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## Thermal storage by thermoreversible chemical reaction systems

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### Abstract

Recent research work on the development of smart pumpable materials for thermal storage at temperatures below 200 °C will be presented. Currently two different systems being analyzed: additive enhanced CO<sub>2</sub>-hydrates for climate and cooling purposes and neutralization reactions of organic acids with nitrogen bases for waste heat utilization. CO<sub>2</sub>-hydrate formation and growth are studied while using hydrogel additives of different morphological structure. In particular hydrogels with a low content of cross-linker significantly promotes the hydrate formation. Several combinations of organic acids and bases are tested in mixing experiments and show that high energy densities can be obtained by these neutralization reactions in liquid systems. Special emphasis is put on the option of long-term-storage of heat. This possibility is demonstrated by distilling off the acid component for the reference reaction system trioctylamine and acetic acid.

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### Nomenclature

DSC	Differential Scanning Calorimeter
ITC	Isothermal Titration Calorimeter
J	Joule
K	Kilo
L	Liter
M	Mega

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m	Milli
$\mu$	Micro
pK <sub>a</sub>	Acid Dissociation Constant
RC	Reaction Calorimeter
t <sub>a</sub>	Time Stirrer Started
t <sub>TP</sub>	Time Turbidity Point
t <sub>Ind</sub>	Induction time
V	Fraction of used cross-linker in the hydrogel sample
(w/w)	Weight-Weight Percentage

## 1. Motivation

Thermochemical heat storage materials offer energy storage densities which are up to 10 times higher than those of sensible and phase change materials respectively. However, current developments of thermochemical heat storage materials concentrate on high temperatures. There is a lack of materials for low temperature applications (below 200 °C) [1]. Moreover, most of the thermochemical heat storage materials under development are based upon solid/gaseous reaction systems, which implicate the utilization of complex and expensive devices in practice. The idea therefore is to develop and optimize cost-efficient fluid thermochemical heat storage materials with high energy storage densities. In particular two different approaches are investigated: CO<sub>2</sub> hydrates with optimized reaction kinetics for cooling and climatization purposes, and nitrogen-based thermoreversible organic reaction schemes for waste heat utilization.

## 2. CO<sub>2</sub> hydrates for cold storage

Gas hydrates are crystalline structures that trap a large amount of gas such as CO<sub>2</sub> in the polyhedral cavities formed by a water-based host matrix (Fig. 1). Carbon dioxide Hydrates show significantly higher energy storage densities (500 kJ kg<sup>-1</sup>) than ice (334 kJ kg<sub>w</sub><sup>-1</sup>) and can be used as pumpable slurries (Carbon dioxide Hydrates Slurries, CHS) for cooling purposes [2]. Nevertheless, their practical utilization is hampered due to the slow and unpredictable kinetics of hydrate formation.

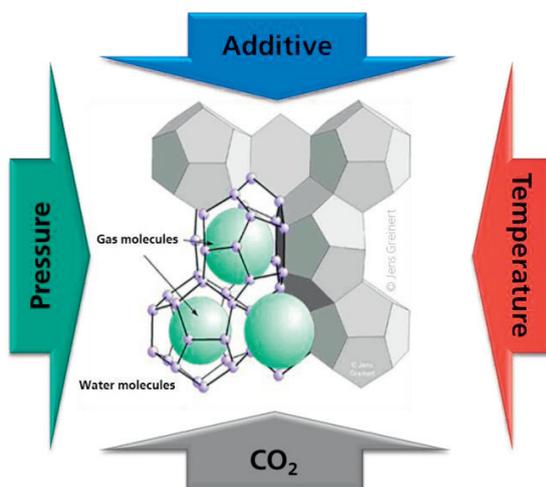


Fig. 1. Cubic structure of gas hydrates and their stimuli (pressure, temperature and gas, additive) to influence formation of CO<sub>2</sub> hydrate.

These hindrances can be overcome by adding an adequate promoting agent. Our investigations focus on the addition of different sodium polyacrylate hydrogels being cross-linked and partly neutralized (75 %). We have carried out first series of reactor experiments using hydrogel samples with variable particle diameter [3] and have found an influence on the induction time which represents an essential key parameter of the hydrate formation. Samples with diameters smaller than approx. 100  $\mu\text{m}$  induced an undesired inhibiting effect.

