



Article Solid–Gas Sorption System for Ammonia Storage and Delivery Driven by Engine Waste Heat for NOx Reduction of Diesel Engine

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Abstract: A new design of a sorption-selective catalytic reduction (SCR) system is proposed to improve ammonia storage density and meet the ammonia demand for high NOx conversion efficiency at a relatively lower temperature (<100 $^{\circ}$ C) compared to urea-SCR systems. The major components are a main unit and a start-up unit that each contain a metal halide ammine as the sorbent. The start-up unit can operate without any external heat source, but spontaneously releases ammonia at the ambient temperature and is only used when the main unit is being warmed up for action. The selection criteria for the metal halide ammine for each unit is discussed. The working pair of SrCl₂ as the main ammine and NH_4Cl as the start-up ammine is further analyzed as an example to be used in the sorption-SCR system for a diesel engine, the NOx emissions of which were experimentally measured in different operation modes. Based on the experimental data of engine emissions and kinetic models of the chemisorption between ammines and ammonia, the dynamic performance of the sorption system with a total capacity of 180 L sorbent composite in different layouts was investigated and compared. It was found that the achievable desorption conversion degree was lower in smaller reactors and was more sensitive to operating conditions in smaller reactors compared to larger reactors. This suggests that a system using a small reactor layout requires some extra volume to completely meet the required capacity compared to a larger reactor layout. However, because systems with large reactors tend to respond slowly, as they have more thermal mass and take a longer time for preparation, there is a design trade-off required to have optimal performance and balance between the main unit and the start-up unit. In the case studied in this work, a system using three rechargeable reactors with a volume of 60 L each was found to be the preferable layout; it could have about a 90% desorption conversion degree and required around 10 min of warm-up time. Meanwhile, the coupled start-up unit should have a capacity of around 165 mL at least.

Keywords: sorption; NOx emissions reduction; SCR; ammonia storage; dynamic performance; metal halide ammine

1. Introduction

Increasingly stringent regulations on the reduction of nitrogen oxide (NOx) emissions have been driving technology development in both combustion and exhaust after-treatment; in particular, the removal of NOx from diesel engine exhaust without compromising fuel economy has received tremendous attention [1–3]. Currently, either a lean NOx trap (LNT) or selective catalytic reduction (SCR) technology is used to control NOx emissions from the engine exhaust, depending on engine size and other factors. For instance, SCR is favored and adopted worldwide for heavy-duty diesel engines as the more cost-effective solution, with higher achievable NOx conversion compared to LNT. More than 99% of new heavy-duty vehicles are diesel in the European Union; therefore, there is an appreciable goal to meet tightening Euro emissions regulations by improving SCR technology.

The SCR technology converts NOx to nitrogen over a catalyst using ammonia as the reductant. Liquid absorption is one of the most common methods for ammonia separation



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and storage [4]. As a low-cost and reversible absorbent, urea has been used in commercial de-NOx products, such as AdBlue, a eutectic 32.5 wt% urea-water that can be injected into the exhaust gas flow for NOx conversion [5]. In addition, ionic liquids (ILs) and deep eutectic solvents (DESs) are researched as alternative green solvents for NH₃ absorption, as they have adjustable structures, higher ammonia storage capacity, and lower volatility than traditional water-based urea solutions [4,6,7]. However, rather than ammonia storage and delivery for SCR reaction, more research focuses on using ILs and DESs to absorb and convert NOx directly [8,9]. There is a dilemma in designing ILs and DESs for ammonia capture. The solubility of ammonia improves with the increasing acidity of solvents, while the increase of acidity will increase the difficulty of the regeneration and storage of solvents [10]. This dilemma limits the performance of ILs and DESs technologies in vehicle applications that require a safe and stable cycle system. A number of drawbacks related to the use of liquid absorption of ammonia, especially urea, encourage the development of alternative solutions for ammonia storage and delivery and are mentioned below [2,3,11,12]:

- The safety issue of liquid-based systems onboard a vehicle;
- The incomplete conversion of urea solution to ammonia at 200 °C forms deposits and even deactivates the SCR catalyst, leading to a sharp reduction of NOx conversion efficiency;
- ➤ Urea solution is corrosive, and the freezing point of −11 °C is too high to avoid freezing in many areas of the world reliably;
- An injector should be carefully designed to disperse fine droplets for evaporation into the exhaust. However, the evaporation of water decreases the exhaust gas temperature, which greatly impacts the activity, especially in the low-temperature region. Additionally, it was found that particles were formed in this injection, which could clog the nozzle [13];
- Mixers and careful design are needed to obtain uniform ammonia concentration at the SCR catalyst face;
- The ammonia storage potential of AdBlue only amounts to 0.201 kg/L (0.184 kg/kg) NH₃/solution, one-third of that of liquefied ammonia.

Some solid compounds have been discussed as alternative means of ammonia storage, with evident improvement in terms of storage density, freezing, and storage stability. These include (1) ammonium salts, for example, ammonium carbamate and ammonium carbonate, which have an ammonia storage density of 0.698 kg/L (0.436 kg/kg) and 0.531 kg/L (0.354 kg NH₃/kg), respectively [3,14–16]; and (2) ammine compounds of metal salts, such as $MgCl_2 \cdot 6NH_3$, $CaCl_2 \cdot 8NH_3$, $SrCl_2 \cdot 8NH_3$. etc., which typically can store at least 2.5 times the ammonia of AdBlue on a volume basis if the compound density is around 1.1~1.3 kg/m³ [3,11,17–21]. Many of these solid compounds can thermally decompose and effectively release ammonia at a relatively low temperature (potentially down to 50~60 °C, considering the atmosphere as the back pressure), and direct gaseous ammonia dosing from these compounds also significantly simplifies the operation of the ammonia delivery system. Systems based on both technologies have been tested for commercial applications, and the use of ammonium carbamate was protected by solid SCR [15,16]. However, unlike the metal ammine compound that releases pure ammonia, the desorption of ammonium salts also yields CO_2 and/or H_2O . Since these are reversible reactions, there is a risk that these resultants recombine to generate solid ammonium carbamate on cold surfaces, which could clog and inhibit dosing systems. Hence, this work focuses only on ammine compounds to explore the feasibility of a solid-gas sorption-SCR system.

