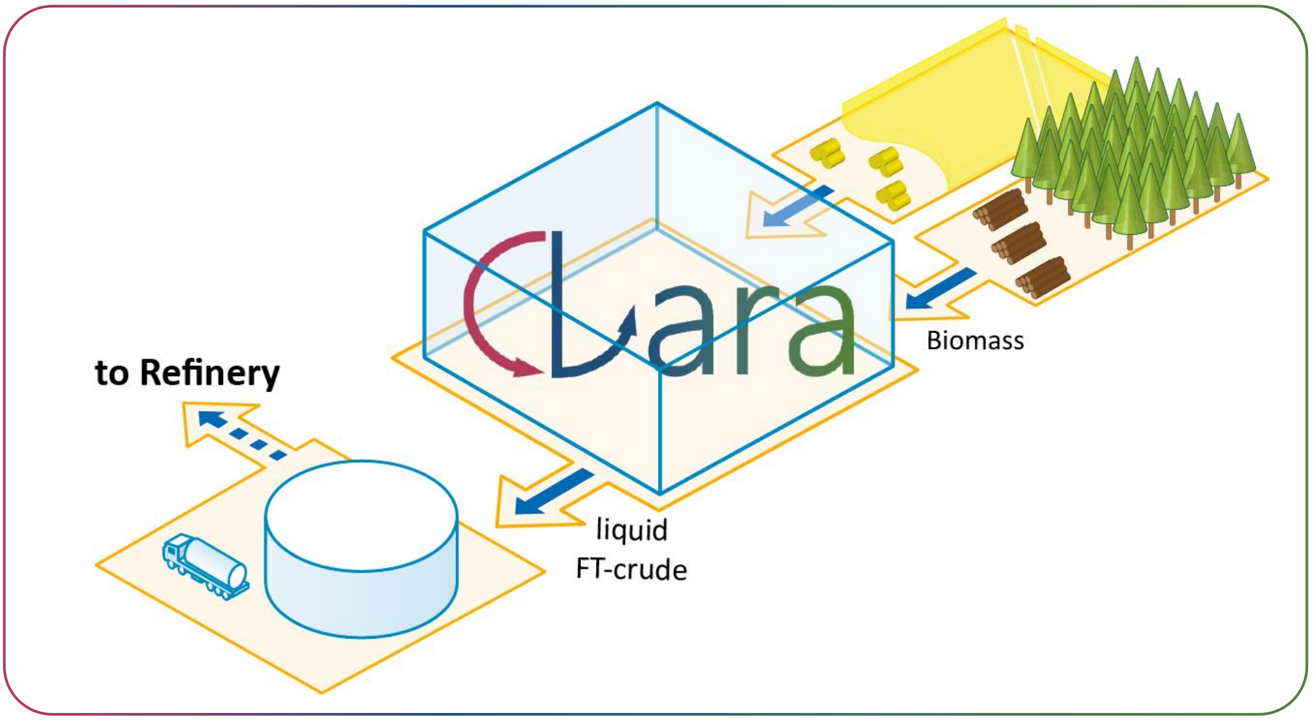
Chemical **L**ooping G**a**sification fo**r** Sustain**a**ble Production of Biofuels

H2020 Research and Innovation action
Grant Agreement no 817841

Public Report II



Authors: Paul Dieringer[1], Jochen Ströhle[1], Ibai Funcia[2], Amir Soleimani[3], Thorsten Liese[4], Frank Buschsieweke[4]

Affiliation: [1]Technische Universität Darmstadt, [2]Centro Nacional De Energías Renovables, [3]Chalmers University of Technology. [4]RWE Power AG.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 817841.

Publication date: 31.10.2020, Access the digital version via this link: https://clara-h2020.eu/public-reports/

Executive Summary

During second year of the CLARA projects, major efforts were focused on advancing the individual technologies of the devised biomass-to-liquid process chain. These include the development of a novel pre-treatment concept for wheat straw (see Chapter 4.1), the deeper investigation of CLG in bench and lab-scale units (see Chapter 4.2), and studies on the innovative sour gas separation concept, required for efficient sulfur recovery (see Chapter 4.3). Moreover, the pilot plant facilities located at the Technical University of Darmstadt were extended by a syngas cleaning plant and a synthesis test rig, allowing for an investigation of the full solid-to-liquid process chain at the pilot plant facilities (see Chapter 4.4).

With the aim of making wheat straw a suitable feedstock for efficient CLG operation, a pre-treatment concept, consisting of torrefaction, washing, pelleting, and additivation has been developed under the lead of *CENER*. To understand the impact of each pre-treatment step, the feedstock quality after each processing step has been studied intensively. On the basis of these insights, a preliminary pre-treatment sequence has been determined. After the final refining of this sequence, the performance of the wheat straw pellets, produced with the novel pre-treatment concept, will be analyzed during CLG operation, to evaluate the merit of the suggested pre-treatment sequence.

Due to the novelty of the CLG technology, gaining a basic understanding of the process fundamentals is essential to allow for its efficient implementation and targeted optimization. With the aim of gaining such essential insights on the CLG process, more than 350 hours of continuous CLG operation was carried out by *CTH* and *CSIC* in continuous 1 kW_{th} and 10 kW_{th} units, using different oxygen carrier materials. The knowledge base gained from these small-scale test campaigns with regard to process control, process efficiency, and the merit of different oxygen carrier materials will be transferred to larger CLG units in future test campaigns.

As syngas cleaning signifies a major share of biofuel production costs in a biomass-to-biofuel process chain, a cost-efficient alternative to the state-of-the-art Rectisol® and Claus® process is under investigation in the CLARA project. By studying the innovative sour gas separation technology in a designated setup, *RWE* was able to determine the fundamentals of the researched reaction system. The knowledge gained from these experiments will now be transferred to a more sophisticated atmospheric glass column module, to obtain more representative values for the conversion rate of H_2S, which can be used for theoretical modeling and the sizing of the required plant components.

In preparation of the full chain biomass-to-biofuel test campaigns at the facilities of *TUDA*, the pilot plant is currently being adjusted and extended. This includes the finalization and commissioning of a novel pilot scale syngas cleaning unit and the integration of the two test rigs provided by the project partner *RWE*. First full-chain test campaigns, including pilot scale gasification and syngas cleaning, as well on-site investigations of fuel synthesis and the novel sour gas separation technology, will take place within the RFCS project Lig2Liq in January 2021.

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.

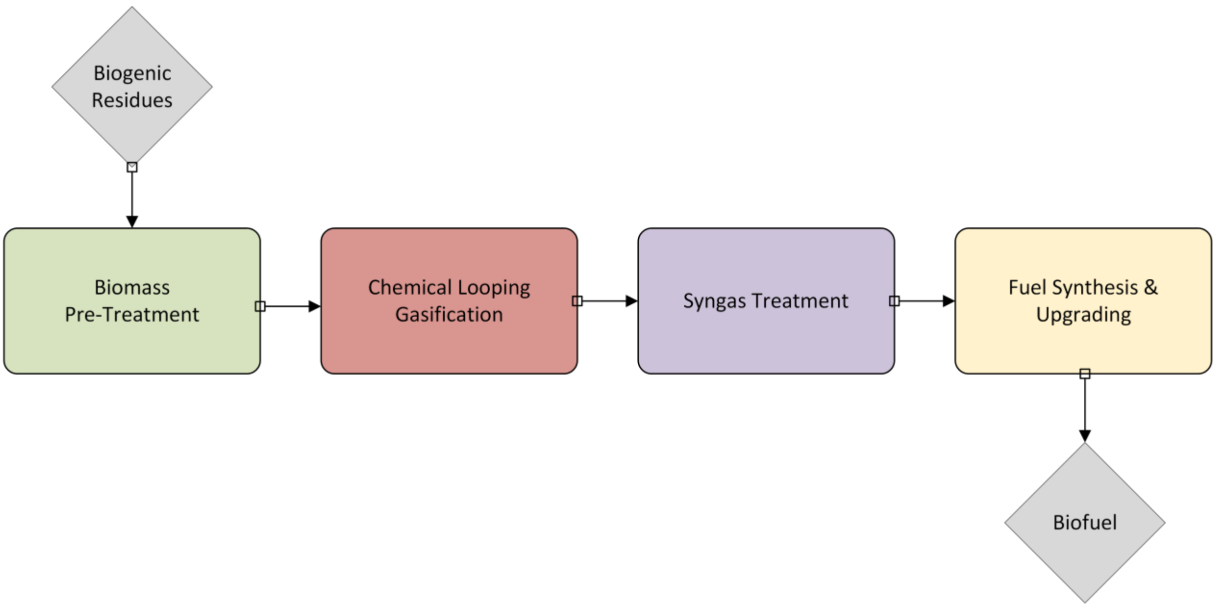


Figure 1: Simplified scheme of full biomass-to-biofuel process chain.

