

Bio methanol production via chemical looping gasification coupled with membrane reactors

Producción de biometanol mediante gasificación con transportadores sólidos de oxígeno y reactores de membrana (Bio-MeGaFuel)

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Abstract

Bio-MeGaFuel is an European project focused on establishing a novel, efficient, and scalable process to convert low-value biogenic residues and organic waste into biomethanol at low cost. By developing chemical looping gasification coupled with membrane reactors, the project aims to achieve Technology Readiness Level 5 (TRL 5) by 2028. The project also aims to intensify the process, reduce the need for downstream treatments, and create synergies with renewable energy sources, such as renewable hydrogen integration. This breakthrough will pave the way for greater adoption of biomethanol in the chemical industry, marine transportation and notably as a feedstock to produce sustainable fuel alternative (SAF) for hard-to-abate sectors such as aviation. By reducing production costs and scaling up biomethanol output, Bio-MeGaFuel aims to offer a renewable, economically viable solution to the fuel challenges faced by sectors critical to the global economy.

Abstract (español)

El proyecto europeo Bio-MeGaFuel tiene por objetivo el desarrollo de un proceso innovador, eficiente y escalable para convertir residuos biogénicos de bajo valor y desechos orgánicos en biometanol a bajo coste. Mediante el desarrollo del proceso de gasificación con transportadores sólidos de oxígeno (Chemical Looping Gasification) acoplada con reactores de membrana, el proyecto tiene como objetivos alcanzar un Nivel de Madurez Tecnológica 5 (TRL 5) para 2028. El proyecto busca también intensificar el proceso, reducir los procesos de limpieza del gas de síntesis y generar sinergias con fuentes de energía renovables mediante la integración de hidrógeno renovable. La innovación propuesta abrirá el camino para un mayor uso del biometanol en la industria química, el transporte marítimo y, especialmente, como materia prima para la producción de combustible sostenible para sectores de difícil descarbonización, como la aviación. Al reducir los costes de producción y aumentar la producción de biometanol, el proyecto Bio-MeGaFuel tiene como objetivo ofrecer una solución renovable y económicamente viable a los desafíos energéticos que enfrentan sectores clave de la economía global.

Introduction

Biofuels play a vital role in decarbonizing the transport sector by providing a low-carbon solution for existing technologies [1]. Biofuel demand in 2022 reached a record high of 170 billion litres [2]. Furthermore, global demand for biofuels is expected to surge, primarily to aid in the decarbonization of sectors where emissions are challenging to mitigate, and alternative solutions are either unavailable or difficult to implement in the near future. These sectors include heavy industry, shipping, aviation, and heavy-duty transport.

Among the currently available types of biofuels, biomethanol, with its unique properties, stands out as one of the clearest alternatives for decarbonizing shipping, and heavy-duty transport. Methanol is a multipurpose fuel that can be used directly in internal combustion engines, blended with other fuels or for producing fuel additives, which improve engine performance. Besides its fuel properties, it is also an important chemical commodity [3]. Methanol is a stable chemical that is in liquid state at ambient temperature and pressure (no need for high pressure and cryogenic conditions), thus making transportation and storage more efficient compared to hydrogen.

However, two key issues may challenge the further uptake of methanol in energy systems: i) methanol is today produced from fossil resources, and ii) methanol is used mainly by chemical industries, leaving small room for the energy sector to count on it.

In fact, with a global production of about 100 million tons of methanol in 2020 (with expectations of increasing to 500 Mt/year by 2050), about 65% is produced by natural gas reforming and ~35% is produced by coal gasification [4]. Only less than 1% of global methanol production is renewable methanol. Therefore, to meet the net zero emission in the near future, the production of renewable methanol must increase significantly to maintain the production of several products we take for granted in modern society. The Bio-MeGaFuel project proposes a novel route that converts low value biomass to methanol via an intensified process with a minimum carbon footprint comparable to conventional methods.

The Bio-MeGaFuel Project

(<https://www.biomegafuelproject.eu/>)

The goal of Bio-MeGaFuel is to establish a novel efficient, and scalable process to convert low-value biogenic residues and organic waste to biomethanol through chemical looping gasification coupled with membrane reactors. Figure 1 schematically shows the novel proposed plant. The process is based on the novel chemical looping gasification (CLG)

concept for producing syngas from biogenic residues and membrane reactors for methanol synthesis from syngas.

