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Review

Advances in Organic Liquid-Gas Chemical Heat Pumps

Compared with inorganic chemical heat pumps (CHPs), organic liquid-gas CHPs are more amenable to be run as a continuous process because the reactants and products can be fed or removed continuously. Therefore, increasing attention has been paid to investigations of CHPs using the organic liquid-gas reaction system. Relevant research topics involved reaction catalyst, chemical reaction kinetics, reactive distillation, energy efficiency evaluation, economic analysis, etc. Nevertheless, the research on an organic liquid-gas CHP system is still in the elementary stage. A detailed review on the current research status of catalyst-assisted CHPs employing an organic liquid-gas reaction system has been performed. Existing problems are identified and future research directions are proposed.

Keywords: Catalytic reaction, Chemical heat pump, Heat recovery, Liquid-gas reaction, Organic reaction system

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1 Introduction

A chemical heat pump (CHP) is a type of device that utilizes the endothermic and exothermic behaviors of reversible chemical reactions to upgrade the temperature level of thermal energy stored in chemical substances [1]. It can not only improve the quality of heat, but also realize heat storage [2]. The chemical reaction system plays an important role in absorbing and releasing the thermal energy [3]. The advantages of high energy storage capacity, long storage time, and low heat losses suggest that CHPs are a strong candidate for energy upgrading of intermittent low-grade heat as well as energy storage. The heat sources driving a CHP could be industrial waste heat, heat of combustion of municipal waste, subterranean heat, solar energy obtained from a collector, and other middle-low temperature heat sources.

The general chemical reaction taking place in a CHP reactor is of the form:

$$A \rightleftarrows B + C \tag{1}$$

Here, the forward and backward reactions occur at two different temperatures, thus causing the upgrading of low-temperature waste heat to a higher temperature. The upgraded heat can be used for heat supply, cooling, dehumidification, power generation, and any other suitable application. The concept of a CHP with a general reversible reaction is illustrated in Fig. 1. For the forward endothermic reaction ($A \rightarrow B + C$), the thermal energy can be supplied to the endothermic reactor from a low-temperature heat source (e.g., waste heat), whilst the backward exothermic reaction ($B + C \rightarrow A$) occurs in the exothermic reactor and releases thermal energy to the sink at high temperature. The alternation of the forward and backward reactions makes the processes proceed continuously.

A variety of chemicals can be used in CHPs for generating chemical reactions. They can be categorized according to different criteria such as inorganic/organic and solid-gas/liquid-gas. A detailed introduction on the chemical substances used in CHPs is reported in [5]. Inorganic CHPs are those systems that normally operate with batch processes involving solid-gas

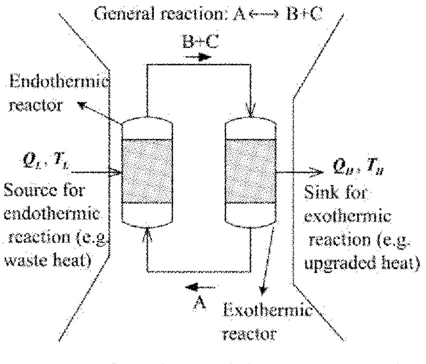

Figure 1. Concept of a chemical heat pump with a general reversible reaction [4].

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or solid-liquid reactions. An organic reaction system contains hydrocarbon and hydrocarbon derivates, e.g., isopropanol/acetone, *tert*-butanol/isobutene, cyclohexane/benzene, and paraldehyde/acetaldehyde (Pa/A) systems. Solid-gas CHPs normally employ an inorganic reaction system and comprise reactor (or adsorber), condenser, and evaporator, while liquid-gas CHPs generally employ an organic reaction system and include at least two reactors (endothermic and exothermic) and other components like condenser, separator, and heat exchanger [6]. In a CHP system, the reactors where the heat and mass transfer, chemical reaction, absorption, and desorption take place, are the most critical components.

Since solid-gas CHPs are based on two successive steps, namely, synthesis and decomposition, they are not suitable for continuous operation. In addition, due to the limitation of the thermal conductivity of the reaction substance and the thermal contact resistance between the reaction substance and reactor, solid-gas CHPs have such disadvantages as slow chemical reaction rate, long reaction time, high heat loss, and low coefficient of performance (COP). For organic liquid-gas CHPs, the reactants and products can be fed or removed continuously due to the liquid-gas reaction. Therefore, an organic liquid-gas reaction system is more amenable to be run as a continuous process. In addition to the continuous operation, organic CHPs have many other advantages, such as high energy density, excellent heat transfer performance, wide temperature range, and relatively low endothermic reaction temperature. Herein, organic CHPs have been extensively studied by many researchers considering the following aspects: reaction catalyst, chemical reaction kinetics, reactive distillation, energy efficiency evaluation, economic analysis, and other related contents.

In 2001, Wongsuwan et al. [5] gave a broad overview and classification for the different types of CHPs and their applications. In their review, the main statements were placed on the inorganic CHPs, and there were few contents concerning with the organic liquid-gas CHP systems. In recent years, great progress has been made with the organic liquid-gas CHPs. The objective of this review is to introduce the current research status of catalyst-assisted chemical heat pumps employing an organic liquid-gas reaction system. On this basis, the existing problems for the organic CHPs are discussed and the future research directions are further pointed out.

2 Principle of Organic Liquid-Gas CHPs

The organic CHPs with various liquid-gas reaction systems have a similar process flow and comprise such essential constituents as endothermic reactor, reboiler, distillation column, condenser, heat exchanger, and exothermic reactor. There are two different ways for these constituents to be connected to conceptually upgrade the temperature level, i.e., the continuous type and storage type [7].

2.1 Continuous Type

The flow diagram of a continuous-type organic liquid-gas CHP system is presented in Fig. 2. The liquid-phase reaction occurs at low temperature (T_L) in the endothermic reactor. The mixture of reactant and product outflows from the endothermic reactor and is fed into the distillation column where the liquid-phase reactant (e.g., isopropanol) is separated from the gas-phase products (e.g., acetone and hydrogen) as a bottom product. Then the liquid-phase reactant is fed back into the endothermic reactor again. After passing through the heat exchanger, the gas-phase products are fed into the exothermic reactor where they are recombined to the gas-phase reactant at high temperature (T_H), and the released reaction heat is recovered for any possible application. After preheating the feed for the exothermic reactor through the heat exchanger, the gas-phase mixture from the exothermic reactor is separated in the distillation column for the continuous cyclic operation. A part of the absorbed waste-heat is used as a heat source for the endothermic reaction and the remaining as a driving force for the distillation process. The thermal energy added to the distillation column is utilized to separate the reaction mixture and finally dissipates to the environment through the condenser. The separation work serves as a driving force for the organic liquid-gas CHP [8].

