Chemical Looping Gasification for Sustainable Production of Biofuels

H2020 Research and Innovation action
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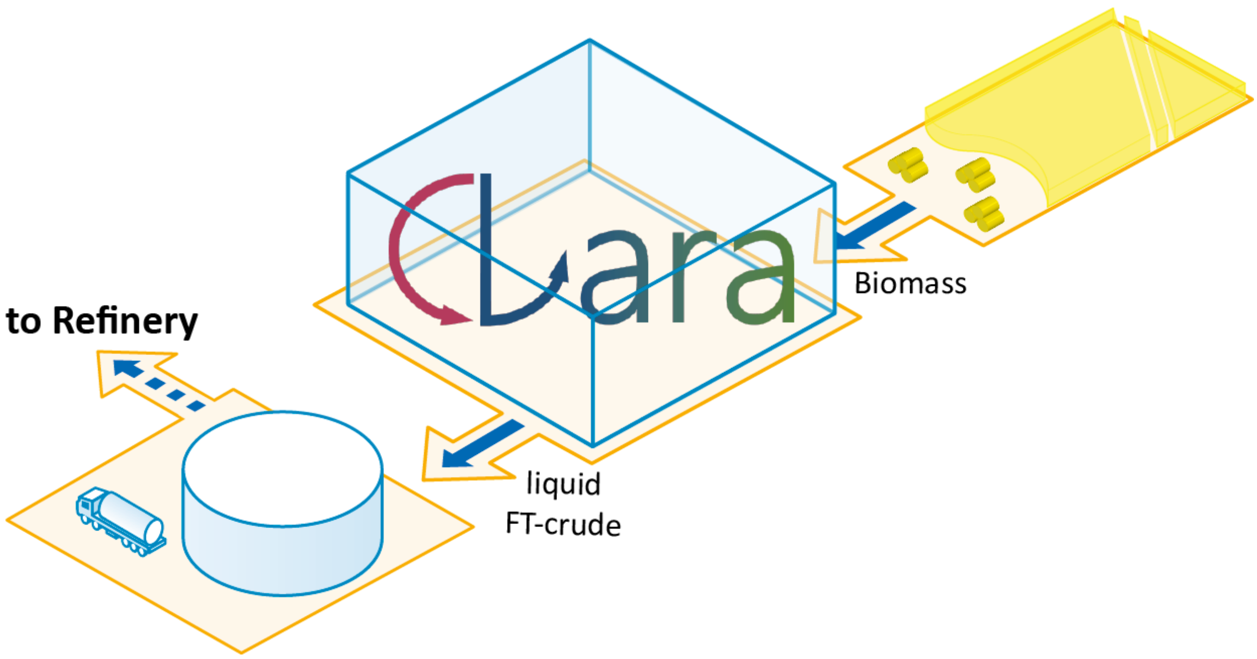
Public Report 3



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Executive Summary

During the third project year, the CLARA partners were not only focused on finalizing the basic design for the Biomass-to-Liquid (BtL) process chain (see Chapter 3) and refining the novel technologies investigated within the project (see Chapter 4), but also made big steps towards the very first full-chain investigation of the entire process chain (see Chapter 5). Moreover, initial advances towards in-depth analyses of the entire process chain, such as risks assessment and techno-economic studies have started (see Chapter 6).

Based on the underlying technologies, *TUDA* and *CERTH* derived an optimized process layout of the entire BtL chain, achieving competitive figures for the most important key performance indicators, such as attaining negative CO_2 emissions or achieving an energetic fuel efficiency of 55 % for the entire process chain. A summary of the most important results on process definition can be found in Chapter 3.1. Moreover, first scale-up studies for the chemical looping gasifier have been completed by *AE*. The results of these are presented in Chapter 3.2, where the very first design of an industrial scale CLG unit is presented.

In terms of technology development, *CENER* refined the newly devised pre-treatment concept of wheat straw, before its ongoing industrial-scale implementation at the *ABT* facilities in Sweden (more details see Chapter 4.1). Building on the insights gathered in their lab-scale test risks, *CTH* and *CSIC* have been able to carry out the first successful test campaigns in a small CLG pilot unit and were able to support the findings made in lab-scale units. These findings are described in greater detail in Chapter 4.2. Lastly, *RWE* was able to successfully demonstrate a new patented sour gas separation concept, allowing for an efficient removal of H_2S from sour gases. More insights into this topic is presented in Chapter 4.3.

In preparation of combining these new technologies in pilot scale for the very first time, *TUDA* is currently implementing final adaptions in their 1 MW_{th} pilot unit for the upcoming test campaigns. Following an elaborate detail engineering of all required plant adjustments, all major equipment is now on site (more details see Chapter 5). Presently, the last open points for the first-full-chain pilot tests in March 2022 are being finalized.

Rounding up the efforts of the CLARA consortium, *RWE*, *ULSTER* and *TU WIEN* have started with the assessment of the BtL full-chain concept. These investigations include risk studies as well as techno-economic considerations, amongst others. A detailed description of the current and upcoming activities in this field is presented in Chapter 6 of this report.

Content

1 Introduction

Within the scope of the *Horizon 2020* project CLARA, a novel biomass-to-biofuel process chain is to be investigated. Through cutting-edge research and interdisciplinary cooperation, the CLARA consortium, consisting of thirteen international members including universities, research institutes and industrial partners, aims to investigate the complete process chain and bring the suggested technologies to market maturity.

Here, the advantages of utilizing locally availably biogenic residues and the economy of scale are combined, through decentralized feedstock pre-treatment facilities and a centralized fuel production plant in the scale of 100-300 MW_{th}. The fuel production plant itself consists of a chemical looping gasifier for the production of a raw syngas, a gas treatment train to provide the required syngas composition for the subsequent synthesis, and a Fischer-Tropsch (FT) reactor to covert the syngas into liquid FT-crude. This crude can then be purified and upgraded to ready-to-use second generation drop-in biofuels in existing state-of-the-art refineries. A schematic overview over the suggested biomass-to-biofuel process chain, with its four main subunits, is shown in Figure 1.

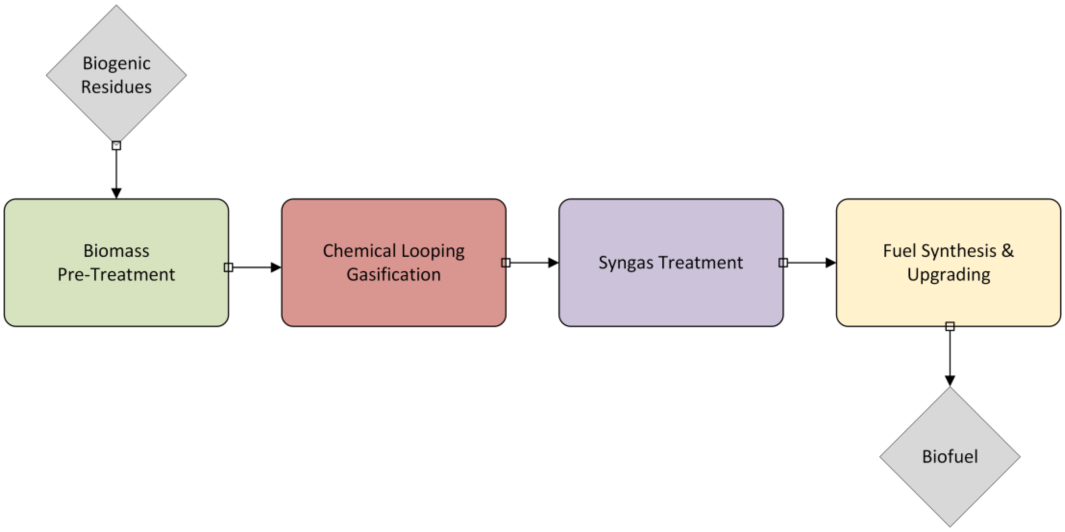

Figure 1: Simplified scheme of full biomass-to-biofuel process chain.

