

**F O S S I L**

DOE/PC/90057--T9  
(DE95001933)

**THE SELECTIVE CATALYTIC CRACKING OF FISCHER-TROPSCH LIQUIDS TO  
HIGH VALUE TRANSPORTATION FUELS**

**Final Report**

**By  
M. M. Schwartz**

**Work Performed Under Contract No. AC22-91PC90057**

**For  
U.S. Department of Energy  
Pittsburgh Energy Technology Center  
Pittsburgh, Pennsylvania**

**By  
Amoco Oil Company  
Naperville, Illinois**

**MASTER**

**DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED**

THE SELECTIVE CATALYTIC CRACKING OF FISCHER-TROPSCH LIQUIDS  
TO HIGH VALUE TRANSPORTATION FUELS

FINAL REPORT

PREPARED BY: M. M. SCHWARTZ

CONTRIBUTORS: W. J. REAGAN, J. J. NICHOLAS, and R. D. HUGHES

WORK PERFORMED UNDER CONTRACT NO. DE-AC22-91PC90057

FOR

U.S. DEPARTMENT OF ENERGY  
PITTSBURGH ENERGY TECHNOLOGY CENTER  
PITTSBURGH, PENNSYLVANIA

BY

AMOCO OIL COMPANY  
RESEARCH AND DEVELOPMENT DEPARTMENT  
P.O. BOX 3011  
NAPERVILLE, ILLINOIS 60566

1 m 6/60

**FINAL REPORT SUBMITTED TO:**

1. A. C. Bose (5 copies)  
Contracting Officer's Representative  
U.S. DOE/PETC  
P.O. Box 10940  
Pittsburgh, PA 15236
2. Cynthia Y. Mitchell  
Contract Specialist  
U.S. DOE/PETC  
P.O. Box 10940, MS 921-118  
Pittsburgh, PA 15236
3. Robert M. Hamilton  
FE-231, C-175/GTN  
19901 Germantown Road  
Germantown, MD 20585
4. Joanne Wastek  
Project Management Assistant  
U.S. DOE/PETC  
P.O. 10940, MS 922-H  
Pittsburgh, PA 15236

**ADDITIONAL CIRCULATION FOR REPORTS TO:**

Amoco Corporation  
Alternative Feedstock Development Department  
P. O. Box 3011  
Naperville, Illinois 60563-7011  
T. H. Fleisch, E-2G

Amoco Oil Company  
P.O. Box 3011  
Naperville, Illinois 60566  
W. J. Reagan, H-6  
F. W. Hauschildt, H-3  
J. J. Nicholas, H-4  
M. M. Schwartz, H-4 (3)  
R. D. Hughes, H-2  
O. P. Mahajan, H-2

TABLE OF CONTENTS

	<u>Page</u>
Executive Summary . . . . .	12
1.0 Background . . . . .	12
2.0 Scope of Work . . . . .	15
2.1 Program Descriptions . . . . .	15
2.2 Task Description . . . . .	15
2.2.1 Project Management Plan	
2.2.2 Preparation of Feedstocks and Equipment Calibration	
2.2.3 Catalytic Cracking Catalyst Screening Program	
2.2.4 Pilot Plant Tests	
2.2.5 Preparation of C <sub>5</sub> -C <sub>8</sub> Ethers	
2.2.6 Evaluation of Gasoline Blending Properties of Ethers and Alcohol Products	
2.2.7 Scoping Economic Evaluation of the Proposed Processes	
3.0 Feedstock Characterization and Equipment Calibration . . . . .	15
3.1 Feedstock Characterization . . . . .	15
3.1.1 Sasol Wax	
3.1.2 Air Products Wax	
3.1.3 Fischer-Tropsch Naphtha from UOP Pilot Plant	
3.2 Equipment Modification . . . . .	18
4.0 Catalytic Cracking Catalyst Screening Program . . . . .	19
4.1 Sasol Wax Feedstock . . . . .	19
4.1.1 Comparison with Gas Oil Feedstock	
4.1.2 Effect of Reaction Severity	
4.1.3 Non-zeolitic Catalysts	
4.1.4 Effect of HZSM-5 Source	
4.1.5 HZSM-5 Zeolite Catalysts Containing Rare Earth	
4.1.6 Y Zeolite Catalysts Containing Rare Earth	
4.1.7 Effect of Coke Deposition	
4.1.8 Low Zeolite-content Catalysts	
4.2 LaPorte Wax Feedstock . . . . .	54
4.2.1 Selective Attrition Experiments	
4.2.2 Catalyst Effects	
4.3 UOP Fischer-Tropsch Naphtha Feedstock . . . . .	81
5.0 Pilot Plant Tests . . . . .	81
5.1 Conversion and Selectivity . . . . .	87
5.2 Product Quality . . . . .	88
5.2.1 Properties of 430-°F Product (Naphtha)	
5.2.2 Properties of 430-650°F Product (LCCO)	
5.2.3 Properties of 650+°F Product (Heavy Cycle Oil)	
6.0 Preparation of C <sub>5</sub> -C <sub>8</sub> Ethers . . . . .	98
6.1 Model Compound Runs . . . . .	98
6.2 Feedstock Variation . . . . .	98
6.3 Etherification Runs . . . . .	105

