5.0 FISCHER-TROPSCH WAX HYDROCRACKING PROGRAM (TASK 3 and Task 6)

The findings of the Fischer-Tropsch wax hydrocracking program are summarized in this section. Most discussion in this section pertains to the hydrocracking of Arge commercial wax (Task 3). Additional pilot plant work was done with Mobil wax. These results are discussed in Section 5.7, Mobil Wax Upgrading (Task 6).

5.1 HYDROCRACKING PROCESS DESCRIPTION

Catalytic hydrocracking is used in the petroleum refinery industry to produce a wide variety of products including light hydrocarbon gases, naphthas, distillates and lubricating oils. This process converts the high molecular weight components in heavy petroleum distillates by a complicated sequence of reactions involving hydrogenation and carbon-carbon bond cleavage. Sulfur, nitrogen and oxygen compounds are removed at the same time, and olefins are saturated. Typical hydrocracker unit charge stocks are vacuum gas oils from petroleum fractionation.

In typical single-stage hydrocracking (Figure 5.1), charge stock is first combined with recycle gas, heated to the desired reactor temperature and processed in the reactor. The reactor effluent enters a high pressure separator, where hydrogen-rich gases are separated and recycled to the reactor inlet. Condensed liquid from the high pressure separator is sent to a flash drum where additional light gases are removed. Condensed liquid from the flash drum is, in turn, sent to fractionation where the desired products are recovered and sent to storage (14).

Two distinct single-stage hydrocracking operations are practiced in commercial petroleum refineries. In the first operation, designated "once-through," reactor temperature is adjusted to maintain the desired conversion level in a single reactor pass. The second type of operation, designated "recycle," involves the return of unconverted charge stock from the fractionator bottoms to the reactor inlet (15). In this fashion, complete conversion of charge stock to lighter products can occur over multiple reactor passes.

Catalytic hydrocracking processes typically use dual function catalysts that possess both acidic cracking and metallic hydrogenation components. The acidic cracking component is either an amorphous silica-alumina support or a crystalline zeolite material. The metallic hydrogenation component is a metal sulfide incorporating nickel, tungsten, cobalt or molybdenum finely dispersed on the support material. The relative strengths of these components influence the interactions of the various hydrocracking reactions, and affect the resulting product yield structure and product quality.

Deactivation of hydrocracking catalysts proceeds by both fouling and poisoning mechanisms. Fouling is caused by the formation of polyaromatic cokes that interfere with active catalyst sites and block catalyst pores. High molecular weight unsaturated hydrocarbons, such as aromatics and asphaltenes, have the highest coke forming tendencies. Poisoning is caused by the chemisorption of feedstock contaminants, such as nitrogen and metallic compounds, on active catalyst sites.

Catalysts deactivated by fouling can be regenerated by oxidation of the coke at elevated temperatures in a controlled oxygen environment. The effects of catalyst poisoning generally cannot be reversed.

5.2 GENERAL REVIEW OF PARAFFIN HYDROCRACKING MECHANISMS

Postulated mechanisms for catalytic hydrocracking have been extensively discussed in the literature (16, 17, 18, 19). These mechanisms are generally based on pure component work. Applying the pure component mechanisms to commercial hydrocracking operations, however, has been only partially successful, because of the complex nature of hydrocracking reactions with typical commercial charge stocks.

Pure component studies have suggested that the mechanisms of hydrocracking normal paraffins involves a carbonium ion intermediate for the cracking of carbon-carbon bonds, coupled with the chemistry of hydrogenation. The reaction path for paraffins initiates at the metallic component of the catalyst with the formation of an olefin by dehydrogenation (Figure 5.2). The olefin is then rapidly adsorbed on an acid site to form a carbonium ion that subsequently isomerizes to a more stable carbonium ion, or cracks at the beta position to form another cation and an olefin. Secondary cracking occurs as the carbonium ion continues to isomerize and crack, while the olefin is saturated at the metallic site to form a paraffin (16, 17).

Product distribution and hydrocarbon types obtained from the hydrocracking of normal paraffins vary depending on the relative strengths of the metallic and acid sites on the catalyst. Dual functional catalysts used in commercial hydrocracking operations generally have high acidity and intermediate hydrogenation activities. The reaction products from these commercial operations typically contain a higher proportion of branched species than the charge stock, indicating a tendency to form more stable tertiary carbonium ion intermediates. Since the formation of primary and secondary carbonium ions is less favorable, the yields of methane and ethane are relatively low. Hydrocracking catalysts with strong hydrogenation activity exhibit more hydrogenolysis reactions, which produce more methane and ethane, and a lower molecular branching ratio (17, 18).

Paraffin hydrocracking is the reaction of primary importance with Fischer-Tropsch waxes. This reaction is also important in the hydrocracking of typical petroleum refinery charge stocks. However, because of the complexity of the petroleum derived material, other reactions (17), outlined below, are also important.

Cycloparaffin hydrocracking typically involves paring reactions in which alkyl groups are selectively removed without breaking the ring itself (Figure 5.3). The formation of carbonium ions from the olefin intermediate during cycloparaffin hydrocracking, followed by isomerization to form the more stable carbonium ion, is consistent with the mechanism previously described for normal paraffin hydrocracking. Accordingly, a high ratio of methylcyclopentane to cyclohexane is observed in the hydrocracked product of cycloparaffins, far in excess of thermodynamic equilibrium. The primary paraffin product is isobutane.

Alkyl aromatic hydrocracking can potentially involve numerous reactions including: isomerization, dealkylation, paring, cyclization and alkyl group migration. Primary reactions include dealkylation and alkyl group transfer. Cyclization reactions may occur if the alkyl group side chain is large enough to form bi-cyclic compounds (Figure 5.4). The reaction mechanism for polyalkyl aromatics is similar to the paring reactions typical of cycloparaffins (Figure 5.5). Minimum ring breakage and methane formation are observed with high yields of isobutane. Xylene products undergo rapid alkyl transfer to form heavier aromatics.

Polycyclic aromatic hydrocracking involves extremely complex reaction mechanisms. The transfer of butyl groups formed by partial hydrogenation and ring cleavage, followed by cyclization to higher ring intermediates that subsequently crack, appears to be the primary reaction pathway (Figure 5.6).

Polycyclic aromatics with higher molecular weights have relatively low reaction rates and are, thus, potential coke precursors. Polycyclic aromatics may also undergo condensation reactions to form highly refractive polynuclear aromatics.

Thermal cracking mechanisms have been proposed that proceed through a free radical type mechanism instead of the previously discussed carbonium ion mechanism (20). Normal paraffin thermal cracking is initiated with the paraffin molecule losing a hydrogen molecule by reaction with a free hydrogen or small hydrocarbon radical (Figure 5.7). The original paraffin, thus, becomes a free radical itself, and may either isomerize to form a more stable radical, or immediately crack at the carbon-carbon bond in the beta position. Cracking at the beta position yields an olefin and another free radical, which in turn can isomerize or recrack at the beta position. Successive cracking produces methyl and ethyl radicals that convert into methane and ethane products.

The mechanisms of hydrocracking are not only dependent upon the catalyst employed and hydrocarbon types undergoing reaction, but also on the presence of contaminants in the charge stock. For example, sulfur and nitrogen compounds in the charge stock will affect the metallic hydrogenation and acidic cracking functions of the catalyst. This typically involves competition for metallic and acidic sites between the various hydrocarbon species and contaminant materials.

Product distributions obtained from hydrocracking reactions depend upon the type of reaction mechanism through which the reaction proceeds. For example, thermal cracking reactions form relatively large amounts of methane and ethane and few branched paraffins. In contrast, acidic type cracking produces relatively small amounts of methane and ethane, with mostly branched paraffins.

5.3 WAX HYDROCRACKING PILOT PLANT PROGRAM

This section details hydrocracking experiments performed by the Allied-Signal Engineered Materials Research Center. Brief descriptions of the pilot plant and feedstock are followed by analyses of process variable and catalyst performance studies.

5.3.1 Pilot Plant Flow Schemes

Two pilot plant configurations were used for the process variable studies. The once-through mode (Figure 5.8) is simpler to operate and is more suitable for surveying process conditions. The recycle configuration (Figure 5.9) is similar to the commercial single-stage flow scheme described in Section 5.1.

Prior to this study, the hydrocracking pilot plant was modified. Heat tracing was applied to any portion of the plant where the high pour point wax would tend to solidify.

5.3.2 Process Variable Studies

Several process variable studies were initiated to determine the effect of pressure, liquid hourly space velocity (LHSV), hydrogen recycle rate, and combined feed ratio (CFR) on hydrocracking operations.

The following key operating parameters were measured to evaluate catalyst performance:

- Catalyst activity
- Catalyst stability
- Product yields
- Product quality

Catalyst activity is the average reactor temperature required at the beginning of an operating cycle to achieve a specific feedstock conversion with a given set of operating conditions. Catalyst stability is the rate at which reactor temperatures must be increased to maintain a specific feedstock conversion level over the life of the catalyst.

5.3.2.1 Process Variable Study -- Pressure

The effect of pressure on catalyst activity, stability and product distribution was studied. The operation was once-through with the reactor temperature adjusted to maintain 100% conversion of Arge wax to 700°F (minus) product.

Lowering the pressure of the wax hydrocracking operations significantly lowered initial catalyst temperature requirements (improved catalyst activity), but decreased the catalyst temperature stability (Table 5.1 and Figure 5.10). Lower pressure increases the rate of the hydrocracking initiation step -- the formation of olefins -- but, at the same time, lower pressure favors formation of coke precursors.

The UOP pilot plant showed that as reactor pressure was increased, the overall distillate yield (300-700°F) first increased, passed through a maximum and subsequently decreased (Table 5.1 and Figure 5.11). As reactor pressure increases, the higher pressure inhibits secondary cracking and lighter product formation. But, on further pressure increase, the effect of higher catalyst temperature dominates over the suppression of secondary cracking. At higher temperatures, more light ends are produced.

5.3.2.2 Process Variable Study -- LHSV

Liquid hourly space velocity (LHSV) measures the total liquid throughput or volumetric rate per unit volume of catalyst. Adjusting LHSV affects both the temperature requirements and product distribution. When feed throughput was increased by a factor of three during once-through operation, the initial catalyst temperature was increased by 53°F in order to maintain 100% conversion (Table 5.2 and Figure 5.12). The higher reactor temperature shifted the product slate to lighter products.

5.3.2.3 Process Variable Study -- Hydrogen Recycle Rate

For a given fresh feed rate to the hydrocracker, the hydrogen recycle rate is a function of the recycle gas compressor output. The hydrogen recycle rate is expressed in terms of standard cubic feet of pure hydrogen per barrel of fresh feed (SCFB).

A decrease in hydrogen recycle rate causes a shift to lighter products (Table 5.3 and Figure 5.13). At the lower recycle rate, C_5/C_6 and gasoline yields increase at the expense of diesel fuel production.