After providing a basic introduction regarding the project motivation and the underlying goals (Section 2), this report will focus on the progress achieved in the past 27 months. Section 3 provides insights into the process definition, optimization, and upscaling, before a deep-dive into the technological development of the individual technologies, being under investigation in the CLARA project, is presented in Section 4. The advances made with regard to the full-chain testing of the entire process chain in the 1 MW_{th} scale are summarized in Chapter 5, while the analysis of the entire process chain in terms of economics and risks is provided in Chapter 6.

More details and project updates can be found on our project website (https://clara-h2020.eu/), where you can also subscribe to the CLARA newsletter to receive regular updates on the project progress. In case you have any remarks or questions, do not hesitate to contact us (jochen.stroehle@est.tu-darmstadt.de).

2 Project Motivation & Project Goals

Significant reductions in greenhouse gas emissions are required to prevent a surge in global average temperatures, exceeding the much discussed 1.5 °C threshold of the Paris Agreement. Here, the de-carbonization of the transport sector, which utilizes over a third of the global final energy [1] and is responsible for almost one quarter of the European greenhouse gas emissions [2], is a key concern on the route to achieve this goal. Particularly, the substitution of fossil fuels in transport sectors for which electrification is presently not viable (e.g. road transport and aviation), remains a major challenge.

To tackle this issue, the European Union has set a target of a share of 14 % renewable energy in the transport sector by 2030 in the Renewable Energy Directive (RED II) in 2018 [3]. This requires the large-scale deployment of biofuels in addition to electrification and the increased deployment of rail transport. Since the wide-spread utilization of energy crops is being strongly criticized publicly, the utilization of biogenic residues, which do not impact food availability and prices negatively, in the energy and transport sector is to be intensified. Therefore, substantial advances in renewable fuel generation are required.

One route to achieve these objectives is the synthesis of advanced biofuels through thermochemical conversion of biomass-based residues. Gasification is a well-established thermochemical biomass conversion technology. Yet, its primary use is the production of heat and electricity, whereas industrial scale gasifiers for the synthesis of advanced biofuels are not available, hitherto [4].

Within the scope of the CLARA project, an efficient technology for the production of liquid fuels based on chemical looping gasification (CLG) of biogenic residues is being developed. The major objective is to further investigate and test CLG up to 1 MW_{th} scale in an industrially relevant environment, elevating the process to market maturity. Furthermore, the project aims at devising and optimizing innovative, cost-efficient technologies for biomass pre-treatment and syngas cleaning. These novel process steps will be supplemented by established fuel synthesis technologies (e.g. Fischer-Tropsch process), yielding the full biomass-to-biofuel process chain.

By focusing on biological non-food-grade precursors, CLARA contributes not only to a sustainable shifting from fossil to renewable resources, but also facilitates the large-scale economic production of biofuels, without detrimental effects on food availability and prices arising. This aspect, in combination with the projected advances in terms of process scalability, CO_2-reduction potential (net negative CO_2 emissions) and projected biofuel costs of 0.7 €/l, make the process investigated within the scope of CLARA an auspicious candidate for a key industry of the 21st century.

3 Process Definition

3.1 Layout of the Process Chain

A schematic illustration of the entire suggested biomass-to-biofuel process chain, highlighting the four main sub-units, biomass pre-treatment, chemical looping gasification, syngas cleaning, and fuel synthesis, is given in Figure 2.

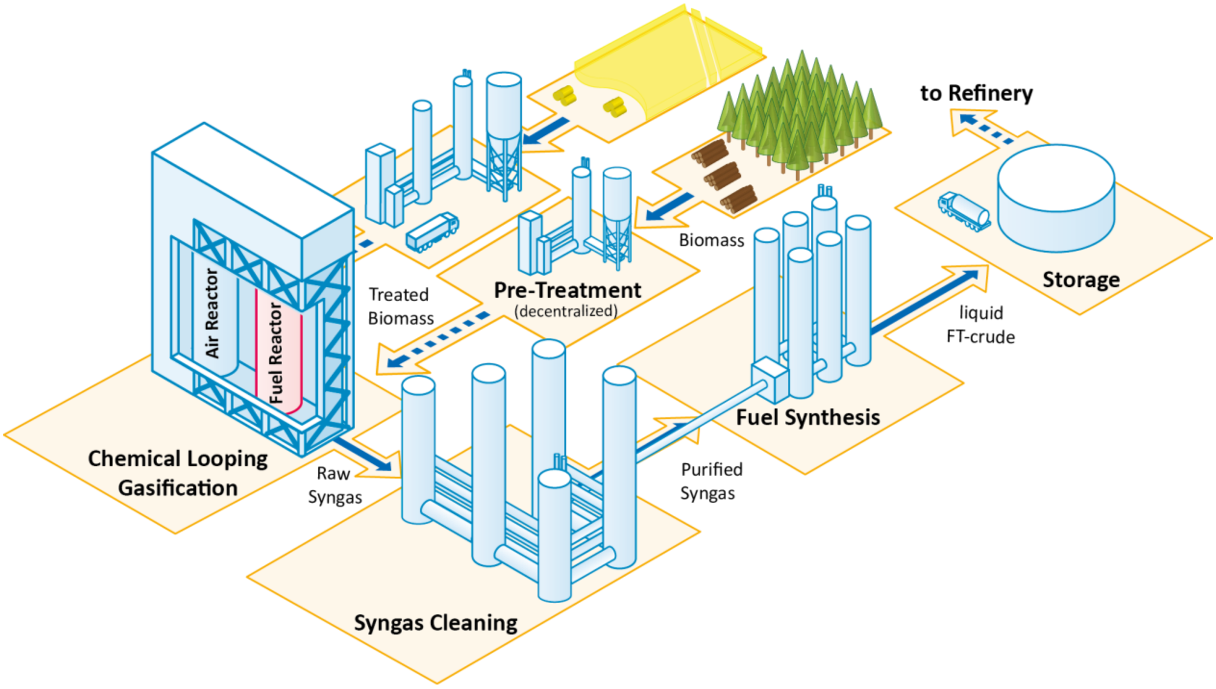

Figure 2: Schematic illustration of the process chain investigated within the CLARA project.

Based on this layout, the full process chain, including all major plant components, was defined in detail, using the insights gathered during technology development (see Section 4), in order to calculate the heat and mass balances for the entire process chain. The process flow diagram of the resulting biomass-to-liquid (BtL) process chain is given in Figure 3. In the first sub-unit, the raw biomass is prepared for transport to the centralized BtL plant site and subsequent gasification. Thereafter, the pre-treated biomass pellets are converted into a raw producer gas containing large fractions of syngas (H_2 & CO) inside the 200 MW_{th} chemical looping gasifier (CLG, more details see Sections 3.2 and 4.2). In the downstream gas cleaning unit, the raw gas is compressed and purified, using water and amine scrubbing as well as an oil-based tar removal unit. This procedure yields a pure syngas which is fine cleaned using a caustic wash, before being converted into the end product, a FT-crude, inside the fuel synthesis unit. The crude is then transported from the BtL plant site to local refineries for final fuel upgrading and refining to drop-in standards. To attain a better utilization of all gaseous species in the fuel synthesis unit, it is equipped with a steam methane reformer (SMR) converting gaseous hydrocarbons to H_2 and CO. Sulphur species (i.e. H_2S) contained in the sour gas coming from the amine wash, which mainly consists of CO_2 (>95 vol-%), are removed using a new cleaning technology (see Chapter 4.3), so that the captured CO_2 can be used for carbon capture and storage or utilization (CCU/S) purposes.

