Steam Consumption on Solvent Recovery Distillation of 1500t/a Propylene Oxide Pilot Plant: Simulation and Optimization

YI-CHUAN LI¹, BEN-XIAN SHEN¹, WEI-GUO XIAO², LEI WANG^{1,2} and JI-GANG ZHAO^{1,*}

¹State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, P.R. China

²Tianjin Dagu Chemical Co., Ltd., Tianjin, P.R. China

*Corresponding author: Fax: +86 21 64252851; Tel: +86 21 64252916; E-mail: zjg@ecust.edu.cn

(Received: 4 December 2012;

Accepted: 9 September 2013)

AJC-14077

China's first pilot-scale hydrogen peroxide to propylene oxide (HPPO) plant has been built in Tianjin in March 2009. In the test duration, it produced qualified propylene oxide but its solvent recovery distillation consumed more energy. In order to improve the energy utilization level of plant, the solvent recovery process was simulated and its steam consumption was optimized by PRO/II with established thermodynamic model. According to the energy-saving optimization results, the actual steam consumption performed in the 1500 t/a plant could be reduced by 6.2 %.

Key Words: Propylene oxide, Direct epoxidation, Solvent recovery distillation, Steam consumption, Simulation, Optimization.

INTRODUCTION

Propylene oxide (PO) is an important chemical raw material and intermediate, which has broad application in polyester industry. However, among the existing methods of industrial production, chlorhydrination has serious pollution to the environment while the co-oxidation produces a large amount of joint products. Neither of them can meet the requirements of sustainable development. In recent years, hydrogen peroxide to propylene oxide (HPPO) process was regarded as an important development trend of propylene oxide green production for its mild reaction conditions, high catalytic activity and high atoms utilization without pollution problems. The world's largest commercial-scale propylene oxide (PO) plant and the first based on the innovative hydrogen peroxide to propylene oxide (HPPO) technology jointly developed by BASF SE (BASF) and The Dow Chemical Company (Dow) has completed its start-up phase in March 2009 and is running stably¹. Both companies are satisfied with the performance of the new process which is regarded as a historical milestone in propylene oxide production. At present, there are no similar device reported in China.

East China University of Science and Technology and Tianjin Dagu Chemical Co., LTD developed a 1500 t/a novel-process HPPO pilot plant applying propylene epoxidation over lamellar TS-1 molecular sieve catalyst^{2,3} in May 2007. The process uses hydrogen peroxide as oxidant and methanol as solvent⁴. After the reaction of propylene oxide from propylene

and H₂O₂ in a tube reactor, high-purity propylene oxide are separated in a rectification column followed by a solvent recovery distillation in which the methanol was recovered from the material flow. Since it was set up the unit has operated stably and accomplished sustain cleaner production of propylene oxide. In order to promote the construction of 10000 t/a propylene oxide plant, better economic performance should be achieved. Considering the energy needed by the solvent recovery tower occupies a large proportion of pilot plant operating cost, the software PRO/II of SIMSIC is employed to simulate the steam consumption of kettle reboiler using established thermodynamic model. Furthermore, the effects of multiple process parameter variations of the solvent recovery distillation are investigated and the values of parameters are determined so that the economic benefits are optimized while the process constraints and specifications are satisfied. The proposed energy-saving solution of solvent recovery process is carried out successfully in the pilot plant.

EXPERIMENTAL

Solvent recovery process statement: After the separation of propylene oxide, 70 % of stream is recycled to reactor directly while the remaining 30 % is put into a distillation column to recover the methanol in the top, then it will be also recycled to the reactor. So the existing solvent recovery ratio is 30 %. Feedstock composition and separation requirements of solvent recovery distillation are shown in Table-1. Except for the produced by epoxidation, most of water in the system

TABLE-1
CONSTRAINTS AND REQUIREMENTS OF
SOLVENT RECOVERY PROCESS

Stream	Mass fraction (%)				
	PO	Methanol	H ₂ O	1,2-PG	PGME
Feedstock	0.2	80.1	17.0	0.3	2.4
Top	-	> 90.0	-	0	0
Bottom	-	0	-	-	-

is imported as solvent of H₂O₂ before reaction. In order to maintain the stability of units the amount of water in the system should be controlled. So that the mass flow rate of water in the bottom have to be equated to the sum of the mass flow rate of water in reactor feed and production rate of water in reactor. Propylene glycol monomethyl ether (PGME) and 1,2-propylene glycol (1,2-PG) are the by-products of propylene epoxidation.

