

Control of an Extractive Distillation System for the Separation of CO₂ and Ethane in Enhanced Oil Recovery Processes

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ABSTRACT: High concentrations of carbon dioxide in natural gas occur when carbon dioxide is used for enhanced oil recovery (EOR). The separation of the CO₂ from the hydrocarbons in the natural gas is complicated by the existence of an azeotrope between ethane (C₂) and CO₂ at the cryogenic temperatures required for distillation. A two-column extractive distillation system using higher molecular weight hydrocarbons as the solvent is used to remove CO₂ out the top of the extractive column. Ethane is recovered from the top of the recovery column, whose bottoms is a C₃+ hydrocarbon mixture called natural gas liquid (NGL). A portion of the bottoms is used as the solvent fed near the top of the extractive column. The purpose of this paper is to develop an effective plantwide control structure for this two-column extractive distillation system. Results show that a conventional extractive distillation control structure using single-end temperature control in both columns and solvent-to-feed and reflux-to-feed ratios does *not* provide tight control of the CO₂ distillate composition from the extractive column. A composition controller is required, but two important issues must be addressed: (1) which of the two impurities (heavy-key component C₂ or a heavy component in the solvent) should be controlled and (2) which of the two available manipulated variables (solvent-to-feed and reflux-to-feed) should be used.

1. INTRODUCTION

The injection of carbon dioxide into oil wells to recover additional amounts of crude oil and natural gas is called enhanced oil recovery (EOR) and has been effectively used for many years. The resulting gas stream from the wells contains significant amounts of carbon dioxide in addition to the usual mixture of hydrocarbons from methane to pentanes. The separation of methane from the other components is accomplished in a high-pressure cryogenic distillation column called a demethanizer. The overhead product is mostly methane. The carbon dioxide goes out in the bottoms stream with the ethane and heavier hydrocarbons. The hydrocarbons are valuable as natural gas liquids (NGL), so the carbon dioxide must be removed and recycled back to the wells.

The separation of the carbon dioxide (CO₂) from the ethane (C₂) is complicated by the existence of a minimum-boiling azeotrope. At 25 atm the azeotropic composition is 32.83 mol % C₂ at a temperature of 256 K. Hong and Kobayashi¹ provided vapor–liquid equilibrium data for this system and proposed using *n*-pentane as a heavy entrainer in an extractive distillation separation flowsheet. Lastari et al.² explored the effects of solvent-to-feed ratio, feed tray location, and solvent composition on reboiler and condenser (refrigeration required) duties in the extractive column. The use of a modified divided-wall column for this separation was studied by Tavan and Hosseini³ and compared to a conventional two-column design.

None of these studies address the issue of plantwide control of the two-column interconnected process. That is the purpose of this paper. The measures of “good” control assumed in this work are (1) the need for closed loop stability, (2) small transient peak deviations, and (3) small steady-state deviations of product compositions from their specified values.

2. PROCESS STUDIED

The flowsheet is given in Figure 1 and is based on the information provided by Tavan and Hosseini³ with some modifications. Both columns have theoretical 51 stages and operate at 24 atm. The gas feed stream is 14 400 kmol/h with a composition of 32.25 mol % CO₂ and 46.23 mol % C₂. The remaining components range from propane (C₃) down to *n*-pentane (nC₅). Aspen simulations are used in the steady-state and dynamic studies with Peng–Robinson physical properties.

2.1. Extractive Column. The feed gas is fed on stage 39 of the extractive column. The solvent at 9072 kmol/h is fed on stage 5 near the top. It is important to note that, unlike conventional extractive distillation, the solvent used in this process is not a distinctly different component that is selected to enhance the separation between the two components (a light key and a heavy key). The solvent is a mixture of the hydrocarbons entering in the feed that contains propane and heavier components. It is the natural gas liquid (NGL) produced in the process with the ethane removed. In the numerical case, the solvent composition is 33.69 mol % C₃, 35.65 mol % iC₄, 15.32 mol % nC₄, and small amounts of iC₅ and nC₅. The concentration of C₂ in the solvent is very small (0.06 mol %) as dictated by the specification in a downstream depropanizer column in which the propane is produced in the distillate. Therefore the solvent is quite similar to the heavy-key component (C₂) in the extractive column (the light-key component is CO₂). The effects of fractionation in this process are different from those in conventional extractive distillation in which the solvent is selected to be distinctly different from the components to be separated.

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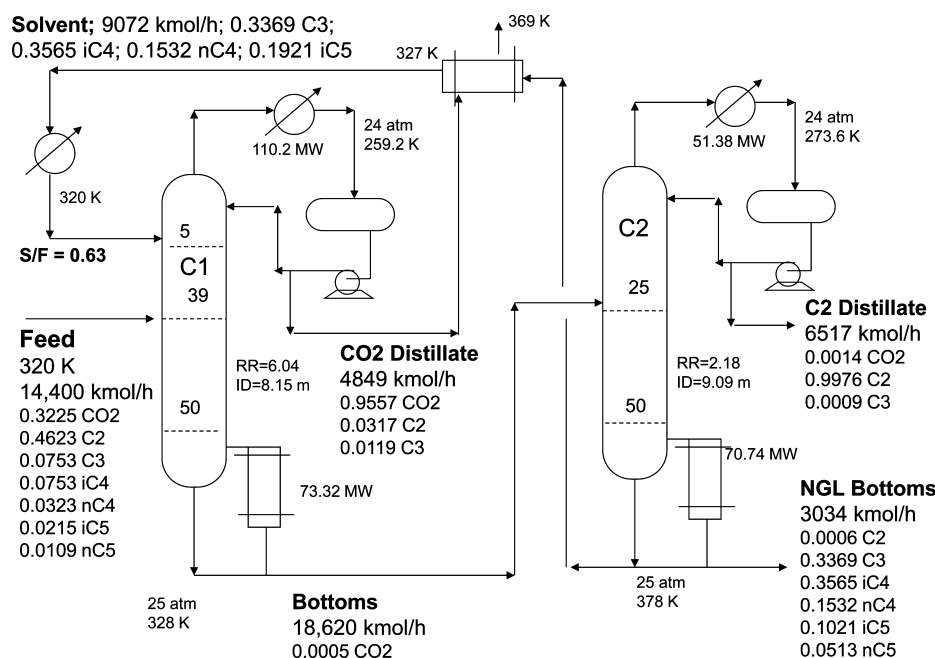


Figure 1. Extractive distillation of CO_2 /ethane with C_3 + solvent.