The main reactions involved in the biomethanol production process are the following:

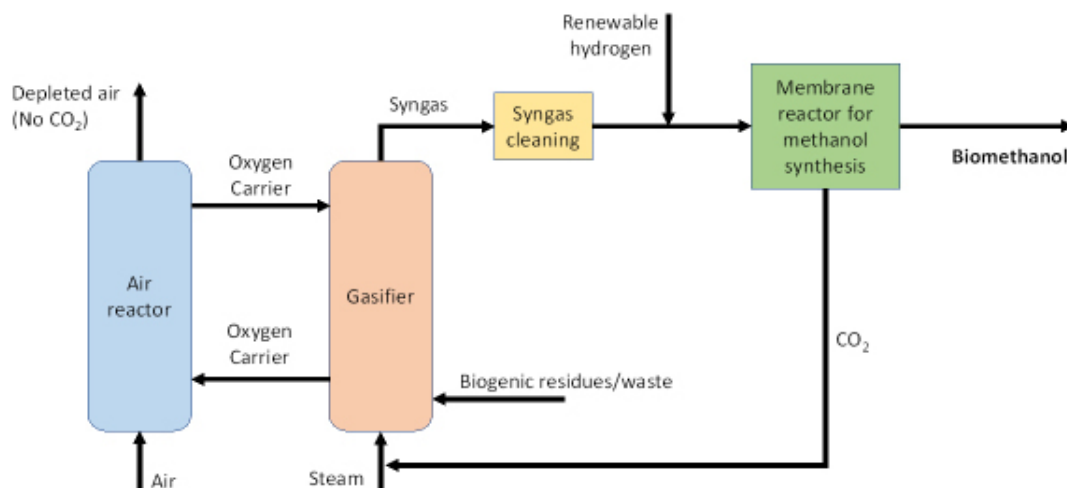
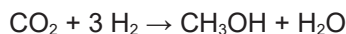
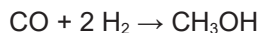


Figure 1. Biomethanol production from biogenic residues and wastes through chemical looping gasification coupled with membrane reactors.

Figura 1. Producción de biometanol a partir de residuos biogénicos mediante gasificación con transportadores sólidos de oxígeno acoplado con reactores de membrana.

Consortium

Bio-MeGaFuel is a collaborative effort between 9 partners from 5 European countries, namely: • RISE Research Institutes of Sweden (Sweden) • GIDARA Energy (Netherlands) • Technische Universität Darmstadt (TUDA) (Germany) • Eindhoven University of Technology (Netherlands) • Spanish National Research Council (CSIC) (Spain) • IVL Swedish Environmental Research Institute (Sweden) • Perpetual Next (Netherlands) • 1CUBE (Netherlands) • Blue World Technologies (Denmark)

The consortium consists of universities, research institutes, end-users and technology providers who individually will investigate and enhance a particular process-step. Many of the partners have been instrumental in the development of included processes and techniques, such as CLG (TUDA and CSIC), membrane reactors for methanol synthesis (TUE), and methanol synthesis through gasification. Dissemination will be also a relevant part of the project.



Figure 2. The Bio-MeGaFuel project value chain.

Figura 2. Cadena de valor del proyecto Bio-MeGaFuel



The following key specific objectives are targeted:

1. Developing biogenic residues and wastes gasification with oxygen carriers to maximize the conversion of biogenic residues and wastes to syngas:

Within Bio-MeGaFuel, it is intended to develop CLG of low-value biogenic residues and wastes in pilot units up to 1 MWth, thus establishing the technology at TRL 5-6. Here, 50-70 tons of biogenic residues will be gasified, and performance will be evaluated.

2. Developing of membrane reactors for methanol synthesis:

TUE will develop novel thin carbon molecular sieve membranes based on the patented technologies developed by TUE (together with Tecnalia) in the past years. The aim is to significantly increase the yield of biomethanol production from syngas by two-fold.

3. Developing Single-step methanol synthesis with recirculation of CO₂ to maximize carbon and biomass conversion:

One of the benefits of Bio-MeGaFuel is the application of membrane technology where unconverted biogenic CO₂ is separated and recirculated back to the gasifier to i) promote the gasification of biomass to reach a higher conversion, and ii) maximize the utilization of the carbon from biomass and its conversion to syngas to increase the syngas yield.

4. Exploitation and whole Value Chain analysis:

Market analysis and product uptakes will be done considering the novel route proposed in Bio-

MeGaFuel, that includes a lower cost and lower GHG emission. Therefore, several aspects of the new production route will be analyzed through production potential and market analysis, conceptual value chain, business models for the biomethanol, and the barriers and analysis of the end users.

