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Short communication

New process for separating propylene and propane by extractive distillation with aqueous acetonitrile

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Abstract

A new process for separating propylene and propane in ethylene production has been put forward in which the extractive distillation with aqueous acetonitrile (ACN) as entrainer is employed. A PRO/II software process simulation has been made with the selection of an appropriate vapor–liquid equilibrium model. The new process, extractive distillation, requires a small number of trays, less energety consumption and small column diameter. In the design of the distillation column a new type of multi-overflow compound slant-hole tray was adopted which has been widely used in the recent years. It is believed that with the new process the industrial separation of propylene and propane is greatly improved. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Propane; Propylene; Extractive distillation; PRO/II; Slant-hole tray

1. Introduction

With the rapid increase of demand for propylene derivatives since 1970s, the production of propylene has become more and more important. Since most of the propylene comes from pyrolysis gases, the separation of propylene in ethylene projects has great commercial significance. In ethylene projects, propylene is purified from a mixture mainly composed of propylene and propane. It is known that the pure component boiling points are very close over a large range of pressure and they are difficult to separate by ordinary distillation. The present paper is therefore focused on the separation of propane and propylene.

In general, separation processes for propane and propylene can be divided into three types: low-pressure distillation, high-pressure distillation and distillation with heat pump [1,2]. The high-pressure distillation uses water for cooling the top of the tower (at temperature above 313.15 K), and the bottom temperature is about 343.15 K, which can be met by ordinary low pressure steam. But the reflux ratio is very high and the number of theoretical trays is very large. Distillation under low pressure will improve the relative volatility of propane and propylene. As a result, the number of theoretical trays and the reflux ratio are obviously reduced. However, a specialized condensing agent is required instead of ordinary water to cool the top of the tower. The top product can be compressed as a cryogen and vaporized at the bottom. Due to the complexity of this process the high-pressure distillation is often preferred. Aiming at the disadvantages of high-pressure distillation such as high reflux ratio and large number of theoretical tray, this paper is intended to optimize the process by adding solvent, namely extractive distillation. The new process takes the advantage of the interaction difference that exists between the solute and solvent. The different electron fluidity of propane and propylene is the foundation for producing different interactions.

Aqueous acrylonitrile (ACN) was selected as entrainer for extractive distillation because of its low cost and low boiling point which would be helpful to retain the advantage of low grade heat in the old process. The physical properties of acrylonitrile, water, propylene and propane are presented in Table 1.

A vapor–liquid equilibrium model was confirmed first by experiments and simulation on the existing process, and the novel extractive distillation process was simulated with the PRO/II software. The column trays were then designed on the basis of the simulation result for application in the novel process in practice.

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Nomenclature

L	liquid flow rate ($m^3\,h^{-1}$)
V	vapor flow rate ($m^3\,h^{-1}$)
α	relative volatility
ρ_L	density of liquid ($kg\,m^{-3}$)
ρ_V	density of vapor ($kg\,m^{-3}$)
σ	surface tension ($N\,m^{-1}$)

Subscripts

1	1-butane
2	1-butene
3	*trans*-2-butene
4	*cis*-2-butene
5	butadiene-1,3

Table 1
The physical properties of ACN, water, propylene and propane

	Molecule weight	Boiling point (K)	Liquid density ($kg\,m^{-3}$)
ACN	41.053	354.8	782
Water	18.015	373.2	998
Propylene	42.081	225.4	612
Propane	44.097	231.1	582

2. Selection of the vapor–liquid equilibrium model and the experimental data

In this work an air-lift apparatus was set up to measure the relative volatility at infinite dilution by inert gas stripping and gas chromatography method [3,4]. The composition of each sample was determined by local SQ-206 equipped with a thermal conductivity cell. Sebaconitrile was used as the fixed agent of the column packing, and hydrogen as the carrier gas. The column packing was at room temperature. The method is based on the variation of vapor phase composition when highly dilute components of liquid mixture are stripped from the solution by a constant flow of inert gas. In the stripping cell the outlet gas flow that is in the equilibrium state with the liquid phase is injected into the gas chromatograph by means of a six-way gas valve at certain intervals. In addition, the method employed in this study involved a modification of equilibrium cell configuration to enlarge the gas–liquid interface and to increase the contact time between gas and liquid phases with spiral path, and the use of a double cell. The experimental results listed in Table 2 were compared with those of references [5] and proved to be reliable. On this basis a series of relative volatilities at infinite dilution of ACN + propane + propylene system was measured and is given in Table 3.