The investigations presented in the following were executed to elucidate the hydrogel effect on hydrate formation due to the degree of cross-linking. On this, different hydrogel samples were synthesized containing varying amounts of cross-linker (e. g. the hydrogel sample named V0.6 has a molar cross-linker content of 0.6 %). Samples with a small fraction of cross-linker swell less in water than samples having a higher cross-linker ratio.

### 2.1. Reactor experiments

In the scope of our lab experiments we use a glass pressure reactor, which allows visual observation of the turbidity point and subsequent hydrate formation steps. Furthermore, we monitor both the pressure and the gas consumption of the reaction. The reactor experiments followed a modified multi-cycle procedure described by Duchateau et al. [4]. The procedure is based on the memory effect of water, which takes advantage of residual structures remaining in the mixture after previous hydrate formation. The stochastic character of hydrate formation could be reduced in the subsequent formation cycles, if the destabilization temperature is not too high.

Each experiment in the reactor consists of three cycles which are divided in four phases: saturation, conditioning, hydrate growth phase, destabilization. Fig. 2 (a) shows one cycle with its four phases. During saturation and cooling the mixture is stirred. The stirrer is subsequently switched off until conditions are constant, then it is started again. Mean induction times are presented in Fig. 2 (b). While ultra-pure water is used in the first two cycles, a small amount of a hydrogel solution is injected into the reactor via a locking system at the beginning of the third cycle. The final concentration of the swollen hydrogel in the whole bulk comprises 0.01 % (w/w) and all hydrogel samples previously had time for swelling overnight. Each experiment was triplicated at least for reproducibility reasons.

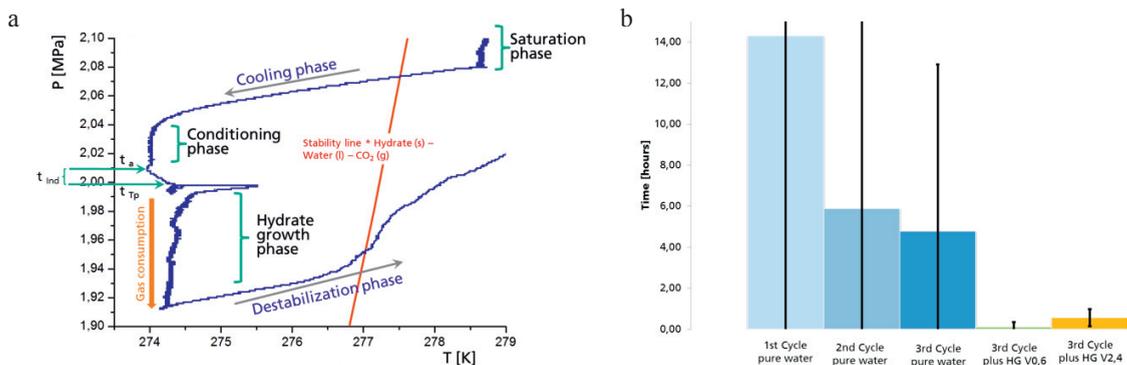


Fig. 2. (a) Cycle with phases of reactor experiments. Stability line [5]  $t_a$ : Time stirrer started;  $t_{TP}$ : Time turbidity point;  $t_{ind}$ : Induction time; (b) Mean induction times with standard deviations. HG: Hydrogel; V – Fraction of cross-linker [mol-%]

As can be seen in Fig. 2 (b), already a small additive concentration of 0.01 % (w/w) reduces the induction time essentially. This is also true for the standard deviations of these experimental runs (strong reproducibility increase).

Another aspect of our investigations is the gas consumption which corresponds to the incorporation of CO<sub>2</sub> into the hydrate cage (Fig. 3 (a)). The gas consumption was calculated on the basis of temperature and pressure data following the Peng-Robinson equation which is described in detail in [6]. Fig. 3 (b) summarizes the results of gas consumption: a hydrogel additive, e. g. sample V0.6, with a small fraction of cross-linker promotes the hydrate growth, whereas a stronger cross-linked hydrogel such as sample V2.4 inhibits the growth.

