Design and Control of Glycerol Tertiary Butyl Ethers Process for the Utilization of a Renewable Resource

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This document is an electronic supplement which provides additional information about this work. It is organized as follows:

Section 1: Information about Process Design of GTBE Production in the Literatures.

Section 2: Cost models for TAC calculation.

Section 3: Design Steps of the Plantwide Process.

Section 4: Alternative Control Configurations and Their Control Performance.

Section 1: Information about Process Design of GTBE Production in the Literatures.

Three different process design alternatives for the manufacture of *h*-GTBE have been described in the literature. In the ARCO process shown in Fig. A1(A),[9] a decanter is placed after the reactor so that unconverted glycerol, *p*-toluenesulfonic acid and mono-ether can then be recovered in the lower phase and then recycled back to the reactor. A lower conversion of glycerol is required to maintain a phase split in the decanter. The upper phase is fed to a stripping column to recover unconverted isobutene. The bottom stream of the stripper is fed to an extraction column and water is used as solvent to remove mono-ether, glycerol and catalyst. In this case, large amount of mono-ether was lost through the waste water stream in the extraction column, thus, a further separation and recycle was also required which was not mentioned in the patent.

In the Bhern and Obendorf process shown in Fig. A1(B),[2] a extraction column is placed after a reactor and glycerol feed is used as a solvent to extract unconverted glycerol, *p*-toluenesulfonic acid and mono-ether. The extract stream is recycled to the reactor while the raffinate stream is fed to a flash tank to recover unconverted isobutene. The bottom stream of the flash tank is fed to a vacuum column to remove remaining mono-ethers, glycerol and traces of catalyst. Because mono-ethers and glycerol are recycled back to the reaction section, higher selectivity and conversion are obtained in this configuration in comparison with the ARCO process.

In the Di Serio, et al. process shown in Fig. A1(C),[3] the problem of the low solubility of MTBG in fuel is solved where a series of extraction steps were proposed. Free fatty acid ester (FAME) is used as the solvent to extract GBTEs (including MTBG, DTBG and TTBG) and water is used as the solvent of another extraction column to wash the glycerol from the product to meet the glycerol specification in fuel additive. The final product, a mixture of FAME and GTBEs, can be used as a component of the gasoline pool.