Table 2
The relative volatilities of C4 at infinite dilution for the *N,N*-dimethylformamide (DMF) + C4 system

	303.15 K	323.15 K	
	This work	This work	The literature (values)
α_{15}	3.92	3.32	3.43
α_{25}	2.35	2.12	2.17
α_{35}	1.96	1.79	1.76
α_{45}	1.69	1.61	1.56

Selecting an appropriate model of vapor–liquid equilibrium is of vital importance in simulating the distillation process. The key for the vapor–liquid equilibrium model is the activity coefficient model. Since the UNIFAC group contribution [6–9] method is the most commonly used model in calculation of extractive distillation, it was also used in this work. From Table 3 it is shown that the calculated values in terms of UNIFAC are in good agreement with experimental data. The software used for simulation was PRO/II.

3. Simulation of two processes

Fig. 1 shows the existing high-pressure distillation process for separation of propane and propylene, which is also the process generally used in industry. Fig. 2 displays the

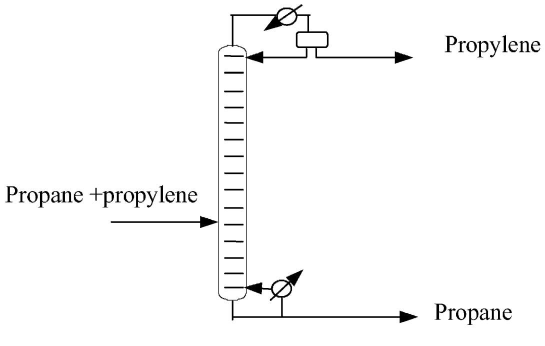

Fig. 1. The high-pressure distillation process for separation of propane and propylene.

Table 3
Comparison of the experimental data and calculated values

Solvent	Temperature (K)	Infinite dilution relative volatility	
		Experimental data	Calculated value of UNIFAC
ACN	292.05	1.69	1.71
ACN	303.15	1.62	1.70
ACN + 10 wt.% H_2O	288.65	1.75	1.85

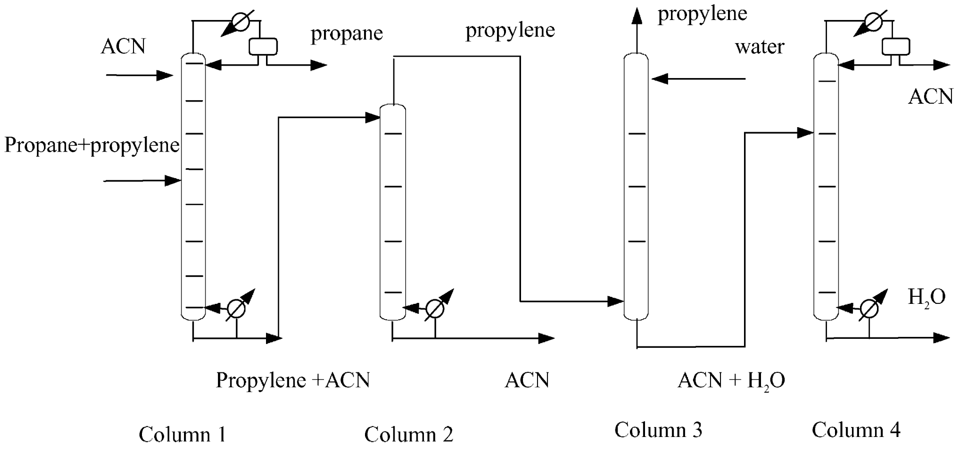

Fig. 2. The new separation process of extractive distillation.

new separation process of extractive distillation. The new process consists of four sections: (1) extractive distillation column; (2) stripping column; (3) water scrubber; (4) recovery tower (for extractive solvent). In the extractive distillation column propane and propylene are separated, and propane can be obtained on the top of the column. In the stripping column the extractive solvent is recovered from the bottom and propylene with high concentration is produced at the top of the column. In the water scrubber trace ACN in propylene is washed down by water and the product propylene is recovered from the top. In the recovery tower the mixture of water and ACN is distillated for recovery of ACN.

