An innovative approach for storing low-grade thermal energy using liquid phase thermoreversible reaction

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HIGHLIGHTS

- The potential of *methanol + acetaldehyde ↔ hemiacetal*, as a thermoreversible reaction, is studied for long-term energy storage.
- A full description of forward and backward reactions is provided.
- The technical issues associated with both forward and backward reactions are discussed.
- The presented approach has a great potential for storing low-grade thermal energy in regional areas of cold weather.

ARTICLE INFO

ABSTRACT

This study investigates the potential of "*methanol + acetaldehyde ↔ hemiacetal*" as a liquid phase thermoreversible reaction for long-term storing of low-grade thermal energy to overcome the mismatch between energy supply and demand. Both forward and backward reactions are studied experimentally and the technical issues associated with employing such a system are discussed. Methanol and acetaldehyde would react via an exothermic reaction ($-\Delta H_r = 31.8 \frac{kJ}{mole}$ *or* $104.7 \frac{kWh}{m^3}$) at low temperature range ($< 15\,°C$) and atmospheric pressure, with a high reaction rate ($k = 26.26 \times 10^2 \exp\left(-\frac{4099}{T}\right)$). The regeneration of parent reactants with high purity occurs at $48\,°C$ which can easily be delivered using low-grade heat. The low operating temperature required for forward reaction and the reduction in backward reaction rate caused by methanol accumulated are the main engineering challenges. These technical problems need to be solved before this reaction could be utilised commercially.

1. Introduction

Management, upgrading, and reusing of energy are of worldwide interest due to the fast-growing energy demand and increasing concerns about the continuous reduction of fossil fuel resources and global warming. The storage and reuse of low-grade waste heat is a promising opportunity for industrial actors or even house owners, however, it is quite problematic because of its low temperature. Sensible and latent heat storage have been developed commercially to capture and store high- and low-grade thermal energies [1–3], and are found suitable for short-term energy storage. To overcome the mismatch between energy supply and demand long terms thermal storage is vital. For example, incident solar radiation on roof of a house in summer is much higher than what is needed, while it can be stored for use in winter [4]. However, long-term thermal storage is problematic and the

technologies are still in early stage of development and hence further research on such an approach is needed. Using thermoreversible chemical reactions is a promising approach to store thermal energy at different temperature levels and recover it when needed [5,6]. In a thermoreversible reaction, two reactants are mixed to undergo an exothermic reaction and release heat through the formation of new chemical bonds. Thermal energy is used to dissociate the reaction product(s) and regenerate the parent reactants via an endothermic process. The separated materials are then stored separately to be remixed for recovering the stored energy on demand [7,8].

Among the different thermoreversible reactions including gas-gas, gas-liquid, gas-solid and liquid-liquid; the gas-solid reactions have been mostly highlighted due to their simplicity, covering a broad range of temperature (80–1000 °C) and having high energy storage density (400–800 kWh/m³ of salt) [9,10]. Systems with solid–gas reactants are

typically catalytic with a low energy recovery efficiency (< 80%) due to the presence of a gas phase and they require a complex system design [11–13]. The energy recovery in such a system highly depends on gas diffusion into the solid structure which diminishes with time due to solid expansion during the process [14]. For example, in a gas-solid system comprising of salt composite and water vapour the salt could expand by > 50% during moisture adsorption (exothermic reaction) [15,16]. Such limitation could block the pores in the host matrix and reduce energy recovery by up to 30% [17,18]. While liquid-liquid thermoreversible reactions seem more suitable from an engineering perspective since they occur with no phase change. They require smaller reaction volume and introduce no heat transfer limitation [19,20]. Hence, to store low-grade thermal energy a liquid-liquid reaction with high reaction rate and enthalpy as well as moderate/low operational conditions would be a more attractive system. However, due to the limitations caused by reaction reversibility and the conditions in which it occurs, there has been limited focus on using liquid-liquid reactions for storing energy.

Diels-Alder, esterification, and alcohol-aldehyde are the liquid phase thermoreversible reactions most studied in the literature. Diels-Alder reaction involves dimerization of a diene at room temperature and has a high energy density, for example, 128.5 kWh/m^3 of cyclopentadiene produced [5,21,22]. However, it typically requires a destructive distillation at > 150 °C to regenerate the original reactant and requires low storage temperature (− 20 °C) to prevent the forward exothermic reaction. Also, it coincides with a mass loss during regeneration step due to the formation of azeotrope which means the system would have to be refueled with the reactant to compensate the loss [23–26]. Esterification is another type of liquid phase thermoreversible reaction, which occurs between a carboxylic acid (R$_1$-COOH) and alcohol (R$_2$-OH) to form an ester (R$_1$-COO-R$_2$) and water. Although it has a relatively low operating temperatures (≤ 80 °C) [27,28], it is a very slow reaction in the absence of a strong acid as catalyst. Moreover, the reaction has a very low energy storage density (< 20 kWh/m^3 product) [29,30].