A solid sorption cycle based on the reversible chemisorption reaction between metal ammine compounds and ammonia has been researched and developed for decades. With interest mainly in thermal applications such as heat pumps and thermal energy storage. Apart from the aforementioned superiority of ammonia storage compared to AdBlue, it is also advantageous for its higher vapor pressure at a low temperature, so energy consumption for heating the materials is not prohibitive. On the other hand, it has a much lower vapor pressure at ambient temperature compared to liquid ammonia, which is desirable for the safe handling of materials. Ammonia-based chemisorption has the feature of monovariant behavior. This indicates that the kinetics can be controlled on demand by adjusting one thermodynamic parameter, either temperature or pressure. Therefore, the release of ammonia can be tuned to match the NOx emissions by controlling the desorption temperature and/or the backpressure.

Elmøe et al. [12] tested a small reactor containing about 260 g of MgCl₂·6NH₃ with a volume of 785 mL and demonstrated the desorption of MgCl₂·6NH₃, which required heating to at least 184.4 °C to initiate the first phase of desorption when the set-point buffer pressure was maintained at 5 bar. A simple ON–OFF controller with the buffer pressure as the control variable was employed to generate an oscillating varying profile of ammonia out-flow around the set-point pressure. By applying such a controlling strategy under the studied operating conditions, it was found that approximately 99% of the ammonia stored in the salt could be delivered for NOx conversion. Johannessen et al. [11,19,20] designed and studied an ammonia storage and delivery system (ASDS/AdAmmine) with two main cartridges containing the sorbent of chloride ammine compound and a start-up unit, and feasibility and great competitiveness over the urea-SCR system were demonstrated for urban driving conditions. AdAmmine, with a dosing temperature of 100 °C, reduced tailpipe NOx emissions by half compared to the urea-SCR system dosing at 180 °C. An electric heater was integrated within the AdAmmine as the only heat source, and the total usage of electric power could be tuned according to the system size and vehicle power. The start-up unit initially consumed 550 W in high-duty engine applications and 250 W in light-duty engine applications; the main units received 150 W to warm up; afterwards, more power was required [19] for the main units. Johannessen et al. also suggested that a high uniformity (>0.98) of ammonia concentration in a shorter mixing length could be achieved by using an ammonia inlet tube with multiple entry points, which releases ammonia at several positions in the exhaust cross-section to give adequate mixing. A low-pressure drop obstacle can be used to provide efficient turbulent mixing of ammonia vapor with the exhaust gas. It is interesting to note that the early generation of AdAmmine developed by Johannessen et al. was a pure metal compound powder that is mechanically compressed into dense bulk (around 1250 kg/m^3), with an ammonia storage capacity of around 600 g/L [11]; in their later works, a new version of AdAmmine was produced from a veiled special formulation with a usable capacity of 450 g/L [21]. It is well-known that the repeatability of the cyclic performance of dense pure-chemical bulk is questionable due to the expansion and agglomeration of chemical materials within a confined space [22,23].

Jiang et al. [24] compared the theoretical ammonia storage capacity of different metal salts mixed with expanded graphite treated with sulfuric acid (ENG-TSA). The ENG-TSA was used as a matrix to enhance heat transfer properties and to avoid the potential performance degradation caused by swelling and agglomeration associated with pure chemicals [25,26]. It was found that the NH₄Cl-ENG-TSA composite slightly excelled over other salts studied under ideal equilibrium conditions, as it only required one-third of the mass and 80% of volume required by AdBlue to satisfy the same NOx reduction, indicating an ammonia storage capacity of around 250 g/L. The addition of a porous host matrix compromises the volumetric sorption capacity of the bulk sorbents. On the other hand, although NH₄Cl has a higher ammonia storage capacity, its high working pressure will require a thicker reactor wall, resulting in a heavier reaction unit [27]. Thus, Wang et al. [27] concluded that $CaCl_2$ and $SrCl_2$ are better ammoniate choices after comprehensive consideration of ammonia sorption capacity and working pressure.

Zhang et al. [28] proposed four types of the sorption-SCR system based on multifunctional multi-stage ammonia production cycles. The first type used a single ASDS unit to provide ammonia. The second type added an ammonia transfer (AT) unit filled with low-temperature ammoniate to the ASDS unit for a lower starting temperature. Then, an ammonia warning (AW) unit containing high-temperature ammoniate was integrated with the second type to provide NH_3 for NOx conversion when the ammonia output from the main ASDS unit was insufficient. The fourth type combined an ASDS unit and an AW unit into one reactor for a more compact system. The test results of using NH₄Cl, NaBr, CaCl₂, SrCl₂, and MnCl₂ as candidate ammoniates show that adding the AT unit is valuable, as it can ensure the starting temperature at 29–38.2 °C. Although adding the AW unit made the lowest ammonia storage density in the fourth-type system (570 g/L) higher than the lowest ammonia storage density in the second-type system (420 g/L), the highest ammonia storage density was in the second-type system. When using NH₄Cl-ENG-TSA in the AT unit, and CaCl₂ -ENG-TSA in the ASDS unit, the ammonia storage density of the second-type sorption-SCR system can reach 710 g/L, and its minimum required mass of sorbent accounts is 28% the needs of AdBlue to obtain the same amount of ammonia.