As an introduction, this report again informs the reader about the project motivation and the underlying goals (Section 2) as well as the different technologies that are being deployed to achieve these (Section 3). Moreover, current findings and highlights unveiled by the CLARA consortium within the last twelve months (Nov. 2019 – Oct. 2020) are presented in Section 4. An summary of this public report can be found in the last Section (Section 5).

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

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 Project Technology

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. In the following, the different technologies deployed within these sub-units will be explained in detail.

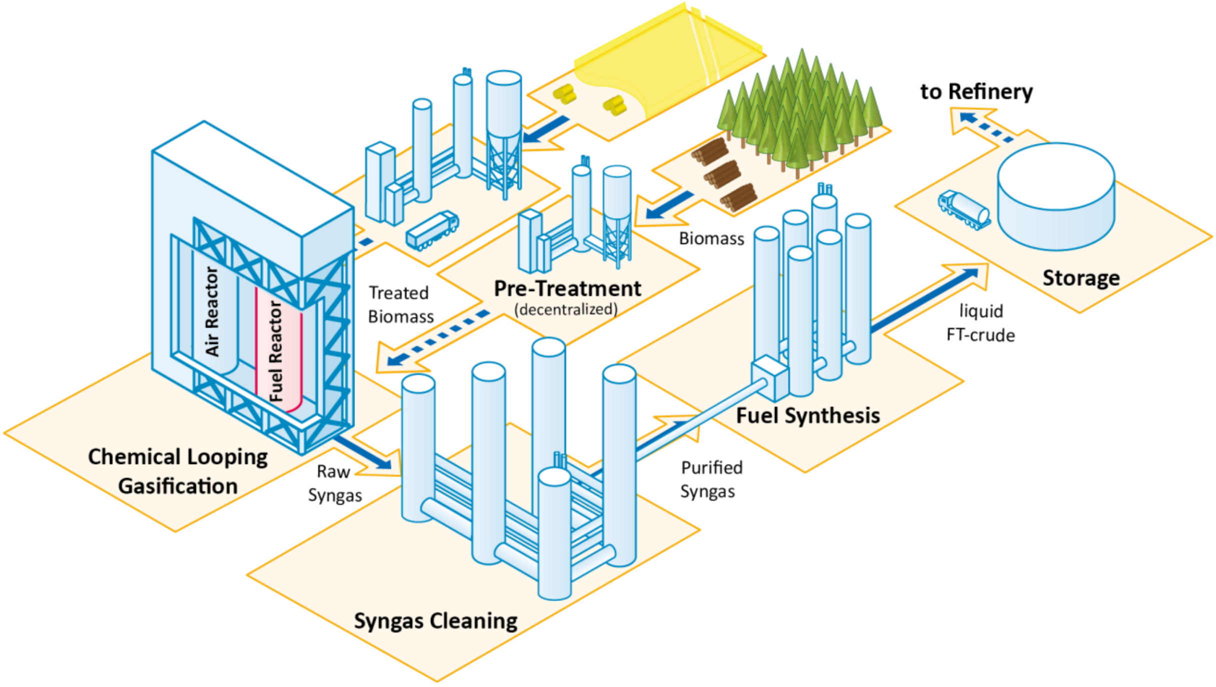


Figure 2: Schematic illustration of the process chain investigated within the CLARA project.

3.1 Chemical Looping Gasification (CLG)

During the chemical looping gasification (CLG) process, schematically shown in Figure 3, the pre-treated feedstock is devolatilized, pyrolyzed and gasified in the FR at temperatures around 850 to 950 °C by means of a gasification agent (H_2O and CO_2) and an oxygen carrier (Me_xO_y). This means that instead of supplying pure O_2, part of the oxygen required for the endothermic biomass gasification is provided by the oxygen carrier, which is regenerated (re-oxidized) in the air reactor at temperatures between 950 and 1050 °C. Typically, oxygen carrier materials are metal oxides such as ilmenite or hematite, exhibiting excellent stability and reactivity. The continuous solid circulation between the air and fuel reactor ensures not only the required oxygen transport, but also the necessary heat transport between the air and fuel reactor to reach autothermal behavior.

As shown in Figure 3, the biomass feedstock is converted into a raw syngas, which is a mixture of CO, H_2, CH_4, CO_2, H_2O, inside the fuel reactor. The latter compounds (i.e. CO_2 and H_2O) are unavoidable to fulfil the heat balance of the gasifier, but can be removed downstream, together with other contaminants formed during the gasification reactions (e.g. H_2S, NH_3 and tars). As all carbon is expected to be converted in the fuel reactor, all carbon dioxide will be present in the syngas stream, amiable for capture. Inside the air reactor, the oxygen carrier is regenerated through the re-oxidation with the oxygen contained in the inlet air, while any unconverted char is combusted. This means that the sole gaseous products leaving the air reactor are nitrogen, oxygen and no or little CO_2. Consequently, the suggested technology constitutes an oxygen-driven gasification process, allowing for net negative CO_2 emissions, which does not require an air separation unit. Hence, CLG of biogenic residues promises significantly reduced biofuel costs when compared to conventional gasification processes, while at the same time providing a pathway to achieve significant reductions in the transport sector's carbon footprint.

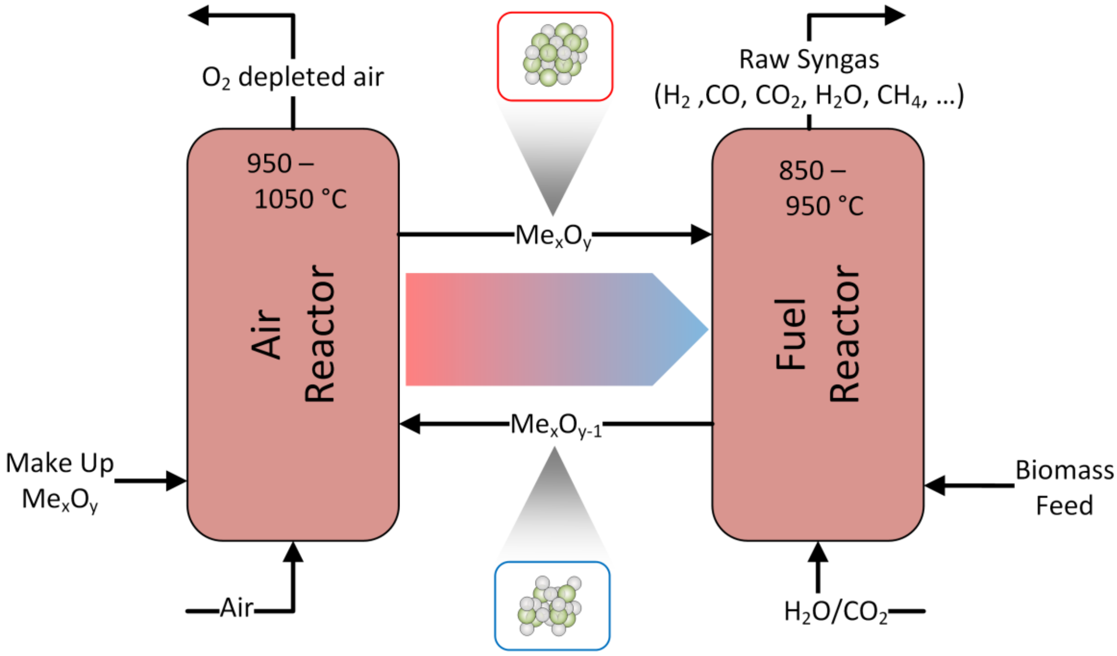


Figure 3: Basic concept of the CLG process.

To unlock these potentials, the CLG process has to be optimized with respect to conversion efficiency, selectivity, tar formation, and operability, while at the same time taking into account specifications for the final usage of the syngas. These performance indicators are influenced by the feedstock properties as well as by the design and operating conditions of the reactors, i.e. temperatures, steam/carbon ratio, solids circulation, and particle residence time. Taking these constraints into account, the CLG process will be investigated within the CLARA project in different bench and pilot scale units, further promoting the process towards market maturity.

3.2 Biomass Pre-Treatment

As fluidized bed systems are in general viable for different kind of fuels, chemical looping gasification can be considered to be a suitable process for feedstocks with high contents of impurities, such as residues from agriculture and forestry. Hence, cheap and abundant biomass precursor materials, such as biogenic residues, are generally viable for the process. Despite the mentioned advantages, issues regarding ash melting, undesired interactions with trace elements, or fouling in the gasifier could potentially arise. Therefore, it is necessary to address this through a proper pre-treatment of the feedstock in order to optimize the process performance. Moreover, pre-treatment facilitates the de-centralized provision of the feedstock through measures such as pelletization or torrefaction, allowing for an easier handling, storage, and transportation of the biomass. Due to these reasons, tailored pre-treatment concepts are being devised for the model biogenic feedstocks wheat straw and pine forest residue within the CLARA project. These concepts are a combination of up to four processes: Physical pretreatment, torrefaction, washing, and pelleting/additivation. Obviously, the stated pre-treatment technologies bring additional energy requirements, costs, and uncertainties. Hence, a tailored combination of the above-mentioned pre-treatment processes, fulfilling the requirements for the chemical looping gasifier and optimizing the economics of the process chain, will be established for each individual feedstock.

