|   |  | EXXON   | GRU. 3P   | JLK                                   | AUFMAN                                 | ECB  | ROWN<br>TR-75-   | F336   | 15-74-(  | C-2036   | ETC (U)  |  |
|---|--|---|---|---------------------------------------|--|--|--|--|--|--|--|--|
| OF  <br>AD<br>AO53 IO6  |  |   |   |                                       | ALTERNATION OF A                       | The second secon |  |  | Antonio di Contra di Contr |  |  |  |
|   | antinue<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>Marine<br>M |   |   |                                       |  |  | in succession in the second se | and the second s   |  |  | DENNISTANG<br>ANTIGENESIS<br>ANTIGENESIS<br>ANTIGENESIS<br>ANTIGENESIS |  |
|   |  |   | internet<br>and a second second<br>second second second<br>second second second<br>second second second second second second<br>second second s | · · · · · · · · · · · · · · · · · · · |  |  |  |  |  |  |  |  |
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|   | Raine and Raine  |   |   |                                       |  |  |  |  |  |  |  |  |
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AFAPL-TR-75-10 Volume III



# EVALUATION OF METHODS TO PRODUCE AVIATION TURBINE FUELS FROM SYNTHETIC CRUDE OILS, PHASE 3

# Volume III

EXXON RESEARCH AND ENGINEERING COMPANY GOVERNMENT RESEARCH LABORATORIES LINDEN, NEW JERSEY 07036

**SEPTEMBER 1977** 

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LEONARD C. ANGELLO Project Engineer

FOR THE COMMANDER ARTHUR V. CHURCHILL 40.52 Chief, Fuels Branch, Starter Carlon Fuels and Lubrication Division USTRADUTOR AVAILABILITY CODES AVAIL. BRE/or SPECIAL 10000

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UNCLASSIFIED CLASSIFICATION OF THIS PAGE (When Date Intered) READ INSTRUCTIONS **REPORT DOCUMENTATION PAGE** BEFORE COMPLETING FORM 2. GOVT ACCESSION NO. RECIPIENT'S CATALOG NUMBER TR-75-1 VOL EVALUATION OF METHODS TO PRODUCE AVIATION Final URBINE EUELS FROM SYNTHETIC CRUDE OILS 76 30 Apr @77. 24 Apr HASE 3 EXXON/GRU. 3PEA. 77 VOLUME III. AUTHOR(.) CONTRACT OR GRANT NUMBER A. R. Cunningham W. F. Taylor 33615-74-C-2036 J. L. Kaufman C. A. Smith E. C. Brown M. G. Luzarraga . PERFORMING ORGANIZATION NAME AND ADDRESS PROJECT, TASK 203F Exxon Research and Engineering Company 6 Government Research Laboratories / P.O. Box 8, Linden, New Jersey 07036 11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Aero Propulsion Laboratory Jun Air Force Wright Aeronautical Laboratories 88 Wright Patterson Air Force Base, OH 45433 ECURITY CLASS. (of Kautman iam Fr laylog J, Unclassified Brown, A.K. unningham DECLASSIFICATION/DOWNGRADING SCHEDULE 18. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, H different from Report) 18. SUPPLEMENTARY NOTES 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Coal Tars Refining Coal Liquefaction Hydrotreating Syncrude Retorting Hydrocracking Jet Fuels **Turbine Fuels** Hydrogenation Coking Thermal Cracking Shale 011 Hydroprocessing ADITRACT (Continue on reverse side if necessory and identify by black number) An engineering planning study was made of the effect of processing shale oil in a refinery processing both shale oil and petroleum to a full product slate including jet fuel. This study was part of an overall program whose object was to investigate the feasibility of producing aviation turbine fuels from synthetic crude oils. In this Phase 3 engineering planning study the results and conclusions (over) DD 1 JAN 73 1473 EDITION OF I NOV 65 IS OBSOLETE UNCLASSIFIED SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered) 391338

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of the Phase 1 state-of-the-art assessment and Phase 2 pilot plant experimental study were further investigated. The Exxon RESCUE Linear Program for Refinery Planning was used to provide a framework for the analysis.

The study which involved a number of arbitrary but well-defined assumptions. was done in the context of a grass roots refinery processing shale oil and petroleum in segregated operations. Shale oil processing was restricted to distillation and hydrotreating of the kerosene and gas oil fractions, whereas petroleum processing involved a full spectrum of refinery processes with a relatively high level of conversion of heavier fractions to lighter fractions to meet a high motor gasoline demand. The hydrotreated shale kerosene was blended to jet fuel product and the bydrotreated shale vacuum gas oil and untreated vacuum resid were blended into fuel oil or liquid plant fuel displacing petroleum fractions which are in turn converted to lighter products. Shale oil was incrementally introduced into the refinery which was initially processing 100 kB/CD of petroleum crude while it was constrained to produce the same volume of prime products. Refinery processing effects and refining cost effects in terms of the average cost per unit of total prime product were calculated. Base case studies were made for processing Paraho, Tosco, and Garrett shale oil. Additional studies were made to explore the sensitivity of the base case results to increased jet fuel demand, increased fuel oil demand and maximum jet fuel production.

The major conclusions of the study are as follows:

- Shale oil may be used to replace or supplement petroleum crude and still meet historical jet fuel demands.
- Jet fuel yield per barrel of shale oil is low. The principal mechanism for producing incremental jet fuel from shale oil is to have shale fuel oil and distillate fractions replace petroleum fractions as fuel oil flux and free heavier petroleum fractions for use as conversion process feed.
- The volume of shale oil that may be run is limited by the availability of fuel oil outlets and the unavailability of conversion outlets.
- A program of developing data on conversion of shale fuel oil fractions should be pursued.

In addition, a 328 gallon sample of aircraft turbine fuel was prepared from Paraho shale oil via initial fractionation followed by catalytic hydroprocessing.

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#### PREFACE

This final report was submitted by Exxon Research and Engineering Company under Contract No. F33615-74-C-2036. The effort was sponsored by the Air Force Aero Propulsion Laboratory, Air Force Systems Command, Wright-Patterson AFB, Ohio under Project 3048, Task 304805 and Work Unit 30480559 with Captain Heidi E. Cron and Mr. L. C. Angello as Project Engineers. Dr. William F. Taylor of Exxon Research and Engineering Company, Government Research Laboratories, Linden, New Jersey, supervised the work. J. L. Kaufman, E. C. Brown, and A. R. Cunningham of Exxon Research and Engineering Company, Exxon Engineering Petroleum Department, Florham Park, New Jersey, conducted the engineering planning study. C. A. Smith and M. G. Luzarraga of Exxon Research and Development Laboratories, Baton Rouge, Louisiana carried out the preparation of a sample of jet fuel from Paraho shale oil.

This report describes the third phase (Phase 3) of a study being carried out by Exxon Research and Engineering Company for the United States Air Force. The study is directed at evaluating the current technology for the production of aviation turbine fuels from synthetic crude oils. The scope of the program involves engineering analyses, experimentation, design projections, and considerations of availability and economics.

Many individuals from the Department of Defense, NASA, and Exxon made valuable contributions to this study. The authors wish to acknowledge the helpful advice and encouragement received from the following individuals: Messrs. H. Shaw, J. P. Longwell, F. H. Kant, and R. B. Long. Dr. J. W. Harrison had overall management responsibility for the project.

# TABLE OF CONTENTS

v -

BACK NOT FILMED

|     |      |         |                        |          |       |      |     |     |     |     |    |   |   |   |   | Page     |
|-----|------|---------|------------------------|----------|-------|------|-----|-----|-----|-----|----|---|---|---|---|----------|
| I.  | SUMM | ARY     |                        |          |       |      |     |     |     |     |    |   |   |   |   | 1        |
| 11. | INTR | ODUCTIO | N                      |          |       |      |     |     | ••  | •   |    | • | • |   | • | 3        |
|     |      |         | ING PLANN<br>SHALE OIL |          |       |      |     |     |     | -   |    |   |   | • | • | 5        |
|     | 3.1  | Introd  | uction                 |          |       |      |     |     |     |     |    |   |   |   | • | 5        |
|     | 3.2  | Genera  | 1 Purpose              | and Lin  | itati | ons  |     |     |     |     |    |   |   |   | • | 5        |
|     | 3.3  | Study : | Bases                  |          | aoup. |      |     |     |     |     |    |   | • |   |   | 5        |
|     |      | 3.3.1   | General.               |          |       |      |     |     |     |     |    |   |   |   |   | 5        |
|     |      | 3.3.2   | Crude Bas              |          |       |      |     | -   | -   | -   |    | • | • | • | • | 6        |
|     |      | 3.3.3   |                        |          |       |      |     |     |     |     |    | • | • | • | • | 9        |
|     |      | 3.3.4   | Refining               |          |       |      |     |     |     |     |    |   | • | • | • | 9        |
|     | 3.4  | Approa  | ch to the              | Study .  |       |      | • • | •   | •   | •   |    | • | • | • | • | 15       |
|     | 3.5  |         | ic Basis.              |          |       |      |     |     |     |     |    |   |   |   | • | 19       |
|     | 3.6  | Discus  | sion of R              | esults . | • •   |      |     |     | •   |     |    |   |   | • | • | 21       |
|     |      |         | General.<br>Series A   |          |       |      |     |     |     |     |    |   |   |   | : | 21<br>21 |
|     |      |         | 3.6.2.1                | Process  | ing E | ffec | ts. |     |     |     |    |   |   |   |   | 30       |
|     |      |         | 3.6.2.2                |          |       |      |     |     |     |     |    |   |   |   |   | 30       |
|     |      |         | 3.6.2.3                | Refinin  | g Cos | t Ef | fec | ts  |     |     |    |   |   |   |   | 32       |
|     |      | 3.6.3   | Series B               | - Incre  | ased  | Jet  | Fue | 1 1 | )en | and | 1. |   |   |   |   | 32       |
|     |      |         | 3.6.3.1                | Refinin  | g Eff | ecte |     |     |     |     |    |   |   |   |   | 36       |
|     |      |         | 3.6.3.2                | Refinin  |       |      |     |     |     |     |    |   |   |   |   | 36       |
|     |      | 3.6.4   | Series C               | - High   | Fuel  | 011  | Den | and | 1.  |     |    | • |   |   |   | 36       |
|     |      |         | 3.6.4.1                | Refinin  | g Eff | ects |     |     |     |     |    |   |   |   |   | 41       |
|     |      |         | 3.6.4.2                | Refinin  |       |      |     |     |     |     |    |   |   |   |   | 41       |
|     |      | 3.6.5   | Series D               | - Maxim  | um Je | t Fu | el. |     |     |     |    |   |   |   |   | 41       |
|     |      |         | 3.6.5.1                | Refinin  | e Eff | ects |     |     |     |     |    |   |   |   |   | 41       |
|     |      |         | 3.6.5.2                | Maximum  |       |      |     |     |     |     |    |   |   |   |   | 41       |
|     | 3.7  | Data N  | eeds                   |          |       |      |     |     |     |     |    |   |   |   |   | 43       |
|     | 3.8  | Conclu  | sions                  |          |       |      |     |     |     |     |    |   |   |   |   | 43       |

#### TABLE OF CONTENTS (continued)

|     |        | E OIL     | PLE OF AIRC | • • •  |       | •   | • • | •••  | •   | • | • | • | • | 44 |
|-----|--------|-----------|-------------|--------|-------|-----|-----|------|-----|---|---|---|---|----|
| 4.1 | Introd | uction .  |             |        |       | •   |     |      |     | • |   | • |   | 44 |
| 4.2 | Experi | mental Pr | ogram       |        |       | •   | • • | •    | •   | • |   | • | • | 44 |
|     | 4.2.1  |           | hale Oil Hy |        | -     |     |     |      |     |   |   |   |   |    |
|     |        | Study .   |             | • • •  |       | •   | • • | •    | •   | • | • | • | • | 44 |
| · · |        | 4.2.1.1   | Feedstock   | and Ca | ataly | st  |     |      |     |   |   |   |   | 44 |
|     |        |           | Unit Opera  |        |       |     |     |      |     |   |   |   |   |    |
|     |        |           | Techniques  |        |       |     | -   |      |     |   |   |   |   | 4  |
|     |        | 4.2.1.3   | Discussion  |        |       |     |     |      |     |   |   |   |   | 4  |
|     | 4.2.2  | Paraho S  | hale Oil Hy | droft  | ontro | Pro | duc | ++   | on  |   |   |   |   |    |
|     | 4.2.2  |           |             |        | -     |     |     |      | .on |   | 5 |   |   | 4  |
|     |        |           |             |        |       |     |     |      | •   |   | • |   | • | 4  |
|     |        |           | Feedstock   |        |       |     |     |      |     |   |   | • | • | 4  |
|     |        | 4.2.2.2   | Unit Opera  |        |       |     | -   |      |     |   |   |   |   |    |
|     |        |           | Techniques  |        |       |     |     |      |     |   | • | • | • | 4  |
|     |        | 4.2.2.3   | Product Qu  |        |       |     |     |      |     |   |   |   |   |    |
|     |        |           | Paraho Sha  |        |       |     |     |      |     |   |   |   | • | 50 |
|     |        | 4.2.2.4   | Unit Opera  | ting H | Exper | ien | ce. | • •  | •   | • | • | • | • | 6  |
|     |        |           | 4.2.2.4.1   | Opera  | atino | Pr  | ohl | em   |     |   |   |   |   | 62 |
|     |        |           | 4.2.2.4.2   |        |       |     |     |      |     |   |   | • | • | 0. |
|     |        |           |             | Activ  |       |     |     |      |     |   |   |   |   | 64 |
|     |        |           | 4.2.2.4.3   |        |       |     |     |      |     |   |   |   |   | 64 |
|     |        |           | 412121415   |        | -Ben  | 001 |     | -p - |     |   | • | • | • | 0- |
| 4.3 | Conclu | sions     |             |        |       |     | • • |      |     |   |   |   |   | 64 |

APPENDIX -- RESCUE LINEAR PROGRAM FOR REFINERY PLANNING. . . . 69

Page

- vi -

# LIST OF TABLES

| No. |  | Page |
|-----|--|------|
| 1   | PETROLEUM CRUDE QUALITIES  | . 7  |
| 2   | RAW SHALE OIL ASSAY QUALITIES                                    | . 8  |
| 3   | PAD II PRODUCT DEMAND SLATE                                      | . 10 |
| 4   | PRIME PRODUCT SPECIFICATIONS                                     | . 11 |
| 5   | TYPICAL U.S. MIDWEST ONSITE PROCESSING FACILITIES                | . 12 |
| 6   | HYDROTREATED SHALE KEROSENE QUALITY                              | . 17 |
| 7   | ECONOMIC BASES   | . 22 |
| 8   | SAMPLE CALCULATION OF AVERAGE REFINING COST                      | 23   |
| 9   | CASE SUMMARY GARRETT-SERIES A                                    | . 24 |
| 10  | CASE SUMMARY TOSCO-SERIES A                                      | . 25 |
| 11  | CASE SUMMARY PARAHO-SERIES A                                     | . 26 |
| 12  | CASE SUMMARY GARRETT-SERIES B                                    | 33   |
| 13  | CASE SUMMARY TOSCO-SERIES B                                      | 34   |
| 14  | CASE SUMMARY PARAHO-SERIES B                                     | 35   |
| 15  | CASE SUMMARY PARAHO-SERIES C                                     | 39   |
| 16  | FEEDSTOCK INSPECTIONS  | 46   |
| 17  | HTT-4-02 DETAILED RUN DATA<br>PARAHO SHALE OIL EXPLORATORY STUDY | 48   |
| 18  | HTT-3-02 DETAILED RUN DATA<br>PARAHO SHALE OIL PRODUCTION RUN    | 51   |
| 19  | HTT-4-03 DETAILED RUN DATA<br>PARAHO SHALE OIL PRODUCTION RUN    | 56   |
| 20  | PARAHO SHALE OIL PRODUCTION RUN<br>15 GAL. COMPOSITES            | 60   |
| 21  | INSPECTIONS OF GUARD CHAMBER FINES                               | 63   |

- vii -

# LIST OF ILLUSTRATIONS

| No. | -  |  | Page |
|-----|----|--|------|
| 1   |    | BASE DEMAND PATTERN BASE CASE                                | 13   |
| 2   |    | SHALE PROCESSING SEQUENCE                                    | 16   |
| 3   |    | AVERAGE REFINING COST VS GARRETT INPUT                       | 27   |
| 4   |    | AVERAGE REFINING COST VS TOSCO INPUT                         | 28   |
| 5   | -  | AVERAGE REFINING COST VS PARAHO INPUT                        | 29   |
| 18  | ı  | BASE DEMAND PATTERN 8 KB/CD GARRETT SHALE PROCESSED          | 31   |
| 6   |    | HIGH FUEL OIL DEMAND PATTERN BASE CASE                       | 37   |
| 68  | 1  | HIGH JET FUEL DEMAND PATTERN 8 KB/CD GARRETT SHALE PROCESSED | 38   |
| 7   |    | AVERAGE REFINING COST VS PARAHO INPUT HIGH FUEL OIL DEMAND   | 40   |
| 8   | 22 | HIGH JET FUEL DEMAND PATTERN BASE CASE                       | 42   |
| 88  | 1  | HTT UNIT FLOW SCHEMATIC                                      | 45   |
| 9   |    | HTT-3-02 ACTIVITY LOG  | 65   |
| 10  |    | HTT-4-03 ACTIVITY LOG  | 66   |
| 11  | -  | HYDROGEN CONSUMPTION VS VOL% AROMATICS REDUCTION             | 67   |
|     |    |  |      |
|     |    | CASE SUMMARY PARABO-SERIES C                                 |      |
|     |    |  |      |
|     |    |  |      |
|     |    |  |      |
|     |    |  |      |
|     |    | ) PARARO SHALK OIL PRODUCTION BUS                            |      |
|     |    |  |      |

No

# LIST OF ABBREVIATIONS AND ACRONYMS

| AGO    | - | Atmospheric Gas 011                           |
|--------|---|---|
| API    | - |   |
| ATF    | - |   |
| BBL    | - | Barrel (42 U.S. gallons)                      |
| CD     | - | Calendar Day                                  |
| DCF    | - |   |
| EOR    | - |   |
| ERDL   |   | Exxon Research and Development Laboratories   |
| FCC    | - | Fluid Catalytic Cracking                      |
| FCP    | - | Final Cut Point of Cat Cracker Recycle        |
| FOEB   | - | Fuel Oil Equivalent Barrel                    |
| HAGO   | - | Heavy Atmospheric Gas 011                     |
| HVN    | - | Heavy Virgin Naphtha                          |
| H/T    | - | Hydrotreater                                  |
| kB/CD  | - | Thousand Barrels per Calendar Day             |
| kB/SD  | - | Thousand Barrels per Stream Day               |
| LAGO   | - | Light Atmospheric Gas 011                     |
| LHSV   | - | Liquid Hourly Space Velocity                  |
| LPG    | - | Liquified Petroleum Gas                       |
| LVN    | - | Light Virgin Naphtha                          |
| LP     | - | Linear Programming                            |
| Lt     | - | Light   |
| Mogas  | - | Motor Gasoline                                |
| MON    | - | Motor Octane Number                           |
| OPEC   | - | Organization of Petroleum Exporting Countries |
| PAD II | - | Petroleum Allocation for Defense District II  |
| P/S    | - | Pipe Still                                    |
| RON    | - | Research Octane Number                        |
| RVP    | - | Reid Vapor Pressure                           |
| Sat    | - | Saturated                                     |
| SCF/B  | - | Standard Cubic Feet per Barrel                |
| SOR    | - | Start of Run                                  |
| Unsat  | - | Unsaturated                                   |
| VGO    | - | Vacuum Gas 011                                |
|        |   |   |

#### SECTION I

#### SUMMARY

An engineering planning study was made of the effect of processing shale oil in a refinery processing both shale oil and petroleum to a full product slate including jet fuel.

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This study was part of an overall program whose object was to investigate the feasibility of producing aviation turbine fuels from synthetic crude oils. In this Phase 3 engineering planning study the results and conclusions of the Phase 1 state-of-the-art assessment and Phase 2 pilot plant experimental study were further investigated. The Exxon RESCUE Linear Program for Refinery Planning was used to provide a framework for the analysis.

The study which involved a number of arbitrary but well-defined assumptions, was done in the context of a grass roots refinery processing shale oil and petroleum in segregated operations. Shale oil processing was restricted to distillation and hydrotreating of the kerosene and gas oil fractions, whereas petroleum processing involved a full spectrum of refinery processes with a relatively high level of conversion of heavier fractions to lighter fractions to meet a high motor gasoline demand. Conversion processing options for shale oil fractions were specifically excluded due to a lack of such data available to the program. The hydrotreated shale kerosene was blended to jet fuel product and the hydrotreated shale vacuum gas oil and untreated vacuum resid were blended into fuel oil or liquid plant fuel displacing petroleum fractions which are in turn converted to lighter products. Shale oil was incrementally introduced into the refinery which was initially processing 100 kB/CD of petroleum crude while the refinery was constrained to produce the same volume of prime products. Refinery processing effects and refining cost effects in terms of the average cost per unit of total prime product were calculated. Base case studies were made for processing Paraho, Tosco, and Garrett shale oil. Additional studies were made to explore the sensitivity of the base case results to increased jet fuel demand, increased fuel oil demand and maximum jet fuel production.

The major conclusions of the study are as follows:

- Shale oil may be used to replace or supplement petroleum crude and still meet historical jet fuel demands.
- Jet fuel yield per barrel of shale oil is low. The principal mechanism for producing incremental jet fuel from shale oil is to have shale fuel oil and distillate fractions replace petroleum fractions as fuel oil flux and free heavier petroleum fractions for use as conversion process feed.
- The volume of shale oil that may be run is limited by the availability of fuel oil outlets and the unavailability of conversion outlets.

• A program of developing data on conversion of shale fuel oil fractions should be pursued.

In addition, a sample of Jet A type aircraft turbine fuel (approximately 328 gallons) was produced from Paraho shale oil via initial fractionation followed by catalytic hydroprocessing which met the following specifications:

- Total sulfur
- Total aromatic content
- Flash point
- Freeze point
- Smoke point
- Viscosity at -30°F
- ASTM distillation
- API gravity

This aviation turbine fuel was produced by hydrotreating a  $310/500^{\circ}$ F cut of Paraho shale oil over HDS-3A catalyst at  $700^{\circ}$ F, 1200 psig, 1 LHSV, and 4000 SCF/B H<sub>2</sub>. At these conditions sulfur content was reduced from 0.74 wt.% to generally less than 10 ppm. No noticeable catalytic hydrodesulfurization deactivation had occurred after thirty days on oil. However, catalyst activity for denitrogenation and aromatics hydrogenation had both declined during the course of the run. Product nitrogen levels increased from less than 5 ppm to 40-100 ppm, and aromatics contact increased from ca. 10 vol.% initially to 15-16 vol.% at the end of approximately 30 days. The hydrogen consumption involved in upgrading the kerosene fraction of a Paraho shale oil to meet Jet A fuel specifications at these process conditions initially was ca. 1050 SCF/B at SOR. Hydrogen consumption was somewhat lower at the end of the run which reflects the decline in catalyst activity for aromatics hydrogenation.

