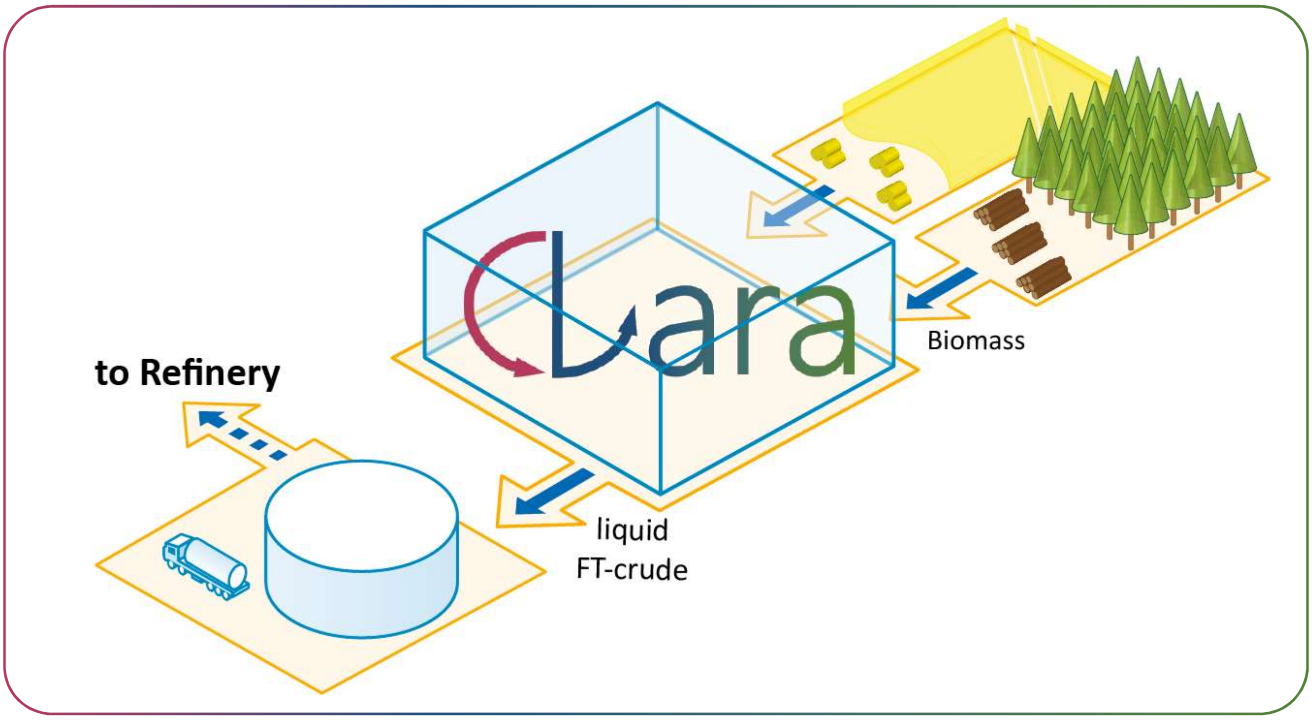
Chemical Looping Gasification for Sustainable Production of Biofuels

H2020 Research and Innovation action
Grant Agreement no 817841

Public Report I



Authors: Paul Dieringer[1], Jochen Ströhle[1], Ibai Funcia[2], Carl Johan Linderholm[3]
Affiliation: [1]Technische Universität Darmstadt, [2]Centro Nacional De Energías Renovables, [3]Chalmers University of Technology.

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

Publication date: 31.10.2019, Access the digital version via this link: https://clara-h2020.eu/public-reports/

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.

