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Original Paper

A study on carbon dioxide emissions reduction in marine diesel engines using a chemical carbon absorber

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Abstract: The shipping industry is responsible for a considerable portion of global carbon dioxide (CO_2) emissions, and reducing these emissions is crucial to mitigate the impacts of climate change. In this study, a chemical carbon absorber (CCA) was used to reduce CO_2 emissions from marine diesel engines, and an experiment was performed to determine the efficiency of the method and quantify the reduction achieved. The experiment consisted of injecting 30% and 100% of aqueous CCA into the exhaust gas pipeline via the nozzle of a selective catalytic reduction system. The CO_2 concentration in the exhaust gas before and after the CCA injection point was measured to monitor the CO_2 emission reduction. The results showed that using CCA can reduce CO_2 emissions from the exhaust gas of marine diesel engines. However, further research is needed to optimize the process and improve its efficiency. Three potential areas for future research include installing reductions within the exhaust pipe to increase reaction contact time, recycling waste heat energy from the engine to increase reaction temperature, and improving mixing units to enhance reaction efficiency at higher engine loads. Overall, the results of this study confirm that using CCA technology can reduce CO_2 emissions from marine diesel engine.

Keywords: CO_2 capture, Marine diesel engines, KOH based metal, Selective catalytic reduction, Carbon capture absorber

1. Introduction

Global warming and climate change have become a global issue, leading to various problems such as rising of sea levels, more frequent and severe extreme weather events, and risks to biodiversity and human health. The international community has recognized the gravity of the situation and taken efforts to improve it. Despite the growing concerns, annual emissions from the shipping industry are close to 1 billion tons of carbon dioxide (CO_2), representing approximately 3% of global emissions **[1]**, and continue to increase owing to the rising demand for maritime trade, with projections indicating that emissions will reach 2–3 billion tons by 2050 **[2]**. To address this issue, the international maritime organization (IMO) has established targets to reduce 40% of CO_2 emissions by 2030 and reach net zero greenhouse gas emissions by 2050, in comparison to 2008 levels, in which international shipping was responsible for emitting 794 million tons of CO_2 **[3]**-[**5**]. As the engines of ships are the primary source of CO_2 emissions in shipping industries, the application of CO_2 capture technology to marine diesel engines has emerged as a viable solution.

CO_2 capture technology has already been effectively employed in various industries, such as power plants, and has been found to considerably reduce CO_2 emissions from marine diesel engines. The integration of CO_2 capture technology into marine diesel engines is critical for the long-term sustainability and profitability of the industry, particularly under the pressure of IMO regulations like the energy efficiency existing ship index **[6]** and carbon intensity indicator **[7]**. Furthermore, considering the increasing public demand for a sustainable shipping industry, companies that do not achieve CO_2 emission reductions are expected to eventually lose space in the market. To address these challenges, this study aimed to perform an applied test employing a chemical carbon absorber (CCA) for the exhaust gas of ship internal combustion engines. The three primary CO_2 capture systems for commercial use encompass pre-combustion, oxy-fuel combustion, and post-combustion methods **[8]-[10]**. Among

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these, post-combustion CO_2 capture is the preferred industrial system, as it can treat substantial flue gas volumes and serves as an appealing end-of-pipe solution **[9]-[11]**. In this experiment the post-combustion method was implemented using the selective catalytic reduction (SCR) equipment, which is already installed on existing commercial ships, to confirm whether SCR components including injection nozzle and dosing unit can be utilized.

In this experiment, CCA was injected in concentrations of 30% and 100% into the exhaust gas pipeline through SCR nozzles to confirm the efficiency of CO_2 absorption by the reaction of CCA with exhaust gases. To monitor CO_2 emissions, the emission rate of CO_2 in the exhaust gas before and after the CCA injection point was measured. The CO_2 emission reduction rate was determined and the amount of CO_2 emission was quantified.

This experiment enabled to verify the potential of using CO_2 capture technology in shipping industries **[12]**.

2. Overall system description

2.1 Marine diesel engine

The experiment was conducted under the following conditions. The experiment was aimed to confirm the actual reduction rate of CO_2 by applying CCA to commercially used engines for maritime shipping. CCA, selected as the experiment subject, is an aqueous solution capable of reducing CO_2 by trapping and converting it into sodium carbonate or potassium carbonate, as described in the following chemical reactions **[13]**.