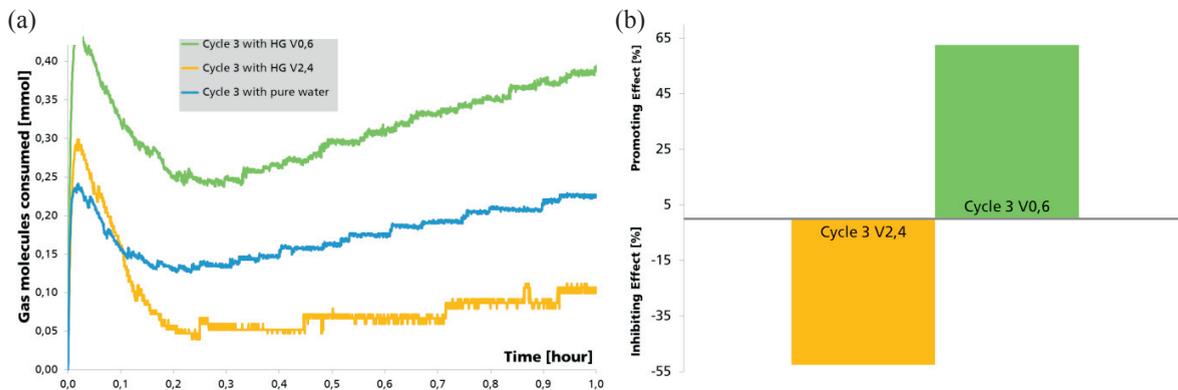


Fig. 3. (a) Mean values of CO<sub>2</sub> consumption starting at turbidity point; (b) Growth effect influenced by the cross-linking degree of the hydrogel

2.2. High pressure DSC experiments

To verify the reactor experiments, we also performed corresponding thermo-analytical measurements with a high-pressure Differential Scanning Calorimeter ( $\mu$ DSC 7 Evo, Setaram). Since the calorimeter cells do not have a stirrer, a modified multi-cycle method [7] was used for these experiments. This method consists of several freezing and thawing cycles (Fig. 4 (a)) producing both ice and CO<sub>2</sub> hydrates during freezing. The thawing temperature was fixed to the melting point of ice, so that the CO<sub>2</sub> hydrates - once formed - are always stable. Consequently, the amount of hydrates increases cycle by cycle. In the last cycle, the sample melts completely. Two peaks are obtained in the thermogram: one for the melting of ice and the other one for the hydrate dissociation (cf. Fig. 4 (b)). The ice peak can be used to calculate the specific hydrate melting heats based on the melting enthalpy of ice ( $334 \text{ kJ kg}_w^{-1}$  [2]), the weighted sample and the observed heat of the hydrate peak.

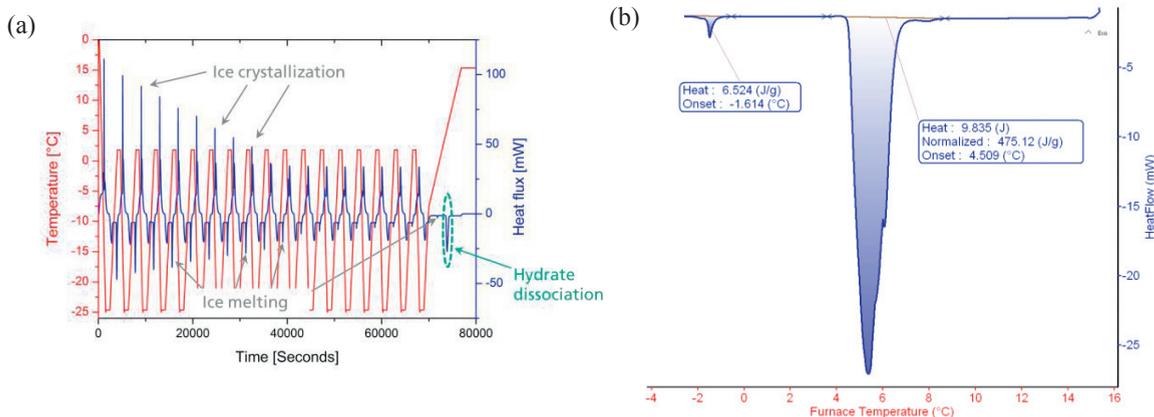


Fig. 4. (a) Principal thermogram with furnace temperature and heat flux over time (multi-cycle method); (b) Thermogram with baseline integration of ice and hydrate peak

