Olefin and Alcohol Production from Wet Natural Gas Holdings

Background

Recently, a "wet" natural gas supply was acquired near a small pilot scale production and research facility. This existing facility became very profitable through the production of small quantities of specialty chemicals. This new raw material supply is very intriguing because it can be used as a feed stock to the existing plant itself or as salable products via the design of new units.

The main goal is to design a plant for the production of C_4 and C_5 olefins and alcohols from the feedstock of wet natural gas. The composition of the natural gas is as follows:

Component	Volume %
Methane	78.00
Ethane	4.75
Propane	6.50
Isobutane	1.60
n-Butane	3.45
Isopentane	4.75
CO_2, N_2, He	0.95

The yearly feed of this supply is approximately 5000 metric tons per year. The designed process consists of four steps:

1. Separation of C_4 and C_5 alkanes from the wet natural gas. Also, included is a column design for the cryogenic separation of propane from the methane and ethane. This propane may either be sold if the market is favorable, or returned to the well with the methane and ethane.

2. Dehydrogenation of the C_4 and C_5 alkanes to mono-olefins.

3. Hydration of the C_4 and C_5 mono-olefins to alcohols.

The block flow diagram (Figure 1) shows how the natural gas plant will be built around the already existing, Semi-Works, plant. The overall plant design consists of three sections: cryogenic separation of the C_4 and C_5 hydrocarbons from the lighter hydrocarbons in the “wet” natural gas, production of mono-olefins from these hydrocarbons, and hydration of these olefins to alcohols. This plant is not only to be designed to produce marketable products, but also to supply the Semi-Works plant with a small supply of heavy hydrocarbons, olefins, and alcohols. These processes are very distinct and are more easily handled separately. The titles of the three processes are Cryogenics Separation, Olefins, and Alcohols. The uniqueness of this design is the time element used. In the Olefin and Alcohol units, the same equipment is used to produce three different products. The plant is set up to make one product for a certain period of time and then new raw materials are added to make different products over the course of a year.

