

GASOLINE RANGE ETHER SYNTHESIS FROM LIGHT NAPHTHA PRODUCTS OF  
FLUID CATALYTIC CRACKING OF FISCHER-TROPSCH WAX.

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The Fluid Catalytic Cracking of Fischer-Tropsch wax ( $C_{20}^+$  paraffins) produces two to four times the concentration of reactive iso-olefins (isobutylene, isoamylenes, isohexenes) than observed from conventional gas oil feedstocks. Methanol reacts with these olefins to form the corresponding tertiary alkyl methyl ethers: MTBE, TAME and MTHE's. These etherification reactions are mildly exothermic and equilibrium limited. The reaction temperature and the olefin molecular structure are important variables for maximum ether yields. The base naphtha research octane number increases by 2-4 numbers after the etherification reaction. The presence of hydrogen has a detrimental effect on ether yields because of hydrogenation of reactive olefins to paraffins. The catalytic cracking of Fischer-Tropsch wax provides a non-conventional source of olefins for ether synthesis that can supplement existing and dwindling petroleum supplies.

#### INTRODUCTION

Fischer-Tropsch (F-T) synthesis technology (1) produces liquid hydrocarbons from synthesis gas (hydrogen and carbon monoxide) derived from the gasification of coal or reforming of natural gas. The F-T liquid product consists of a broad range of normal paraffins ( $C_3$ - $C_{30}^+$ ) and a small quantity of oxygenates and olefins. The distillate fraction,  $C_{12}$ - $C_{18}$ , is an excellent quality fuel. The largest product fraction,  $C_{18}^+$ , is primarily wax and is useless as a transportation fuel. These products are further treated by conventional petroleum processes, such as hydrotreating, reforming and catalytic cracking to produce conventional gasoline and distillate fuels. (2) Fluid catalytic cracking and hydrocracking studies have been reported by Mobil (3) and UOP. (4) Heavy wax ( $C_{20}^+$ ) fractions have also been treated with hydroisomerization and hydrocracking processes at Exxon. (5) Hydrodewaxing and catalytic cracking treatments of heavy wax from slurry F-T processing are also reported by Mobil. (6) In addition, pure component cracking studies (decanol, decanal) over the intermediate - pore zeolite HZSM-5 have been reported. (7) The catalytic cracking of F-T liquids was examined in some detail by Wojciechowski over large-pore Faujasite (zeolite Y) and over HZSM-5 zeolite catalysts. (8,9) Governmental regulations, most recently in the Clean Air Act Amendments of November, 1990, have resulted in the phase-out of lead additives, lowering of the Reid vapor pressure of gasoline and in some geographical areas, the mandated use of oxygenates. Several types of ethers are now commercially produced and used as gasoline blending components. (10) Recent studies of methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME) suggest that these compounds may reduce automotive carbon monoxide emissions, have high blending gasoline octane ratings, R+M/2, (MTBE=108, TAME=102) and have low Reid vapor pressure. These ethers are produced commercially by the etherification of the appropriate olefin by methanol (MTBE, isobutylene; TAME, isoamylenes). (11,12) There is less information in the open literature about the etherification reactions of  $C_6$  olefins that are also present in significant quantities in fluid catalytic cracking product naphthas. The Etherol process (13) produces a mixed ether product from  $C_6$ - $C_7$  reactive iso-olefins in naphthas. One report (14) provides some information about the reaction of  $C_6$  iso-olefins with methanol to produce the higher ethers, MTHE's, methyl tertiary hexyl ethers. MTBE has attracted the most attention in recent years. The growth rate for its production could reach 25% per year by 1995. (15,16) There is a growing need for alternative sources of olefins for ether syntheses as demand for these materials escalates beyond the capacity of conventional petroleum processes. There are no reported studies of the catalytic cracking processing of F-T liquids to produce  $C_3$ - $C_6$  olefins as feedstocks for the synthesis of gasoline range ethers.

