CONVERGE

CarbON Valorisation in Energy-efficient Green fuels

A H2020 Research and Innovation Action project, Grant Agreement number 818135

D5.1 – Report on the technical specifications for the CONVERGE unit

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WP 5: Socio-techno-economic assessment

Task 5.1: Technical specifications of the CONVERGE process

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Technical References

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[1] PU = Public

PP = Restricted to other programme participants (including the Commission Services)

RE = Restricted to a group specified by the consortium (including the Commission Services)

CO = Confidential, only for members of the consortium (including the Commission Services)

History of Changes

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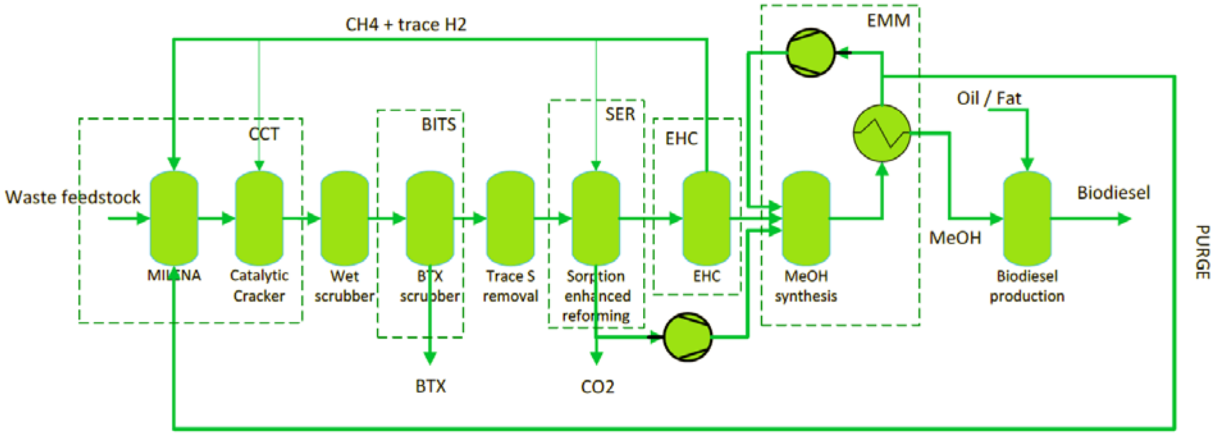
00	25/02/2019	Original version by POLIMI
01	05/03/2019	Revisions of IFE, TNO, UBB included
Final	08/03/2019	Approved by Giampaolo Manzolini

Disclaimer

Executive Summary

The CONVERGE project will validate an innovative route for green biodiesel production starting from secondary biomass. This new route which is more efficient and less expensive than current processes: it will take advantage of five innovative technologies specifically selected to improve each conversion step required from secondary biomass to biodiesel from both efficiency and costs. The CONVERGE solution is built around the concept of developing a set of five new technologies:

- **CCT**: Catalytic cracking of tars from an indirectly heated gasifier to below green C8
- **BITS**: Recovery of refinery products including aromatics for green C6-C8 fraction (BTX)
- **SER**: Sorption-Enhanced Reforming of C1-C6 for excess-carbon removal, and H_2 production
- **EHC**: Highly efficient electrochemical compression of green H_2 with by-product fuel
- **EMM**: Enhanced Methanol Membrane to ensure efficient green biodiesel production



This report summarizes the operating conditions of each component (temperature, pressure and composition of the inlet/outlet streams). These conditions will be used as starting point to develop the different units.

This report is not intended to determine the performance of the CONVERGE system as there is no optimization and heat integration between the components.

Heat and mass balances are determined through a simplified code to predict the performance of each component.

This report points out the synergies between the different technologies integrated in the CONVERGE unit which provides (i) a**good flexibility** with respect to the feedstock, (ii) **production of BTX** (benzene, toluene, xylenes) together with methanol and (iii) a CO_2 stream ready for storage or other utilization options thus delivering **negative CO_2 emissions**.

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Nomenclature/Acronyms

Comp	Compressor
CCT	Catalytic Cracker of Tar
C&C	Cleaning & Conditioning
BITS	Recovery of BTX
BTX	Benzene, Toluene, Xylenes
EHC	Electrochemical Hydrogen Compressor
HP	High pressure
LP	Low pressure
MET	Methanation reactor
SER	Sorption Enhanced Reforming
WGS	Water Gas Shift

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1 Introduction

1.1 Purpose of the deliverable

The CONVERGE project will validate an innovative route for green biodiesel production starting from secondary biomass. This new route is more efficient and less expensive than current technologies will take advantage of five innovative technologies specifically selected to improve each conversion step required from secondary biomass to biodiesel from both efficiency and costs. The main rationale behind CONVERGE is process intensification, applied to a biomass-to-fuel production unit, minimizing the energy losses related to processing steps and producing 100% biogenic methanol as feedstock for biofuels production. The goal will be reached through the reduction of the number of processes in the transformation chain and eventually increasing the overall efficiency compared to state-of-the-art approaches.

The CONVERGE solution is built around the concept of developing a set of five new technologies.

The project started in November 2018 and in the first four months of the project, a simplified CONVERGE flow sheet was developed to identify the initial operating conditions of each component. These conditions will be used as starting point to develop the different units.

This report is not intended to determine the overall performance of the CONVERGE system as in this first iteration there is no optimization and heat integration between the components. In addition, there is no comparison between the CONVERGE unit and reference technologies.

The aim of this report is to provide to all the consortium partners and, in particular to the technology developers, **an initial set of operating temperatures, pressure and compositions for each operation unit as well as their respective product specifications**.

Heat and mass balances are determined through a simplified code to predict the performance of each component.

This report already points out the synergies between the different technologies integrated in the CONVERGE unit which provides (i) **good flexibility** with respect to the feedstock, (ii) **production of BTX** (benzene, toluene, xylenes) together with methanol and (iii) CO_2 stream ready for storage producing **negative CO_2 emissions**.

