4.0 FEEDSTOCKS

Petroleum-derived LPG blends were purchased for use in the Huels CSP and Cyclar pilot plant studies. Other program tasks for upgrading naphtha via reforming were completed with coal-derived feedstock from a commercial F-T facility, but long-distance transport of coal-derived LPG for the Cyclar study proved to be impractical.

4.1 HUELS CSP FEEDSTOCKS

The pilot plant feedstock compositions were estimates of a commercial combined feed (Figure 4.1). Such estimates are necessary when a once-through pilot plant simulates the performance of a commercial process with recycle. For a highly olefinic feedstock, the Huels CSP combined-feed ratio (CFR) is in the range of 20 to 30. The CFR is defined as:

$$CFR = (\text{Fresh Feed} + \text{Recycle}) \,/\, \text{Fresh Feed}$$

As a result of the high CFR, fresh-feed and combined-feed compositions were drastically different. For example, the LPG from an Arge F-T reactor (Huels CSP fresh feed) would have more than 60 wt-% olefins, but the Huels CSP-combined feed would have about 3 wt-% olefins.

Two feed blends were processed in the Huels CSP pilot plant (Table 4.1). CSP Blend 1 was based on an estimate of C_3-C_5 LPG produced by an Arge F-T reactor. The low pentene levels in CSP Blend 1 made pentene conversion data difficult to interpret; hence the need for a blend richer in pentenes. CSP Blend 1 was diluted with normal butane, and then olefins (weighted toward pentenes) were added. Normal butane is inert, and so the net effect was to create a new feedstock (CSP Blend 2) in which pentenes were a larger percentage of total olefins.

4.2 PURE COMPONENT CYCLAR FEEDSTOCKS

Pure component runs with propane and butane were conducted to reference the Cyclar pilot plant performance. The Cyclar process was originally developed to convert LPG paraffins into aromatics. The reference runs in this program were essential to tie into the majority of existing data and experience.

Propylene and butylene feedstocks were run to investigate Cyclar performance with a pure olefin feed. Nitrogen from a separate cylinder was blended-on line with the pure olefins to dilute the feed. An undiluted 100% olefin feed was considered unviable because it would cause the catalyst to deactivate too rapidly and could result in excessive coke formation in the reactor.

4.3 DIRECT CYCLAR FEEDSTOCKS

The Cyclar study was conducted in a once-through pilot plant, whereas the commercial Cyclar process recycles unconverted LPG. Direct Cyclar blends were made to simulate a combined Cyclar feed consisting of F-T LPG (Cyclar fresh feed) and recycle material (Figure 4.2).

In the Direct Cyclar process, LPG is processed by the Cyclar unit without the upstream saturation of LPG olefins by a Huels CSP unit. The composition of the Direct Cyclar combined feed depends on the F-T reactor technology producing the fresh feed. Three Direct Cyclar feed blends were used in this program (Table 4.2). The blends simulated Cyclar-combined feed when processing Arge F-T LPG (Direct Blends 1 and 2) and Synthol F-T LPG (Direct Blend 3). Determining the Cyclar combined-feed composition was an iterative procedure. The composition of the recycle stream depends on the conversion per pass and the selectivity attained during the run. Direct Blend 1 was the first estimate for a combined-feed composition using Arge-derived LPG. Direct Blend 2 was a refined estimate for the Arge case based on actual pilot plant data. The Synthol feed composition (Direct Blend 3) was more easily determined by drawing on experience from the Arge blends.

Some pentanes were included in Direct Blends 1 and 2 to study Cyclar as a route for upgrading at least a portion of the C_5 entering the F-T upgrading complex.

4.4 INDIRECT CYCLAR FEEDSTOCK

The Indirect Cyclar feed blend (Indirect Blend 1) is described in Table 4.3. This feed blend was mixed on-line with ethane from a separate cylinder to produce pilot plant feed. The final feed composition for each test period (Runs 13-16) is given in Appendix B.

