ADCONIP 2014 Hiroshima

Dynamic Start-up Policies of Extractive Distillation for Dehydration of Iso-propyl Alcohol Process

Kuo-Chun Weng, Hao-Yeh Lee

Abstract—**In this work, dehydration of iso-propyl alcohol process is studied to demonstrate as an example for the start-up of extractive distillation. This study that consists of two kinds of policy with various reflux flow and reboiler heating steps is carried out a better operating procedure to reduce the period of start-up. It is found that total reflux policy with close loop operation illustrates a better dynamic behavior and faster response to complete whole start-up period than other cases. And this best start-up policy can reduce total start-up time 99.2% than the total distillate operating policy.**

I. Introduction

In chemical engineering process, distillation is an important method for product purification. However start-up of distillation columns is one of the most difficult operations in the chemical industry. Since the startup often has a long period of time, leads to off-spec products, and costs much energy. Because the process is unproductive during the startup period, it is desired to shorten this period by optimizing startup operation policies [1].

Single column start-up policies have been proposed to improve the startup performance with various approaches. For example, total reflux (Ruiz et al. [2]) and total distillate (Kruse et al. [3]) policies together with a large reboiler duty have been proposed for conventional distillation with single column. The reflux flow switching time from total reflux or total distillate to values at their nominal operating value is determined when the difference between the temperature at the steady state on some trays and their measured value reaches the minimum.

Extractive distillation process is widely used in azeotropic mixture separation. However, study of start-up policies for azeotropic mixture is quite rare in the open literature. There is no study report for start-up of extractive distillation process. The essential difficulty in modelling column startup lies in the fact that it is a quite complicated dynamic process. And most of research on start-up has studied by using the customized formulation and did the simulation case by case in conventional distillation. Therefore studying start-up of extractive distillation process by using Aspen Plus Dynamics™ in this paper can use some modularized units to simplify overall process modeling, and it is also valuable for better understanding dynamic behavior of column during start-up period. In this paper, two kinds of start-up policies with five cases will be studied for the dehydration of iso-propyl alcohol process.

*Resrach supported by National Science Council of R.O.C under grant No: NSC102-2221-E-011-144.

All authors are with the Chemical Engineering Department, National Taiwan University of Science and Technology, Taipei, CO 10607 Taiwan (corresponding author phone: 886-2-27376613; fax: 886-2-27336634; e-mail: haoyehlee@ mail.ntust.edu.tw).

II. Process Flowsheet and its Control Schemes

Isopropyl alcohol (IPA) is widely used in the semiconductor industry as a cleaning agent, thus the recovery of this cleaning agent from the waste solvent stream is an important topic worthy of detailed study. This waste solvent stream contains mainly isopropyl alcohol and water which contains a minimum-boiling azeotrope and, thus, is difficult to separate. According to Arifin and Chein's [4] study, they designed an extractive distillation process via dimethyl sulfoxide (DMSO) as entrainer for dehydration of iso-propyl alcohol process. In this process, the extractive column (C1) contains 41 stages. Feed location of IPA-water mixture and entrainer are 35th and 7th trays, respectively. Feed flow rate of IPA mixture and overall entrainer into extractive distillation are 100 and 102.5 kmol/hr. Notice that the fresh makeup of entrainer is quite tiny comparing with overall entrainer feed into the extractive distillation column. The top product of C1 is IPA product. The bottom stream of C1 is feeding into 9th tray of entrainer recovery column (C2). DMSO is recovered from bottom product of C2. The control scheme is shown in Fig. 1 which is used to operate in nominal condition and its main stream table is shown in Table 1.