#### SECTION II

#### INTRODUCTION

Domestic petroleum product production is now, and is forecast to continue to be (National Petroleum Council, 1973), heavily dependent on foreign crude oil feedstocks. Wide recognition of this dependence has led to renewed interest in the production of hydrocarbon liquids from coal and shale deposits to augment the domestic fuel base. The degree to which synthetic fuels developments mitigate foreign dependence is of obvious significance to the logistics support planning of the Armed Forces.

This program is a three phase effort sponsored by the U.S. Air Force Systems Command to determine the feasibility of producing aviation turbine fuels, in particular, from other-than-normal petroleum sources. In Phase 1, literature data relating to the extent of domestic mineral resources and to the many proposed processes for the extraction or transformation to crude fuel liquids were assessed. Approaches to the production of finished fuels from the crude liquids, based on current petroleum oil technology, were also assessed. Phase I concluded that shale-derived oils should be preferentially investigated as a source of aviation turbine fuels, both because they more nearly resemble natural petroleum than do other synthetic crudes, and because significant quantities of shale oil are expected to come onto the market before coal-derived materials are available. The properties of coal-derived liquids, on the other hand, make them ideal for the production of other finished products, such as certain motor gasolines, and could add indirectly to aviation turbine fuel availability by permitting back-out of regular petroleum crude from gasoline manufacture.

In Phase II, the experimental segment of the program, the objective was to determine whether specification JP-4 and/or Jet A aviation fuels could be produced from synthetic crude oils via hydrotreatment of selected synthetic crude oil fractions. Three shale oils and two coal liquids, obtained from the respective process developers, were investigated. Feed fractions encompassing the jet fuel boiling range were distilled from the starting crude oils and hydrotreated at varying severity over nickel and/or cobalt-molybdenum catalysts. Final narrow-cut (Jet A) and/or wide-cut (JP-4) jet fuels oils were blended from the hydrotreated products. From the inspections obtained on the final jet fuel blends, including results of the Jet Fuel Thermal Oxidation Tests (JFTOT), it was concluded that the production of jet fuels from shale oil-derived crude oils is technically feasible, and apt to be much more straightforward than would be the comparable production from coal-derived oils. Hydroprocessing severity is important to the production of specification fuels. Production of specification jet fuel from shale liquids will require at least a moderate severity operation employing a 1500 psi total pressure. Final fuels prepared from coal-derived fuels, however, did not meet density specifications unless hydrotreated at high

severity conditions employing 2200 psi pressure. Increased processing severity, in general, improved the thermal stability and decreased the aromatic and nitrogen content of the product fuel. Sulfur levels of the processed fuels were all well below specifications at all processing severity levels.

In the Phase 3 portion of the program described in this report an engineering planning study of the effect of processing shale oil in a refinery processing both shale oil and petroleum crude was carried out. In addition, the preparation of a 300 gallon sample of Jet A type fuel, prepared to the Air Force requirements from Paraho shale oil was carried out. This work is also described in this report.

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#### SECTION III

#### AN ENGINEERING PLANNING STUDY OF THE EFFECT OF PROCESSING SHALE OIL IN A CONVENTIONAL REFINERY

#### 3.1 Introduction

The purpose of this study was to determine the refining impact of producing aviation turbine fuels from synthetic crude oils. Planning Engineering did this study as the third phase (engineering phase) of an overall assessment of producing aviation turbine fuels (ATF) from domestic synthetic crude sources. Briefly, Phase One was an overview of the problem considering raw material availability, synthetic crude production, optimum processing paths and ATF production. Phase Two was an experimental phase in which analyses of the synthetic oils were obtained and test runs made on hydrotreating synthetic crude oil ATF fractions. The Phase Three engineering work took advantage of the results and conclusions of Phases One and Two.

#### 3.2 General Purpose and Limitations

The overall objective of the engineering planning study was to explore the impact of producing jet fuel from a refinery crude slate including both shale oil and petroleum. The framework for the analysis was the results and conclusions of the previous work in the program; however, to an extent the quantitative bases for the study although well defined, was arbitrary. Thus, the significance of the study lies not so much in the quantitative results presented but in the qualitative and/or directional effects which were obtained. The refining cost effects shown should not be construed to represent an absolute, real cost for producing jet fuel from shale oil. Likewise, the processing sequence chosen for the shale oil, although a logical extension of work in the previous two phases of the program, should not be construed as an optimum processing sequence.

The reader will find much data in this study on refining costs, refinery crude runs, product yields, energy consumption, etc. The derivation of this data, and the bases and assumptions behind them is well documented in this study. However, bases and assumptions become outdated as they are set, especially when they apply to a relatively new field such as refining of shale oils. The real objective of this study is to provide a framework upon which further consideration of how best to process shale oil in refineries may be based, and the significance of this study is not in the quantitative data presented herein but in the qualitative discussions.

#### 3.3 Study Bases

#### 3.3.1 General

It is likely that as shale oil comes into significant commercial production, it will be processed in conventional petroleum refineries along with petroleum crudes rather than in refineries designed specifically for shale oil refining. This approach will minimize the processing required to produce salable products from shale oil as well as reduce the performance and quality risk normally associated with the introduction of new products. Shale oil production will most likely reduce foreign crude imports otherwise needed to meet increasing product demand in the U.S.

The U.S. Midwest - Petroleum Allocation for Defense District II (or PAD II) - was chosen as the basis for defining raw materials characteristics and availability, product volume and quality, and processing capabilities for this study. PAD II was chosen because it is thought to be typical of the entire U.S. and it is a possible recipient, via pipeline, of shale oil. Definition of the refining capabilities of PAD II is based on recent petroleum industry and U.S. Bureau of Mines data. Current operation was chosen as a basis over a forecast of future demand, raw material supply, etc. to make the results more understandable and to avoid jeopardizing the validity of the results with an erroneous forecast. 1975 is used as the base year for defining investments and operating costs.

Although the base refinery is modeled after present day, average PAD II operation in terms of raw materials, demand slate and processing sequence, the base case as well as all other cases in this study are based on grass roots refining capacity. No attempt was made to define existing refining capability or existing spare capacity in PAD II. This approach allows evaluation of the full impact of the shale oil on the base refinery.

#### 3.3.2 Crude Basis

Several different types of crude are processed in the PAD II district. For simplicity and clarity of calculations and analyses, this broad petroleum crude slate was modeled as a 67/33 mixture of South Louisiana, a low sulfur domestic crude, and Arabian Light, a high sulfur foreign crude. This mixture is similar in density, sulfur content and distillation characteristics to the average of all crudes run in PAD II. A comparison of qualities for these two model crudes is shown in Table 1.

Only synthetic crude oils resulting from shale are considered in the Phase Three work. Phase One considered several synthetic crude oil sources. Phase Two considered only five sources, three from shale and two from coal. Analysis of the Phase Two data indicated that conventional specification ATF could not be produced from the coal-derived synthetic crudes without extreme processing steps. Thus, the Phase Three work was limited to the three shale-derived crudes - Garrett, Tosco and Paraho.

Shale oils from three different production processes are considered in this study. Only raw shale oils with no mine-site upgrading are considered. <u>Garrett</u> shale oil results from in-situ retorting of shale rock. <u>Tosco</u> shale oil is produced by a hot ceramic ball retorting process. <u>Paraho</u> shale oil is produced by a gas combustion retorting process. Assay data for the raw shale oils were developed as part of the Phase Two program. Qualities of the three shale oils and shale oil fractions are summarized in Table 2.

#### TABLE 1

# PETROLEUM CRUDE QUALITIES

|                      |                 | So. Louisiana | Arabian Light                           |
|----------------------|-----------------|---------------|---|
|                      |                 |               |   |
| Whole Crude          |                 |               |   |
| Sp. Gravity (°API)   |                 | .8438(36.2)   | .8529(34.4)                             |
| Sulfur, wt%          |                 | .19           | 1.69                                    |
| Nitrogen, wt%        |                 | .06           | .04                                     |
| C4-, LV% on Crude    |                 | 1.4           | 2.0                                     |
| out , in or or or or |                 | - 1001 B      |   |
| Light Virgin Naphtha | (C5/160)        |               |   |
| LV% on Crude         |                 | 3.8           | 6.1                                     |
| Sp. Gravity          |                 | .6578         | .6524                                   |
| Sulfur, wt%          |                 | .001          | .023                                    |
| ,                    |                 |               | 2 2 2 2 2 2 2 2 3 2 3 2 3 2 3 2 3 2 3 2 |
| Heavy Virgin Naphtha | (160/375)       |               |   |
| LV% on Crude         |                 | 19.9          | 20.4                                    |
| Sp. Gravity          |                 | .767          | .775                                    |
| Sulfur, wt%          |                 | .01           | .03                                     |
| 146.                 |                 |               |   |
| Kerosene (375/460)   |                 |               |   |
| LV% on Crude         |                 | 10.8          | 8.9                                     |
| Sp. Gravity          |                 | .817          | .798                                    |
| Sulfur, wt%          |                 | .03           | .11                                     |
| Light Atmospheric Ga | 0 011 (460/550) |               | Atomstice 18                            |
| LV% on Crude         | s 011 (400/330) | 13.6          | 9.3                                     |
|                      |                 | .841          | .828                                    |
| Sp. Gravity          |                 |               | .80                                     |
| Sulfur, wt%          |                 | .05           | .00                                     |
| Heavy Atmospheric Ga | s 011 (550/650) |               |   |
| LV% on Crude         | 0 011 (000,000) | 14.2          | 9.8                                     |
| Sp. Gravity          |                 | .862          | .858                                    |
| Sulfur, wt%          |                 | .125          | 1.38                                    |
|                      |                 |               |   |
| Vacuum Gas Oil (650/ | 1050)           |               |   |
| LV% on Crude         |                 | 29.3          | 30.5                                    |
| Sp. Gravity          |                 | .903          | .916                                    |
| Sulfur, wt%          |                 | .34           | 2.36                                    |
| Vacuum Resid (1050+) |                 |               |   |
| LV% on Crude         |                 | 7.0           | 13.0                                    |
| Sp. Gravity          |                 | .986          | 1.025                                   |
| Sulfur, wt%          |                 |               | 4.19                                    |
| ourier, were         |                 | .87           | 4.17                                    |
|                      |                 |               |   |

Notes:

(1) Numbers in parentheses next to cut names represent boiling ranges and are given in °F based on 15/5 distillation.

#### TABLE 2

## RAW SHALE OIL ASSAY QUALITIES

|                       | Garrett     | Tosco       | Paraho        |
|-----------------------|-------------|-------------|---------------|
| Whole Shale Oil       |             |             |               |
| Sp. Gravity (°API)    | .9042(25.0) | .9279(21.0) | .9383(19.3)   |
| Sulfur, wt%           | .64         | .67         | .71           |
| Nitrogen, wt%         | 1.30        | 1.85        | 2.00          |
| Viscosity, CS @ 100°F | 15.8        | 27.1        | 78.5          |
| Pour Point, °F        | 50          | 70          | 85            |
| Naphtha (310-) (1)    |             |             |               |
| Yield on Crude, LV%   | 1.26        | 7.10        | 0             |
| Sp. Gravity           | .814        | .762        | 200 - 201 LUK |
| Sulfur, wt%           | .43         | .90         | a niaite oran |
| Kerosene (310/500)    |             |             |               |
| Yield on Crude, LV%   | 14.04       | 13.86       | 6.80          |
| Sp. Gravity           | .841        | .824        | .847          |
| Sulfur, wt%           | . 58        | .82         | .71           |
| Smoke Point, mm       | 14          | 17          | 16            |
| Luminometer No.       | 32          | 40          | 32            |
| Nitrogen, wt% (2)     | 1.06        | .78         | 1.36          |
| Bromine No. (2)       | 23          | 23          | 23            |
| Aromatics, LV% (2)    | 38.9        | 29.9        | 39.4          |
| Gas 0il (500/1050)    |             |             |               |
| Yield on Crude, LV%   | 80.2        | 61.4        | 84.2          |
| Sp. Gravity           | .906        | .941        | .936          |
| Sulfur, wt%           | . 54        | .65         | .62           |
| Nitrogen, wt%         | 1.36        | 2.10        | 1.96          |
| Con Carbon, wt%       | .5          | 1.5         | 1.3           |
| Pour Point, °F        | 74          | 86          | 87            |
| Pitch (1050+)         |             |             |               |
| Yield on Crude, LV%   | 4.5         | 17.6        | 9.0           |
| Sp. Gravity           | 1.059       | 1.034       | 1.034         |
| Sulfur, wt%           | 1.32        | . 53        | .48           |
| Nitrogen, wt%         | 1.98        | 2.32        | 3.06          |
| Pour Point, °F        | >120        | 125         | bless monou   |

### Notes:

(1) Numbers in parentheses next to cut names represent boiling ranges and are given in °F based on 15/5 distillation.

(2) These data not obtained from assays but rather from subsequent Phase Two results.

- 8 -

The three shale oils are chemically similar to petroleum crude oils. As refinery feedstock, shale oils have relatively high nitrogen and sulfur content although only the nitrogen level is unusually high compared to petroleum crudes. Shale oils are more dense than petroleum crudes. This is reflected in a lower API gravity (19-25°API for the shale oils). The shale oils also have less material boiling in the naphtha and kerosene boiling range (500°F boiling point or lower) than do petroleum crudes. This is an important difference since the U.S. has a relatively high demand for light products (e.g. motor gasoline). The fuel oil fractions of shale oil have higher pour points than corresponding petroleum fractions.

#### 3.3.3 Product Demand Basis

The base demand pattern for refining products in the U.S. Midwest is summarized in Table 3. Refining products are broken down into five broad categories: LPG (liquified petroleum gas) - motor gasoline (mogas) including regular, premium and unleaded grades - Jet Fuel, both naphtha type and kerosene type - distillates including diesel oil, heating oil, kerosene and other distillate products - residual fuel oil including fuel oil as well as asphalts, waxes and lubes. PAD II like most of the U.S. requires a relatively high level of conversion of fuel oil and distillate to naphtha to meet a high (58% on total liquid product) motor gasoline demand. Product specifications for these five products are summarized in Table 4.

Throughout this report the terms Jet Fuel and ATF (Aviation Turbine Fuel) will be used interchangeably. Two general types of Jet Fuel are produced in the U.S. Midwest - Jet A and JP-4. Jet A is an aviation turbine fuel used primarily in commercial aircraft. JP-4 is the so called "wide cut" or "naphtha type" Jet Fuel used in military aircraft. In the U.S. Midwest, Jet Fuel production is approximately 80% Jet A/20% JP-4. Total jet fuel production in PAD II is 5% of total liquid product. By comparison, in 1974 jet fuels averaged 6.3% of total U.S. domestic production (1).

#### 3.3.4 Refining Basis

The hypothetical grass roots petroleum refinery used as a basis in this study produces 100 kB/CD(2) of products from petroleum with a process sequence typical of the present day refining industry in PAD II. No attempt was made to define existing capacity or possible spare available capacity. Onsite processing equipment considered typical of PAD II is listed in Table 5.

A process flow scheme for the Base Case is shown in Figure 1. Crude oil is separated into several fractions in a two stage distillation train of atmospheric and vacuum distillation. In the atmospheric tower crude oil is separated into light ends gas (material that boils below  $70^{\circ}$ F), naphtha, kerosene, light atmospheric gas oil (LAGO), heavy atmospheric gas oil (HAGO), and atmospheric residuum (material boiling above  $650^{\circ}$ F typically). The atmospheric resid ( $650^{\circ}$ F+) is further distilled in a vacuum distillation step

F. H. Kant et. al, "Effects of Changing the Proportions of Automotive Distillate and Gasoline Produced by Petroleum Refining" EPA-460/3-74-018, July 1974.

<sup>(2)</sup> In accordance with SI conversion  $k = 10^3$ ,  $M = 10^6$ .

The three shale oils an unmitcally and in to percoleme which with a collect struck, shale oils have relatively high contened suffur costent situated only the sitrogen level is unmanily high contened to set them crodes. Shale oils are not dense then percolemented. The shale oils also have less astacial (19-25° API for the shale oils). The shale oils also have less astacial (slifte in thermaph is and kerusene to nithe the the structed of boots of boots the shale oils). The shale oils also have less astacial (slifte in thermaph is and kerusene to nithe the the structed of boots the structed the shale oils also be also at a structed to be and the structed in the the the structed of the structed of the structed of the structed of the struct of the structed of the structed of the structed of the struct of the structed of the fuel of the structed of the structed of the struct of the fuel of the structed of the structed of the struct of the fuel of the structed of the structed of the struct of the structed of the fuel of the structed of the structed of the structed of the struct of the struct of the structed of the structed

#### TABLE 3

# PAD II PRODUCT DEMAND SLATE

| Product                       |           |
|-------------------------------|-----------|
| LPG                           |           |
| Motor Gasoline                | 58.0      |
| Jet Fuel (1)                  |           |
| Naphtha Type<br>Kerosene Type |           |
| Distillate                    | 23.5      |
| Fuel Oil                      | 11.0      |
|                               |           |
| Total Liquid Pr               |           |
| Total Prime Pro<br>(ex. LPG)  | duct 97.5 |
|                               |           |

#### Notes:

(1) The terms Jet Fuel and Aviation Turbine Fuel (ATF) are used synonymously in this report.

#### TABLE 4

#### PRIME PRODUCT SPECIFICATIONS

• Motor Gasoline

87.5 min. (RON + MON)/2RVP, psi Lead, cc/gal 7-10.5 • Jet A ("Kerosene Type" Jet Fuel) Sp. Gravity .775-.830 Sulfur, wt% .2 max. Luminometer No. 45 min. Aromatics, LV% 20 max. Freeze Point, °F -36 max. JP-4 ("Naphtha Type" Jet Fuel) Sp. Gravity .751-.802 Sulfur, wt% .3 max. Luminometer No. 50 min. RVP, psi 2-3 Aromatics, LV% 20 max. Freeze Point, °F -53 max. Distillate Sp. Gravity .890 max. Sulfur, wt% .3 max. Fuel Oil Sulfur, wt% .7 max. Viscosity, CS @ 122°F 10-350

- 12 -

#### TABLE 5

#### TYPICAL U.S. MIDWEST ONSITE PROCESSING FACILITIES

Distillation

Atmospheric Pipestill Vacuum Pipestill Crude Light Ends Facilities Unsaturated Light Ends Facilities

#### Hydrotreating

Naphtha Hydrotreater Kerosene Hydrotreater Heavy Atmospheric Gas Oil Hydrotreater Vacuum / Coker Gas Oil Hydrotreater

#### Fuel Oil Conversion

Fluid Catalytic Cracking Delayed Coking

#### Mogas Processes

Catalytic Reforming

#### Miscellaneous

Merox Treating - LPG - Cat Naphtha MEA Scrubbing of H<sub>2</sub>S Rich Gas Hydrogen Production Claus Plant (With Tail Gas Cleanup) so, Greviej Suliur, Wiž Luminometer No. RVP, pel Aromatice, LVZ.

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Sulfur, wil Viscosity, CS G 122°F



- 13 -

producing a vacuum gas oil (VGO) and vacuum resid (material boiling above 1050°F typically). The light ends and naphtha are sent to a series of fractionation towers (light ends or gas plant) which recovers a gas, containing ethane and methane for use as refinery fuel, propane for LPG sales, butanes for mogas blending, light virgin naphtha (LVN) for JP-4 and mogas blending and heavy virgin naphtha (HVN). Most of the HVN is processed in a catalytic reformer to make a high octane motor gasoline blending stock while a small portion is blended into JP-4.

Kerosene is mildly hydrotreated to improve its physical properties (odor, color, etc.) and is then blended either into Jet Fuel or to distillate products such as automotive diesel oil or home heating oil. LAGO and HAGO are blended to distillate products or fuel oil, or used as feed, along with VGO, to a Fluid Catalytic Cracking (FCC) unit. The FCC converts the atmospheric and vacuum gas oils mainly into naphtha to help meet the mogas demand. Other FCC products include unsaturated light ends, cat distillate and cat plant "bottoms" which is a tar-like substance. The light ends go to a separate unsaturated light ends plant where refinery fuel gas, FCC C<sub>3</sub>'s (propane and propylene) and C<sub>4</sub>'s (butanes and butenes) material used as LPG or as Alkylation plant feed are recovered. The Alkylation plant is a unit that produces high octane motor gasoline by chemically combining propylene or butene with isobutane. Cat distillate is blended either to distillate or fuel oil dispositions. Cat plant bottoms is blended to fuel oil.

Vacuum resid  $(1050^{\circ}F+)$  is either blended to fuel oil dispositions or converted to lighter products in a Coker. The Coker produces unsaturated light ends, coker naphtha and coker gas oil. The coker light ends are processed in a common plant with FCC light ends. Coker naphtha and heavy coker gas oil are fed to the FCC. Light coker gas oil goes to distillate and fuel oil dispositions.

In addition to these onsite process facilities, all offsite support facilities required for the refinery such as utility, pollution control, tankage and general offsite facilities are also included. The definition of offsite support facilities is based on historical data and experience.

Utility facilities cover such operations as steam generation, power distribution, cooling water circulation, refinery fuel distribution, and other miscellaneous utilities associated with operating a petroleum refinery.

Pollution control facilities provided are for a "restrictive location," typical of what would be required to build a refinery in the U.S. today. Primary and secondary wastewater treating is included. A Claus Sulfur plant followed by a tail gas cleanup plant is provided to treat sulfur rich refinery gases. All high sulfur feed to the refinery's fluid cat cracker is desulfurized. A total refinery limit of 10 LT/CD (for 100 kB/CD products) of SO<sub>2</sub> is imposed. General offsites facilities include interconnecting lines, safety facilities, fire protection, crude receipt and product shipping, blending, chemicals handling, building, site development, civil improvements and other miscellaneous facilities typical of a petroleum refinery. Tankage includes crude tankage, product storage and any necessary intermediate tankage.

The onsite processing facilities described above and in Table 5 refer to processing of petroleum crude only. For this study it is assumed that shale oil is processed in facilities segregated from the petroleum crude. This approach avoids any problems with compatibility of shale oil fractions with petroleum fractions and problems associated with the quality of shale/petroleum mixture fractions as feed to conventional petroleum refining units neither of which has been commercially demonstrated. No conversion facilities are provided for shale oil fractions since only limited data on employing the best current technology for such operations are available.

The processing sequence for processing the raw shale oil (shown in Figure 2) is as follows. The shale oil is fractionated in an atmospheric tower producing a  $500^{\circ}F^-$  (15/5 distillation) overhead, primarily kerosene, and a  $500^{\circ}F^+$  (15/5 distillation) resid. The  $500^{\circ}F$  (15/5 distillation) backend on the kerosene is a conservative approximation for shale kerosene representing industry average Jet A quality.

The Phase Two work indicated that Jet-A quality material can be produced from shale kerosene, if the shale kerosene is hydrotreated to reduce sulfur, nitrogen and aromatics content, and to improve burning characteristics. The 500°F<sup>-</sup> overhead is hydrotreated and fractionated into kerosene and naphtha. The Phase Two effort demonstrated that hydrotreating process conditions for shale kerosene are more severe than those normally required for petroleum kerosenes. The process basis for the hydrotreater is to produce a kerosene of Jet A quality. Table 6 summarizes the, quality of the hydrotreater product. Process and economic information for the severe hydrotreater is based on evaluation and extrapolation of data from the Phase Two work.