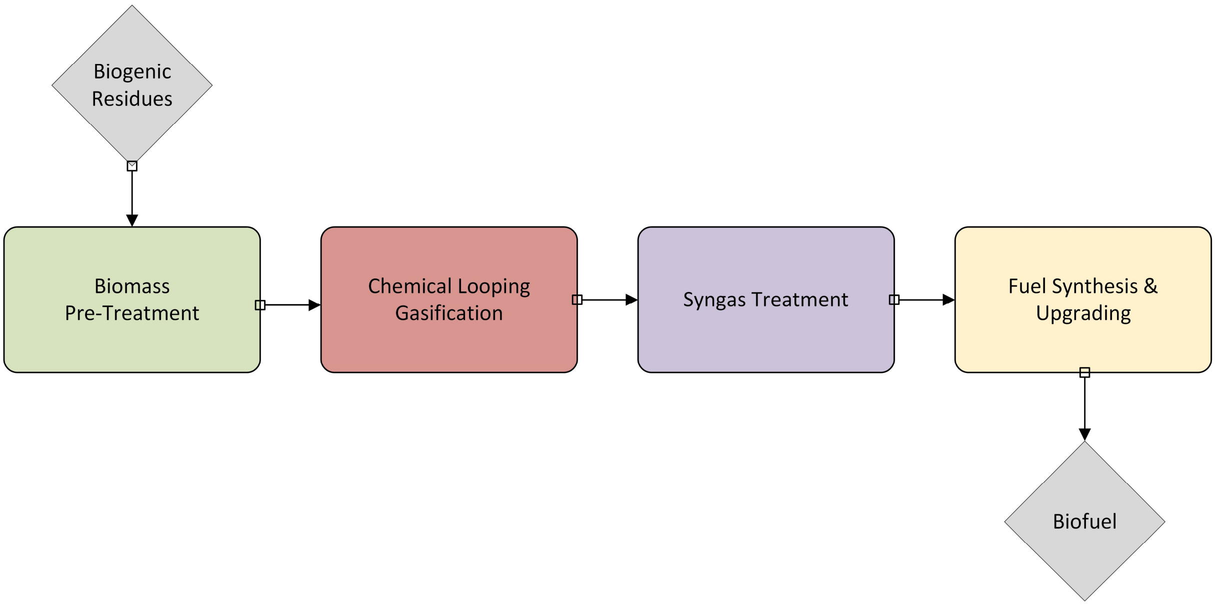


Figure 1: Simplified scheme of full biomass-to-biofuel process chain.

This report 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 are presented in Section 4. An executive summary of this public report can be found in the last 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.