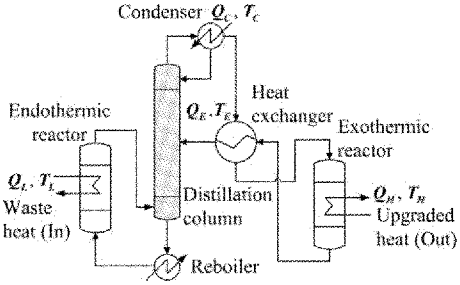

Figure 2. Flow diagram of a continuous-type organic liquid-gas CHP system [8].

In a closed-loop system, the relationship between temperature and pressure at the equilibrium state can be described by the Clausium-Clapeyron equation [9, 10]:

$$\ln(P_{\mathrm{eq}}) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{2}$$

Here, P_{eq} is the pressure at the equilibrium state, ΔH is the change of enthalpy, ΔS is the change of entropy, and R is the perfect gas constant. By means of Eq. (2), the working status of the gas medium in a CHP cycle system can be plotted in a Clapeyron diagram. For a continuous-type organic liquid-gas CHP, its Clapeyron diagram is illustrated in Fig. 3. At a gas pressure equaling to the pressure in the condenser (point 2), the endothermic decomposition reaction of an organic compound (e.g., isopropanol) occurs at low temperature T_L and absorbs the low-temperature heat Q_L (point 1). At a pressure equaling to the pressure in the heat exchanger (point 3), the organic compound is regenerated at high temperature T_H, and the upgraded heat Q_H (point 4) is released. The work cycle runs in the 1-2-3-4-1 order continuously. Based on the Clapeyron diagram, a thermodynamic analysis of an organic CHP can be conducted for system design.

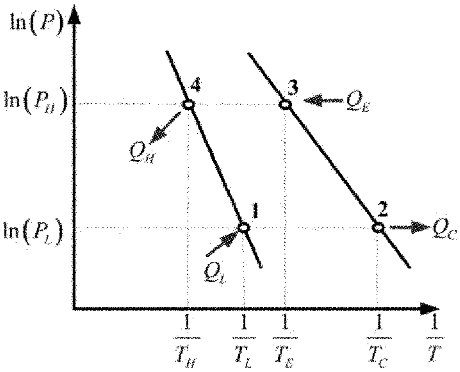

Figure 3. Clapeyron diagram of a continuous-type organic liquid-gas CHP.

2.2 Storage Type

Fig. 4 represents the flow diagram of a storage-type CHP employing an isopropanol/acetone/hydrogen reaction system. The gas-phase overhead products in the distillation column are introduced from the condenser to the hydrogen-storing metal at T_C. Hydrogen at atmospheric pressure is stored in the metal hydride reactor with hydriding heat removed at T_C, and heat is regenerated at high pressure by heating the metal hydride at T_L. After mixing with the condensate in separator-1, the pressurized hydrogen is then fed into the exothermic reactor via the heat exchanger, where hydrogenation heat is produced at the high temperature of T_H. After preheating the feed for the exothermic reactor, the reaction mixture from the exothermic reactor enters into separator-2. The separated liquid-phase components are then fed into the distillation column through the valve and eventually flow back into the endothermic reactor where the liquid-phase isopropanol is dehydrogenated at T_L.

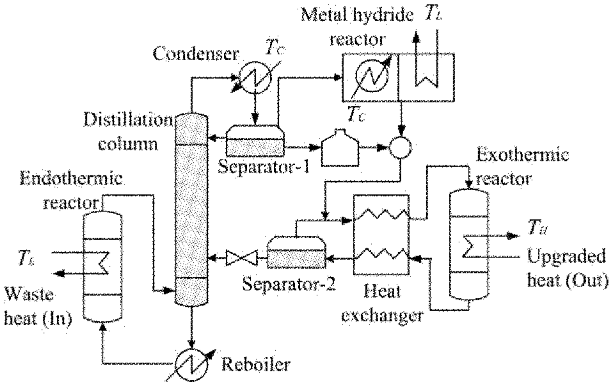

Figure 4. Flow diagram of a storage-type organic liquid-gas CHP system [7].

3 Research Overview on Organic Liquid-Gas CHPs

3.1 Organic Reaction System

To utilize low-temperature waste heat effectively, a key is to choose a suitable reaction system fitting to the temperature level of the used heat source. As a long-term running closed-loop system, an organic CHP has a very strict requirement for the reaction system [11]. The following conditions should be satisfied [12, 13]:

- The reaction process has a good reversibility.
- To obtain the maximum reaction heat, the reaction system has a very high conversion and selectivity for the main chemical reaction.
- The reactant must be separated from the products easily.
- There are few types of substances involved in the reaction.

From the published literature, the main investigations on the organic reaction system in CHPs were focused on the isopropanol/acetone/hydrogen system, the *tert*-butyl alcohol/isobutylene/water system, the cyclohexane/benzene/hydrogen system, and the paraldehyde/acetaldehyde (Pa/A) system. The details of these organic reaction systems and their reaction characteristics are summarized in Tab. 1.