A. Conventional Example. Let us consider a typical example of conventional extractive distillation, the separation of acetone (light key, LK) and methanol (heavy key, HK) using a heavy entrainer solvent, dimethyl sulfoxide (DMSO). The feed flow rate in this example is 540 kmol/h of a 50/50 molar mixture of acetone and methanol. Figure 2 shows how the purity and impurities in the distillate from the extractive column vary with the solvent flow rate (S) and the reflux ratio (RR). These results are generated by specifying fixed values of S and RR while holding the bottoms composition at 0.01 mol % acetone by varying the distillate flow rate in an Aspen Design spec/vary function.

Figure 2a shows that, as expected, higher solvent flow rate produces higher purity acetone in the extractive column distillate $x_{D1}(\text{acetone})$. However, for a given solvent flow rate, there is a non-monotonic effect of the reflux ratio. This interesting phenomenon occurs because of the effect of the reflux ratio on solvent impurity in the distillate and on solvent dilution. As shown in Figure 2b, too little reflux permits more solvent and methanol to go out the top of the column, which reduces distillate purity. On the other hand, too much reflux dilutes the solvent and permits methanol to go out the top and reduce distillate purity.

Increasing the reflux ratio *always* decreases the impurity of the solvent in the distillate (lower graph in Figure 2b). The effect of increasing solvent flow rate is *always* to improve distillate acetone purity. As we demonstrate in the following, these two effects are *not* true in the CO_2/C_2 system using the NGL solvent.

B. CO_2 /Ethane Extractive Distillation. The extractive column is designed to produce a distillate of mostly CO_2 (95.57 mol %). The effects of the solvent flow rate (S) and reflux ratio (RR) on the separation are shown in Figure 3. These results are generated by specifying fixed values of S and RR while holding the bottoms composition at 0.06 mol % CO_2 by varying the distillate flow rate in an Aspen Design spec/vary function.

The same nonmonotonic relationship with the reflux ratio occurs in this system, but with two important differences. Unlike conventional extractive distillation, the effect of higher solvent flow rates depends on the reflux ratio. In the higher RR range,

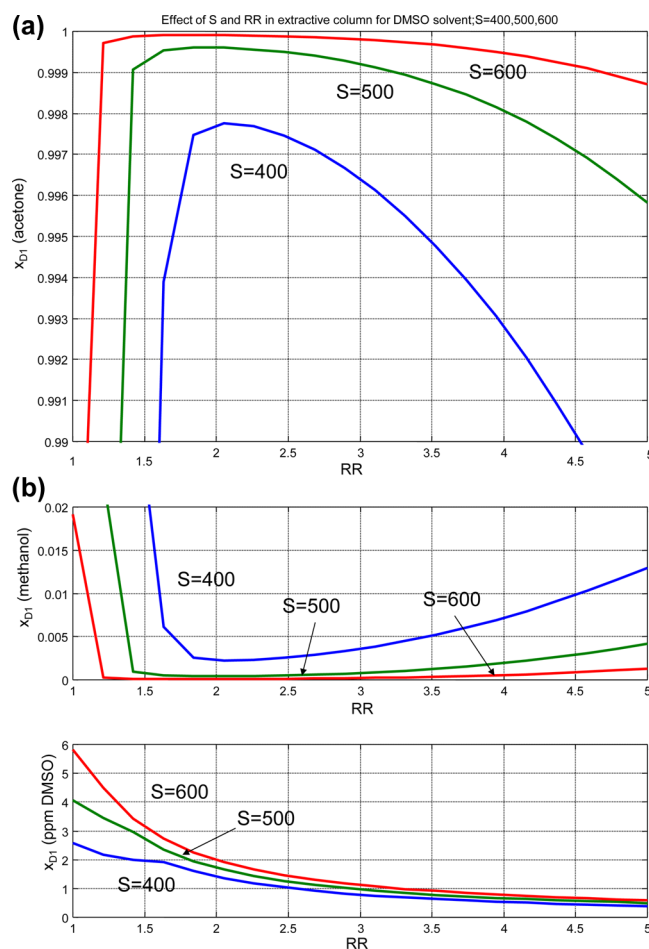


Figure 2. (a) Effect of RR and solvent on acetone product purity with DMSO solvent. (b) Effect of RR and solvent on impurities in acetone product with DMSO solvent.

increasing the solvent flow rate increases the distillate CO_2 purity (Figure 3a). However, in the lower RR range, the opposite occurs.

