Sulphur – solar fuel for on demand power generation

Int. Workshop on Solar Thermochemistry, Juelich, Germany

Dennis Thomey, Christos Agrafiotis, Nicolas Overbeck, Martin Roeb, Christian Sattler

Co-funded by the Horizon 2020 Framework Programme of the European Union

Contents

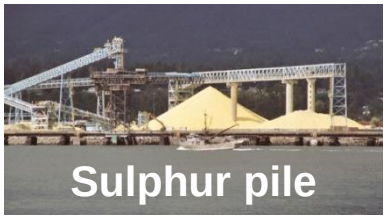
- Sulphur as industrial commodity
- Sulphur as thermochemical storage
- Solar sulphur power generation
- Background of DLR on sulphur cycles
- European project PEGASUS
- Conclusions and outlook

Comparison of energy storage densities

Technology	Energy density (kJ/kg)	
Hydrogen	141,886	1
Gasoline	47,357	1
Sulphur	**9,281**	2
Molten Salt	282	2
Lithium Ion Battery	580	2
Elevated water Dam (100m)	1	2

[1]College of the Desert
[2]General Atomics

Sulphur in industrial processes


Sulphur pile

- Sulphur is required for **sulphuric acid** (SA) production
  - SA is world's most produced chemical
    ⇒ Global annual rate **>200 Mio. tons**
  - SA is measure of industrial development
  - SA is mainly needed for **fertiliser production**


Sulphuric acid plant

- Sulphur from **desulphurisation of hydrocarbons** via Claus process

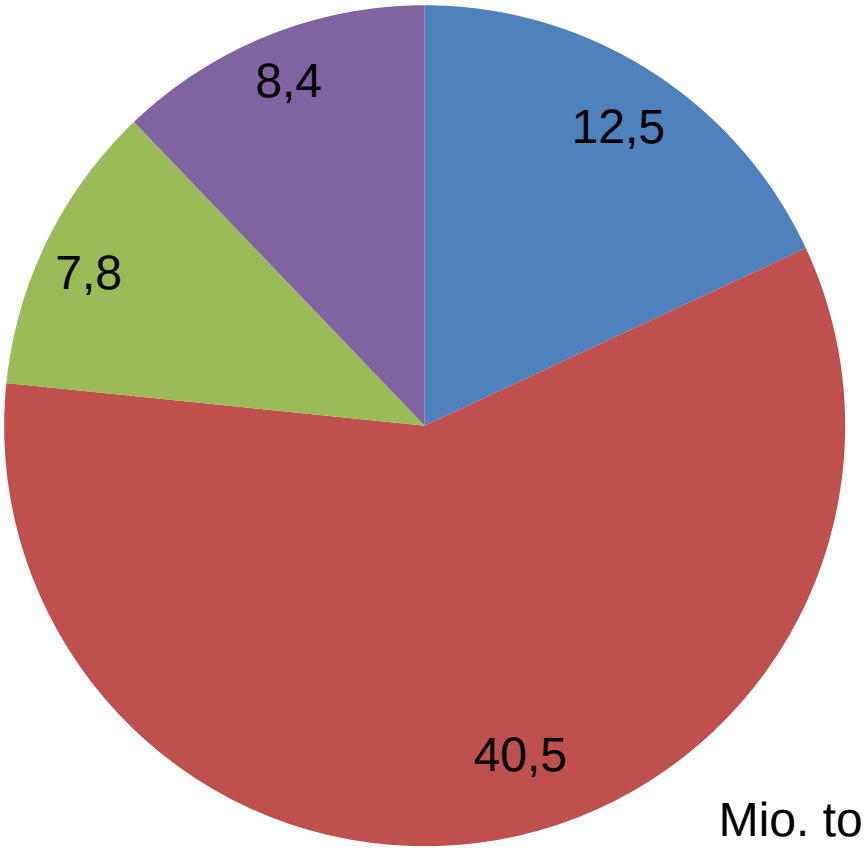

Claus process

- Sulphur is by-product of **metallurgic processes**


Ore roasting

Sulphur world production 2014

Total of 69.1 Mio. tons (avg. world price of US$160 per ton)



- Metallurgy (smelting of sulphide ores)
- By-product sulphur from refineries etc. (processing natural gas, petroleum and oil sands)
- Mining (pyrite, native sulphur, underground deposits)
- Other

