DELIVERABLE

Acronym / Number	**WASTE2GRIDS / 826161**
Title	Converting <u>WASTE</u> to offer flexible <u>GRID</u> balancing <u>S</u>ervices with highly-integrated, efficient solid-oxide plants
Duration	24 months
Start date	01.01.2019

Deliverable Number	D3.2
Deliverable Name	Technical bottlenecks and possible measures
Lead beneficiary	SOLIDpower SA
Authors (beneficiary)	Ligang Wang (EPFL), Stefan Diethelm (SP), Paolo Deiana and Claudia Bassano (ENEA), Yi Zong (DTU)
Type (R/DEC/...)	R
Disse. level (PU/CO/CI)	PU
Delivery date expected	31.10.2020 (M22)
Actual delivery date	30.12.2020 (M24)
Comments	

Summary

This deliverable summarizes the critical bottlenecks and considerations to enable the large-scale deployment of the W2G plants. It involves the identification of the considerations at different levels (material, component, system and grid integration). The information was based on literature review, expert knowledge from the partners, or the findings of this project. The major conclusions are further highlighted in terms of different components, including gasifier, gas cleaning, stack, methanation, system and deployment considerations.

Contents

1. Introduction

This deliverable is based on all previous deliverables, D1.1, D1.2, D2.1, D2.2 and D3.1, to identify the critical bottlenecks or considerations to enable the large-scale deployment of the W2G plants. This involves the identification of the considerations at different levels including:

- Material level: the critical materials, their characteristics and operating issues (e.g., carbon decomposition, species immigration and contamination, formation of nonconductive species, delamination, carburization, high-temperature corrosion, acid corrosion), pollutant resistance (e.g., HCl, H_2S, tar or others).
- Component level: complexity, key elements, performance, degradation/durability, operating flexibility and off-design operating issues, new issues raised by the optimized operating conditions identified in the case studies, size ranges, cost and main drivers, etc.
- Plant level: existing and newly identified system-integration issues (e.g., heat exchange between high-temperature components), major mode-switch obstacles.
- Supply chain level: the logistics of available wastes, the competition of waste utilization technologies, centralized or distributed waste supply for large-scale plants.
- Grid integration level: critical requirements for offering long-term grid services, possibility and challenges to offer short-time grid services (frequency regulation).

The deliverable is organized as follows: Section 2 reports the summary of the bottlenecks of the subsystem/component level including the material issues described. In section 3, the plant design and integration considerations are introduced. In section 4, the plant deployment bottlenecks, including biomass supply chain and grid integration considerations, are summarized.

2. Subsystem/component bottlenecks

2.1 Biomass gasification

2.1.1 Biomass gasifier

There are many different gasification reactors. All are based on one of three generic types: fixed-bed, fluidized-bed and entrained-flow reactors [1]. Fixed-bed updraft is featured with fuel flexibility and the principal advantages are their simple construction and high thermal efficiency.

Gasification systems differ if air or oxygen is used as an **oxidizing agent**. Furthermore, the **biomass feeding method** varies with the considered system: the biomass can be fed either in pellet or chips, either in dry powder or in a mixture. The **flow geometry**, which determines how the fuel and the oxidant come into contact, the temperature, the pressure and the characteristics of the produced syngas differ from one gasifier to another. Finally, different types of gasifiers also differ according to the **mineral-removing methods** in form of dry ash or slag.
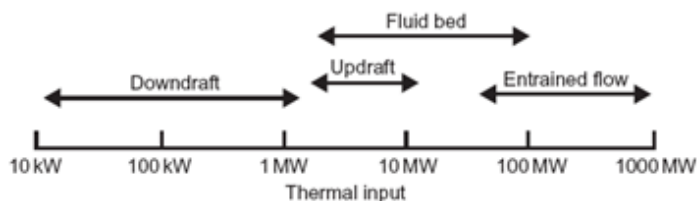
Figure 1 Range of applicability biomass gasifier type.

For fixed-bed gasifiers it is possible to differentiate two reactor type: updraft configuration (countercurrent) when biomass move from the top and the gasifying agent from the bottom; downdraft configuration (concurrent), when the biomass and the gasifying agent move together from the top to the bottom of the reactor.
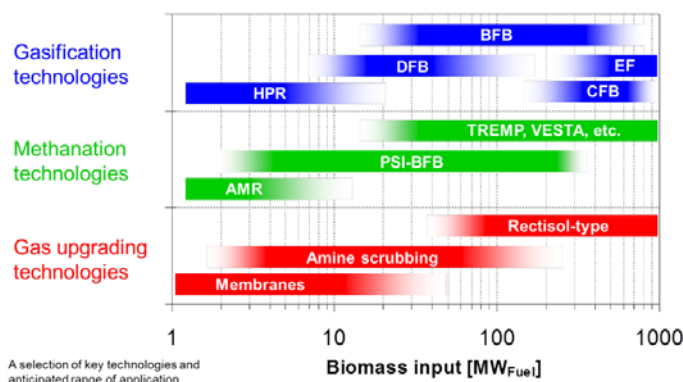

Figure 2 Key technologies for SNG production application range (HPR Heat Pipe Reformer, DFB dual Fluidized Bed, Bubbling Fluidized Bed, CFB Circulating Fluidized Bed, EF Enatrined Flow). [2]

As shown in Figure 1, fixed-bed reactors are generally used in a small-scale application while large coal gasifiers are usually fluidized-bed or entrained–flow type. For small-scale power generation plants of 10 MWth fixed bed gasifiers are considered the best choice. The fluidized-bed type is more appropriate for intermediate units (5–100 MWth); entrained-flow reactors are used for large-capacity units (>50 MWth) [1].

The gasifier type choice generally depends on the final syngas application. Figure 2 shows selected key technologies (gasification, methanation and gas upgrading) for SNG production in function of biomass input.

Table 1 Characteristics and main operating conditions of different gasifier types.

Gasifier type	Entrained flow bed	Twin fluidized bed (FICFB)
Technology	Complex construction	Complex construction
Particle size, fuel, mm	<0,15 mm	<6 mm
Maximum fuel moisture (%)	<15%	11–25
Gas LHV (MJ/Nm^3)	4–6	5.6–6.3
Tar (g/Nm^3)	**0.01–4**	**0.2–2**
Ash and particles in syngas	**Low**	**High**
Ash melting point	>1250 °C	>1000 °C

Syngas output temperature	>1260 °C	800–1000 °C
Residence time	Very short (few seconds)	Particles spend substantial time in bed.
Voidage, %	0.98-0.99	0.5-0.8
Carbon conversion efficiency	High	High
Bed material, particle size, mm	None	0.1-0.5
Gas superficial velocity, m/s	15-25	0.1-1.5
Temperature gradients	Low	High
Process flexibility	Very limited. Size and energy content of the fuel must be in a narrow range.	Flexible to loads less than design
Temperature profile	Temperatures above the ash melting temperature	Constants in each reactor
Hot gas efficiency	80%	90–95%

The choice of gasifier technology for centralized applications has been made considering TRL, integration complexity, scale-up capability and computational requirement. For gasifier technology, we consider entrained-flow gasifier (EFG) for large-scale applications (100–1000 MWth), twin (dual) fluidized-bed gasifier (e.g. FICFB) for medium-scale applications (10–100 MWth).

Table 1 shows that generally gasifiers operate below 900-950 °C, or lower due to ash issues since high-temperature potentially causes **ash agglomeration** problems. Only entrained flow gasifiers operate at markedly higher temperatures, in this condition ash is melted and is removed as a free-flowing slag. Additional advantage is the thermal decomposition of tars and hydrocarbons at these high-temperatures.

2.1.2 Critical issues

(1) Corrosion

Gasifiers are generally built with materials such as pipes, sheets and steel plates. The crucial areas and aspects include:

- **High-temperature corrosion of the grate and nozzles**. Thus, **stainless steels or inconel** are usually used to avoid the softening of mild steels.
- **Chemical corrosion of mild steel components due to organic acid, Cl and S**. Corrosion occurs in areas where water condenses or collects as gasifier water often contains organic acids. In these cases, steel should be replaced by **corrosion-resistant materials such as stainless steel** and should be considered also the adoption of **chromium ferritic alloys** [3]. Biomass may contain larger amounts of chlorine and smaller amounts of sulfur than coal, so there is a risk of higher degree of **chlorine-induced corrosion**. Using a carbon steel shell decreases **stress corrosion cracking** caused by HCl.
- **Corrosion caused by the melting of salts contained in the ash and gaseous reaction products**. These molten salts were found to be very aggressive towards the refractory lining of the gasifier. Some gaseous reaction products were found to penetrate the refractory lining and condense on the cold shell gasifier where problems of material degradation have been highlighted. Laboratory tests reported in Ref. [3] indicated that a **chromium-containing**

ferritic or duplex steel would be expected to achieve satisfactorily in that environment. A 300 series stainless steel would be expected to be resistant to any of the organic acids that might condense on the shell, but the probable for **chloride stress corrosion carking** would make those stainless steels a less desirable choice.

(2) Design

The design of a gasifier is composed of both **process and hardware**. The process design gives the type and yield of the product, operating conditions, and the basic size of the reactor. Hardware design involves structural and mechanical components. Some considerations of gasifier design can be summarized as the following underlining critical issues.

Fluidized-bed gasifier [4]

- **Residence time for sulfur capture and tar conversion/cracking**. For sulfur removal, limestone is fed into the fluidized-bed gasifier since virgin biomass contains little or no sulfur, but some waste biomass fuels do. The height of the gasifier (freeboard and bed) should be adequate to allow the residence time needed for the desired sulfur capture. The depth of the gasifier should be such that the gas residence time is adequate for the desired tar conversion/cracking.
- **Pressure drop**. A deeper bed causes a higher pressure drop across it, leading to higher cost and energy consumption of air compression.
- **Carbon loss**. The freeboard correct height allows entrained particles to drop back into it and avoid carbon loss.

Dual Fluidized Bed Gasifier [5]

Dual fluidized bed gasifier is composed of two fluidized bed chambers, one is a gasification chamber and the other is a combustion chamber. Critical aspects of this gasifier type are:

- Difficult to maintain the continuous circulation of particles
- Relatively complex construction makes it expensive
- Difficult to avoid slight gas mixing between two chambers.

Entrained flow gasifier [5]

Critical aspects of this gasifier type are:

- Fuel preparation cost is high due to very fine particle size requirement
- More sophisticated reactor design due to high-temperature operation
- The thickness of the refractory and insulation used is to be chosen with care due to the high operating temperature and pressure
- Some fuels can form corrosive slag which may damage the inner wall. Slag is corrosive for ceramic inner walls that serve to protect the gasifier outer wall. Limestone can be mixed with the fuel prior to gasification to lower the ash fusion temperature [6].
- Low cold gas efficiency

- Higher amount of gasifying agent requirement.
- Frequent maintenance of critical equipment such as wall refractory and injectors.

Plasma gasifier [5]

Critical aspects of this gasifier type are:

- Highly energy-consuming process
- High capital cost
- Net energy production is small or sometimes negative.

Critical aspects, scale up potential of the three types of gasifiers and the bottlenecks are shown in table Table 2.

