

# Improving Hydrogen Production in a Reactive Distillation via Economic Optimization and Control

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**Abstract** – Sulfur/iodine cycles have a considerable potential for thermochemical hydrogen production. This contribution studied section III (HI decomposition) of sulfur/iodine by using a reactive distillation. The commercial process simulator has been applied for simulation in the steady and dynamic states to investigate optimization and control strategy of a reactive distillation column for hydrogen production. From simulation studied, it is found that the reflux ratio and distillate rate affect the product quality in the reactive distillation. The optimal configuration for the reactive distillation consists of reflux ratio 6.9 and distillate rate 194.4 kmol/hr. Under this condition indicated that the composition at the top of column consists of hydrogen 9.2%. From economic optimization investigated, it is observed that the number of stage and the feed location is a very important variable on total annual cost (TAC). The resultant optimum process design contains 24 stages and is fed at stage 21. The disturbances of feed flowrate ( $\pm 5\%$ ) are used to evaluate the control performance of hydrogen production process. The control structure is considered, it performs well and good disturbance rejection is observed.

**Key Words**-- Hydrogen production, HI decomposition, reactive distillation, optimization, control

## 1. Introduction

The world energy demand has increased rapidly because of emerging industrial countries. Combustion of fossil fuels, used to power transportation, generate electricity, heat homes and fuel industry provides 86% [1] of the world's energy. Drawbacks to fossil fuel utilization include limited supply and carbon dioxide emissions from their combustion are thought to be responsible for global warming. Hydrogen appears as one of the most attractive energy for the future that has the potential to displace fossil fuels. One of the promising approaches to produce large quantity of hydrogen in an efficient way using the nuclear energy is the iodine-sulfur (IS) thermo-chemical water splitting cycle.

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Date of modification: 8 March 2012. Some information of graph is improved.

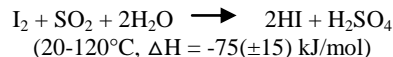
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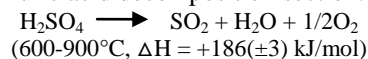
Sulfur-iodine (SI) cycle was first described by General Atomics. General Atomics chose Aspen Plus as the process simulator, and tried to develop the thermodynamic model based on the electrolytic NRTL (ELEC/NRTL) model built in Aspen Plus [2]. For the HI decomposition section, Neumann proposed an NRTL (Non-Random, Two Liquids) model in 1987 that describes thermodynamic interaction between constituent molecules (HI-H<sub>2</sub>O binary solution and HI-H<sub>2</sub>O-I<sub>2</sub> ternary mixture) [3]. Belaisaoui et al. [4] studied hierarchical approach for the preliminary design of reactive distillation columns that is extended to systems involving vapor phase chemical reaction and is successfully applied to the HI vapor phase decomposition to produce H<sub>2</sub>. Novel model predictive control (MPC) based on a sequence of reduced-order models is developed for a ternary batch distillation operated in an optimal reflux policy. [5]

Sulfur-iodine (SI) cycle consists of 3 sections: [6]

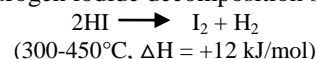
Section I Bunsen section:



Section II Sulfuric acid decomposition section:



Section III Hydrogen iodide decomposition section:



The purpose of the present work is to study hydrogen iodide decomposition for the production of hydrogen by using a reactive distillation. Simulation studies of hydrogen production process are performed using commercial process simulator to investigate effects of operating parameters in order to improve the product quality. The effects of the number of stage and the feed location on the total annual cost (TAC) are investigated. This leads to optimize the total annual cost (TAC), design the control structure of hydrogen production process by using commercial process simulator and evaluate the performance of the control structures based on the process disturbances.

## 2. Process simulation

Simulation of hydrogen production process is performed by using commercial process simulator. The procedures for developing the process consist on selecting the chemical components for the process, thermodynamic model, chemistry model and reaction model must be all selected and specified.