Main parameters of column are showed in Table-2. The kettle reboiler is heated by steam at 750 KPa. The mass of steam consumed by the reboiler gives expression to its heat load when one ton of propylene oxide is produced.

TABLE-2
MAIN PARAMETERS OF COLUMN

Parameters	Value
Number of stage	40
Feeding stage	26
Distillate pressure (kPa)	300
Stage pressure drop (kPa)	0
Reflux ratio	0.3
Steam consumption (t tPO ⁻¹)	10.0

Thermodynamic model foundation

Gaseous phase: In phase equilibrium calculation, The virial equation terminated at the second coefficient is a simple but accurate predicting method for the fugacity of gas mixture under low pressure. the most convenient form of the virial equation to be used is

$$z \equiv \frac{Pv}{RT} = 1 + \frac{BP}{RT} \quad (1)$$

where v is the molar volume and, in a mixture of N components

$$B = \sum_{i=1}^N \sum_{j=1}^N y_i y_j B_{ij}(T) \quad (2)$$

Here y is the mole fraction and B_{ij}(T) is the second virial coefficient characterizing pair interactions between an 'i' and a 'j' molecule, a function only of temperature. The vapour fugacity is given by

$$f_i^v = y_i P \phi_i \quad (3)$$

where the fugacity coefficient is given by

$$\ln \phi_i = \left(2 \sum_{j=1}^N y_j B_{ij} - B_m \right) \frac{P}{RT} \quad (4)$$

where B_{ij} is pure-component or cross second virial coefficient, B_m is the virial coefficient of mixture. However, the virial equation is not valid for substances which associate very strongly,

such as methanol and water. As gas mixtures are highly non-ideal, the 'chemical theory' for nonideality can give good predictions in such cases when an equilibrium constant for association is available⁵. B_{ij} should be given by Hayden - O'Connell equation⁶ which recommend

$$B_{ij} = B_{ij}^F + B_{ij}^D \quad (5)$$

Here B_{ij}^F is physical contribution, B_{ij}^D is chemical contribution. If only take the binary associating of methanol into consideration, the fugacity coefficient of component 'i' is given by

$$\phi_i = \frac{Z_i}{y_i} \exp \left(\frac{B_i^F p}{RT} \right) \quad (6)$$

where y_i is the apparent mole fraction of component i, Z_i is the real mole fraction of component i.

Liquid phase: Since the system contains methanol, water and other non-ideal polar components, the nonrandom two-liquid (NRTL) activity coefficient model was used for the thermodynamic modeling of the system. The nonrandom two-liquid equation is applicable not only to the strongly non-ideal liquid, but also to the miscible and partially miscible system. For the binary system, its expression is⁷

$$\ln \gamma_1 = x_2^2 \left(\frac{\tau_{12} G_{21}^2}{(x_1 + x_2 G_{21})^2} + \frac{\tau_{12} G_{12}^2}{(x_1 + x_2 G_{12})^2} \right) \quad (7)$$

$$\ln \gamma_2 = x_1^2 \left(\frac{\tau_{12} G_{12}^2}{(x_2 + x_1 G_{12})^2} + \frac{\tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} \right) \quad (8)$$

Here

$$\tau_{12} = (g_{12} - g_{22})/RT, \tau_{21} = (g_{21} - g_{11})/RT \quad (9)$$

$$G_{12} = \exp(-\alpha_{12} \tau_{12}), G_{21} = \exp(-\alpha_{21} \tau_{21}) \quad (10)$$

where g_{ij} is binary interaction energy parameters (g₁₂ = g₂₁), α_{ij} is the mixed nonrandom characteristic constant of component i-j (α₁₂ = α₂₁).