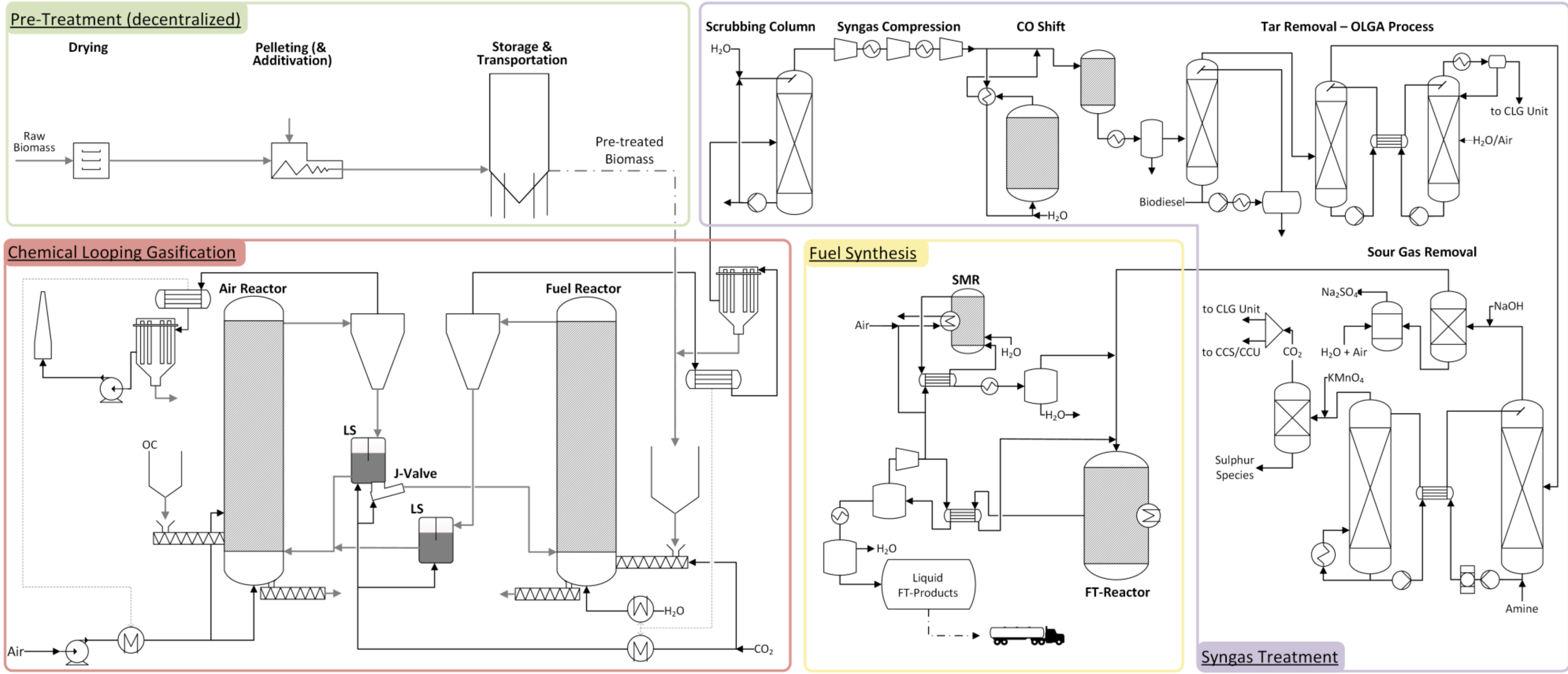

Figure 3: Simplified version of the process flow diagram for the CLARA biomass-to-liquid process chain.

For process optimization, the entire process chain was evaluated using two performance indicators. Firstly, the carbon utilization (CU), which relates the carbon contained in the final FT-crude to the carbon contained in the pre-treated feedstock:

$$CU = \frac{\dot{m}_{carbon,FT-crude}}{\dot{m}_{carbon,feedstock}} \tag{1}$$

And secondly, the energetic fuel efficiency (EFE), which is given by the fraction of the energy contained in the pre-treated feedstock and the energy contained in the final FT-crude:

$$EFE = \frac{\dot{m}_{FT-crude} \cdot LHV_{FT-crude}}{\dot{m}_{feedstock} \cdot LHV_{feedstock}} \tag{2}$$

The heat and carbon balance for the optimized BtL plant layout for the model feedstock pine forest residue (PFR) are illustrated in Figure 4 and Figure 5, respectively. Inside the CLG unit, a cold gas efficiency (CGE) of around 80 % is achieved. A total of 1 % of the energy accounts for heat losses, while the remaining energy is used for pre-heating of the inlet streams (~10 %) and for steam generation (~9 %) for usage in other plant units (e.g. gas cleaning). The heat losses of the gas cleaning & conditioning unit are minor, while the main heat losses of the process are observed in the FT-synthesis unit (~23%), due to the highly exothermic Fischer-Tropsch reactions as well as the partial syngas combustion for steam reforming of longer hydrocarbons in the fuel synthesis unit. In summary, an EFE around 52-53% is achieved, meaning that more than half of the chemical energy contained in the initial feedstock is found in the final product of the process (i.e. FT-crude).

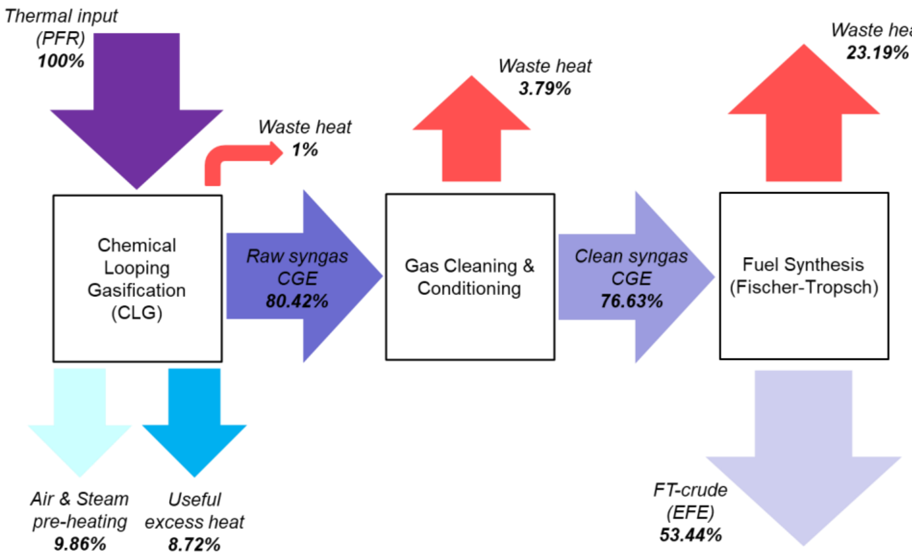

Figure 4: Heat balance for the entire BtL process chain for the model feedstock PFR.

In terms of the carbon balance, the majority of carbon (~87.5%) contained in the pre-treated feedstock is transferred to the producer gas inside the industrial-scale CLG unit, while the remainder (~12.5%) is combusted in the air reactor of the CLG unit, providing necessary process heat. Subsequently, after a significant carbon transformation from CO to CO_2 via the CO-shift reaction in the gas treatment unit, a high percentage of carbon (~45%) is captured in the form of pure CO_2 in the acid gas removal unit. A small part of the captured CO_2 is recycled back to the CLG unit along with any tars removed via oil washing, while the carbon left in clean syngas (i.e. CO & CH_4) is directed to the FT-synthesis unit. There, partial syngas/carbon combustion for the heat demands of the SMR takes place (~10%), while the remaining carbon is integrated into long-chained hydrocarbons during FT-synthesis and is thus found in the valuable FT products, yielding a CU equal to around 32.5 %.

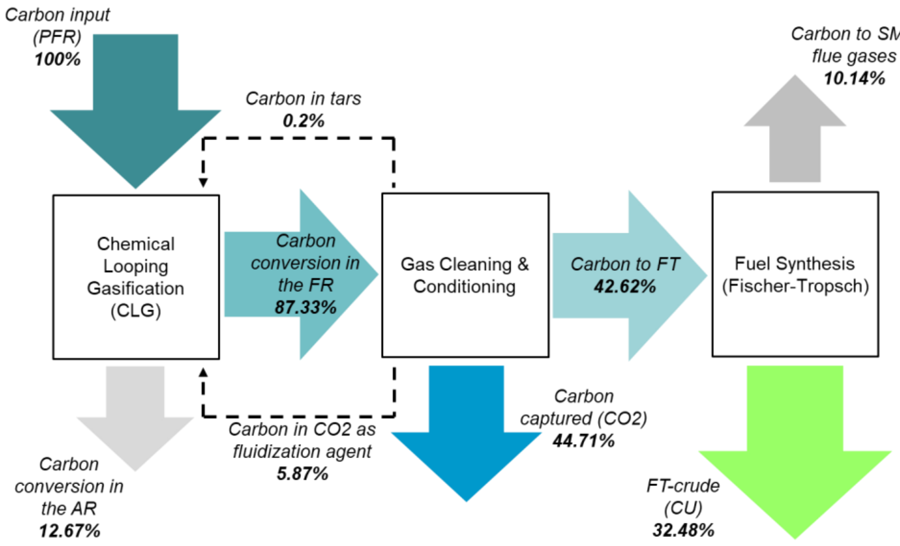

Figure 5: Carbon balance for the entire BtL process chain for the model feedstock PFR.