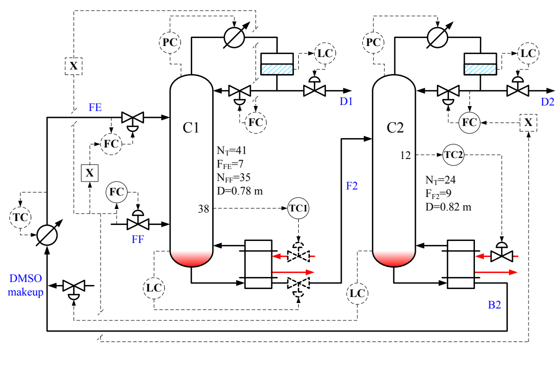

Figure 1. Concept design of IPA dehydration extractive distillation process

TABLE I. STREAM TABLE OF NOMINAL OPERATING CONDTION

	FF	D1	D2	F2	B2
F(kmol/hr)	100	49.95	50.05	152.5	102.5
X(mol%)					
IPA	0.5	0.999999	0.000999	0.00033	8.15e-20
H_2O	0.5	8.29e-7	0.999	0.328	5.56e-7
DMSO	0	1.77e-7	8.91e-8	0.672	0.999999

The control scheme can not be applied for the start-up operation. Before the process start-up, the column is full with nitrogen. The condition is called cold empty state. There are two different operations which compare with simple distillation need to be considered while start-up of extractive distillation. The first different operation is initial feed flow rate of DMSO. Because the make-up stream is too small to maintain the feed ratio of IPA mixture and DMSO, additional entrainer feed is required for the start-up phase. The second operation which needs to be considered is purging the excess amount of DMSO during the start-up period. The modified control scheme is shown in Fig. 2. There are five additional streams required for this process start-up. Streams FN1 and FN2 are used to remove nitrogen during the C1 and C2 start-up. The entrainer DMSO is fed by stream FEI in the beginning of start-up. Because total amount of entrainer cannot be estimated easily in the start-up period, the excess entrainer DMSO needs partial drawn out to prevent accumulation in whole process. Therefore the excess DMSO is designed to purge out by stream FEO at the bottom of C2. During start-up period, the process control operation will be quite different with nominal condition. Unlike the nominal condition, the sump level of C2 is maintained by bottom stream flow rate. The reflux drum level of each column is controlled by its reflux flow rate in the start-up period.

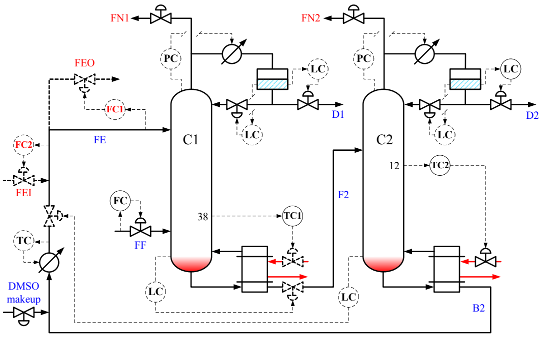

Figure 2. Flowsheet and control structure of IPA process for start-up

III. START-UP POLICIES AND DYNAMIC BEHAVIORS

In this section, total reflux and total distillate policies are considered to investigate for the time period of start-up. In each policy, the important key points are reflux flow/distillate switch time selection and reboiler duty operation of each column. Because two products are very pure, the overall start-up period will be finished when two product composition satisfy Eq.(1). $X_{p,i}$ is the IPA and water product compositions. $X_{p,iss}$ is the nominal product compositions under steady-state. For start-up procedure design, two columns are assumed to operate in the same start-up setting.

$$\left| X_{p,i} - X_{p,iss} \right| \le 0.001 \qquad (1)$$

A. Start-up by total distillate strategy

The concept of total distillate policy is operating column without any reflux flow initially. After reflux flow switch time, the reflux flow is set as nominal operating value. The procedures of total distillate policy are designed in following steps:

