# Catalyst-assisted chemical heat pump for upgrading low-quality heats

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## ABSTRACT

A chemical heat pump system has been proposed for upgrading waste heats of 90°C to 200°C with use of catalytic dehydrogenation of 2-propanol and acetone hydrogenation and also by using catalytic methanol decomposition and synthesis from 200°C to 250°C at the sacrifice of heat removal with the ambience for both reaction couples. In order to attain high thermal efficiencies, superheated liquid-film states were indispensable for the catalyst at the endothermic side. The Aspen plus process simulation to estimate the thermal efficiencies of this chemical heat pump was applied, from which dehydrogenation conversions and total pressures were elucidated to be very important as variable parameters.

## 1. Introduction

Some chemical reactions proceed reversibly, with endothermic and exothermic reaction heats accompanied. These magnitudes are actually the same irrespective of reaction temperatures, because both the standard enthalpy change ( $\Delta H^0$ ) and entropy change ($\Delta S^0$ ) of a certain chemical reaction are insensitive to temperatures, bringing us a linear correlation of the standard Gibbs energy change ( $\Delta G^0$ ) with temperature ( T ) [ Fig. 1 ].

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (1)$$

A mixture of some chemical substances with different boiling points is easy to separate into individual components by applying fractional distillation. It is to be noted that entropy decrease due to separation from the product mixture makes it possible to start the reaction again and, consequently, the endothermic reaction at low temperature and the exothermic reaction at high temperature proceed simultaneously and stationarily.

A chemical heat pump system was proposed with the constituents of an endothermic reactor afforded with low-quality heats, an exothermic reactor for recovering upgraded heats and

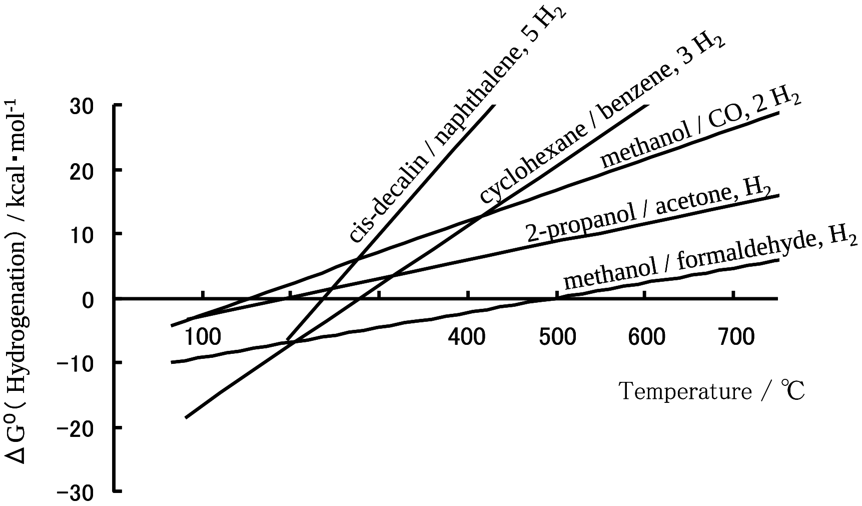


Fig. 1 Standard Gibbs energy change of hydrogenation / dehydrogenation couple as a function of temperature

a condenser operated at the ambient temperature [ Fig. 2 ] [1].

In this presentation, a coupled chemical heat pump with use of alcoholic substances is introduced, in which the waste heat at 90°C is upgraded to 250°C at the sacrifice of heat removal with ambience. All through these chemical processes, essentially-important technology relates with catalysis [2].

## 2. Constitution of catalyst-assisted chemical heat pump

A catalyst-assisted 2-propanol / acetone / hydrogen chemical heat pump system (CHP) was proposed for the first time in 1984, aiming at thermal improvements of waste heats in factories [1].