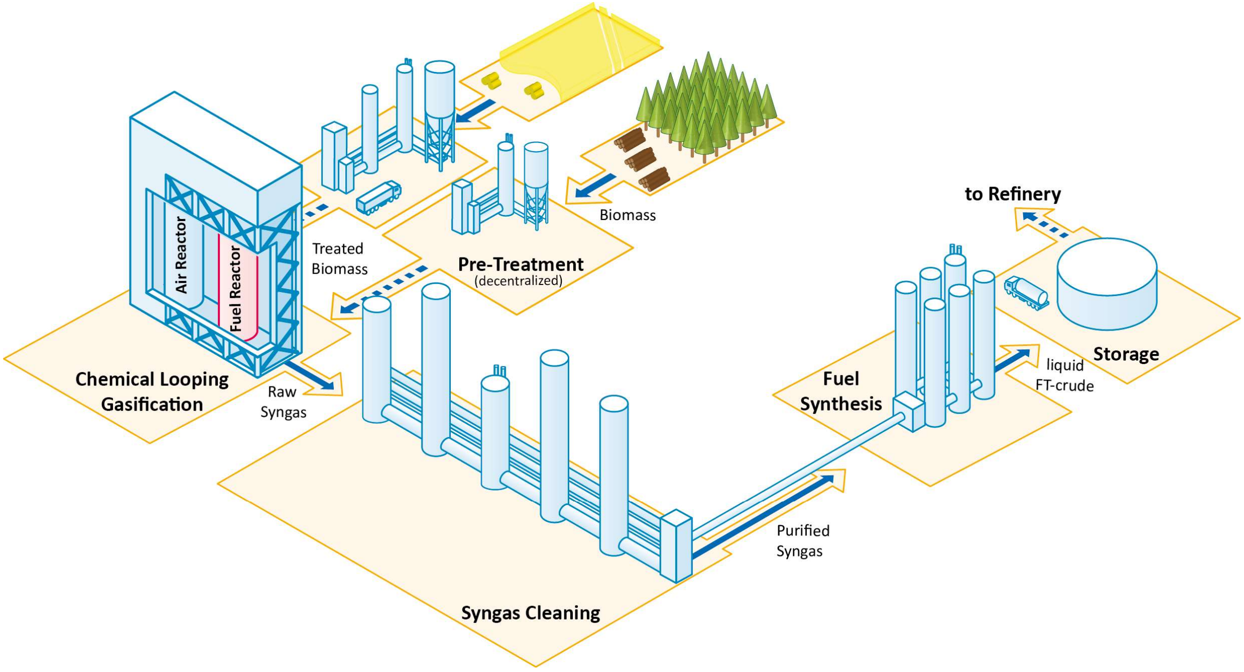


Figure 2: Schematic illustration of the process chain investigated within the CLARA project.

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.

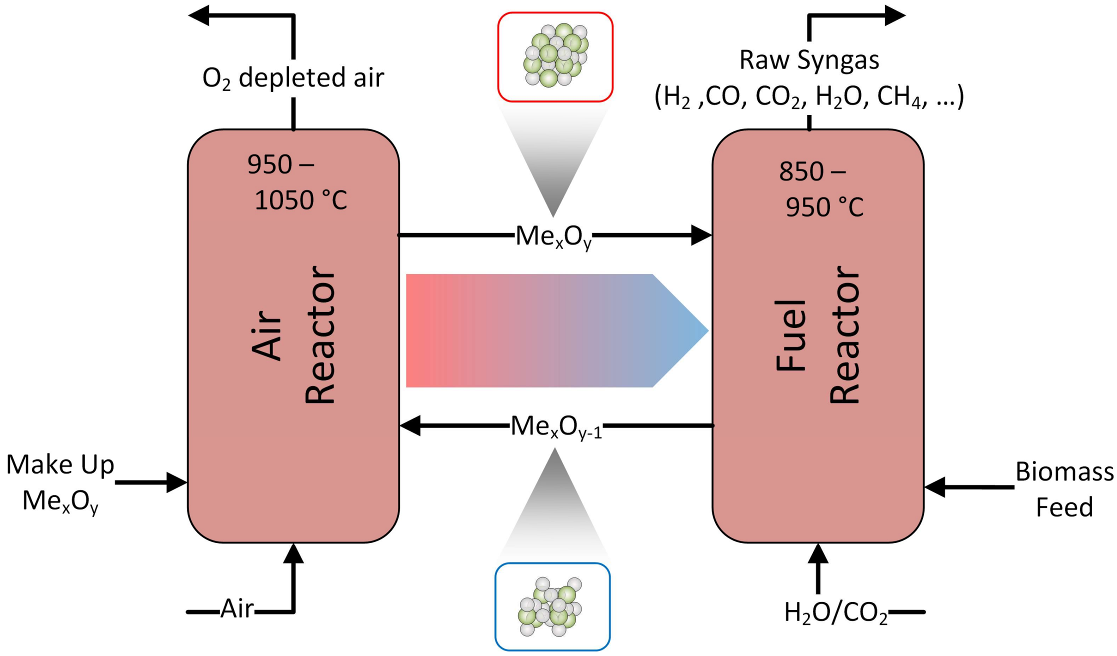


Figure 3: Basic concept of the CLG process.

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. 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® process, relying on costly solvent refrigeration.

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 Selection of Biomass Feedstock

Since the suggested biomass-to-biofuel process should allow for the conversion of a wide variety of biogenic residues, three model feedstocks were selected as reference materials, which are to be investigated within the scope of CLARA, considering technical, ecological and economic factors. The selected precursor materials are:

- Wheat straw from sourcing regions close to the CENER facility in Spain and close to ABT facilities in Sweden as a representative for agricultural residues;
- Pine wood residues from sourcing regions close to the CENER facility in Spain and close to ABT facilities in Sweden as a representative for forestry residues;
- Industrial wood pellets of considerable low grades as a representative for commoditized & densified biogenic carbon carriers;

These feedstocks were subsequently analyzed with regard to their composition, heating value, bulk density and ash melting behavior. Moreover, an in-depth market assessment was carried out for all selected feedstock materials. A detailed description of the feedstock selection is available in the publicly available deliverable D1.1.