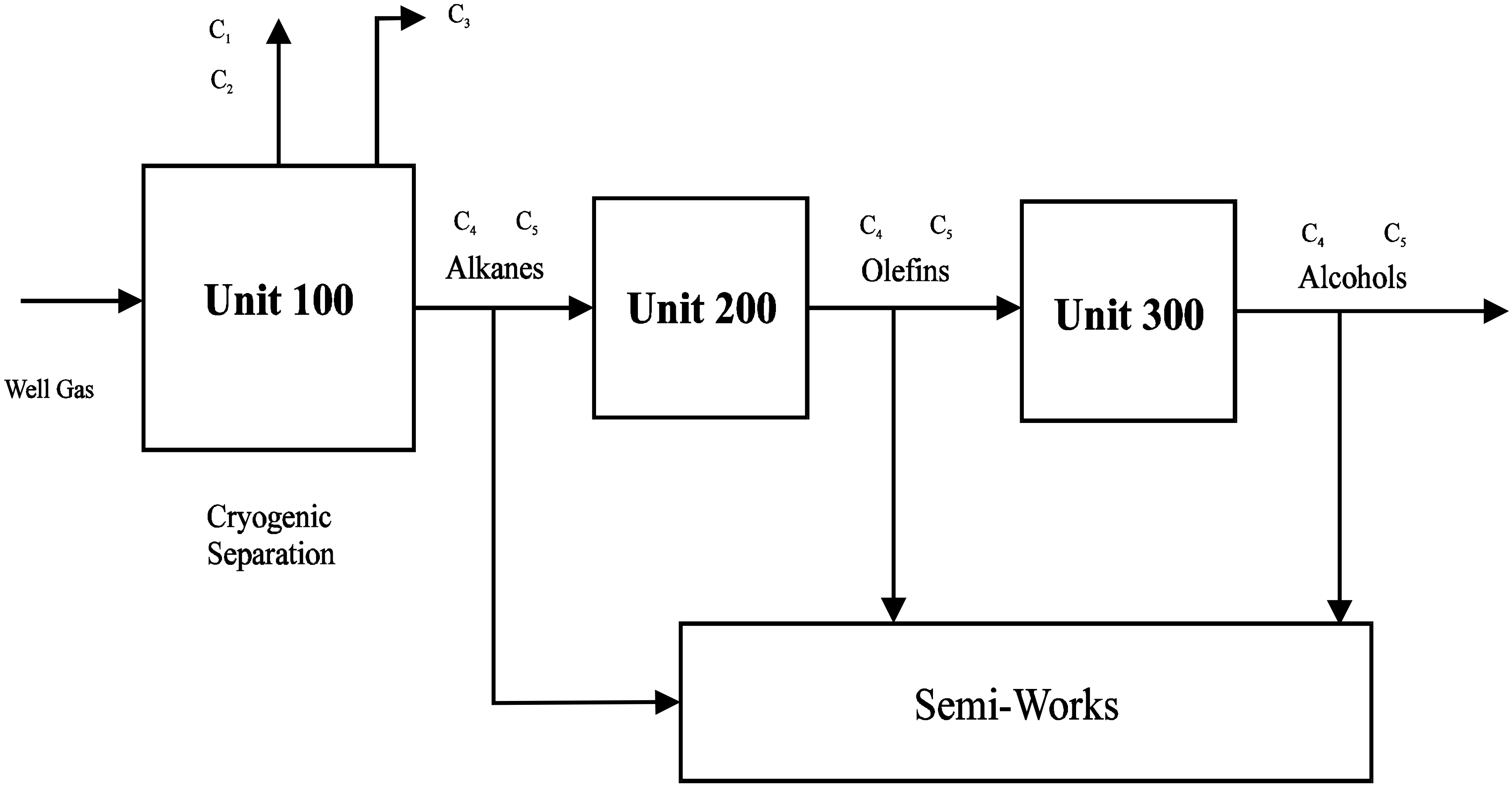


Figure 1: Block Flow Diagram

Unit 100 -- Cryogenic Separation

Background

The purpose of this section is to separate higher hydrocarbons from the natural gas stream. A preliminary PFD for the unit is shown in Figure 2 along with the PFD for the refrigeration system in Figure 3. The flow summary is given in Table 1. A flash is used to separate most of the methane and ethane from the propane, n-butane, i-butane, and i-pentane. The next step involves the further separation of the propane and remaining methane and ethane from the higher hydrocarbons. Another separation tower is used to separate the methane and ethane from the propane. The methane and ethane are returned to the well while the propane is sold for profit if desired. Most of the heavier hydrocarbons are sent on to the next unit for further processing. But some are supplied to the Semi-Works plant when needed.

Process Description

The natural gas, which is a mixture of C_1-C_5 hydrocarbons, is fed to this process at 10°C and 8 bar (Figure 2). The gas is piped through two heat exchangers, E-101 & E-102, which lowers Stream 6 to a temperature of -23°C using the outlets from the flash, V-101. It is then sent through another heat exchanger, E-103, cooling Stream 7 to -63°C. The natural gas is then flashed at -63°C and 7.4 bar in V-101. The top product, predominately methane and ethane, is sent back to the well. The bottom product, mainly C_3 and higher hydrocarbons, is sent to distillation column, T-101, where C_1-C_3 hydrocarbons are separated from the C_4-C_5 hydrocarbons which will be further processed in the olefins plant. The top product is sent back to the well. The bottoms out of T-101, Stream 14 consists mostly of n-butane, i-butane, and i-pentane. It is sent to a distillation tower, T-102, where the C_5 is separated from the C_4's. The distillate, Stream 17, from this tower is sent to a third column, T-104. Here the iC_4 is separated from the nC_4. The C_5, iC_4, and nC_4 streams (Stream 18, Stream 19, and Stream 20) are then sent to holding tanks. From here, theses higher hydrocarbons are sent to the Semi-Works plant or to the olefin unit for further processing.

The refrigeration loop for the system (Figure 3) compresses and expands ethylene for cryogenic cooling. The ethylene is compressed to 100 bar in C-102. Heat exchanger, E-104, cools the stream from 167°C to 45°C. E-105 cools Stream 28 further to 10°C with refrigerated water. The pressure is then released to 4 bar. By releasing the pressure, the ethylene cools to -76.2°C. The flash vessel, V-102, separates the liquid and vapor of Stream 21. The liquid is used in the condenser of T-101. Stream 23 is vaporized at a temperature of -75°C. Stream 24 is mixed with the vapor stream from flash vessel, V-102. Stream 25, the combined stream at -75.7°C and 4 bar, is used as the coolant in heat exchanger, E-103. Stream 26, -49.6° and 3.7 bar, is sent back to compressor, C-102.

[There are a few extra pieces of equipment on the PFD (Figure 2). Compressor, C-101, and distillation tower, T-103, are only to be used when the sale of propane is desirable. Propane is typically sold at a pressure of 20 bar. Therefore the system needs to be run at a higher pressure. Therefore, the process needs to be adjusted for the increase of pressure throughout the system. When selling propane, T-103 is needed to separate the lower carbons, methane, ethane, and propane. With the addition of T-103, the cryogenic loop needs to be adjusted for the low temperature of the heat exchanger, E-110.]

Necessary Information and Simulation Hints

When optimizing the separation towers, the number of stages, sequencing of columns, and operating pressure need to be varied in order to minimize the EAOC. The major cost of the cryogenic plant is the refrigeration loop (Figure 3). The electricity cost of the compressor is high due to the large amount of refrigerant needed to cool the feed from 10°C to -63°C. Using two heat exchangers, one with cooling water and one with refrigerated water, reduced the utility costs. The significant savings can also be obtained by optimizing the refrigeration loop. The use of different refrigerants in a temperature cascade should be considered.

