Urban Biogas Workshop
“Biogas upgrading”
- Biogas cleaning methods -

Michael Beil, Fraunhofer Institute for Wind Energy and Energy System Technology

Urban Biogas Workshop, Riga/Latvia, 2012-10-25


[IWES]


[Beil]


[CorelI]

Fraunhofer IWES

Contents
Biogas cleaning methods for:

- H_2O
- H_2S
- Other unwanted gas compounds:
  - Organic silicon compounds (siloxanes)
  - NH_3

Contents

- **Separation of water / drying**
- Desulphurization / Reduction of sulphur
- Separation of other unwanted gas compounds:
  - Organic silicon compounds (siloxanes)
  - NH_3

Separation of water / drying:
Cooling

- Mostly at the inlet of the upgrading plant
- Always after compressors to avoid unwanted condensation effects
- Including condensate separator
- Mostly not suitable to reach sufficient low dew points for grid injection

Separation of water / drying:
Adsorption

- Mostly at the outlet of the upgrading plant (if using scrubbers)
- Suitable to reach sufficient low dew points for grid injection (- 60°C to – 90°C)
- Typical adsorbents: e.g. molecular sieves or silica gel
- Regeneration is needed (e.g. by a TSA Temperature Switch Adsorption system – one column is loaded, the other one is regenerated by heated gas)

Contents

- Separation of water / drying
- **Desulphurization / Reduction of sulphur**
- Separation of other unwanted gas compounds:
  - Organic silicon compounds (siloxanes)
  - NH_3

Overview desulphurization methods

Method	H_2S - Output-concentration	Neces-sity of O_2	Internal / External	Primary desulph.	Precision desulph.
Internal biological H_2S reduction (in the digester)	50 - 200 ppm	Yes	Internal	**X**	
External biological H_2S reduction (out of the digester in a sprinkling filter)	10 - 200 ppm	Yes	External	**X**	
Combination of external biological H_2S reduction with lye scrubber	20 - 100 ppm	(Yes)	External	**X**	
Chemical precipitation using iron salts (sulphide precipitation)	100 - 150 ppm	No	Internal	**X**	
Chemical precipitation using iron hydoxide	100 - 150 ppm	No	Internal	**X**	
Iron oxide or iron hydroxide (in an external column)	< 1 ppm	(Yes)	External		**X**
Adsorption / catalytic oxidation using impregnated activated carbon	< 1 ppm	Yes	External		**X**
Zinc oxide	< 1 ppm	No	External		**X**

Green marked methods have currently most relevance for biogas upgrading!

Desulphurization:
Internal biological desulph. (in the digester)

$2\ H_2S + O_2 \rightarrow 2\ S + 2\ H_2O$

$S + H_2O + O_2 \rightarrow H_2SO_3$

- Air dosing: 2 – 12 %
- Cheap
- Dilution of biogas with nitrogen

Desulphurization:
Internal biological desulph. (in the digester)

Alternative:

Pure oxygen by oxygen generation at the plant. Provided by a small air separation system (PSA).

Fraunhofer IWES

Desulphurization:

Internal biological desulph. (in the digester)

Alternative:

Pure oxygen provided by an oxygen tank (from external production):

- Not common
- Relatively expensive

Desulphurization:
Internal biological desulph. (in the digester)


[Corell]


[Corell]