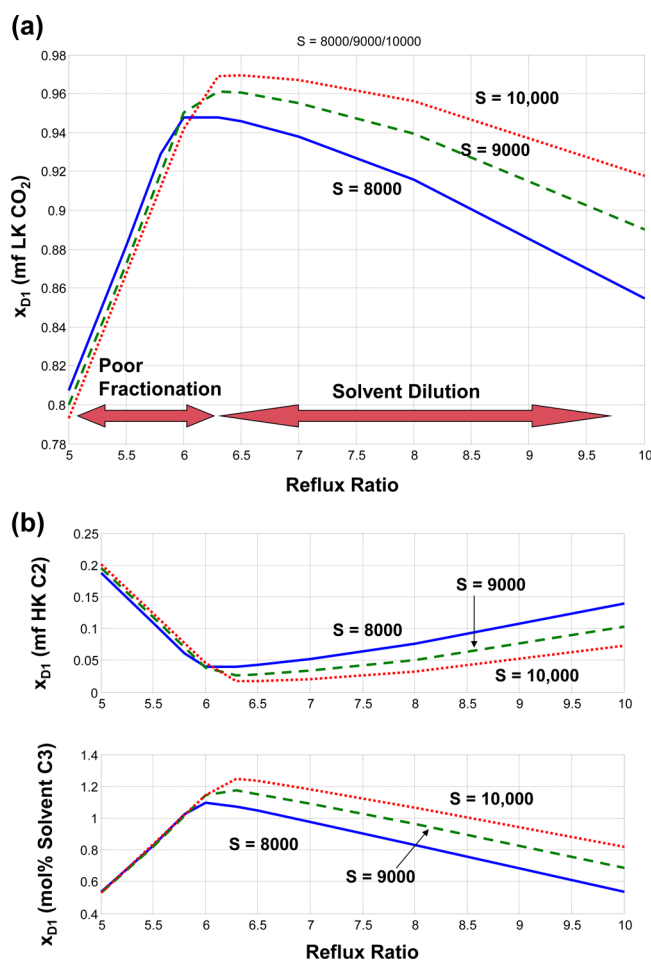


Figure 3. (a) Effect of RR and solvent on CO₂ purity. (b) Effect of RR and solvent on CO₂ impurities.

The impact of this nonlinear relationship on the control structure is discussed in section 3.1.

Figure 3b shows that there are nonmonotonic relationships between RR and both of the distillate impurities (C₂ and C₃), but they are opposite in shape. The C₂ curve (the HK component) reaches a minimum. The C₃ curve (the lightest of the components in the NGL solvent) reaches a maximum. They are also opposite in the effect of the solvent flow rate. More solvent decreases C₂ impurity, but more solvent increases C₃ impurity.

These differences between a conventional extractive distillation process and the NGL process under study are due to the solvent being quite similar to the LK component being separated from the CO₂.

The minimum solvent flow rate is found that meets the two specifications for the extractive column while operating at the lower of the two possible reflux ratios. As shown in Figure 1, the solvent flow rate is 9072 kmol/h and the reflux ratio is 6.035. The resulting heat exchanger duties are 73.32 MW in the reboiler (low-pressure steam with the base temperature of 328 K) and 110.2 MW in the refrigerated condenser (259.2 K in the reflux drum).

The distillate flow rate is 4849 kmol/h of mostly CO₂ with impurities of 3.17 mol % C₂ and 1.19 mol % C₃. The bottoms flow rate is 18 620 kmol/h and contains most of the C₂ and heavier components. The column diameter is 8.15 m with two-pass trays.

2.2. Recovery Column. The bottoms stream of the extractive column is fed on stage 25 of the recovery column. Its design specifications are 0.09 mol % C₃ in the distillate and 0.06 mol % C₂ in the bottoms. The small amount of CO₂ in its feed goes overhead with the C₂ product as an impurity (0.14 mol % CO₂), which gives a C₂ product with a purity of 99.76 mol %.

The required reflux ratio to meet these specifications is 2.177. The reboiler duty is 70.74 MW, and the condenser duty is 51.38 MW. The column diameter is 9.09 m with two-pass trays.

The bottoms stream is split into the NGL product (3034 kmol/h) and the solvent fed to the extractive column. The NGL stream goes to a sequence of distillation column for separation into C₃, iC₄, nC₄, and C₅ product streams.

Notice that one of the unique features of this system is that the solvent used is *not* a third component that must be added to the system with solvent losses in the product streams requiring a makeup stream. The solvent is a mixture of the C₃ and heavier components that enter in the original gas feed to the system.

3. PLANTWIDE CONTROL

The control of extractive distillation columns has been studied for many years. The pioneering work by Grassi⁴ set the standard configuration that has been successfully applied in many systems. The recommended control structure uses single-end temperature control in both columns with the flow rate of solvent ratioed to the feed flow rate. Unlike the original control scheme, in which reflux flow rates are fixed, in this paper we use reflux-to-feed ratios in both columns. The selection of the temperature control tray is shown to be critical.

Results demonstrate that the conventional control structure does *not* provide effective composition control of the distillate CO₂ product from the extractive column. This occurs because the solvent in this system is quite similar to the light-key component C₂. A composition controller is required to maintain product specifications, and the selection of what composition to control and of what to manipulate is not obvious.

Tray temperatures are controlled by manipulating reboiler duties. These loops contain 1-min deadtimes and are tuning by running a relay-feedback test and applying Tyreus–Luyben tuning rules. Column pressures are controlled by manipulating condenser duties using Aspen default tuning. Reflux-drum and base levels are controlled using proportional controllers ($K_C = 2$) by manipulating bottoms and distillate flow rates, respectively.

3.1. Extractive Column. Figure 4a gives the temperature profile. Two possible temperature control trays are suggested by looking at the slope of the temperature profile. The use of either stage 48 or stage 25 is explored. Figure 4b gives the composition profiles of the key components in the extractive column. Since the compositions of the key components (CO₂ and C₂) are changing rapidly from tray to tray around stage 25, we would expect that location to provide more effective control, which the results presented below verify.

A feed composition sensitivity analysis is performed to provide guidance for selecting the second control degree of freedom. Should we hold the reflux-to-feed ratio constant or hold the reflux ratio constant? For feed flow rate disturbances, it should not matter since all flows ratio directly with throughput (in theory, at least, if there are no changes in tray efficiencies or pressure effects on phase equilibrium). However, for feed composition disturbances, the ratios change differently when the two products are maintained at their specifications.