1.2 Deliverable structure

In Section 2, the main components of the CONVERGE process and their features are presented, together with the proposed integration for the whole transformation chain from biomass-to-methanol.

Section 3 of this report also includes a preliminary simulation of the complete CONVERGE process, aimed at providing to the developers of the different technologies a comprehensive framework for defining the components operating conditions and their interactions.

2 CONVERGE process configuration

The CONVERGE process includes the whole transformation chain from biomass to methanol. The main steps involved are biomass gasification, syngas conditioning and methanol synthesis. Although this scheme is a well-known pathway for bio-chemicals and bio-fuels production, the novelty of CONVERGE process is the integrated approach that involves five innovative technologies, which are listed below:

- **CCT**: Catalytic cracking of tars from an indirectly heated gasifier to below green C8
- **BITS**: Recovery of refinery products including aromatics for green C6-C8 fraction (BTX)
- **SER**: Sorption-Enhanced Reforming of C1-C6 for excess-carbon removal, and H_2 production
- **EHC**: Highly efficient electrochemical compression of green H_2 with by-product fuel
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A schematic integration of the processes is presented in Figure 2.1.

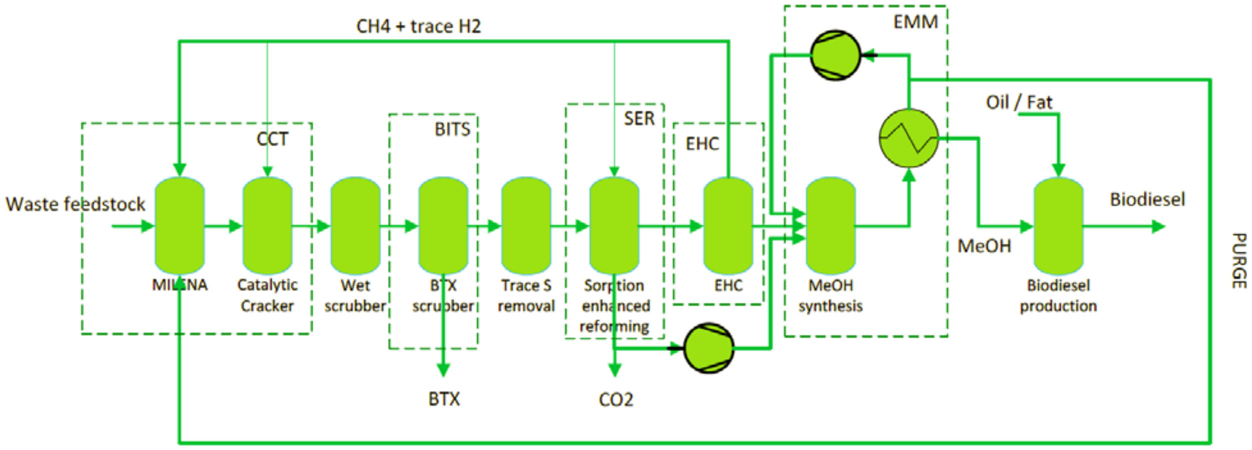

Figure 2.1 – CONVERGE process integration

Because of the presence of such processes, still not commercially available off-the-shelf, a preliminary evaluation of the interactions and of the operating conditions has been performed through simulation. The simulation approach for each section and the main assumptions are presented in the next sections, while in Chapter 3 the results are discussed.

2.1 Biomass drying and gasification

The plant is fed with secondary biomass and should be capable of converting different feedstocks. In this preliminary analysis, residual wood is considered as reference case due to the relative stability of its characteristics and the availability of data for gasifier simulation. Other options will be investigated during the project according to the results of techno-economical screening, focusing on solid biomass.

The "as received" biomass has a variable amount of moisture, so a pre-treatment including drying and grinding must be considered whenever the moisture content is above 25%. In the simulations, the pre-treatment section includes a tube bundle drier fed with saturated steam (6 bar, 160°C) and using ambient air as humidity sweep gas.

The biomass gasification is performed by an indirect gasifier, i.e. the MILENA technology developed by ECN-TNO. The indirect gasifier contains separate sections for gasification and combustion. This separation of functionalities allows the production of a producer gas with low N_2 content, which is important for cost-effective and efficient downstream processing, especially with respect to the methanol synthesis loop. The gasification section consists of three parts: gasifier riser, settling chamber and downcomer. The combustion section consists of only one part.

Biomass is fed into the gasifier riser using lock hoppers. A small amount of superheated steam is added from below to allow solids circulation. Hot bed material (typically sand or olivine) enters the gasifier riser from the combustor through a hole in the gasifier riser (opposite of the biomass feeding point). The typical circulation rate on a mass basis is 40 times the amount of biomass fed to the gasifier riser. The bed material heats the biomass to the desired temperature in the gasification section. The heated biomass particles degasify and are partially converted into gas. The volume created by the gas from the biomass results in a vertical velocity increase over the length of the gasifier riser. It will ultimately create a “turbulent fluidization” regime in the gasifier riser and carrying over of the bed material together with the degasified biomass particles (char). The vertical velocity of the gas is reduced in the settling chamber, causing the larger solids (bed material and char) to separate from the gas and fall down into the downcomer. The producer gas leaves the reactor from the top and is sent to the gas cleaning section. The typical residence time of the gas is several seconds.

The combustor operates as a bubbling fluidized bed (BFB). The downcomer transports bed material and char from the gasification section into the combustor. Tar and dust, separated from the producer gas, are also transported to the combustor. Char, tar and dust are burned with air to heat the bed material. Flue gas leaves the reactor to be cooled, de-dusted and emitted. The heated bed material leaves the bottom of the combustor through a hole into the gasifier riser. Usually, no additional heat input is required since all heat for the gasification process is produced by the combustion of the char and tar in the combustor. However additional fuel can be burnt in the combustor, if required. Since the gasification and the combustion steps are separated, pure oxygen is not necessary and nitrogen dilution of the product gas is avoided.

