

EuroBioRef

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Executive summary

This report describes the achievements realized in WP7.3, Task 7.3.7, which ran from M12 to M36. The main objective of this work package was to run a pilot scale test rig facility for alcohols synthesis from syngas for testing the long-term stability of the optimum HAS catalyst developed in WP6.3.2 and ultimately produce 5k g of higher alcohols.

Based on the outcome of WP6.3.2, a K/Ni/Mo₂C catalyst developed in CERTH was chosen for the testing. CERTH and CNRS-UCCS worked towards catalyst development, while Nykomb contributed in conceptual process design. The long term test lasted 17 days (11/6/2013 – 28/6/2013) and allowed the monitoring of catalyst stability and the production of 3.5 kg of product. The product was less than the initially anticipated 5 kg due to catalyst deactivation with time-on-stream. Relatively fast deactivation was observed for the first 6 days, while the deactivation rate was much less in the next days with a stabilizing trend. Further optimization of the catalyst structure and possibly shape and particle size is needed in order to avoid deactivation. Moreover, the pilot testing also proved that the process can be up-scaled and operated continuously without any significant hurdles for a significant amount of time.

The produced amount of higher alcohols is available in CERTH for the needs of the EuroBioRef project.

Results and discussion

Description of the deliverable objective and content

The contents in Deliverable 7.3.9 pertain to the work performed in WP7.3, Task 7.3.7. The initial description of the work to be performed according to the DoW was to design and build a mobile test rig facility for alcohols synthesis from syngas with a capacity of 10kg/year. This mobile test rig would then be used to test the long term stability of the optimum catalysts developed for higher alcohols synthesis in WP6.3 and ultimately produce ~5 kg of higher alcohols for further uses in the project. It was identified early within the project (during the 1st year) that it would be possible to perform the above described work in the bench scale test rig for HAS synthesis that was constructed in CERTH as part of the work in WP6.3 after necessary modifications, which would include the use of a larger reactor, mass flow controllers and product collection system. The request for modification was accepted.

The bench scale test rig for the evaluation of higher alcohol synthesis catalysts was constructed during the 1st year of the project and was used to perform all catalyst screening tests as part of Task 6.3.2, as reported in the respective deliverable D6.3.2. In view of the work for Task 7.3.7 regarding the demo testing, we completed the necessary modifications and began the pilot plant testing of the optimum higher alcohol synthesis catalytic formulation (identified in WP6.3) in April 2013. The test was performed with a K/Ni/Mo₂C catalyst that was developed in CERTH as part of WP6.3 and was identified as the catalyst with the highest space time yield for higher alcohols production from all the materials investigated in the relevant work package. The long term test lasted 17 days (11/6/2013 – 28/6/2013) and allowed the monitoring of catalyst stability and the production of 3kg of product. The product was less than the initially anticipated 5kg due to catalyst deactivation with time-on-stream.

Brief description of the state of the art

WP6.3 ran from M1 to M36 with the main objective to develop improved catalysts for the hydrogenation of CO to higher alcohols. CERTH and CNRS-UCCS worked towards catalyst development, while Nykomb contributed in conceptual process design. The work performed in this task advanced the scientific knowledge in higher alcohols synthesis from syngas and led to the development of efficient catalytic materials for the process. The ambitious target initially set was a space-time-yield (STY) of 200 gC₂₊OH/kg_{cat}.h with a reference yield of 5 gC₂₊OH/kg_{cat}.h. Although the target was not met, the catalysts developed reached **35% of the target** and improved the reference state-of-the-art yield by more than 1000%. CNRS-UCCS developed **Fe-10Cu10Co/Al₂O₃** catalyst with very high activity in CO conversion, although low selectivity to higher alcohols, demonstrating a space

time yield of 51 gC₂₊OH/kg_{cat}.h. The **K/Ni/Mo₂C** catalyst developed in CERTH exhibited the highest space time yield (70 gC₂₊OH/kg_{cat}.h) at 60bar with additionally high selectivity to C₂₊ alcohols. Milestone M6.5 which was planned at M24 and concerned the decision to move to pilot plant tests for heavier alcohols production in WP7.3 was met successfully, as it demanded that the new HAS catalyst performance should be equivalent or better than that of the reference catalyst. As shown in Figure 1 which presents the reference point, the target yield set for the end of the project and the best yields achieved by the teams of CERTH and CNRS-UCCS, it is clear that compared to the base case the developed catalysts perform better in terms of higher alcohols space time yield.