#### EXPERIMENTAL.

The feedstock for this work is a sample of reactor wax from a commercial fixed bed F-T unit operated by Sasol, Limited. The analytical characterization of this feedstock is available in other studies. (4) The small scale (1 gram of feed, 3-5 grams of catalyst) catalytic cracking tests were performed on a Micro Activity Test unit (MAT) similar in design to the unit described in ASTM procedure, D3907-86. This test unit is equipped for detailed analyses of gas and liquid products and coke yields. The pilot plant tests were conducted in a circulating catalyst unit similar to a design described by ARCO. This unit operates with 2 to 3 kilograms of

catalyst and feed rates of 10-30 grams/minute. The ether synthesis experiments were carried out in a conventional high pressure micro-reactor. Three FCC catalysts, containing zeolite Y, zeolite Beta and zeolite HZSM-5 are the primary catalysts for the FCC studies. The Y zeolite catalyst is an Ultrastable Y faujasite (USY) zeolite catalyst taken from one of Amoco's commercial FCC units. The HZSM-5 catalyst is a commercial sample produced by Intercat Corp. The Beta sample was prepared in our laboratory by spray drying a commercially available Beta zeolite and a conventional silica-alumina matrix. Two commercial ion exchange resin catalysts, Rohm and Haas's Amberlyst 15 and Bayer's K 2634, were used in the ether synthesis runs.

## RESULTS AND DISCUSSION.

### A. Catalytic Cracking Tests.

Initial catalytic cracking runs with the small scale test system provide some insights into the catalytic cracking behavior of the wax feedstock. The initial choice of fluid catalytic cracking (FCC) catalyst and process conditions focuses on comparisons with conventional gas oil, the usual feedstock to commercial FCC units. At these conditions, (970°F reaction temperature, 3 catalyst to oil weight ratio), the wax feedstock readily converts (85%+ conversion) to high yields of C<sub>4</sub>- gas (high in propylene and C<sub>4</sub> olefins) and naphtha (C<sub>5</sub>-430°F). A summary of this comparison is presented in Table I. The conversion level is defined by convention as the sum of the products: naphtha, gas and coke. This high catalytic cracking conversion level for the wax feedstock agrees with the published Mobil data (3,6) on F-T wax cracking. In addition, historical pure component hydrocarbon cracking studies (17) suggest that long chain paraffins crack at much greater rates than the shorter chain paraffins. The low coke yield of the wax feedstock will be an important parameter when commercial heat balanced operations are evaluated. The relatively low octane number of the wax product naphtha results from the higher concentrations of low octane number paraffins compared to the gasoline from the more aromatic gas oil feedstocks. The octane numbers in the Table I are estimated results from detailed naphtha analyses by gas chromatography and correlations with octane engine tests. The target of these studies is to optimize the yields of branched olefin intermediates (isobutylene and isoamylenes) for ether synthesis. Three FCC catalysts, containing zeolite Y, zeolite Beta, and zeolite HZSM-5, were tested for wax conversion and product selectivity as a series of blends with an inert solid. Table II presents the detailed product distributions for the three catalysts at a similar conversion level of about 83%. Both the Beta and HZSM-5 catalysts produce much higher yields of the desirable olefins. However, this occurs at the expense of naphtha product. In addition, the HZSM-5 catalyst produces very high yields of propylene. These screening test results show that FCC catalyst variations can provide for widely different product distributions.

### B. Pilot Plant Catalytic Cracking Tests.

Some initial wax catalytic cracking screening tests on the pilot plant unit are presented in Table III. The high conversions of the wax feedstock in the pilot plant agree with the small scale test results. The Beta zeolite catalyst converts a greater fraction of the wax feedstock to light olefins, including propylene, isobutylene and isoamylenes, than the Y zeolite catalyst. The higher olefin yields are offset by a significantly lower naphtha yield for the Beta zeolite catalyst compared to the standard Y zeolite catalyst. The test results for the HZSM-5 catalyst mixture are similar to the Beta zeolite. High yields of the target light olefins are produced but the naphtha yield is much lower than the Y zeolite catalyst. This trade-off of light olefin and naphtha yields can be adjusted by the amount of the HZSM-5 additive. The total liquid products from several pilot plant catalytic cracking runs were combined and distilled (ASTM Method D-2892) to produce light naphtha (<200°F) fractions for the etherification studies.