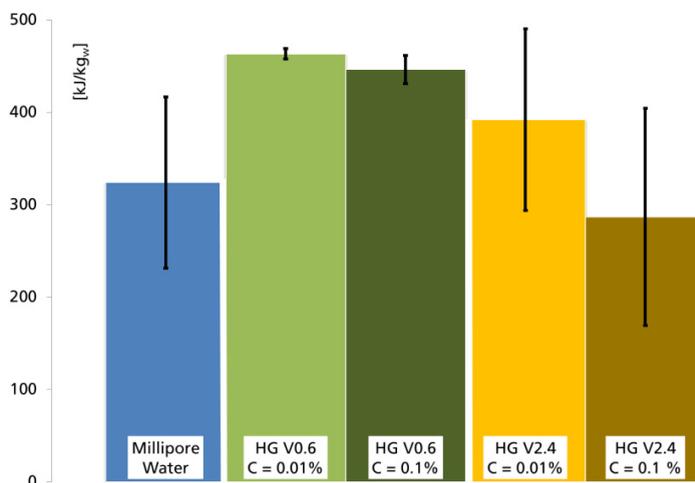


Fig. 5. Average hydrate melting heats with standard deviation measured via DSC

Fig. 5 exemplifies that the use of 0.01 % (w/w) solutions with hydrogel sample V0.6 leads to significantly higher CO<sub>2</sub> hydrate melting heats than the application of ultrapure water. This phenomenon is consistent with the observed higher gas consumption and incorporation of CO<sub>2</sub> into the hydrate structure respectively (Fig. 3). However, higher concentrations such as 0.1 % (w/w) do not improve this promoting effect.

If we use the more cross-linked hydrogel sample V2.4 instead of V0.6, it seems that smaller specific melting enthalpies for the hydrate are obtained. However, the standard deviation increases within the experimental run not allowing an absolute assessment and require further measurements.

### 3. Thermoreversible reactions between organic acids and amines

Additionally to the research on CO<sub>2</sub>-hydrates, investigations of organic reaction schemes were carried out to elicit adequate thermochemical heat storage materials for application temperatures below 200°C. For this purpose we had already tested substances undergoing thermo-reversible Diels-Alder reactions in the framework of previous investigations [3]. Our current focus deals with reactions between organic acids and nitrogen bases, mainly tertiary amines. Most of these chemicals are liquid, widely available and react according to a pure neutralization mechanism without any tendency for an undesired side reaction. To gain pumpable storage systems the resulting neutralization products need to be also liquid. This is generally true when tertiary amines are used as base.

The reaction between sulfuric acid and ammonia represents a good reference system for the announced type of heat storage system. It delivers 2.200 MJ/m<sup>3</sup> (energy related to the volume sum of ammonia and sulfuric acid, both in liquid state) indicating the potential energy density for these neutralization reactions. On the other hand, this reaction involves many disadvantages: it results in a solid product and has to be conducted under pressure to keep the ammonia liquid. In addition, just half of the ammonia can be recovered in the low temperature range. We therefore used a combination of acetic acid and trioctylamine (Fig. 6) for our first investigations. This bulk reaction system is always liquid and most likely thermo-reversible below 200°C.

### 3.1. Storage mechanism

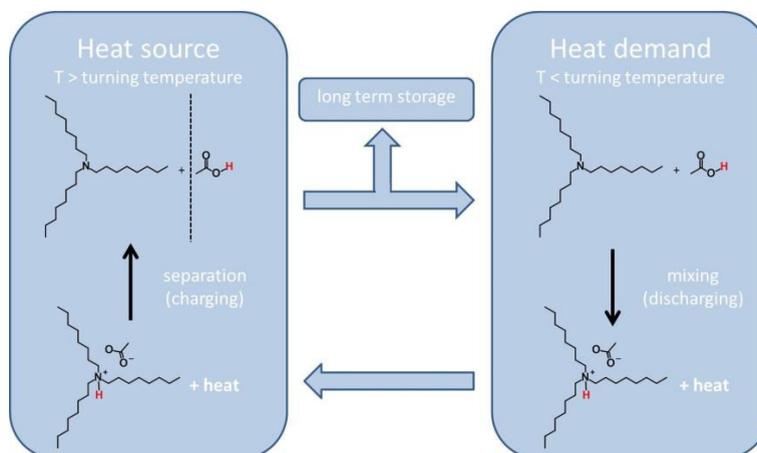


Fig. 6. Heat storage principle illustrated by system triethylamine and acetic acid