Source: 2014 Minerals Yearbook, SULFUR, U.S. Geological Survey

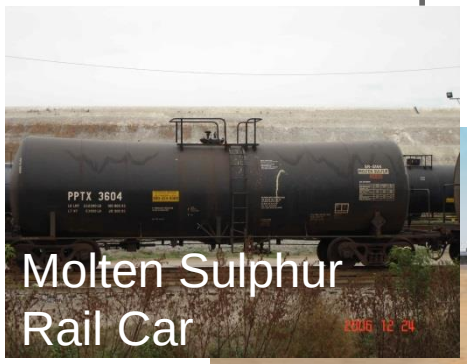
Transportation and storage of sulphur

In solid or liquid form

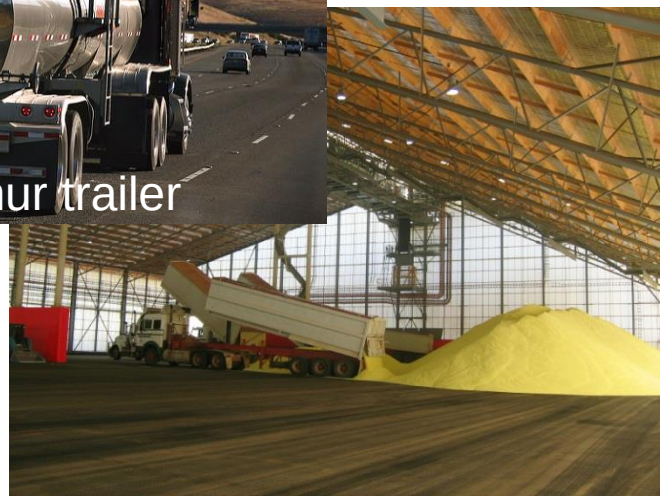
Pipeline

Molten sulphur in heated pipelines (~140 °C)

Train



Truck



Ship

Thermochemical sulfur storage cycle for on-demand solar power production

$2\ H_2O + 3\ SO_2 \Rightarrow 2\ H_2SO_4 + S$
<200 °C (liq. phase)

ΔH = -254 kJ/mol

$SO_2 + H_2O$

SO_2

Sulphuric Acid Decomposition

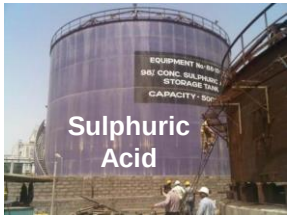
SO_2 Disproportionation

Sulphur Combustion

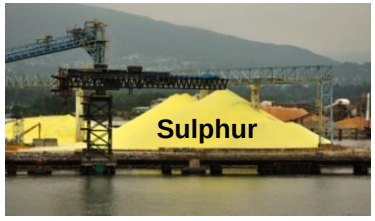
$2\ H_2SO_4 \Rightarrow 2\ H_2O + 2\ SO_2 + O_2$
>800 °C

