6.0 CYCLAR PILOT PLANT WORK

A total of 18 Cyclar pilot plant runs were conducted. Table 6.1 presents an overview of the experimental program. Feed composition, temperature, pressure, and space velocity were varied in the study. The data-reduction procedure is described in Appendix A. Detailed results for each Cyclar pilot plant run are in Appendix B.

6.1 CATALYST

The Cyclar catalyst formulation was not a variable in this program. Fresh loadings of Cyclar catalyst from the same batch of commercial prototype material were used in each pilot plant test. After every run, the carbon level of the spent catalyst was measured. The results are reported as received, without adjustment for LHSV or conversion-level differences. The carbon level for Cyclar Run 3 was chosen as the reference and assigned a value of 1.00. All other spent-carbon levels are compared with this reference as a weight ratio. This ratio is referred to as the "relative carbon on spent catalyst" listed in Table 6.1. A value of 0.5 would indicate that the spent catalyst contained half the carbon of the Run 3 spent catalyst.

6.2 INTERPRETATION OF PILOT PLANT DATA

A fixed-bed once-through pilot plant was used to model a multistage commercial unit with recycle of unconverted feed. Unlike the pilot plant, commercial Cyclar is a moving-bed system. Spent catalyst is continuously removed from the last reactor, regenerated, and then returned to the first reactor. Despite these differences, the pilot plant is able to give tremendous insight into how the commercial unit will function. This section describes the pilot plant test methodology and the effect of variables on performance. These parameters are summarized in Table 6.2.

6.2.1 Pilot Plant Test Methodology

All pilot plant runs in this program used the same test methodology. The electric heating elements surrounding the reactor were adjusted to achieve and then maintain a specified reactor-inlet temperature. This inlet temperature was held constant throughout the run. All the liquid product from a given period was collected (composite sample), and separator overhead gas samples were analyzed hourly by on-line GC and then averaged for each period.

The LPG conversion was defined as the disappearance of LPG (all C_3-C_5 hydrocarbons). The LPG may be converted to hydrogen, fuel gas (C_1 and C_2), or aromatics. The gradual increase of LPG in the separator overhead reflects catalytic activity loss due to coke formation. As less LPG is converted, the production rate (grams/hour) of aromatics will decline. This decline does not mean that selectivity is lower, because selectivity pertains only to LPG converted out of the C_3-C_5 range. In general, aromatic selectivity increases as conversion declines in Cyclar pilot plant tests.

Conversion and selectivity results are all in units of weight-percent (wt-%) in this report. For each period, the LPG conversion is the wt-% of the LPG that entered the reactor and was converted to something other than LPG. The selectivity data indicate what wt-% of the converted material became fuel gas (fuel gas selectivity), hydrogen (hydrogen selectivity) or liquid product (aromatics selectivity). The sum of these three selectivities is 100 wt-% by definition.

Liquid product from each test period was analyzed to determine the distribution of the aromatic product. The results are expressed as a wt-% of all C_6+ hydrocarbons detected. Trace aromatics present in the separator off gas are considered liquid product, although they only have a minor impact on the results.

6.2.2 Evaluation of Results

When evaluating a run, the first area to consider is catalytic activity and stability (temperature performance). As stated previously, Cyclar pilot plant tests are run at constant reactor-inlet temperature. The conversion obtained for each period measures activity. The rate of conversion decline as a function of time reflects stability. Figure 6.1 shows three hypothetical cases that serve as examples of good and bad temperature performance.

Activity and stability are both important catalyst properties. High activity means high LPG conversion and, therefore, less unconverted feed recycle in a commercial unit. The temperature required to obtain a given conversion is important because this variable affects commercial fixed costs (such as heater design and metallurgy) and operating costs (utilities consumption).

Stability measures how fast a catalyst deactivates. In a fixed-bed commercial unit, a pilot plant stability assessment would be used to estimate run length. When modeling a CCR process like Cyclar with a fixed-bed pilot plant, stability assesses the rate of continuous catalyst regeneration that is needed to maintain optimum catalyst performance. Lower stability means a larger and, therefore, more expensive regenerator and also higher catalyst costs.

Besides conversion stability, the coke level on spent catalyst provides critical information for designing the CCR section of a commercial unit. The carbon level of the spent catalyst (wt-% carbon) affects regenerator design. Two catalysts with the same end-of-run conversion will not necessarily have the same spent-catalyst carbon level.

Midrun comparisons are particularly meaningful data from a fixed-bed pilot plant for modeling a moving-bed CCR system, such as in the

Cyclar process (see Section 2.2.3). This comparison approximates an average catalytic performance between that of fresh catalyst (regenerated catalyst to reactor 1) and spent catalyst (catalyst from the final reactor). The exact choice of the pilot plant midpoint is not pivotal because a commercial CCR section operates independently of the reactor section.

Product selectivities and selectivity stability are important catalyst-performance parameters. The amount of desired products (aromatics and hydrogen) produced relative to the undesired side product (fuel gas) and the changes in selectivities as conversion declines are critical factors for commercial operation.

A fixed relationship exists between aromatics, hydrogen, and fuel gas selectivities. As Cyclar makes aromatics from propane, it simultaneously produces hydrogen in an amount determined by stoichiometry. Hydrogen selectivity increases with aromatics selectivity. In the Cyclar process, yield loss is from cracking reactions that form fuel gas (C_1 + C_2 hydrocarbons). Therefore, fuel gas selectivity moves inversely to aromatics selectivity. These fixed relationships simplify comparing selectivity differences between runs.

The last performance consideration discussed here is the liquid-product distribution. Cyclar produces primarily benzene (C_6), toluene (C_7), and xylenes plus ethylbenzene (C_8). Also produced is a heavy aromatic product that is referred to as A_9+ (nine or more carbon number aromatics). The composition of the aromatic product varies according to the feedstock and process conditions.

Liquid-product composition is important for a variety of reasons. If the Cyclar unit were in an aromatics complex, benzene and xylenes would be more valuable than toluene and A_9+ aromatics. If the Cyclar product were blended into a gasoline pool, the benzene content would be critical, given possible environmental regulations placing strict ceilings on benzene levels in gasoline.

6.3 PURE COMPONENT PILOT PLANT WORK

Most of the pilot plant work conducted during the development of the Cyclar process has focused on pure propane or butane feedstocks. Pure paraffin feedstocks were run in this program to establish base-case performance as well as to examine the effects of process pressure. Runs were also performed with propylene and _n_-butene to investigate performance with pure olefin feeds.

6.3.1 Propane Feedstock at Base-Case Conditions (Run 1)

Pure propane was run at previously established base conditions (Run 1). As shown in Figure 6.2, Run 1 displayed good activity and stability.

Aromatics, hydrogen, and fuel gas selectivities are plotted as a function of time for Run 1 (Figure 6.3). Based on previous experience, the selectivities and selectivity stabilities were as expected for this catalyst. Selectivity was relatively insensitive to time on-stream (and, therefore, conversion). Selectivity to aromatics improves slightly as the run progresses and as the catalyst activity declines via coking.

The liquid-product distribution (Figure 6.4) was as expected for a propane feedstock. A direct route to benzene (dimerization of a C_3 molecule) and the A_9 aromatic (propylbenzene, a C_3 trimer) exists, but the significant production of toluene (C_7) and xylenes (C_8) reveals that other mechanisms, such as transalkylation and dealkylation, are also important.

6.3.2 Butane Feedstock at Base-Case Conditions (Run 9)

A pure butane feedstock was run at base-case conditions (Run 9), which were identical to those used for propane in Run 1. As indicated in Figure 6.5, butane conversion is higher for any given test period (butane is more reactive), and butane results in slightly better stability.

Midrun results from propane and butane feeds tested at base conditions are compared in Table 6.3. Butane gives higher total aromatics selectivity.

Aromatic-product breakdowns at similar conversion levels are compared for propane and butane feeds (Figure 6.6). Butane tends to make an aromatic product leaner in benzene and richer in xylenes than propane. This result is expected because the most direct route to benzene would result from the dehydrocyclodimerization of two propane molecules. A similar reaction for two butane molecules would tend to make C_8 aromatics (xylenes + ethylbenzene).

6.3.3 Pressure Increase with Pure Component Feeds (Runs 8 and 10)

The effect of pressure on Cyclar performance was investigated in Runs 8 and 10. The only change from base conditions was a pressure increase to P2 (1.5 x base pressure). For each feed, higher process pressure was shown to improve conversion. Higher conversion at elevated pressure is more pronounced for propane (Figure 6.7) than butane (Figure 6.8) because propane has a significantly lower conversion at P1 than butane.

Higher pressure benefits conversion, but it has an adverse impact on aromatics selectivity. Aromatics selectivity plotted as a function of conversion for propane (Figure 6.9) and butane (Figure 6.10) shows that the selectivity offset was not attributable to the conversion differential. Selectivity was relatively stable in both tests.

Liquid-product distributions obtained at P1 and P2 are compared for propane (Figure 6.11) and butane (Figure 6.12). The propane-feed product shows a shift from benzene to xylenes as pressure increases. Butane feed shows a shift from benzene to alkyl aromatics.

6.3.4 Pure Olefin Feeds

Runs were conducted with pure propylene (Run 11) and butene (Run 12) to provide information for Direct Cyclar yield estimates. Both runs were performed at P2, which is 1.5 times the base pressure. Pure olefin feeds were diluted with nitrogen via on-line blending. The criterion for nitrogen blending was to have a similar mol-% pure component olefin as Direct Blend 1 (see Section 4.3) but to replace all other hydrocarbons with nitrogen. This space velocity effectively maintained LHSV 1 (of Direct Cyclar) with respect to the pure component without the complications introduced by multiple reactants in the feed. Olefins are known to be extremely reactive, and the Cyclar catalyst would be too unstable if a pure olefin feed were run at base conditions without nitrogen dilution.

6.3.4.1 Propylene Feed (Run 11)

Before comparing propylene and propane test results, the two types of conversion must be defined. *Propylene conversion* is the disappearance of propylene (C_3H_6) across the Cyclar reactor. Propylene hydrogenated to propane shows up as propylene conversion. *LPG conversion* is the disappearance of LPG, defined here as all C_3-C_5 molecules. The hydrogenation of propylene does not constitute LPG conversion.

In commercial Cyclar, LPG is recycled back to the reactor. This recycle means that LPG conversion is of primary concern because conversion of propylene outside of the LPG range unburdens the recycle loop but the conversion of propylene to propane does not. Generally, this report discusses conversion to products other than LPG.

For the pure component olefin feed study, looking at the component conversion as well as the LPG conversion must be examined. In Run 11, the propylene conversion was nearly complete throughout the run, but the LPG conversion dropped steadily (Figure 6.13). Although propylene remains extremely reactive, olefin hydrogenation becomes increasingly significant as the catalyst deactivates. This point is demonstrated in Figure 6.14. The propane content of the reactor effluent is shown to increase steadily, but the light ends (C_1 and C_2) formed by cracking tend to stay relatively constant and then decline toward the end of the run.

Midrun results show propylene has better aromatic-product selectivity than does propane (Table 6.4). The high selectivity results because the propane dehydrogenation step of the Cyclar reaction pathway (see Section 2.2.2) is bypassed. The aromatics selectivity and LPG conversion advantage for propylene was maintained throughout the run, as shown in Figure 6.15.

Liquid-product compositions (Figure 6.16) indicate a shift from benzene to xylenes and heavy aromatics with propylene. Propylene is likely to form an intermediate trimer, which then converts to a nine-carbon aromatic.

Results with a propylene feed are directionally consistent compared to propane. However, making strict comparisons is not possible because of a difference in test methodology (nitrogen dilution, see Section 4.3).

6.3.4.2 Butene Feed (Run 12)

In most respects, butene behaved similar to propylene. Butene is very reactive, and LPG conversion drops with respect to butene conversion (Figure 6.17). In Run 12, even the butene conversion began to drop at the end of run (EOR). This result is consistent with the extremely high EOR coke level (7.9 x base) for the spent catalyst

(Table 6.1). Hydrogenation of butene to butane became more prevalent with time (Figure 6.18). The reactor effluent shows an increasing level of butane (hydrogenation product), with a decreasing level of C_1 and C_2 (cracking and dealkylation products).

Midrun results for butene and butane are compared in Table 6.5. Just as with the C_3 olefin, butene resulted in significantly better aromatics selectivity than its paraffin analog. As was the case with propylene, butene aromatics selectivity is superior to that of paraffin at any conversion measured (Figure 6.19). A liquid-product distribution shift from benzene toward xylenes and heavy aromatics is observed for butene (Figure 6.20). The shift is similar to that observed with propylene. This shift is another indication that olefins may tend to form trimers as an intermediate which increases the production of A_9+ aromatics.

Again, the key difference in test methodology between the pure component paraffin and olefin tests must be stressed. Nitrogen was blended on-line with the olefin. The olefin versus paraffin comparisons are made to help interpret some of the Direct Cyclar results discussed next.

6.4 DIRECT CYCLAR PILOT PLANT STUDY

The pilot plant work described in Section 6.3 was all done with pure component feeds. The Direct Cyclar study was performed with LPG feed blends. The blends, which are described in Section 4.3, vary in carbon number distribution as well as olefinicity. A common feature of the Direct Cyclar blends was the high olefin level, ranging between 38 and 73 wt-% of the pilot plant feedstock.

6.4.1 Direct Cyclar at Base Conditions (Run 3)

Direct Cyclar Blend 1 (DB1) was run at base conditions in Run 3.

Compared to propane, DB1 results in slightly higher conversion (Figure 6.21). Conversion was not as high as expected, considering that DB1 contains butane, propylene, and butene. All three converted more than propane in the pure component work. Aromatics selectivity with DB1 was higher than with propane (Table 6.6), which was as expected based on pure component results. Finally, the liquid-product distribution shifted from benzene to xylenes and A_9+ material as expected (Figure 6.22).

6.4.2 Direct Cyclar Pressure Study (Runs 3, 5, and 6)

In the Cyclar process, conversion increases with pressure (Figure 6.23), and conversion stability improves. At P1, the LPG conversion decline was about 4 wt-% per test period. The conversion decline was slightly over 2 wt-% per test period at P3.

Aromatics selectivity declined with increasing pressure as demonstrated in Figure 6.24. Despite the decline, the aromatics selectivity for DB1 was still good at P3 (3 x base pressure). This result was encouraging because Direct Cyclar operated at higher pressure (higher conversion) and still maintained high aromatics selectivity with respect to a paraffin feedstock. A shift in the liquid-product distribution from benzene to xylenes and heavy aromatics (Figure 6.25) was consistent with the pure component results.

6.4.3 Pressure Study at Reduced Temperature (Runs 2, 4, and 7)

The same pressure sequence described previously was repeated at 520°C, a 20°C reduction from base temperature. At base pressure, the temperature reduction lowered initial activity but improved stability so that the conversion coincided for periods 6 through 9 (Figure 6.26). As pressure increased (Figures 6.27 and 6.28), the stability advantage of the lower temperature operation gradually disappeared. At P3, a nearly constant conversion offset was observed throughout the run. The rates of conversion decline become similar because higher temperature operation has better stability at elevated pressure.

The decline at elevated pressure of aromatics selectivity is plotted in Figure 6.29. A comparison of Figures 6.24 (540°C) and 6.29 (520°C) reveals that the total aromatics selectivity was relatively insensitive to temperature. The conversion benefit from the temperature increase of 520°C to 540°C was not offset by a measurable loss in aromatics selectivity.

Pressure affected the liquid-product distribution similar to that at 540°C at 520°C (Figure 6.30). As pressure increased, less benzene and more xylenes and heavy aromatics were present. Comparing the product distributions at 520°C and 540°C shows some interesting results. Lower temperature suppresses the relative amount of benzene in the liquid product at the base pressure, but the levels begin to converge at P3 (Figure 6.31). Heavy aromatics formation has equivalent sensitivity to pressure changes at 520°C and 540°C, as shown in Figure 6.32.

6.4.4 Variation in Feedstock Olefinicity (Runs 6, 17, and 18)

Three Direct Cyclar blends (DB1, DB2, and DB3 as described in Section 4.3 of this report) covered a range of 38 to 73 wt-% olefins in the pilot plant feed. All three feedstocks were evaluated at the same conditions. Aromatics selectivity improved as the feed olefinicity increased (Table 6.7).

Conversion stabilities for the three Direct Cyclar feeds at identical conditions were plotted (Figure 6.33). Each feed resulted in similar stability for the first six periods. However, conversion stability deteriorated after this point depending on feed olefinicity. Stability deterioration was also observed for butene feed (Run 12), as described in Section 6.3.4. Relative spent carbon levels (Table 6.1) correlate to feed olefinicity as well as the point of departure from the midrun deactivation rate. Higher olefin levels lead to higher coke levels.

An increase in feed olefinicity causes a shift from benzene to xylenes (Figure 6.34). The heavy aromatics in the liquid product were the same at 38 and 73 wt-% olefins.

6.4.5 Direct Cyclar Spent-Catalyst Coke Levels

The effects of temperature and pressure on the end-of-run coke level of the catalyst are shown in Figure 6.35. As might be expected, more coke was produced at the higher temperature. Surprisingly, the coke level was observed to increase with pressure. This result runs counter to the trends observed with reforming catalysts, where high hydrogen partial pressures promote catalyst stability and low levels of coke production.

Figure 6.32 shows the effects of temperature and pressure on Ag+ aromatics yields. These trends were directionally consistent with the coke levels. However, as feed olefinicity increased, the values for Ag+ aromatics (Figure 6.34) in the liquid product did not explain the trend in coke levels (Figure 6.36). Possibly the oligomerization process described previously is different with high olefin feeds. Perhaps in this case, olefin polymerization (forming tars and then polymeric coke) progresses along with the heavy aromatics condensation route to coke.