R1	$2KOH+CO_2 \leftrightarrow K_2CO_3+H_2O$	Overall reaction
R2	$K_2CO_3+CO_2+H_2O \leftrightarrow 2KHCO_3$	
R3	$CO_2+OH^- \leftrightarrow HCO_3^-$	Bicarbonate formation
R4	$HCO_3^-+OH^- \leftrightarrow H_2O$	Carbonate formation
R5	$CO_2+H_2O \leftrightarrow H_2CO_3$	
R6	$H_2CO_3+OH^- \leftrightarrow HCO_3^-+H_2O$	
R7	$CO_2(aq)+H_2O \leftrightarrow HCO_3^-+H^+$	
R8	$K_2CO_3 \leftrightarrow 2K^++CO_3^{2-}$	Dissolution of K_2CO_3 in water
R9	$CO_3^{2-}+H_2O \leftrightarrow HCO_3^-+OH^-$	Hydrolysis of CO_3^{2-}
R10	$2H_2O \leftrightarrow H_3O^++OH^-$	Ionization of water

The marine diesel engine used in the experiment was an STX-MAN engine (6 cylinder, in-line type), as shown **Figure 1**, which is mainly used in cargo ships, tankers, Ro-ro vessels, and tugboats. This engine can use multiple types of fuel including marine gas oil, marine diesel oil, and heavy fuel oil, and it emits approximately 100 tons of exhaust gas per hour. The specifications of the diesel engine and fuel are listed in **Table 1 [14]**.

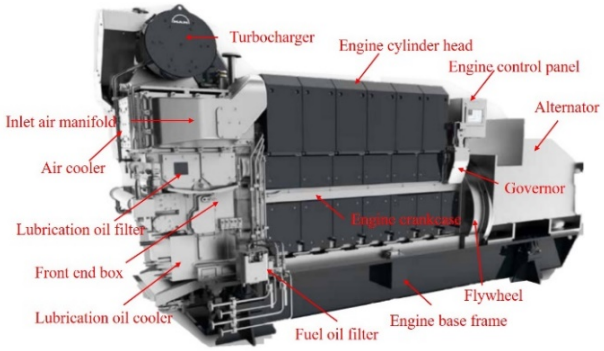

Figure 1: STX-MAN marine diesel engine

Table 1: Specifications for marine diesel engine and fuel

Engine model	STX-MAN 6L21/31-MK1
Cylinder bore × Stroke	210 × 310 mm
Rated power at speed	1320 kw at 900 rpm
Exhaust gas flowrate	Average 310℃
Kind fuel	ISO-F-DMC (ISO 8217 Specifications of marine fuels-2005ed)

2.2 Measurement of CO_2 capture ratio

Horiba MEXA (**Figure 2**), a widely used measurement tool in the maritime field, was selected for the analysis of exhaust gas emissions. The equipment was used to measure the carbon ratio in the generated exhaust gas. The substances measured from the exhaust gas are NOx, CO_2, O_2, and total hydrocarbons (THC) **[15]**. Based on the measurement results, the influence of other environmental pollutants in addition to CO_2 can be confirmed.

Figure 2: Exhaust gas analyzer (Horiba MEXA)

2.3 Measuring and injection equipment

Many ships have SCR systems installed to reduce NOx emissions considering environmental factors. The principle of SCR

systems to reduce NOx is the chemical reaction between urea/catalyst and NOx in the exhaust gas to change from NOx to Nx and H_2O. The STX-SCR system consists of SCR controller, pump unit, dosing unit, mixer, nozzle, catalyst, and reactor, as shown in **Figure 3**. The SCR operation sequence is as follows:

① Exhaust gas emission from engine → ② SCR controller → ③ Pump unit → ④ Dosing unit → ⑤ Nozzle & mixer → ⑥ Catalyst → ⑦ Elimination of NOx from the emission exhaust gas

⑤ step in **Figure 3** is the chemical reaction to produce ammonia from N, N_2 in the exhaust gas as follows **[16]**:

$(NH_2)_2CO \rightarrow (NH_2)2CO\ (s) + H_2O$

$(NH_2)_2CO \rightarrow NH_3\ (g) + HNCO$

$HNCO\ (g) + H_2O \rightarrow NH_3\ (g) + CO_2$

⑥ step in **Figure 3** is the chemical reaction to produce Nx, H_2O from ammonia as follows **[16]**:

$4NO + 4HN_3 + O_2 \rightarrow 4N_2 + 6H_2O$

$2NO + 2NO_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O$

$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$

Through steps ⑤ and ⑥, NOx becomes Nx and H_2O. Exhaust gas analysis (utilizing MEXA equipment in **Figure 2** is conducted in step ⑦ to confirm NOx elimination from the exhaust gas.

For this experiment, the STX-SCR system in **Figure 3** was installed with STX-MAN diesel engine and urea was replaced by CCA to confirm the CO_2 capture rate. The reactor was also replaced by a straight pipe 500 A, as a catalyst was not required, and utilized for NOx reduction.

The applicability of the nozzle for injecting urea and the dosing unit in SCR systems for controlling the injection amount were also examined. Two types of flow meter of the dosing unit were evaluated: electromagnetic type and gear type, whose specifications are listed in **Table 2**. These two types of flow meter were sequentially installed in the dosing unit to check the conductivity of the fluid and confirm the flow detection range. The experiment results indicated that the gear type had a measurement range of 0.1–50.0 L/h, whereas the electromagnetic type had a measurement range of 30.0–120 L/h. Therefore, the electromagnetic type flow meter was selected as the experiment equipment to be installed in the existing dosing unit.

Table 2: Type of flowmeter to apply in the dosing unit.

Flowmeter Type	Electromagnetic type	Gear type
Detection of fluid conductivity	Applicable	Applicable
Detecting range	3~120 liter/h	0.1~50 liter/h

The expected CCA (Concentration: 100% and 30%) consumption at each engine load, as described in **Table 3**, was calculated assuming a CO_2 capture amount of 30%. The spray condition was not an issue.

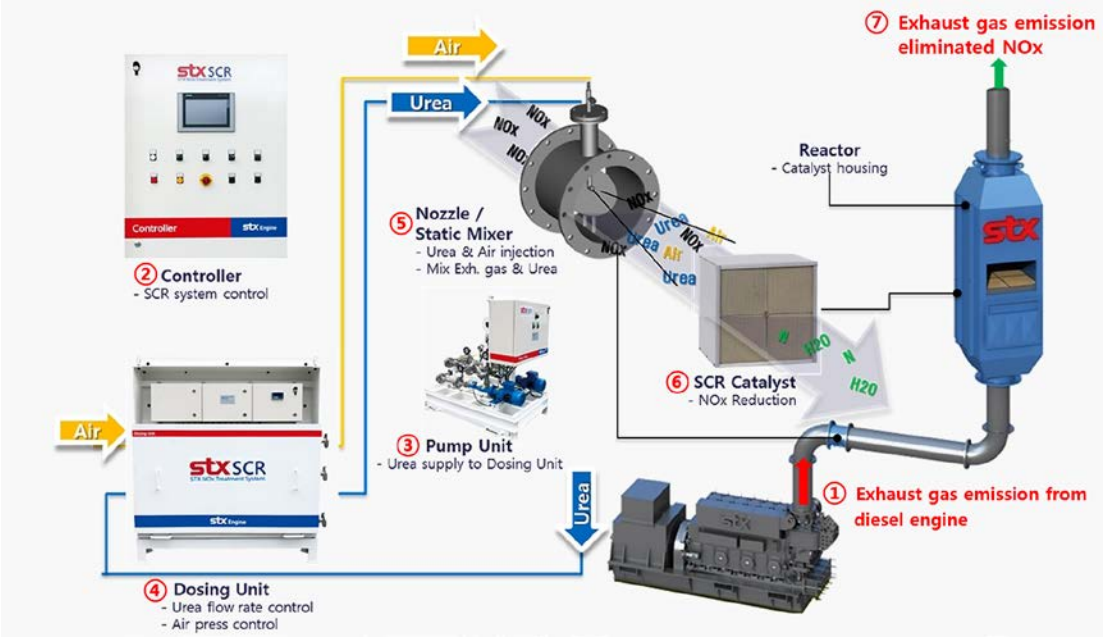

Figure 3: SCR system configuration

Table 3: Estimated CCA consumption rate considering 30% CO_2 capture condition.