The exothermic reaction between acetic acid and triethylamine to triethylammonium acetate represents the discharging step of the heat storage. In order to initiate the reverse reaction, the product is brought to a high temperature level far above the turning temperature of the reaction, where the equilibrium constant  $K$  is equal to “1”. The equilibrium shifts consequently back toward the educts again forming a mixture of acid and base. If one component is removed from the mixture there is the possibility to generate a long-term storage system. This worked out in the case of the system acetic acid and triethylamine via distilling off the acid at 150°C under a slight vacuum (cf. chapter 3.3.).

### 3.2. Screening experiments

In the following screening experiments several combinations of organic acids and amines are monitored by an EasyMax apparatus (Mettler Toledo) under isoperibolic conditions. The aim was to determine the relative energy densities for different neutralization systems.

On the one hand we applied substances with variable acidity and basicity strength. Table 1 and Table 2 detail the specific acid dissociation constants (pKa) of different acids and bases. We anticipate that using acids with strong acidity (low pKa) will result in high reaction enthalpies. This may also be true if we use amines with strong basicity (high pKa) for the neutralization. On the other hand small molar volume should be favorable in order to optimize the energy densities and application properties in the reaction system. For instance, the carbon chain lengths of trialkylamines (cf. Table 2) should affect both the energy density and aggregation state of the resulting neutralization product.

An additional idea was the utilization of polymeric components that may offer particularly high concentrations of functional groups which can react. Two different polymer types were applied (Fig. 7 (b)). We first tested two aqueous solutions of partially hydrolyzed polyvinyl formamides (Hercobond 6363, Ashland and Lupamin 1595, BASF), showing a linear molecular structure. Due to their moderate solubility in water, the polymer mass fraction does not exceed 15 % (w/w) in solution. Secondly, we applied 50 % (w/w) aqueous solutions of two branched polyethylenimines with different average molecular masses (Lupasol G100 with  $M_w = 5000$ g /mol, BASF and Product 408719 with  $M_w = 800$ g /mol, Sigma-Aldrich).

Table 1. Monofunctional organic acids used for the screening experiments.

	Methane-sulfonic acid	Trifluoroacetic acid	Pyruvic acid	Formic acid	Lactic acid	Vinylacetic acid	Acetic acid	Nonanoic acid
$pK_a$ (25 °C)	-1.900	0.520	2.390	3.750	3.860	4.340	4.756	4.960
molar volume [mL/mol]	64.900	76.600	70.100	37.700	74.400	85.100	57.500	174.900

Table 2. Monofunctional organic nitrogen bases used for the screening experiments.

Name	Tridodecylamine (Alamine 304-1)	Trioctylamine (Alamine 300)	Trihexylamine	Tripentylamine	1,1,3,3-Tetramethylguanidine	1-Methylimidazole
$pK_a$ (25 °C)		~11.0			13.6	7.1
molar volume [mL/mol]	652.5	442.1	337.7	290.8	124.4	79.3

For each screening experiment, equimolar amounts of acid and base were mixed in a 10 ml reactor of the EasyMax apparatus (Mettler-Toledo). The overall volume of the mixture continuously comprises 9 mL. Peltier elements of the EasyMax apparatus kept the reactor jacket temperature at a constant level of 15 °C and both reactants were tempered prior to mixing. After reaching a constant temperature one component was quickly poured into the other while the mixture was intensively stirred. The exothermic effect was then monitored by recording the temperature difference between the reaction mixture and reactor jacket until it remained constant again (Fig 7 (a)).

