LINDE's activities to develop the CO$_2$ purification for the Oxyfuel combustion process

Roland Ritter, Linde AG

Wuhan, 29$^{th}$ October 2015
Carbon Capture and Usage
Linde offers solutions in all three pathways

<table>
<thead>
<tr>
<th>Technology</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Combustion</td>
<td>ASU ➔ Gasifier ➔ CO Shift ➔ Gas cleaning (Rectisol) ➔ CO₂ purification &amp; compression ➔ CO₂</td>
</tr>
<tr>
<td>Oxyfuel</td>
<td>ASU ➔ Boiler ➔ DeSOx ➔ DeNOx ➔ CO₂ purification &amp; compression ➔ CO₂</td>
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Linde's scope at Oxyfuel-Pilot Plant Schwarze Pumpe/ Germany

- **Air Separation Unit (ASU)**
  - Oxygen supply: 6600 Nm³/h

- **Gas Processing Unit (GPU)**
  - CO₂ Purification and Liquefaction: 240 t/d
Pilot Plant Schwarze Pumpe
Linde's Project Milestones

2006  Contract signature  (Scope: Engineering, Procurement, Construction and Start-up)

2008  Mechanical Completion, Commissioning and Start-up

2008  Signature of Technology Partnership for ASU and GPU with VATTENFALL

2008  Service Agreement for maintenance and operation of the ASU and GPU signed by Linde Gas

2010  Implementation and test of the DeNOx test facility (Linde Cold DeNOx - LICONOX®)

2011  Delivery of liquid CO₂ to Ketzin (underground CO₂ injection and migration)

2014  End of Project
**Oxyfuel technology**

Air separation plant (pilot plant Schwarze Pumpe)

**Client**
Vattenfall

**Location**
Schwarze Pumpe/Germany

**Process**
Oxygen supply

**Capacity**
6,600 Nm³/h Oxygen

**Purity**
> 99.5 vol % O₂

**Scope of work**
Turnkey plant

**Start-up**
2008

→ Commercial available technology
Main results  Air Separation Plant

All guaranteed parameter were shown during operation

— Overall capacity, product flow rates
— $O_2$, $N_2$ purity and pressure
— turn down and load change capability
— utility consumption

Learning's about some power related specialties

— The requirements for load following capability of ASUs for Oxyfuel Power Plants are higher than for conventional applications. During the operation at Schwarze Pumpe requested load changes between 4 and 8% could be verified and the applicability of Cryogenic Air Separation Processes for Oxyfuel was confirmed
— uninterrupted product supply for different operating modes, coal and flue gas qualities were successfully tested
— integration of the ASU operation, start-up and shut down procedures, were optimized within the overall Oxyfuel Process
— Linde ASU technology ready for commercial application also in Oxyfuel and CCS

a conventional and proven ASU design could be applied, referenced also in other areas
Oxyfuel technology
CO₂ purification and liquefaction plant (pilot plant)

Client
Vattenfall

Location
Schwarze Pumpe/Germany

Process
Drying, compression, liquefaction, rectification with CO₂ recycling and liquid storage

Capacity
7 000 Nm³/h flue gas
240 t/d CO₂ liquid

Purity
> 99.7 vol % CO₂

Scope of work:
Turnkey plant

→ Commercial available technology

Start-up: 2008
Main results  Gas Processing Unit (GPU)

All guaranteed parameter were shown during operation

- Overall capacity
- CO₂ recovery rate
- CO₂ purity
- Turn down and load change capability
- Utility consumption

Based on long experiences in design and operation of ASU and CO₂ Plants.

Learning's about some power related specialties like

- Experiences for different cases, coal and flue gas qualities
- Operation of GPU with all other processes within overall power plant configuration could be verified
- Load changes around 4%/minute verified
- Optimization of start-up and shut down procedures in combination with a power plant
- Dryer adsorbents and corrosion resistance for CO₂ plants
Pilot Plant Schwarze Pumpe
Captured and liquified CO$_2$ in Linde's GPU

$t$ CO$_2$ captured

Year of Operation

<table>
<thead>
<tr>
<th>Year</th>
<th>CO$_2$ captured (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008</td>
<td>91</td>
</tr>
<tr>
<td>2009</td>
<td>1824</td>
</tr>
<tr>
<td>2010</td>
<td>3593</td>
</tr>
<tr>
<td>2011</td>
<td>4735</td>
</tr>
<tr>
<td>2012</td>
<td>418</td>
</tr>
<tr>
<td>Total</td>
<td>10661</td>
</tr>
</tbody>
</table>
CO₂ injection
Linde supplies CO₂ for injection tests in Ketzin

