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Design of a Chemical Heat Pump based on Methylcyclohexane, Toluene and Hydrogen

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ABSTRACT

The conceptual design and performance of a novel Methylcyclohexane-Toluene-Hydrogen based chemical heat pump was studied using steady state simulations. The distillation operating parameters of the chemical heat pump were optimized to maximize the Coefficient of Performance based on heat quantity (COP) and its corresponding Coefficient of Performance based on electric work input (COP_W) was calculated. The best operating temperature ranges of the endothermic and exothermic reactor are 200°C-225°C and 250°C-275°C respectively. An endothermic temperature of 200°C and an exothermic temperature of 250°C results in a COP of 0.1357 and a COP_W of 13.3. By integrating this chemical heat pump with a vapor compression heat pump COP increased to 0.1445 while COP_W reduced to 4.9.

Keywords: Chemical heat pump, Energy Efficiency, Toluene, Methylcyclohexane, Hydrogen

INTRODUCTION

Chemical heat pumps convert low temperature heat to high temperature heat with only a small amount of electricity or work requirements. Organic chemical heat pumps are based on reversible organic reactions. The key unit operations in a chemical heat pump include an endothermic reactor, an exothermic reactor, and a distillation column [1]. Low temperature heat input (primarily waste heat) is given to the endothermic reactor and high temperature heat is released from the exothermic reactor. Because the reactions approach equilibrium, the distillation column separates the reactants from the products to establish the necessary driving forces. Ideally, the distillation column reboiler can be powered by waste heat at the same or lower temperature as the endothermic reactor.

The most researched organic chemical heat pump is the isopropanol + acetone based chemical heat pump. It is generally best used for lifting heat from about 80-90°C to about 150-210°C [1]. In this work, we examine a chemical set (methylcyclohexane and toluene) that could lift heat from about 200°C to about 250°C that has not been studied previously for chemical heat pump applications. Drying in textile and distillation in chemical industries are some of the processes that require heat in the range 200°C-250°C [2]. The methylcyclohexane and toluene based reversible system has been widely explored in other applications, such as a liquid organic hydrogen carrier. In that application, the hydrogen is stored in the form of methycyclohexane by using hydrogenation of toluene. Hydrogen is released during the dehydrogenation of methyl cyclohexane as shown:

$$C_7H_{14} \rightleftharpoons C_7H_8 + 3H_2 \quad (1)$$

Usman *et al.* [3] studied the dehydrogenation kinetics of methylcyclohexane in the temperature range of 340°C-380°C. Castano *et al.* [4] studied the toluene hydrogenation kinetics in the temperature range of 100°C-250°C. These studies provide evidence that the reversible reaction is feasible within the desired temperature ranges suitable for our proposed chemical heat pump application. Toluene and methylcyclohexane have a difference in boiling point by around 10°C, which enables their separation in a distillation column. Additionally, toluene and methylcyclohexane also meet the ozone depletion potential and global warming potential screening criteria as per [5].

In this work, we designed a novel methylcyclohexane–toluene–hydrogen (MTH) based chemical heat pump (CHP) and determined its key performance indicators using Aspen Plus process simulations.

