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Chemical Heat Pump (CHP) Simulation, Energy and Exergy Analysis

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***Abstract*- A suitable heat pump coupled to low-temperature sources can upgrade heat to higher temperatures. This is commonly achieved by consumption of electricity (vapor compression heat pumps) or by thermal means (vapor absorption and solid–gas sorption heat pumps). However, vapor compression and vapor absorption heat pumps are frequent, intensive research on chemical heat pumps conducted in recent years. Since no mechanical compression is required for attaining a considerable temperature rise, chemical heat pumps expected to take an important role in the utilization of solar, geothermal or waste-heats. They do not require electric power and generally have higher thermodynamic efficiencies than mechanical heat pumps. This paper present a detailed simulation of Isopropanol-Acetone-Hydrogen Chemical Heat Pump. The CHP system was simulated using ASPEN PLUS and further analyzed and optimized for the energy efficiency. Under the optimum distillation column condition (Table 2), the COP and exergy efficiency was considered0.25 and 0.33 respectively, which proved that simulation results are greater than the reported results. The developed model can be invoked as a guide for understanding the reaction kinetics for CSTR reactor.**

***Index Terms*—Chemical Heat Pump; Process simulation; Process optimization; ASPEN PLUS.**

I. INTRODUCTION

A suitable heat pump coupled to low-temperature sources can upgrade heat to higher temperatures. This is commonly achieved by consumption of electricity (vapor compression heat pumps) or by thermal means (vapor absorption and solid–gas sorption heat pumps). Though vapor compression and vapor absorption heat pumps are common, intensive research on chemical heat pumps is done in recent years [1]. Since no mechanical compression is required for attaining a large temperature rise, chemical heat pumps are expected to take an important role in the utilization of solar, geothermal or waste-heats [2]. They do not require electric power and generally have higher thermodynamic efficiencies than mechanical heat pumps [3].

A chemical heat pump in principle consists of two different chemical reactions each run at two different temperatures [4]. For example, it can be based on dehydrogenation of alcohols and hydrogenation of aldehydes or ketone, as shown below:

Alcohol ↔ Aldehyde (or Ketone) + Hydrogen

The most obvious property is the absence of any overall reaction. The reaction sequence functions to upgrade thermal energy, with no theoretical consumption or production of chemicals [5]. So, chemical heat pump systems comprise of two main units: an endothermic reactor (low-temperature heat is supplied) and an exothermic reactor (high-temperature heat is released) [6]. The feasibility of a chemical heat pump system based on dehydrogenation of *i*-propanol and hydrogenation of acetone has been proven experimentally [7]. The alcohol produced by hydrogenation reaction of aldehyde or ketone and hydrogen is recycled for dehydrogenation reaction. Since two reverse reactions running at different temperature levels are involved, at least two reactors and one heat exchanger are used in the system cycle [8]. A distillation column (the reboiler of which serves as endothermic reactor) is used to separate the outlet flow of the reactors into products and residual reactants. Part of low-level thermal energy supplied is upgraded to high-level energy and the rest was removed by condenser at ambient temperature. No mechanical energy as a driving force is necessary.

II. THE ISOPROPANOL-ACETONE-HYDROGEN CHEMICAL HEAT PUMP

The IAH-CHP, shown in Fig 1, is composed of two reactors, one for endothermic and the other for exothermic reactions. The endothermic reaction is dehydrogenation of isopropanol taking place at 80 – 90 and the exothermic reaction is hydrogenation of acetone taking place at 170– 210°C. The reaction equations are shown below. [9]

$(CH_3)_2CHOH$ (l) → $(CH_3)_2CO$ (g) + H_2 (g) ΔH = 100.4 kJ/mol(A)

$(CH_3)_2CO$ (g) + H_2 (g) → $(CH_3)_2CHOH$ (g) ΔH = -55.0 kJ/mol (B)Since the Gibbs free energy of dehydrogenation reaction ($\Delta G°$=13.9 kJ/mol) is positive, the reaction can be proceeded catalytically.

