Jiang L, Xie XL, Wang LW, Wang RZ, Wang YD, Roskilly AP.

[Investigation on an innovative sorption system to reduce nitrogen oxides of diesel engine by using carbon nanoparticle.](#)

Applied Thermal Engineering 2018, 134, 29-38

Copyright:

© 2018. This manuscript version is made available under the [CC-BY-NC-ND 4.0 license](#)

DOI link to article:

<https://doi.org/10.1016/j.applthermaleng.2018.01.116>

Date deposited:

21/02/2018

Embargo release date:

31 January 2019

This work is licensed under a

[Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International licence](#)

Investigation on an innovative sorption system to reduce nitrogen oxides of diesel engine by using carbon nanoparticle

L.Jiang^{a,b,*}, X.L. Xie^b, L.W. Wang^a, R.Z. Wang^a, Y.D. Wang^b, A.P. Roskilly^b

^a Institute of Refrigeration and Cryogenics, Shanghai Jiao Tong University, Shanghai, 200240, China

^b Sir Joseph Swan Centre for Energy Research, Newcastle University, Newcastle NE1 7RU, UK

Abstract: A novel sorption system is proposed to reduce nitrogen oxides (NO_x) emission, which is regarded as an alternative solution to conventional urea selective catalytic reduction (SCR) technology. Nanoparticle i.e. carbon coated aluminum (Al@C) plays dual roles at the beginning and end of this system. One is used to prepare novel fuel blend, which is expected to reduce NO_x emission due to low fuel consumption. The other is selected for developing composite sorbent for ammonia storage reactor. NO_x emission of a diesel engine is tested in terms of various fuel blends. Based on these testing results, working performance of novel sorption SCR system is evaluated. It is indicated that the lowest annual required mass of composite SrCl₂ with Al@C is about 98 kg, which is one quarter of urea solution. Comparably, the highest annual required volume of urea solution is 25.6% higher than that of composite SrCl₂ with Al@C. Annual required mass ranges from 98 kg to 475 kg whereas annual required volume is in the range from 243 L to 446 L. Feasibility of novel sorption SCR system is further verified, which reveals vast potentials for reducing NO_x emission in terms of conversion efficiency and cost.

Keywords: Selective catalytic reduction, Carbon coated aluminum, Sorption, Composite sorbent

* Corresponding author. Tel. +86-21-34206309

Email: maomaojianglong@sjtu.edu.cn (L. Jiang)

1 Nomenclature

Adblue	Urea solution
Al@C	Carbon coated aluminum
BMEP	Brake mean effective pressure
B0	Diesel
B0E4	Diesel with 4% ethanol
B0E4N30	Diesel with 4% ethanol and 30ppm Al@C
EGR	Exhaust gas recirculation
ENG	Expanded natural graphite
MTS	Middle temperatue salt
LTS	Low temperatue salt
NH ₃	Ammonia
NO _x	Nitrogen oxides
Ni@C	Carbon coated nickel
Q	Heat (kW)
SCR	Selective catalytic reduction
TEM	Transmission electron microscope

2 Greek letters

Δx	Cycle sorption capacity ($\text{kg}^{-1} \cdot \text{kg}^{-1}$)
------------	---

3 Subscripts

am	Ammonia
c	Cycle
de	Desorption
eq	Equilibrium
eva	Evaporation
h	High
i	Theoretical

l	Low
max	Maximum
R	Reaction
r	Real situation
s	Sorption
sor	Sorbent

4

5 **1. Introduction**

6 Since the issue of Volkswagen emissions violation, nitrogen oxides (NO_x) emissions have once again
7 become a hot topic which attracts burgeoning numbers of attentions. NO_x emissions of diesel engine have been
8 verified as a major source for air pollution, which contributes to the formation of smog and acid rain[1]. Thus
9 reducing NO_x emissions has become an urgent challenge for environmental protection and energy saving.

10 It is extensively acknowledged that fuel is not only characterized as power of vehicles but also source of
11 emissions[2]. Thus there are two feasible approaches to realize effective NO_x reduction. One is to decrease the
12 production of NO_x inside engine whereas the other is to take reaction to reduce its emissions. For former
13 methods, exhaust gas recirculation (EGR)[3, 4] is generally considered as a mature technology. Since the exhaust
14 gas replaces some of the excess oxygen in the pre-combustion mixture, it inhibits the production of NO_x .
15 Nonetheless, combustion efficiency of diesel engine is more or less influenced in terms of various working
16 conditions. Also worth noting that development of novel fuel blends by using nanoparticles have been
17 investigated by various researchers for reducing NO_x emissions. Soukht Saraee et al.[5] explored the function of
18 blending cerium oxide and cerium dioxide on engine performance. It was indicated that brake specific fuel
19 consumption and NO_x emissions were decreased by adding nanoparticles. Although nanoparticles have an
20 positive influence on NO_x emissions, the limited improvement could be accomplished, which is usually less than

5%[6]. Another method to reduce NO_x emission is to use dual fuel for diesel engine i.e. ammonia will take effect inside engine. Reiter et al.[7] investigated combustion and emission characteristics of a compression-ignition engine through a dual fuel approach. It was demonstrated that combustion efficiency and emissions were improved by adopting direct ammonia/diesel injection strategies. Later, fumigation of the premixed ammonia was attempted to be applied for a diesel engine. Simulation results revealed that NO_x emissions decreased with little ammonia fumigation and increased with high ammonia fumigation[8]. At present, dual fuel technology for diesel engine mainly concentrates on numerical simulation. It may take a long time to realize real application since the engine is inevitably modified.