Based on the fact that the reaction system can absorb huge amounts of reaction heat at a relatively low temperature and has fewer hazards than other reaction systems [15], the isopropanol/acetone/hydrogen CHP has been extensively studied, being a promising representative CHP type [4, 7, 8, 15, 22–27]. The endothermic dehydrogenation reaction of liquid isopropanol at about 353 K and 0.1 MPa proceeds with proper catalysts (e.g., Ru/C, Ru-Pt/C, Ru-Pd/C, Raney nickel, etc.) [15, 28–30], as indicated in Eq. (3). The gaseous reaction products (acetone and hydrogen) can be continuously removed from the reaction media. With the aid of other catalysts (e.g., Ni-Cu/alumina, Raney nickel) at 473 K and 0.1 MPa [15, 31], the exothermic hydrogenation reaction of gas-phase acetone into isopropanol is carried out in packed-bed reactors (see Eq. (4)). To finish the CHP cycle, the condensation separation of gas-phase isopropanol from the gaseous mixture has to be fulfilled (see Eq. (5)).

$$\begin{aligned}&(CH_3)_2CHOH(l)\rightarrow(CH_3)_2CO(g)+H_2(g),\\&\Delta H = 100.4\,\mathrm{kJ\,mol^{-1}}\end{aligned} \tag{3}$$

$$\begin{aligned}&(CH_3)_2CO(g)+H_2(g)\rightarrow(CH_3)_2CHOH(g),\\&\Delta H_1 = -55.0\,\mathrm{kJ\,mol^{-1}}\end{aligned} \tag{4}$$

$$\begin{aligned}&(CH_3)_2CHOH(g)\rightarrow(CH_3)_2CHOH(l),\\&\Delta H_2 = -45.4\,\mathrm{kJ\,mol^{-1}}\end{aligned} \tag{5}$$

For the *tert*-butanol/isobutene/water system, the reversible chemical reactions are indicated in Eqs. (6)–(8). The dehydration of *tert*-butanol (tBA) and hydration of isobutene (iB) proceed reversibly through the use of an acid solid catalyst [18].

Table 1. Organic reaction systems and their characteristics [1, 14–21].

Organic reaction system	Endothermic reaction		Exothermic reaction		Reaction heat [kJ mol^{-1}]
	Temperature [K]	Pressure [MPa]	Temperature [K]	Pressure [MPa]	
Isopropanol/acetone/ hydrogen	~353	0.1	~473	0.1	100.4
tert-Butanol/isobutene/ water	~343	0.15	~383	1.34	56.6
Cyclohexane/benzene/ hydrogen	~473	0.1	~623	1.96	207
Paraldehyde/ acetaldehyde	~286	0.1	~313	0.075	189.5
Hemiacetal/ acetaldehyde/alcohol	~343	0.1	~293	0.1	–

The feasibility of this type of CHP was examined experimentally, and the possibility of using the CHP to upgrade heat from around 50–80 °C to 90–120 °C was also demonstrated [16]. Nevertheless, because water generated in the dehydration process of tBA is easily absorbed by the catalyst, the reaction is significantly inhibited, which results in a relative low conversion. From Tab. 1 it can be seen that the exothermic reaction pressure (1.34 MPa) for a *tert*-butanol/isobutene/water system is much higher than that for an isopropanol/acetone/hydrogen system (0.1 MPa), i.e., the exothermic reaction conditions are more rigorous in the *tert*-butanol/isobutene/water system. In addition, the reaction heat of the former is also less than that of the latter.

$$(CH_3)_3COH(l) \rightarrow (CH_3)_2CCH_2(l) + H_2O(l),\quad \Delta H = 56.6\,\mathrm{kJ\,mol^{-1}} \tag{6}$$

$$(CH_3)_2CCH_2(l) + H_2O(l) \rightarrow (CH_3)_3COH(l),\quad \Delta H_1 = -38.0\,\mathrm{kJ\,mol^{-1}} \tag{7}$$

$$(CH_3)_2CCH_2(g) \rightarrow (CH_3)_2CCH_2(l),\quad \Delta H_2 = -18.6\,\mathrm{kJ\,mol^{-1}} \tag{8}$$

According to the numerical estimations [21, 32–34], the organic CHP based on the benzene-hydrogenation/cyclohexane-dehydrogenation reversible reaction (see Eq. (9)) is very promising for the temperature range of 423–523 K. For a CHP employing such a reaction system, large reaction heat and high temperature upgrading are its main advantages. However, the benzene-hydrogenation exothermic reaction pressure (1.96 MPa) must be much higher than the cyclohexane-dehydrogenation endothermic reaction pressure (0.1 MPa), so as to achieve the heat-pump effect. Therefore, the exothermic reaction conditions are harsher in the benzene-hydrogenation reaction system than in the isopropanol/acetone/hydrogen reaction system.

$$C_6H_{12} \rightleftarrows C_6H_6 + 3H_2,\ \Delta H = 207\ \mathrm{kJ\ mol^{-1}} \tag{9}$$

The paraldehyde (Pa)/acetaldehyde (A) reaction system can be used in an organic CHP for cooling purpose [1]. The chemical reaction equations of depolymerization and vaporization are indicated in Eqs. (10) and (11). One mole liquid paraldehyde (2,4,6-trimethyltrioxane) is depolymerized into three moles gaseous acetaldehyde with an acid catalyst [35, 36]. The depolymerization reaction is endothermic (189.5 kJ as the sum of reaction heat and vaporization heat) and reversible and can be promoted by the vaporization of acetaldehyde (endothermic). In spite of the strong reaction heat, this type of organic CHPs can only upgrade the temperature level from 286 K to 313 K. In addition to the Pa/A reaction system, an acetal hydrolysis reaction can also be employed for a cooling system. An investigation of the acetal hydrolysis system for cooling was conducted by Watanabe et al. [37].

$$C_6H_{12}O_3(l) \rightleftarrows 3CH_3CHO(l),\ \Delta H_{298K} = 110.3\ \mathrm{kJ\ mol^{-1}} \tag{10}$$

$$CH_3CHO(l) \rightleftarrows CH_3CHO(g),\ \Delta H_{298K} = 26.4\ \mathrm{kJ\ mol^{-1}} \tag{11}$$

The reaction between alcohol and aldehyde is exothermic and reversible. Hemiacetal as reaction product only exists in the liquid state. If an acid appears in the mixture, it can become a catalyst for a further reaction producing an acetal. The acetal-producing reaction is irreversible and cannot be adopted in a cycle. Unless acid exists in the system, hemiacetal is the final reaction product. Tanisho et al. [14] measured the temperature rise due to the alcohol-aldehyde reaction and found that the highest temperature rise was obtained with a methyl alcohol-acetaldehyde reaction system (see Eq. (12)).

$$CH_3OH + CH_3CHO \rightleftarrows C_3H_8O_2 \tag{12}$$

As an exothermic reaction, the equilibrium constant or conversion of the alcohol-aldehyde reaction is high at low temperature and rapidly decreases with increasing temperature. A large temperature rise (50 K) can be achieved when the liquid reactants are at a low temperature. Based on the reaction, a heat transport and upgrading system was proposed by Tanisho et al. [14], as illustrated in Fig. 5.