Table 1 shows how reflux ratio (RR) and reflux flow rate change over a range of feed compositions, while maintaining

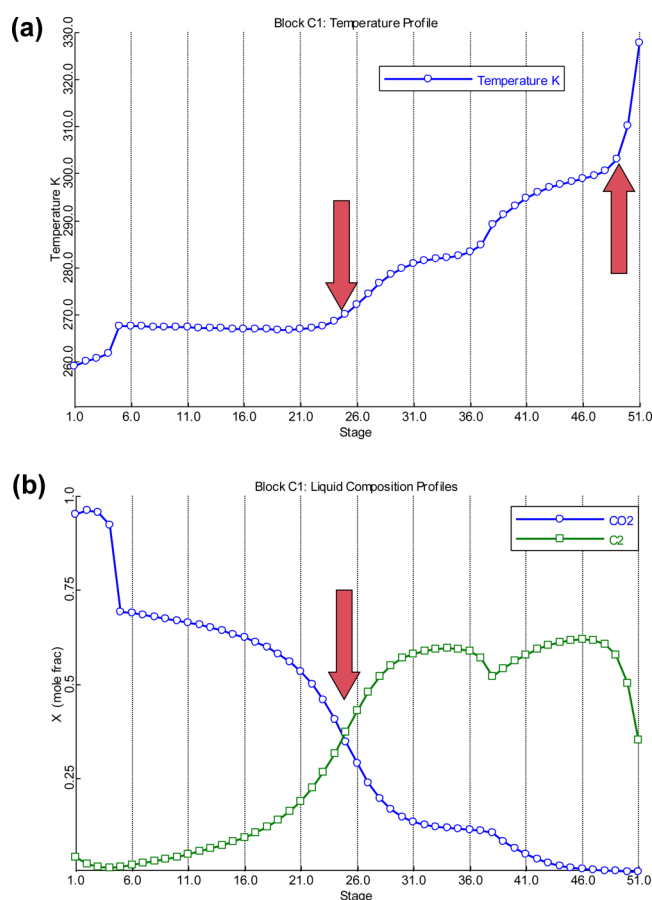


Figure 4. (a) Extractive column temperature profile. (b) Extractive column composition profiles.

Table 1. Feed Composition Sensitivity: Extractive Column^a

	feed composition (mol %)		RR	reflux flow rate (kmol/h)
	CO ₂	C2		
design	37.25	41.23	5.054	28 487
	32.25	46.23	5.999	29 265
	27.25	51.23	7.253	29 887
% change			37	4.8

^aFeed flow rate = 14 400 kmol/h.

product specifications at both ends of the column using two Aspen Design spec/vary functions. The two specifications are 0.06 mol % CO₂ in the bottoms and 3.17 mol % C2 in the distillate. The reflux-to-feed ratio structure is clearly better.

One issue that should be mentioned is the control of the reflux-drum level in a high reflux ratio column. Conventional distillation control wisdom suggests that, for columns with reflux ratios greater than about 3, the reflux-drum level should be controlled by manipulating the reflux. Using distillate to control the level can result in large changes in the distillate flow rate, which can upset downstream processes. The reflux ratio in the extractive column is 6.15, so level control using the reflux is recommended. However, this precludes the use of a reflux-to-feed control structure, which should handle feed composition disturbances more effectively. In this application, rapid and frequent disturbances should be infrequent since the feed stream is coming from a natural gas well. Therefore, the selection between R/F and RR should not be critical. Simulation results presented later do not display large or rapid changes in the distillate flow rate.

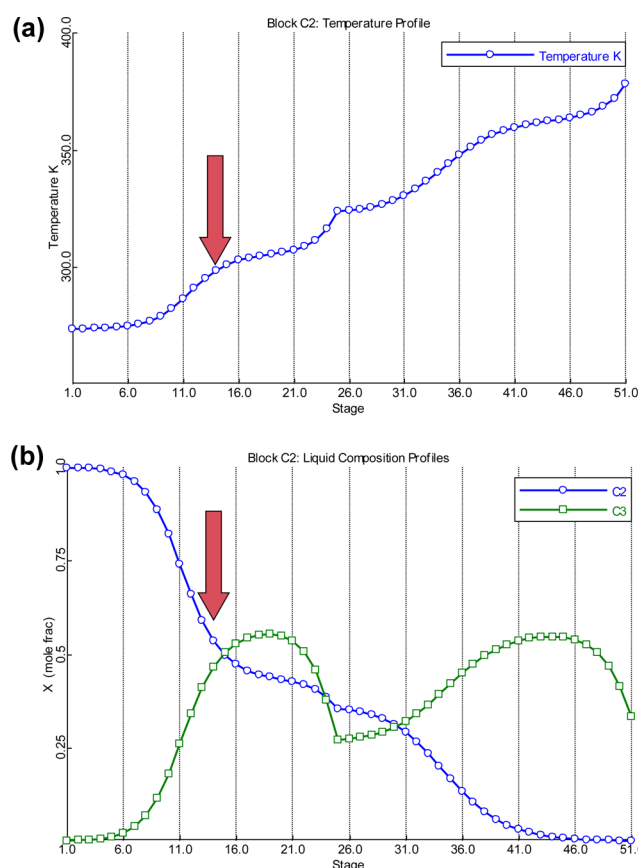


Figure 5. (a) Recovery column temperature profile. (b) Recovery column composition profiles.

3.2. Recovery Column. Figure 5a gives the temperature profile and Figure 5b gives the composition profiles of the key components (C2 and C3). Since both the temperatures and the compositions of the key components are changing rapidly from tray to tray around stage 14, we would expect that location to provide effective control.

