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Utilization of alumina-supported K_2CO_3 as CO_2-selective sorbent: A promising strategy to mitigate the carbon footprint of the maritime sector

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ABSTRACT

This paper investigates the application of K_2CO_3 supported onto porous alumina, as sorbent for selective CO_2 capture in marine applications. Alumina-functionalized sorbents were prepared by incipient wetness impregnation achieving K_2CO_3 loadings from 3.6 to 14.1% wt. Carbonation tests were performed in a fixed-bed column at temperatures between 60 and 105 °C, as those typically occurring at the outlet of a scrubber and/or a waste heat recovery unit, with a model diesel engine exhaust (5% vol. CO_2, 5% vol. H_2O, balance N_2). According to the carbonate loading, the sorbents may reach conversion degrees of carbonate up to 90% and overall capture capacity up to 0.66 mol kg^{-1} sorbent. Experimental data showed higher conversion degree and capture capacity compared with unsupported K_2CO_3, which is affected by significant intraparticle diffusion limitations. Steam regeneration tests performed in a fixed-bed column on the sorbent with 3.6% wt K_2CO_3 loading revealed that a temperature of 120 °C assures almost complete recovery of captured CO_2 while preserving the sorbent carbonation degree for 10 consecutive carbonation/regeneration cycles. The preliminary design of a temperature swing carbonation/regeneration unit for on-board ship installation was performed for the reference case study of a passenger ship equipped with a 4.35 MW marine engine fueled with marine gas oil and with a commercial seawater scrubber for SO_2 removal. The proposed unit appeared able to cut up to 30% carbon dioxide emission by using the sorbent containing 3.6% wt K_2CO_3 and operating the carbonation and regeneration stage at 60 and 120 °C, respectively.

1. Introduction

In 2016, there was a record increase in global warming effects caused by greenhouse gases (GHG) and, in particular, by CO_2 emissions, mainly deriving from electricity and heat production, industry and transport sectors [1]. The maritime sector accounts for nearly 2.0% of global CO_2 emissions [2].

Due to the high margins of improvement for ships and engines designs, the European Community set the target of 40% reduction in CO_2 emissions compared to 2005 levels to be achieved by 2050 [3]. This cut is largely expected to be provided by energy efficiency improvements and alternative power generation (as wind or solar energy). Contextually, the Marine Environment Protection Committee (MEPC) of the International Maritime Organization (IMO) recently adopted new regulations (MARPOL 73/78–Annex VI) and guidelines [4,5] to increase energy efficiency on-board ships. Among these measures, the Energy Efficiency Design Index (EEDI) is the parameter that better quantifies the most effective strategies to increase the energy efficiency of new-built ships. The Regulation 21 of IMO MARPOL 73/78–Annex VI established a time route with specific EEDI reduction targets for different classes of ships (according to their type and size). In particular, two size classes are identified for each ship type as a function of its dead weight tonnage (DWT): a 30% decrease of EEDI compared with the 2010 standards should be attained from 2025 onwards for ships belonging to the larger size class.

The most common actions to reduce CO_2 emissions in the maritime sector are mainly related to the improvement of energy efficiency of ships and can be classified into six main groups: hull design, economy of scale, power and propulsion, speed, fuels and alternative energy sources, weather routing and scheduling [5–7]. The recent analysis reported by Bouman et al. [6] and by Di Natale and Carotenuto [7] indicates that the use of biofuels and speed optimization are mitigation

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options with high potential for reducing CO_2 emissions in the maritime sector with conventional internal combustion engines. On the other hand, the Authors also concluded that emission reduction over 75% within 2050 can be only attained by adopting a proper combination of several mitigation measures [6]. In the European Community different projects funded under the European Research and Innovation Framework Program HORIZON 2020 are currently active, aiming at demonstrating at real scale the effectiveness of energy saving and emission reduction technologies in the maritime sector. For example, the LeanShips project (Low Energy And Near To Zero Emissions Ships) aims at developing seven demonstrators that combine several technologies for efficient and less polluting vessels with the targets of up to 25% fuel saving and at least 25% CO_2 reduction (http://www.leanships-project.eu/demo-cases/).

In this framework, the adoption of high-efficiency and low-cost purification technologies for CO_2 capture from flue-gases on-board ships is considered to play a relevant role to achieve the target of reducing the emissions of this greenhouse gas in the naval sector. Currently, few options for post-combustion CO_2 capture from exhaust gases have been proposed for naval applications so far. In 2012, Det Norske Veritas (DNV) and Process Systems Enterprise Ltd. (PSE) developed a design concept for the integration of Carbon Capture and Storage (CCS) units on-board ships based on CO_2 chemical absorption into amine solutions followed by a thermal regeneration step and a final CO_2 liquefaction [8]. However, the use of aqueous amine solutions (e.g. monoethanolamine, MEA) suffers many drawbacks, such as high-energy consumption for solvent regeneration, equipment corrosion and solvent degradation [9]. Recently, Zhou and Wang [10] proposed a CO_2 capture process for marine applications based on the following steps: i) CO_2 absorption into a NaOH solution to form sodium carbonate; ii) reaction of Na_2CO_3 with CaO in the aqueous medium to obtain precipitated $CaCO_3$ with simultaneous regeneration of the caustic soda absorbent. This process is meant to provide the fixation of CO_2 into a solid $CaCO_3$ form (a product with a market value) which avoids the CO_2 liquefaction stage of typical CCS schemes, thus reducing power requirements while saving space on-board [10,11].