2.2 Syngas cleaning and conditioning

The product gas obtained from biomass gasification has a composition that strongly depends on the characteristics of the feedstock. On the other hand, the synthesis section requires a specific ratio between reactants according to the stoichiometry of the reactions. In addition, the presence of Chlorine, Sulphur and other metallic species in the biomass results in a non-negligible amount of pollutants in the syngas that could cause issues in the downstream processes (e.g. catalysts deactivation). The cleaning and conditioning of the product gas to optimize the yield of the synthesis process is one of the main issues present in all the biomass-to-liquid processes. Besides these general considerations, the indirect gasification also generates tars and BTX because of the lower operating temperature.

The CONVERGE process addresses the issue of tailoring the raw syngas through a chain of cleaning processes:

- *High temperature filtration*, by means of cyclones
- *Tar removal* is performed by means of a catalytic cracking reactor (CCT). The syngas is heated up by means of external combustion and the catalytic reaction converts long chain condensable hydrocarbons (C8+).
- *Water wet scrubbing* section at low temperature removes pollutants such as ammonia, hydrogen cyanide, hydrogen chloride and a small amount of carbon dioxide.

- *BTX scrubber* removes BTX compounds (benzene, toluene, xylenes) that are recovered from the sorbent stripping as a valuable byproduct. The BTX scrubber is also capable of removing much of the organic sulphur species.
- *Sulphur removal process*, for which the Lo-cat technology has been proposed. This solution uses a proprietary liquid redox iron-based catalyst that converts H_2S to solid elemental sulfur by carrying out the direct oxidation of H_2S. The resulting elemental Sulphur particles are very small, with high surface area and moisture content is suitable for agricultural applications.
- *Guard beds*, required to meet the very strict requirement of the downstream catalytic processes, removing traces of pollutants. The use of activated carbon or iron oxide at low temperature has been suggested. An alternative is the use of a hydrogenation bed followed by a high temperature (200°C) bed of ZnO.

The presence of the cleaning and conditioning components is mandatory for the correct operation of the plant and to avoid irreversible damages to the devices, but the influence on the general syngas composition and energy balance can be estimated using some simplified assumptions.

2.3 Sorption-enhanced Reformer (SER)

Sorption-Enhanced Reforming is an alternative reforming process to the conventional steam reforming of methane. The SER process involves the use of a high temperature CaO-based solid CO_2 sorbent together with a reforming catalyst. In the process, reforming, water gas shift and CO_2 capture (through carbonation) occur simultaneously:

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \qquad \Delta_R h^0 = 206.1\ kJ/mol$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad \Delta_R h^0 = -41.2\ kJ/mol$$

$$CaO + CO_2 \leftrightarrow CaCO_3 \qquad \Delta_R h^0 = -178\ kJ/mol$$

Since CO_2 is a product of the reforming/water gas shift reactions, its in-situ removal moves the thermodynamic equilibrium towards higher hydrogen yields. In addition, the combination of the three reactions is close to being thermally neutral. These reactions occur in a first fluidized bed reactor (reformer), after which the solid sorbent and catalyst are sent to a second reactor (regenerator) where the sorbent is regenerated (calcined) by means of external indirect heating. In order to keep a sufficient driving force for calcination and to avoid catalyst oxidation, steam and a small quantity of hydrogen are added to the reactor. The regenerated sorbent, together with the catalyst, are then returned to the reforming reactor to start a new cycle. In the CONVERGE process, the SER generates two streams:

- An almost pure CO_2 flow that can be used for methanol synthesis and/or exported externally for storage or utilisation.
- A flow containing all the remaining species (mainly H_2, H_2O, CH_4, N_2 with traces of CO_2 and CO) that is sent to a compression and separation step to obtain pressurized pure hydrogen for methanol synthesis.

The alternative of using a catalyst that is less active in methane reforming will also be considered, since this option reduces the heat demand of the process and prevents the adoption of a toxic and expensive catalyst. Additionally, the heating value of methane would be not available for the synthesis, increasing the energy content of the off-gas.

The SER process is coupled to a methanation reactor on the syngas outlet stream and a polishing reactor on the CO_2 rich stream. The first removes the CO and CO_2 traces resulting from water gas shift reaction in the reforming unit, since carbon monoxide and to some extent CO_2 are poisoning the membranes of the downstream EHC. The latter removes the residual hydrogen and CO from the CO_2 stream; this system consists in a catalytic oxidation and requires pure oxygen injection.

2.4 Reactants compression

The syngas stream at SER outlet is cooled down and sent to an electrochemical hydrogen compressor. This modular system allows to compress the hydrogen through a membrane. The working principle involves hydrogen ions transfer applying an electrical potential between an anode and a cathode on the two sides of the membrane. The process is highly selective to hydrogen, despite a certain amount of water and carbon dioxide migrates also through the separator. The consequent advantage of the process is the simultaneous pressurization and purification of hydrogen.

The CO_2 stream compression is performed by means of a conventional intercooled compressor.

After the compression, the two streams are mixed, generating a syngas tailored for methanol synthesis, i.e. with a stoichiometric module equal to 2[1]. Since the flows are pure H_2 and CO_2, this is equivalent to achieving a H_2/CO_2 ratio of 3, as required by the simple methanol synthesis reaction stoichiometry. The excess CO_2 can be exported for sequestration or for alternative uses.

2.5 Methanol synthesis

The final step of the process is the synthesis of methanol which could be a final product (e.g. used as fuel), an intermediate for chemical industry or for the synthesis of more complex fuels (e.g. biodiesel). In the CONVERGE project, the purification of methanol to high quality specification is not foreseen, assuming its use as an intermediate intended for other industrial processes.