ΔH = 551 kJ/mol

H_2SO_4



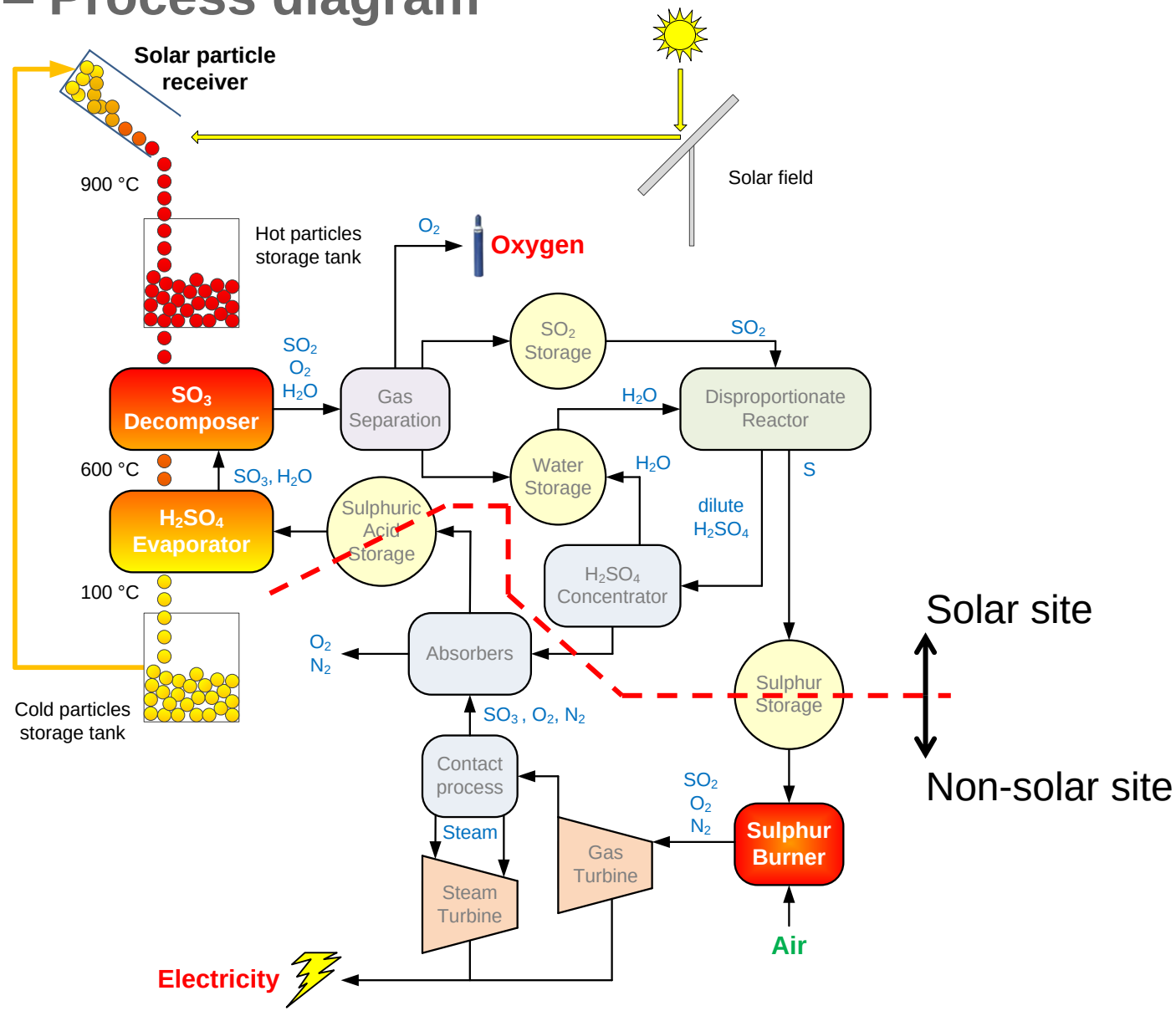
S



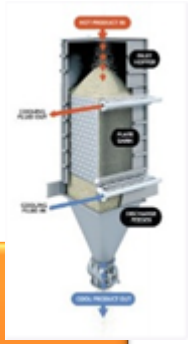
$S + O_2 \Rightarrow SO_2$
>1000 °C

ΔH = -297 kJ/mol

PEGASUS – Process diagram



Integration of solar sulphur power generation



Solar particle plant

Hot particles

Particle reactor (sulphuric acid splitting)