Fig. 5a) outlines a heat transport system consisting of a distillation column and a reactor, where the methyl alcohol-acetaldehyde reaction takes place. By absorbing the waste heat, acetaldehyde and methyl alcohol are separated in the distillation column due to their different boiling points and then remixed in the exothermic reactor at 293 K. The liquid-phase reaction product is heated by the released heat to 343 K and then transported to a consumer center. Fig. 5b) displays a double-distillation column heat transport system. Based on the vapor-liquid equilibrium data of the methyl alcohol-acetalde-

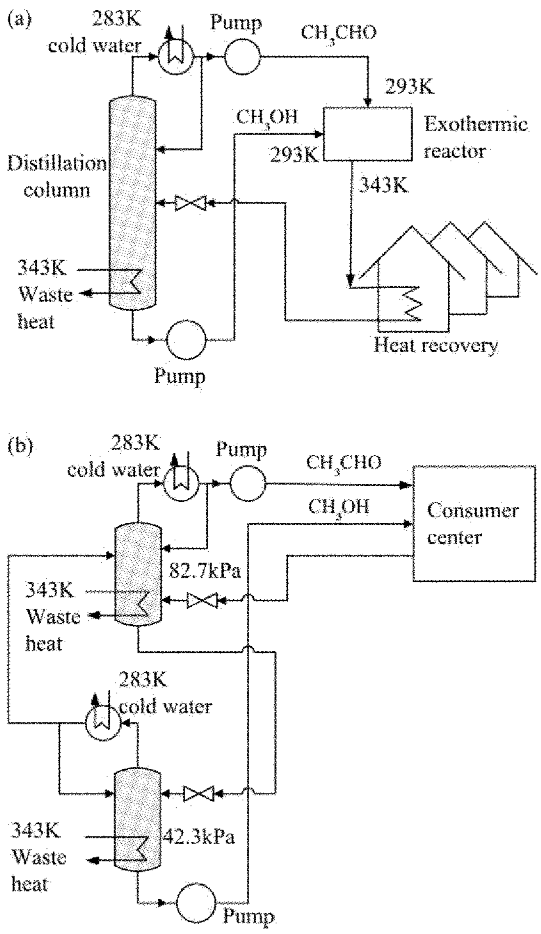

Figure 5. Heat transport and upgrading system employing the methyl alcohol-acetaldehyde system. (a) With a distillation column operated with 343 K waste heat and 283 K cold water; (b) with split-type distillation column operated with 333 K waste heat and 283 K cold water.

hyde reaction, this type of distillation separation is to use the right half of the 82.7 kPa equilibrium curves in one column for CH_3CHO and the left half of the 43.3 kPa curves in the other column for CH_3OH.

3.2 Organic Catalytic Reaction

Up to now, many investigations on a suitable catalyst have been conducted for both endothermic and exothermic organic chemical reactions. In the sixties of the last century, Memas et al. [28, 30] examined the dehydrogenation activity of a nickel catalyst prepared by sodium borohydride reduction for isopropanol. With Raney nickel as a catalyst, Kim et al. [15] studied the liquid-phase endothermic dehydrogenation of *i*-propanol occurring at 353 K and the gas-phase exothermic hydrogenation reaction of acetone taking place at 473 K and 1 atm. The maximum hydrogenation of acetone was obtained when the mole ratio of acetone to hydrogen was 4.0. In addition, they found that the acetone concentration controlled the reaction rate in the dehydrogenation reaction. The rate equation was defined as:

$$V = 0.1C_P(1 + 7.0C_A) \qquad (13)$$

where C_P and C_A are the concentrations of *i*-propanol and acetone, respectively.

In a kinetic study, Ali and Zaera [38] obtained the kinetic data for the selective oxidation of 2-propanol over oxygen-pretreated nickel foils by using a microbatch reactor with mass spectrometry detection. By studying the high-temperature acetone hydrogenation at atmospheric pressure over alumina and titania-supported nickel and cobalt catalysts, Gandia and Montes [39] found that 2-propanol and methyl isobutyl ketone (MIBK) were the main reaction products. The MIBK selectivity of the alumina-supported catalysts decreased with increasing the reduced temperature. KlinSoda et al. [25] investigated all major components (endothermic reactor, exothermic reactor, and distillation column) individually in organic CHP systems. Raney nickel as a catalyst was packed in both the endothermic and exothermic reactors. Maximum conversions of 8.32 % and 13.02 % for the endothermic and exothermic reactions, respectively, were achieved (18 % for the equilibrium conversion [24]). On the basis of the component research, a demonstration unit of an isopropanol-acetone-hydrogen organic CHP system was presented. This organic CHP system can reach a steady state within 1 h, and the conversions in the endothermic and exothermic reactors were around 8.5 % and 11.6 %, respectively. The temperature was raised from 353 K to 409 K. The thermodynamic efficiency for such a CHP system was about 27 %, and the heat conversion was 38 %.

With a composite Ru-Pt/carbon catalyst, Ito et al. [40] observed the synergetic promotion in an experiment of 2-propanol dehydrogenation. The composite Ru-Pt catalyst and its surface modification with $Pt(acac)_2$ or $Pd(acac)_2$ exhibited an activity enhancement [41]. With Ru-Pd/C as a catalyst, Gaspillo et al. [23] measured the reaction rate of gas-phase isopropanol in a fixed-bed reactor and found that the conversion was limited to 10.8 % at 363 K due to the equilibrium. Subsequently, Doi et al. [42] further studied the dehydrogenation reaction of isopropanol when using carbon-supported Ru-Pd as a catalyst. By conducting the dehydrogenation reaction of 2-propanol with Ru or Ru-Pt catalyst, Meng et al. [43] found that the thermal efficiency of an isopropanol-acetone-hydrogen CHP could be greatly improved. A high value was attained for both the fraction of heat used for the endothermic reaction (25.6 %) and the exergy efficiency (58.6 %). Mooksuwan and Kumar [4] experimentally determined the performance of dehydrogenation of 2-propanol using a suspended catalyst (10 wt-% Ru-Pt/activated C) in the temperature range of 333–353 K. The maximum initial reaction rate of 54 mmol $h^{-1}g^{-1}$ was obtained in the reaction temperature range of 348–353 K with 400 mg catalyst suspended in 300 mL 2-propanol. Among Ru-Pt/C, Ru-Pd/C, Ru/C catalysts, Taneda et al. [44] found that Ru-Pd/C had an excellent activity and selectivity in liquid-phase dehydrogenation and produced the least amount of by-product as compared with Ru-Pt/C and Ru/C.