$(CH_3)_2CHOH$ (*liq*) → $(CH_3)_2CO$ (*gas*) + $H_2$  $\Delta H^0 = 100.4\ \mathrm{kJmol^{-1}}$ ( dehydrogenation )
$(CH_3)_2CO$ (*gas*) + $H_2$ → $(CH_3)_2CHOH$ (*gas*)  $\Delta H^0 = -45.4\ \mathrm{kJmol^{-1}}$ ( hydrogenation )
$(CH_3)_2CHOH$ (*gas*) → $(CH_3)_2CHOH$ (*liq*)  $\Delta H^0 = -55.0\ \mathrm{kJmol^{-1}}$ ( condensation )

On the other hand, methanol decomposition / synthesis chemical heat pump is designed for upgrading from 200° C to more valuable temperatures ( e. g., 250°C ) under pressurized conditions.

$CH_3OH$ (*liq*) → CO + 2 $H_2$  $\Delta H^0 = -128.9\ \mathrm{kJmol^{-1}}$(decomposition)
$CH_3OH$ (*gas*) → $CH_3OH$ (*liq*)  $\Delta H^0 = 35.3\ \mathrm{kJmol^{-1}}$(condensation)

$CO + 2\,H_2 \rightarrow CH_3OH$ (*liq*) $\Delta H^0 =$ 93.6 kJmol$^{-1}$(synthesis)

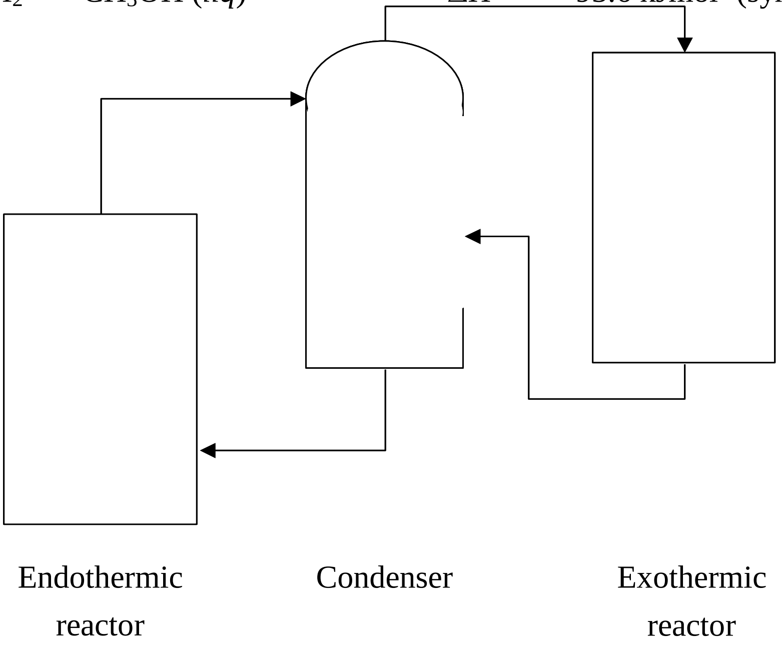


Fig. 2 Scheme of catalyst-assisted chemical heat pump system

Under boiling and refluxing conditions in a batch-wise reactor, catalytic dehydrogenation of 2-propanol (b.p. 82.4°C) or decomposition of methanol (b.p. 64.5°C) can proceed, until all of the liquid substrates are converted into the products owing to separation of gaseous components from the reaction medium. On the other hand, one-pass conversions of dehydrogenation or decomposition are essentially important a continuous-type reactor for attaining high thermal efficiencies in the chemical heat pump system.