Table 1 summarizes the key performance indicators (KPI) for the BtL process chain. It can be seen that for the model feedstock PFR, values within the range of the project targets are obtained. Approaches to further optimize the KPIs, will be investigated within the on-going up-scaling studies (see Section 3.2), using the latest findings from technology development (see Section 4) and the pilot tests (see Section 5), carried out within the CLARA project.

Table 1: KPIs for the full-scale BtL process for PFR pellets.

KPI	Results from Heat & Mass Balance	Project Targets
Carbon conversion in the CLG (CC)	100%	98%
Cold Gas Efficiency (CGE)	80.42%	82%
Carbon utilization (CU)	32.48%	33%
Energetic Fuel Efficiency (EFE)	53.44%	55%
FT-crude yield (kg/$kg_{feedstock}$)	0.206	nA

3.2 Process Chain Up-Scaling

Using the insights gathered in the CLARA project so far, a basic design for a full-chain chemical looping gasifier has been devised. The basic design data to develop a 200 MW CLG unit derives from the heat and material balance based on a numerical simulation (see Chapter 3.1) as well as from some typical operational data of the 1 MW_{th} pilot unit, provided by EST at the Technische Universität Darmstadt. The current result of the design study, carried out by AE, is shown in Figure 6.

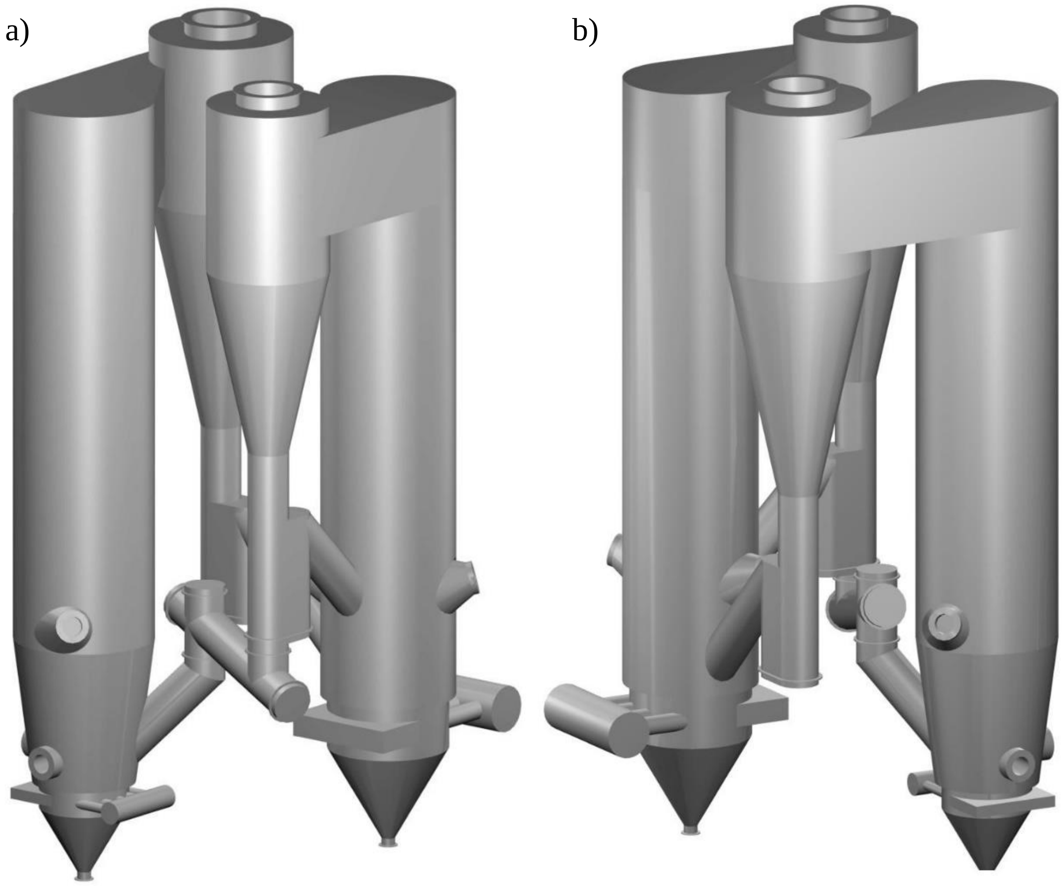

Figure 6: a) FR at left side, AR at right side; cyclone AR at front, cyclone FR in the back; J-Valve visible below the middle, b) FR at right side, AR at left side; cyclone FR at front, cyclone AR in the back.

Based on this data, the cross-sectional area and the inner diameter of the Air Reactor (AR) and the Fuel Reactor (FR) have been calculated. All dimensions and the performance of the cyclones for the AR and the FR have been designed according the heat and material balance. The geometry of the return legs, stand pipes, J-Valves and the two Loop Seals result from the design of the cyclones and the circulation mass flows. The minimum total height of the combined components cyclone, the loop seal, and return leg, are fixed for the AR and the FR. To achieve the maximum possible circulating mass flow between the two reactors, necessary for optimized KPIs of the CLG process, the height of each reactor should be minimized, limited by the minimum height of the two cyclone assemblies, as well as restrictions resulting from the combination of the two reactors and the necessity to exchange the bed material by gravity from one to the other. Another influence on the final geometry and arrangement is the design of all the hot components of the whole process group. These include the reactors themselves and all components of the solids separation and recycle, starting from the flange at the solid fuel feed to the FR and ending at the gas outlet flanges of the cyclones at AR and FR as well as the bed material outlet flanges at the reactor bottom cones. Each of these components are composed of a self-supporting steel shell structure with an inner insulation of a two-layer refractory lining of 250 mm thickness. This type of a two-layer lining with a high insulating layer covered by a high abrasion resistant layer, together with its selected thickness, will be an optimum in heat loss, surface temperature and the weight of the individual units.

4 Technology Development

4.1 Biomass Pre-Treatment

Different representative feedstocks for the CLARA project were selected based on technical and market criteria in order to identify biogenic residues that maximize the chances for reaching a higher technological readiness level (TRL) while at the same time being representative as feedstocks with high European sustainable sourcing potentials. The selected representative feedstocks for the CLARA project were wheat straw (agricultural residues), pine wood residues (forestry residues) and industrial wood pellets of considerable low grades.

It is well know that Chemical Looping Gasification (CLG) is rather flexible with respect to the feedstock used and particularly suited for fuels with a high content of impurities. Hence, biogenic residues from agriculture and forestry could be applicable as a cheap and abundant feedstock for biofuel production using CLG.

Cereal straw is, in particular, an attractive lignocellulosic materials for use in energy production, since it is one of the most abundant renewable resources whose potential is similar to the sum of both forest and non-forest woody residues. However, straw residues are especially problematic feedstocks, due to their undesired properties with regard to their gasification in fluidized beds:

- Low energy density leading to increased costs for transport and problems with feeding
- Low ash melting point leading to agglomeration and slagging
- High content of volatile inorganics such as alkali and chlorine that promote corrosion and fouling

This makes it difficult to handle, transport and store efficiently limiting its commercial use being necessary to perform some pre-treatment prior to the gasification step. Therefore, the aim of the feedstock pre-treatment is to improve wheat straw residues characteristics for CLG obtaining a solid feedstock with a high calorific value and a high energy density, while at the same time avoiding ash-related operational issues considering technical, economic and environmental impacts in the value chain. Hence, an efficient and cost-effective pre-treatment concept is being derived within the CLARA project, allowing for a large-scale utilization of wheat straw in industrial gasification processes.