Equipment Description

E-101	Cooler
E-102	Cooler
E-103	Cooler (Cryogenic loop)
E-104	Cryogenic loop cooler (CW)
E-105	Cryogenic loop cooler (RW)
E-106	C_1, C_2, C_3 condenser (Cryogenic loop)
E-107	C_4, C_5 reboiler
E-108	C_4’s condenser
E-109	C_5 reboiler
E-110	C_1, C_2 condenser
E-111	C_3 reboiler
E-112	i-C_4 condenser
E-113	n-C_4 reboiler

P-101	Pump
P-102	C_1, C_2, C_3 reflux pump
P-103	C_4’s reflux pump
P-104	C_1, C_2 reflux pump
P-105	i-C_4 reflux pump
C-101	Optional compressor if propane is desired for sale
C-102	Cryogenic loop compressor
V-101	Flash vessel
V-102	Cryogenic loop flash vessel
T-101	C_1-C_5 distillation tower
T-102	C_4, C_5 distillation tower
T-103	C_1, C_2, C_3 distillation tower
T-104	C_4’s distillation tower

Table 1: Stream Table for Unit 100

Stream	1	2	3	4	5	6
Temp. (°C)	10.0	10.0	10.0	-21.0	-25.0	-22.6
Press. (bar)	8.0	8.0	8.0	7.7	7.7	7.7
Vapor Fraction	1.0	1.0	1.0	0.9	0.9	0.9
Total Flow (kg/h)	593.75	359.70	234.05	359.70	234.05	593.75
Total Flow (kmol/h)	25.41	15.39	10.02	15.39	10.02	25.41
Component Flows (kmol/h)						
Methane	19.76	11.97	7.79	11.97	7.79	19.76
Ethane	1.20	0.73	0.47	0.73	0.47	1.20
Propane	1.64	1.00	0.65	1.00	0.65	1.64
I-Butane	0.41	0.25	0.16	0.25	0.16	0.41
I-Pentane	1.20	0.73	0.47	0.73	0.47	1.20
N-Butane	0.88	0.53	0.35	0.53	0.35	0.88
Nitrogen	0.08	0.05	0.03	0.05	0.03	0.08
Carbon Dioxide	0.08	0.05	0.32	0.05	0.03	0.08
Helium	0.15	0.09	0.06	0.09	0.06	0.15
Ethylene	--	--	--	--	--	--

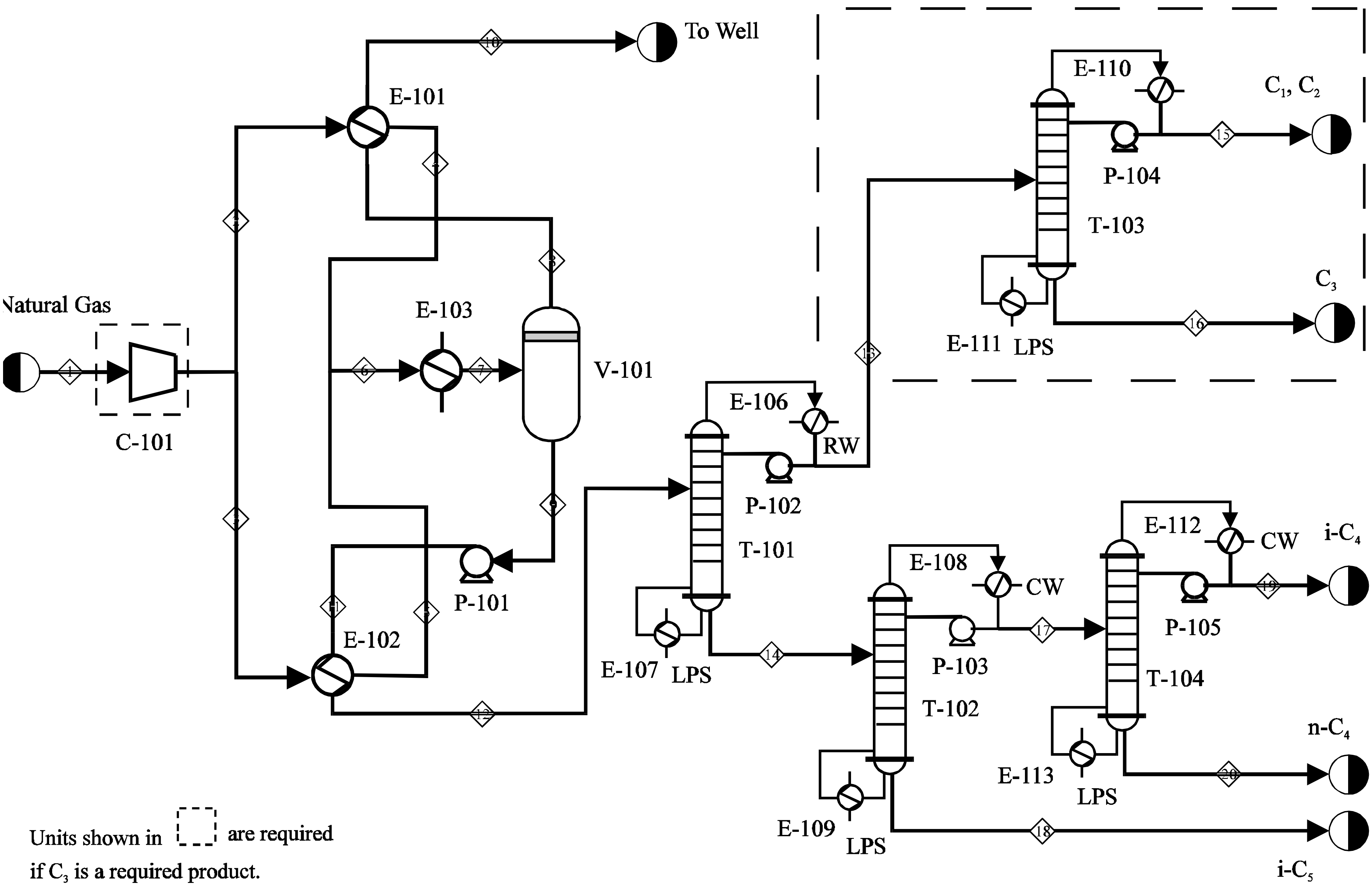
Stream	7	8	9	10	11	12
Temp. (°C)	-63.0	-63.0	-63.0	4.4	-62.9	4.0
Press. (bar)	7.4	7.4	7.4	7.1	12.3	12.0
Vapor Fraction	0.8	1.0	0.0	1.0	0.0	0.1
Total Flow (kg/h)	593.75	359.95	233.80	359.95	233.80	233.80
Total Flow (kmol/h)	25.41	20.85	4.56	20.85	4.56	4.56
Component Flows (kmol/h)						
Methane	19.76	19.30	0.47	19.30	0.47	0.47
Ethane	1.20	0.83	0.37	0.83	0.37	0.37
Propane	1.64	0.35	1.29	0.35	1.29	1.29
I-Butane	0.41	0.02	0.38	0.02	0.38	0.38
I-Pentane	1.20	0.01	1.19	0.01	1.19	1.19
N-Butane	0.88	0.03	0.85	0.03	0.85	0.85
Nitrogen	0.08	0.08	**	0.08	**	**
Carbon Dioxide	0.08	0.07	0.01	0.07	0.01	0.01
Helium	0.15	0.15	**	0.15	**	**
Ethylene	--	--	--	--	--	--