If we use the EasyMax as a simple calorimeter under isoperibolic conditions, we may assume that the temperature difference  $\Delta T$  is proportional to the overall heat flow between reactor content and reactor jacket. Further, we consider that the main part of the heat flow is being caused by the reaction, while thermal losses are neglected:  $dq_r/dt = f\Delta T + dq_{loss}/dt - dq_{stirr}/dt \approx f\Delta T$  [8] (with  $dq_r/dt$ ,  $q_{loss}/dt$ ,  $q_{stirr}/dt$ : heat flows caused by reaction, by heat losses and by stirring, respectively, f: constant factor). Thus, the area of the first peak in Fig. 7 (a) provides a rough amount for the specific reaction heat of three different amines with acetic acid ( $q_r \approx f\Delta T dt$ ). In the case of the reaction with tetramethylguanidine, a second peak occurs. This effect can be attributed to the crystallization of the neutralization product, which eventually becomes solid.

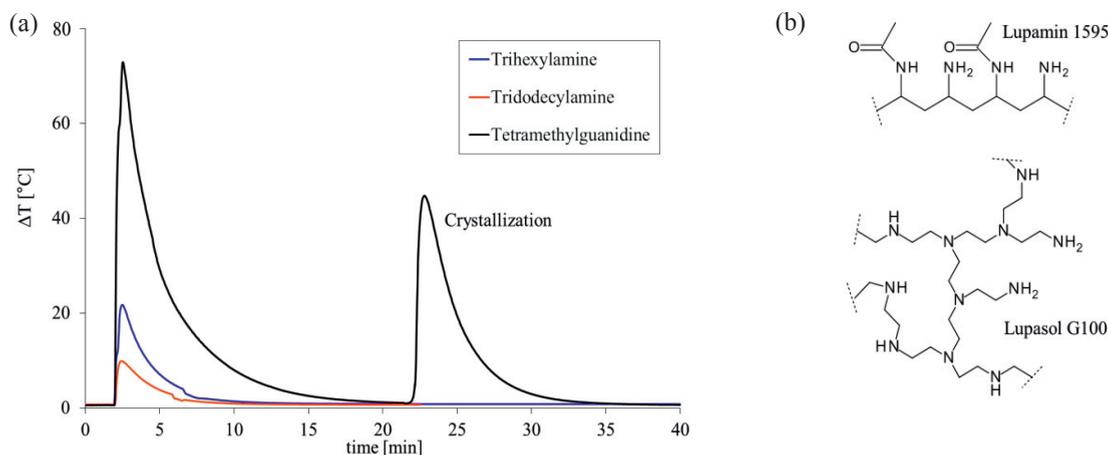
Fig. 7. (a)  $\Delta T$  of reactions between acetic acid and different amines; (b) polymeric amines selected for screening tests

Fig. 8 visualizes the volume-based peak areas as relative energy densities of the investigated reaction systems.

Few combinations lead to solid products, in particular when strong bases such as tetramethylguanidine are involved. As expected stronger acids and bases as well as combinations with small molecules result in higher energy

densities. Furthermore, high concentrations of polymeric amine groups as they exist in the aqueous solution of the branched polyethylenimine Lupasol G100 induce also a high release of thermal energy. Due to its strong dilution mixtures of partially hydrolyzed polyvinyl formamides such as Lupamin 1595 yield rather small energy densities.

The run of screening experiments allows an easy semi-quantitative assessment of energy storage densities for the selected reaction systems in Fig. 8. Further investigations will focus on a more comprehensive characterization of promising reaction systems.