In order to accomplish this development, an experimental study was performed regarding pre-treatment of straw based on the combination of different technologies such as heat treatment (torrefaction), washing and use of additives. The underlying goal was to obtain optimized feedstock properties. The quality of wheat straw after processing with the different pre-treatment steps and combinations of them was comprehensively studied to allow for inferences regarding its performance during gasification. Since inorganics behavior in solid fuels is a complex topic, pre-treated fuel samples produced by CENER were characterized not only based on biofuel standards but also by advanced techniques. On the one hand, FJZ has tested the influence of pre-treatment on the release of volatile inorganics during gasification as well as well as the melting behavior of the residual ashes by hot stage microscopy. On the other hand, UNIVAQ performed continuous steady-state gasification tests and dynamic pressure measurements to evaluate gas yield and its composition as well as the sintering phenomena and interactions with different oxygen carriers (OC).

Finally, physical pre-treatments such as chopping and/or pelleting should be considered as part of the pre-treatment concept since these allow an easier handling, storage, and transportation reducing overall costs. Pelleting, for example, raises the volumetric energy density of the feed-stock and improves its handling properties, which will facilitate gasifier feeding and gasification process control, impacting the value chain from a technical and economical operation point of view.

Since the improvement of each pre-treatment step on biomass performance for CLG application should have a clear effect, the final selection for the optimized pre-treatment process conditions was based in the following criteria: suitability for CLG gasification (fluidization behavior and interactions with oxygen carrier), feasibility/cost of transport, feeding requirements for CLG plant and production cost.

Therefore, the selected pre-treatment concept established for wheat straw in order to develop a concept for production of advanced liquid biofuels based on chemical looping gasification (CLG) was finally based on chopping, pelleting and additivation.

Feedstocks preparation for all subsequent small-scale CLG test campaigns in the CLARA project has been carried out inside the pre-treatment pilot plant of CENER (see Figure 7). Additionally, the pre-treatment concept is being applied in the (semi-)industrial scale at the facilities of ABT, for the pilot tests conducted at TUDA. Based on the findings of these CLG test campaigns, the merit of the suggested pre-treatment concept will be evaluated, allowing for further advances towards it large-scale application in industrial environments.

Figure 7: Biomass pre-treatment unit at CENER facilities (BIO2)

4.2 Chemical Looping Gasification

Chemical looping gasification (CLG) requires in-depth analyses of multiple phenomena to attain a stable and efficient process allowing for continuous conversion of solid biomass-based feedstocks to a high-quality syngas. Using lab and bench scale chemical looping units, *CTH* and *CSIC* have the possibility to investigate CLG at realistic conditions, using different fuels and oxygen carriers at varying boundary conditions (e.g. reactor temperatures, air-to-fuel equivalence ratio, etc.).

During the third year of the project, CTH and CSIC were focused to investigate the performance of the selected oxygen carriers, from the pre-screening task, in the 10 kW_{th} at CTH, and 1.5 kW_{th} and 50 kW_{th} at CSIC. The selected OCs from the prescreening tests were ilmenite, LD slag and Tierga iron ore. For evaluation of these selected oxygen carriers during continuous operation in the pilot plants, a total of 600 hours of CLG operation has been carried out in the pilot plants at CTH and CSIC at realistic conditions, using different fuels at various operating conditions (e.g. reactor temperatures, air-to-fuel equivalence ratio, etc.). After a vast experimental evaluation, summarized in Table 2, it has been confirmed that using oxygen carriers in CLG has a positive effect on gasification of biomass by reducing tar formation, increasing syngas yield, biomass conversion, and H_2/CO ratio compared to conventional steam gasification using silica sand as bed. Among the tested oxygen carriers, Ilmenite ilmenite, and LD slag showed better biomass gasification performance compared to Manganese ores (Elwaleed B and Moanda) and Tierga ore. LD slag has a lower lifetime than ilmenite and needs heat pretreatment, but a higher syngas yield and H_2/CO.

Table 2: Summary of CLG results for Ilmenite and LD slag during continuous operation.

		Unit	**Oxygen Carrier**			
			CTH S/B=0.95, T=970ºC, λ=0.2, Fuel=PFR		CSIC S/B=0.6, T=950ºC, λ=0.35, Fuel=PFR	
			Ilmenite	LD slag	Ilmenite	LD slag
Gas Composition	CO_2, CO	%vol, %vol	37, 22	35, 20	41.5, 21.1	38.1, 23.1
	H_2, CH_4	%vol, %vol	29, 8	34, 8	23.6, 10.2	29.5, 8.1
	C2-C3	%vol	4	3	3.4	1.2
Biomass conversion, X_b		%	93	95	98.9	97
H_2/CO Ratio			1.5	1.7	1.1	1.3
Syngas yield, Y		m^3/kg dry biomass	0.65	0.71	0.53	0.70
Tar		g/Nm^3	8-18	2-5	1-2	2-3
Lifetime		hour	850	800	630	275
Cost*		USD/Ton	200	NA	200	NA

Therefore, ilmenite has been selected for subsequent tests in larger CLG pilots and the final demonstration at TUDA (WP5), considering the operational performance, availability of the material at multi-ton scale, lifetime and pretreatments required for the material prior to CLG operation. In a first step towards large-scale demonstration, CSIC has performed a first test campaign in their 50 kW_{th} pilot unit using ilmenite as oxygen carrier and pre-treated straws as fuel. The layout of 50 kW_{th} unit is illustrated in Figure 8. In the 50 kW_{th} pilot unit at CSIC, CH_4 and C2, C3 concentrations were similar to those found in the 1.5 kW_{th} unit. Also, no agglomerates were found and pellets maintained the shape inside the fuel reactor. Currently, CTH is modifying the 100 kW_{th} unit for safe handling of CLG. The risk assessment report for CLG operation has been prepared and the fuel feeding system has been modified. The plan is to further investigate the performance of ilmenite during continuous CLG operation in the 100 kW_{th} unit using pine forest residue and pretreated straw (see also Chapter 4.1).

Apart from the testing of CLG in the pilots of CTH and CSIC, gasification kinetics for pine forest residue pellets and industrial wood pellets were determined, to allow for modelling of the conversion of the biomass char inside the CLG unit. In order to do so, the resistance to the gas diffusion happening in the pellets of the biomass char has been determined by CSIC. In addition, the kinetics of the selected oxygen carrier, ilmenite, has been established under CLG conditions. Kinetic equations and parameters regarding both the reduction and oxidation reactions to be used in the CLG process have been established, paving the way for future modelling endeavors in the CLARA project.

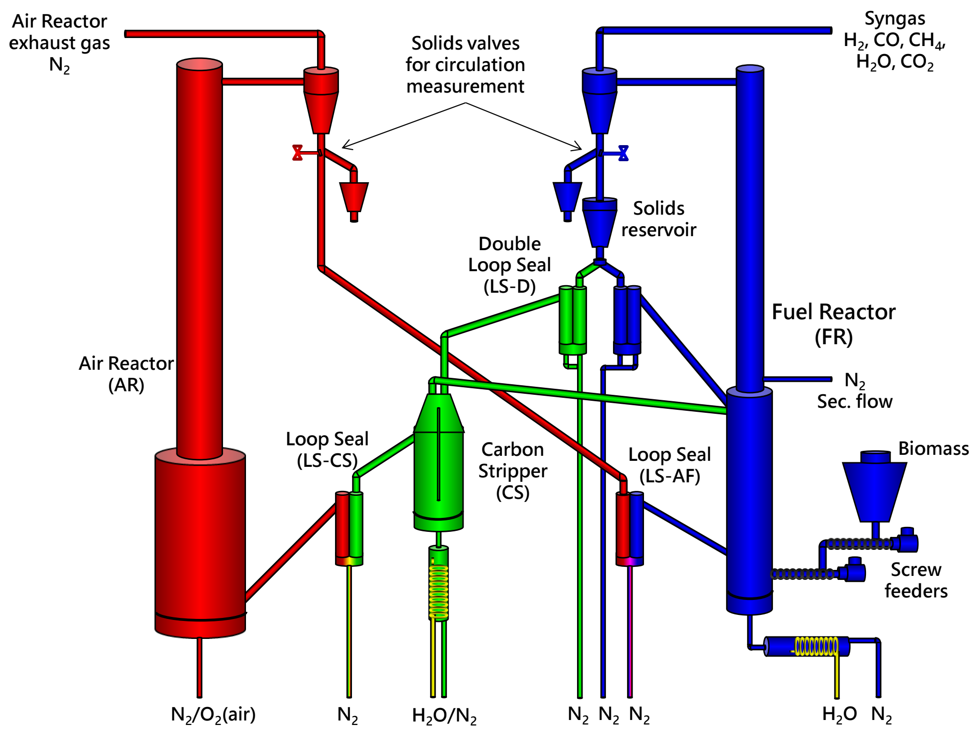

Figure 8: Layout of the CSIC facility (50 kW_{th}) used for biomass fuelled CLG.