There is another influential factor that also should be taken into account, but has been barely discussed in previous research for determining the real size of sorption-based SCR system: the reaction kinetics of the ammine compound. Based on intrinsic kinetics, it is essential to strategically control the thermodynamic conditions, heating conditions, and/or working pressure for the ammonia desorption to meet the demanding mass flow rate of ammonia. However, there is very limited literature on this topic, nor detailed in-depth investigation of dynamic performance.

The present paper proposes a new solid–gas sorption-SCR system design by integrating a secondary reactor as a start-up unit with the main sorption reactors. This small start-up unit should operate spontaneously under cold start conditions to completely eliminate the need for an electric heater, while the main reactor uses the existing waste heat onboard the vehicle, either engine coolant or engine exhaust. Moreover, to obtain more insight into optimal reactor design, this paper investigates the interrelation between reactor sizing and dynamic dosing performance by examining experimental data of NOx emissions from a heavy-duty diesel engine and the chemisorption kinetics of the ammonia–metal ammine compound reaction.

2. Working Principle

The proposed sorption-based SCR system schematic is illustrated in Figure 1, which outlines the integrated design mainly comprised of main reactor(s), one start-up unit, dosing valves, temperature and pressure sensors, and a dosing control unit (DCU). The main reactor(s) is filled with a ammonia sorbent and constructed with sufficient heat exchange space for engine coolant or engine exhaust to flow through for efficient heat transfer. The start-up unit with a comparatively smaller volume contains a secondary ammonia sorbent, which has a lower equilibrium temperature than the main sorbent at the same working pressure. Namely, the desorption of this secondary sorbent occurs at a lower temperature so that it can extract heat from ambient surroundings to carry out endothermic desorption of ammonia. Ideally, the equilibrium pressure corresponding to the ambient temperature should be higher than the engine exhaust pressure (\approx 1 bar) to have the proper equilibrium drop as the driving force. The start-up unit should be thermally isolated from the main reactor to avoid heat exchange.

The *P*–*T* diagram shown in Figure 2 exemplifies the state points of synergistic operation between the main and secondary sorbents. The start-up unit has a pressure higher than the exhaust pressure when at ambient temperature (Point 1 in Figure 2); consequently, when Valve 1 in Figure 1 opens as the engine starts, the desorption in the start-up unit is triggered by the pressure difference and the ammonia is released into the exhaust line. In the meantime, the inside pressure of the main reactor(s) climbs from Point 2 as it is heated by engine coolant, for example. Once the pressure in the main reactor reaches Point 3, where the equilibrium pressure is higher than both the start-up pressure and the exhaust pressure, Valve 2 opens to release the ammonia from the main reactor for NOx conversion. At the same time, the start-up reactor is also receiving ammonia from the main reactor to refill it for the next cold-start operation. A certain amount of equilibrium pressure difference ($P_{ms} > P_{ss} > P_{exh}$), as shown in Figure 2, is required to activate the desorption and drive the process at the desired reaction rate.



Figure 1. Schematics of sorption-SRC system with a start-up unit and main reactors.



Figure 2. Clausius-Clapeyron diagram of the sorption-SCR system.

Temperature and pressure sensors are used in a feedback control algorithm conducted by the DCU to control the backpressure of desorption to ensure sufficient ammonia dosing into the exhaust line at the desired mass flow rates. The DCU communicates with the engine control unit to acquire information on ammonia demand and combines the temperature/pressure feedback to work out the control algorithm and tune the dosing valve for ammonia release.

3. Materials

Composites that consist of metal halide ammines (MHA) and porous matrix have been developed and studied for sorption systems. They benefit system performance with improved thermal conductivity, a supporting porous structure for sufficient mass transfer, and by preventing the storage capacity from degrading over multiple cycles due to swelling and agglomeration of chemicals [25]. In this work, expanded natural graphite treated with sulfuric acid (ENG-TSA) can be used as a supporting matrix. The thermal conductivity of the ENG-TSA composites was reported to be 44 times higher than that of ENG-based consolidate and 400 times higher compared to ordinary granular pure salt, while the permeability is potentially improved by more than 100 times if compared to pure granular salt after adsorption [29].

There is a great number of MHAs that can react with ammonia in a wide temperature range (50~350 °C) [30]. In a complete cycle, they undertake endothermic desorption with ammonia release in one-half cycle and experience exothermic adsorption in the other half cycle when returning to the initial state. The thermodynamic equilibrium of the most commonly studied MHAs with a desorption temperature below 150 °C at atmospheric pressure is plotted in the *P*–*T* Clausius–Clapeyron diagram in Figure 3. The properties of each MHA composite in terms of specific ammonia concentration, ammonia storage density, volume ratio of MHA composite to the AdBlue with the same ammonia content, and equilibrium temperature/pressure of the MHA-NH₃ reaction at some key points are summarized in Table 1, where the bulk density of the composites is assumed at 800 kg/m³, with a mass ratio between MHAs and ENG-TSA of 5:1.



Figure 3. Clausius–Clapeyron diagram of typical metal halide ammines in equilibrium reaction with ammonia.

The first criterion for the candidate MHAs of the start-up unit is that the equilibrium pressure at the ambient temperature should be higher than its backpressure in the exhaust line that is close to atmospheric pressure. Namely, the equilibrium line should be located in the grey-shadowed zone in Figure 3, with the assumed ambient temperature at 25 °C. In this instance, only MHAs No. 1–6 are shortlisted. However, only three of them, i.e., NH₄Cl, NaBr, and BaCl₂, can provide appealing improvement in ammonia storage density compared to AdBlue, as they reduce the volume to less than half of the AdBlue, while the PbCl₂ and SnCl₂ composites are radically ruled out since they have smaller ammonia storage density than AdBlue. Considering the mass transfer issue within the densely compressed composites, the BaCl₂ will be screened out because its equilibrium pressure at

No.