6.5 INDIRECT CYCLAR PILOT PLANT STUDY

Four Indirect Cyclar runs were conducted. Two process variables, LHSV and pressure, were investigated. The Indirect-Cyclar feed blend had a low olefin level, as indicated in Section 4.4. The low olefin level in a commercial unit would result from a Huels CSP unit upstream of the Cyclar unit. However, some olefins are present in the combined feed, which contains olefins introduced from the recycle stream.

6.5.1 LHSV Effect at P1 (Runs 13 and 14)

A 25% increase in space velocity lowered conversion about 8 wt-%, as would be expected (Figure 6.37). Perhaps more important, the space velocity increase did not change the aromatics selectivity (Figure 6.38). Figure 6.38 shows that if the capacity of a commercial unit is pushed, aromatics selectivity would not suffer from the space velocity change. The LHSV increase also had marginal impact on the liquid-product distribution, as shown in Figure 6.39. Slightly less benzene is made at higher space velocity.

6.5.2 LHSV Effect at P3 (Runs 15 and 16)

Space velocity was doubled at P3, and the LPG conversion was significantly lower. The 25% LHSV increase at P1 caused the conversion to shift, but stability appeared unchanged. The 100% LHSV increase at P3 altered the conversion stability and reduced conversion (Figure 6.40).

On average, aromatics selectivity was considerably better at the higher space velocity (Figure 6.41). However, where the conversions overlap, near 77 wt-% LPG conversion, the selectivities are about the same. In this case, aromatics selectivity is a significantly more pronounced function of conversion. The conversion shifted with the LHSV change, and a new region of the same selectivity versus conversion line was explored at the high space velocity. The composition of liquid product obtained at different LHSV's was almost identical (Figure 6.42).

6.5.3 Pressure Effect at LHSV 2 (Runs 14 and 15)

The pressure increase from P1 to P3 produced all the expected trends, based on pure component and Direct Cyclar findings. Higher conversion and greater stability were achieved at P3 (Figure 6.43). The aromatics selectivity decline shown in Figure 6.44 was expected. Finally, higher pressure induced a shift in the liquid-product distribution from benzene to xylenes and heavy aromatics (Figure 6.45).

6.6 CONCLUSIONS

Some of the following conclusions are based on pure component work and apply to Cyclar in general. These conclusions are also consistent with both the Direct and Indirect Cyclar results. Conclusions specific to either Direct or Indirect Cyclar are drawn separately.

6.6.1 Butane vs. Propane

- Butane is more reactive than propane; for any given test period (at identical process conditions), butane conversion is higher. Conversion stabilities are similar, with perhaps a slight advantage with butane.
- Butane feedstock results in higher aromatics selectivities than did propane.
- The liquid product made from butane has less benzene and more xylenes than did the liquid product made from propane.
- The hydrogen-to-carbon weight ratio for butane (C_4H_{10}) is lower than that for propane (C_3H_8). Therefore, the theoretical maximum hydrogen selectivity (weight basis) for butane is lower than that of propane. This result explains why the pilot plant hydrogen selectivities for propane and butane are about the same despite the higher aromatics selectivities obtained with butane.

6.6.2 Paraffins vs. Olefins

- Olefins are extremely reactive. With respect to the reactivity of the corresponding paraffin, the conversion of a pure olefin feed is significantly higher. As a run progresses, conversion out of the C_3-C_5 range declines, but olefin hydrogenation increases. Therefore, the olefin content of the reactor effluent remains low throughout the run.

- Olefins result in higher aromatics selectivities than do the corresponding paraffin at all conversion levels.
- The liquid product made from an olefin has less benzene and more xylenes and A_9+ aromatics than does liquid product made from a paraffin.

6.6.3 Effect of Pressure

- An increase in pressure results in higher conversion.
- Higher pressure suppresses aromatics and hydrogen selectivities.
- An increase in pressure shifts the liquid products distribution. Less benzene and more xylenes are present in liquid product made at higher pressure.

6.6.4 Direct Cyclar Conclusions

- Direct Cyclar pilot plant testing demonstrates that processing highly olefinic Cyclar feedstocks is technically feasible.
- With respect to more paraffinic feeds, Direct Cyclar (olefinic) feeds result in higher aromatics selectivities.
- A 20°C inlet temperature reduction (to 520°C) improved conversion stability at P1 with respect to 540°C operation. As pressure is increased, the conversion stability observed with lower temperature operation disappears.
- Aromatics and hydrogen selectivities were about the same at 520°C and 540°C inlet temperatures. At P1, the liquid product from the 520°C run has less benzene and more

xylenes than does that made with a 540°C inlet temperature. As pressure increases to P3, the liquid products become closer in composition.

- Olefinic feeds lend themselves to higher pressure operation, which capitalizes on higher conversion. With respect to base case Cyclar (paraffin feed and low process pressure), the detrimental effect of pressure on aromatics selectivity is offset by the improved aromatics selectivities for olefinic feeds.
- Spent catalyst carbon levels are higher for Direct Cyclar. This disadvantage at least partially offsets the aromatics and hydrogen selectivities advantages discussed above. Spent-catalyst carbon levels correlate well with feed olefinicity.
- Pressure also has an effect on spent-catalyst carbon levels. Higher pressure results in more spent-catalyst carbon.

6.6.5 Indirect Cyclar Conclusions

- Indirect Cyclar results are similar to pure paraffin results.
- An LHSV study demonstrates that LHSV changes shift conversion, with minimal impact on conversion stability.
- LHSV variation does not affect aromatics or hydrogen selectivities, when adjusted for conversion.
- Increased pressure improves conversion and conversion stability but lowers aromatics selectivity.

TABLE 6.1

Overview of Direct and Indirect Cyclar Pilot Plant Runs

Run No.	Feed (a)	Diluent	Rx Temp, °C	Pressure (b)	LHSV (c)	Relative Carbon on Spent Catalyst (d)
1	Propane	--	540	P1	LHSV 1	0.5
2	DB1	--	520	P1	LHSV 1	0.6
3	DB1	--	540	P1	LHSV 1	1.0
4	DB1	--	520	P3	LHSV 1	1.5
5	DB1	--	540	P3	LHSV 1	2.7
6	DB1	--	540	P2	LHSV 1	1.5
7	DB1	--	520	P2	LHSV 1	1.2
8	Propane	--	540	P2	LHSV 1	0.4
9	Butane	--	540	P1	LHSV 1	0.5
10	Butane	--	540	P2	LHSV 1	0.7
11	Propylene	Nitrogen	540	P2	LHSV 1A	1.2
12	Butylene	Nitrogen	540	P2	LHSV 1B	7.9
13	IB1	Ethane	540	P1	LHSV 1	0.7
14	IB1	Ethane	540	P1	LHSV 2	0.7
15	IB1	Ethane	540	P3	LHSV 2	0.6
16	IB1	Ethane	540	P3	LHSV 3	0.6
17	DB2	--	540	P2	LHSV 1	3.8
18	DB3	--	540	P2	LHSV 1	7.3

Notes:

(a) DB1, DB2, and DB3 refer to Direct Blends 1, 2, and 3 as described in Section 4.3. DB1 and DB2 are Arge-type blends, and DB3 is a Synthol-type blend. IB1 is an Indirect Cyclar blend (Arge type).

(b) P2 = 1.5 x P1
P3 = 3.0 x P1

(c) LHSV 2 = 1.25 x LHSV 1
LHSV 3 = 2.50 x LHSV 1
LHSV 1A = with respect to propylene content of DB1
LHSV 1B = with respect to butene content of DB1

(d) Run No. 3 carbon chosen as reference and defined as 1.00. All other runs are weight ratios with the Run No. 3 carbon level in the denominator.

TABLE 6.2

Cyclar Pilot Plant Performance

Parameter	Measurement in Cyclar Pilot Plant	Impact on Commercial Unit
Catalytic Activity	Conversion (wt-%) of LPG feed out of the C_3-C_5 hydrocarbon range for a specific reactor inlet temperature.	Unit size, recycle rate, heater design, utility consumption, catalyst requirements.
Conversion Stability	Rate of conversion declines as a function of time on-stream.	CCR size and catalyst circulation rate.
Aromatics Selectivity	Mass of all aromatics products divided by the total mass of LPG converted.	Liquid product yield.
Hydrogen Selectivity	Mass of hydrogen product divided by the total mass of LPG converted.	Coproduct hydrogen yield.
Fuel Gas Selectivity	Mass of C_1 + C_2 product divided by the total mass of LPG converted.	Net utility import and export.
Spent-Catalyst Coke	Wt-% carbon on spent catalyst.	CCR design (to accomplish regeneration).
Liquid-Product Distribution	Distribution (wt-%) of benzene, toluene, xylenes + EB and heavy aromatics in liquid product.	Value of liquid product.

TABLE 6.3

Comparison between Propane and Butane Feedstocks at Base Conditions

	Feedstocks	
	Propane	Butane
Run No.	1	9
Temperature, °C	540	540
Pressure	P1	P1
LHSV, 1/hr	LHSV 1	LHSV 1
Midrun Conversions, Wt-%		
C_3=	--	--
C_3	67.4	--
C_4=	--	--
C_4	--	95.7
C_5=	--	--
C_5	--	--
C_3-C_5	64.3	77.2
Midrun Selectivities, Wt-%		
H_2	5.2	4.8
$C_1 + C_2$	37.0	30.8
Benzene	19.2	17.1
Toluene	24.2	28.2
Xylenes + EB	9.9	13.9
C_9+ Aromatics	4.5	5.2
Total Aromatics	57.8	64.4

TABLE 6.4

Comparison between Propane and Propylene Feedstock Results

	Feedstocks	
	Propane	Propylene
Run No.	8	11
Temperature, °C	540	540
Pressure	P2	P2
LHSV, 1/hr	LHSV 1	LHSV 1
Midrun Conversions, Wt-%		
$C_3=$	--	99.2
C_3	75.8	--
$C_4=$	--	--
C_4	--	--
$C_5=$	--	--
C_5	--	--
C_3-C_5	73.5	90.1
Midrun Selectivities, Wt-%		
H_2	4.3	2.1
$C_1 + C_2$	41.7	25.3
Benzene	16.1	18.3
Toluene	22.6	30.8
Xylenes + EB	10.1	14.8
C_9+ Aromatics	5.2	8.7
Total Aromatics	54.0	72.6

TABLE 6.5

Comparison between Butane and Butylene Feedstock Results

	Feedstocks	
	Butane	Butylene
Run No.	10	12
Temperature, °C	540	540
Pressure	P2	P2
LHSV, 1/hr	LHSV 1	LHSV 1
Midrun Conversions, Wt-%		
C_3=	--	--
C_3	--	--
C_4=	--	100.0
C_4	98.9	--
C_5=	--	--
C_5	--	--
C_3-C_5	81.7	84.1
Midrun Selectivities, Wt-%		
H_2	4.1	1.8
C_1 + C_2	34.8	25.1
Benzene	15.3	14.8
Toluene	26.5	31.4
Xylenes + EB	13.3	18.1
C_9+ Aromatics	6.0	8.8
Total Aromatics	61.1	73.1

TABLE 6.6

Comparison between Propane and Direct Blend 1 Feedstock Results

	Feedstocks	
	Propane	Direct Blend 1
Wt-% Paraffins	100	62
Wt-% Olefins	0	38
Run No.	1	3
Temperature, °C	540	540
Pressure	P1	P1
LHSV, 1/hr	LHSV 1	LHSV 1
Midrun Conversions, Wt-%		
$C_3=$	--	92.5
C_3	67.4	28.5
$C_4=$	--	98.2
C_4	--	83.3
$C_5=$	--	100.0
C_5	--	100.0
C_3-C_5	64.3	65.1
Midrun Selectivities, Wt-%		
H_2	5.2	4.1
$C_1 + C_2$	37.0	26.0
Benzene	19.2	17.5
Toluene	24.2	30.2
Xylenes + EB	9.9	15.8
C_9+ Aromatics	4.5	6.4
Total Aromatics	57.8	69.9

TABLE 6.7

Effects of Direct Cyclar Feed Olefinicity

Feedstock	DB1	DB2	DB3
Wt-% Olefins	38.04	46.88	72.77
Run No.	6	17	18
Temperature, °C	540	540	540
Pressure	P2	P2	P2
LHSV, 1/hr	LHSV 1	LHSV 1	LHSV 1
Midrun Conversions, Wt-%			
C_3=	95.6	96.1	97.0
C_3	50.7	39.3	-19.3*
C_4=	92.0	98.9	99.4
C_4	99.0	89.5	62.2
C_5=	100.0	100.0	--
C_5	100.0	100.0	--
C_3-C_5	76.8	77.8	73.3
Midrun Selectivities, wt-%			
H_2	3.5	3.7	3.2
C_1 + C_2	31.0	26.7	22.2
Benzene	16.0	15.2	14.9
Toluene	27.9	29.5	32.1
Xylenes + EB	14.1	15.9	18.7
C_9+ Aromatics	7.5	9.0	8.9
Total Aromatics	65.5	69.6	74.6

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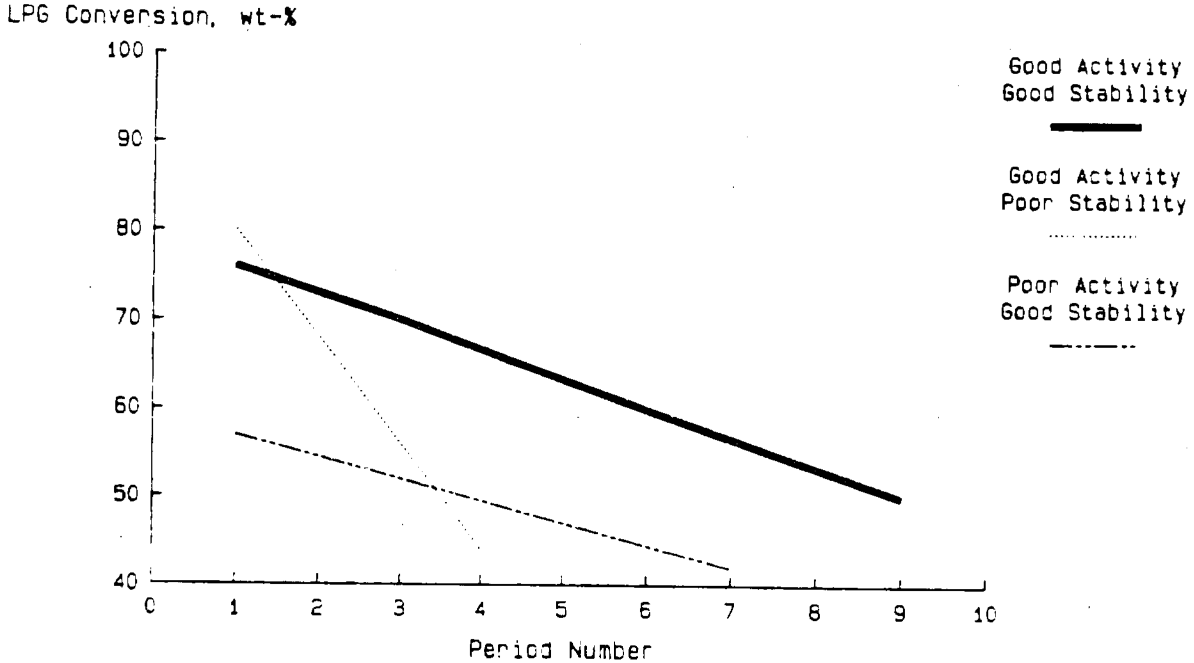
* Negative number indicates accumulation across reactor rather than conversion.