From above summary, it is difficult to remarkably reduce NO_x production through improved method in terms of engine part. Thus selective catalytic reduction (SCR) technology is adopted to further reduce NO_x emissions outside engine[9], which is characterized with excellent selectivity with reasonable combustion efficiency remained[10]. For conventional SCR, urea solution (adblue) serves as a source of ammonia to react with NO_x , which will result in some drawbacks i.e. low ammonia storage density, low NO_x conversion efficiency and crystallization at low ambient temperature[11]. In order to further improve NO_x conversion efficiency, various novel catalysts are developed and investigated in catalytic converter of conventional SCR system. Wang et al.[12] developed a novel Cu-chabazite catalyst, which indicated a significant breakthrough for removing NO_x . Li et al.[13] prepared a novel catalyst with a core-shell structure by using a chemical deposition method. Results demonstrated that the catalyst revealed a relatively high NO conversion efficiency at a temperature range from 110°C to 220°C. Due to the limitation of conventional urea SCR system by injecting adblue directly to the catalytic converter, NO_x conversion efficiency could not be further improved only through novel catalysts[14].

Under this scenario, a novel sorption SCR technology is proposed in our previous work, which reveals the advantages of efficient ammonia storage and generation[15]. Monovariant chemisorption reaction process is

flexibly adjusted to external conditions by using various metal halides[16], which has been widely applied for various fields such as refrigeration[17], heat pump[18], energy storage[19] and electricity generation[20], etc. Since ammonia acts as gas form in diesel vehicles, safety of this novel technology could be guaranteed. Composite sorbents have been verified to be a suitable candidate for sorption SCR[21], which could overcome the drawbacks of granular metal chlorides with an improved sorption and desorption characteristic[22]. Recently carbon coated metal and expanded natural graphite (ENG) were investigated as combined additives for enhancing heat and mass transfer performance of composite sorbents[23]. This novel composite sorbents are also expected to have a better performance with regard to sorption SCR technology.

Our previous researches about composite sorbents by using carbon nanoparticles were applied for thermal energy storage. In this paper, a novel sorption SCR system is presented for reducing NO_x of diesel engine by using carbon coated metal. It is the first time that fuel blends are prepared by adding carbon coated aluminum (Al@C). Composite sorbent is developed with Al@C and ENG for improved desorption and sorption characteristic. Performance of novel sorption SCR system is analyzed and compared in terms of various fuel blends and composite sorbents, which reveals combined efficacy on reducing NO_x from source to emission.

2. Concept of sorption selective catalytic reduction

Layout of novel sorption SCR system in diesel vehicle is indicated within the dashed line of Fig.1. Ammonia storage reactor of sorption SCR system could be installed in the position where adblue tank is originally installed, which is on left or right side of the underframe of diesel vehicle. Ammonia storage reactor is nearby the exhaust pipe, which is expected to utilize exhaust heat more conveniently with less modification of original SCR system.

Fig.1. Layout of novel sorption SCR system in diesel vehicle.

The detailed schematic diagram of novel sorption SCR system is demonstrated in Fig.2, which is adopted for further illustrating the layout as shown in Fig.1. As Fig.2a shows, the system is mainly composed of two temperature and NO_x sensors at the inlet and outlet of catalytic converter, an ammonia nozzle, a catalytic converter, a pressure sensor, an electric control unit and an ammonia storage reactor. Since an improved performance is expected by using novel fuel blend, source part i.e. diesel engine is also included in sorption SCR, which is a little different from our previous work with only regard to ending part i.e. emission[21]. The structure of ammonia storage reactor is depicted in Fig.2b. Compared with conventional urea SCR system, there are two major advantages of novel sorption SCR system. One is that sorption reactor could be heated and driven by exhaust gas in stable working condition. The other is that adblue pump won't be required for ammonia storage reactor. The main working processes of novel sorption SCR system for reducing NO_x are as follows:

- (1) Desorption process (NO_x reduction process): In this process, electric heater is used to heat the reactor at the initial stage of starting diesel engine since exhaust temperature could not reach desorption temperature of composite sorbent for desorbing ammonia. In stable working condition, ammonia storage reactor will be heated by exhaust gas. When the outlet NO_x concentration of catalytic converter is higher than standard value, ammonia storage reactor will eject ammonia through nozzle. Ammonia is mixed first and then reacts with NO_x in the catalytic converter. Electric control unit will adjust the injection capacity in this working process until NO_x emission concentration is in the standard range.
- (2) Sorption process (ammonia replenishment process): When ammonia in storage reactor is almost depleted, the reactor will be taken out and replenished in a sorption process. Ammonia storage reactor and liquid ammonia tank will be mutually connected. In this process, the reactor will be immersed and

cooled in ambient cooling medium for releasing sorption heat of Q_s . Liquid ammonia tank is maintained at environmental temperature by consuming evaporation heat of Q_{eva} . When composite sorbent reaches the saturated state, sorption storage process will be finished. The weighing method will be applied to ensure filling capacity. Finally, ammonia is stored in form of chemical potential inside sorption working pair.