3.3 Gas Treatment

Treatment of the raw syngas formed during CLG is required to obtain syngas properties fulfilling the requirements of the subsequent Fischer-Tropsch synthesis unit. These requirements are a H_2/CO ratio of around 2, the reduction of inert species like CO_2 to minimize unnecessary gas flows, as well as the removal of condensable gases (such as tars) and impurities (i.e. H_2S, COS, HCN, NH_3 < 0.1 ppmv), in order to prevent catalyst deactivation. Moreover, the gas treatment must be reliable since the catalysts require high stability and activity at the designated operating conditions, to achieve high product yields in the preferred range during an economically sufficient life time. Taking into account this prerequisite, one major challenge is to minimize the costs for the gas cleaning equipment, which contributes a considerable share to the overall plant costs. For gas conditioning and contaminant removal, the suggested process relies on a number of well-established technologies (e.g. a biodiesel washing column for tar removal). The novel subdivision of the syngas treatment train is an innovative acid gas removal concept operating at moderate temperature levels, which promises significant reductions in CAPEX and OPEX when compared to the state-of-the-art Rectisol® and Claus® process, relying on costly solvent refrigeration and highly selective processes.

3.4 Conversion to Liquid Fuels

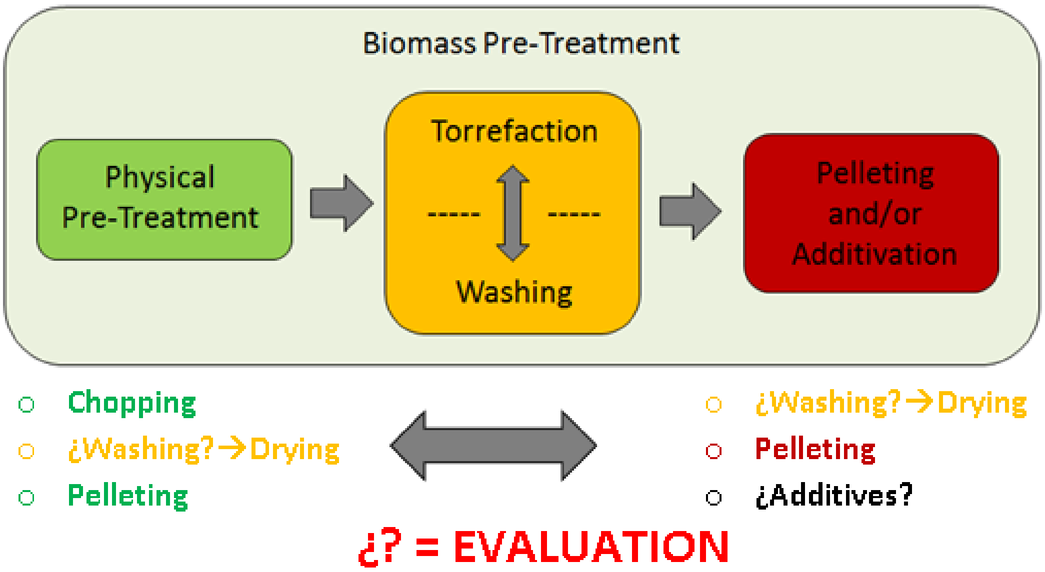
The innovative process sub-units are supplemented by the established Fischer-Tropsch (FT) process, allowing for a continuous conversion of the treated syngas to an easily storable and transportable liquid crude. This crude can subsequently be purified and upgraded using conventional refining technologies. As state-of-the-art refineries are available globally, the final fuel upgrading step will be outsourced to existing refineries, which have the required infrastructure and know-how at their disposal and hence can undertake this step efficiently and at minimal cost.

4 Novel Findings & Highlights

4.1 Development of a Novel Pre-Treatment Concept for Wheat Straw

Wheat straw is an abundant, yet "problematic" feedstock, due to its undesired properties with regard to ash melting, contaminant release, and low calorific value, amongst others. 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.

As shown in Figure 4, the suggested biomass pre-treatment concept is based on the combination of different technologies, allowing for an improvement of feedstock characteristics. The quality of wheat straw after processing with different pre-treatment steps and combinations of them has been studied intensively to allow for inferences regarding its performance during gasification. By combining heat treatment (torrefaction), washing, and the use of additives, the novel pre-treatment aims to improve conversion efficiency of the feedstock. This means obtaining a solid biofuel with a high calorific value and a high energy density, while at the same time avoiding ash-related operational issues with focus on the elimination of certain undesirable inorganic elements to reduce the level of emissions (K, Cl, N and S) and increasing the ash melting temperature of the mineral fraction in the bottom ashes.



Step	Torrefaction	Washing	Additives
Effect on	NCV, CHN, Cl	Inorganics + S & Cl	Molar Ratios

Figure 4: Scheme of the pre-treatment experimental study

Since inorganics behaviour in solid fuels is a complex topic, pre-treated fuel samples produced by *CENER* are being characterised not only based on biofuel standards but also by advanced techniques. On the one hand, *FJZ* is testing the influence of pre-treatment on the release of volatile inorganics during gasification as well as well as the melting behaviour of the residual ashes by hot stage microscopy. On the other hand, *UNIVAQ* is performing continuous steady state gasification tests and dynamic pressure measurements to evaluate gas yield and its composition and the sintering phenomena and interactions with different oxygen carriers (OC). Besides, *CENER* and *FJZ* are investigating the effect of pre-treatment steps on biomass behaviour by thermochemical modelling.

The effect of torrefaction on wheat straw composition is shown in Figure 5. Depending on torrefaction temperature, it was found that the net calorific value (NCV) increases by 20-28 %, volatile matter decreases by 8-15 %, while the nitrogen content is slightly increased. Additionally, a de-chlorinating effect was observed during torrefaction, with about 45-55% of the initial chlorine being removed. Hence, torrefaction allows for an improvement of the feedstock quality not only through an increase in the net calorific value, but also through a significant decrease in the chlorine content, which translates into reduced amounts of Cl being released during gasification.

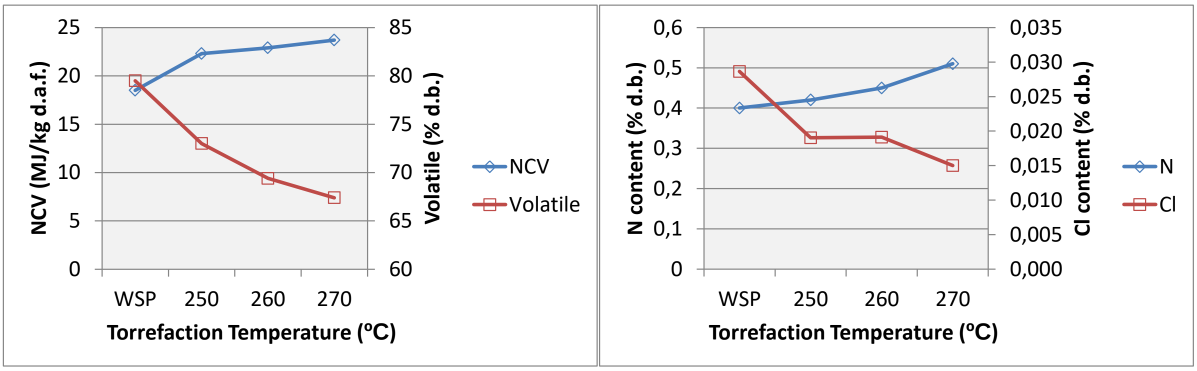


Figure 5: Wheat Straw properties changes during torrefaction: NCV, Volatile, Nitrogen and Chlorine content.

Results for devotalization tests carried out by *UNIVAQ* showed that an increase in devolatilization/gasification temperature leads to an increase in the product gas yield, the H_2/CO ratio, and in carbon conversion, which means that a more efficient conversion of carbon into permanent gases is attained at elevated temperature. Moreover, as shown in Figure 6, an increase in torrefaction temperature produces a slight increase in gas yield, yet for all torrefied feedstocks, the gas yield is lower, when compared to the raw wheat straw, as volatile matter (esp. moisture) is already removed during torrefaction, leading to a higher quality synthesis gas. Furthermore, the H_2/CO ratio increases with torrefaction temperature, whereas the methane and carbon dioxide content in the product gas is not impacted distinctly. These considerations show that (a) higher gasification temperatures are beneficial to increase quantity and enhance the quality of the produced syngas and (b) torrefied feedstocks not only outperform the raw material in terms of contaminant release (e.g. Cl) during gasification, but also with respect to the major raw syngas species.

Despite these positive trends, torrefied wheat straw can still be considered to be a problematic feedstock, due to its relatively high ash content, rich in potassium alumino-silicates and therefore low melting point. Hence, a combination of torrefaction, leaching, and additivation is under investigation to reduce the concentration of problematic ash compounds or to modify their chemistry, which is directly related to bed agglomeration & de-fluidization phenomena because of their low melting temperatures. Through this, CLG operation with bed temperatures between 850 – 950 °C, not exhibiting the afore-mentioned issues is facilitated.