Riousx and Vannice [45] carried out an experimental investigation on vapor-phase isopropyl alcohol (IPA) dehydrogenation in a differential fixed-bed reactor over carbon-supported Cu, UHP Cu powder, and Cu chromite catalysts. The results indicated that Cu had a low dispersion (ca. 0.02–0.17) on an activated carbon for all these catalysts. Subsequently, Riousx and Vannice [46] further examined the kinetics of isopropyl alcohol dehydrogenation over carbon-supported Pt and three bimetallic Cu–Pt catalysts and compared their results with previous results for carbon-supported Cu. The research revealed that Pt was more active than Cu and all catalysts were 100 % selective to acetone. Bimetallic Cu-Pt catalysts were less active than their monometallic counterparts, but exhibited a kinetic behavior similar to that of the monometallic catalysts. The possible suitability of various metal oxide-supported (e.g., Cu/Al_2O_3, Cu/Cr_2O_3, Cu/SiO_2, and Cu/TiO_2) Cu catalysts for isopropanol dehydrogenation and acetone hydrogenation has also been investigated by Cunningham et al. [27]. For acetone hydrogenation over Cu/Al_2O_3 and Cu/SiO_2, the temperature range extended over 423–550 K. However, it was restricted to 423–473 K over Cu/Cr_2O_3 and Cu/TiO_2. Similar temperature ranges were found to be necessary for obtaining the adequate activity and selectivity for dehydrogenation of isopropanol vapor over oxide-supported Cu catalysts. In 2010, Rahman [47] has presented an excellent review on acetone hydrogenation under different conditions with various homogeneous and heterogeneous catalysts, and some new strategies to develop economic and environmentally benign approaches for acetone hydrogenation were also proposed.

For the dehydration reaction of *tert*-butyl alcohol, catalysts such as ion-exchange resin, solid acid, and Amberlyst-15 can be applied [19, 48–51]. Honkela et al. [50] studied the dehydration of *tert*-butyl alcohol to isobutylene by using an ion-exchange resin catalyst in the temperature range of 333–363 K and obtained a temperature-dependent equilibrium constant for the dehydration reaction. In addition, they found that the best model with physically meaningful parameters was of the Langmuir-Hinshelwood type in which isobutene does not adsorb on the catalyst. The experiment of the *tert*-butanol dehydration conducted by Knifton et al. [51] indicated that such solid acids, e.g., zeolite β, hydrogen-fluoride-treated β-zeolites, and HF-treated montmorillonite clays could be used as catalysts for the *tert*-butanol/isobutylene/water reaction system.

As mentioned above, the catalyst plays an important role in both endothermic and exothermic organic chemical reactions for improving the reaction conversion. An ideal catalyst is expected to have such characteristics as high activity at low temperature, excellent diffusibility in liquids, and durability. Possible catalysts for various organic liquid-gas reaction systems are summarized in Tab. 2.

Table 2. Possible catalysts for various organic liquid-gas reaction systems.

Catalyst	Application
Ru/C; Cu /C; Ru-Pt/C; Cu-Pt/C; Ru-Pd/C; Raney nickel; Cu/metal oxide (e.g., Cu/Al_2O_3, Cu/Cr_2O_3, Cu/SiO_2 and Cu/TiO_2)	Dehydrogenation of isopropanol and hydrogenation of acetone [4, 15, 23, 25, 27, 28, 40, 42, 45, 46, 52]
Pt/Al_2O_3	Dehydrogenation of cyclohexane to benzene
Amberlyst-15; ion exchange resins	Dehydration of *tert*-butanol [19, 48–50]
Solid acid	Depolymerization of paraldehyde [36], dehydration of *tert*-butanol [51]

3.3 Reactive Distillation

As described in Eqs. (3) and (4), the dehydrogenation of isopropanol is reversible and strongly limited by the equilibrium (0.108 at 363 K). On the other hand, in the liquid phase, the produced acetone is a strong inhibitor due to its adsorption on the catalyst. Thus, the conversion of reaction is very low. To solve these problems, Gastauer et al. [53] proposed a particular design for the vapor-phase dehydrogenation reactor similar to the liquid-phase reactor. In their proposal, the internal structure of the distillation column is very complicated. In addition, the operation has a very strict requirement for the pressure balance in the system. Later, Gaspillo et al. [23] proposed a simpler design by using a reactive distillation column and found that the separation of acetone and 2-propanol was substantially influenced by the feed flow rate, temperature of the heat source, and reflux ratio. The conversion and the molar fraction of acetone in the column could reach 100 % for the selected conditions (less than $0.04\,mmol\,s^{-1}$ feed flow rate in their work), and the reaction rate is independent of the mole fraction of acetone in the feed. At the same time, Doi et al. [42] studied the dehydrogenation reaction distillation process of isopropanol in a solar organic CHP, including the effect of heat supplied, reflux ratio, and stirrer speed on the distillate flow.

Based on the fact that the reactive distillation can facilitate a complete conversion of the reaction by overcoming the limitation of equilibrium and strong inhibition in the liquid phase, it can also be applied to the *tert*-butanol/isobutene/water reaction system. By using the reactive distillation technology, a complete tBA conversion of more than 99 % has been achieved in the temperature range of 323–393 K [51]. Abella et al. [48] conducted an experiment on dehydration of *tert*-butanol in a reactive distillation column. They found that the use of the reactive distillation could facilitate a complete conversion of the *tert*-butanol dehydration by avoiding the strong inhibition of water. The conclusion was restated by Zhao et al. [19] through their experimental investigation and theoretical simulation. Due to the importance of reactive distillation in an organic CHP, more and more attention has been paid to the reactive distillation process of *tert*-butanol, including rectifying process analysis, thermodynamic and kinetic analysis, experimental investigation, modeling, and simulation [50, 51, 54–57].