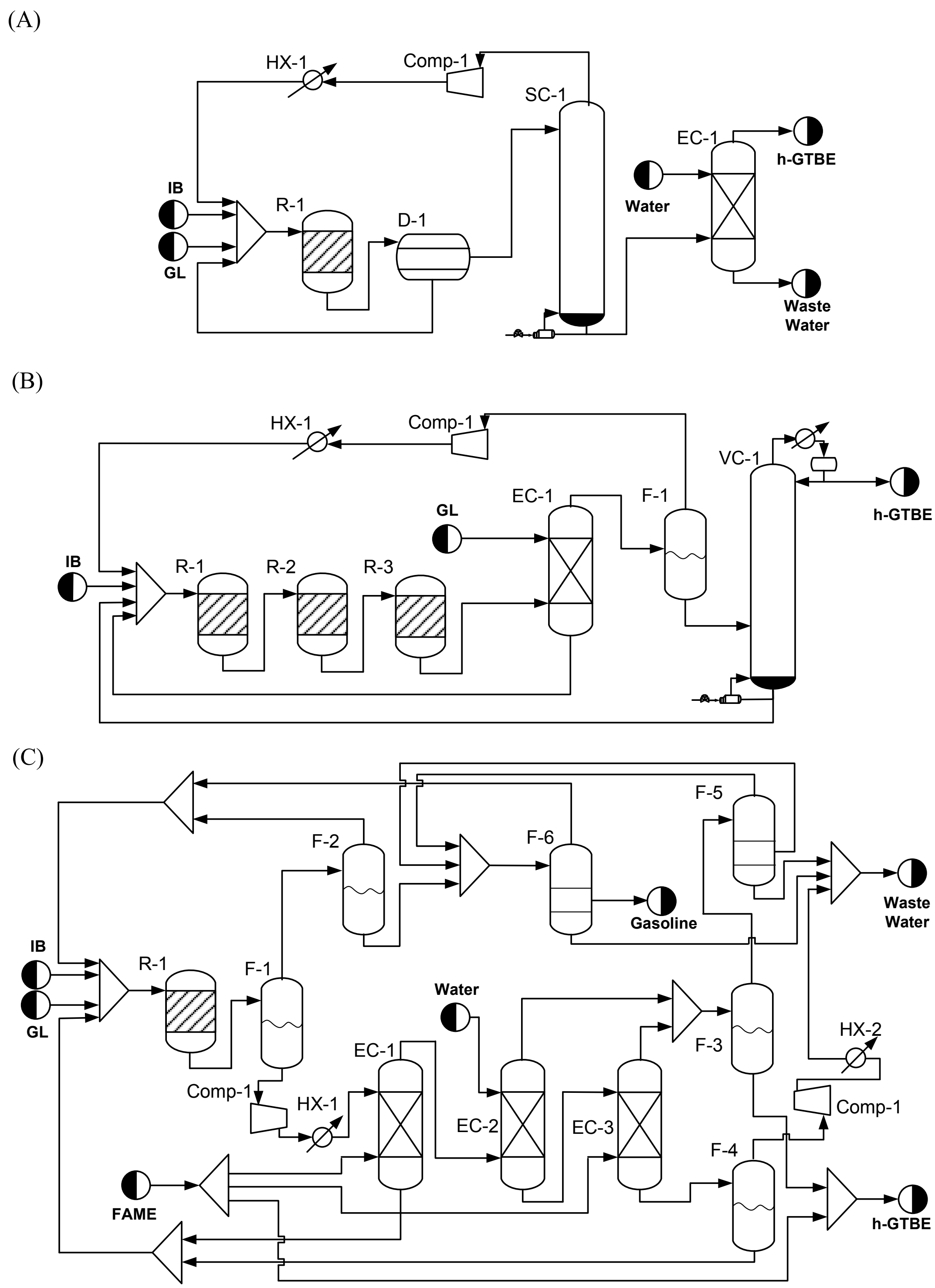


Fig. A1. Plant-wide processes for glycerol etherification: (A) the ARCO process,[9] (B) the Bhern and Obendorf process[2] and (C) the Di Serio, et al. process.[3]

Section 2: Cost models for TAC calculation.

The evaluation of equipments follows the procedure of Seider et al. (2009). A payback period of 8-year is assumed and a CE index of 539.1 (for January, 2010) is applied in the calculation. Materials of construction are stainless steel. The equipment is sized as follows:

(1) Reboiler Heat Transfer Area (A_R)

$$A_R[ft^2] = \frac{Q_R}{U_R \cdot \Delta T_R} \tag{A-1}$$

where Q_R [Btu/hr] is the reboiler duty, the overall heat-transfer coefficient U_R is assumed 250 Btu/(hr*ft^2), and the temperature driving force ΔT_R [^{o}F] in the reboiler depends on the steam.

(2) Condenser Heat Transfer Area (A_C)

$$A_C[ft^2] = \frac{Q_C}{U_C \cdot \Delta T_C} \tag{A-2}$$

where Q_C [Btu/hr] is the condenser duty, the overall heat-transfer coefficient U_C is assumed 150 Btu/(hr*ft^2), and the log-mean temperature driving force ΔT_C [^{o}F] depends on the dew points and bubble points for a total condenser.

(3) Column Length (L_C)

$$L_C[ft] = 2.4 N_T \tag{A-3}$$

where N_T is the total number of trays.

The capital and operating costs are calculated according to:

(1) Cost of Towers

$$\text{Purchase Cost, } C_P\ [\$] = \frac{\text{CE}}{550}\left(F_M C_V + C_{PL}\right) \tag{A-4}$$

where C_V, C_{PL} and F_M are

$$\text{Cost of empty vessel, } C_V\ [\$] = exp\left\{7.2756 + 0.18255\left[ln(W)\right] + 0.02297\left[ln(W)\right]^2\right\} \tag{A-5}$$

$$\text{Weight of shell, W [lbs]}=\pi\left(D_i+0.4947\right)\left(L+0.8D_i\right)\times 0.4947\times 0.284 \quad \text{(A-6)}$$

$$\text{Material factor, } F_M = 1.7 \text{ (for Stainless Steel 304)} \quad \text{(A-7)}$$

$$\text{Cost of platforms and ladders, } C_{PL} = 300.9D_i^{0.63316}L^{0.80161} \quad \text{(A-8)}$$