Stream	13	14	15	16	17	18
Temp. (°C)	-74.7	100.5	-106.3	32.3	82.7	124.1
Press. (bar)	12.0	12.0	12.0	12.0	12.0	12.0
Vapor Fraction	0.0	1.0	0.0	0.0	0.0	0.0
Total Flow (kg/h)	76.01	157.80	19.24	56.77	71.41	86.39
Total Flow (kmol/h)	0.17	2.43	0.84	1.29	1.23	1.20
Component Flows (kmol/h)						
Methane	0.47	--	0.47	--	--	--
Ethane	0.37	--	0.35	0.02	--	--
Propane	1.29	**	0.02	1.27	**	--
I-Butane	**	0.38	--	**	0.38	**
I-Pentane	--	1.19	--	--	**	1.19
N-Butane	--	0.85	--	--	0.84	0.01
Nitrogen	**	--	**	--	--	--
Carbon Dioxide	0.01	--	0.01	--	--	--
Helium	**	--	**	--	--	--
Ethylene	--	--	--	--	--	--

Stream	19	20	21	22	23	24
Temp. (°C)	73.6	87.3	-76.2	-76.2	-76.2	-75.0
Press. (bar)	12.0	12.0	4.0	4.0	4.0	4.0
Vapor Fraction	0.0	0.0	0.6	1.0	0.0	1.0
Total Flow (kg/h)	22.17	49.24	2358.40	1350.40	1008.00	1008.00
Total Flow (kmol/h)	0.38	0.85	84.01	48.14	35.93	35.93
Component Flows (kmol/h)						
Methane	--	--	--	--	--	--
Ethane	--	--	--	--	--	--
Propane	**	--	--	--	--	--
I-Butane	0.38	**	--	--	--	--
I-Pentane	--	**	--	--	--	--
N-Butane	**	0.84	--	--	--	--
Nitrogen	--	--	--	--	--	--
Carbon Dioxide	--	--	--	--	--	--
Helium	--	--	--	--	--	--
Ethylene	--	--	84.01	48.14	35.93	35.93

Stream	25	26	27	28	29
Temp. (°C)	-75.7	-49.6	166.9	45.0	10.0
Press. (bar)	4.0	3.7	100.0	100.0	100.0
Vapor Fraction	1.0	1.0	1.0	1.0	1.0
Total Flow (kg/h)	2358.40	2358.40	2358.40	2358.40	2358.40
Total Flow (kmol/h)	84.01	84.01	84.01	84.01	84.01
Component Flows (kmol/h)					
Methane	--	--	--	--	--
Ethane	--	--	--	--	--
Propane	--	--	--	--	--
I-Butane	--	--	--	--	--
I-Pentane	--	--	--	--	--
N-Butane	--	--	--	--	--
Nitrogen	--	--	--	--	--
Carbon Dioxide	--	--	--	--	--
Helium	--	--	--	--	--
Ethylene	84.01	84.01	84.01	84.01	84.01

** Very small traces



Units shown in ⬚ are required if C_3 is a required product.