Methanol synthesis reactions can be described by the following general reactions:

$$CO + 2H_2 \leftrightarrow CH_3OH$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

where the equilibrium is defined by two of the reactions, i.e. the third is a linear combination of the others. Other parasitic reactions are present (e.g. small amounts of ethanol and other alcohols synthesis), the formation of which requires a kinetic model to include. Conventional methanol synthesis reactors are high pressure catalytic beds (fixed or slurry), requiring large recycles due to the thermodynamic limitation of single-pass conversion. In addition, the reaction is strongly exothermic, and heat integration is applied to optimize the productivity of the system either by gas quenching, intermediate cooling or active bed cooling.

The CONVERGE process includes an innovative membrane reactor. The presence of membranes selective to methanol and water allows to remove the product in-situ, removing the thermodynamic limitation and strongly increasing the yield.

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[1] The module M is defined as $M = \frac{H_2 - CO_2}{CO + CO_2}$ on molar basis

2.6 Off-gas internal recovery and heat integration

The CONVERGE process produces two main off-gases streams:

- Residual syngas from electrochemical compression, still containing a significant amount of hydrogen, and enriched in methane and CO_2, which can be tuned by the performance of SER.
- Purge from methanol synthesis, to avoid inert gases accumulation in the reactors recycling loop that is mainly composed by hydrogen, CO_2 and methanol.

In general, off-gas production should be minimized to reduce the loss of reactants and increase the global yield of the process. On the other hand, the off-gas production will contribute to the thermal demand of some process units, namely:

- The gasifier, whether the combustion of residual char from gasification is not sufficient. In this case, the additional fuel could be either a fraction of the inlet biomass or part of the off-gas from the downstream units. In the state-of-the-art solution, the tars could also be separated and fed back to the gasifier as extra fuel, but the CONVERGE process has chosen to valorize this product stream separately.
- Catalytic Cracking of Tars, which requires a thermal input to heat the syngas up to the required operating temperature. In this case, the heat is produced by means of an external combustor and transferred through a heat exchanger, requiring a clean fuel such as an off-gas stream.
- The Sorption-Enhanced Reforming unit that requires heat for sorbent calcination to be provided by external combustion of a clean fuel.

In addition to the internal off-gas recovery, several heat sources at different temperature are available in the process. They can be effectively recovered to increase the process efficiency, by producing and preheating the process steam and producing electricity. The heat integration and waste heat recovery will be object of investigation during the project. Heat integration is beyond the scope of this deliverable.

3 Simulation approach, assumptions and preliminary results

In this section, the main assumptions and models used for estimating the operating conditions and the characteristics of material and heat streams in the plant are presented. The second part of the chapter presents two sets of results which differ for the assumed methane conversion in the SER unit.

3.1 Aspen model description

The plant is simulated using Aspen Plus. The physical properties and the composition of the main streams at the interfaces among the different process units are calculated.

For the calculation of the thermodynamic properties, the Redlich-Kwong-Soave-Boston-Mathias (RKS-BM) equation of state is used for this preliminary evaluation. Specific equations of state will be selected where necessary for further detailed modelling of components (e.g. water scrubber).

3.1.1 Secondary Biomass

Secondary biomass is not a conventional substance with an unambiguous set of thermodynamic properties, so it is included in Aspen simulation as a non-conventional component. This kind of components allow for the definition of properties (specific heat, density, heat of combustion) without the knowledge of the detailed chemical structure of the substance. The same approach is also used to define the ash properties.

In Aspen Plus, the model available for coal is adapted and used for biomass and ashes. The Aspen models for coal are HCOALGEN for enthalpy and DCOALIGT for density calculations. This last is not relevant at this stage in the evaluation and will not be discussed further here.

HCOALGEN model requires the definition of ultimate and proximate analysis, potentially also including the Sulphur analysis (organic, pyritic, sulfate). Several sub-models and correlations are available for coal properties calculation. The general ones are selected and summarized in Table 3.1.

Table 3.1 - Non-conventional components sub-models

	BIOMASS		ASH	
Property	Aspen Option	Value	Aspen Option	Value
Heat of combustion	6 (HCOMB)	HHV dry basis	1 (BOIEC)	Standard correlation
Standard heat of formation	1	From heat of combustion	1	From heat of combustion
Heat capacity	1 (CP1C)	Fitted on correlation for biomass [1]	1 (CP1C)	Standard correlation
Enthalpy basis	1	Standard state at 298.15 K and 1 bar	1	Standard state at 298.15 K and 1 bar

For biomass, the heat of combustion is given, considering the relations between LHV and HHV at different humidity:

$$LHV_d = LHV_{AR} \cdot (1 + y_{d,m}) \tag{3.1}$$

$$LHV_d = HHV_d - \left(y_{d,m} + y_{d,H} \cdot \frac{M_{w,water}}{M_{w,H_2}} \right) \cdot \Delta h_{eva} \tag{3.2}$$

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$$LHV_{d,y'_{d,m}} = LHV_{d,y_{d,m}} + \left(y_{d,m} - y'_{d,m}\right) \cdot \Delta h_{eva} \qquad (3.3)$$

where y_d are weight fraction dry basis and Δh_{eva} is 2.442 $\mathrm{MJ/kg_{water}}$; LHV and HHV are expressed on dry basis. A calculator is implemented to convert the LHV_{dry} to the input requested by the model. Properties are verified modeling the complete combustion of the biomass and comparing the calculated LHV with the input one.

Heat capacity model follows the formulation:

$$c_{p,d} = \sum_j \left(a_{1,j} + a_{2,j}T + a_{3,j}T^2 + a_{4,j}T^3\right) \cdot y_j \qquad (3.4)$$

where $c_{p,d}$ is given on dry basis, j is each component of ultimate analysis and y_j are weight fraction on dry basis. Aspen requires the parameters in appropriate units to obtain $c_{p,d}$ in cal/gram°C with temperature in °C.

