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## Thermodynamic efficiencies of hydrogen storage processes using carbazole-based compounds

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### ABSTRACT

Carbazole-based compounds are promising candidates for hydrogen storage materials, and recent research has focused on finding components with higher hydrogen storage capacity and desirable physical properties. In this paper, thermodynamic efficiencies of hydrogenation and dehydrogenation reactions were analyzed assuming an idealized process. The physical properties and thermodynamic efficiencies of three carbazole-based compounds (n-ethylcarbazole, n-propylcarbazole, n-acetylcarbazole) were investigated for use as liquid organic hydrogen carriers (LOHCs). Unavailable physical and thermodynamic properties were estimated using molecular modeling or group-contribution methods. Process simulations were performed for hydrogen storage and release processes using a commercial simulation package to evaluate the thermodynamic efficiencies of three candidate molecules. Even though there might be additional loss of exergy upon practical implementation of the whole process, the framework developed in this study can be useful for screening candidate LOHC molecules.

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### Introduction

Hydrogen storage is a key technology for the sustainable use of hydrogen energy. Various methods to store hydrogen have been proposed, such as sorption materials or chemical hydride materials [1]. Liquid organic hydrogen carriers (LOHCs)

are regarded as effective ways to store hydrogen using chemical reactions of unsaturated organic compounds such as benzene, naphthalene and toluene [2–5]. In systems using such LOHCs, hydrogen can be safely provided at a moderate pressure by reversible hydrogenation and dehydrogenation. On the other hand, cyclic organic compounds like cyclohexane require high temperatures and large amounts of

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energy due to their highly endothermic dehydrogenation reactions. Organic cyclic compounds that contain heteroatoms may be attractive alternatives for further development of LOHCs [6]. Brückner [7] and Müller [8] reported that the liquid mixture of isomeric dibenzyltoluene had desirable transport properties and could store up to 6.2wt% hydrogen.

Reversible hydrogen storage using aromatic compounds with N-heteroatoms was proposed by Pez et al. [9,10]. Among the proposed hetero-cyclic compounds, n-ethylcarbazole can store hydrogen reversibly at ambient temperature. In the hydrogenation of n-ethylcarbazole, full storage of hydrogen can be achieved with suitable kinetics using a ruthenium-based catalyst [11]. In the dehydrogenation of dodecahydro-n-ethylcarbazole, full recovery of hydrogen can be accomplished with a palladium-based catalyst [12–14]. Thus, n-ethylcarbazole is regarded as a promising candidate LOHC, and it has a hydrogen capacity of 5.79wt%, which is higher than the target (5.5wt% by 2020) suggested by the US Department of Energy (DOE) [15]. However, other physical properties such as the melting point and viscosity were not suitable for practical applications, and the thermodynamic efficiency of the hydrogenation/dehydrogenation processes have not been evaluated. Research to find better candidate molecules that have the desired hydrogen storage capacity, physical properties and thermodynamic efficiency is on-going.

Molecular modeling and process simulation tools can be used for evaluating candidate LOHCs without expensive and time-consuming chemical synthesis and physical property measurements. Recent advances in these fields allow us to effectively evaluate possible candidates with improved accuracy. Emelyanenko and coworkers [16] calculated the enthalpies of reaction for hydrogenation and dehydrogenation by combining quantum-chemical calculations and experimentally measured vaporization enthalpy data. They also calculated enthalpies of reactions for n-isopropyl-, n-propyl- and n-butyl-carbazole, and they concluded that the low enthalpies of reaction allow for low temperature hydrogen generation reactions. Only enthalpies of reactions were compared in their study, and they did not analyze the efficiency of the hydrogenation and dehydrogenation processes. In this study, we show that an exergy analysis of hydrogenation and dehydrogenation processes may be useful for screening of candidate LOHC components.

Three carbazole-based components (n-ethylcarbazole, n-propylcarbazole, n-acetylcarbazole) were investigated and evaluated for use as LOHCs. Normal and hydrogenated carbazole-based components used in this study are shown in Fig. 1. N-propylcarbazole is a potential alternative due to its lower melting point and favorable hydrogenation kinetics [17]. N-acetylcarbazole can also be considered as a LOHC candidate due to its higher ideal hydrogen capacity of 6.32 wt%. The thermodynamic properties of some compounds were unavailable. Therefore, these properties were estimated using Density Functional Theory (DFT) calculations and group contribution methods. After we collected the relevant physical and thermodynamic data, simulations of hydrogen storage/emission processes were performed using the ASPEN plus package (version 8.0). The thermodynamic efficiencies were compared based on exergy analyses using the three carbazole-based components mentioned above.

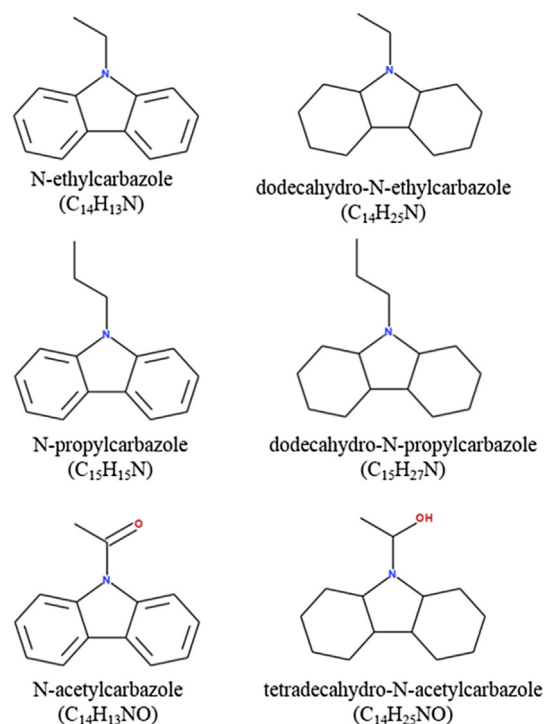


Fig. 1 – The molecular structures of carbazole-based compounds (left) and hydrogenated forms (right).

## Preparation of process simulation

### Estimation of thermodynamic properties

In order to model the process of reversible hydrogenation/dehydrogenation reactions, the enthalpies of formation, Gibbs free energies of formation, and ideal gas heat capacities must be known. These properties for 6 components (normal and hydrogenated forms of the 3 components of interest) were obtained using DFT calculations employing the Perdew, Burke and Ernzerhof (PBE) gradient-corrected functional [18] and double numerical plus d-function (DND) 4.4 basis set. The stereoisomers of compounds were distinguished before the calculations. After the geometry optimization of all the compounds, the most stable compound was selected for the calculation of thermodynamic properties. The most stable conformer of each compound provided the smallest steric energies at  $T = 0$  K ( $E_0$ ) as shown in Fig. 2.

Enthalpies of formation were calculated from enthalpies of theisodesmic reaction. To verify the current estimation method, literature values for n-ethylcarbazole and dodecahydro-n-ethylcarbazole were compared with calculated values. Calculated values were 171.1 kJ/mol, –149.9 kJ/mol, respectively, and these agreed reasonably well with the literature values of 167.7 kJ/mol [19] and –151.4 kJ/mol [20].

The entropy of each compound at  $T = 298.15$  K was obtained by calculating the optimized structure and frequency of each compound using the DFT method. Entropies of formation ( $\Delta_f S_{298.15}^0$ ) were calculated on the basis of the

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