### 2.1 Chemical components

The following pure components have been used in the commercial process simulator models:

**Table 1** Components in HI decomposition section

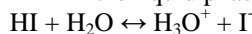
Component ID	Formula	Description
H2O	H <sub>2</sub> O	Water
HI	HI	Hydrogen iodide
I2	I <sub>2</sub>	Iodine
H2	H <sub>2</sub>	Hydrogen
H3O+	H <sub>3</sub> O <sup>+</sup>	Hydrated hydronium ion
I-	I <sup>-</sup>	Iodide ion

### 2.2 Thermodynamic model

The physical properties model used is the ELECNRTL model. This thermodynamic model captures the non-ideality of the ionic liquid solutions, but needs to be coupled with “chemistry” models that describe the dissociation and complication reactions that occur in solution. [2]

### 2.3 Chemistry model

In the liquid phase, the solvation equilibrium occurs:



The solvation equilibrium constant  $K_a(T)$  is expressed as follows:

$$\ln K_a(T) = -228.84 + \frac{12587.48}{T} + 40.686 \ln T - 0.098T \quad \text{with } T \text{ in K. [2]}$$

### 2.4 Reactions model

Power law kinetic expression

$$r = k \left(\frac{T}{T_0}\right)^n e^{-\left(\frac{E}{R}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)}$$

Kinetic rate constants of the reactions are necessary information for process simulation. This work focuses on the production of hydrogen from decomposition reaction of hydrogen iodide.

**Table 2** The values of kinetic constant for HI decomposition

No.	Reaction	A	$\beta$	$E_0$ (cal/mol)
1	$2HI \rightarrow I_2 + H_2$	$3.59 \times 10^{15}$	0.0	49 280
2	$I_2 + H_2 \rightarrow 2HI$	$1.23 \times 10^{15}$	0.0	40 940

$$k = AT^\beta \exp\left(-\frac{E_0}{RT}\right) \quad \text{with } T \text{ in K [7]}$$

$$R = 1.987207 \text{ cal / mole K}$$

### 2.5 Process flowsheet

In this research, all simulations are carried out using RADFRAC of commercial process simulator. The column is constituted by 11 stages including the condenser and the reboiler. The HI decomposition reaction takes place in all the 11 stages. The HI-I<sub>2</sub>-H<sub>2</sub>O product of Section I is pumped up to 22 bar and heated to the feed temperature (262°C) of the reactive distillation column (COLUMN) with a molar fraction of 51% of water, 39% of iodine and 10% of HI and is set at stage 10. The overhead product of the column is scrubbed in a packed column (SEP at 22 bar and 298 K) with water to remove the residual hydrogen iodine from the hydrogen. [4]

**Table 3** Operating conditions for hydrogen production

Parameter	Value
feed flowrate (kmol/hr)	360
reflux ratio	5
distillate flowrate (kmol/hr)	200.07
E1(MW)	-2.537
E2 (MW)	0.715

All system performances are considered in terms of yield of hydrogen defined as follows;

$$Y_{\text{Hydrogen}} = \frac{\text{Molar flowrate of hydrogen}}{\text{Molar feed flowrate of hydrogen iodide}} \times 100$$

## 3. Optimization and Control

### 3.1 Optimization of reactive distillation (steady-state)

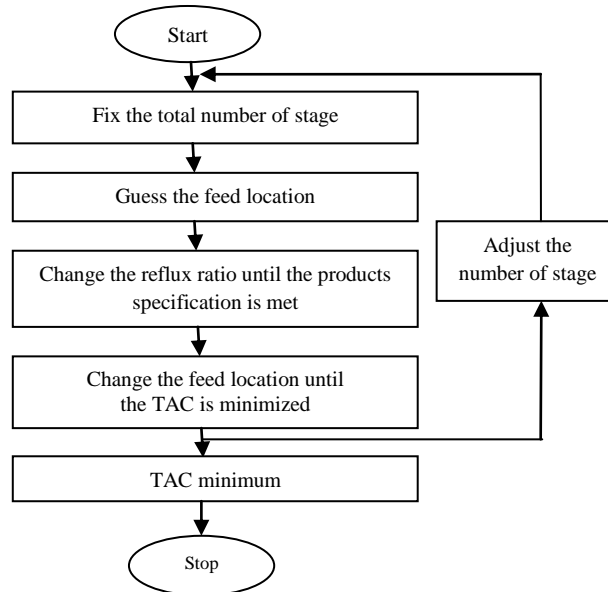
Fig.1 the minimization of total annual cost (TAC) is chosen as the economical objective function for the optimization of a reactive distillation column. Using a payback period of three years, the TAC is defined as:

$$TAC = \text{Operating cost} + \frac{\text{Capital cost}}{3}$$

The operating cost includes the cost of steam and cooling water. The capital cost covers the cost of column, trays, and heat exchangers. The costs of equipment and utilities are estimated with the formulas that are adopted from the book by Douglas (1988) [8] and Seider et al. (2010). [9]

Purity constraints:  $y_{\text{Hydrogen}} \geq 0.092$

The product has been kept on their specification with the careful adjustment of the reflux ratio.



**Fig.1** A method for the optimization of a RD column

### 3.2 Control structure

Fig. 2 shows the schematic of dynamic structure and controller positions of hydrogen production process. Proportional (P) controllers are used for drum level, sump level and separation level. Proportional-integral (PI) controllers are used for feed flowrate and pressure (condenser and separation).

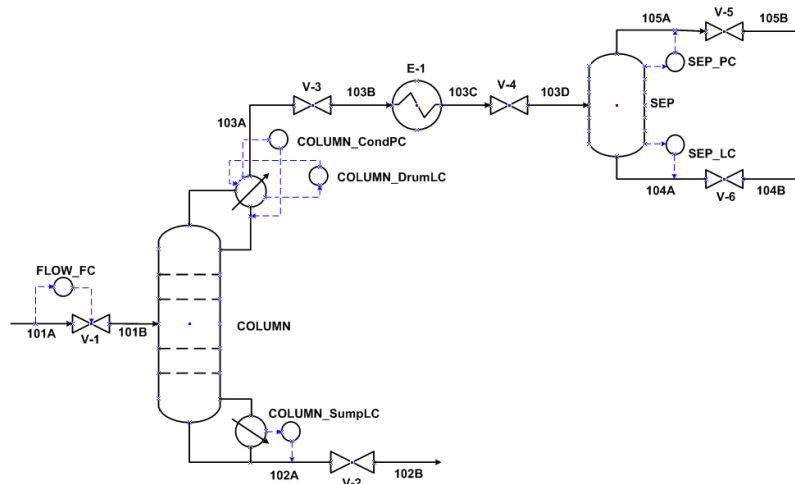


Fig.2 Schematic of control structure of hydrogen production process

## 4. Results and discussion

### 4.1 Steady-state simulation

From the simulation results, the top of the column has a number of water are 91%, hydrogen iodide 0.1% and hydrogen 8.9%. The stream 105B has a production rate of hydrogen 17.74 kmol/hr.

#### 4.1.1 Effect of reflux ratio

The reflux ratio is important variable that affects the efficiency of reaction and separation in the RD column. Operating conditions of reactive distillation are set as standard case. There is only the reflux ratio which has changed from 0.1 to 10 as shown in Fig 3. Notice that the reflux ratio of more than 6.9 the yield of hydrogen will be greater than 99.5%.

