Newsletter V, April 2021



WHAT IS CLARA?

CLARA is a Horizon 2020 project, funded by the EU, involving 13 partners from across Europe, which aims at developing an efficient technology for the production of 2nd generation liquid biofuels based on chemical looping gasification (CLG) of biogenic residues.

Chemical Looping Gasification for Sustainable Production of Biofuels

H2020 Research and Innovation action Grant Agreement n° 817841

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ABOUT THE PROJECT

The de-carbonization of the transport sector is a key factor to achieve significant reductions in greenhouse gas emissions that are required to prevent a surge in global average temperatures, exceeding the 1.5 °C Paris Agreement threshold. To tackle this issue, the large-scale deployment of biofuels, in addition to electrification and the increased deployment of rail transport, is necessary. Therefore, substantial advances in renewable fuel generation, not affecting food availability and prices, are required. One route to achieve these objectives is the synthesis of advanced biofuels through thermochemical conversion of biomass-based residues. Within the scope of CLARA, 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 MWth 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.



PROJECT HIGHLIGHTS

- By integrated combination of different technologies such as torrefaction, washing, use of additives and pelleting, the quality of wheat straw residues has been improved for CLG application.
- Tests in small continuous units have proven that ilmenite and LD-slag (by-product from steel industry) are suitable oxygen carrier materials for CLG.
- Ilmenite has been chosen for the further investigation of CLG in pilot scale and the demonstration of the full process chain at TUDA.
- Chemical looping gasification of biomass pellets was successfully demonstrated in a 50 kW_{th} unit.
- Sour gas separation using H_2O_2 has been investigated in detail using different experimental setups, showing little promise of the solvent for the designated purpose. Nevertheless, the suggested innovative gas cleaning concept is still promising as alternative solvents, which will be investigated in the future, are viable for the sour gas separation step.
- The newly erected syngas treatment train of the 1 MWth pilot plant at TUDA was successfully commissioned in two test campaigns.

For more information on the project progress visit: <u>https://clara-h2020.eu/</u>.

In case you want to receive regular updates on the project, you can <u>subscribe to the biannual newsletter</u>.

Project Progress

Within the last six project months (Nov. 2020 – April 2021), progress was made in WP2 (*Development of a Concept for Pre-Treatment of Straw*), WP3 (*Development of Chemical Looping Gasification*), WP4 (*Development of a Novel Gas Cleaning Concept*), and WP5 (*Demonstration of the Full Process Chain*). This progress is briefly summarized in the following.

DEVELOPMENT OF A CONCEPT FOR PRE-TREATMENT OF STRAW

- Based on initial findings made in WP2, a first batch of pre-treated wheat straw has been produced for CSIC to conduct CLG experiments in their 50 kWth unit, assessing the effect of certain pre-treatment steps on bed agglomeration phenomena.
- On the basis of these tests at larger CLG scale (50 kW_{th}) the final pre-treatment concept, consisting of additivation & pelleting, was defined.

DEVELOPMENT OF CHEMICAL LOOPING GASIFICATION

- Selected oxygen carriers were investigated for continuous CLG in 10 kW_{th} and 1.5 kW_{th} units, with total operational times of over 600 h. After the evaluation of the performance of oxygen carriers in continuous operation, ilmenite was selected for the scale up of the process. An alternative material showing outstanding characteristics during CLG is LD-slag (shown on the right).
- \bullet CLG of biomass was demonstrated in a 50 kW $_{th}$ unit using ilmenite as oxygen carrier at CSIC. The process performance is similar to the one obtained in the 10 kW $_{th}$ and 1.5 kW $_{th}$ units.
- \bullet The 100 kW $_{th}$ at CTH is under preparation and modification for continuous CLG operation.
- A 1.5D CLG process model was developed, requiring kinetic data of biomass gasification and oxygen carrier reactions. Gasification kinetics of char obtained from different biomass pellets have been measured and the determination of the redox reactions of ilmenite is on-going.