Fig.2. Schematic diagram of novel sorption SCR system (a) desorption process; (b) sorption process.

Fig.3 indicates P - T schematic diagram of novel sorption SCR system. During NO_x reduction process, ammonia storage reactor will be heated with exhaust heat Q_{de} at a temperature of T_{de} , which happens at point A. Ammonia will be desorbed and ejected into exhaust pipe through a nozzle, reacting with NO_x in the catalytic

converter. Theoretical equilibrium desorption process should proceed from point A to point B whereas real desorption process is usually non-equilibrium process, which probably proceeds from point A to point B'. Thus real desorption process is displayed with a dashed line. During ammonia replenishment process, the reactor is cooled by cooling medium to release sorption heat Q_s at a temperature of T_s whereas evaporation heat Q_{eva} produced by liquid ammonia tank will be consumed by environmental medium at a temperature of T_{eva} . Sorption process happens from point C to point D. The main reaction processes between NO_x and ammonia could be referred to equations 1-2.

Fig.3. P - T schematic diagram of working processes of novel sorption SCR system.

3. Materials

3.1 Carbon coated metal

As a type of nanoparticles, carbon coated metal is characterized with core-shell structure. Carbon coating plays a role of protecting metal core as external condition, which could maintain excellent core properties.

Fig.4 indicates transmission electron microscope (TEM) image of Al@C and carbon coated nickel (Ni@C), which could refer to our previous work[24]. The encapsulated structure of Al@C could be observed in Fig.4a. It is worth noting that aluminum cores are completely surrounded by carbon shells with a thickness ranging from 2 nm to 4 nm. Fig.4b reveals core-shell structure of Ni@C with a diameter ranging from 30 nm to 100 nm. Core-shell structure of nanoparticles with metallic core and carbon shell could protect metal core in the

sorption/desorption process due to the fact that carbon materials are stable even in severe conditions.

It is suggested that the carbon shell of the nanoparticles consisted of both ordered graphitic layers and amorphous carbon. EDX result shows strong Ni element peaks, further indicating the Ni@C nanoparticles contain Nickel element (Fig. 2(c)). Copper signal is come from the copper mesh as sample holder in TEM observation. The encapsulated structures of Al@C nanoparticles are clearly seen in Figs. 2(d)–(e), where cores with spherical shape and diameter between 50nm and 100 nm are dominant. The TEM images reveal that the aluminum cores are completely surrounded by carbon shells with thickness of only 2 nm to 4 nm, including approximately 6 to 11 ordered graphitic layers. EDX result of Al@C nanoparticles shows a strong Al element peak indicating aluminum element as well(seen Fig. 2(f)). Core-shell structure of the nanoparticles with metallic core and carbon shell could shield metal core from environmental degradation during ammonia adsorption/desorption process because carbon materials are stable even in harsh conditions, providing effective enhancement of thermal conductivity in a long-term.

In order to evaluate the mixing

(a)

(b)

Fig.4. TEM image of carbon coated metal (a) Al@C; (b) Ni@C[24].

3.2 Preparation of novel fuel blends

Two kinds of carbon coated metals i.e. Al@C and Ni@C are selected for comparing their different influence on fuel blends. The developing processes of novel fuel blend are described as follows: carbon coated metal is first mixed with ethanol as surfactant in ultrasonic bath. Then the mixture will be combined with oil in ultrasonic bath for 30 minutes.

Fig.5 indicates the photo of fuel blends by using Al@C and Ni@C. It could be observed that Al@C and Ni@C are well mixed in fuel blends on the first day. After one night, Ni@C particles are almost separated with oil where Al@C still maintains well mixed, which indicates that Al@C is more suitable as an additive for novel fuel blend. Difference of fuel blends by using Al@C and Ni@C is probability related with Van der Waals force between nanoparticles and oil molecules. Van der Waals force of Al@C is stronger than its gravity whereas Ni@C has a stronger gravity than its van der Waals force[26].

In order to seek for an optimal mass ratio of novel fuel blend, different mass ratios of Al@C, i.e. 30 ppm, 60 ppm and 90 ppm are adopted for further comparison which are shown in Fig.6. It is worth noting that sample with a ratio of 30 ppm remains stable during two weeks whereas sample with 60 ppm precipitates some particles on the bottom. Comparably, sample with 90 ppm has a significant deposit. It is demonstrated that phase separation becomes obvious with the increase of mass ratio of Al@C due to the fact there is a weak gel structure of particles in ethanol. This structure results in a strong van der Waals force for particles in suspension.

Fig.5. Fuel blends by using carbon coated metal (a) just finished; (b) one day after.