TABLE OF CONTENTS  
(Continued)

	<u>Page</u>
7.0 Evaluation of Gasoline Blending Properties of Ether . . . . .	106
8.0 Scoping Economic Evaluation of the Proposed Processes . . . . .	107
8.1 Product Value of FCC Pilot Plant Runs . . . . .	107
8.1.1 Propylene Valued as Fuel Gas	
8.1.2 Propylene Valued as Feedstock to Di-isopropyl Ether Unit	
8.2 Calculation of Hydrocracking Product Values and Comparison with Pilot Plant FCC Product Values . . . . .	121
9.0 Conclusions . . . . .	126
10.0 References . . . . .	126

LIST OF TABLES

<u>Table</u>	<u>Description</u>	<u>Page</u>
I	Viscosities of Sasol and LaPorte Waxes . . . . .	18
II	Chemical Analysis of LaPorte Wax . . . . .	19
III	GC-MS of UOP Fischer-Tropsch Naphtha . . . . .	20
IV	MYU Tests: F-T wax vs Conventional Gas Oil Feedstocks . . . . .	22
V	MYU Tests: Effect of Catalyst Diluent . . . . .	23
VI	MYU Tests: Effect of Catalyst to Oil Ratio . . . . .	25
VII	MYU Tests: Catalyst Comparisons at 880°F . . . . .	31
VIII	MYU Tests: Comparison of Amorphous Catalyst at 970°F . . . . .	32
IX	MYU Tests: Various HZSM-5 Catalysts . . . . .	38
X	MYU Tests: Rare Earth/HZSM-5 Catalysts . . . . .	39
XI	MYU Tests: Rare Earth/USY Catalysts . . . . .	43
XII	Chemical Composition of Zeolite FCC Catalysts . . . . .	54
XIII	Physical Properties of Zeolite FCC Catalysts . . . . .	61
XIV	MYU Tests: Selective Attrition Experiments . . . . .	62
XV	MYU Tests: Sasol vs LaPorte Wax Feedstocks . . . . .	79
XVI	MYU Tests: UOP F-T Naphtha Feedstock at 880°F . . . . .	82
XVII	MYU Tests: UOP F-T Naphtha Feedstock at 970°F . . . . .	83
XVIII	FCC Pilot Plant Run Data with Sasol Wax Feedstock . . . . .	86
XIX	Analysis of IBP-430°F Products from FCC Pilot Plant Runs . . . . .	89
XX	Analysis of 430-650°F Products from FCC Pilot Plant Runs . . . . .	92
XXI	Analysis of 650+°F Products from FCC Pilot Plant Runs . . . . .	93
XXII	Hydrocarbon Composition of 200-°F Naphthas "A," "B," and "C" from FCC Pilot Plant Runs . . . . .	99
XXIII	Etherification Runs with Naphtha "A" . . . . .	100
XXIIIa	Reactive Iso-olefins Conversion to Ethers . . . . .	101
XXIV	Etherification Runs with Naphtha "B" . . . . .	102
XXV	Etherification Runs with Naphtha "C" . . . . .	103
XXVI	Summary of Etherification Run Data . . . . .	104
XXVII	RON and MON of Etherification Run Products . . . . .	109
XXVIII	C <sub>4</sub> -C <sub>6</sub> Isomer Distribution of FCC Pilot Plant Products . . . . .	110
XXIX	Economic Analysis of FCC Pilot Plant Run 939-1; USY Catalyst . . . . .	111
XXX	Economic Analysis of FCC Pilot Plant Run 939-2; USY Catalyst . . . . .	112
XXI	Economic Analysis of FCC Pilot Plant Run 939-4; USY Catalyst . . . . .	113
XXXII	Economic Analysis of FCC Pilot Plant Run 939-5; Steamed USY Catalyst . . . . .	114
XXXIII	Economic Analysis of FCC Pilot Plant Run 940-1; Steamed Beta Catalyst . . . . .	115
XXXIV	Economic Analysis of FCC Pilot Plant Run 940-2; Steamed Beta Catalyst . . . . .	116
XXXV	Economic Analysis of FCC Pilot Plant Run 941-1; Blend 25% Steamed HZSM-5 with USY Catalyst . . . . .	117
XXXVI	Economic Analysis of FCC Pilot Plant Run 942-2; Blend 50% USY Catalyst with Diluent Catalyst . . . . .	118
XXXVII	Summary of Net Product Values for FCC Pilot Plant Runs with Propylene valued as Feedstock to a Di-isopropyl Ether Unit . . . . .	119
XXXVIII	Summary of Net Product Values for FCC Pilot Plant Runs . . . . .	120
XXXIX	Propylene Properties Used in Economic Analysis . . . . .	121
XL	F-T Wax Hydrocracking Case Price Structure Calculations . . . . .	122
XLI	Economic Analysis of F-T Wax Hydrocracking Case . . . . .	123