5.3.2.4 Process Variable Study -- CFR

When a single-stage hydrocracker operates in the recycle mode, the unconverted feedstock is recycled from the fractionator bottom to the reactor inlet for conversion in multiple cycles. Combined feed ratio (CFR) provides a measure of feedstock conversion per reactor pass, and is defined by the equation:

$$\text{CFR} = \frac{\text{Feedstock Rate} + \text{Recycle Liquid Rate}}{\text{Feedstock Rate}}$$

As shown in Figure 5.14, recycle operation shifted the product distribution to higher carbon number ranges. The biggest yield shift (Table 5.4, Figure 5.15) was seen when operation was changed from once-through (CFR = 1.0) to recycle (CFR = 1.5).

Diesel fuel material produced by hydrocracking Arge wax displayed excellent product quality. This material could be blended with inferior product quality materials, such as light cycle oil, to increase the diesel fuel yield of the overall upgrading complex.

5.3.3 Catalyst Comparison Study

Two catalysts, A and B, were compared in this study. Process conditions are summarized in Table 5.5. Catalyst B is significantly more active than Catalyst A at these operating conditions (Figure 5.16). This superior activity could be taken advantage of in commercial operations through a variety of methods. For example, it may be advantageous to operate at higher LHSV, lower pressure, lower recycle gas rate, or a combination of the above. Trade-offs between these options would have to be carefully considered with respect to capital and operating costs and product yields and quality.

In commercial refinery operations, Catalyst B would be expected to display significantly better stability than Catalyst A. Because catalyst deactivation rates were extremely low when processing Arge wax in this study, no stability comparison was possible.

The distillate yields of both catalysts at different LHSV's are presented in Figure 5.17. As previously shown, the distillate yield with Catalyst A significantly decreases at higher LHSV's. With Catalyst B, the distillate yield hardly changed at higher LHSV's; in fact, the distillate yield of Catalyst A is higher than that of Catalyst B at 1.0 hr^{-1} LHSV while at 3.0 hr^{-1} LHSV the reverse is observed. This result again suggests the major role catalyst temperature plays in the hydrocracking of Arge wax. Although at lower LHSV's Catalyst A displays higher distillate yields, this advantage cannot be maintained over the more active Catalyst B at higher LHSV's, because of the relatively higher temperatures required with Catalyst A to maintain conversion.

Table 5.5 summarizes the catalyst activities and stabilities and distillate product yields and properties for once-through operations with the two catalysts.

5.4 PRODUCT YIELDS

In this study, the various product yield categories are defined as follows:

1. Light gases, C_1-C_4
2. Light naphtha, C_5-C_6
3. Heavy naphtha, C_7-300°F
4. Jet fuel, 300-550°F
5. Diesel fuel, 550-700°F

A vacuum column endpoint of 700°F was chosen for pilot plant testing. The sum of the jet and diesel fraction, 300-700°F, is called distillate.

Product yield distributions were measured by three methods:

1. Gas chromatography boiling range (GCBR)
2. Oldershaw fractionation
3. Gel permeation chromatography (GPC)

5.4.1 Gas Chromatography Boiling Range (GCBR) Yields

The GCBR analysis is the quickest and least expensive means of determining product yields. Generally, GCBR skews the yields to show more light liquids, such as gasoline, than would be experienced commercially. This shift is partially caused by the chromatograph's ability to fully resolve components of a mixture. The chromatograph is equivalent to thousands of theoretical plates. Distillation vessels, commercial or laboratory, are unable to achieve this degree of resolution.

Tabular summaries of each Arge wax hydrocracking run include process conditions (Table 5.6), liquid product gravities and distillations (Table 5.7) and GCBR yields (Table 5.8).

5.4.2 Oldershaw Yields

Oldershaw distillations are done in a laboratory column at high reflux. After the batch distillation is performed, a smaller amount of lighter material is added back to the distillate until the flash point specification of the distillate is reached. Oldershaw yields provide the best indication of commercial yields.

Liquid material from a representative test period was selected from six Arge wax runs. Oldershaw fractionation results are summarized (Table 5.9) along with liquid product properties for the individual Oldershaw fractions.

Run 910 at 1.5 CFR achieved the highest Oldershaw distillate yields. The 300-700°F material was 86.8 wt-% of fresh feed.

5.4.3 Gel Permeation Chromatography (GPC) Yields

Gel permeation chromatography allows yields to be shown on the basis of carbon number. This technique was mainly used for yield models discussed in Appendix B.

5.5 COMPARISON OF ARGE WAX AND PETROLEUM VGO HYDROCRACKING

Arge wax is compared in Table 5.10 to a typical Arabian petroleum vacuum gas oil. The Arge wax is mostly straight-chain paraffins with minimum concentration of nitrogen and metal compounds. It is essentially free of aromatics and asphaltenes.

Table 5.11 compares results for hydrocracking Fischer-Tropsch wax versus the Arabian VGO. Twice the pressure, lower LHSV and similar gas rate are required for processing the VGO with the same catalyst, flow scheme, CFR and conversion. The wax is so easy to process that the catalyst was 50°F more active and no catalyst deactivation was measured. The product yields are similar but petroleum feedstock yielded 2 wt-% more distillate. Based upon the once-through results, the wax could give higher yields of distillate at lower pressures. The comparison shows that one-third the hydrogen required to process petroleum feed was required for the wax. Hydrogen consumption is an important operating cost.

5.6 ARGE WAX HYDROCRACKING CONCLUSIONS

The DOE sponsored Arge wax hydrocracking program conclusively proved that Fischer-Tropsch wax hydrocracking is a viable process for producing distillate for diesel fuel applications. The study gave many new and interesting results. Some of these were:

1. <u>The effect of pressure on initial catalyst activity</u>; as pressure increases initial catalyst activity decreases, because dehydrogenation is the rate limiting step.

2. <u>The effect of LHSV on distillate product yield</u>; as LHSV increases distillate product yield decreased for amorphous catalyst A. For Catalyst B, LHSV had no effect on product yield.

For maximum distillate yield with the Arge Fischer-Tropsch wax feedstock the following results were found:

1. Pressures lower than 1000 psig may yield more distillate (500-1000 psig).

2. Higher gas rates yield more distillate.

3. Lower LHSV for Catalyst A may yield more distillate. For Catalyst B, increasing the LHSV had no effect on distillate yield. At higher throughput, Catalyst B would be the choice over Catalyst A for producing maximum distillate.

4. A single-stage recycle flow scheme gives higher distillate yields than once-through operations. Higher CFR yields more distillate.

Finally, high catalyst activities and no catalyst deactivation at low pressures with low hydrogen consumption makes Arge wax hydrocracking appear to be a very attractive process.

5.7 MOBIL WAX HYDROCRACKING (TASK 6.0)

The objective of the hydrocracking pilot plant run was to demonstrate the processibility of the Mobil wax and compare the processibility to that of the Arge Fischer-Tropsch wax. The operating conditions are listed in Table 5.12. The conditions are the same as the optimum cases in the once-through and recycle liquid flow schemes for the Arge F-T wax runs.

The Mobil wax contains 133 ppm of iron from the catalyst in the Fischer-Tropsch slurry reactor. Hydrocracking of the Mobil wax was done without iron removal. Results are shown in Table 5.13 and compared to the Arge F-T wax hydrocracking runs. These results indicate no significant differences in catalyst activity between the two feeds. Also, over the two-week run period, the higher iron content of Mobil wax did not cause any catalyst stability problems. But, Mobil wax produced greater amounts of lighter C_6- material and consumed more hydrogen during the hydrocracking operation. This was expected due to the higher concentration of olefins, oxygenates and branched molecules in the Mobil wax.

Oldershaw fractionation results are summarized (Table 5.14) along with liquid product properties for the individual Oldershaw fractions. A comparison of Arge and Mobil wax Oldershaw yields is consistent with that based on gas chromatography. Mobil wax produced more light ends and less distillate than Arge wax. Distillate product quality was similar for the two waxes.

5.7.1 Iron Removal

The 133 ppm iron content of the Mobil wax did not cause any catalyst stability problems over the two-week run period. Although the iron did not induce any measurable catalyst deactivation, iron was accumulating in the reactor section of the pilot plant. A material balance of the feedstock iron showed that at least 50% of the iron remained in the reactor. By the end of the run, the differential pressure across the reactor was increasing, possibly as a result of iron accumulation. Also, it was more difficult to unload the reactor because the quartz preheater section was stuck together in solid chunks. Metal analysis by atomic adsorption (AAS) revealed higher than normal concentration of iron on the preheater and catalyst. No iron was observed in the vacuum fractionator overhead product but small amounts were found in the fractionation bottoms.

Attempts to remove iron from Mobil wax prior to pilot plant processing were not successful. Bench-scale filtration techniques did not work because of the high wax viscosity coupled with the small size of the iron particles. Several attempts were made to convert iron into iron carbonyl by reacting iron with carbon monoxide. The experiments were done in both shaking and continuous autoclaves at pressures ranging between 165-495 psig and temperatures ranging between 480-570°F. The iron concentrations of the Mobil wax did not decrease in any of the experiments.

Table 5.1

Pilot Plant Data Summary

Once-Through Process Variable Study: Effect of Pressure

Feedstock: Commercial Arge Wax

Run	901	903	902
Pressure, psig	500	750	1,000
LHSV, hr^{-1}	1.0	1.0	1.0
H_2 Recycle, SCFB	10,000	10,000	10,000
Catalyst Activity, °F	B-16	B-7	Base (B)
Catalyst Deactivation, °F/BPP	35	19	Not Measurable
GC Product Yields, wt-% (Fresh Feed Basis)			
C_1-C_4	5.2	3.6	3.9
C_5-C_6	10.3	7.3	8.3
C_7-300°F	16.1	13.1	14.7
300-550°F	35.5	39.8	43.2
550-700°F	32.8	37.2	31.1
Chemical H_2 Consumption, SCFB	456	531	581
Distillate Product (300-700°F), wt-%	68.3	77.0	74.3
API	--	--	50.0
Cetane No.	--	--	70
Flash Point, °F	--	--	135
Cold Filter Plugging, °F	--	--	0
Pour Point, °F	--	--	-35
Cloud Point, °F	--	--	9
Viscosity at 100°F, cSt	--	--	2.64

Table 5.2

Pilot Plant Data Summary

Once-Through Process Variable Study: Effect of LHSV

Feedstock: Commercial Arge Wax

Run	902	905
Pressure, psig	1,000	1,000
LHSV, hr^{-1}	1.0	3.0
H_2 Recycle, SCFB	10,000	10,000
Catalyst Activity, °F	Base (B)	B + 53
Catalyst Deactivation, °F/BPP	0	0
GC Product Yields, wt-% (Fresh Feed Basis)		
C_1-C_4	3.9	7.9
C_5-C_6	8.2	13.2
C_7-300°F	14.7	16.5
300-550°F	43.2	37.3
550-700°F	31.1	27.4
Chemical H_2 Consumption, SCFB	581	677
Distillate Product (300-700°F), wt-%	74.3	64.7
API	50.0	50.3
Cetane No.	70	70
Flash Point, °F	135	135
Cold Filter Plugging, °F	0	30
Pour Point, °F	-35	5
Cloud Point, °F	9	30
Viscosity at 100°F, cSt	2.64	2.58