DEVELOPMENT OF A NOVEL GAS CLEANING CONCEPT

- Numerous tests in stirred glass reactors with variation of several operation parameters like H_2S concentration in feed gas, H_2O_2 concentration in gas cleaning solvent, temperature, or concentration of catalyst have been performed. Only little conversion rate has been observed due to short contact times, which are typical for large scale application in baffle tray columns. Test runs in technical scale columns verify these results.
- Alternative approaches guaranteeing the viability of the suggested gas cleaning concept, such as the investigation of alternative reactants, are currently underway.
- The amine section, which is the core of the gas cleaning concept, and the caustic scrubbing step have been modelled successfully. The sulfur recovery section involving alternative reactants is due to be developed and aligned with the updated experimental activities.



DEMONSTRATION OF THE FULL PROCESS CHAIN

- Operation of the 1 MW_{th} pilot in CLG mode leads to the production of significant quantities of syngas. In order to remove this gas safely, a novel syngas removal train is being engineered at TUDA. Erection of this pilot plant extension is scheduled for the last quarter of 2021.
- The HAZOP analysis for the 1 MW_{th} chemical looping gasifier is underway, preparing the pilot plant for safe operation.
- Accurate control of the pilot plant during operation requires a specifically engineered process control system (PCS). This PCS is currently being programmed.
- The newly erected syngas treatment train (see right), financed through the German research project FABIENE, has been commissioned in two test campaigns & first fullchain experience has been gathered.

Detail view from the top level of the newly erected syngas treatment train at TUDA.

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Chalmers University of Technology (CTH) is located in Gothenburg, Sweden and it was founded in 1829. It was transformed into an independent foundation in 1994 and is one of the leading technical universities in northern Europe. The research group at the division of <u>Energy Technology at Chalmers</u> is world leading in chemical-looping combustion It has been working with the development of reactor concepts and oxygen-carrier material for such processes since 1998 and was the first to successfully demonstrate the process in sustained operation, which was achieved 2003 in a 10 kW prototype unit for gaseous fuel. Chalmers was also first to demonstrate chemical-looping combustion of solid fuels in another 10 kW prototype in 2006.



CHALMERS

The research has been carried out in a range of national and international projects, including the EU-projects GRACE, CLC GAS POWER, CACHET, INNOCUOUS, NOCO2, the ECSC/RFCS-projects CCCC and ACCLAIM, and together with Alstom, the RFCS-project ECLAIR and solid fuel CLC work within EU-project ENCAP.

Chalmers currently has four chemical-looping reactor units for gaseous/solid/liquid (G/S/L) fuels: 300 W (G/L), 10 kW (G/L), 10 kW (S) and 100 kW (S), that have totally been in operation with fuel for >4000 h, using >60 different oxygen carrier materials. This involves the first successful demonstration of chemical-looping combustion with oxygen carriers based on nickel, iron and manganese oxides, as well as natural minerals and combined oxides (e.g. CaMnO3- δ), using natural gas, syngas, bituminous coal, pet coke, wood char, kerosene, fuel oil and heavy oil residues as fuels. Further, Chalmers has investigated more than 500 different oxygen carrier materials in laboratory. Chalmers has >300 publications on CLC, of which >170 are reviewed and 18 are PhD theses.

Other major experimental & modelling work at the division has been related to combustion & gasification, with strong focus on fluidized bed technology. Current main activities are related to oxygen-carrier aided combustion of biomass and indirect gasification of biomass. For these activities, the division has access to a unique 12 MW circulating fluidized bed research boiler and gasifier located at Chalmers. It should also be pointed out that the city of Gothenburg is home of the GoBiGas project, which is one of the world's largest industrial plants for production of biogas from biomass by gasification. This facility utilizes technology developed by CTH.



CTH research team in front of the 300 Wth, 10 kWth, & 100 kWth chemical looping unit.