Engine load (%)	10	25	50	75	100
Fuel consumption (liter/h)	40.5	76.2	132.0	193.8	263.4
100% CCA consumption (liter/h)	21.1	39.6	68.6	100.8	136.9
30% CCA consumption (liter/h)	61.6	115.8	200.6	294.6	400.3

Equations (1) and **(2)** represent the calculation formulas for consuming 100% and 30% CCA, respectively.

$$100\%\ CCA_{consumption\ rate} = Fuel_{consumption}\ C_f \times 15\% \times 1.1 \quad (1)$$

Equation (1) was used to calculate the expected CCA consumption rate considering a CO_2 emission reduction from exhaust gas of 30% when the CCA was diluted to 100%. The non-dimensional conversion factor, C_f **[17]**, is the ratio of the fuel consumption [g] and CO_2 emission [g] based on the carbon content of the fuel. In this case, the C_f had a value of 3.151040. Based on the result of the experiment, the CCA consumption rate was estimated to be 15% when CO_2 emissions in the exhaust gas were reduced by 30%. Thus, the expected CCA consumption rate to CO_2 emission reduction was calculated by multiplying the fuel consumption by 15%. The final CCA consumption rate was estimated by applying the CCA flow uniformity coefficient of 1.1, which is a factor that accounts for the uneven distribution of CCA in the exhaust gas.

$$30\%\ CCA_{consumption\ rate} = Fuel_{consumption}\ C_f \times 43.79\% \times 1.1 \quad (2)$$

Equation (2) was used to calculate the expected CCA consumption rate to a CO_2 emission reduction from the exhaust gas of 30% when the CCA was diluted to 30%. The non-dimensional conversion factor, C_f, was the ratio of the fuel consumption [g] and CO_2 emission [g], based on the carbon content of the fuel. In this case, C_f had a value of 3.151040. Previous **Equation (1)** indicated that the CCA consumption rate was estimated to be 15% when CO_2 emissions in the exhaust gas were reduced by 30%, based on the result of the experiment. **Equation (2)** is different from **Equation (1)** in that it considers the dynamic viscosity of CCA (9.4 mPa.s). This means that to achieve the same effect of reducing CO_2 by 15%, 2.9256 times more diluted CCA must be injected. The expected CCA consumption rate to CO_2 emission reduction was calculated by multiplying the CCA consumption rate (15%). The final CCA consumption rate was estimated by applying the CCA flow uniformity coefficient of 1.1.

The selection of the flow meter was based on a thorough assessment of the available range of flow supply, calculated CCA consumption rate in **Table 3**, CCA viscosity, and visual inspection of the spray state.

Furthermore, the experiment was conducted considering the flow allowance range of the existing SCR equipment utilized for NOx reduction. The maximum detection range of the electromagnetic flowmeter considering the error tolerance (±2%) confirmed that it can be applied to an engine load of up to 10%. Consequently, the CO_2 capture experiment was conducted with a maximum engine load set at 10%.

2.4 Experimental diesel engine configuration

The configuration of the experiment system was same as that of the pre-existing SCR system installed in ships. This system configuration consists of engine, pipe lines, mixer, nozzle, and exhaust gas analyzer, as shown in **Figure 4**.

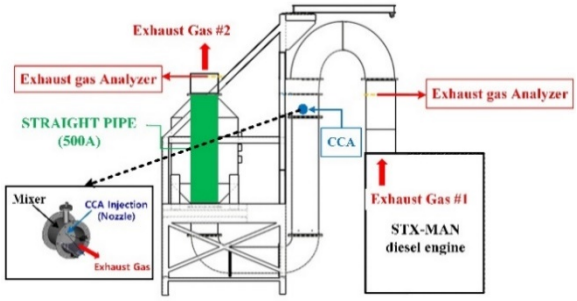

Figure 4: Experiment system configuration.

Figure 5: Experiment facility, STX-MAN diesel engine.