Depending on the performance of the LPG recovery section of a commercial Cyclar unit, some ethane and ethylene are recycled with the unconverted LPG. Ethane and ethylene are specified in the Indirect Cyclar feeds to accommodate greater flexibility in the recovery section design, eliminating the need to make a nearly perfect C_2-C_3 split. Allowing C_2 into the recycle stream improves the recovery of LPG because C_3 levels in the fuel gas will be extremely low.

The LPG feed blend was purchased with a specified C_3-C_5 composition as well as a small amount of ethylene. Ethane was purchased in a separate cylinder and blended on-line in the pilot plant. This on-line blending was similar to diluting pure olefin feeds with nitrogen as described in Section 4.2.

TABLE 4.1

Feedstocks for Huels CSP Pilot Plant Study

Component, wt-%		CSP Blend 1		CSP Blend 2
Propylene		1.46		1.87
Propane		43.76		6.03
Isobutenes		0.40		0.51
n-Butenes		1.00		1.31
Isobutane		8.91		0.81
n-Butane		35.56		87.90
Isopentenes		0.00		0.00
n-Pentenes		0.20		0.70
Isopentanes		0.40		0.02
n-Pentane		8.31		0.85
Total		100.00		100.00
Hydrocarbon Type, wt-%				
Total Paraffins	96.94		95.61	
Isoparaffins		9.31		0.83
n-Paraffins		87.63		94.78
Total Olefins	3.06		4.39	
Isoolefins		0.40		0.51
n-Olefins		2.66		3.88
	100.00	100.00	100.00	100.00
Olefin Ratios, wt/wt				
Propylene/Total Olefin		0.48		0.42
Isobutenes/Total Olefin		0.13		0.12
n-Butenes/Total Olefin		0.33		0.30
n-Pentenes/Total Olefin		0.06		0.16
Isobutenes/Propylene		0.27		0.27
n-Butenes/Propylene		0.68		0.70
n-Pentenes/Propylene		0.14		0.37

TABLE 4.2

Direct Cyclar LPG Blend Compositions

Component, wt%	Direct Blend 1	Direct Blend 2	Direct Blend 3
Propylene	20.42	22.34	37.53
Propane	41.95	31.97	18.52
Butylenes	16.72	22.34	35.24
Isobutane	3.50	3.41	1.90
n-Butane	12.81	12.93	6.81
Pentenes	0.90	2.20	0.00
Isopentane	0.00	1.10	0.00
n-Pentane	3.70	3.71	0.00
	100.00	100.00	100.00
Carbon Number Distribution, wt-%			
C_3	62.37	54.31	56.05
C_4	33.03	38.68	43.95
C_5	4.60	7.01	0.00
Hydrocarbon Type, wt-%			
Total Paraffins	61.96	53.12	27.23
Total Olefins	38.04	46.88	72.77

TABLE 4.3

Indirect Cyclar LPG Blend Composition*

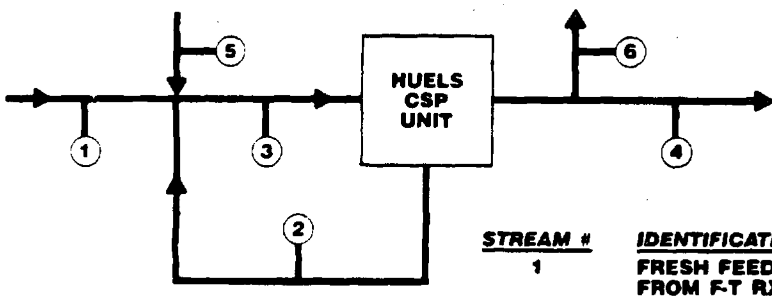
Component	Wt-%
Ethylene	1.10
Propylene	2.60
Propane	52.10
Butylenes	1.00
Isobutane	7.70
n-Butane	29.20
Pentenes	0.00
Isopentane	0.80
n-Pentane	5.50
	100.00

* Ethane was added from a cylinder via on-line blending. See Appendix B for net reactor-inlet compositions.