1

2

3456789

10

11

12 13

14

PbCl₂

NaBr

BaCl₂

SnCl₂

CaCl₂

SrCl₂

CaCl₂

 $ZnCl_2$

ZnCl₂

LiCl

MnCh

MgCl₂

278.2

102.97

208.23

189.7

111.68

158.52

111.68

136.69

136.69

42.44 125.84

95.3

3.25

0

0

1 2 2

ambient temperature is lower than 4 bar, which is a recommended threshold of working pressure without the concern of mass transfer limitation [31]. Therefore, NH_4Cl and NaBr are the final candidates for the secondary sorbent in the start-up unit. These two sorbents have the lowest working temperatures at -10.8 °C and -3.7 °C, respectively, at a backpressure of 1 bar, making these two candidates adoptable in cold winter. The sorptions of these two sorbents are formulated as follows:

$$NH_4Cl + 3NH_3 \leftrightarrow NH_4Cl \cdot 3NH_3 + 3\Delta H_r$$
 (1)

$$NaBr + 5.25NH_3 \leftrightarrow NaBr \cdot 5.25NH_3 + 5.25\Delta H_r$$
 (2)

1.04

0.29

0.38

2.28

0.66

0.37

1.07

1.26

1.51

0.44

0.59

0.48

 $-5.1 \\ -3.7$

5.7

17.1

32.0

38.2

42.3

59.0

59.7

62 5

85.1

139.4

4.74 5.24

2.74

1.54

0.68

0.49

0.39

0.15

0.15

0.11

0.04

0.002

Salt	Molecular Weight (g/mol)	Initial Mole of NH3	Final Mole of NH ₃	kg NH ₃ Per kg Composite	NH ₃ g Per Liter Composite	Volume Factor (Norm to AdBlue)	Desorption Temp. (°C, at 1 Bar)	NH ₃ Vapour Pressure (Bar, at 25 °C)
SnCl ₂	189.7	4	9	0.330	264	0.76	-26.9	14.91
NH₄Ĉl	53.5	0	3	0.953	763	0.26	-10.8	5.05

0.242

0.867

0.653

0.110

0.378

0.678

0.233

0.200

0.166

0.572

0.425

0.526

Table 1. The properties of different reactant salts for the composite sorbents [32].

194

693

522

88

303

542

187

160

133

458

340

421

Likewise, the potential MHA candidates for the main reactors could be SrCl₂ and LiCl. Although MgCl₂ has a volume factor of less than 0.5, it requires the demanding condition of high temperature for desorption. The chemical formulas of these two main MHA candidates are expressed in Equations (3) and (4). The salts are specified in Table 1.

$$SrCl_2 \cdot NH_3 + 7NH_3 \leftrightarrow SrCl_2 \cdot 8NH_3 + 7\Delta H_r$$
 (3)

$$LiCl \cdot NH_3 + 2NH_3 \leftrightarrow LiCl \cdot 3NH_3 + 2\Delta H_r$$
 (4)

4. Analytical Methods

8 5.25

8 4

8

8

4

6

6

3

6

6

Limited information about the kinetics of solid–gas sorption between MHAs and ammonia could be found. The authors only found published data for SrCl₂, but unfortunately, none for LiCl. This work will take the analysis and discussion of the potential performance of a solid–gas sorption-SCR system using SrCl₂ as a case study.

The dynamic evaluation of ammonia desorption from sorbent highly depends on the kinetic models used. However, the kinetic models determined by different methods deviate from each other mainly due to the different heat and mass transfer conditions of the used experimental apparatus. To obtain more insights for reactor and system design, the current study used two different kinetic models to analyze the proposed sorption-SCR system. One represents the ideal performance of the sorbent and reactor with extremely good heat and mass transfer, while the other one represents a relatively practical scenario with limited heat and mass transfer.

The kinetic model developed by Veselovskaya and Tokarev is based on the large temperature jump (LTJ) method [33]. A monolayer of sorbent weighing 0.833 g is placed on flat metal support in the LTJ test unit so that the ammonia adsorption and desorption can process with negligible influence of heat and mass transfer. The LTJ method emulates real operation conditions where the adsorption/desorption is driven by a temperature jump at isobaric conditions. The time-dependent variation of conversion degree, x(t), is expressed by the following equation:

$$\mathbf{x}(t) = \exp(-t \cdot k) \tag{5}$$

where *x* is the conversion degree from 0 to 1; the rate constant *k* is believed to have a linear relationship with the temperature equilibrium drop, ΔT_{eq} , as expressed in Equation (6).