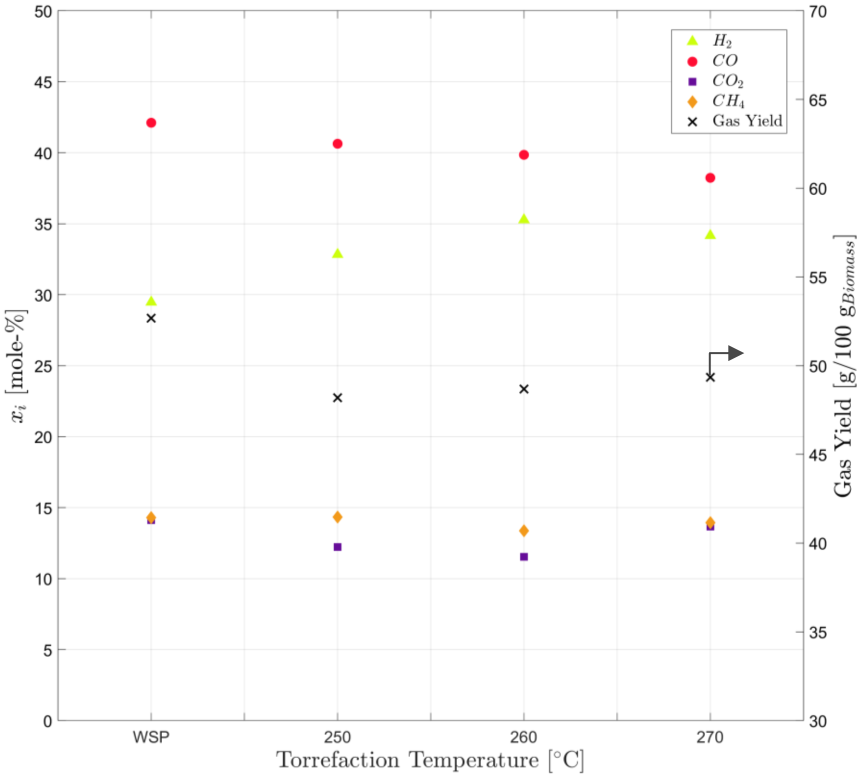


Figure 6: Results for devolatilization tests at 900 °C with ilmenite for wheat straw (WSP) and straw torrefied and different temperatures.

In the case of the washing step, the potential of inorganic matter removal was established by the chemical fractionation procedure [5]–[7], using water as the leaching solvent. None or scarce differences in S, K and Cl removal from non-torrefied and torrefied samples tested were observed, as about 60-85 % of the S, 40-70 % of the K almost all the Cl present can be removed for all samples during washing.

The release experiments, carried out by *FJZ* with the hot gas analysis performed with a Molecular Beam Mass Spectrometry (MBMS) detector, give indications on the behavior of volatile species during gasification. As shown in Figure 7 (left), some species (particularly: K, Cl and S) showed a double step reaction, leading to their release: a devolatilization (pyrolysis; blue area) and a char gasification and ash reaction step (red area). Additionally, Figure 7 shows that an increased potassium (K) release was observed for the torrefied biomass when compared to the raw material. On the other hand, leached or washed biomass did not show a release of potassium during the ash reaction. Therefore, it can be concluded that washing reduces the presence of inorganic species, influencing the release of inorganics such as KCl, HCl, and H_2S during gasification. This means that washing enhances the gasification properties of the feedstock as the release of undesired contaminants (e.g. KCl , H_2S) is reduced and hence post-processing requirements in the syngas cleaning unit (see also Chapter 4.3) are diminished.

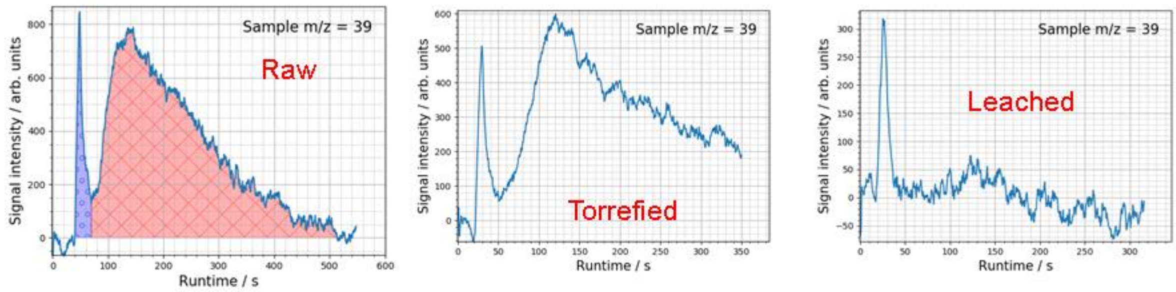


Figure 7: Effect of torrifying/leaching biomass on volatile species (potassium).

Lastly, dynamic pressure measurements were conducted, to evaluate sintering/agglomeration phenomena and interactions of the pre-treated feedstocks with different oxygen carriers (OC) such as ilmenite (ILM) (see Figure 8) and hence reproduce the fluidized bed behaviour in a chemical looping gasifier at representative conditions. In this particular case, better fluidization behavior was obtained for torrefied biomasses (WSP-TX) compared to wheat straw pellets (WSP) or pine forest residues pellets (RPR). Yet, no differences were observed for torrefied (WSP-TX) and washed wheat straw (WSP-TXW). This means that torrefaction can be considered to be a mandatory requirement to allow for an efficient gasifier operation at sufficiently high temperatures, while the washing step is an optional approach to optimize the process efficiency.

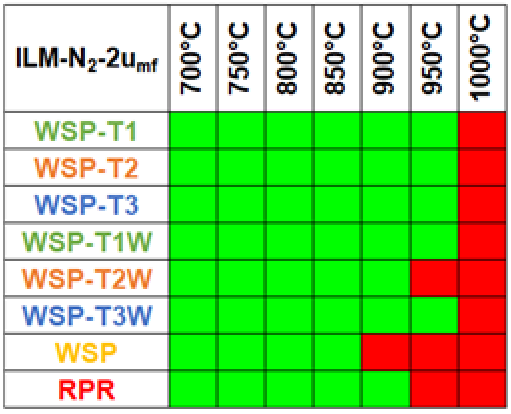


Figure 8: Behavior of torrified/washed biomass during dynamic pressure fluidization test; green = bubbling bed, red = no bubbling.

Therefore, it can be concluded that torrefied wheat straw has some advantages compared with raw wheat straw or pine forest residues for CLG. These are a higher calorific value, a reduced chlorine content, higher H_2/CO ratios in the gas phase during gasification, and an enhanced sintering/agglomeration behavior. On the other hand, when an additional washing step is conducted, only a reduction in the level of emissions is observed, whereas the ash melting temperature of the mineral fraction in the bottom ashes remains unchanged.

The last innovative step being tested in wheat straw pre-treatment is to include or combine additives in the final formulation of the pre-treated biomass to modify ash chemistry during CLG to increase ash melting temperature in the fuel reactor bed. To accomplish this task, three industrial wastes (bentonite, Ca-based, and P-based additive) were previously selected and evaluated as potential additives to improve the CLG efficiency. Based on thermochemical modeling, the Ca-based additive has been selected for further testing according to the previously mentioned techniques in torrefied and torrefied and washed wheat straws. The results of these tests will allow for final inferences regarding the most suitable and economic pre-treatment concept for wheat straw, which will be applied to prepare the feedstock for all subsequent small-scale CLG test campaigns in the CLARA project, inside the pre-treatment pilot plant of *CENER* (see **Figure 9**). Additionally, the pre-treatment concept will be applied in the (semi-)industrial scale at the facilities of *ABT*, to prepare the wheat straw pellets 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 9: Schematic (a) and photograph (b) of biomass pre-treatment unit at CENER facilities (BIO2C).

4.2 Investigation of CLG in Continuous Lab and Bench Scale Units

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 first two years of the project, the research focused on the selection of oxygen carriers suitable for CLG of biomass to a syngas, compatible with the downstream Fisher-Tropsch process. Initially, seven raw materials of low cost, available at industrial scale, were selected as an oxygen carrier. Then, selected oxygen carriers have been evaluated at different scales, with a range of methods, at *CTH* and *CSIC*, to develop a comprehensive understanding and establish a portfolio of suitable oxygen carriers. These materials are iron and manganese ores of different origins. The selected materials were first characterized regarding their reactivity with H_2 and CH_4 during consecutive redox cycles in TGA and a batch fluidized bed reactor. The ability of the oxygen carriers to convert hydrocarbons in volatile matters was also tested at *CTH* using a 300 W gas-fueled chemical looping unit for more than 300 hours of continuous operation. Furthermore, their attrition behavior was analyzed using the ASTM Jet attrition test, while their physical and chemical characteristics were investigated by a range of different techniques (e.g. elemental analysis). Based on the prescreening tests in TGA, batch reactors, and continuous operation in 300 W unit, three oxygen carriers, Ilmenite, LD slag and Tierga ore, shown in Figure 10, were selected for the CLARA project. The performance of these oxygen carriers during continuous CLG operation in the 10 kW_{th} unit of *CTH* (see Figure 11a) and 1.5 kW_{th} CLG unit of *CSIC* (see Figure 11b) is currently being tested and evaluated.