LIST OF FIGURES

<u>Figure</u>	<u>Description</u>	<u>Page</u>
1	Simulated Distillation of Sasol and LaPorte Wax . . . . .	16
2	Normal Paraffin Distribution of Sasol and LaPorte Wax . . . . .	17
3	Sasol Wax MYU Data: Effect of Temperature on Conversion . . . . .	24
4	Sasol Wax MYU Data: Effect of Temperature on Isobutylene Yield . . . . .	24
5	Sasol Wax MYU Data: Effect of Diluent on Boiling Point Distribution . . . . .	27
6	Sasol Wax MYU Data: Effect of Diluent on Conversion . . . . .	27
7	Sasol Wax MYU Data: Effect of Conversion on Isoamylenes Yield . . . . .	28
8	Sasol Wax MYU Data: Effect of Conversion on Isobutylene Yield . . . . .	28
9	Sasol Wax MYU Data: Effect of Conversion on Propylene Yield . . . . .	29
10	Sasol Wax MYU Data: Effect of Conversion on C <sub>3</sub> + C <sub>4</sub> Yield . . . . .	29
11	Sasol Wax MYU Data: Effect of Conversion on C <sub>5</sub> -430°F Naphtha Yield . . . . .	30
12	Sasol Wax MYU Data: Effect of Conversion on Coke . . . . .	30
13	Sasol Wax MYU Data: Effect of C/O in Coke . . . . .	33
14	Sasol Wax MYU Data: Effect of Conversion on Aromatics Formation . . . . .	34
15	Sasol Wax MYU Data: C <sub>5</sub> Isomer Distribution . . . . .	35
16	Sasol Wax MYU Data: C <sub>4</sub> Isomer Distribution . . . . .	36
17	Sasol Wax MYU Data: Effect of C/O on Conversion with HZSM-5 Catalysts . . . . .	37
18	Sasol Wax MYU Data: Effect of Conversion on Propylene Yield with HZSM-5 Catalysts . . . . .	40
19	Sasol Wax MYU Data: Effect of Conversion on Isobutylene Yield with HZSM-5 Catalysts . . . . .	40
20	Sasol Wax MYU Data: Effect of Conversion on Isoamylenes Yield with HZSM-5 Catalysts . . . . .	41
21	Sasol Wax MYU Data: Effect of Conversion on C <sub>5</sub> -430°F Naphtha Yield with HZSM-5 Catalysts . . . . .	41
22	Sasol Wax MYU Data: Effect of Conversion on Aromatics Formation with HZSM-5 Catalysts . . . . .	42
23	Sasol Wax MYU Data: Effect of Conversion on Olefins Yield with HZSM-5 Catalysts . . . . .	42
24	Sasol Wax MYU Data: Effect of C/O on Conversion with Rare Earth/USY Catalysts . . . . .	45
25	Sasol Wax MYU Data: Effect of Conversion on Propylene Yield with Rare Earth/USY Catalysts . . . . .	45
26	Sasol Wax MYU Data: Effect of Conversion on Isobutylene Yield with Rare Earth/USY Catalysts . . . . .	46
27	Sasol Wax MYU Data: Effect of Conversion on Isoamylenes Yield with Rare Earth/USY Catalysts . . . . .	46
28	Sasol Wax MYU Data: Effect of Conversion on C <sub>5</sub> -430°F Naphtha Yield with Rare Earth/USY Catalysts . . . . .	47
29	Sasol Wax MYU Data: Effect of Conversion on C <sub>3</sub> + C <sub>4</sub> Yield with Rare Earth/USY Catalysts . . . . .	47