$$k = c\Delta T_{\rm eq} = \frac{\alpha \cdot S}{\Delta H_{\rm r} \cdot \Delta N} \cdot \Delta T_{\rm eq} \tag{6}$$

where *S* denotes the surface area of the heat exchanger, equal to the surface of the metal plate $(1.96 \times 10^{-3} \text{ m}^2 \text{ in [24]})$, α is the heat transfer coefficient between the grains and the metal plate, which was calculated as $90 \pm 10 \text{ W/(m}^2\text{K})$ in [33], ΔH_r is the enthalpy of the chemical reaction, and ΔN is the maximal amount of ammonia exchanged; hence, the multiplication of $\Delta H_r \cdot \Delta N$ in Equation (6) represents the total enthalpy change during the adsorption/desorption of the tested composite. The value of *c* can be calculated to be 0.000333 K⁻¹ s⁻¹ based on the parameters given in [33]. ΔT_{eq} is the main driving force for the chemical reaction in the isobaric sorption process, and can be calculated by Equation (7):

$$\Delta T_{\rm eq} = T_{\rm eq}(P_{\rm c}) - T_{\rm c} \tag{7}$$

where T_{eq} is the equilibrium temperature of the sorbent corresponding to the working pressure P_c ; T_c is the constrain temperature, which is equal to the heat-exchanging fluid temperature and approximates the sorbent temperature in the test. Although this model was developed based on BaCl₂ test data, considering the similarity of MHA reaction activity and heat and mass transfer performance on the grain scale, it is reasonable to apply it to other MHAs under similar conditions. The value of *c* for SrCl₂ in the current work was calculated to be 0.000129 K⁻¹ s⁻¹ using the enthalpy change of SrCl₂-ammonia sorption.

Another kinetic model of $SrCl_2$ -NH₃ sorption expressed in Equation (8) was reported by Huang et al. [34] using a test rig that consisted of a cylindrical reactor and an evaporator/condenser. The cylindrical sorbent had a diameter of 150 mm and length of 100 mm, with an 8 mm hole in the center for gas diffusion; the volume of the sorbent was around 1.8 L, and the mass amount was in the magnitude of hundreds of grams.

$$\frac{dx}{dt} = s_{\rm d} \exp\left(\frac{-E_{\rm d}}{RT}\right) (1-x)^{m_{\rm d}} \frac{P_{\rm c} - P_{\rm eq}(T)}{P_{\rm eq}(T)} \tag{8}$$

where *T* is the sorbent temperature and P_{eq} is the equilibrium pressure corresponding to the sorbent temperature. The kinetic parameters s_d , E_d , and m_d were determined as 0.125 s^{-1} , 9000 J/mol and 3.02, respectively, for desorption by fitting to experimental results. This model is intended to be a local model; only the local degree of conversion can be referred to and the use of an experimental global degree of conversion to fit the kinetic model must be avoided. Huang et al. built heat and mass transfer equations together with a kinetic model for small elements to determine those parameters. Hence, theoretically, Huang et al.'s model depresses the influence of heat and mass transfer on kinetics. However, to some extent, the model still reflects the relatively practical performance of the sorbent and reactor with limited heat and mass transfer.

With the calculated desorption rate, the released ammonia flow rate \dot{m}_{NH3} can be calculated by the following equation:

$$\dot{m}_{\rm NH3} = \frac{dx}{dt} \frac{\rho V f}{M_{\rm s}} \gamma M_{\rm NH3} \tag{9}$$

where ρ is the bulk density of the sorbent, *V* is the sorbent volume, *f* is the salt mass fraction in the sorbent, γ is the stoichiometric coefficient of the sorption, and *M*_s and *M*_{NH3} are the molar mass of the salt and ammonia, respectively.

5. NOx Emissions of a Diesel Engine

A heavy-duty diesel engine (Cummins ISBe 5) was experimentally tested to obtain NOx emissions data under different operating conditions. The schematic diagram of the

diesel engine test bench is shown in Figure 4. The specifications of the tested engine are shown in Table 2. All exhausts were measured by a HORIBA[©] MEXA 1600D gas analyzer, and solid particle data were collected by a HORIBA[©] MEXA 1000 SPCS. The diesel engine ran for more than 30 min for warm-up prior to it being considered to have steady-state performance. A more detailed description of this engine test can be found in the previous work [24].



Control unit

Figure 4. Experimental test rig of NOx emissions of diesel engine [24].

Table 2. Specification of the tested diesel engine [24].

Specification	Values			
Engine type	Vertical-inline, turbo-charged, water cooling, 4-stroke			
Cylinder	4			
Chamber	ω type			
Displacement	4.5 L			
Bore \times Stroke	$107~\mathrm{mm} imes124~\mathrm{mm}$			
Max. power	152 kW@2300 rpm			
Max. torque	760 Nm@1400 rpm			
Compression ratio	17.3			
Emissions standard	Euro V			

According to the European stationary cycle, 12 different operation modes with three different rotation speeds (1680 rpm, 1810 rpm, and 1940 rpm) and four load levels ranging from 25% to 100% were tested. The specification of the operation modes is shown in Table 3. The real-time NOx emissions of 10 modes are presented in Figure 5 (the other two curves overlap and tangle with other curves, so they are not shown for the sake of clear presentation). The highest average NOx emission of 196 mg/s occurred in Mode 8 with a 25% load and the highest exhaust flow rate; the lowest average NOx emission of 112 mg/s happened in Mode 6 with the same load, but the lowest rotation speed. The emission data of operation Mode 6 and 8, respectively, representing two extreme cases, will be considered in the performance evaluation and comparison for the proposed sorption-SCR

system. In each operation mode, the instantaneous NOx emission appeared in a slightly wavy profile, but was almost stable with a small amplitude. Therefore, it is sensible to use the average NOx emission for stable engine operation. The average emissions are also presented in Table 3.

Mode	Engine Speed (rpm)	Load (%)	Weight (%)	NOx Emission (mg/s)	NH ₃ Flow Rate Required (mg/s)
1	1680	100	8	132.26	72.34
2	1810	50	10	157.55	86.17
3	1810	75	10	152.06	83.17
4	1680	50	5	159.82	87.41
5	1680	75	5	145.02	79.32
6	1680	25	5	111.67	61.08
7	1810	100	9	142.77	78.09
8	1810	25	10	196.08	107.25
9	1940	100	8	135.04	73.86
10	1940	25	5	172.93	94.59
11	1940	75	5	131.10	71.71
12	1940	50	5	182.10	99.60

Table 3. European stationary cycle test modes and corresponding average NOx emission [24].