Table 2 Gasifier type comparison, with each type ranked from ● (poor) to ●●●●● (good). [7]

Gasifier type	Feedstock tolerance	Syngas quality	Scale up potential	Costs
EFG	● Preparation to <1mm, 15% moisture, low ash %, composition unchanging over time	●●●● Very low CH_4, C2+and tars, high H2and CO	●●●●● Very large gasifiers and plants possible	●●●● High efficiency. Expensive pre-treatment if decentralised
FICFB	●●●● <75mm, 10-50% moisture, care with ash	●●● C2+and tars present, high H_2, but high CH_4. Particles	●●● Some projects planned, but only modest scale up	●●●● Potential for low syngas production costs
Plasma	●●●● No specific requirements	●●●●● No CH_4, C2+and tars High H_2 and CO	● Only small scale, modular systems	● Very high capital costs, low efficiency

2.1.3 Operation considerations

Generally important monitoring and operating procedures to be considered for suitable plant operation include the start procedure (cold and warm start), normal operation, normal shutdown procedure and emergency stop [8]. It is suggested to develop and realize start-up, normal operation and shutdown routines for the entire gasification plant (preheating, gasifier ignition, normal operation, etc.) to avoid human error in manual operation. Also, fail-safe routines have to be part of the plant operation concept. Recommendations and critical aspects regarding operating and monitoring procedures are summarized subsequently.

Normal start-up and shutdown procedures

- At start-up it is recommended to remove the oxygen inside the plant by inertizing the system with for instance nitrogen.
- Experience shows that most accidents take place at start-up and shutdown. Therefore, operators should be instructed not to stay unnecessarily close to system components (gasifier, cyclone bins, filters, etc.) containing flammable materials during start-up and shutdown.
- At start-up and emergency shutdown or in the case where valves get stuck, the gas must be flared.

- If the gas engine were to be shut-down for whatever reason, any residual gas should be immediately flared by switching valves by the automation and control system. If the engine cannot be re-started (after two attempts), the emergency stop procedure should be initiated.

Normal operation procedure

Procedures for manual intervention during operation of the plant should be documented properly in the O&M manual.

Emergency shut-down procedure

- The development of the plant operational manual and appropriate scada control must consider the implications identified within the Hazid and Hazop. Each emergency shutdown procedure is therefore highly specific and customized to the individual application.
- Typical emergency shutdown measures include: stop feeding to the gasifier; stop air supply to the gasifier; direct the gas to the flare; note: inerting the gasifier with nitrogen is not effective as the gasifier normally contains a lot of fuel and charcoal.

Other critical aspects of fluidized-bed gasifiers and entrained flow gasifiers are listed below.

Fluidized bed [4]

One major critical aspect regarding the operating of fluidized-bed gasifiers is the entrainment of fine char with the product gas, contributing to major carbon loss. A tall freeboard can reduce the problem, but that has a cost penalty. Alternatively, fluidized-bed gasifiers can use a cyclone and a recycle system to return the entrained char particles back to the gasifier.

Entrained-flow gasifier

For an entrained flow gasifier, the start-up procedure consists in heating up with a start-up burner the reactor vessel wall that is lined with heavy refractory and therefore takes a long time. During this time, the reactor vessel is not pressurized. When the thick refractory wall is heated to 1100 °C, the start-up burner is withdrawn and the fuel is injected along with the oxidizer (Weigner et al., 2002). The reactor is pressurized slowly once the main fuel is ignited.

2.2 Syngas cleaning

Synthesis gas produced from biomass is considered an attractive and reliable route to produce chemicals, hydrogen, biofuels. Syngas production can be divided in biomass pretreatment (drying and grinding), gasification, gas cleaning up and conditioning (including the removal of particulates, tar, and inorganic), Water Gas Shift, CO_2 elimination, and possibly H_2 purification.

2.2.1 Syngas composition and contaminants

Typical gas composition of raw syngas from biomass gasification is given in Table 3.

Table 3 Gas composition of raw syngas from biomass gasification [9].

Compound	Oxygen gasification (entrained flow)	Oxygen gasification (fluidized bed)	Steam gasification (indirect)
CO (vol%)	40–60	20–30	20–25
CO2 (vol%)	10–15	25–40	20–25
H2 (vol%)	15–20	20–30	30–45
CH4 (vol%)	0–1	5–10	6–12
N2 (vol%)	0–1	0–1	0–1
LHV (MJ m^{-3})	10–12	10–12	10–14
Tar content(g Nm^{-3})	<0.1	1–20	1–10

Gas cleaning is an essential component of any biomass gasification plant to meet the specifications of the syngas end user. Contaminants in syngas are mainly classified as particulate matter, dust, soot, inorganic pollutants and organic pollutants (tars) fly ash, alkali, nitrogen (NH_3, HCN), sulfur (H_2S, COS), halides and trace elements. These contaminants are responsible for the problems in the gasifier such as **corrosion, obstruction and catalyst deactivation**. They also make syngas unsuitable for biofuel production, FT synthesis, fuel cells and other applications.

2.2.2   Syngas cleaning requirement

Syngas downstream process and cleaning levels required are reported in Table 4.

Table 4 Cleaning levels required as a function of the downstream process. [10]

Contaminant	Syngas End Use					
	Methanol Synthesis (mg/m3)	Ethanol (ppmv)	FTS (ppmv)	Hydrogen (ppmv)	SNG (ppmv)	SOFC stack (ppmv)
PM	<0.02	0	0	0	0	0
Tars	<0.01	<0.5	<0.01 §	<1–2 ; <2–5	<2–5	Light tar may be as fuel
Alkali	<0.005	N.A.	<0.01	N.A.	N.A.	-
Nitrogen	<0.1	<1–10	<0.02–10	<1–10	<30	-
Sulphur	<0.5 ; <1	<1–50; 50–100 ++	<0.01–1	<1–50; 50–100 ++	<0.1 *	<1
Halides	<0.001; <0.1	N.A.	<0.01	N.A.	<10	<1
Siloxanes						<0.01
Benzene						Fuel

Consequently, syngas treatment it's necessary prior to its usage.

The effects of the impurities on the SOFC systems usually focus on the nickel-based catalyst used in the fuel processing unit (usually reformer) and the reactant electrode of the solid-oxide cell. The data and explanations given below are mostly based on Ref. [11]. For the reformer, recent research focused on the impact of the H_2S, light hydrocarbons and siloxanes. With the target of our sister EU project Waste2Watts**,** the tolerance of **the reformer** has been set as

- 1 ppm for sulfur (H_2S, org. sulfur (COS, CS_2, mercaptans))

- 0.01 ppm for Siloxanes (D4, D5, …)
- 20 ppm for Halogens (X)
- 1000s ppm for other VOC (linear HC, aromatics).

For the gasification integrated with SOFC, usually, the reformer is not necessary; thus, the contaminant tolerance is mainly from the stack. The adsorption or deposition of contaminants at the three-phase boundary (TPB) of the SOFC anode can drastically reduce the lifetime of cells and stacks. Contaminants can also affect stack components (namely interconnects and sealant); however, the region which seems the most sensitive to contamination and related degradation is the electrode interface with the electrolyte, where the electro-chemical reactions occur. Hence, the durable performance of a SOFC is strongly tied to the characteristics and evolution of electrodes' interfaces during operation.

The mechanisms and tolerances of the poisoning of **the stack** depend on the nature of impurity. Sulfur at low and high concentrations causes adsorption-type and reaction-type degradation. The impact level depends on the H_2S concentration:

- < 1 ppm H_2S concentration: reversible degradation due to the deactivation of steam-reforming and water gas shift reactions. The performance remains stable after stopping the sulfur supply.
- < 2 ppm H_2S concentration: long-term operation may be affected by a significant irreversible degradation.
- >100 ppmv H_2S concentrations: sulfur will react with nickel and bulk sulfidation (NiS, Ni3Sx) occurs, causing irreversible damage to the anode catalyst.

The effects of HCl, and other chlorine compounds, CH_3Cl and Cl_2. For HCl poisoning mechanism, Cl is more likely to be absorbed onto Ni to reduce the triple-phase boundary (TPB). The impact level also depends on the contaminant concentration level:

- < 8 ppm: No obvious degradation. At higher concentrations, Cl_2 and CH_3Cl cause more server degradation than HCl.

Siloxanes decompose at high temperatures and form SiO_2 (s), and even at low concentrations, Si could affect Ni-based anodes via the formation of NiSi and Ni_2Si. Thus, the presence of siloxane can cause deposition-type degradation. A significant performance drop has been observed for the D4 concentration of 69 ppbv - 3 ppmv. **The degradation caused by Siloxanes can only be partially recovered; thus, siloxanes must be removed completely from the biogas feeding the SOFC. Even trace contamination of the fuel feed at ppb level can affect the SOFC Ni anode, leading to fast degradation.**
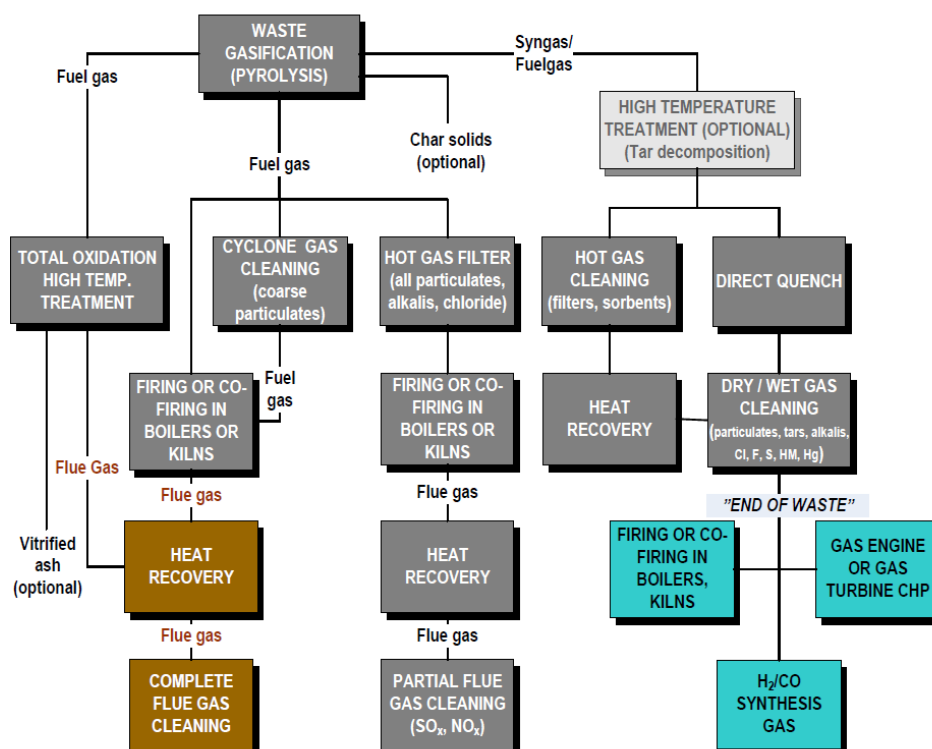
2.2.3   Syngas cleaning technology

Figure 3 Examples of syngas cleaning process chains. [12]

Syngas purification can be divided into hot gas and cool gas cleaning. Hot cleaning systems increase gasification efficiency by around 3–4%, since the syngas loses its energy content when it is cooled. In Table 5 are summarized relevant cleaning technologies for the main syngas contaminants.