LIST OF FIGURES  
(Continued)

<u>Figure</u>	<u>Description</u>	<u>Page</u>
30	Sasol Wax MYU Data: Effect of Conversion on RON with Rare Earth/USY Catalysts . . . . .	48
31	Sasol Wax MYU Data: Effect of Conversion on MON with Rare Earth/USY Catalysts . . . . .	48
32	Sasol Wax MYU Data: Power Law Plot of Propylene vs Conversion with Rare Earth/USY Catalysts . . . . .	49
33	Sasol Wax MYU Data: Power Law Plot of Isobutylene Yield vs Conversion with Rare Earth/USY Catalysts . . . . .	49
34	Sasol Wax MYU Data: Power Law Plot of Isoamylenes Yield vs Conversion with Rare Earth/USY Catalysts . . . . .	50
35	Sasol Wax MYU Data: Power Law Plot of C <sub>5</sub> -430°F Naphtha Yield vs Conversion with Rare Earth/USY Catalysts . . . . .	50
36	Sasol Wax MYU Data: Effect of Multiple Runs on Conversion with HZSM-5 Catalyst . . . . .	51
37	Sasol Wax MYU Data: Effect of Conversion on Propylene Yield in Multiple Runs with HZSM-5 Catalyst . . . . .	51
38	Sasol Wax MYU Data: Effect of Conversion on Isobutylene Yield in Multiple Runs with HZSM-5 Catalyst . . . . .	52
39	Sasol Wax MYU Data: Effect of Conversion on Isoamylenes Yield in Multiple Runs with HZSM-5 Catalyst . . . . .	52
40	Sasol Wax MYU Data: Effect of Conversion on C <sub>5</sub> -430°F Naphtha Yield in Multiple Runs with HZSM-5 Catalyst . . . . .	53
41	Sasol Wax MYU Data: Effect of Conversion on C <sub>3</sub> + C <sub>4</sub> Yield in Multiple Runs with HZSM-5 Catalyst . . . . .	53
42	Sasol Wax MYU Data: Parity Plot of MYU and Simulated Distillation Methods for Conversion Calculation with Low Zeolite Content Catalysts . . . . .	55
43	Sasol Wax MYU Data: Effect of Conversion on Propylene Yield with Low Zeolite Content Catalysts . . . . .	56
44	Sasol Wax MYU Data: Effect of Conversion on Isobutylene Yield with Low Zeolite Content Catalysts . . . . .	57
45	Sasol Wax MYU Data: Effect of Conversion on Isoamylenes Yield with Low Zeolite Content Catalysts . . . . .	58
46	Sasol Wax MYU Data: Effect of Conversion on C <sub>5</sub> -430°F Naphtha Yield with Low Zeolite Content Catalysts . . . . .	59
47	Sasol Wax MYU Data: Effect of Conversion on LCCO Yield with Low Zeolite Content Catalysts . . . . .	59
48	Sasol Wax MYU Data: Effect of Conversion on 650-800°F Cycle Oil Yield with Low Zeolite Content Catalysts . . . . .	60
49	Sasol Wax MYU Data: Effect of Conversion on 800+°F Cycle Oil Yield with Low Zeolite Content Catalysts . . . . .	60
50	SEM Photomicrograph of Base FCC Catalyst; 4200 ppm Iron . . . . .	64
51	SEM Photomicrograph of FCC Catalyst Contaminated with F-T Catalyst Fines; 10500 ppm Iron . . . . .	65
52	SEM Photomicrograph of FCC Catalyst Contaminated with F-T Catalyst Fines; 10500 ppm Iron (Higher Magnification) . . . . .	65

