American Institute of Chemical Engineers

STUDENT CONTEST PROBLEM

1974

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SITUATION

You are responsible for evaluating potential improvements to the catalytic polymerization plant at the Conservation Oil Company refinery. The polymerization plant consumes a propylene feed stream which is diluted with propane to 40 volume percent propylene. The propylene polymerizes to form olefinic polymers in the C_6 to C_{12} + boiling range. (The average molecular weight of the polymer is approximately 133.) The polymer is sold to a chemical company as feed for an Oxo-alcohol plant.

A supplier representing Catalysts Unlimited, Ltd., gives you pilot-plant-based data for its new catalyst, XP-23. Your assignment is to evaluate the new catalyst and to recommend its use if it is significantly more profitable and if it causes no insurmountable operating problems in the existing plant facilities.

CATALYST SUPPLIER DATA

The XP-23 catalyst data, which were obtained in a pilot plant packed-bed reactor having approximate similitude with your plant reactors, are supplied in graphical form. Figure 1 is a plot of the percentage of propylene conversion as a function of space velocity (U.S. gallons per hour of total feed per pound of catalyst in the reactor) and is based on a constant reactor outlet temperature of 400°F. Figure 2 shows the effect of outlet temperature on conversion. Figure 3 shows the effect of catalyst age on conversion, where catalyst age is expressed in gallons of polymer produced per pound of catalyst in the reactor. Figure 4 is a plot of the catalyst pressure-drop factor as a function of catalyst age and weighted average reactor-outlet temperature. Figure 4 illustrates the common problem of polymerization catalysts, that increasing the reactor temperatures accelerates the pressure-drop increases.

The representative of the catalyst supplier tells you that the best operating range for outlet temperature depends on the local economic situation but that most users of this new catalyst find that the range is between 410° and 435°F. Below this range conversion becomes too low, and above this range the run length, fixed by the maximum pressure drop, becomes too short. He advises that the inlet temperature be constant and be equal to the average outlet temperature, $\bar{T}$, which is defined in the instructions for Figure 4.

PLANT DATA

Figure 5 is a diagram of the polymerization plant. The temperatures and pressures shown on this figure are typical of current plant operations and should be used as the basis for the current catalyst evaluation. For the purpose of evaluating the new XP-23 catalyst, several bases and unit limitations are given:

1. The total feed to the unit feed drum will be 15,000 bbl./day (630,000 U.S. gallons per day) and should be assumed to be constant. The feed is 40 volume percent propylene, and the remainder can be assumed to be propane.
2. Five reactors are available. Normally, four will be on stream, and one will be down for cleaning. Each reactor holds 20,000 pounds of catalyst, which is discarded at the end of a run because catalyst regeneration is too expensive. The reactors are the tubular type with exothermic reaction heat removal by a shell-side pressurized water-steam drum system. The polymerization unit is a net producer of 125 lb./sq. in. gauge steam, which is valued at steam cost.
3. The feed rates to the individual reactors are controlled by automatic flow controllers. The outlet temperatures on each reactor are controlled by pressure control of the steam drum associated with the pressurized water system. The set-points for feed rate and outlet temperature do *not* have to be identical for all reactors at any point in time or constant with time.
4. The feed drum is none too large. The holdup in this drum between the level (LI) taps is about 1,500 barrels. Therefore, care must be exercised that the sum of the feed rates to the individual reactors does not overflow or drain the feed drum.
5. Past data indicate that it is a good assumption to consider the barrels of polymer formed per barrel of propylene as constant and equal to 0.715 barrel of polymer per barrel of propylene. The heat of reaction is 533.4 B.t.u./pound of propylene.
6. The length of time that any reactor is on stream is fixed by the maximum reactor pressure drop. When the pressure differential across the reactor reaches 100 lb./sq. in., the reactor must be shut down for catalyst dumping and recharging. Feed rate, however, may be reduced to extend the length of any run if the feed rate to the other reactors is increased to compensate. (See item 4 above.)
7. The propane is separated from the polymer product in a depropanizer. The depropanizer overhead stream is sent to a facility which blends propane streams for LPG sales. The maximum propylene level in LPG should be considered 4 volume percent for this evaluation.
8. The depropanizer has the capacity to adequately separate the propane and propylene from the polymer (essentially no propane or propylene in tower bottoms). However, the tower is currently operating at maximum vapor loading at the feed tray; consequently the feed temperature must be 170°F. or less for optimum fractionation. The water control valve to the depropanizer feed cooler is operating at 75 percent of maximum flow under conditions shown in Figure 5. The cooling-water pump has a maximum rated capacity of 600 gal./min.
9. The feed preheater furnace uses 1,000 B.t.u. per standard cubic feet of fuel gas and is 60 percent efficient.
10. Enthalpy data for typical reactor feed and product streams are provided in Tables 1 and 2.