SO_2

Disproportionate reactor

Sulphuric acid

Sulphuric acid plant

SO_3

Sulphur

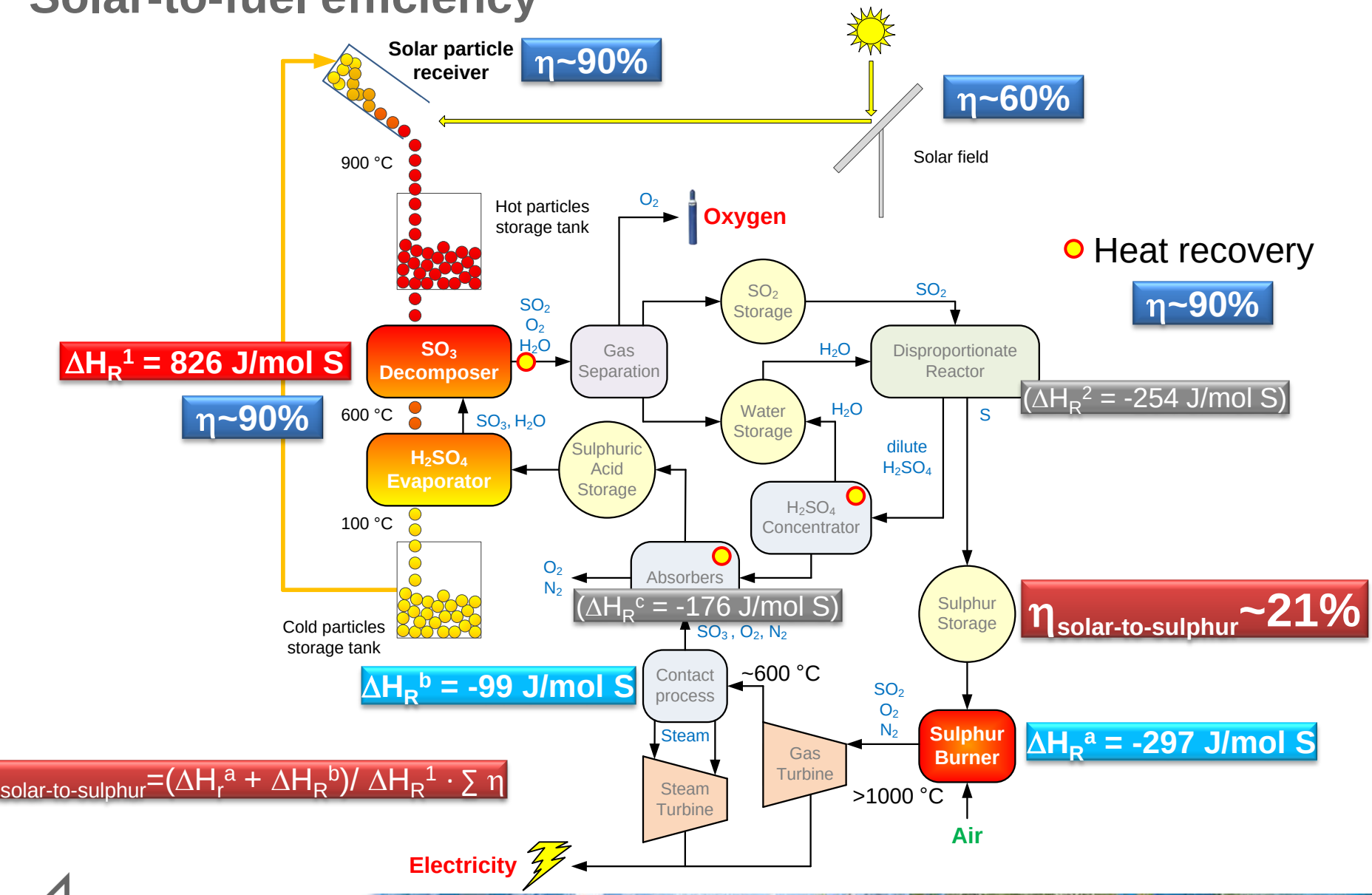
Refinery

Electrical power

Sulphur gas turbine plant

DLR

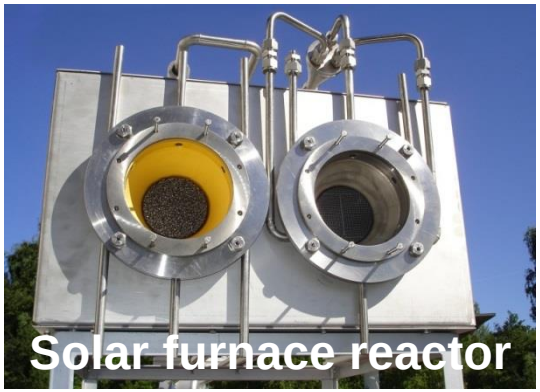
Solar-to-fuel efficiency



Research of DLR on sulphur cycles

- Experience on solar sulphuric acid cracking since more than 20 years
- Research on Hybrid Sulphur Cycle in European projects HYTHEC, HycycleS and SOL2HY2 (2004 – 2016)
  - Development and on-sun testing of receiver/reactors in solar furnace
  - Construction of pilot unit and demo operation on solar tower
  - Modelling of reactors
  - Testing of catalysts and construction materials
  - Flowsheeting and techno-economics of HyS process
  - Scale-up concepts


Catalyst testing


Solar furnace reactor


Solar tower demo

Project Baseload (Sulfur Based Thermochemical Heat Storage for Baseload Concentrated Solar Power Generation)