Table 2 give results of the feed composition sensitivity analysis, which suggests a reflux-to-feed control structure. The reflux ratio

Table 2. Feed Composition Sensitivity: Recovery Column^a

	feed composition (mol %)		RR	reflux flow rate (kmol/h)
	C2	C3		
design	39.99	16.58	1.830	13 569
	34.99	21.58	2.174	14 102
	29.99	26.58	2.617	14 552
% change			36	7

^aFeed flow rate = 18 620 kmol/h.

in this column is 2.16, so there is no conflict with distillation wisdom.

Figure 6 gives the conventional plantwide control structure for the two-column extractive distillation process using the basic Grassi structure that is tested for effectiveness.

3.3. Results. A. Stage 48 Temperature Control. Figure 7a gives extractive column results for 20% disturbances in feed flow rate when stage 48 is selected as the temperature control tray. The solid lines are for increases and the dashed lines are for decreases. The stage 48 temperature is well controlled by

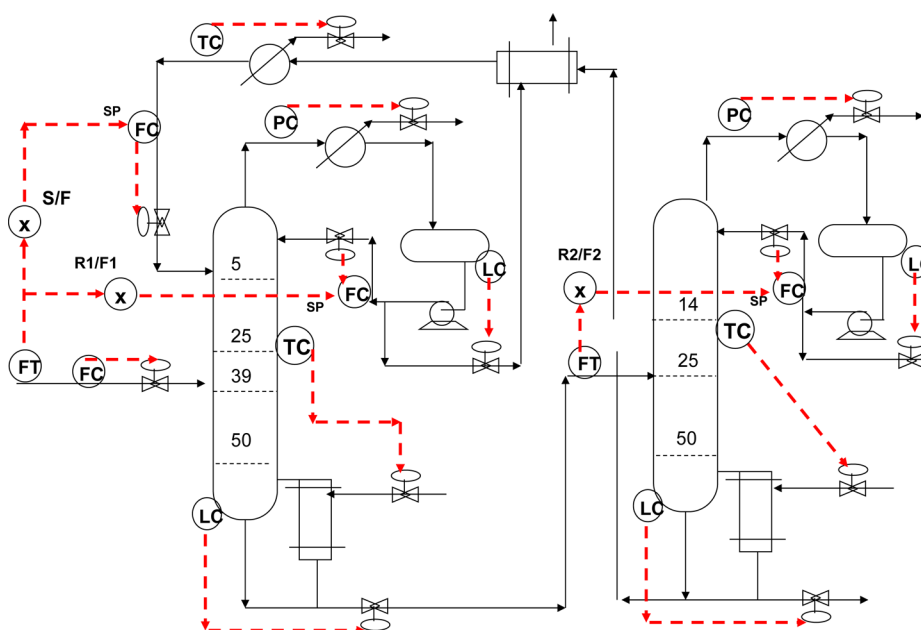


Figure 6. Conventional extractive distillation control structure.

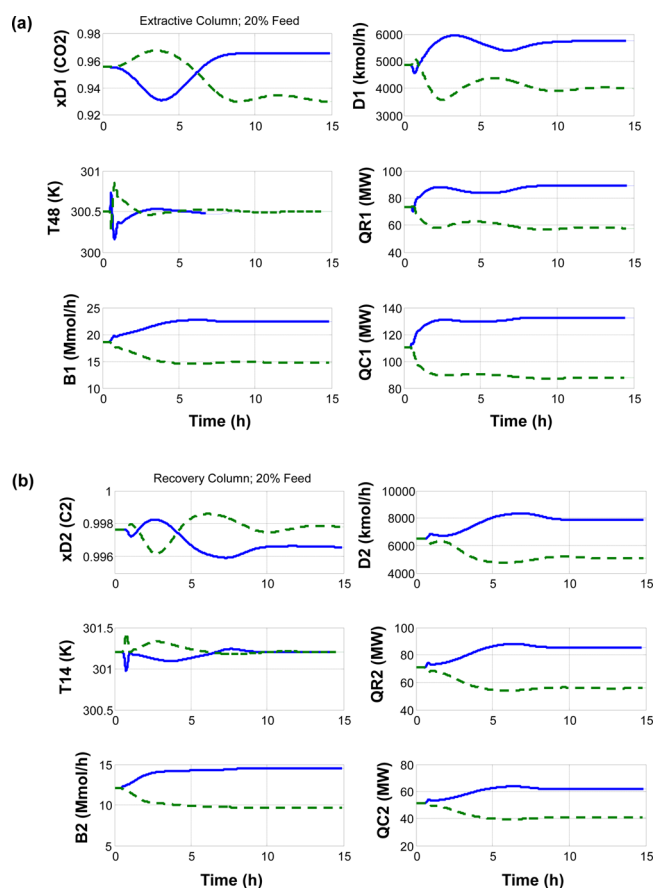


Figure 7. (a) Extractive column: stage 48; 20% feed flow rate disturbances. (b) Recovery column: stage 14; 20% feed flow rate disturbances.

manipulating the reboiler duty. The changes in the distillate and bottoms flow rates are gradual due to the proportional reflux-drum and base level controllers. Figure 7b shows that the distillate composition and temperature in the recovery column are well controlled.

However, distillate purity in the extractive column $x_{D1}(\text{CO}_2)$ drops significantly for the decrease in throughput. This occurs because we are controlling a temperature near the base of the column, which is far from the distillate stream. The lower throughput means lower vapor and liquid flow rates up and down the column, which result in less pressure drop through the trays. The smaller tray pressure drop means that the pressure on stage 48 is lower since the pressure in the condenser is held constant. At a constant controlled temperature but lower pressure, there is less of the light-key component (CO_2) and more heavy-key component C2 on stage 48, which means that the composition profile is shifted up in the column and more C2 impurity appears in the distillate.