170

171 Fig.6. Comparison of fuel blends with various mass ratios of Al@C (a) just finished; b) two weeks later.

172

173 3.3 Development of novel composite sorbent

174 Detailed developing processes of novel composite sorbent with ENG and Al@C are illustrated in Fig.7.

175 First, Al@C is dispersed in ethanol with ultrasonic bath for 30 minutes to prevent aggregation (a₁ process).

176 Meanwhile, metal chloride is stirred and dissolved in the water (a₂ process). Then ENG is dried in an oven at a

177 controlled temperature of 120°C for 2 h. ENG, Al@C and metal chloride solution are stirred and mixed together

178 in ultrasonic bath for another 30 minutes (b process). After that, the mixture will be dried in an oven at 200°C for

179 48 h (c process). Composite sorbent is developed, and it will be put into ammonia storage reactor and pressed by

180 a compressing machine (d process). Finally, consolidated composite sorbent of the reactor will be tested (e

181 process), which is to simulate desorption/sorption performance of novel sorption SCR system.

182

Fig.7. Developing process of novel composite sorbent by using ENG and Al@C.

4. Diesel engine testing

Fig.8 indicates the photo of diesel engine bench for exhaust testing, which is mainly composed of a diesel engine, an oil tank, a dynamometer, an intercooler, an air flow meter, a turbo charger and exhaust gas analyzers. A heavy-duty diesel engine is adopted for testing which is produced by Cummins, and detailed information is indicated as in Table 1. A common rail fuel injection system has four solenoid injectors for each cylinder with a maximum pressure of 1800 bar. Through intake system and fuel control system, fuel enters the combustion chamber of diesel engine. Exhaust turbocharger and intercooler is also equipped in the intake and exhaust system to control flowrate and temperature during the combustion process. Eddy current dynamometer is able to achieve multipoint of choice and control. Testing apparatus with their accuracies are listed in Table 2. All exhausts are measured by HORIBA MEXA 1600D gas analyzer.

In this experiment, three different types of fuel blends are selected for further comparison, namely diesel (B0), diesel with 4% ethanol (B0E4) and diesel with 4% ethanol and 30ppm Al@C (B0E4N30).

Fig.8. Photo of engine testing bench.

Table 1. Specification of diesel engine ISBe 5.

Specification	Explanation
Cylinder	4
Chamber	ω type
Peak torque	760 N·m
Displacement	4.5 L
Governed speed	2500 rpm
Stroke	124 mm
Bore	107 mm
Compression ratio	17.3
Emission standard	Euro V

Table 2. The main testing apparatus for testing bench.

Apparatus	Type	Testing scope	Accuracy
Dynamometer	Eddy current	0-230kW	$\pm 0.3R$

Temperature sensor	K	0-1200°C	±0.1°C
Pressure sensors	PTX	0-10 bar	±0.1%
HORIBA	1600D	0-500 g·kW ⁻¹ ·h ⁻¹	±0.2%

Fig.9 demonstrates overall NO_x emissions in terms of different brake mean effective pressure (BMEP) and fuel blends when speed is 1810 rpm. It is demonstrated that overall NO_x emissions by using various fuel blends decrease remarkably with the increase of BMEP. The highest NO_x emission could reach 222.6 mg·s⁻¹ by using B0E4 whereas B0E4N30 reveals the lowest NO_x emission in terms of different BMEP. The reasons are elaborated as follow: It is widely acknowledged that NO_x emission is usually related with fuel consumption. Fuel blend by mixing Al@C have a higher thermal conductivity and lower viscosity than that of other two, which will result in larger heat release. Less fuel will be consumed in this case. Thus overall NO_x emission of novel fuel blend with Al@C will be further reduced.

Fig.9. Overall NO_x emissions vs. different BMEP.

Fig.10 demonstrates instantaneous NO_x emissions by using various fuel blends i.e. B0 (Fig.10a), B0E4 (Fig.10b) and B0E4N30 (Fig.10c) when diesel engine operates under stable working conditions i.e. 30 minutes of warming-up in advance. The highest instantaneous NO_x emission could be obtained when BMEP is 0.25. This is mainly because air-fuel ratio is decreased with the decrease of BMEP. With regard to higher BMEP i.e. higher peak pressure in combustion chamber, NO_x emission will be reduced. Similarly the lowest NO_x emission could be obtained when BMEP reaches 0.93. When BMEP is 0.25, it represents a working condition with a quite low

load, which almost doesn't appear in real operation of diesel vehicle. Thus sorption SCR system will be evaluated based on experimental NO_x emission in terms of high BMEP i.e. 0.5, 0.76 and 0.93.

(a)

(b)

(c)

Fig.10. Instantaneous NO_x emission of different fuel blends vs. time (a) B0; (b) B0E4; (c) B0E4N30.

5. Sorption SCR system

5.1 Composite sorbent characterization

Considering temperature range of exhaust gas and tolerance limit of vehicle materials, middle temperature salt (MTS) and low temperature salt (LTS) could be selected for ammonia storage reactor of sorption SCR system since their desorption temperature is no more than 150°C with regard to 30°C condensation temperature. Several metal chlorides i.e. CaCl₂, SrCl₂, NH₄Cl and BaCl₂ are selected for further comparison in terms of equilibrium desorption temperature, molar mass, maximum cycle sorption capacity, experimental cycle sorption capacity and unit price, which are shown in Table 3. Reaction processes of these sorbents with ammonia could refer to equations 3-8 without sorption hysteresis. Also for chemisorption working pair, working pressure is generally determined by working temperature, which can be according to Clapeyron equation 9. To simplify the description of chemisorption process of sorbents, phrases of CaCl₂ 8/2, SrCl₂ 8/1, BaCl₂ 8/0 and NH₄Cl 3/0 are used in this paper. E.g. SrCl₂ 8/1 represents the process in which SrCl₂ ammoniate reacts with ammonia from 1 moles to 8 moles. Besides, CaCl₂ 8/2 is actually composed of CaCl₂ 8/4 and CaCl₂ 4/2.