ECONOMIC BASIS

The following economic basis applies to this evaluation:

1. The value of the polymer product is 20 cents/gal. of polymer.
2. The value of the depropanizer overhead stream to LPG sales is 10 cents/gal.
3. The cost of the new XP-23 catalyst is the same as that of the present catalyst, 30 cents/lb. Catalyst bed densities for the present and XP-23 catalysts are approximately the same.
4. The time necessary for dumping and recharging catalyst is 250 man-hours. The availability of manpower requires that 5 days of elapsed time should be made available for a turnaround. Manpower costs $12/hr. including all overhead.
5. The present catalyst has an average life (catalyst age at end of run) of 55 gal. of polymer/lb. of catalyst. The average propylene conversion is 94 percent at conditions shown in Figure 5. These results are currently achieved by decreasing the feed rate to and increasing the outlet temperature from

TABLE 1—Enthalpy Data for Typical Reactor Feed Stream (40 vol.% propylene & 60% propane)

Temperature °F.	Pressure lb./sq. in. gauge	Mole fraction vaporized	Enthalpy, B.t.u./lb.
-459.40	1100	0.0	0
100.00		0.0	256.90
125.00		0.0	274.83
137.84		0.0	284.68
163.54		Dew point	300.50
175.66		1.0	309.62
187.83		1.0	319.01
200.00		1.0	328.74
233.39		1.0	359.03
243.13		1.0	368.72
266.78		1.0	393.59
290.00		1.0	417.90
330.00		1.0	454.27
370.00		1.0	485.87
410.00		1.0	515.50
422.50		1.0	524.56
450.00		1.0	544.33

each reactor as the cataylst ages. Operators make changes every 4 to 5 days with the present catalyst.

6. Utility costs:

Fuel gas	@50 cents/million B.t.u.
Cooling water	@2.2 cents/thousand gal.
125 lb./sq. in. gauge steam	@50 cents/thousand lb.

REPORT

Your final report should address the following questions:

1. Is the new catalyst significantly better than the present one? A significant improvement is one that yields a net increase in profit of at least $50,000/yr.
2. What are the optimum conditions of feed rates and outlet temperatures for the new catalyst? You should present the optimum reactor feed rates and outlet temperatures as a function of days on stream. Be sure to allow for turn-around times and to specify the frequency of reactor startups (for example, that a new reactor should come on stream every 5.5 days).
3. Do you anticipate any problems with the new catalyst or with the run conditions you have specified? Consider the limitations of existing equipment and the limited availability of the operator's time for involved control variable manipulations that your reactor feed rate and outlet temperature specifications may require.

It is not required that you redesign any equipment that needs modifications. Your report should only identify those items that require redesign.

TABLE 2—Enthalpy Data for Typical Reactor Product Stream (67.2 vol.% propane, 2.7% propylene and 30.1% polymer)

Temperature, °F.	Pressure lb./sq. in. gauge	Mole fraction vaporized	Enthalpy, B.t.u./lb.
-459.40	250	0.0	0
100.00		0.0	240.62
115.25		0.0	249.69
130.50		0.0	258.89
145.75		Bubble point	268.23
148.17		0.10	278.77
153.20		0.25	295.37
161.31		0.40	313.72
170.25		0.50	327.98
187.45		0.61	347.94
229.15		0.73	383.49
270.84		0.80	415.78
312.54		0.86	449.22
354.24		0.93	485.28
395.94		Dew point	523.94
413.96		1.0	535.05
431.98		1.0	546.28
450.00		1.0	557.63
-459.40	1050	0.0	0
200.00		0.0	305.74
222.96		0.0	323.81
236.42		0.0	335.49
245.92		0.0	344.71
264.74		0.0	370.11
268.88		Bubble point	379.53
270.81		0.03	380.10
292.20		0.33	396.95
315.51		0.54	411.37
338.83		0.69	425.24
362.15		0.81	441.31
385.47		0.92	458.30
408.78		Dew point	476.48
410.00		1.0	477.55
422.52		1.0	488.44
436.26		1.0	500.14
450.00		1.0	511.60