Client
German Research Centre for Geosciences
GFZ, Potsdam, Germany

Location
Ketzin/ Germany

Capacity
3,600 kg/h CO₂
pressure adjustable up to 100 bar

Purity
Food grade CO₂

Scope of work
Turnkey plant

Start-up
2008

→ since 2011 CO₂ from Schwarze Pumpe was injected
Storage and Injection
CO$_2$ injection pilot plant – Maxdorf/ Germany

Client
PEG (Gaz de France)

Location
Maxdorf/ Germany

Capacity
16 – 32 t/h CO$_2$
from coal power plant

Purity
> 99.7 vol% CO$_2$

Scope of work
Turnkey plant

Operation and CO$_2$
injection were not
allowed by the federal
state Sachsen-Anhalt/
Germany by law
## Basic data of the Demonstration Plant in Jänschwalde

<table>
<thead>
<tr>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>3000 MW (el.) 6 blocks, 500 MW each</td>
</tr>
<tr>
<td>Construction</td>
<td>1976… 1989</td>
</tr>
<tr>
<td>Upgrades</td>
<td>1995 (retrofitting of FGD)</td>
</tr>
<tr>
<td></td>
<td>since 1996 gradual upgrade of the turbines</td>
</tr>
<tr>
<td>Lignite Coal</td>
<td>14 Mio t/yr (approx. 1 kg lignite coal per 1 kWh)</td>
</tr>
<tr>
<td>Efficiency</td>
<td>35… 36 %</td>
</tr>
<tr>
<td>Emissions</td>
<td>approx. 1.1 kg CO₂/kWh</td>
</tr>
</tbody>
</table>

Construction of an Oxyfuel-Demonstration Plant for approx. 250 MW\(_{el}\) at the Jänschwalde Power Plant site

- Capture of approx. 1,3 Mio t/yr CO₂

Project stopped in Germany by political reasons – no public acceptance
Development of a large scale concept
Study for 250 MW\textsubscript{el} Oxyfuel Demo-Plant
Jänschwalde

The detailed design of all equipment as well as the creation of an 3D model

- true to scale arrangement of all equipment and connecting pipes
- integration of ASU and CO\textsubscript{2}-plant in the whole demonstration plant
- assessment of accessibility to equipment, machinery and measurement points (operability of controls and instruments, assessment of maintenance spaces etc.)
- assessment of mounting and construction concepts
- dynamic simulation of ASU and GPU and investigation of behavior in overall plant scheme
Principle units for Oxyfuel technology
Development of the Linde-concept for Oxyfuel technology

Oxyfuel pollutants compared to air fired power plants
3 to 5 times SO₂ due to recycle → serious corrosion at boiler
- FGD before recycle is required
1.5 times NOₓ due to partially reduction in boiler
- High dust NH₃-SCR not feasible → high volume flow
- Tail end NH₃-SCR not feasible → low temperatures

New development by Linde
Wet scrubber system with washing fluid regeneration
LINDE-concept alkaline wash unit  
LICONOX™ (“Linde cold DeNOx”)

**NO and SO₂ Oxidation:**
- NO + ½ O₂ → NO₂  
- SO₂ + NO₂ → SO₃ + NO

**Alkali based wash unit:**
- SO₂ + 2 NH₃ + H₂O → (NH₄)₂SO₃  
- SO₃ + 2 NH₃ + H₂O → (NH₄)₂SO₄  
- NO + NO₂ + 2 NH₃ + H₂O → 2NH₄NO₂  
- 2 NO₂ + 2NH₃ + H₂O → NH₄NO₂ + NH₄NO₃  
- 2 NO + O₂ + 2 NaOH → NaNO₂ + NaNO₃ + H₂O  
- 2 NO₂ + 2 NaOH → NaNO₂ + NaNO₃ + H₂O

**Regeneration/ reduction:**
- NH₄NO₂ → N₂ + 2 H₂O (Nitrite-decomposition > 60°C)

**advantages:**
- pre-purified, compressed gas  
- moderate temperature  
- small gas stream (low volume flow rate)  
- smaller equipment  
- high conversation rate  
- no acid mixture (corrosion problem)