4.2 Conception of the Biomass-to-Biofuel Process Chain

Due to the innovative nature of the suggested biomass-to-biofuel process, a holistic consideration of the entire process chain, taking into account the special characteristics, requirements and constraints of each individual subsection, is necessary. Especially the focus on biogenic residues, requiring a preceding biomass pre-treatment and the novelty of the suggested CLG and syngas treatment concept, demand for a detailed description of the entire process, where each sub-section is accurately tailored according to its upstream and downstream requirements (see Figure 4).

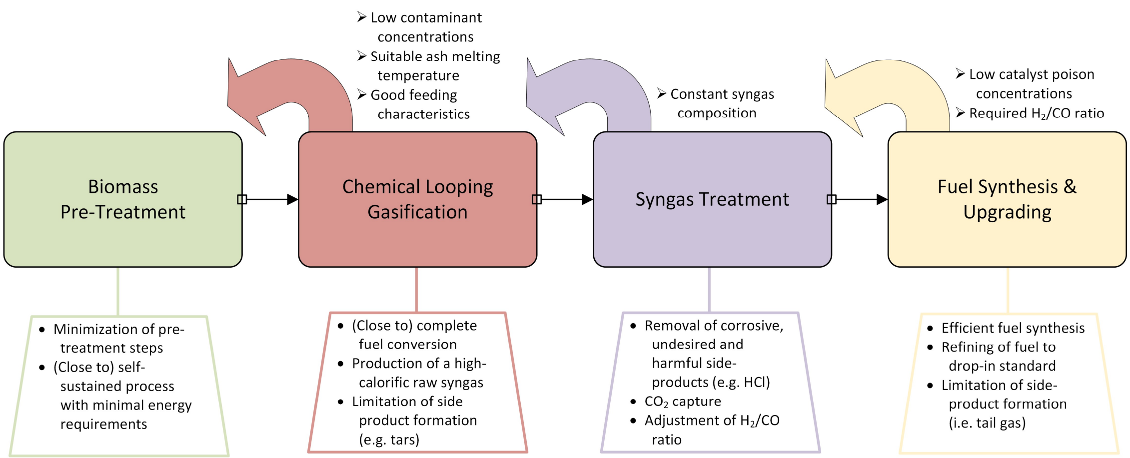


Figure 4: Sub-units of the biomass-to-biofuel process chain with associated requirements to upstream unit (top) and inherent technological targets (bottom).

Within the last twelve months, TUDA, AE, CTH, RWE and CERTH have developed a process concept for the entire process chain, allowing for an efficient production of biofuels from biomass, while at the same time limiting process bottlenecks and reducing associated costs and risks. Especially, a tailored alignment of the gasifier, syngas treatment, and fuel synthesis unit, facilitating an efficient limitation, avoidance, and conversion of side products formed during the CLG process was achieved. This means that through the suggested process chain excellent material and energetic utilization of the feedstock is accomplished. Moreover, the resulting waste and side product streams are minimized and, if possible, used internally, resulting in process synergies.

Using this process scheme as a starting point, CERTH devised a process model for the entire process chain, stretching from gasification to fuel synthesis and upgrading, in order to estimate heat and mass balances of the process.[1] For the chemical looping gasifier, a validated chemical looping combustion model [5] was provided, scaled-up and optimized by TUDA, allowing for an accurate modelling of the gasification process. By conducting simulations for all model feedstocks investigated within the scope of CLARA (i.e. wood pellets, wheat straw, and pine forest residue), the suitability of the suggested process for bio-based precursors of different origin and composition was assessed in detail. For these feedstocks, the key performance indicators listed in Table 1 were computed. Clearly, chemical looping gasification facilitates a close to complete conversion of the utilized feedstock in the fuel reactor, while at the same time retaining the majority of the input energy in the gaseous product stream. Moreover, the process scheme not only allows for an efficient conversion of carbon to the final transport fuel, but also promises major CO_2 capture rates, allowing for net-negative CO_2 emissions. The given indicators will be used in subsequent stages of the project to assess the prospect of different optimization strategies and the impact of required process adaptions on the process efficiency.