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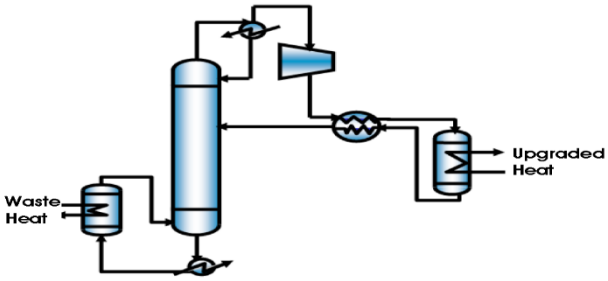

Fig 1. Isopropanol-Acetone-Hydrogen Chemical Heat Pump.

A. Constitution of the CHP system

Essential system constituents of the chemical heat pump are as follows:

Endothermic reactor R_L: the reaction heat (Q_L) is absorbed by the liquid-phase endothermic reaction (equation (A)) at the temperature of T_L

Exothermic reactor R_H: the reaction heat (Q_H) is generated by the gas-phase exothermic reaction (equation (B)) at the temperature of T_H.

Distillation column D: evaporation heat (Q_R) for reboiling in distillation is supplied at the temperature of $T_R$out of the mixture of 2-propanol, acetone and hydrogen, carried in from both endothermic reactor R_L and exothermic reactor R_H, 2-propanol is separated by the condensation procedure, with the condensation heat (Q_C removed with coolant at the temperature of T_C.

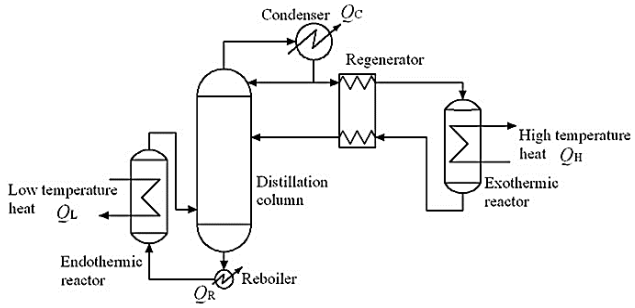

Fig. 2. Heat flow and material balance in the loop of chemical heat pump system composed of the reversible reaction couple of acetone hydrogenation and 2-propanol dehydrogenation and separation procedure.

In order to operate the present system more efficiently, it is necessary in addition to set the heat exchanger **E** for recovering high temperature heat carried out from exothermic reactor R_H with its outlet gas, by preheating its inlet gas, which is supplied from the top of distillation column.

B. CHP system design and evaluation of performance

The performance of an organic CHP can be characterized by such parameters as the upgrading temperature, specific power production, coefficient of performance (COP, i.e., enthalpy efficiency), and exergy efficiency.

Saito et al. [8] calculated the energy efficiencies (enthalpy efficiency and exergy efficiency)

The enthalpy efficiency

$$COP \text{ or } \eta_H = \frac{Q_H}{Q_L} (1)$$

and exergy efficiency could be calculated as:

$$\eta_\varepsilon = \frac{Q_H(1 - T_o/T_H)}{Q_L(1 - T_o/T_L)} (2)$$

For a reversible cycle, the maximum efficiency value only depends on the temperature levels at which heat is exchanged [9]:

$$\eta_{max} = \frac{[1 - (T_C/T_L)]}{[1 - (T_C/T_H)]} (3)$$

However, for engineering purposes the use of effectiveness (ξ) is more significant:

$$\xi = \frac{\eta_H}{\eta_{max}} (4)$$

Where:

η_H is chemical heat pump efficiency (or COP = coefficient of performance).
η_{max} is maximum chemical heat pump efficiency.
ξ is heat pump effectiveness.
Q_L is endothermic reaction heat.
Q_H is exothermic reaction heat.
T_o is surrounding temperature.
T_L is endothermic reaction temperature.
T_H is exothermic reaction temperature.
T_C is condensation temperature.

