

Renewable methanol production for the shipping industry



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Document Approval

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Executive Summary

Crude methanol samples are produced from carbon dioxide and hydrogen in the existing methanol synthesis pilot plant at Air Liquide Forschung & Entwicklung GmbH (ALFE) at the Innovation Campus Frankfurt (Germany). The samples are analysed, collected and sent to the Centre for Research and Technology Hellas (CERTH), Thessaloniki (Greece) for laboratory scale distillation tests with the goal of defining optimal operating conditions for the distillation regarding the production of Maritime Methanol.

Methanol Production at Air Liquide Innovation Campus Frankfurt

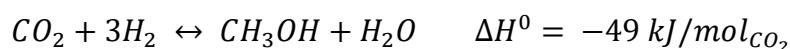
Maritime transport relies mainly on fossil fuels. As a result, as of 2021, waterborne shipping was responsible for 3-4% of all EU CO₂ emissions (1). In response to the high demand for maritime decarbonized fuel, M²ARE will deliver a methanol synthesis demonstration plant using the existing pilot plant located at the Air Liquide Innovation Campus Frankfurt, Germany.

The existing pilot plant was developed to valorise steel off gases by converting them into methanol. The process development was part of an EU-funded project called “i3upgrade”.¹ The novel process consists of a multi-stage, once-through or low-recycling methanol synthesis concept. The configuration of the pilot plant to produce the crude methanol for CERTH is operated in a four stage setup without recycling. Each reactor is followed by an inter-stage condensation and product separation. Moreover, each reactor is filled with a dedicated commercial methanol catalyst delivered by Clariant, member of the advisory board. The pilot unit is shown in Figure 1.



Figure 1: Multi-stage methanol pilot plant at Air Liquide Innovation Campus Frankfurt

For the production of the crude methanol in the pilot plant carbon dioxide and hydrogen are used. Nitrogen is added as an inert. The methanol synthesis is based on the hydrogenation of carbon oxides (CO₂ and CO) and the Reverse Water Gas Shift reaction (RWGS) (2):



¹ The i3upgrade project has received funding from the Research Fund for Coal and Steel under grant agreement No 800659.



As a consequence the methanol synthesis produces besides methanol also water. The hydrogenation reaction as well as the RWGS reaction are equilibrium reactions. By separation of the product mixtures immediately after each reactor stage the equilibrium is shifted further to the product side (Le Chatelier's Principle).

In addition the multi-stage, once-through or low-recycle process concept can handle a wide range of gas compositions, including high levels of inert gases (e.g. methane and/or nitrogen). Typically, high recycle rates in conventional reactor designs can lead to accumulation of such inerts in the synthesis loop and reduce the response time of the plant towards fluctuations. (3)

In order to produce the crude methanol samples needed for the distillation tests at CERTH a dedicated test campaign has been performed in the pilot plant. The feed of the pilot plant consisting of hydrogen, carbon dioxide and nitrogen (H₂: 74.3 vol.%, CO₂: 24.7 vol.%, N₂: 1 vol.%) has been used to produce a methanol/water mixture suitable for further distillation tests at CERTH. The reaction temperature was set to 240 °C and the reaction pressure to 80 barg.

The Crude Methanol Samples

The water content of the crude methanol sample is determined using volumetric Karl Fischer titration and the impurities are analysed by gas chromatography. The results are given in Table 1.

Table 1: Water content and impurities in the crude methanol.

Component	Unit	Result
Methanol (calculated)	wt.%	62.26
Water	wt.%	37.7
Alcohols (excl. methanol)	wt.ppm	31
Ketones	wt.ppm	1
Ethers	wt.ppm	1
Esters	wt.ppm	337
Hydrocarbons	wt.ppm	0

The crude methanol samples were collected from the pilot plant in stainless steel barrels (**Figure 2**) and filled into appropriate canisters for shipment to CERTH. A safety data sheet has been generated for these crude methanol samples. The samples were shipped to CERTH on 06 March 2024 from ALFE and received at CERTH on 19 March 2024.



Figure 2: Barrel used for the collection of crude methanol from the pilot plant

Crude Methanol Distillation Tests at Centre for Research and Technology Hellas

The crude methanol produced by Air Liquide R&D is distilled in a fully automated laboratory scale distillation unit consisting of 15 theoretical plates (**Figure 3**). The reflux ratio of the distillation unit is 4/1 and the unit is flexible to allow different cuts.



Figure 3: Fully automated lab-scale distillation apparatus at CERTH

The samples are used to carry out exploratory distillation tests to define the optimum distillation conditions. The test results will be crucial in defining the conditions needed to purify the crude methanol provided according to the specifications for methanol use as maritime fuel (e.g. the water content in the fuel).

References

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