Table 1: Range of key performance indicators calculated for the suggested biomass-to-biofuel process chain for different biomass feedstocks.

KPI	Definition	Range	Target
Carbon utilization	Fraction of carbon in initial feedstock that is converted to the fuel.	31-35 %	> 33 %
Carbon conversion	Fraction of carbon in feedstock that is converted to gas in the gasifier.	96-98 %	> 98 %
Cold gas efficiency	Fraction of chemical energy in feedstock that is transferred to syngas in the gasifier.	75-77 %	> 82 %

[1] Due to the lack of literature data for the novel gas cleaning concept, the model considers the state-of-the-art Rectisol® process for the acid gas removal, in this initial approach.

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

As described in Section 3, biomass pre-treatment is an essential component of the suggested biomass-to-biofuel process chain. Here, the most crucial prerequisite is allowing for an efficient preparation of "difficult" feedstocks for gasification. Therefore, a novel pre-treatment concept for wheat straw, a precursor material which is widely available, yet scarcely used due to its unfavorable characteristics (e.g. high alkaline & chlorine content), is being developed at CENER.

Torrefaction is the core technology of the suggested pre-treatment concept. Initial experiments showed that this process step is exothermic for wheat straw, meaning that the process can be conducted in a self-sustained manner. Moreover, it was found that with increasing torrefaction degree, contaminant concentrations decrease, whereas the net calorific value of the feedstock increases. Figure 5 shows changes in Net Calorific Value (NCV), volatile matter, nitrogen and chlorine content depending on final Anhydrous Weight Loss (AWL) for untreated wheat straw. It can be highlighted that the higher AWL, the lower the chlorine content, while nitrogen slightly increased above 26 % AWL. The observed de-chlorinating effect eases the risk of corrosion in the CLG unit, while the reduction of other minor species (e.g. nitrogen) decreases downstream syngas cleaning system requirements. Moreover, the higher NCV positively influences the energy content of the feedstock allowing for higher gasifier efficiencies.

Nevertheless, torrefied wheat straw is still a problematic feedstock due to its relatively high ash content, rich in potassium alumino-silicates, and therefore low melting point. As bed temperatures during CLG are in the range of 850-950 ºC, torrefied straw ashes could be a problematic feedstock, causing bed de-fluidization because of their low melting temperatures. Hence, a combination of torrefaction, leaching, and additivation is under investigation, in order to improve its behavior in CLG units. The main goal is to reduce the concentration of problematic compounds or to modify the potassium alumino-silicates chemistry directly related to de-fluidization and melting phenomena.

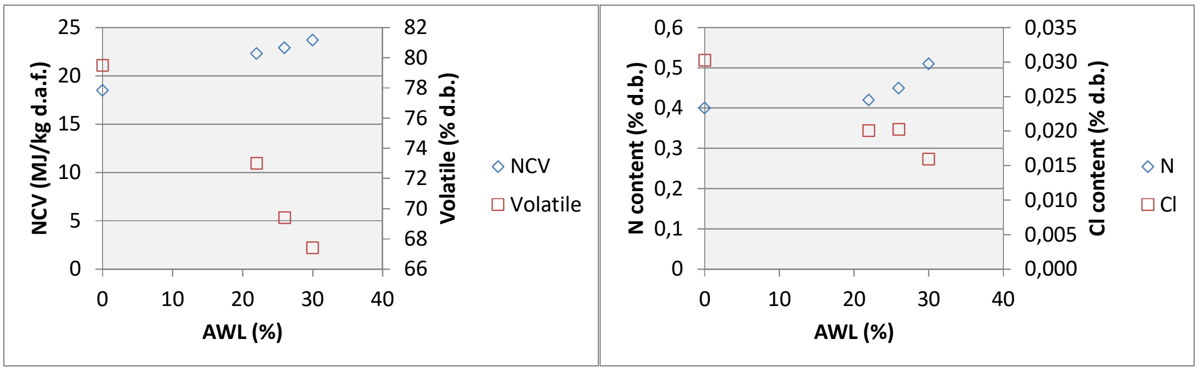


Figure 5: Wheat Straw properties changes during torrefaction: NCV, Carbon, Nitrogen and Chlorine content.