Whatever hydrotreated shale naphtha is recovered is blended to JP-4 or motor gasoline. The kerosene is blended only to Jet Fuel. The  $500^{\circ}F^+$  resid is distilled in a vacuum tower producing a vacuum gas oil (VGO) and a small volume of vacuum resid. The VGO is hydrotreated to reduce sulfur and nitrogen content. The treated shale VGO and the vacuum resid are blended into either fuel oil for sales or liquid plant fuel, displacing petroleum fractions which are in turn converted to lighter products. These same shale fractions are allowed to displace refinery gas from use as plant fuel to fuel gas sales.

#### 3.4 Approach to the Study

The refining impact of producing ATF (Jet Fuel) from shale oil includes changes in processing, energy requirements, grass roots capital investment, raw materials requirement, etc. These changes manifest themselves as an increase in total refining cost. The increased cost is due



- 16 -

# TABLE 6

#### HYDROTREATED SHALE KEROSENE QUALITY

|                       | Garrett             | Tosco | Paraho |
|-----------------------|---------------------|-------|--------|
| Sp. Gravity, °API     | 43.0                | 45.1  | 44.5   |
| Sulfur, wt% (Max.)    | 0.2                 | 0.2   | 0.2    |
| Aromatics, LV% (Max.) | 20.0                | 20.0  | 20.0   |
| Luminometer No.       | 48                  | 54    | 48     |
| Smoke Point, MM       | 22.                 | 24    | 22     |
| Nitrogen, wt%         | 0.3                 | 0.3   | 0.4    |
| Bromine No.           | refined at 1 mother | 1     | 1.1.1  |

action of class (Series 6) for such chais oil, with an even increasing volume of shale oil in the crude slate. Binner, in this study, shale oil fractions "oiling share 100" reason he conversed to lighter products, there is a greecies! Hight is to now such shale oil way be introduced into the crude slate. This light is reached then Firskally all of the feel oil and place fuel demond has been estimized by shale oil derived feel oil. For each of the these oile, the first is approximately 15 13/CD (per 100 kD/CD of product Further discussion on deriving this inhis and the inglications of methods to be produced by the first is approximately 15 13/CD (per 100 kD/CD of product to be consisted of the first is approximately with follows.

Approximate setter of cases (Sector 3) bringing shale oil into a second braw religing producing a bisher volume of dat Pick is also prosented in this report. The product reals for this parity of cases is shown balley:

both to the cost of facilities required to process the shale oil and to the increased conversion of heavy petroleum fractions required as shale oil fractions displace petroleum fractions from fuel oil and plant fuel dispositions.

The study is done with the aid of a refinery, linear programming, computer model. Linear programming (LP) is a mathematical technique for finding the optimum configuration of a complex system. LP is widely used throughout the petroleum industry as well as other industries. As applied to this situation LP is being used to define the optimum refinery processing sequence for both petroleum and shale oil consistent with product demand, crude availability, product quality, heat and material balance constraints.

The Base Case for this study is a grass roots refinery producing 100 kB/CD of liquid product (97.5 kB/CD of prime product - i.e. ex LPG) according to the base demand pattern in Table 3 by processing a 100% petroleum crude slate (67/33 So. Louisiana/Arabian Light) in refining facilities typical of PAD II. The product yield is shown below:

| Motor Gasoline      | 58.0 kB/CD |
|---------------------|------------|
| Jet Fuel*           | 5.0 kB/CD  |
| Distillate          | 23.5 kB/CD |
| Fuel Oil            | 11.0 kB/CD |
| Total Prime Product | 97.5 kB/CD |

\*"Jet Fuel" represents a 4/1 combination of Jet A/JP-4.

Increments of each shale oil are brought into the crude slate, replacing Arabian Light crude, while the refinery is forced to meet the same prime product demand as the Base Case. Production of LPG and refinery fuel gas, both relatively low volume products, is allowed to vary. This results in a series of cases (Series A) for each shale oil, with an ever increasing volume of shale oil in the crude slate. Since, in this study, shale oil fractions boiling above 500°F cannot be converted to lighter products, there is a practical limit as to how much shale oil may be introduced into the crude slate. This limit is reached when virtually all of the fuel oil and plant fuel demand has been satisfied by shale oil derived fuel oil. For each of the shale oils, the limit is approximately 16 kB/CD (per 100 kB/CD of product). Further discussion on deriving this limit and the implications of reaching it is contained in the discussion of results which follows.

Another series of cases (Series B) bringing shale oil into a second base refinery producing a higher volume of Jet Fuel is also presented in this report. The product yield for this series of cases is shown below:

| Motor Gasoline      | 58.0 kB/CD  |
|---------------------|-------------|
| Jet Fuel            | 10.0 kB/CD  |
| Distillate          | 23.5 kB/CD  |
| Fuel Oil            | 11.0 kB/CD  |
| Total Prime Product | 102.5 kB/CD |

This second series is meant to show the effect of producing Jet Fuel at a higher rate, relative to other prime products, than current PAD II demand indicates.

Two additional sensitivities are also considered in this report. The first (Series C) is sensitivity of the Series A results to an increased fuel oil demand. This is considered since the fuel oil plus plant fuel demand effectively controls the maximum volume of shale oil in the crude slate. Series C is run only for Paraho shale oil, since Paraho has the largest  $500^{\circ}F^+$  yield of the three shale oils and thus is the most severely limited. The product yield for Series C is shown below:

| Motor Gasoline      | 58.0 kB/CD  |
|---------------------|-------------|
| Jet Fuel            | 5.0 kB/CD   |
| Distillate          | 23.5 kB/CD  |
| Fuel Oil            | 15.0 kB/CD  |
| Total Prime Product | 101.5 kB/CD |

The second additional sensitivity (Series D) is an attempt to determine the maximum amount of Jet Fuel that can be produced from processing shale oil given the crude, demand, quality and processing constraints in this study. Demand for motor gasoline, distillate and fuel oil is maintained at the Series A level; petroleum crude availability is fixed at 100 kB/CD of the 67/33 So. Louisiana/Arabian Light mix. Tosco shale oil is allowed to come into the crude slate and Jet Fuel (maintaining a 4/1 Jet A/JP-4 ratio) production is allowed to reach its maximum. This maximum is about 20 kB/CD and is discussed, in detail, in the results section of this report. Tosco shale oil is chosen for this sensitivity since it has the highest kerosene yield of the three shale oils and as such produces the most Jet Fuel per barrel.

It should be pointed out that the (approximate) 100 kB/CD of products that is the basis for this study is chosen arbitrarily for ease of calculation. This study does not mean to imply that all, or even most, of the PAD II refineries process something close to the average crude slate or produce the average product slate using the typical process equipment. Some refineries run domestic crude, some a combination of domestic and foreign. Some refineries have more conversion capacity than others. The base refinery in this study is a purely hypothetical, average PAD II refinery. Similarly, data given in this report on shale crude runs of zero to 16 kB/D (based on 100 kB/CD products) does not imply that all refiners will be investing in equipment to process these small volumes of shale oil. Some refiners will process shale oil, others will not. Those that do will be building facilities of practical refining capacity. Thus, investment and operating cost levels for the shale oil processing equipment in this study are based on costs consistent with practical refining capacity.

#### 3.5 Economic Basis

Commercial shale oil production is not expected to be a reality until the mid-1980's or beyond. Cost escalation, inflation and raw materials cost in general and the development of shale oil projects in particular will depend on prevailing economic conditions at some time in the future. The timing of shale oil projects will depend on U.S. energy demand, OPEC's position, U.S. Government policy, rate of discovery of new domestic petroleum resources and other factors that are impossible to forecast. Rather than arbitrarily attempt to predict an economic/political scenario for some indeterminate time in the future, a historical basis of 1975 costs was chosen to define investment and operating cost levels.

To properly perform the economic analyses required for this study, it is necessary to arbitrarily set raw materials costs and by-product values. Prime product values are not required since each series of cases is run at a constant prime product production. Crude oil - including foreign, domestic and shale oil - cost is set at \$12.50/BBL (or approximately \$13.50/FOEB)(1). Other raw material and by-product values are approximately in cost parity with this crude price assumption. Refinery fuel gas value is set at \$15.00/FOEBor \$1.50/FOEB over crude. Propane LPG and imported butanes are set at an average value of \$5.CO/FOEB and \$6.00/FOEB above crude (\$11.10/BBL and \$13.05/BBL) respectively. It should be emphasized that the above values are completely arbitrary and are not meant to reflect present day or projected values at any particular location.

Investments presented in this study are based on 1975 costs and provide for onsite as well as all offsite support facilities required for the refinery. As is typical for a study of this type, a 20% contingency is included in the investments.

The economic results of this study are given in terms of average refining cost per barrel of prime products. This represents the minimum amount that a refiner would have to charge for the average barrel of prime products to recover refining expenses plus achieve a return on investment with the return criteria and economic bases used in this study. Average refining cost is defined as the total refining cost less by-product credits. Refining cost includes the following items:

- Raw Materials
- o Fuel
- Utilities
- · Manning
- Maintenance .
- Catalyst and Chemicals
- General Expenses
- Cost of Capital

(1) One Fuel Oil Equivalent Barrel (FOEB) = 6.05 x 10<sup>6</sup> BTU (LHV).

No working capital items such as crude and product inventory or warehouse spares are included in these costs since the basis for such items is highly location/ situation dependent. These costs could represent a significant addition to the average refining costs presented in this report. By-products include LPG and refinery fuel gas, low volume products the volumes of which are allowed to vary in this study, as well as delayed coke and sulfur. Raw materials and fuel values were discussed previously. Power cost is indexed to the \$15.00/FOEB fuel value. All other operating costs are given typical 1975 values. The annual capital recovery factor assumed is 20.4%/yr. This provides a 10% DCF after tax return assuming a 16 year project life, 50% tax rate, sum-of-theyear's-digits depreciation, centroid of investment one year prior to startup and no salvage value.

As already stated, these economic bases are completely arbitrary. Sufficient information is provided, in the case summaries for each series of cases, to adjust the economic results presented in this report to any alternate economic basis. The economic bases used in this report are summarized in Table 7.

#### 3.6 Discussion of Results

#### 3.6.1 General

As previously discussed, this study is done with the aid of a linear programming (LP) computer model of a refinery. LP is a mathematical technique to find the optimum configuration of a complex system. The word optimum as used here is in the mathematical sense. The LP model in this study is finding the optimum of a very constrained refining system (i.e. product demands and processing sequence fixed; crude slate essentially fixed) or in mathematical terms a local optimum. Identification of the more universal optimum, i.e. the most efficient way of processing shale oil in U.S. refineries requires a much more extensive study beyond the scope of this work.

Much of the data presented in this study and discussed in the following pages is given in terms of average refining cost. As suggested in the discussion of the economic basis used in this study, the economic basis is arbitrary. For this reason, sufficient information is presented for each case for the reader to substitute an alternate economic basis for the one used here. A sample calculation of average refining cost is given in Table 8.

#### 3.6.2 Series A - Base Demand Pattern

The Series A cases involved bringing increments of Garrett, Tosco and Paraho shale oils into the base refinery crude slate while forcing the refinery to maintain the base demand pattern. Case summaries for the Garrett, Tosco and Paraho shale oil Series A are presented in Tables 9 thru 11 respectively. Average refining cost for each of the Series A cases is plotted vs. shale oil input in Figures 3 thru 5.

#### TABLE 7

#### ECONOMIC BASES

- Raw Materials Cost
  - + Crude
  - + Butanes (Avg.)
- By-Product Values
  - + Refinery Fuel Gas
  - + LPG
  - + Coke
  - + Sulfur
- Utilities
  - + Fuel
  - + Power
  - + Raw Water
- Capital Recovery<sup>(2)</sup>

\$15.00/FOEB<sup>(1)</sup> \$11.10/BBL \$34/LT \$30/LT

\$12.50/BBL

\$13.05/BBL

\$15.00/FOEB 3.2¢/KWH 60¢/kGal

20.4%/yr of Total Investment

#### Notes:

One fuel oil equivalent barrel (FOEB) = 6.05 x 10<sup>6</sup> MBtu (LHV).
Provides 10% DCF return.

The Sories & cases involved bringing increments of Gernett, Toro at Parabo shale oils into the base refinery crude side while inverse the situer in antatain the base denote pattors. Gare somether for the Gern seco and Parabo shale oil beries & are presented in Fables 5 through seperificity. Average celluling cost for each of the Series & cases is botted vs. choic oil legat in Figures 3 through.

## - 23 -

# TABLE 8

SAMPLE CALCULATION OF AVERAGE REFINING COST

| Basis: Garrett Series A - 8 kB/CD Case (see Table                               |                          |
|---|--------------------------|
| • Raw Materials   | <u>Cost</u> , k\$/CD     |
| + Crude (100.76 $\frac{\text{kB}}{\text{CD}} \times \$12.50/\text{BBL}$ ) =     | 1259.5                   |
| + Butanes (6.22 $\frac{\text{kB}}{\text{CD}} \times \$13.05/\text{BBL}$ ) =     | 81.2                     |
| • Utilities   |                          |
| + Fuel (8.65 $\frac{\text{k FOEB}}{\text{CD}} \times $15.00/\text{FOEB}$ ) =    | 129.8                    |
| + Power (29.6 MW x 24 $\frac{\text{HR}}{\text{CD}}$ x \$.032/KWH) =             | 22.7                     |
| + Water (11.1 $\frac{M Gal}{CD}$ x \$.60/k Gal) =                               | 6.7                      |
| • Other Costs   |                          |
| + Manning, Maintenance and General Expenses                                     | 83.0                     |
| + Chemicals and Catalyst  | 7.0                      |
| 10 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1  |                          |
| • Capital Recovery  |                          |
| + .204 $\overline{YR} \times 334$ M\$ x $\frac{1}{365} \frac{YR}{CD}$           | 187.0                    |
| • By-Product Credits  |                          |
| + LPG $(2.44 \frac{\text{kB}}{\text{CD}} \times \$11.10/\text{BEL}) =$          | (27.1)                   |
| + Ref. Gas $(1.41 \frac{\text{k FOEB}}{\text{CD}} \times $15.00/\text{FOEB}) =$ | (21.2)                   |
| + Coke (266 $\frac{LT}{CD} \times $34.00/LT$ ) =                                | (9.0)                    |
| + Sulfur (50 $\frac{LT}{CD}$ x \$30.00/LT) =                                    | (1.5)                    |
| • Total Net Refining Cost   | 1718.1 k\$/CD            |
| • Average Refining Cost   |                          |
| 1718 1 k\$ 1  | Secondel Dista           |
| + 1718.1 $\frac{k\$}{CD} \times \frac{1}{97.5 \frac{kB}{CD}} =$                 | 17.62 \$/BBL<br>of Prime |
| 2.08 2.23 0.08 2.03 0.08  | Product                  |

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# - 24 -

## TABLE 9

#### CASE SUMMARY

GARRETT SERIES A

| Sha | ale Oil Input       |                      | 0 kB/CD | 4 kB/CD | 8 kB/CD | 12 kB/CD | 16 kB/CD |
|-----|---------------------|----------------------|---------|---------|---------|----------|----------|
| •   | Refinery Inputs     |                      |         |         |         |          |          |
|     | + Crudes, kB/CD     |                      |         |         | ID .    |          |          |
|     | South Louisian      | 3                    | 66.67   | 66.67   | 66.67   | 66.67    | 66.67    |
|     | Arabian Light       |                      | 32.77   | 28.54   | 26.09   | 22.80    | 21.99    |
|     | Garrett Shale       | 011                  | 0.00    | 4.00    | 8.00    | 12.00    | 16.00    |
|     | Total Crude         | Input                | 99.44   | 99.21   | 100.76  | 101.47   | 104.66   |
|     | + Butanes, kB/CD    |                      |         |         |         |          |          |
|     | Isobutane           |                      | 1.89    | 1.83    | 1.77    | 1.67     | 1.68     |
|     | Normal Butane       |                      | 4.37    | 4.43    | 4.45    | 4.47     | 4.49     |
|     | Total Butane        | Input                | 6.26    | 6.26    | 6.22    | 6.14     | 6.17     |
| •   | Refinery Outputs    |                      |         |         |         |          |          |
|     | + Prime Products,   | kB/CD <sup>(1)</sup> | 97.5    | 97.5    | 97.5    | 97.5     | 97.5     |
|     | + By-Products       |                      |         |         |         |          |          |
|     | LPG, kB/CD          |                      | 2.27    | 2.36    | 2.44    | 2.57     | 2.48     |
|     | Refinery Gas k      | FOE/CD               | 0.45    | 0.17    | 1.41    | 1.69     | 4.31     |
|     | Coke, LT/CD         |                      | 317     | 281     | 266     | 246      | 243      |
|     | Sulfur, LT/CD       |                      | 53      | 50      | 50      | 49       | 50       |
|     | Refinery Fuel, kFOE | /cd <sup>(2)</sup>   |         |         |         |          |          |
|     | + Process and Steam | m Gen.               |         |         |         |          |          |
|     | Liquid Fuel         |                      | 2.34    | 2.44    | 4.02    | 4.53     | 7.44     |
|     | Gas Fuel            |                      | 4.31    | 4.37    | 3.00    | 2.64     | 0.00     |
|     | + Carbon on FCC Ca  | talyst               | 1.57    | 1.56    | 1.63    | 1.80     | 1.78     |
|     | Total Fuel Co       | onsumption           | 8.22    | 8.37    | 8.65    | 8.97     | 9.22     |
| •   | Utilities           |                      |         |         |         |          |          |
|     | + Power, MW         |                      | 27.6    | 28.5    | 29.6    | 30.5     | 31.8     |
|     | + Water, M Gal/CD   |                      | 10.8    | 10.9    | 11.1    | 11.2     | 11.4     |
| •   | Economic Data (3)   |                      |         |         |         |          |          |
|     | + Total Investment  |                      | 307.5   | 318.0   | 334.0   | 349.0    | 368.5    |
|     | + Manning, Mainten  |                      |         |         |         |          |          |
|     | General Expenses    |                      | 80.0    | 80.5    | 83.0    | 85.5     | 88.5     |
|     | + Chemicals and Ca  | talyst, k\$/CD       | 6.0     | 6.5     | 7.0     | 7.0      | 7.5      |

Notes:

(1) Breakdown as follows: Mogas 58.0 kB/CD, Jet Fuel 5.0 kB/CD, Distillate 23.5 kB/CD, Fuel 011 11.0 kB/CD.

(2) One fuel oil equivalent barrel (FOER) =  $6.05 \times 10^6$  Btu (LHV). (3) Economic data based on 1975 average cost.

#### - 25 -TABLE 10

CASE SUMMARY

TOSCO-SERIES A

| h | ale Oil Input                          |      | 0 kB/CD | 4 kB/CD | 8 kB/CD | 12 kB/CD | 16 kB/CD |
|---|--|------|---------|---------|---------|----------|----------|
|   | Refinery Inputs                        |      |         |         |         |          |          |
|   | + Crudes, kB/CD                        |      |         |         |         |          |          |
|   | South Louisiana                        |      | 66.67   | 66.67   | 66.67   | 66.67    | 66.67    |
|   | Arabian Light                          |      | 32.77   | 29.25   | 26.52   | 22.81    | 21.67    |
|   | Tosco Shale Oil                        |      | 0.00    | 4.00    | 8.00    | 12.00    | 16.00    |
|   | Total Crude Input                      |      | 99.44   | 99.92   | 101.19  | 101.48   | 104.34   |
|   | + Butanes, kB/CD                       |      |         |         |         |          |          |
|   | Isobutane                              |      | 1.89    | 1.82    | 1.79    | 1.68     | 1.69     |
|   | Normal Butane                          |      | 4.37    | 4.41    | 4.45    | 4.46     | 4.49     |
|   | Total Butane Input                     |      | 6.26    | 6.23    | 6.24    | 6.14     | 6.18     |
|   | Refinery Outputs                       |      |         |         |         |          |          |
|   | + Prime Products, kB/CD <sup>(1)</sup> |      | 97.5    | 97.5    | 97.5    | 97.5     | 97.5     |
|   | + By-Products                          |      |         |         |         |          |          |
|   | LPG, kB/CD                             |      | 2.27    | 2.37    | 2.40    | 2.53     | 2.44     |
|   | Refinery Gas, k FOE/CD                 |      | 0.45    | 0.85    | 1.86    | 1.74     | 4.26     |
|   | Coke, LT/CD                            |      | 317     | 286     | 270     | 246      | 235      |
|   | Sulfur, LT/CD                          |      | 53      | 51      | 52      | 50       | 51       |
|   | Refinery Fuel, k FOE/CD <sup>(2)</sup> |      |         |         |         |          |          |
|   | + Process and Steam Gen.               |      |         |         |         |          |          |
|   | Liquid Fuel                            |      | 2.34    | 3.12    | 4.49    | 4.58     | 7.40     |
|   | Gas Fuel                               |      | 4.31    | 3.70    | 2.55    | 2.56     | 0.00     |
|   | + Carbon on FCC Catalyst               |      | 1.57    | 1.57    | 1.59    | 1.79     | 1.77     |
|   | Total Fuel Consumption                 |      | 8.22    | 8.39    | 8.63    | 8.93     | 9.17     |
|   | Utilities                              | 44.8 |         |         |         |          |          |
|   | + Power, MW                            |      | 27.6    | 28.5    | 29.3    | 30.1     | 31.3     |
|   | + Water, M Gal/CD                      |      | 10.8    | 10.9    | 11.1    | 11.2     | 11.4     |
|   | Economic Data <sup>(3)</sup>           |      |         |         |         |          |          |
|   | + Total Investment, M\$                |      | 307.5   | 318.0   | 331.5   | 344.0    | 361.0    |
|   | + Manning, Maintenance and             |      | 50115   | 510.0   | 551.5   | 51110    |          |
|   | General Expenses, k\$/CD               |      | 80.0    | 81.0    | 83.0    | 85.0     | 88.0     |
|   | + Chemicals and Catalyst, k\$/         | CD   | 6.0     | 6.5     | 7.0     | 7.0      | 8.0      |

## Notes:

(1) Breakdown as follows: Mogas 58.0 kB/CD, Jet Fuel 5.0 kB/CD, Distillate 23.5 kB/CD, Fuel 011 11.0 kB/CD.