FIGURE 6.1

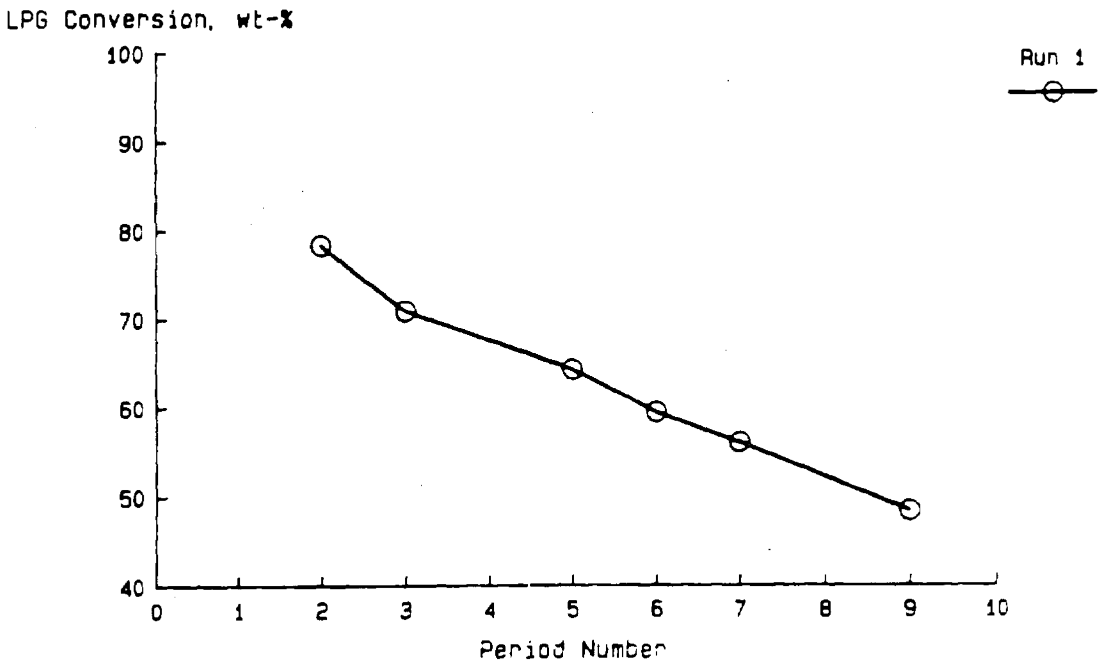
Activity and Stability Information



Propane Feedstock
540 C / P1 / LHSV1
Prototype Catalyst

FIGURE 6.2

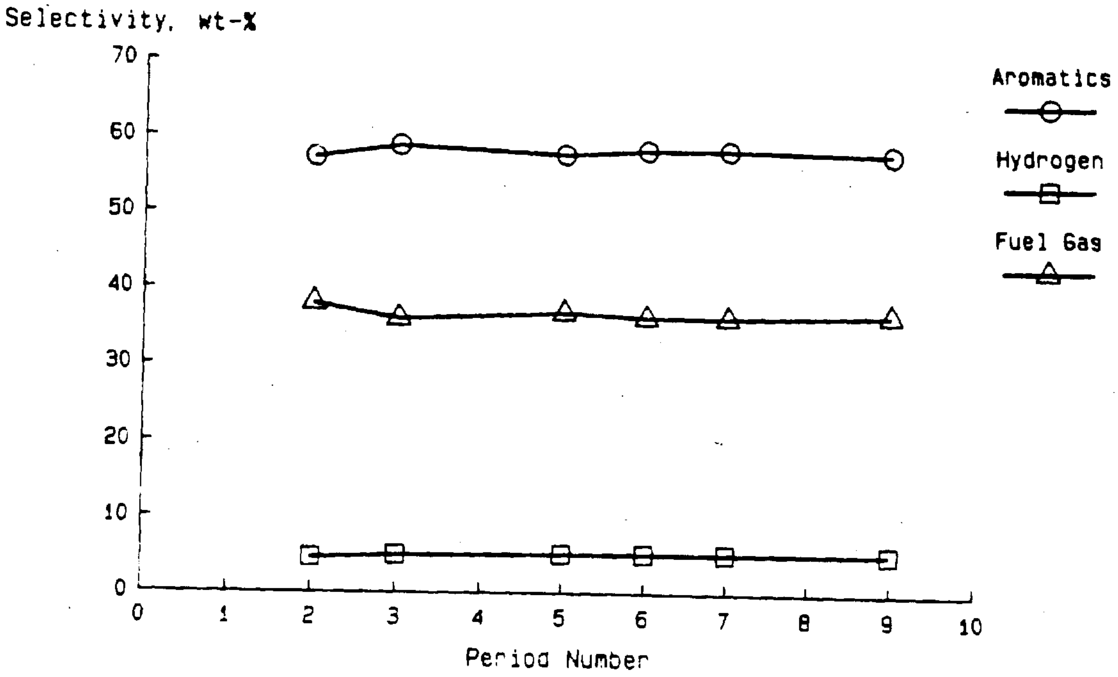
Propane Feedstock at Base Case Conditions



Propane Feedstock
540 C / Pi / LHSV 1
Prototype Catalyst

FIGURE 6.3

Aromatics, Hydrogen and Fuel Gas Selectivities

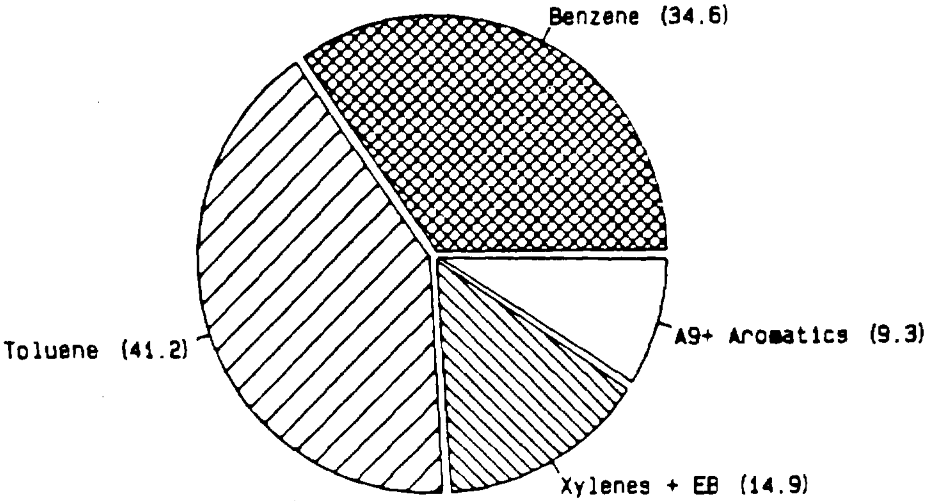


Propane Feedstock
540 C / P1 / LHSV 1

UOP 1681-17

FIGURE 6.4

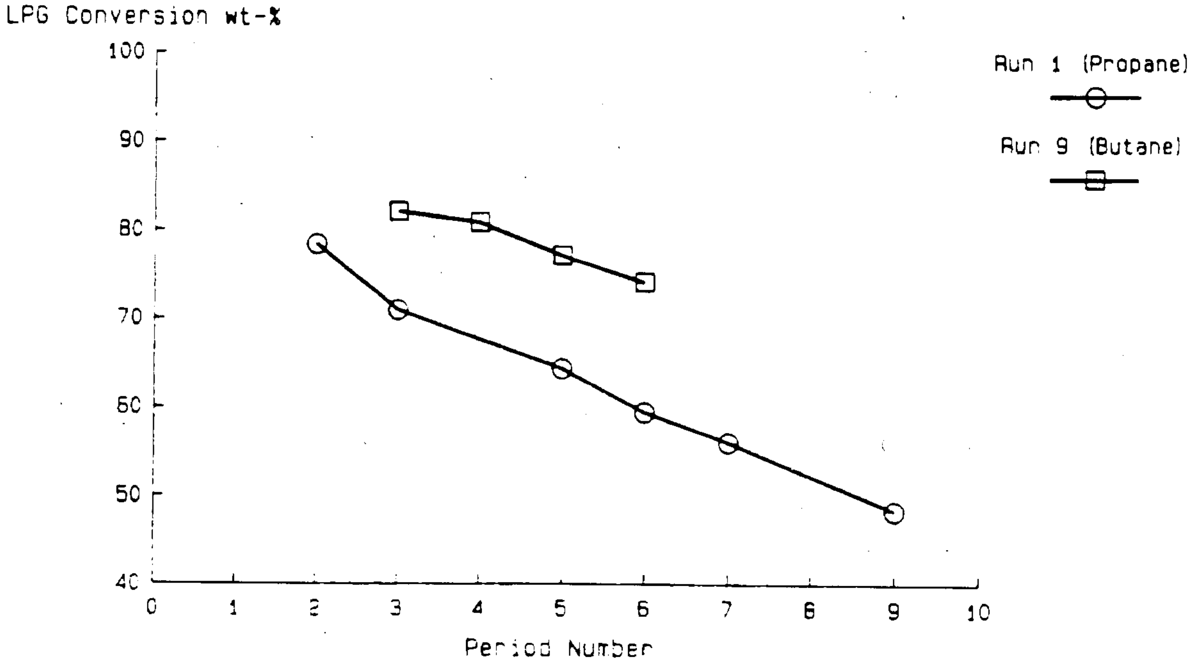
Aromatics Breakdown for Propane Feedstock
( ) = wt-% of Liquid Product



540 C / P1 / LHSV 1
Run 1 / Period 2
78.4 wt-% Conversion

FIGURE 6.5

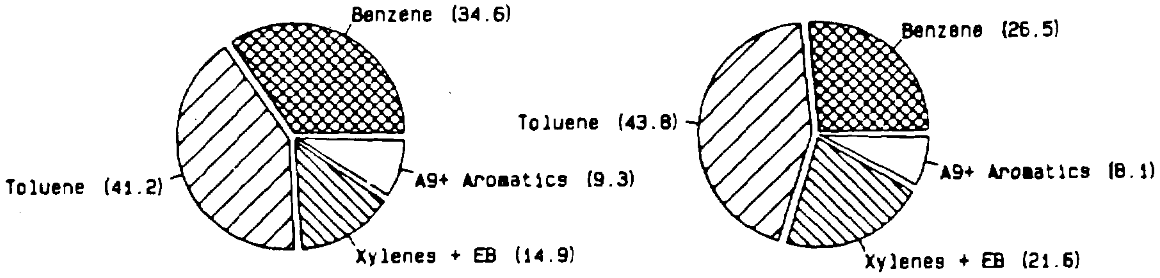
Propane vs Butane Temperature Performance



Pure Component LPG Feeds
540 C / P1 / LHSV 1

FIGURE 6.6

Aromatics Breakdown for Propane and Butane Feeds
( ) = wt-% of Liquid Product



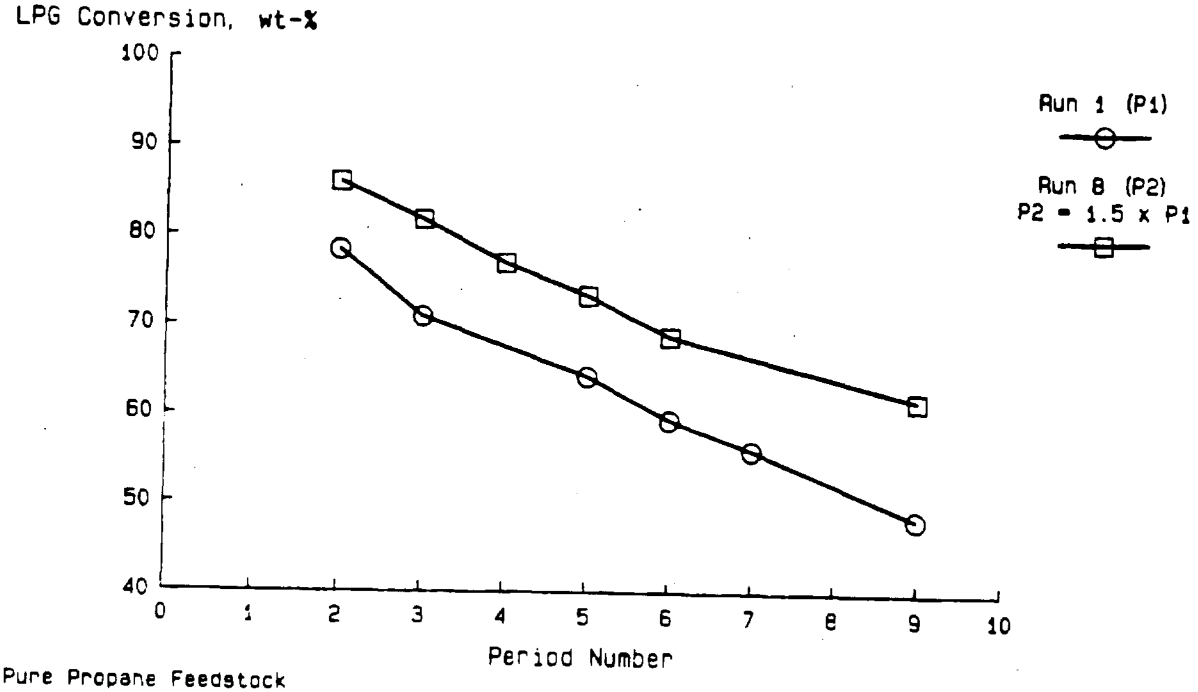
Propane Feedstock
78.4 wt-% LPG Conversion

Butane Feedstock
77.2 wt-% LPG Conversion

540 C / P1 / LHSV 1
Propane: Run 1 / Period 2
Butane: Run 9 / Period 5

FIGURE 6.7

Effect of Pressure on Conversion
Pure Propane Feedstock

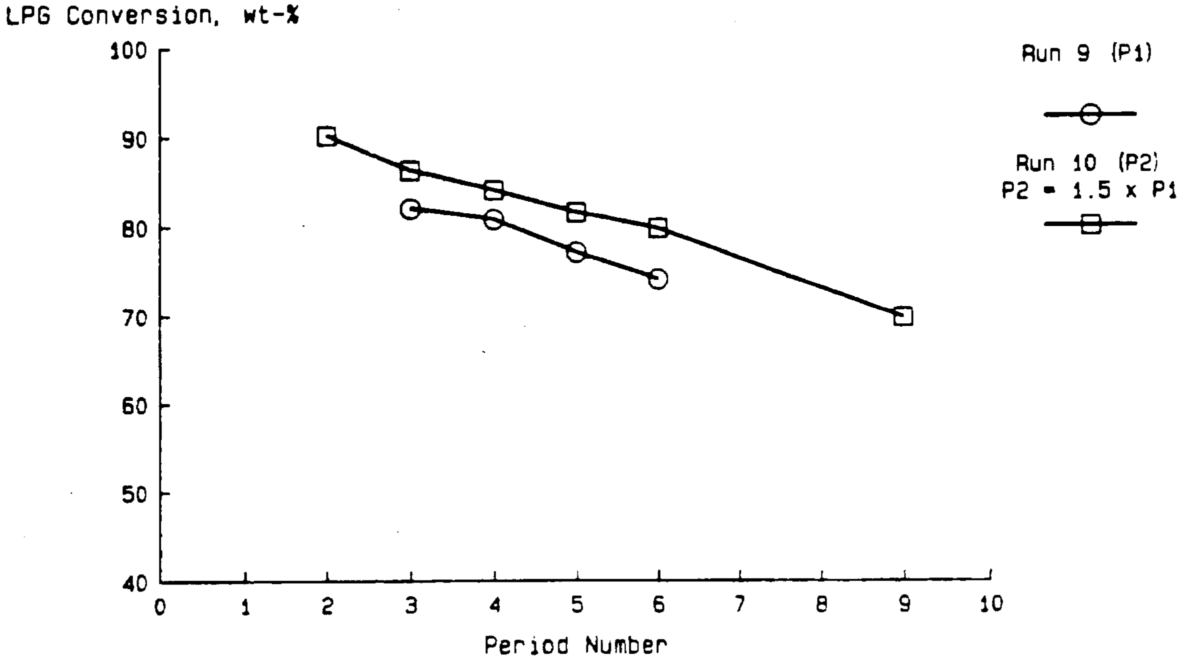


Pure Propane Feedstock
540 C / LHSV 1
Prototype Catalyst

UOP 166-2

FIGURE 6.8

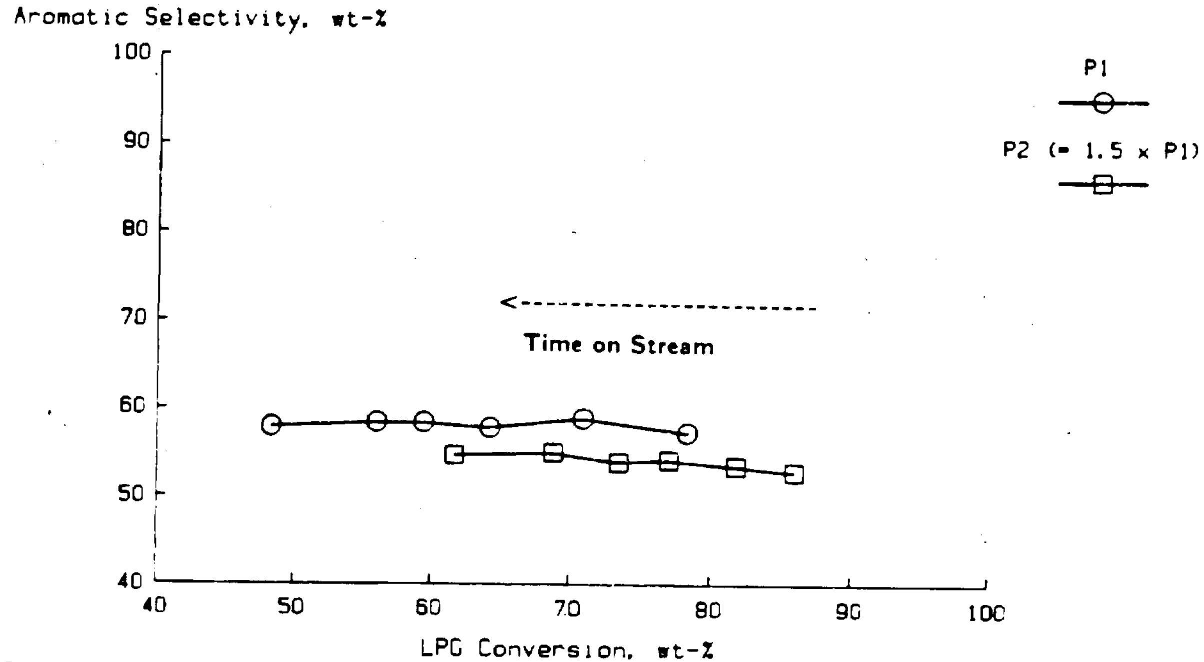
Effect of Pressure on Conversion
Pure Butane Feedstock



