B.11 PRODUCTION OF HEPTENES FROM PROPYLENE AND BUTENES [1], UNIT 1200

The background information for this process is taken from Chauvel et al. [1]. This example is an illustration of a preliminary estimate of a process to convert a mixture of C_3 and C_4 unsaturated hydrocarbons to 1-heptene and other unsaturated products. The market for the 1-heptene product would be as a highoctane blending agent for gasoline or in the production of plasticizers. Based on preliminary market estimates, a production capacity of 20,000 metric tons per year of 1-heptene using 8000 operating hours/y was set. This process differs from the other examples in Appendix B in several ways. First, the raw materials to the process contain a wide variety of chemicals. This is typical for oil refinery and some petrochemical operations. Second, no specific kinetic equations are given for the reactions. Instead, the results of laboratory tests using the desired catalyst at different conditions and using different feed materials are used to guide the process engineer to an optimum, or close to an optimum, reactor configuration. The flowsheet in Figure B.11.1 and stream, equipment summary, and utility summary tables, Tables B.11.1–B.11.3, have been developed using such information. It should be noted that a preliminary economic analysis, and hence the feasibility of the process, can be determined without this information, as long as yield and conversion data are available and the reactor configuration can be estimated.

[Material on pages 133-137 was not relevant to the heptenes process and has been removed.]

B.11.1 Process Description

Two liquid feed streams containing propylene and butene and a stream of catalyst slurried with 1-hexene are mixed at a pressure of approximately 8 bar prior to being sent to the reactor. The reactor consists of five essentially well-mixed sections, with similar concentrations in each section. Heat removal is achieved by using pump-arounds from each stage through external heat exchangers. The reactor effluent is partially vaporized before being fed to the first of three distillation columns. The first column (T-1201) removes the unreacted C_3 and C_4 components, which are used subsequently as fuel (Stream 7) or sent to LPG storage (Stream 6). The next column (T-1202) separates the 1-hexene product overhead (Stream 10) and sends the bottoms stream to the final column (T-1203). In T-1203, the main 1-heptene product (Stream 13) is taken overhead, and the C_8 and heavier compounds are taken as the bottoms product (Stream 14). The bottoms product is processed off-site to remove the heavy material and to recover spent catalyst.

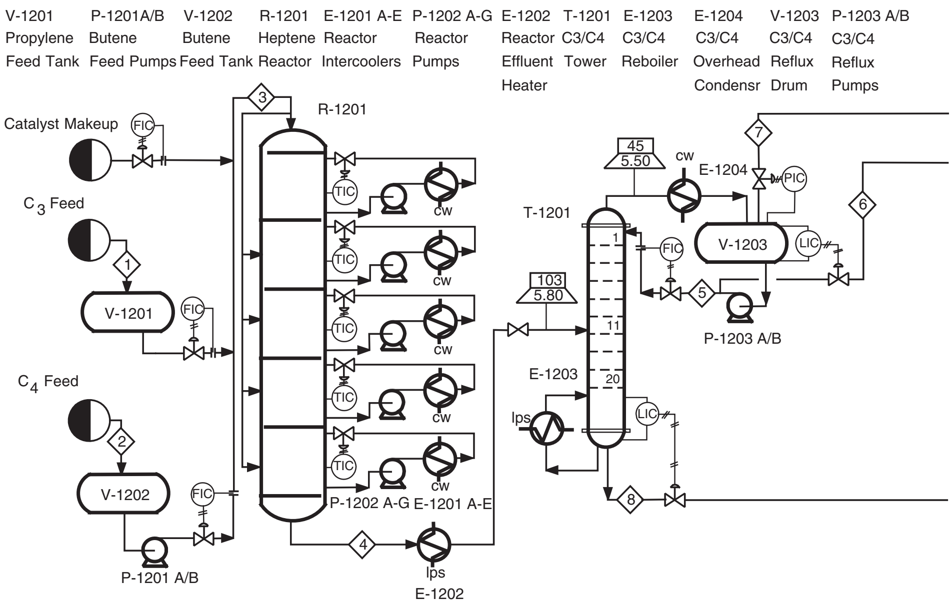

Figure B.11.1 Unit 1200: Production of Heptenes from Propylene and Butenes PFD

B.11.2 Reaction Kinetics

The process given in Figure B.11.1 is based on the liquid-phase catalytic co-dimerization of C_3 and C_4 olefins using an organometallic catalyst. This catalyst is slurried with a small volume of the hexenes product and fed to the reactor with the feed streams. The volume of the catalyst stream is small compared with the other streams and is not included in the material balance given in Table B.11.1. In 1976 (CEPCI = 183), consumption of catalyst amounted to \$9.5/1000 kg of 1-heptene product [1].