Table 5 Syngas relevant cleaning technologies. [13]

Technique employed	Process	Principle	T (°C)	Removal η (%)	Comments
Tar					
Hot Gas Cleaning Technique (HGC)	Thermal Cracking	Employing high T to crack tar	1100–1300	~80	Expensive, results in low process efficiency
	Catalytic cracking	Employing catalyst to crack tar at comparatively low T	Vary	Vary	Operational challenges vis-a-vis catalytic activity due to coking, sintering and poisoning
	Non-thermal plasma	Decomposition of tar by plasma	~400 (pulsed corona plasma)	Vary	Complex, high energy demand
Cold gas cleaning technique (CGC)	Wet scrubbing	Absorption of tar components in H_2O	< 100	Vary	Waste H_2O needs treatment prior to discharge
Particulates					
HGC	Cyclones	Inertial separation	> 1000	90	e.g. – conventional and enhanced cyclones

	Filtration	Diffusion, inertial impaction, gravitational settling	~ 250 (fabric) ~600 (panel bed) ~1000 (metal barrier)	~99	e.g. – fabric filter, panel bed filter, metal barrier filter & rigid filter
	Electro-static separations	Difference in dielectric properties under electric field	~ 400	– a	e.g. – parallel plate precipitator, tube type
CGC	Wet scrubbing	(i) separation by inertial force (ii) electrostatic force (iii) T gradient (iv) liquid vapour pressure	< 100	~95 (PM5) ~70 (submicron) (dynamic scrubber)	e.g.- spray (scrubber, wet dynamic scrubber, cyclonic scrubber, impact wet scrubber)
Alkalis					
HGC	Condensation	Condensation and agglomeration of alkali vapours	~600	–	–
	Adsorption	Adsorption by sorbents	~840	98 (activated Al_2O_3) 99 (Bauxite)	Removal η & T range are function of nature of SO_2 sorbent
CGC	Wet scrubbing	Condensation of alkali vapours	< 300	–	Most alkalis are removed along with tars and particulates
N					
HGC	Thermal catalytic decomposition	Cracking of NH_3 in the presence of catalyst to N_2 and H_2	500–800	80 (WC, WZ catalysts) 92 (Ni/MnO_3/ Al_2O_3)	Different catalysts have different removal η at different T
CGC	Wet scrubbing	Absorption in H_2O	<100	Vary with NH_3 concentrations	Other cold gas methods such as adsorption and biological treatments are not feasible on account of cost and CO_2 generation issues
S					
HGC	Physical and chemical adsorption	Physical absorption is based on Vander Waal's inter-molecular dipole interactions whereas chemisorption employs covalent bonding of adsorbate molecules	400–600 (Z-sorbIII) > 600 (Mn mixed with V and Cu)	99	S adsorption occurs in 3 stages – reduction, sulphidation and regeneration
CGC	Chemical solvent methods	Absorption by amines	< 100	–	COS can't be removed. Continuous solvent replacement is needed.
	Physical absorption	Absorption by methanol and DME	<100	–	COS/H_2S can be removed. High energy requirement.
	Liquid redox process	Wet scrubbing in the presence of catalyst	< 100	100	Non-toxic reactions. Process flexibility. Elemental regeneration
Halides					
HGC	Adsorption	Adsorption by sorbents	500–550	80 (Ca-based powders at 600 – 1000 °C)	Activated carbon, alumina, trona, Ca-based powders are commonly employed sorbents

CGC	Wet scrubbing	Removal of HCl and NH$_4$Cl via absorption	<100	–	Reduction in process η because of acidic compounds and filter coke formation

^{a} Data are not available in the original literature

2.2.4 Tar removal bottlenecks

Tars formation is one of the biggest problems to be solved in the gasification process. Tar is constituted by the condensable products of pyrolysis, composed of a complex mixture of organic compounds and can account for up to 50 % of the weight of the former biomass. **Tar is a complex mixture of condensable hydrocarbons comprising single-ring to 5-ring aromatic compounds plus other oxygen-containing hydrocarbons and complex polyaromatic hydrocarbons**. Tar represents a serious problem in biomass gasification since it can condense in pipes, filters and heat exchangers, causing obstruction of the downstream section of the plant and reduction of the heat transfer efficiency. For these reasons, tars must be separated after the gasifier and before the further syngas treatment section where they can cause the deactivation of the catalysts used for the refining syngas processes.
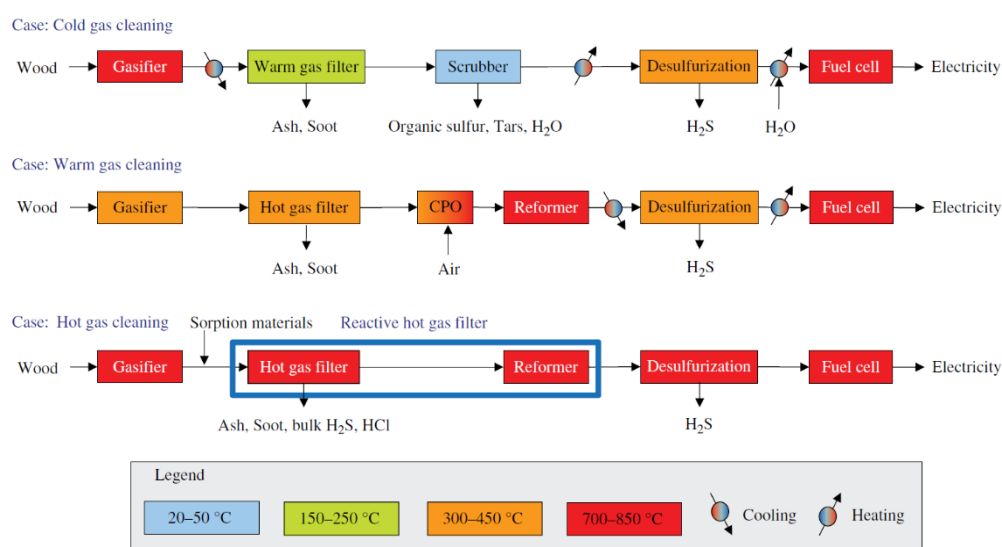

Figure 4 Examples of some cold, warm, and hot gas cleaning process chains (CPO catalytic partial oxidation). [14]

Tar management can be achieved through two strategies: reduction of tar formation inside the gasifier, with the so-called primary methods, or separation after the gasification process, with secondary methods. Primary methods include the optimal design of the gasifier, the optimization of process parameters, and possibly (depending on the specific technology) the use of suitable additives or catalysts.

Secondary methods comprise thermal or catalytic cracking, or mechanical methods such as the use of cyclones and electrostatic filters, as well as the use of wet scrubbers.

Mechanical methods such as the use of cyclones and electrostatic filters, as well as the use of wet scrubbers, remove or capture the tar from product gases, while the energy in tar is lost. The thermal

or catalytic cracking tar methods can not only reduce the tar but also convert the tar into useful gases [15].

Primary methods

Regarding the primary methods, gasifier operating parameters have a very significant role in the tar reduction during biomass gasification and their influence can be summarized as follow:

- Tar yield from biomass gasification decreased drastically from 15 to 0.54 g/Nm3 [15], as the average temperature increased from 970 to 1090.
- Equivalence ratio (ER) increase also has a beneficial effect on reducing tar formation, however, the heat value of product gases will decrease with enhancing ER.

The use of suitable additives or catalysts in the gasifier bed is another method. For example, in a fluidized bed gasifier, active bed material can be applied to achieve lower overall tar contents in the produced raw gases. Dolomite or olivines are naturally occurring minerals that are used for this purpose. Also, catalysts for in-bed tar reforming can be used.

Secondary method
(1) Physical Tar Removal
- Wet scrubbers collect tar aerosols and soluble tar compounds but tar removal efficiencies of wet scrubbers are often not rigorous enough and the treatment of the contaminated liquid is costly.
- OLGA process is a multiple-stage scrubber tar removal concept.

Tar separated by physical removal can be collected and recycled to the gasifier.

An example of tar removal by physical methods is water spray quenching. The syngas produced in **EFG** is often cooled and separated from other gasification products in a quench (following the hot gasification reactor) prior to further upgrading in a series of downstream processes. In the case of **water spray quenching**, a resulting issue is the proper handling of the quench water. In commercial operation, the quench water needs to be circulated and reused without causing operational problems due to accumulation of contaminants. In order to choose the correct combination of water treatments (e.g. coagulation/flocculation, filtration and sedimentation), thorough characterization of the process water is needed in order to tailor proper cleanup techniques. Besides turbidity and acidity, the quench water is defined by the dissolved organic substances (e.g. aliphatics, benzene and polyaromatic hydrocarbons).

(2) Thermal cracking [16]

Tars are decomposed into lighter hydrocarbons at high temperatures or partial oxidation where tar is cracked by increasing the temperature by adding air or pure oxygen to the producer gas. Disadvantage: expensive alloys resisting the high temperatures must be used for thermal cracking.

The heating value of the producer gas decreases significantly by partial oxidation and CO levels could increase at the cost of conversion efficiency.

(3) <u>Catalytic Tar Removal</u>

Catalytic tar removal can be applied in the gasifier or downstream. Catalyst cracking is generally used to decompose or reduce tar with the advantage of conserving the energy content of the tar components. The disadvantages of catalytic tar removal options are catalyst deactivation and costs, especially for synthetic catalysts. In order to get highly efficient tar decomposition, the temperature of thermal cracking needs to be very high, which results in an operating cost increase. The chemical treatments catalytic reforming of tar into gas is one of the most promising, allowing the enhancement of the syngas quality increasing the amount of CO and H_2.

The use of carbonaceous materials, such as **<u>char and activated carbon</u>**, for tar removal and/or cracking offers several advantages over the traditional Ni-based catalysts. Activated carbon as a result of its extensive surface area is an attractive material for tar abatement. The char exhibits quite a high abatement capacity but high deactivation; however, being cheap material always available in the plant, it can be a very interesting solution for the first step of tar abatement placed before a catalytic reactor.

Lessons learnt from GoBiGas project

The analysis and critical aspects of syngas cleanup to produce biofuels were addressed in the Gobigas project. The Gothenburg Biomass Gasification plant (2015) [17] is currently the largest plant in the world producing biomethane (20 $MW_{biomethane}$) from woody biomass. The goal of the GoBiGas project is to produce biomethane (BioSNG) by biomass gasification. The gasifier is a dual fluidized bed system (DFBG).
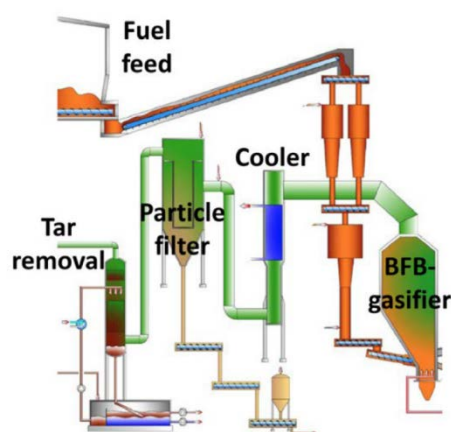

Figure 5 GoBiGas Plant Gasifier section

A characteristic of dual fluidized bed system is the low temperature can lead to a significant level of tar. Aiming to limit the tar yield in the Gobigas plant two innovative approaches were followed:

- A**ctive bed material** is used, thereby avoiding fouling or deactivation in the downstream equipment. As active material olivine was chosen for its ability to reduce the yield of tar and

its tendency not to agglomerate at these process temperature levels. However, to achieve the desired catalytic behavior, olivine needs to be activated. The approach used to active olivine in the GoBiGas plant is based on the addition of potassium.

- A **scrubber fed by a continuous flow of fresh rapeseed methyl ester (RME)**. Using rapeseed methyl ester (RME) as the absorbent liquid the condensable tar is separated. The emulsion of tar and bio-oil is not discharged from the system as waste stream, but is brought into the combustor, where it is combusted and provides additional energy to the system.

The experience gained from the Gothenburg Biomass Gasification plant indicates several measures improving the efficiency, including the use of additives (potassium and sulfur), high-temperature pre-heating of the inlet streams and improved insulation of the reactors. Also, the recirculation of the ash streams within the process is an important issue since the presence of the alkali salt in the systems was identified as highly important for control of the tar species. More aspects of the experience gained from the demonstration of GoBiGas wood-based biomethane production plant can be found in Ref. [18].