Pure Butane Feedstock
540 C / LHSV 1
Prototype Catalyst

FIGURE 6.9

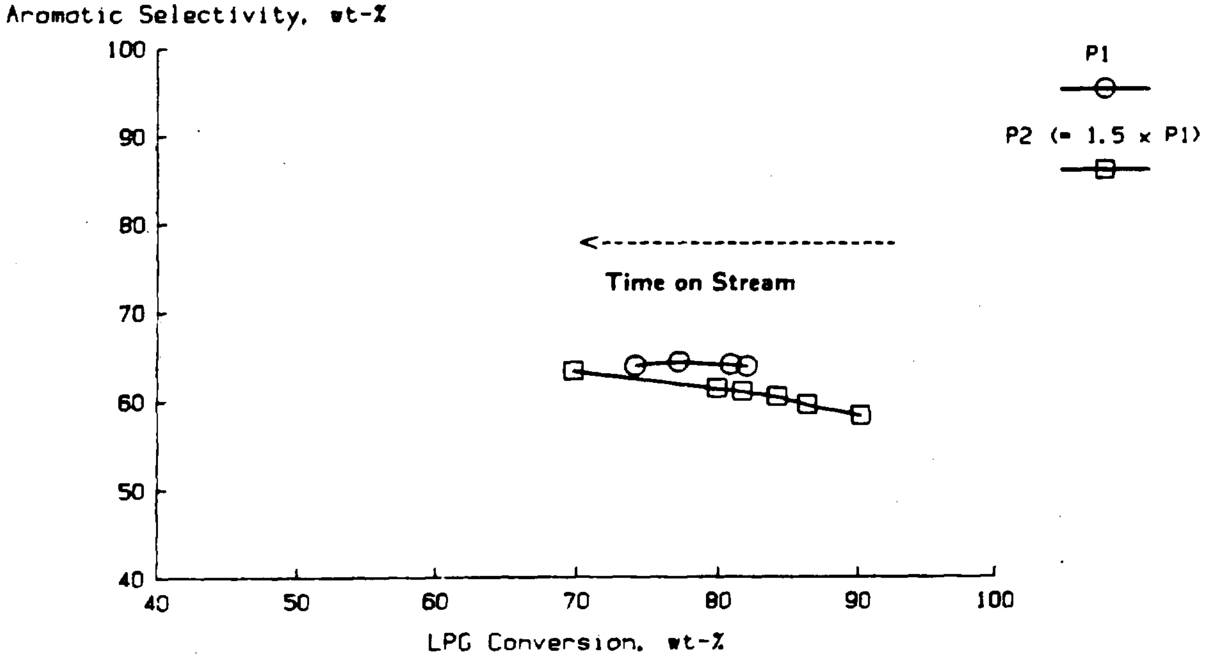
Effect of Pressure on Aromatic Selectivity
Propane Feedstock



540 C / LHSV 1
P1: Run 1
P2: Run 8

FIGURE 6.10

Effect of Pressure on Aromatic Selectivity
Butane Feedstock

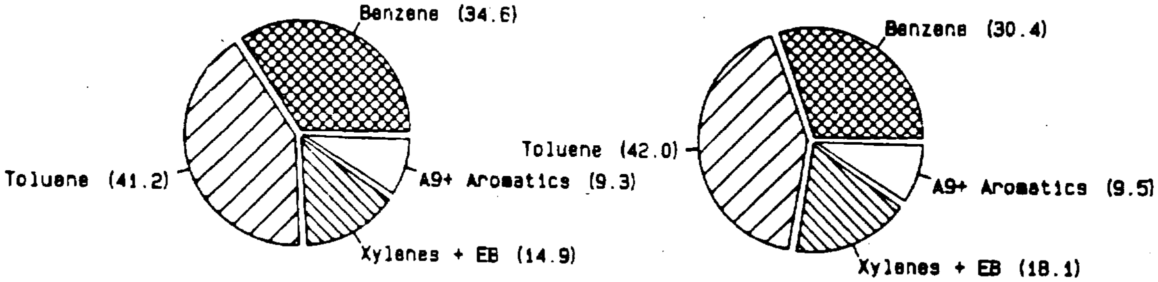


540 C / LHSV 1
P1: Run 9
P2: Run 10

UOP 1681-24

FIGURE 6.11

Effect of Pressure on Liquid Product
Propane Feedstock
( ) = wt-% of Liquid Product



Base Pressure, P1
78.4 wt-% LPG Conversion

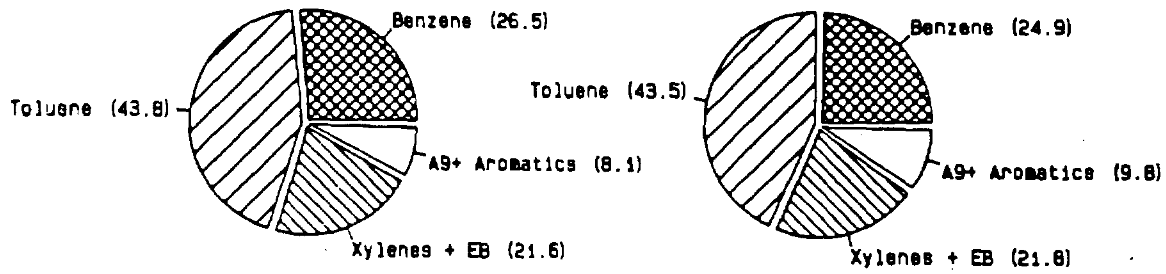
P2 = 1.5 x P1
77.1 wt-% LPG Conversion

540 C / LHSV 1
P1 = Run 1 / Period 2
P2 = Run 8 / Period 4

UOP 1681-25

FIGURE 6.12

Effect of Pressure on Liquid Product
Butane Feedstock
( ) = wt-% of Liquid Product



Base Pressure, P1
77.2 wt-% LPG Conversion

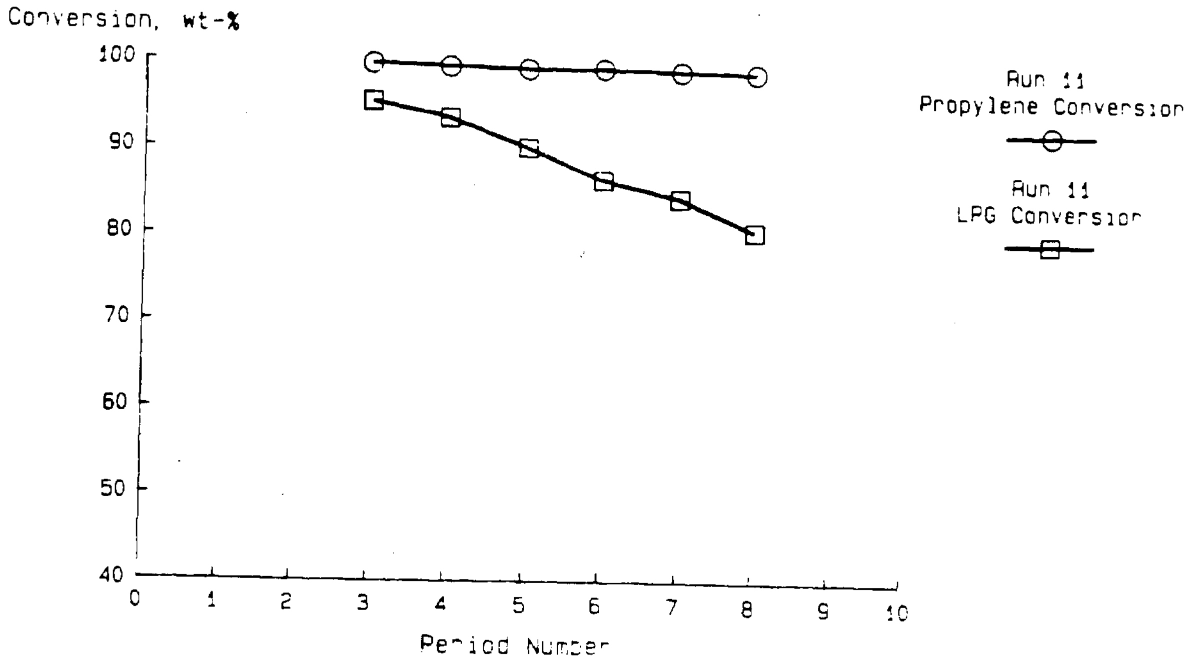
P2 = 1.5 x P1
81.7 wt-% LPG Conversion

540 C / LHSV 1
P1 = Run 9 / Period 5
P2 = Run 10 / Period 5

UOP 166[illegible]-26

FIGURE 6.13

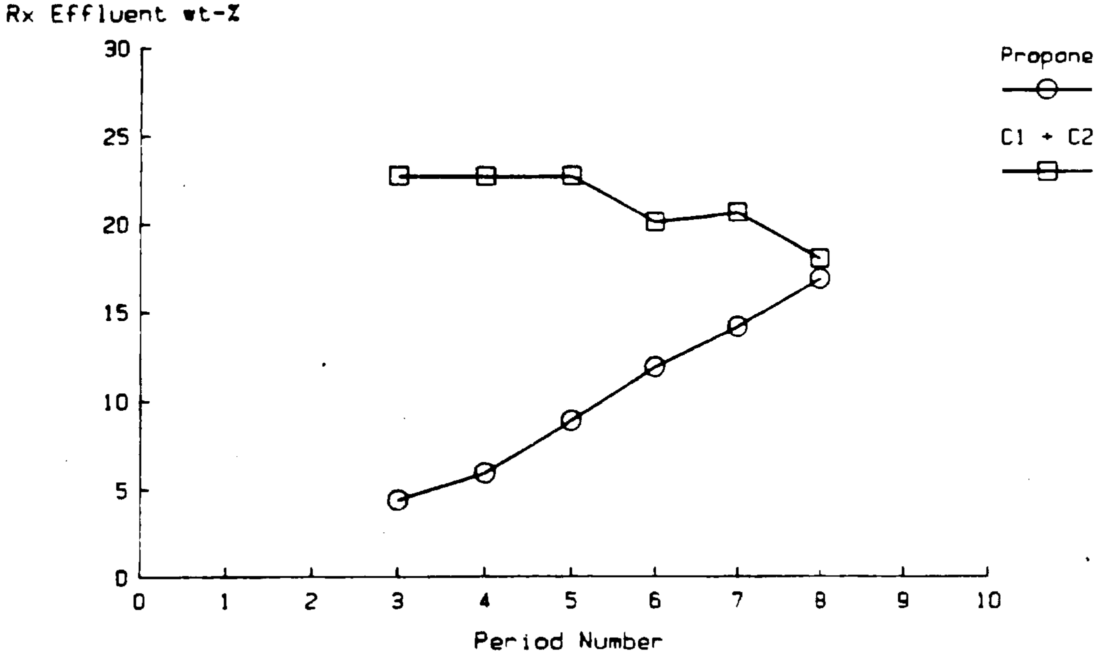
Propylene vs LPG Conversion



Propylene / N2 On-line Feed Blending
540 C / P2

FIGURE 6.14

Hydrogenation of Propylene
Run 11 Reactor Effluent Compositions

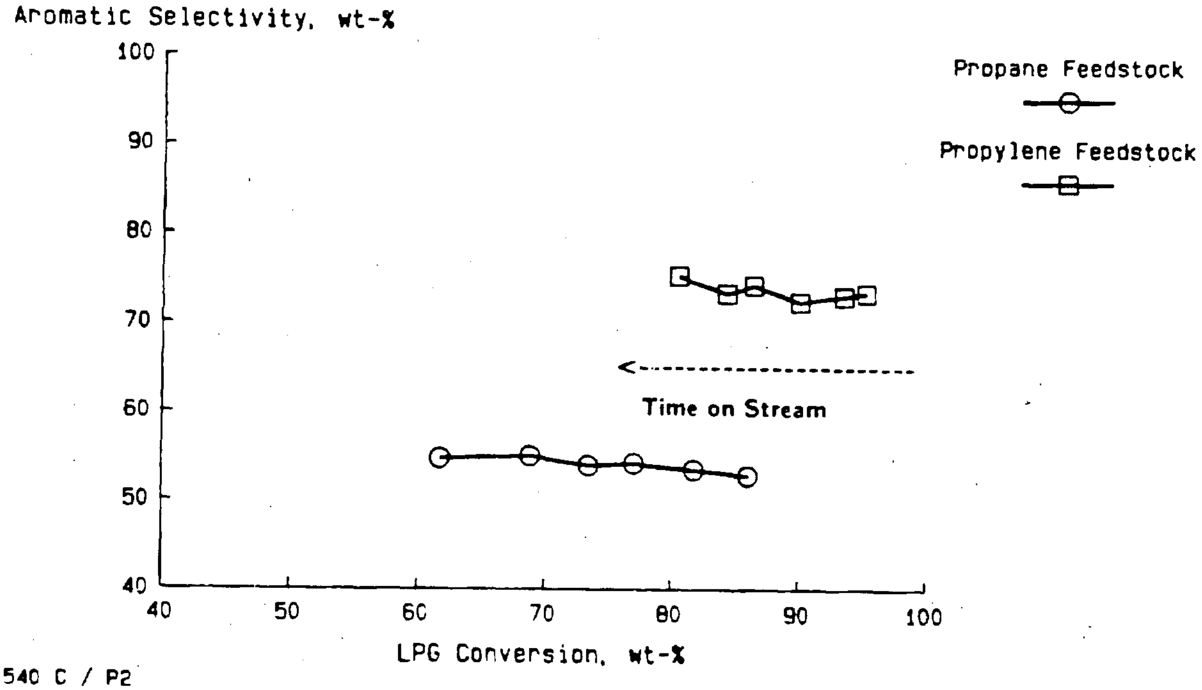


540 C / P2
Pure Propylene Feedstock

UOP 164-25

FIGURE 6.15

Aromatic Selectivity vs LPG Conversion
Propane / Propylene Comparison

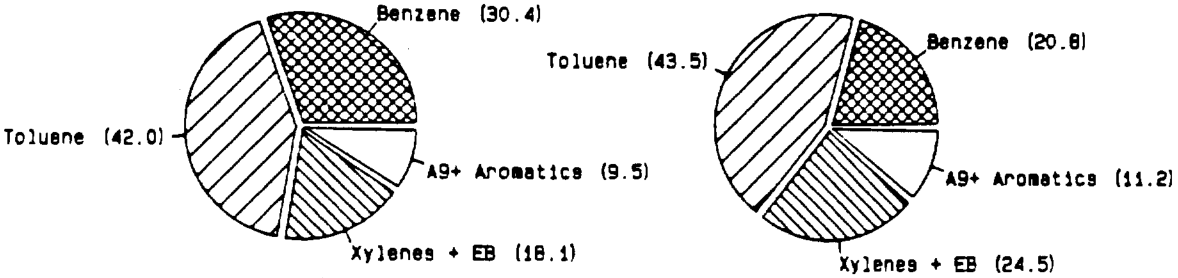


540 C / P2
Propane: Run 8
Propylene: Run 11

UOP 168- 29

FIGURE 6.16

Effect of Olefins on Liquid Product
Propane vs Propylene Feedstock
( ) = wt-% of Liquid Product



Propane Feedstock
77.1 wt-% LPG Conversion

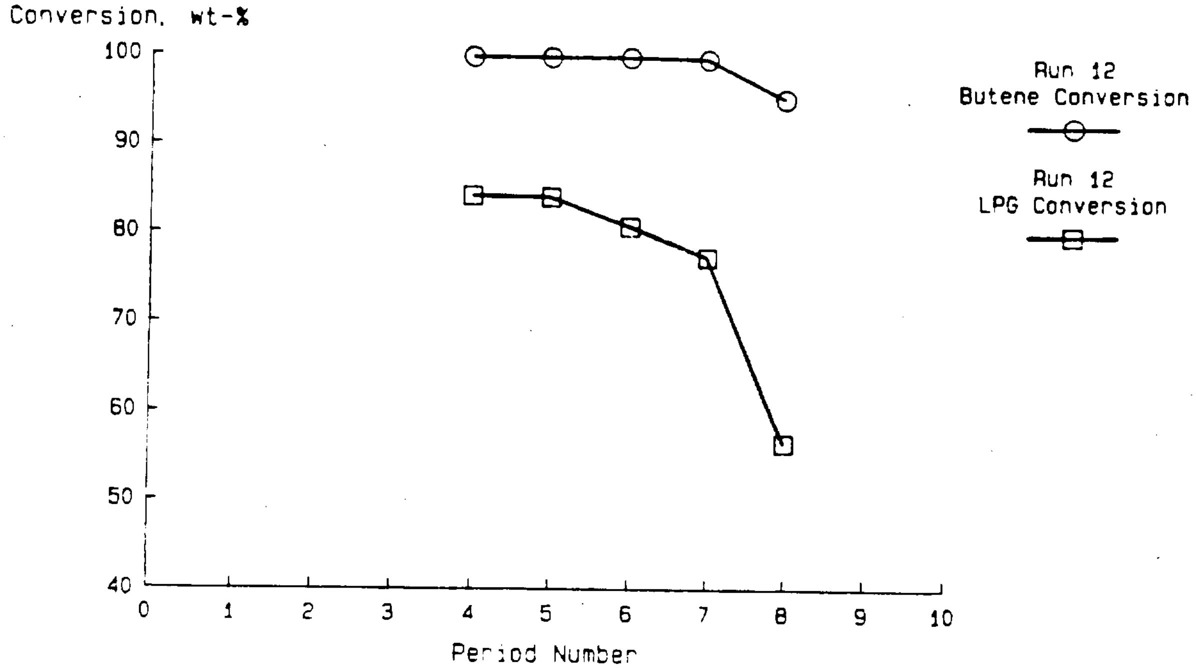
Propylene Feedstock
80.6 wt-% LPG Conversion