### C. Ether Synthesis.

Since the reaction of isobutylene and methanol to form MTBE is well known, this study will focus on the production of TAME and MTHE ethers from the light naphtha products of the pilot plant wax cracking studies. A small, fixed bed unit was used for these etherification studies. The initial test runs involve the reaction of 2-Methyl-2-butene with methanol to produce TAME. Table IV shows the comparison of TAME yields (conversion of isoamylenes to TAME: moles TAME out/moles isoamylenes in\*100). The test conditions are: variable temperatures, 200 PSIG unit pressure, 0.66 WHSV (olefin) and 1.2 mole ratio of methanol/olefin. The catalyst for these runs is Amberlyst 15, a commercial etherification catalyst. The reaction temperature is a major factor in this etherification reaction. The sharp

rise in TAME yield at 150°F and the decline at 200°F suggests that equilibrium limitations exist at these temperatures and reaction conditions. The maximum yields of ethers will occur at these equilibrium conditions. Table V presents the detailed composition of the light naphtha samples from the pilot plant wax catalytic cracking runs. The iso-olefin contents of the samples, feeds "B" and "C", are higher from the pilot plant wax catalytic cracking runs than the light naphtha sample, feed "A". This is due to the use of high olefin selective FCC catalysts, Beta and HZSM-5, in the pilot plant runs, Nos. 940-01,02 and 941-01. The same Y zeolite catalyst was used in the runs for feed "A" and "C". The high iso-olefin content of feed "C" results from the lower conversion level. The reactive isoamylenes, 2-Methyl-2-butene and 2-Methyl-1-butene for TAME synthesis and the reactive C<sub>6</sub> iso-olefins, 2-Methyl-1-pentene, 2-Methyl-2-pentene, 2,3-Dimethyl-1-butene, and cis and trans 3-Methyl-2-pentene for MTHE synthesis are the important components. This light naphtha, feed "A" sample and methanol are the feedstock for a series of etherification runs at the same process conditions for the 2-Methyl-2-butene/methanol tests. Due to the limited availability of the naphtha, only two reaction temperatures are available. A summary of the conversion of the various C<sub>5</sub> and C<sub>6</sub> iso-olefins to their respective methyl ethers, Table VI, shows that reaction temperature is a major factor in the etherification reaction. The decrease in conversion with the increase in the carbon number of the iso-olefin agrees with other literature etherification studies. (18,20) The reaction products from these runs have a significant yellow color, especially at the higher reaction temperature of 150°F. This color is not present for the pure component 2-Methyl butene-2 tests. It is likely that polymerization of olefins to C<sub>10</sub>+ hydrocarbon "color bodies" is responsible for the colored product. The color of the ether product could be a significant product quality issue. Table VII presents the results of the etherification runs with the "B" and "C" light naphthas at 150°F. In these runs, both Amberlyst 15 and another commercial etherification catalyst, Bayer's K2634 are under study. The Bayer catalyst contains a noble metal in addition to the strong acid functionality. The noble metal is available for olefin isomerization and diolefin saturation, in the presence of hydrogen. The nominal reaction conditions from the previous set of runs, 200 PSIG, 2.9 grams of catalyst, methanol 1.37 g/hr, naphtha, 5.5 g/hr are the same except that only one reaction temperature, 150°F, is available. The iso-olefin conversion results are similar for both catalysts and the three feedstocks, in the absence of hydrogen gas in the reactor. The calculated research octane values for the products of these etherification runs are 2-4 numbers higher than the starting light naphtha feedstocks, Table VIII. As expected, this octane increase depends to some extent upon the concentrations of the ethers in the product. Blending octane numbers for the mixed ether light naphtha fractions are also shown in Table VIII. There is a fair agreement with the calculated (by GC) octane numbers. When hydrogen gas is present, Run No. 034-1, Table VIII, there is a major loss of iso-olefin conversion. These reaction conditions result in the hydrogenation of both reactive iso-olefins and linear olefins. This is an undesirable result since both the production of ethers and the octane number of the product decreases significantly. The run with added hydrogen gas, 034-1, has a lower research octane rating (79.5) than the feedstock (84.6) or the run with no added hydrogen, 034-3, (85.8). This octane loss is due to the conversion of high octane value olefins to low octane value paraffins. There is a significant improvement in the color of the etherification products in the presence of hydrogen gas.