III. CHP PROCESS SIMULATION AND EXERGY ANALYSIS

Table below summarizes the main units of CHP used in the Aspen Plus flow sheet and the operating conditions simulated.

Table 1. Equilibrium and Kinetic reactor required operating conditions.

Parameter	Endothermic reactor (RCSTR)	Distillation column (Redfrac)	Endothermic reactor (Rstoic)
Temperature	80 ℃	-	200 ℃
Pressure	1 atm	1 atm	1 atm
Residence time	30 min	-	-
Initial reflux ratio	-	1.2	-
Distillate/ feed ratio	-	0.5	-
Conversion %	-	-	98 (based on acetone)

A. Process description

Based on the below Fig. 3, the feed contain isopropanol is feed to endothermic reactor when the it takes place at low temperature acetone and hydrogen are produced. The absorbed heat will be carried by these chemical species and is transported to the exothermic part of the system by separating these two chemical species from isopropanol (unreacted) in a partial condensation distillation column. Isopropanol as a bottom product of the distillation is fed into the endothermic reactor. Acetone and hydrogen are then sent, compressed, and reacted in the exothermic reactor, where the hydrogenation taking place, to produce isopropanol. The compressor is to compensate for the pressure drop in the system. The high-temperature heat will be released from the system to a process. The product from the reactor exchanges heat with reactor feed through a heat exchanger and is fed into distillation column and the process operate continuously.

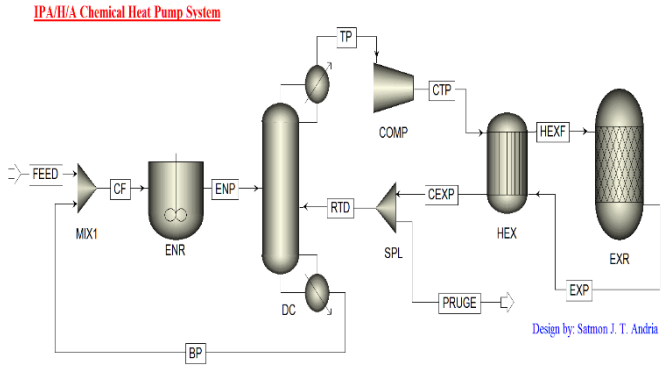

Fig. 3. Overall process flow diagram for continuous IHA chemical heat pump system

IV. SIMULATION RESULTS

A. Thermodynamic analysis

The below figure shows the binary mixture analysis between isopropanol and acetone versus temperature at 1 atm

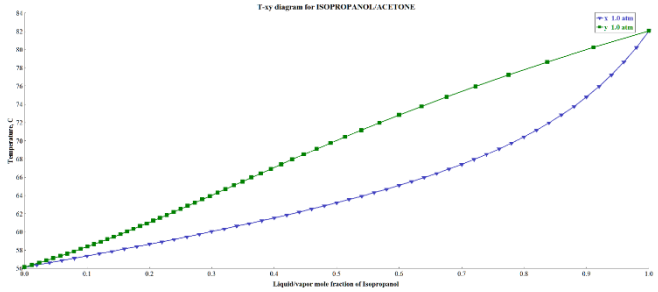

Fig. 4. Binary mixture of isopropanol and acetone

B. Endothermic reactor analysis

Fig. 5, shows that pressure has an effect on the conversion of isopropanol, an increasing of pressure decrease isopropanol conversion. Nevertheless, its obviously in Fig. 6, high temperature increases conversion but for our system, temperature is determined variable. Therefore, from this analysis low pressure and temperature are preferable.