(2) Cost of Tray

$$\text{Cost of Tray, } C_T = N_T F_{NT} F_{TT} F_{TM} C_{BT} \quad \text{(A-9)}$$

where N_T (the number of trays), F_{NT}, F_{TT}, F_{TM} and C_{BT} are

$$F_T\text{=1 (if } N_T\text{<20) and } F_T\text{=}\frac{2.25}{1.0414^{N_T}} \text{ (if } N_T\text{<20)} \quad \text{(A-10)}$$

$$F_{TT}\text{=1 (for Sieve)} \quad \text{(A-11)}$$

$$F_{TM}\text{=}1.189+0.0577D_i \text{ (for Stainless Steel 303)} \quad \text{(A-12)}$$

$$C_{BT}\text{=}4.68\,exp\left(0.1739D_i\right) \quad \text{(A-13)}$$

(3) Cost of Shell-and-Tube Heat Exchangers

$$\text{Purchase Cost, } C_P \text{ [\$]}=F_P F_M F_L C_B \quad \text{(A-14)}$$

where

$$F_P\text{=1} \quad \text{(A-15)}$$

$$F_M\text{=}2.7+\left(\frac{A}{100}\right)^{0.007} \quad \text{(A-16)}$$

$$F_L\text{=1} \quad \text{(A-17)}$$

$$C_{BT}\text{=}exp\left\{11.967 - 0.8709\left[ln\left(A\right)\right]+0.09005\left[ln\left(A\right)\right]^2\right\} \quad \text{(A-18)}$$

(4) Double-Pipe Heat Exchangers

$$\text{Purchase Cost, } C_P \text{ [\$]}=F_P F_M C_B \quad \text{(A-19)}$$

$$F_P\text{=1} \quad \text{(A-20)}$$

$$F_M\text{=3} \quad \text{(A-21)}$$

$$C_{BT}\text{=}exp\left\{7.1460+0.16\left[ln\left(A\right)\right]\right\} \quad \text{(A-22)}$$

(5) Cost of Vertical Vessels

$$\text{Purchase Cost, } C_P\ [\$]=\frac{\text{CE}}{550}\left(F_M C_V + C_{PL}\right) \quad \text{(A-23)}$$

where C_V, C_{PL} and F_M are

$$\text{Cost of empty vessel, } C_V\ [\$]=exp\left\{7.0132+0.18255\left[ln\left(W\right)\right]+0.02297\left[ln\left(W\right)\right]^2\right\} \quad \text{(A-24)}$$

$$\text{Weight of shell, W [lbs]}=\pi\left(D_i+1.0176\right)\left(L+0.8D_i\right)\times1.0176\times0.284 \quad \text{(A-25)}$$

$$\text{Material factor, } F_M = 1.7 \text{ (for Stainless Steel 304)} \quad \text{(A-26)}$$

$$\text{Cost of platforms and ladders, } C_{PL}=361.8D_i^{0.73960}L^{0.70684} \quad \text{(A-27)}$$

(6) Cost of Extractor

$$\text{Purchase Cost, } C_P\ [\$]=\frac{\text{CE}}{550}\left(320F_M S^{0.84}\right) \quad \text{(A-28)}$$

where F_M and S are

$$F_M=2 \quad \text{(A-29)}$$

$$\text{Size factor, S}=\left(\text{HETP}\times N_T+6\right)D^{1.5}$$

$$\text{HETP [ft]}=4$$

$$D\text{ [ft]}=\left(\frac{4\times\text{cross-sectional area for flow}}{\pi}\right)^{0.5} \quad \text{(A-30)}$$