These etherification runs clearly demonstrate that the light naphtha fractions from the catalytic cracking of Fischer-Tropsch wax are excellent ether synthesis feedstocks.

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#### REFERENCES

1. Anderson, R. B. The Fischer-Tropsch Synthesis; Academic (New York), 1984.
2. Stuart, J. S., et al. Oil & Gas Journal, August 31, 1981, 62.
3. Kuo, J. C. W., et al. 1988 AIChE Annual Meeting (Washington, DC, 11/17/88, Preprint No. 61D); 1984 AIChE Annual Meeting (Anaheim, California, Preprint No. 11D); Department of Energy, Final Report, October, 1985, DOE/PC/60019-9A.
4. Shah, P. P., et al. "F-T Wax Characterization and Upgrading"; Final Report, Department of Energy, June 6, 1988, DOE/PC/80017-T1.
5. Exxon R&E Company, U.S. 4,832,819, May 23, 1989.

6. Mobil Oil Company, U.S. 4,684,756, August 4, 1987.
7. Riley, M.; Anthony, R. G. J. Catal., 103, 87-94, 1987.
8. Abbot, J.; Wojciechowski, B. W. Ind. Eng. Chem. Prod. Res. Dev. 1985, 24, 501-507.
9. Kobolakis, I.; Wojciechowski, B. W. Can. J. Chem. Eng., 63, April 1985, 269-277.
10. Piel, W. J. Energy Progress, 8, No. 4, 201, 1988; Oil & Gas J., December 4, 1989, 40.
11. Reychler, A. Bull. Soc. Chim. Belg.; 21, 71 (1907).
12. Ancillotti, F., et al., J. Catalysis; 46, 49-57 (1977).
13. Halsig, C. P., et al., NPRA, 1986 Annual Meeting, Paper AM-86-94.
14. Krause, A. O. I., et al., 8th Int. Cong. Catal., 5, 553, 1984.
15. Oil & Gas J., January 27, 1992, 21.
16. Oil & Gas J., November 30, 1992, 48.
17. Gorra, A.; Wojciechowski, B. W. Catal. Rev.-Sci. Eng., 27(1), 29-150, 1985

TABLE I

**INITIAL COMPARISONS OF FISCHER-TROPSCH MAX CRACKING AND CONVENTIONAL GAS OIL FEEDSTOCKS**

MAT Test Results: 970°F, 3 C/O, Equilibrium Catalyst  
Product Distribution and Product Properties

	Gas Oil	Max
Conversion, wt%	61.6	88.1
<b>Products, wt%:</b>		
C <sub>1</sub>	2.6	1.8
C <sub>2</sub> + C <sub>3</sub>	11.6	31.4
C <sub>4</sub>	6.9	15.9
C <sub>5</sub> - 430°F	36.2	36.8
430°F+	38.4	11.9
Coke	4.3	2.2
Isobutylene	1.3	4.5
Isoamylenes	2.3	5.8
Naphtha, RON	90.4	85.8
MON	79.8	77.6