◆Start-up of extractive column

1. At t = 0.05 hr, IPA/water mixture initial charge is started until sump level of C1 reach 1.5 m. Starting to heat column.
2. Nitrogen is started to purge by FN1 stream and turn on the pressure controller of C1. Setpoint is 1.1 atm.
3. Using top product stream of C1 to maintain reflux drum level, setpoint is 0.44 m.
4. Until temperature of stage 1 of C1 reach 82 ^{o}C (temp. of azeotrope), Starting to feed DMSO in 102.5 kmol/hr.
5. Waiting for 0.05 hr and closing nitrogen purge valve.
6. Until temperature of stage 1 of C1 reach nominal operating value 84.5 ^{o}C, starting to feed fresh IPA/water mixture continuously.
7. When sump level of C1 reaches 1.9 m, turn on the level control in auto, and setpoint is 1.26 m as nominal operating value. Then starting to purge out nitrogen of C2.
8. Until switch point, reflux flow rate is set as nominal operating value 31.67 kmol/hr

◆Start-up of entrainer recovery column

1. Until sump level reach 0.1 m, start to heat column and turn on control pressure in auto mode. And assign its setpoint nominal operating value 1.1 atm.
2. Turn on the drum level controller to control level by top product stream. And assign its setpoint nominal operating value 0.2663 m.
3. Until temperature of stage 1 of C2 reach 102.7 ^{o}C (boiling point. of water), then wait 0.05 hr and close C2 nitrogen purge valve.
4. Waiting for sump level of C2 reaches 1.9 m and starting to control sump level of C2 by bottom product, set point is set as 1.2 m.
5. Turn on bottom product temperature controller (TC in Fig. 2), setpoint is 72 ^{o}C.
6. Turn on overall entrainer flow controller (FC1 in Fig. 2), setpoint is 102.5 kmol/hr.
7. Until reflux switch point, reflux flow rate is set as nominal operating value 22.31 kmol/hr.

Reboiler heating steps are an important key factor under start-up period. In conventional operation, energy supplied is operated by the operator and gradually increase in manual during all start-up period. This is called open loop operation. Some open literatures have studied how to optimize the heating steps in open loop operation. Another idea in this paper is that the condition of column maybe is easier to achieve nominal operating condition if temperature controller of column can be applied in some moment during the process start-up. This is so called close loop operation. These two kinds of operations for reboiler heating are considered in this study.

The steps of these two operations are shown as follows:

1. Reboilier duty of C1 and C2 is adjusted from 0%, 50%, 100% to 150% of its nominal operating values, and the interval of each change is set equal to 0.1 hr.

TD-Case 1 Open loop operation

2. Until temperature of sensitive stage equal to the nominal value, then reboilier duty is set as its nominal operating value directly.

TD-Case 2 Close loop operation

2. Until temperature of sensitive stage equal to the nominal value, then turn on column temperature controller in auto mode.

Because the total distillate policy does not have reflux flow in the beginning of start-up, a switch time is required to turn on the reflux flow rate to its nominal operating value. Therefore, the reflux switch time selection of total distillate policy is determined by MT function which was proposed by Kruse et al. [3]. MT-function is present in Eq.(2). Where $T_j(\tau)$ and T_j^{SS} are the current temperature of jth stage and the corresponding nominal operating value. The reflux switch time is selected by the smallest value of MT-function. The reflux switch time selection result of TD-Case 1 and TD-Case 2 are shown in Fig. 3. The switch point of C1 is 0.593 hr and C2 is 1.1 hr for TD-Case 1. For TD-Case 2, the switch point of C1 is 0.596 hr and C2 is 1.06 hr.