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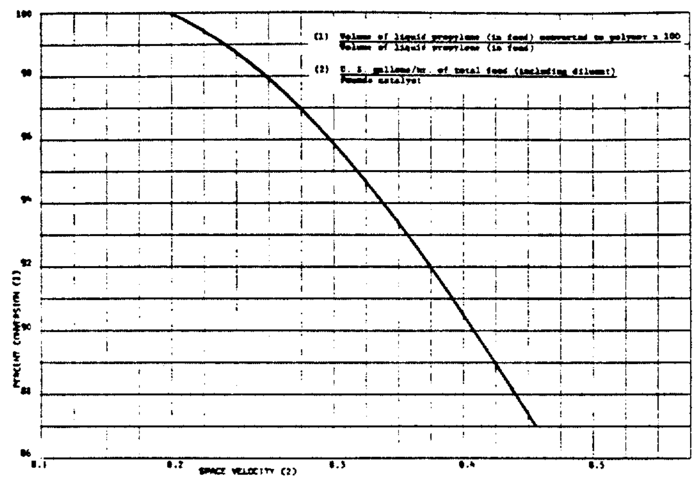

Fig. 1. Propylene conversion at 400°F. outlet temperatures for CU-Ltd. catalyst XP-23.

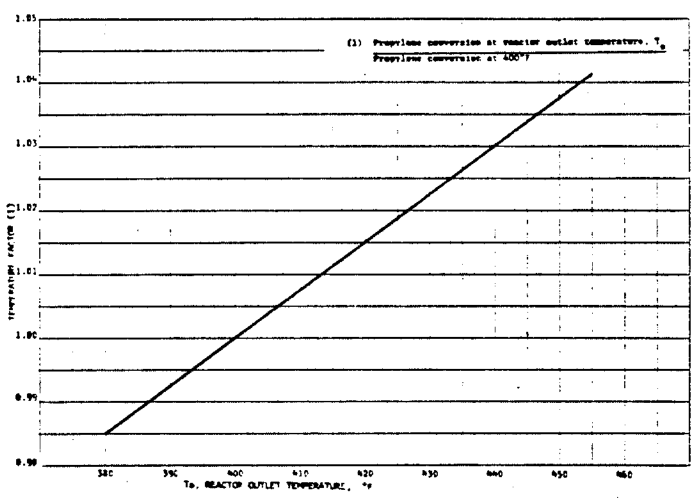

Fig. 2. Conversion–temperature factor for CU-Ltd. catalyst XP-23.

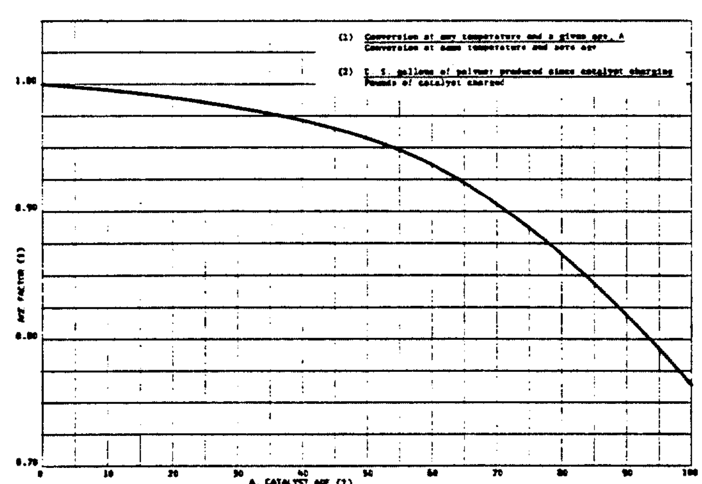

Fig. 3. Conversion–catalyst-age factor for CU-Ltd. catalyst XP-23.