(2) One fuel oil equivalent barrel (FOEB) =  $6.05 \times 10^6$  Btu (LHV). (3) Economic data based on 1975 average cost.
### - 26 -

### TABLE 11

### CASE SUMMARY

PARAHO-SERIES A

| Shale Oil Input  |                                     | 0 kB/CD                             | 4 kB/CD                             | 8 kB/CD                             | 12 kB/CD                            | 16 kB/CD                            |
|--|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| • Refinery Inputs  |                                     |                                     |                                     |                                     |                                     |                                     |
| + Crudes, kB/CD<br>South Louisiana<br>Arabian Light<br>Paraho Shale Oil  |                                     | 66.67<br>32.77<br><u>0.00</u>       | 66.67<br>29.42<br><u>4.00</u>       | 66.67<br>26.58<br><u>8.00</u>       | 66.67<br>23.39<br><u>12.00</u>      | 66.67<br>22.16<br><u>16.00</u>      |
| Total Crude Input  |                                     | 99.44                               | 100.09                              | 101.25                              | 102.26                              | 104.83                              |
| + Butanes, kB/CD<br>Isobutane<br>Normal Butane<br>Total Butane Input   |                                     | $\frac{1.89}{4.37}$                 | 1.82<br><u>4.42</u><br>6.24         | 1.77<br><u>4.45</u><br>6.22         | 1.67 $4.46$ $6.13$                  | 1.67<br><u>4.48</u><br>6.15         |
| <ul> <li>Refinery Outputs</li> </ul>   |                                     |                                     |                                     | (1)                                 | 60149236                            | C (resiled)                         |
| <ul> <li>Kernery Outputs</li> <li>+ Prime Products, kB/CD<sup>(1)</sup></li> <li>+ By-Products<br/>LPG, kB/CD<br/>Refinery Gas, kFOE/CD<br/>Coke, LT/CD<br/>Sulfur, LT/CD</li> </ul> |                                     | 97.5<br>2.27<br>0.45<br>317<br>53   | 97.5<br>2.44<br>0.97<br>308<br>52   | 97.5<br>2.42<br>1.88<br>266<br>52   | 97.5<br>2.53<br>2.27<br>242<br>51   | 97.5<br>2.66<br>4.15<br>296<br>56   |
| • Refinery Fuel, kFOE/CD <sup>(2)</sup>  |                                     |                                     |                                     |                                     |                                     |                                     |
| <ul> <li>+ Process and Steam Gen.</li> <li>Liquid Fuel</li> <li>Gas Fuel</li> <li>+ Carbon on FCC Catalyst</li> <li>Total Fuel Consumption</li> </ul>                                | 21.0<br>01.0<br><u>1.52</u><br>8.39 | 2.34<br>4.31<br><u>1.57</u><br>8.22 | 3.17<br>3.71<br><u>1.56</u><br>8.44 | 4.53<br>2.47<br><u>1.62</u><br>8.62 | 5.17<br>1.97<br><u>1.79</u><br>8.93 | 7.39<br>0.00<br><u>1.82</u><br>9.21 |
| • Utilities  |                                     |                                     |                                     |                                     |                                     |                                     |
| + Power, MW<br>+ Water, M Gal/CD   |                                     | 27.6<br>10.8                        | 28.6<br>10.9                        | 29.7<br>11.1                        | 30.7<br>11.2                        | 32.2<br>11.6                        |
| • Economic Data <sup>(3)</sup>   |                                     |                                     |                                     |                                     |                                     |                                     |
| + Total Investment, M\$<br>+ Manning, Maintenance and  |                                     | 307.5                               | 320.0                               | 336.0                               | 351.0                               | 373.5                               |
| General Expenses, k\$/CD<br>+ Chemicals and Catalyst, k\$  | /CD                                 | 80.0<br>6.0                         | 81.0<br>6.5                         | 83.5<br>7.0                         | 86.0<br>7.5                         | 90.0<br>8.0                         |

### Notes:

Breakdown as follows: Mogas 58.0 kB/CD, Jet Fuel 5.0 kB/CD, Distillate 23.5 kB/CD, Fuel 011 11.0 kB/CD.

(2) One fuel oil equivalent barrel (FOEB) =  $6.05 \times 10^6$  Btu (LIV). (3) Economic data based on 1975 average cost.



- 27 -





1

- 29 -

### 3.6.2.1 Processing Effects

How does the grass roots refinery processing change with the introduction of shale oil into the crude slate? It is important to first examine the Base Case refinery balance in more detail. In order to meet the relatively high demand for light products (principally mogas), conversion of some, but not all, fuel oil and distillate fractions in the Fluid Cat Cracker and Delayed Coker is required. Referring to Figure 1, some heavy atmospheric gas oil (HAGO) and even some hydrotreated vacuum gas oil (VGO) bypass the cat cracker (FCC). Some potential cat reformer feed bypasses to JP-4 blending. The motor gasoline (mogas) pool is made up largely of reformate and cat naphtha. The distillate pool consists of light and heavy atmospheric distillate, cat distillate and kerosene. The fuel oil pool contains cat distillate and cat fractionator bottoms, atmospheric distillate, hydrotreated VGO and vacuum pitch.

As shale oil is brought into the crude slate, VGO and then HAGO originally bypassed are introduced into the FCC. This happens for two reasons. First, shale oil 500°F+ fractions displace petroleum blendstocks in the fuel oil pool necessitating more conversion of petroleum fuel oil stocks. Secondly, the yield of reformable naphtha on total crude decreases requiring more cat naphtha to meet mogas demand. The volume of coking decreases commensurate with the decrease in yield of petroleum 1050°+. Cat distillate is blended into the distillate pool to make more room for additional shale 500°F+ fractions in the fuel oil pool and to compensate for atmospheric gas oil being withdrawn from the distillate pool for cat cracker feed. Liquid plant fuel begins to displace refinery gas as a means of increasing outlets for shale based fuel oil.

As even more shale oil is brought into the crude slate the above effects are intensified. The FCC, having exhausted all possible sources of feed, begins to recycle more cat distillate than normal. This increases cat naphtha yield making up for an ever decreasing yield of reformate and aids in destroying cat distillate thus making room in the sales fuel oil pool for more shale fuel oil. This higher recycle FCC operation produces more gas than normal at the same time that gas is becoming less valuable as a refinery fuel. Thus fuel gas export starts to increase rapidly. The refinery, unable to convert any more petroleum liquids from the base crude run, must import more crude to meet the same prime product demand. These effects may be seen in Table 9 for Garrett shale oil. Bringing in 4 kB/D of Garrett shale oil - from zero to 4 kB/D on the total crude slate - backs about 4 kB/D of Arabian Light out of the crude slate. The same incremental shale oil import - from 12 kB/D to 16 kB/D - backs out less than 1 kB/D of Arabian Light. The effect of the introduction of shale oil on the base case refinery process flow scheme is illustrated in Figure 1a, which shows the 8 kB/CD Garrett shale oil case results.

### 3.6.2.2 Maximum Shale Volume

As demonstrated by the above analysis there is a practical limit to the volume of shale oil that can be processed under the given processing and demand constraints. That is, without the opportunity to convert shale fuel oil fractions to lighter products, the volume of shale oil processed is effectively limited by the available plant fuel and fuel oil outlets. This



- 31 -

limit for each of the shale oils is approximately 16.0 kB/CD (per 100 kB/CD liquid product).

The realization of this limit accentuates the need for determining a philosophy for how shale oil will be processed in petroleum refineries. Traditional residual fuel oil outlets may decrease in the future with the growth of coal and nuclear energy industries. The question of whether shale fuel oil fractions should be converted to lighter products or blended to sales fuel oil depends on several factors. Among these factors are the economics of conversion, the quality of resulting conversion products, the volumes of shale oil that refineries will be required to process, etc. This question cannot be answered until data are available on conversion of shale oil fractions.

Another point to consider is whether this maximum is optimistic from a product quality point of view. Although sulfur, viscosity and nitrogen levels for the shale oil fractions are acceptable, these fractions have unusually high pour points compared to petroleum crude fractions (see Table 2). This presents little problem for the plant fuel pool which is a stream internal to the refinery. However, as shale fractions comprise more and more of the sales fuel oil pool, fuel oil pour points may rise to levels unacceptable in the current market. There are several unknowns that cloud an evaluation of the magnitude of this problem. Among them are the effect of blending petroleum derived and shale derived fuel oils on pour point, the effect of hydrotreating shale VGO on its pour point, the applicability of petroleum pour point blending techniques to shale oil pour points. It is expected, however, that this potential pour point problem could be handled via relatively minor modifications to oil movement and storage facilities and/or special product formulation techniques.

### 3.6.2.3 Refining Cost Effects

Using Figure 3, the Series A refining costs for Garrett shale oil, as an example average refining costs per barrel of prime product increases as shale oil is brought into the crude slate. At first the rise is slow representing the phase in which potential conversion process feeds, originally bypassed, are converted to lighter products. The slope of the curve gradually increases as available conversion process feeds become fully utilized and the refinery is forced to import more crude to meet the same prime product demand.

### 3.6.3 Series B - Increased Jet Fuel Demand

The Series B cases differ from Series A only in the volume of Jet Fuel produced. The Series B cases produce 10 kB/CD of Jet Fuel keeping all other prime product volumes constant. This series is designed to show the effect on the theoretical grass roots refinery of producing a higher volume of Jet Fuel on the overall demand slate. Case summaries for the Garrett, Tosco and Paraho Series B cases may be found in Tables 12 thru 14. Figures 3 thru 5 show the comparison of the Series A and Series B costs.

### - 33 -TABLE 12

### CASE SUMMARY

GARRETT-SERIES B

|       | 0 kB/CD  | 4 kB/CD   | 8 kB/CD   | 12 kB/CD   | 16 kB/CD   |
|-------|--|---|---|--|--|
|       |  |   |   |  |  |
|       | 66.67  | 66.67   | 66.67   | 66.67  | 66.67  |
| 09.75 | 38.06<br>0.00  | 33.85   | 30.60<br><u>8.00</u>                                  | 27.13<br><u>12.00</u>  | 26.31<br><u>16.00</u>  |
|       | 104.73   | 104.52  | 105.27  | 105.80   | 108.98   |
|       | 1 96   | 1.83  | 1.79  | 1 78   | 1.76   |
|       | 4.30   | 4.32  | 4.39  | 4.45   | 4.45   |
|       | 6.26   | 6.15  | 6.18  | 6.23   | 6.21   |
|       |  |   |   |  |  |
|       | 102.5  | 102.5   | 102.5   | 102.5  | 102.5  |
|       | 2.10   | 2.39  | 2.46  | 2.44   | 2.46   |
|       | 350  | 316   | 295   | 273  | 270  |
|       | U.   | 50  | 50  |  |  |
|       |  |   |   |  |  |
|       | 2.22 4.41  | 2.32 4.61   | 3.38 3.78   | 4.05 3.29  | 6.97<br>0.61   |
|       | 1.70   | 1.65  | 1.61  | 1.60   | 1.63   |
|       | 8.33   | 8.58  | 8.77  | 8.94   | 9.21   |
|       |  |   |   |  |  |
|       | 28.3<br>10.9   | 29.4<br>11.2  | 30.4<br>11.3  | 31.1<br>11.4   | 32.4<br>11.7   |
|       |  |   |   |  |  |
|       | 321.5  | 332.5   | 345.0   | 357.5  | 377.0  |
| CD    | 83.5   | 84.5  | 86.0  | 87.5   | 90.5   |
|       | 1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411<br>1411 | $ \begin{array}{r} 66.67\\38.06\\0.00\\104.73\\1.96\\4.30\\6.26\\102.5\\2.10\\0.49\\350\\61\\2.22\\4.41\\1.70\\8.33\\28.3\\10.9\\321.5\\83.5\end{array} $ | $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ | 66.67 $66.67$ $66.67$ $66.67$ $38.06$ $33.85$ $30.60$ $0.00$ $4.00$ $8.00$ $104.73$ $104.52$ $105.27$ $1.96$ $1.83$ $1.79$ $4.30$ $4.32$ $4.39$ $6.26$ $6.15$ $6.18$ $102.5$ $102.5$ $102.5$ $2.10$ $2.39$ $2.46$ $0.49$ $0.00$ $0.62$ $350$ $316$ $295$ $61$ $58$ $56$ $2.22$ $2.32$ $3.38$ $4.41$ $4.61$ $3.78$ $1.70$ $1.65$ $1.61$ $8.33$ $8.58$ $8.77$ $28.3$ $29.4$ $30.4$ $10.9$ $11.2$ $11.3$ $321.5$ $332.5$ $345.0$ $83.5$ $84.5$ $86.0$ | 66.67 $66.67$ $66.67$ $66.67$ $66.67$ $38.06$ $33.85$ $30.60$ $27.13$ $0.00$ $4.00$ $8.00$ $12.00$ $104.73$ $104.52$ $105.27$ $105.80$ $1.96$ $1.83$ $1.79$ $1.78$ $4.30$ $4.32$ $4.39$ $4.45$ $6.26$ $6.15$ $6.18$ $6.23$ $102.5$ $102.5$ $102.5$ $102.5$ $102.5$ $2.10$ $2.39$ $2.46$ $2.44$ $0.49$ $0.00$ $0.62$ $0.98$ $350$ $316$ $295$ $273$ $61$ $58$ $56$ $55$ $2.22$ $2.32$ $3.38$ $4.05$ $3.33$ $8.58$ $8.77$ $8.94$ $28.3$ $29.4$ $30.4$ $31.1$ $10.9$ $11.2$ $11.3$ $11.4$ $321.5$ $332.5$ $345.0$ $357.5$ $83.$ |

### Notes:

(1) Breakdown as follows: Mogas 58.0 kB/CD, Jet Fuel 10.0 kB/CD, Distillate 23.5 kB/CD, Fuel Oil 11.0 kB/CD. (2) One fuel oil equivalent barrel (FOEB) =  $6.05 \times 10^6$  Btu (LHV). (3) Economic data based on 1975 average cost.

### - 34 -TABLE 13

### CASE SUMMARY

TOSCO-SERIES B

| Sh | ale Oil Input   | 0 kB/CD | 4 kB/CD | 8 kB/CD | 12 kB/CD | 16 kB/CD |
|----|---|---------|---------|---------|----------|----------|
| •  | Refinery Inputs   |         |         |         |          |          |
|    | + Crudes, kB/CD<br>South Louisiana  | 66.67   | 66.67   | 66.67   | 66.67    | 66.67    |
|    | Arabian Light   | 38.06   | 33.90   | 30.11   | 27.43    | 25.59    |
|    | Tosco Shale Oil   | 0.00    | 4.00    | 8.00    | 12.00    | 16.00    |
|    | Total Crude Input   | 104.73  | 104.57  | 104.78  | 106.10   | 108.26   |
|    | + Butanes, kB/CD  |         |         |         |          |          |
|    | Isobutane   | 1.96    | 1.82    | 1.80    | 1.81     | 1.76     |
|    | Normal Butane   | 4.30    | 4.31    | 4.40    | 4.44     | 4.44     |
|    | Total Butane Input  | 6.26    | 6.13    | 6.20    | 6.25     | 6.20     |
| •  | Refinery Outputs  |         |         |         |          |          |
|    | + Prime Products, kB/CD <sup>(1)</sup>  | 102.5   | 102.5   | 102.5   | 102.5    | 102.5    |
|    | + By-Products   | 102.5   | 102.5   | 102.5   | 102.5    | 102.5    |
|    | LPG, kB/CD  | 2.10    | 2.42    | 2.42    | 2.38     | 2.41     |
|    | Refinery Gas, kFOE/CD   | 0.49    | 0.00    | 0.16    | 1.33     | 3.09     |
|    | Coke, LT/CD   | 350     | 317     | 292     | 277      | 261      |
|    | Sulfur, LT/CD   | 61      | 58      | 55      | 56       | 56       |
| •  | Refinery Fuel, kFOE/CD <sup>(2)</sup>   |         |         |         |          | Surfrom. |
|    | + Process and Steam Gen.  |         |         |         |          |          |
|    | Liquid Fuel   | 2.22    | 2.32    | 2.89    | 4.40     | 6.49     |
|    | Gas Fuel  | 4.41    | 4.61    | 4.24    | 2.94     | 1.05     |
|    | + Carbon on FCC Catalyst  | 1.70    | 1.65    | 1.59    | 1.54     | 1.63     |
|    | Total Fuel Consumption  | 8.33    | 8.58    | 8.72    | 8.88     | 9.17     |
|    | Utilities   |         |         |         |          |          |
|    | + Power, MW   | 28.3    | 29.4    | 30.0    | 30.7     | 31.9     |
|    | + Water, M Gal/CD   | 10.9    | 11.2    | 11.2    | 11.4     | 11.6     |
| •  | Economic Data <sup>(3)</sup>  |         |         |         |          |          |
|    | <ul> <li>+ Total Investment, M\$</li> <li>+ Manning, Maintenance and</li> </ul> | 321.5   | 331.0   | 340.0   | 353.0    | 368.5    |
|    | General Expenses, k\$/CD  | 83.5    | 84.5    | 85.0    | 87.0     | 89.5     |
|    | + Chemicals and Catalyst, k\$/CD  | 6.5     | 6.5     | 7.0     | 7.5      | 8.5      |

### Notes:

(1) Breakdown as follows: Mogas 58.0 kB/CD, Jet Fuel 10.0 kB/CD, Distillate 23.5 k\$/CD. Fuel Oil 11.0 kB/CD.

(2) One fuel oil equivalent barrel (FOEB) =  $6.05 \times 10^6$  Btu (LHV). (3) Economic data based on 1975 average cost.

| - | 35 | - |
|---|----|---|
|   |    |   |

TABLE 14

### CASE SUMMARY

PARAHO-SERIES B

| Shale | e Oil Input                          | 0 kB/CD | 4 kB/CD | 8 kB/CD  | 12 kB/CD | 16 kB/CI |
|-------|--------------------------------------|---------|---------|----------|----------|----------|
| R     | efinery Inputs                       |         |         |          |          |          |
| +     | Crudes, kB/CD                        |         |         |          |          |          |
|       | South Louisiana                      | 66.67   | 66.67   | 66.67    | 66.67    | 66.67    |
|       | Arabian Light                        | 38.06   | 33.86   | 30.62    | 28.26    | 27.13    |
|       | Paraho Shale Oil                     | 0.00    | 4.00    | 8.00     | 12.00    | 16.00    |
|       | Total Crude Input                    | 104.73  | 104.53  | 105.29   | 106.93   | 109.80   |
| +     | Butanes, kB/CD                       |         |         | A STREET |          |          |
|       | Isobutane                            | 1.96    | 1.83    | 1.79     | 1.80     | 1.78     |
|       | Normal Butane                        | 4.30    | 4.32    | 4.39     | 4.44     | 4.45     |
|       | Total Butane Input                   | 6.26    | 6.15    | 6.18     | 6.24     | 6.23     |
| R     | efinery Outputs                      |         |         |          |          |          |
|       | Prime Products, kB/CD <sup>(1)</sup> | 102.5   | 102.5   | 102.5    | 102.5    | 102.5    |
| +     | By-Products                          |         |         |          |          |          |
|       | LPG, kB/CD                           | 2.10    | 2.39    | 2.46     | 2.40     | 2.53     |
|       | Refinery Gas, kFOE/CD                | 0.49    | 0.00    | .63      | 2.07     | 4.06     |
|       | Coke, LT/CD                          | 350     | 314     | 291      | 274      | 322      |
|       | Sulfur, LT/CD                        | 61      | 58      | 57       | 58       | 63       |
| R     | efinery Fuel, kFOE/CD <sup>(2)</sup> |         |         |          |          |          |
| +     | Process and Steam Generation         |         |         |          |          |          |
|       | Liquid Fuel                          | 2.22    | 2.33    | 3.40     | 5.22     | 7.58     |
|       | Gas Fuel                             | 4.41    | 4.58    | 3.72     | 2.11     | 0        |
| +     | Carbon on FCC Catalyst               | 1.70    | 1.65    | 1.60     | 1.56     | 1.60     |
|       | Total Fuel Consumption               | 8.33    | 8.56    | 8.72     | 8.89     | 9.18     |
| U     | tilities                             |         |         |          |          |          |
| +     | Power, MW                            | 28.3    | 29.5    | 30.4     | 31.4     | 32.8     |
| +     | Water, M Gal/CD                      | 10.9    | 11.2    | 11.3     | 11.4     | 11.8     |
| E     | conomic Data <sup>(3)</sup>          |         |         |          |          |          |
| +     | Total Investment, M\$                | 321.5   | 332.5   | 345.5    | 361.0    | 383.0    |
| +     | Manning, Maintenance and             |         | 1 10000 |          |          |          |
|       | General Expenses, k\$/CD             | 83.5    | 84.5    | 86.0     | 88.0     | 92.0     |
| +     | Chemicals and Catalysts, k\$/CD      | 6.5     | 6.5     | 7.0      | 8.0      | 8.0      |
|       |                                      |         |         |          |          |          |

### Notes:

(1) Breakdown as follows: Mogas 58.0 kE/CD, Jet Fuel 10.0 kB/CD, Distillate 23.5 kB/CD, Fuel 011 11.0 kB/CD.

(2) One fuel oil equivalent barrel (FOEB) =  $6.05 \times 10^6$  Btu (LHV). (3) Economic data based on 1975 average cost.

### 3.6.3.1 Refining Effects

The refining effects of the incremental Jet Fuel production can be best understood by first comparing the base cases (100% petroleum crude) for Series A and Series B (Figures 1 and 6, respectively). The most obvious difference is that Series B requires a higher level of crude run to make the incremental volume of liquid product. The refinery produces the incremental Jet Fuel by blending kerosene that made up part of the distillate pool in Series A to Jet Fuel. Another important effect is that considerably less atmospheric gas oil is cat cracked in the Series B base case. This reflects a lowered required conversion of crude to mogas in Series B as demonstrated by the lower yield of mogas per barrel of prime product (56.5% in Series B vs. 59.5% in Series A). The effect of the introduction of shale oil on the high jet fuel demand refinery process flow scheme is illustrated in Figure 6a, which shows the 8 kB/CD Garrett shale oil case results.

What is the effect of bringing shale oil into the crude slate of this Series B base refinery? The effect is qualitatively the same as in Series A. The main difference is that problems associated with limited availability of shale fuel oil outlets in Series A are postponed to a slightly higher volume of shale oil since the base Series B case processes less of the potential cat cracker feed than Series A.

### 3.6.3.2 Refining Cost Effects

Average refining cost as a function of shale input is compared for Series B vs. Series A in Figures 3 thru 5 (representing Garrett, Tosco, and Paraho shale oils, respectively). Due to the lower level of conversion required to produce the Series B demand pattern, the overall level of refining cost per barrel of prime product is actually lower for Series B than for Series A. The same trends apply in Series B as in Series A. That is, there is an initial phase in which available conversion unit feeds are optimized (postponed slightly in Series B) followed by a phase of rapidly increasing cost in which the refinery, short on available conversion feed, imports higher volumes of petroleum crude to meet prime product demand. The maximum volume of shale oil that can be processed in the Series B scenario is essentially the same as for Series A since the volume of the ultimate disposition of shale fuel oil cuts, i.e., shale fuel oil plus liquid refinery fuel, was essentially unchanged.

### 3.6.4 Series C - High Fuel Oil Demand

As discussed under Series A the limited availability of outlets for fuel oil and liquid plant fuel limits the volume of shale oil that can be run to approximately 16 kB/CD. This limitation is most severe for Paraho shale oil since among the three shale oils considered, Paraho has the highest fuel oil yield (see Table 2). Series C is an attempt to discover how the base refinery processing sequence would change with a higher fuel oil demand. The case summary for Series C may be found in Table 15. Average refining costs for Series C are compared to Paraho Series A in Figure 7.