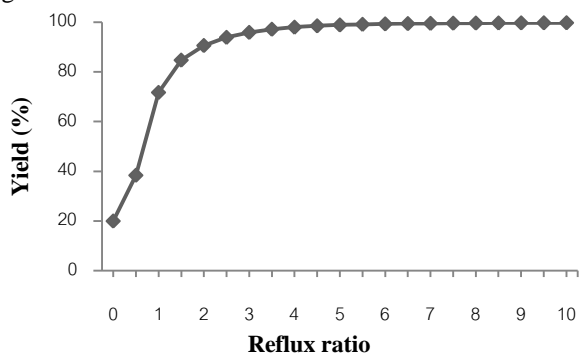


Fig.3 Effect of reflux ratio on yield of hydrogen

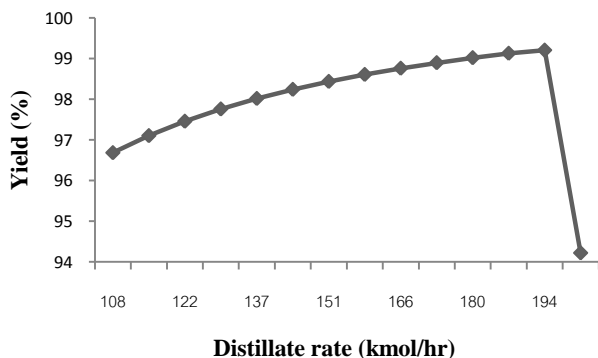


Fig.4 Effect of distillate rate on yield of hydrogen

#### 4.1.2 Effect of distillate rate

Figure 4 shows the effect of distillate rate on the yield of hydrogen. The operating parameters are the same as the standard condition. The distillate rate more than 194.4 kmol/hr, the yield of hydrogen will be reduced.

From simulation studies, it is found that the optimal configuration for the reactive distillation with reflux ratio of 6.9 and distillate rate 194.4 kmol/hr. Fig 5-6 show the temperature profile and composition profile in the reactive distillation with the optimal configuration. It can be seen that the composition at the top of column consists of water 90.8% and hydrogen 9.2%. The hydrogen production rate equals to 17.87 kmol/hr.

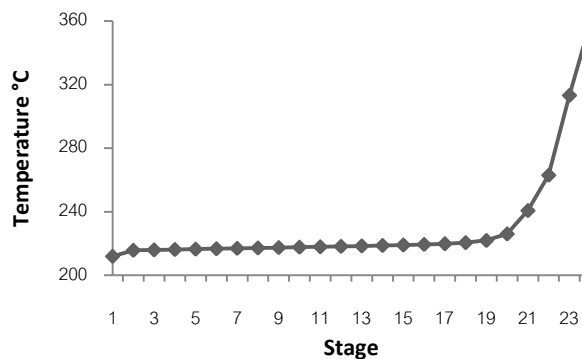


Fig.5 Temperature profile in the reactive distillation

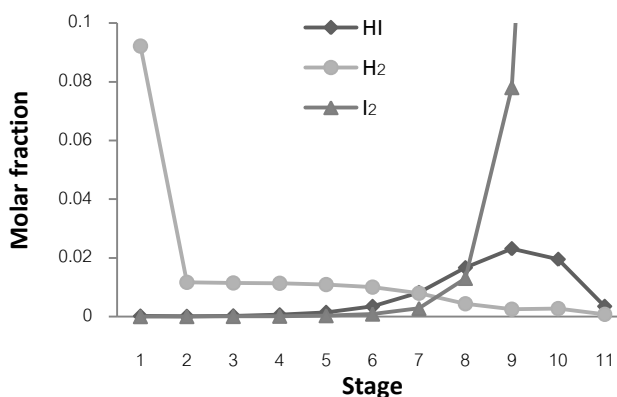


Fig.6 Composition profile in vapor phase along the reactive distillation column

The temperature profile along in the reactive distillation column is showed on Fig.5. In the upper part of the column, the temperature decrease is related to the increase in the light boiling compound hydrogen content. The temperature increase observed in the lower part of the column can be related to the increase in the heavy boiling compound iodine content.

The vapor composition profile in vapor phase along the reactive distillation column is showed on Fig.6. This figure shows that hydrogen production is obtained only for very low iodine content in the upper part of the column because iodine has high boiling point. HI decomposition mostly occurs in the upper part of the column that leads to the recovery of hydrogen. In the lower part of the column, almost pure iodine is recovered at the bottom in the liquid residue.