Table 5.3

Pilot Plant Data Summary

Once-Through Process Variable Study: Effect of Hydrogen Recycle Rate

Feedstock: Commercial Arge Wax

Run	905	906
Pressure, psig	1,000	1,000
LHSV, hr^{-1}	3.0	3.0
H_2 Recycle, SCFB	10,000	5,600
Catalyst Activity, SOR, °F	Base (B)	B + 4
Catalyst Deactivation, °F/BPP	--- Not Measurable ---	
Conversion to 700°F Minus, %	100	100
GC Product Yields, wt-% (Fresh Feed Basis)		
C_1/C_2	0.1	0.1
C_3/C_4	7.9	8.1
C_5/C_6	13.2	15.8
C_7-300°F	16.5	18.6
150-550°F	37.3	35.3
290-700°F	27.4	23.3
Chemical H_2 Consumption, SCFB	677	748

Table 5.4

Pilot Plant Data Summary

Combined Feed Rate Process Variable Study

Feedstock: Commercial Arge Wax

Run	902	910	911
Pressure, psig	1,000	1,000	1,000
LHSV, hr^{-1}	1.0	1.0	1.0
H_2 Recycle, SCFB	10,000	10,000	10,000
CFR	1.0	1.5	2.0
Catalyst Activity, °F	Base (B)	Base (B)	B + 4
Catalyst Deactivation, °F/BPP	<------Not	Measurable	------>
GC Product Yields, wt-% (Fresh Feed Basis)			
C_1-C_4	3.9	2.7	3.3
C_5-C_6	8.2	5.4	6.2
C_7-300°F	14.7	10.0	10.5
300-550°F	43.2	34.0	32.6
550-700°F	31.1	48.1	48.3
Chemical H_2 Consumption, SCFB	581	518	524
Distillate Product (300-700°F), wt-%	74.3	82.1	80.9
API	50.0	48.4	48.6
Cetane No.	70	74	73
Flash Point, °F	135	135	135
Cold Filter Plugging, °F	0	32	28
Pour Point, °F	-35	10	-15
Cloud Point, °F	9	32	32
Viscosity at 100°F, cSt	2.64	3.58	3.48

Table 5.5

Pilot Plant Data Summary
Catalyst Comparison Study

Feedstock: Commercial Arge Wax

Run	902	905	907	909
Catalyst	A	A	B	B
Pressure, psig	1,000	1,000	1,000	1,000
LHSV, hr^{-1}	1.0	3.0	1.0	3.0
Gas Recycle, SCFB	10,000	10,000	10,000	10,000
Catalyst Activity, °F	Base (B)	B + 53	B - 67	B - 25
Catalyst Deactivation, °F/BPP	Not Measurable			
GC Product Yields, wt-% (Fresh Feed Basis)				
C_1-C_4	3.9	7.9	3.5	3.9
C_5/C_6	8.2	13.2	9.9	9.4
C_7-300°F	14.7	16.5	17.3	17.3
300-550°F	43.2	37.3	42.5	36.8
550-700°F	31.1	27.4	27.9	34.0
Chemical H_2 Consumption, SCFB	581	677	673	555
Distillate Product (300-700°F), wt-%	74.3	64.7	70.4	70.8
API	50.0	50.3	51.4	51.0
Cetane No.	70	70	73	75
Flash Point, °F	135	135	135	135
Cold Filter Plugging, °F	0	30	-43	45
Pour Point, °F	-35	5	10	19
Cloud Point, °F	9	30	34	48
Viscosity at 100°F, cSt	2.64	2.58	2.41	2.59

Table 5.6

Arge Wax Hydrocracking Pilot Plant Program

Run	901	902	903	904	905	906	907	909	910	911
Mode*	OT	OT	OT	OT	OT	OT	OT	OT	R	R
Catalyst	A	A	A	A	A	A	B	B	A	A
Pressure, psig	507 (5)	1000 (3)	751 (6)	1000 (6)	998 (5)	999 (2)	1000 (2)	1000 (2)	1001 (3)	1000 (1)
LHSV, hr^{-1}	0.99 (0.05)	1.00 (0.01)	1.00 (0.02)	1.99 (0.02)	2.99 (0.02)	2.98 (0.04)	1.00 (0.01)	2.96 (0.04)	1.01 (0.02)	1.01 (0.02)
Recycle H_2, SCFB	9440 (500)	9456 (173)	10038 (253)	10864 (1636)	10039 (295)	5622 (318)	10684 (155)	10863 (909)	10823 (674)	10713 (640)
CFR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.51	2.00
H_2 Consumption, SCFB	456 (43)	581 (43)	531 (48)	581 (63)	677 (52)	748 (106)	673 (44)	555 (63)	518 (90)	524 (670)
Conversion, Wt-%	96.2 (4.1)	100.7 (2.2)	100.5 (1.8)	100.0 (0.9)	100.0 (0.4)	99.7 (0.8)	98.9 (3.5)	98.7 (3.4)	99.4 (4.5)	98.3 (5.3)
Weight Recovery, Wt-%	97.7 (7.3)	97.9 (3.3)	97.8 (2.2)	100.0 (3.5)	98.6 (3.0)	100.8 (1.8)	98.4 (4.4)	96.8 (3.5)	99.0 (6.5)	98.3 (4.7)

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* OT = Once-Through
R = Recycle

( ) = 1 standard deviation for estimate of mean value

Table 5.7

Arge Wax Hydrocracking Liquid Product Gravity and Distillation Summary

Run	901	902	903	904	905	906	907	909	910	911
Liquid Product API	55.8 (2.2)	56.0 (1.5)	55.5 (1.7)	57.1 (1.7)	63.2 (2.8)	63.3 (2.0)	59.2 (0.5)	59.2 (2.7)	53.7 (1.1)	53.7 (1.1)
D-86 90% Pt	692 (7)	662 (17)	679 (9)	668 (10)	672 (21)	673 (16)	648 (10)	702 (36)	684 (14)	683 (9)
D-86 EP	702 (5)	687 (18)	703 (7)	695 (7)	690 (9)	692 (10)	688 (12)	708 (36)	697 (10)	694 (12)

( ) = 1 standard deviation for estimate of mean value

Table 5.8

Arge Wax Hydrocracking Gas Chromatography Boiling Range (GCBR) Yields*

Run	901	902	903	904	905	906	907	909	910	911
C_1	0.05 (0.01)	0.05 (0.01)	0.05 (0.01)	0.05 (0.01)	0.06 (0.01)	0.05 (0.01)	0.05 (0.01)	0.05 (0.01)	0.06 (0.01)	0.05 (0.01)
C_2	0.07 (0.02)	0.07 (0.01)	0.08 (0.01)	0.08 (0.02)	0.07 (0.01)	0.8 (0.02)	0.03 (0.01)	0.07 (0.01)	0.07 (0.01)	0.06 (0.01)
C_3	0.50 (0.04)	0.45 (0.02)	0.48 (0.03)	0.39 (0.04)	0.55 (0.08)	0.72 (0.21)	0.36 (0.03)	0.43 (0.07)	0.42 (0.05)	0.43 (0.06)
C_4	4.53 (0.24)	3.46 (0.28)	2.98 (0.62)	4.05 (0.19)	7.28 (2.42)	7.44 (0.80)	3.06 (0.22)	3.32 (0.43)	2.18 (0.38)	2.73 (0.25)
C_5	4.81 (0.55)	3.74 (0.30)	3.43 (0.58)	4.44 (0.77)	6.59 (0.16)	7.86 (0.23)	4.56 (0.40)	4.24 (0.25)	2.42 (0.53)	2.98 (0.28)
C_6	5.52 (0.92)	4.41 (0.27)	3.87 (0.67)	4.74 (1.03)	6.57 (1.24)	7.95 (0.47)	5.30 (0.57)	5.17 (0.45)	2.93 (0.55)	3.23 (0.32)
C_7-300	16.10 (0.38)	14.66 (1.26)	13.05 (1.82)	13.91 (1.84)	16.50 (3.64)	18.59 (1.50)	17.33 (1.02)	17.33 (1.97)	10.03 (0.91)	10.47 (0.93)
300-550	35.50 (0.71)	43.23 (0.95)	39.81 (1.75)	40.50 (0.59)	37.31 (1.78)	35.33 (1.06)	42.50 (2.20)	36.79 (1.63)	34.04 (2.17)	32.55 (0.89)
550-EP	32.82 (2.52)	31.09 (1.36)	37.16 (3.57)	33.08 (4.28)	27.41 (2.50)	23.25 (0.65)	27.88 (0.96)	34.03 (3.45)	48.11 (3.91)	48.27 (1.85)
C_7 plus	84.42	88.98	90.02	87.49	81.22	77.17	87.71	88.15	92.18	91.29

---

* GCBR Yields will not sum to 100 due to hydrogen consumption and are reported on Fresh Feed (FF) basis.

( ) = 1 standard deviation for estimate of mean value

Table 5.9

Arge Wax Hydrocracking
Oldershaw Yields and Product Qualities
(P = 1000 psig, Recycle H_2 = 10,000 SCFM)

Run	902	905	907	909	910	911
Catalyst	A	A	B	B	A	A
LHSV, hr^{-1}	1.0	2.99	1.0	2.96	1.01	1.01
CFR	1.0	1.0	1.0	1.0	1.51	2.00
Oldershaw Fraction, Wt-%						
C_7-300°F	9.2	14.6	13.5	16.1	5.4	5.7
300-700°F	79.7	66.6	74.2	72.1	86.8	85.6
Product Quality, C_7-300°F						
API	69.9	68.5	69.6	69.1	69.9	70.5
Specific Gravity	0.7026	0.7075	0.7036	0.7054	0.7026	0.7005
Product Quality, 300-700°F						
API	50.0	50.3	51.4	51.0	48.4	48.6
Specific Gravity	0.7796	0.7783	0.7736	0.7753	0.7865	0.7857
Cetane No.	69.5	69.9	72.6	74.8	74.0	73.3
Cold Filter Plugging, °F	0	30	-43	45	32	28
Flash Point, °F	135	135	135	135	135	135
Pour Point, °F	-35	5	10	19	10	-15
Cloud Point, °F	9	30	34	48	32	32
Viscosity @ 100°F	2.643	2.583	2.414	2.586	3.577	3.475

Table 5.10

Comparison Between Arge Wax and Petroleum VGO

	Wax	Arabian VGO
API	22.3	20.3
Specific Gravity	0.9200	0.9321
Boiling Range, IBP, °F	597	655
Boiling Range, EP, °F	1036	1103
Sulfur, ppm	80	15200
Nitrogen, ppm	16	1720
Carbon, Wt-%	85.2	85.6
Hydrogen, Wt-%	14.7	12.0
Oxygen, Wt-%	0.1	0.14
Aniline Point, °F	293	185
Pour Point, °F	205	105
Viscosity, cSt	7.59 @ 250°F	8.16 @ 210°F
Conradson Carbon, Wt-%	0.01	0.68
Emission Metals, ppm	5.9	1.3
Aromatics, Wt-%	0	51.4