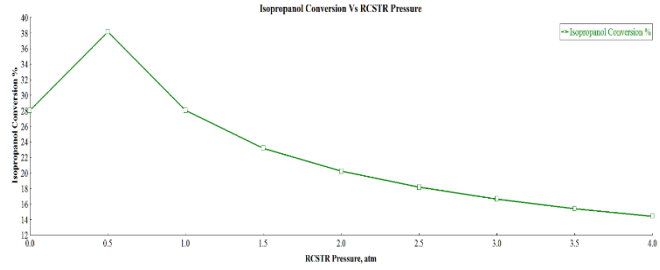

Fig. 5. Effect of pressure on the isopropanol conversion

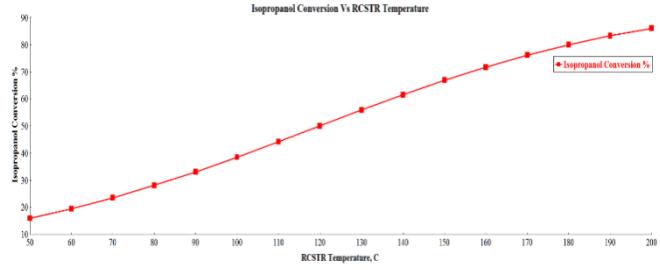

Fig. 6. Effect of pressure on the isopropanol conversion

C. Distillation column analysis

Sensitivity analysis was done to see the possible way of optimizing the distillation unit related to exergy analysis. Fig. 7. Indicated that distillate to feed ratio is directly proportional to reboiler and condenser duties. Also, increase in distillate to feed ratio increases acetone molar flow (see Fig. 8) in top production, which is a clear indication for an increase in condenser duty.

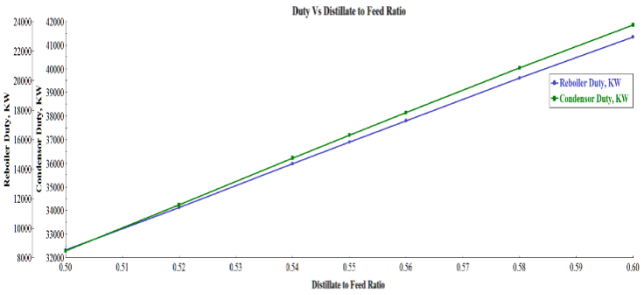

Fig. 7. Variation of distillate to feed ratio on reboiler & condenser duties

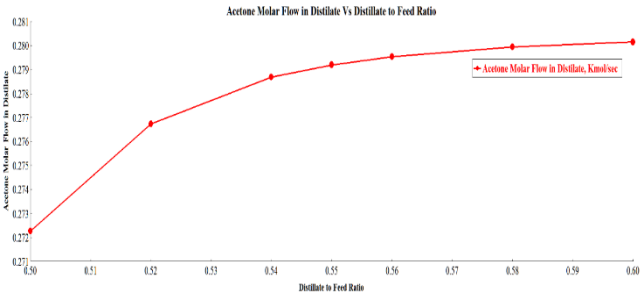

Fig. 8. Variation of distillate to feed ratio on acetone molar flow

D. Energy and exergy analysis

It was worth mentioned that, for high COP and exergy efficiency the CHP system must be optimized especially the distillation column. Therefore, from the sensitivity analysis we found the optimum operating conditions for distillation column as follows:

Table 2. Distillation column optimum operating conditions.

Parameter	Distillation column (Redfrac)
No of Stage	15
Reflux ration	1.6
Distillate to feed ratio	0.423
Feed location	8
Recycle location (from exothermic reactor)	10