540 C / P2
Propane = Run 8 / Period 4
Propylene = Run 11 / Period 8

UOP 1681-30

FIGURE 6.17

Butene vs LPG Conversion

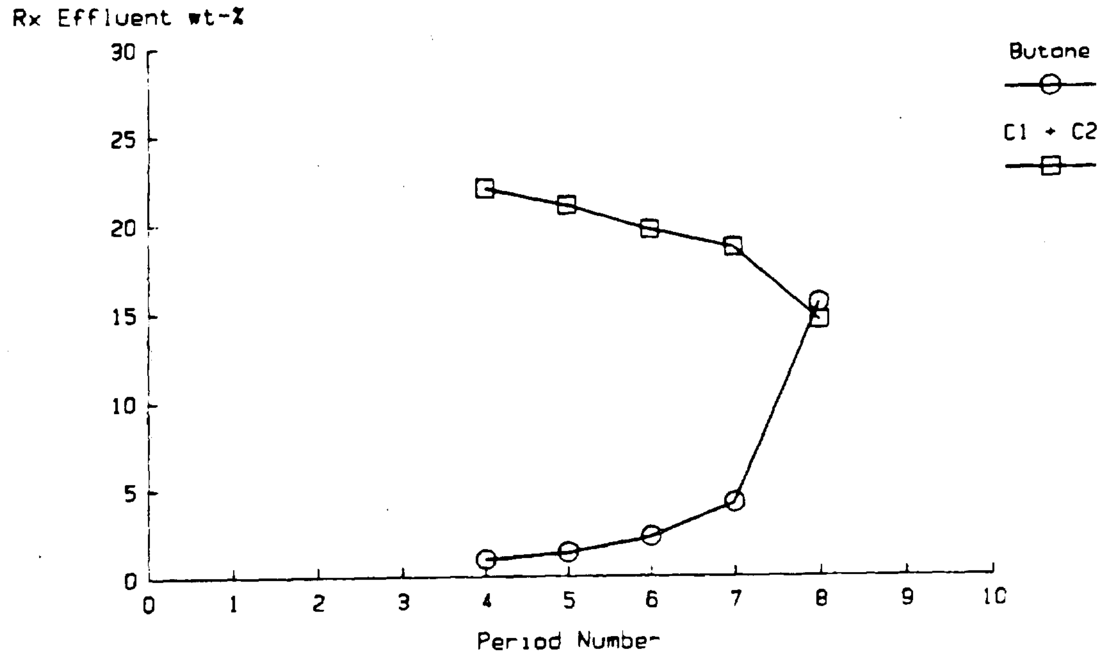


Butene / N2 On-line Feed Blending
540 C / P2

UOP 1561-3

FIGURE 6.18

Hydrogenation of Butene
Run 12 Reactor Effluent Compositions

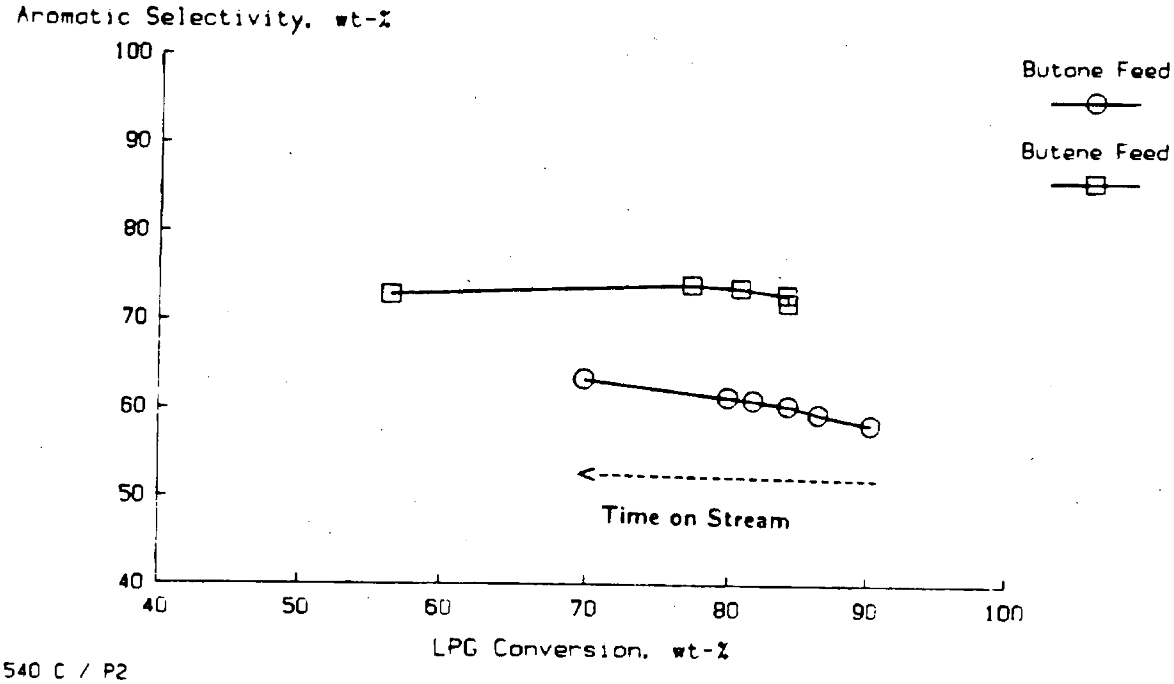


540 C / P2
Pure Butene Feedstock

UOP [illegible]

FIGURE 6.19

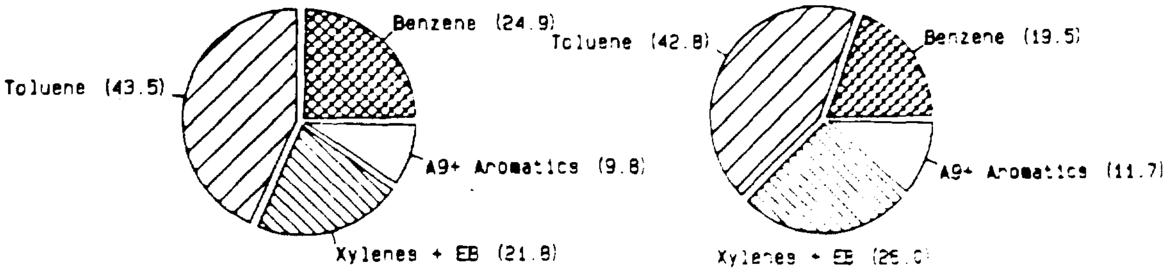
Aromatic Selectivity vs LPG Conversion
Butane / Butene Comparison



540 C / P2
Butane: Run 10
Butene: Run 12

FIGURE 6.20

Effect of Olefins on Liquid Product
Butane vs Butene Feedstocks
( ) = wt-% of Liquid Product



Butane Feedstock
81.7 wt-% LPG Conversion

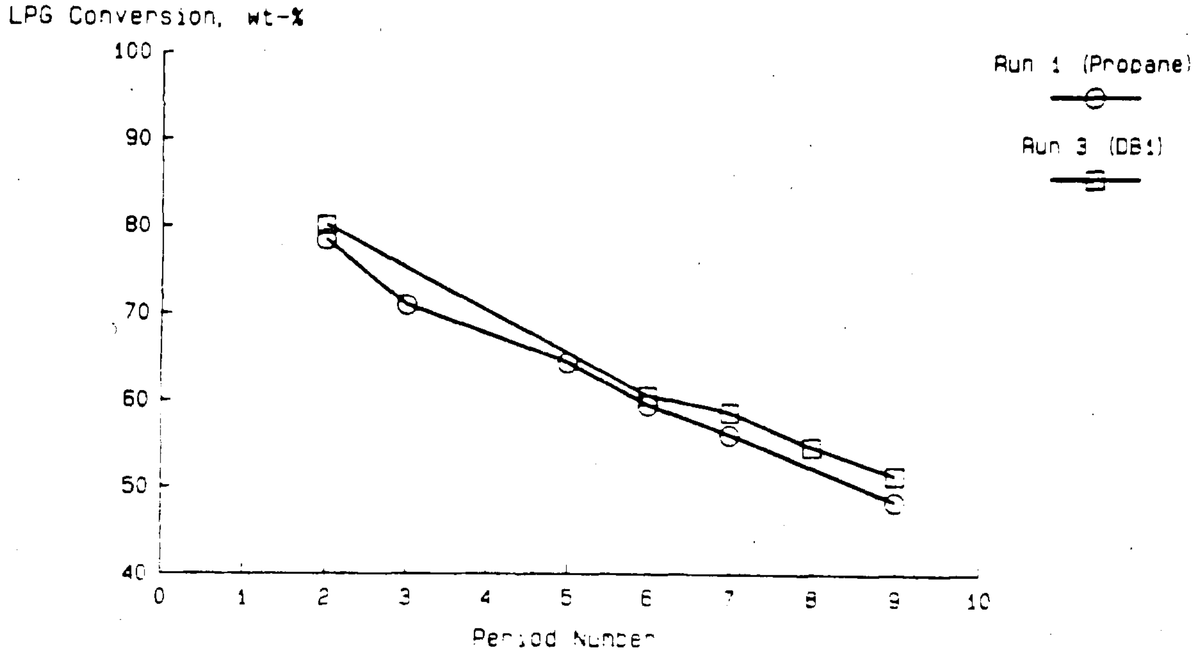
Butene Feedstock
80.8 wt-% LPG Conversion

540 C / P2
Butane = Run 10 / Period 5
Butene = Run 12 / Period 6

[illegible]

FIGURE 6.21

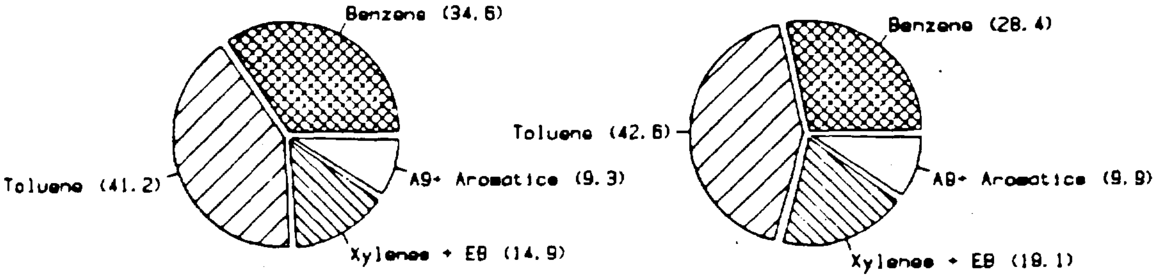
Direct Blend 1 Temperature Performance
Comparison to Propane Feedstock



540 C / P1 / LHSV 1 (Base Conditions)
Propane (Run 1)
DB1 (Run 3)

FIGURE 6.22

Direct Cyclar Blend 1 Liquid Product
Comparison to Propane at Base Conditions
( ) = wt-% of Liquid Product



Propane Feedstock
78.4 wt-% LPG Conversion

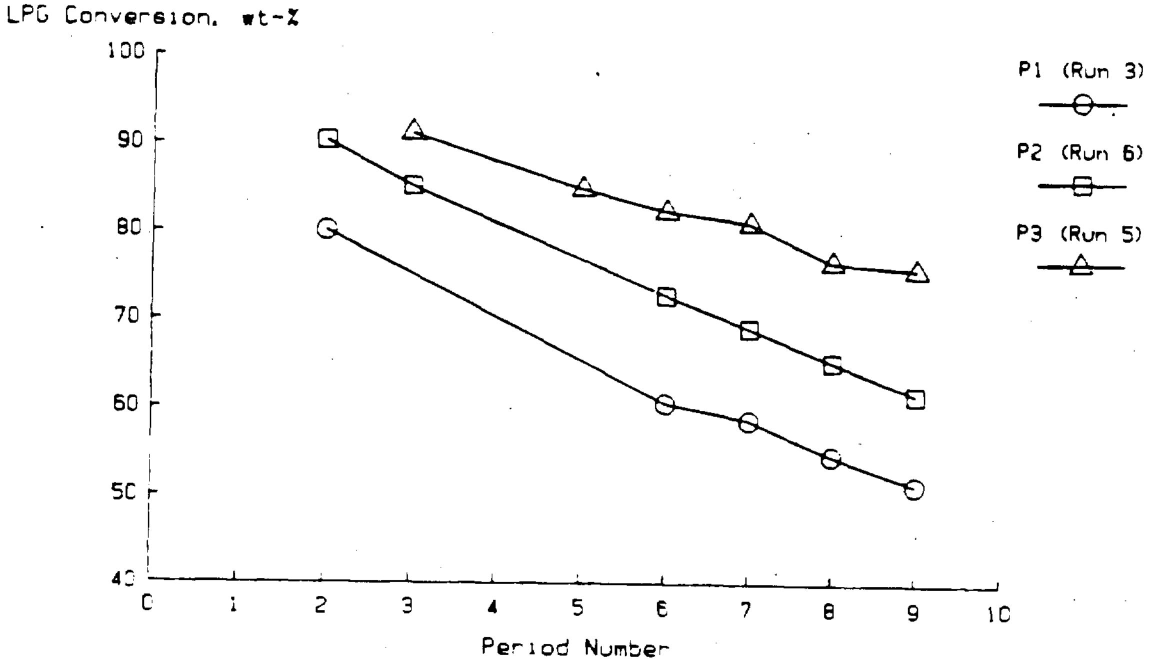
Direct Blend 1
80.1 wt-% LPG Conversion

54C C / P1 / LHSV 1
Propane: Run 1 / Period 2
DB1: Run 3 / Period 2

UOP 166[illegible]

FIGURE 6.23

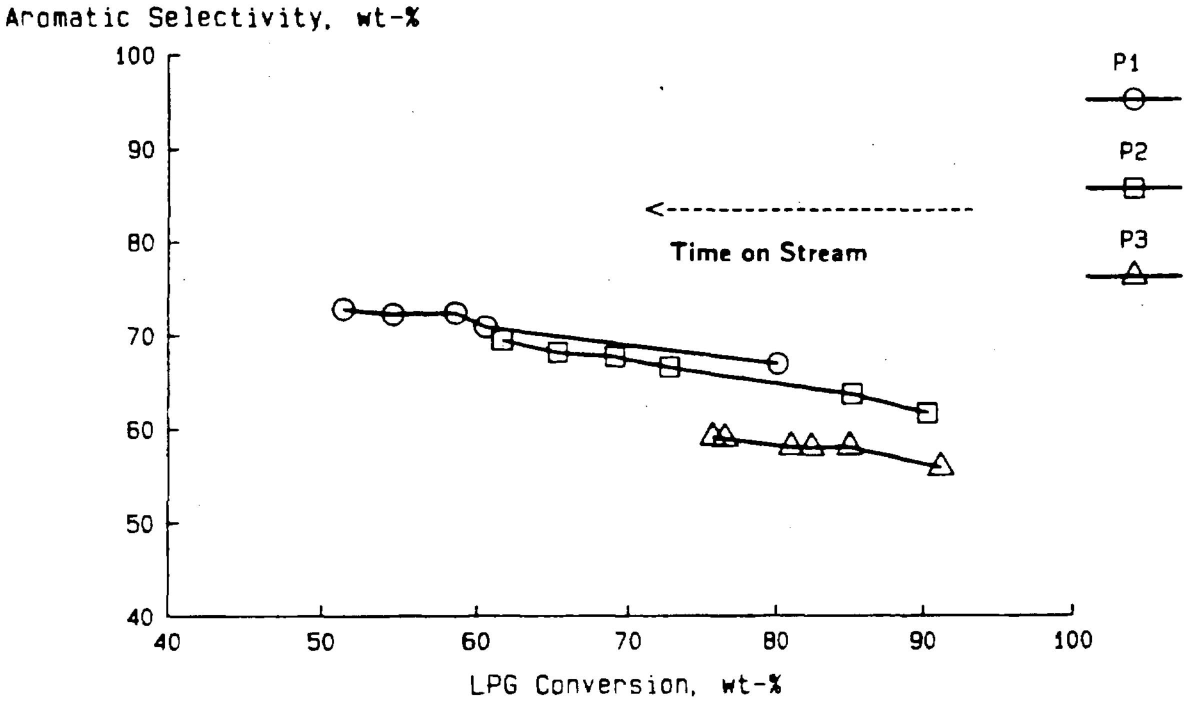
Effect of Pressure on Conversion
Direct Blend 1