- 37 -



- 38 -

### - 39 -TABLE 15

### CASE SUMMARY

PARAHO-SERIES C

| Shale Oil Input   | 0 kB/CD                        | 4 kB/CD                             | 8 kB/CD                             | 12 kB/CD                            | 16 kB/CD                            |
|---|--------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| • Refinery Inputs   |                                |                                     |                                     |                                     |                                     |
| + Crudes, kB/CD<br>South Louisiana<br>Arabian Light<br>Paraho Shale Oil   | 66.67<br>36.79<br><u>0.00</u>  | 66.67<br>32.68<br>4.00              | 66.67<br>29.59<br><u>8.00</u>       | 66.67<br>26.47<br><u>12.00</u>      | 66.67<br>23.39<br><u>16.00</u>      |
| Total Crude Inpu  | t 103.46                       | 103.35                              | 104.26                              | 105.14                              | 106.06                              |
| + Butanes, kB/CD<br>Isobutane<br>Normal Butane<br>Total Butane Inp  | 1.97<br><u>4.31</u><br>6.28    | $\frac{1.81}{4.32}$ 6.13            | 1.82<br><u>4.41</u><br>6.23         | 1.76 $4.44$ $6.20$                  | 1.67<br><u>4.46</u><br>6.13         |
| • Refinery Outputs  |                                |                                     |                                     |                                     |                                     |
| + Prime Products, kB/C<br>+ By-Products   | nd <sup>(1)</sup> 101.5        | 101.5                               | 101.5                               | 101.5                               | 101.5                               |
| LPG, kB/CD<br>Refinery Gas, kFOE<br>Coke, LT/CD<br>Sulfur, LT/CD  | 2.03<br>2/CD 0.40<br>319<br>57 | 2.37<br>0.02<br>280<br>55           | 2.31<br>0.94<br>260<br>53           | 2.37<br>1.52<br>236<br>54           | 2.46<br>2.04<br>211<br>52           |
| • Refinery Fuel, kFOE/CD  | (2)                            |                                     |                                     |                                     |                                     |
| <ul> <li>+ Process and Steam Generation</li> <li>Liquid Fuel</li> <li>Gas Fuel</li> <li>+ Carbon on FCC Cataly</li> <li>Total Fuel Consumption</li> </ul> | 2.24<br>4.43<br>1.59           | 2.35<br>4.54<br><u>1.62</u><br>8.51 | 3.65<br>3.42<br><u>1.57</u><br>8.64 | 4.57<br>2.67<br><u>1.62</u><br>8.86 | 5.36<br>2.03<br><u>1.78</u><br>9.17 |
| • Utilities   |                                |                                     |                                     |                                     |                                     |
| + Power, MW<br>+ Water, M Gal/CD  | 27.9<br>10.8                   | 29.2<br>11.0                        | 30.0<br>11.2                        | 31.0<br>11.3                        | 32.0<br>11.5                        |
| • Economic Data <sup>(3)</sup>  |                                |                                     |                                     |                                     |                                     |
| + Total Investment, MS<br>+ Manning, Maintenance  | and                            | 328.0                               | 341.0                               | 355.5                               | 371.0                               |
| General Expenses, k<br>+ Chemicals and Cataly   |                                | 83.5<br>6.5                         | 84.5<br>7.0                         | 87.0<br>7.5                         | 89.0<br>8.0                         |

### Notes:

(1) Breakdown as follows: Mogas 58.0 kB/CD, Jet Fuel 5.0 kB/CD, Distillate 23.5 kB/CD, Fuel 011 15.0 kB/CD.

(2) One fuel oil equivalent barrel (FOEB) =  $6.05 \times 10^6$  Btu (LHV). (3) Economic data based on 1975 average cost.



- 40 -

### 3.6.4.1 Refining Effects

Compared to the Series A base case the Series C base case (see Figure 8) requires an overall lower level of conversion. This is reflected by a lower atmospheric gas oil feed to the cat cracker in Series C.

As expected, raising the volume of fuel oil outlet allowed a greater volume of Paraho shale oil to be introduced into the refinery. The practical limit for shale oil increased from about 16 kB/CD to 20 kB/CD (per 100 kB/CD liquid product).

### 3.6.4.2 Refining Cost Effects

As may be seen in Figure 7, the overall level of average refining costs for Paraho Series C is lower than for Series A due primarily to a reduced level of conversion. The Series C curve remains in a "low slope" phase longer than the Series A curve reflecting the increased availability of fuel oil outlets.

### 3.6.5 Series D - Maximum Jet Fuel

Perhaps the most significant series of all, Series D attempts to define how the theoretical grass roots refinery would make incremental barrels of Jet Fuel (with reference to the base demand pattern) by processing incremental barrels of shale oil (with reference to the base crude slate). Tosco shale oil is chosen for this sensitivity since it gives the highest yield of Jet Fuel per barrel shale oil of the three shale oils considered. The product demands and crude runs for this case are as follows:

| Cri                                     | ude Run   | Pro   | duct Demand  |
|---|---|---|--|
| So. Louisiana<br>Arabian Light<br>Tosco | 66.7 kB/CD Fixed<br>33.3 kB/CD Fixed<br>Unlimited | Mogas<br>Jet Fuel<br>Distillate<br>Fuel Oil | 58.0 kB/CD Fixed<br>5.0 kB/CD Minimum*<br>23.5 kB/CD Fixed<br>11.0 kB/CD Fixed |

\*Ratio of 4/1 Jet A/JP-4 is maintained.

### 3.6.5.1 Refining Effects

As Jet Fuel demand is increased product blending is rearranged such that potential Jet Fuel blendstocks that were going to other products (e.g. kerosene to heating oil or to fuel oil as a diluent) now get blended to Jet Fuel. As these sources of kerosene are exhausted the initial cutpoint of the kerosene is lowered (reducing cat reformer feed) to increase Jet Fuel production. This operation, of course, is limited by the need for reformate in the mogas pool both to maintain mogas volume and more importantly, to meet specification on mogas.

### 3.6.5.2 Maximum Jet Fuel Volume

Under the constraints previously described the maximum practical volume of Jet Fuel that can be produced is about 20 kB/CD (per fixed volume of other liquid products). This volume is limited by two factors. The



- 42 -

first, as discussed above is that incremental Jet Fuel production from the petroleum fractions is at the expense of cat reformer feed and the volume and quality of the mogas pool suffers. The second, as discussed under Series A, is that producing Jet Fuel from the Tosco shale oil also produces fuel oil as a co-product and fuel oil outlets are limited.

### 3.7 Data Needs

Throughout this report, mention is made of additional data that would be required for further definition of the impact of producing Jet Fuel from shale oils. The most basic of these needs is for data on the compatability of petroleum and shale crude oil fractions. Can petroleum and shale oil be processed in admixture? Are the resulting admixed fractions suitable as feed to downstream process units or as products in themselves?

As discussed previously, both the total volume of shale oil that could be processed and the maximum volume of Jet Fuel that could be produced (within the context of the demand slate) are limited because no conversion options are available to shale fuel oil fractions in this study. Data should be developed as to the suitability of shale fuel oil fractions as feed to such processes as Fluid Cat Cracking, Coking, Visbreaking, Hydrocracking. Data should also be developed on the cat reformability of shale naphthas.

### 3.8 Conclusions

Phase Two experimental work demonstrated that conventional quality Jet Fuel could be produced from shale kerosene. This Phase Three work has demonstrated that historical yields of Jet Fuel in the U.S. Midwest can be met with up to 16% shale oil in the region's crude slate. In fact, up to twice the historical yield can be achieved. Jet Fuel yields on shale oil are relatively low. The principle mechanism for producing incremental Jet Fuel from shale oil is to have shale distillate and fuel oil fractions replace petroleum fractions in existing distillate and fuel oil dispositions allowing petroleum fractions to be converted to lighter products.

Data should be developed on conversion of shale fuel oil fractions to lighter products. This study has shown that without conversion options, the volume of shale oil that can be processed is limited by the availability of shale fuel oil outlets. Such data are required before a study on the most efficient way of processing shale oil in petroleum refineries can be done.

Average refining costs per barrel of prime product increase as the volume of shale oil in the refinery crude slate increases. This occurs for two reasons. First, the high level of processing required for raw shale oil fractions increases costs. Secondly, the low yield of light fractions (boiling below approximately 500°F) on raw shale oil requires increased conversion of heavy (500°F+) material to meet the same product demands.

### SECTION IV

### PREPARATION OF A SAMPLE OF AVIATION TURBINE FUEL FROM PARAHO SHALE OIL

### 4.1 Introduction

As part of the Phase III program a sample, ca. 330 gallons, of Jet A quality aviation turbine fuel was prepared for the Air Force by hydrotreating a 310/500°F cut of Paraho shale oil over HDS-3A catalyst at 700°F, 1200 psig, 1 LHSV, and 4000 SCF/B H<sub>2</sub>. Prior to this production run, an exploratory study was conducted to verify the process conditions required to meet Jet A fuel specifications. The results of these studies are presented in this portion of the report.

### 4.2 Experimental Program

The experimental program consisted of a short exploratory run designed to confirm the hydrotreating conditions and the actual production run. Both pilot plant studies were conducted in HTT unit which consists of four independent reactor systems. Each reactor has its own temperature and pressure control. A unit schematic is shown in Figure 8a.

### 4.2.1 Paraho Shale Oil Hydrofining Exploratory Study

### 4.2.1.1 Feedstock and Catalyst

Paraho shale oil (125 barrels) was distilled at the Exxon Crude Assay Laboratory in Baytown, Texas. The feedstock utilized in this program was the 310/500°F cut (approximately 380 gallons) obtained from this raw Paraho shale oil. Detailed inspections of this feedstock are given in Table 16.

The catalyst utilized in this pilot plant study was HDS-3A which is the same commercially available NiMo catalyst which was used in the Phase II portion of the program.

### 4.2.1.2 Unit Operations and Analytical Techniques

In this run the reactor was charged with 60 cc of HDS-3A catalyst diluted with approximately 70 cc of mullite to maintain a uniform temperature in the reactor. The reactor was constructed from 3/4" schedule 160 stainless steel (type 304, 27" in length) and was operated in a downflow mode. A 10% H<sub>2</sub>S in hydrogen blend was used to sulfide the catalyst. Typical pilot plant operating procedures were discussed in detail in the Phase II final report. Initial operating conditions of the pilot plant unit were as follows:



### TABLE 16

### FEEDSTOCK INSPECTIONS

- 46 -

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| Feedstock<br>ERDL F.S. No.       | 310/500°F Paraho Shale Oil<br>4119 | Once-Through Mildly H/T<br>310/500°F Paraho Shale Oil<br>4202 |
|----------------------------------|------------------------------------|---|
| API Gravity, 60/60               | 36.3                               |   |
| Sulfur, Wt. %<br>Nitrogen, Wt. % | 0.743<br>1.158                     | 0.149<br>0.342  |
| Carbon, Wt. %                    | 84.67                              | 85.63   |
| Hydrogen, Wt. %                  | 12.55                              | 13.83   |
| Bromine No., cg/g                | 66.4                               | 8.3   |
| FIA, Vol. %                      |                                    |   |
| Aromatics                        | 36.9                               |   |
| Olefins                          | 24.3                               |   |
| Saturates                        | 30.6                               |   |
| PM Closed Cup Flash Pt., °F      | 162                                |   |
| Smoke Pt., mm                    | 15                                 | 25  |
| Kin. Viscosity @ -30°F, cs       | 11.42                              | 9.17  |
| ASTM D-86                        |                                    |   |
| IBP/5%                           | 342/374 <sup>(1)</sup>             | 258/309   |
| 10/20                            | 384/390                            | 335/368   |
| 30/40                            | 397/402                            | 380/392   |
| 50/60                            | 407/416                            | 402/410   |
| 70/80                            | 419/431                            | 416/430   |
| 90/95                            | 436/446                            | 443/455   |
| FBP                              | 469                                | 473   |
| % Recovery                       |                                    | 100   |
| <pre>% Residue</pre>             |                                    | 0   |
| % Loss                           |                                    | 0   |

(1) Average based on distillations of ten drums of FS-4119

| Unit                                    | HTT                        |
|---|----------------------------|
| Reactor                                 | 4                          |
| Catalyst                                | HDS-3A                     |
| Volume, cc                              | 60                         |
| Feedstock                               | 310/500°F Paraho Shale 011 |
| ERDL F.S. No.                           | 4119                       |
| Process Conditions                      |                            |
| LHSV                                    | 1.0                        |
| Pressure, Psig                          | 1500                       |
| Temperature, <sup>•</sup> F             | 700                        |
| Treat Gas, SCF/B (100% H <sub>2</sub> ) | 4000                       |

These conditions were set to correspond to the base case conditions utilized in earlier pilot plant studies conducted by the Government Research Laboratories with a slightly different kerosene cut from Paraho shale oil. During this exploratory study the effect of reducing total pressure to 1200 psig on product quality was also investigated. At the higher pressure initial indications were that the aromatics content was well within specifications although the flash point was slightly low. Lowering pressure could conceivably reduce the amount of hydrocracking, and thus increase the flash point. Also, it was expected that the level of aromatics hydrogenation would be less at the lower pressure which would tend to reduce hydrogen consumption.

Detailed run conditions are described in Table 17. Product inspections included gravity, sulfur, nitrogen, bromine number, carbon/hydrogen, FIA, PM closed cup flash point, freeze point, smoke point, kinematic viscosity @ -30°F, and ASTM D-86. Product sulfur and API gravity were determined daily for unit control. Carbon/hydrogen analyses were also obtained on a daily basis in order to determine hydrogen consumption. These results are also shown in Table 17.

4.2.1.3 Discussion of Results

As shown in the following table, most Jet A fuel specifications were easily met at the hydrotreating conditions employed in this study. Initial indications from the exploratory study (see Table 17) were that flash point would be the limiting specification in meeting fuel quality requirements. As expected, lowering pressure to 1200 psig resulted in a decrease in both the smoke point and the level of aromatics hydrogenation. TABLE 17

HTT-4-02 DETAILED RUN DATA PARAHO SHALE OIL EXPLORATORY STUDY

| . (6).  | Reactor No.<br>Run No.<br>Balance No.  | 401    | 400    | 4 N N       | 4 0 4                                 |            | • ~ ~ . | 100    | CN 60  | • • • | 201   |
|---|--|--------|--------|-------------|---------------------------------------|------------|---------|--------|--------|-------|-------|
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$   | FREESTOCK<br>Catalyst<br>ERDL Cat. No.<br>Volume, cc   |        |        |             | 300/500<br>4119<br>HDS-3A<br>NNM-4680 | F Shale 01 |         |        |        |       |       |
| No.         1.045         1.077         0.927         0.915         1.015         0.955         1.055         1   | Weight, gms<br>Process Conditions  |        |        |             | 43.6                                  |            |         |        |        |       |       |
| X/B         LUOW H_J         3331         3720         4340         4333         3720         4340         3333         1372         1395         1356         1355         1356         1356         1356         1356         1356         1356         1356         1356         1356         1356         1356         1356         1356  | THEN   | 1.043  | 1.077  | 0.927       | 0.915                                 | 1.019      | 1.133   | 0.955  | 1.055  | 966'0 | 1.    |
| metre, Paig         1471         1500         1435         1503         1477         1434         1135         1155  | FRC Rate, SCF/B (100% H <sub>2</sub> )<br>WTM Rate SCF/B   | 3831   | 3720   | 4340        | 4404                                  | 3959       | 3529    | 4213   | 3800   | 4038  | 39.05 |
| Terrer     703.6     703.1     704.7     702.9     702.6     703.2     703.2     703.3  | Reactor Pressure, Psig   | 1472   | 1509   | 1493        | 1503                                  | 1477       | 1494    | 1195   | 1185   | 1183  | E     |
|   | r, rurtuu rressure, rsia<br>Témperature, °F  | 703.6  | 705.1  | 704.7       | 702.9                                 | 702.6      | 703.2   | 703.2  | 703.3  | 703.3 | 703.5 |
|   | Liquid Product   |        |        |             |                                       |            |         |        |        |       |       |
| 110       272       187       64       35       54       273       167 $114$ $11.45$ $11.45$ $11.3$ $25.57$ $85.98$ $86.10$ $86.20$ $54.20$   | ERDL Sample No.  | 290021 | 290023 | 290025      | 290026                                | 290027     | 290028  | 290029 | 720031 |       |       |
| 113     5.5 <td>S. X-TAY, WPPM<br/>N WINN</td> <td>4110</td> <td>272</td> <td>187</td> <td>49 5</td> <td>38</td> <td>43.1</td> <td>48.2</td> <td>173</td> <td></td> <td></td>   | S. X-TAY, WPPM<br>N WINN   | 4110   | 272    | 187         | 49 5                                  | 38         | 43.1    | 48.2   | 173    |       |       |
| 19.8     14.45     14.33     <  | the state of the s | CEIC   | 21 98  | 00<br>95 07 | 24<br>05 C3                           | 11.3       | 0.0     | 4.0    | 0. 24  |       |       |
| 19.8     1.3     0.25     0.20     0.24     0.2       23.3     10.8     9.8     9.7     9.7     11.1     12.1     13.0       23.3     10.8     9.8     9.7     9.7     11.1     12.1     13.0     12.3       6.0     0.8     11.0     0.8     11.2     12.1     13.0     12.3       70.7     88.4     89.5     89.1     87.7     81.8     81.3       70.7     88.4     89.5     89.1     87.7     81.8     81.3       70.7     88.4     89.5     89.1     87.7     81.8     81.3       70.7     88.4     89.5     89.1     87.7     81.4     48.1     47.7       70.7     89.0     77.4     7.96     7.52     7.63     7.52     7.19     7.19       21     7.65     7.53     7.53     7.53     7.53     7.50     7.90     7.90       21.1.81     7.85     7.74     7.96     7.52     7.19     7.19     7.19       21.1.81     7.85     7.56     7.53     7.53     7.53     7.53     7.19     7.19       21.1.81     7.85     7.56     7.55     7.53     7.55     7.19     7.19  | H. K   |        | 14 45  | 12.00       | 14 41                                 | 10.00      | 80 71   | 14 37  | 14 28  |       | 14    |
| 23.5       10.8       9.8       9.7       9.7       11.1       12.1       13.0       12.3         70.7       88.4       89.5       89.1       87.7       87.1       86.2       86.4         70.7       88.4       89.5       89.1       87.7       87.1       86.2       86.4         70.7       88.4       89.5       89.1       87.7       87.1       86.2       86.4         70.7       88.4       89.5       89.1       87.7       87.1       86.2       86.4         70.7       89.0       9.7       47.4       48.0       47.4       48.1       47.7       48.3         1200       94       -49.0       -222.07       49.0       -222.07       49.0       104       104         11.81       7.85       7.74       7.96       7.52       7.80       29.0       7.19       7.19       7.19         215.5       -447.2       -49.0       -7.52       7.63       7.52       7.19       7.19       7.19       7.19         211.81       7.85       7.56       7.55       7.53       7.53       7.55       7.19       7.19       7.19         255       7.55 <td< td=""><td>Br No.</td><td>19.8</td><td>1.3</td><td></td><td>0.25</td><td></td><td>0.20</td><td>0.24</td><td></td><td></td><td></td></td<>  | Br No.   | 19.8   | 1.3    |             | 0.25                                  |            | 0.20    | 0.24   |        |       |       |
| 23.5     10.8     9.8     9.7     9.7     9.7     11.1     12.1     13.0     12.3       70.7     88.1     1.0     0.8     11.2     1.2     0.8     1.3       70.7     88.4     88.5     89.1     87.7     87.7     86.3       70.7     88.4     88.5     89.1     87.7     87.1     87.7     48.3       70.7     88.5     89.5     89.5     89.1     87.7     86.3     86.4       70.7     88.5     89.5     89.1     100     106     110     108     104       712.5     -47.2     -49.0     -22.07     -49.0     -22.07     -49.0     29.0     29.0       21     26.5     7.74     7.96     7.52     7.63     7.52     7.19     7.19       21     7.85     7.74     7.96     7.52     7.63     7.52     7.19     7.19       21     7.85     7.74     7.96     7.52     7.63     7.52     7.19     7.19       304     336/349     35753     365/359     365/359     365/359     365/359     365/359       567/359     563/359     567/359     365/359     365/359     365/359     365/359       514  | FIA, Vol. %  |        |        |             |                                       |            |         |        |        | 1     | 1     |
| 70.7     88.4     87.3     89.5     87.4     87.4     87.4     87.4     87.4     86.5     86.4       120     94     96     100     106     110     108     104     104       120     94     80.5     89.5     89.5     89.1     87.4     86.3     86.4       120     94     90     -49.0     -22.07     -49.0     -45.5     -48.1     46.3       121     26.5     52.0     32     50.2     28.0     29.0     29.0       21     7.85     7.74     7.96     7.52     7.19     7.19       21     7.85     7.74     7.96     7.52     7.19     7.19       21     7.85     7.74     7.96     7.52     7.19     7.19       364     36.499     35.759     36.5/379     365/379     365/379       365/375     365/379     365/379     365/379     365/379       367/39     406/416     407/416     407/416     407/416       465     514     99     90     90     90       0.5     0.5     91     91     90     91       0.5     0.5     90     91     91     91  | Aromatics  | 23.3   | 10.8   | 8.6         | 0.0                                   | 2.6        | 1.11    | 12.1   | 13.0   | 12.3  | 13.   |
| 56.3     47.2     47.4     48.0     47.4     48.1     47.7     48.3       120     94     94     96     100     106     110     108     104     104       121     26.5     52.0     -49.0     -22.07     -49.0     -45.5     -48.1     48.1       21     26.5     32.0     32     50.2     28.0     29.0     29.0       21     26.5     7.74     7.96     7.52     7.19     7.19       21     26.5     7.74     7.96     7.52     7.19     7.19       21     26.5     7.74     7.96     7.52     7.19     7.19       21     26.5     7.74     7.96     7.52     7.19     7.19       304     317     342/552     363/395     365/395     365/395       365/397     365/395     365/395     365/395     365/395       366/416     426/438     407/416     407/416       465     514     99     90       0.5     0.5     0.5     91       0.5     0.5     99     90       0.5     0.5     1055     100  | Saturates  | 2.02   | 0.0    | 2 08        | 0.0                                   | 1.4        | 1.4     | 0.0    | 0.0    | C.1   |       |
| 120         94         96         100         106         101         108         104         104           -15.5         -47.2         -49.0         -22.07         -49.0         -45.5         -48.1         -48.1         -46.3           21         26.5         32.0         32         30.2         28.0         29.0         29.0           11.81         7.85         7.74         7.96         7.52         7.19         7.19           304         30.2         30.2         38.0         29.0         29.0         29.0           356/349         356/349         356/349         357/397         342/352         7.19         7.19           356/349         356/349         356/349         356/349         356/349         356/349         7.19           356/349         356/349         356/349         356/349         356/349         7.19         7.19           356/349         356/349         356/349         356/349         356/349         356/349         7.16         7.19           366         406/416         406/416         406/416         407/416         407/416         406/416         406/416         406/416         406/416         406/416         40  | API Gravity  | 36.3   | 47.2   | 47.4        | 48.0                                  | 47.4       | 48.4    | 48.1   | 47.7   | 4.00  | 48.   |
| -15.5 -47.2 -49.0 -22.07 -49.0 -45.5 -48.1 -46.3<br>21 26.5 32.0 32 29.0 29.0 29.0 29.0<br>11.81 7.85 7.74 7.96 7.52 7.19 7.19<br>304 317 356/349 317 317 317 317 317 356/379<br>356/349 356/349 356/349 317 317 356/379<br>366/416 406/416 407/416 407/416 407/416 407/416 407/416 406/416 406/416 407/416 407/416 407/416 90 107/416 407/416 90 107 100 100 100 100 100 100 100 100 10  | Flash Pt., PM Closed Cup, "F   | 120    | 94     | 96          | 100                                   | 106        | 110     | 108    | 104    | 104   | . 86  |
| 21         26.5         32.0         32         50.2         29.0         29.0         29.0         7.19         7.114         7.114         7   | Freeze Pt., *F   | -15.5  | -47.2  | -49.0       | -22.07                                | -49.0      | -45.5   | -48.1  | -48.1  | -46.3 | -46   |
| 11.81     7.85     7.74     7.96     7.52     7.52     7.19     7.19       304     304     317     317     317       356/349     365/379     365/379     365/379       356/349     356/349     342/352       356/349     365/379     365/379       356/349     365/379     365/379       365/379     365/379     365/379       365/379     365/379     365/379       365/379     365/379     365/379       365/379     365/379     365/379       365/379     365/379     365/379       365/379     365/379     365/379       365/379     365/379     365/379       365/379     365/379     365/379       365/379     365/379     365/379       365/379     365/379     365/379       365/379     365/379     365/379       365/379     365/379     406/416       406/416     426/438     406/416       99     90     9       0.5     0     0  | Smoke Pt., mm  | 21     | 26.5   | 32.0        | 32                                    | 30.2       | 28.0    | 29.0   | 29.0   | 29.0  | 29.   |
| 304<br>304<br>336/349<br>336/349<br>335/357<br>335/357<br>335/357<br>335/357<br>335/357<br>335/357<br>335/357<br>335/357<br>335/357<br>335/359<br>342/416<br>405/416<br>405/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>407/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/416<br>400/410<br>400/4100/4100000000000000000000 | Viscosity, kin C -30°F, cs   | 11.81  | 7.85   | 7.74        | 7.96                                  | 7.52       | 7.63    | 7.52   | 7.19   | 7.19  | 7.3   |
| 304     317       336/349     317       336/349     342/352       355/357     355/357       355/357     352/352       355/357     352/352       355/357     352/352       355/357     352/352       355/357     352/352       355/357     352/352       355/357     352/352       355/357     352/352       355/357     352/352       356/416     407/416       455     450       3514     99       95     1       0.5     0       571     99       0     1030       1030     1030  | ASTM D-86, Vol. 1  |        |        |             |                                       |            |         |        |        |       | -     |
| 365/375     365/375       367/397     365/379       387/397     365/379       387/397     369/398       387/397     389/398       387/397     389/398       387/397     389/398       387/397     389/398       387/397     389/398       387/397     389/398       387/397     389/398       406/416     407/416       455     450       455     450       514     99       91     99       0.5     1126       501     99       0.5     1126   | 5\$/10\$   |        |        | 336/349     |                                       |            | 342/352 |        |        |       | 333   |
| 387/397     389/398       387/397     389/398       406/416     407/416       405/416     407/416       455     456       465     450       514     90       90     91       0.5     1176       567/B     1089  | 20/30  |        |        | 363/375     |                                       |            | 365/379 |        |        |       | 381   |
| 406/416     407/416       425/439     426/438       455     456/438       465     456/438       514     501       99     99       0.5     1126       567/B     1030       1030     1126       1030     1030   | 40/50  |        |        | 387/397     |                                       |            | 389/398 |        |        |       | 385   |
| 465<br>465<br>514<br>514<br>50<br>99<br>0.5<br>0<br>501<br>0.5<br>1080<br>1030<br>1126<br>1050<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1010<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>10                        | 0//09  |        |        | 406/416     |                                       |            | 407/416 |        |        |       | 406   |
| 514 501<br>99 99<br>0.5 1<br>0.5 0<br>SCF/B - 1089 1039 1126 1056 1031 1050 1010  | 96   |        |        | 465         |                                       |            | 450     |        |        |       | 448   |
| 99 99 99 99 99 99 99 99 99 99 91 91 91 9  | FBP  |        |        | 514         |                                       |            | 201     |        |        |       | 505   |
| 0.5 0.5 0<br>0.5 0<br>SCF/B - 1089 1039 1126 1056 1031 1010 -   | kecovery, 1  |        |        | 66          |                                       |            | 66      |        |        |       | 995   |
| 0 0.5 0<br>SCF/B - 1089 1039 1126 1056 1031 1010 -  | Residue  |        |        | 0.5         |                                       |            | -       |        |        |       | 0.5   |
| SCF/B - 1080 1039 1136 1055 1051 1010 -   | F033   |        |        | c.0         |                                       |            | 0       |        |        |       | •     |
|   |  |        | 1089   | 1039        | 1176                                  | 1065       | 1033    | 1050   | 0101   |       | 000   |