(a)

(b)

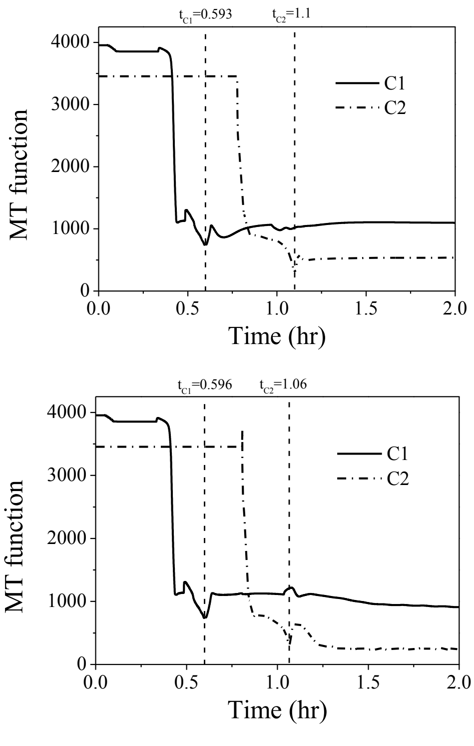

Figure 3. Switch point selection of (a) TD-Case 1 open loop strategy (b) TD-Case 2 close loop strategy

The overhead compositions of C1 for both TD-Case 1 and 2 are shown in Fig. 4. The red dash line represents the reflux switch point. It is obvious that the IPA composition of TD-Case 1 increase faster than TD-Case 2 in the beginning of start-up. After t = 1.5 hr, the trend of IPA composition become mildly increase for both cases. In the beginning of both operations, it is found that the overheads contain a little DMSO. After the reflux switch time, DMSO composition is monotonic decrease. Until t = 1.2 hr, DMSO becomes quite tiny in the overhead of C1. From the Fig. 4, the total start-up period spends about 4.8 hr for TD-Case 1. Comparing with TD-Case 2, it is interesting that the start-up period is only half of TD-Case 1. It can be found that the behavior of TD-Case 2 is quite similar to TD-Case 1 before the reflux switch time. After switch point, Unlike IPA composition of TD-Case 1, the response goes down first and then up later. The response of TD-Case 2 can quickly increase to nominal value by close loop operation. Comparing the result of TD-Case 1 with TD-Case 2, it is shown that the close loop operation has shorter start-up period than open loop operation.

$$MT(\tau)=\sum_{j=1}^{N}\left|T_j(\tau)-T_j^{ss}\right| \tag{2}$$

(a)

(b)

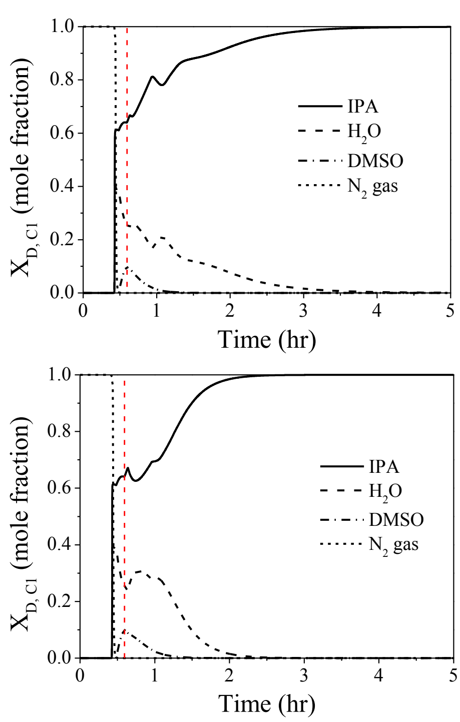

Figure 4. Start-up result of IPA composition of C1 overhead for (a) TD-Case 1 open loop operation and (b) TD-Case 2 close loop operation

B Start-up by total reflux policy

Based on the result of previous section, close loop operation is applied to total reflux policy. Total reflux policy is also a common approach for conventional column start-up. It is unlike total distillate policy, the process operated in total reflux in the beginning of start-up before reflux switch time. After this switch point, the reflux flow is set as nominal operating value, and the distillate is used to control reflux drum level. For reflux switch time selection, Yasuoka et al. [5] showed that MT-function is suitable to be applied in total reflux policy. Therefore, the MT-function method proposed by Yasuoka et al. [5] is named TR-Case 1. The start-up procedure by total reflux policy is shown in following steps:

◆Start-up of extractive column (C1)

1. At t = 0.05 hr, IPA/water mixture initial charge is started until sump level of C1 reach 1.5 m. Starting to heat column.
2. Nitrogen is started to purge by FN1 stream and turn on the pressure controller of C1. Setpoint is set in 1.1 atm as nominal operating value.
3. Using reflux flow rate of C1 to maintain drum level, then setpoint is set as nominal operating value 0.44 m.
4. Until temperature of stage 1 of C1 reach 82 ^{o}C (temp. of azeotrope), Starting to feed DMSO in 102.5 kmol/hr.
5. Waiting for 0.05 hr and closing C1 purge valve.
6. When sump level of C1 reaches 1.9 m, Starting to control level automatically, set point is 1.26 m. starting to purge out nitrogen of C2.
7. After switch point, reflux flow rate is set as nominal operating valve 31.67 kmol/hr.
8. After the reflux flows of both two columns are switched, the fresh IPA/water restarts to feed into C1 continuously.

◆Start-up of entrainer recovery column (C2)

1. Until sump level reach 0.1 m, start to heat column and turn on control pressure in auto mode. And assign its setpoint nominal operating value 1.1 atm.
2. Turn on the drum level control level by reflux flow. And assign its setpoint nominal operating value 0.2663 m.
3. Until temperature of stage 1 of C2 reach 102.7 ^{o}C (b.p. of water), then wait 0.05 hr and close C2 nitrogen purge valve.
4. Waiting for sump level of C2 reach 1.9 m and starting to control sump level of C2 by bottom product, set point is 1.2 m.
5. Turn on bottom product temperature controller (TC in Fig. 2), setpoint is 72 ^{o}C.
6. Turn on overall entrainer flow controller (FC1 in Fig. 2), setpoint is 102.5 kmol/hr.
7. Until reflux switch point, reflux flow rate is set as nominal operating value 22.31 kmol/hr.

The result of switch time with TR-Case 1 is shown in Fig. 5. The switch point of C1 is t = 0.58 hr and C2 is t = 0.98 hr for TR-Case 1. The start-up result of TR-Case 1 is shown in Fig. 6. The response shows that the composition of IPA can have faster raise up response in the beginning. However when composition of IPA is near 0.8, the response of IPA composition goes down and becomes oscillatory. The start-up time of TR-Case 1 is 2.54 hr.

The comparison of start-up behavior by total distillate and total reflux policy is shown in Fig. 7. Notice that the results of TD-Case 2 is better than TD-Case 1 in last section so TD-Case 2 and TR-Case 1 are used in comparison. In case of Fig.7, the reboiler duty is used by close loop operation and switch points are selected by MT-function. Fig. 7 shows IPA composition increase slower by total distillate strategy. The response of IPA composition goes down and becomes oscillatory with total reflux policy during t = 0.7 to 1.1 hr. The result of Fig. 7 still displays that start-up time of total reflux policy is shorter than total distillate policy.