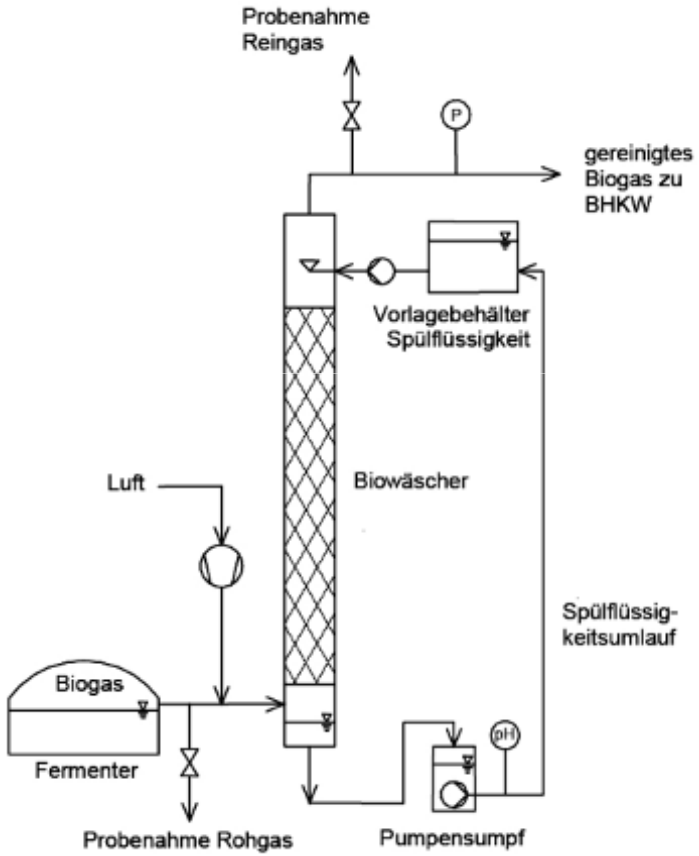
Fraunhofer IWES

Desulphurization:
Internal biological desulph. (in the digester)

Method	H_2S - Output-concentration	Neces-sity of O_2	Internal / External	Primary desulph.	Precision desulph.
Internal biological H_2S reduction (in the digester)	**50 - 200 ppm**	**Yes**	**Internal**	**X**	
External biological H_2S reduction (out of the digester in a sprinkling filter)	10 - 200 ppm	Yes	External	**X**	
Combination of external biological H_2S reduction with lye scrubber	20 - 100 ppm	(Yes)	External	**X**	
Chemical precipitation using iron salts (sulphide precipitation)	100 - 150 ppm	No	Internal	**X**	
Chemical precipitation using iron hydoxide	100 - 150 ppm	No	Internal	**X**	
Iron oxide or iron hydroxide (in an external column)	< 1 ppm	(Yes)	External		**X**
Adsorption / catalytic oxidation using impregnated activated carbon	< 1 ppm	Yes	External		**X**
Zinc oxide	< 1 ppm	No	External		**X**

Fraunhofer IWES

Desulphurization:
External biological desulph. (out of the digester)



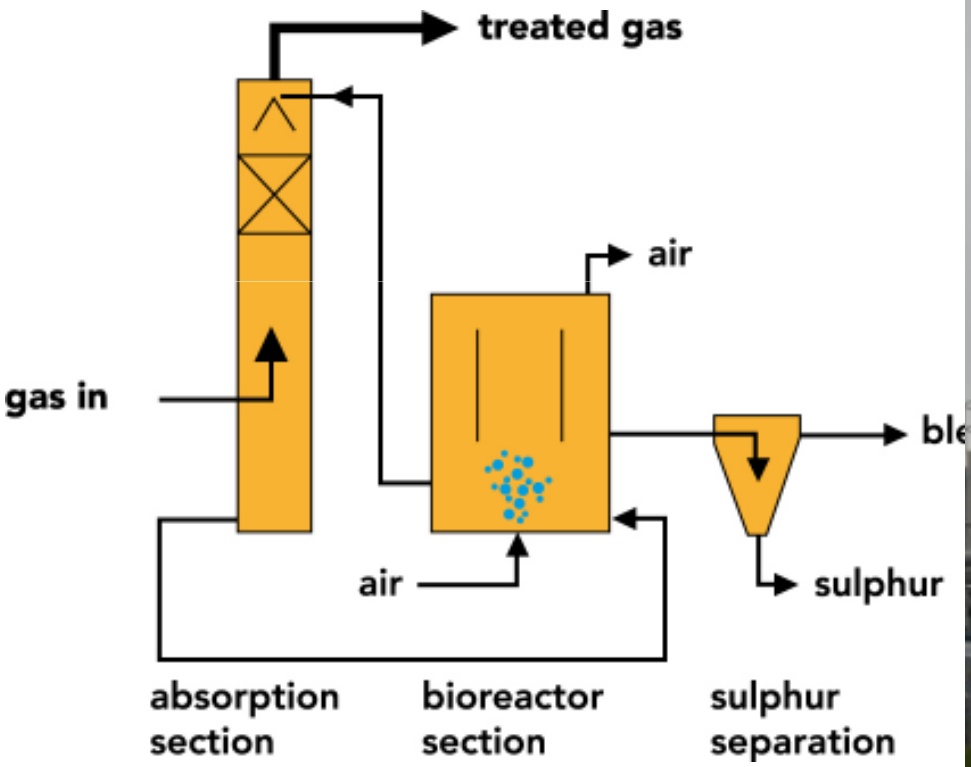
[Köhler-Ziegler GmbH]