2.3 RSOC stack and balance of Plant

The cost of the RSOC stack represents a significant share of the full system cost. This is due to the expensive materials that are used, the small production scale and the limited lifetime of the stack components due to their degradation over time. The latter is a material related topic **that could hinder the commercialization of RSOC**. In what follows, we will give a brief overview of the main materials involved in the construction of RSOC, their prevailing degradation mechanism and, when available, mitigation measures that are proposed**.**

2.3.1 Cell/stack materials and degradation

Materials and structures

RSOC stack has the same construction as SOFC. The core element is the cell, which is made of three layers: the central solid oxide electrolyte and the two electrodes. The positive electrode, where the oxygen evolves, is usually made of perovskite-type oxides or sometimes a mixture of this oxide with fluorite-type oxide (ZrO_2, CeO_2) to improve its adhesion to the electrolyte. The first generation of oxygen electrode were composed of $(La,Sr)MnO_3$ (LSM) or LSM-YSZ. The second generation is based on $(La,Sr)(Fe,Co)O_3$ (LSCF), which requires the addition of a barrier layer between the electrolyte and the positive electrode to prevent the formation of Sr-zirconate, known as a poor electrical conductor, which would increase the cell's internal resistance. The solid electrolyte is mainly Yttrium stabilized zirconia (YSZ). Scandium doped zirconia (ScDZ) has recently been used as an alternative electrolyte because of its higher ionic conductivity, in particular with electrolyte supported cells in which the resistance of the electrolyte is the main contributions to the cell losses due to its relatively large thickness (50-100 micron). Doped ceria (mainly Gd-doped CeO_2) has also been considered because of its higher conductivity but, due to the presence of significant electronic conductivity at high temperature, its use is restricted to operating temperatures around $600°C$.

The negative electrode is predominantly Ni-cermet. Where the electrode is the support, Ni-YSZ is preferred, whereas in electrolyte-supported cells, Ni-CGO is preferred. More recently, alternative negative electrodes have been considered based on perovskite oxides such as Sr-titanite and La-chromite, but the conductivity and activity of these materials are far below that of nickel.

The other stack components besides the cell are the metallic interconnect (MIC) that prevents the air and the fuel from direct mixing when the cells are stacked in series, the gas distribution layers (GDL) that ensure an even distribution of the reactive gases all over the active area, the gas manifolds and the sealings. Figure 6 presents a schematic picture of a single repeating unit with its main components.
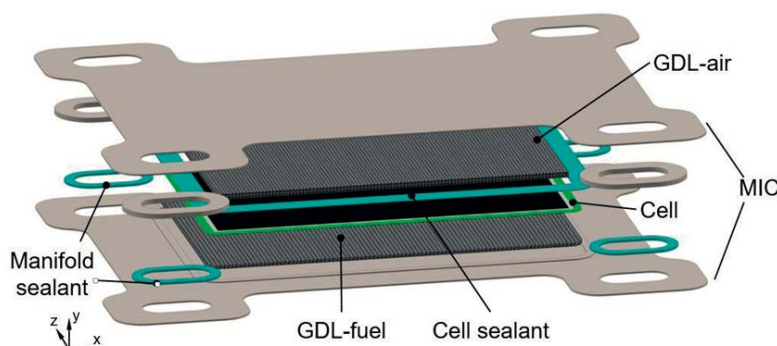
Figure 6: exploded picture of a basic repeating unit of a stack, showing the main components: metallic inter-connect (MIC), gas diffusion layer (GDL), sealant and cell.

Degradation

There are many detailed reviews of degradation in RSOC such as in Ref. [19]. We will here only give a short overview. One of the major degradation mechanisms in SoA negative electrodes is related to the **evaporation of Ni** from the functional layer in the vicinity of the electrolyte, resulting in the reduction of the active triple phase boundary (TPB) sites, where the electrochemical reactions take place. This mechanism translates into an increase of the effective electrolyte thickness and consequently in an increase of the ohmic resistance of the cell. This phenomenon affects more severely the negative electrode when operated in electrolysis mode than in fuel cell mode. Different mechanisms have been proposed to explain the loss of contact between the Ni particles and the zirconia backbone and their removal. The simple formation of volatile $Ni(OH)_2$ in presence of steam is not sufficient to explain the high evaporation rates [19]. One of the assumed mechanisms implies the formation of zirconia nanoparticles at the TPB by fracture due to high local temperature gradients provoked by the neighboring Joule and Peltier heat sources. This mechanism is specific to the electrolysis mode but does not occur in fuel cell mode because then the Joule and the Peltier effects tend to compensate [19]. As a mitigation measure, CGO infiltration in Ni-YSZ cermets was observed to reduce the Ni-migration [20].

Another explanation is related to the wetting properties of nickel on zirconia, which is characterized by the dihedral contact angle (θ_{Ni}) between zirconia and the Ni particle. This angle is assumed to depend upon the polarisation of the electrode [21]. The proposed Ni removal mechanism is depicted in Figure 7: Under electrolysis polarisation, the dihedral contact angle tends to reduce by

electrowetting, favoring the migration of Ni far from the TPB (B). Ultimately, this would result in the removal of the Ni particle (C). In this case, a possible mitigation measure could be to increase the wettability of Ni by alloying with Ti, for instance [22].
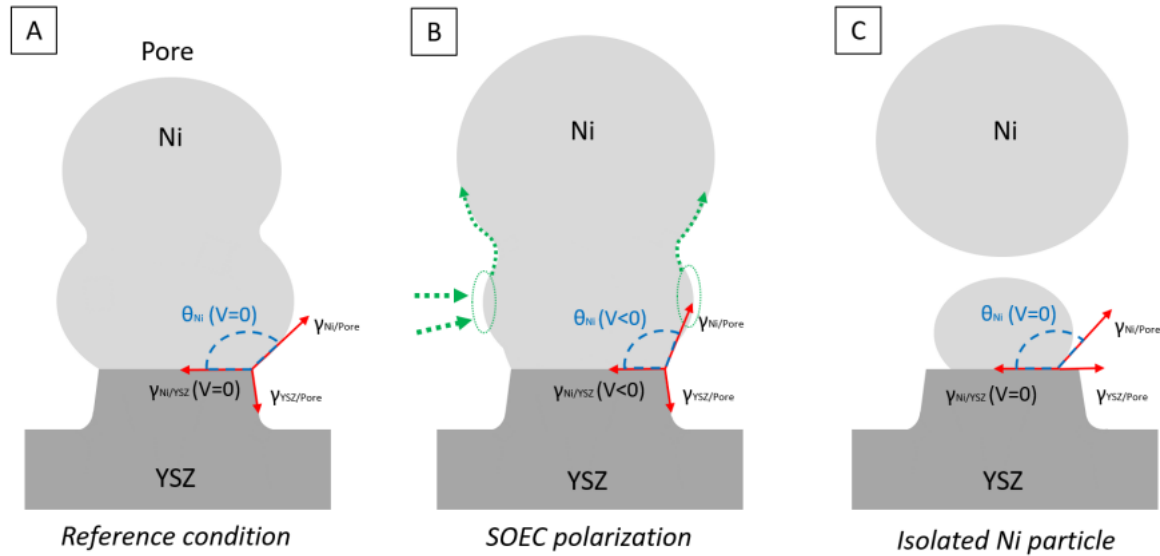

Figure 7: proposed mechanism for the loss of Ni based on electrowetting. Refer to text for explanation [22].

Impurity impact

Another cause of degradation is electrode poisoning by **impurities** either contained in the raw materials of the cells or generated in the other the components of the stack (sealings, MIC,...) or the BoP (HEX,...). The syngas produced by biomass gasification, is known to generate a large amount of impurities that are detrimental to RSOC: in particular sulphur containing compounds, tars, halogens and alkali metals. Beside abundant literature, there are two on-going FCH-JU H2020 projects that are specifically investigating the effect of impurity levels on the performance and durability of SOC: Waste2Watts for biogas and BLAZE for woodgas.

Si and Na tend to form glassy deposits at the TPB, thereby blocking their activity in an irreversible manner. The only mitigation measure is to use scavenger materials in the electrode that will capture the impurities before they deposit on active sites. Addition of SrO and La_2O_3 have been considered therefore. CeO_2 can also be an efficient trap for Si in its reduced form [19].

Cr is a well-studied oxygen electrode poison. It either originates from the MIC or from metallic hot BoP materials. SOFC degradation rates have significantly decreased since spinel oxide coatings have been applied on the MIC to hinder the evaporation of Cr. Sr-containing oxide contact layers have also be shown to be efficient Cr-getters. The main drawback is the formation of $SrCrO_4$, which has a poor electrical conductivity. Such Cr-getters have also been suggested upstream of stacks to capture volatile Cr-species originating from the hot BoP components. Cr-traps consisting of $(La,Sr)CoO_3$ coated ZrO2 honeycomb have been implemented and successfully tested [23].

Carbon deposition and high-temperature corrosion

Carbon containing fuels are prompt to crack on the Ni-particles and form **carbon deposit**. The carbon that diffuses in the Ni grain tends to accumulate at the gain boundaries and grow as carbon-whiskers that remove Ni-particle from the bulk. This phenomenon is known as metal dusting and results in the reduction of the active electrochemical sites. Addition of steam, CO_2, H_2 or eventually air can help gasify the deposited carbon and prevent the irreversible detrimental metal dusting. Carbon deposition is particularly at risk with heavier hydrocarbons ($\geq$C2) but can also occur with CO and CH_4. Ni-ceria is less sensitive to C-deposition than Ni-zirconia because of the ability of ceria to act as an oxygen buffer. Regarding the Waste2GridS case, the tars produced during the gasification of biomass wastes are particularly critical: light tars tend to favour carbon deposition and heavy tars tend to plug the pores of the cells and provoke fuel starvation. A thorough removal is therefore required. Mitigation measures have been considered such as using less carbon sensitive metals, passivation of Ni with sulphur or exsolution of the Ni particles [19].

Another material related aspect that could be critical is **high temperature oxidation** of metals. Refractory alloys are used; where electrical conduction is required (MIC), ferritic steels are preferred, whereas for BoP components such as HEX, oxidiser and reformer, austenitic steels are selected. The resistance to oxidation often stems from the high levels of Cr (>20%) that from a Cr_2O_3 scale in oxidising environment. The growth of the scale can be hindered by addition of reactive elements such as Ce, La or Y that reduce the mobility of oxygen in the scale. On the other hand, the addition of Mn favours the formation of spinel $(Cr,Mn)_3O_4$ that increases the conductivity of the scale [24].

Currently used alloys for RSOC are also being considered as supports for oxygen separation membrane (OSM) applications in which the materials are exposed to oxygen concentration up to 100% at 800°C [25]. High O_2 concentration however seems to be less detrimental to metal oxidation than humidity [26].

Table 6 summarises the material related threats and proposed mitigation solutions.

Table 6: Summary of material related components' lifetime issues with their associated mitigation measures.

Material	Bottlenecks	Mitigation measures
Negative electrode	Ni-evaporation	CGO infiltration Ni-alloying with Ti
Negative electrode	Impurities	MIC coatings (Cr) Upstream cleaning getters
Negative electrode	C-deposit	Less C-sensitive metals, Ni-passivation
Metal parts	Metal corrosion	coatings
Positive electrode	Impurities	Getters

Beside components' lifetime issues, the question of availability of raw material should also be mentioned as a potential bottleneck in the future. In particular, the question of rare earth elements (REE) that are widely used in many renewable technologies such as electrical engines and generators (magnets), batteries (electrodes), photovoltaics (semiconductors) and fuel cells (electrodes, electrolyte, etc). The growing demand will be confronted in the future to many challenges:

geopolitical (in 2015, China represented >85% of the world production), environmental (mining, radioactive ore) and recycling (mature industrial-scale recycling of REE is inexistent) [27]

2.3.2 Key components

The key components that build-up a RSOC system are, beside the SOC stack modules, the heat exchanger network, the air blower, the steam generator and the post-combustor. The RSOC also requires power electronics (bidirectional DC-DC boosters and AC-DC converters). For RSOC operating at atmospheric pressure (<100mbar overpressure), the design of the heat exchangers might be challenging in order to optimize the heat recovery, implying a large exchange area, while minimizing the pressure drops. This is particularly true in the electrolysis mode, where the stack is operated close to the thermo-neutral voltage and therefore the approach temperature is small. In many practical cases, electrical heating is used to ensure the final heating of the gas streams (cf. SUNFIRE and Haldor Topsoe) but with an efficiency penalty.