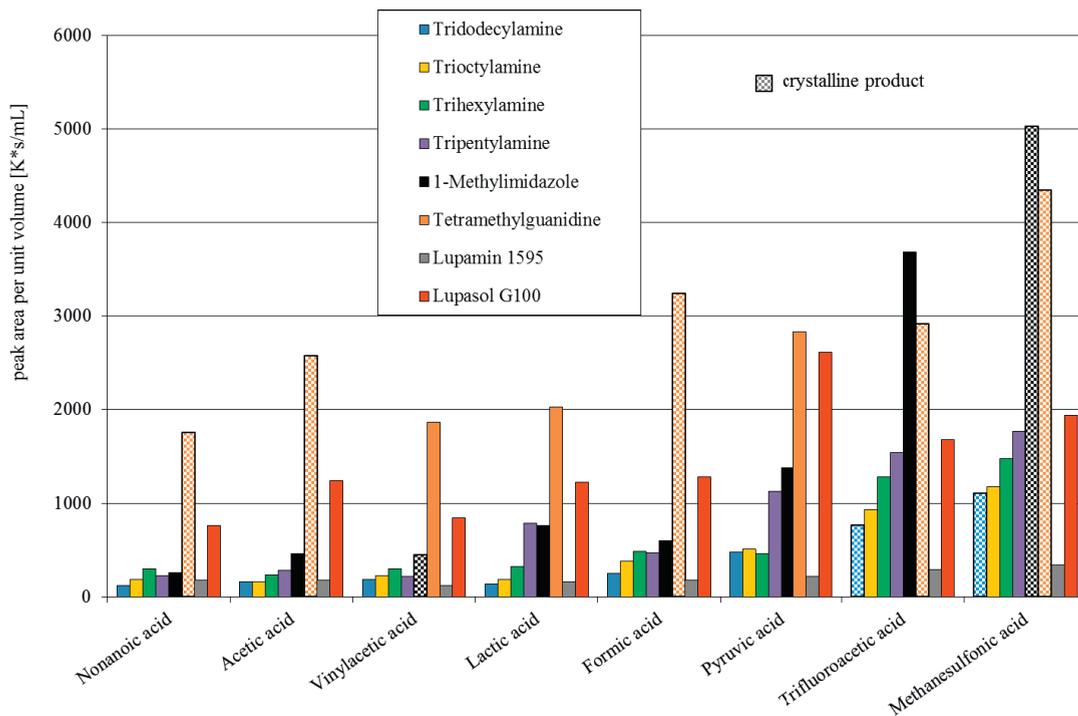


Fig. 8. Screening experiments: Relative energy densities obtained by mixing different organic acids and bases

### 3.3. Characterization and up-scaling

For an adequate assessment of thermochemical storage materials some parameters are of particular interest: energy density, turning temperature and cycling stability. The achievable energy density at a certain working temperature is affected by both the reaction enthalpy, the equilibrium constant  $K$  and the stoichiometry of reaction. We determined these parameters via isothermal calorimetric methods using a differential scanning calorimeter (DSC) and an isothermal titration calorimeter (ITC). To determine the enthalpy of reaction, we initially used an isothermal DSC method with open mixing cells (Fig. 9 (a)). Both reactive components were filled into separated chambers of the mixing cell. One of the educts was added in a 4- to 5-fold molar excess. Then the mixing cell was placed in the calorimeter ( $\mu$ DSC 7 Evo, Setaram). After thermal equilibration at a specific temperature the heat flow measurements gave a stable baseline and the separation between both chambers was removed by pressing a piston. The piston was connected to an electric motor and was used to stir the mixture until the heat flow remained constant again. Fig. 9 (a) exemplifies the typical exothermic peak in the thermogram that is obtained from such isothermal DSC measurements.

