

Martin Haaf

# **Utilization of Waste-Derived Fuels in the Carbo-nate Looping Process: Experimental Demonstra-tion and Techno-Economic Assessment**



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Demonstration and Techno-Economic Assessment





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Vom Fachbereich Maschinenbau  
an der Technischen Universität Darmstadt  
zur  
Erlangung des Grades eines Doktor-Ingenieurs (Dr.-Ing.)  
genehmigte

## **Dissertation**

vorgelegt von

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aus Wertheim am Main

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# Preface

The Ph.D. thesis "Utilization of Waste-Derived Fuels in the Carbonate Looping Process: Experimental Demonstration and Techno-Economic Assessment" was developed during my work as research scientist at the Institute for Energy Systems and Technology (EST) at the Technische Universität Darmstadt between October 2014 and December 2019.

I would like to thank Prof. Dr.-Ing. Bernd Epple, the Head of the Institute and supervisor of my Ph.D. thesis for the possibility to conduct my own research under his supervision.

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# Abstract

The economic and environmental threat of climate change due to the anthropogenic rise of the CO<sub>2</sub> concentration in the earth's atmosphere is widely accepted and addressed. Several pathways are being considered in order to diminish the emissions of CO<sub>2</sub> at sufficient mass and time scale. In addition to efficiency improvements, the reduction of energy consumption and the intensive utilization of renewable energy sources such as wind, solar and biomass, the application of carbon capture and storage processes in energy-intense industries seems to be unavoidable.

Through these processes, the CO<sub>2</sub> contained in an exhaust gas stream is separated, purified and subsequently stored in an appropriate long-term storage side. Balancing the CO<sub>2</sub> emissions along the whole process chain, CO<sub>2</sub> reductions of more than 90 % are feasible. The process of CO<sub>2</sub> capture from the respective exhaust gas streams represents the most energy-intensive part of such a process chain which leads to growing research activities in the field of CO<sub>2</sub> capture processes. The carbonate or calcium looping (CaL) process is a second generation CO<sub>2</sub> capture process based on the reversible reaction of calcium oxide and CO<sub>2</sub>. The limestone-based sorbent is exposed to cyclic carbonation-calcination reaction regimes, which is realized by means of two interconnected fluidized bed reactors.

In addition to traditional energy-intensive industries such as fossil-fired thermal power plants or the production processes for steel and clinker, waste-to-energy (WtE) plants represent a stationary CO<sub>2</sub> emitter that is reasonably large for the integration of carbon capture and storage processes. WtE plants are predicted to be widely used in future waste treatment strategies, which increases the need to cope with the related CO<sub>2</sub> emissions even further. Due to the organic waste fractions, part of the emitted CO<sub>2</sub> is regarded as carbon-neutral. Once this part is captured and stored, negative CO<sub>2</sub> emissions are feasible, thus CO<sub>2</sub> is removed from the atmosphere.

This thesis evaluates the utilization of waste-derived fuels in the CaL process. In the first step, the feasibility of continuous CO<sub>2</sub> capture by means of a waste-derived fuel fired CaL process was successfully demonstrated by experimental investigations at a 1 MW<sub>th</sub> pilot plant. In these investigations, the boundary conditions were adapted to an application in WtE plants. Over the course of the test series, it was shown for the first time worldwide that CO<sub>2</sub> capture rates of more than 90 % are feasible, while the CaL process was fueled by commercially available solid recovered fuel.

Based on the experimental data, a CaL process was validated and subsequently applied for the determination of heat and mass balances for the retrofit of a 60 MW<sub>th</sub> WtE plant. The techno-economic assessment bases on the key performance indicators such as levelized cost of electricity (LCOE) and the cost per avoided CO<sub>2</sub> (CAC). It was found that the LCOE increases from 80 EUR/MWh<sub>e</sub> up to 176 EUR/MWh<sub>e</sub> in case of the CaL retrofit. This further leads to CAC of 112 EUR/t<sub>CO2,av</sub>. Even though this cost range seems high, it needs to be noted that the application of the CaL process in the framework of WtE plants represents a cost-efficient solution for the achievement of negative CO<sub>2</sub> emissions in comparison to competitive negative emission technologies.



# Kurzfassung

Die wirtschaftlichen und ökologischen Gefahren des Klimawandels aufgrund des anthropogenen Anstiegs der CO<sub>2</sub>-Konzentration in der Erdatmosphäre sind weithin anerkannt. Es werden verschiedene Ansätze zur Reduktion dieser CO<sub>2</sub>-Emissionen diskutiert. Neben Effizienzsteigerungen, der Reduzierung des Energieverbrauchs und der Nutzung erneuerbarer Energiequellen wie beispielsweise Wind, Sonne und Biomasse scheint die Anwendung von Verfahren zur Abscheidung und Speicherung von CO<sub>2</sub> in energieintensiven Industrien unumgänglich zu sein.