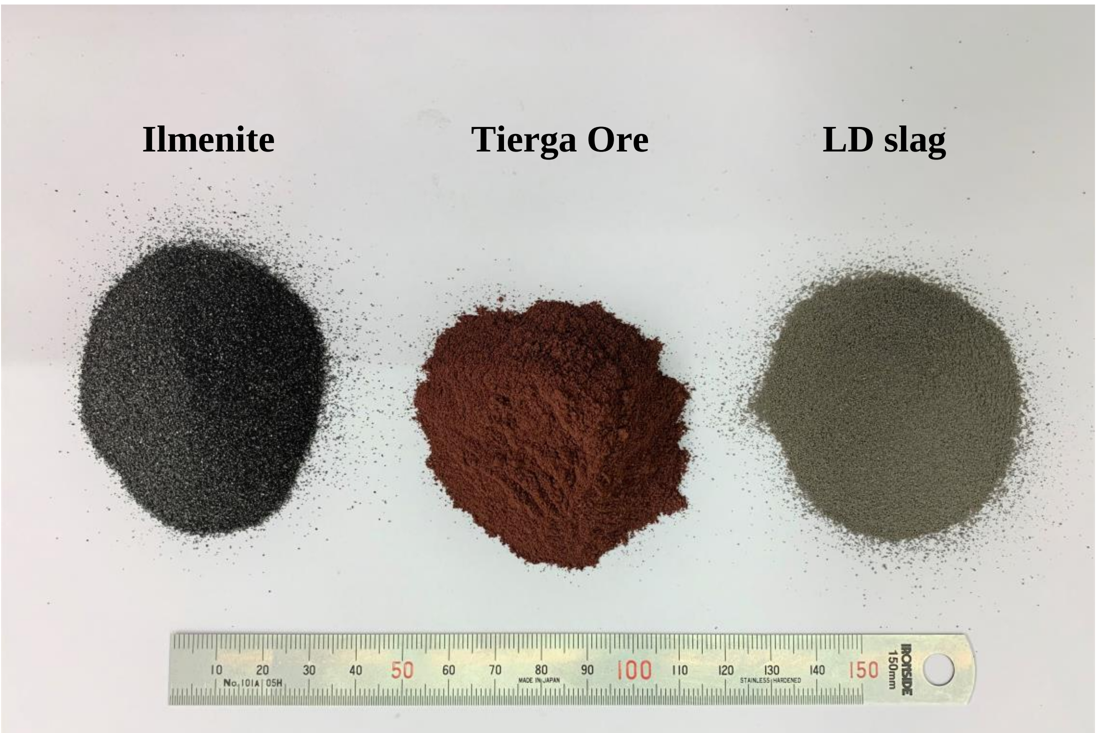


Figure 10: Photograph of the three oxygen carriers selected for the CLARA project.

Figure 11: a) Photograph of the research team at *CTH* in front of the 300 W_{th} (left), 10 kW_{th} (center), and 100 kW_{th} unit (right) b) Photograph of the research team of *CSIC* in front of the 1.5 kW_{th} unit.

So far, more than 350 hours of continuous operation has been carried out using the three selected oxygen carriers at *CTH* and *CSIC*. The effect of the operating conditions on the process performance (syngas generation, biomass conversion, tar emissions) were analyzed. The tests demonstrated that it is possible to obtain a high purity syngas, with lower tar production in relation to other gasification processes (i.e. dual-fluidized bed gasification). It was found that the main operating variable affecting the performance was the air-to-fuel equivalence ratio (λ) used in the process, while the effect of the temperature and the water to biomass ratio were of lower impact. The highest syngas yield was obtained at low λ values, reaching values up to

40 vol% H_2 and 20 vol% CO, and the syngas gas quality decreases with increasing λ value. This is due to the increase of the combustion reactions over the gasification and reforming reactions. However, it should be considered that autothermal CLG conditions should be reached for the selected boundary conditions (i.e. no external energy input). A preliminary study carried out showed that λ values in the range 0.3-0.4 are required in order to fulfil the heat balance of an autothermal CLG process. There is not a clear effect of λ on the H_2/CO ratio, since both H_2 and CO decrease at higher λ values. Values of H_2/CO ratio between 1.5 and 2 were obtained. In Figure 12, the effect of λ on syngas yield is shown for the oxygen carriers Ilmenite and Tierga ore during CLG of pine forest residue at 940 ºC.

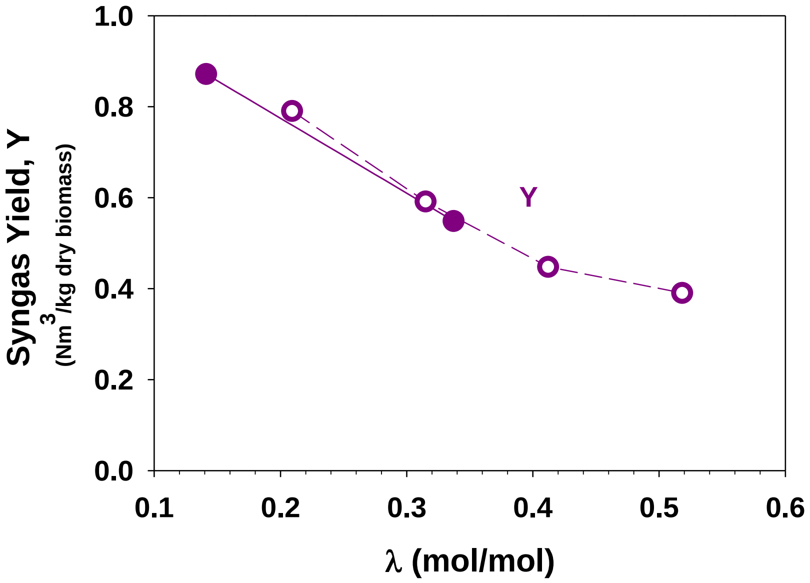


Figure 12: Effect of oxygen-to-fuel ratio on the CLG process for two different oxygen carriers. Ilmenite (continues lines), Tierga ore (discontinuous lines) with pine forest residue. T=940 ºC. Steam/Biomass=0.6.

In addition, the effect of different biomass fuels, wheat straw pellets, pine forest residue, and steam exploded wood pellets , on CLG has been investigated. The results show that the H_2 to CO ratio for the straw pellets is 1.5 and higher than the ratio obtained by using pine forest residue or black pellets. This can be due to the high ash content in straw which acts as a catalyst for the water gas shift reaction and increase the yield of H_2 [8]. However, values between 58 and 64 vol-% were obtained in terms of the syngas content (i.e. H_2 + CO concentration), at λ values in the range 0.3-0.4, which shows the different composition of fuels has negligible effects on the syngas yield.

Regarding tar formation, less tar has been formed compared to conventional dual fluidized bed gasification technologies, however, higher amounts of tars were found when using Tierga iron ore in comparison to Ilmenite and LD slag.

In addition to the continuous operation test in 1.5 kW_{th} and 10 kW_{th} units, *CSIC* has currently determined the gasification kinetics corresponding to the pine wood pellets from *TUDA*. Kinetic parameters were in the range of normal values for these types of fuels. In a later step, the kinetics corresponding to the torrefied pellets of washed straw will also be determined (see Chapter 4.1).

The kinetic data, together with the kinetic reaction for the selected oxygen carriers will be introduced in several models to determine the optimum configuration and operating conditions in an industrial scale CLG plant.

Last but not least, an experimental procedure for investigating the fate of tar surrogates has been developed at Chalmers. The conversion of tar species, i.e. benzene, toluene and ethylene, was measured in batch fluidized beds. From the experiments, it was found that oxygen carriers can reduce the amount of tar formation by partial oxidation and catalytic cracking of tar surrogates. The benzene conversion is increasing with the degree of oxidation and the CLG operating temperature from 800 to 950 °C. Therefore, Mn ores, which exhibit a higher oxygen transport capacity compared to iron ores and iron waste material, can achieve a higher conversion of benzene as a tar precursor at the same operating conditions.