- 48 -

|                             | Jet A Spec    | Hydrotreated Para | ho Shale Oil |
|-----------------------------|---------------|-------------------|--------------|
| Reactor No.                 | Ler-pauly 702 | 4                 | 4            |
| Run No.                     | -             | 2                 | 2            |
| Balance No.                 | -             | 3                 | 10           |
| Process Conditions          |               |                   |              |
| Catalyst                    | -             | HDS-3A            | HDS-3A       |
| LHSV                        | -             | 1.0               | 1.0          |
| P, Psig                     | -             | 1500              | 1200         |
| T, °F                       | -             | 700               | 700          |
| Treat Gas, SCF/B            | - 305         | 4000              | 4000         |
| Liquid Product              |               |                   |              |
| S, wppm                     | Max. 3000     | 187               | 190          |
| Aromatics, FIA (Vol.%)      | Max. 20       | 9.8               | 13.4         |
| PM Closed Cup Flash Pt., °F | Min. 105      | 96                | 98           |
| Freeze Pt., °F              | Max36         | -49.0             | -46.3        |
| Smoke Pt., mm               | Min. 25       | 32.0              | 29.0         |
| Kin. Viscosity @ -30°F, cs  | Max. 15       | 7.74              | 7.30         |
| ASTM D-86                   |               |                   |              |
| 10%                         | Max. 400      | 349               | 347          |
| 50%                         | Max. 450      | 397               | 397          |
| FBP                         | Max. 550      | 514               | 505          |
| API Gravity                 | 39-51         | 47.4              | 48.3         |

### Effect of Pressure on Product Quality

### 4.2.2 Paraho Shale Oil Hydrofining Production Run

### 4.2.2.1 Feedstock and Catalyst

The feedstock utilized for the majority of this run was a 310/500°F kerosene cut (FS-4119) obtained from a raw Paraho shale oil. Detailed inspections are provided in Table 16. In order to meet the contract obligation for 300 gallons of Jet A quality aviation turbine fuel, however, towards the end of the run it was necessary to hydrotreat off spec material that had been mildly hydrotreated at low temperature during unit startups and shutdowns. Detailed inspections of this feedback (FS-4204) are also shown in Table 16.

The catalyst utilized in this pilot plant study was also HDS-3A which is a commercially available NiMo catalyst.

### 4.2.2.2 Unit Operations and Analytical Techniques

In this run each reactor was charged with 900 cc of HDS-3A catalyst. The reactor for each unit consisted of six tubes (3/4" schedule 160 x 34" Lg.) placed in series, each having a nominal internal volume of 165 cc. Mullite was placed at both ends of each tube for preheat purposes and to limit catalyst attrition. In addition, a guard chamber charged with 10 cc of catalyst and operated at the same temperature as the reactor was positioned ahead of each reactor bundle to help diagnose and prevent plugging problems. An electronic differential pressure cell was used to monitor pressure drop across the guard chamber. A 10% H<sub>2</sub>S in hydrogen blend was used to sulfide the catalysts. Operating conditions of the pilot plant unit were as follows:

| Unit                                    | HTT                        |
|---|----------------------------|
| Reactor                                 | 3 4                        |
| Catalyst                                | HDS-3A                     |
| Volume, cc                              | 900                        |
| Feedstock                               | 310/500°F Paraho Shale 011 |
| ERDL F.S. No.                           | 4119                       |
| Process Conditions                      |                            |
| LHSV                                    | 1.0                        |
| Pressure, Psig                          | 1200                       |
| Temperature, °F                         | 700                        |
| Treat Gas, SCF/B (100% H <sub>2</sub> ) | 4000                       |

For the production run, the operating pressure was maintained at 1200 psig since data obtained in the exploratory study had indicated that Jet A quality material could be produced at these conditions. Also, it was felt that better activity maintenance information would be obtained at the lower pressure.

Detailed run conditions are described in Tables 18 and 19. Product inspections included gravity, sulfur, nitrogen, bromine number, carbon/hydrogen, FIA, PM closed up flash point, freeze point, smoke point, kinematic viscosity @ -30°F, and ASTM D-86. Product sulfur, nitrogen, and API gravity were determined daily for unit control. FIA analyses were obtained periodically to measure catalyst deactivation for arcmatics hydrogenation. Carbon/hydrogen analyses were also obtained regularly to determine hydrogen consumption. These results are also shown in Tables 18 and 19.

### 4.2.2.3 Product Quality of Hydrotreated Paraho Shale Oil

Operating conditions for the production run were set at  $700^{\circ}$ F, 1200 psig, 1 LHSV and 4000 SCF/B H<sub>2</sub>. At these conditions a total of 296 gallons of product was collected in 21 nominal 15-gallon composites. In order to meet the 300-gallon contract obligation, additional hydrotreating of off spec material that had been mildly hydrotreated was required. Inspections of the composites are shown in Table 20. An overall sample inspection was calculated by arithmetically averaging the individual composite inspections. As shown in the following table the overall sample inspections all meet those required for Jet A aviation turbine fuel. TABLE 18

HTT-3-02 DETAILED RUN DATA PARAHO SHALE OIL PRODUCTION RUN

| <b>Date</b><br><b>Balance</b> No.<br>Fedstock  | 2/9<br>1<br>310/500°F                          | 2/10<br>2<br>Paraho                                   | 2/10 2/11 2<br>2 3 4<br>Paraho Shale Oil        | 2/12   | 2/13<br>S                                     | 2/15   | 2(12)   | 2/20<br>8                                      | 2/21<br>9                                      | 2/£3)<br>11                                    | 2/24<br>12   |   |
|--|--|---|---|--|---|--|---|--|--|--|--|---|
| ERUL F. S. No.<br>Catalyst<br>ERUL Cat. No.<br>Volume, cc<br>Meight, gms   | 4119<br>HDS-3A<br>NNM-4680<br>900<br>657.6     |   |   |  |   |  | (Guard ch.<br>charged w/cat)<br>910<br>664.9    | Ŧ  |  |  |  |   |
| Process Conditions<br>LHSV<br>Treat Gas, SCF/B (1004 H <sub>2</sub> )<br>Exit Gas, SCF/B<br>Reactor Pressure, Psig<br>H, Partial Pressure, Psia<br>Tëmperature, "F | 0.953<br>4197<br>2575<br>1358<br>1096<br>708.6 | 1.009<br>3959<br>2353<br>2353<br>1199<br>954<br>707.5 | 1.042<br>3838<br>2784<br>1195<br>999<br>706.9   | 0.888<br>4499<br>3164<br>1202<br>1006<br>705.7 | 1.019<br>3927<br>2814<br>1203<br>977<br>707.3 | 0.987<br>4054<br>3132<br>1213<br>999<br>706.1    |   | 0.9628<br>1853<br>2846<br>1254<br>994<br>503.0 | 1.2642<br>1574<br>1717<br>1233<br>855<br>697.4 | 0.9632<br>4149<br>3148<br>1225<br>999<br>698.0 | 0.9939<br>4022<br>3037<br>1199<br>972<br>698.9                 |   |
| Liquid Product<br>Matl. Balance Sample No.<br>5. wppm<br>N. wppm<br>C. wt. 9<br>H. wt. 8<br>Br. No.  | 720034<br>119<br>3.0                           | 720035<br>153<br>4.0                                  | 720036<br>260<br>0.43<br>86.08<br>14.29<br>0.24 | 720037<br>163<br>4.7                           | 720038<br>161<br>7.9                          | 720039<br>61.2<br>53.0<br>86.26<br>14.28<br>0.34 | 720046<br>283.5<br>334<br>86.37<br>14.08<br>0.6 | 720049<br>432<br>10,825                        | 720054(1)<br>143,30(1)<br>369                  |  | 720064 (1) 720072 (1)<br>28.3, 9.1 (1) 90.7,54.6 (1)<br>89 283 | 8 |
|  | 48.3   | 48.3  | 9.8<br>0.6<br>89.5<br>48.3                      | 48.2   | 48.1  | 14.2<br>0.7<br>85.0<br>47.8                      | 16.8<br>0.7<br>82.5<br>45.8                     | 38.2   | 45.8<br>8                                      | 46.0   | 45.8   |   |
| ASTM D-86, F<br>TBP/54<br>10/20<br>30/40<br>50/60<br>70/80<br>90/95  |  |   |   |  |   |  |   |  |  |  |  |   |
| <pre>* necovery * Loss * Loss * Residue Matl. Balance, Mt. % Mydrogen Consumption by C/H Analysis, SCF/B</pre>   | 98.3   | 99.3  | 96.7<br>1038                                    | 103.27   | 99.21   | 95.64<br>1007                                    |   | 91.46  | 75.64  | 98.43  | 95.39  |   |

- 51 -

| T     |
|-------|
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| cont  |
| 18    |
| TABLE |
|       |

## HTT-3-02 DETAILED RUN DATA PARAHO SHALE OIL PRODUCTION RUN

| Date<br>Balance No.   | 2/25<br>13  | 2/26<br>14                                | 2/27<br>15                                 | 2/28<br>16                              | 3/1   | 3/2<br>18                    | 3, .<br>19   |
|---|---|---|--|---|---|------------------------------|--|
| ERDL F. S. No.<br>Catalyst<br>ErDL Cat. No.<br>Volume, cc   |   |   |  | 510/500<br>4119<br>HDS-3A<br>NNM-4680   | -110/500 F Paraho Shale 011<br>-4119                    |                              |  |
| Process Conditions  |   |   |  | 664.9                                   |   |                              |  |
| Treat Gas, SCF/B (100% H <sub>2</sub> )   | 0.9699<br>4118  | 0.9971<br>3975<br>2057                    | 1.0045<br>3943                             | 1.0219<br>3911<br>3978                  | 0.9865 4054 2100  | 0.9898 4038                  | 0.9929<br>4022   |
| Reactor Pressure, Psig<br>H, Partial Pressure, Psig<br>Témperature, °F  | 9140<br>1194<br>974<br>698.5                            | 1213<br>1213<br>980<br>696.1              | 1178<br>1178<br>858<br>697.9               | 20/0<br>1173<br>954<br>699.0            | 1224<br>1007<br>702.8                                   | 2014<br>1219<br>991<br>697.7 | 203/<br>1211<br>993<br>699.4                                       |
| Liquid Product<br>Matl. Balance Sample No.<br>S, wppm<br>N, wppm<br>C, wt. 8<br>H, wt. 8<br>Br. No.                               | 720076(1)<br>0, 0.8(1)<br>318<br>86.16<br>14.03<br>0.62 | 720078<br>21.3, 7.2 <sup>(1)</sup><br>352 | 720080<br>20.1, 12.0 <sup>(1)</sup><br>391 | 720082<br>24.5, 0 <sup>(1)</sup><br>495 | 720084<br>13.1, 0.3(1)<br>75<br>85.99<br>14.05<br>14.05 | 720086<br>185, 31.7(1)<br>68 | 720094<br>12.6, 8.2 <sup>(1)</sup><br>63<br>86.21<br>14.21<br>0.27 |
| FIA, Vol. 4<br>Aromatics<br>Olefins<br>Saturates<br>API Gravity<br>PM Closed Cup Flash Pt., *F<br>Freeze Pt., *m<br>Smoke Pt., *m | 18.6<br>0.6<br>80.7<br>45.8                             | 47.0                                      | 462  | 8.<br>8                                 | 15.6<br>0.7<br>83.7<br>46.4                             | 47.5                         | 16.2<br>1.0<br>82.8<br>47.3  |
| Kin. Viscosity 0 -30°F, cs<br>ASTM D-86, °F<br>IBP/5%<br>10/20<br>30/40<br>50/60<br>70/80   |   |   |  |   |   |                              |  |
| FBP<br>% Recovery<br>% Loss<br>% Residue<br>Matl. Balance, Mt. %  | 95.54   | 94.62                                     | 94.88                                      | 95.23                                   | 93.19   | 89 ,34                       | 90.42  |
| Hydrogen Consumption by C/H<br>Analysis, SCF/B  | 883   |   | NI 210                                     | •                                       | 914   |                              | 1017   |

(1) Mercury treated

- 52 -

TABLE 18 (continued)

## HIT-3-02 DETAILED RUN DATA PARAHO SHALE OIL PRODUCTION RUN

| Dete<br>Teltance No.                              | 3/4                            | 3/5          |      | 3/6        | 3/7                        | 3/8                        | 3/9                       |
|---|--------------------------------|--------------|------|------------|----------------------------|----------------------------|---------------------------|
| Feedstock   |                                |              |      |            | 310/500°F Paraho Shale Oil | o Shale Oil                |                           |
| catalyst<br>ERDL Cat. No.                         |                                |              |      |            | 411941194119               |                            |                           |
| Volume, cc<br>Weight, gms                         |                                |              |      |            | 910                        |                            |                           |
| Process Conditions                                |                                |              |      |            |                            |                            |                           |
| Lrisv<br>Treat Gas. SCF/B (100% H_)               | 0.9960                         | 0.9464       |      | 0.9657     | 0.9539                     | 0.9611                     | 0.9718                    |
| Exit Gas, SCF/B                                   | 2941                           | 3259         |      | 3180       | 3180                       | 2750                       | 3180                      |
| Reactor Pressure, Psig<br>H Partial Pressure Deia | 1206                           | 1205         |      | 1187       | 1196                       | 1193                       | 1189                      |
| Temperature, 'F                                   | 638.9                          | 698.4        |      | 698.3      | 696.3                      | 704.9                      | 704.4                     |
| Liquid Product<br>Matl. Balance Samle No.         | 720106                         | 011022       |      | 720122     | 301067                     | 120130                     | 720140                    |
| S. wppm   | (I)0 °0                        | 30.7, 3.4(1) | 4(1) | 47.4, 0(1) | 15.5, 2.9 <sup>(1)</sup>   | 63.5, 10.8 <sup>(1)</sup>  | 123.8, 7.1 <sup>(1)</sup> |
| N, vppm<br>C, vt. 1<br>H, vt. 1<br>Br. No.        | 87 .<br>85.90<br>13.94<br>0.28 | 60           |      | 59         | Ø                          | -<br>86.39<br>14.18<br>0.3 | 81                        |
| FIA, Vol. 4                                       |                                |              |      |            |                            | 141 and 141                |                           |
| Olefins   | 0.7                            |              |      |            |                            | 1.0                        |                           |
| API Gravity                                       | 84.5                           | 46.4         |      | 47.0       | 47.2                       | 83.9                       | 46.1                      |
| PM Closed Cup Flash Pt., "F<br>Freeze Pt "F       |                                |              |      |            |                            |                            |                           |
| Smoke Pt., mm<br>Kin. Viscosity 0 -30°F. cs       |                                |              |      |            |                            |                            |                           |
| ASTM D-86, *F                                     |                                |              |      |            |                            |                            |                           |
| 10/20<br>10/40                                    |                                |              |      |            |                            |                            |                           |
| 20/60   |                                |              |      |            |                            |                            |                           |
| 70/80<br>90/95                                    |                                |              |      |            |                            |                            |                           |
| FBP   |                                |              |      |            |                            |                            |                           |
| Loss  |                                |              |      |            |                            |                            |                           |
| % Residue<br>Matl. Balance. Mt. %                 | 93.28                          | 91.62        |      | 91.88      | 93.09                      | 60.62                      | 95.73                     |
| Hydrogen Consumption by C/H                       | 67.6                           |              |      |            | ALL BUS U                  |                            |                           |

(1) Mercury treated

- 53 -

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TABLE 18 (continued)

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# HTT-3-02 DETAILED RUN DATA PARAHO SHALE OIL PRODUCTION RUN

| Balance No.<br>Fredstock<br>ERDL F. S. No.<br>Catalyst<br>ERDL Cat. No.<br>Volume, cc<br>Weight, gms.   | 8  |                    | 27  | 28   | 30(3)<br>30(500°F P<br>-4119<br>-HDS-3A<br>NNM-4680      | 30(3) 31<br>310/500°F Paraho Shale Oil<br>4119 | 32   | 8   |
|---|--|--------------------|---|--|--|--|--|---|
| Process Conditions<br>LHSV<br>Treat Gas, SCF/B (100% H <sub>2</sub> )<br>Exit Gas, SCF/B<br>Reactor Pressure, Paig<br>H Partial Pressure, Psia<br>Tëmperature, *F   | 0.9615<br>4165<br>3196<br>1196<br>977<br>700.4 | 1                  | 0.9405<br>4245<br>1081<br>1202<br>893<br>704.3            | 0.9351<br>4277<br>3339<br>1190<br>979<br>700.0 | 0.9427<br>0.9427<br>4245<br>2433<br>1213<br>963<br>715.5 | 0.9681<br>4134<br>3100<br>1204<br>992<br>717.4 | 0.972<br>4118<br>1187<br>1187<br>709.1                       | 0.961<br>4165<br>3048<br>1198<br>986<br>706.1 |
| Mall Froduct<br>Mall Balance Sample No.<br>S, wppm<br>N, wppm<br>C, wt. 5<br>Br. No.<br>Br. No.   | 720156<br>114.4, 14.6 <sup>(1)</sup><br>141    | 4.6 <sup>(1)</sup> | 720166 (1)<br>13.2, 0(1)<br>137<br>86.26<br>13.96<br>0.33 | 720176<br>10.8, 0(1)<br>171                    | 7201881)<br>71, 911)<br>53                               | 270190 (1)<br>29, <1<br>62                     | 720199<br>79.3, 35.1 <sup>(1)</sup><br>166<br>86.41<br>14.01 | 720208<br>18.2, 10.6(1)<br>127                |
| rin, vol. *<br>Aromatics<br>Aromatics<br>Saturates<br>API Gravity<br>PM Closed Cup Flash Pt., *<br>Freeze Pt., *<br>Smoke Pt., *<br>S | 45.7   |                    | 45.2  | 45.5   | 46.9   | 46.0   | 16.9<br>0.3<br>82.7<br>46.0                                  | 46.2  |
| 50/60<br>70/80<br>90/95<br>FBP<br>* Recovery<br>* Loss<br>* Residue<br>Mail. Balance, Wt. *<br>Hydrogen Consumption by C/H<br>Analysis, SCF/B   | 93.59  |                    | 94.35<br>821  | 95.13<br>-                                     | 94.72<br>-   | 94.15<br>-                                     | 126.95<br>820  | 106.03  |

Mercury treated
 Shutdown due to high pressure
 Guard chamber plugged during balance 29