- Funding: United States Department of Energy (DOE)
  - 2 project phases from 2010 to 2013
  - GO/NO-GO review after phase I
  - Phase I completed in Mar. 2012
  - GO recommendation for Phase II (May 2012 – Oct. 2013)

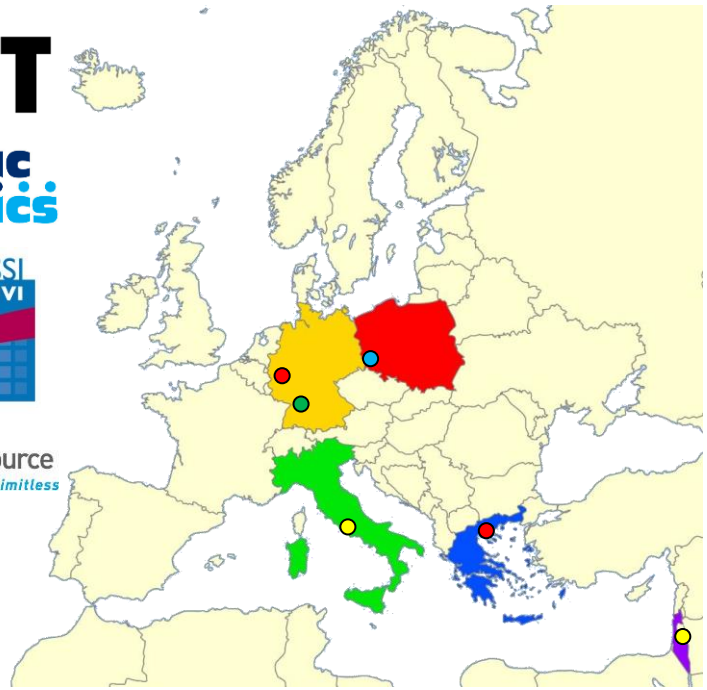
- Coordinator: General Atomics (GA), USA
  - SO_2 disproportionation
  - Sulfur combustion
  - Experiments, plant design, flowsheeting, economics

- Subcontractor: German Aerospace Center (DLR)
  - H_2SO_4 decomposition
  - Experiments, modeling
  - Funded work and in-kind contribution

PEGASUS partners

- **DLR**, Germany (Coordinator)
  - Solar tower/simulator owner/operator
  - Solar receiver/reactor developer
- **APTL/CERTH**, Greece
  - Catalyst materials developer
- **KIT**, Germany
  - Combustion specialist
- **Baltic Ceramics**, Poland
  - Advanced ceramics manufacturer
- **Processi Innovativi**, Italy
  - Power plant designer/contractor
- **BrightSource**, Israel
  - CSP plant designer/contractor

- Research institute
- University
- SME
- Industry



PEGASUS – Work plan

- WP1: Catalytic particles development, manufacturing – APTL, Baltic Ceramics
- WP2: Centrifugal particle solar receiver – DLR
  - Preparation of existing test receiver
  - On-sun test operation with catalytic particles (WP1)
- WP3: Sulphur trioxide decomposer + WP4: Sulphuric acid evaporator – DLR
  - Development and construction of moving bed reactors with direct (WP3) and indirect (WP4) heat transfer
  - Off-sun test operation
- WP5: Sulphur Combustor – KIT
  - Development, construction and operation of sulphur burner
- WT6.1, 6.5, 6.6:Overall concept evaluation – Processi Innovativi, BrightSource
  - System modelling, flowsheeting, techno-economy
- WT6.2-6.4: System integration, test operation – DLR
  - Integrated operation of solar receiver (WP2) and sulphuric acid splitting reactors (WP3, WP4)

Centrifugal particle solar receiver optimization

Application of pilot receiver developed in CentRec project

- Centrifugal particle receiver was erected on scaffold in front of Juelich Solar Tower
  - Nominal power: 2.5 MW_{th}
  - Diameter of aperture: 1.13 m
  - Max. particle temperature: 1000 °C
- Commissioning is in progress
- Solar testing of CentRec pilot planned to start in autumn 2017

Project PEGASUS

- Pre-testing of catalytic particles in CentRec pilot
- Integrated testing together with particle reactors for sulphuric acid splitting planned in last project year