4.3 Development of a Cost-Efficient Syngas Treatment Technology

As described in Section 3.3, gas cleaning is an essential part of the full process chain with respect to CAPEX and OPEX. In case of processes using catalysts, which are poisoned mainly by sulfur species, mature technologies are very complex and use severe operation conditions. With respect to this, Rectisol® has to be mentioned as world leading state-of-the-art technology. It uses numerous gas cleaning sections to get a highly concentrated H_2S in CO_2 stream for further use in a so-called Claus® oven for sulfur recovery. Furthermore, it uses methanol as solvent at very low temperatures of around -40 °C, which leads the need of refrigeration technology. Both aspects result in high investment and operation costs as a significant portion of the overall Biomass-to-Liquid (BtL) technology.
Less selective technologies for gas cleaning find application in refinery processes. One such technology, which requires moderate operating conditions with respect to pressure and temperature, is amine scrubbing. Yet, the resulting H_2S concentrations in the sour gas leaving the amine desorber mean that the Claus® process cannot be utilized for sulfur recovery. Hence, an alternative technology becomes necessary. At this point, the main innovative idea of *RWE*, investigated within the scope of CLARA, is to use H_2O_2 as oxidant for the H_2S in the sour gas coming from the desorber of the main gas cleaning section to recover sulfur from the sour gas.

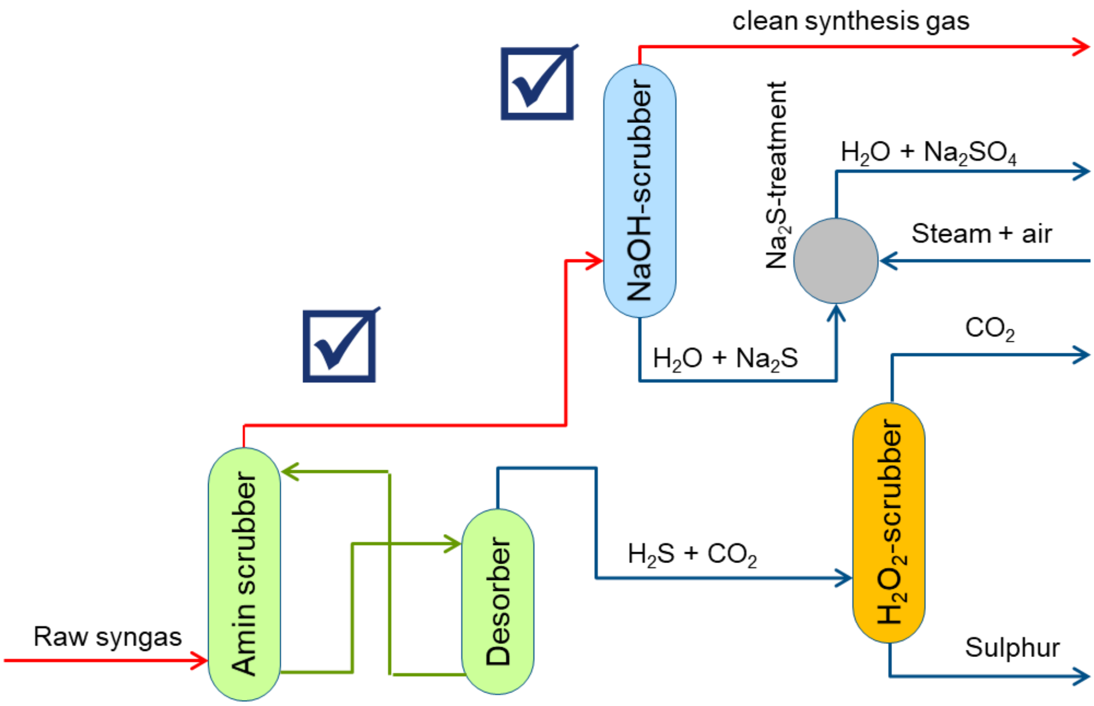


Figure 13: Flowsheet of the innovative syngas cleaning concept.

For the investigation of this new idea, a mobile gas cleaning test rig has been built-up in a transportable standard container (see Figure 14, left side). Beside the common part of gas inlet and outlet, including safety installations as well as the control room, the technical part consists of three different modules (see Figure 14, right side), which can be operated individually. These modules are:

- Cascade of three stirred glass bottles for atmospheric pressure

- Glass column containing solvent cycle for atmospheric pressure
- Steel column containing solvent cycle for elevated pressure

As the basic gas cleaning steps (using amines and caustic solvent under pressure) are already mature technologies and established data are available for modeling, sizing, and economical calculations, the module with the pressurized steel column is not in operation within the CLARA project.

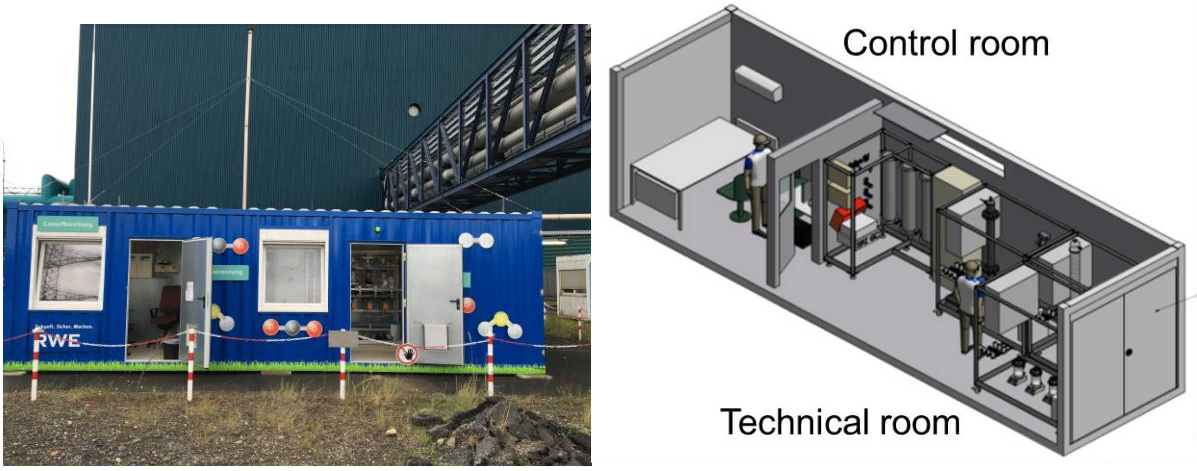


Figure 14: Outside view and internal arrangement scheme of gas cleaning test rig

This means the focus of the research is placed on the atmospheric operation of the H_2O_2 system, which is investigated in two steps. First, basic kinetic data is measured in the stirred glass bottles, which can be understood as one ideal bottom or tray in a column. Based on the results of such tests, a starting point can be set for the second step, using the atmospheric glass column module. At this point the more “realistic” values of conversion rate of H_2S oxidation in H_2O_2 solvent will finally be used for theoretical modeling of such process and the sizing of the single installations in a technical scale, leading to the economical evaluation in comparison to the above mentioned state-of-the-art technologies.

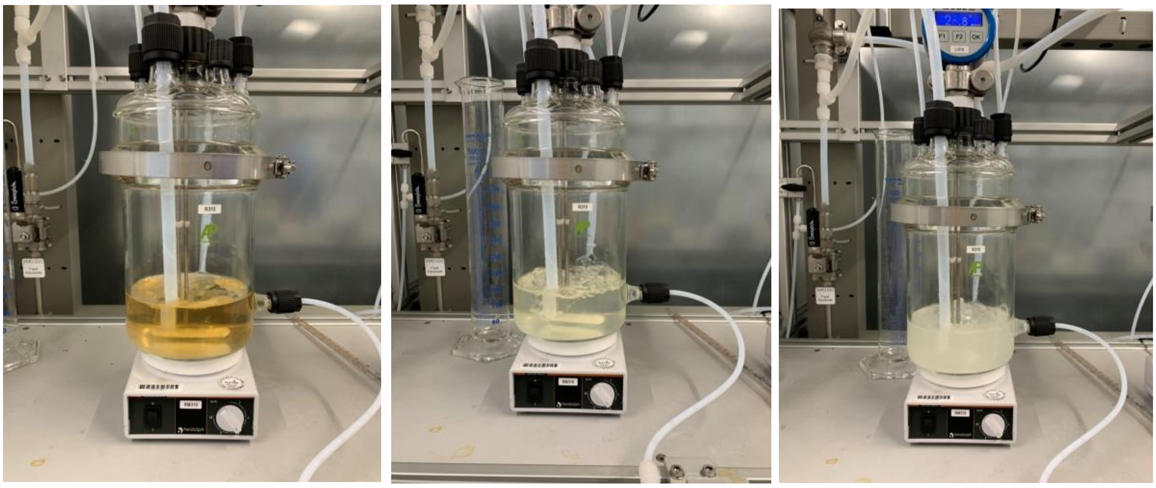


Figure 15: Time depending status of reaction of H_2S in H_2O_2 solvent

During the last year, numerous tests with the stirred glass bottles have been completed at a wide range of operation parameters, such as concentration of H_2S in the gas, volume flow of the gas, concentration of H_2O_2 in the solvent, residence time of the gas in the liquid, concentration of additional catalyst, and temperature of the solvent. Currently, final evaluations of the results are being carried out and last tests to yield conclusive answers are being completed, so that detailed results on the novel gas cleaning technology will be available shortly.