(6) Cost of Vacuum System for jet ejector

$$\text{Purchase Cost, } C_P\ [\$]=\frac{\text{CE}}{550}\left(F_{CM}\right)\left(1690\times S^{0.41}\right) \quad \text{(A-31)}$$

where F_{CM} and S are

$$\text{Cost Multiplying Factor, } F_{CM}=2.1 \text{ (for three stages)} \quad \text{(A-32)}$$

$$\text{Size factor, S}=\frac{W}{P} \quad \text{(A-33)}$$

Amount of air leakage, W [lb/hr]=

$$5+\left\{0.0298+0.03088\left[ln\left(P\right)\right]-0.0005733\times\left[ln\left(P\right)\right]^2\right\}V^{0.66}$$

P [ft^3]= vessel volume

$$P \text{ [torr]= absolute operating pressure} \tag{A-34}$$

(7) Cost of Compressor

$$\text{Purchase Cost, } C_P \text{ [\$]=} \frac{\text{CE}}{550} F_D F_M C_B \tag{A-35}$$

where F_D, F_M and C_B are

$$F_D = 1.25 \text{ (for a gas turbine)} \tag{A-36}$$

$$F_M = 2.5 \text{ (for stainless steel)} \tag{A-37}$$

$$C_B = exp\left\{8.1238 + 0.7243\left[ln\left(P_C\right)\right]\right\} \text{ (for screw compressor)} \tag{A-38}$$

(8) Cost of Installation

$$\text{Bare-module Cost, } C_{BM} = F_{BM} C_P \tag{A-39}$$

whrer F_{BM} (Bare-Module Factors) is as shown as below

Equipments	F_{BM}
Shell-and-tube heat exchangers	3.17
Double-pipe heat exchangers	1.80
Vertical pressure vessels	4.16
Gas compressors and drivers	2.15

(9) Cost of Cooling Water

$$\text{Cooling water cost [\$/year]=}\left[\frac{\$}{\text{year}}\right] = \frac{\$0.03}{1000\text{gal}}\left(\frac{1\text{ gal}}{8.34\text{ lb}}\right)\left(\frac{Q_C}{30}\right)\left(8150\frac{\text{hr}}{\text{year}}\right) \tag{A-40}$$

(10) Cost of Steam

$$\text{Steam cost [\$/year]=}\frac{\$3.73}{1000\text{lb}} \times \left(\frac{Q_H}{774.9}\right)\left(8150\frac{\text{hr}}{\text{year}}\right) \text{ (for Stripping Column)} \tag{A-41}$$

$$\text{Steam cost [\$/year]=}\frac{\$4.21}{1000\text{lb}} \times \left(\frac{Q_H}{895.1}\right)\left(8150\frac{\text{hr}}{\text{year}}\right) \text{ (for Vacuum Column)} \tag{A-42}$$

(11) Cost of Electricity

$$\text{Electricity cost [\$/year]=\$}\left(0.006\right) \times \left(\text{Electricity input, kW - hr / year}\right)\left(8150\frac{\text{hr}}{\text{year}}\right) \tag{A-43}$$

Section 3: Design Steps of the Plantwide Process.

After identifying 6 design variables in section 3.2 of the manuscript, a systematic design procedure is devised for flowsheet generation. All the simulations are carried out in Aspen Plus. Given the production rate and product specifications, the design steps of the proposed process (see Fig. 3 in the manuscript) are:

(1) Given the fresh glycerol feed flowrate (F_{GL}=5 kmol/hr) and the fresh isobutene feed flowrate (F_{IB}=11 kmol/hr)

(2) Guess the residence time of the 1st reactor ($\tau_{R\text{-}1}$).

(3) Guess the residence time of the 2nd reactor ($\tau_{R\text{-}2}$).

(4) Guess a number of trays in the extraction column ($NT_{C\text{-}1}$).

(5) Guess a number of trays in the vacuum column (NT_{VC}) and a feed location in the vacuum column ($NF_{F,VC}$).

(6) Guess a number of trays in the stripping column ($NT_{C\text{-}3}$).

(7) Guess a value of *h*-GTBEs composition in the bottoms of the vacuum column ($x_{VC,hGTBEs}$).

(8) Change the reflux ratio of the the vacuum column (*RR*) until the product specification is met.

(9) Go back to (7) and vary $x_{VC,hGTBEs}$ until the TAC is minimized.

(10) Go back to (6) and vary $NT_{C\text{-}3}$ is minimized.

(11) Go back to (5) and vary NT_{VC} *and* $NF_{F,VC}$ until the TAC is minimized.