Fraunhofer IWES

Desulphurization:
Internal biological desulph. (in the digester)

Method	H_2S - Output-concentration	Neces-sity of O_2	Internal / External	Primary desulph.	Precision desulph.
Internal biological H2S reduction (in the digester)	**50 - 200 ppm**	**Yes**	**Internal**	**X**	
External biological H2S reduction (out of the digester in a sprinkling filter)	**10 - 200 ppm**	**Yes**	**External**	**X**	
Combination of external biological H_2S reduction with lye scrubber	20 - 100 ppm	(Yes)	External	**X**	
Chemical precipitation using iron salts (sulphide precipitation)	100 - 150 ppm	No	Internal	**X**	
Chemical precipitation using iron hydoxide	100 - 150 ppm	No	Internal	**X**	
Iron oxide or iron hydroxide (in an external column)	< 1 ppm	(Yes)	External		**X**
Adsorption / catalytic oxidation using impregnated activated carbon	< 1 ppm	Yes	External		**X**
Zinc oxide	< 1 ppm	No	External		**X**

Desulphurization: Combination of external biological H_2S reduction with a lye scrubber



[www.paques.nl]

[IWES]

Fraunhofer IWES

Desulphurization: Combination of external biological H_2S reduction with a lye scrubber

Method	H_2S - Output-concentration	Neces-sity of O_2	Internal / External	Primary desulph.	Precision desulph.
Internal biological H2S reduction (in the digester)	**50 - 200 ppm**	**Yes**	**Internal**	**X**	
External biological H2S reduction (out of the digester in a sprinkling filter)	**10 - 200 ppm**	**Yes**	**External**	**X**	
Combination of external biological H_2S reduction with lye scrubber	**20 - 100 ppm**	**(Yes)**	**External**	**X**	
Chemical precipitation using iron salts (sulphide precipitation)	100 - 150 ppm	No	Internal	**X**	
Chemical precipitation using iron hydoxide	100 - 150 ppm	No	Internal	**X**	
Iron oxide or iron hydroxide (in an external column)	< 1 ppm	(Yes)	External		**X**
Adsorption / catalytic oxidation using impregnated activated carbon	< 1 ppm	Yes	External		**X**
Zinc oxide	< 1 ppm	No	External		**X**

Fraunhofer IWES

Desulphurization:
Chemical precipitation (iron hydroxide)

$2\ Fe(OH)_3 + H_2S \rightarrow 2\ Fe(OH)_2 + S + H_2O$

$Fe(OH)_2 + H_2S \rightarrow FeS \downarrow + 2\ H_2O$


[IWES]

Fraunhofer IWES

Desulphurization:
Chemical precipitation (iron chloride)