The RSOC stack is expected to have a lifetime shorter (5-8 years) than the rest of the BoP (15 years). The system design should therefore allow to replace the stack modules in a convenient way. Ideally, it should allow the replacement of the individual stack modules without stopping the whole plant. This could be achieved with modules that could be stopped, disconnect and restarted independently from the rest of the plant. This concept is discussed in deliverable 3.1 (Development path and upscale strategy) and will be detailed below. Other disposable components such as filters should be replaced on a yearly basis during annual maintenance.

2.3.3 Process and systems

In D3.1, a pathway for the RSOC scale-up strategy was presented to reach the multi-MW scale. The approach relied on 100-400kW stack modules that could be started and stopped independently to allow their replacement without stopping the whole plant. This implies that the stack module includes some BoP components such as heat exchangers (air and fuel recuperators) and a burner for the controlled heat-up. The syngas resulting from the biomass gasification should go through a purification step (tar removal and desulfurisation,…) before entering the RSOC modules. Depending on the chosen technology for purification, the clean syngas will be distributed either close to ambient temperature or at a higher temperature (>400°C) (cf. D2.1: Optimal conceptual plant design). In order to allow more easy isolation and disconnection of the individual RSOC modules, syngas should be distributed at a temperature below 200°C. This would also be the case for the steam feed to the RSOC. On the contrary, air would be distributed at ambient temperature. The following figure gives a schematic representation of the multi-MW concept. Each RSOC module is fed with air, syngas and superheated steam. Each line has its own control and shut-off valve in order to allow the modules to be operated independently and eventually stopped and restarted if required. Shut-off valves are also installed at the outlets for the hydrogen and/or flue gas for the same purpose.
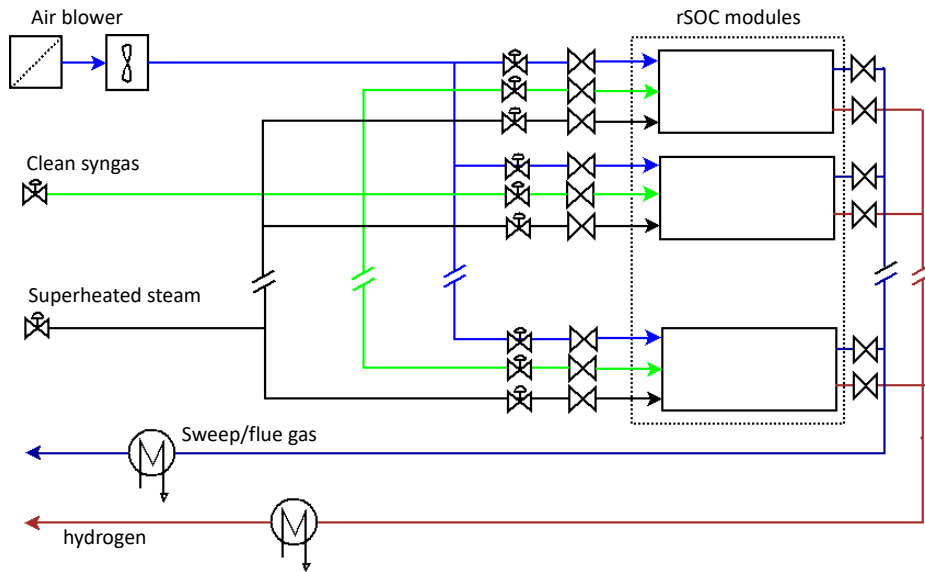
Figure 8: schematic representation of the modular approach followed for multi-MW scale RSOC

Fulfilling grid-balancing services requires the ability to switch from the electrical power production mode to power storage mode within less than 15 minutes [28]. Although the electrochemical response of the RSOC is very fast, the thermal changes are slow due to the high heat capacity of materials used in the stacks. Similar thermal inertia occurs with the heat exchangers, the steam generator and the gasifier. Therefore, the switching between modes must be done in such a way that the initial and final state should not differ too much from a thermal point of view. However, operating the RSOC in power generation mode on syngas is highly exothermic and therefore requires large air cooling, whereas electrolysis is operated preferably close to thermo-neutral voltage for higher efficiency. Alternatively, if the RSOC would be operated in fuel cell mode with methane rather than syngas and with significant internal reforming, this would allow to reduce the air flow to a value closer to the sweep flow used in electrolysis mode.

The electrical architecture of a multi-MW RSOC plant has also been discussed in D3.1. Power electronics favours high voltage and low current. whereas the single RSOC stack rather operate at low voltage and high current. It would therefore be advantageous to connect the stacks within a module or the modules themself in series in order to increase the voltage. This would however, imply technological complications since the stacks or modules should be electrically floating and therefore electrically insulated from one another. Alternatively, the voltage of each stacks/modules could be increased by using DC-DC boosters. However, every additional electronic component would increase the cost of the system and decrease its efficiency. Figure 9 illustrates three possible electrical connections: A) corresponds to the case where the RSOC stacks/modules are connected in series to a centralised bidirectional DC-AC converted before an AC-transformer brings the voltage to the grid requirement. In B), the stacks/modules are connected to individual DC-DC booster before the centralised DC-AC converter. Finally, in C), the stacks/modules are connected in parallel to a centralised DC-DC booster before the DC-AC converter.
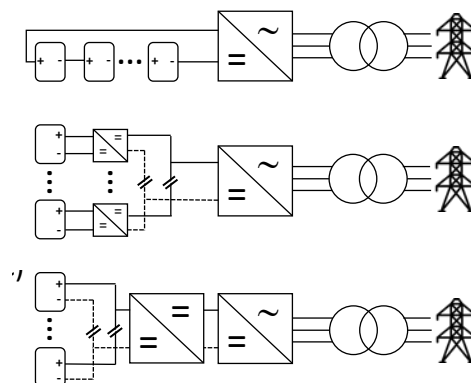
Figure 9: schematic representation of three different power connection configuration: A) RSOC stacks or modules assembled in series; B) stacks or modules with bidirectional DC-DC converters in parallel; C) stacks or modules in parallel.

2.4 Methanation [29]

There have been many methanation technology under development, as shown in Figure 10. The catalytic methanation reaction has been known since 1902. Since the oil crisis in the 1970s, the use of methanation for the production of SNG from synthesis gas has gained increasing interest. CO_2 methanation for SNG production has also been investigated for decades. Several reactor concepts (mostly fixed-bed) for large scale coal-to-gas plants have been developed. Catalytic methanation reactors are typically operated at temperatures between 200 C and 550 C and at pressures ranging from 1 to 100 bar. Several metals such as Ni, Ru, Rh, and Co may be used as the catalyst for the methanation reaction. However, **most often Ni is considered to be the optimum catalyst choice due to its relatively high activity, good CH_4 selectivity, and low raw material price**. However, nickel based catalysts require a high purity of the feed gas (with respect to halogeneous and sulphurous compounds, among others).

The methanation reaction is highly exothermic. **The methanation reactor is to realise good temperature control in the reactor in order to prevent thermodynamic limitation and catalyst sintering.** In order to meet this essential objective, several steady-state reactor concepts have been developed, namely fixed-bed, fluidized-bed, three-phase and structured reactors. **Fluidized-bed reactors as well as fixed-bed reactors are established technologies**, while the other reactor concepts are in the development phase. **Different methanation reactor concept offers a different approach to overcome the issue related to the reaction heat removal.**

For adiabatic fixed-bed reactors, the usual approach relies on a series of adiabatic reactors, typically 2-5, **with intercooling and sometimes with gas recirculation**. Due to the adiabatic mode of operation, the catalyst must be able to withstand a broad temperature range (250-700 C). The main concerns for the catalyst are possible **cracking or sintering**. Alternatively, cooled fixed-bed reactors can be applied for methanation. Usually, such a reactor contains cooling tube bundles; a further possibility is the use of cooled plates. Due to the cooling, the process setup is simpler than for adiabatic reactors, however, the reactor itself is more expensive.

In fluidized-bed reactors, the mixing of fluidized solids leads to almost isothermal conditions in the reactor facilitating the control of the operation. Offering more effective heat removal is the major advantage of this concept, which allows for using one single reactor with a rather simplified design. Nevertheless, due to high mechanical load resulting from fluidization, attrition processes take place in relation tothe catalyst as well as thewall of the reactor. As a consequence, the catalyst is eventually deactivated. A further disadvantage can be the incomplete CO_2 conversion caused by bubbling. In addition, a fluidized-bed reactor is limited by superficial gas velocity within the reactor: it cannot be too low in order to assure minimum fluidization conditions and cannot be too high in order to avoid catalyst elutriation.
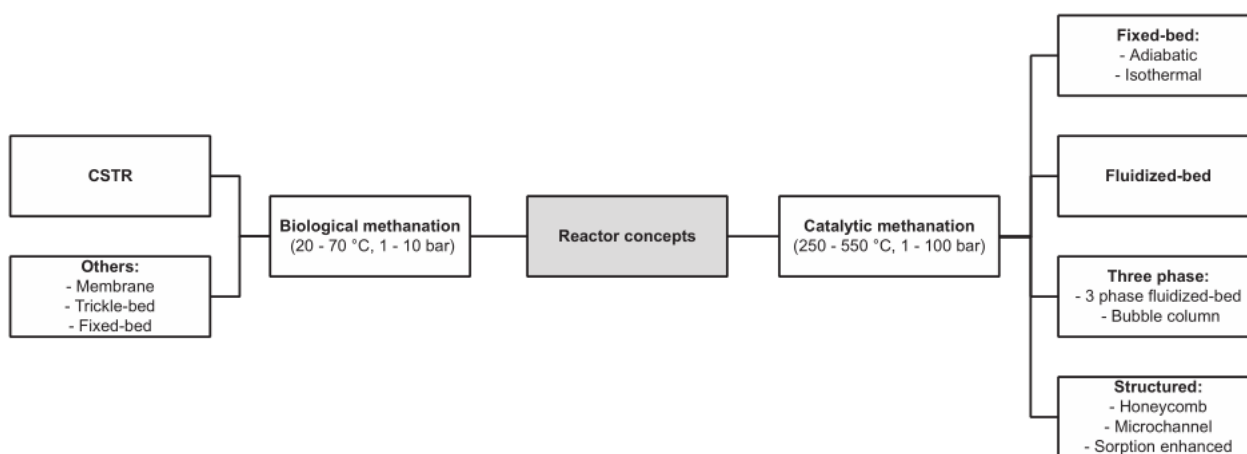
Figure 10: Methanation technology.

The methanation subprocess is working under PowSto and PowNeu modes, while in the PowGen mode, it will be kept under a warm state. Dynamic performance is involved. Under dynamic operation, the reactor temperature can severely change if the reactor heating or cooling cannot be adapted quickly enough. This strong temperature variation can lead to catalyst cracking or sintering which diminishes the catalyst lifetime. The major way to overcome the temperature variation issue is to adapt methanation reactor concepts for dynamic temperature regulation.

The summary of methanation bottlenecks is given below:

- The size of fixed-bed methanator system can be very large to tens of MWth.
- Few results are published about the dynamic operation of methanation reactors.
- Recent results indicate that the dynamic operation is not significantly reducing the catalyst stability.
- The control of the reactor temperature of adiabatic reactors is difficult; consequently cooled fixed-bed reactors are under investigation to handle the above mentioned issue.