The primary reactions that take place are as follows:

$$C_3H_6 + C_3H_6 \rightarrow C_6H_{12}$$

1-*hexene*

$$C_3H_6 + C_4H_8 \rightarrow C_7H_{14}$$

1-*heptene*

$$C_4H_8 + C_4H_8 \rightarrow C_8H_{16}$$

1-*octene*

$$C_3H_6 + 2C_4H_8 \rightarrow C_{11}H_{22}$$

1-*undecene*

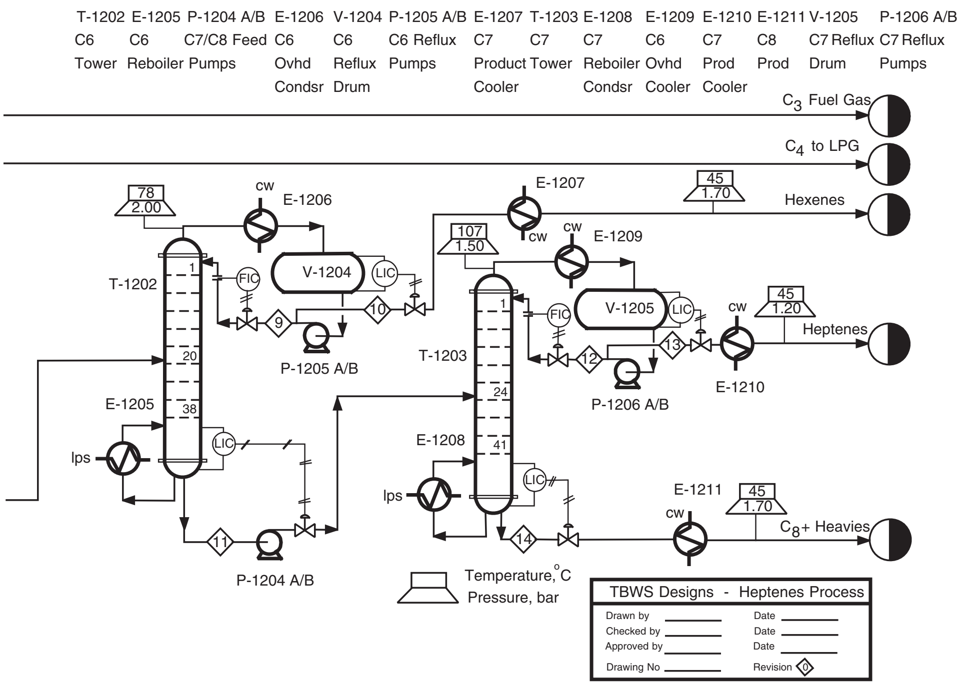

Figure B.11.1 (*Continued*)