#### 4.2 Economic optimization of reactive distillation

From calculation the total annual cost of initial configurations (11 stage and feed stage 10), the total annual cost (TAC) is 2,975,731.86 \$/year.

##### 4.2.1 Effect of feed location on total annual cost

The column has a total of 11 stages with HI decomposition reaction takes place in all the 11 stages. The effects of feed location on the total annual cost are investigated. The feed location is a very important variable and it is found that feeding on the ninth stage of the reactive distillation column is most advantageous (minimum TAC), the total annual cost (TAC) equals to 1,720,612.92 \$/year.

##### 4.2.2 Effect of number of stage on total annual cost

Fig. 8 shows that the number of stage affects on total annual cost (TAC). If the number of stage is increased, the RD column becomes taller, but its diameter becomes smaller because reboiler heat input decreases (figure 7). This decreases heat exchanger costs and operating costs (steam cost and cooling water cost). However, the cost of the RD column increases because it is longer. So the effect of increasing the number of stage is to increase the capital cost of the RD column and to decrease the capital cost of the heat exchangers and operating costs.

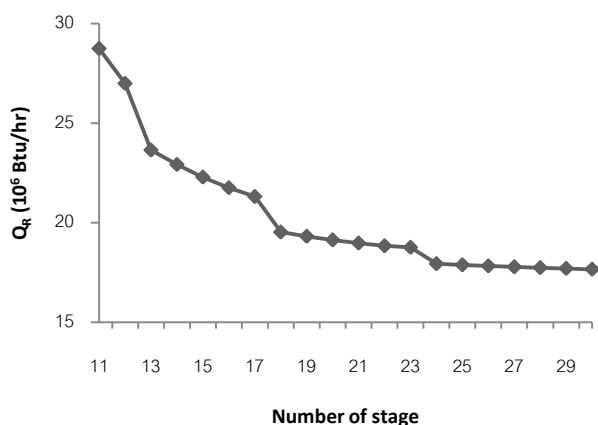


Fig.7 Effect of the reboiler heat duty on total annual cost (TAC).

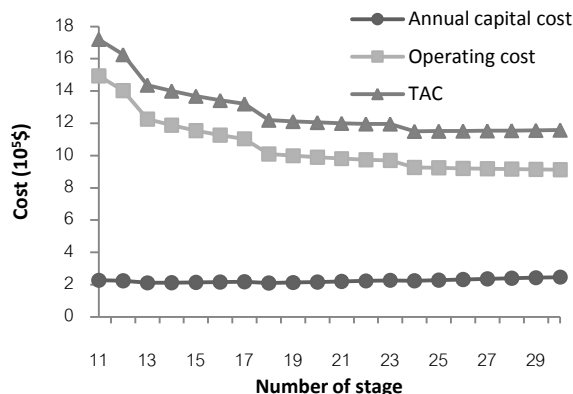


Fig.8 Effect of the number of stage on total annual cost (TAC).

From table 4, regarding the comparison between the initial configurations adopted and the optimum process designs obtained. A considerable reduction has been secured in the capital cost, operating cost, and TAC. The resultant optimum process design contains 24 stages with HI decomposition reaction takes place in all the 24 stages and is fed at stage 21, the total annual cost (TAC) equals 1,150,648.47 \$/year.

Table 4 Effect of the number of stage and feed location on the total annual cost (TAC).