The specific heat of dry wood can be estimated through the correlation:

$$c^0_{p,d} = 0.003867 \cdot T + 0.1031 \qquad (3.5)$$

The heat capacity model from [1] takes into account also the additional contribution of energy absorbed by the wood-water bonds

$$c_{p,d} = \frac{c^0_{p,d} + y_{hum} \cdot c_{p,water}}{1 + y_{hum}} + A \qquad (3.6)$$

where $c^0_{p,d}$ is the specific heat of dry wood, $c_{p,water}$ is the specific heat of water (about 4.186 kJ/kgK) and A is a correction term:

$$A = (0.02355 \cdot T - 1.326 \cdot y_{hum} - 6.191) \cdot y_{hum} \qquad (3.7)$$

with T in K. This correction is valid between 280 and 420 K; above this temperature (fiber saturation temperature), the simple law of mixture is valid (A = 0). Parameters $a_{i,j}$ are regressed on this correlation, obtaining the results in Table 3.2. The error between (3.4) and (3.6) is about 2% between 10% and 50% water content.

Table 3.2 – Coefficients for biomass specific heat

	$a_{1,j}$	$a_{2,j}$	$a_{3,j}$	$a_{4,j}$
Biomass	0.5712	0.00257	-	-
Moisture	-6.9561	0.03768	-	-

For ashes, the standard Aspen ashes are assumed.

As mentioned before, the reference secondary biomass for this preliminary evaluation is wood type biomass, whose composition is reported in Table 3.3. The biomass is assumed to be heated up to 80°C and dried from the initial moisture content of 17.3 $\%_{w,ar}$ to $10\%_w$. The energy required by the drier is provided as steam and a flow of air removes the water from the system, resulting in 80% RH at outlet for exhaust air. No volatile release is considered at this temperature.

Table 3.3 – Reference wooden biomass properties before and after drying

		As received	**Dried**
LHV	*MJ/kg*	15.36	16.93
PROXIMATE analysis			

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Moisture	*%ar*	17.30	10.00
FC	*%dry*	17.75	17.75
VM	*%dry*	81.25	81.25
Ash	*%dry*	1.00	1.00
ULTIMATE analysis			
C	*%dry*	50.12	50.12
H	*%dry*	6.01	6.01
N	*%dry*	0.38	0.38
Cl	*%dry*	0.09	0.09
S	*%dry*	0.06	0.06
O	*%dry*	42.34	42.34

3.1.2 Gasification and syngas cleaning sections

The syngas composition at MILENA gasifier outlet is estimated considering fixed residual char and hydrocarbons yield (CH_4, C_xH_y) production, provided from previous simulations performed by ECN-TNO with detailed models. The presence of H_2, H_2O, CO and CO_2 is evaluated through water gas shift reaction equilibrium. Steam addition to the gasifier is determined by the assumed steam to carbon ratio of 0.3 on mass basis. Once the composition is defined, the ASPEN component RYield is used to calculate the energy balance of the gasification section. The amount of solid material (olivine) that circulates between the gasifier and the combustor is calculated so as to keep the former at constant temperature (800°C). The char separation in the gasifier is simulated by cyclones with an assumed efficiency of 99% and the residual char is sent to the combustor. The combustor is fed with preheated air, with an excess calculated to have 3 vol.% content of oxygen in flue gases. If the combustion of char is not sufficient to heat the solids up to the required temperature (850°C), additional biomass is burnt in the combustor. Flue gases are cooled down to 300 °C for heat recovery and then the residual sensible heat is used for air preheating. A solid purge from the combustor (2 wt.% of the biomass entering the system) is included to avoid ashes build up; because of the corresponding olivine loss, a makeup flow is calculated for compensation.

As mentioned before in the plant description, in this preliminary analysis the gas cleaning section is simulated with a lumped approach. All the residual solids are removed from the syngas stream assuming ideal filters. The CCT reactor is simulated as an isothermal reactor operating at 800 °C and is assumed to convert all C9+ hydrocarbons to BTX and syngas (H_2, CO and CO_2). The reaction heat is provided by means of external combustion of the purge off-gas from the methanol synthesis section.

The resulting gas is cooled down to 25°C to condense the water and the BTX together with the organic Sulphur components are separated by the BITS reactor.

3.1.3 SER, methanation and polishing

The Sorption-Enhanced reforming process is simulated using two equilibrium reactors (RGibbs). The first reactor performs the reforming and water gas shift reactions, achieving chemical equilibrium at 650°C. Methane reforming reaction can be deactivated, simulating the behavior of different catalysts (see cases discussion in next section). Steam at 500°C is fed to the SER reformer according to S/C ratio of 3.5, to avoid carbon formation. A solids flow composed of supported CO_2 sorbent (CaO) and supported catalyst (Ni or Fe) is fed to the reactor. The quantity of circulating solid is selected in order to remove the maximum quantity of CO_2 (limited by chemical equilibrium governed by CO_2 partial pressure in syngas at the operating temperature) assuming a CaO conversion to $CaCO_3$ of 65%. The heat provided by the solids that cool from

850 to 650 °C adds to the heat of the exothermic reactions system and the SER reactor has to be cooled. The thermal power to be removed is calculated by the model from the reactor energy balance.

Solid are entirely separated in a cyclone assumed to have 100% efficiency and sent to a calciner in which sorbent is regenerated by heating up to 850°C. Steam is added to reduce the CO_2 partial pressure and keep a sufficient driving force for the calcination reaction. A CO_2 fraction of $50\%_{vol}$ is assumed at the SER calciner exit. When Ni-based catalyst (active on CH_4 reforming) is used, hydrogen is also fed to the calciner to keep a reducing atmosphere and avoid catalyst oxidation with steam.

The calciner is heated by means of external combustion of methanol reactor off-gas and EHC purge off-gas, burnt in air. Combustion air is controlled to obtain $3\%_{vol}$ O_2 content in the flue gases.

Downstream the SER reformer, a methanation reactor is included to reduce CO concentration according to EHC specifications. Downstream the calciner, a polishing unit consisting in a catalytic combustor fed with pure oxygen is assumed to oxidize hydrogen (if present) from the CO_2-rich stream.

The methanation reactor is calculated assuming chemical equilibrium at 400 °C, allowing to obtain few ppm of CO at outlet.