The existing process of high-pressure distillation was simulated with the practical operation conditions to verify the validity of the simulation by PRO/II software. Then the two processes were simulated and compared.

The design conditions and the comparison of simulation results with the measured values from the practical plant are listed in Tables 4 and 5, respectively, for high pressure distillation.

The agreement of the simulation results with measured values proves the reliability of the simulation by PRO/II.

Table 4
Operation parameters of high pressure distillation

Feed ($kg\,h^{-1}$)	32040
Feed concentration of propylene (mol%)	84
Feed tray	90
Feed temperature (K)	318.15
Feed pressure (kPa)	1910
Top pressure (kPa)	1910
Column pressure drop (kPa)	60
Reflux ratio	15
Top product ($kg\,h^{-1}$)	26500
Bottom product ($kg\,h^{-1}$)	5540

The two processes were simulated with PRO/II under the same separation requirement (Table 6) and the results of calculation was listed in Table 7. From Table 7 it can obviously seen that the novel process is superior to the existing one and the thermal loads of condenser and reboiler are reduced by 79.1 and 13.2%, respectively. The save of heat duty of the condenser is very large and the number of theoretical trays is cut down by 25%.

Vapor–liquid load of a majority of trays in the columns for the existing process and the extractive distillation process (columns 1 and 2) is respectively given in Tables 8 and 9. The whole distribution of vapor–liquid load in the columns is illustrated in Figs. 3 and 4. The results turn out that the vapor–liquid load decreases rapidly for the extractive distillation process.

4. The design of column plates

Bearing in mind the high pressure used for separation of propane and propylene, a plate column was selected for design and operation. There are many types of plates employed in plate columns such as the slant-hole tray, floating valve tray and sieve tray, among which the slant-hole tray

Table 5
Comparison of simulation results and measured values of high pressure distillation

	Simulated value	Measured value
Top temperature (K)	319.75	319.45
Bottom temperature (K)	328.45	331.25
Concentration of propylene in top product (mol%)	99.3	99.2
Concentration of propylene in top product (mol%)	7.62	8.2
Heat duty of reboiler ($kJ\,h^{-1}$)	122.2	123.3
Heat duty of condenser ($kJ\,h^{-1}$)	122.0	122.5

Table 6
Process controlled parameters for two processes

Feed rate (kg h^{-1})	Composition of propylene in feed (mol%)	Product rate (kg h^{-1})	Composition of product propylene (mol%)
32000	84	26500	≥99.3

Table 7
Energy consumption of the two process

	Existing process	Novel process				Saving (%)
		Column 1	Column 2	Column 3	Column 4	
Condenser (10^6 kJ h^{-1})	122.2	9.8	0	0	15.8	79.1
Reboiler (10^6 kJ h^{-1})	122.0	49.0	37.4	0	19.5	13.2
Number of theoretical tray	120	50	10	10	20	25.0

Table 8
The vapor–liquid load in the column of the existing process

Plate no.	V (m^3 h^{-1})	L (m^3 h^{-1})	ρ_V (kg m^{-3})	ρ_L (kg m^{-3})	σ (N m^{-1})
1–90	9967	860.2	42.7	464.2	0.00408
91–120	9737	948.1	44.1	459.0	0.00395

Table 9
The vapor–liquid load in the column of the extractive distillation process

Plate no.	V (m^3 h^{-1})	L (m^3 h^{-1})	ρ_V (kg m^{-3})	ρ_L (kg m^{-3})	σ (N m^{-1})
Column 1					
3–22	1981	425.9	40.8	632.5	0.02557
23–50	2538	536.1	38.1	589.1	0.02200
Column 2					
1–10	10201	315.5	3.4	709.4	0.02601