FIGURE 4.1

HUELS CSP STREAM IDENTIFICATIONS

COMMERCIAL CSP UNIT



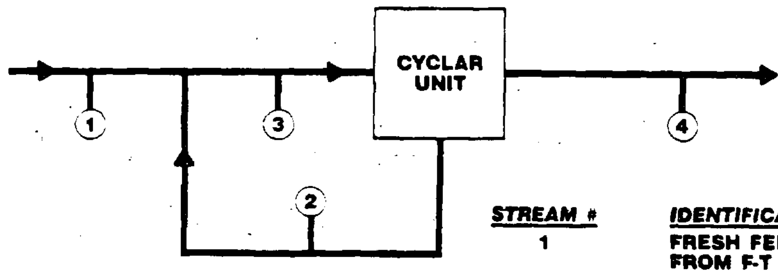
STREAM #	IDENTIFICATION	OLEFIN LEVEL
1	FRESH FEED (LPG) FROM F-T RX	HIGH
2	RECYCLE STREAM	LOW
3	COMBINED FEED	INTERMEDIATE
4	CSP PRODUCT TO CYCLAR UNIT	LOW
5	HYDROGEN FEED FROM CYCLAR	NONE
6	VENT GAS	LOW

NOTE: ONCE-THROUGH PILOT PLANT FEED COMPOSITION SAME AS STREAM #3 IN A COMMERCIAL (RECYCLE) UNIT

FIGURE 4.2

DIRECT CYCLAR STREAM IDENTIFICATIONS

COMMERCIAL FLOW SCHEME



STREAM #	IDENTIFICATION
1	FRESH FEED (LPG) FROM F-T REACTOR
2	RECYCLE FROM CYCLAR LPG RECOVERY SECTION
3	CYCLAR COMBINED FEED
4	CYCLAR PRODUCTS (TO SEPARATION AND RECOVERY)

NOTE: ONCE-THROUGH CYCLAR PILOT PLANT FEED COMPOSITION SAME AS STREAM #3 IN COMMERCIAL (RECYCLE) SCHEME

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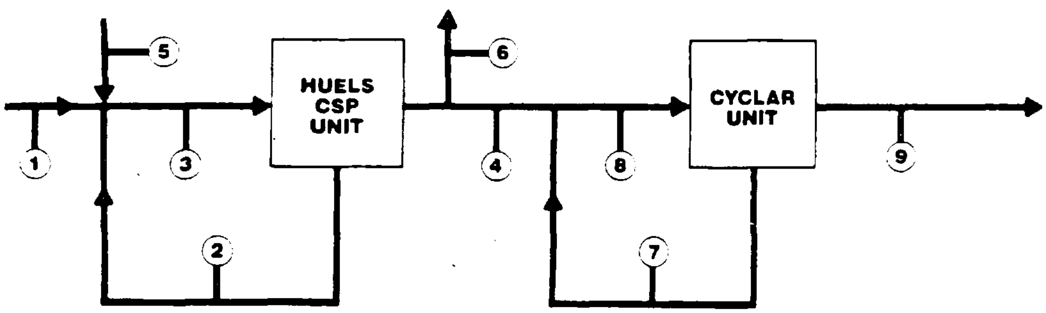
FIGURE 4.3

INDIRECT CYCLAR STREAM IDENTIFICATIONS

COMMERCIAL FLOW SCHEME



STREAM #	IDENTIFICATION
1	FRESH FEED (LPG) FROM F-T RX
2	CSP RECYCLE
3	CSP COMBINED FEED
4	CSP PRODUCT TO CYCLAR UNIT
5	HYDROGEN FEED (FROM CYCLAR)
6	VENT GAS
7	RECYCLE FROM CYCLAR LPG RECOVERY SECTION
8	CYCLAR COMBINED FEED
9	CYCLAR PRODUCTS (TO SEPARATION AND RECOVERY)

NOTE: *ONCE-THROUGH CYCLAR PILOT PLANT FEED COMPOSITION SAME AS STREAM #6 IN COMMERCIAL (RECYCLE) SCHEME*

5.0 HUELS CSP PILOT PLANT WORK

The objective of the Huels CSP study was to process olefinic C_3-C_5 feeds at commercial conditions and to provide data for commercial yield estimates. Experiments were performed in a once-through pilot plant, but the commercial process has a recycle stream (see Section 4.1). Therefore, the feed blends in the CSP pilot plant matched the expected commercial combined-feed composition (commercial reactor-inlet composition).