Biomass Chemical Looping Gasification: Ongoing activities at ICB-CSIC

The Combustion and Gasification research group of the Instituto de Carboquímica (ICB-CSIC) is involved in developing biogenic residues and wastes gasification with oxygen carriers. In this sense, Biomass Chemical Looping Gasification (BCLG) represents an innovative process with the potential of reducing costs and emissions compared to other gasification technologies [5-7]. In BCLG, a solid oxygen carrier circulates between two interconnected fluidized bed reactors, fuel and air reactors, providing the oxygen needed for partial oxidation of the solid fuel and the heat necessary for the endothermic reactions taking place for syngas production. The main advantage of BCLG is the production of high-quality syngas with reduced tar content, non-diluted in nitrogen, without using costly pure oxygen and without CO₂ emissions to the atmosphere. In fact, BCLG process can operate at autothermal conditions with all the carbon compounds exiting the system in the fuel reactor stream. The separation and further storage of the CO₂ present in the syngas allows CLG operation without any emission.

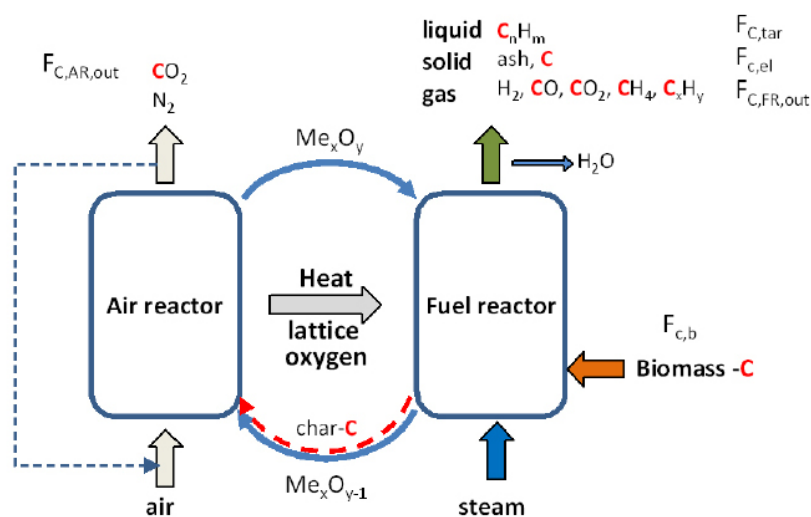


Figure 3. Scheme of the Chemical Looping Gasification process.

Figura 3. Esquema del proceso de gasificación con transportadores sólidos de oxígeno.

The schematic illustration of this process is shown in Figure 3. The biomass is converted into gaseous (pyrolysis gas), liquid (tar) and solid (char) products in the fuel reactor and then these products may be partially oxidized by the oxygen carrier and the gasifying agent. Thus, solid fuel is converted to synthesis gas and the oxygen carrier is reduced in parallel. The oxygen carrier is denoted by Me_xO_y and Me_xO_{y-1} , where Me_xO_y is a metal oxide and Me_xO_{y-1} its reduced compound. The reduced oxygen carrier goes to the air reactor where it is regenerated in air

atmosphere to begin a new cycle. Moreover, the reactions that occur in the air reactor are exothermic, so the required heat for fuel gasification is provided by the oxygen carrier circulating from the air to the fuel reactor.

A relevant feature in the process operation is the method for controlling oxygen used for gasification. This oxygen can be perfectly controlled by feeding the required amount in the air reactor, that it is fully transferred to the oxygen carrier and then to the fuel for gasification. To allows operation, a part

of the nitrogen obtained at the air reactor outlet is recirculated for fluidization. The main advantages of this method are that the oxygen transferred from the air reactor to the fuel reactor does not depend on the solid circulation flow, allowing high flows of oxygen carrier circulation, and the possibility of obtaining pure nitrogen in the outlet stream of the air reactor.

The oxygen carrier to be used in the project will be ilmenite. Ilmenite is a natural ore mainly composed by iron titanium oxide, FeTiO_3 , that needs to be oxidised previously to be used in the process. The redox pair $\text{FeTi}_2\text{O}_5/\text{FeTiO}_3$ is system used in the process to transport oxygen from air to the fuel for gasification.

The potential feedstock includes abundantly available biogenic residues and wastes in five categories: biogenic waste (B-wood), waste streams (RDF), agricultural residue (olive pits, buckwheat husk, etc.), woody biomass and forestry residue, and microalgae. In fact, micro-algae can be an interesting precursor for third-generation biofuels and with no effect on the food change.