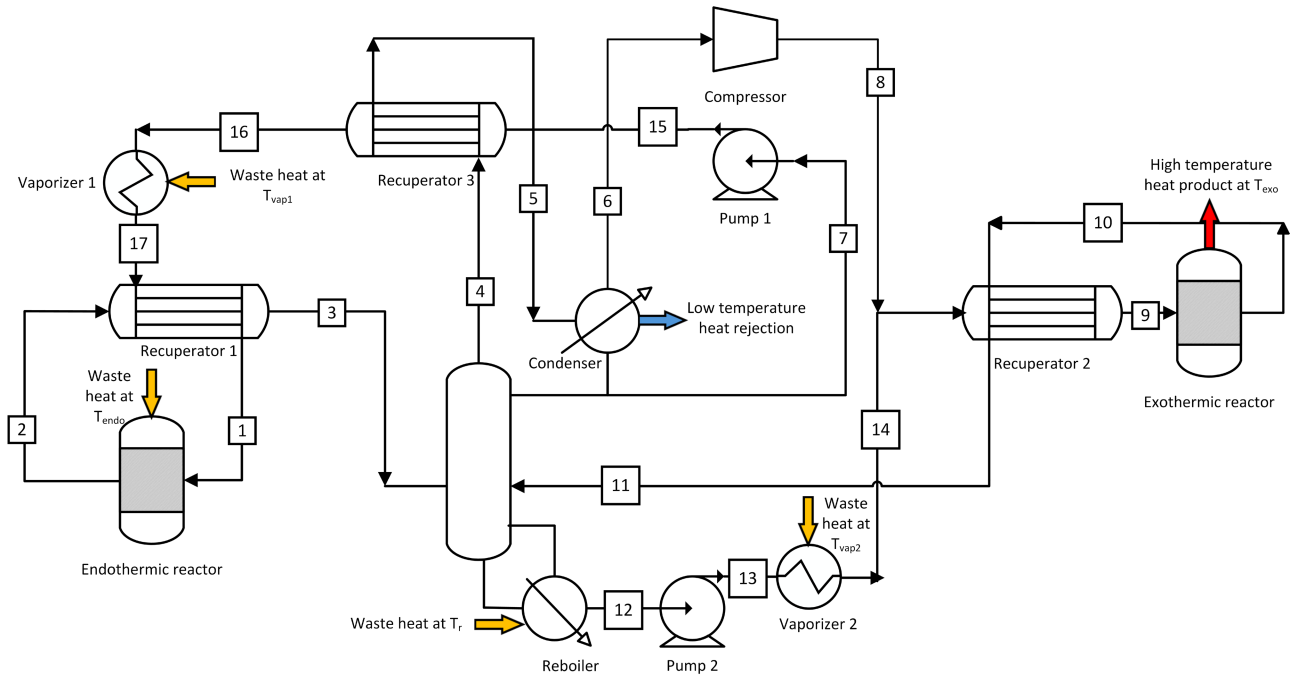

Figure 1. Process scheme of MTH-CHP

Table 1: Stream details of MTH-CHP at for T_{endo} = 200°C, T_{exo} = 250°C when COP is maximized

Stream number	Tempera-ture, °C	Pressure, bar	Mole Flow ratio (Stream X / Stream 1)	Methylcyclo-hexane mole fraction	Hydrogen mole frac-tion	Toluene mole frac-tion
1	190	1.23	1.00	0.6174	0.0028	0.3798
2	200	1.13	1.10	0.5321	0.0923	0.3756
3	113	1.10	1.10	0.5321	0.0923	0.3756
4	92	1.06	1.70	0.4419	0.2903	0.2678
5	86	1.06	1.70	0.4419	0.2903	0.2678
6	35	1.01	0.54	0.0638	0.9098	0.0264
7	35	1.01	1.00	0.6174	0.0028	0.3798
8	59	1.30	0.54	0.0638	0.9098	0.0264
9	240	1.28	0.61	0.1146	0.7969	0.0885
10	250	1.18	0.52	0.2002	0.7580	0.0418
11	83	1.15	0.52	0.2002	0.7580	0.0418
12	107	1.10	0.08	0.4729	-	0.5271
13	107	1.35	0.08	0.4729	-	0.5271
14	113	1.30	0.08	0.4729	-	0.5271
15	35	1.30	1.00	0.6174	0.0028	0.3798
16	82	1.30	1.00	0.6174	0.0028	0.3798
17	110	1.25	1.00	0.6174	0.0028	0.3798