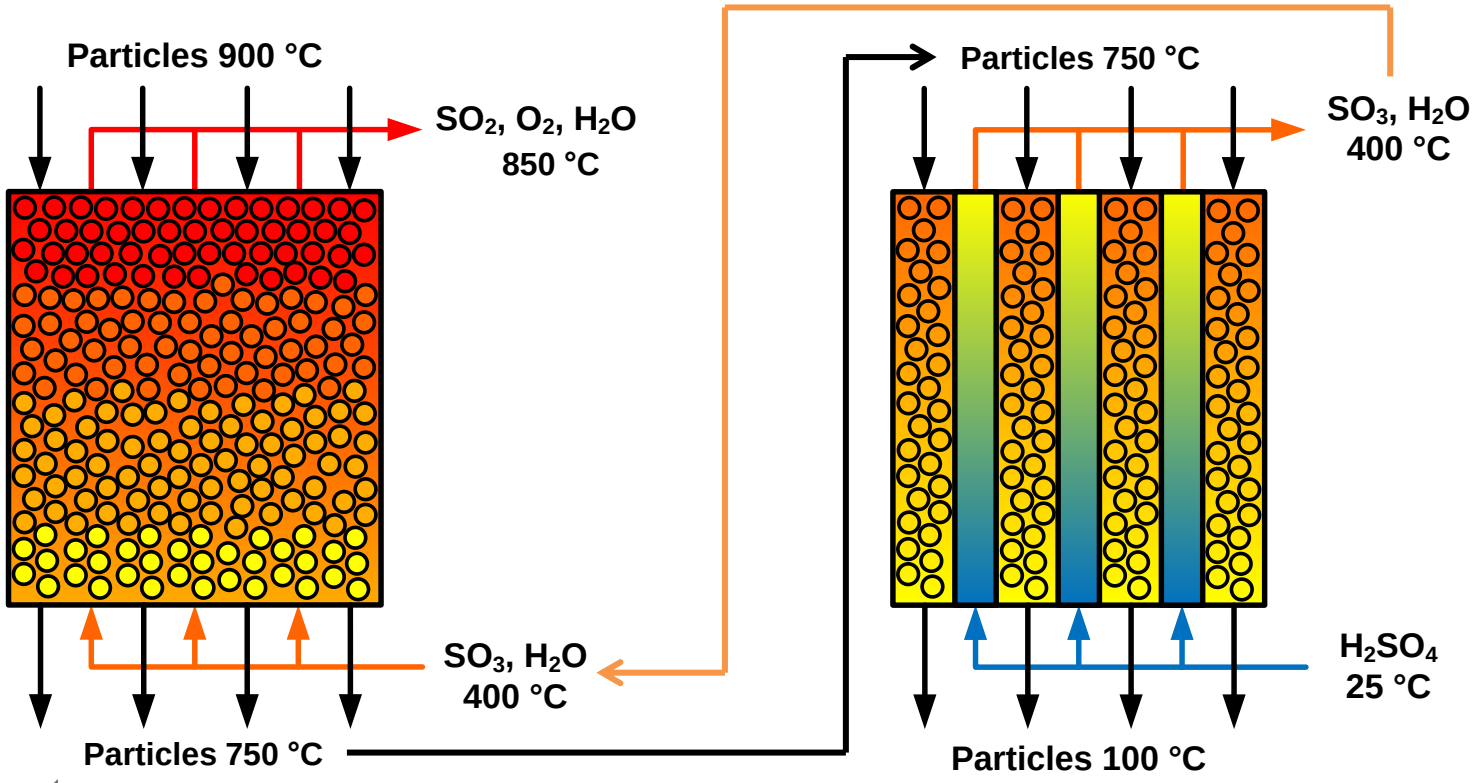
Design options for decomposer and evaporator

SO_3 decomposer

- Direct contact

Sulphuric acid evaporator

- Indirect heat transfer (tube/plate HX)



Conclusions and outlook

- Sulphur is one of the most important commodity of chemical industry
- Sulphur has high thermochemical energy density
- Transportation and storage of solid or liquid sulphur is industrial practice
- Solar sulphur cycle for baseload and on-demand power production
  - Estimated solar-to-fuel efficiency of ~21%
- Potential for integration of sulphur cycle into existing sulphuric acid plants
- Investigation of solar sulphur cycle in European project PEGASUS
  - Development of catalytically active solar particles
  - Construction of particle reactor for sulphuric acid splitting
  - Prototype development of sulphur burner for SO_2 gas turbine

Thank you for your attention!

Co-funded by the Horizon 2020 Framework Programme of the European Union