$FeCl_2 + H_2S \rightarrow FeS \downarrow + 2\ HCl$

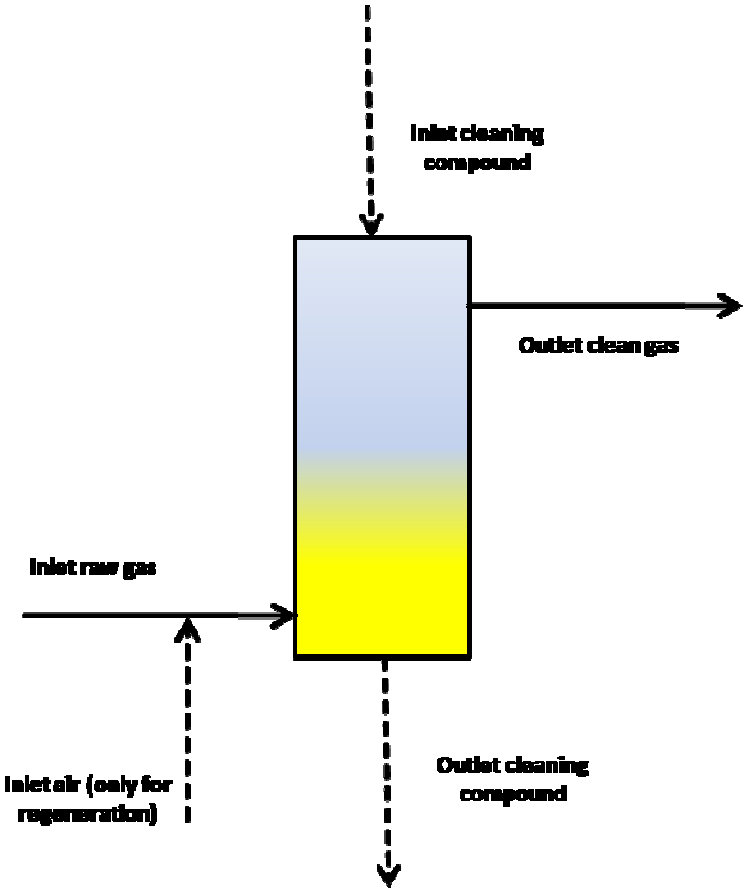
Fraunhofer IWES

Desulphurization:
Internal biological desulph. (in the digester)

Method	H_2S - Output-concentration	Neces-sity of O_2	Internal / External	Primary desulph.	Precision desulph.
Internal biological H2S reduction (in the digester)	50 - 200 ppm	Yes	Internal	X	
External biological H2S reduction (out of the digester in a sprinkling filter)	10 - 200 ppm	Yes	External	X	
Combination of external biological H_2S reduction with lye scrubber	20 - 100 ppm	(Yes)	External	X	
Chemical precipitation using iron salts (sulphide precipitation)	**100 - 150 ppm**	**No**	**Internal**	**X**	
Chemical precipitation using iron hydoxide	**100 - 150 ppm**	**No**	**Internal**	**X**	
Iron oxide or iron hydroxide (in an external column)	< 1 ppm	(Yes)	External		X
Adsorption / catalytic oxidation using impregnated activated carbon	< 1 ppm	Yes	External		X
Zinc oxide	< 1 ppm	No	External		X

Fraunhofer IWES

Desulphurization:
Iron oxide or hydroxide in an external column



[IWES after Eisenmann]

Fraunhofer IWES

Desulphurization:
Iron oxide or hydroxide in an external column

Method	H_2S - Output-concentration	Neces-sity of O_2	Internal / External	Primary desulph.	Precision desulph.
Internal biological H2S reduction (in the digester)	**50 - 200 ppm**	**Yes**	**Internal**	**X**	
External biological H2S reduction (out of the digester in a sprinkling filter)	**10 - 200 ppm**	**Yes**	**External**	**X**	
Combination of external biological H_2S reduction with lye scrubber	20 - 100 ppm	(Yes)	External	**X**	
Chemical precipitation using iron salts (sulphide precipitation)	**100 - 150 ppm**	**No**	**Internal**	**X**	
Chemical precipitation using iron hydoxide	**100 - 150 ppm**	**No**	**Internal**	**X**	
Iron oxide or iron hydroxide (in an external column)	**< 1 ppm**	**(Yes)**	**External**		**X**
Adsorption / catalytic oxidation using impregnated activated carbon	< 1 ppm	Yes	External		**X**
Zinc oxide	< 1 ppm	No	External		**X**