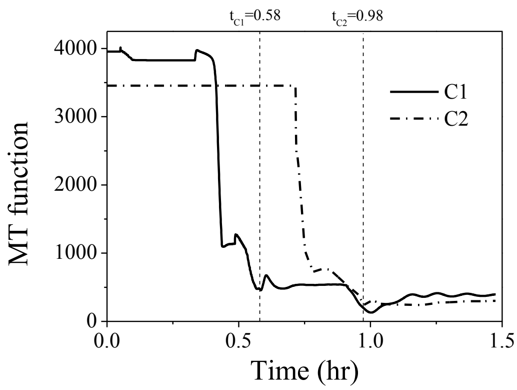

Figure 5. Switch point selection of TR-Case 1

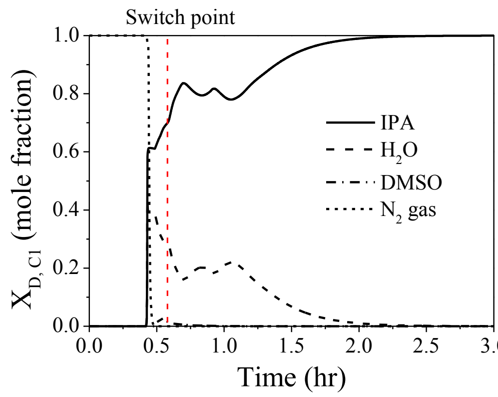

Figure 6. Start-up result of IPA composition of C1 overhead for TR-Case 1

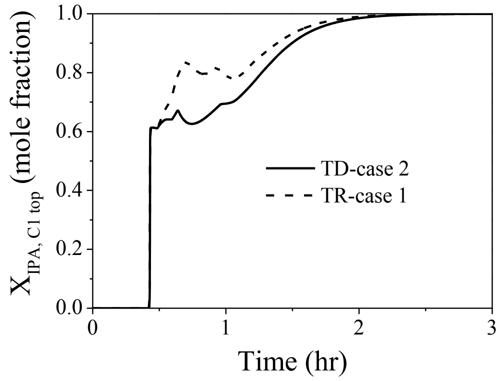

Figure 7. Comparison of total reflux and total distillate strtegy

It is interesting that the behavior of composition profile of C1 can be observed by three component phase diagram. Fig. 8 shows the behavior of C1 from entrainer feeding to start-up finished by TR-Case 1 as example. The dash line is iso-volatility curve. t = 0.486 hr is the point to feed entrainer. Until t = 0.58 hr, composition profile of column top section has crossed iso-volatility curve. When t = 0.6 hr, bottom composition has a trajectory from water side to DMSO side. This is because more and more DMSO is fed into C1, and its composition becomes more significantly in the bottom of C1. At t = 1.15 hr, the composition profile of bottom section has nearly achieved nominal operating profile. At t = 2.59 hr, start-up is finished and the composition profile is the same with nominal operating condition.

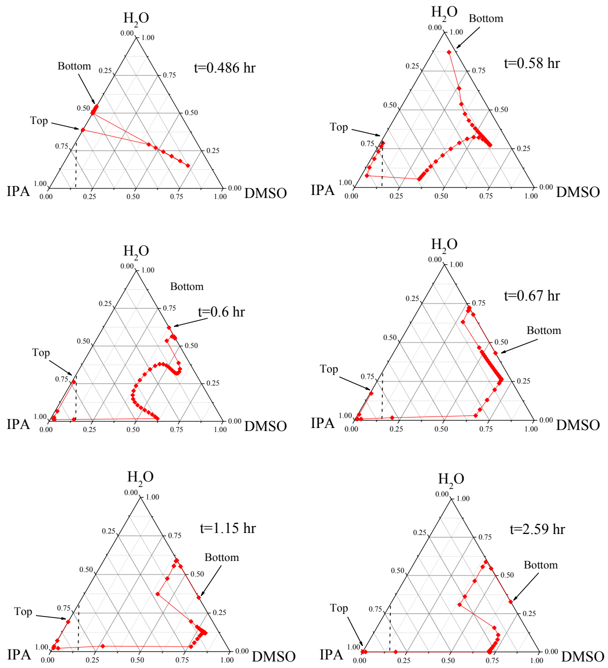

Figure 8. Composition profile change of C1 during start-up

C. *Effect of different reflux switch point selecting method for total reflux policy*

The comparison result shows that total reflux policy is more suitable than total distillate policy for extractive distillation process. However, the reflux switch time selecting tool, MT-function, is not easy to be applied in industrial column because temperatures of all stages need to be measured. Wendt et al. [6] proposed another simple method to select the switch point. They observed the bottom temperature of column and set the reflux switch time at the point while temperature is not increasing.