Figure 2: Unit 100 -- Initial Separation

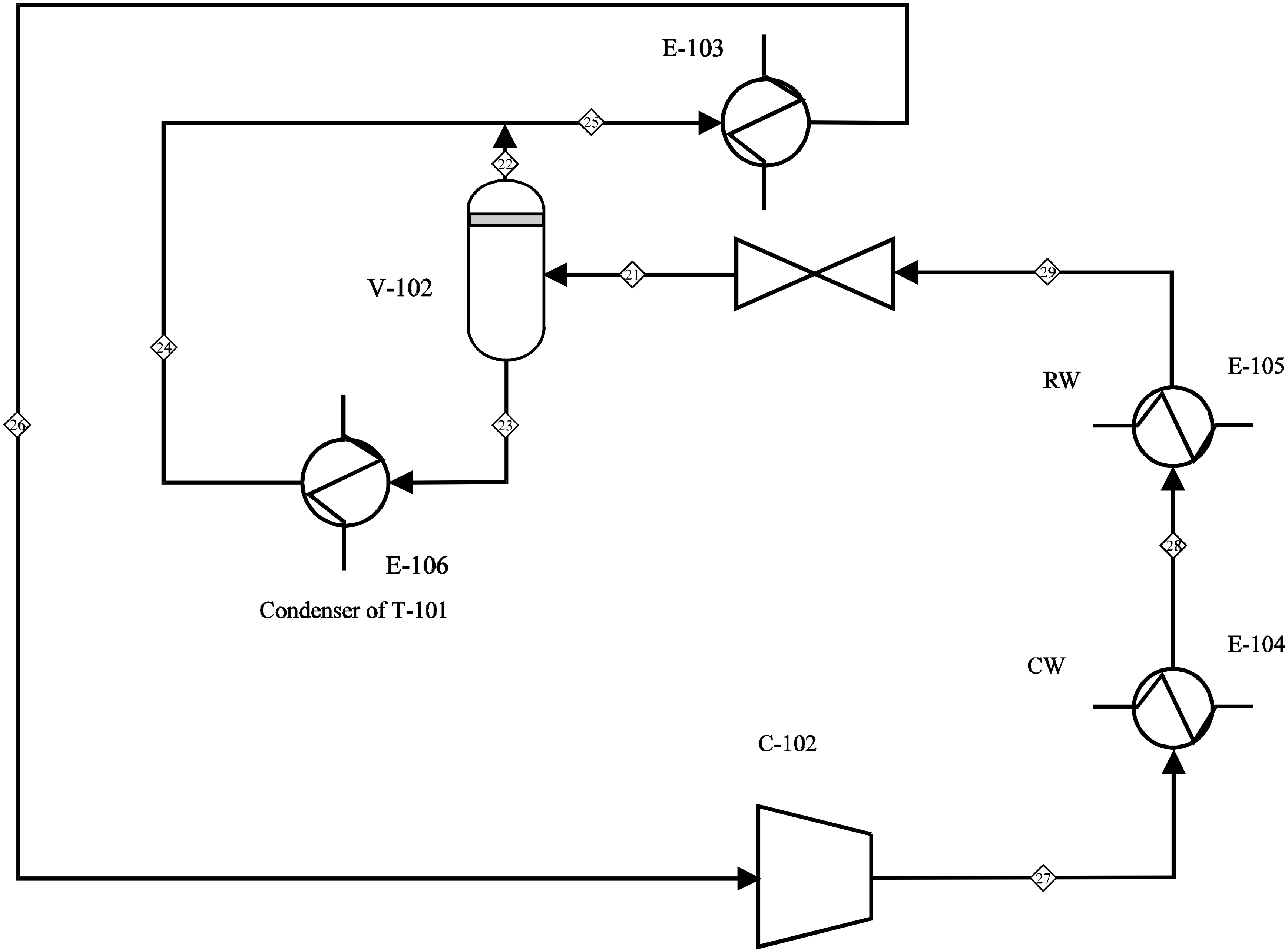


Figure 3: Unit 100 -- Refrigeration Cycle

Unit 200 -- Olefins

Background

The olefin production facility processes the higher hydrocarbons (n-butane, isobutane, and isopentane), separated in the cryogenics plant, into their respective olefins. N-butane is converted to n-butene, isobutane is converted to isobutene, and isopentane is converted to 2-methyl-1-butene.

$$2C_4H_{10} \Leftrightarrow C_4H_8 + C_3H_6 + 3H_2 + C(\text{Coke})$$
$$2CH(CH_3)_3 \Leftrightarrow C_4H_8 + C_3H_6 + 3H_2 + C(\text{Coke})$$
$$3(CH_3)_2CHCH_2CH_3 \Leftrightarrow C_5H_{10} + C_4H_8 + C_3H_8 + C_2H_4 + 3H_2 + C(\text{Coke})$$

The production of olefins involves the catalytic dehydrogenation of alkanes. The process uses chromium-alumina oxide catalyst in a fixed bed reactor. The reactor operates at approximately isothermal conditions, and is run at high temperatures and low pressures to achieve the desired conversion and selectivity.