Fraunhofer IWES

Desulphurization: Adsorption / catalytic oxidation using impregnated activated carbon

Demand:

- **Oxygen (compared to stoichiometric needed):**
  - **> 2 x (impregnated)**
  - **~ 4 x (not impregnated)**
- **Humidity (rel.): 30 – 80 %**
- **Retentation time: 2 – 6 s**

[IWES]

Desulphurization:
Iron oxide or hydroxide in an external column

Method	H_2S - Output-concentration	Neces-sity of O_2	Internal / External	Primary desulph.	Precision desulph.
Internal biological H2S reduction (in the digester)	**50 - 200 ppm**	**Yes**	**Internal**	**X**	
External biological H2S reduction (out of the digester in a sprinkling filter)	**10 - 200 ppm**	**Yes**	**External**	**X**	
Combination of external biological H_2S reduction with lye scrubber	20 - 100 ppm	(Yes)	External	**X**	
Chemical precipitation using iron salts (sulphide precipitation)	**100 - 150 ppm**	**No**	**Internal**	**X**	
Chemical precipitation using iron hydoxide	**100 - 150 ppm**	**No**	**Internal**	**X**	
Iron oxide or iron hydroxide (in an external column)	**< 1 ppm**	**(Yes)**	**External**		**X**
Adsorption / catalytic oxidation using impregnated activated carbon	< 1 ppm	Yes	External		**X**
Zinc oxide	< 1 ppm	No	External		**X**

Fraunhofer IWES

Contents

- Separation of water / drying
- Desulphurization / Reduction of sulphur
- **Separation of other unwanted gas compounds:**
  - **Organic silicon compounds (siloxanes)**
  - **NH_3**

Overview siloxanes:

Name	Abbrev.	Formula	M [g/mol]
Tetramethylsilane	TMS		
Trimethylsilanol	MOH		
Hexamethyldisiloxane	L2	$C_6H_{18}OSi_2$	162
Octamethyltrisiloxane	L3	$C_8H_{24}O_2Si_3$	236
Decamethyltetrasiloxane	L4	$C_{10}H_{30}O_3Si_4$	310
Dodecamethylpentasiloxane	L5	$C_{12}H_{36}O_4Si_5$	384
Tetradecamethylhexasiloxane	L6	$C_{14}H_{42}O_5Si_6$	459
Hexadecamethylheptasiloxane	L7	$C_{16}H_{48}O_6Si_7$	533
Octadecamethyloctasiloxane	L8	$C_{18}H_{54}O_7Si_8$	607
Hexamethylcyclotrisiloxane	D3	$C_{12}H_{18}O_3Si_3$	222
Octamethylcyclotetrasiloxane	D4	$C_8H_{24}O_4Si_4$	297
Decamethylcyclopentasiloxane	D5	$C_{10}H_{30}O_5Si_5$	371
Dodecamethylcyclohexasiloxane	D6	$C_{12}H_{36}O_6Si_6$	445
Tetradecamethylcycloheptasiloxane	D7	$C_{14}H_{42}O_7Si_7$	519
Hexadecamethylcyclooctasiloxane	D8	$C_{16}H_{48}O_8Si_8$	593

[IWES, 2010]