The actual experiment facility, assembled engine, and SCR unit excluding the reactor are shown in **Figure 5**. **Figure 6** shows the simplified flow for the CO_2 capture system in this experiment, indicating the exhaust gas flow and measuring locations before

and after CCA injection. The exhaust gas coming from the engine first traverses an exhaust duct, wherein the CO_2 content undergoes initial analysis (referred to as 'Exhaust Gas #1' in **Figure 4**).

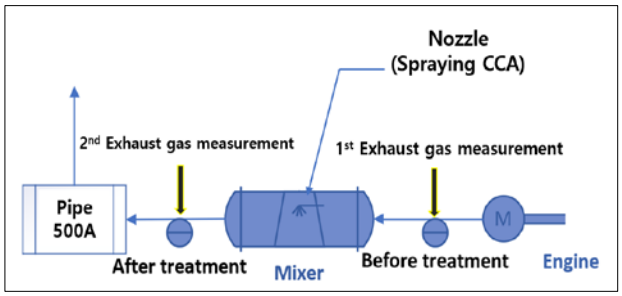

Figure 6: Simplified flow for the CO_2 capture system

The value derived from this analysis serves as the reference for emissions. Subsequently, the exhaust gas is directed through a mixer. Despite inducing an increase in back pressure, the mixer ensures uniform distribution within the exhaust pipe, facilitating the required chemical reactions. Upon the atomization of the CCA in a vaporized state via a nozzle within the mixer, the CO_2 capture process is initiated. In sequence, the exhaust gas passes through a 500A pipe before being expelled externally. Prior to this discharge, the CO_2 content undergoes a secondary analysis (referred to as 'Exhaust Gas #2' in **Figure 4**) within the mixer. The CO_2 capture rate is determined by comparing the primary and secondary analyses values.

3. Experimental conditions and results

3.1 Experiment conditions to measure CO_2 capture rate

The first experiment, as detailed in **Table 4**, was designed to measure the amount of CO_2 captured by the system under different injection amounts of 100% CCA and 30% CCA. During this experiment, the engine was maintained at a load of 0% and the amount of CCA injected into the system was gradually increased. The conditions were set to confirm the CO_2 capture rate according to the change in the amount of CCA.

The second experiment, as detailed in **Table 5**, was conducted to measure the amount of CO_2 captured when a fixed amount of CCA was injected under gradually increasing engine load conditions up to 10%. The conditions were set to confirm the CO_2 capture rate according to the change in the load condition from 0% to 5% and to 10%.

3.2 Experiment result of CO_2 reduction

The first experiment shown in **Figure 7** was conducted to measure the CO_2 capture rate at no load. Case 1 refers to the application of CCA in a concentration of 100% and measurement of the CO_2 emission before and after the mixing pipe.

Table 4: Experiment condition at variable CCA injection amount and engine load 0% for 10 min.

Case No.	Engine load	CCA consumption
Case 1 (100% CCA)	0%	31.0 kg/h
		40.6 kg/h
		50.5 kg/h
		61.2 kg/h
Case 2 (30% CCA)		31.0 kg/h
		40.3 kg/h
		50.0 kg/h
		61.3 kg/h

Table 5: Experiment condition at variable engine load with fixed CCA injection amount for 10 min.

Case No.	Engine load	Fuel consumption	CCA consumption
Case 3 (100% CCA)	0%	21.6 kg/h	61.2 kg/h
	5%	30.6 kg/h	61.2 kg/h
	10%	40.8 kg/h	60.0 kg/h
Case 4 (30%CCA)	0%	21.6 kg/h	61.3 kg/h
	5%	30.6 kg/h	60.0 kg/h
	10%	40.8 kg/h	60.0 kg/h

The CO_2 capture rate was gradually increased with the increase of the CCA injection amount from 31.0 L/h to 61.2 L/h. As shown in **Figure 7**, the CO_2 emission decreased as the injection volume increased. Case 2 refers to the application of CCA in a concentration of 30% and measurement of the CO_2 emission before and after the mixing pipe. As observed in **Figure 8**, the CO_2 capture rate did not considerably change even when the injection quantity increased from 30.1 L/h to 61.2 L/h.