The polishing reactor is calculated as an adiabatic reactor with oxygen added in stoichiometric proportion. The equilibrium temperature is given by the energy balance on the reactor.

3.1.4 Reactants compression and methanol synthesis

Hydrogen-rich stream is compressed by means of an electrochemical compressor, able to compress and purify hydrogen at the same time. For this preliminary evaluation, a separation efficiency of 90% is assumed. Compressed hydrogen is not entirely pure, but water and CO_2 permeate together with H_2, resulting in an assumed hydrogen purity of 99.5% on dry basis and a moisture content of 3%. An estimate of the V-I curve has been provided by HyET from which the electrical consumption is estimated.

CO_2 rich stream is compressed assuming a two-stage intercooled compression. The outlet temperature from the intercooler is set to 40°C.

The final pressure for both the stream is fixed to 80 bar, which is the expected operating condition of methanol synthesis membrane reactor according to TNO. An optimization of the operating pressure will be performed once the development of the reactor section will be more advanced.

The pressurized H_2 and CO_2 streams are mixed in order to obtain the composition required by the synthesis section (M=2, corresponding to $H_2/CO_2 = 3$). The excess of high purity CO_2 from the SER calciner is considered to be exported from the plant for use or storage. The inlet stream may be mixed with a fraction of raw methanol gas separated from the reactor outlet and recirculated for increasing the total gas-to-methanol conversion of reactants to products.

Since a detailed model of the methanol membrane reactor is not available yet, the mass balance is calculated by (i) setting the amount of produced methanol permeating through the membrane and (ii) assuming the retentate at chemical equilibrium. A fraction of water and hydrogen also permeates together with the permeate. The membrane selectivity of water over H_2 is set at 15 and methanol over H_2 at 5, while CO and CO_2 are assumed not to permeate. Both permeate (low pressure) and retentate (high pressure) streams are cooled and flashed at 40°C to separate the methanol (mixed with water) from the off-gas. In this preliminary analysis, the reactor is modelled as a black box and off-gas streams from both the separators are used to cover the thermal demand in CCT and SER sections as discussed before. So, the overall methanol yield is tuned so that the energy content of the off-gas matches the total energy demand of the upstream units of the plant.

3.2 Simulated plant integration results

The abovementioned model is used to estimate the mass and energy balances of the integrated plant for a 10 MW_{LHV} biomass input. Since the model includes only mass and energy balances that do not depend on the actual plant size, the results (i.e. mass flows and thermal duties) can be linearly scaled proportionally to the biomass input.

Table 3.4 – Input biomass for the 10 MW_{th} plant

BIOMASS		**As received**	**Dried**
T	*°C*	25	80
P	*bar*	1	1
Mass flow	*kg/s*	0.651	0.598
LHV power	*MJ/kg*	10.00	10.12

Two cases are assessed in this preliminary analysis:

A. SER with reforming of all hydrocarbons, which could be obtained by means of a conventional reforming with a Ni-based catalyst

B. SER with reforming of the higher hydrocarbons, but not of methane. This solution could be obtained by means of an alternative Fe-based catalyst

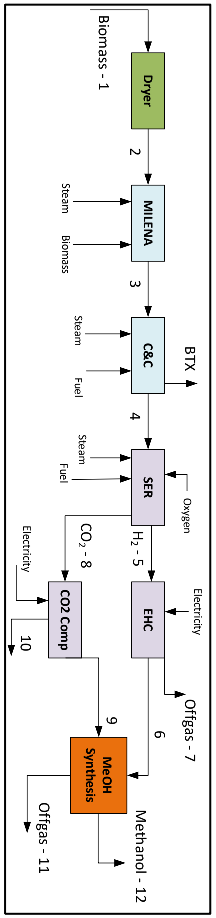
These two solutions differ in the capacity of converting methane by steam reforming: the first resulting in a conversion at chemical equilibrium, the latter in a zero methane conversion. Both of them are assumed to completely convert higher hydrocarbons into CO and H_2 and to bring the WGS reaction to the chemical equilibrium.

In the next sections, the properties of the main streams and components are presented for the two cases.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 818135

3.2.1 Case with reforming of all hydrocarbons

Table 3.5 – CONVERGE process main stream properties (case with methane reforming in SER)