4.4 Investigation of CLG in Lab and Bench Scale Units

Chemical looping gasification (CLG) is a novel technology requiring 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, Chalmers and CSIC have the possibility to investigate CLG with different fuels and oxygen carriers at varying boundary conditions (e.g. reactor temperatures, air-to-fuel equivalence ratio, etc.).

During the past year, the research focused on the preselection of oxygen carriers suitable for CLG of biomass. Initially some raw materials of low cost, available at industrial scale were selected. These materials are iron and manganese ores of different origins. The selected materials were characterized regarding their reactivity with H_2 and CH_4 during consecutive redox cycles in a batch fluidized bed reactor. 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).

Moreover, some of the preselected materials were tested in the continuous 1.5 kW_{th} CLG unit of CSIC, using pine as the biomass feedstock. Initially, different options to supply the amount of oxygen required for CLG, were investigated. The effect of the operating conditions on the process performance (syngas generation, biomass conversion, tar emissions) were analyzed using ilmenite as the oxygen carrier. It was found that the main operating variable affecting the performance was the air-to-fuel equivalence ratio (lambda) used in the process, while the effect of temperature and the water/biomass ratio were of lower impact.

Oxygen carrier materials are also being tested in the Chalmers 300 W gas-fueled chemical looping unit. Two materials have been used in operation, and a third one is in progress. The first material, a manganese ore called Sibelco Calcined (SC), was used in continuous operation for 25 hours. The H_2/CO ratio was around 1, and high concentration of methane was observed in all experiments. Furthermore, no de-fluidization or agglomeration was experienced, and the particle attrition was low, indicating high expected particle lifetime. Figure 6 shows the obtained gas fractions of total carbon as a function of fuel-reactor inventory with SC as oxygen carrier. The second material subjected to tests in the 300 W unit was “Elwaleed B” – also a manganese ore. Important observations include: (i) activation by syngas highly increased the CLOU properties so that after the activation, the gas phase oxygen concentration increased from 1.2% to 4% at 925°C; (ii) 100% methane conversion at 900 °C using a low fuel flow rate (0.6 L/min) and synthetic “biomass volatiles“ (BMV) as fuel, and (iii) some problems with agglomeration were encountered, which were observed as interruptions of the solids circulation, especially at temperatures above 900 °C.

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, is measured in batch fluidized beds. From the initial experiments, it was found that the benzene conversion is increasing with the degree of oxidation and the CLG operating temperature from

800 to 950 °C. Full conversion of benzene is possible at 950 °C and highly oxidizing conditions in the reactor. Therefore, Mn ores with 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.