Nonrandom two-liquid equation has the advantage of correlating with strongly polar system. Furthermore, without introducing specific parameters of multiple system, it can be calculated with the related parameters of binary system. The missing binary interaction parameters among components could be supplied by UNIFAC group contribution method⁸ (Tables 3-5).

TABLE-3
COMPONENT GROUP ASSIGNMENT

Component	m.f.	Group assignment					
Methanol	CH ₃ OH	1 CH ₃ OH					
H ₂ O	H ₂ O	1 H ₂ O					
PO	C ₃ H ₆ O	1 CH ₃	1 CH	1 FCH ₂ O			
PGME	C ₄ H ₁₀ O ₂	1 CH ₃	1 CH	1 CH ₂	1 OH	1 CH ₃ O	
1,2-PG	C ₃ H ₈ O ₂	1 CH ₃	1 CH	1 CH ₂	2 OH		

RESULTS AND DISCUSSION

Process simulation: The distillation module of PRO/II was used to simulate the solvent recovery column and the simple HX module was used to calculate the heat load of

TABLE-4
GROUP VOLUME AND SURFACE-AREA PARAMETERS

	CH ₃ OH	H ₂ O	CH ₃	CH	CH ₂	OH	FCH ₂ O	CH ₃ O
R _k	1.4311	0.9200	0.9011	0.4469	0.6744	1.0000	0.9183	1.1450
Q _k	1.4320	1.4000	0.8480	0.2280	0.5400	1.2000	1.1000	1.0880

TABLE-5
GROUP INTERACTION PARAMETERS

	CH ₃ OH	H ₂ O	CH ₂ (CH ₃ ,CH)	OH	CH ₂ O(FCH ₂ O,CH ₃ O)
CH ₃ OH	0	-181.0	16.51	249.1	-180.6
H ₂ O	289.6	0	580.6	229.1	-400.6
CH ₂	697.2	1318	0	986.5	251.5
OH	137.1	353.5	156.4	0	28.06
CH ₂ O	339.7	634.2	83.36	237.7	0

TABLE-6
SIMULATION RESULTS OF DISTILLATION

Stream	Temp. (°C)	P (kPa)	F (kg h ⁻¹)	Mass fraction				
				PO	Methanol	H ₂ O	1,2-PG	PGME
Feedstock	67	200	1837.5	0.0020	0.8010	0.1700	0.0030	0.0240
Top	50	300	282.7	0.0024	0.9467	0.0510	0.0000	0.0000
Bottom	134	300	1554.8	0.0000	0.0000	0.8245	0.0195	0.1560

reboiler. According to the simulation results, the material balance lists are presented in Table-6 and the calculated heat load of reboiler is presented in Table-7, which is compared with the actual steam consumption.

TABLE-7
SIMULATION RESULTS OF REBOILER

Reboiler	Temp. (°C)	Steam consumption (t tPO ⁻¹)
Simulated value	134	9.90
Measured value ⁹	137	10.0
Relative error	-	1.0 %

The thermodynamic model and calculation method established can accurately predict the solvent recovery distillation. They can be applied to explore energy-saving solution of our process to carry out economic optimization.

Optimization: In regard to our process, influences on separation accuracy and energy consumption by feed position, reflux ratio and solvent recovery ratio are investigated and exhibited in Fig. 1.

It can be seen from Fig. 1a that when the feed position is lower than the 32th plate, energy needed by reboiler soars drastically and methanol concentration in the top of tower decreases slightly. The separation accuracy and steam consumption hardly vary with the perturbation of feed position from 18th to 30th, so the existing feed position is appropriate.