4.4 Demonstration of Entire Biomass-to-Biofuel Process Chain in Pilot Scale

At the facilities of the Institute of Energy Systems & Technologies (EST) at the Technical University of Darmstadt (*TUDA*), the entire biomass-to-biofuel process chain, advanced within the CLARA project, is to be demonstrated in pilot scale. In order to achieve this, the existing 1 MW_{th} pilot plant (see Figure 16), which has been erected in 2010 within the framework of the projects COORETEC – LISA and RFCS – ÉCLAIR, is being adapted, so that a conversion of biomass into synthesis gas via CLG can be achieved.

To accomplish this ambitious target, previous knowledge from both, chemical looping combustion [9]–[11] as well as gasification [12], [13] test campaigns conducted within this pilot, were combined, to derive a suitable process concept. Different approaches to obtain a stable and efficient CLG process were evaluated using different process models, yielding the associated mass and energy balances for CLG operation in the 1 MW_{th} pilot scale [14]. Based on these calculations, the required plant adaptions required were identified and are currently being prepared and implemented, so that the CLARA full-chain pilot test campaigns can commence in 2021.

Figure 16: Photograph of the 1 MW_{th} TUDA pilot plant.

During CLG operation, a slipstream of approx. 200 Nm^3/h of the raw synthesis gas produced within the CLG pilot plant will be transferred to the novel gas treatment plant, which is currently being constructed within the framework of the research project COORETEC – FABIENE. In this novel extension of the pilot plant, side products (e.g. CO_2, H_2O) and contaminants (e.g. tars) are being removed from the raw syngas produced within the pilot gasifier, thus preparing it for its utilization in different chemical syntheses (e.g. FT-synthesis). Within the last months, the construction and final preparations were completed, so that the plant commissioning of the novel syngas treatment unit is scheduled to begin in November 2020.

To test the merit of the gas treatment plant, a slipstream the purified syngas will be used to synthesize methanol in a test rig supplied by the project partner *RWE*. The containerized test rig was transport to Darmstadt in September (see Figure 17a), prior to its integration into the pilot plant environment with regard to piping and electricity. The synthesis test rig will be operational during the gas treatment commissioning in November 2020, allowing for the first-time realization of a full chain process for the production of high value chemicals from syngas produced in the pilot-scale gasifier at the facilities in Darmstadt. For the CLARA project, the same test rig will be utilized to synthesize FT-fuels from the purified syngas leaving the gas treatment plant. To allow for this, the boundary conditions (e.g. temperature, pressure) in the reactor and separators contained in the test rig (see Figure 17b) will be adjusted accordingly and a state-of-the-art low temperature cobalt-based FT-catalyst, supplied by the project partner *UniCRE*, will be utilized (see Figure 17c).

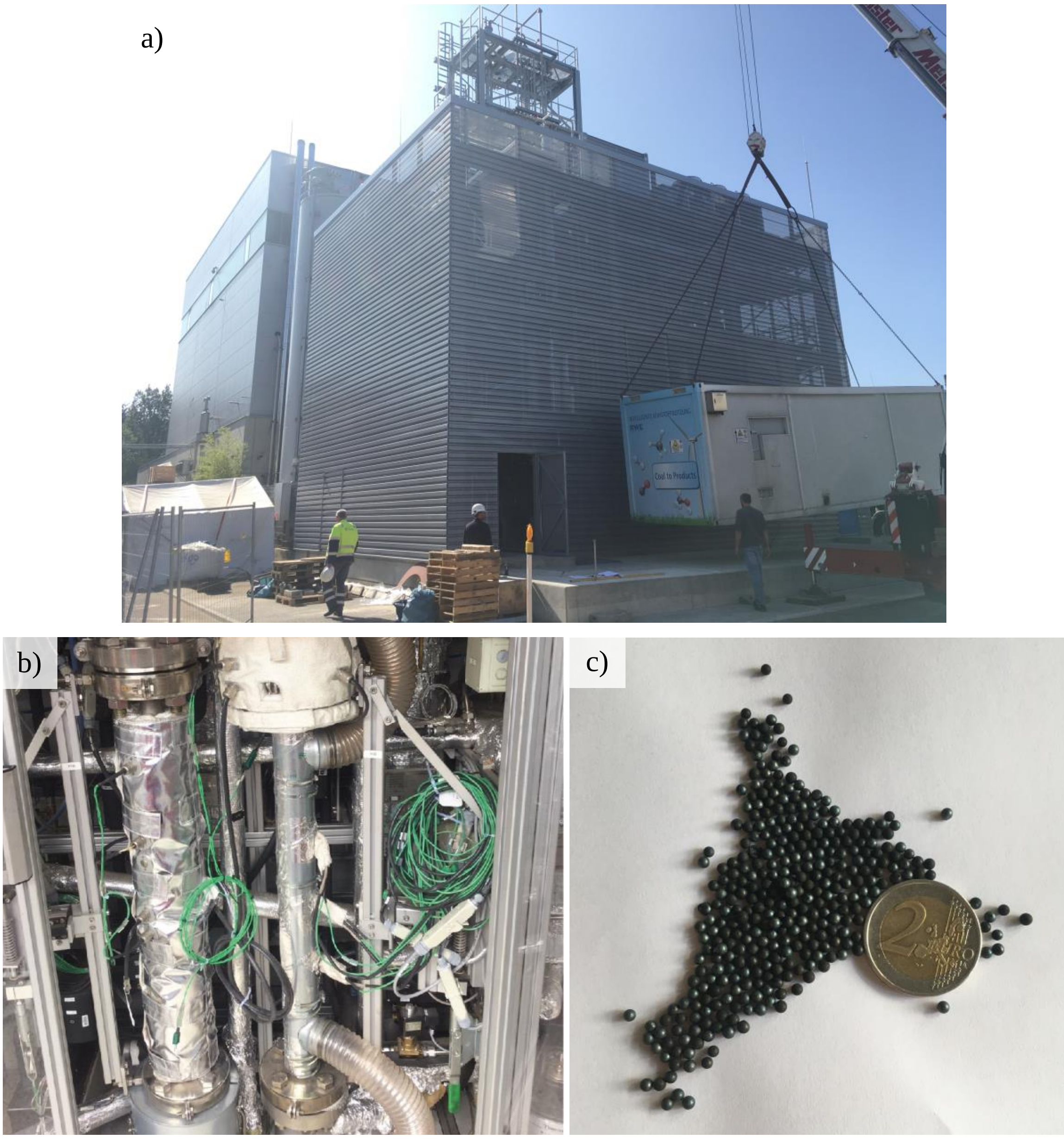


Figure 17: a) Image of the delivery of the *RWE* synthesis test rig container to the *TUDA* facilities with the gas treatment plant and pilot plant in the background; b) Inside view of the synthesis test rig; c) Image of *UniCRE* low temperature FT-catalyst.

In addition to synthesis test rig, a second test rig of the project partner *RWE*, allowing for a deeper investigation of the novel syngas cleaning concept, will be integrated into the pilot plant facility in Darmstadt. This mobile gas cleaning test rig facilitates an investigation of the downstream processing of the sour gas mixture leaving the desorber column of the gas treatment plant, chiefly consisting of carbon dioxide (CO_2) and hydrogen sulfide (H_2S), in a hydrogen peroxide (H_2O_2) scrubber. This innovative sour gas post-processing concept, which has been devised and investigated by *RWE* (see Chapter 4.3), will be put to the test in a full chain environment (i.e. with a genuine sour gas stemming from an amine washing unit) for the first time at the pilot plant in Darmstadt. Currently, preparations for the arrival of the test rig, which is expected in Darmstadt after the finalization of the experiments of *RWE* on the H_2O_2 scrubber in Niederaußem (Germany) in December 2020, are underway. After its arrival, first full-chain experiments with the test rig will be conducted after its integration and commissioning in January 2021 within the RFCS project Lig2Liq.

In its unity, the pilot plant setup, consisting of the CLG reactor setup, the gas treatment plant, and the *RWE* test rigs (see Figure 18), will facilitate an investigation of all relevant technologies of the biomass-to-biofuel process chain, investigated within the scope of CLARA, in an industrially relevant environment and thus will allow for meaningful inferences on process efficiency and scale-up.