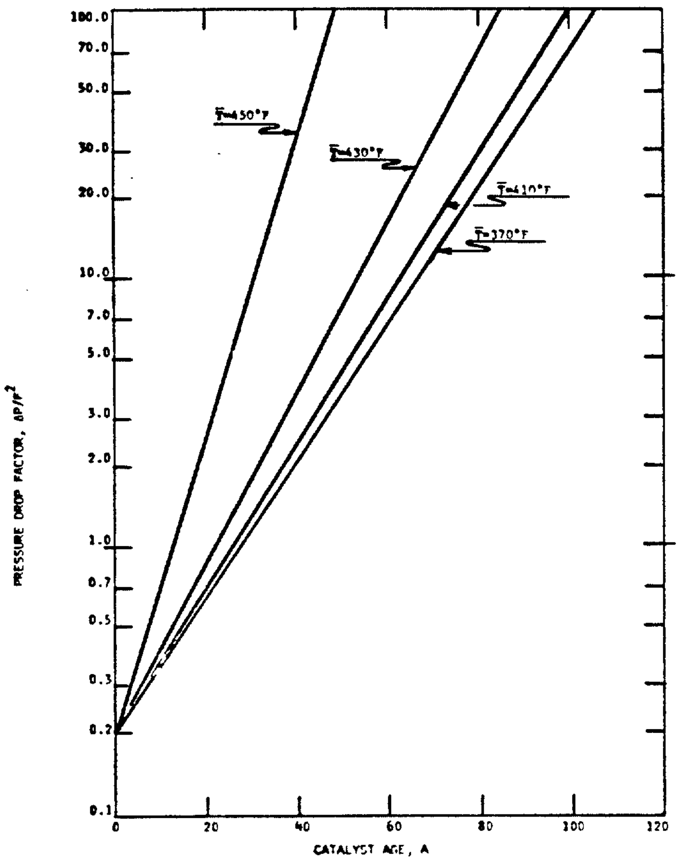

Fig. 4. Pressure-drop factor for CU-Ltd. catalyst XP-23.

INSTRUCTIONS FOR USE OF FIGURE 4

Definitions:

$$\text{Pressure-drop factor} = \frac{\Delta P}{F^2}$$

where ΔP = reactor pressure drop, lb./sq. in.
and F = reactor total feed rate, thousand barrels/day

Average reactor outlet temperature (to time, D) = $\overline{T}$

defined as

$$\overline{T} = \frac{\int_0^D F(t)\, T_o(t)\, dt}{\int_0^D F(t)\, dt}$$

where t = time, days
D = time (in days) at which $\overline{T}$ and $\Delta P/F^2$ are to be calculated
T_o = reactor outlet temperature, °F.
F = reactor total feed rate, thousand barrels/day

Catalyst-age factor = A

defined as

$$A = \frac{\left[\int_0^D F(t)\, dt\right] \times \text{[conversion factors to gallons of polymer]}}{\text{[pounds of catalyst]}}$$

where A = U.S. gallons of polymer/pound catalyst

The lines of pressure-drop factor are linear with catalyst age on semi-log coordinates. The intercept for catalyst age = 0 is $\Delta P/F^2$ = 0.2 in each case. The catalyst-age intercepts at $\Delta P/F^2$ = 100 are given for the following average reactor outlet temperatures:

$\overline{T}$, °F.	Catalyst age
370	105.97
390	102.81
410	99.83
415	98.70
420	96.18
425	91.63
430	84.90
435	76.36
440	66.84
445	57.21
450	48.21

EXAMPLE: A reactor has been operating for some time. The catalyst age (A) is currently 60 gal. of polymer/lb. of catalyst, and the accumulated average reactor outlet temperature ($\overline{T}$) is 410°F. If the current feed rate is 3,000 bbl./day, what is the pressure drop?

Reading Fig. 4 at A = 60 and using the line for $\overline{T}$ = 410°F. gives

$$\frac{\Delta P}{F^2} = 8.3 \frac{\text{lb./sq. in.}}{\text{(thousand barrels of feed)}^2}$$

because F^2 = 9.0, ΔP = 74.7 lb./sq. in.