It is worth noting that the maximum cycle sorption capacities are evaluated under equilibrium condition whereas experimental sorption capacities are based on real testing condition, which could refer to our previous work[27, 28]. It is indicated that composite NH₄Cl has the largest experimental cycle sorption capacity of 0.65 kg·kg⁻¹ whereas composite BaCl₂ shows lowest value of 0.379 kg·kg⁻¹. Also composite SrCl₂ has the smallest difference between theoretical and experimental cycle sorption capacity whereas composite BaCl₂ has the largest

difference, which is decreased by 41.6%. This is mainly because theoretical sorption capacity is obtained under equilibrium condition i.e. sufficient reaction duration and large temperature driving potential whereas non-equilibrium reaction process proceeds in experiment with limited reaction duration and heat transfer. Prices of metal chlorides could refer to that of China pharmaceutical group. Some metal chlorides are usually in the form of hydrated salts, and their prices are also calculated for granular salts.

Among these composite metal chlorides, it is indicated that composite CaCl_2 and SrCl_2 are suitable to be selected for sorption SCR system when considering both experimental sorption capacity and unit price. Nonetheless, CaCl_2 proceeds two reaction processes in the selected temperature range. Thus two working pressures are generated in the desorption process, which will increase the complexity for electric control and reduce its thermal stability. Therefore, composite SrCl_2 will be selected as an example for further analyzing its performance of novel sorption SCR system.

Table 3. The main parameters of selected metal chlorides.

Sorbent	Equilibrium desorption temperature (°C)	Molar mass (kg)	Maximum cycle sorption capacity $\Delta x_{\max}$ (kg·kg ⁻¹)	Experimental cycle sorption capacity Δx (kg·kg ⁻¹)	Price per kg (RMB)
CaCl_2 8/2	99	110.8	0.93	0.613	60
SrCl_2 8/1	96	158.4	0.75	0.626	100
BaCl_2 8/0	56	208.2	0.65	0.379	68
NH_4Cl 3/0	48	53.4	0.96	0.65	300

$$\ln(P_{\text{eq}}) = -\frac{\Delta H_{\text{R}}}{RT_{\text{eq}}} + \frac{\Delta S}{R} \quad (9)$$

Since composite SrCl_2 is selected for novel sorption SCR system, desorption and sorption characteristic of composite sorbent by using Al@C as the additive are key parameters for further analysis. It is widely acknowledged that global conversion rate, i.e. the percentage of composite sorbent that reacts with the refrigerant, is often used to assess performance of working pairs[29]. Thus global conversion rate of composite SrCl_2 with and without Al@C are experimentally investigated and compared, which is shown in Fig.11. The detailed testing processes by using specially designed testing unit could be referred to our previous work[23]. Desorption and sorption performance are indicated in Fig.11a and Fig.11b, respectively. It is worth noting that composite SrCl_2 with Al@C has a faster desorption and sorption rate than that without Al@C . Al@C will be conducive to reduce sorption and desorption time. When the reaction proceeds 70% of desorption process i.e. global conversion rate is 0.3, it takes about 8.1 minutes for composite SrCl_2 with Al@C , which is about 1.7 minutes less than that without Al@C . Similarly when global conversion rate is 0.7 in the sorption process, it takes 17.9 minutes for composite SrCl_2 with Al@C , which is 3.1 minutes less than that without Al@C under the condition of 10°C evaporation temperature. The faster sorption rate results in less time to fill ammonia storage reactor in the replenishing process, which indicates the higher working efficiency and lower cost. The reduced desorption time will also decrease the heat input for ammonia sorption reactor, which is conducive to overall energy efficiency of diesel vehicles.

Fig.11. Desorption/sorption characteristic of composite SrCl_2 (a) desorption process; (b) sorption process.

5.2 Performance analysis

Since diesel engine mainly operates at 50% load in real application, the concerning testing results of NO_x emission will be selected for investigating the performance of sorption SCR system based on experimental cycle desorption capacity of composite SrCl_2 . Annual required mass and volume are considered as two paramount parameters, which determines the size of ammonia storage reactor for diesel vehicles. Ammonia storage reactor is assumed to be replaced and filled once a year, and annual required mass and volume of composite SrCl_2 and adblue are evaluated by equation 10, which are shown in Fig.12 in terms of different fuel blends.