Reaction of CO_2 with porous sorbents is a promising technique for CO_2 removal but, to the best of our knowledge, it has not been investigated for maritime applications so far. The interest for on-board ships installation of a CO_2 reactive adsorption unit can be justified by the possibility of using non-hazardous solid materials that circumvent the risks associated with the handling of corrosive, toxic or caustic liquid solutions proposed for CO_2 absorption. Moreover, adsorption has several advantages. For example, due to their design, fixed-bed reactors present high operating flexibility, being able to manage variable inlet concentrations and gas flow rates. This is very important for an unsteady application as for diesel engines. Besides, the tunability of chemico-physical and microstructural properties of sorbents generates a large variety of materials suitable to accomplish the specific tasks [12–21].

However, the potential use of sorbents for CO_2 capture in marine applications should consider the peculiarities of the process at hand. The exhaust gases of low speed marine diesel engines are rarely hotter than 250 °C and, depending on the fuels, contain up to 600 ppm of sulphur [7]. To improve energy efficiency, waste heat recovery units (WHRU) are placed after the engine and the temperature is lowered to a value from 110 to 190 °C, depending on the sulphur content in the fuel: the higher the sulphur content, the higher the minimum temperature.

To reduce sulphur emission below the limits imposed by the MARPOL Annex VI regulation 14 guidelines, seawater scrubber (SWS) are placed after the WHRU. Since sulphur dioxide can compete with carbon dioxide for reactive adsorption with different sorbents, such as metal carbonates or hydroxides, a CO_2 removal unit should be placed after a SWS, if the sulphur content is high, or directly after the WHRU if ultra-low sulphur fuels (ULSF) or LNG are used. In the first case, the CO_2 removal unit should operate at almost 60 °C while, in the second case, it is reasonable for the unit to operate at 110 °C.

Indeed, while these temperatures are critically low for many sorbents, chemically reactive alkali metal carbonates (Na_2CO_3 and K_2CO_3) convert CO_2 into bicarbonates under humid conditions and temperatures below 100 °C [22]. It was also proved that these solids can be regenerated for cyclic applications at temperatures generally lower than 200 °C [22–24]. Besides, carbonates are harmless, easy to handle and store, available worldwide and cost effective, thus representing potentially good candidates for on-board ship applications.

The pertinent literature usually focuses on the use of this class of sorbents for the selective removal of carbon dioxide from exhaust gases of stationary combustion sources, whose compositions are quite different from those of marine diesel engines. In particular, fossil fuel power plant exhausts usually contain CO_2 concentrations around 15% vol., while diesel engine exhausts contain about 5% vol. of CO_2. The lower concentration affects the process performances by reducing the sorbent conversion degree and influencing the process dynamics. However, for a fortuitously condition, the marine diesel engine exhausts contain almost as much water as it is needed by the stoichiometry of the carbonate reaction with CO_2. This means that there is no need to artificially add steam to the gas before the decarbonation process.

In a former experimental study performed by this research group, it was observed that for raw K_2CO_3 having particle size 300–630 μm the maximum sorbent utilization degree was about 2%. This result was ascribed to the occurrence of a shell-and-core reaction mechanism determined by the occurrence of slow intraparticle diffusion rates [25]. Nevertheless, the pertinent literature clearly demonstrated that the dispersion of the active phase onto supports with large surface area (e.g. activated carbons, alumina etc.) determined greater utilization factor of the sorbent and faster reaction kinetics [22,26–30].

This paper aims to provide a preliminary assessment of the potential applicability of alkali metal carbonates for the mitigation of CO_2 emissions from marine diesel engines. To this end, we report results of CO_2 removal from a model flue-gas mimicking the composition of a marine diesel engine exhaust (5% vol. CO_2, 5% vol. H_2O, 90% vol. N_2) by means of potassium carbonate supported onto porous alumina at different active phase loading (3.6, 7.1, 10.5 and 14.1% wt). Experimental carbonation tests were performed in a fixed-bed reactor at different operating temperatures (60, 75, 90 and 105 °C). The sorbent exhibiting the greatest utilization factor of the active phase was subjected to multiple carbonation/regeneration cycles, by performing the carbonation step at 60 °C and the regeneration step using steam at 120–200 °C. The lab-scale results provided indications for the preliminary design of a full-scale CO_2 capture unit for on-board ships application. The reference case study of a Ro-Ro (Roll-On/Roll-off) passenger ship equipped with a 4.35 MW main engine and running over a route of 1 h was analysed. It was assumed that the ship run with a MGO fuel and has a conventional seawater scrubber installed to contain sulphur emissions.

2. Materials and methods

2.1. Sorbent materials

The starting materials used for the preparation of alumina-supported K_2CO_3 sorbents were a commercially available potassium carbonate (Carlo Erba Reagents), as the active phase for CO_2 capture, and a γ-Al_2O_3 (1 mm diameter spheres, supplied by Sasol), adopted as support. The raw substrate bulk density is 770 $kg\,m^{-3}$ with a fixed-bed void fraction of 0.4.

The supported sorbents were prepared by incipient wetness impregnation, namely by adopting a ratio of K_2CO_3 solution volume to substrate mass comparable with the specific pore volume of the raw support, in order to ensure a homogeneous distribution of the active phase. More specifically, a K_2CO_3 aqueous solution, at specific initial concentrations (equal to 0.13, 0.28, 0.44 or 0.63 $g\,mL^{-1}$) was added