540 C / LHSV 1
P2 = 1.5 x P1
P3 = 3.0 x P1

FIGURE 6.24

Effect of Pressure on Aromatic Selectivity
Direct Blend 1 at 540 C Rx Inlet

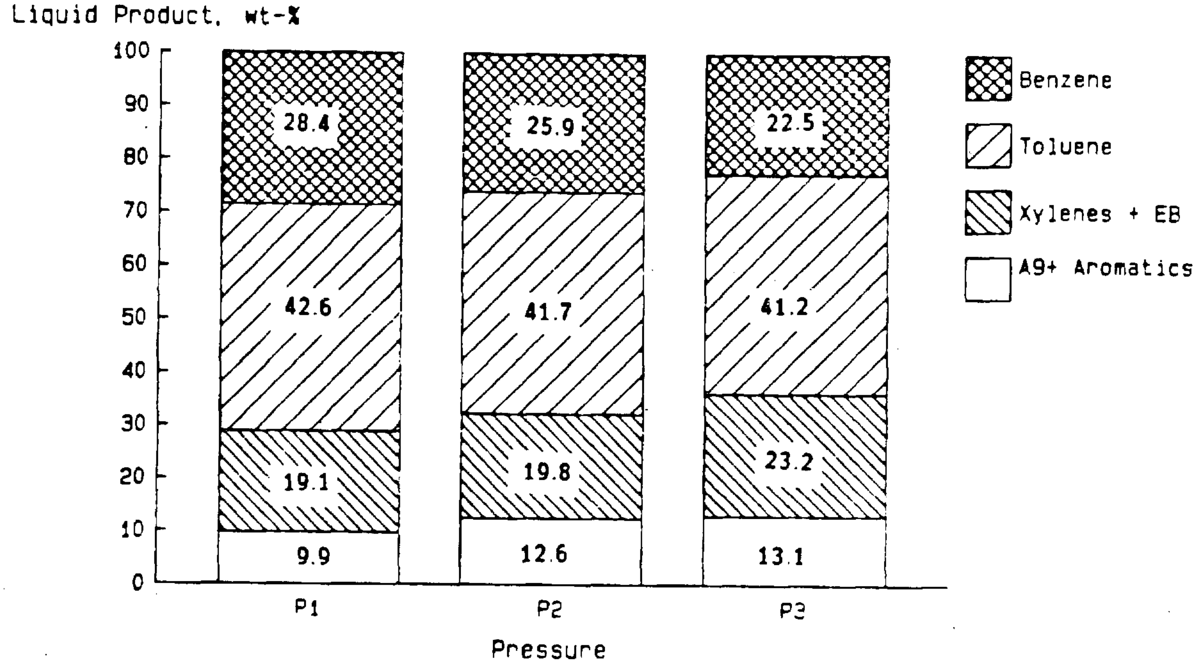


540 C / LHSV 1
P1 (Run 3) / P2 (Run 6) / P3 (Run 5)
P2 = 1.5 x P1 / P3 = 3.0 x P1

UOP 1681-36

FIGURE 6.25

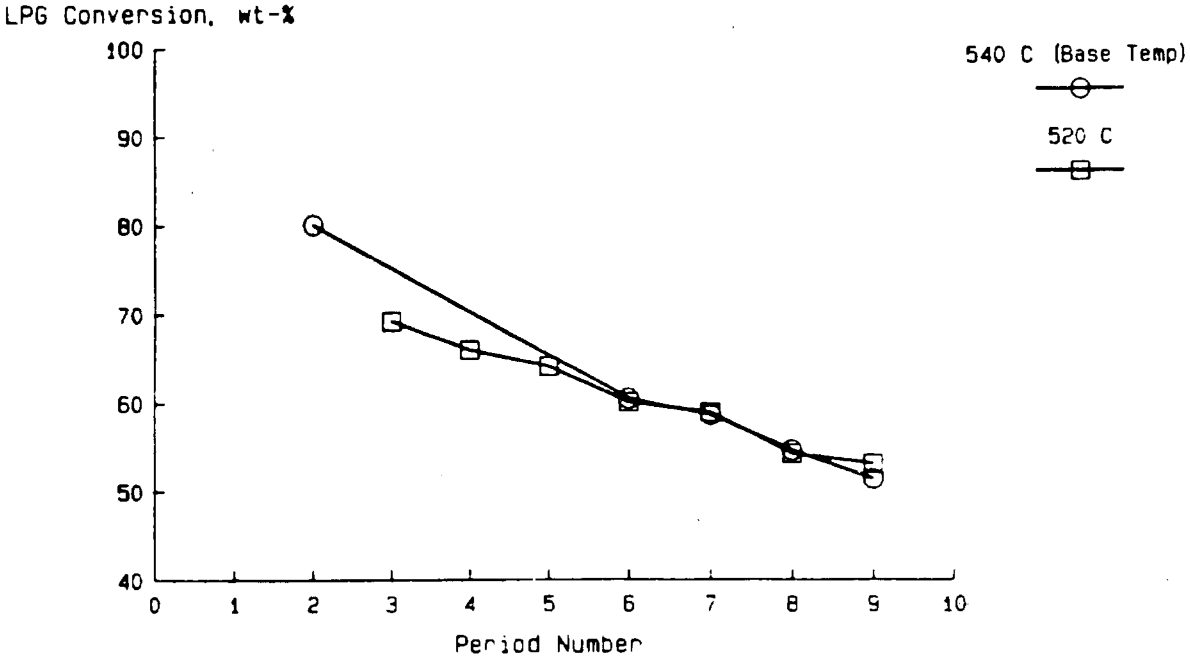
Effect of Pressure on Liquid Product
Direct Blend 1 / 38 wt-% Olefins in Feed



540 C / LHSV 1
P2 = 1.5 x P1
P3 = 3.0 x P1

FIGURE 6.26

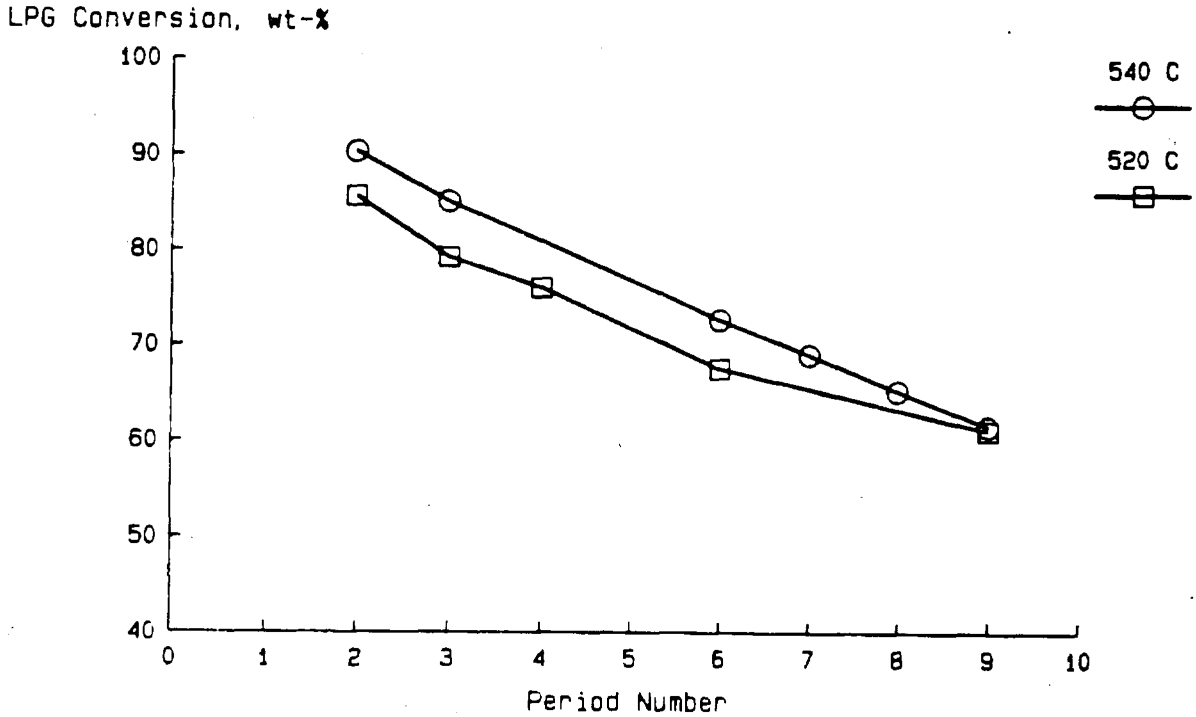
Effect of Temperature on Conversion
Direct Blend 1 Feedstock



P1 / LHSV 1
540 C (Run 3)
520 C (Run 2)

FIGURE 6.27

Effect of Temperature on Conversion
Direct Blend 1 Feedstock at P2

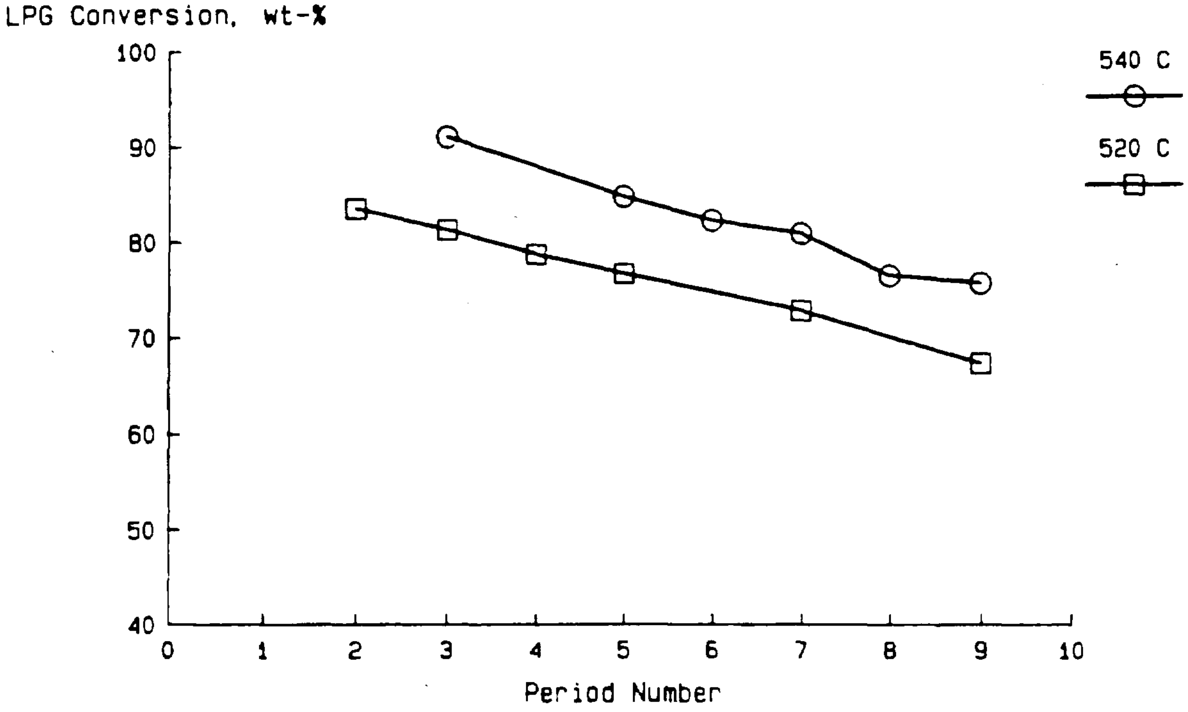


P2 / LHSV 1
540 C (Run 6)
520 C (Run 7)

UOP 1681-41

FIGURE 6.28

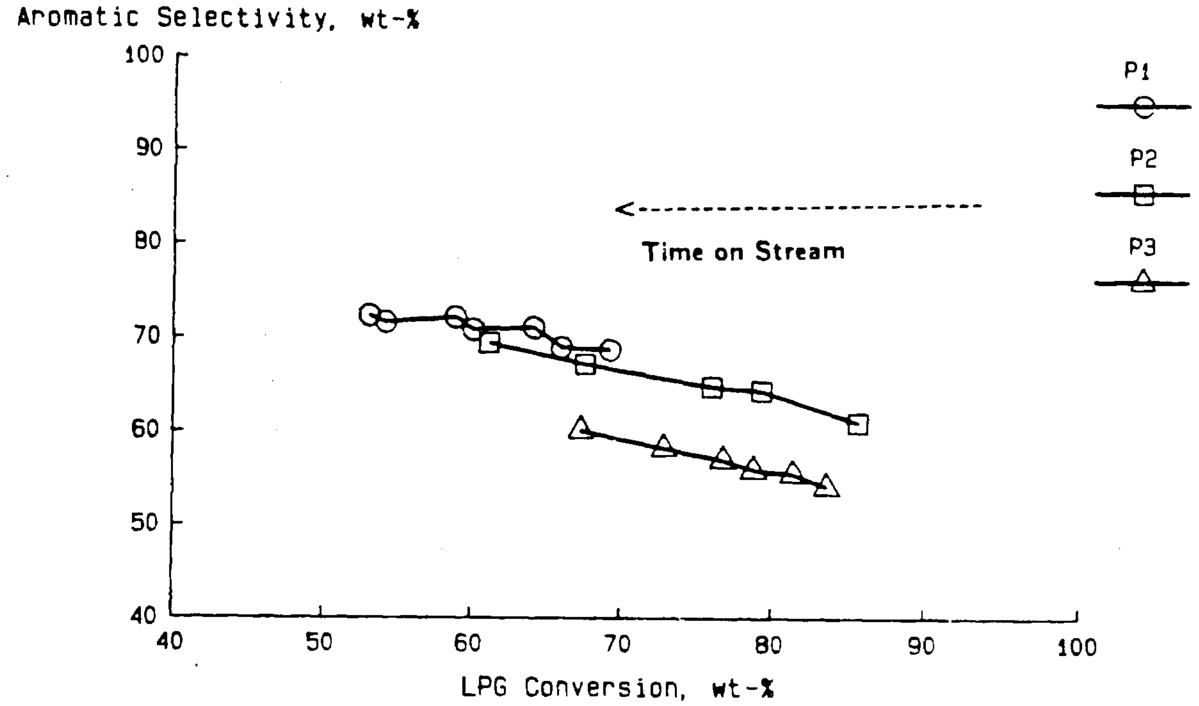
Effect of Temperature on Conversion
Direct Blend 1 Feedstock at P3



P3 / LHSV 1
540 C (Run 5)
520 C (Run 4)