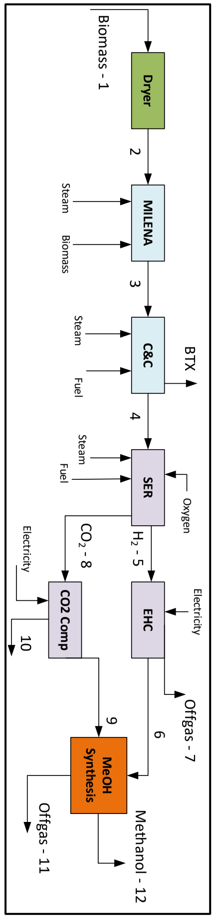
		Milena outlet	Cleaning outlet	H2 from SER+MET	H2 after ECC	Offgas ECC	CO2 to MET	CO2 excess	Methanol	Offgas LP	Offgas HP
Stream		**3**	**4**	**5**	**6**	**7**	**9**	**10**	**12**	**11**	**11**
T	*°C*	800	200	40	60	40	282	282	40	40	40
p	*bar*	1.02	1.02	1.02	80	1.02	80	80	2	2	80
Mass flow	*kg/s*	0.6432	0.6449	0.1172	0.0643	0.0529	0.3552	0.3689	0.2571	0.0036	0.1588
Molar flow	*kmol/s*	0.0286	0.0299	0.0311	0.0257	0.0054	0.0081	0.0084	0.0105	0.0007	0.0130
Mole fraction (wet)											
H2		21.52%	38.24%	89.12%	96.98%	51.52%	-	-	0.01%	89.54%	74.84%
O2		-	-	-	-	-	-	-	-	-	-
H2O		19.29%	5.81%	5.73%	3.01%	18.70%	0.71%	0.71%	55.12%	2.08%	0.08%
CO		26.28%	8.91%	0.00%	-	0.00%	-	-	0.00%	-	1.71%
CO2		16.49%	32.44%	0.00%	0.00%	-	99.29%	99.29%	0.52%	-	23.02%
CH4		9.87%	9.44%	4.27%	-	24.67%	0.00%	0.00%	0.00%	-	0.00%
N2		0.71%	0.83%	0.80%	-	4.64%	-	-	-	-	-
AR		0.01%	0.01%	0.01%	-	0.04%	-	-	-	-	-
C2/2+		5.44%	4.25%	-	-	-	-	-	-	-	-
METHANOL		-	-	-	-	-	-	-	44.34%	8.38%	0.35%
Others		0.40%	0.08%	0.07%	-	0.43%	-	-	-	-	-
Mole fraction (dry)											
H2		26.66%	40.60%	94.53%	100.00%	63.37%	-	-	0.03%	91.44%	74.90%
O2		-	-	-	-	-	-	-	-	-	-
CO		32.56%	9.46%	0.00%	-	0.00%	-	-	0.00%	-	1.71%
CO2		20.43%	34.44%	0.00%	0.00%	-	100.00%	100.00%	1.16%	-	23.04%
CH4		12.23%	10.02%	4.53%	-	30.35%	0.00%	0.00%	0.00%	-	0.00%
N2		0.89%	0.89%	0.85%	-	5.70%	-	-	-	-	-
AR		0.01%	0.01%	0.01%	-	0.05%	-	-	-	-	-
C2/2+		6.73%	4.51%	-	-	-	-	-	-	-	-
METHANOL		-	-	-	-	-	-	-	98.80%	8.56%	0.35%
Others		0.49%	0.08%	0.08%	-	0.53%	-	-	-	-	-

Table 3.6 – CONVERGE components operating conditions (case with methane reforming in SER)

DRYER		
Heat demand	200	*kW*
Air flow mass flow rate	0.14	*kg/s*
MILENA gasifier		
Additional steam required	0.03	*kg/s*
Circulating solids to the gasifier	17.43	*kg/s*
of which Olivine	16.93	*kg/s*
Olivine makeup	0.18	*kg/s*
Heat recovery from flue gases	448	*kW*
Additional biomass to combustor	0.00	MW_{th}
Combustion air	0.67	*kg/s*
Blowers consumption	29	kW_{el}
Syngas production	1.08	kg_{wet}/kg_{biom}
Steam to Carbon (total)	0.226	*mol basis*
Carbon conversion in the gasifier	82.30%	
M	0.117	
Catalytic Cracking		
Steam required	0.64	*kg/s*
Heat demand	262	kW_{th}
BTX recovered	0.022	*kg/s*
BTX energy content	890	kW_{th}
Sorption-enhanced Reformer		
Steam to reformer	0.4262	*kg/s*
Steam to calciner	0.2716	*kg/s*
Hydrogen to calciner	0.0013	*kg/s*
Heat from reformer	2186	kW_{th}
Heat to calciner	4054	kW_{th}
Heat recovery from reformed syngas	1547	*kW*
Heat recovery from calciner flue gases	1976	*kW*
CH_4 conversion	91.32%	
CO_2 separated	90.61%	*of inlet C*
	97.03%	*of total* CO_2
CaO conversion	65.00%	
Methanation cooling duty	146	*kW*
CO methanation outlet	2.30	*ppm*
Oxygen to polishing reactor	0.010	*kg/s*
Polishing reactor temperature	952	*°C*
Electrochemical hydrogen compressor		
Electrical consumption	769.3	kW_{el}
Specific consumption	3.324	kWh_{el}/kg_{H2}
H_2 recovery	90%	
H_2 selectivity	96.98%	
Off-gas heating value	1741.2	kW_{LHV}
CO_2 compressor		
Electrical consumption	334	kW_{el}
Cooling duty	219	kW_{th}
Methanol synthesis unit		
Reactor inlet module M	2.01	
Reactor duty (cooling)	202	kW_{th}
Methanol production (pure)	0.150	*kg/s*
C to methanol (reactor)	62.18%	
C to product methanol (total)	60.81%	
Methanol recovery (membrane)	41%	
Membrane selectivity	15	H_2O/H_2
	5	$MeOH/H_2$
Offgas balance		
Off-gas from EHC	1.741	MW_{th}
Off-gas from methanol synthesis	2.638	MW_{th}
Thermal demand of CCT	0.262	MW_{th}
Thermal demand of SER	4.054	MW_{th}

3.2.2 Case without methane reforming in SER

Table 3.7 – CONVERGE process main stream properties (case without methane reforming in SER)