2.5 Auxiliaries

There are many different technologies, including cryogenic air separation units, pressure swing adsorption and vacuum pressure swing adsorption. The cryogenic distillation process are **mature** and **dominating**. The sizes of air separation unit can be very large. Air Liquide Engineering &

Construction provide oxygen, nitrogen, argon and rare gases production plants, ranging from units with a capacity of **a few hundred tons per day of oxygen to** Mega **ASU multi-train complexes capable of producing more than 20 000 tons per day of oxygen**. **The major challenge might be the frequent start-up and stop, coupled with oxygen storage.**
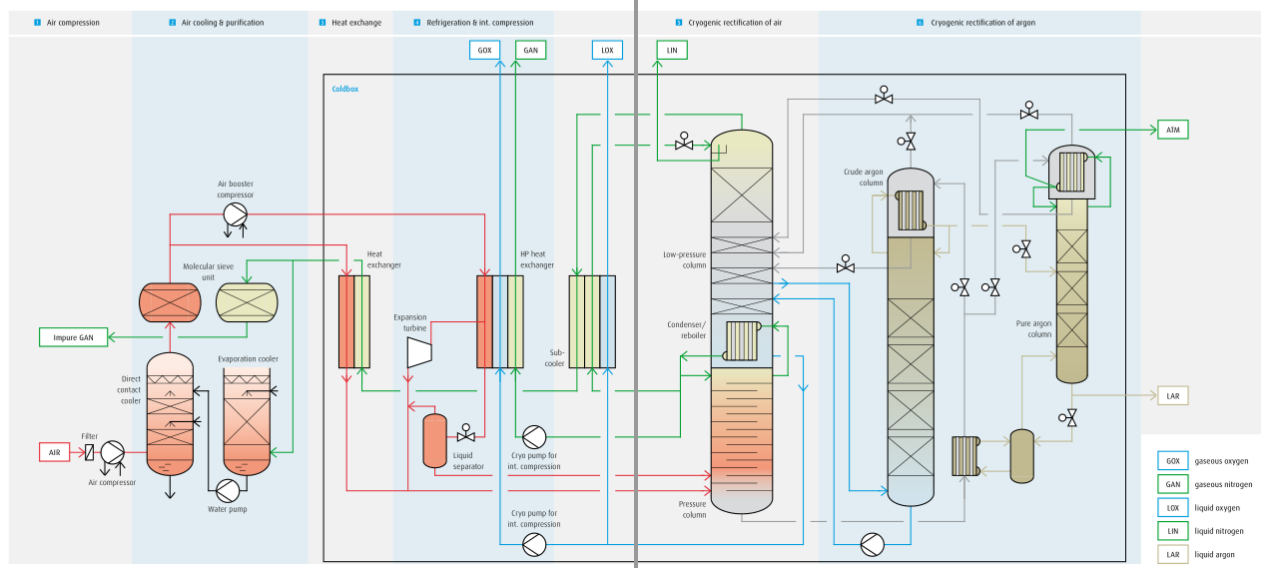

Figure 11: Typical cryogenic air separation process [30].

3. Plant design and integration bottlenecks

The plant design and integration bottlenecks are related to D2.1 and D2.2. They can be summarized in the following category:

Plant design: For the plants with the same stack sizes, different plant designs realize different characters to interact with the electrical, gas grids. This will affect the overall economic feasibility. The design involves the selection of technology combinations, including gasification, syngas cleaning, solid-oxide cell stack, methanation subsystem, electrolysis mode. According to D2.1 and our recent publication [31], the major conclusion of the process design investigation are:

- The increase in efficiency results in an increased cell area for a given biomass feed. There is no big difference (less than 5% points) in efficiency among various process options of the same type of gasifier. The efficiencies reached can be up to 50%–60% (power generation), 72%–76% (power storage) and 47%–55% (power neutral). Those with fluidized bed gasifier can realize higher efficiencies than those with entrained flow gasifier.
- The steam turbine network plays a significant role to enhance the efficiencies of all modes by converting available process heat to electricity. With the promotion of syngas converted

electro-chemically via penalizing syngas burnt, the Rankine cycle can still generate power of 0.21–0.24 kW/kW-LHVdb, thanks to its optimal deployment. The efficiencies of all three modes can drop by up to 20% points if the steam turbine network is discarded.

- By penalizing the syngas burnt, the optimal designs in the pool obtained has limited variation of grid interactions, particularly for the process options with entrained flow gasifier. The ratio of power between power storage and generation modes can vary within 2.4–3.0, while that of the gas between power storage and power neutral modes varies around 3.5. However, those with fluidized bed gasifier allows for an enlarged ability of grid interactions.

- For all three modes, the overall biomass-to-product processes are highly exothermic. Due to the electricity feed, the PowSto mode results in more process heat (0.9 kW/kW-LHVdb) above 250 C than the PowGen and PowSto modes (0.6–0.7 kW/kW-LHVdb). Thus, it is a challenge to design a common heat exchanger networks to satisfy the heat transfer of all three modes.

Combining the major conclusions from D2.2, the following findings are highlighted:

- Technology combination: Fludized-bed gasifier seems to be preferred than the entrained flow gaisifer. Steam electrolysis shows advantage in terms of stack durability. The steam turbine network should be properly sizing to maximize the heat utilization of the three modes.

- The plant size is largely limited by the biomass supply chain, and should be below several hundreds of MWth. The major sizing issue comes from the stack. It is needed to scale the stack technology to several tens of MWe (PowGen mode). Therefore, reliable scale-up of the solid-oxide technology is one critical aspect to enable the W2G concept contribute significantly to the expected grid balancing.

Mode switch and operational flexibility: The HEN enables the feasibility of mode switch. However, the real operation needs the plant to smoothly switch between different modes within a minimum switch time. This would require the subsystems to be operated in different ways:

- Gasification and syngas cleaning: stable, steady-state, continuous operation if no maintenance is needed
- Stack: Leading the switch of modes; stack thermal management during mode switch; centralized or distributed flow organization methods; under operation if no maintenance
- Methanation: The subsystem is not working during the PowGen mode and under partial-load operation in the PowNeu mode; therefore, thermal mangement of the methanation units become important during the standby periods.

Heat exchanger network (HEN): The HEN is a key to realize the high efficiency of all three modes. The charateristics of the hot and cold streams are rather different in three modes. The components involved in mode switching are also different, as discussed above. Designing a specific feasible HEN, which could manage the heat exchange of all three modes efficiently with the **minimization of its investment costs**, is critical to make the W2G plant. This involves the optimization of HEN with the optimal spliting and matching of hot and cold streams considering **multiple operating periods**, and

stuctural design to enable a compact HEN with a minimized heat loss. Particularly, due to the operation variation of different subsystems in different modes:

- **The HEN for the gasification and syngas cleaning subsystems** should be designed more for one period, since it is expected not to change under different modes. Thus, the HEN for this subsystem should be designed and integrated considering only the hot and cold flows within the subsystem, while its integration with the subsequent subsystems is via end-of-pipe utilization to minimize the impact of mode switch of downstream subsystems.
- **The HEN for the stack and methanation subsystems** should be more interacted to reach the stack operation requirement and to realize the following points: (1) the maximization of the utilization of end-of-pipe streams from the gasification/syngas cleaning subsystems, (2) the utilization of methanation heat (when available) for stack subsystem heat requirement, and (3) the utilization of heat from the stack subsystem to keep methanation ready-to-use during standby periods.

To EPFL's best knowledge, there has been no practice for such a complex HEN for the power generation and storage sector.

Mode switch and partial-load operation of the methanation subsystem: The W2G plants are not expected to operate with load shifting but only operates with mode switching. The W2G plants will be operated at a full load of each mode. The methanation reactors work under full load at the PowSto mode but partial load at the PowNeu mode. The methanator subsystem design needs to consider whether the reactor will be centralized or modulized.

4. Plant deployment bottleneck

4.1 *Biomass supply chain*

The biomass supply chain plays a crucial role in the deployment of the triple-mode grid-balancing plants, influencing their economic potential and restricted to a specific geographical area. Thus, the tailored biomass supply chain is designed and dimensioned to fulfill the biomass requirements of the W2G power plants by optimizing the supply chain capital and operating expenditure. Based on the optimization results for the DK1 area and Italy case study, it can be found that the total annual cost of the biomass supply chain is approximately linear related to the yearly balancing biomass requirements in two ranges: 0 – 10 TWh /year and 10 – 40 TWh/year.
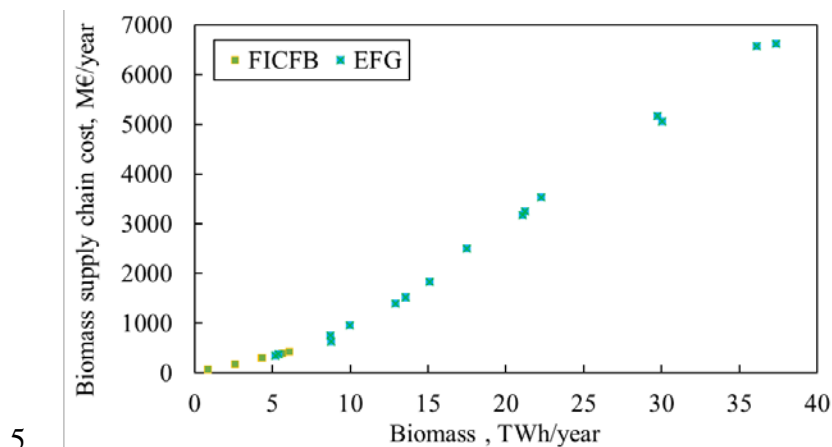
Figure 12: The total annual cost of biomass supply chain changing along with yearly balancing biomass requirements.

The total cost of the biomass supply chain consists of raw material purchase cost, transportation cost, production cost, indirect cost and capital investment cost. According to a detailed cost breakdown analysis, the raw biomass purchase cost is higher than half of the total cost (54 – 75%) and the proportion decreases along with the yearly biomass requirements increasing, while the proportion of the indirect cost is ignorable (less than 1%).

With the yearly biomass requirements increasing, the biomass collection geographic range increases and the transportation cost increases, but the share presents a slight fluctuation from 8% to 15%. On the one hand, transportation cost consists of fuel cost (related to the transportation distances) and the load/unload cost (related to the amount of biomass). On the other hand, the share is influenced by the change of other costs, e.g., the rise of the production cost.

For the production cost, when the yearly biomass requirements less than 10 TWh, the share of production is similar to that of the transportation at 10%. However, the proportion performs a significant increase from 10% to 30% when the biomass requirements rise. The increment of the production cost is derived from various biomass use and pre-treatment. The biomass with higher LHV and lower moisture content is a prior option in the supply chain but with limited available capacity, with the biomass requirements increasing, the biomass with lower LHV and higher moisture content will be used and cause a larger drying cost. For the capital investment cost, it increases with the biomass requirements increasing but the share decreases from 5% to 1% since the scale-up effect and the significant change in production cost.

4.2 Grid integration

Firstly, the pre-qualifications for new technologies (e.g. P2X) to provide ancillary services are updated based on currently on-going/ finished projects in this section. Secondly, the test results of a 3-year European Union H2020 project QualyGridS (launched in 2017), which aims to establish standardized testing protocols for electrolysers to perform electricity-grid services, are summarized as a reference for RSOC based Waste2Grids plant grid integration in the near future. Finally, technology competition and business models for grid integration of the RSOC based Waste2Grids plant are investigated, followed by a suggestion of future work.

4.2.1 Pre-qualifications for new technologies to provide grid services

High penetration of renewables (wind, photovoltaic), and other CO_2 neutral power production plants together with the development of new technologies, such as renewable fuels and Power2X technology, demand side aggregated units (e.g. heat pumps, cooling equipment and household & industrial customers), combined with the fact that all conventional coal-fired power plants are expected to experience a reduction in operation, triggers the consequence that ancillary services deliveries in practice should be able to be delivered from all kinds of resources for TSOs.