LIST OF FIGURES  
(Continued)

<u>Figure</u>	<u>Description</u>	<u>Page</u>
53	SEM Photomicrograph of FCC Catalyst Contaminated with F-T Catalyst Fines after Selective Attrition; 6200 ppm Iron . . . . .	66
54	SEM Photomicrograph of Catalyst Fines from Selective Attrition; 29600 ppm Iron . . . . .	67
55	SEM Photomicrograph of Catalyst Fines from Selective Attrition; 29600 ppm Iron (Higher Magnification) . . . . .	67
56	LaPorte vs Sasol Wax MYU Data: Effect of C/O on Conversion . . . . .	68
57	LaPorte vs Sasol Wax MYU Data: Effect of Conversion on Coke . . . . .	69
58	LaPorte vs Sasol Wax MYU Data: Effect of Conversion on Hydrogen Yield . . . . .	70
59	LaPorte vs Sasol Wax MYU Data: Effect of Conversion on Propylene Yield . . . . .	71
60	LaPorte vs Sasol Wax MYU Data: Effect of Conversion on Isobutylene Yield . . . . .	72
61	LaPorte vs Sasol Wax MYU Data: Effect of Conversion on Isoamylenes Yield . . . . .	73
62	LaPorte vs Sasol Wax MYU Data: Effect of Conversion on C <sub>5</sub> -430°F Naphtha Yield . . . . .	74
63	LaPorte vs Sasol Wax MYU Data: Effect of Conversion on LCCO Yield . . . . .	75
64	LaPorte vs Sasol Wax MYU Data: Effect of Conversion on 650-800°F Cycle Oil Yield . . . . .	76
65	LaPorte vs Sasol Wax MYU Data: Effect of Conversion on 800+°F Cycle Oil Yield . . . . .	77
66	LaPorte vs Sasol Wax MYU Data: Effect of Conversion on RON . . . . .	78
67	UOP F-T Naphtha MYU Data: Effect of Temperature on C <sub>5</sub> -Conversion . . . . .	84
68	UOP F-T Naphtha MYU Data: Effect of C <sub>5</sub> - Conversion on Isobutylene Yield . . . . .	84
69	UOP F-T Naphtha MYU Data: Effect of C <sub>5</sub> - Conversion on Isoamylenes Yield . . . . .	85
70	Sasol Wax FCC Pilot Plant Data: Effect of USY Zeolite Catalyst Acidity on PIANO Distribution by Compound Type in IBP-430°F Naphtha . . . . .	94
71	Sasol Wax FCC Pilot Plant Data: Effect of USY Zeolite Catalyst Acidity on PIANO Distribution by Carbon Number in IBP-430°F Naphtha . . . . .	95
72	Effect of Reaction Temperature on Etherification of 2-Methyl-2-butene with Methanol . . . . .	105
73	Engine Test RON vs Calculated RON for Mixed Ether Reaction Products . . . . .	108
74	Schematic of Basis Refinery Configuration for Hydrocracking Case Economics . . . . .	124
75	Net Product Values from FCC Pilot Plant Runs vs Hydrocracker Case . . . . .	125

LIST OF APPENDICES

<u>Appendix</u>	<u>Description</u>	<u>Page</u>
A	MYU Run Data . . . . .	129
B	Product Value Calculations used in Economic Analyses . .	140

**DISCLAIMER**

This report is an account of work sponsored by the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.