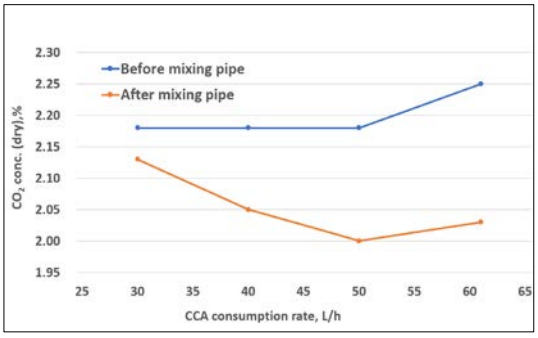

Figure 7: Experiment results at varying CCA (100%) injection amounts with engine load 0%

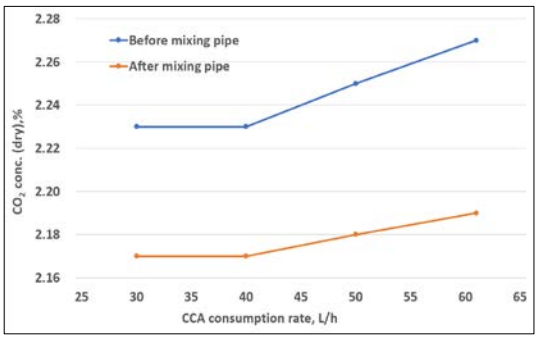

Figure 8: Experiment results at varying CCA (30%) injection amounts with engine load 0%

Table 6: CO_2 capture rate for varying CCA injection amounts with engine load 0%.

Case No.	CCA Injection amount	CO_2 Emission		CO_2 capture rate
		Before reaction	After reaction	
Case 1 (100% CCA)	31.0 liter/h	2.18%	2.13%	2.5%
	40.6 liter/h	2.18%	2.05%	6.1%
	50.5 liter/h	2.18%	2.00%	8.4%
	61.2 liter/h	2.25%	2.03%	9.7%
Case 2 (30% CCA)	30.1 liter/h	2.23%	2.17%	2.3%
	40.6 liter/h	2.23%	2.17%	2.7%
	50.5 liter/h	2.25%	2.18%	3.0%
	61.2 liter/h	2.27%	2.19%	3.1%

Table 6 lists the CO_2 capture rates when the injection amount for each CCA concentration tested (case 1 – 100% and case2 – 30%) was changed at a fixed load. The CO_2 capture rate in case 1 gradually increased up to 9.7%, whereas that in case 2 did not considerably improve. **Figure 9** shows that the carbon capture rate increased as the CCA injection rate increased under 0% engine load with relatively low exhaust gas volume. In addition, considering CCA concentrations of 100% and 30% (CCA diluted in water), the CO_2 capture rate relatively increased as the CCA injection rate increased for a concentration of 100%, whereas it slightly changed for a concentration of 30%. This means that the CCA concentration and injection amount are important factors to obtain better CO_2 capture efficiency. Based on these results, the CCA injection amount and concentration are key factors for achieving an optimized CO_2 capture rate in future investigations or experiments. To further enhance the CO_2 capture efficiency, a pumping control system in the dosing unit could be implemented. This system could utilize a proportional–integral–derivative control with a feedback mechanism to optimize the injection process.

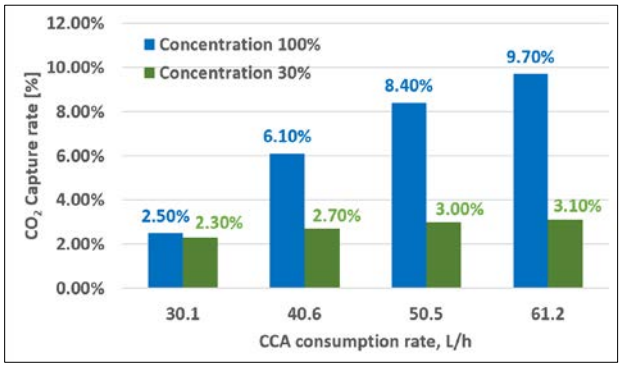

Figure 9: CO_2 capture efficiency results according to CCA concentration at 0% engine load

Table 7: CO_2 capture rate at varying CCA injection amounts and varying engine loads.