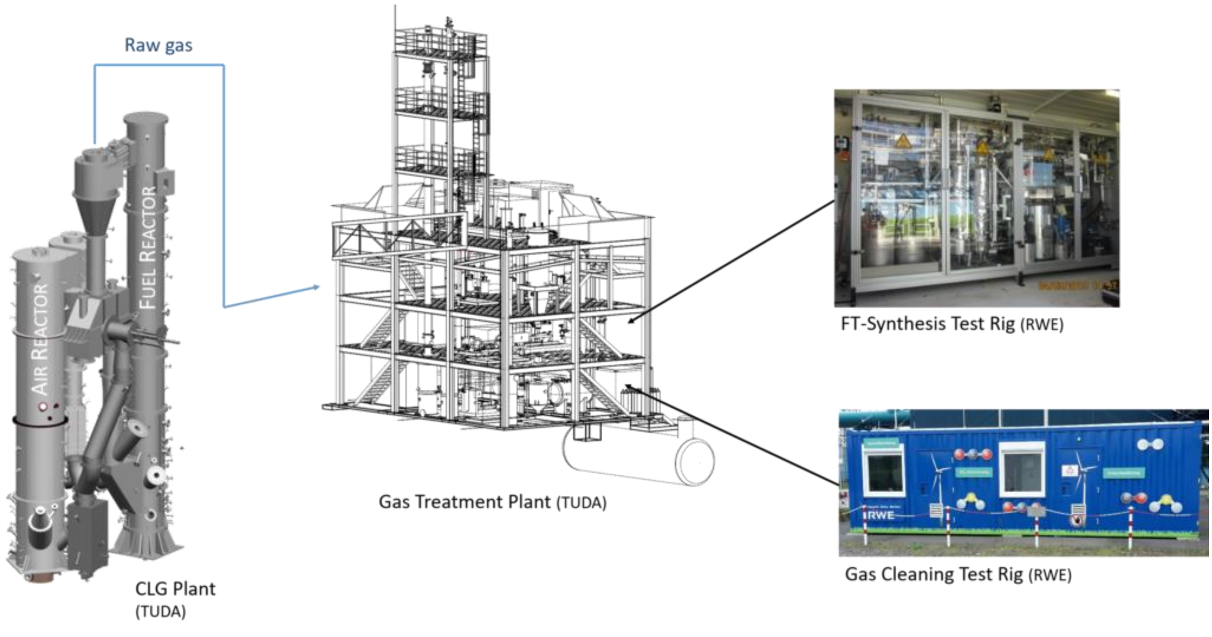


Figure 18: Scheme of the novel pilot plant configuration at the Technical University Darmstadt.

5 Conclusions

In the following, the major advances and most important findings made within the second year of the CLARA project with regard to the development of a novel pre-treatment concept for wheat straw (see Chapter 4.1), the deeper investigation of CLG (see Chapter 4.2), studies on the innovative sour gas separation concept (see Chapter 4.3), and the preparation of the pilot plant facilities for full chain operation (see Chapter 4.4) are summarized.

Investigations on the feedstock quality after each suggested processing step of the novel pre-treatment sequence showed that:

- Torrefaction not only reduces the moisture content and thus increases the net heating value of the feedstock, but also leads to a reduction in the release of contaminant species (e.g. Cl) during CLG. Moreover, it has been shown that torrefaction reduces sintering and agglomeration effects at elevated temperatures in the presence of oxygen carrier materials, meaning that it facilitates a stable hydrodynamic behavior in the fluidized bed during CLG.
- The subsequent washing of the feedstock, allows for a close to complete removal of inorganic species such as potassium (K) and chlorine (Cl), which means that their release during CLG and hence the associated syngas post treatment requirements are reduced significantly.
- Additivation with a Ca-based additive promises further enhancements with regard to agglomeration and ash melting.

By conducting different experiments in different continuous CLG lab and bench scale units with different oxygen carriers, the CLARA consortium established the following:

- Variations in the different boundary conditions (e.g. temperature, oxygen carrier material, steam to biomass ratio) showed that the air-to-fuel equivalence ratio is the most important process material affecting not only the quality of the product syngas, but also the overall heat balance, distinctly.
- When compared to “standard” dual fluidized bed gasification, tar formation in the FR is significantly reduced in the CLG process due to the presence of an oxygen carrier material.

Fundamental studies on the novel sour gas separation system by *RWE* analyzed the effect of inlet concentration, the residence time, and temperature on the oxidation of H_2S, contained in the sour gas, with H_2O_2, paving the way for experimental investigations of the concept in a more sophisticated reactor system.

The preparation of the pilot plants facilities of *TUDA*, for full chain biomass-to-biofuel test campaigns is underway. These preparations include:

- Adaptions of the 1 MW_{th} gasifier to allow for CLG operation.
- The finalization of the erection & commissioning of the novel syngas cleaning unit, capable of treating up to 200 Nm^3/h of raw syngas produced in the pilot-scale gasifier.
- The integration of the fuel synthesis test rig from *RWE*, in which the conversion of the purified syngas into valorized liquid products will take place, into the pilot plant environment.
- Preparations for the transport of the second test rig of *RWE*, facilitating the investigation of the novel sour gas separation concept, to Darmstadt.

References

[1] International Energy Agency, *Key World Energy Statistics 2018*. OECD, 2018.

[2] “Transport emissions - A European Strategy for low-emission mobility,” *Transport emissions*. https://ec.europa.eu/clima/policies/transport_en (accessed Aug. 23, 2019).

[3] “DIRECTIVE (EU) 2018/ 2001 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL - of 11 December 2018 - on the promotion of the use of energy from renewable sources,” p. 128.

[4] J. E. Carrasco, A. Monti, J. Tayeb, J. Kiel, and F. Girio, “Strategic Research and Innovation Agenda 2020,” EERA. Accessed: Jun. 01, 2019. [Online]. Available: http://www.eera-bioenergy.eu/publications/#sria-2020.

[5] P. Teixeira, I. Gulyurtlu, N. Lapa, and H. Lopes, “Use of chemical fractionation to understand partitioning of biomass ash constituents during co-firing in fluidized bed combustion.,” *Fuel*, 2011, doi: 10.1016.

[6] R. Pöykiö, H. Nurmesniemi, O. Dahl, and M. Mäkelä, “Chemical fractionation method for characterization of biomass-based bottom and fly ash fractions from large-sized power plant of an integrated pulp and paper mill complex,” *Trans. Nonferrous Met. Soc. China*, vol. 24, no. 2, pp. 588–596, Feb. 2014, doi: 10.1016/S1003-6326(14)63099-5.

[7] M. Zevenhoven, B. Onderwater, J. Skrifvars, R. Backman, M. Hupa, and J.-P. Blomquist, “The prediction of behaviour of ashes from five different solid fuels in fluidised bed combustion,” *Fuel*, vol. 79, no. 11, pp. 1353–1361, 2000, doi: 10.1016/S0016-2361(99)00280-X.

[8] L. Jiang *et al.*, “Catalytic effects of inherent alkali and alkaline earth metallic species on steam gasification of biomass,” *Int. J. Hydrog. Energy*, vol. 40, no. 45, pp. 15460–15469, Dec. 2015, doi: 10.1016/J.IJHYDENE.2015.08.111.

[9] P. Ohlemüller, J. Ströhle, and B. Epple, “Chemical looping combustion of hard coal and torrefied biomass in a 1 MW th pilot plant,” *Int. J. Greenh. Gas Control*, vol. 65, pp. 149–159, Oct. 2017, doi: 10.1016/j.ijggc.2017.08.013.

[10] P. Ohlemüller, J.-P. Busch, M. Reitz, J. Ströhle, and B. Epple, “Chemical-Looping Combustion of Hard Coal: Autothermal Operation of a 1 MWth Pilot Plant,” *J. Energy Resour. Technol.*, vol. 138, no. 4, p. 042203, Jul. 2016, doi: 10.1115/1.4032357.

[11] J. Ströhle, M. Orth, and B. Epple, “Chemical looping combustion of hard coal in a 1 MW th pilot plant using ilmenite as oxygen carrier,” *Appl. Energy*, vol. 157, pp. 288–294, Nov. 2015, doi: 10.1016/j.apenergy.2015.06.035.

[12] P. Herdel, D. Krause, J. Peters, B. Kolmorgen, J. Ströhle, and B. Epple, “Experimental investigations in a demonstration plant for fluidized bed gasification of multiple feedstock’s in 0.5 MW th scale,” *Fuel*, vol. 205, pp. 286–296, Oct. 2017, doi: 10.1016/j.fuel.2017.05.058.

[13] D. Krause, P. Herdel, J. Ströhle, and B. Epple, “HTW^{TM}-gasification of high volatile bituminous coal in a 500 kWth pilot plant,” *Fuel*, vol. 250, pp. 306–314, Aug. 2019, doi: 10.1016/j.fuel.2019.04.014.

[14] P. Dieringer, F. Marx, F. Alobaid, J. Ströhle, and B. Epple, “Process Control Strategies in Chemical Looping Gasification—A Novel Process for the Production of Biofuels Allowing for Net Negative CO2 Emissions,” *Appl. Sci.*, vol. 10, no. 12, Jun. 2020, doi: https://doi.org/10.3390/app10124271.

Abbreviations

BtL	Biomass to Liquid	OC	Oxygen Carrier
CAPEX	Capital Expenditure	OPEX	Operating Expenditure
CLG	Chemical Looping Gasification	REDII	Renewable Energy Directive
FT	Fischer-Tropsch	RPR	Pine Forest Residue Pellets
ILM	Ilmenite	WSP	Wheat Straw Pellets
MBMS	Molecular Beam Mass Spectrometry	WSP-TX	Wheat Straw Pellets torrefied at temperature TX
NCV	Net Calorific Value	WSP-TXW	Washed wheat Straw Pellets torrefied at temperature TX

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 Renovables	*UniCRE*	Unipetrol Centre for Research and Education, a.s.
UNIVAQ	University of L'Aquila		