

3.0 PROCUREMENT OF FISCHER-TROPSCH MATERIAL (TASK 1.0)

UOP procured several materials from the product pool of a fixed-bed commercial Arge reactor. The fixed-bed Arge Fischer-Tropsch process operates at lower temperatures when compared to the circulating bed Synthol process. The product distribution ranges from methane to C₂₅₀₊ hard waxes (5). Typical product selectivities from a commercial fixed bed reactor are shown in Table 3.1.

Gasoline from a fixed-bed process has a very low octane value. This gasoline fraction requires upgrading using processes such as UOP Platforming before inclusion in a typical gasoline pool with an unleaded octane specification of 89. Diesel from a fixed-bed process, on the other hand, is of extremely high quality with very high cetane numbers. This diesel fraction can be blended with low-value refinery products such as LCO to increase the volume of the diesel pool. The carbon number fraction, higher than diesel, from the Fischer-Tropsch reactor is labelled reactor wax. The Fischer-Tropsch Arge wax from a commercial operation was used as feedstock for the hydrocracking work described in Task 3.0 and the characterization program described in Task 2.0.

3.1 DESCRIPTION OF PRODUCTS FROM A COMMERCIAL ARGE UNIT (6,7)

In a commercial Arge unit, the liquid F-T synthesis product is separated into three process streams: reactor wax, hot condensate and cold condensate (Refer to Figure 3.1). The tail gas, before being sent to the reformer, is washed with heptane to recover hydrocarbons as rectisol condensate, followed by a methanol wash to remove carbon dioxide. The hot and cold condensate are combined in a commercial Arge facility and sent to the atmospheric column, where they are separated into the desired product fractions. Atmospheric bottoms, containing 650°F plus material is blended back into the reactor wax to produce the desired product wax properties. Note that for Task 3.0: Wax Hydrocracking, this atmospheric bottoms fraction was not blended into the reactor wax feedstock to the pilot plant.

3.2 MATERIALS PROCURED

Table 3.2 lists all the procured products from a commercial Arge fixed-bed process, as well as some pilot-plant produced waxes used in Task 2.0: Wax Characterization and refinery LCOs used in Task 4.0: Blending Study.

3.2.1 Commercial Arge Unit

As mentioned earlier, the Arge wax was used in Task 2.0: Wax Characterization and Task 3.0: Wax Hydrocracking. Table 3.3 summarizes the commercial wax properties. For the purpose of the blending study, hot condensate and cold condensate were combined and separated into desired fractions. Table 3.4 lists properties of hot and cold condensate before and after blending. C₅/C₆ material was fractionated from the rectisol condensate and used as feedstock to the oligomerization pilot plant as described in Task 4.0: Blending Study. Table 3.5 lists properties of the Rectisol condensate as received from the commercial Arge unit and also, the composition of the C₅/C₆ material from the Rectisol condensate. Oligomerized Fischer-Tropsch C₅/C₆ product is a good blending component for maximum diesel fuel production.

3.2.2 Pilot Plant Waxes

Three other waxes were also procured in this program (Table 3.3). These waxes were produced in pilot plants at Union Carbide Corporation, Air Products and Chemicals, Inc. and Mobil Corp. All these waxes were fully characterized but, only the Mobil wax was hydrocracked in Task 6.0 to compare processibility with commercial Arge wax.

The Air Products wax was produced with a promoted cobalt catalyst at approximately 500°F, 1.0 CO/H₂ feed ratio and 300 psig reactor

pressure (8). The Union Carbide wax was produced with promoted cobalt catalysts in a series of pilot plant runs at approximately 465-500°F, 1.0 CO/H₂ feed ratio and 300 psig reactor pressure (9).

The Mobil wax was produced in a two-stage slurry reactor system at approximately 535°F, a low H₂/CO ratio of 0.7, 165 psig and with a precipitated iron catalyst (10).

3.2.3 Refinery LCO's

Three refinery LCO's (Table 3.6) were procured to increase the volume of diesel pool. LCO represents low-value refinery blend components and offers a source of aromatics in the blends.

Table 3.1
Fixed-Bed Arge Reactor

Product Distribution

		C Atom Basis, %
Arge Reactor	CH ₄	2.0
	C ₂ H ₄	0.1
	C ₂ H ₆	1.8
	C ₃ H ₆	2.7
	C ₃ H ₈	1.7
	C ₄ H ₈	3.1
	C ₄ H ₁₀	1.9
	C ₅ -C ₁₁ (gasoline)	18
	C ₁₂ -C ₁₈ (diesel)	14
	C ₁₉ -C ₂₃	7
	C ₂₄ -C ₃₅	20
	C ₃₅ + } Wax	25
	NACs*	2.7