Lastly, CSIC developed a 1.5D fluidized bed model for the entire CLG reactor system considering the core/wall structure along the height of the circulating fluidized beds. This model includes both the fluid-dynamic of the solids present in the bed and the kinetic parameters for the biomass char and oxygen carrier (ilmenite). Moreover, TUDA is currently preparing 3D CFD models for the 50 kW_{th} unit of CSIC and the 1 MW_{th} CLG pilot plant in Darmstadt. In the coming months, simulations will be carried out, using data both CLG units, to validate and optimize the given modelling approach. Based on this, further fine tuning of the full-scale unit (see Chapter 3.2) will be carried out.

4.3 Syngas Cleaning

For removal of CO_2 and Sulphur containing components from the syngas for subsequent synthesis processes, the Rectisol® process, using methanol as solvent, is mainly applied worldwide. As this technology shows high CAPEX and OPEX due to necessary refrigeration of the solvent, an alternative novel concept will be used in this project (see Figure 9). The innovative idea is to use solvents already known partly from other applications. At first, it is foreseen to combine an amine wash (T-01) for main desulphurization with a subsequent caustic wash (T-04) for fine cleaning of the syngas. For Sulphur recovery, the sour gas from the amine regeneration (T-02) will be treated in a H_2O_2 wash (T-03), where oxidation to pure Sulphur will occur. In first investigations at RWE including mass- and energy balances with ChemCad, this combination showed significant potential for savings in CAPEX as well as in OPEX.

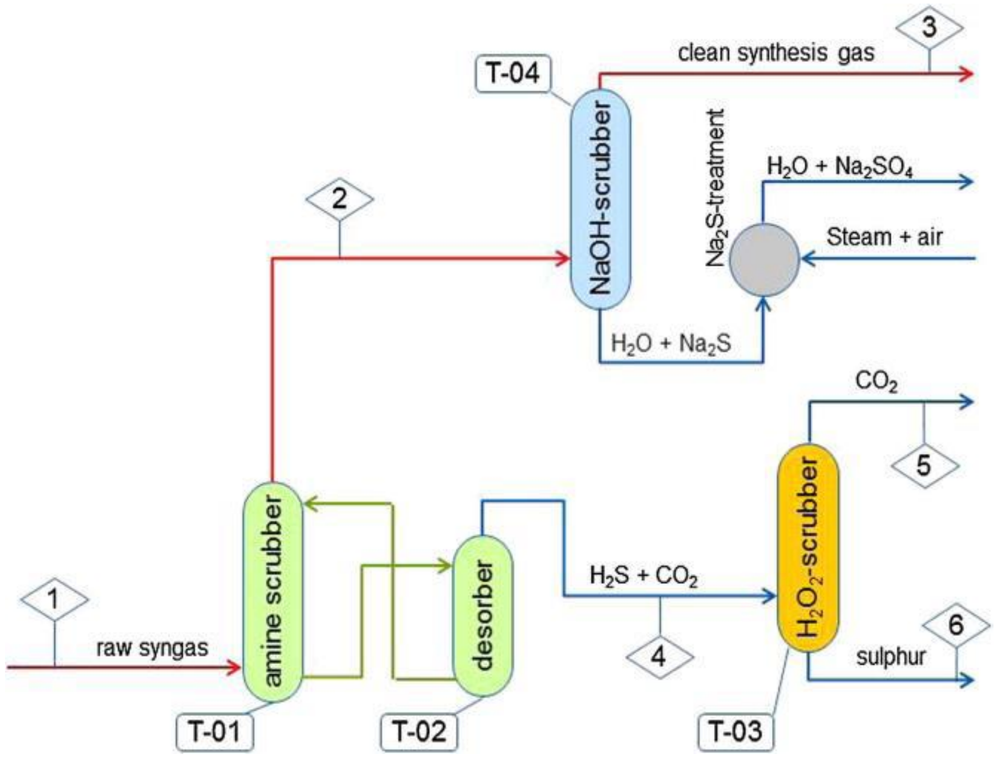

Figure 9: Block flow diagram of innovative gas cleaning concept

The new concept for acid gas (CO_2 and H_2S) removal from the CLG syngas were tested in a mobile small-scale test rig at RWE. While amine wash is a mature technology, well-known from several large-scale gas cleaning projects and can be again demonstrated during full chain test runs at pilot scale in the plant at TU Darmstadt, two main topics were defined for experimental investigations within the mobile small-scale test rig:

1. Which minimal level of Sulphur impurities can be reached in the syngas exiting the caustic wash?
2. How effective is the H_2O_2 contact, i.e. will the reaction of H_2S really end up at elemental Sulphur or will further oxidation occur. Will it be effective enough for such H_2S contents in the sour gas and what are the side-effects of the high CO_2 content?

The mobile small-scale gas washing test rig consists of three different absorption modules (see Figure 10). They have been designed for operation with all foreseen solvents and could be operated at the different conditions / gas specifications suitable for the respective cleaning steps (1, 3 and 4 in Figure 9).

A module with a pressurized metal column is applied for tests of caustic and amine wash, while two different modules – one with stirred glass bottles and one with glass column - are used for atmospheric Sulphur recovery with H_2O_2.

In a first operation phase when basic parameters were tested at the RWE Innovation Centre Niederaußem, the needed gas compositions were supplied by mixing of synthetic pure gases from bottles. In a second operation phase, the mobile small-scale test rig will be operated at TUDA behind the already existing pilot scale gas cleaning unit of the 1 MW_{th} chemical-looping gasifier (see Chapter 5).

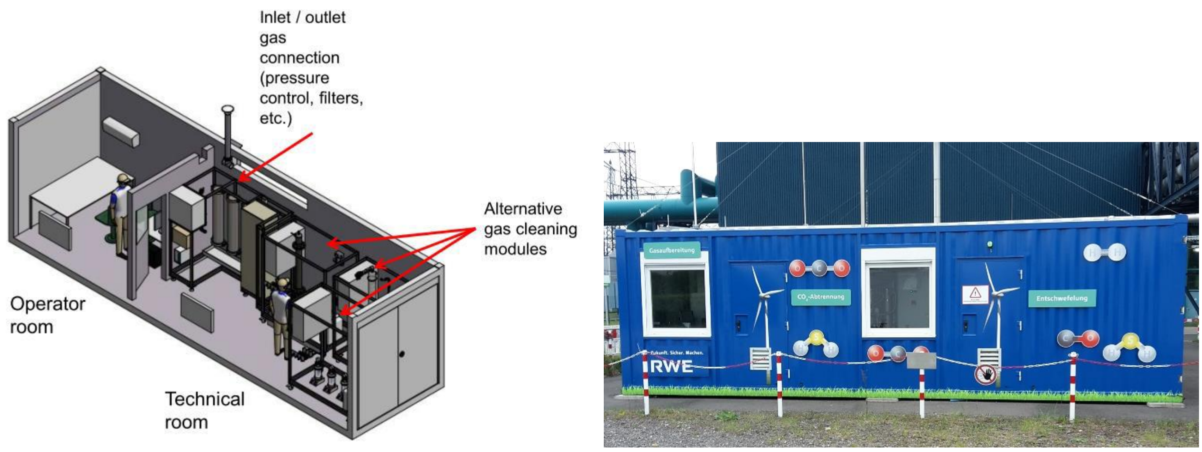

Figure 10: 3D view and photo of mobile small-scale gas washing test rig

During the first operation phase at RWE numerous trials with H_2O_2 under different operating conditions and with different parameters like H_2O_2 concentration in the liquid, H_2S concentration in the gas, operating temperature, amount of additional catalyst, etc. have been performed. Unfortunately, no significant conversion of H_2S to pure Sulphur could be found. Therefore, it was decided to use potassium permanganate ($KMnO_4$) as alternative chemical. Although this leads to several alterations such as the type and the composition of Sulphur containing product stream, the overall goal of saving CAPEX and OPEX is expected to be reached. This alternative combination of processes for the innovative gas cleaning has now been applied for patent and first experimental results are presented below.