Figure 5. Real-time NOx emission in different operation modes, specifications of the operation modes are given in Table 3 [24].

According to the reactions between NOx and NH_3 described by Equations (10) and (11), to fully converse NOx to nitrogen and water, the required molar ratio of ammonia to NOx is 1:1.

$$4NH_3 + 4NO + O_2 \leftrightarrow 4N_2 + 6H_2O \tag{10}$$

$$2NH_3 + NO + NO_2 \leftrightarrow 2N_2 + 3H_2O \tag{11}$$

6. Results and Discussion

The ammonia charging of the start-up unit occurs simultaneously when the SCR chamber receives ammonia dominantly from the main reactors. This requires a pressure difference between the main reactor and the start-up unit. For example, if NH₄Cl, which has an equilibrium pressure of 5 bar at the ambient temperature (assumed as 25 °C in this work), is used as the start-up MHA, the desorption pressure of the main MHA has to be higher than 5 bar to expel ammonia to the start-up unit and SCR chamber at the same time. This therefore sets a threshold of desorption temperature for the main MHA. This work evaluated the performance of the sorption-SCR system using the SrCl₂ (main)/NH₄Cl (start-up) pair based on two different kinetic models, as explained in Section 4. The desorption temperature of the main MHA was set as 80 °C, 90 °C, and 100 °C, with an allowance of more than 1 bar pressure equilibrium drop for the adsorption of the NH₄Cl ammine at the ambient temperature.

In general, a full AdBlue tank is designed to enable the average user to continue driving for one year. The size of the AdBlue tank depends on many factors, including the diesel vehicle's engine and mileage, as well as several additional factors, such as the type of driving, the ambient temperature, or the type of journey. The estimated average use of AdBlue vs. diesel for trucks is between 4% and 8%, so approximately 500 L AdBlue is needed for local distribution in one year [35]. According to the volume factor of SrCl₂ ammine/ENG-TSA composite shown in Table 1, it can be estimated that a sorption ammonia storage system using such a composite needs a main unit with an overall 180 L capacity for one-year operation. Different layouts using different sizes of replaceable reactors (from 10 L to 180 L) were discussed and compared; for example, a possible layout could be 9×20 L, 6×30 L, 3×60 L, 2×90 L, or 1×180 L.

6.1. LTJ Model and Huang et al.' Model

Comparing the dynamic desorption based on two different kinetic models, as shown in Figure 6, the LTJ model represents the more desirable kinetics with a faster reaction rate. In contrast, the curves of Huang's model change rapidly before the desorption conversion degree reaches 0.4. Afterward, the reaction rate slows down quickly, and the ammonia conversion degree hardly changes once it goes beyond 0.8. It is not shown in Figure 6, but the ammonia conversion degree is still lower than 0.9 after 3 h of reaction. The LTJ model reflects relatively pure chemical reaction kinetics in a microscopic grain scale, as the equilibrium drop dominates the evolution and almost eliminates all other possible influences. These excluded influences, such as the heat conduction at the pellet level, should have been coupled into heat transfer property and have a prominent impact on the reaction rate of bulk reactant. Huang et al.'s model was developed by fitting the experimental results on a reactor containing a few hundred grams of bulk reactant. At such a testing scale, besides the dependence of pressure and temperature, the kinetics also involve a function of conversion degree, f(x), which is the term representing the reactant reactivity as the progression of the reaction and the changes in the physical structure of the reactant [36,37]. The reaction rate is directly related to the conversion degree, as shown in Equation (8). The higher the conversion degree is, the lower the reaction rate. The reaction rate drastically decreases when the desorption is halfway through. This implies that the quantity/scale of the bulk MHA directly impacts the reaction rate and the final conversion degree, and therefore the actual capacity of ammonia storage and delivery.

6.2. The Main Reactor

As described in Section 5, when the diesel engine operates at a stable condition, the NOx emissions can be considered at a constant rate; therefore, a stable ammonia dosing rate is required, as given in Table 3. However, it is the nature of the MHA-ammonia chemical reaction that the desorption rate of MHA is an extremely unstable process if it is subject to a fixed constraint pressure and temperature. The desorption is violent within the first few minutes and then slows down quickly. Therefore, the current study proposed using a

pressure valve to adjust the backpressure to achieve stable ammonia dosing. This valve is located downstream of the reactor, but upstream of the exhaust mixer, as shown in Figure 1. The opening area of the orifice of the valve is adjusted by the signal given by the DCU after processing the pressure signal.



Figure 6. Kinetic curves of SrCl2-ammonia desorption based on LTJ model and Huang et al.'s model.

The constraint pressure that should be imposed on the sorbent to generate the ammonia stream at a required flow rate is shown in Figure 7 when the engine operates with the highest NOx emissions (Mode 8). If using the LTJ model, i.e., the heat and mass transfer of the reactor are under ideal conditions, the unrestrained kinetics enable ammonia release for a longer time, and all the ammonia stored in the sorbent composite can be released, regardless of different reactor layouts; the backpressure of desorption can be almost constant, and there is no need for it to go down for the purpose of creating a higher pressure difference to propel ammonia release. The operation duration of the whole unit is almost the same, independent of the heating temperature and layout design. It is noticeable that there is a small point-down tail on the curves of the 10 L reactor; this small tail gradually disappears as the reactor size becomes larger, as shown in Figure 7. Since the LTJ kinetic model has no item directly representing the conversion degree, the calculated conversion degree is solely time-dependent. However, for a comparatively small reactor, the constraint pressure has to decrease to a relatively lower level to release the last bit of ammonia. For a relatively larger reactor, the larger total reactive ammonia ensures that the ammonia dosing can be persistently supplied at a required rate, even when the desorption rate is low as it approaches reaction completion. This is more evident in Equation (9).