(12) Go back to (4) and vary $NT_{C\text{-}1}$ until the TAC is minimized.

(13) Go back to (3) and vary $\tau_{R\text{-}2}$ until the TAC is minimized.

(14) Go back to (2) and vary $\tau_{R\text{-}1}$until the TAC is minimized.

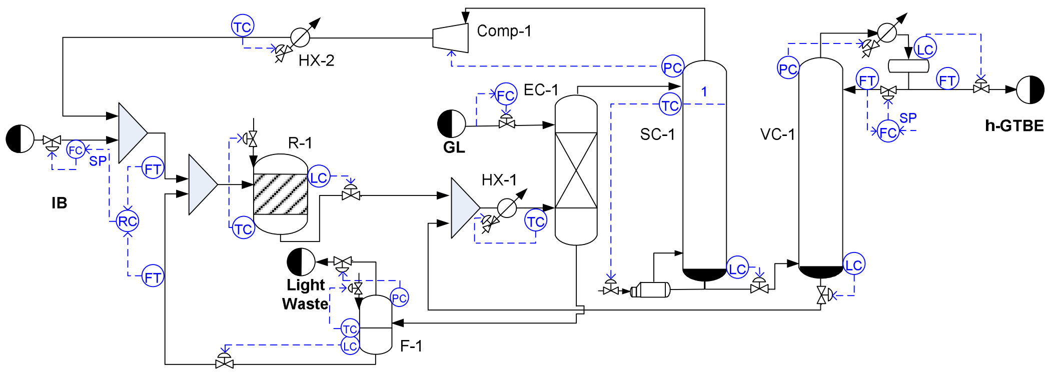
Section 4: Alternative Control Structures and Their Control Performance.

Two alternative control structures are considered, which are:

1. CS-A: Fix the reflux flow rate in the vacuum column (Figure A2(A))
2. CS-B: Fix the ratio of the reflux flow rate in the vacuum column to the feed flow rate to the vacuum column (Figure A2(B)).

The plant-wide controls of CS-A and CS-B are also tested for the same disturbance sequence of feed flow and composition changes, as shown in Figure A3 and A4 respectively. The results show that there is no significant improvement in the settling time compared to the control structure of fixing reflux ratio (Figure 9 in the manuscript).

(A)



(B)

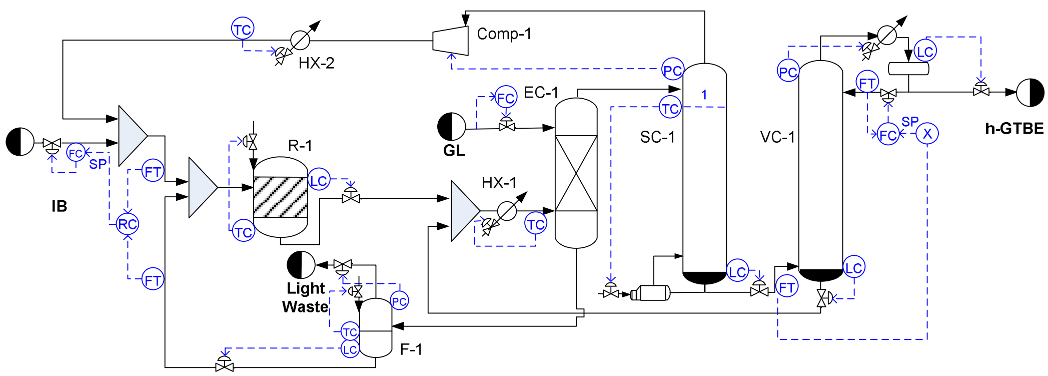


Fig. A2. Alternavitve control structures: (A) CS-A: Fix the reflux flow rate in the vacuum column and (B) CS-B:Fix the ratio of the reflux flow rate in the vacuum columnto the feed flow rate to the vacuum column.