Table 5.11

Processing Conditions for Producing Distillate

Feedstock	Arge Wax	Arabian VGO
Catalyst	A	A
CFR	1.5	1.5
Total Conversion, Wt-%	100	100
Fractionation EP, °F	700	700
Pressure, psig	1,000	2,250
LHSV, hr^{-1}	1.00	0.84
Recycle H_2 Rate, SCFB	10,000	12,100
Initial Activity, °F	Base	Base + 54
Deactivation Rate, °F/BPP	None	12
GC Product Yield, Wt-% (FF)		
C_1-C_4	2.7	3.1
C_5/C_6	5.4	3.9
C_7-300°F	10.0	8.0
300-500°F	34.0	36.7
550-700°C	48.1	48.5
Chemical H_2 Consumption, SCFB	518	1660
300-550°F		
API	54.2	41.7
Aromatics, Vol-%	0	16.7
Smoke Point, mm	>50	20.7
Flash Point, °F	116	102
Freeze Point, °F	-45	
550-700°F		
API	44.9	37.1
Cetane No.	>74.3	65
Flash Point, °F	325	325
Pour Point, °F	19.4	

Table 5.12

Mobil Wax Hydrocracking: Operating Conditions

	Once-Through	Recycle
Pressure, psig	1,000	1,000
LHSV, hr^{-1}	1.00	1.00
CFR	1.00	1.50
Recycle H_2 Rate, SCFB	10,000	10,000
Conversion, wt-%	100	100
Fractionation EP, °F	700	700
H_2 Purity, mole-%	>90	>90
Reactor Delta T, °F	50	50

Catalyst was presulfided using laboratory plant operated at 775°F for 3 hours using a 10% H_2S/90% H_2 blend at 1.5 CFH gas rate.

Table 5.13

Fischer-Tropsch Wax Hydrocracking

Results

Feedstock	Arge		Mobil	
CFR	1.0	1.5	1.0	1.5
Average Reactor Temp., °F	Base	Base	Base -4	Base -7
Average Conversion, Wt-%	100.7	99.4	101.1	101.5
GC Product Yields, Wt-% FF				
C_1-C_4	4.0	2.7	5.6	5.1
C_5/C_6	8.2	5.4	11.5	10.7
C_7-300°F	14.7	10.0	15.5	14.4
300-550°F	43.2	34.0	40.8	31.5
550-700°F	31.1	48.1	27.5	39.1
300-700°F	74.3	82.1	68.3	70.6
Chem. H_2, SCFB	581	518	836	822

Table 5.14

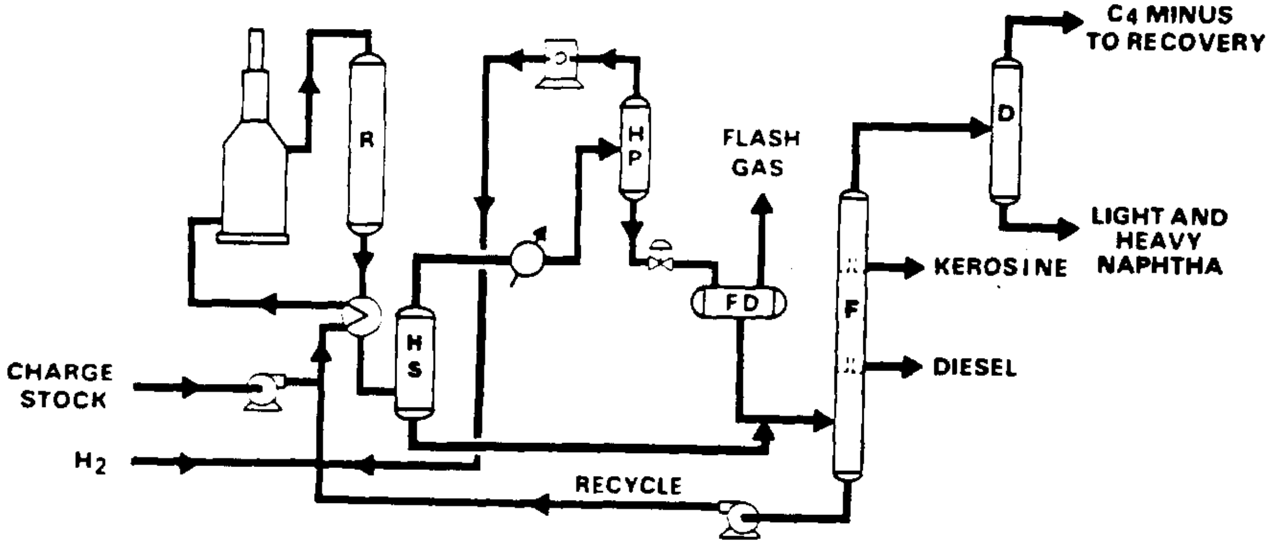
Fischer-Tropsch Wax Hydrocracking
Oldershaw Yields and Product Qualities
(P = 1000 psig, Recycle H_2 = 10,000 SCFM, LHSV = 1.0 hr^{-1})

Feedstock	Arge Wax		Mobil Wax	
Catalyst	A	A	A	A
CFR	1.0	1.5	1.0	1.5
Oldershaw Fraction, Wt-%				
C_7-300°F	9.2	5.4	12.4	10.4
300-700°F	79.7	86.8	71.4	74.6
Product Quality, C_7-300°F				
API	69.5	69.9	69.0	68.8
Specific Gravity	0.7026	0.7026	0.7058	0.7065
Product Quality, 300-700°F				
API	50.0	48.4	50.0	48.4
Specific Gravity	0.7796	0.7865	0.7795	0.7867
Cetane No.	69.5	74.0	66.7	72.2
Cold Filter Plugging, °F	0	32	N/A	N/A
Flash Point, °F	135	135	136	144
Pour Point, °F	-35	10	-44	7
Cloud Point, °F	9	32	14	39
Viscosity @ 100°F	2.643	3.577	2.663	3.559
Freeze Point, °F	N/A	N/A	22	42

N/A: Not Available

FIGURE 5.1

TYPICAL FLOW DIAGRAM OF SINGLE STAGE HYDROCRACKER



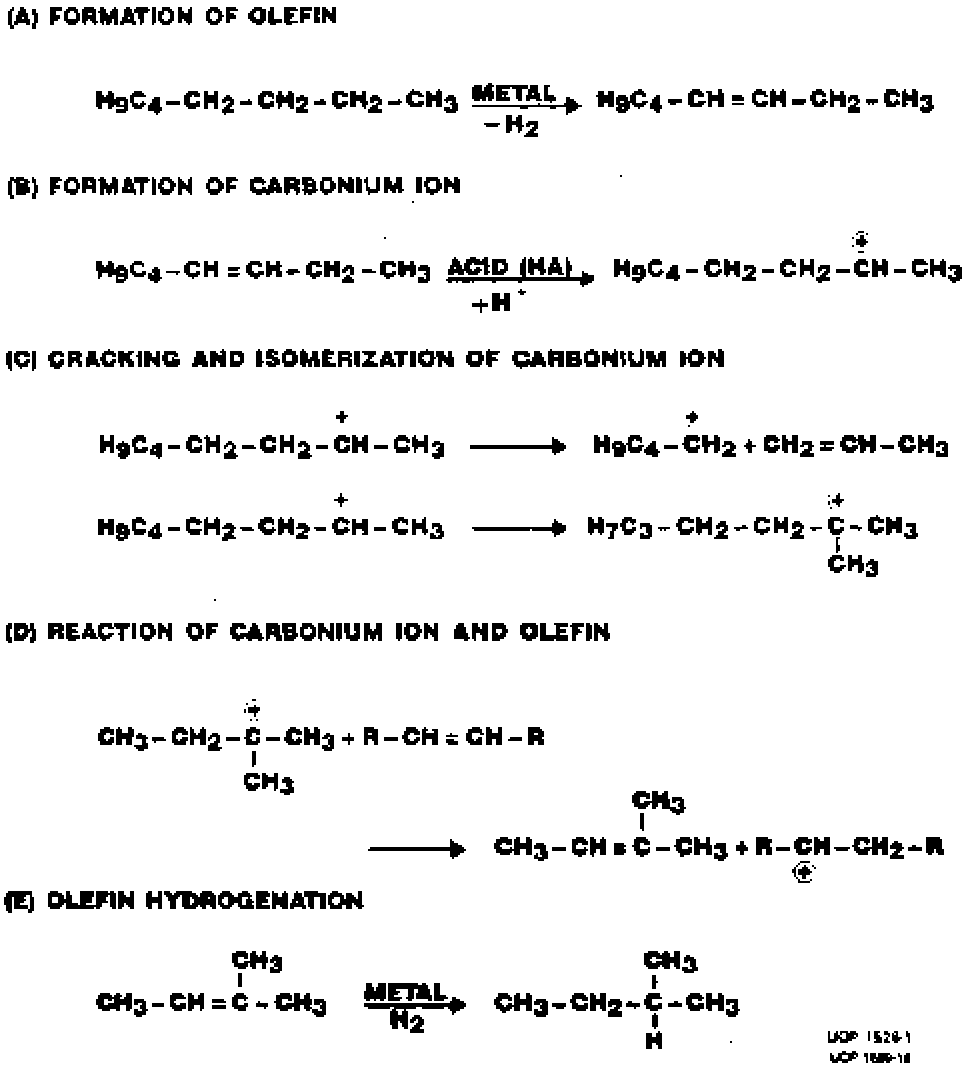
LEGEND

R = REACTOR
HP = HIGH PRESSURE SEPARATOR
HS = HOT SEPARATOR
FD = FLASH DRUM
D = DEBUTANIZER
F = FRACTIONATOR

UOP 812-1
UOP 1589-17

FIGURE 5.2

POSTULATED CRACKING MECHANISM FOR *n*–PARAFFIN



(A) FORMATION OF OLEFIN

$$H_9C_4-CH_2-CH_2-CH_2-CH_3 \xrightarrow[-H_2]{METAL} H_9C_4-CH=CH-CH_2-CH_3$$

(B) FORMATION OF CARBONIUM ION

$$H_9C_4-CH=CH-CH_2-CH_3 \xrightarrow[+H^+]{ACID\ (HA)} H_9C_4-CH_2-CH_2-\overset{\oplus}{C}H-CH_3$$

(C) CRACKING AND ISOMERIZATION OF CARBONIUM ION

$$H_9C_4-CH_2-CH_2-\overset{+}{C}H-CH_3 \longrightarrow H_9C_4-\overset{+}{C}H_2 + CH_2=CH-CH_3$$

$$H_9C_4-CH_2-CH_2-\overset{+}{C}H-CH_3 \longrightarrow H_7C_3-CH_2-CH_2-\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}-CH_3$$

(D) REACTION OF CARBONIUM ION AND OLEFIN

$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}-CH_3 + R-CH=CH-R \longrightarrow CH_3-CH=\overset{\overset{CH_3}{|}}{C}-CH_3 + R-\underset{\oplus}{C}H-CH_2-R$$