Technical concepts such as system inertia and voltage stability are characteristics of the electrical transmission system having system robustness against frequency disturbances and other incidents in the grid. Today the inertia of the system depends on the stored energy in the rotating masses of electrical machines i.e. generators and motors (the spinning reserves). Alternative providers must be established to supplement, provide and in the long term even replace inertia coming from large convention generators. Caused by an increasingly larger amount of renewable energy production, which comes from converter-based technologies, there will be a corresponding reduction in inertia since these technologies do not contribute to natural mechanical inertia. These facts have initiated research and development tasks providing ancillary services from production and demand facilities [32].

The energy market is characterised by rapid changes, where new technologies can contribute to greater flexibility and liquidity in the market, provided that there are no unnecessary barriers to entry for new technologies in the market. This is useful in terms of ensuring high system security while maintaining a high proportion of renewable energy. It is found that there is without a doubt technical potential for delivery of ancillary services from new types of converter-based generation units with source from wind and sun, wind turbines and photovoltaic plants. Demand side units, such as large heat pumps or aggregated cooling equipment, which are also increasingly being supplied via converters, can already supply ancillary services or are being prepared for delivering ancillary services, when dimensioning the associated thermal and/or mechanical systems are accordingly taken account of. Supplementary deliveries of ancillary services from Power-to-X technologies are possible today. The technical potential is available, and the amount of plants will supposedly expand in the coming 5-10 years [32].

Before the service provider enters the market, **it is a prerequisite to pass a pre-qualification test through which the grid operator can assess the service provider's ability against the technical requirements of the targeted service**. Units (e.g. Waste2Grids plants) that would like to offer balancing services to electricity grid operators, pre-qualification, in terms of its technical ability/metering and communication setup, is often required. It is **pre-qualification** that is a process, where a grid operator makes an assessment of a service provider's capability against the technical requirements of targeted service. It is therefore a prerequisite for the participation in tendering procedures for services that are critically important. In principle, detailed pre-qualification testing procedures are well defined by the TSOs in each country. Pre-qualification, in general, is initiated by potential service providers (e.g. the owners of the Waste2Grids plants), who have to make

applications to the TSOs. **Once all the required certificates, protocols and other documents are received by the TSO, pre-qualification tests will be arranged under framework/bilateral agreements** [33]. The duration of a pre-qualification test can vary from short (i.e. a few minutes) to medium (i.e. up to 2 hours) to long (i.e. up to weeks). The short-duration tests are normally made to examine one or more individual technical aspects. The medium and long tests are conducted to test sustainability. The detailed test manual and requirements for the Danish TSO can be found in reference [34] and the deliverable 1.1 of Waste2Grids project.

The technical characteristics and qualification requirements for grid services requested by the DSOs are more or less the same as those for the TSOs. Acquisitions of the DSOs' grid services are normally managed through bilateral contracts. In practice, the grid services are applied to address techno-economic issues of an individual power system. Therefore, the requirements even for the same type of grid services can be different from one grid operator to another. Regarding different aspects of grid services, technical requirements and pre-qualification standards, the technical report "Grid service catalogue for water electrolysers (WE) " [35] published by the QualyGridS [36] consortium presents a detailed overview of grid services applied by the grid operators in Europe.

For the RSOC-based Waste2Grids plant always running at warm states, it could target at the replacement reserves (**RR**). **RR** are mostly referred to as manual reserves or regulating power, which are actually two parts of the same market – the availability market (reserve market) and the activation market (regulating power market). The physical purpose of regulating power is for the TSO Energinet.dk to replace the activated primary and secondary reserves with manual regulating power and thereby ensure that as much primary and secondary reserve capacity as possible is available for stabilizing the grid frequency. Furthermore, the TSO also use regulating power proactively by forecasting imbalances and taking pre-emptive action to avoid imbalances. This is done by activating downward or upward regulation. The TSO will procure upward regulation in hours where less electricity is produced than is consumed, and conversely the TSO will procure downward regulation when more electricity is produced than consumed. Reserve agreements are made in order to ensure that there are always sufficient bids on the manual regulating power market for the TSO to call upon. The manual reserve market is a marginal price market, where the last bid accepted sets the price. If a reserve agreement is not made, the actors can still submit regulating power offers. Offers can be made and adjusted **until 45 minutes before the hour of operation**. Also, in this market the price is determined by the marginal pricing system, meaning that the most/least expensive unit sets the price for all accepted bids, depending on whether it is up or down regulation. In order to be able to participate in this market, the unit **must be able to ramp up to the quantity offered within 15 minutes after activation**. **Once activated the unit is guaranteed a minimum operation of 30 minutes.** In addition, currently the minimum bid size of 10 MW applies for the bids given by the BRP, but these can consist of **several smaller aggregated bids**. This means that also units with a capacity below 10 MW can participate in this market if the BRP is able to pool several units to a combined capacity of more than 10 MW [37].

In addition, depending on in which place and to which voltage level an electric unit is connected to, the unit may need to be follow certain grid codes, such as voltage support, frequency support etc. A

grid code is a technical specification, which defines the parameters that a facility connected to a public electric grid has to ensure safe, secure and economic proper functioning of the electric system [38]. For example, in order to provide secure and stable grid services, current WEs need to revise the control strategy according to local grid code requirement (See the details in the following sub-section).

4.2.2   Lessons learnt from the current market and technical barriers for P2X (e.g. electrolysers)

Balancing means all actions and processes through which TSOs continuously ensure the maintenance of system frequency within a predefined stability range, as well as compliance with the amount of reserves needed with respect to the required quality. There are specific rules related to different types of grid services, in terms of a unit/a group of units' technical ability. Often, the ability requirement covers capacity, speed of reaction, ramping ability, duration etc. Balancing energy in Europe is organized in up to five steps: (1) Frequency containment reserve (*FCR*); (2) Imbalance netting (*IN*); (3) Frequency restoration reserves with automatic activation (*aFRR*); (4) Frequency restoration reserves with manual activation (*mFRR*); (5) Replacement reserves (*RR*). The detailed description of the current balancing market and balance settlement both in Denmark and Italy can be found in the Deliverable 1.1 of the Waste2Grids project. Detailed requirements for balancing services of *FCR, FRR, RR* in different countries can be found in Ref. [35].

Power-to-X (P2X) is expected to be a key element in a cost-effective transition to a clean, renewable energy supply, which can convert renewable electricity production via electrolysis into hydrogen, and further process into gaseous and liquid fuels etc. The trading strategy for P2X technology can be designed in many different ways depending on the specific plants, but based on current energy market **the most relevant markets for a P2H plant are the spot (day-ahead) market and the regulating power market**. The primary and secondary reserve markets are relatively small in DK1 (West Denmark) compared to the other markets. **The tertiary reserve market (regulating power market) is more interesting for flexible demand such as electrolysis.** In this market, bids of just one hour can be offered and these bids can be changed until 45 minutes before operation. With this option, it is easier for a plant to participate in multiple markets and adjust the production plan according to the need for hydrogen. One strategy could be to buy the needed electricity for the coming day on the spot market and within the day of operation offer upward and downward regulation in the regulating power market to the extent that electricity is dispensable or extra electricity can be consumed. In addition to this strategy, the intraday market could also be used as a way of balancing the produced hydrogen and the demand for hydrogen.

Consumers and BRPs (Balancing Responsible Parties) have **recommended more changes for the balancing market requirement** (listed in the following summary) [32]. Especially concerning integration of more ancillary services delivered from consumers and new technologies, for example, the minimum bid of 5 MW of *mFRR* is most important regarding demand bids, and lowering to 1 MW will presumably result in faster introduction of demand bids [32]. These recommendations on revising the grid codes create great opportunities for the RSOC based triple-mode grid balancing plant (power generation, power storage and power neutral) to participate in the balancing market.

- ***FCR-D*** (Disturbances): min. bid 0.3 MW lowered to 0.1 MW

- ***FCR-N*** (Normal operation): min. bid 0.3 MW lowered to 0.1 MW

- ***aFRR***: min. bid 1 MW lowered to 0.5 MW

- ***mFRR***: min. bid 5 MW lowered to 1 MW

Some on-going and finished hydrogen-related demonstration projects in Denmark show that Electrolyser (PowerStore Mode for W2G plants) can provide ancillary services for frequency regulation to the Danish power grid. For example, the electrolyser unit (1 MW alkaline electrolyser - aggregated portfolio of reserves) at the BioCat [39] Avedøre has been approved by Energinet to participate in the **DK2 *FCR-N*** market. The unit can also participate in the spot market and the regulating power market with ***mFRR*** (***aFRR*** is not relevant in DK2-East Denmark) [32]. The HyBalance project [40] demonstrates the use of hydrogen in energy systems. The hydrogen produced from WE, can not only store cheap renewable electricity from wind turbines, but also can help balance the grid. For example, the 1.2 MW Polymer Electrolyte Membrane (PEM) WE unit- aggregated portfolio of reserves can participate in the **DK1 *FCR*** frequency market, the spot market and the regulating power market with ***mFRR*** as well as the automatic reserves ***aFRR*** [32].

By conducting many tests on different WEs in EU H2020 QualyGrids project [36], it is highlighted that **although flexibility is often more associated to the PEM WEs, advanced Alkaline WEs have the same flexibility in terms of ramping and load following ability** [36]. Results have also shown that there are multiple factors that could influence the qualification of an electrolyser for grid services, such as electrolyser technologies and system design, the selected range of load variation, configuration issues related to the inclusion of balance-of-plant (BOP) or not, delays caused by communication and other limitations of test benches, etc. Other issues such as a variation in the stack impedance during constant-load periods and the capability of the rectifier technologies applied can also influence the power-performance stability of the electrolyser. What has been particularly observed during the test is that, although power regulation of the electrolyser load can be achieved by changing the electrolyser DC-current set-points in real time, it is challenging to achieve highly accurate active-power control due to the variation in stack impedance. It is therefore **highly recommended to use a dedicated power controller** when the required accuracy level of the electrolysers' power performance is high [41]. In a word, it has been identified that the difficulties to participate in grid services are from the BOP of WEs. The power electronics and the control must be formulated the right way for dynamic operation. For example, smoothly power-controllable BOP system should be a nice-to-have feature to allow grid service not only for rectifier input but also for the full system in a flexible and dynamic manner [36].

The test knowledge and experience of WEs in QualyGrids project, not only can bring relevant stakeholders and society multifold benefits, e.g. facilitating mutual understanding between the electricity industry and the hydrogen industry, supporting further improvement of the developed testing protocols, guiding the design and selection of relevant techno-economic case studies and business models, but also can serve as a good reference on how to design and operate on Waste2GridS

plants including its BOP and communication systems for the purpose of providing grid services in the near future.

4.2.3 Technology competition and business models for grid integration

The RSOC is still extreme expensive for system level application. If with potential subsidies through green-initiative legislation and improved efficiencies with more research, the economic benefits can be increased. Especially, due to the high operation temperatures of water electrolysis, there is also potential to include them in the district heating network and thereby reducing the need for CHP [42].

There is a realistic potential for establishing P2X systems in Denmark during the next 5-10 years. However, an analysis [43] also shows that the regulations – including electricity tariffs – have a major impact on profitability and the choice of a connection model. Tariffs can have a significant impact on the profitability of P2X, as they can represent a significant part of the final electricity price. Yet, it is still the raw electricity price that has the greatest impact. Despite all kinds of advanced model analysis, it is still notoriously difficult to predict future electricity prices because so many factors – regulatory, macroeconomic and system-related – come into play [43].