SYSTEM DESCRIPTION

The process scheme of the MTH-CHP is shown in Figure 1 with corresponding stream conditions in Table 1. It consists of an endothermic reactor, an exothermic reactor, a distillation column, recuperators, pumps and a compressor. The methylcyclohexane dehydrogenation takes place in the endothermic reactor and the toluene hydrogenation occurs in the exothermic reactor. Both the reactor effluents, containing all the chemicals, enter the distillation column for separation. The distillation column bottom consists of mostly toluene since it is the heaviest component. The distillate consists of hydrogen and methylcyclohexane. The hydrogen and methylcyclohexane need to be separated since hydrogen is required in

the exothermic reactor and methylcyclohexane is required in the endothermic reactor. A partial condenser facilitates this separation. Because the reactions happen in the gas phase, methylcyclohexane in the partial condenser liquid product and toluene at the distillation bottom and need to be fully vaporized (vaporizer 1 and 2 respectively). To reduce the heat duty of vaporizer 1, recuperator 3 is present to recover some of the heat from the distillate. Recuperator 1 and recuperator 2 recover heat from the endothermic and exothermic reactor outlet respectively.

The MTH-CHP requires waste heat at four different temperatures as shown in Figure 1. Out of all the four, the heat input at the endothermic reactor will have the highest temperature since the methylcyclohexane dehydrogenation is only feasible above 150°C at atmospheric pressure. The temperature of the reboiler, vaporizer 1 and vaporizer 2 is determined by the bubble point of the mixture at those pressure conditions.

METHODOLOGY

Modelling and simulation

A steady state simulation model was created using the software Aspen Plus V14. The PRMHV2 (Peng–Robinson equations of state with modified Huron–Vidal mixing rules) property method is chosen since the model phase equilibrium predictions are in close agreement with the NIST experimental data [10], as shown in Figure 2. The flow sheet was solved using Equation Oriented (EO) mode. Convergence was achieved by first solving the flowsheet in sequential modular mode with one or more loops broken (a.k.a. manual tearing), such that the solver converges but there is a small error in the global mass and energy balances. Then the loops are closed programmatically using the connections feature in EO, and the previous inaccurate solution is used as an excellent initial guess. The final converged EO solution satisfies all mass and energy balances.

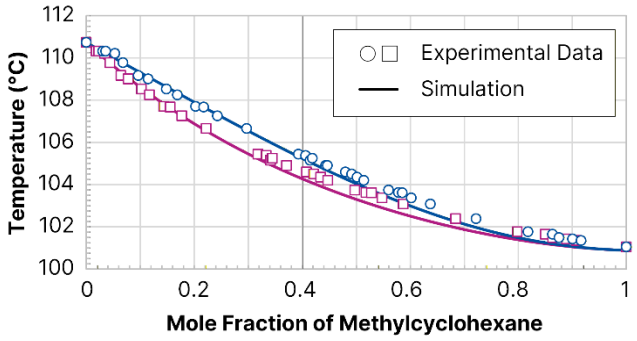

Figure 2. A comparison of the PRMHV2 vapor-liquid equilibria predictions for methylcylohexane and toluene vs. experimental data.

RADFRAC was chosen for modelling the distillation column in equilibrium made. The Design Spec feature in RADFRAC was used to meet the column top and bottom purity specs. The partial condenser temperature in RADFRAC was chosen as 35°C which maximized the separation between hydrogen and organics. The operating pressure of condenser is set as atmospheric. For both the endothermic and exothermic reactor, RGIBBS was used, which gives the maximum conversion possible since chemical equilibrium is assumed. The reactor assumes isothermal condition. 100% selectivity was assumed for both the reactors (in other words, we ignore potential side reactions not mentioned in this paper so as to achieve an optimistic performance bound). All the recuperators and vaporizers were modelled using HEATX and HEATER models respectively. The vapor fraction of vaporizer 1 is considered as 0.95 to reduce its heat duty, while the recuperator present in the downstream handles the remaining heat load. The approach temperature, defined as the temperature difference between hot inlet and cold outlet stream, is set to be 10°C for all the recuperators. The COMPR model was used for the compressor and the default isentropic efficiency of 0.72 was assumed. Pumps were modelled using PUMP with the default pump efficiency. Pumps and compressor are present to account for the pressure drops in the system. The pressure drop of the reactor, vaporizer, partial condenser and recuperators were assumed to be 0.1, 0.05, 0.05 and 0.025 bar respectively. A tray pressure drop of 0.005 bar per tray was considered [6].