The thermal efficiency $\eta$ is defined as ratio of the recovered heat $Q_H$ at high temperature $T_H$ devided by the supplied heat $Q_L$ at low temperature $T_L$.

$$\eta = Q_H / Q_L \qquad (2)$$

From the thermodynamical conservation laws on energy and entropy,

$$Q_L = Q_H + Q_C \qquad (3)$$

$$Q_L / T_L = Q_H / T_H + Q_C / T_C \qquad (4)$$

where the removed heat $Q_C$ at the cooling temperature $T_C$ is incorporated for separation. The maximum magnitude of thermal efficiencies is derived from the equations ( 2 ) ~ ( 4 ) as

$$\eta_{max} = ( 1 - T_C / T_L ) / ( 1 - T_C / T_H ) \qquad (5)$$

which is generally accepted for thermo-driven heat pump in the temperature-upgrading mode.

The low-quality thermal reservoirs or waste heats to be upgraded are devided into the reaction heat $Q_{react}$ and the evaporation heat $Q_{evap}$ inside the endothermic reactor.

$$Q_L = Q_{react} + Q_{evap} \qquad (6)$$

An actually-equal amount of heat is recovered at high temperature in the exothermic reactor as $Q_H$ owing to the temperature insensitivity of $\Delta H^0$.

$$Q_H = Q_{react} \qquad (7)$$

Therefore, the thermal efficiency in these chemical heat pump systems is determined substantically by efficient allotment to the reaction heat in the endothermic reactor within the framework of themodynamical limit.

$$\eta = Q_{react} / ( Q_{react} + Q_{evap} ) < \eta_{max} \qquad (8)$$

## 3. Importance of superheated liquid-film state for endothermic catalyst

Catalytic hydrogen evolution from 2-propanol, carried out in a batch-wise reactor under boiling and refluxing conditions, was found to be quite sensitive to concerning different amounts of substrate with a constant amount of a dehydrogenation catalyst the initial reaction rates and conversions. A sharp contrast of catalyst performance was pointed out between the suspended state and the liquid-film state, the latter of which was named for describing such a catalyst state that its surface was covered with a thin film of liquid substrate. The temperature of the catalyst in this case, just immersed or narrowly wetted, was higher than the boiling point of the liquid phase under the reaction conditions.