Hierbei wird das in einem Abgasstrom enthaltene CO<sub>2</sub> abgetrennt, aufbereitet und anschließend in Langzeitlagerstätten gespeichert. Bei einer Bilanzierung der CO<sub>2</sub>-Emissionen entlang der gesamten Prozesskette sind CO<sub>2</sub>-Reduktionen von mehr als 90 % möglich. Der Prozessschritt der CO<sub>2</sub>-Abscheidung stellt hierbei den energieintensivsten Teil dar, was zu wachsenden Forschungsaktivitäten im Bereich der CO<sub>2</sub>-Abscheideverfahren führt. Das Carbonate- oder Calcium-Looping (CaL) Verfahren ist ein CO<sub>2</sub>-Abscheideverfahren der 2. Generation, welches auf der reversiblen Reaktion zwischen Kalziumoxid und CO<sub>2</sub> beruht. Das auf Kalkstein basierende Sorbents ist hierbei zyklischen Karbonisierungs-Kalzinierungsreaktionsregimen ausgesetzt, die innerhalb zweier, miteinander gekoppelter Wirbelschichtreaktoren realisiert werden. Der Wärmebedarf des CaL-Prozesses wird durch eine Oxyfuel-Verbrennung von zusätzlichem Brennstoff gedeckt.

Neben den traditionellen energieintensiven Industrien wie fossil-befeuerete, thermische Kraftwerke oder den Produktionsprozessen für Stahl und Klinker stellen Müllverbrennungsanlagen (MVA) einen stationären CO<sub>2</sub>-Emittenten dar, der für die Integration von CO<sub>2</sub>-Abscheidungs- und Speicherprozessen angemessen groß ist. Es ist zu erwarten, dass Müllverbrennungsanlagen in Zukunft im großen Umfang in Abfallsorgungsstrategien berücksichtigt werden, was die Notwendigkeit, die damit verbundenen CO<sub>2</sub>-Emissionen zu bewältigen, noch weiter erhöht. Aufgrund der organischen Abfallfraktionen wird ein Teil des emittierten CO<sub>2</sub> als klimaneutral angesehen. Sobald dieser Teil abgetrennt und gespeichert wird, sind negative CO<sub>2</sub>-Emissionen möglich, wodurch bereits emittiertes CO<sub>2</sub> aus der Atmosphäre entfernt wird.

Diese Dissertation bewertet die Nutzung von Ersatzbrennstoffen (EBS) im CaL-Prozess. Im ersten Schritt konnte die CO<sub>2</sub>-Abscheidung aus einem MVA-ähnlichen Abgas durch einen EBS-gefeuerten CaL-Prozess anhand von experimentellen Untersuchungen im 1 MW<sub>th</sub>-Maßstab erfolgreich nachgewiesen werden. Im Rahmen der Versuchsreihen wurde weltweit erstmals gezeigt, dass CO<sub>2</sub>-Abscheidungsraten von mehr als 90 % realisierbar sind, während der CaL-Prozess mit kommerziell erhältlichen EBS befeuert wird.

Basierend auf den experimentellen Daten wurde ein CaL-Prozessmodell validiert und anschließend zur Bestimmung von Massen- und Energiebilanzen für die Nachrüstung einer MVA eingesetzt. Die technisch-wirtschaftliche Bewertung basiert auf wichtigen Leistungsindikatoren wie den Stromgestehungskosten und den CO<sub>2</sub>-Vermeidungskosten. Die Stromgestehungskosten einer MVA steigen im Falle einer CaL-Prozess Nachrüstung von 80 EUR/MWh<sub>e</sub> auf ca. 176 EUR/MWh<sub>e</sub>. Dies führt weiter zu CO<sub>2</sub>-Vermeidungskosten von ca. 112 EUR/tCO<sub>2,vermieden</sub>. Auch wenn diese Kostenspanne relativ hoch erscheint, ist zu beachten, dass die Anwendung des CaL-Prozesses im Rahmen von MVAs einen kosteneffizienten Weg zur Erzielung negativer CO<sub>2</sub>-Emissionen darstellt.