After calculation, the minimum reflux ratio of solvent recovery tower should be 0.2 otherwise the concentration of methanol in the top will not meet separation requirements. The results showed in Fig. 1b indicate that with the rise of reflux ratio from 0.2 to 0.3, steam consumption and methanol concentration climb obviously. From 0.3 to 0.4 the methanol concentration levels out while steam consumption increases continuously. Therefore the reflux ratio of 0.25 is suggested, as it can not only reduces the energy consumption of solvent recovery tower, but also achieves the accuracy of separation at that operating point.

The alteration of solvent recovery ratio implies to change the handling capacity of tower. During the simulation it is found that when the solvent recovery ratio is less than 23 %, the amount of water in the system will increase inevitably. With the recovery ratio rising from 23 to 40 %, steam consumption decreases slightly and then increases rapidly. So the reasonable point should be located at between 25 to 30 % according to the curve in Fig. 1c.

Validation: On the basis of the optimization some validations have been obtained in the pilot plant. An energy-saving solution compared with the experimental results is showed in Table-8.

TABLE-8
ENERGY-SAVING VALIDATION OF SIMULATION

Parameters	Value	
	Pre-optimized	Optimized
Number of stage	40	40
Feeding stage	26	22
Reflux ratio	0.3	0.25
Solvent recovery ratio	30 %	28 %
Methanol concentration	0.947	0.926
Experiment (t tPO ⁻¹)	10.0	9.38
Simulation (t tPO ⁻¹)	9.90	9.27

By optimizing the operating conditions of feed position, reflux ratio and solvent recovery ratio, the practical steam consumption of solvent recovery tower reduced from 10.0 t tPO⁻¹ to 9.38 t tPO⁻¹, reduced by 6.2 %.

Conclusion

The virial equation and non-random two-liquid activity coefficient method are employed to simulate the solvent recovery distillation of 1500 t/a propylene oxide pilot plant by PRO/II process simulation software. The thermodynamic model and calculation method established can accurately predict and simulate the energy consumed by the reboiler. They

Fig. 1. Sensitivity analysis results

are applied to explore energy-saving solution of our process to accomplish cost reduction by investigating operating conditions such as feed position, reflux ratio and solvent recovery ratio. Based on the simulation results some verification of economic optimization have been carried out in the pilot plant. After comparison, the actual steam consumption of solvent recovery tower dropped from 10 t tPO⁻¹ to 9.38 t tPO⁻¹, declined by 6.2 percentage points. The results of simulation and optimization do have some significance to improve the energy utilization level of 1500 t/a propylene oxide pilot plant and give impetus to the direct epoxidation process scale-up.

ACKNOWLEDGEMENTS

The authors are grateful to the National High Technology Research and Development Program of China (863 Program: 2012AA040306) and Tianjin Dagu Chemical Co., Ltd. (China) for financial support.

REFERENCES

1. <http://www.basf.com/group/pressrelease/P-09-154>
2. W.G. Xiao, B.X. Shen, J.G. Zhao, et al., CN Patent 100351176 (2007).
3. B.X. Shen, W.G. Xiao and J.G. Zhao, et al., CN Patent 100558461 (2009).
4. J. Zhao, B. Shen, W. Xiao, C. Zhang and L. Wang, *Energ. Source A*, **31**, 108 (2009).
5. K.H. Nothnagel, D.S. Abrams and J.M. Prausnitz, *Ind. Eng. Chem. Process Des.*, **12**, 25 (1973).
6. J.G. Hayden and J.P. O'Connell, *Ind. Eng. Chem. Process Des.*, **14**, 209 (1975).
7. W. Xu, *Advanced Chemical Engineering Thermodynamics*, Tianjin University Press, Tianjin, p. 163 (2004).
8. B.L. Larsen, P. Rasmussen and A. Fredenslund, *Ind. Eng. Chem. Res.*, **26**, 2274 (1987).
9. Tianjin Dagu Chemical Co., Ltd., Project Completion Report of 1500t/a direct epoxidation from propylene to propylene oxide, Tianjin, 5 (2010).