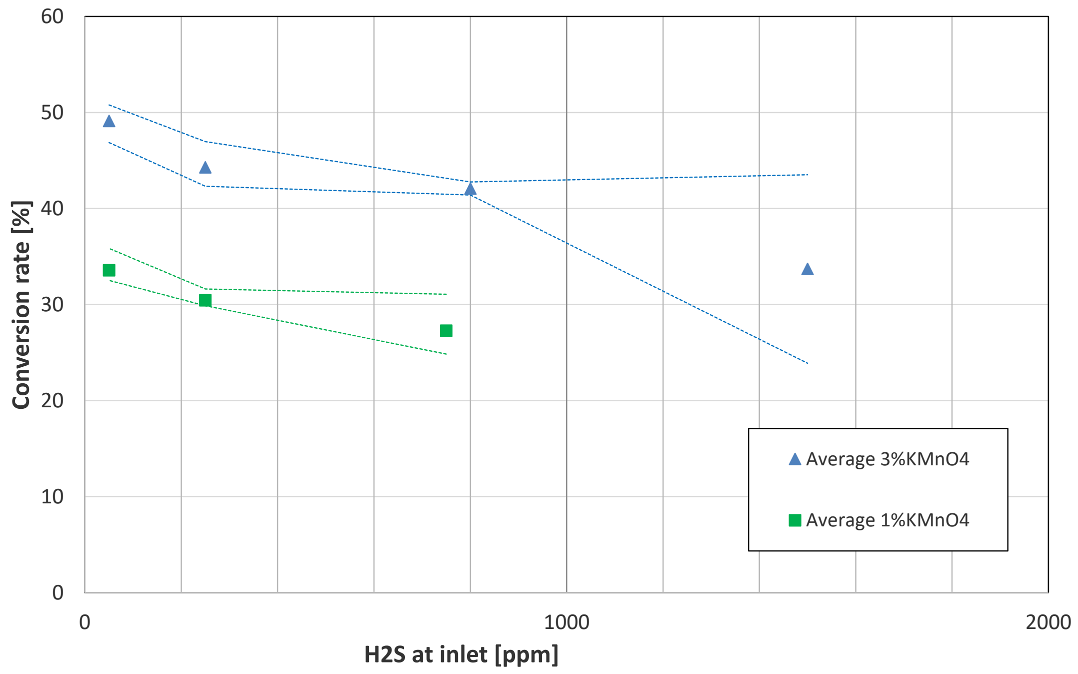

Figure 11: Conversion of H_2S to sulphur using $KMnO_4$.

Due to a tight time schedule, only a few test runs could be performed with $KMnO_4$. During these, H_2S concentrations in the gas were varied up to 1500 ppm, the concentration of $KMnO_4$ in the liquid was set to 1 and 3 wt%. The main outcome is that especially for very small concentrations of H_2S, significant conversion rates could be found. This is important because it can be stated that full cleaning of the sour gas (H_2S containing CO_2) is possible as requested for further use of the CO_2 e.g. for solid fuel feeding to or inerting purpose of the gasifier, use in synthesis processes, venting to atmosphere, or other usage. Further on, as generally expected, it can be seen that the conversion rate depends on the concentration of KMnO4 in the liquid.

As mentioned above, further tests will be done during full-chain test runs at TU Darmstadt. These will be carried out at the conditions shown above, yet using a "real" sour gas coming from the pilot-scale gas cleaning unit. To get a complete picture of the reaction system with $KMnO_4$, more tests will be performed at RWE in subsequent projects.

The modelling procedure of the novel gas cleaning concept will be adapted to the latest experimental findings. CERTH is working on updating the gas cleaning unit that has been developed for the process chain definition and modeling (see Chapter 3.1), by including the novel Sulphur recovery unit. The results will be presented in the next public report.

5 Full-Chain Pilot Testing

In preparation of the upcoming full-chain pilot tests at the facilities in Darmstadt, the 1 MW_{th} pilot gasifier is being prepared. This includes installation of new equipment, adaptions of existing plant sections (e.g. steam supply for the FR), as well as maintenance of the existing measurement and control systems. Moreover, the pilot plant is currently being extended by a syngas removal facility (concept see Figure 12a), in order to be able to handle and dispose the raw gas produced in the gasifier safely. Construction works for the plant extension have started in November 2021, with the foundation work having been finished in December. Thereafter, the main components shown in Figure 12, a thermal oxidizer (see Figure 12b+c) and a hot gas filter (see Figure 12d), were installed on the base plate in January 2022. Currently, piping and insulation, connecting the gasifier and the syngas removal unit are being installed, before commissioning of the new plant unit will take place at the end of February in 2022.

Figure 12: **Concept (a) and progress at the construction site (b-d) of the novel syngas removal unit at the 1 MW_{th} pilot plant facilites in Darmstadt.**

During steady-state CLG operation, a slipstream of approx. 200 Nm^3/h of the raw synthesis gas produced within the CLG pilot will be transferred to the novel gas cleaning plant, which was successfully commissioned within the framework of the German research project FABIENE. In the gas cleaning plant, side products (e.g. CO_2, H_2O) and contaminants (e.g. tars) are removed from the raw syngas produced within the pilot gasifier. The treated syngas is then used for Fischer-Tropsch synthesis inside a test rig, provided by the project partner RWE. This test rig was successfully commissioned and operated during two previous tests campaigns within the research projects FABIENE and Lig2Liq. Moreover, a side stream of sour gas (mainly consisting of CO_2, H_2O, and H_2S) from the gas treatment plant is utilized to test the novel sour gas separation concept, investigated within the project CLARA, in the full-chain configuration for the very first time inside a second dedicated container. This container is currently being integrated into the pilot facility. An image providing an overview over the novel gas treatment plant and the two containerized test rigs is shown in Figure 13.

Figure 13: **Image of the novel gas treatment plant (background) and the two RWE test rigs (lower container behind cladding: fuel synthesis test rig, upper container: gas treatment test rig).**

During each of the three scheduled two-week test campaigns, roughly 75 tons of pre-treated biomass pellets will be converted into a raw syngas inside the 1 MW_{th} chemical looping gasifier. To have these amounts of pre-treated biomass in the desired quality at disposal, AB Torkapparater (ABT) has started pelletizing raw wheat straw according to the recipe from CENER (see Chapter 4.1), in their industrial scale facilities in Sweden. ABT currently has roughly 10 t of fully prepared straw pellets, shown in Figure 14, ready for shipment to Darmstadt. Moreover, preparations to pelletize the second model feedstock, pine forest residue (PFR), are underway. Once fully prepared, the entire feedstock batches will be stored in a decentralized facility, before being transported to Darmstadt prior to the test campaigns. Here, the pre-treated pellets will be stored in a dedicated fuel silo, prior to being fed to the FR during full-chain operation.

Starting in March 2021, the entire full-chain pilot plant will be in operation for the very first time, facilitating an investigation of all relevant technologies of the biomass-to-biofuel process chain. Thereby, important insights for process scale-up (see Chapter 3.2) and the analysis and investigation of the full process chain (see Chapter 6.1 & 6.2) will be obtained.

Figure 14: **Straw pellets manufactured at ABT**

6 Analysis & Investigation of the Full Process Chain

6.1 Risk Assessment

During the risk assessment study, the following aspects are being considered by the project consortium:

- Health and safety
- Environment
- Society
- Technology
- Economy

The health and safety issues are assessed by RWE (with support from CENER, TU WIEN, AE, and TUDA) with respect to the full-scale biomass-to-end-use chain based on the processes defined at the beginning of the CLARA project. One focus is on the handled materials including solids (oxygen carrier, feedstock, dust, ash, etc.), liquids (biodiesel from gas cleaning unit, biofuel-products, solvents for gas washing, etc.), as well as gaseous components (H_2, CO, CO_2, etc.) and their hazardous potential for workers and local residents. Particular attention is drawn to the process itself and the potential safety risks in case of a malfunction of the unit and preventive measures. The partners already agreed on certain criteria and the methodology, but as the assessment has just started, no results can be presented yet.