For brevity, only the most relevant details are contained in this paper. The model has been released to the public as supplementary material (see link at end of article). Full details of the model and steam converged conditions of a representative case can be found there.

Performance analysis

The COP of MTH-CHP is calculated by the formula:

$$COP = \frac{Q_{exo}}{Q_{endo}+Q_{vap1}+Q_{vap2}+Q_r} \quad (2)$$

where Q_{exo} is the rate of high temperature heat produced from the exothermic reactor, Q_{endo} is the rate of the heat consumed in the endothermic reactor needed for the reaction and to raise the feed stream to reaction temperature, Q_r is the reboiler heat duty, Q_{vap1} is the heat duty of vaporizer 1 and Q_{vap2} is the heat duty of vaporizer 2 (all in kW).

To enable the comparison with mechanical heat pumps, the COP_w for a chemical heat pump is defined as follows:

$$COP_W = \frac{Q_{exo}}{W_{in}} \quad (3)$$

where $W_{in} = W_c + W_{p1} + W_{p2}$ and W_c, W_{p1}, W_{p2} is the power

of compressor, pump 1 and pump 2 in kW.

Optimization framework

The performance of MTH-CHP depends on many design parameters such as endothermic and exothermic reactor temperatures and distillation column parameters. Hence, multiparameter optimization is carried out to maximize the performance. The optimization problem is defined as follows:

$$\max_{d} COP$$

$f(x) = 0$ [all equations in Aspen Plus, & eq 2]

$g(x) \leq 0$ [all inequalities in Aspen Plus]

$L \leq d \leq U$ [all decision variable bounds]

The particle swarm optimization algorithm (PSO) was used for optimization using the method described in [7]. There are 6 total degrees of freedom. 4 degrees of freedom were taken as decision variables d described in Table 2. The remaining 2 degrees of freedom are the total number of stages in the distillation column (N_{stages}), and the ratio of the molar flow rate of hydrogen to toluene at the exothermic reactor inlet ($r_{H2/tol}$). These two were fixed or taken as parameters. The objective function is theoretically maximized at infinite N_{stages}, and so reasonable upper bounds much be chosen as described later. Although out of the scope of this work, they can be decision variables if the objective function were based on economic or other metrics that balance capital (N_{stages}) versus operating ($r_{H2/tol}$) tradeoffs.

Table 2 Decision variables considered for optimization.

d No	Description	Lower Bound	Upper Bound
1	Mole fraction of toluene in the partial condenser condensate stream	0.01	0.99
2	Mole fraction of methylcyclohexane in distillation bottom stream	0.01	0.99
3	Feed Tray Location of endothermic feed (tray 1 is partial condenser)	2	$N_{stages} - 1$
4	Feed Tray Location of exothermic feed (tray 1 is partial condenser)	2	$N_{stages} - 1$

The number of particles considered for all runs is 40. The maximum number of iterations is set as 100. Each case was run for at least twice to ensure that the result was consistent. The arbitrary upper and lower bounds for d_1 and d_2 were wide enough such that d_1 and d_2 at the optimum was never at a bound.

Table 3 COP variation with number of stages at T_{endo} = 200°C, T_{exo} = 250°C, $r_{H2/tol}$ =3

N_{stages}	d_3	d_4	COP
5	4	2	0.1176
8	5	3	0.1181
10	7	3	0.1183
15	8	4	0.1183
20	9	2	0.1183

Prior to solving the full optimization problem, N_{stages} was set to 10 based on a preliminary sensitivity study. In that preliminary study, N_{stages} was varied around a base case of a "very good" design candidate with T_{endo} = 200°C, T_{exo} = 250°C, d_1 = 0.43 and d_2 = 0.45. The values for d_1 and d_2 were chosen in accordance with our previous work for a different chemical heat pump system where "sloppy distillation" is optimal from efficiency point of view [7]. $r_{H2/tol}$ was set as 3, which is stoichiometrically balanced (eq. 1). Then, for each value of N_{stages} considered in the preliminary sensitivity study, the other two decision variables d_3 and d_4 were optimized using simple enumeration of the possible feed tray location combinations, to find the combination that yielded the maximum COP. It was found that the COP increased with N_{stages} up to 10 stages. $N_{stages} > 10$ did not improve the COP meaningfully. The results are populated in Table 3. N_{stages} is relatively small mainly because the vaporizer duty represents the largest quantity of heat load and reboiler duty is not the dominant term.