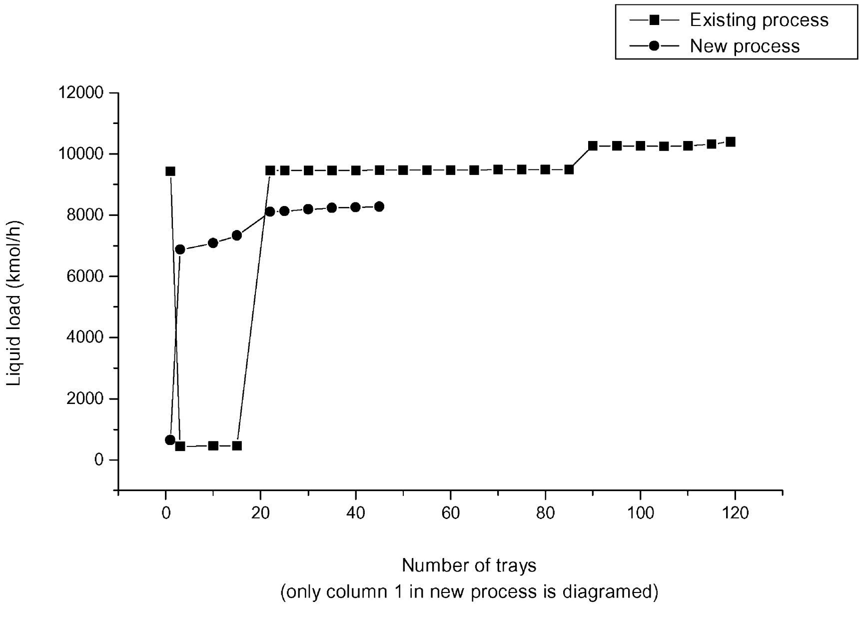

Fig. 3. Liquid load in the column for the two processes.

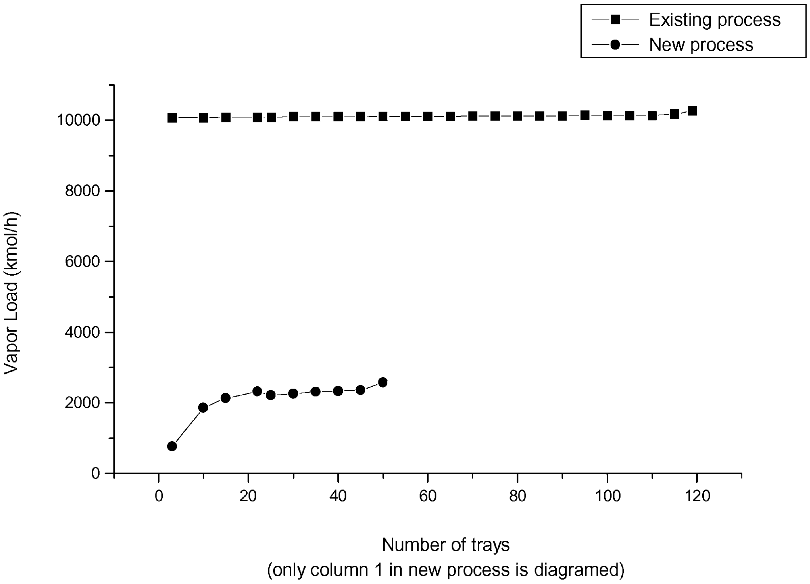

Fig. 4. Vapor load in the column for the two processes.