Process Description

Processing the alkanes is set on a rotating schedule that takes up a whole year (351 days). It was determined that the alkanes could be processed one at a time in the same set of equipment. One alkane is processed while storing the other two in tanks. The processing time for the alkanes is adjusted so that the flowrates are approximately equal and this flowrate was used to size the equipment. The processing times are as follows: n-butane – 117 days, isobutane – 47 days, and isopentane – 187 days.

The olefin process flow diagram is shown in Figure 4 and consists of four major components. The first section is the feed preparation system. In this section, the process stream is heated from around 0°C to a temperature of 650°C and the pressure is lowered from 10 to 0.5 atmospheres.

After the feed has been adjusted to the reactor operating conditions, it is sent to the reactor system. The reaction process is cyclical in nature and uses a multi-reactor system to ensure continuous operation. An assumed conversion of 50% is used. The reduction of the catalyst following the regeneration is counter-balanced by the use of at least three reactors. One reactor processes the alkanes, one is regenerated using air, and the one is on stand-by. A purge is used to stop the build up of lighter hydrocarbons in the recycle and is used as fuel gas, Stream 6.

The reactor effluent is then sent to the separation system. This system consists of a flash and a series of distillation columns. In the flash, the non-condensable hydrogen is separated from the hydrocarbons. Depending on the alkene, either two or three columns are needed to separate the olefin, unreacted alkane, and the by-products. The butanes require two columns, while three columns are necessary for isopentane. All three olefin processes use the same equipment with slightly different piping systems (Figure 4). The unreacted alkane is recycled and mixed with fresh feed where it is sent to the reactor to be processed again. The olefins are sent to the alcohol plant and the other distillation products such as propylene, propane, and ethylene can be used as a fuel source or returned to the natural gas well.

Necessary Information and Simulation Hints

For a given reactor, the total cycle time ranges from 15 to 30 minutes. The regeneration step is necessary for two reasons. The first is to regenerate the catalyst because during the dehydrogenation of the alkanes coke is deposited on the catalyst bed. The coke is burned off during the regeneration step, which involves passing hot air through the catalyst bed.

Secondly, since the dehydrogenation reaction is endothermic, heat must be supplied to the reaction to maintain an isothermal process. The majority of the heat of reaction is added to the process during regeneration – reheat step from several sources. These include:

1. Combustion of coke deposited during the dehydrogenation step.
2. Sensible heat from the hot regeneration air stream.
3. Reduction of the catalyst following the regeneration.

N-butane and isobutane only require two distillation columns, while isopentane requires three. This means that a third tower must be used when processing the isopentane (Figure 6-8).

Equipment Description

E-201	Reactor inlet heater
R-201 A/C	Reactor
E-202	Reactor effluent cooler
C-201	Compressor
E-203	Pre-flash cooler
E-204	Pre-flash cooler
V-201	Flash
E-205	Heater (only used in the production of 1-Butene)
T-201	Hydrogen distillation tower
E-206	Condenser
E-207	Reboiler
V-202	Reflux drum

P-201	Reflux pump
T-202	Distillation tower
E-208	Condenser
E-209	Reboiler
P-202	Reflux pump
T-203	Distillation tower
E-210	Condenser
E-211	Reboiler
P-203	Reflux pump