B. Stage 25 Temperature Control. Figure 8 gives a direct comparison between controlling the stage 48 temperature (solid

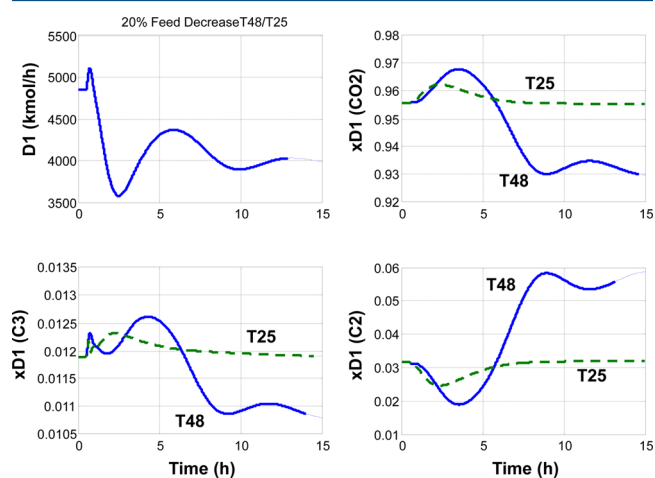


Figure 8. Extractive column with T48 or T25: 20% decrease in feed flow rate.

lines) or controlling the stage 25 temperature higher up in the column (dashed lines) for a 20% decrease in throughput. The extractive column distillate purity is held quite close to its specification because the C2 impurity changes very little.

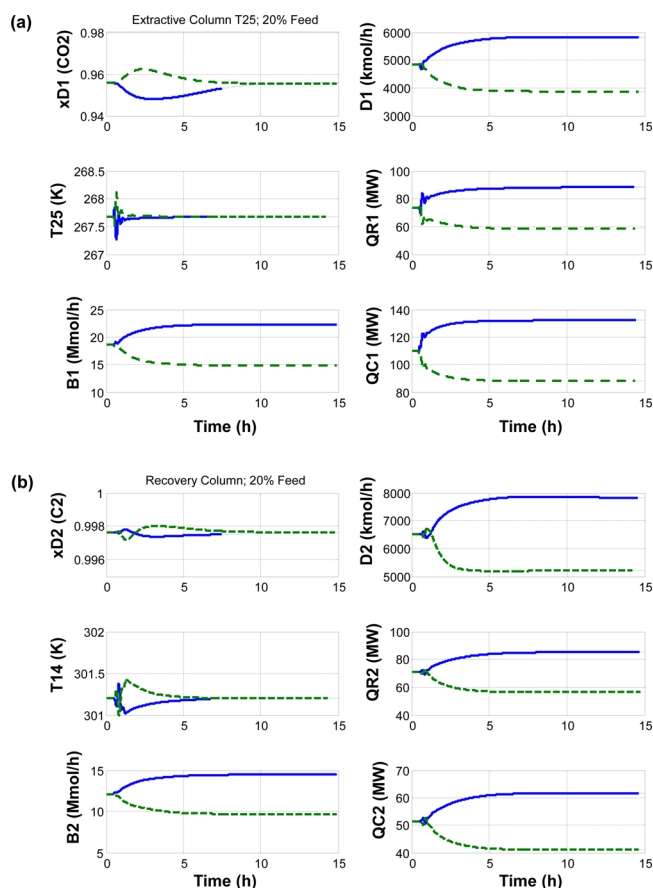


Figure 9. (a) Extractive column: stage 25; 20% changes in feed flow rate. (b) Recovery column: stage 14; 20% changes in feed flow rate.

Figure 9 shows the responses of the two columns for 20% disturbances in throughput with stage 25 controlled in the extractive column. Solid lines are increases and dashed lines are decreases. Both product purities are held close to their specifications.

Figure 10 gives results for feed composition disturbances. The solid lines are when the CO_2 feed composition is increased from 32.25 to 37.25 mol % CO_2 with a corresponding reduction in the C_2 feed composition from 46.23 to 41.23 mol % C_2 . The dashed lines are when the CO_2 feed composition is decreased from 32.25 to 27.25 mol % CO_2 with a corresponding increase in the C_2 feed composition from 46.23 to 51.23 mol % C_2 . Increasing the CO_2 feed composition produces more extractive column distillate ($D1$) and less bottoms ($B1$). Reboiler duty ($QR1$) and condenser duty ($QC1$) both increase. The recovery column is well controlled (Figure 10b).

However, the distillate purity in the extractive column decreases to 94.5 mol % CO_2 (Figure 10a). We assume that this variability is unacceptable, so a composition controller is necessary to keep the CO_2 distillate product from the extractive column closer to its specified value.

C. Extractive Column Distillate Composition Control. The conventional practice when controlling the composition in a distillation column is to control the *impurity*, not the purity, because the composition of the impurity is more sensitive to changes in the both the manipulated variables and the disturbances. For example, the concentration of the heavy-key component in the distillate is controlled by manipulating one of the two manipulated variables: reflux or reboiler duty.