There are still some challenges for the grid integration of the RSOC based Waste2Grids plant. Firstly, it needs to compete with other energy storage/flexible technologies, which may have better techno-economic abilities (e.g. grid-connected battery). Secondly, new business models, such as Wind/PV+ RSOC hybrid plants, energy sector coupling by combining with district heating systems through heat recovery (including low temperature and ultra-low temperature district heating) should be investigated, including the optimal sizing and placing (grid-connection) [44]. Finally, technology improvements on control strategy, power electronics and communication systems should be further conducted in order to adapt the grid codes and energy market's requirements. Future research should more focus on the system energy efficiency. When P2X units (e.g. WE electrolysers) are coupled with renewables, where times of operation and idle periods alternate, will potentially influence its performance because of the degrading mechanisms occurring [45].

5. Summary

This deliverable is further summarized as follows:

- Gasification
    - Materials to resist corrosion caused by high-temperature, chemical (organic acid, Cl and S) and the melting of salts
    - Process and design: tar generation control with proper bed materials; residence time for sulfur capture and tar conversion; pressure drop and carbon loss; expensive; the scale-up ability and product impurity of FICFB gasifier
- Syngas cleaning
    - Materials to resist corrosion caused by high-temperature, chemical (organic acid, Cl and S)
    - Tar removing or conversion process

- Deep syngas cleaning to reach the stack requirement: < 1 ppm H2S, <8 ppm chlorine compounds, no Siloxanes
- Innovative, less expensive deep gas cleaning process and units needed
- Stack
  - Metal to resist high-temperature corrosion, various impurities (S, Cl, etc)
  - Cheaper and better performing cell materials, particularly not using Co
  - Cell/stack durability with impurity tolerance enhancement and advanced process control to reduce degradation and carbon deposition
  - Scale-up and manufacturing
- Methanation
  - Cheaper, durable, highly selective catalyst
  - Reactor and process design to realize good temperature control, and high controllability
  - Dynamic operation
- System
  - Matching of plant design and application
  - Steam turbine network to enhance the overall performance
  - Mode switch and operational flexibility to reduce the switch time and proper management of the standby mode of methanation reactors
  - Heat exchanger design to enable multiple operating mode with components under different operating schemes
- Deployment
  - Size strongly limited by the biomass supply chain: very large single plants up to 1000 MWth not feasible
  - Grid integration: service qualification with the plant established and tested.

References

1. PrabirBasu Biomass Gasification and Pyrolysis Practical Design 2010, Pages 167-228.
2. Production of Biomethane/Synthetic Natural Gas (SNG) from Dry Biomass – A Technology Review 2015.
3. Materials Issues In Biomass Gasification by James R Keiser, Samuel A Lewis Sr, Raynella M Connatser, Donovan N Leonard. CORROSION 2018 Conference & Expo April, 2018.
4. Biomass Gasification, Pyrolysis and Torrefaction Practical Design and Theory Basu 2013 https://doi.org/10.1016/C2011-0-07564-6
5. Chanchal Loha, Malay K. Karmakar, Santanu De and Pradip K. Chatterjee Gasifiers: Types, Operational Principles, and Commercial Forms Coal and Biomass Gasification, Energy, Environment, and Sustainability, 2018 https://doi.org/10.1007/978-981-10-7335-9_3
6. Chapter 3 - Gasifier Types G.Speight https://doi.org/10.1016/B978-0-12-799911-1.00003-0
7. Review of Technologies for Gasification of Biomass and Wastes E4tech, June 2009
8. GASIFICATION GUIDE Potential hazards and good design principles
9. Yanan Zhang et al. Economic and environmental potentials for natural gas to enhance biomass-to-liquid fuels technologies. Green Chem., 2018, 20, 5358–5373
10. A. Molino et al. Biofuels Production by Biomass Gasification: A Review. Energies 2018, 11, 811; doi:10.3390/en11040811
11. Lanzini, A., Madi, H., Chiodo, V., Papurello, D., Maisano, S., & Santarelli, M. (2017). Dealing with fuel contaminants in biogas-fed solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC) plants: Degradation of catalytic and electro-catalytic active surfaces and related gas purification methods. Progress in Energy and Combustion Science, 61, 150-188.
12. Lars Waldheim, Gasification of waste for energy carriers A review IEA 2018
13. Sikarwar et al. Progress in biofuel production from gasification. Progress in Energy and Combustion Science Volume 61, July 2017, Pages 189-248
14. Urs Rhyner Synthetic Natural Gas from Coal, Dry Biomass, and Power-to-Gas Applications Chapter 3 Gas Cleaning 2016 John Wiley & Sons, Inc.
15. Jun Han, Heejoon Kim. The reduction and control technology of tar during biomass gasification/pyrolysis: An overview. Renewable and Sustainable Energy Reviews Volume 12, Issue 2, February 2008, Pages 397-416
16. Urs Rhyne Chapter 3 Gas Cleaning Synthetic Natural Gas from Coal, Dry Biomass, and Power to Gas Applications
17. Alamia A. et al. Performance of large-scale biomass gasifiers in a biorefinery, a state-of-the-art reference. Int. J. Energy Res. 2017; 41:2001–2019
18. H. Thunman et al. Advanced biofuel production via gasification – lessons learned from 200 man-years of research activity with Chalmers' research gasifier and the GoBiGas demonstration plant. Energy Science and Engineering 2018; 6(1): 6–34
19. M.B. Mogensen, M. Chen, H.L. Frandsen, C. Graves, J.B. Hansen, K.V. Hansen, A. Hauch, T. Jacobsen, S.H. Jensen, T.L. Skafte and X. Sun, Reversible solid-oxide cells for clean and sustainable energy, Clean Energy, 2019, Vol. 3, No. 3, 175–201
20. Ovtar S, Tong X, Bentzen JJ, et al. Boosting the performance and durability of Ni/YSZ cathode for hydrogen production at high current densities via decoration with nano-sized electrocatalysts. Nanoscale 2019; 11:4394–406.
21. A. Nakajo, G. Rinaldi, P. Caliandro, G. Jeanmonod, L. Navratilova, M. Cantoni, J. Van herle, Evolution of the Morphology Near Triple-Phase Boundaries in Ni – Yttria Stabilized Zirconia Electrodes Upon Cathodic Polarization, Journal of Electrochemical Energy Conversion and Storage, 2020; 17: 041004-1-13
22. Giorgio RINALDI, Long-term evolution of solid oxide fuel and electrolysis cell 3-D microstructure, Thesis 9381, EPFL, 2019.
23. J.A. Schuler A.J. Schuler, D. Penner, A. Hessler-Wyser, C. Ludwig, J. Van herle, Mitigating Cr Contamination by Hot Air Filtering in Solid Oxide Fuel Cells, Electrochemical and Solid-State Letters, 14(12):B132
24. M. Bianco, M. Linder, Y. Larring, F. Greco, J. Van herle. Lifetime Issues for Solid OxideFuel Cell Interconnects. Solid Oxide Fuel Cell Lifetime and Reliability. Academic Press.2017.
25. Ragnar Kiebach, Kurt Engelbrecht, Kawai Kwok, Sebastian Molin, Martin Søgaard, Patrick Niehoff, Falk Schulze-Küppers, Ralf Kriegel, Jens Kluge, Peter Vang Hendriksen, Joining of ceramic Ba 0.5 Sr 0.5 Co 0.8 Fe 0.2 O 3 membranes for oxygen production to high temperature alloys, Journal of Membrane Science 506 (2016) 11–21
26. Manuel Bianco, Analysis of High Temperature Degradation in Metals for SOFC Power Generators, EPFL thesis
27. Tanushree Dutta, Ki-Hyun Kim, Minori Uchimiya, Eilhann E. Kwon, Byong-Hun Jeon, Akash Deep, Seong-Taek Yun, Global demand for rare earth resources and strategies for green mining, Environmental Research 150 (2016) 182–190
28. ENTSO-E, ELECTRICITY BALANCING IN EUROPE: AN OVERVIEW OF THE EUROPEAN BALANCING MARKET AND ELECTRICITY BALANCING GUIDELINE, November 2018
29. Götz, M., Lefebvre, J., Mörs, F., Koch, A.M., Graf, F., Bajohr, S., Reimert, R. and Kolb, T., 2016. Renewable Power-to-Gas: A technological and economic review. *Renewable energy*, *85*, pp.1371-1390.
30. https://www.leamericas.com/en/images/Cryogenic%20air%20separation%20brochure19_4353_tcm136-414865.pdf

31 Wang, L., Zhang, Y., Li, C., Pérez-Fortes, M., Lin, T.E., Maréchal, F. and Yang, Y., 2020. Triple-mode grid-balancing plants via biomass gasification and reversible solid-oxide cell stack: Concept and thermodynamic performance. Applied Energy, 280, p.115987.

32 Energinet report, "Ancillary services from new technologies: Technical potentials and market integration", December 2019. https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&ved=2ahUKEwiv0_rHuI_tAhVVr4sKHYNxCAwQFjAAegQIAhAC&url=https%3A%2F%2Fenerginet.dk%2F-%2Fmedia%2F229625DCEA984813BF322090E7926844.pdf&usg=AOvVaw3k8L34fx_O9D9Qvk-KsV3u

33 Energinet report, "Prequalification of units and aggregated portfolios", https://en.energinet.dk/Electricity/Rules-and-Regulations/Approval-as-supplier-of-ancillary-services---requirements

34 Energinet, "Test manual and conditions reserves", https://en.energinet.dk/-/media/23C3E874506D446C81BB6A4C1087801D.pdf?la=en&hash=7B76C6722F45DEE007EFD5E98209B5C8CC708D64

35 Shi You, Chresten Træholt and Yi Zong et al. "Electrical Grid Service Cataloguefor Water Electrolyser", https://www.qualygrids.eu/app/uploads/sites/5/2017/02/Deliverable-1.1-Electrical-Grid-Service-Catalogue-for-Water-Electrolysers-27-11-2017.pdf

36 EU H2020 QualyGridS project, https://cordis.europa.eu/project/id/735485/results

37 Power2Hydrogen, WP1 report "Potential of hydrogen in energy systems", http://hybalance.eu/wp-content/uploads/2017/01/Power2Hydrogen-WP1-report-Potential-of-hydrogen-in-energy-systems.pdf

38 Roland Bründlinger, "Grid Codes in Europe for Low and Medium Voltage", 6th International Conference on Integration of Renewable and Distributed Energy Resources, Kyoto November 18, 2014, https://www.nedo.go.jp/english/ired2014/program/pdf/s2/s2_4_roland_bruendlinger.pdf

39 BioCAT project, http://biocat-project.com/

40 EU H2020 HyBlance project, https://cordis.europa.eu/project/id/671384

41 Shi You, Regine Reissner, Christoph Imboden and Cyril Bourasseau et al. "Facilitating water electrolysers for electricity-grid services in Europe through establishing standardized testing protocols", Clean Energy, 2020, 1–10, doi: 10.1093/ce/zkaa015

42 Yi Zong, Jiawei Wang and ShiYou, et al. "Identifying the System-related Conditions and Consequences of Power-to-X Solutions for a High Renewables Penetration in Denmark", the 4th IEEE Energy Internet and Energy System Integration, Wuhan, China, Oct.31-Nov.1, 2020.

43 Energinet report, "PTX IN DENMARK BEFORE 2030-Short term potential of PtX in Denmark from a system perspective", April 2019. https://energinet.dk/Analyse-og-Forskning/Analyser/RS-Analyse-April-2019-PtX-i-Danmark-foer-2030

44 Jiarong Li, Jin Lin, and Yonghua Song, et al. "Operation optimization of power to hydrogen and heat (P2HH) in ADN coordinated with the district heating network", IEEE transactions on sustainable energy, vol. 10, no. 4, October 2019.

45 A. Weiß et al "Impact of Intermittent Operation on Lifetime and Performance of a PEM Water Electrolyzer", Journal of The Electrochemical Society, 166 (8) F487-F497 (2019)

Acknowledgment