It is demonstrated that annual required mass of composite SrCl_2 is much less than that of adblue whereas annual required mass of composite SrCl_2 with Al@C is slightly less than that of composite SrCl_2 without Al@C. This is mainly because sorption SCR technology is more conducive to system compactness when compared with conventional urea SCR system. Also worth noting that the lowest annual required mass of composite SrCl_2 with Al@C is about 98 kg, which is almost one quarter of adblue by using the same fuel blend. Comparably, difference of annual required volume between composite SrCl_2 and adblue become closer due to the fact that density of adblue is higher than that of composite SrCl_2 . Moreover, results reveal that the highest annual required

volume of adblue could reach 446 L, which is 25.6% higher than that of composite SrCl_2 with Al@C. By using different SCR technologies, annual required mass ranges from 98 kg to 475 kg whereas annual required volume is in the range from 243 L to 446 L.

$$m_{\text{sor}} = \frac{m_{\text{am}}}{\Delta x_c} \quad (10)$$

Fig.12. Annual required mass and volume of SCR technologies vs different fuel blends (a) mass; (b) volume.

Table 4 shows overall comparison between novel sorption SCR system and conventional urea SCR system in terms of system compactness, fuel consumption, energy input, mechanical and thermal stability, NO_x reduction and total cost. Since less annual required mass and volume could be obtained, system compactness is further improved by novel sorption SCR system. Also worth noting that sorption SCR with Al@C is conducive to fuel consumption, which will reduce NO_x emissions of diesel engine. SCR systems without Al@C don't take effect on fuel consumption.

For sorption SCR system, electric and exhaust heating could be mutually combined. Electric heater is used for heating ammonia storage reactor at initial stage of starting diesel engine since exhaust temperature couldn't reach desorption temperature of composite SrCl_2 . This combined heating mode will not only reduce NO_x emission but also lower the outlet temperature of exhaust, which results in an improved energy efficiency. In

contrast, conventional urea SCR system will consume part of electricity by using adblue pump.

Sorption SCR system by using composite sorbent has a higher mechanical and thermal stability than urea SCR system by using adblue which is flexible to adjust working pressure of ammonia with a higher ammonia content. Also worth noting that sorption SCR could solve the problems such as crystallization or coking by supplying ammonia into the catalytic converter directly rather than adblue through the pump, which could remarkably improve NO_x conversion efficiency. Since Al@C plays dual roles by developing fuel blend and composite sorbents, NO_x will be further reduced by sorption SCR with Al@C than without Al@C. Besides, pump is removed from sorption SCR system, which reduces system complexity. One remarkable fact is that sorption SCR by using Al@C has a lower cost than other two SCR systems due to the fact that less fuel is consumed and no fluid pump is required. In order to further illustrate the advantage of sorption SCR, system cost is compared in details as follow.

Table 4. Comparison between novel sorption SCR and conventional urea SCR.

Type	System compactness	Fuel consumption	Energy input	Mechanical& thermal stability	NO _x reduction	Cost
Sorption SCR with Al@C	High	Reduced	Electricity & Exhaust heat	High	High	Low
Sorption SCR without Al@C	High	No change	Electricity & Exhaust heat	High	Moderate	Moderate
Urea SCR	Moderate	No change	Electricity	Moderate	Low	High

Since system cost is reduced by novel fuel blends and sorption SCR technology, it is reasonable to be analyzed separately. Fig.13a shows the hourly cost by using various fuel blends whereas Fig.13b demonstrates relative fuel consumption in terms of different BMEP. It is indicated that when BMEP is higher than 0.25, fuel of B0E4N30 indicates the lowest cost. This is mainly because B0E4N30 will has a positive relative fuel

consumption whereas B0E4 has a negative relative consumption when compared with that of B0. The highest positive and negative relative consumption is about 0.07 and -0.09, which indicate an improved performance of fuel blend by using Al@C. Also worth noting that when BMEP is 0.25, cost and fuel consumption of B0E4 and B0E4N30 is lower than B0. The reasons are elaborated as follows: for low BMEP, ethanol as a surfactant will result in an ignition delay due to its high evaporation latent heat. Under this scenario, capacity of intake air is increased, and fuel consumption of B0 is lower than that of fuel blends without ethanol. Comparably, fuel consumption of B0E4N30 constantly maintains low with the increase of BMEP due to the fact that Al@C is conducive to heat release. Fig.14 demonstrates cost of various SCR systems i.e. urea SCR, sorption SCR with and without Al@C. It is indicated that cost of sorption SCR system is around two-thirds of adblue system. Sorption SCR without Al@C has a higher cost than that of sorption SCR with Al@C. This is because the larger sorption capacity could be obtained by composite SrCl_2 with Al@C. Since mass ratio of Al@C is relatively small with regard to the total mass of fuel blend and composite sorbent, it almost doesn't increase the cost of sorption SCR system.

Fig.13. Comparison of fuel blends vs. different BMEP (a) fuel cost; (b) relative fuel consumption.

Fig.14. Cost of SCR technologies vs different fuel blends.

6. Conclusions

A novel sorption SCR system is proposed to reduce NO_x emissions of diesel engine by using carbon nanoparticle, in which Al@C plays dual roles for developing fuel blend and composite sorbent. Performance of SCR system with Al@C and without Al@C is analyzed and compared with urea SCR system based on the testing results of different fuel blends. Conclusions are yielded as follows:

[1] Overall NO_x emission of fuel blend decreases remarkably with the increase of BMEP. The highest

NO_x emission could be obtained by using B0E4 whereas B0E4N30 shows the lowest NO_x emission.