Based on these results, the K/Ni/Mo₂C catalyst was selected for the pilot plant testing as part of the work in WP7.3.

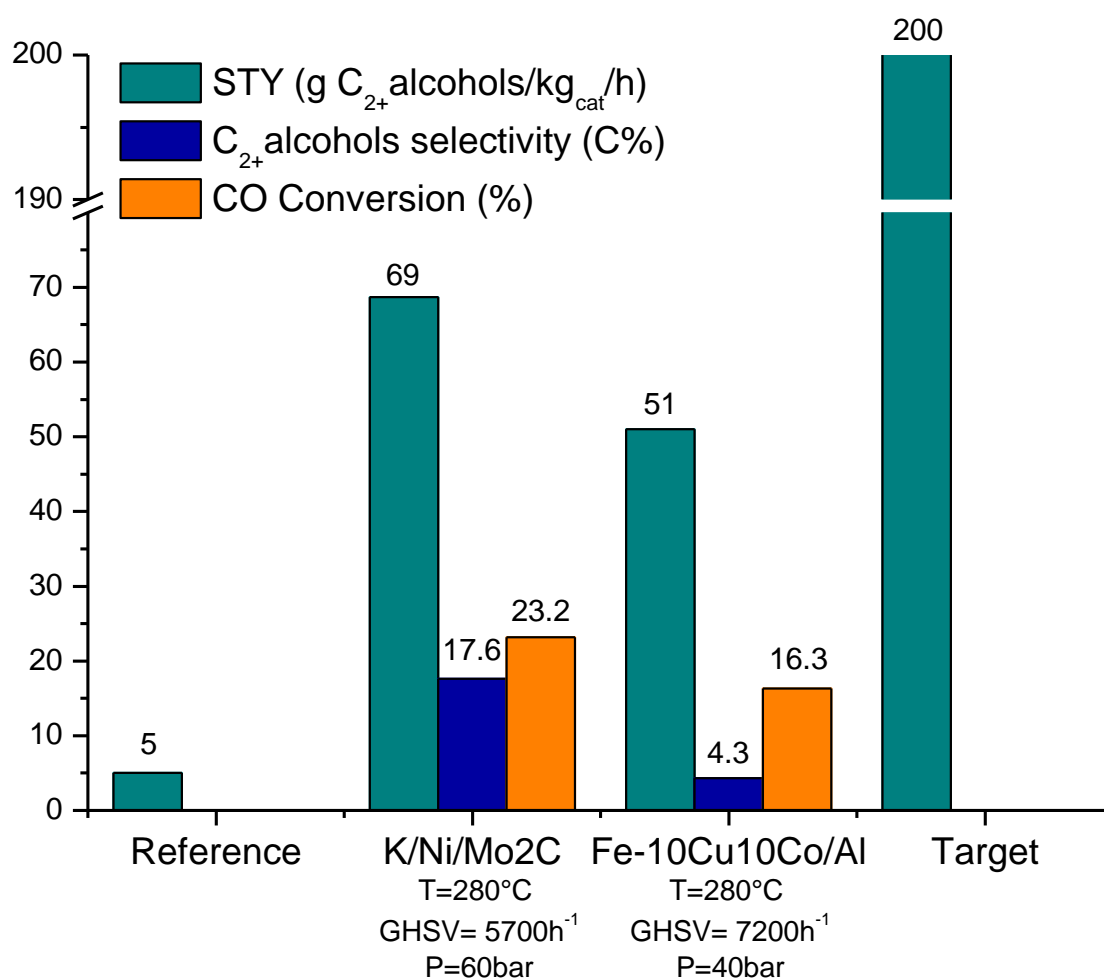


Figure 1. Space time yield of higher alcohols: reference point, target and best yields achieved by the teams of CERTH and CNRS-UCCS