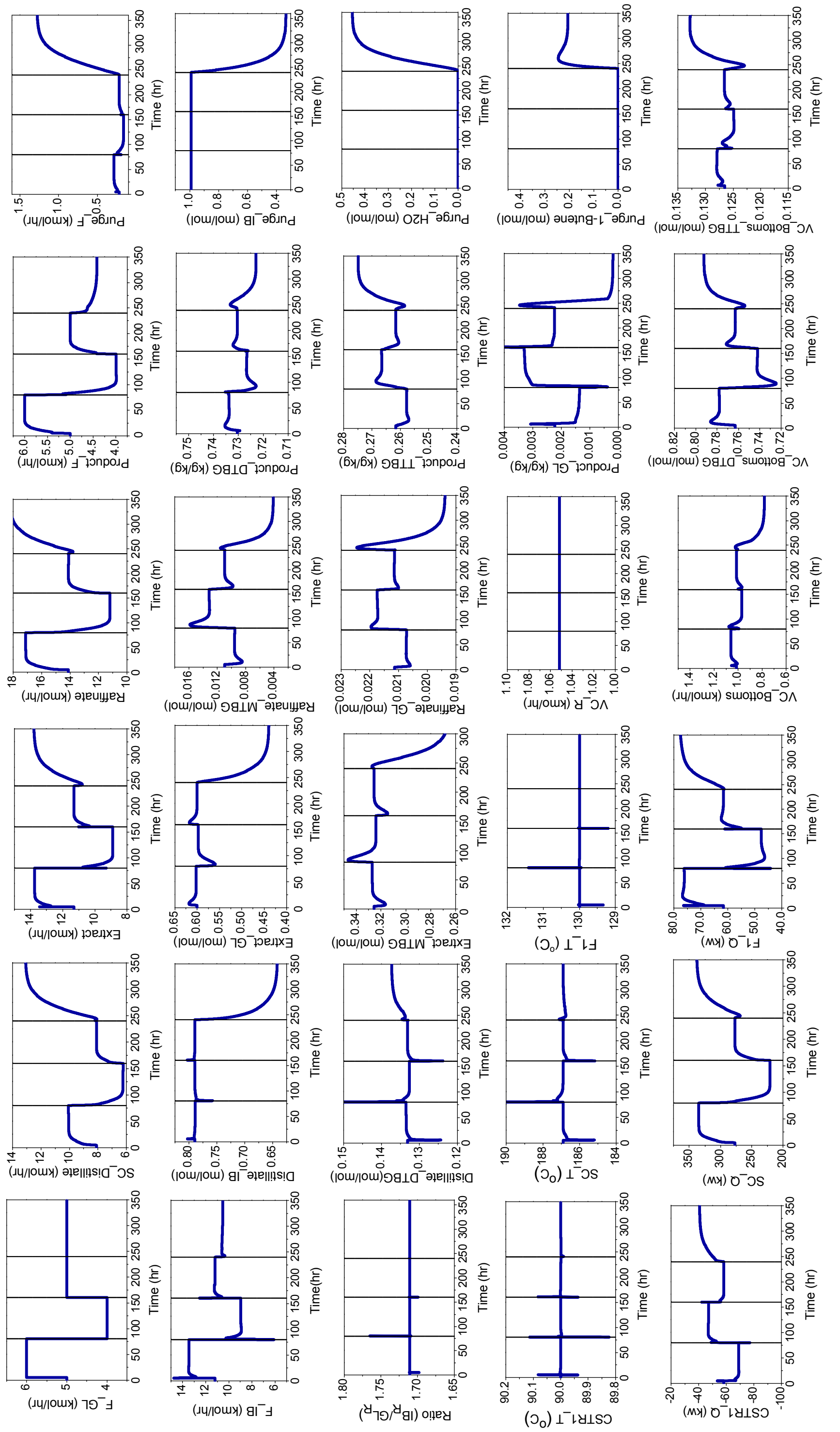


Fig. A3. Dynamic response of CS-A for the following load sequence: increasing glycerol fresh feed rate from 5 to 6 kmol/hr at t=5 hr, decreasing glycerol fresh feed flow rate from 6 to 4 kmol/hr at t=80 hr, returning the original production rate at t=160 hr and finally introducing impurity in both feeds (97.5wt% glycerol/2.5wt% water and 97.5wt% isobutene/2.5wt% 1-butene) at t=240 hr.