3.4 System Design and Evaluation of Performance and Economy

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), coefficient of amplification (COA), and exergy efficiency. Definitions and expressions of these parameters are described in [5].

Saito et al. [7] calculated the energy efficiencies (enthalpy efficiency and exergy efficiency) for both continuous-type and storage-type organic CHP systems whose design parameters are summarized in Tab. 3.

The amounts of all components in the exothermic reactor were determined according to the equilibrium constant. Due to a high catalytic activity of acetone hydrogenation, the output gas of the exothermic reactor is the equilibrium mixture with a temperature of 473 K and atmospheric pressure. The temperature of heat supplied to the endothermic reactor or the reboiler is set at 353 K. The bottom vapor in the distillation column, containing the generated hydrogen (taking 1.0 in molar as reference) and the saturated 2-propanol/acetone vapor, is presumed to be 351 K. The minimum reflux ratio is set at 1.42. The components of the overhead product are the sum of refluxing component and cold stream component in the heat exchanger. The hot stream in the heat exchanger is used to preheat its cold stream up to 473 K and is then fed into a distillation column from the midplane.

On the basis of the data in Tab. 3, the enthalpy efficiency and exergy efficiency could be calculated as:

$$\eta_H = Q_H/Q_L \tag{14}$$

$$\eta_\varepsilon = \frac{Q_H(1 - T_0/T_H)}{Q_L(1 - T_0/T_L)} \tag{15}$$

where T_0 is the surrounding temperature. For the continuous-type CHP, a maximum enthalpy efficiency of 36 % is attained around $T_H = 473$ K. For the storage-type CHP, a remarkable improvement in energy efficiency is achieved at the high-temperature range. The maximum exergy efficiency of 60 % together with the enthalpy efficiency of 21 % was obtained at $T_H = 543$ K. Thus, it can be concluded that there is an optimal upgrading temperature (T_H) to acquire the maximum enthalpy efficiency and exergy efficiency. Nevertheless, the investigation conducted by Gandia and Montes [22] indicated a different conclusion, as depicted in Fig. 6.

It is seen that the exergy efficiency decreases with the increase of T_L. This is due to the fact that the 2-propanol content of the vapor leaving the reboiler increases with increasing temperature. The higher 2-propanol content results in a larger amount of degraded heat in the condenser, which lowers the exergy efficiency. In addition, it is also found that the exergy efficiency remains almost unaltered when T_H increases from 433 K to 493 K for any given value of T_L. Obviously, it is contradictory to the conclusion by Saito et al. [7].

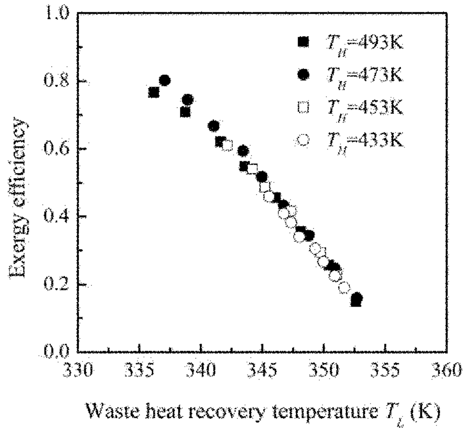

Figure 6. Exergy efficiency against waste heat recovery temperature T_L (data from [22]).

Based on their experimental investigation, Kim et al. [15] designed a continuous organic CHP whose optimal design specification is presented in Tab. 4. In this design, the organic CHP system consists of a dehydrogenation reactor, a distillation column, and a hydrogenation reactor. The hydrogenation reactor is a plug-flow-type tubular reactor. In order to improve the conversion of acetone, a mole ratio of more than 4.0 (about 4.3) is used for hydrogen/acetone. The driving temperature (dehydrogenation reaction) and delivery temperature (hydrogenation reaction) are 351–353 K and 463–473 K, respectively. The total tray number is 20 and the position number of the feed tray is 11. The reflux ratio is set at 0.67. For such an organic CHP, the energy efficiency (enthalpy efficiency) is 18 % (lower than 36 % in [7]) and increases with increasing conversion of acetone into *i*-propanol in the hydrogenation reactor and the total plate number of the distillation column. Nevertheless, when the total plate number exceeds 28, the energy efficiency indicates no further significant improvement.

As an extension of the work by Kim et al. [15], Chung et al. [8] conducted an optimal design for the 2-propanol/acetone/hydrogen organic CHP, whose process flow diagram is displayed in Fig. 2. The efficiency of the organic CHP system mainly depends on the performance of the distillation column, which is usually determined by the number of trays and the reflux ratio. Fig. 7 illustrates the effect of the total stage number of the distillation column on the efficiency of the organic CHP system.

It is seen that the enthalpy efficiency increases with increasing total stage number, but does not

Table 3. Design specification of the organic CHP proposed by Saito et al. [7].

System constituent		Temperature [K]	Amount in molar unit			
			2-Propanol	Acetone	Hydrogen	Total
Exothermic reactor	Input	473	0.05	2.34	11.70	14.09
	Output	473	1.05	1.34	10.70	13.09
Distillation column with reboiler as endothermic reactor	Feed	341	1.05	1.34	10.70	13.09
	Bottom vapor	351	2.89	0.68	1.00	4.57
	Overhead product	330	0.18	5.59	11.70	17.47
	Reflux	330	0.13	3.25	0.00	3.38

Table 4. Design specification of the organic CHP proposed by Kim et al. [15].