Deviation from objectives and corrective actions

The up-scaling of the thermochemical synthesis of higher alcohols from bio-syngas and the long-term testing of the optimum HAS catalyst was initially supposed to finish at M36. A 6-month extension of the task to M42 was requested and was granted, due to a delay in the delivery of the optimum catalytic formulation in WP6.3.2. Moreover, the product attained is less than the 5kg initially anticipated due to catalyst deactivation with time-on-stream. Still, as indicated in the DoW, a lower limit of about 30% less than expected is still acceptable.

Innovation brought and technological progress

The long-term testing of a K/Ni/Mo₂C catalyst developed in CERTH for the production of higher alcohols from syngas on pilot scale showed that the process can be up-scaled without any significant hurdles. Of course, for further up-scaling, special attention should be paid to the heat management of the unit, as the reaction is exothermic. Moreover, it was demonstrated that the reaction can run unattended from several days on stream. Concerning the catalytic material, deactivation problems occurred, leading to a reduction of catalyst activity with time-on-stream. Relatively fast deactivation was observed for the first 6 days, while the deactivation rate was much less in the next days with a stabilizing trend. Characterization of the used sample with BET and XRD showed that deactivation is probably due to sintering, as great reduction of the catalyst surface area was recorded (fresh catalyst: 6.1 m²/g, used catalyst: 0.47 m²/g). The crystal structure of the catalyst was however retained, indicating that the conversion loss is not due to an alteration of the catalytic active sites.

Analysis of the results

Test unit description and upgrading to pilot scale

As described above, the pilot scale testing was performed on the bench scale test rig used for the evaluation of higher alcohol synthesis catalysts as part of Task 6.3.2 after necessary modifications. The unit consists of 3 mass flow controllers, a 3 zone furnace, a fixed bed reactor and a pressure regulator for pressure control. Liquid products after leaving the reactor are headed through the cooled line to a liquid collection container, for further offline analysis, while gaseous products are led directly to a Gas Chromatographer (GC) for online analysis, as it is shown in Figure 2. Product analysis is performed with a GC Agilent 7890A equipped with two detectors (FID & TCD) and three columns (MS, Porapak Q and DB-FFAP) in a series-bypass configuration.

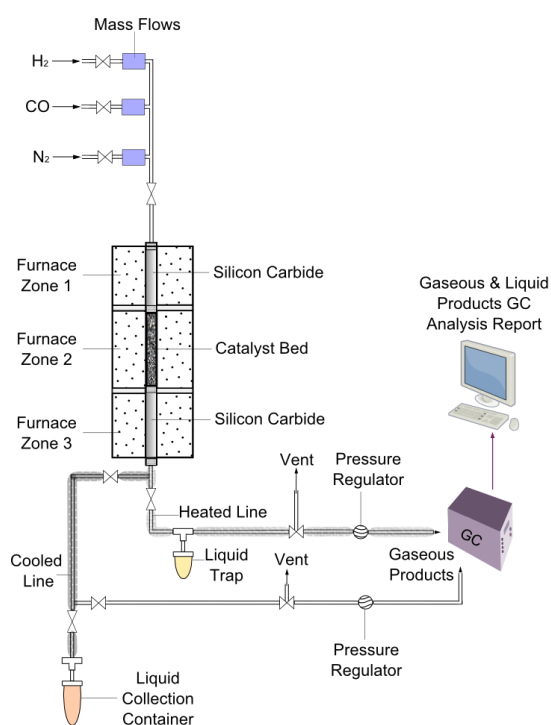


Figure 2. CERTH higher alcohol synthesis unit

The modifications that took place to upscale the unit were the following:

- Larger mass flow controller. Specifically the 0-500 cm³/min H₂ mass flow controller was upgraded to 0-1000 cm³/min.
- Larger reactor with a bulk bed volume of 83cm³.
- Higher capacity liquid product collection system (up to 5kg of liquid product).
- New pressure regulator (mity mite) in order for the unit to run unattended

Experimental conditions

The higher alcohol synthesis reaction at pilot scale was investigated at the temperature of 280°C and pressure of 60bar, W/F ratio of 0.68 g/s/cm³ and inlet feed composition H₂/CO=2. 10g of K/Ni/Mo₂C catalyst developed in CERTH was loaded in the fixed bed reactor, in a 4:1 dilution with silicon carbide of 355-425µm particle size, and the pressure was raised at 60bar using 500 ml/min CO and 1000 ml/min H₂ flow, respectively. When the pressure was reached, the temperature was raised according to the temperature program shown in Figure 3. The steady-state activity measurements were taken after at least 24 h on-stream.

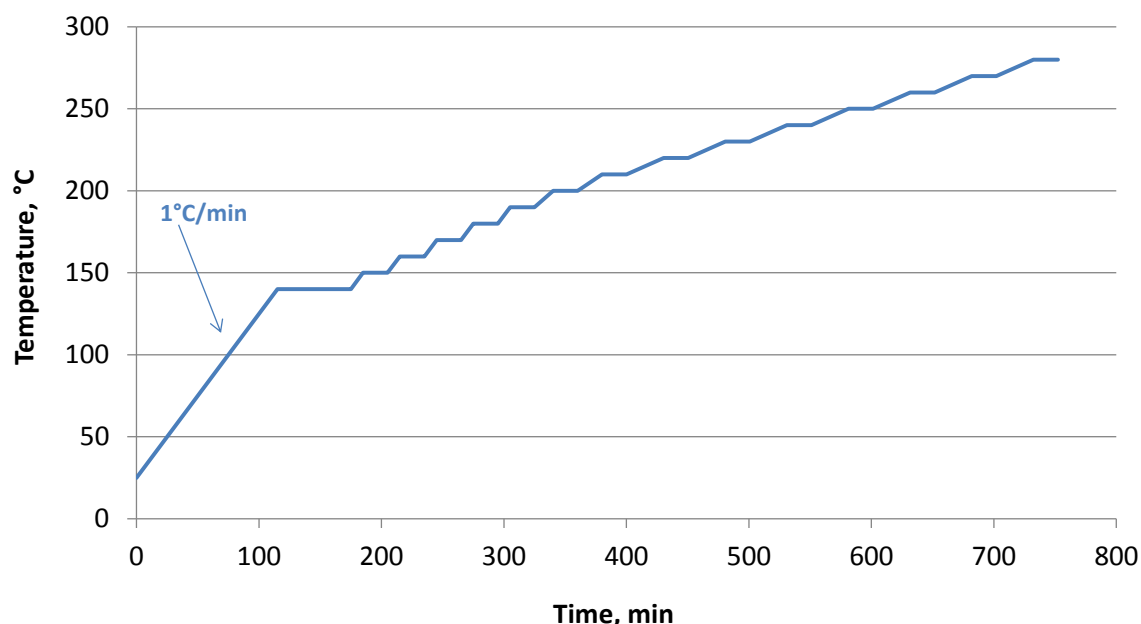


Figure 3. Temperature program used to achieve the desired temperature

Preliminary experiments

Before the steady-state experiment, we initially loaded the reactor with 10g of catalyst, in a 2:1 dilution with silicon carbide of 355-425µm particle size, and started raising the temperature with a rate of 3°C/min up to 270°C, the standard rate that we were using for the bench scale test experiments. Figure 4 presents the conversion of the reactants (CO and H₂) and the temperature of the reactor and the controller as a function of time. The system was let at this temperature to stabilize, while at the same time we started recording the catalytic performance. After two days of stable