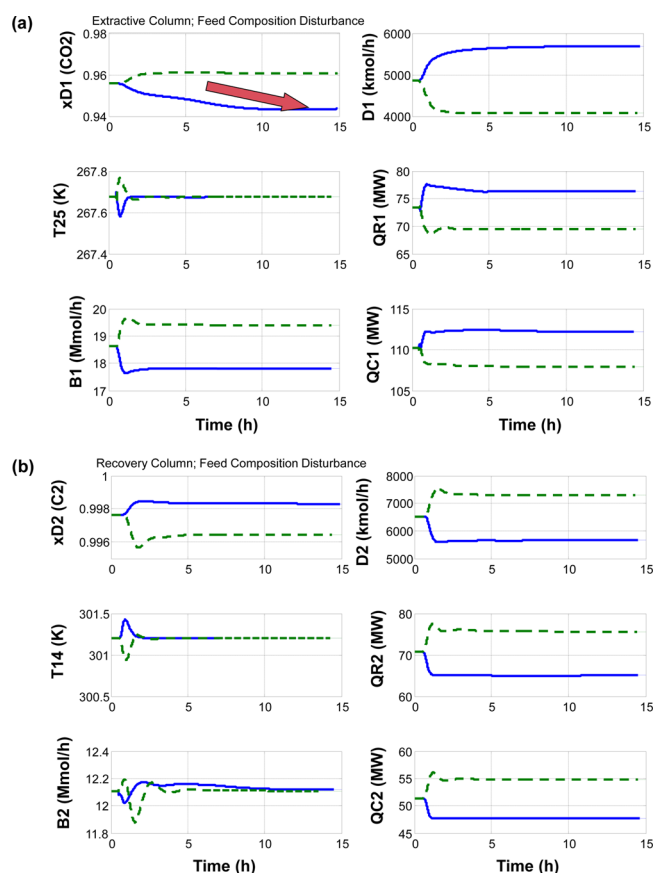


Figure 10. (a) Extractive column: stage 25; feed composition disturbances. (b) Recovery column: stage 14; feed composition disturbances.

In an extractive distillation column, the distillate has two impurities: the solvent and the heavy key component. An extractive column also has three manipulated variables: solvent flow rate, reflux flow rate, and reboiler duty. Therefore, the first question is which distillate impurity should be controlled. Then an equally important question is which manipulated variable should be used.

The design flowsheet given in Figure 1 shows that the compositions of the two impurities in the distillate are 3.17 mol % C_2 (the heavy-key component) and 1.19 mol % C_3 (the lightest component in the solvent stream). Since the C_2 is larger, we select this impurity to be controlled ($x_{D1(\text{C}_2)}$). Notice that this impurity of the solvent is much larger in this NGL extractive distillation system than is typical in conventional extractive distillate in which the solvent is chosen to be much less volatile than either of the two key components. Solvent impurity in the extractive column distillate is usually very small in order to reduce solvent losses and to maintain a high-purity distillate product.

The reboiler duty has been selected to control the stage 25 temperature, and this keeps the light-key component CO_2 from dropping out the bottom. Should we use the solvent-to-feed (S/F) ratio to control $x_{D1(\text{C}_2)}$, or should we use the reflux-to-feed ratio?

The curves shown in the upper graph in Figure 3b predict that increasing the S/F ratio should reduce $x_{D1(\text{C}_2)}$ at high reflux ratios. However, at low reflux ratios, the opposite is true. Thus it is not obvious what action the composition controller should have. Simulation studies in which the S/F ratio was manipulated by a C_2 composition controller were found to be closed-loop

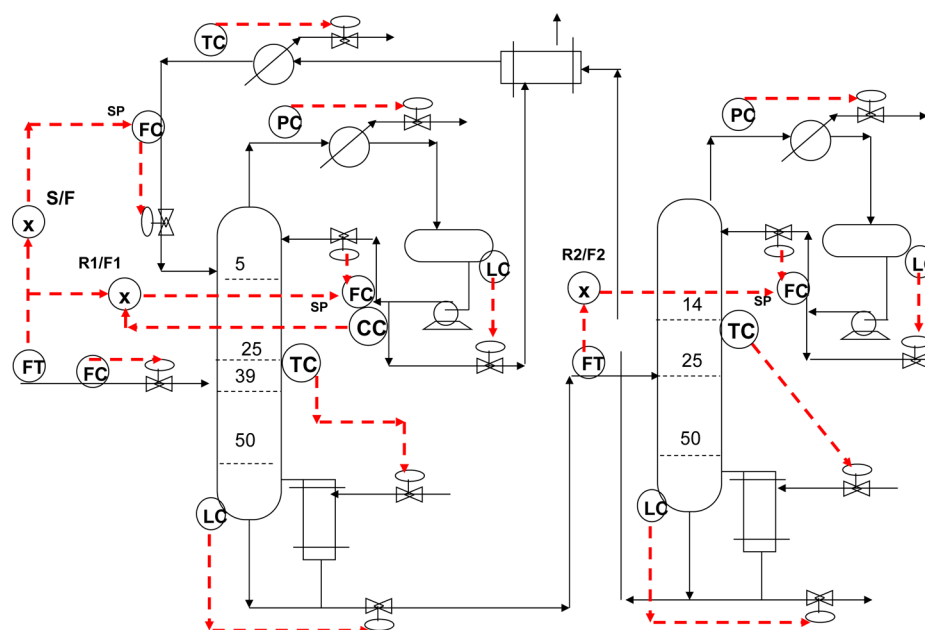


Figure 11. Proposed extractive distillation control structure.

unstable when the action of the composition controller was either *direct* (an increase in C2 concentration increases the S/F ratio) or *reverse*. Neither controller action provided stable control. The reason for this interesting phenomenon is probably that we are operating right at the minimum point in these curves (RR = 6.15 and $S = 9072$ kmol/h).

On the other hand, if the composition controller manipulates the R/F ratio (which changes the reflux flow rate and hence the RR) and has *reverse* action, the tuning of the controller is successful. The reverse action means that an increase in C2 concentration is counteracted by a decrease in the reflux ratio. This implies that the “solvent dilution effect” of reflux is the dominating phenomenon in the column, and we are operating in the region to the right of the minimum in the curves shown in the upper graph in Figure 3b.

The final proposed control structure is shown in Figure 11. The composition controller (CC) is holding the C2 impurity in the extractive column distillate at 3.17 mol % C2. A 3-min deadtime is used in the loop, and the controller is tuned by running a relay-feedback test and using Tyreus–Luyben tuning rules. The controller input range is 0–10 mol % C2, and the controller output range is 0–4 R/F ratio. The controller gain had to be reduced to eliminate oscillations. Final controller settings are $K_C = 0.3$ and $\tau_I = 33$ min.