GETTING TO KNOW THE PARTNERS - CTH

Producing a high-quality syngas from various feedstocks is a challenging task. Here, Chemical Looping Gasification, being employed within the scope of CLARA, offers several advantages. CTH leads the research efforts in further developing the CLG concept for the efficient and reliable conversion of biogenic residues into syngas. We had the chance to talk to Dr. Amir Soleimanisalim and Prof. Tobias Mattisson from CTH, to learn about the advantages & promises of this novel technology and how it is being further developed within the project.

What appealed to you in the CLARA project, sparking the interest to get involved in it?

Tobias: Well, we had done some preliminary work regarding CLG earlier, so it was in some way in-line what we were doing. The fullchain concept as proposed by TUDA, was quite appealing to us, so it was an exciting project to be a part of. Further, we had also started to focus more and more on negative emission technology during that time. We see CLG as an excellent way of producing fuel but also as a viable technology to capture carbon dioxide. In contrast to normal indirect gasification, in CLG we obtain a more concentrated stream of CO₂ together with the syngas, applicable for capture. Then of course, CLG can have other advantages, as we are exploring in the project.

What is your role in the project and what expertise do you bring to the consortium?

Amir: Chalmers is leading work package which is developing chemical looping gasification. This is one of the main work packages in CLARA which evaluate different parameters for chemical looping gasification. Chemical looping group at Chalmers has more than 20 years of experience on CLC. As Tobias mentioned above, we also had some experience with CLG, but this is the first project where we really explore this process in more detail. So far, we have made over 600 h of testing in pilots, and we have really obtained valuable data. \mathbf{N}

Why do you think CLARA is an important project for society, academia, and industry?

Amir: CLARA will move production of the second generation of biofuels from biomass through chemical looping gasification to TRL6-7. This process can achieve the net negative CO₂ emission and will reduce the carbon footprint from the transportation and energy industries. Also, the feedstock for CLARA is biogenic residues to avoid the negative impact of biofuels on the food production and land use. The use of biogenic residues and operation of decentralized supply plants to centralized CLG plants may also strengthen the economy of rural areas.

Tobias: I think that the whole-value chain project really is the key. Often projects, even integrated projects, look at one issue or part of the chain, here we really see all parts and how they fit together.

What are the biggest challenges in your work within CLARA?

Amir: We have several tasks in the work package of developing chemical looping gasification and they are mostly experimental. In principle, this has gone well, with several hundreds of hours of experiments at Chalmers and CSIC. Of course, these types of tests have a lot of inherent challenges, but I would actually say that the main challenge was the COVID-19 pandemic, and we have had difficulties to access the laboratories and perform experiments using our pilot plants.

Currently, CTH working on the development of the novel Chemical Looping Gasification (CLG) process. What role does CLG play in biomass-to-biofuel process chains? In which way can it influence the product quality or the process efficiency?

Amir: I think CLG is the heart of biomass-to-biofuel process chains, which convert the solid biomass to gases products. Operational condition in CLG can affect to quality of the gas products, i.e. H2/CO ratio, tar content, etc. Therefore, tuning the CLG conditions based on the gas quality required for the Fischer-Tropsch can increase the efficiency and reduce the cost of gas cleaning after CLG.

Tobias: Also, I think that the possibility to actually combine carbon capture with fuel production is a very big advantage of CLG, something which I believe is not emphasized enough.

How can your findings be beneficial to other projects and how do you see them being utilized in industrial processes?

Tobias: As with any chemical-looping technology, I think the viability of the oxygen carriers with regard to performance, attrition behavior and such is going to be an important outcome. Further, the viability with these types of residue fuels and at highly reducing conditions will be valuable information for further exploitation of the technology.

Amir: We have dedicated a lot of efforts and resources in the work package of developing CLG to evaluate the viable options for oxygen carriers and the effects of the operational parameters on the performance of CLG operation. Our findings can accelerate the development of the CLG process to a commercialized level. In this work package, chemical looping gasification of biogenic residues has been demonstrated up to 100 kW_{th} and proved to produce the high-quality syngas with lower tar content compared to conventional gasification processes. The results from this work package are therefore very valuable for further development of CLG processes.

What was your biggest success in the project so far?