RESULTS AND DISCUSSION

The optimization problem described in the previous section was solved for different $r_{H2/tol}$ of 3, 6, 9 and 12 and for T_{endo} = 200°C, T_{exo} = 250°C. Performance was recorded in terms of COP and COP_W.

Table 4 Solutions to the maximize COP problem for each $r_{H2/tol}$ value taken as a parameter, with the corresponding COP_W shown.

$r_{H2/tol}$	COP	COP_W
3	0.1202	19.6
6	0.1341	16.7
9	0.1357	13.3
12	0.1357	10.4

Toluene hydrogenation which is the exothermic reaction is favored at higher $r_{H2/tol}$ and there is a COP increase initially. However, the COP does not increase

further when $r_{H2/tol}$ is above 9 because a major portion of the heat released from the exothermic reactor is used for heating the excess H_2 to exothermic reaction temperature. COP_W reduces with higher $r_{H2/tol}$ due to higher work requirement in compressor. Based on these results, $r_{H2/tol}$ is fixed at 9 for further runs.

Finally, T_{endo} and T_{exo} were varied and the maximized COP obtained by the optimization procedure described earlier and its corresponding COP_w is populated in Table 5. Increasing the T_{exo} for the same T_{endo} reduces COP because the heat liberation from the exothermic reactor (Q_{exo}) reduces at higher temperatures. The rate of methylcyclohexane dehydrogenation (Q_{endo}) increases with increase in endothermic reactor temperature and the rate of toluene hydrogenation decreases with increase in exothermic reactor temperature. This leads to more toluene and hydrogen in the system at higher endothermic and exothermic reactor temperatures. This causes increase in the compressor load and hence there is a drop in COP_W at higher reactor temperatures. For the same reason, the toluene concentration in the partial condenser condensate increases, while the methylcyclohexane concentration in the distillation bottom decreases as the reactor temperature increases (Table 6). Energy flows per unit of product heat produced are shown in Table 7 for a representative case.

T_{exo} of 300°C and above is not feasible for the MTH-CHP. This is because the sensible heat required to heat the feed inlet stream from 290°C to 300°C is more than the exothermic heat liberated at 300°C.

Table 5 Variation of maximized COP with T_{endo} and T_{exo}

T_{endo}, °C	T_{exo}, °C	COP	COP_W
175	225	0.0632	18.3
200	250	0.1357	13.3
200	275	0.0766	4.5
225	275	0.1614	4.8

Table 6: Decision variable values for the maximized COP case

T_{endo}, °C	T_{exo}, °C	d_1	d_2	d_3	d_4
175	225	0.2307	0.7371	6	7
200	250	0.3798	0.4729	5	2
200	275	0.7490	0.1285	8	2
225	275	0.7607	0.1277	9	4

Integration with vapor compression heat pump

The vaporizer 1 heat duty represents the majority of heat consumption as shown in Table 7. A design improvement of MTH-CHP could consist of including a conventional vapor compression heat pump. The function of a vapor compression heat pump is to take part of the partial condenser heat duty as its heat source and deliver heat at a higher temperature to vaporizer 1. Thus, this hybrid system not only reduces the hot utility demand of vaporizer 1, but also the cold utility demand of the partial condenser, although at the penalty of additional work/electricity requirements.

