Diploma Thesis

Simulation and experimental analysis of a thermochemical reactor for high temperature heat storage

Frederic Krakau

Course: Energie- und Verfahrenstechnik
Matr.-Nr. 313542

Submitted: February 2014

Technische Universität Berlin
Fakultät III - Prozesswissenschaften
Institut für Energietechnik
Fachgebiet für Energieverfahrenstechnik und Umwandlungstechniken regenerativer Energien (EVUR)

Advisor: Prof. Dr. rer. nat. habil. Frank Behrendt (EVUR)
Supervisor: Dipl.-Ing. Johannes Wellmann (EVUR)
Supervisor: Dipl.-Ing. Matthias Schmidt (DLR)

Acknowledgement

The present paper at hand has been composed within my employment at the institute of Technical Thermodynamics at DLR in Cologne.

First and foremost I want to thank my advisor Matthias Schmidt for the excellent supervision. I appreciate all the effort, time and ideas he contributed to my work. Without his support and thought-provoking impulses this thesis would not exist as it is now.

Second I owe Johannes Wellmann a debt for his superb mentoring. I am grateful for his support which enabled me to have a valuable experience at DLR.

Furthermore I would like to thank all my colleagues from the institute of Technical Thermodynamics in Cologne joyful and friendly cooperation.

Thanks also to Prof. Behrendt for his assessment of this thesis and his engagement at the department of Energy Process Engineering and Conversion Technologies of Regenerative Energies.

Further thanks to the employees of the company Steag for their assistance in questions regarding the simulation software Ebsilon and the unconventional provision of a license over the time of my thesis.

Finally, I want to thank my family and friends for their unconditional support throughout my life.

Declaration of Authorship

Hereby I declare that I have composed the diploma thesis at hand on my own and that I have not used any other references or aid than stated within this thesis.

Berlin, February 10th, 2014

(Frederic Krakau)

Abstract

Thermal energy storage has recently attracted much attention as a promising option to decouple power generation from the availability of renewable energy sources. Especially solar thermal power plants in combination with thermal energy storage systems offer a dispatchable, efficient and cost-competitive energy production system among all the different renewable options. Additionally, thermal energy storage can lower the production costs and consumption of fossil fuels in energy intensive industries.

Although thermochemical heat storage is still at an early stage of development, the method offers several advantages compared to sensible or latent heat storage. For example, the endothermal dehydration of calcium hydroxide to calcium oxide combines low material costs and a large gravimetric energy storage density within a favorable temperature range from 400 to 560°C. The feasibility to store heat with this material system has already been demonstrated in a pilot scale reactor at DLR. Nevertheless, to evaluate the benefits of a thermochemical storage system, an efficient integration into the process, especially of the reaction gas supply, still needs to be investigated. Not until then the performance of the overall process can be determined.

Within this thesis, a mathematical model of the calcium hydroxide storage reactor has been developed in order to develop efficient process integration concepts. By means of experimentally gained results this model was validated and integrated as a new component in the commercial simulation tool for thermodynamic cycles, “Ebsilon Professional”. Consequently, a reference plant was modeled where available excess heat was incorporated to charge the thermochemical storage system. The maximum possible amount of converted storage material within the reference configuration was determined by varying the heat input of the solar field. Based on these results, the control system of the plant was optimized whereby the possible heat input from the solar field was increased up to a factor of two, compared to the reference plant without storage system. With this plant configuration, 1100 tons of Ca(OH)2 could be converted during an eight hours charging cycle. Finally, the discharge process was simulated where the necessary heat to run the power plant was only supplied out of the storage system. The steam supply to drive the hydration reaction of the storage in turn was realized through a low pressure steam extraction from the turbine. Overall, the plant operation could be maintained for an additional 7.7 hours at a part load power of 77% for the applied system configuration.

Zusammenfassung

Die thermische Energiespeicherung hat in letzter Zeit an Bedeutung, als eine erfolgversprechende Option zur Entkopplung der Stromerzeugung von der Verfügbarkeit erneuerbare Energiequellen, gewonnen. Unter den verschiedenen erneuerbaren Optionen ermöglichen solarthermische Kraftwerke in Kombination mit thermischen Energiespeichern eine regelbare, effiziente und kostengünstige Stromerzeugung. Zusätzlich können thermische Energiespeicher die Produktionskosten und den Verbrauch von fossilen Brennstoffen in energieintensiven Industrien senken.