(E) OLEFIN HYDROGENATION

$$CH_3-CH=\overset{\overset{CH_3}{|}}{C}-CH_3 \xrightarrow[H_2]{METAL} CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

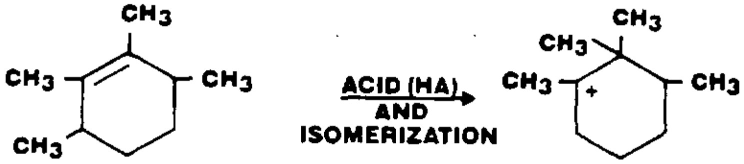
UOP 1526-1
UOP [illegible]

FIGURE 5.3

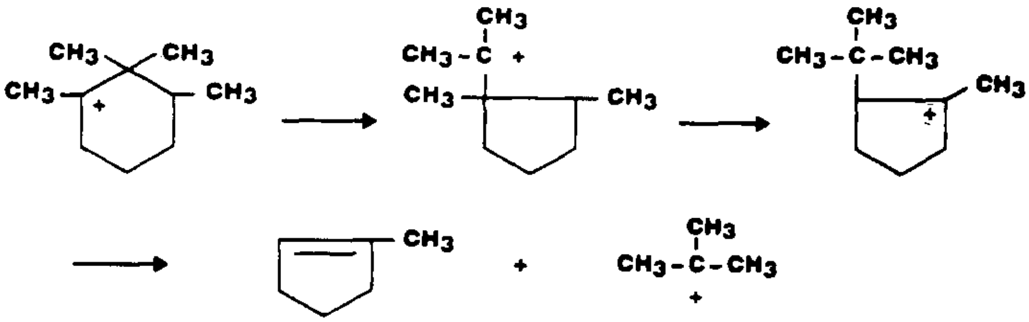
POSTULATED CRACKING MECHANISM FOR CYCLOPARAFFINS

(A) OLEFIN FORMATION

(B) CARBONIUM ION FORMATION

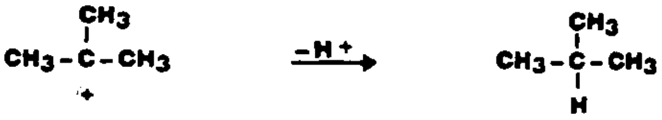


(C) ISOMERIZATION AND CRACKING



(D) HYDROGENATION

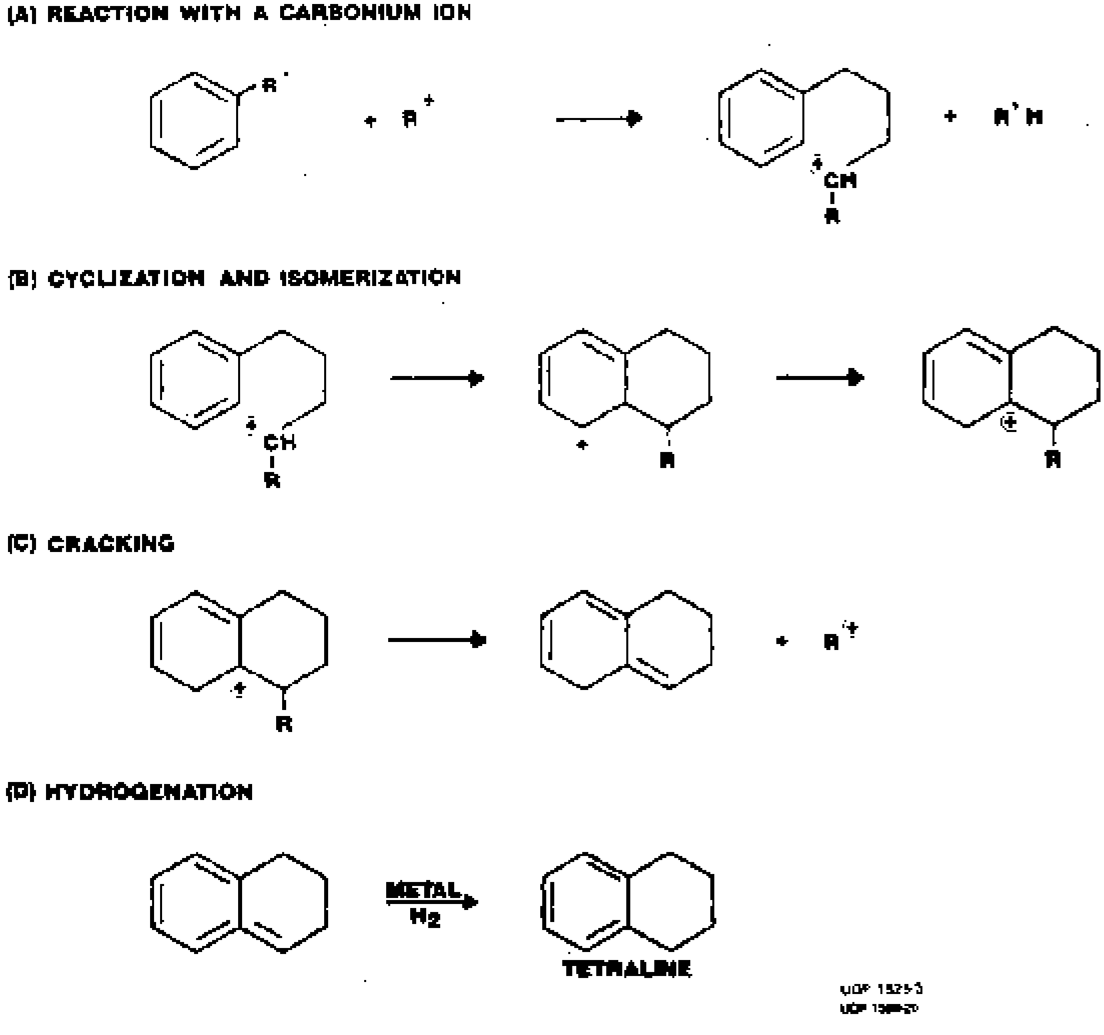
(E) HYDRIDE ION TRANSFER



UOP 1526 2
UOP 1589-19

FIGURE 5.4

POSTULATED CRACKING MECHANISM FOR ALKYL AROMATICS

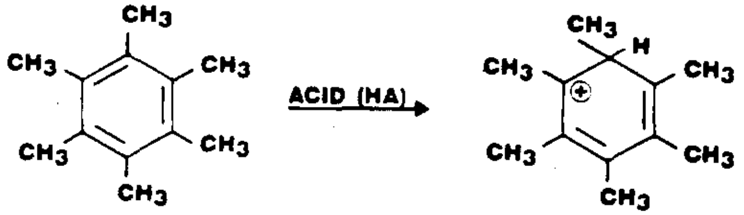


UOP 1525-3
UOP 1599-20

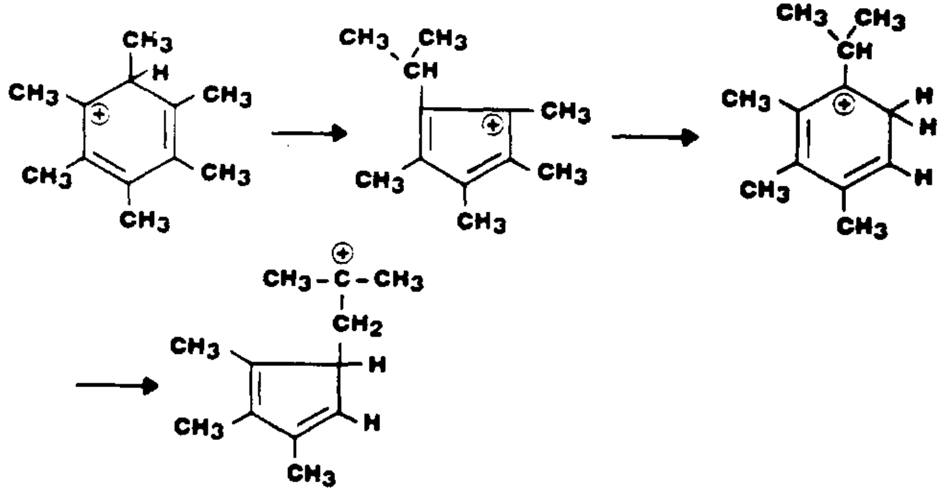
FIGURE 5.5

POSTULATED CRACKING MECHANISM FOR POLYALKYL AROMATICS

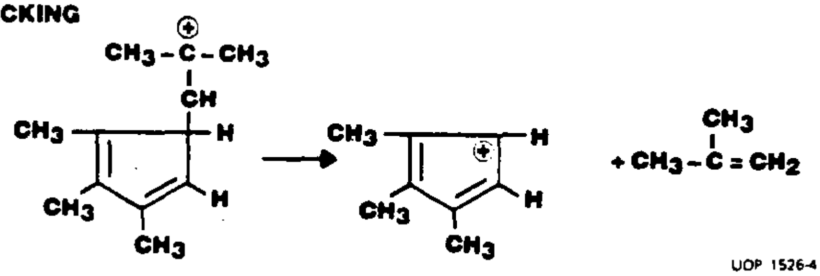