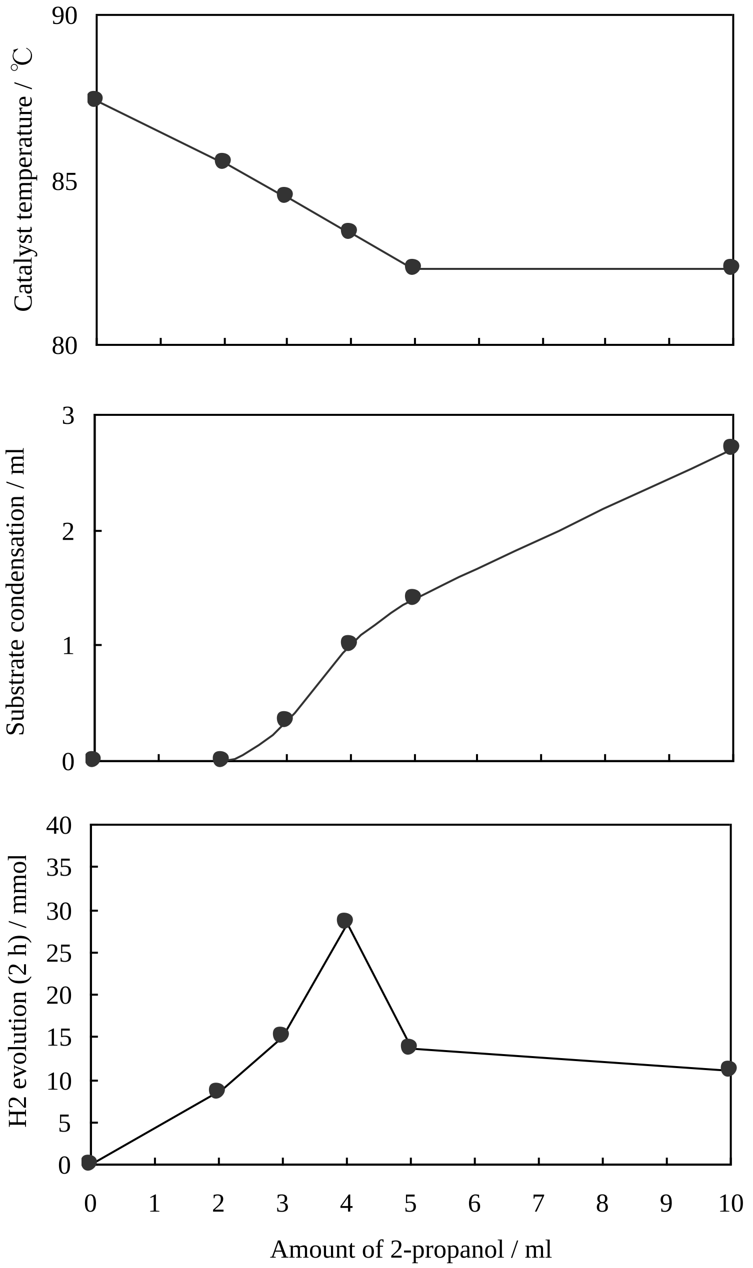
The catalyst layer, set at the superheated zone under boiling conditions, could behave advantageously in the gas-evolving reactions such as 2-propanol dehydrogenation or methanol decomposition. The temperatures of the catalyst layer, the initial rates of substrate condensation and the 2 h conversion of $H_2$ evolution from 2-propanol were plotted as a function of substrate amounts given at the start of catalytic dehydrogenation [Fig. 3]. The temperature of carbon granules as the catalyst support without the metallic component was plotted as a function of external heating temperatures in order to contrast the suspended and liquid-film states [Fig. 4]. At the region of temperatures higher than the boiling point, the suspension gave the same boiling temperature irrespective of the external heating temperatures. On the other hand, the catalyst layer in the liquid-film state was superheated at the extent corresponding to the temperature difference between inside and outside of the reactor wall.

A schematic contrast between the suspended and liquid-film states was depicted in addition to the sand-bath state [Fig. 5]. It was ascertained that the catalysts in these states obeyed the Langmuir-type rate equation well,

$$v = k / ( 1 + K \, [\text{product}] ) \qquad (9)$$

where the product in the substrate solution took the role of rate retardation [3]. Experimental results have revealed that the kinetic parameters of rate constant k and retardation constant K were quite different between the suspended and liquid-film states for the same catalyst and the same substrate; large k and small K were obtained with the superheated liquid-film state [4].

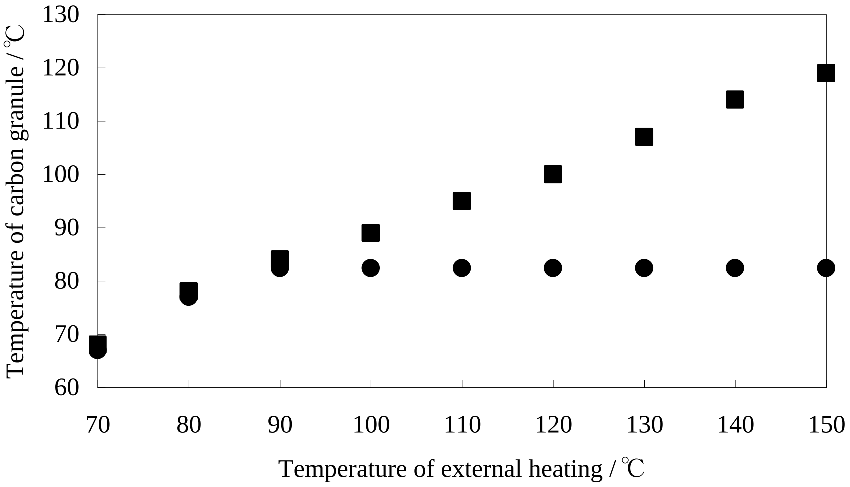
With regard to the endothermic catalysts, nanosize bimetallic particles supported on carbon granules were found to be quite effective [5].