The following figures are distillation column profiles under optimum condition

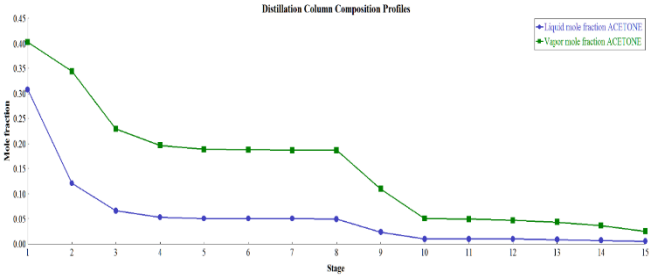

Fig. 9. Variation of acetone vapor/liquid mole fraction to stage number

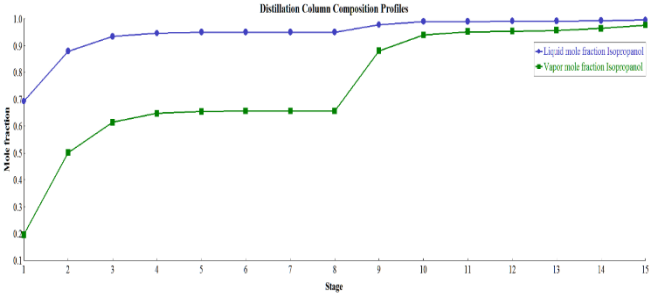

Fig. 10. Variation of isopropanol vapor/liquid mole fraction to stage number

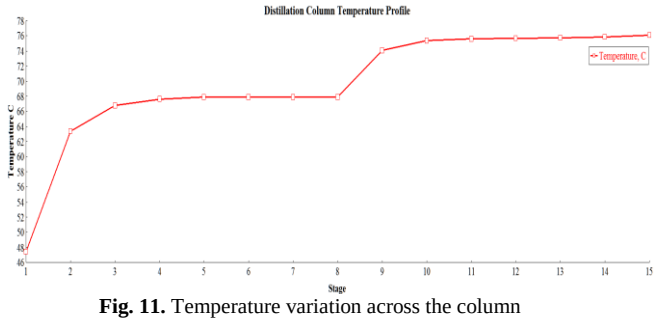

Fig. 11. Temperature variation across the column

The above optimum condition shows the highest COP and exergy efficiency as in Table 3 and in comparison with previous studies (Table 4 and 5).

Table 3. COP and exergy efficiency results.

Parameter	Value
COP	0.25
η_ε	0.33
η_{max}	0.50
ξ	0.67

Table 4. Initial and optimal design for CHP under design variables (J. Guo et al. [10]).

One initial and the optimal design schemes under three design variables conditions.

	R	x_0	T_H (K)	N_H	N_L	N	r_F	Q_R (MW)	Q_L (MW)	Q_{EH} (MW)	Q_F (MW)	Q_{EL} (MW)	COP	η	G'
Initial	5.61	1.54	471.3	3	7	8	0.342	9.62	15.78	0.45	2.68	2.22	0.087	0.187	0.116
Optimal	4.89	2.95	473.2	3	10	15	0.400	1.57	20.69	0.68	3.51	2.83	0.127	0.268	0.168

Table 5. Initial and optimal design for CHP under design variables (J. Guo et al. [11]).

One initial and the optimal design schemes under four design variables conditions.

	R	x_0	T_H (K)	T_L (K)	T_R (K)	N_H	N_L	N	r_F	Q_R (kJ)	Q_L (kJ)	Q_C (kJ)	Q_M (kJ)	Q_H (kJ)	COP	η
Initial	3.48	2.61	489.0	372.2	353.15	3	7	8	0.282	990	1460	2350	860	234	0.071	0.161
Optimal	3.45	1.72	466.3	372.6	353.15	4	11	14	0.392	340	2030	2340	570	388	0.132	0.259

Below figure is the optimized CHP system

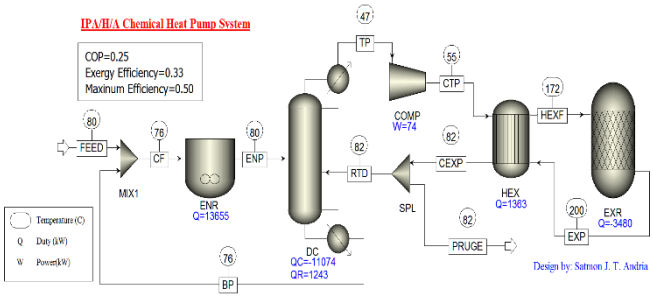

Fig. 12. Optimized process diagram for continuous IHA chemical heat pump system.

V. CONCLUSION

The CHP system was simulated using ASPEN PLUS and further analyzed and optimized for the energy efficiency. COP and exergy efficiency was found to be 0.25 and 0.33 respectively.

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