performance we attempted to reach the final reaction temperature of 280°C. As shown in Fig. 4, during this final temperature increase we observed fluctuations in the temperature in the catalyst bed. At the same time, CO and H₂ conversion also decreased or increased based on the temperature fluctuations. When the reaction temperature target approached the 280°C target, a violent run-away occurred with an instant increase of temperature from 280°C to 530°C, accompanied by almost total CO conversion and exclusive production of methane and ethane (not shown). At this point, pressure increased also rapidly due to sintering/coking of the catalyst and the unit automatically shut down the reactants flow

to prevent over-pressure in the system. The results of this first experiment show that due to the exothermic character of the higher alcohol synthesis reaction special attention should be paid to the heat management of the unit. In order to achieve good temperature control and avoid runaways, we followed the temperature programmed described in Fig. 3 (experimental conditions) with which we were able to adequately control the temperature. However, for larger scale experiments, it would be necessary to install an appropriate reactor heat removal system to achieve good control of the reaction temperature.

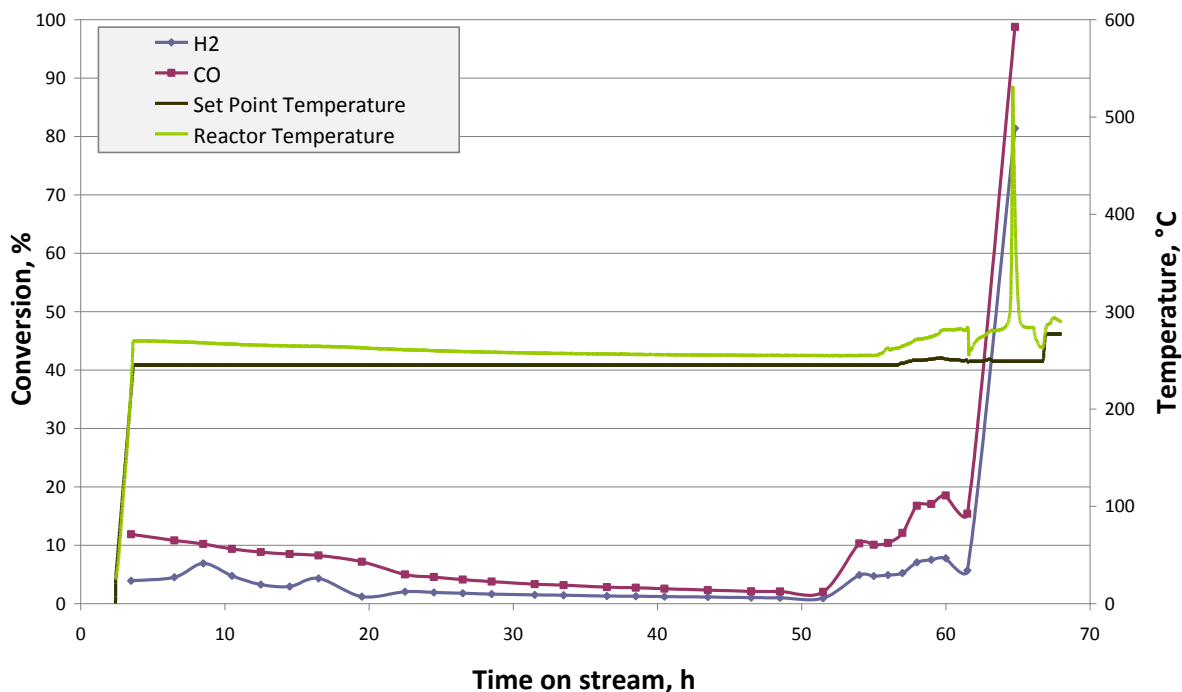


Figure 4. Reactants conversion and temperature as a function of time-on-stream (conditions: $P=60\text{bar}$, $H_2/CO=2$ molar ratio)

Catalyst stability at steady-state operation

The conversion of the reactants (CO and H_2) and the carbon-based selectivity of the different products are shown as a function of time in Figures 5 and 6 respectively.