Amir: Seven oxygen carriers, which are natural ores and industrial wastes, were preselected as the most promising options for CLG based on the experiences from CTH, CSIC and TUDA. We have evaluated all the seven oxygen carriers in our pilot plants and investigated effects of the operational parameters on the CLG performance of each oxygen carrier. The experimental work has been very extensive, and we could demonstrate chemical looping gasification of biogenic residues in our pilot plant as a viable option for high quality syngas production. We have proven that the conversion of biomass residue in CLG is higher than conventional steam gasification and the tar content in the gas product is lower.

Tobias: I would agree with Amir, that the main success is the long operations with many oxygen carriers at quite severe conditions. The lower tar content Amir mentioned is really important because all biomass gasification techniques see this as major problematic, and many times a show stopper. To have a technology which where we can produce a liquid fuel with carbon capture, and thus negative emissions, with lower emissions of tars and nitrogen, that would really be an important process in my opinion.



Amir Soleimanisalim has a PhD in chemical engineering and a diploma in engineering management. Since May 2019, Amir has been working as the leader of work package of chemical looping gasification at Chalmers University of Technology. Amir has been working more than 6 years on chemical looping combustion and gasification, carbon capture technologies and gas treatment processes. He has been received several awards and scholarships for his contribution to the development of carbon capture technologies.



<u>Tobias Mattisson</u> is professor within sustainable fuel conversion at Chalmers, and has worked with chemicallooping technologies for more than two decades. He has made contributions in a number of areas, including development of oxygen carrier materials for chemicallooping. He has over 150 peer-reviewed publications in the area, which are widely cited.

Dissemination Activities

Scientific publications

- Dieringer, P.; Marx, F.; Alobaid, F.; Ströhle, J.; Epple, B. "Process Control Strategies in Chemical Looping Gasification—A Novel Process for the Production of Biofuels Allowing for Net Negative CO2 Emissions", <u>Applied Sciences 2020</u>, 10 (12), 4271.
- Condori, O.; García-Labiano, F.; de Diego, L. F.; Izquierdo, M. T.; Abad, A.; Adánez, J. "Biomass Chemical Looping Gasification for Syngas Production Using Ilmenite as Oxygen Carrier in a 1.5 KWth Unit", Chemical Engineering Journal 2021, 405, 126679.
- A. Di Giuliano, I. Funcia, R. Pérez-Vega, J. Gil, K. Gallucci, "Novel Application of Pretreatment and Diagnostic Method Using Dynamic Pressure Fluctuations to Resolve and Detect Issues Related to Biogenic Residue Ash in Chemical Looping Gasification", Processes 2020, 8 (9), 1137
- A. Di Giuliano, S. Lucantonio, K. Gallucci, "Devolatilization of residual biomasses for chemical looping gasification in fluidized beds made up of oxygen-carriers", Energies 2021, 14 (2), 311
- A. Hedayati, A. H.Soleimanisalim, C. J. Linderholm, T. Mattisson, A. Lyngfelt, "Experimental Evaluation of Manganese Ores for Chemical Looping Conversion of Synthetic Biomass Volatiles in a 300 W Reactor System", Journal of Environm. Chemical Engineering, 2020

Conference Contributions

- "Chemical Looping Gasification A Novel Process for the Sustainable Production of Biofuels", 6th CEBC, Graz, 22/01/20
- "Biomass Chemical Looping Gasification (BCGL) Using Ilmenite as Oxygen Carrier", 6th CEBC, Graz, 22/01/20
- "Novel concept for the pre-treatment of cereal straw", European Pellet Conference 2020, 04/03/2020
- "Advanced Fischer-Tropsch biofuels production from syngas derived from Chemical Looping Gasification: A preliminary process simulation study", eEUBCE2020, 06/07/2020

Other publications

- "Chemical Looping Gasification A Novel Process for the Production of Biofuels Allowing for Net Negative CO2 Emissions", European Energy Innovation, Spring 2020 Edition
- "Production of Biofuels exhibiting a net-negative CO2 Footprint", Open Access Government, July Edition



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