In this paper, we have made a modification for Wendt et al's [6] method. The nominal value of C1 bottom temperature is chosen as switch point. Because C1 bottom contains water and DMSO mixture, bottom temperature will not stay in a constant value except for the composition quite close to pure DMSO. This approach may maintain bottom temperature easily at the start-up period.

Therefore, there are another two methods will be studied in this section. Except for the MT-function case proposed by Yasuoka et al. [5], the case proposed by Wendt et al. [6] is named TR-Case 2. The modified method from Wendt et al. [6] is named TR-Case 3.

The results of switch time with two cases are shown in Fig. 9. The switch point of C1 is t = 1.15 hr and C2 is t = 0.97 hr for TR-Case 2. The switch point of C1 is t = 0.58 hr and C2 is t = 0.98 hr for TR-Case 3. It can be observed that switch time of C2 for these two cases is quite close. However the switch time of C1 in these two methods is very different. Furthermore, it is easy to observe that the switch time sequence is in reverse order for these two cases. Comparing with TR-Case 1, the switch point sequence of TR-Case 3 is the same. However C1 reflux switch point is a little lag by using TR-Case 3.

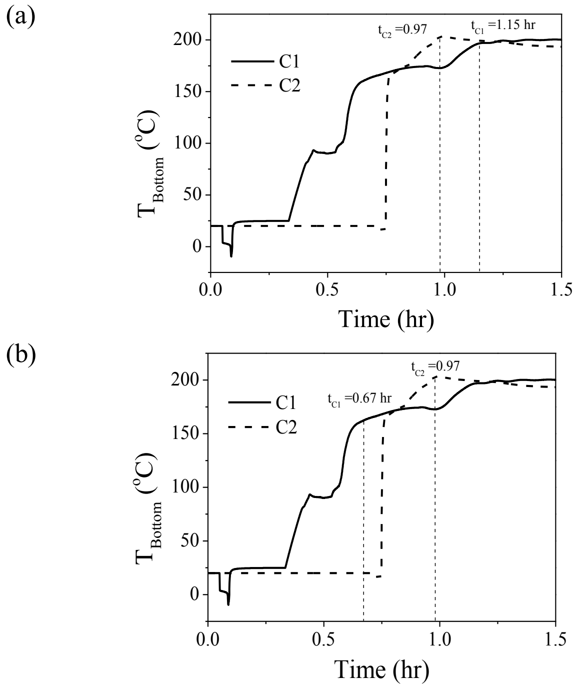

Figure 9. Switch point selection of (a) TR-Case 2 (b) TR-Case 3

The overhead compositions of C1 for these three cases are shown in Fig. 10. From Fig. 10, it can be seen the IPA composition increases fast before 0.5 hr. However after IPA composition is over 0.7 mole fraction, the trend of IPA composition increasing has various raring rates.

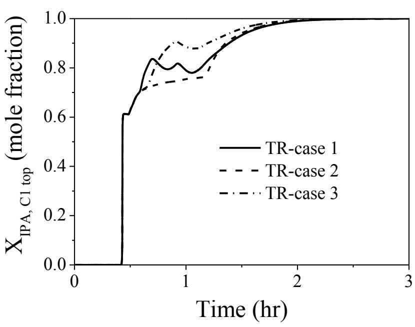

Figure 10. Comparison of three cases of total reflux strtegy

In case of the TR-Case 2, it would have a longer period for C1 on the total reflux condition. The response of IPA composition in overhead becomes more flat than others. This is because the overhead composition is quite close to the IPA/water azeotrope, and this composition is always refluxed before the reflux switch point. After switch point, the IPA composition in overhead of C1 increases like an open-loop response of first-order transfer function to the product specification. The total start-up time of TR-Case 2 is 2.58 hr.