Figure 7. Working pressure and desorption conversion degree of sorption-SCR system in Mode 8, calculated with LTJ model and Huang et al.'s model: (a) 10 L reactor; (b) 20 L reactor; (c) 180 L reactor.

The conversion degree of the sorbent has an evident impact on the reaction rate in Huang et al.' model. In the case of a bulk reactor/sorbent with limited heat transfer, as the ammonia content within the sorbent decreases with the evolving desorption, the equilibrium pressure drop should increase to retain the continuously stable ammonia stream at the required flow rate with a given desorption temperature. For this instance, the constraint pressure P_c should decline to create the equilibrium drop required. Once the ammonia conversion degree reaches around 0.4–0.5, it can be observed in Figure 7 that P_c declines drastically; when P_c decreases to 1 bar (exhaust pressure), there is still some ammonia detained within the sorbent.

Figure 8 shows the final desorption conversion degree in each reactor with different volumes and heating temperatures. The value of the conversion degree in a reactor with 100 °C heating temperature for Mode 6 and Mode 8 is an average of 0.86% and 1.05% higher than that with 80 °C heating temperature, respectively, because higher heating temperature leads to higher equilibrium pressure, resulting in a higher equilibrium drop to maintain the required ammonia dosing rate for a longer time. Meanwhile, the reactor volume has a significant influence on the conversion degree. To meet the required ammonia flow rate, a relatively larger desorption rate (dx/dt) is required for a smaller reactor, according to Equation (9), leading to a quicker drop in ammonia content. In a mutual coupling of a vicious circle, the decrease in the value of x results in a declining reaction rate. In this instance, as the desorption is ongoing, a larger equilibrium drop, according to Equation (8), is the only way to achieve the desired desorption rate. However, since there is a floor limit of desorption backpressure, the equilibrium drop cannot infinitely be enlarged with a given desorption temperature. Consequently, when the conversion degree reaches a certain value, the smaller reactor becomes incapable of providing the required ammonia flow rate. For example, for the operation of Mode 6 at the same heating temperature of 80 °C, when the conversion degree reaches 69.1%, the ammonia output from 2.5 L reactor cannot meet the flow rate demand (107.25 mg/s). In contrast, a 10 L reactor can still provide the required ammonia until the conversion degree grows to 80.5%. The actual achievable ammonia storage capacity of a small reactor deviates more from its theoretical expectation than a large reactor. Another obvious indication is that, unlike the results of the LTJ model, the duration of the effective ammonia release in a 30 L reactor is not straightforwardly half that of a 60 L reactor but less; likewise, a 180 L reactor lasts longer than two 90 L reactors combined. Hence, using a layout consisting of small reactors requires a large total volume of the main unit for a certain storage capacity or requires more frequent reactor replacement or ammonia charging. For example, for the operation of Mode 8, a system with a 6 \times 30 L reactor layout would need an extra 25 L sorbent composite to fulfill the total 180 L capacity, not to mention the collateral volume penalty of fitting and piping arrangements between reactors.

6.3. The Start-Up Unit

The start-up unit was adopted to deliver ammonia during the warm-up time of the main unit. As a matter of fact, a layout with a few small replaceable reactors composing the main unit is preferable over one large reactor if considering the warm-up time for the main unit. Since the storage tank and the whole bulk of sorbent should be heated up until the sorbent reaches the desorption point with proper working pressure in order to activate ammonia release, the less its thermal mass, the faster the unit can begin to function effectively. Alternatively, to offset the relatively retarded action at the outset, the size and capacity of the start-up unit can be enlarged so that it can last a longer time before the main reactor is ready.



Figure 8. Desorption conversion degree using three different heating temperatures.

This warm-up time has been calculated using the common design of double-tube reactors for the main unit as an example. In a double-tube reactor, the heat-exchange fluid flows through the inner tube and the solid sorbent is compressed into the annular space between the inner and outer tubes. The geometric parameters of the reactors in different sizes are assumed and given in Table 4. The reactor is not necessarily straight; meandering in multiple U shapes or spiral shapes could be possible, especially for large volume design. According to the ratio of coolant water flow rate to brake power as a function of engine speed [38], the coolant water flow rate can be estimated for engine operation Mode 6 and Mode 8 at about 0.31 ± 0.01 kg/s. The temperature of the coolant water entering the reactor is assumed to be 90 °C. The start-up unit using NH₄Cl/ENG-TAS composite has an equilibrium pressure of around 5 bar at 25 °C and begins to adsorb ammonia when it is subject to a pressure equilibrium drop of 1 bar. This means that the main reactor should be heated and pressurized up to around 6 bar before it can release ammonia for both NOx conversion and for charging the start-up unit. After that, the required volume of the start-up unit can be estimated based on the ammonia storage capacity of the used start-up MHA and the NOx emissions during the warm-up period.

Table 4. Parameters of different reactors and the corresponding start-up units.