TABLE II

**MAT TEST RESULTS--CATALYST COMPARISONS AT 880°F**

Catalyst Type	Zeolite T	Zeolite Beta	Zeolite HZSM-5
Run No.	031	042	055
Conversion, wt%	83.0	83.3	83.8
<b>Product Yields, wt%:</b>			
C <sub>1</sub>	0.6	0.6	1.5
C <sub>2</sub>	7.4	8.9	17.5
C <sub>3</sub>	0.8	0.9	2.7
C <sub>4</sub>	13.2	17.7	27.4
C <sub>5</sub>	3.7	3.6	3.6
C <sub>6</sub>	11.7	13.5	13.9
C <sub>7</sub>	3.6	2.2	2.0
C <sub>8</sub> -430°F	41.7	35.8	15.3
430°F+	17.0	16.8	16.2
Coke	0.3	0.2	0.1
Isobutylene	5.8	9.4	12.3
Isoamylenes	7.7	9.2	9.8
C <sub>5</sub> -430°F	57.0	51.4	31.1
RON	85.2	84.4	84.4
MON	76.2	74.6	76.0

TABLE III  
PILOT PLANT RUNS

RUN NO.	939-05	940-2	941-1
Reaction Temp., °F	879	910	965
C/O Ratio	2.25	3.35	2.84
WHSV (hr <sup>-1</sup> )	42.2	61.5	54.61
Catalyst	Steamed eq. USY	Steamed Beta	Steamed eq. USY (75%)/HZSM-5 (25%)
Conversion, wt%	85.0	96.5	89.0
Product Yields, wt%:			
C <sub>2</sub>	0.51	0.66	1.22
C <sub>2</sub> <sup>n</sup>	6.28	13.68	16.03
C <sub>3</sub>	0.90	1.81	2.47
iC <sub>3</sub>	3.40	7.66	3.40
nC <sub>3</sub>	0.99	2.09	1.92
iC <sub>3</sub> <sup>n</sup>	6.75	12.99	12.95
tC <sub>3</sub> <sup>n</sup>	3.19	5.44	5.33
cC <sub>3</sub> <sup>n</sup>	2.31	3.98	3.76
iC <sub>4</sub>	3.35	3.73	2.16
nC <sub>4</sub>	0.96	1.51	1.40
Total C <sub>3</sub> <sup>n</sup>	10.54	10.24	12.47
C <sub>7</sub> -430°F	46.08	31.53	24.81
430°F+	14.06	3.67	11.60
Coke	0.68	1.00	0.47

TABLE IV  
TAME PRODUCTION  
Methanol/2-Methyl-2-butene feedstock

Reaction Temperature, °F	TAME YIELD <sup>a</sup>
125	50
150	80
200	59

<sup>a</sup>TAME YIELD = moles TAME out/moles isoamylenes in \* 100.

TABLE V  
HYDROCARBON COMPOSITION OF 200°F NAPHTHAS

Feed ID:	92-0490-01A Feed A <sup>a</sup>	93-0024-01A Feed B	93-0024-01C Feed C
Pilot Plant Run Nos.	939-01, + 02 eq. USY catalyst conversion = 93.6%	940-01, 02 941-01 Beta/HZSM-5 catalyst Conversions = 90, 96%	939-04 eq. USY catalyst conversion = 83%
Total Paraffins wt%	6.69	8.44	4.32
Total Iso-paraffins wt%	42.71	17.64	22.88
Total Aromatics wt%	1.74	2.62	0.35
Total Naphthenes wt%	3.96	5.55	3.16
Total Olefins wt%	44.51	64.47	68.6
Reactive iso-olefins wt%			
C5's			
2-methyl-1-butene	1.25	2.15	1.76
2-methyl-2-butene	4.26	5.67	5.64
C6's			
2,3-dimethylbutene	0.8	0.73	0.97
2-methyl-1-pentene	2.35	2.49	3.02
2-methyl-2-pentene	4.01	5.27	5.46
3-methyl-trans-2-pentene	2.49	3.13	3.29
3-methyl-vis-2-pentene	3.98	5.48	5.35

TABLE VI  
**REACTIVE ISO-OLEFINS CONVERSION TO ETHERS**  
 Reaction Temperature (Averages of Three Weight Balance Tests)