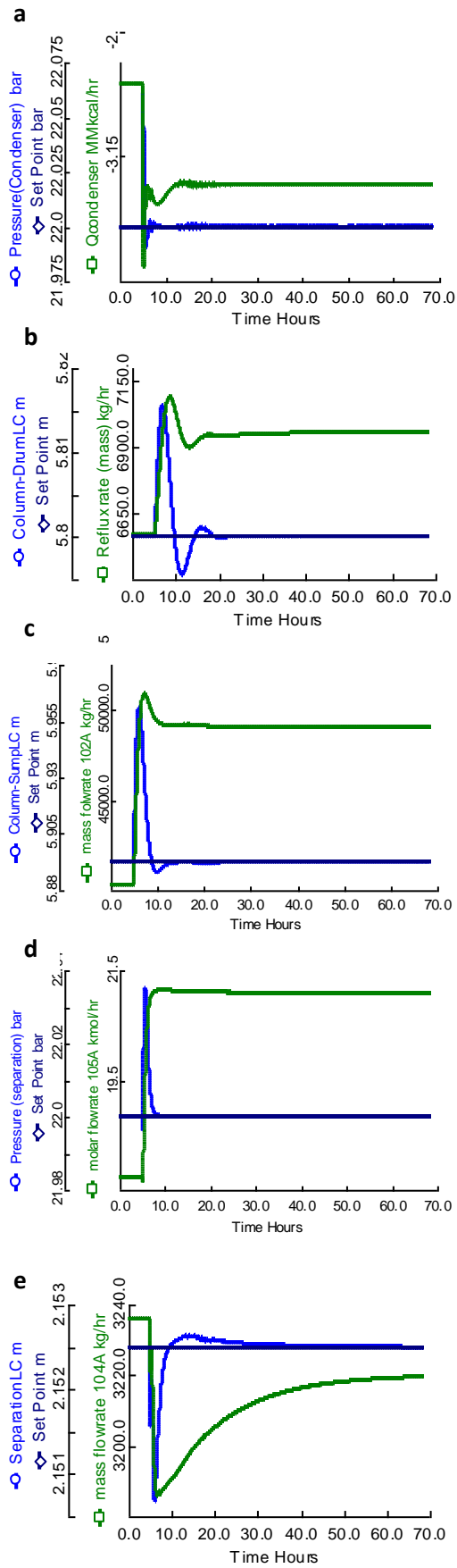
	11	11	24
feed stage	10	9	21
reflux ratio	6.9	3.51	1.85
Diameter (ft)	10.28	7.71	6.07
Q <sub>c</sub> (10 <sup>6</sup> Btu/hr)	-44.85	22.85	12.03
Q <sub>r</sub> (10 <sup>6</sup> Btu/hr)	50.77	28.76	17.94
A <sub>c</sub> (ft <sup>2</sup> )	1450.29	738.79	389.09
A <sub>r</sub> (ft <sup>2</sup> )	4513.21	2556.45	1594.8
Column cost (10 <sup>5</sup> \$)	2.91	2.12	3.38
Heat exchanger cost(10 <sup>5</sup> \$)	6.91	4.68	3.34
Operating cost (10 <sup>5</sup> \$/year)	26.48	14.94	9.26
TAC(10 <sup>5</sup> \$/year)	29.76	17.206	11.506