- 54 -

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## HTT-3-02 DETAILED RUN DATA PARAHO SHALE OIL PRODUCTION RUN

| Date<br>Balance No.<br>Feedstock  | 3/20<br>34<br>310,                              | 3/21 3/22<br>35<br>-310/500°F Paraho Shale Oil | 3/22<br>36<br>1e 011                                    | 3/29<br>37  | 3/30<br>38<br>Mildly Hydrot                   | 3/30 3/31<br>38 39 39<br>-Mildly Hydrotreated FS 4119 | 4/1<br>40   |
|---|---|--|---|---|---|---|---|
| ERDL F. S. No.<br>Catalyst<br>ERDL Cat. No.<br>Volume, cc.<br>Meight, gms.  | 41194119  | -4119  |   |   |   |   |   |
| Process Conditions<br>LHSV<br>Treat Gas, SCF/B (100% H <sub>2</sub> )<br>Exit Gas, SCF/B (100% H <sub>2</sub> )<br>Reactor Pressure, Psig<br>H <sub>2</sub> Partial Pressure, Psia<br>Tëmperature, <sup>*</sup> F | 0.9784<br>4086.<br>3037<br>1187<br>975<br>709.2 | 0.9865<br>4054<br>2846<br>1187<br>977<br>708.1 | 0.9775<br>4086<br>3021<br>1201<br>986<br>701.2          | 0.9424<br>425<br>3895<br>1199<br>1015<br>702.6                      | 0.9430<br>4245<br>890<br>1203<br>874<br>709.3 | 0.9414<br>4245<br>3831<br>1205<br>1018<br>709.0       | .9674<br>4134<br>327<br>1219<br>1031<br>708.2       |
| Liquid Product<br>Matl. Balance Sample No.<br>S. vppm<br>N. vr. 4<br>H. vt. 4<br>Br. No.  | 720220<br>26.9, <1.0 <sup>(1)</sup><br>126      | 720224<br>28, 11.6(1)<br>151                   | 720286<br>39.9, 3.3(1)<br>119<br>86.10<br>14.00<br>0.31 | 720306<br>14.2, 2.3 <sup>(1)</sup><br>1.59<br>8.81<br>14.52<br>0.53 | 720309<br>24.2, <1 <sup>(1)</sup><br>19       | 720314<br>5.4, 3.1(1)<br><0.1                         | 720324<br>3.8, <0.1<br>0.1<br>86.20<br>14.33<br>0.3 |
| FIA, Vol. 4<br>Aromatics<br>Alexatics<br>Saturates<br>API Gravity<br>PM Closed Cup Flash Pt., °F<br>Freeze Pt., "P<br>Smoke Pt., m<br>Kin. Viscosity 0 -30°F, cs<br>ASTM D-86, °P                                 | 16.9<br>0.3<br>82.7<br>47.1                     | <b>6.4</b>                                     | 16.3<br>0.7<br>83.0<br>46.5                             | 8.2<br>0.7<br>91.1<br>47.7  | 47.8  | 47.9  | 9.9<br>1.1<br>89.0<br>47.8                          |
| 10/20<br>30/40<br>50/60<br>70/80<br>90/95<br>FEP<br>* Recovery<br>* Loss<br>* Residue<br>* Residue<br>* Residue<br>* Matl. Balance, Mt. %<br>Hydrogen Consumption by C/H<br>Analysis, SCF/B                       | 92.92<br>-                                      | 94.68  | 94.72<br>882  | 95.77<br>320  |   | - 94.90   | 93.89   |

- 55 -

Mercury treated
 Shutdown due to high pressure
 Guard chamber plugged during balance 29

TABLE 19

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## HTT-4-03 DETAILED RUN DATA PARAHO SHALE OIL PRODUCTION RUN

| Date Date No.<br>Belance No.<br>Feedstock   | 2/15                                 | 2/16                 | 3/17                 | 2/18   | 2/19<br>5                     | 2/20<br>6<br>310/50                | 0 2/21 2/22<br>7 8<br>310/500°F Paraho Shale Oil | 2/22<br>8<br>ale Oil        | 2/23<br>9                        | 2/24<br>10                  | 3/2                                    |
|---|--------------------------------------|----------------------|----------------------|--|-------------------------------|------------------------------------|--|-----------------------------|----------------------------------|-----------------------------|--|
| catalyst<br>Catalyst<br>Volume, cc.<br>Weight, gms.   |                                      |                      |                      |  |                               | 4119<br>HDS-3A<br>NNM-4680-<br>910 | 80   |                             |                                  |                             |  |
| Process Conditions<br>LHSV<br>Treat Gas, SCF/B (1004 H_)  | 0.984 4070                           | 1.0034<br>3990       | .9943                | .9906  | .9918<br>4038                 | .9918<br>3975                      | 1.3321<br>3005                                   | 0.9848<br>4070              | 0.9822<br>3995                   | 0.9426<br>4245              | 0.9309<br>4293                         |
| Exit Gas, SCF/B   | 2957                                 | 2893                 | 2925                 | 3005   | 2925                          | 3005                               | 2178   | 350                         | 2941                             | 3370                        | 3402                                   |
| H, Partial Pressure, Psia   | 992<br>992                           | 066                  | 583<br>706 7         | 980  | 969<br>211 8                  | 987                                | 914<br>910 0                                     | 802<br>802<br>707 0         | 974<br>976                       | 979<br>576                  | 124/<br>991                            |
| Liquid Product<br>Natl. Balance Sample No.<br>5, wppm<br>N, wrpm<br>H, wt. 8<br>Br. No.   | 720041<br>93<br>4.0<br>86.2<br>14.28 | 720045<br>122<br>5.4 | 720044<br>670<br>5.0 | 720047<br>720047<br>283.1<br>5.0<br>14.29<br>0.3 | 720050<br>139, 127(1)<br><1.0 |                                    |  |                             | 720066 (1)<br>91.5, 0(1)<br><1.0 | 720074(1)<br>7.6, 0<br>41.0 | 7200 <b>88</b> (1)<br>80, 5.9(1)<br>32 |
| FIA, Vol. 4<br>Aromatics<br>Olefins<br>Saturates<br>API Gravity<br>PM Closed Cup Flash Pt., °F<br>Freeze Pt., °F<br>Stoke Pt., mm | 10.9<br>0.8<br>88.3<br>48.6          | 48.7                 | 48.6                 | 11.5<br>0.8<br>87.7<br>48.5                      | 48.6                          | 48.1                               | 4<br>8.3   | 14.9<br>0.7<br>84.5<br>48.1 | 47.7                             | 47.2                        | 47.3                                   |
| ALL. V1200311Y - JU F, CS<br>ASTM D-86. *F<br>10/20<br>30/40<br>50/60<br>70/80<br>90/95<br>FBP<br>* Recovery                      |                                      |                      |                      |  |                               |                                    |  |                             |                                  |                             |  |
| <pre>% Loss<br/>% Residue<br/>Matl. Balance, Wt. %<br/>Hydrogen Consumption by C/H<br/>Accounting Construction</pre>              | 99.66                                | 96.89                | 98.73                | 99.47  | 98.79                         | 88.01                              | 72.79  | 85.99                       | 95.75                            | 94.07                       | 95.37                                  |
| Analysis, SCF/B   | 1077                                 |                      |                      | 1078   | •                             | ·                                  |  |                             |                                  |                             |  |

(1) Mercury treated

- 56 -

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## HTT-4-03 DETAILED RUN DATA PARAHO SHALE OIL PRODUCTION RUN

| Date<br>Balance No.<br>Feedstock<br>ERDL F. S. No.  | 3/3<br>12  | 3/4<br>13  | 3/5<br>14<br>2                                 | 3/6 3/7<br>15<br>310/500 <sup>6</sup> F Paraho Shale Oil | 3/7<br>16<br>Shale Oil                                    | 3/8<br>17   | 3/9<br>18                                      | 3/10<br>19                                       |
|---|--|--|--|--|---|---|--|--|
| Catalyst<br>ERDL Cat. No.<br>Volume, cc.<br>Weight, gms.  |  |  | <b>Ξ</b> Ζ Ο Ξ                                 | -HDS-5A<br>-NNM-4680<br>-910<br>-664 9-                  |   |   |  |  |
| Process Conditions<br>LHSV<br>Treat Gas, SCF/B (100% H <sub>2</sub> )<br>Exit Gas, SCF/B<br>Reactor Pressure, Psig<br>H <sub>2</sub> Partial Pressure, Psia<br>Temperature, *F                      | 0.9459<br>4229<br>3084<br>1235<br>1010<br>707.4          | 0.9458<br>4229<br>2941<br>1225<br>993<br>706.2         | 0.9472<br>4229<br>3132<br>1216<br>992<br>705.3 | 0.9627<br>4149<br>3052<br>1220<br>991<br>704.4           | 0.9582<br>0.9582<br>4181<br>3037<br>1232<br>1001<br>704.1 | 0.9610<br>4165<br>874<br>1208<br>863<br>703.7           | 0.9792<br>4086<br>3021<br>1231<br>998<br>704.1 | 0.9606<br>4165<br>3100<br>11225<br>1010<br>704.1 |
| Liguid Product<br>Mati. Balance Sample No.<br>S. wppm<br>C. wt. %<br>H. wt. %<br>Br. No.  | 720096<br>34.1, 3.8(1)<br><1.0<br>86.08<br>14.14<br>0.27 | 720108<br>17.1, 3.4(1)<br>1.0<br>86.19<br>14.28<br>0.3 | 720112<br>34.5, 7.9 <sup>(1)</sup><br><0.1     | 720124<br>39.7, 10.7(1)<br><0.1                          | 720128<br>60.5, 17.6 <sup>(1)</sup><br><1.0               | 720132<br>34.7, 20.2(1)<br>18<br>86.12<br>14.17<br>0.14 | 720142<br>33.0, 1.0<br><1.0                    | 720158<br>101.1, 6.7 <sup>(1)</sup><br>3.2       |
| FIA, Vol. <b>*</b><br>Aromatics<br>Aromatics<br>Olefins<br>Saturates<br>API Gravity<br>PM Closed Cup Flash Pt., *F<br>Freeze Pt., *<br>Smoke Pt., mm<br>Kin. Viscosity 0 -30°F, cs<br>ASTM D-86, *F | 14.8<br>0.8<br>84.4<br>47.4                              | 14.3<br>0.6<br>85.1<br>46.6                            | 46.6   | 47.3   | 47.1  | 14.5<br>0.8<br>84.6<br>47.0                             | 46.6   | 46.6   |
|   |  |  |  |  |   |   |  |  |
| <pre>% Residue<br/>Matl. Balance, Mt. %<br/>Hydrogen Consumption by C/H<br/>Analysis, SCF/B</pre>   | 95.46<br>983   | 91.04<br>1049  | 93.85<br>-                                     | 93.39<br>-   | 93.03   | 98.98<br>948  | 93.24<br>-                                     | 93.61<br>-                                       |

(1) Mercury treated

- 57 -

TABLE 19 (continued)

## HTT-4-03 DETAILED RUN DATA PARAHO SHALE OIL PRODUCTION RUN

| Date<br>Balance No.  | 3/11<br>20   | 3/15<br>21  | 5/14<br>42  | 3/15<br>23  | 3/16<br>24   | 3/17<br>25  |  |
|--|--|---|---|---|--|---|--|
| Feedstock<br>ERDL F. S. No.<br>Catalyst<br>ERDL Cat No.<br>Volume, cc.   |  | 510/500°F<br>4119<br>HDS-3A<br>910                      | -510/500°F Paraho Shale Oil<br>4113                   | -   |  |   |  |
| Meight, gms.<br><u>Process Conditions</u><br><u>LHSV</u><br>Treat Gas, SCF/B (100% H <sub>2</sub> )<br>Exit Gas, SCF/B (100% H <sub>2</sub> )<br>Exit Gas, SCF/B (100% H <sub>2</sub> )<br>Exit Gas, SCF/B (100% H <sub>2</sub> )<br>Temporature, °F | 0.9475<br>0.9475<br>4229<br>715<br>1228<br>866<br>704.7      | 664.9<br>0.9466<br>4229<br>3116<br>1222<br>997<br>704.4 | 0.9730<br>118<br>4118<br>2089<br>1204<br>976<br>705.0 | 0.9600<br>4165<br>3005<br>1213<br>984<br>705.0          | 0.9574<br>0.9574<br>4181<br>2766<br>1276<br>980<br>980 | 0.9778<br>4086<br>3100<br>1200<br>988<br>705.3    |  |
| Liquid Product<br>Natl. Balance Sample No.<br>S. wppm<br>N. wppm<br>C. wt. %<br>H. wt. %<br>Br. No.  | 720168 0(1)<br>128.8, 0(1)<br><1.0<br>86.16<br>14.08<br>0.29 |   | 720182<br>40.7, 11.2 <sup>(1)</sup><br>14             | 720184<br>52.3, 51.4(1)<br>3.9<br>86.03<br>14.05<br>0.3 | 720186<br>65.1, 1.0 <sup>(1)</sup>                     | 72019 <b>2</b><br>79.0, <1.0 <sup>(1)</sup><br>21 |  |
|  | 16.3<br>0.9<br>82.9<br>48.3                                  | 46.7  | 46.6  | 16.3<br>0.6<br>83.1<br>46.8                             | 46.6   | 66.<br>8  |  |
| ASTM D-86, F<br>18/55, 50/40<br>50/40<br>50/60<br>70/80<br>90/95<br>FBP<br>FBP   |  |   |   |   |  |   |  |
| <pre>% Loss % Residuo % Matl. Balance, Nt. % Hydrogen Consumption by C/H Analysis, SCF/8</pre>   | 95.07<br>893   | 94.82   | 99.7  | 94.32<br>923  | 92.80  | 93.33   |  |

- 58 -

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(1) Mercury treated

TABLE 19 (continued)

## HTT-4-03 DETAILED RUN DATA PARAHO SHALE OIL PRODUCTION RUN

| Date<br>Balance No.<br>Feedstock<br>ERDL F. S. No.   | 3/18<br>26   | 3/19<br>27                                   | 3/20<br>28<br>210/500°F<br>4119             | 3/20 3/21<br>28 29<br>310/500°F Paraho Shale Oil<br>4119 | 3/22<br>30                                    | 3/29<br>31<br>Mild1<br>4202-               | 5/30<br>32<br>Mildly Hydrotreated<br>4202    | 3/31<br>33<br>F.S.  | 4/1<br>34<br>4119                          |   |
|--|--|--|---|--|---|--|--|---|--|---|
| ERDL Cat. No.<br>Volume, cc.<br>Weight, gms.   |  |  | 910   |  |   |  |  |   |  |   |
| Process Conditions<br>LHSV<br>Treat Gas, SCF/B (100% H <sub>2</sub> )<br>Exit Gas, SCF/B (100% H <sub>2</sub> )<br>Reactor Pressure, Psig<br>H <sub>2</sub> Partial Pressure, Psia<br>Témocrature. | 0.9774<br>4086<br>572<br>1179<br>822<br>703.7                      | .9715<br>4118<br>541<br>1185<br>825<br>703.9 | .9851<br>.054<br>41<br>1215<br>783<br>704.4 | .9953<br>4022<br>4022<br>1215<br>784<br>704.9            | .9854<br>4054<br>2973<br>1203<br>985<br>704.0 | .9471<br>4229<br>238<br>1222<br>823<br>823 | .9447<br>4229<br>700<br>1225<br>873<br>703.5 | .9436<br>.9436<br>4245<br>3752<br>3752<br>1224<br>1031<br>703.2 | .9618<br>4165<br>620<br>1225<br>862<br>862 | 9 <b>9</b>  |
| Liquid Product<br>Matl. Balance Sample No.<br>S, wppm<br>N, wppm<br>C, wt. \$<br>H, wt. \$<br>Br. No.  | 720201<br>22.6, 17.5 <sup>(1)</sup><br>36<br>86.24<br>14.02<br>0.3 | 720<br>28.                                   |   |  |   |  |  |   |  | 720323<br>0.1, <0.1 <sup>(1)</sup> -<br>86.08<br>14.39<br>0.4 |
| FIA, Vol. 4<br>Aromatics<br>Olefins<br>Saturates<br>API Gravity<br>Prece Pt. F   |  | 46.4   | 47.1  | 46.6   | 15.1<br>1.4<br>83.5<br>46.4                   | 48.0                                       | 48.0   | 48.0  | 8.5<br>90.6<br>47.8                        |   |
| Smoke Pt., mm<br>Kin. Viscosity C -30°F, cs<br>ASTM D-86, °F<br>IBP/50<br>30/40  |  |  |   |  |   |  |  |   |  |   |
| 50/60<br>50/60<br>70/80<br>90/95<br>FBP<br>F Recovery  |  |  |   |  |   |  |  |   |  |   |
| % Residue<br>Matl. Balance, Wt. %<br>Hydrogen Consumption by C/H<br>Analysis, SCF/B  | 123.62<br>-  |  | 92.92                                       | 92.21<br>-   | 93.89<br>913                                  | 95.94                                      | 93.09  | 95.18   | 95.25                                      | S   |

(1) Mercury treated

|                            |         |                  | PARA     | PARAHO SHALE | COMPOSITIES | OIL PRODUCTION RUN | RUN     |         |          |         |         |         |
|----------------------------|---------|------------------|----------|--------------|-------------|--------------------|---------|---------|----------|---------|---------|---------|
|                            |         |                  |          |              |             |                    | 1       |         |          |         |         |         |
| Composite No.              | -       | 2 <sup>(2)</sup> | m        | 4            | Q           | 9                  | 2       | 80      | 6        | 01      | n       | 12      |
| Composite Sample No.       | 720040  | 720045           | 720194   | 720195       | 720196      | 720212             | 720213  | 720214  | 720215   | 720300  | 720301  | 720048  |
| Composite Br. Check No.    | R-6529  | R-6536           | R-6584   | R-6585       | R-6586      | R-8212             | R-8211  | R-8210  | R-8209   | R-8229  | R-8230  | R-6543  |
| Inspèctions                | 3       | 1                | 1        |              |             |                    |         |         |          |         |         |         |
| S. wppm                    | 100(1)  | (1)869           | 346.5(1) | 26.3         | 43.2        | 35.8               | 30.3    | 61.8    | 24.7     | 9.3     | 70.2    | 350(1)  |
| Mqcw .N                    | 6.7     | 10.0             | 260.0    | 347.0        | 268.0       | 84                 | 48      | 100     | 105      | 146     | 142     | 13.0    |
| FIA, Vol. X                |         |                  |          |              |             |                    |         |         |          |         |         |         |
| Aromatics                  | 10.8    | 12.4             | 17.6     | 17.9         | 16.6        | 15.8               | 15.2    | 15.8    | 16.6     | 17.2    | 16.0    | 1.11    |
| Olefins                    | 0.7     | 1.5              | 0.8      | 0.8          | 0.9         | 0.6                | 0.6     | 1.6     | 0.8      | 0.7     | 0.7     | 0.8     |
| Saturates                  | 88.5    | 86.1             | 81.7     | 81.4         | 82.5        | 83.6               | 84.2    | 82.7    | 82.7     | 82.1    | 83.3    | 38.1    |
| PM Closed Cup Flash Pt.,°F | 100.0   | 120.0            | 136      | 134          | 126         | 134                | 128     | 132     | 134      | 139     | 130     | 112     |
| Freeze Pt., °F             | -47.2   | -52.6            | -35.5    | -34.6        | -39.0       | -44.5              | -45.4   | -39.1   | -40.9    | -40.0   | -35.2   | -51.7   |
| Snoke Pt., mm              | 31.0    | 25.0             | 25.0     | 25.5         | 25.0        | 27.0               | 28.0    | 25.0    | 25.0     | 24.0    | 27.0    | 27.0    |
| Kin. Viscosity @ -30°F. cs | 7.19    | 7.63             | 9.94     | 10.33        | 9.39        | 8.84               | 8.84    | 10.03   | 10.49    | 10.05   | 9.51    | 7.30    |
| ASTM D-86, "F              |         |                  |          |              |             |                    |         |         |          |         |         |         |
| IBP/5%                     | 282/322 | 305/336          | 340/366  | 342/372      | 320/362     | 326/359            | 329/353 | 345/368 | 350/372  | 332/370 | 330/357 | 305/337 |
| 10/20                      | 336/357 | 345/365          | 375/386  | 382/394      | 371/381     | 366/375            | 358/372 | 376/385 | 380/391  | 378/385 | 365/380 | 350/367 |
| 30/40                      | 373/385 | 376/328          | 393/408  | 393/412      | 393/402     | 387/395            | 382/392 | 397/405 | 401/411  | 397/405 | 391/400 | 379/389 |
| 50/60                      | 396/405 | 398/408          | 417/427  | 419/428      | 412/420     | 403/411            | 400/408 | 415/423 | 418/427  | 415/422 | 410/419 | 397/404 |
| 70/30                      | 415/426 | 416/426          | 437/447  | 154/524      | 430/440     | 419/429            | 417/425 | 432/442 | \$37/445 | 430/441 | 429/439 | 410/417 |
| 30/95                      | 438/455 | 436/453          | 452/480  | 462/479      | 454/472     | 440/458            | 437/449 | 456/472 | 450/473  | 455/470 | 450/465 | 426/439 |
| FBP                        | 494     | 491              | 500      | 504          | 494         | 502                | 492     | 513     | 518      | 507     | 505     | 472     |
| % Recovery                 | 98.5    | 0.02             | 97.5     | 98.5         | 97.5        | 98.5               | 0.99    | 66      | 98.5     | 98.5    | 99.5    | 98.5    |
| Z Loss                     | 0.5     | 0                | 0.5      | 0            | 1.0         | 0                  | 0.0     | 0.0     | 0.5      | 0.5     | 0.      | 0.5     |
| % Residue                  | 1.0     | 1.0              | 2.0      | 1.5          | 1.5         | 1.5                | 1.0     | 1.0     | 1.0      | 1.0     | 0.5     | 1.0     |
| API Gravity, 60/60         | 47.7    | 46.8             | 44.6     | 44.2         | 45.0        | 45.8               | 45.8    | 45.8    | 44.8     | 44.8    | 45.1    | 47.6    |
| Net Ht., Lbs               | 96.5    | 92.0             | 81       | 71           | 107         | 83                 | 108     | 107     | 109      | 66      | 76.5    | 85      |
| Net Gallons                | 14.7    | 13.:             | 12.1     | 10.5         | 16.0        | 12.5               | 16.3    | 16.1    | 16.3     | 14.8    | 11.5    | 12.9    |

(2) Composite withheld from shipment to produce several gallons of JP-5 quality material