(A) CARBONIUM ION FORMATION



(B) ISOMERIZATION AND SIDE CHAIN GROWTH



(C) CRACKING



UOP 1526-4
UOP 1589-21

FIGURE 5.5
CONTINUED

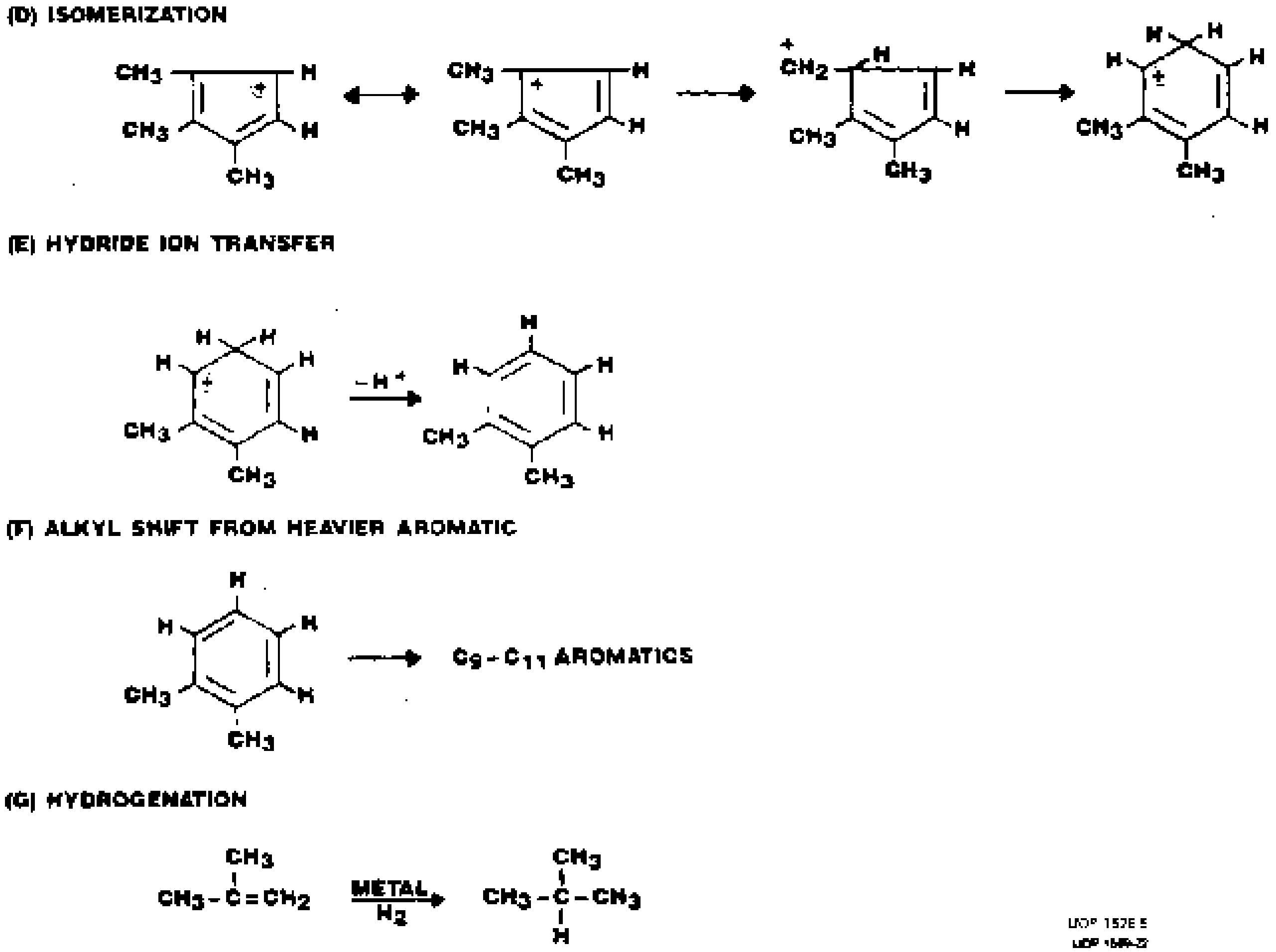
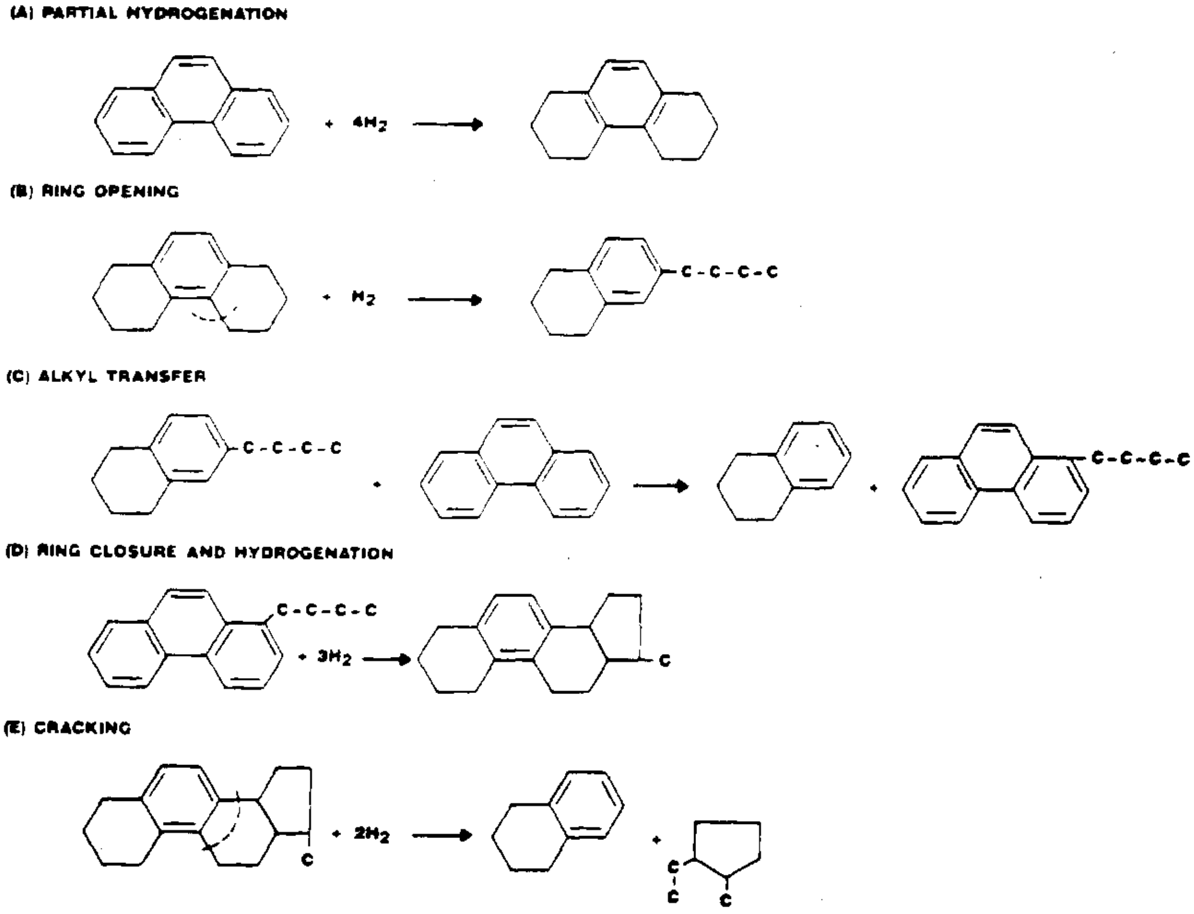


FIGURE 5.6

POSTULATED CRACKING MECHANISM FOR POLYNUCLEAR AROMATICS



UOP 1526-C
UOP 1589-23

FIGURE 5.7

POSTULATED THERMAL CRACKING MECHANISM FOR PARAFFINS

(A) FREE RADICAL FORMATION

$$R_1-CH_2-CH_2-CH_2-CH_2-R_2 \longrightarrow R_1-CH_2-CH_2-CH_2\cdot + \cdot CH_2-R_2$$

(B) CRACKING

$$R_1-CH_2-CH_2-CH_2\cdot \longrightarrow R_1-CH_2\cdot + CH_2=CH_2$$

$$R_1-CH_2\cdot \longrightarrow CH_2=CH_2 + \cdot CH_3$$

(C) PROPAGATION OF FREE RADICAL FORMATION

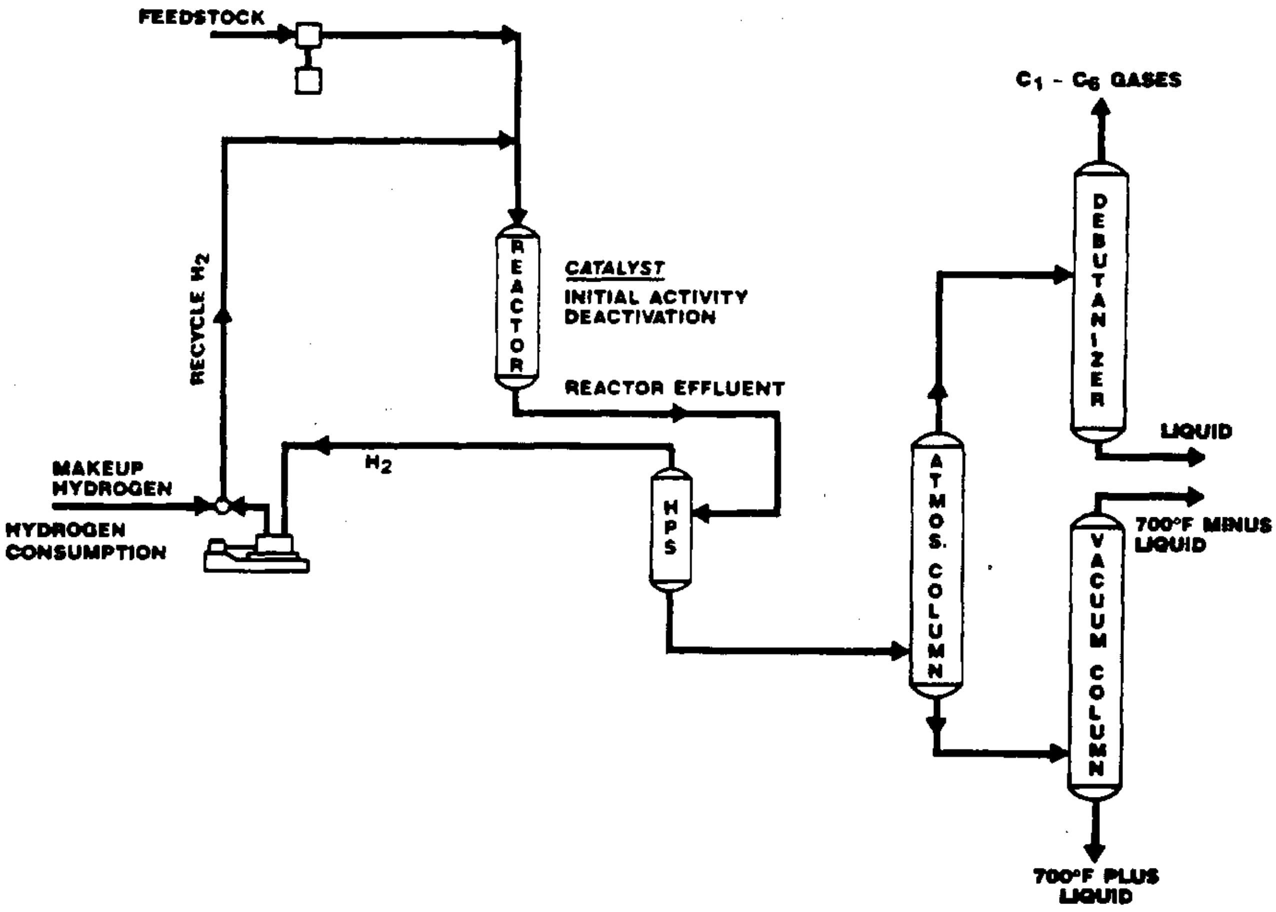
$$\cdot CH_3 + R-CH_2-CH_2-CH_3 \longrightarrow CH_4 + R-CH_2-\underset{\bullet}{C}H-CH_3$$

(D) PROPAGATION OF REACTIONS IN STEP (B) AND (C)