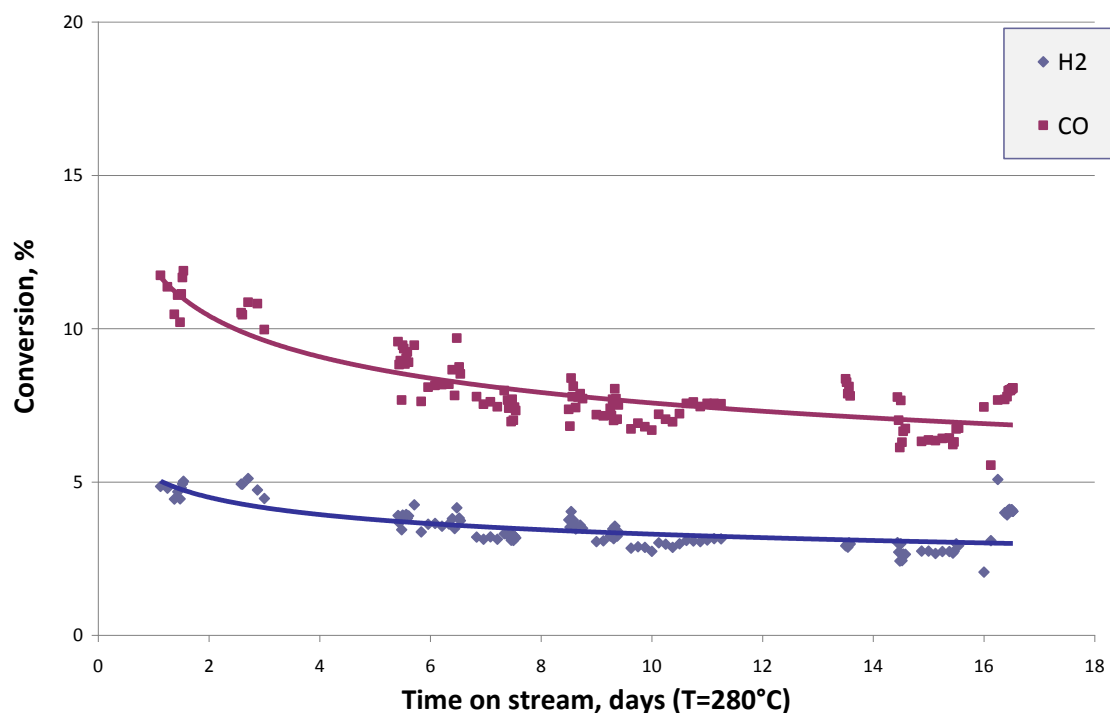


Figure 5. Reactants conversion as a function of time-on-stream (conditions: $P=60\text{bar}$, $\text{H}_2/\text{CO}=2$ molar ratio)