Lowering the flow rate to 2,000 bbl./day would reduce the pressure drop (F^2 = 4.0, ΔP = 33.2 lb./sq. in.) substantially. Reducing the outlet temperature can also reduce the pressure drop, but because $\overline{T}$ is averaged over the total time of reactor operation, considerable time would elapse before any significant effect in $\overline{T}$ is noted, and by then the catalyst age would have increased to offset the benefit.

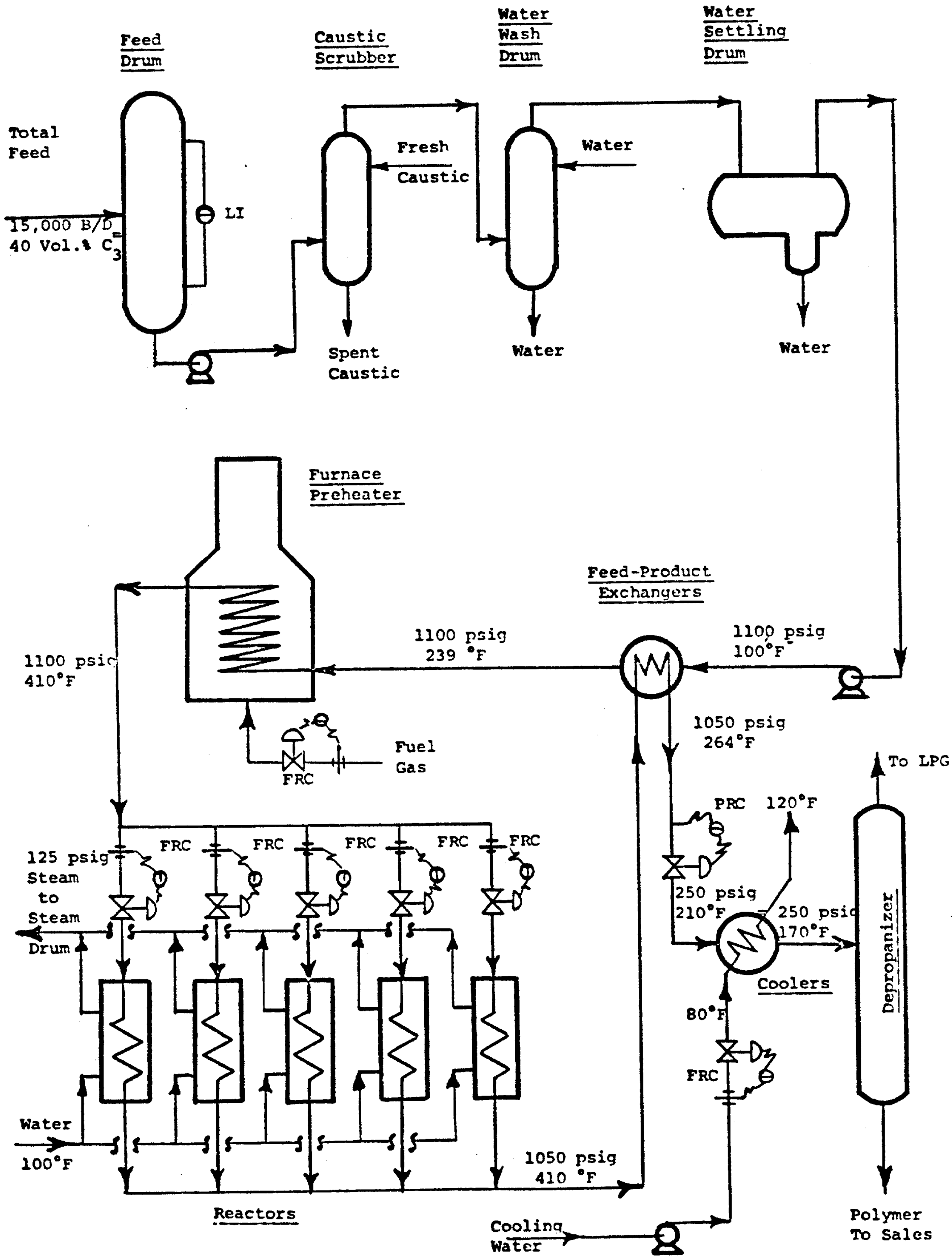

Fig. 5. Conservation Oil Company catalytic polymerization unit.

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