● : Pt-Fe (10:1) / carbon catalyst (1.0 g)

Boiling and refluxing conditions by heating at 90°C and cooling at 5°C

Fig. 3 Rates of substrate evaporation and $H_2$ evolution together with temperature of carbon-supported catalyst as a function of 2-propanol amount



Carbon granule (800 mg) immersed with 2-propanol of
10 ml as suspension (●) and 4 ml as liquid-film state (■)

Fig. 4 Temperature of carbon support as a function of external temperature

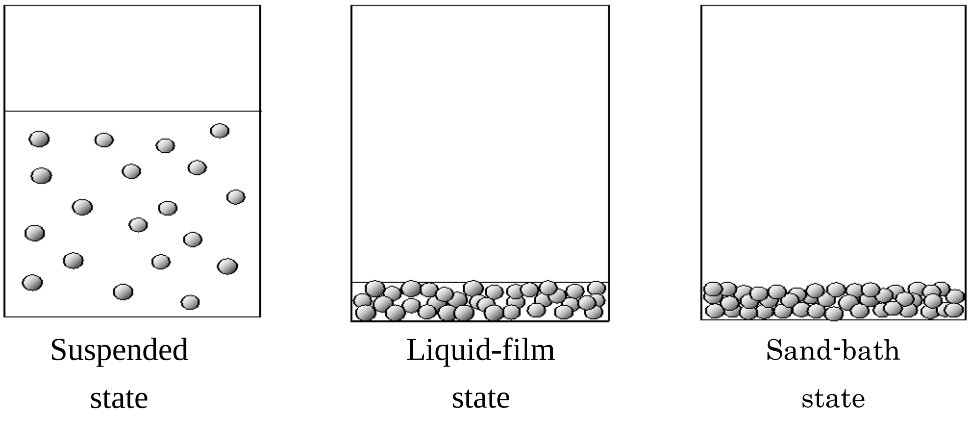


Fig. 5 State of carbon-supported metallic nano-particle catalyst varied with amount ratio of substrate to catalyst

The catalyst layer in the superheated liquid-film state will keep a certain extent of temperature gradient stationarily, the dynamics of which is important from the standpoint of the failure on local equilibrium concerning heat the flow from the active site on the catalyst surface to the boiling solution.

Under thermal equilibrium conditions, the Gibbs energy change $\Delta G$ is described as

$$\Delta G = \Delta H - T\Delta S \qquad (10)$$

Under thermally-unequilibrated conditions,

$$\Delta G^* = \Delta H - \Delta(S\,T) = \Delta H - T\Delta S - S\Delta T \qquad (11)$$

Under boiling conditions of $T_{ext} > T_{boil}$, we have

Table Continuous-type Catalytic Dehydrogenat°Cion of 2-Propanol under Boiling

| Catalyst* | Heating | liquid amount | $H_2$ evolution rate | evaporation | Conversion / % | |
|---|---|---|---|---|---|---|
| mg-metal | ˚C | ml | mmol / h | mmol / h | One-pass | equilibrium |
| 50 | 90 | 100 | 26 | 993 | 2.9 | 11.3 |
| 50 | 90 | 5 | 26 | 322 | 10.6 | 11.3 |
| 50 | 83 | 5 | 20 | 97 | 20.9 | 9.47 |

*Carbon-supported Pt-Ru composite catalyst (1:1, 5 wt%), prepared by impregnation 1.0 g

$$\Delta G - \Delta G^* = S\Delta T > 0 \qquad (12)$$

Consequently, endothermic catalysts in the superheated liquid-film states are able to proceed the reaction beyond chemical equilibrium at a moderate temperature range. This is an example of heat-and-mass-transfer coupling in the irreversible thermodynamics [6].