Obwohl die thermochemische Wärmespeicherung noch in einer frühen Entwicklungsphase ist, bietet die Technik mehrere Vorteile gegenüber sensibler oder latenter Wärmespeicherung. Die endotherme Dehydratisierung von Calciumhydroxid in Calciumoxid zum Beispiel kombiniert niedrige Materialkosten und eine große gravimetrische Energiespeicherdichte innerhalb des bevorzugten Temperaturbereichs von 400 bis 560 °C. Die Möglichkeit Wärme mit diesem Materialsystem zu speichern wurde bereits in einem Reaktor im Technikumsmaßstab am DLR nachgewiesen. Um jedoch die Vorteile eines thermochemischen Speichersystems zu bewerten, steht eine effiziente Integration in den Prozess, insbesondere der Reaktionsgasversorgung, noch aus.

Im Rahmen dieser Arbeit wurde ein mathematisches Modell des Calciumhydroxid Speicherreaktors entwickelt um effiziente Integrationskonzete zu entwickeln. Anhand von experimentellen Ergebnissen wurde dieses Modell validiert und als neue Komponente in das kommerzielle Simulationsprogramm für thermodynamische Kreisprozesse „Ebsilon Professional“ integriert. Infolgedessen wurde ein Referenzkraftwerk modelliert, wobei vorhandene Überschusswärme genutzt wurde um das thermochemische Speichersystem zu beladen. Durch die Variation des Wärmeeintrags des Solarfeldes wurde die maximale Menge an umgewandeltem Speichermaterial innerhalb der Referenzkonfiguration ermittelt. Der Mögliche Wärmeeintrag des Solarfeldes konnte gegenüber dem Referenzkraftwerk ohne Speicher verdoppelt werden. Mit dieser Konfiguration konnten 1100 Tonnen CaO während einer achtstündigen Beladungsphase produziert werden. Zum Schluss wurde der Entladungsvorgang simuliert, wobei die benötigte Wärme zum Betrieb des Kraftwerks nur aus dem Speicher bereitgestellt wurde. Der für die Hydratisierungsreaktion des Speichers notwendige Wasserdampf wurde dabei der Niederdruck-Turbine entnommen. Insgesamt

konnte durch diese Konfiguration der Kraftwerksblock mit 77 % der Nennleistung für weitere 7,7 Stunden Strom erzeugen.

Table of Contents

List of Figures

List of Tables

Nomenclature

Acronyms

BRICS	Brazil, Russia, India, China and South Africa
CLHS	Cascaded latent heat system
CSP	Concentrated Solar Power
DLR	Deutsches Zentrum für Luft- und Raumfahrt
DSG	Direct steam generation
EES	Engineering Equation Solver
HEX	Heat exchanger
HTF	Heat transfer fluid
IEA	International Energy Agency
LEC	Levelised Energy Cost
LHS	Latent heat storage
PCM	Phase Change Material
SEGS	Solar Energy Generating Systems
TCS	Thermochemical heat storage
TCM	Thermochemical Material
TES	Thermal Energy Storage
UNFCCC	United Nations Framework Convention on Climate Change

Latin Letters

A	Heat transfer area	[m^2]
c	Volumetric specific heat capacity/ Volumetric storage capacity/density	[kWh_t/m^3]
c_p	Specific heat capacity at constant pressure	[J/(kg*k)]
Δh_{pc}	Specific heat of fusion	[J/kg]
Δh_R	Specific heat of reaction	[J/mol]
k	Reaction rate constant	[1/s]
M	Molar mass	[kg/mol]
m	Mass	[kg]
$\dot{m}$	Mass flow	[kg/s]
n	Amount of Substance	[mol]

$\dot{n}_R$	Molar mass flow of reaction	[mol/s]
p	Pressure	[bar]
P	Electric Power	[W]
Q	Heat	[J]
$\dot{Q}_R$	Chemical Reaction heat flow	[W]
T	Temperature	[°C]
ΔT	Temperature Difference	[°C]
t	Operation Time	[s]
U	Overall heat transfer coefficient	[W/(m²*K)]
x	Conversion	[-]

Greek Letters

ε	Porosity	[-]
η	Energy conversion efficiency	[-]
η_{work}	Modified energy conversion efficiency	[-]
$\Delta\vartheta_{ln}$	Log mean temperature difference	[K]
λ	Thermal conductivity	[W/(m*K)]
μ	Velocity	[m/s]
ρ	Density	[kg/m³]

Subscripts

Bed	Reaction bed
Eq	Equilibrium
In	Inlet
Out	Outlet
pc	Phase Change
R	Reaction
TCM	Thermochemical Material