#### 4.3 Control performance

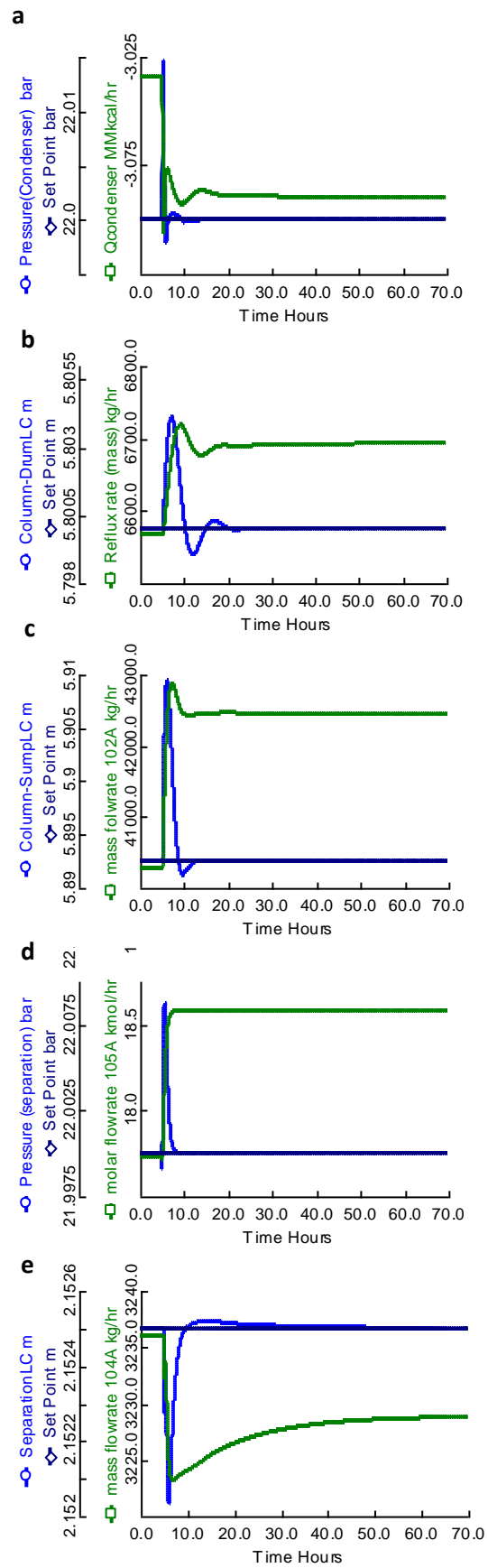
The change in the molar flowrate of feed as the disturbance  $\pm 5\%$  is imported to hydrogen production process to illustrate what occurs throughout the process and the control system responses.

##### 4.3.1 Condenser pressure controller

Fig. 9(a) and Fig. 10(a) show the effectiveness of condenser pressure controller to  $\pm 5\%$  disturbances of feed flowrate. Oscillations of condenser pressure are damped by increasing dynamic simulation time. Molar flowrate of feed increasing causes that condenser pressure is increased at initial times. Condenser pressure controller has a small offset that can neglect it.



**Fig.9** Control responses for +5% disturbances (molar flowrate of feed) a) pressure condenser b) column-drum LC c) column-sump LC d) pressure separation e) separation LC



**Fig.10** Control responses for -5% disturbances (molar flowrate of feed) a) pressure condenser b) column-drum LC c) column-sump LC d) pressure separation e) separation LC

#### 4.3.2 Condenser and reboiler level controllers

For  $\pm 5\%$  disturbances of molar flowrate of feed, the condenser and reboiler liquid level controllers actually work quite well as shown in Fig.9 (b-c) and Fig.10 (b-c). The final effects of increasing molar flow rate of feed are increases in manipulated variable (mass reflux rate and mass flowrate 102A). Condenser and reboiler liquid level controllers haven't offset.

#### 4.3.3 Separation pressure controller

Fig.9(c) and Fig.10(c) show the performances of separation pressure controller. The disturbances are 5% increase and decrease in molar flowrate of feed. Molar flowrate of feed increasing cause that molar flowrate of 309A is increased. The pressures go back to their set-point for both positive and negative disturbances.

#### 4.3.4 Separation level controller

For  $\pm 5\%$  molar flowrate of feed changes, the response of separation level controller are rather symmetrical as shown in Fig.9 (e) and Fig.10 (e). The separation levels are increased and return to set- point after the liquid level reach to maximum overshoots. The steady-state offsets are quite small.

### 5. Conclusion

In this work, optimization and control strategy of a reactive distillation for hydrogen production is investigated. The commercial process simulator has been applied for simulation of the reactive distillation column in the steady and dynamic states. Results under the standard condition indicated that hydrogen of the top product equal 8.9%. The simulation results showed that when reflux ratio 6.9 and distillate rate 194.4 kmol/hr are set in the reactive distillation, the hydrogen purity of 9.2% can be achieved.

From economic optimization based on a total annual cost (TAC) analysis, the optimal configuration of reactive distillation column consists of 24 stages and is fed at stage 21. The minimum total annual cost (TAC) is 1,150,648.47 \$/year. The effect of increasing the number of stages is to increase the capital cost of the column. But the diameter of column becomes smaller because reboiler heat input decreases, this leads to decreases heat exchanger costs and operating costs.