- 60 -

TABLE 20 (continued)

|                             |          |         |          |         | COLE CO TTOO |         | 1       |         |          |                    |                    |
|-----------------------------|----------|---------|----------|---------|--------------|---------|---------|---------|----------|--------------------|--------------------|
| Composite No.               | 13       | 14      | 15       | 16      | 17           | 18      | 19      | 2       | 21       | 22                 | 23                 |
| Composite Sample No.        | 720197   | 720198  | 720216   | 720217  | 720219       | 720219  | 720302  | 720303  | 720326   | 720334             | 720335             |
| Composite Br. Check No.     | R-6528   | R-6589  | R-8203   | R-8213  | R-8214       | R-8215  | R-8231  | R-8232  | R-8244   | R-8252             | R-8253             |
| Inspections                 |          |         | 1        |         |              |         |         |         | 12       |                    |                    |
| S wppm                      | 203.3(1) | 16.4    | 157.9(1) | 31.3    | 26.1         | 29.7    | 5.5     | 125.9   | 224.9''' | 15.3               | 8.0                |
| N, wppm                     | 7.0      | 0.6     | ₽        | 4.81    | 3.57         | 7.44    | 30      | 40      | 112      | 3.9                | 3.2                |
| FIA, Vol. X                 |          |         |          |         |              |         |         |         |          |                    |                    |
| Aromatics                   | 14.0     | 14.6    | 13.5     | 11.9    | 12.5         | 16.3    | 15.8    | 16.4    | 14.9     | 9.0 <sup>(2)</sup> | 7.6 <sup>(2)</sup> |
| Olefins                     | 9.0      | 0.6     | 1.5      | 0.0     | 1.9          | 0.9     | 1.0     | 0.6     | 0.8      | 0.5                | 1.2                |
| Saturates                   | 85.4     | 84.8    | 85.0     | 88.1    | 85.6         | 82.8    | 83.2    | 83.0    | 84.3     | 90.6               | 91.2               |
| PM Closed Cup Flash Pt., *F | 122      | 136     | 130      | 122     | 132          | 128     | 134     | 122     | 128      | 130                | 126                |
| Freeze Pt., "F              | -43.6    | -45.4   | -43.6    | -45.4   | -43.6        | -42.7   | -43.6   | -40.0   | -43.5    | -42.7              | -41.8              |
| Snoke Pt., mm               | 27.5     | 26.0    | 28.0     | 28.0    | 25.5         | 26.0    | 24.0    | 24.0    | 25.0     | 32.0               | 32.0               |
| Kin. Viscosity 6 -30°F,cs   | 8.18     | 8.40    | 8.84     |         | 9.28         | 9.39    | 9.50    | 9.17    | 19.6     | 9.39               | 9.39               |
| ASTM D-66, °F               |          |         |          |         |              |         |         |         |          |                    |                    |
| 18P/5%                      | 322/357  | 336/355 | 324/360  | 327/353 | 330/360      | 342/358 | 334/359 | 323/357 | 319/358  | 326/358            | 333/357            |
| 10/20                       | 365/374  | 363/374 | 367/375  | 363/573 | 368/377      | 368/330 | 368/378 | 354/375 | 368/350  | 367/376            | 368/378            |
| 30/40                       | 385/394  | 324/394 | 386/394  | 384/394 | 333/397      | 369/353 | 390/399 | 389/393 | 392/400  | 338/397            | 390/398            |
| 50/60                       | 400/407  | 401/408 | 402/409  | 401/410 | 405/415      | 406/415 | 408/417 | 407/415 | 408/415  | 407/413            | 407/415            |
| 70/83                       | 414/420  | 417/425 | 417/425  | 418/427 | 424/433      | 424/433 | 425/435 | 425/435 | 423/433  | 422/433            | 423/433            |
| 56/05                       | 427/447  | 438/450 | 448/455  | 438/451 | 445/458      | 445/458 | 448/460 | 449/451 | 445/461  | 450/456            | 447/465            |
| FBP                         | 464      | 480     | 490      | 494     | 455          | 499     | 495     | 497     | 492      | 506                | 515                |
| X Recovery                  | 98.0     | 93.0    | 0.62     | 65      | 98.5         | 98.5    | 98.5    | 65      | 66       | 66                 | 66                 |
| # Loss                      | 0.5      | 0.5     | 0.5      | 0.5     | 0.5          |         | 0.5     | 0       | 0        | 0                  | 0                  |
| % Residue                   | 1.5      | 1.5     | 0.5      | 0.5     | 1.0          | 1.5     | 1.0     | 1.0     | 1.0      | -                  | -                  |
| API Gravity, 60/60          | 46.6     | 46.1    | 43.5     | 45.8    | 45.7         | 48.7    | 45.4    | 45.4    | 45.9     | 46.9               | 47.0               |
| Net Wt., Lbs                | 105      | 79.5    | 96       | 105     | 108          | 06      | 101     | 75      | 87.5     | 109                | 108                |
| Net Gallons                 | 15.9     | 12.0    | 14.5     | 16.0    | 16.2         | 13.8    | 15.2    | 11.3    | 13.2     | 16.5               | 16.4               |

- 61 -

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|                             | Jet A Spec | Hydrotreated Paraho Shale 011 |
|-----------------------------|------------|-------------------------------|
| Total Sulfur Content, wppm  | Max. 3000  | 115                           |
| FIA Aromatics, Vol.%        | Max. 20    | 14.3                          |
| PM Closed Cup Flash Pt., °F | Min. 105   | 127.6                         |
| Freeze Pt., °F              | Max36      | -42.7                         |
| Smoke Pt., mm               | Min. 25    | 26.6                          |
| Kin. Viscosity @ -30°F, cs  | Max. 15    | 9.13                          |
| ASTM D-86                   |            |                               |
| 10%, °F                     | Max. 400   | 366                           |
| 50%, °F                     | Max. 450   | 407                           |
| F3P                         | Max. 550   | 496                           |
| API Gravity                 | 39-51      | 46.0                          |

## Product Quality of Hydrotreated Paraho Shale Oil

#### 4.2.2.4 Unit Operating Experience

## 4.2.2.4.1 Operating Problems

For both units during the production run, smooth operations were interrupted by recurrent plugging problems both in the guard chamber located just ahead of the reactor tube bundle and in the transfer line between the reactor outlet and the high pressure separator. As shown in Table 21, inspections of the discharged material from the guard chamber indicate that it is not coke due to the relatively low carbon and hydrogen content. Much of the material appears to be iron and iron sulfide, although the overall material balance with the inspections that were obtained was less than one hundred percent. The high  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> concentrations with trace amounts of CoO and MoO<sub>3</sub> indicate that catalyst fines were also contained in the material discharged from the guard chamber.

Due to the large quantities of liquid that were being processed in the unit, accurate measurement of product contaminant levels was difficult. As a result, very limited kinetic information was obtained. Of particular difficulty was the product sulfur content. The hydrotreated product contains a certain amount of dissolved H2S, most of which is removed after nitrogen stripping. In the presence of air, however, any residual H<sub>2</sub>S will readily oxidize to form elemental sulfur which is retained in the liquid product. While exposure of the sample to air was limited as much as possible, a certain amount of oxidation was unavoidable due to the high concentration of H2S present in the liquid product. Thus, total product sulfur concentration as measured by x-ray will reflect the elemental sulfur content as well as that sulfur not removed during hydrotreating. For the bulk of the pilot plant program, liquid product samples were mercury treated to remove elemental sulfur. This explains the discrepancy in the sulfur values shown on the activity plot for each unit (Figures 9 and 10) and those reported for the 15-gallon composites in Table 20.

# TABLE 21

# INSPECTIONS OF GUARD CHAMBER FINES

| ERDL Sample No.<br>Sample Description            | 720351<br>HTT-3-02 & HTT-4-03<br>Guard Chamber Fines |  |
|--|--|--|
| Inspections                                      |  |  |
| C, Wt. %   | 9.7  |  |
| H, Wt. %   | 1.05   |  |
| S, Wt. %   | 15.7   |  |
| Ni, Wt. %  | 0.383  |  |
| V, Wt. %   | 0.026  |  |
| Fe, Wt. %  | 27.9   |  |
| CoO, Wt. %                                       | 0.084  |  |
| Mo0 <sub>2</sub> , Wt. %                         | 2.22   |  |
| $\alpha$ -AI <sub>2</sub> O <sub>2</sub> , Wt. % |  |  |
| Si0, Nt. %                                       | 17.0<br>12.5   |  |

The advance of indrogen command is tograding the serveres fraction of a raw fitters which to must let A fuel encifications at the process conditions endoted in this sends is on 1050 SCD/9 at 800. Due to sho stands that as consists tothet for around the bride gradient, by friger of I measure to KOK was senewhet lower. Nedergan communics as a function of I measure to the graph rectared in Figure 11. In general, the data lower section of the graph rectared in Figure 11. In general, the data data gives on 10 Morth the community of SCD places while that is the to second field the section of the graph rectared to Figure 11. In general, the data gives on 10 Morth the community of a community of the to second to a lower of a community of the section of the data field to the section of the graph rectared to the section of the second to the section of the section of the section of the second to the section of the section of the section of the second to the section of the section of the section of the second to the section of the sectors of the section of the second to the section of the section of the sectors of the section of the sec

The data at 1500 paig operating pressure shown is rights if one obtained in the exploratory study. Within the Haffettane of the outboal hodrogen sublitede which is used to deterthis hodregen consumption, there are no observed difference in the abount of hydrogen consumption, there is estudy out that research at 1200 paig.

4.3 CONCLUME TO B

A somple of let A type aviation turbine feel was produced troc a 910/200°F con from Parako shale oil by hydrotrouting over 1008-34 cataiyet at 100°F, 1200 years, 1-146V and 4000 SCF/B of H- which are the following specifications:

> - Total soliur content - Total \* content - Ylash roint

## 4.2.2.4.2 Catalyst Activity and Activity Maintenance

## a. Desulfurization

As shown in Figures 9 and 10, sulfur content was reduced from 0.74 wt.% to generally less than 10 ppm at the process conditions employed in this study. No noticeable decline in catalytic hydrodesulfurization activity had occurred after thirty days on oil.

## b. Denitrogenation

Catalytic hydrodenitrogenation activity at these conditions declined during the course of the run. Product nitrogen levels increased from less than 5 ppm to 40-100 ppm at EOR. The unusually high nitrogen levels on HTT-3 around day 10 were probably the result of poor operations due to plugging during that time period.

## c. Aromatics Hydrogenation

At the process conditions utilized in this pilot plant program, catalyst activity for aromatics hydrogenation declined substantially during the course of the run. Aromatics content as determined by FIA analysis increased from ca. 10 vol.% at SOR to 15-16 vol.% at EOR.

# 4.2.2.4.3 Hydrogen Consumption

The amount of hydrogen consumed in upgrading the kerosene fraction of a raw Paraho shale to meet Jet A fuel specifications at the process conditions employed in this study is ca. 1050 SCF/B at SOR. Due to the steady decline in catalyst activity for aromatics hydrogenation, hydrogen consumption at EOR was somewhat lower. Hydrogen consumption as a function of % aromatics reduction is illustrated in Figure 11. In general, the data in the upper portion of the graph represent SOR values while that in the lower portion represent those observed at EOR. Linear regression of these data gives ca. 10 SCF/B hydrogen consumption per volume percent reduction in aromatics. Increased hydrogen consumption, of course, increases the cost of processing synthetic fractions to jet fuel.

The data at 1500 psig operating pressure shown in Figure 11 was obtained in the exploratory study. Within the limitations of the carbon/ hydrogen analysis which is used to determine hydrogen consumption, there was no observed difference in the amount of hydrogen consumed at this pressure and that measured at 1200 psig.

## 4.3 Conclusions

- A sample of Jet A type aviation turbine fuel was produced from a 310/500°F cut from Paraho shale oil by hydrotreating over HDS-3A catalyst at 700°F, 1200 psig, 1 LHSV and 4000 SCF/B of H<sub>2</sub> which met the following specifications:
  - Total sulfur content
  - Total aromatics content
  - Flash point



- 65 -





- Freeze point
- Smoke point
- Viscosity at -30°F
- ASTM distillation
- API gravity
- At the process conditions employed in this study no noticeable decline in catalyst hydrodesulfurization activity had occurred after thirty days on oil. Sulfur content was reduced from 0.74 wt.% to generally less than 10 ppm.
- Catalyst hydrodenitrogenation activity at these conditions declined during the course of the run. Product nitrogen levels increased from less than 5 ppm to 40-100 ppm at the end of approximately 30 days.
- Catalyst activity for aromatics hydrogenation also declined during the run. Product aromatics content increased from ca. 10 vol.% at the start of the run to 15-16 vol.% at the end of approximately 30 days.
- At the process conditions investigated in this study, initial hydrogen consumption was approximately 1050 SCF/B. Due to the steady decline in catalyst activity for aromatics hydrogenation, hydrogen consumption was somewhat lower at the end of the run.
- Within the limitations of the carbon/hydrogen analysis which is used to determine hydrogen consumption, there was no observed difference in the amount of hydrogen initially consumed at 1500 psig versus that initially consumed at 1200 psig operating pressure.

- 68 -

# APPENDIX I

# EXXON RESEARCH & ENGINEERING COMPANY

## RESCUE LINEAR PROGRAM FOR REFINERY PLANNING

ER&E's RESCUE Linear Program for Refinery Planning is a flexible planning tool often used in refinery optimization studies. It helps optimize process selection, determine blending operations, select crudes and product mixes, etc. The following sections describe what refinery linear programming (LP) is, ER&E LP capability, and the specific LP model used by ER&E Planning Engineering.

## Why LP in Refinery Planning

The requirements of a typical refinery project could be satisfied in a great many ways. These alternatives, and their interactions, are so complex that only a limited number can be studied were it not for LP techniques. Thus, the use of LP can determine the optimum project configuration, which might otherwise be missed. Furthermore, the cost of the planning effort is substantially reduced by the use of LP.

Linear programming is a technique of creating a model of various available business, logistic, and technical altheratives, and selecting the optimum combination of these alternatives. In a petroleum refinery situation, these alternatives typically include the selection of crudes, processes and their conditions, and product blending components.

The linear programming model contains all these alternatives and their economics, as well as restrictions on the selection of these alternatives. These restrictions include material balances, product quality requirements, product demands, feed availability, and equipment limitations. The structure of the model is that of a number of linear equations, each describing one of these restrictions. Typically, there are many more alternatives (variable in the equations) than there are equations, so there is more than one solution. From these alternatives, the linear program determines that particular solution which is the economic optimum.

## ER&E Began LP in Early 60's

ER&E has extensive experience in the development and running of linear programs. The planning group began about 15 years ago developing and using LP, and were among the first in industry to incorporate this technique into planning studies for actual refinery projects. Over the years, many models for various specific applications have evolved. These applications range from hemispheric supply models, which involve simplified refinery process representations, to highly detailed representations of the processing alternatives for a single refinery. These models have been developed and run for Exxon Corporation affiliates, as well as selected potential licensees of ER&E technology. The continual use and growth of LP work has resulted in a large up-to-date data bank, which accurately details crudes, processing alternatives, product qualities, operating costs, utilities, etc. In addition, this experience provides background and techniques for setting up models with the required degree of complexity, and efficiently selecting alternative scenarios to be examined. These data, and the experience of ER&E planning, are available with RESCUE.

## A Comprehensive Tool for Refinery Planning

RESCUE is a dynamic, flexible tool used in refinery planning studies to optimize the process selection and develop running plans. Some of the features of the model are outlined below:

- Crudes Many of the high volume North American, South American, Mid-East, and Far East crudes can be simulated by the model. Other crudes can be added if sufficient characterization data are available to adequately estimate processing effects.
- Processes Over 30 refinery processes are included in the model. Where significant, a range of operations for the process units is given. For example, these include Powerformate octane level, Flexicracker severity, and RESIDFINER product sulfur level. Thus, not only do the LP results show the processing sequence that should be used, but they also point to the specific operation for many of the units. A list of most of the processes is shown in Table A.

The process data can be modified to more accurately reflect a specific refinery situation. This, along with simple procedures for selecting only those of the many available process options which are applicable, can result in a model which is highly specific for any particular refinery. Information can be added on other processes from data already in-house. These include many competitive processes, for which non-confidential data are already available at ER&E.

• Products/Product Qualities - All critical qualities are tracked in the model for a full range of products, to ensure that specifications are met. As an example, for each grade of gasoline, the model follows Research Octane, Reid Vapor Pressure, sulfur content, gravity, volatilities, and derived specs. Distillate specifications include sulfur content, flash point, gravity, cloud point, and volatilities. A list of the products and the qualities typically followed is shown in Table B.

- Utility Requirements The requirements for power, cooling water, and steam have been provided in the model for each processing option. The LP thus determines the total utilities for the optimum set of processing alternatives. In developing the overall steam requirements, the LP ensures that a high and low pressure steam supply and demand are both in balance. This is done via options to select major process drivers using either electric motors, condensing steam or back pressure steam. Thus the model, in effect, provides an initial energy optimization/driver selection for the entire refinery.
- Refinery Fuel and Emissions The LP solution balances the fuel needs of the refinery - liquid and gaseous refinery fuel and hydrogen plant feed. The sulfur content of the refinery fuel is also tracked. By providing options for low sulfur components to enter the refinery fuel oil pool, as well as a flue gas desulfurization option, total sulfur emissions specifications can be met. Additionally, the offsite investments include allowances for waste treatment to the specifications currently typical of the United States.
- Tankage and General Offsites The amount of feed, intermediate and product tankage, and an allowance for the general offsite support facilities is also estimated for each onsite process option. Thus, the LP representation of the refinery is a complete one, rather than just accounting for onsites alone.
- Investments Investment data for all facilities are based on up-to-date feedback from Exxon's refinery projects around the world. Provisions are available in the model for selecting the unit cost of many of the critical process units at the appropriate size range.
- Economics Investments for each onsite unit, each utility, the tankage and general offsites are available in sufficient decail so that adjustments to the specific economic conditions at any particular refinery can easily be made. The economic factors that can be individually tailored include the labor situation, desired return levels, escalation rates, etc. In addition, the cost of purchased power can be easily adjusted to the specific location.

Most of the information required for a planning study are already available, stored within the data bank. The additional information required to create a model which is specific to a particular refinery is relatively simple. It consists of the desired specifications for each of the products, crude and product prices, and economic bases, such as time, location, and return rate. A listing of the typical information required for an LP study is presented in Table C. The results from the linear program directly provide the information of interest in a planning study. This includes, for the optimum process sequence, a complete material balance, size and type of process, onsite and offsite investments, utility requirements, details of product blending, sulfur emissions, and operating costs.

A typical planning study for a licensee would involve an LP model of 300-400 rows and 600-800 activities. These small models can easily be generated from the large data bank, excluding activities which are not of interest. This results in more efficient, faster running LP's. The data bank, on the other hand, is large - about 700 rows by 2300 activities.

# LP Model & Techniques Constantly Updated

RESCUE is dynamic. It is currently being used in a number of Exxon affiliate and licensee applications. In the course of this work, the existing data are constantly being updated, and new processing alternatives developed. Techniques for setting up and running the LP are also continually being enhanced. These improvements are immediately incorporated into our LP technology, and become available to the next user of the program. In addition, a new data management system is under development.

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# TABLE A PROCESS CAPABILITIES

#### Ceneral

- Capability to handle a wide range of conventional crudes as well as synthetic crudes from coal, shale oil and tar sands.
- Crude specific approach to processing and blending for greater accuracy.
- Capability to restrict overall refinery sulfur dioxide emissions.

# APS

- Overhead and sidestream cutpoint flexibility
- Flash tower for segregated crude operation.

#### VPS

• Flexibility to distill RESIDFINED product.

# Naphtha HYDROFINING

## Kero HYDROFINING

 Flexibility for hydrosweetening or high severity hydrotreating to meet smoke point specifications.

#### AGO HYDROFINING

#### Saturated Light Ends

• Choice of LPG recovery levels.

# U-JHC Hydrocracking

- Capability to handle virgin atmospheric and vacuum gas oils as well as cat/coker gas oils.
- Operations to maximize LPG, naphtha, jet fuel or distillate.
- Single stage and two stage operations.
- Production of SNG feedstocks.
- Production of aromatics precursors.

# - 73 -

## FLEXICRACKING

- Capability to handle virgin atmospheric and vacuum gas oils as well as coker gas oil and coker naphtha. These stocks can be processed untreated or after desulfurization.
- Operations to maximize production of olefins, naphtha or distillate.
- Heat balance formulation maintains energy balance around cat unit including the fractionator and cat light ends.
- Flexibility to add regenerator flue gas scrubbing.
- Production of ethylene/propylene for use as chemical feedstocks.
- Production of carbon black feedstock.

## Cat Naphtha Splitting

• Naphtha cutpoint flexibility to optimize distillate/heavy cat naphtha split.

#### Unsaturated Light Ends

• Choice of light ends recovery levels.

#### Cat Naphtha HYDROFINING

- Mild or severe hydrotreating to meet projected mogas sulfur specifications.
- Flexibility to blend desulfurized cat naphthas directly to mogas.
- Hydrotreated naphtha available for aromatics extraction.

## Cat Gas Oil HYDROFINING

• Range of severities.

## Coker Naphtha HYDROFINING

• Treated naphtha available as SNG feedstock.

# Coker Distillate HYDROFINING

• Product can be tailored for aviation or mogas.

# iC, Recovery

# iC5 Recovery

## LVN Isomerization/Mol Sieve

- Can isomerize with or without sieving.
- High purity iC5/iC6 available to mogas.
- Option for molecular sieving of LVN to provide  $nC_5/nC_6$  for steam cracker feed.

## POWERFORMING

- Cyclic and semi-regenerative reforming.
- Range of octane severities.
- Feedstock cutpoint flexibility.
- Wide range of feeds including virgin stocks, hydrocracked naphthas. and cat/coker naphthas.
- Option to split reformates for optimum mogas blending and recovery of aromatics.
- Option to maximize aromatics production for chemicals.

## GO-FINING

• Capability to handle virgin and cracked stocks.

## RESIDFINING

- Range of product sulfur levels.
- Option to desulfurize deasphalted oil.

# Fluid Coking

## FLEXICOKING

• Range of coke gasification levels available.

Delayed Coking

Deasphalting

Asphaltene Flaking

Steam Reformer (H<sub>2</sub> Production)

• Range of suitable feeds and fuels from reformer tail gas to light virgin naphtha.

Cryogenic H<sub>2</sub> Recovery

Sulfur Plant & MEA

Sulfur Plant Tail Gas Cleanup

Flue Gas Desulfurization

# - 77 -

# TABLE B

# Products and Product Qualities

| Product   | Qualities                                |                                     |
|---|--|-------------------------------------|
| LPG (Propane)   | M <b>ax</b> . % C4<br>Min. % Propylene   |                                     |
| LPG (Butane)  | Min. % C <sub>4</sub><br>Max. % Butylene |                                     |
| Gasoline (2 grades)   | RON Clear<br>MON Clear<br>RVP            | % Sulfur<br>Volatility              |
| Sales Naphtha (3 grades)  | Distillation                             |                                     |
| Jet Fuel/Kerosene   | Freeze Point                             |                                     |
| Diesel Fuel   | Wt% Sulfur<br>Flash<br>Gravity           | Cetane Index<br>Cloud<br>Volatility |
| lleating Oil  | Wt% Sulfur<br>Gravity                    | Volatility                          |
| Fuel 0il (4 grades)   | Wt% Sulfur<br>Viscosity                  | Heating Value                       |
| Refinery Fuel (Two Systems;<br>H <sub>2</sub> Plant feed and Other) | Sulfur                                   |                                     |
| SNG   | 1000 BTU/SCF                             |                                     |
| Sulfur  |  |                                     |

Coke

# - 78 -

# TABLE C

# TYPICAL INPUT INFORMATION FOR LP PLANNING STUDY

# I. Required Product Specifications

Specifications for all products of interest, as shown in Table B.

## II. Required Economic Information

Crude Prices, \$/B, and Availability

Capital Recovery Factor

DCF return Depreciation method Project life Tax rate

Major Product Price Spreads, \$/B

Mogas Kerosene Dicsel Fuel Heating Oil LSFO

## Investment Basis

Time Location

# Utilities

Purchased power, c/kwhr Cooling water, c/M gal

# Purchase Options (if any)

iC<sub>4</sub>-, \$/B Others

# Byproduct Credits

Coke, \$/ton Sulfur, \$/ton

\*U.S.Government Printing Office: 1978 - 757-080/357