Table 7: Heat duties and electric power per unit of product heat delivered for T_{endo} = 200°C, T_{exo} = 250°C for the maximized COP case

Ratio	Value
Q_{vap1}/Q_{exo}	5.38
Q_{vap2}/Q_{exo}	0.38
Q_{endo}/Q_{exo}	1.36
Q_r/Q_{exo}	0.25
W_{in}/Q_{exo}	0.08

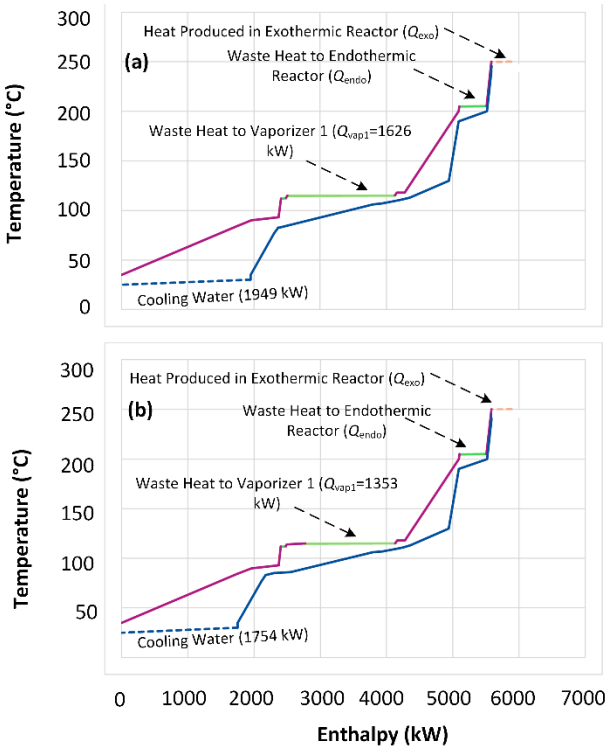

Figure 3. (a) Composite curve of MTH-CHP for T_{endo} = 200°C, T_{exo} = 250°C . (b) Composite curve of the hybrid heat pump design when 10% of the partial condenser heat duty is used as a heat source for the vapor compression heat pump. Both systems produce the same amount of exothermic heat, but the second system requires less waste heat consumption.

To look at the possibilities of mechanical heat pump integration, a composite curve was constructed for the MTH-CHP, using Aspen Energy analyzer. Figure 3a shows the composite curve of MTH-CHP without any heat integration for T_{endo} of 200°C and T_{exo} of 250°C. For this composite curve, a pinch temperature of 5°C was

chosen. Figure 3b shows what the composite curve would be if 10% of the partial condenser heat were upgraded and used for vaporizer 1 with a vapor compression heat pump, with a pinch temperature of 5°C. We assume a COP_w of 3.5 for the vapor compression heat pump where the heat source temperature is around 85°C and heat sink temperature is around 115°C [8]. This increases the high-quality heat product generated per unit waste heat consumed by about 14%. This was repeated for 5% and 25% of partial condenser duty upgrading, with results summarized in Table 8.

Table 8: Performance result of hybrid heat pump

Heat source of vapor compression heat pump	COP	% Increase	COP_W
25% of condenser duty	0.1955	44%	1.4
10% of condenser duty	0.1546	14%	3.0
5% of condenser duty	0.1445	6.5%	4.9

The COP presented in Table 8 reflects the result of heat integration already present as per Figure 1 as well as the contribution from the mechanical heat pump integration. The results show that this hybrid system allows the increase of COP at the cost of COP_w. Increasing the scale of the vapor compression heat pump to 5% -10% of the partial condenser duty would result in COP_w being in the same range as that of many mechanical heat pumps. Currently there is at least one mechanical heat pump at TRL 9 that can supply heat up to 280°C [9].

CONCLUSIONS

The performance of novel chemical heat pump based on methylcyclohexane, hydrogen, toluene was studied. The most promising results are obtained at T_{endo} of 200°C and T_{exo} of 250°C, where we achieve a COP of 0.136 and a COP_w of 13. Increasing the temperature lift beyond 50°C significantly reduces the COP for this chemical heat pump. Furthermore, a new configuration of hybrid system combining both chemical heat pump and mechanical vapor compression heat pump was studied. This configuration resulted in higher COP at reduced COP_w. Very few commercial heat pumps currently operate within this range, and future economic assessments will determine whether this MTH-CHP is commercially viable.

DIGITAL SUPPLEMENTARY MATERIAL

The aspen plus simulation file of the MTH-CHP is available in LAPSE at https://psecommunity.org/LAPSE:2026.0022.

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