5.1 HUELS CSP PROCESS VARIABLE STUDY

Temperature and space velocity were varied over established commercial ranges to generate yield and conversion data. The pressure was maintained at a constant value, which was high enough to ensure a single liquid phase. At commercial operating conditions, conversion was nearly stoichiometric and was controlled by adjusting the hydrogen addition rate. Two target olefin conversions (66% and 80%) were examined over a range of temperatures and space velocities.

CSP Run 1 is summarized in Table 5.1. The target conversion levels were achieved, and hydrogen consumption was virtually complete. The individual conversion levels for C_3 and C_4 (Figure 5.1) show propylene was preferentially converted (saturated) relative to butene. Conversion of component i was defined as follows:

$$\text{Mol-\% Conversion i, \%} = 1 - \frac{\text{Mol-\% (i) Product}}{\text{Mol-\% (i) Feed}} \times 100$$

The conversion of pentenes during CSP Run 1 was difficult to interpret. The feed pentene level was low (0.2 wt-%), and so small (0.1 wt-%) GC errors in the product pentene content resulted in significant errors in conversion measurement.

5.2 HUELS CSP PENTENE CONVERSION STUDY

The pentene content of the CSP Run 1 feed was enhanced (see Section 4.1) to provide a new feed for CSP Run 2. The purpose of this run was to examine the pentene conversion levels at both intermediate and high conversion per pass. The hydrogen injection rate was set to achieve 66% and 100% conversion. The actual conversions (Table 5.2) were lower, probably because of a leak in the hydrogen injection system. However, pentene conversion was similar to butene conversion. When corrected to target conversion, the CSP Run 2 propylene and butene conversion values were similar to those of CSP Run 1, and so repeating the run was not necessary.

5.3 CONCLUSIONS OF HUELS CSP PILOT PLANT TESTING

Huels CSP pilot plant runs demonstrated C_3-C_5 olefins hydrogenation at commercial conditions. The rate of the addition of hydrogen controls the degree of olefin saturation. When the molar ratio of hydrogen to olefins was less than one, propylene hydrogenated more readily than butenes or pentenes. Butenes and pentenes were hydrogenated to a similar extent at commercial conditions.

TABLE 5.1

Average Yields and Conversions for Huels CSP Run 1

Test Period	1	2	3	4	5	6	7	8
Temperature, °C(a)	T_1	T_2	T_4	T_5	T_1	T_3	T_5	T_5
LHSV(b)	$LHSV_1$	$LHSV_1$	$LHSV_1$	$LHSV_1$	$LHSV_2$	$LHSV_2$	$LHSV_2$	$LHSV_3$
Target Conversion, Mol-%	66	66	66	66	80	80	80	80
Yields, Wt-%:								
C_3=	0.15	0.14	0.09	0.10	0.05	0.05	0.05	0.06
C_3	41.87	42.69	42.16	42.67	42.38	42.07	41.96	41.42
C_4=	0.97	0.93	0.88	0.03	0.62	0.57	0.62	0.64
i-C_4	9.26	9.20	9.26	9.20	9.31	9.35	9.35	9.37
n-C_4	37.86	37.40	37.83	37.51	37.96	38.19	38.22	38.51
C_5=	0.15	0.14	0.13	0.13	0.09	0.08	0.09	0.09
i-C_5	0.44	0.43	0.44	0.43	0.43	0.44	0.44	0.45
n-C_5	9.28	9.02	9.19	9.01	9.15	9.26	9.28	9.45
Total Olefins	1.27	1.21	1.10	1.16	0.76	0.68	0.76	0.80
Conversions, Mol-%								
C_3=	89.5	89.7	93.1	92.1	96.2	96.5	96.2	95.7
C_4=	34.4	37.4	39.5	36.8	58.4	61.5	58.5	57.0
Overall	63.6	65.1	67.4	66.0	78.3	79.9	78.3	77.4