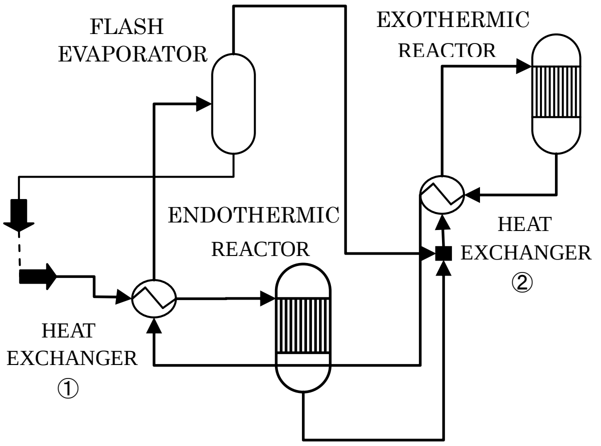
Catalytic 2-propanol dehydrogenation in a continuous-type reactor, proceeded with two kinds of substrate amounts corresponding to the suspended and liquid-film states and different external heating temperatures over the same amount of common catalyst, revealed that ( 1 ) decrement of liquid substrate was effective to reduce the evaporation rate, ( 2 ) decrement of external heating temperature was also effective to reduce the evaporation rate, and ( 3 ) the liquid-film conditions at a modest heating temperature brought us the chemical surpass over equilibrium conversion calculated from the heating temperature and 1 atm conditions [ Table ].

Another example of equilibrium surpass was encountered for the case of catalytic decalin dehydrogeno-aromatization [7].

## 4. Catalyst-assisted chemical heat pump system

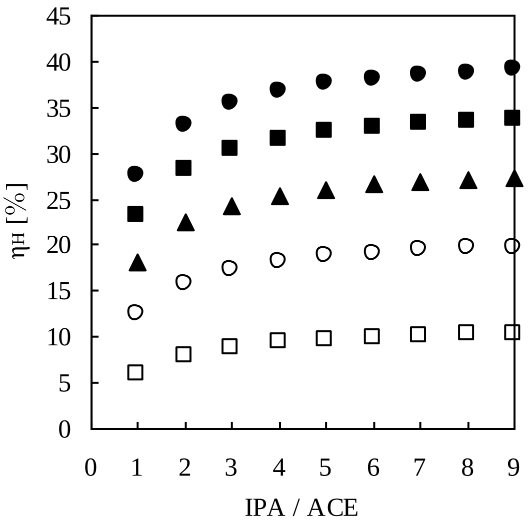
In order to upgrade the low-quality heats at ca. 90°C upto ca.200°C, 2-propanol / acetone / hydrogen chemical heat pump system is proper to be utilized [1]. The system thermal efficiency for obtaining 200°C from 90°C with the heat sink at 25°C was examined with Aspen Plus process simulation [ Fig. 6, 7 ]. Apparently, the role of endothermic one-pass conversions was decisive, suggesting the potential importance of superheated liquid-film state of dehydrogenation catalysts. Methanol decomposition / synthesis chemical heat pump [4] is suited for upgrading from ca. 200°C to ca. 250°C. The selection or combination of these two systems would enlarge the possibility of utilization of waste heats.

Cascade-type utilization of thermal energy along with the level down of temperatures is an important approach to energy-saving technology. Chemical heat pump in the temperature-upgrading mode will play a certain helpful role to save waste heats again. For this purpose, how-to-prepare and how-to-use the endothermic catalysts are essentially important.



$T_H$ = 200°C, $T_L$=90°C, $T_C$ = 25°C

Fig. 6 2-Propanol / acetone / hydrogen chemical heat pump system examined with process simulation



Dehydrogenation conversion : 10%(ڤ), 20%(○), 30%(▲), 40%(■), 50%(●)

Fig. 7 System thermal efficiency as a function of dehydrogenation conversion

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