UOP 1526-6
UOP 1569-24

FIGURE 5.8

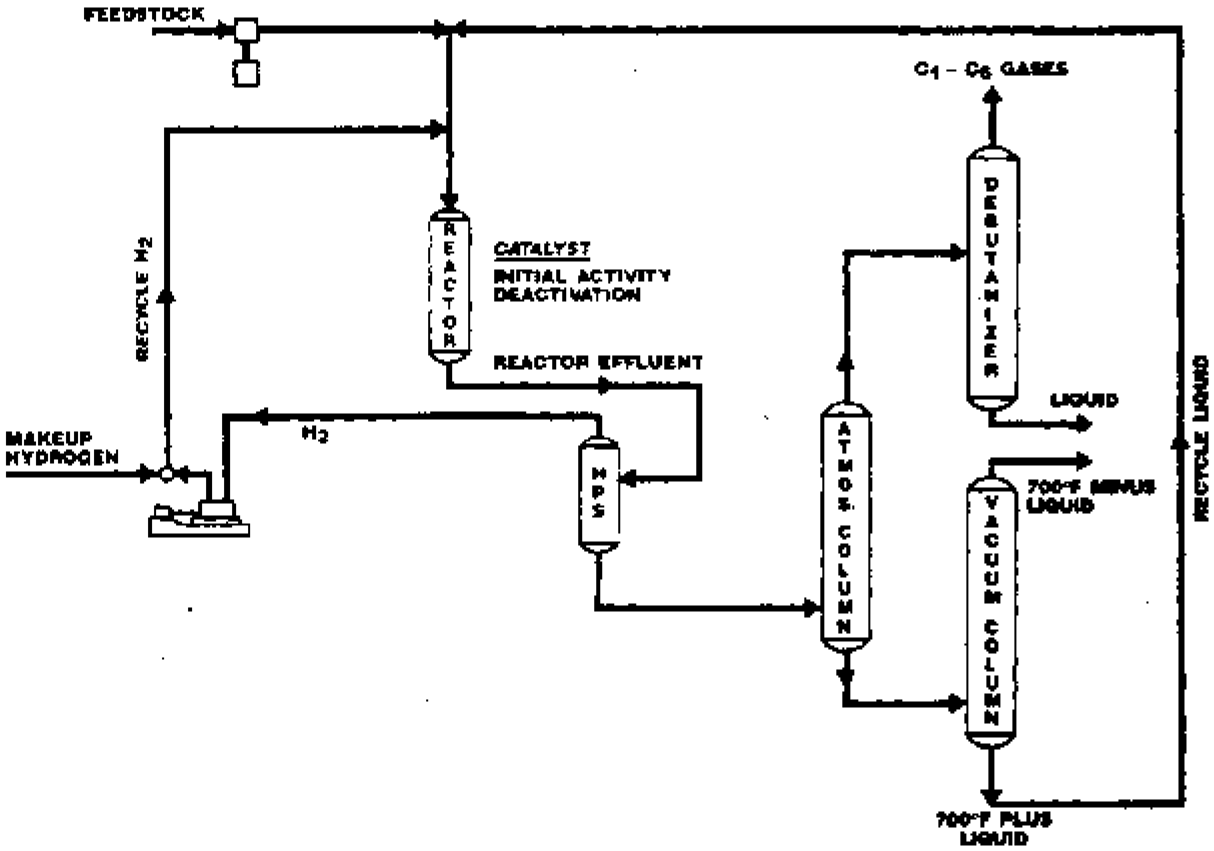
PILOT PLANT ONCE-THROUGH FLOW SCHEME



UOP 1589-25

FIGURE 5.9

PILOT PLANT RECYCLE LIQUID FLOW SCHEME



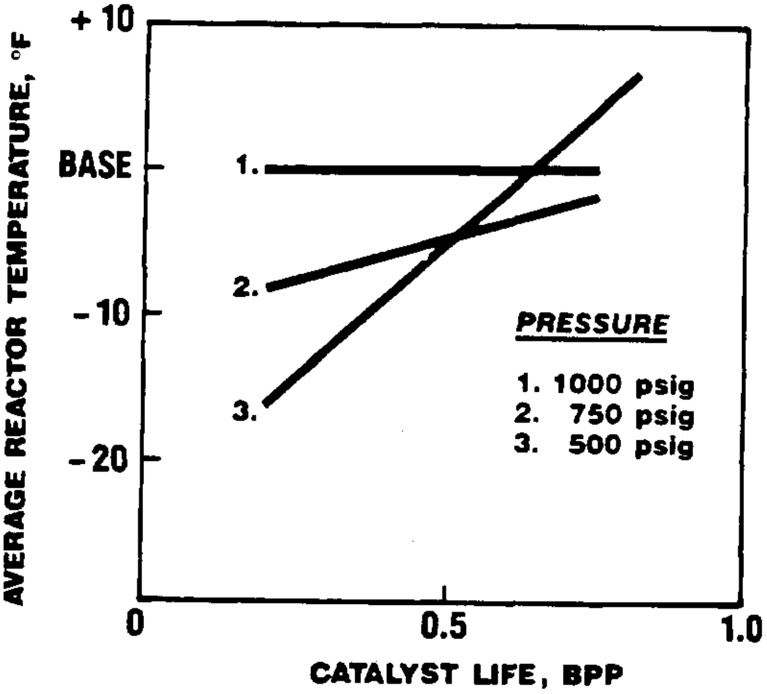
UOP 1589-26

FIGURE 5.10

PRESSURE EFFECT

CATALYST ACTIVITY AND STABILITY PERFORMANCE

ONCE – THROUGH OPERATION



OPERATING CONDITIONS

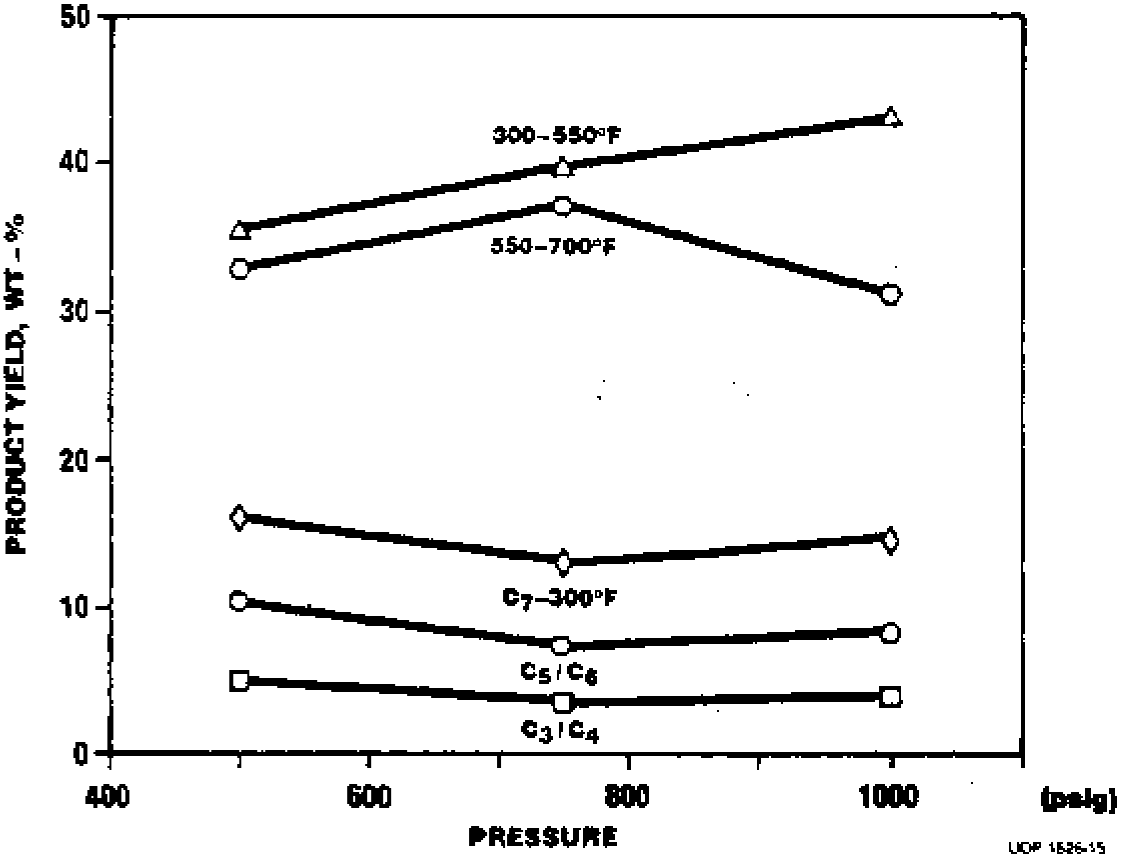
FEEDSTOCK = ARGE WAX
CONVERSION = 100%
PRODUCT = 700°F ENDPOINT
GAS RECYCLE = 10,000 SCFB
LHSV = 1.0 hr^{-1}