	Dehydrogenation reactor		Distillation column			Hydrogenation reactor	
				Output			
	Input	Output	Input	Top	Bottom	Input	Output
Acetone [mol h^{-1}]	31.0	200.0	400.0	369.0	31.0	369.0	200.0
i-Propanol	569.0	400.0	600.0	31.0	569.0	31.0	200.0
Hydrogen	0.0	169.0	1600.0	1600.0	0.0	1600.0	1431.0
Temperature [K]	354	351	341	332.1	354	463	473
Pressure [MPa]	0.10	0.10	0.104	0.104	0.104	0.1	0.1

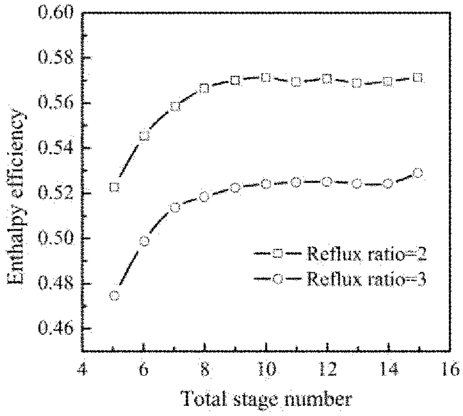

Figure 7. Efficiency changes with the total stage number (data from [8]).

increase any more when the number of stages is over 9. This point was also revealed from the profile of temperature, composition, and flow rate of the distillation column in [8]. Chung et al. [8] did not observe obvious improvements in separation performance when the stage number of the distillation column exceeded 9. In addition, the enthalpy efficiency of such an organic CHP system showed its maximum around a reflux ratio of 1.0. In the results presented by Chung et al. [8], the enthalpy efficiency decreases with the increase of hydrogenation reaction temperature (exothermic temperature) and increases with increasing the dehydrogenation reaction temperature (endothermic temperature). Therefore, lower exothermic temperatures and higher endothermic temperatures were concluded as preferred for this type of organic CHP systems. However, this conclusion seems to be inconsistent with the previous results obtained by Saito et al. [7] and Gandia and Montes [22].

Based on the catalytic dehydrogenation of alcohols at low temperature and hydrogenation of aldehydes or ketone at high temperature, Karaca et al. [58] compared the economic costs for the organic CHPs employing methanol/formaldehyde/hydrogen (M-F-H), ethanol/acetaldehyde/hydrogen (E-AL-H), *i*-propanol/acetone/hydrogen (*i*P-A-H), and *n*-butanol/butyraldehyde/hydrogen (*n*B-B-H) reaction systems. The results are summarized in Tab. 5.

Although the production rates of aldehyde or ketone are almost the same, their concentrations in the liquid mixture are rather different for the different dehydrogenation pressures. This will affect considerably the capacity of the reactor and the amount of the catalyst that should be used. As seen in Tab. 5, the values of Q_H and Q_L that make organic CHPs more economical are as follows: $Q_H > 264$ kW and $Q_L > 511$ kW for M-F-H organic CHPs; $Q_H > 649$ kW and $Q_L > 1602$ kW for E-AL-H organic CHPs; $Q_H > 1782$ kW and $Q_L > 3362$ kW for *i*P-A-H organic CHPs; $Q_H > 1766$ kW and $Q_L > 4045$ kW for *n*B-B-H organic CHPs. Though the economics of these heat pumps are almost in the same range between $30.339 \cdot 10^{-3}$ and $30.935 \cdot 10^{-3}$ \$ kWh^{-1}, it can be concluded that the M-F-H and E-AL-H organic CHPs are suitable for low heat duties, while the *i*P-A-H and *n*B-B-H organic CHPs are better for higher heat duties.

To compare the COPs of organic CHPs with the conventional compression heat pumps, Kato and Pritchard [17] proposed an isobutene/*tert*-butanol/water CHP system for upgrading waste heat from about 343 K to 383 K, as illustrated in Fig. 8.

The system combines the organic chemical reaction with a compressor. In addition, the system is equipped with catalytic reactors for dehydration of tBA and hydration of iB. A high-concentration tBA stream enters the dehydration reactor, which is packed with a solid catalyst. The endothermic dehydration reaction proceeds in the liquid phase at low temperature and pressure. The low-temperature heat is thus stored chemically in the product stream of iB and the water generated by the reaction. Because the atmospheric boiling point is much lower for iB (266.1 K) than for water (373 K) and tBA (355.5 K), the product is readily separated into gas and liquid phases in the separator. The gas-phase product is compressed by the compressor to a sufficiently high pressure for the prod-

Table 5. Comparison of various organic CHPs (data from [58]).

Organic CHPs	Dehydrogenation pressure [atm]	η	Q_H [kW]	Q_L [kW]	G^a [kg h^{-1}]	$x_{AD}{}^b$	$LTC^c \cdot 10^{-3}$ [\$ kWh^{-1}]
M-F-H	1	0.447	264	590	332	0.056	30.935
	2	0.516		511	334	0.099	
E-AL-H	1	0.373	649	1739	1774	0.224	30.501
	2	0.405		1602	1797	0.435	
*i*P-A-H	1	0.379	1782	4702	6541	0.243	30.344
	2	0.530		3362	6566	0.674	
*n*B-B-H	1	0.400	1766	4420	6766	0.263	30.339
	2	0.437		4045		0.485	

[a] Flow rate of ketone; [b] concentration of ketone; [c] levelized total annual cost.

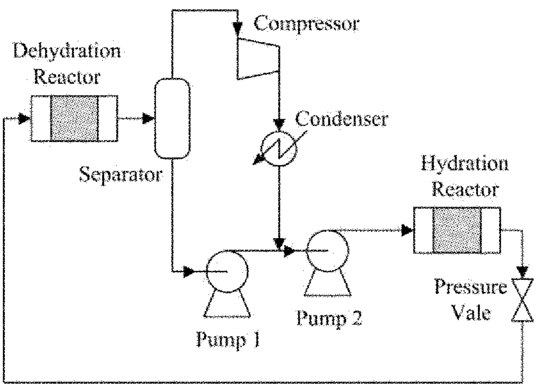

Figure 8. Isobutene/*tert*-butanol/water organic CHP system [17].

uct to be condensed by cooling water in the condenser. The mixture of water and unreacted tBA is pressurized by pump 1, and then mixed with the condensate from the condenser. The final mixture is pumped by pump 2 to the hydration reactor, where iB and water react exothermically on the solid catalyst. The heat of hydration with high temperature is utilized as a heat source. The tBA returns to the dehydration reactor after the pressure is reduced by a pressure valve, and then the cycle is completed. A process simulation based on experimental data indicates that the proposed organic CHP system has a COP value of 6.4 at 343–383 K, which is greater than that of the conventional compression heat pump (4.0) under the same conditions. In addition, the proposed heat pump has also a higher exergy efficiency value than the conventional compression heat pump.