For different fuel blends, the highest NO_x emission could be obtained when BMEP is 0.25. When

BMEP is 0.93, the lowest NO_x emission could be obtained.

[2] Composite SrCl₂ by using Al@C has a faster desorption and sorption rate than that without Al@C.

Thus Al@C is conducive to reduce sorption and desorption time. When the reaction proceeds 70% of

desorption process, it takes about 8.1 minutes for novel composite SrCl₂ with Al@C, which is about

1.7 minutes less than that without Al@C. Similarly when global conversion rate is 0.7 in the sorption

process, it takes 17.9 minutes for novel composite SrCl₂ with Al@C, which is 3.1 minutes less than

that without Al@C.

[3] The lowest annual required mass of composite SrCl₂ with Al@C is about 98 kg, which is one quarter

of adblue. Comparably, difference of annual required volume between composite SrCl_2 and adblue become close. Also the highest annual required volume of adblue could reach 446 L, which is 25.6% higher than that of composite SrCl_2 with Al@C. By using different SCR technologies, annual required mass and volume range from 98 kg to 475 kg and from 243 L to 446 L, respectively.

[4] Al@C is conducive to fuel consumption and sorption characteristic which will play dual roles for reducing system cost. Cost of sorption SCR system is about two-thirds of adblue system. Sorption SCR with Al@C has a lower cost than that of sorption SCR without Al@C. Fuel blend and composite sorbent by adding Al@C almost doesn't increase the cost of sorption SCR system.

With high ammonia conversion efficiency and low fuel consumption by using carbon coated metal, the proposed sorption SCR system may be an alternative method to reduce NO_x emission from diesel vehicles. Improved performance could be verified under steady-state condition. The main challenge of sorption SCR is how to accurately control dynamic behavior of sorption storage reactor in the process of NO_x reduction, which is related with chemical kinetics of working pairs. Dynamic performance analysis on this novel technology will be further carried out in our future work.

Acknowledgements

This research was supported by National Natural Science Foundation of China under contract number (51606118), Innovative Research Groups under contract number (51521004) and Heat-STRESS project (EP/N02155X/1) funded by Engineering and Physical Science Research Council of the UK.

References

[1] S.K. Hoekman, C. Robbins, Review of the effects of biodiesel on NO_x emissions, Fuel Processing Technology, 96 (2012) 237-249.

401 [2] L. Chen, Z. Liang, H. Liu, S. Ding, Y. Li, Sensitivity analysis of fuel types and operational parameters on the
 402 particulate matter emissions from an aviation piston engine burning heavy fuels, *Fuel*, 202 (2017) 520-528.

403 [3] M.V. De Pours, A.P. Sathiyagnanam, D. Rana, B. Rajesh Kumar, S. Saravanan, 1-Hexanol as a sustainable
 404 biofuel in DI diesel engines and its effect on combustion and emissions under the influence of injection timing
 405 and exhaust gas recirculation (EGR), *Applied Thermal Engineering*, 113 (2017) 1505-1513.

406 [4] B.L. Salvi, K.A. Subramanian, Experimental investigation on effects of exhaust gas recirculation on flame
 407 kernel growth rate in a hydrogen fuelled spark ignition engine, *Applied Thermal Engineering*, 107 (2016) 48-54.

408 [5] H. Soukht Saraee, H. Taghavifar, S. Jafarmadar, Experimental and numerical consideration of the effect of
 409 CeO₂ nanoparticles on diesel engine performance and exhaust emission with the aid of artificial neural network,
 410 *Applied Thermal Engineering*, 113 (2017) 663-672.

411 [6] A. Fayyazbakhsh, V. Pirouzfard, Comprehensive overview on diesel additives to reduce emissions, enhance
 412 fuel properties and improve engine performance, *Renewable and Sustainable Energy Reviews*, 74 (2017)
 413 891-901.

414 [7] A.J. Reiter, S.-C. Kong, Combustion and emissions characteristics of compression-ignition engine using dual
 415 ammonia-diesel fuel, *Fuel*, 90 (2011) 87-97.

416 [8] A. Boretta, Novel dual fuel diesel-ammonia combustion system in advanced TDI engines, *International*
 417 *Journal of Hydrogen Energy*, 42 (2017) 7071-7076.

418 [9] Z.-b. Xiong, J. Liu, F. Zhou, D.-y. Liu, W. Lu, J. Jin, S.-f. Ding, Selective catalytic reduction of NO_x with
 419 NH₃ over iron-cerium-tungsten mixed oxide catalyst prepared by different methods, *Applied Surface Science*,
 420 406 (2017) 218-225.

421 [10] J. Rodríguez-Fernández, A. Tsolakis, R.F. Cracknell, R.H. Clark, Combining GTL fuel, reformed EGR and
 422 HC-SCR aftertreatment system to reduce diesel NO_x emissions. A statistical approach, *International Journal of*

423 Hydrogen Energy, 34 (2009) 2789-2799.

424 [11] J. Hwang, H.-J. Ha, J. Ryu, J.-J. Choi, C.-W. Ahn, J.-W. Kim, B.-D. Hahn, W.-H. Yoon, H. Lee, J.-H. Choi,
 425 Enhancement of washcoat adhesion for SCR catalysts to convert nitrogen oxide using powder spray coating of
 426 TiO₂ on metallic honeycomb substrate, Catalysis Communications, 94 (2017) 1-4.