Table B.11.1 Stream Table for Unit 1200

Stream Number	1	2	3	4	5	6	7
Temperature (ºC)	25	25	26	45	45	45	45
Pressure (bar)	11.6	3.0	8.0	7.7	7.5	6.5	5.0
Vapor fraction	0.0	0.0	0.0	0.0	0.0	0.0	1.0
Mass flow (tonne/h)	3.15	9.29	12.44	12.44	3.68	6.66	0.13
Mole flow (kmol/h)	74.57	163.21	237.78	178.10	64.41	116.45	3.00
Component flowrates (kmol/h)							
Propane	3.56	0.00	3.56	3.56	0.31	0.56	3.00
Propylene	71.06	0.00	71.06	0.00	0.00	0.00	0.00
i-Butane	0.00	29.44	29.44	29.44	16.19	29.28	0.00
n-Butane	0.00	34.41	34.41	34.41	18.65	33.72	0.00
i-Butene	0.00	8.27	8.27	8.27	4.53	8.19	0.00
1-Butene	0.00	90.95	90.95	44.94	24.61	44.49	0.00
1-Hexene	0.00	0.14	0.14	21.21	0.12	0.21	0.00
1-Heptene	0.00	0.00	0.00	26.53	0.00	0.00	0.00
1-Octene	0.00	0.00	0.00	7.41	0.00	0.00	0.00
1-Undecene	0.00	0.00	0.00	2.34	0.00	0.00	0.00
Stream Number	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Temperature (ºC)	151	78	78	135	107	107	154
Pressure (bar)	5.8	4.5	4.5	2.5	4.0	4.0	2.0
Vapor fraction	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mass flow (tonne/h)	5.64	5.79	1.86	3.79	4.30	2.53	1.26
Mole flow (kmol/h)	58.65	69.84	22.44	36.22	43.78	25.76	10.46
Component flowrates (kmol/h)							
Propane	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Propylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
i-Butane	0.16	0.50	0.16	0.00	0.00	0.00	0.00
n-Butane	0.69	2.15	0.69	0.00	0.00	0.00	0.00
i-Butene	0.08	0.25	0.08	0.00	0.00	0.00	0.00
1-Butene	0.45	1.40	0.45	0.00	0.00	0.00	0.00
1-Hexene	21.00	64.70	20.79	0.21	0.36	0.21	0.00
1-Heptene	26.52	0.84	0.27	26.26	43.28	25.47	0.79
1-Octene	7.41	0.00	0.00	7.41	0.14	0.08	7.33
1-Undecene	2.34	0.00	0.00	2.34	0.00	0.00	2.34

Table B.11.2 Preliminary Equipment Summary Table for Unit 1200

Equipment	P-1201 A/B	P-1202 A-G*	P-1203 A/B	P-1204 A/B	P-1205 A/B	P-1206 A/B
MOC	Carbon steel	Carbon steel	Carbon steel	Carbon steel	Carbon steel	Carbon steel
Power (shaft) (kW)	6.75	5.13	2.75	0.66	2.15	1.93
Efficiency	40%	70%	40%	40%	40%	40%
Type/drive	Centrifugal/ electric	Centrifugal/ electric	Centrifugal/ electric	Centrifugal/ electric	Centrifugal/ electric	Centrifugal/ electric
Temperature (°C)	25	45	45	151	78	107
Pressure in (bar)	2.97	8.00	5.50	2.50	2.00	1.50
Pressure out (bar)	9.00	9.00	7.55	4.00	4.47	4.00

*Seven identical pumps: five operating + two spares.

(*continued*)

Table B.11.2 Preliminary Equipment Summary Table for Unit 1200 (*Continued*)

Equipment	V-1201	V-1202	V-1203	V-1204	V-1205
MOC	Carbon steel	Carbon steel	Carbon steel	Carbon steel	Carbon steel
Diameter (m)	1.40	1.90	1.10	0.95	0.92
Height/length (m)	4.20	5.7	3.30	2.85	2.75
Orientation	Horizontal	Horizontal	Horizontal	Horizontal	Horizontal
Internals	—	—	—	—	—
Pressure (barg)	20.0	5.0	4.5	1.0	0.5

Equipment	R-1201	T-1201	T-1202	T-1203
MOC	Carbon steel	Carbon steel	Carbon steel	Carbon steel
Diameter (m)	3.00	1.05	1.10	0.90
Height/length (m)	13.0	20.7	26.0	27.3
Orientation	Vertical	Vertical	Vertical	Vertical
Internals	Reactor split into 5 equal sections	20 SS sieve plates @ 24″ spacing	38 SS sieve plates @ 18″ spacing	41 SS sieve plates @ 18″ spacing
Pressure (barg)	7.0	5.0	1.5	1.0

Table B.11.2 (*Continued*)