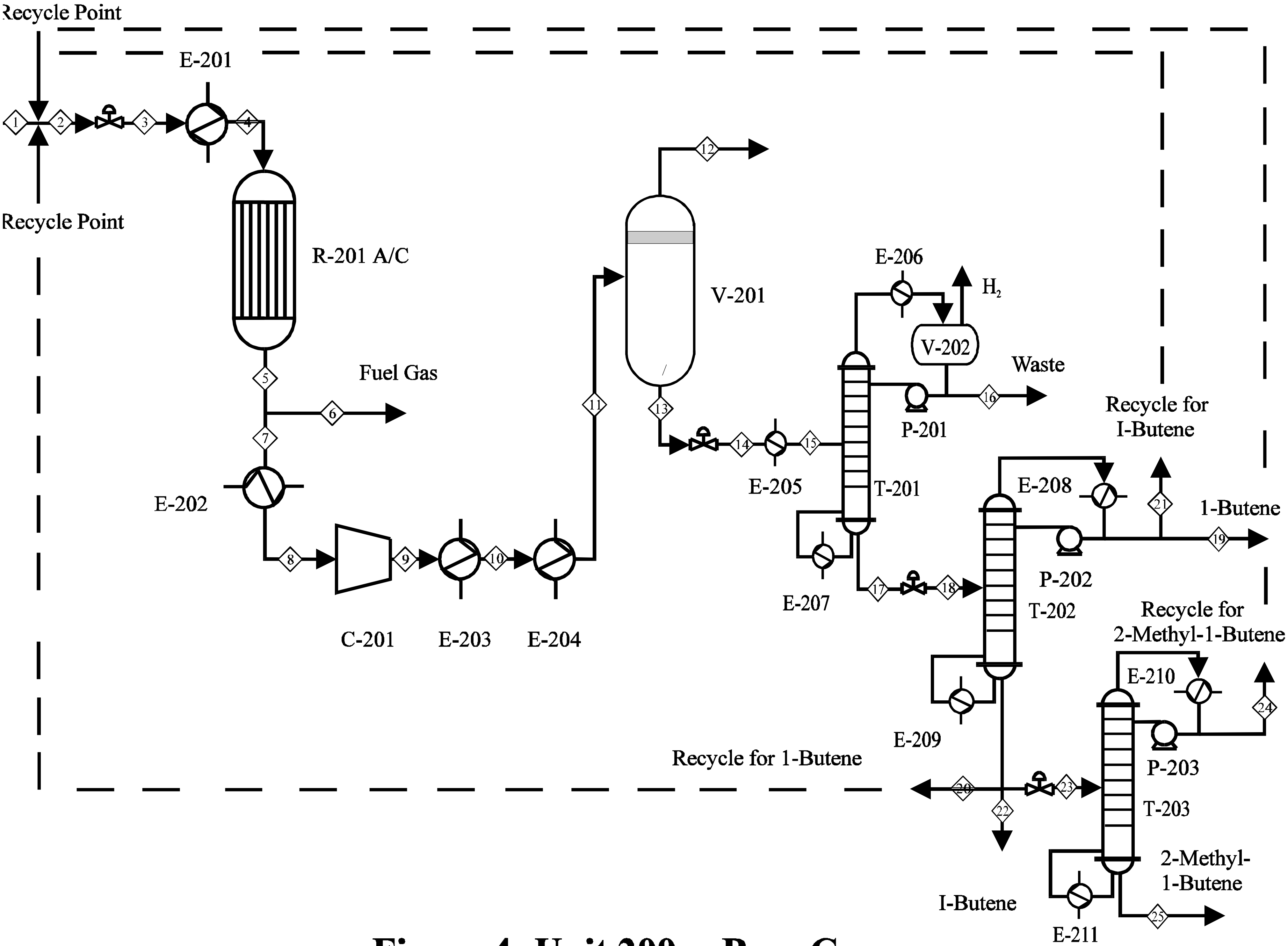


Figure 4: Unit 200 -- Base Case

**T-103 is only required
for 2-methyl-1-butene

Unit 300 -- Alcohols

Background

Following the conversion of the alkanes to olefins (isobutene, 1-butene, and 2-methyl-1-butene), the olefin products are fed to the alcohol production plant where they are converted to alcohols by the reaction:

$$C_nH_{2n} + H_2O \rightarrow C_nH_{2n+1}OH$$

The process is based on U.S. Patent # 4,182,920 (1), by Dow Chemical Company. The abstract for this patent describes the process as “an improved process for making alcohol by hydration of an olefin.” The “improvements” refer to higher conversions and yields, as well as a reduction in the amount of solvent needed. The catalyst for the process is an ion-exchange resin. Acetone is used as the solvent in this process and serves to keep the products from accumulating at the catalyst surface.

Like the patented process, which converts olefins to alcohols, the proposed production scheme consists of three reactors each followed by a heat exchanger. The alcohol products, specifically tert-butanol, sec-butanol, and 2-methyl-2-butanol, are to be produced with a minimum purity of 98 percent by weight. The reaction takes place in the liquid phase at relatively low temperatures (less than 100°C) and a pressure of approximately 10 bar.

Process Description

The process flow diagram for the alcohol production plant is shown in Figure 9. The plant is designed to produce three different alcohol products from three different alkenes. The plant handles the alkenes, one at a time. The sequencing of feeds is spaced out through the year to maintain a continuous process. Three different raw material feeds may enter the system. N-butene and isobutene are pumped to a pressure of 10 bar by pump P-301. 2-methyl-1-butene enters at 2.0 bar. The feed stream in use is then fed to a horizontal mixing tank, TK-301, to insure a well-mixed feed. Stream 4, containing acetone and water, is fed to the mixing tank. The acetone serves as a solvent and the water is a raw material. Two recycle streams (Stream 18 and Stream 19) enter the mixing tank to recover some raw materials and a small amount of product. From the mixing tank the unified stream, Stream 5, enters the reaction system.

The reaction system consists of a heat exchanger, E-301, which heats the feed to 70°C, followed by a packed bed reactor. No kinetics are available, so a fractional conversion of 0.88 is assumed. This is the minimum conversion, given in any example in the patent (1). Upon exiting the reactor system, the effluent travels through an anion exchange bed (A-301). This anion exchange bed removes any formic or acetic acid that were formed as side products. Stream 8, exiting the anion exchange bed, passes through heat exchanger, E-302, to insure the proper temperature for the flash. Stream 9 is flashed to purge olefins in order to avoid excessive build up in the system. The liquid and vapor streams exiting the flash vessel (V-301) are then fed to two more flash vessels (V-302 and V-303) to further purify the streams. The liquid stream (Stream 17) from the bottom of V-303 is sent to a distillation column (T-301) where the individual components are purified. The distillate, Stream 19, is the raw material recycle. The bottoms, Stream 20, is the purified product (98% by weight).