UOP 1418-24
UOP 1589-27

FIGURE 5.11

FISCHER-TROPSCH WAX HYDROCRACKING

PRESSURE EFFECT



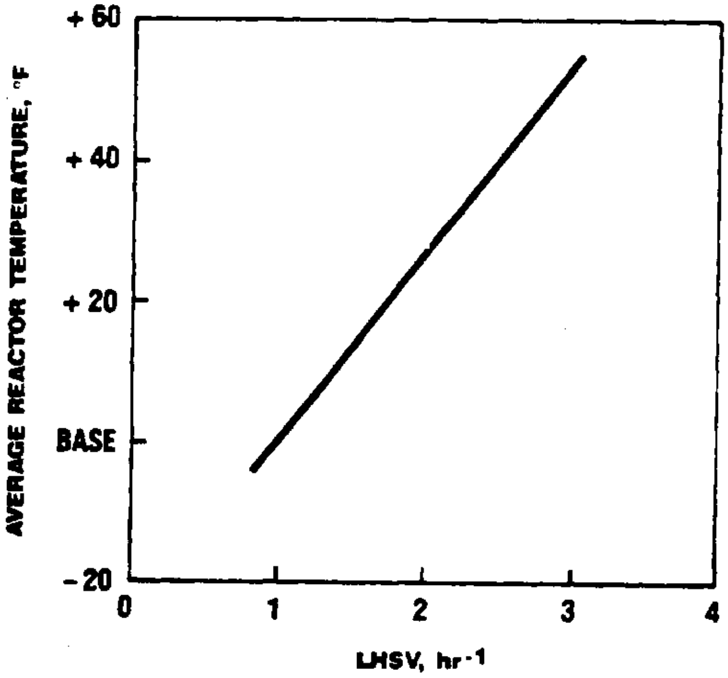
UOP 1526-15
UOP 1589-28

FIGURE 5.12

EFFECT OF LHSV

CATALYST ACTIVITY PERFORMANCE vs. LHSV

ONCE – THROUGH OPERATION



OPERATING CONDITIONS

FEEDSTOCK = ARGE WAX
CONVERSION = 100%
PRODUCT = 700°F ENDPOINT
PRESSURE = 1000 psig
GAS RECYCLE = 10,000 SCFB

UOP 1416-4
UOP 1589-29

FIGURE 5.13

FISCHER-TROPSCH WAX HYDROCRACKING

RECYCLE GAS EFFECT

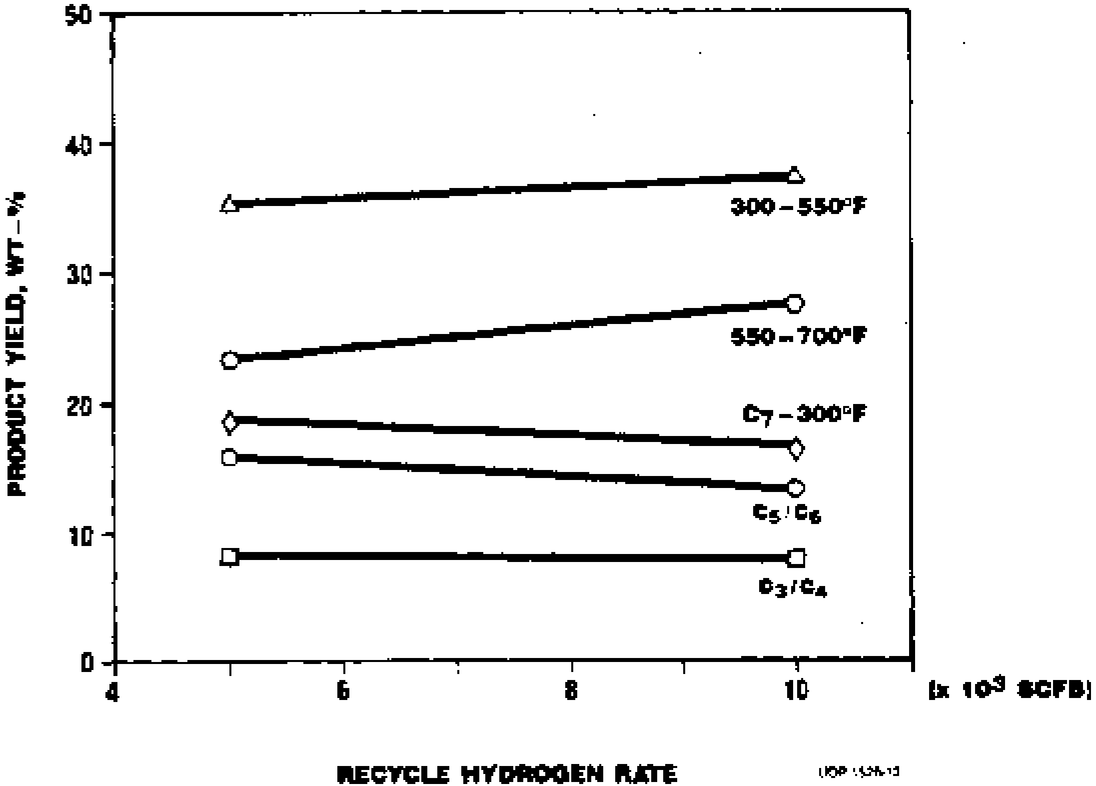
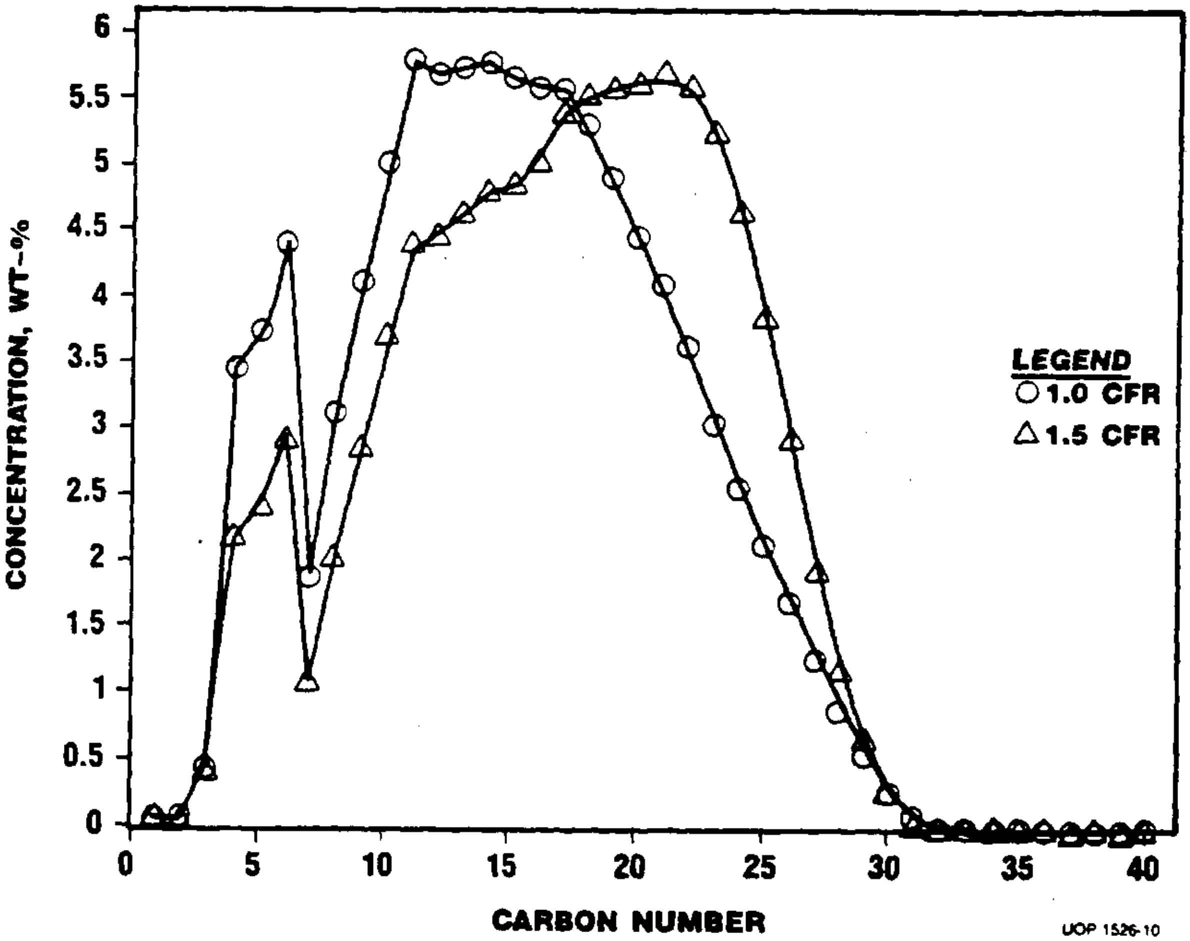


FIGURE 5.14

EFFECT OF CFR
FISCHER-TROPSCH WAX HYDROCRACKING



UOP 1526-10
UOP 1589-31

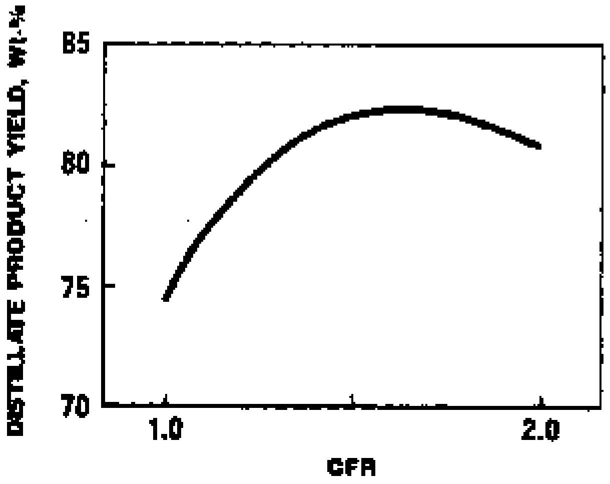
$$\text{CFR} = \frac{F + R}{F}$$

FIGURE 5.15

EFFECT OF CFR

PRODUCT DISTILLATE YIELD vs. CFR

RECYCLE OPERATION



OPERATING CONDITIONS

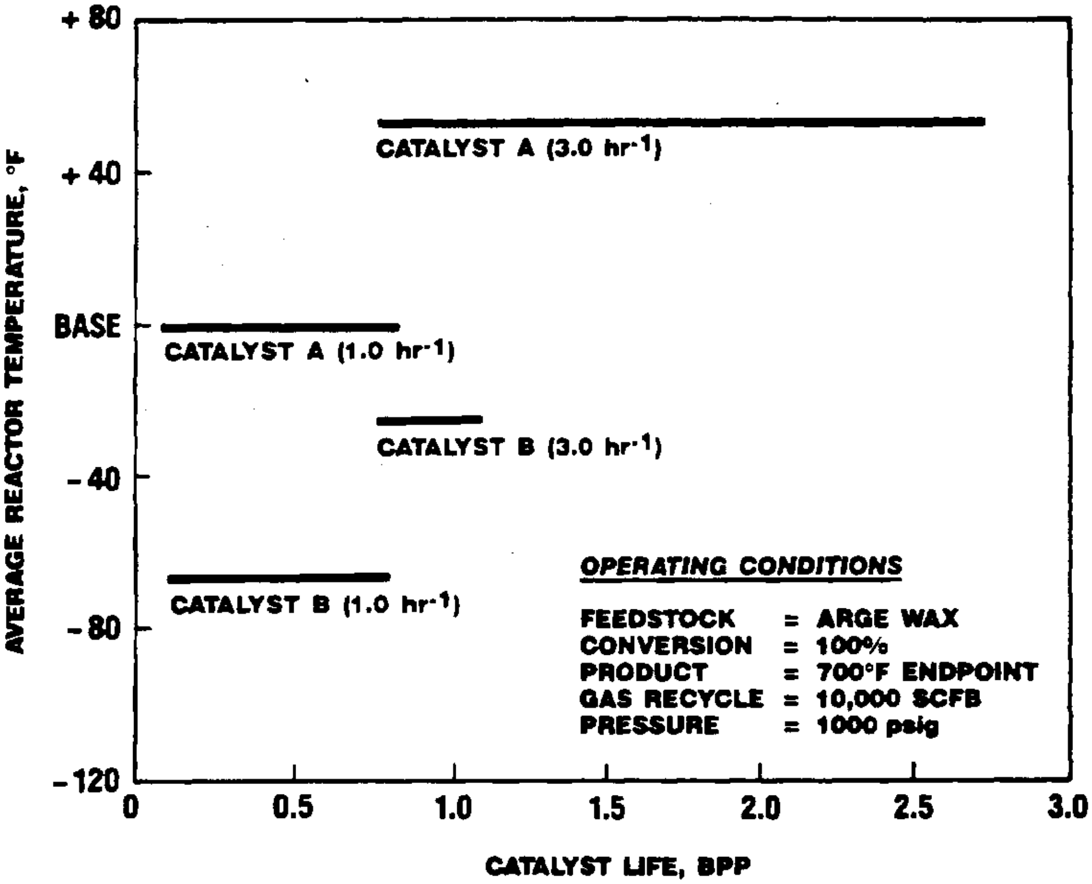
FEEDSTOCK = ARGE WAX
CONVERSION = 100%
PRODUCT = 700°F ENDPOINT
GAS RECYCLE = 10,000 SCFB
PRESSURE = 1000 psig

UOP 1418-7
UOP 1585-32

FIGURE 5.16

CATALYST ACTIVITY AND STABILITY COMPARISON

ONCE – THROUGH OPERATION



UOP 1418-15
UOP 1589-33

FIGURE 5.17

PRODUCT DISTILLATE YIELD vs. LHSV

CATALYST COMPARISON