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# Nomenclature

## Latin symbols

$a$	Decay constant of the solid volume fraction in the lean region	[1/m]
$A$	Cross-section area	[m <sup>2</sup> ]
$a_1, a_2$	Limestone specific deactivation parameter	[–]
$A_i$	Abrasion coefficient	[wt. %/h]
$A_{incr}$	Incremental abrasion coefficient	[wt. %/h]
$A_{tot}$	Total cumulative sorbent abrasion coefficient	[wt. %]
$b$	Limestone specific deactivation parameter	[–]
$c$	Concentration	[mol/m <sup>3</sup> ]
$CAC$	Cost of CO <sub>2</sub> avoided	[EUR/t <sub>CO<sub>2</sub>,av</sub> ]
$d$	Diameter	[m]
$d_p$	Particle diameter	[m]
$d_p^*$	Dimensionless particle diameter	[m]
$e$	Specific gaseous emissions	[mg/MJ <sub>th</sub> ], [g/MJ <sub>th</sub> ]
$E$	CO <sub>2</sub> absorption efficiency, CO <sub>2</sub> capture efficiency	[%]
$F$	Molar flow rate	[mol/s]
$f_1, f_2$	Limestone specific deactivation parameter	[–]
$f_{active}$	Active fraction of Ca-particles in a bed	[–]
$f_{calc}$	Degree of calcination	[–]
$f_{carb}$	Degree of carbonation	[–]
$f_m, f_w$	Limestone specific deactivation parameter	[–]
$f_l$	Average volume concentration of solids in the lean region of a riser	[–]
$FC$	Fuel costs	[EUR]
$FCF$	Fixed charge factor	[–]
$FOC$	Fixed operating costs	[–]
$G_s^*$	Saturated solid mass flow rate in a riser	[kg/m <sup>2</sup> s]
$\Delta H^0$	Heat of reaction	[kJ/mol]
$h$	Height	[m]
$HR_{Cal}$	CaL process heat ratio	[–]
$k$	Sorbent deactivation constant	[–]
$k_0$	Carbonation reaction rate constant	[–]
$l$	Length	[–]
$LCOE$	Levelized cost of electricity	[EUR/MWh <sub>e</sub> ]
$m$	Mass	[kg]
$\dot{m}$	Mass flow rate	[kg/s]
$M$	Molar mass	[kg/kmol]
$N$	Number of complete carbonation-calcination cycles	[–]

$n$	Molar quantity	[mol]
$O_{2,spec}$	Specific oxygen demand	[kg $_{O_2}$ /kg $_{CO_2,capt}$ ]
$p$	Pressure	[N/m <sup>2</sup> ], [bar]
$P$	Accumulated distributional sum	[–]
$P_{el}$	Electrical Power	[MW]
$PR_{CaL}$	CaL process gross power ratio	[–]
$P_{th}$	Thermal Power	[MW]
$\dot{Q}$	Heat flux	[MW]
$Q_{spec}$	Specific heat demand	[MJ <sub>th</sub> /kg $_{CO_2,capt}$ ]
$r$	Interest rate	[–]
$r_N$	Fraction of particles having $N$ cycles between carbonator and calciner	[–]
$r_{N,age}$	Fraction of particles having $N_{age}$ full carbonation-calcination cycles	[–]
$R$	Retention rate	[%]
$R_{CO_2}$	CO <sub>2</sub> Recovery rate	[%]
$S_0$	Initial specific surface area of Ca-particles	[m <sup>2</sup> /m <sup>3</sup> ]
$S_N$	Specific surface area of Ca-particles having $N$ complete carbonation-calcination cycles	[m <sup>2</sup> /m <sup>3</sup> ]
$SAR$	Secondary air ratio	[–]
$SPECCA$	Specific primary energy consumption per CO <sub>2</sub> avoided	[MJ <sub>th</sub> /kg $_{CO_2,av}$ ]
$t$	Time	[s]
$T$	Temperature	[°C]
$\Delta T$	Temperature difference	[K]
$u_0$	Superficial gas velocity	[m/s]
$u_0^*$	Dimensionless superficial gas velocity	[–]
$u_{mf}$	Superficial gas velocity at minimum fluidization conditions	[m/s]
$u_t$	Terminal velocity of a particle	[m/s]
$V$	Volume	[m <sup>3</sup> ]
$V_m$	Molar volume	[cm <sup>3</sup> /mol]
$\dot{V}$	Volumetric flowrate	[m <sup>3</sup> /s]
$VOC$	Variable operating cost	[EUR]
$w$	Width	[m]
$W_s$	Solid inventory of fluidized bed	[kg]
$W_{s,spec}$	Specific solid inventory of fluidized bed	[kg/m <sup>2</sup> ]
$x$	Mass concentration	[wt. %] [–]
$X$	Molar conversion	[mol <sub>CaCO<sub>3</sub></sub> /mol <sub>Ca</sub> ]
$X_{ave}$	Average molar conversion	[mol <sub>CaCO<sub>3</sub></sub> /mol <sub>Ca</sub> ]
$X_{max,ave}$	Maximum average sorbent activity	[mol <sub>CaCO<sub>3</sub></sub> /mol <sub>Ca</sub> ]
$X_{max,N}$	Maximum average sorbent activity having $N$ complete carbonation-calcination cycles	[mol <sub>CaCO<sub>3</sub></sub> /mol <sub>Ca</sub> ]
$X_r$	Residual sorbent conversion capacity	[mol <sub>CaCO<sub>3</sub></sub> /mol <sub>Ca</sub> ]
$y$	Volumetric concentration	[vol. %][–]