From Fig. 10, the responses show the start-up period of TR-Case 1 goes down and becomes oscillatory. And the response of TR-Case 2 spends too long time at total reflux condition. For TR-Case 2, the process studied by Wendt et al. [6] was a simple binary mixture process. When the bottom temperature does not increase in their process, it means that the bottom temperature is quite close to the boiling point of pure component. However there is still a mixture with water/DMSO in the bottom of extractive distillation column for this process. The switch point of each column is selected in the time that bottom temperature reach nominal operating value is TR-Case 3. The TR-Case 3 provides a faster response and IPA composition does not decrease much than TR-Case 1. The result shows the switch point should be chosen by TR-Case 3.

The overall start-up time and energy consumption during star-up period are shown in Table II and Table III respectively. Table II shows the policy TR-Case 3 can shorten the start-up 99.2 % comparing with total distillate in open loop operation. And Table III also shows the lower start-up time is with lower energy consumption. The start-up time of the worst case is twice than the best one. Furthermore the energy consumption of the worst case is triple than the best one.

TABLE II. START-UP TIME OF ALL TESTS

	Total distillate		Total reflux		
	TD-Case 1	*TD-Case 2*	*TR-Case 1*	*TR-Case 2*	*TR-Case 3*
t	4.8 hr	2.63 hr	2.54 hr	2.58 hr	2.41 hr
%	99.2	9.1	5.4	7.1	-

TABLE III. ENERGY CONSUMPTION OF ALL TESTS

	Total distillate		Total reflux		
	TD-Case 1	*TD-Case 2*	*TR-Case 1*	*TR-Case 2*	*TR-Case 3*
Q	36.7 GJ	19.4 GJ	14.58 GJ	17.97 GJ	13.61 GJ
%	169.6	42.5	7.1	32	-

D. Effect of entrainer feed flow in start-up

For extractive distillation, the initial feed flow rate of entrainer is an important variable in the beginning of start-up. In this section, various entrainer feed flow rate in the beginning of start-up will be investigated. Notice that the overall entrainer flow into C1 will be set as nominal operating value while entrainer from C2 recycle back to C1. At the time of this condition, FEI stream will close and excess DMSO will be purge by FEO stream. To observe the effects on start-up time, all simulations are based on the TR-Case 3. The test result is shown in Fig. 11. The optimal entrainer flow rate is 120% of nominal operating value in the beginning of start-up. If operating initial entrainer feed flow rate in 120% of normal operating value in TR-Case 3, the start-up time can be reduced from 2.41 hr to 2.35 hr.

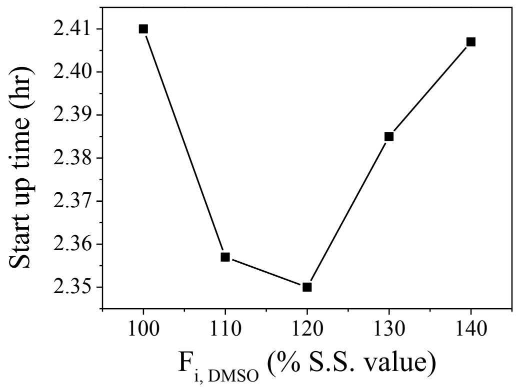

Figure 11. Test result of initial entrainer flow rate

IV. CONCLUSION

The start-up of extractive distillation for IPA dehydration process has been studied in this paper. It is found that total reflux policy with close loop operation illustrates a better dynamic behavior and faster response to complete whole start-up period than other cases. And this best start-up policy can reduce total start-up time near 99 % than the total distillate policy in open loop operating. Furthermore the energy consumption at the start-up period can be reduced to 13.61 GJ. From the result, TR-Case 3 shows the better behavior than other case. And the entrainer initial flow rate should be set in 120% nominal operating value.

ACKNOWLEDGMENT

This financial supports from the National Science Council of R.O.C under grant No: NSC102-2221-E-011-144 which is gratefully acknowledged.

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