Fraunhofer IWES

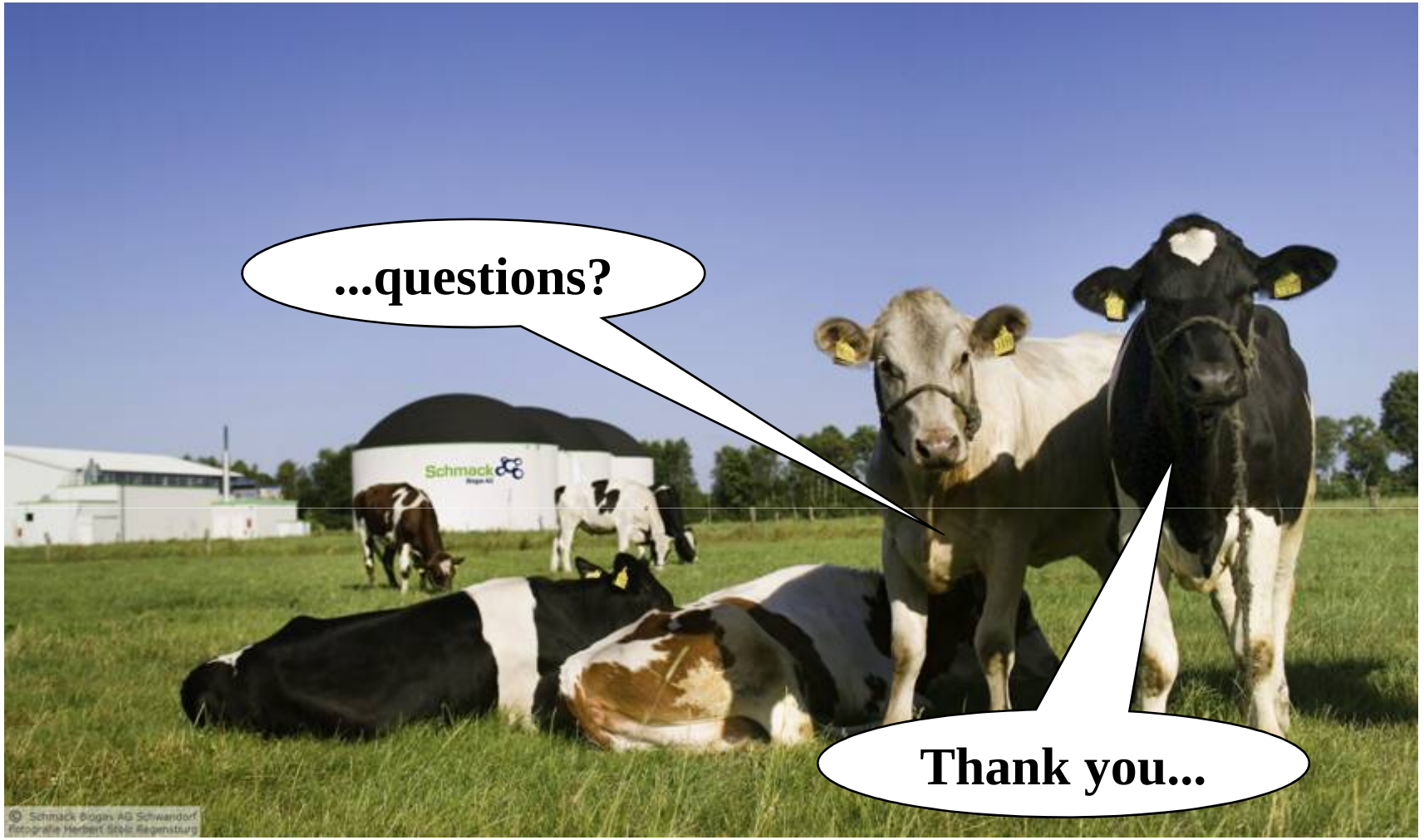
Siloxane separation:

Most common and suitable methods:

- Cooling (cryogenic):
  - -25°C → -26%
  - -30°C → -27%
  - -70°C → -99%
- Adsorption (using activated carbon filters)
- Combination of cooling and adsorption

Ammonia separation

- Activated carbon filters
- Scrubbers:
  - Water scrubber
  - Amine scrubber
  - (Genosorb® scrubbers)
- Membranes



[Copyright: Schmack Biogas AG]

Contacts

Michael Beil
Fraunhofer-Institute IWES
Division Bioenergy System Technology
Königstor 59
34119 Kassel/Germany
+49/561/7294-421
michael.beil@iwes.fraunhofer.de

Fraunhofer IWES