427 [12] J. Wang, H. Zhao, G. Haller, Y. Li, Recent advances in the selective catalytic reduction of NO_x with NH₃ on
 428 Cu-Chabazite catalysts, Applied Catalysis B: Environmental, 202 (2017) 346-354.

429 [13] S. Li, B. Huang, C. Yu, A CeO₂-MnO_x core-shell catalyst for low-temperature NH₃-SCR of NO, Catalysis
 430 Communications, 98 (2017) 47-51.

431 [14] B. Samojeden, M. Motak, T. Grzybek, The influence of the modification of carbonaceous materials on their
 432 catalytic properties in SCR-NH₃. A short review, Comptes Rendus Chimie, 18 (2015) 1049-1073.

433 [15] L. Jiang, X.L. Xie, L.W. Wang, R.Z. Wang, A.P. Roskilly, Performance analysis on a novel self-adaptive
 434 sorption system to reduce nitrogen oxides emission of diesel engine, Applied Thermal Engineering, 127 (2017)
 435 1077-1085.

436 [16] H. Bao, Z. Ma, A.P. Roskilly, Integrated chemisorption cycles for ultra-low grade heat recovery and
 437 thermo-electric energy storage and exploitation, Applied Energy, 164 (2016) 228-236.

438 [17] L. Jiang, Y.J. Lu, K. Tang, Y.D. Wang, R. Wang, A.P. Roskilly, L. Wang, Investigation on heat and mass
 439 transfer performance of novel composite strontium chloride for sorption reactors, Applied Thermal Engineering,
 440 121 (2017) 410-418.

441 [18] A. Freni, G. Maggio, A. Sapienza, A. Frazzica, G. Restuccia, S. Vasta, Comparative analysis of promising
 442 adsorbent/adsorbate pairs for adsorptive heat pumping, air conditioning and refrigeration, Applied Thermal
 443 Engineering, 104 (2016) 85-95.

444 [19] M. Gaeini, H.A. Zondag, C.C.M. Rindt, Effect of kinetics on the thermal performance of a sorption heat

445 storage reactor, *Applied Thermal Engineering*, 102 (2016) 520-531.

446 [20] L. Jiang, L.W. Wang, C.Z. Liu, R.Z. Wang, Experimental study on a resorption system for power and
447 refrigeration cogeneration, *Energy*, 97 (2016) 182-190.

448 [21] Z.X. Wang, L.W. Wang, P. Gao, Y. Yu, R.Z. Wang, Analysis of composite sorbents for ammonia storage to
449 eliminate NO_x emission at low temperatures, *Applied Thermal Engineering*, 128 (2018) 1382-1390.

450 [22] L. Jiang, L.W. Wang, Z.Q. Jin, R.Z. Wang, Y.J. Dai, Effective thermal conductivity and permeability of
451 compact compound ammoniated salts in the adsorption/desorption process, *International Journal of Thermal
452 Sciences*, 71 (2013) 103-110.

453 [23] L. Jiang, R.Z. Wang, Y.J. Lu, A.P. Roskilly, L.W. Wang, K. Tang, Investigation on novel modular sorption
454 thermal cell with improved energy charging and discharging performance, *Energy Conversion and Management*,
455 148 (2017) 110-119.

456 [24] Q. Wu, X. Yu, H. Zhang, Y. Chen, L. Liu, X. Xie, K. Tang, Y. Lu, Y. Wang, A.P. Roskilly, Fabrication and
457 thermal conductivity improvement of novel composite adsorbents adding with nanoparticles, *Chinese journal of
458 mechanical engineering*, 6 (2016) 1114-1118.

459 [25] T. Shaafi, K. Sairam, A. Gopinath, G. Kumaresan, R. Velraj, Effect of dispersion of various nanoadditives
460 on the performance and emission characteristics of a CI engine fuelled with diesel, biodiesel and blends—A
461 review, *Renewable and Sustainable Energy Reviews*, 49 (2015) 563-573.

462 [26] J.A. Eastman, S.R. Phillpot, S.U.S. Choi, P. Keblinski, Thermal Transport in Nanofluids¹, *Annual Review
463 of Materials Research*, 34 (2004) 219-246.

464 [27] L. Jiang, L.W. Wang, Z.S. Zhou, F.Q. Zhu, R.Z. Wang, Investigation on non-equilibrium performance of
465 composite adsorbent for resorption refrigeration, *Energy Conversion and Management*, 119 (2016) 67-74.

466 [28] L. Jiang, L.W. Wang, W.L. Luo, R.Z. Wang, Experimental study on working pairs for two-stage

467 chemisorption freezing cycle, Renewable Energy, 74 (2015) 287-297.

468 [29] T. Yan, R.Z. Wang, T.X. Li, L.W. Wang, I.T. Fred, A review of promising candidate reactions for chemical

469 heat storage, Renewable and Sustainable Energy Reviews, 43 (2015) 13-31.

470