TU Wien has developed a preliminary list of environmental risks that will be further assessed by the whole project group, which include but are not limited to risks related to land use and harvesting, soil preparation, soil contamination by pesticides/fertilizers, the effects of downstream utilization and/or deposition of residual solids and liquid, as well as the energy consumption of the Biomass-to-Liquid plant on the environment. In addition to the technology-specific risks outlined above, safety concerns that could generally result in environmental problems, such as explosions, fire hazards, and operator failures may also be included in the analysis. The analysis of the above mentioned risks, which is a preliminary compilation and is subject to change, is currently ongoing using a qualitative approach that is mainly based on a literature survey and will be later on complemented through an interactive workshop.

In addition to environmental risks, potential risks to society are being assessed by BEST (Bioenergy and Sustainable Technologies GmbH), utilizing a qualitative approach, i.e. a literature search and stakeholder interviews. The risks related to society that have been identified can be clustered three groups illustrated in Figure 14.

Selected results on risks related to socioeconomic factors include but are not limited to potential effects on demand that distort markets and a resulting competition for resources with food/feed production, unintended steering effects for biomass utilization and exacerbated competition for specific feedstocks due to subsidies and the risk of the economic exclusion of micro-scale SMEs. On the other hand, there is a major potential for regional development and added value through the CLARA plant. Selected results of the risk analysis related to political and legal framework include but are not limited to: lack of security regulations that could endanger society due to flawed approval procedures, as well as uncertainties around future political frameworks with regards to e.g. CO_2 pricing for fossil based energy technologies. The latter could result in the risk that CLARA technology may not succeed from an economic standpoint. Finally, several of the identified risks related to social acceptance include concerns about emissions, waste generation, food safety, and biodiversity as well as concerns that increased migration and inequitable benefit sharing could lead to adverse changes in the local social structure or community. The so-called NIMBY (not in my backyard) effect could potentially also be observed for the CLARA project, as the local population may theoretically be in favor of the use of renewable feedstock but may not want a BtL plant in their neighborhood. It is important to note that the examples above merely represent a selection of risks that are being analyzed. A more detailed report on this analysis will be available once first mitigation strategies have been discussed in a workshop in March 2022.

Figure 14: Three clusters of potential risks to society through the CLARA approach.

6.2 Techno-Economic, Socio-Economic and Environmental Assessment

The final part of the CLARA project, bringing cohesion to the research work carried out by all other project partners, consists of the following activities for selected options:

- Estimate capital investment and annual operating cost of industrial scale gasification and fuel synthesis facilities.
- Establish techno-economic models
- Calculate cost and revenue flows
- Identify and analyze economic risks derived from feedstock prices, project budget estimate and technological risks.

Based on the design and mass and energy balance of the plant (see Chapter 3), the cost models of the full-scale biomass chemical looping gasification process for the synthesis of liquid fuel production will be developed; capital investment and operational costs for industrial sized gasification and fuel synthesis plants will be estimated by using the ECLIPSE suite of the process simulation and economics software. Moreover, a realistic comparison will be performed.

When implementing capital and operating costs, a comprehensive techno-economic analysis (TEA) of the CLARA BtL process chain will be conducted, including revenue flows, net present value (NPV) and internal rate of return (IRR). Thus, the results provide a good basis for illustrating economic advantages and disadvantages of different biofuel production decisions and can be used to establish future applications.

The activity of economic risk analysis involves identifying potential economic risks that influence the project objectives. In addition to the technological risk assessment, more detailed economic risks are identified and analyzed for the whole CLARA process chain, including additional project cost reserves, rising feedstock prices, and component failures in operation. The aim of this risk analysis is to derive economic risk mitigation strategies to tackle the vulnerability amplified by the single chain links in the way of scaling up a pilot scale to the demonstration-scale process. To carry out economic risk assessment for the CLARA concept, the Monte Carlo simulation tool @Risk 8 will be used. The results from this activity will be used assess risks emerging from the diffusion of biofuel production chains based on organic residues.

7 Summary & Conclusions

In the following, the major advances and most important findings made within the third year of the CLARA project with regard to process chain definition (see Chapter 3), technology development (see Chapter 4), pilot testing (see Chapter 5) and the investigation of the BtL chain (see Chapter 6) are summarized.

- The entire biomass-to-liquid process chain has been defined and subsequently modelled, yielding an process exhibiting an energetic fuel efficiency of 53.4 % and a carbon utilization of 32.5 %
- Based on the findings made in terms of the advancement of CLG in the CLARA project and during the design of the 1 MW_{th} chemical looping gasifier, AE devised a design for a full scale 200 MW CLG unit.
- Using technical and economic considerations, an optimized pre-treatment concept has been developed, allowing an efficient utilization of straw for gasification processes. This pre-treatment concept is currently being implemented and tested in industrial scale.
- On the basis of lab-scale tests, the very first successful CLG campaigns in a small pilot unit were carried out. The findings made during these experiments confirm those made during lab tests. Further tests in 50 and 100 kW_{th} pilots will be conducted shortly, casting further light onto the CLG technology itself, related optimization strategies, and their technical implementation.
- A novel, patented sour gas treatment concept, using $KMnO_4$ as sorbent for H_2S separation from sour gases has been investigated in lab-scale. Initial findings verify excellent Sulphur removal from different sour gases, animating further investigations for potential large-scale application.
- The necessary adaptions on the pilot facilities in Darmstadt are currently being finalized in preparation of the first full-chain experiments. The first 1 MW_{th} tests campaigns will commence in March 2022, yielding important insights into all technologies under consideration in the CLARA concept.
- Investigations of the entire process chain with regard to risk analysis and techno-economic considerations have commenced and will be supplemented using insights from the other activities in the CLARA project in the upcoming months.

In summary, the CLARA consortium was able to fully define individual sub-units and further investigate the entire BtL concept during the third project year. Holistic considerations of the entire process chain have started, to allow for an assessment of the investigated process chain beyond purely technological indicators. In the fourth project year, all sub-units of the process chain will be fully defined and optimized, before being modelled and scaled to industrial size. This endeavor will be complemented by in-depth risk studies as well as socio-economic analyzes, which allow for an elaborate 360° view of the suggested BtL chain. The upcoming 1 MW_{th} full-chain tests will form the backbone of these efforts, providing important insights into the individual technologies, tested in an industrially relevant environment.

8 References

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Abbreviations

BtL	Biomass-to-Liquid	NCV	Net Calorific Value
CCU/S	Carbon Capture & Storage or Utilization	NIMBY	Not-in-my-Backyard
CAPEX	Capital Expenditure	NPV	Net Present Value
CGE	Cold Gas Efficiency	OC	Oxygen Carrier
CLG	Chemical Looping Gasification	OPEX	Operating Expenditure
CU	Carbon Utilization	PFR	Pine Forest Residue
EFE	Energetic Fuel Efficiency	REDII	Renewable Energy Directive
FT	Fischer-Tropsch	TEA	Techno Economic Analysis
IRR	Internal Rate of Return	TRL	Technological Readiness Level
KPI	Key Performance Indicator		

Project Consortium

TUDA	Technische Universität Darmstadt	*TU WIEN*	Vienna University of Technology
AE	AICHERNIG Engineering GmbH	*FJZ*	Forschungszentrum Jülich
CTH	Chalmers Tekniska Högskola AB	*ABT*	AB Torkapparater
CSIC	Agencia Estatal Consejo Superior de Investigaciones Cientificas	*ULster*	University of Ulster
RWE	RWE Power AG	*CERTH*	Centre for Research & Technology Hellas
CENER	Centro Nacional de Energías Ren-ovables	*UniCRE*	Unipetrol Centre for Research and Education, a.s.
UNIVAQ	University of L'Aquila		