		Milena outlet	Cleaning outlet	H2 from SER+MET	H2 after ECC	Offgas ECC	CO2 to MET	CO2 excess	Methanol	Offgas LP	Offgas HP
Stream		**3**	**4**	**5**	**6**	**7**	**9**	**10**	**12**	**11**	**11**
T	*°C*	800	200	40	60	40	282	282	40	40	40
p	*bar*	1.02	1.02	1.02	80	1.02	80	80	2	2	80
Mass flow	*kg/s*	0.6431	0.6449	0.1282	0.0442	0.0840	0.2414	0.3841	0.2582	0.0054	0.0220
Molar flow	*kmol/s*	0.0286	0.0299	0.0241	0.0175	0.0066	0.0055	0.0088	0.0105	0.0011	0.0014
LHV	*MJ/kg*	13.30	11.59	57.80	92.74	39.40	0.00	0.00	12.14	54.78	10.69
LHV power	*MW*	8.55	7.48	7.41	4.10	3.31	0.00	0.00	3.13	0.30	0.24
Mole fraction (wet)											
H2		21.52%	38.25%	78.32%	96.92%	28.73%	-	-	0.00%	89.27%	66.31%
O2		-	-	-	-	-	0.00%	0.00%	-	-	-
H2O		19.29%	5.81%	5.73%	3.01%	12.99%	0.71%	0.71%	53.16%	2.02%	0.08%
CO		26.28%	8.91%	0.00%	-	0.02%	-	-	0.00%	-	2.06%
CO2		16.49%	32.43%	0.05%	0.07%	-	99.29%	99.29%	0.07%	-	31.18%
CH4		9.87%	9.44%	14.75%	-	54.08%	-	-	-	-	-
N2		0.71%	0.83%	1.04%	-	3.80%	-	-	-	-	-
AR		0.01%	0.01%	0.01%	-	0.03%	-	-	-	-	-
C2/2+		5.44%	4.25%	0.00%	-	0.00%	-	-	-	-	-
METHANOL		-	0.00%	0.00%	-	0.00%	-	-	46.76%	8.72%	0.37%
Others		0.40%	0.08%	0.10%	-	0.35%	-	-	-	-	-
Mole fraction (dry)											
H2		26.66%	40.61%	83.09%	99.93%	33.01%	-	-	0.01%	91.10%	66.36%
O2		-	-	-	-	-	0.00%	0.00%	-	-	-
CO		32.56%	9.46%	0.00%	-	0.02%	-	-	0.00%	-	2.06%
CO2		20.43%	34.43%	0.05%	0.07%	-	100.00%	100.00%	0.15%	-	31.20%
CH4		12.23%	10.02%	15.64%	-	62.15%	-	-	-	-	-
N2		0.89%	0.89%	1.10%	-	4.37%	-	-	-	-	-
AR		0.01%	0.01%	0.01%	-	0.04%	-	-	-	-	-
C2/2+		6.73%	4.51%	0.00%	-	0.00%	-	-	-	-	-
METHANOL		-	0.00%	0.00%	-	0.00%	-	-	99.84%	8.90%	0.37%
Others		0.49%	0.08%	0.10%	-	0.41%	-	-	-	-	-

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Table 3.8 – CONVERGE components operating conditions (case without methane reforming in SER)

DRYER		
Heat demand	200	*kW*
Air flow mass flow rate	0.14	*kg/s*
MILENA gasifier		
Additional steam required	0.03	*kg/s*
Circulating solids to the gasifier	17.36	*kg/s*
of which Olivine	16.85	*kg/s*
Olivine makeup	0.18	*kg/s*
Heat recovery from flue gases	448	*kW*
Additional biomass to combustor	0.00	MW_{th}
Combustion air	0.67	*kg/s*
Blowers consumption	29	kW_{el}
Syngas production	1.08	kg_{wet}/kg_{biom}
Steam to Carbon (total)	0.226	*mol basis*
Carbon conversion in the gasifier	82.30%	
M	0.118	
Catalytic Cracking		
Steam required	0.64	*kg/s*
Heat demand	262	kW_{th}
BTX recovered	0.022	*kg/s*
BTX energy content	890	kW_{th}
Sorption-enhanced Reformer		
Steam to reformer	0.4263	*kg/s*
Steam to calciner	0.2556	*kg/s*
Hydrogen to calciner	0.0000	*kg/s*
Heat from reformer	2195	kW_{th}
Heat to calciner	3514	kW_{th}
Heat recovery from reformed syngas	1783	*kW*
Heat recovery from calciner flue gases	1614	*kW*
CH_4 conversion	0.00%	
CO_2 separated	79.92%	*of inlet C*
	96.85%	*of total* CO_2
CaO conversion	65.00%	
Methanation cooling duty	80	*kW*
CO methanation outlet	24.21	*ppm*

Oxygen to polishing reactor	0.00	*kg/s*
Polishing reactor temperature	850	*°C*
Electrochemical hydrogen compressor		
Electrical consumption	529.1	kW_{el}
Specific consumption	3.324	kWh_{el}/kg_{H2}
H_2 recovery	90%	
H_2 selectivity	96.92%	
Off-gas heating value	3308.6	kW_{LHV}
CO_2 compressor		
Electrical consumption	288	kW_{el}
Cooling duty	189.5	kW_{th}
Methanol synthesis unit		
Reactor inlet module M	2.01	
Reactor duty (cooling)	195	kW_{th}
Methanol production (pure)	0.157	*kg/s*
C to methanol (reactor)	91.39%	
C to product methanol (total)	89.56%	
Methanol recovery (membrane)	89%	
Membrane selectivity	15	H_2O/H_2
	5	$MeOH/H_2$
Offgas balance		
Off-gas from EHC	3.309	MW_{th}
Off-gas from methanol synthesis	0.531	MW_{th}
Thermal demand of CCT	0.262	MW_{th}
Thermal demand of SER	3.514	MW_{th}

Results demonstrate the tight interaction between the different plant components which must be considered in the research and development activity. The following points can be outlined:

- The conversion of methane in the SER requires lower conversion efficiencies in the methanol reactor and increases the electric consumption of the EHC as consequence of the higher amount of hydrogen available;
- SER can produce different H_2 and CO_2 quantities according to the set operating conditions providing good flexibility to the system.
- Together with methanol, a relevant amount of BTX is also produced giving flexibility to the system;
- With respect to the membrane reactor, the defined selectivities in combination with the relatively low utilization of the reactants results in a fairly low cross-reactor change of the stoichiometric M ratio.

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4 Conclusions

This document described the CONVERGE concept and presented preliminary process simulations of the system. The aim of this deliverable is not to calculate overall process performance, but to provide inputs on the expected gas properties and expected initial operating conditions to the developers of the single technologies.

The report provides to the different technologies developed within CONVERGE (CCT, BITS, SER, EHC and EMM), the operating temperature and pressure together with the stream composition at the inlet-outlet of each system. Starting from these indications, the research activity will identify the optimal energy integration between the different components together with single technology improvement.

References

[1] TenWolde A, McNatt JD, Krahn L. Thermal properties of wood and wood panel products for use in buildings. Martin Marietta Energy Systems / US DOE; 1998.