FIGURE 6.29

Effect of Pressure on Aromatic Selectivity
Direct Blend 1 at 520 C Rx Inlet

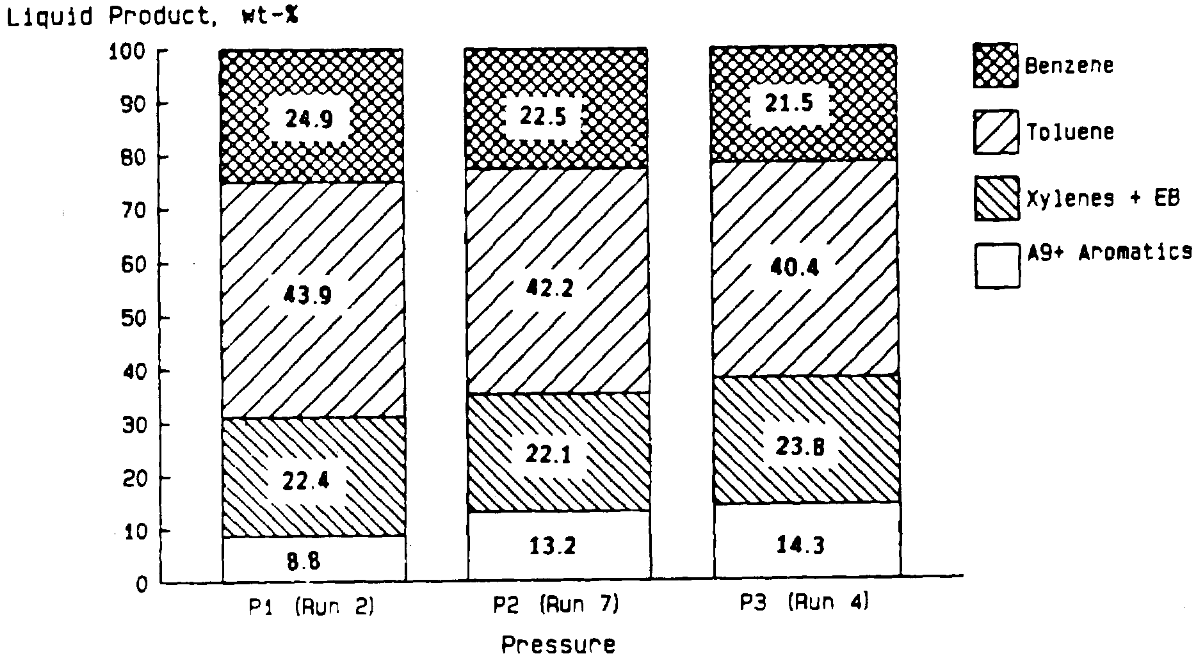


520 C / LHSV 1
P1 (Run 2) / P2 (Run 7) / P3 (Run 4)
P2 = 1.5 x P1 / P3 = 3.0 x P1

UOP 1681-43

FIGURE 6.30

Effect of Pressure on Liquid Product
520 C Reactor Inlet Temperature

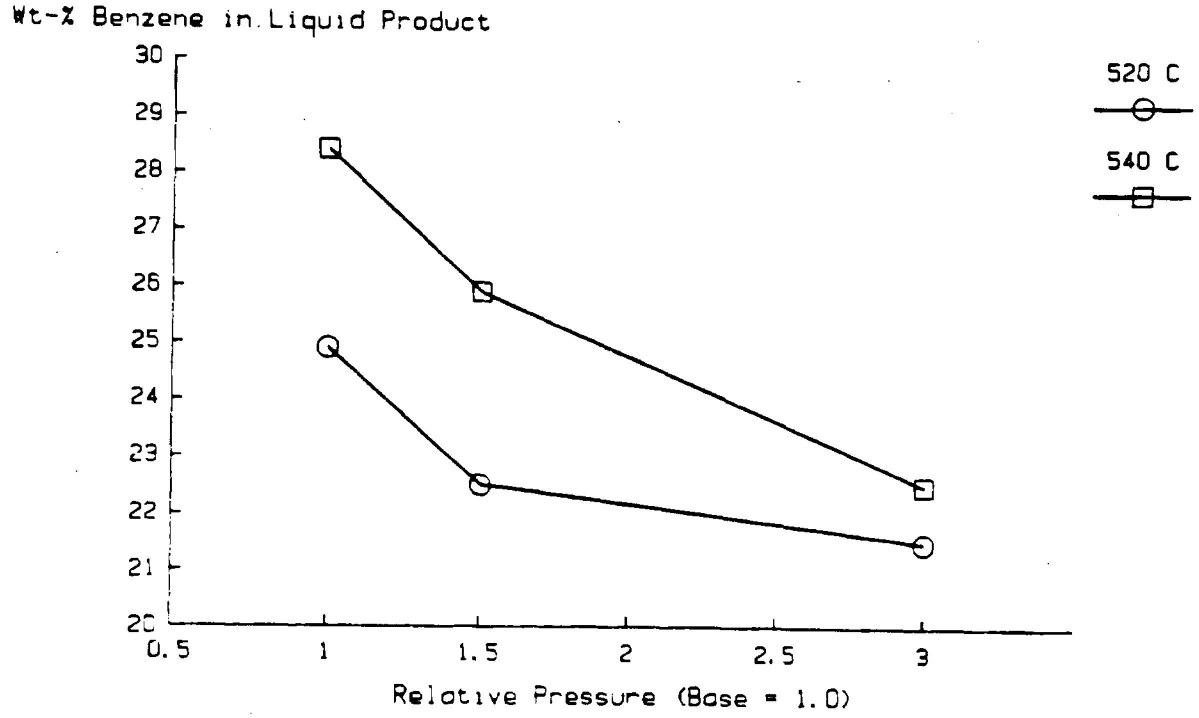


520 C / LHSV 1
P2 = 1.5 x P1
P3 = 3.0 x P1

UOP 1681-44

FIGURE 6.31

Benzene in Liquid Product
Direct Blend 1 Feedstock

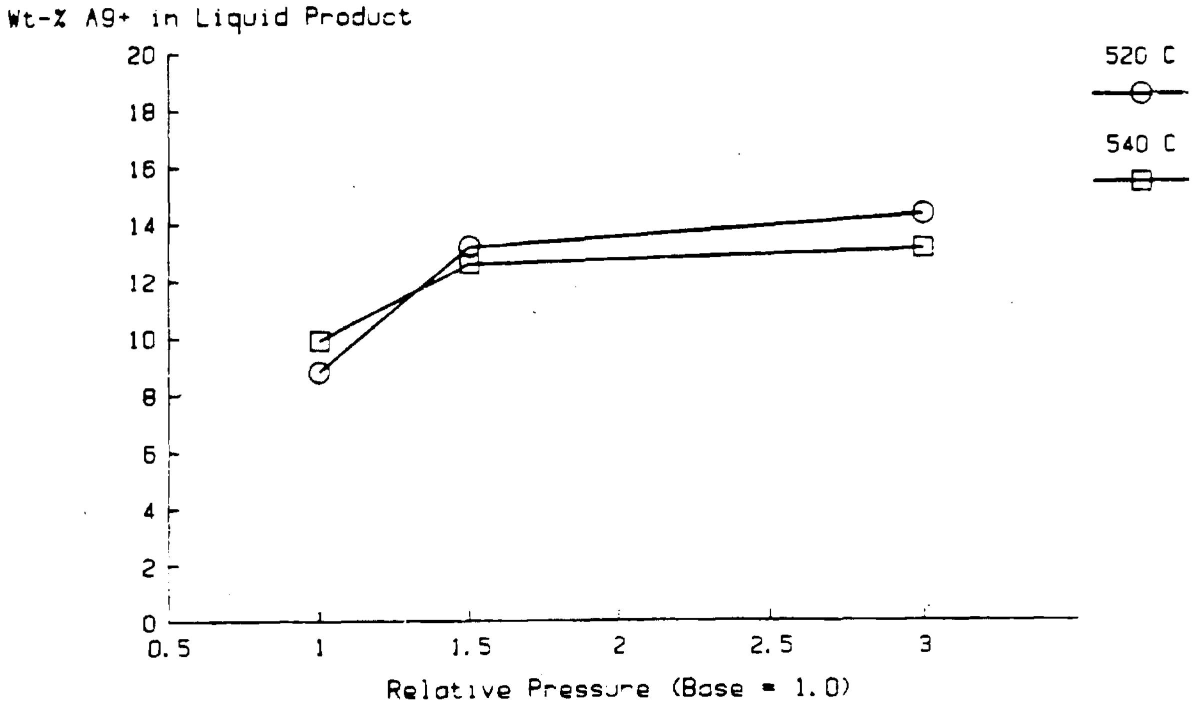


All Data at LHSV 1

UOP 1681-45

FIGURE 6.32

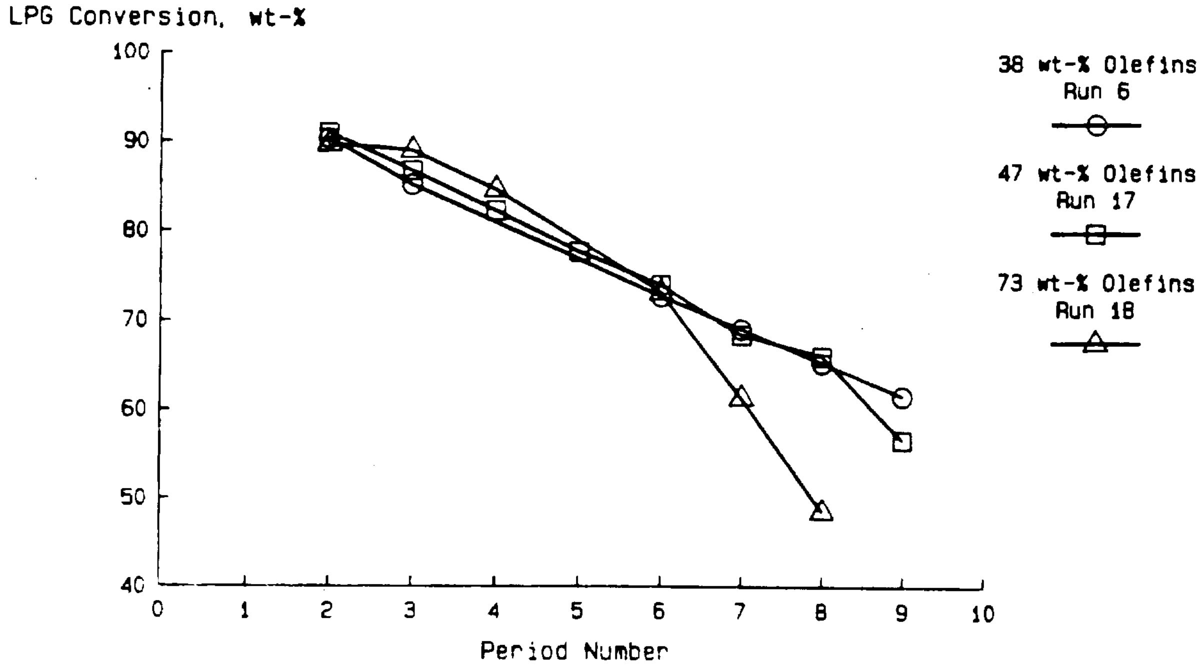
A9+ Material in Liquid Product
Direct Blend 1 Feedstock



All Data at LHSV 1

FIGURE 6.33

Effect of Olefin Level on Conversion
Direct Cyclar Blends 1, 2 and 3

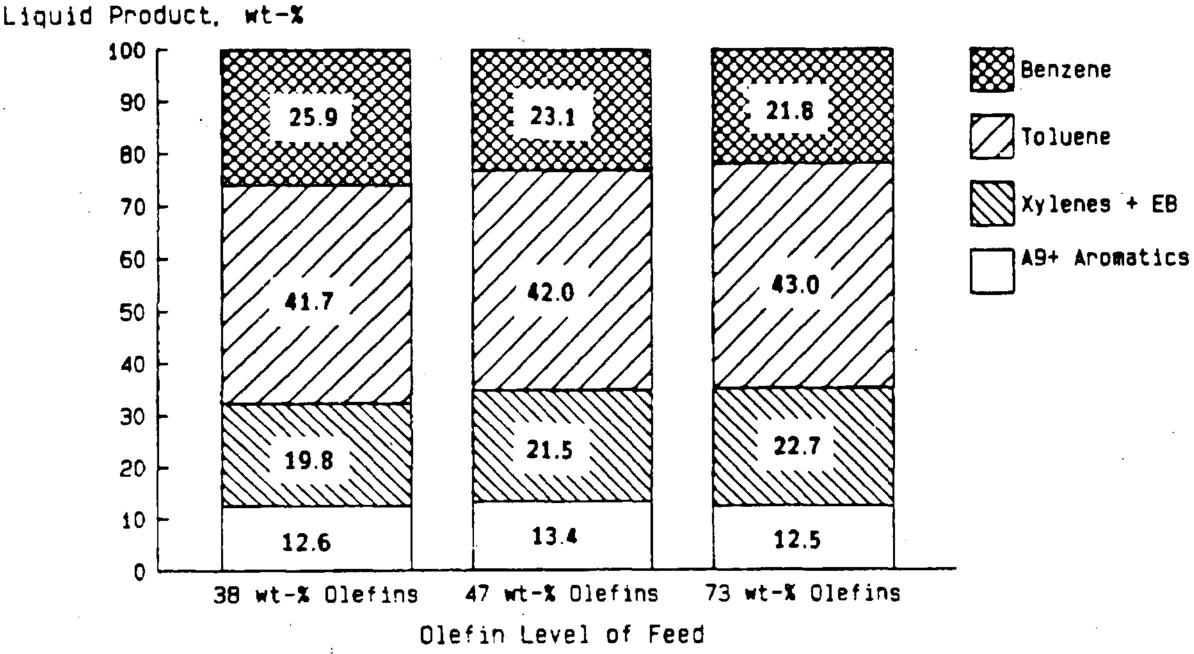


540 C / P2 / LHSV 1

JOP 168-47

FIGURE 6.34

Effect of Feed Olefinicity On Liquid Product Distribution

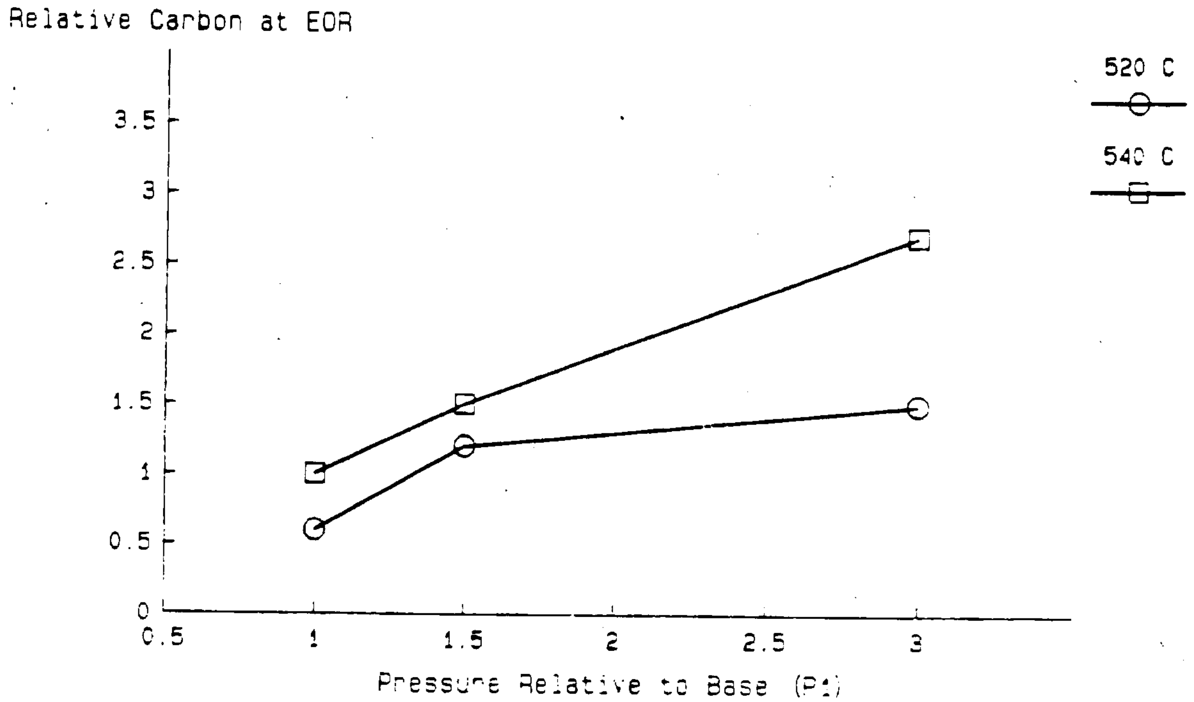


540 C / P2 / LHSV 1
DB1 (Run 6) / DB2 (Run 17) / DB3 (Run 18)
Liq Prod from Periods 3, 4 and 4 Respectively

UOP 1661-48

FIGURE 6.35

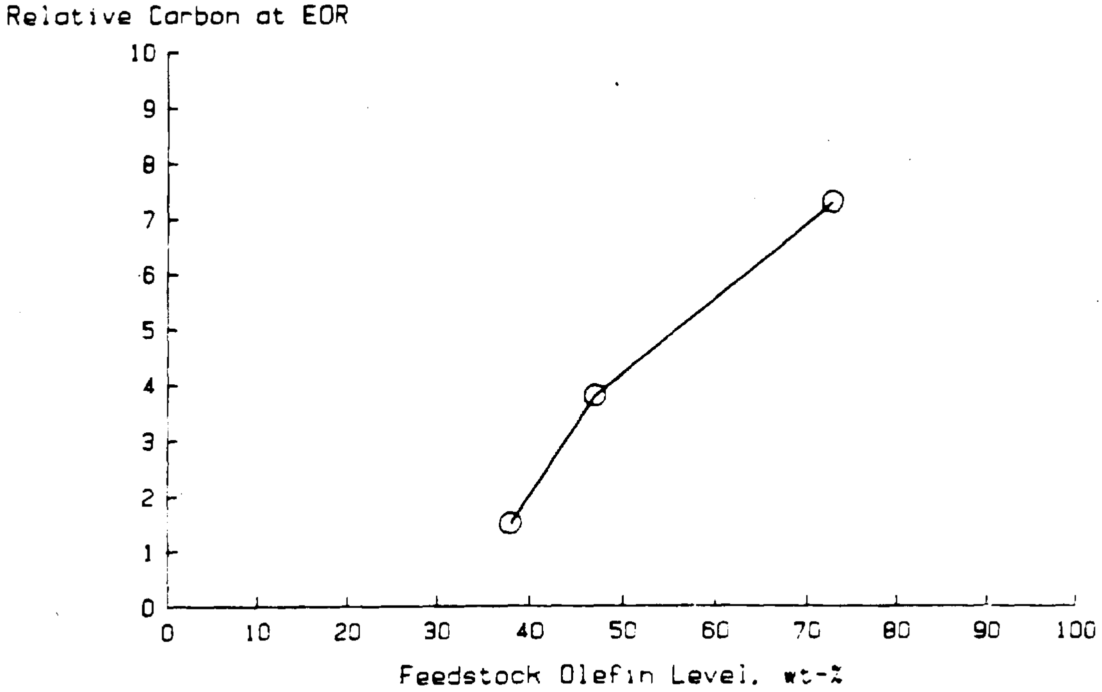
Spent Catalyst Coke
Impact of Temperature and Pressure



LHSV 1
Direct Cyclar Blend 1, 38 wt-% Olefins
Run 3 Relative Carbon Defined as 1.00

FIGURE 6.36

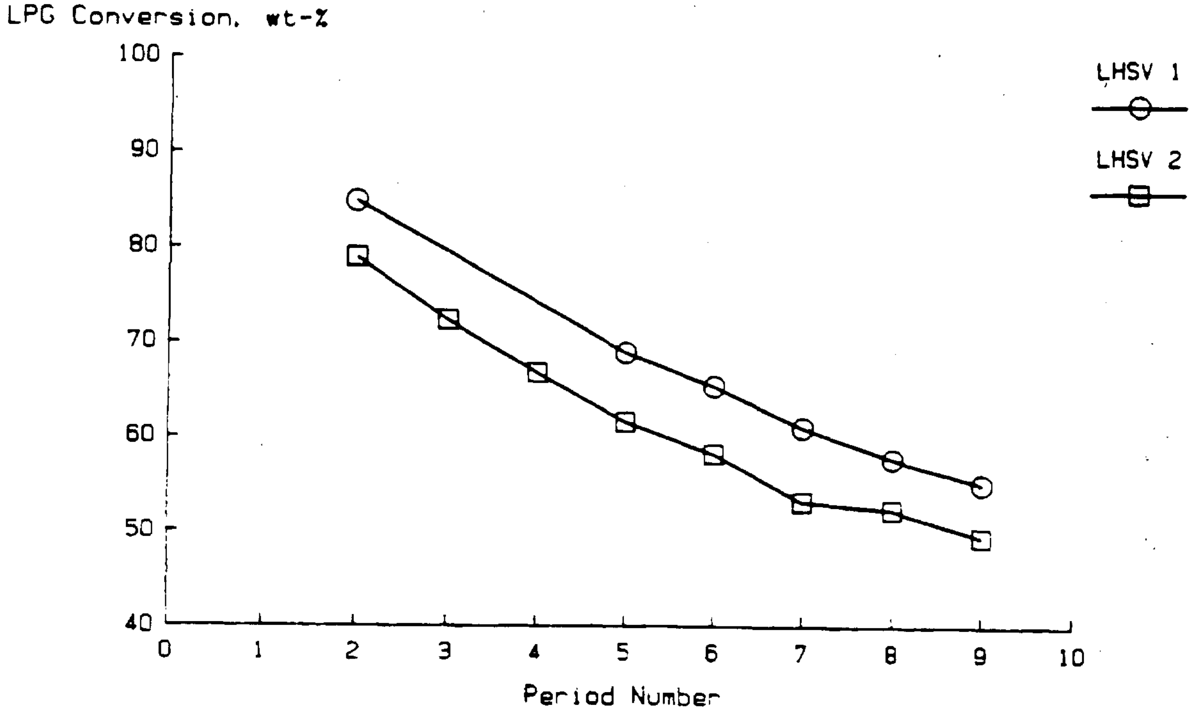
Spent Catalyst Coke vs Feed Olefinicity
Direct Cyclar Feed Blends