Note: Pressure = Constant

(a) T_1 = Base Temp + 15°C
T_2 = Base Temp + 10°C
T_3 = Base Temp + 8°C
T_4 = Base Temp + 5°C
T_5 = Base Temp

(b) $LHSV_1$ = Base Case
$LHSV_2$ = 1.75 $LHSV_1$
$LHSV_3$ = 2 $LHSV_1$

TABLE 5.2

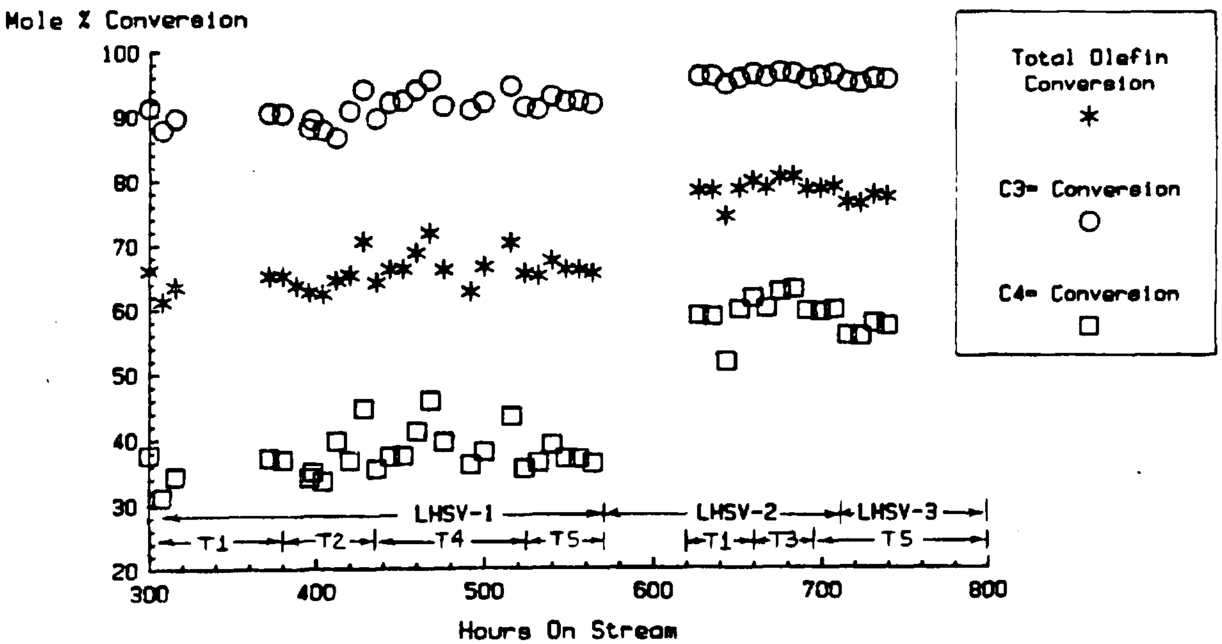
Average Product Yields and Conversions for Huels CSP Run 2 Pentene-Enriched Feed

Target Conversion Mol-%	100	66
Temperature, °C	T2	T2
LHSV, 1/hr	$LHSV_1$	$LHSV_1$
Yields, Wt-%		
C_3=	0.04	0.64
C_3	6.14	5.36
i-C_4=	0.05	0.43
n-C_4=	0.09	0.88
i-C_4	0.92	0.53
n-C_4	91.60	91.01
C_5=	0.05	0.49
i-C_5	0.01	0.00
n-C_5	1.10	0.67
Conversions, Mol-%		
C_3=	97.8	66.0
C_4=	92.6	28.0
C_5=	92.2	29.3
Overall	95.5	49.1

FIGURE 5.1

HUELS CSP STUDY

OLEFIN CONVERSION



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