPTION OF CAT.-CRACKING EXPERIMENTS

<u>Run No.</u>	<u>Catalyst ID</u>	<u>Catalyst Description</u>	<u>Feed^a</u>	<u>Temp. °F</u>	<u>Table No.</u>
58802	1030-25-1	20% US-Y-Cr, 40% NH ₄ -SMM (S/A = 2.16), 40% silica-alumina-magnesia	H	900	21
58803	"	"	H	1000	21
61404	"	"	U	900	30
61405	"	"	U	1000	30
58902	1030-25-2	" 40% silica-alumina-zirconia			
58806	"	"	H	900	21
61407	"	"	H	1000	21
61406	"	"	U	900	30
58606	1030-23-3	" 40% clay	U H	1000 900	30 21
58701	"	"	H	1000	21
61306	"	"	U	900	30
61305	"	"	U	1000	30