* Non acid chemicals

Table 3.2
Materials Procured

<u>Material</u>	<u>Quantity</u>	<u>Source</u>
<u>Commercial F-T Products</u>		
F-T Arge Wax	500 gallons	Arge Commercial Unit
Hot Condensate	60 liters	Arge Commercial Unit
Cold Condensate	60 liters	Arge Commercial Unit
Rectisol Condensate	240 liters	Arge Commercial Unit
<u>LCOs for Blending Study</u>		
Light Cycle Oil 1	1 gallon	Clark Refinery
Light Cycle Oil 2	1 gallon	Ashland Refinery
Light Cycle Oil 3	1 gallon	Union Refinery
<u>Pilot Plant F-T Products</u>		
Union Carbide F-T Wax	550 grams	Union Carbide
Air Products F-T Wax	800 grams	Air Products
Mobil F-T Wax	42 kg	DOE/PETC

Table 3.3
Product Properties
Fischer-Tropsch Waxes

<u>Analysis Type</u>	<u>Commercial Arge Wax</u>	<u>Union Carbide</u>	<u>Air Products</u>	<u>Mobil Wax</u>
API	22.3	29.9	39.0	20.4
Specific Gravity	0.9200	0.8767	0.8299	0.9317
IBP, °F	597	547	417	518
Carbon, wt-%	85.2	85.3	85.2	84.4
Hydrogen, wt-%	14.7	14.7	14.8	15.3
Elemental Oxygen, wt-%	0.1			N/A
Sulfur, ppm	80	<100	<100	4
Nitrogen, ppm	16	0.1	10	3
Aniline Point, °F	293	258	239	298
Melting Point, °F	220	196	156	203
Viscosity, cSt @ 250°F	7.59	3.70	2.31	12.44
Conradson Carbon, wt-%	<0.1	<0.1	<0.1	<0.1
n-C ₂ H ₁₆ Insolubles, wt-%	24.4	0.44	<0.1	22.6
Metals, ppm	5.9	3.5	1.7	135*

* 133 ppm iron

N/A Not Available

Table 3.4
Product Properties

<u>Hot Condensate</u>	
API	45.9
Distillation, °F	
IBP	475
10%	538
30%	581
50%	617
70%	657
<u>Cold Condensate</u>	
API	53.8
Distillation, °F	
IBP	214
10%	286
30%	361
50%	423
70%	486
<u>Hot + Cold Condensate</u>	
API	48.3
Specific Gravity	0.7870
Distillation, °F	
IBP	302
10%	379
30%	473
50%	540
70%	603
90%	689
95%	698
EP	--
Cetane Number	74.9
Flash Point, °F	102
Pour Point, °F	80
Viscosity cSt @ 100°F	2.16
Bromine Number	7.1
Smoke Point, mm	>50

Table 3.5
Product Properties

<u>Rectisol Condensate</u>	<u>SIMDIS</u>	<u>(D-86)</u>
Distillation, °F		
180	23	129
10%	149	167
30%	207	208
50%	248	237
70%	264	266
90%	345	331
EP	907	421
GC Analysis, wt-% (paraffins/naphthenes)		
C ₄ -	1.3	
C ₅	4.7	
C ₆	13.7/0.1	
C ₇	24.8/0.4	
C ₈	25.2/0.4	
C ₉	14.9/0.2	
C ₁₀	5.8/0.1	
C ₁₁	8.3	
C ₁₂		
C ₁₃ +		
Gravity, API @ 60°F	66.9	
Carbonyl Number	63	
Bromine No.	58.4	
Diene Value (Maleic Anhydride)	12.2	
Sulfur (Houston-Atlas), ppm	<0.1	
Total Nitrogen, wt-ppm	1.22	
Water, wt-%	0.19	
<u>C₅/C₆ Fraction from Rectisol Condensate</u>		
(Feed to Oligomerization Plant)		
Feed Composition, wt-%*		
Total C ₃ 's	0.3	
Total C ₄ 's	13	
Total C ₅ 's	34.0	
Total C ₆ 's	44.6	
Total C ₇ 's	8.0	
Total C ₈ 's	0.1	

* Paraffin/Olefin distribution could not be determined due to interference from oxygenates

Table 3.6
Product Properties
Refinery Light Cycle Oil Analysis*

	<u>LCO 1</u>	<u>LCO 2</u>	<u>LCO 3</u>
API	21.1	16.1	14.1
Distillation, °F			
IBP	437	435	477
5%	489	482	498
10%	504	496	513
30%	550	534	554
50%	572	559	592
70%	601	595	637
90%	640	644	687
95%	662	660	702
EP	689	693	723
Cetane Number	27	21	17
Aromatics, wt-%	63.8	72.6	79.1
Paraffin/Naphthane, wt-%	36.2	20.6	18.2
Olefins, wt-%	--	6.8	2.7
Freeze Point, °F	+24	+29	+17
Pour Point, °F	+10	0	-25
Flash Point, °F	163	204	191
Smoke Point, mm	6	5	4
Viscosity, cSt, @ 100°F	3.343	3.932	3.226

* LCO is a Fluid Catalytic Cracking (FCC) Unit Product

Figure 3.1

Arge Reactor Products