Necessary Information and Simulation Hints

It might prove valuable to study the effects of interstage cooling in the reactor. A recommended design is the use of three packed bed reactors in series with intercooling.

In this case, the single-pass fractional conversion is raised to 93 percent, which is the value obtained from the patent example after which the operating conditions were modeled (1). The new production schedule is as follows: t-butanol --58 days, sec-butanol -- 103 days, and 2-methyl-1-butanol -- 189 days.

Reference

1. Giles, J.H., J.H. Stultz, and S.W. Jones, "Process for Hydration of Olefins to Produce Alcohols," U.S. Patent #4,182,920, 1980.

Equipment Description

TK-301	Mixing tank
P-301	Pump
TK-302	Mixing Tank
E-301	Cooler
R-301	Packed Bed Reactor
A-301	Anion Exchange Bed
E-302	Heater
V-301	Flash Vessel
E-303	Cooler
E-304	Heater
V-302	Flash Vessel
V-303	Flash Vessel
T-301	Alcohol Purification Tower
P-302	Reflux Pump
E-305	Condenser
E-306	Reboiler

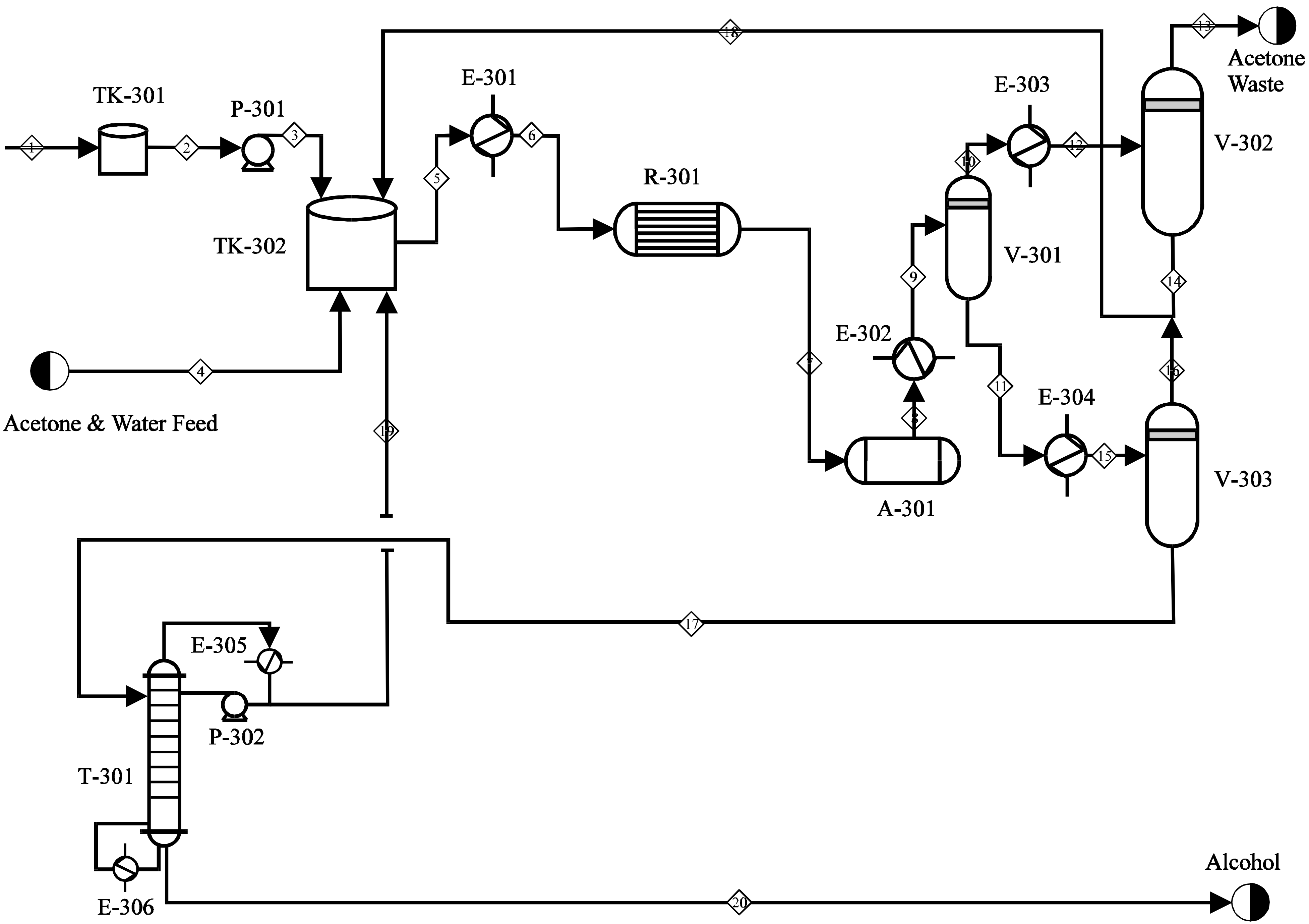


Figure 9: Unit 300 -- Alcohol Production