Equipment	E-1201 A-E*	E-1202	E-1203	E-1204	E-1205	E-1206
Type	Fixed TS	Float-head partial vap.	Float-head reboiler	Fixed TS condenser	Float-head reboiler	Fixed TS condenser
Duty (MJ/h)	846	3827	1251	3577	2184	2630
Area (m^2)	61.4	33.8	32.1	128.5	21.1	20.0
Shell side						
Max. temp (ºC)	45	160	160	45	160	78
Pressure (barg)	8.0	5.0	5.0	4.0	5.0	1.0
Phase	L	Cond. steam	Cond. steam	Cond. vapor	Cond. steam	Cond. vapor
MOC	Carbon steel	Carbon steel	Carbon steel	Carbon steel	Carbon steel	Carbon steel
Tube side						
Max. temp (ºC)	40	103	151	40	135	40
Pressure (barg)	3.0	6.7	4.8	3.0	1.5	3.0
Phase	L	L+V	Boiling liq.	L	Boiling liq.	L
MOC	Carbon steel	Carbon steel	Carbon steel	Carbon steel	Carbon steel	Carbon steel

*Area and duty given for one exchanger; five identical exchangers are needed.

(*continued*)

Table B.11.2 Preliminary Equipment Summary Table for Unit 1200 (*Continued*)

Equipment	E-1207	E-1208	E-1209	E-1210	E-1211
Type	Double pipe	Float-head reboiler	Fixed TS condenser	Double pipe	Double pipe
Duty (MJ/h)	146	2026	2146	372	330
Area (m^2)	2.1	75.3	9.7	3.9	2.4
Shell side					
Max. temp (ºC)	78	160	107	107	154
Pressure (barg)	1.0	5.0	0.5	0.3	0.7
Phase	L	Cond. steam	Cond. vapor	L	L
MOC	Carbon steel	Carbon steel	Carbon steel	Carbon steel	Carbon steel
Tube side					
Max. temp (ºC)	40	154	40	40	40
Pressure (barg)	3.0	1.0	3.0	3.0	3.0
Phase	L	Boiling liq.	L	L	L
MOC	Carbon steel	Carbon steel	Carbon steel	Carbon steel	Carbon steel

Table B.11.3 Utility Summary Table for Unit 1200

Utility	cw	lps	lps	cw	lps	cw	cw	lps	cw	cw	cw
Equipment	E-1201 A-E	E-1202	E-1203	E-1204	E-1205	E-1206	E-1207	E-1208	E-1209	E-1210	E-1211
Temperature in (°C)	30	160	160	30	160	30	30	160	30	30	30
Temperature out (°C)	40	160	160	40	160	40	40	160	40	40	40
Flow (tonne/h)	20.20*	1.84	0.60	85.50	1.05	62.90	3.49	0.97	51.30	8.90	7.89

*Flow of cooling water shown for one exchanger only.

In order to maximize the selectivity of the heptene reaction, several reactor configurations were considered [1]. The reactor configuration that maximized the heptene production, in a minimum volume, was found to be a plug flow reactor in which the butene feed was introduced at one end and the propylene stream was injected along the side of the reactor. However, due to other considerations such as reactor complexity, it was finally decided to use a reactor with five equal stages in which the concentration in each stage is maintained approximately the same. Heat removal and mixing in each stage are accomplished by withdrawing a stream of material and pumping it through an external heat exchanger and back into the same stage of the reactor. The liquid cascades downward from stage to stage by means of liquid downcomers. The inside of the reactor can thus be considered similar to a five-plate distillation column (without vapor flow). The distribution of the feeds into the different stages is not shown in Figure B.11.1, and the dimensions of the reactor are taken directly from Chauvel et al. [1].

B.11.3 Simulation (CHEMCAD) Hints

All the hydrocarbon components used in the simulation can be considered to be well behaved, that is no azeotrope formation. The simulations were carried out using the SRK VLE and enthalpy packages using the CHEMCAD simulator.

B.11.4 Reference

1. Chauvel, A., P. Leprince, Y. Barthel, C. Raimbault, and J-P Arlie, *Manual of Economic Analysis of Chemical Processes*, trans. R. Miller and E. B. Miller (New York: McGraw-Hill, 1976), 207–228.