540 C / P2 / LHSV 1
Direct Cyclar Blends 1, 2 and 3
Run 3 Relative Carbon Defined as 1.00

FIGURE 6.37

Effect of Space Velocity on Conversion at P1
Indirect Cyclor

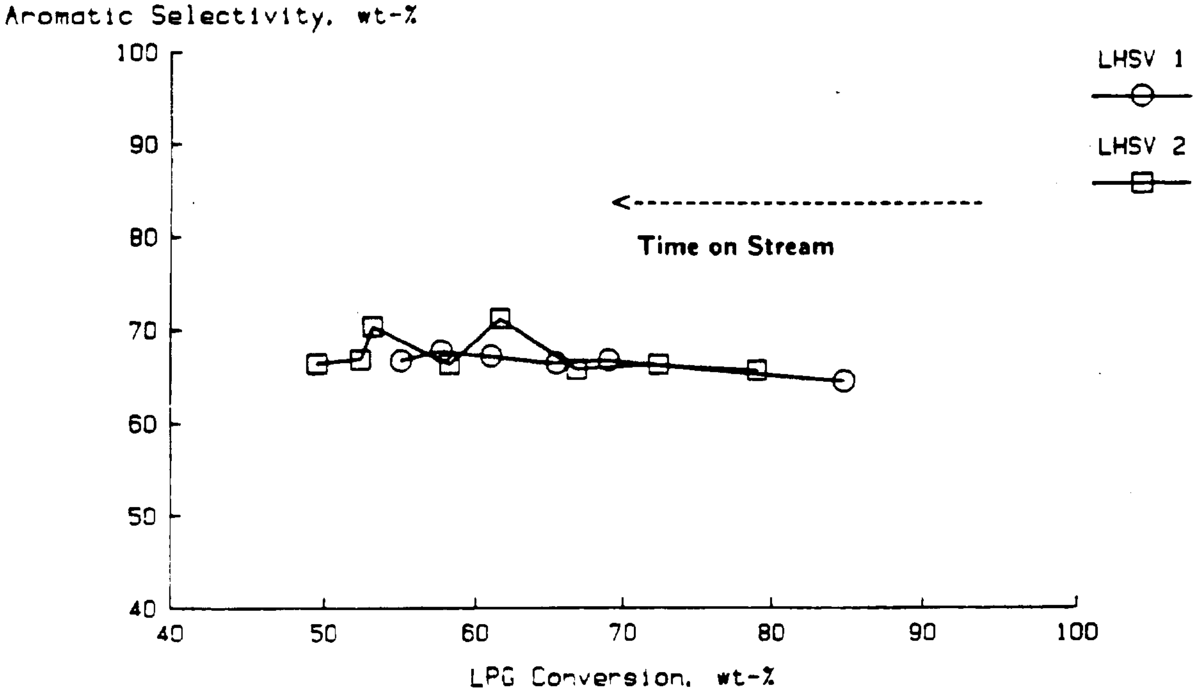


540 C / P1
LHSV 1 (Run 13) / LHSV 2 (Run 14)
LHSV 2 = 1.25 x LHSV 1

UOF 156 3

FIGURE 6.38

Effect of LHSV on Aromatic Selectivity at P1
Indirect Cyclar

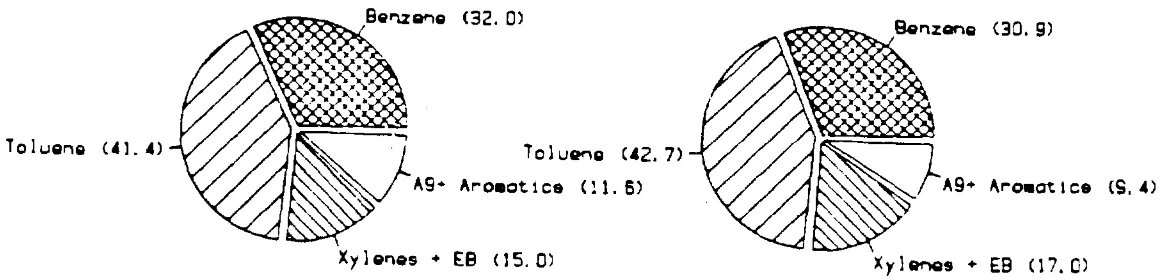


540 C / P1
LHSV 1 (Run 13) / LHSV 2 (Run 14)
LHSV 2 = 1.25 x LHSV 1

UOP 1681-52

FIGURE 6.39

Indirect Cyclar Liquid Product
Effect of LHSV at P1
( ) = wt-% of Liquid Product



LHSV 1
84.9 wt-% LPG Conversion

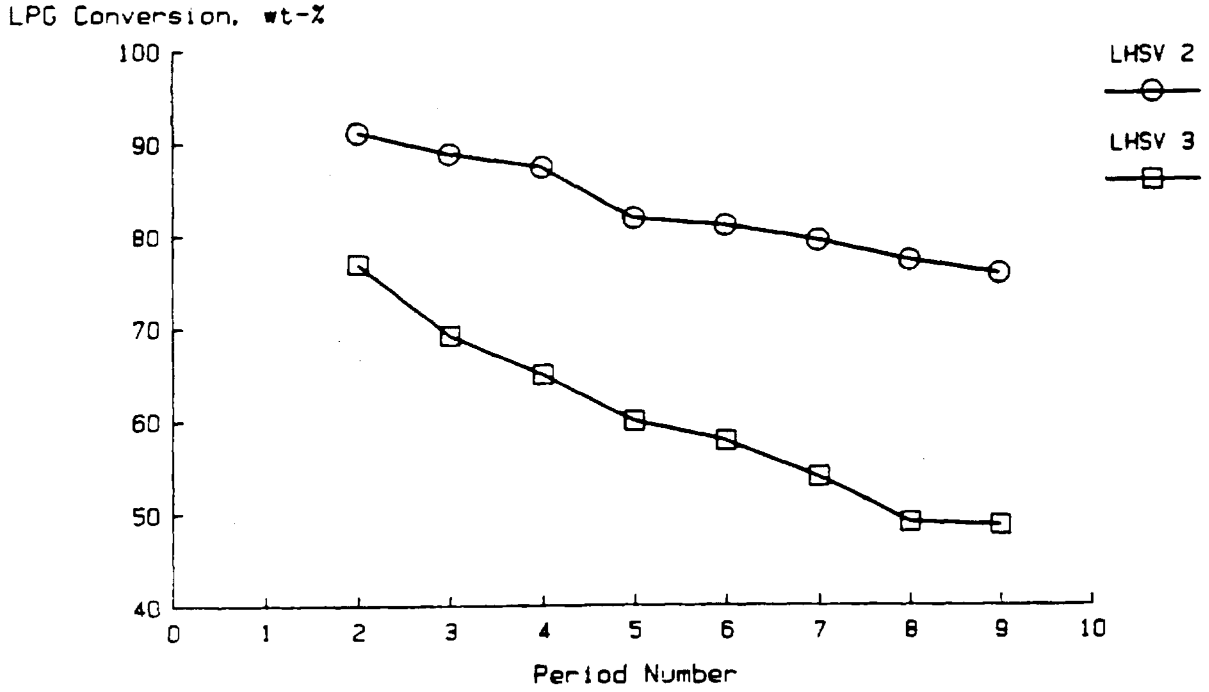
LHSV 2
79.0 wt-% LPG Conversion

540 C / P1
LHSV 1, Run 13 / Period 2
LHSV 2, Run 14 / Period 2

UOP 158-51

FIGURE 6.40

Effect of Space Velocity on Conversion at P3 Indirect Cyclar

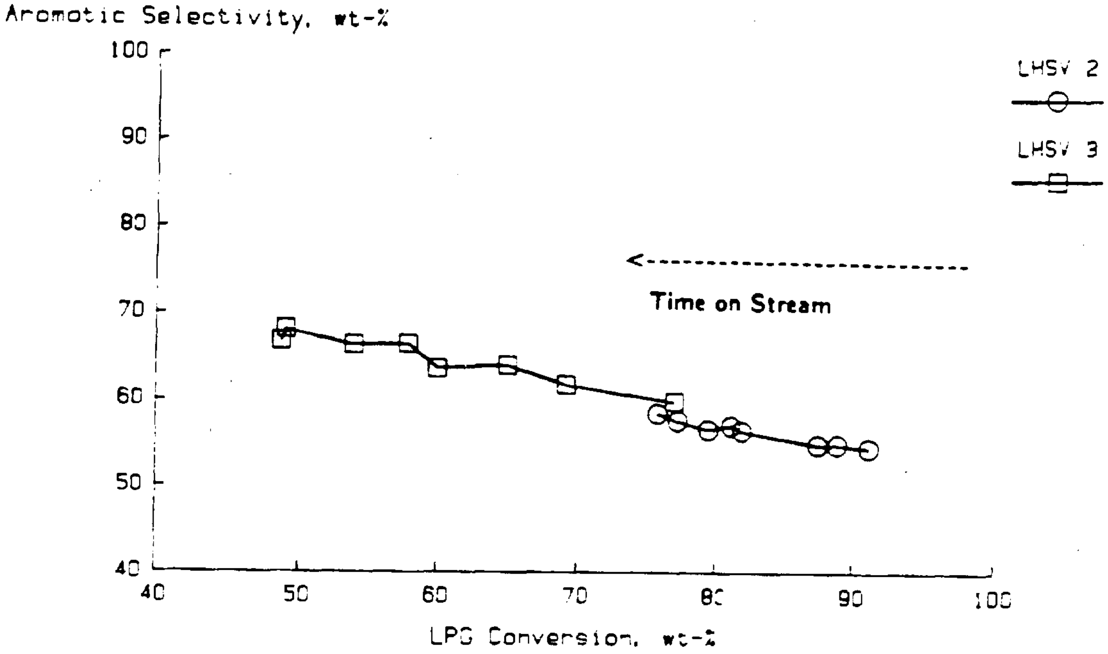


540 C / P3
LHSV 2 (Run 15) / LHSV 3 (Run 16)
LHSV 2 = 1.25 x LHSV 1 / LHSV 3 = 2.50 x LHSV 1

UOP 1681-54

FIGURE 6.41

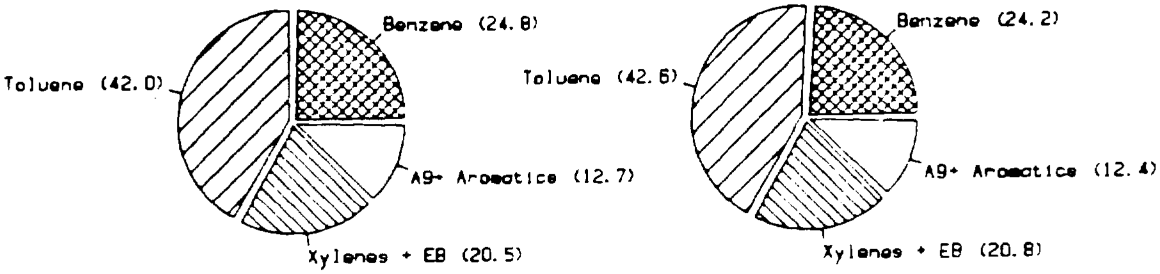
Effect of LHSV on Aromatic Selectivity at P3
Indirect Cyclar



540 C / P3
LHSV 2 (Run 15) / LHSV 3 (Run 16)
LHSV 2 = 1.25 x LHSV 1 / LHSV 3 = 2.50 x LHSV 1

FIGURE 6.42

Indirect Cyclar Liquid Product
Effect of LHSV at P3
( ) = wt-% of Liquid Product



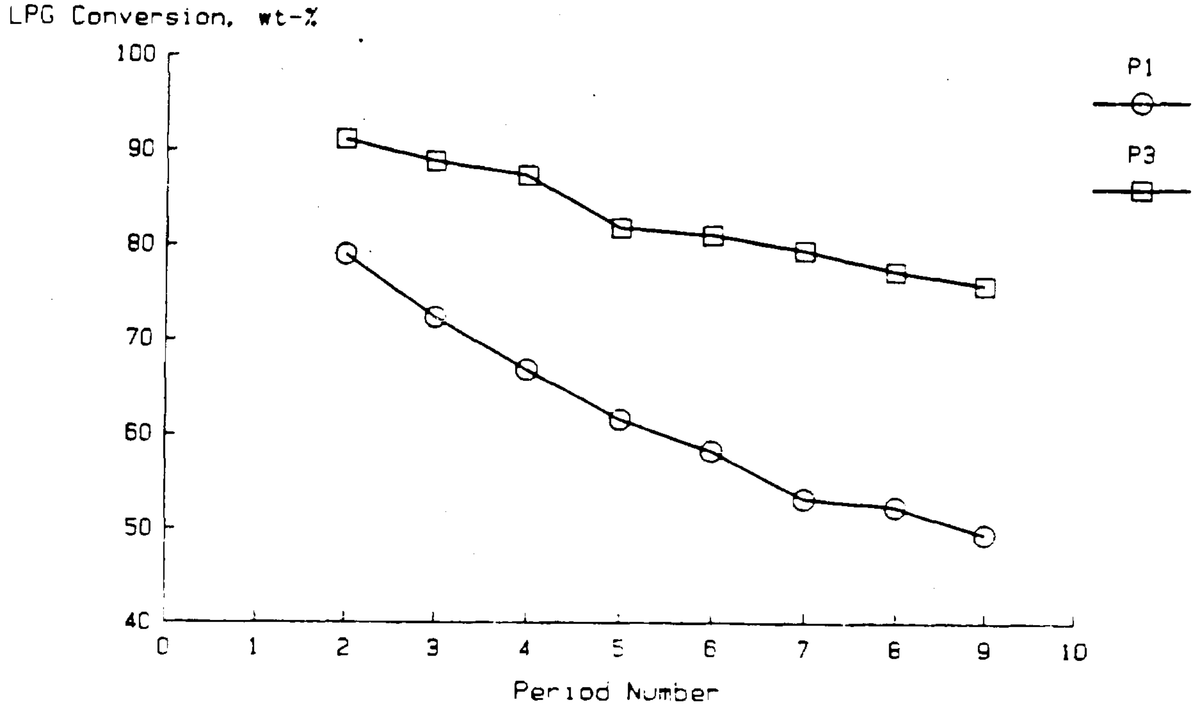
LHSV 2
81.2 wt-% LPG Conversion

LHSV 3
77.0 wt-% LPG Conversion

540 C / P3
LHSV 2, Run 15 / Period 6
LHSV 3, Run 16 / Period 2

FIGURE 6.43

Effect of Pressure at LHSV 2
Indirect Cyclar

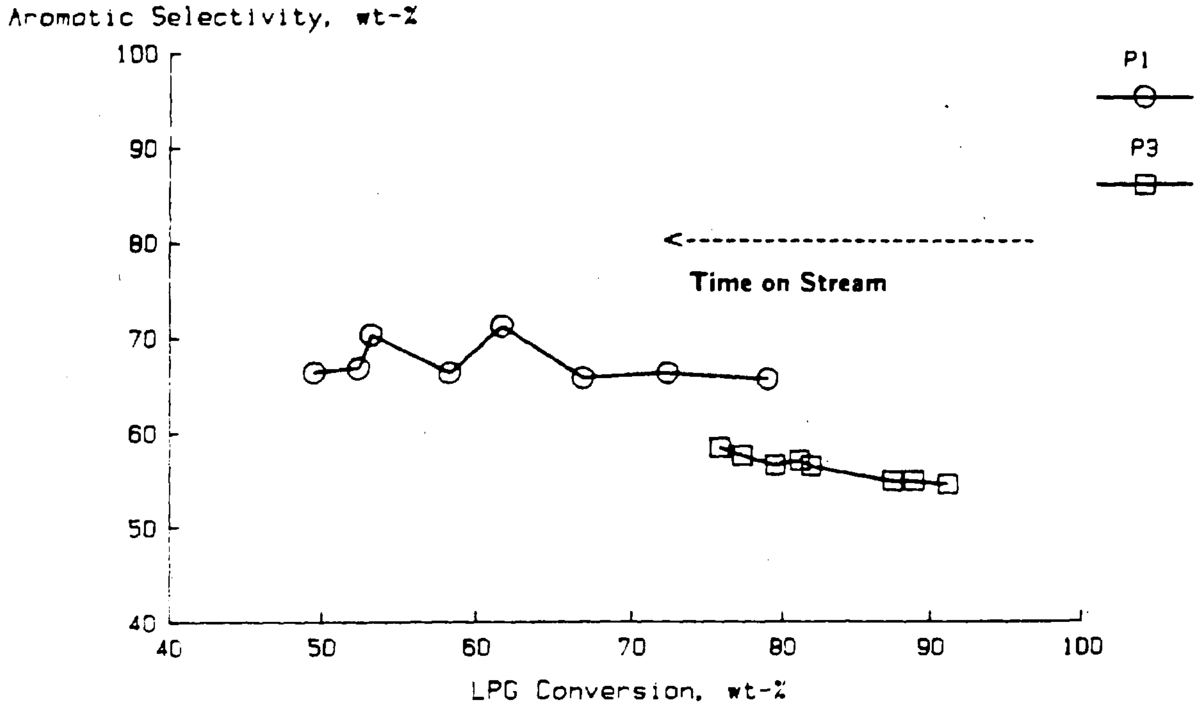


540 C / LHSV 2
P1 (Run 14) / P3 (Run 15)
P3 = 3.0 x P1

UOP [illegible]

FIGURE 6.44

Effect of Pressure on Aromatic Selectivity
Indirect Cyclar

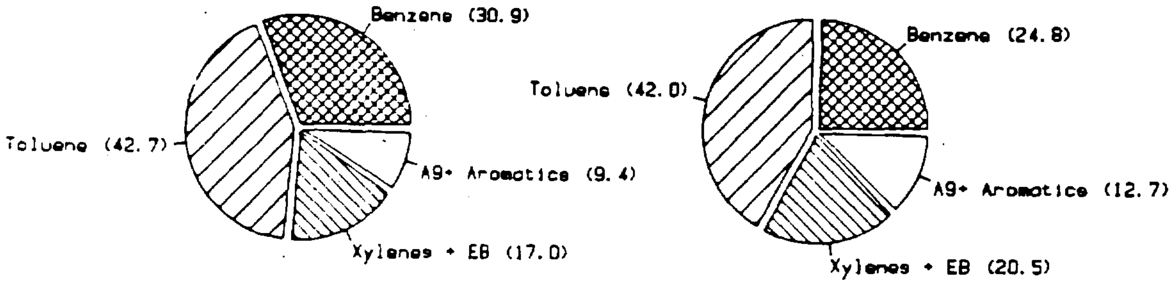


54C C / LHSV 2
P1 (Run 14) / P3 (Run 15)
P3 = 3.0 x P1

UOP 1681-58

FIGURE 6.45

Indirect Cyclar Liquid Product
Effect of Pressure on Composition
( ) = wt-% of Liquid Product



P1
79.0 wt-% LPG Conversion

P3
81.2 wt-% LPG Conversion

540 C / LHSV 2
P1, Run 14 / Period 2
P3, Run 15 / Period 6

JOP 168-59