The effectiveness of the structure is demonstrated in Figure 12 for feed composition disturbances and for feed flow rate disturbances in Figure 13. Good control of both product compositions is achieved.

Notice that the composition controller changes the R1/F1 ratio when feed composition disturbances occur. More CO₂ in the feed requires a lower R/F ratio (upper right graph in Figure 12a). However, for feed flow rate disturbances, there are transient changes in R1/F1 but the ratio lines out at the steady-state design value.

It is interesting to compare the responses of the two alternative control structures in the extractive column (only temperature control and temperature plus composition control) to feed flow rate disturbances. Comparing Figure 9 (single-end temperature structure) and Figure 13 (temperature plus composition

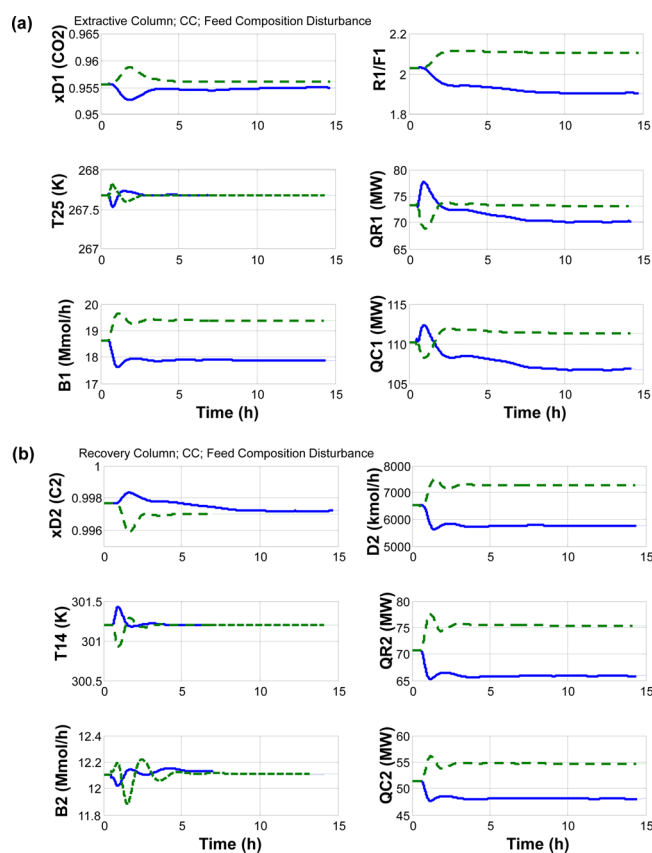


Figure 12. (a) Extractive column with CC: feed composition disturbances. (b) Recovery column: CC in extractive column; feed composition disturbances.

dual-end structure) shows that the extractive column distillate composition is more closely controlled, as we would expect. However, the recovery column distillate composition $x_{D2(C2)}$ has larger peak transients. Therefore tightening up on the control of the first column increases the magnitude of the disturbances to the second column. This is indicated in the response of the second

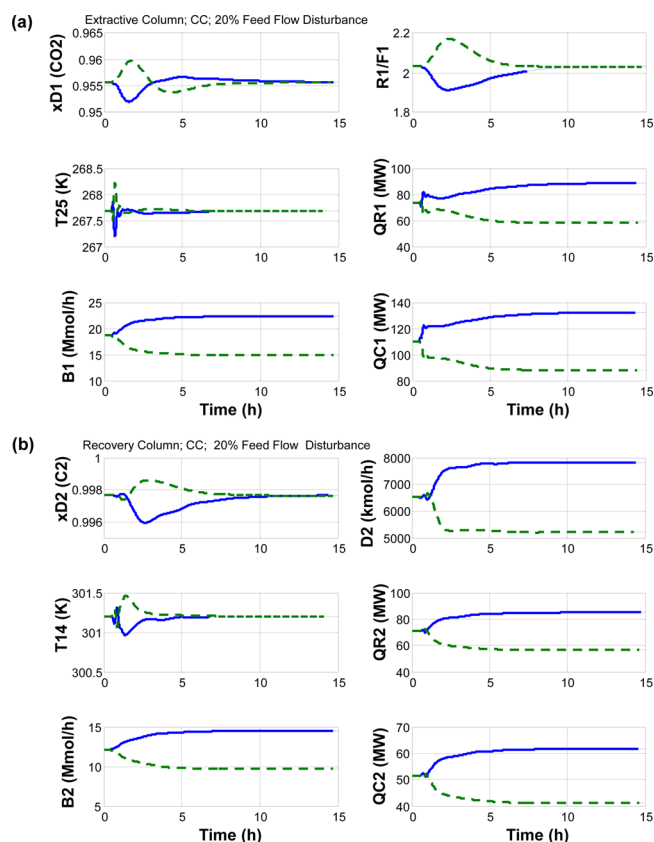


Figure 13. (a) Extractive column with CC: feed flow rate disturbances. (b) Recovery column: CC in extractive column; feed flow rate disturbances.

column distillate D2, which changes more quickly with the dual-end structure. However, the final composition in the recovery column is held closer to its specification when the dual-end structure is used.

4. CONCLUSION

A new extractive distillation column control structure is developed for CO₂/ethane separation. Since the solvent used in this system (NGL) is fairly similar to the heavy-key component ethane, conventional single-end temperature control in the extractive column is unable to maintain CO₂ product purity in the face of feed composition disturbances.

The composition controller holds the ethane impurity in the extractive column distillate by manipulating the reflux-to-feed ratio. Simulations show that the alternative of manipulating the solvent-to-feed ratio leads to instability.

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Notes

The authors declare no competing financial interest.

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