According to the criteria like temperature, pressure, reaction enthalpy, and so on, Spoelstra et al. [26] assessed 33 organic and inorganic CHP systems and found that there are no obvious winners. Organic systems show a bad score on selectivity and conversion as compared with inorganic systems, while inorganic systems perform worse on mass and heat transfer. In spite of this fact, a technical assessment and economic evaluation had been accomplished by modeling the system with help of the ASPEN Plus[reg] program for the isopropanol organic CHP and a spreadsheet model for the salt/ammonia vapor inorganic CHP. The calculation results indicate that the salt/ammonia inorganic CHP has higher enthalpy efficiency and COP and does not suffer from by-product formation, i.e., it provides a better technical performance than the isopropanol organic CHP. Concerning economical aspects, the difference between these two CHPs is even greater. The isopropanol organic CHP is not economically feasible, while the salt/ammonia inorganic CHP shows a good IRR which represents the internal rate of return, an economic indicator, being 14 % for the salt/ammonia inorganic CHP [26].

4 Existing Problems and Future Research Directions

As compared with the traditional mechanical heat pump (MHP), the CHP has many advantages such as wide temperature range, possibility of energy storage, high energy density, and low hazard. In the meantime, however, some disadvantages become obvious, such as complicated operation, high investment cost, by-product formation, catalyst deactivation, and limited industrial applications [6]. Within CHPs, inorganic and organic systems are also up against the different circumstances. Some inorganic CHP systems have stepped into the validating phase and even metal hydride systems have been put into practical operation in some countries. In comparison, the installation of organic CHP systems is still in the laboratory stage and many problems need to be studied and solved further.

Currently, the biggest problem of the organic liquid-gas CHP systems is the relative low thermal efficiency and exergy efficiency due to the low conversions of the endothermic and exothermic reactions. There are three main factors influencing the conversion of reaction, i.e., by-product formation, distillation performance, and heat transfer in the endothermic and exothermic reactors. As for the reactive distillation, many investigations have been conducted and excellent achievements have also been realized. The by-product formation is closely related to the catalyst used. Although the catalyst-assisted organic reaction has been extensively studied, it is still a problem for a long-running closed CHP system. The performance of heat transfer in the reactors is another factor limiting the conversion and stability of the organic CHP system. In order to attain a high chemical reaction rate, complete heat transfer characteristics must be evaluated. In an actual process flow, the heat transfer in the reactors is coupled with the organic chemical reaction. However, most of the investigations neglected the effect of heat transfer on chemical reaction, or heat transfer and chemical reaction were separated for individual studies. In general, the theoretical calculation of the system performance was done by simply assuming a constant reaction rate, leading to the different results among the different researchers. Even the conclusions were sometimes contradictory to each other, e.g., the effect of endothermic temperature (T_L) and exothermic temperature (T_H) on system performance (see Sect. 3.4).

Aiming at resolving the existing problems mentioned above, the following possible research directions for the organic liquid-gas CHPs are proposed:

(1) Development of new liquid-gas organic reaction systems and their catalytic reaction properties. The organic reversible chemical reaction is anticipated to have a large enthalpy change in order to obtain more energy by extending the temperature range of endothermic and exothermic reactions. Therefore, the research and development of organic reaction systems with a large enthalpy change and their catalytic characteristics are imperative.

(2) Study of the chemical reaction mechanism in multiphase, multicomponent systems and heat and mass transfer characteristics. The synergy between organic chemical reaction kinetics and heat and mass transfer plays an important role in the overall performance of the organic CHP systems. It is necessary to investigate the reversible catalytic reaction kinetics, characteristics, and influencing factors of fluid flow and heat transfer accompanied by the chemical reaction. Measures of enhancing the heat transfer as well as promoting the chemical reaction are expected to be proposed. In-depth investigations

are needed to reveal clearly the chemical reaction mechanism of a multiphase, multicomponent system, the characteristics of heat and mass transfer, and the coupling effect between the heat mass transfer and chemical reaction.

(3) Construction, optimization, and control of an organic CHP cycle system with high efficiency. With different heat sources (e.g., industrial waste heat, solar heat, heat of combustion of municipal waste, subterranean heat), the organic CHP systems have certain differences due to their own characteristics (e.g., temperature level, fluctuation, intermittence, and so on). It is important and necessary to construct a cycle system according to the characteristics of low-grade heat sources. The research includes thermodynamic analysis of the cycle performance, dynamic effect of various parameters on the system performance, and improvement of thermodynamic analysis methods. For the stable operation of an organic CHP and the effective use of energy, the control system is also very important, but so far little attention has been paid to this aspect. This is unfavorable for the realization of practical applications. The system work needs efficient collaboration among the researchers in the fields of chemical engineering, thermal engineering, and automation engineering.

(4) Research and development of advanced heat exchangers. Heat exchangers play an important role in an organic CHP system. Their performances will decide the heat transfer rate which influences the chemical reaction rate.

(5) Comprehensive evaluation involving economy and performance of organic CHP systems. Generally, the economic analysis is separately investigated from the performance evaluation of an organic CHP system. It is necessary to develop a comprehensive method for evaluating the economy and performance of organic CHP systems.

5 Conclusions

An overview on the catalyst-assisted CHPs employing organic liquid-gas reaction systems was presented considering the organic reaction system, organic catalytic reaction, reactive distillation, system design, and evaluation of performance and economy. The existing problems with organic liquid-gas CHPs were addressed. The future research directions from both the system level and component level were further pointed out.

Overall, rapid progress has been achieved for inorganic CHPs, but some inherent shortages restrict its large-scale utilization and further development. The authors believe that the organic liquid-gas CHP system is the main trend for future development due to its easy continuous operation and scale applications, although it is yet in the fundamental research stage around the world.

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Symbols used

C_A	[mol L^{-1}]	concentration of acetone
C_P	[mol L^{-1}]	concentration of *i*-propanol
ΔH	[J mol^{-1}]	change of enthalpy
P_{eq}	[Pa]	pressure at the equilibrium state
Q	[kW]	quantity of heat exchange
R	[J mol^{-1}K^{-1}]	perfect gas constant
ΔS	[J mol^{-1}K^{-1}]	change of entropy
T	[K]	temperature
V	[mmol g^{-1}min^{-1}]	reaction rate

Greek symbols

η_H	[–]	enthalpy efficiency
η_ε	[–]	exergy efficiency

Subscripts

C	condensing
H	high, high temperature
L	low, low temperature
0	surrounding

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