Several installations will be used in the project to produce pure syngas through BCLG. Figure 4 shows the schemes of the different CLG continuous units. Lab-scale gasification tests will be carried out in a 1.5 kWth CLG reactor at CSIC under continuous operation using ilmenite as the oxygen carrier and five biogenic fuels. Tests will be conducted at different temperatures and with two gasification agents (H_2O or CO_2 and their mix) to define viable gasification conditions. Thus, a comprehensive screening of fuels and operating conditions will be carried out based on the results obtained. Then, three types of biomasses (one of them being micro-algae) will be tested in a 20 kW CLG unit at CSIC using steam/ CO_2 as gasifying agent. The results obtained will be considered for the selection of two types of feedstocks and the definition of operating conditions during pilot testing at 1 MWth scale at TUDA (Germany). Syngas composition obtained at 1 MWth scale will be used at TUE for the optimum design, production and testing of the membrane for biomethanol production.

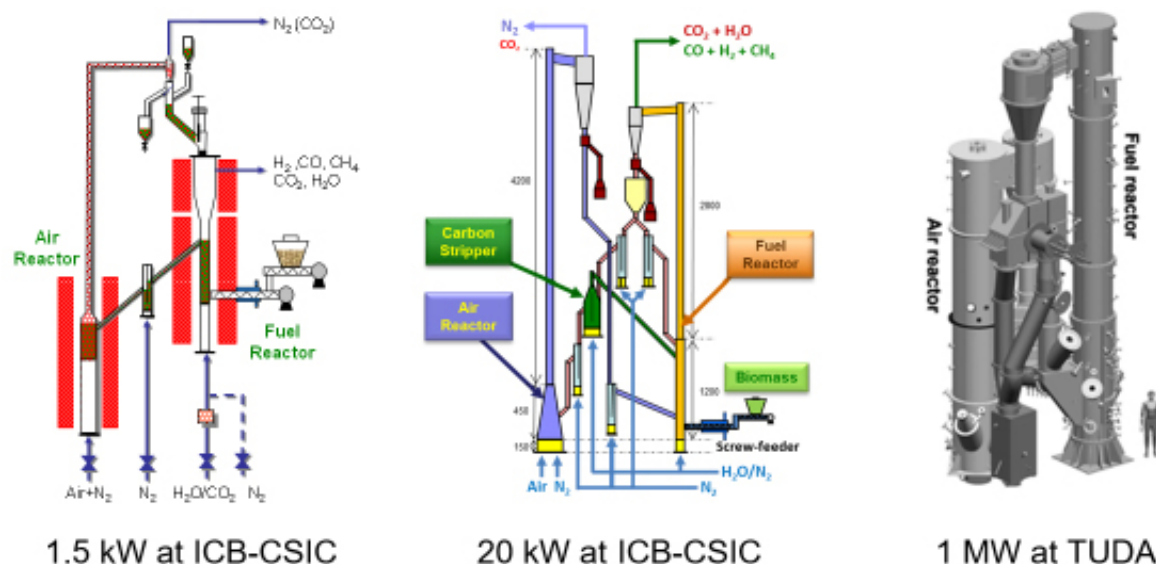


Figure 3. Scheme of the CLG continuous units.

Figura 3. Esquema de las plantas de gasificación con transportadores sólidos de oxígeno.

Acknowledgements

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References

- [1] Make Transport Greener (2021), European Commission.
- [2] Renewable Energy Market Update (2023), IEA.
- [3] A. G. Chaplin, Renewable methanol-An Analysis of technological potentials in light of the EU biofuels policy objectives of Greenhouse Gas Savings, Security of Supply and Employment, (2013).
- [4] G. Dolan, Methanol: Emerging Global Energy Markets. in 16th Annual State of the Energy Industry Forum (2020).
- [5] T. Mendiara, F. García-Labiano, A. Abad, P. Gayán, L.F. de Diego, M.T. Izquierdo, J. Adánez, Negative CO_2 emissions through the use of biofuels in chemical looping technology: A review, *App. Energy* 232 (2018) 657–684.
- [6] O. Condori, F. García-Labiano, L. F. de Diego, M. T. Izquierdo, A. Abad, J. Adánez, Biomass chemical looping gasification for syngas production using ilmenite as oxygen carrier in a 1.5 kWth unit, *Chem. Engn. J.* 405 (2021) 126679.
- [7] O. Condori, A. Abad, M. T. Izquierdo, L. F. de Diego, F. García-Labiano, J. Adánez, Assessment of the chemical looping gasification of wheat straw pellets at the 20 kWth scale, *Fuel* 344 (2023) 128059.