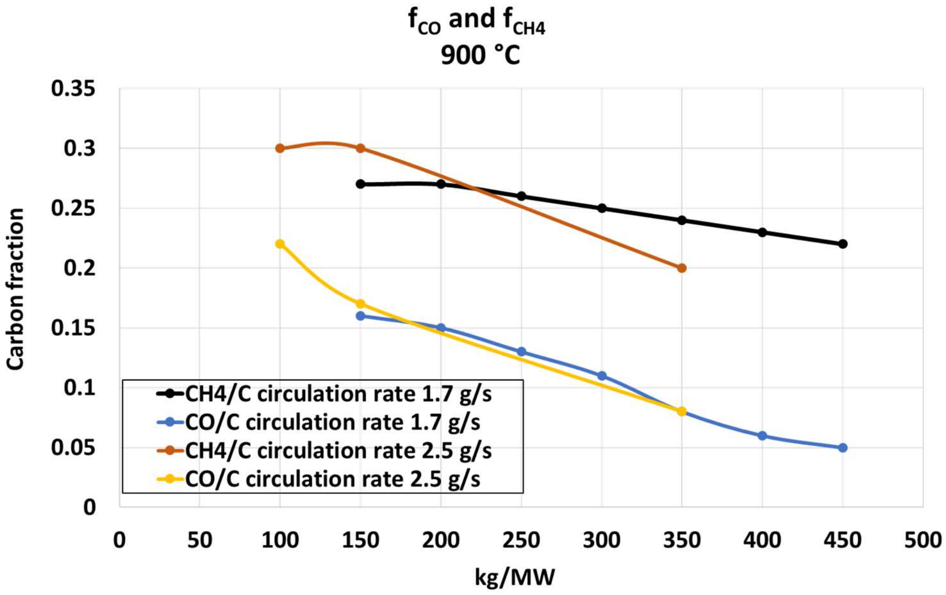


Figure 6: SC used in 300 W unit (Chalmers): Gas fractions of total carbon vs. FR inventory.

5 Executive Summary

During the first twelve-month period of the *Horizon 2020* project CLARA, the groundwork for the in-depth investigation and optimization of a novel biomass-to-biofuel process chain has been laid.

First and foremost, the full process chain, stretching from the selected raw biomass residue precursor material (i.e. wood pellets, wheat straw and pine forest residue) to the finalized drop-in biofuel, has been defined. Here, special focus was placed on achieving maximum material and energy usage of the deployed feedstocks materials, by minimizing the formation of unusable side products and waste streams. For the suggested process chain, cold gas efficiencies reaching 77 % and carbon utilization factors up to 35 % were attained in steady-state process simulations. Based on this reference scenario, further adaptions and optimizations will be pursued, to further boost the process efficiency.

On the technological front, the conception of a novel pre-treatment concept for wheat straw is underway. First experiments revealed that torrefaction of the raw biomass leads to enhanced feedstock characteristics, facilitating higher gasifier efficiencies and reducing post treatment requirements. In order to further enhance the fluidized bed characteristics of the treated feedstock, effective leaching and additivation strategies, promising an increase in ash melting temperatures, are being assessed.

Furthermore, the novel gasification process, chemical looping gasification (CLG), is being investigated by the project consortium. For this technology, the characteristics of eight abundant oxygen carrier materials have been analyzed under different CLG boundary conditions, to assess their suitability for the gasification process. First results showed that generally iron and manganese based ores are suitable for a continuous conversion of the biomass precursor materials to syngas. Yet, systematic process optimization is required to attain the desired efficiency and stability of the process. One issue requiring detailed consideration, is tar formation inside the gasifier, which leads to undesired reactor blockages and lower process efficiency. To alleviate this problem, an experimental procedure to investigate the fate of tar surrogates during the CLG process has been developed.

In the upcoming months, the pre-treatment concept is to finalized on the basis of experimental considerations. Moreover, first long-term CLG test campaigns are planned in bench scale, allowing for major insights into this novel gasification technology and the establishing of suitable operating conditions for the upcoming pilot tests. In terms of the synthesis gas treatment unit, a new scrubber, allowing for an efficient separation of the formed acid gas (i.e. CO_2 and H_2S) has been designed at RWE. The first findings for this new separation technology are expected within the next calendar year. Based on these findings, the fully integrated biomass-to-biofuel process chain will be further optimized, allowing for higher plant efficiencies. These findings will be presented in Newsletter III (May/June 2020) and Public Report II (October/November 2020).

References

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

[2] "Transport emissions - A European Strategy for low-emission mobility," *Transport emissions*. [Online]. Available: https://ec.europa.eu/clima/policies/transport_en. [Accessed: 23-Aug-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.

[5] P. Ohlemüller, F. Alobaid, A. Abad, J. Adanez, J. Ströhle, and B. Epple, "Development and validation of a 1D process model with autothermal operation of a 1 MW th chemical looping pilot plant," *Int. J. Greenh. Gas Control*, vol. 73, pp. 29–41, Jun. 2018.

Abbreviations

ASTM	American Society for Testing and Materials	FT	Fischer-Tropsch
AWL	Anhydrous Weight Loss	NCV	Net Calorific Value
BMV	Biomass Volatiles	OPEX	Operating Expenditure
CAPEX	Capital Expenditure	REDII	Renewable Energy Directive
CLG	Chemical Looping Gasification	SC	Sibelco Calcined
CLOU	Chemical Looping with Oxygen Uncoupling		

Project Partners

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		