	Inner Tube Diameter (mm)	Outer Tube Diameter (mm)	Length (m)	Total System Volume (litre)	Volume of the Start-Up Unit Required (mL)	Warm-Up Time (min)
10 L	20	100	1.35	10.60	91	5.95
20 L	20	100	2.7	21.20	104	6.75
30 L	20	100	4	31.42	117	7.63
60 L	20	100	8	62.83	165	10.78
90 L	20	100	11.95	93.85	219	14.25
120 L	20	100	15.95	125.27	274	17.9
180 L	20	100	23.9	187.71	387	25.25

Table 4 shows the warm-up time required for different sizes of reactors and the required volume of the start-up unit corresponding to different layouts. The warm-up time of the main unit is from 5.95 min to 25.25 min, with the reactor size of the main unit ranging from 10 L to 180 L. Although the start-up volume increases from 0.104 L to 0.387 L,

this volume is at least two orders of magnitude smaller than that of the main unit. As aforementioned, a smaller main unit requires less warm-up time, so the start-up unit can be smaller. However, the volume difference between start-up units for different layouts cannot offset the extra volume required for the layout with smaller reactors compared to that with a larger reactor. In fact, the capacity of the start-up unit onboard the vehicle should be rationally designed greater than that calculated in Table 4 for more reliable operation and resistance to unexpected driving conditions. On the other hand, considering the potential safety issue of ammonia leakage from high-pressure containers (>1 bar) at the ambient temperature in the scenario of eruption, the capacity of the start-up unit should be as small as possible.

Therefore, choosing a layout with a higher conversion degree and shorter warm-up time would be preferable. However, these two values are contradictory. Consequently, a trade-off is necessary for optimal performance, as one or the other is compromised. It is reasonable to compromise the desorption conversion slightly and choose the smaller reactor, i.e., a 60 L reactor, with a much shorter warm-up time and an acceptable conversion degree larger than 0.9.

7. Conclusion

This work studied a new design of sorption-SCR system for improved ammonia storage density and delivery for high NOx conversion efficiency at a relatively lower driven temperature (<100 °C) compared to urea-SCR systems. The system mainly consists of a main unit and a start-up unit that contain, respectively, the main metal halide ammine and a secondary metal halide ammine as sorbents. The selection criteria of metal halide ammine for each unit have been discussed. Taking the SrCl₂ and NH₄Cl as working pairs for an example, the dynamic performance of the sorption system in different layouts has been investigated. Ammonia demand for 100% NOx conversion efficiency was compared between two kinetic models.

Although the actual NOx emissions from engines in real driving conditions are more complex, the European stationary cycle test data of a diesel engine was used to explore the feasibility of this sorption-SCR system as a preliminary study. The modeling results indicated that this system is promising. Some conclusions are given as follows:

(a) Among the commonly used metal halide ammines, NH₄Cl and NaBr can be the ideal candidates for the start-up unit due to their relatively high equilibrium pressure at ambient temperature; and SrCl₂ and LiCl have the potential to be competent as the main metal halide ammine.

(b) A 20 °C growth in desorption temperature can lead to a 1% improvement of utilization efficiency of ammonia storage. Although the volume of the reactor had a significant influence on the conversion degree of the sorbent, larger reactors benefit from the final desorption conversion degree. The conversion degree of a system with a 10 L reactor is 16.6% higher than that with a 2.5 L reactor under a heating temperature of 80 °C for Mode 8. Namely, a larger reactor can release more ammonia than the combination of several small reactors with the same overall sorbent volume.

(c) When the volume of main reactor was increased from 10 L to 180 L, the warm-up time was extended by 19.3 min. Due to the thermal mass of the reactor and the solid sorbent, larger reactors require longer warm-up times before they can effectively deliver the ammonia at the desired flow rate. This necessitates a larger capacity of the start-up unit to cover up the warm-up period and increases the risk of unsatisfied ammonia delivery during non-ideal driving conditions. The optimal design should be a trade-off between the total desorption conversion degree and the warm-up time.

(d) For further work, a more suitable kinetic model based on a reactor design similar to a real system will be needed. A better kinetic model influenced by more practical factors and closer to true kinetic behavior can provide more insights for system design. **Author Contributions:** Conceptualization, C.W. and S.C.; methodology, C.W.; software, C.W.; validation, C.W., S.C. and L.J.; formal analysis, C.W.; investigation, S.C.; resources, Y.W., H.B. and L.J.; data curation, C.W. and S.C.; writing—original draft preparation, C.W.; writing—review and editing, Y.W. and H.B.; visualization, C.W.; supervision, Y.W. and H.B.; project administration, H.B.; funding acquisition, H.B. All authors have read and agreed to the published version of the manuscript.

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Nomenclature

ΔN	Ammonia exchange amount [mol]
ASDS/AdAmmine	Ammonia storage and delivery system
AT	Ammonia transfer
AW	Ammonia warning
ΔH_{r}	Chemisorption enthalpy $[J/mol (NH_3)]$
x	Conversion degree [–]
DESs	Deep eutectic solvents
ρ	Density $[kg/m^3]$
DCU	Dosing control unit
ENG-TSA	Expanded graphite treated with sulfuric acid
R	Gas constant [J/(mol K)]
S	Heat exchange area (m^2)
α	Heat transfer coefficient [–]
ILs	Ionic liquids
LTJ	Large temperature jump
LNT	Lean NOx trap
m	Mass flow rate [kg/s]
MHA	Metal halide ammine
М	Molar mass [kg/mol]
NOx	Nitrogen oxides
т	Parameter in kinetic model [–]
Ε	Parameter in kinetic model [J/mol]
С	Parameter in kinetic model $[K^{-1} s^{-1}]$
S	Parameter in kinetic model $[s^{-1}]$
Р	Pressure [Pa]
k	Rate constant [s ⁻¹]
f	Salt mass fraction in composite $[-]$
SCR	Selective catalytic reduction
γ	Stoichiometric coefficient $[-]$
Т	Temperature [°C]
ΔT	Temperature difference [°C]
t	Time [s]
V	Volume [m ³]
Subscripts	
amb	Ambient
NH ₃	Ammonia
С	Constrains
d	Desorption
eq	Equilibrium
exh	Exhaust
ms	Main salt
sou	Source
SS	Start-up salt

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