The reactions between an alcohol and an aldehyde seems more promising since they have a high energy density (up to 124 kWh/m^3 product) and relatively low operating temperatures, < 80 °C [31–33]. Of the most studied five different alcohol-aldehyde reactions, methanol-acetaldehyde pair has shown a higher energy density (104–124 kWh/m^3 product) and lower operating temperatures (< 20 °C for forward reaction) [31,33–38]. However, to our knowledge, only Fahim, Al-Sahhaf [31] have developed a kinetic model for the forward reaction, with no information provided on kinetic of the backward reaction. Also the potential technical issues associated with using such a thermoreversible reaction for energy storage have not been discussed. Hence, the study presented in this paper aims to develop a basic understanding of this reversible reaction and provide a complete description of both forward and backward reactions, for the first time in literature. In addition, the technical issues which may arise during development of such energy storage system are discussed.

2. Materials and methods

2.1. Forward reaction

The reaction between methanol (M) and acetaldehyde (A) is an equimolar exothermic reaction which results in the formation of hemiacetal (Fig. 1). As both reactants as well as the product are miscible liquids, no solvent is required, which would otherwise reduce energy density. The reactants spontaneously react and generate heat at any temperature below 20 °C. The applicable temperature at atmospheric pressure is limited by the boiling point of acetaldehyde (20.2 °C). The need to operate at low temperature may limit the applications of this reaction. However, it has still a great potential for storing energy in regional areas of cold weather with high solar
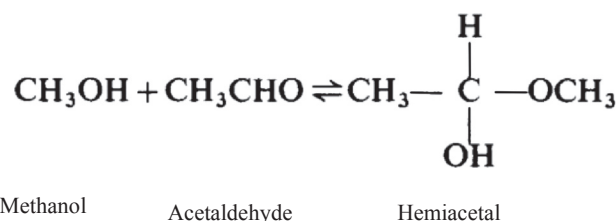

Fig. 1. Reversible reaction between methanol and acetaldehyde.

radiation similar to arctic climate. In such climate, the solar power would be used (stored) for decomposition of hemiacetal into the parent materials during the daytime, and the exothermic reaction can be used for space/water heating at night or after any unlimited period of time.

2.1.1. Heat of reaction

To calculate the enthalpy of the exothermic reaction between methanol and acetaldehyde, a known volume of acetaldehyde (0.3–0.5 ml) was added to a large volume of methanol (20 ml) in an insulated glass reactor at different temperatures (− 5 to 10 °C). This experimental procedure is similar to that suggested by Fahim, Al-Sahhaf [31]. The temperature rise was recorded and the reaction enthalpy (heat released) was calculated calorimetrically according to Eq. (1). As the quantity of acetaldehyde was small, the physical properties of methanol were used to represent the system.

$$\sum m_i C_{Pi} \Delta T_{reactor} = n \Delta H_r + (UA)_{ave.}(T_{amb.} - T_{reactor}) \qquad (1)$$

where m_i and C_{pi} are the mass and heat capacity of different components (i.e. reactor body and methanol), $\Delta T_{reactor}$ is the temperature changes in reactor due to reaction, n is numbers of mole of acetaldehyde, ΔH_r is heat of reaction, UA is the loss heat transfer coefficient of the reactor, and $T_{amb.}$ and $T_{reactor}$ are the ambient and reactor temperatures, respectively. The $(UA)_{ave.}$ of the reactor was measured for the same experimental set-up at non-reacting condition using Eqs. (2) and (3). The reactor was filled with 20 ml of methanol at different initial temperatures (− 10 to 10 °C) and allowed to gain energy from ambient (21 °C).

$$m_M C_{PM} \frac{dT_{reactor}}{dt} = -(UA)_{T_i}(T_{reactor} - T_{amb.}) \qquad (2)$$

Thus:

$$\ln(T_{reactor} - T_{amb.}) = \frac{-(UA)_{T_i}}{m_M C_{PM}} t + \ln((T_{reactor} - T_{amb.})_0) \qquad (3)$$

2.1.2. Kinetic modelling

To develop a kinetic model for the exothermic reaction, the temperature rise of the reaction was monitored while a small volume of acetaldehyde (0.25–0.4 ml) was added to a large quantity of methanol (20 ml) in a glass reactor. As reaction rate is a function of temperature, and to minimize temperature rise during the reaction period, the reactor was immersed in a water bath at controlled temperature (− 5 to 10 °C). A thermocouple (type K) was placed inside the reactor to record the small temperature rise due to reaction. The reactants were mixed when both methanol and acetaldehyde were at water-bath temperature. A new UA for the new experimental conditions was also calculated using Eqs. (2) and (3) based on a non-reacting system. This has been done by placing 20 ml of methanol at an initial temperature into the glass reactor and allow it to cool down by losing heat into the surrounding water bath sustained at − 10 °C.

2.2. Backward reaction

As stated earlier, the backward reaction has not been studied experimentally before. To study the reversibility of the reaction and