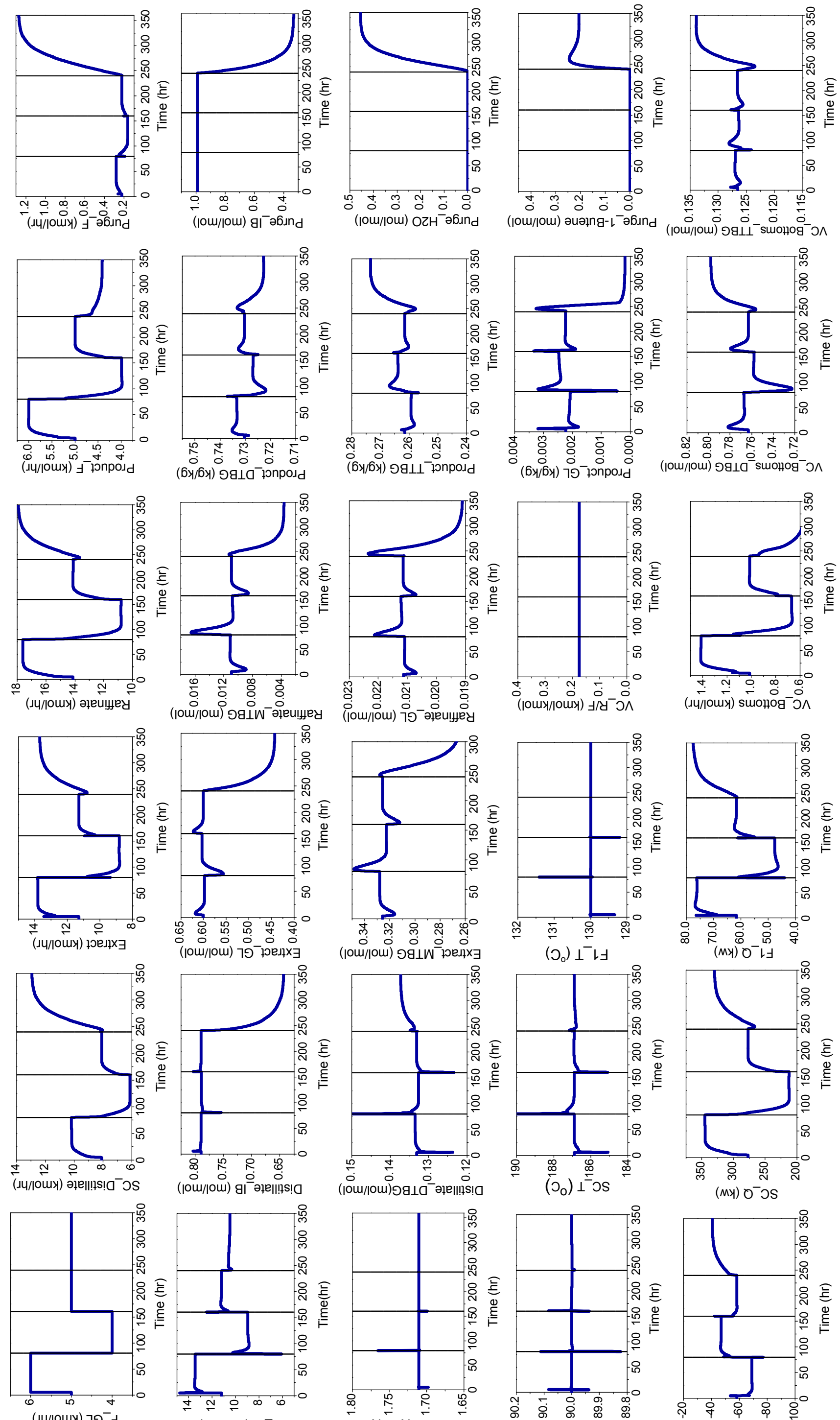


Fig. A4. Dynamic response of CS-B for the following load sequence: increasing glycerol fresh feed rate from 5 to 6 kmol/hr at t=5 hr, decreasing glycerol fresh feed flow rate from 6 to 4 kmol/hr at t=80 hr, returning the original production rate at t=160 hr and finally introducing impurity in both feeds (97.5wt% glycerol/2.5wt% water and 97.5wt% isobutene/2.5wt% 1-butene) at t=240 hr.