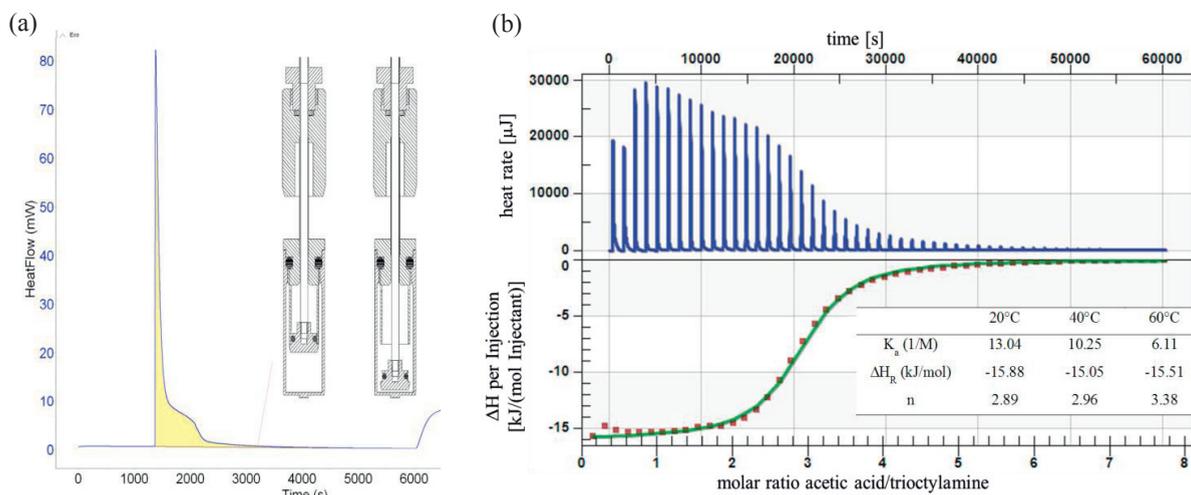


Fig. 9. (a) Isothermal DSC experiment and closed and open mixing cell (Setaram); (b) ITC: titration of acetic acid into trioctylamine

The isothermal titration calorimetry (ITC) can be equally applied to quantify the reaction enthalpy. Moreover, the equilibrium constant  $K$  and the stoichiometry of reaction are also accessible through this. For this purpose we used the instrument TAM III with nano ITC (TA Instruments) and one reactant was added in incremental steps of the same volume to the second reactant. The heat of every titration step was recorded and the values obtained were plotted against both reactants (cf. Fig. 9(b)). The data points had a sigmoid distribution and were fit by a curve that based on a mathematical model of the heat difference (independent model implemented in software “NanoAnalyze”, TA Instruments). Fitting parameters were the stoichiometric ratio  $n$  of the reactants, the change in enthalpy per unit substance amount of titrant and the equilibrium constant  $K$ .

ITC measurements of acetic acid/trioctylamine show the expected decrease of the equilibrium constant  $K$  with increasing temperature (cf. table of Fig. 9 (b)). High temperatures shift the reaction equilibrium from ammonium salt to acid and amine. At the turning temperature  $T^*$  the equilibrium constant  $K$  is equal to “1” [9], which can be consequently achieved from further measurements at higher temperatures.

Although a neutralization of one amine molecule requires just one molecule of acid a ratio of 1:3 (trioctylamine:acetic acid) was determined. This stoichiometry is known for other amine/acid mixtures like triethylamine and acetic acid [10] and is considered as the formation of a stable complex.

Both DSC and ITC apply sample amounts in mg scale and may not mirror the real behavior of the reaction system using large material amounts. Thus, we carried out an additional up-scaling experiment for the system acetic acid and trioctylamine with a laboratory reaction calorimeter (RC1, Mettler-Toledo). Table 3(a) shows the reaction enthalpies obtained by the three different calorimetric techniques. The results of all methods are consistent with those of literature for the neutralization of 1 molar sodium hydroxide solution with 1 molar hydrochloric acid. The outcomes of the system acetic acid and trioctylamine show the same good agreement.

Table 3. (a) Comparison of calorimetric methods; (b) Distillation results

(a)	$\mu$ DSC [kJ/mol]	ITC [kJ/mol]	RC [kJ/mol]	(b)	Recovery [%]	Pressure [mbar]	T <sub>Max</sub> [°C]
1M NaOH + 1M HCl (lit.: -57,6 kJ/mol)	-54,3	-57,0	-57,8	Acetic Acid + Trioctylamine	~ 100	60	150
Acetic Acid + Trioctylamine	-48,4	-45,9	-45,9	Lactic Acid + Triethylamine	94	400	150
				Methanesulfonic Acid + Triethylamine	7	6	200

The equipment of the laboratory calorimeter additionally provides the option to separate the reactants through distillation and this enables a long-term storage of heat. Acetic acid is the more volatile component in the mixture of acetic acid and trioctylamine - it can be easily distilled off under moderate vacuum (cf. Table 3(b)). Nearly 100% of the acid was recovered as a distillate and corresponding IR spectra of the remainder and the distillate confirmed the purity of the recovered reactants. We correspondingly tested the reaction system of lactic acid/ triethylamine and methanesulfonic acid/ triethylamine, wherein the base triethylamine can be potentially removed by distillation. While the main fraction of the amine was recovered from the reaction mixture in the first case, the highly exothermic reaction of methanesulfonic acid and triethylamine was nearly irreversible up to a temperature of 200 °C. This outcome demonstrates the strong impact of the reaction enthalpy on the turning temperature and on the thermoreversibility of the investigated reactions in the low temperature range.

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