Feed A		
Iso-olefin Component	125°F	150°F
	wt%	wt%
C5		
2-Methyl-1-butene	85.4	89.9
2-Methyl-2-butene	29.9	65.5
C6		
2,3-Dimethyl-1-butene	56.5	83.4
2-Methyl-1-pentene	65.9	87.5
2-Methyl-2-pentene	20.7	48.6
3-Methyl-cis-2-pentene	21.7	38.6
3-Methyl-trans-2-pentene	20.8	29.8

TABLE VII  
**REACTIVE ISO-OLEFINS CONVERSION TO ETHERS**

	Feed A	Feed B				Feed C	
200°F- Naphtha	92-049-01A	92-0024-01A				93-0024-01C	
Reaction Temp, °F	150	150	150	150	150	150	
Catalyst	Amberlyst 15	Amberlyst 15	K2634	K2634	K2634	K2634	
			No H2	H2	H2	No H2	
<i>iso-olefin component</i>							
C5's							
2-Methyl-1-butene	89.9	90.2	87.1	77.2	78.1	87.7	
2-Methyl-2-butene	65.5	62.2	66.2	42.9	38.2	61.2	
C6's							
2,3,0imethyl-1-butene	83.4	---	---	---	---	---	
2-Methyl-1-pentene	87.5	85.5	84.1	72.2	78.6	86.9	
2-Methyl-2-pentene	48.6	56.1	62.7	44.2	31.5	51.5	
3-Methyl-cis-2-pentene	38.6	31.0	43.4	23.8	7.3	25.8	
3-Methyl-trans-2-pentene	29.8	32.2	43.7	25.9	20.7	33.3	

TABLE VIII  
**LIGHT NAPHTHA ETHERIFICATION RUNS HYDROCARBON COMPOSITION OF FEED AND PRODUCTS**

Run No.	Reaction Temp	Catalyst	Research Octane Number*	Blending Research Octane Number
<b>Feed A</b>				
92-0490-01A	---	---	80.92	66.9
15586-024-2	125°F	Amberlyst 15	80.09	77.9
15586-024-6	150°F	Amberlyst 15	83.76	79.9
15586-024-8	150°F	Amberlyst 15	83.88	---
<b>Feed B</b>				
93-0024-01A	---	---	83.12	83.9
15586-031-2	150°F	Amberlyst 15	87.43	87.9
05586-033-1	150°F	Bayer K2634	87.48	85.9
15586-033-3	150°F	Bayer K2634	85.78	84.9
<b>Feed C</b>				
93-0024-01C	---	---	84.56	95.9
15586-034-1	150°F	Bayer H2 K2634	79.47	88.0
15586-034-3	150°F	Kayer no H2 K2634	85.78	95.9

\*Calculated

TABLE VIII  
**LIGHT NAPHTHA ETHERIFICATION RUNS HYDROCARBON COMPOSITION OF FEED AND PRODUCTS**  
 (Continued)

Run No.	Paraffins	Iso-paraffins	Aromatics	Naphthenes	Olefins	Oxygenates	Unknowns
<b>Feed A</b>							
92-0490-01A	6.689	42.712	1.736	3.956	44.507	0.071	0.33
15586-024-2	7.804	40.230	1.995	4.474	33.762	11.406	0.34
15586-024-6	6.463	40.429	2.247	4.574	29.671	16.296	0.32
15586-024-8	6.337	40.466	2.263	4.586	29.58	16.436	0.33
<b>Feed B</b>							
93-0024-01A	8.437	17.637	2.623	5.349	64.472	0.17	1.11
15586-031-2	7.417	17.989	3.687	6.424	41.847	21.815	0.821
05586-033-1	7.381	17.340	3.691	6.583	41.716	22.445	0.844
15586-033-3	8.205	17.668	3.62	6.512	45.889	17.277	0.83
<b>Feed C</b>							
93-0024-01C	4.315	22.881	0.353	3.161	68.651	0.15	0.49
15586-034-1	14.535	24.733	2.405	5.436	35.369	17.382	0.19
15586-034-3	5.921	22.489	1.977	4.497	43.51	21.192	0.415

\*Calculated