Case No.	Engine Load (%)	CCA Injection amount	CO_2 Emission		CO_2 capture rate
			Before reaction	After reaction	
Case 3 (100% CCA)	0%	61.2 kg/h	2.25%	2.03%	9.7
	5%	61.2 kg/h	3.04%	2.80%	7.8
	10%	60.0 kg/h	2.23%	3.52%	6.3
Case 4 (30% CCA)	0%	61.3 kg/h	2.23%	2.17%	3.1
	5%	60.0 kg/h	3.05%	2.97%	2.6
	10%	60.0 kg/h	3.76%	3.68%	2.3

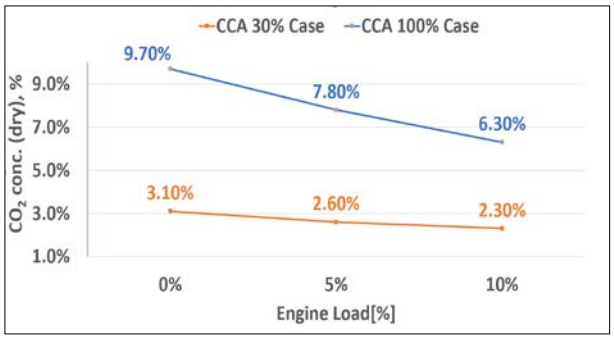

Figure 10: Experiment results for varying engine loads and CCA concentrations of 100% and 30%

Cases 3 and 4 in **Table 7** were expanded from Cases 1 and 2, respectively. Experiments were conducted on CO_2 reduction by sequentially increasing the load to 0%, 5%, and 10%. **Figure 10** is a schematic of the CO_2 reduction amount, confirming that the reduction amount depends on the load.

As shown in **Figure 11**, the CO_2 capture rate was higher for 100% CCA compared to the case with 30% CCA for all engine loads tested. Based on the experiment results, as the engine load

increased, the exhaust gas volume increased proportionately.

Therefore, a larger injection volume is required to achieve an optimal CO_2 capture efficiency. Additionally, a higher CO_2 capture rate can be expected as the CCA concentration increases.

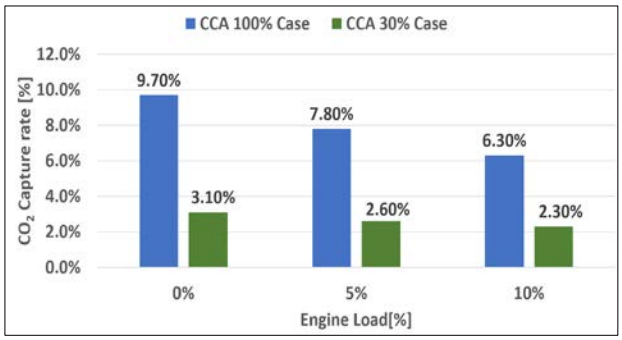

Figure 11: CO_2 capture efficiency according to engine load (0%, 5%, and 10%) and CCA concentration (100% and 30%)

4. Conclusion

In this study, CCA was investigated as a CO_2 capture agent for the exhaust gas of a marine diesel engine. The experiment was conducted under conditions that closely resemble those of a currently operating engine of a ship, without the use of additional devices or equipment to increase CO_2 capture.

The results indicated that the CO_2 capture rate increased as the CCA concentration and injection flow rate increased. The maximum capture rate achieved using 100% concentration of CCA was 9.7% at 0% load, 7.8% at 5% engine load, and 6.3% at 10% engine load. However, the results also indicated that the reaction time between CCA and the exhaust gas decreased as the engine load increased, leading to a decrease in CO_2 capture efficiency.

By addressing these study areas, the CO_2 capture efficiency of marine diesel engines could be improved, contributing to reducing greenhouse gas emissions from shipping.

Future research can include improving the mixing unit to extend the reaction time for more efficient reactions between exhaust gas and CCA at higher engine loads. It could also include research on capturing the chemical reaction products of CCA, such as potassium carbonate and H_2O, and using them as ballast water or desiccants on ships.

Author Contributions

Conceptualization, K. S. Ko; Methodology, Y. G. An; Formal Analysis, Y. G. An; Investigation, K. S. Ko; Resources, Y. G. An; Data Curation Y. G. An; Writing-Original Draft Preparation, K. S. Ko; Writing-Review & Editing, Y. D. Son; Visualization, Y. G. An; Supervision, Y. D. Son.

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