For  $\pm 5\%$  disturbances of molar flowrate of feed, the performance of control structure for hydrogen production process is evaluated. Good disturbance rejection is observed for these control structures. From the simulation results of control, it comes to a conclusion that the processes are resilient for disturbances of molar flowrate of feed.

### Appendix

The capital costs of individual equipment are estimated using the following equation:

$$\text{Column cost [\$]} = \frac{M\&S}{280} (101.9D^{1.066}H^{0.802} (2.18 + F_c))$$

Where  $F_c = F_m F_p$

$$\text{Tray cost [\$]} = \frac{M\&S}{280} (4.7D^{1.55}HF_c)$$

Where  $F_c = F_s + F_t + F_m$

$$\text{Heat exchanger [\$]} = \frac{M\&S}{280} (101.3A^{0.65} (2.29 + F_c))$$

Where  $F_c = (F_d + F_p)F_m$

The operating cost includes the costs of steam and cooling water.

$$\text{Steam cost} \left[ \frac{\$}{\text{year}} \right] = \frac{\$C_s}{1000\text{lb}} \times \left( \frac{Q_H}{\lambda_H} \right) \left( 8150 \frac{\text{hr}}{\text{year}} \right)$$

Where  $\lambda_H$ : heat of vaporization

$C_s$ : steam cost

$$\text{Cooling water cost} \left[ \frac{\$}{\text{year}} \right] = \frac{\$C_w}{1000\text{gal}} \times \left( \frac{1\text{gal}}{8.34\text{lb}} \right) \left( \frac{Q_c}{30} \right) \left( 8150 \frac{\text{hr}}{\text{year}} \right)$$

Where  $C_w$  = cooling water cost

### Reference

- [1] International Energy Outlook 2000: DOE/EIA-0484(2000), The Energy Information Administration of the Department of Energy ([www.eia.doe.gov](http://www.eia.doe.gov)).
- [2] Brown LC, Besenbruch GE, Lentsch RD, Shultz KR, Funk JF, Pickard PS, et-al. High efficiency generation of hydrogen fuels using nuclear power 2003, general atomics, final technical report, GA-A24285 Rev. 1 for the period August 1, 1999 through September 30, 2002.
- [3] Neumann D. Phasengleichgewichte von H<sub>2</sub>/H<sub>2</sub>O/J<sub>2</sub>-Losungen, Thesis, Lehrstuhl für Thermodynamik, RWTH Aachen, 5100 Aachen, Germany, January 1987.
- [4] Belaisaoui B, Thery R, Meyer XM, Meyer M, Gerbaud V, Joulia X. Vapour reactive distillation process for hydrogen production by HI decomposition from HI-I<sub>2</sub>-H<sub>2</sub>O solutions. Chem Eng Process 2008;. doi:10.1016/j.cep.2007.01.018.
- [5] Weerawun Weerachaipichasgul, Paisan Kittisupakorn, Aritsara Saengchan, Kwantip Konakoma, Iqbal M. Mujtaba. Batch distillation control improvement by novel model predictive control. Journal of Industrial and Engineering Chemistry 2010; 16: 305–313.
- [6] Huang Dan. Sulfur - iodine thermochemical cycle for hydrogen production. Bachelor Thesis, June 2009:5-9.
- [7] Yanwei Zhang, Junhu Zhou, Zhihua Wang, Kefa Cen, Detailed kinetic modeling and sensitivity analysis of hydrogen iodide decomposition in sulfur-iodine cycle for hydrogen production, Int. J. Hydrogen Energy, 2008;33: 627 – 632.
- [8] Douglas, J.M., 1988. Conceptual Design of Chemical Processes. McGraw-Hill, New York, USA.
- [9] Seider, W.D., Seader, J.D., Lewin, D.R., 2003. Product and Process Design Principles: Synthesis, Analysis, and Evaluation. John Wiley and Sons, Inc., New York, USA.