**Ammonia water …**
- reaction of NO and NO₂  
- reaction of SO₂ and SO₃

**results are nitrite and nitrate …**
- reaction to a mix of nitrogen and sulfur fertilizer  
- reduction to N₂ and H₂O possible (De-nitrification)
Alkaline wash unit with real flue gas from oxy-boiler – installation in the CO\textsubscript{2}-pilot plant Schwarze Pumpe

capacity:
200… 700 Nm\textsuperscript{3}/h
30… 40 (80) °C
5… 20 bar

NO/NO\textsubscript{2}-concentration adjustable with additional dosing (cylinder)

using of
15 wt% ammonia water or
33 wt% sodium hydroxide
Development of the kinetic model

determination of kinetic rate constants

\[
\frac{\partial [NO]}{\partial t} = -k_1[NO][O_2] + k_2[NO][NO_2]
\]

\[
\frac{\partial [NO]}{\partial t} = -[NO]^2[O_3] + \left( k_1 + k_2 \frac{[NO]}{[NO_2]} \right) - [NO]^2[O_3] \cdot k_3
\]

NO-conversation versus pH-value

\[
4 \text{NO} + \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{NH}_3 \rightarrow 4 \text{NH}_4\text{NO}_2
\]

\[
4 \text{NO} + 3 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 4 \text{HNO}_3
\]

Kinetic model confirmed

⇒ Good correlation between measured data and kinetic model
Reduction of spent salt solution (test phase in Schwarze Pumpe)

possible reduction of spent salt solution:
- NO-NO₂ removal with 15wt%- ammonia water → 100% (Basis)
- NO-NO₂ removal with 33wt%- sodium hydroxide → ca. 46%
- NO-NO₂ removal with ammonia water and reduction → ca. 23%

Regeneration/ reduction:
\[ \text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O} \] (Nitrite-decomposition)

Nitrite-content after reduction versus temperature
Increasing of CO₂-recovery rate – using PSA-unit

Application for requirement of high CO₂ recovery rates

⇒ maximum 99%
⇒ higher spec. energy consumption (additional recycle)

installation of a pressure swing adsorption unit

⇒ CO₂-rich fraction for regeneration and fed back into process before pre-compression
⇒ CO₂-lean fraction could be fed to the ASU
Linde partnering with Aerojet Rocketdyne on their development of "Pressurized Fluidized Bed Combustion"


Zero Emissions Power and Steam (ZEPS™) plant

Pilot plant 1 MW_{th} in erection phase: Ottawa/Canada

start-up: June 2016

— The ZEPS™ plant utilizes an oxy-combustion process with near stoichiometric coal combustion in a pressurized fluidized bed that enables:
  ● High power conversion efficiencies
  ● Low electricity costs with CO\textsubscript{2} capture

— Key technology elements of the ZEPS™ plant
  ● A novel, high heat flux, high carbon conversion, once-through, bubbling, pressurized bed combustor (PFBC) with an in-bed heat exchanger
Conclusions

The cooperation with Vattenfall and all other partners was a major step for Linde in developing Oxyfuel-Technology

Linde's core technology like ASU and CO₂ purification and liquefaction (GPU) could be verified under real conditions of a lignite fired power plant.

Significant improvements (e.g. new DeNOx technology) to improve the overall Oxyfuel Power Plant were developed and successful tested.

Special power plant requirements like fast load changes could be shown for ASU and GPU.

Concepts for a large size Demonstration plant (Jänschwalde) were developed and are the basis for next projects.

New oxyfuel-concept with pressurized fluidized bed will be developed and tested in Ottawa/Canada.

→ ASU and GPU are commercial available for Oxyfuel Power Plants and other applications
Thank you for your attention

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CO₂ capture unit and injection plant
Snøhvit Hammerfest/Norway

Client
StatoilHydro ASA

Location
Snøhvit Hammerfest/Norway

Process
BASF aMDEA®
Drying, precompression, liquefaction, postcompression

Capacity
824 000 Nm³/h natural gas with 2 000 t/d CO₂; high-dense CO₂

Purity
> 99 vol % CO₂

Use of CO₂
Injection into 150 km pipeline for storage at 2 600 m deep

Scope of work
Turnkey plant

Start-up
2008