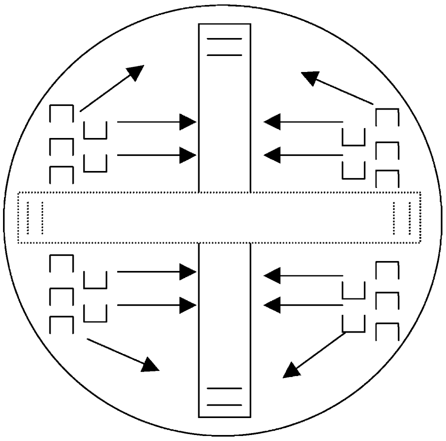

Fig. 5. Configuration of multi-overflow (double flow) slant-hole tray.

has the advantages of high performance and low cost. On the slant-hole tray straggly slanting holes are arranged which can produce liquid and vapor streams and horizontal ejection can enable high gas rates. The evenly distributed gas on the slant-hole tray can avoid continually accelerated gas flow and retain a steady liquid layer. This kind of plate has the features of high production capacity and high efficiency, based upon which the column plate was designed. A new-type multi-overflow compound slat-hole tray was developed for high liquid and vapor load. The new-type multi-overflow compound slant-hole tray adopts two down-flow pipes similar to a multidowncomer tray and has the advantages of simple construction, long liquid flow path and high production capacity and plate efficiency. The replacement of sieve trays by slant-hole trays also improved the production capacity and plate efficiency.

The configuration of our double overflow slant-hole trays is pictured in Fig. 5. In terms of the vapor and liquid load of the column, we obtain the tray parameters by tray software that we have programmed for the sake of modification of column 3. The function of the tray software is presented in detail in the reference [10]. These parameters listed in Tables 10 and 11 are valid because the designed values are in the range of normal operation condition.

The results of design display obvious enhancement of production efficiency with large reduction of column radius (from 5 to 3 m) in the novel process.

Table 10
The results of design on the existing process column trays

Plate no.	1–90	91–120
Column diameter (m)	5	5
Tray spacing (m)	0.6	0.6
Slant-hole area ratio (%)	8	8
Overflow type	Double overflow	Double overflow
Weir length (m)	18	18
Weir width (m)	0.4	0.4
Weir height (m)	0.03	0.03
Downcomer gap (m)	0.1	0.1
Downcomer area (m^2)	3.6	3.6
Overflow intensity ($m^3\,m^{-1}\,h^{-1}$)	47.79	52.67
Vapor velocity for diameter ($m\,s^{-1}$)	0.141	0.138
Hole *F*-factor	11.52	11.44
Liquid height in the tray (mm)	69.11	71.73
Tray pressure drop (mmH_2O)	65.20	66.42
Downcomer pressure drop (mmH_2O)	90.08	109.43
Liquid height in the downcomer (mmH_2O)	155.29	175.85
Residence time (s)	7.99	7.24
Vapor entrainment	0.003	0.003

Table 11
The results of design of column tray in the new extractive distillation process

Plate no.	Extractive distillation column		Stripping column
	3–22	23–50	1–10
Column diameter (m)	3	3	3
Tray spacing (m)	0.45	0.45	0.45
Slant-hole area ratio (%)	6	6	6
Overflow type	Double overflow	Double overflow	Double overflow
Weir length (m)	10	10	10
Weir width (m)	0.4	0.4	0.4
Weir height (m)	0.03	0.03	0.03
Downcomer gap (m)	0.1	0.1	0.1
Downcomer area (m^2)	2	2	2
Overflow intensity ($m^3\,m^{-1}\,h^{-1}$)	42.59	53.61	31.55
Vapor velocity for diameter ($m\,s^{-1}$)	1.30	1.66	6.68
Hole *F*-factor	8.29	10.27	12.33
Liquid height in the tray (mm)	66.22	72.22	59.65
Tray pressure drop (mmH_2O)	44.76	55.28	52.77
Downcomer pressure drop (mmH_2O)	49.69	78.73	27.27
Liquid height in the downcomer (mmH_2O)	94.44	134.01	80.04
Residence time (s)	6.42	5.10	8.67
Vapor entrainment	0.0011	0.0021	0.0041

5. Conclusion

The existing and the new extractive distillation processes were simulated respectively on the basis of UNIFAC group contribution method with PRO/II software. The results of the design lead to the conclusion that the new process flow-scheme is much superior to the existing one with the saving of 13.2% reboiler load and 79.1% condenser load and the reduction of theoretical trays by 25%. The design of column plates was made according to the results of the simulation. With the selection of slant-hole tray in design, the radius of plate can be declined from 5 to 3 m.

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