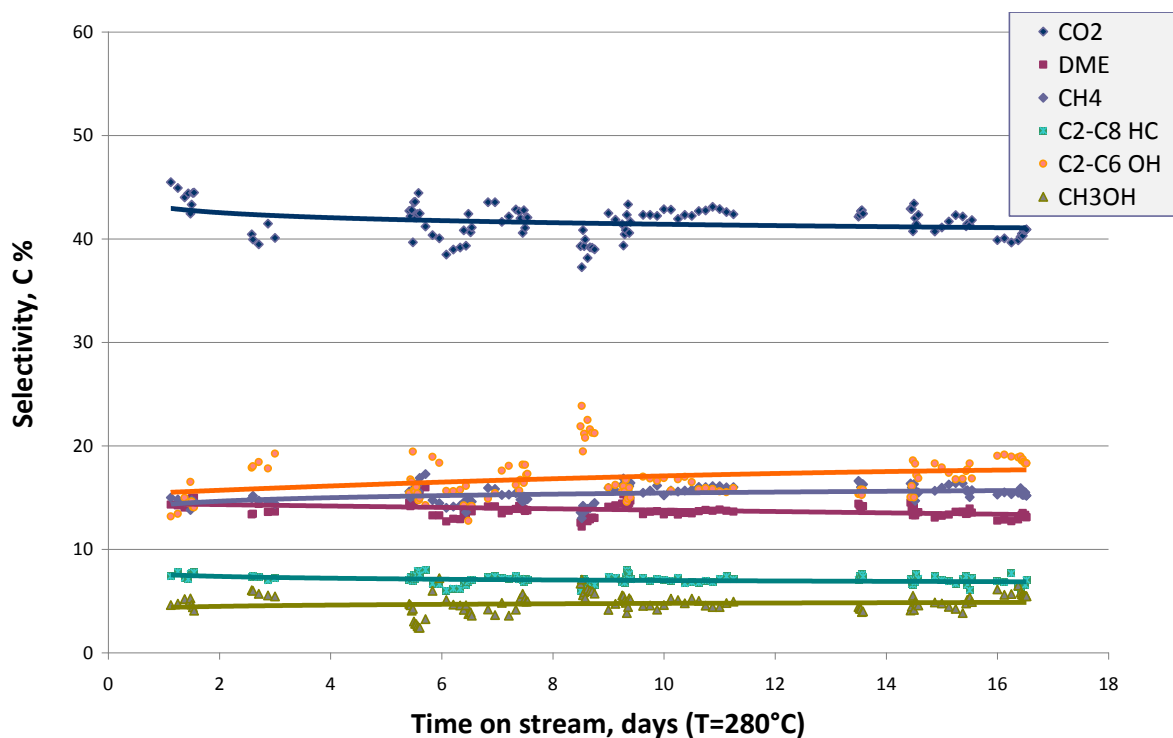


Figure 6. Selectivity to products as a function of time-on-stream (conditions: $P=60\text{bar}$, $\text{H}_2/\text{CO}=2$ molar ratio)

The initial CO conversion was around ~13%, which is close to the value of the 20% conversion that was attained in the bench scale experiments using the same catalyst (see D6.3.2). The reduction recorded could be due to up-scaling effects. The catalyst exhibited a constant deactivation during the

first 6 days of operation, with the activity dropping by about ~30%. The catalytic behavior seems to continue to decline but with a much milder deactivation rate, leading to an extra 15% loss in conversion after 17 continuous days of operation. In terms of selectivity, the target product higher alcohols are produced with a selectivity of around 18%, which is close to the expected value based on the bench test experiments. Besides alcohols, CO₂ is produced at high quantities, followed by the formation of CH₄, DME, methanol and small amounts of higher hydrocarbons. The selectivity does not vary significantly with time-on-stream indicating that the nature of the active sites does not change. This is in line with XRD characterization of the used catalyst that showed no change in the crystal phases of the material, i.e. no decomposition of the molybdenum carbide to oxide. A small increasing trend in HAS formation at the expense of DME and CO₂ production is observed with time-on-stream, which is however due to the decrease in CO conversion. The loss in the conversion is probably due to the reduction of the number of active sites due to sintering. Measurement of the surface area of the used sample showed great reduction in the surface area (close to zero), supporting the above. Carbon deposition could also be a reason, however coke cannot be easily measure on the sample as it is a carbide material to begin with.

Obtained product

The operation of the pilot plant unit for consecutive 17 days resulted in the production of 3.5 kg of higher alcohols. The liquid products were collected and a representative sample from the entire product was analyzed. The detailed composition is shown in Figure 7. The sample is available in CERTH for the needs of the EuroBioRef project. A picture is shown in Figure 8.

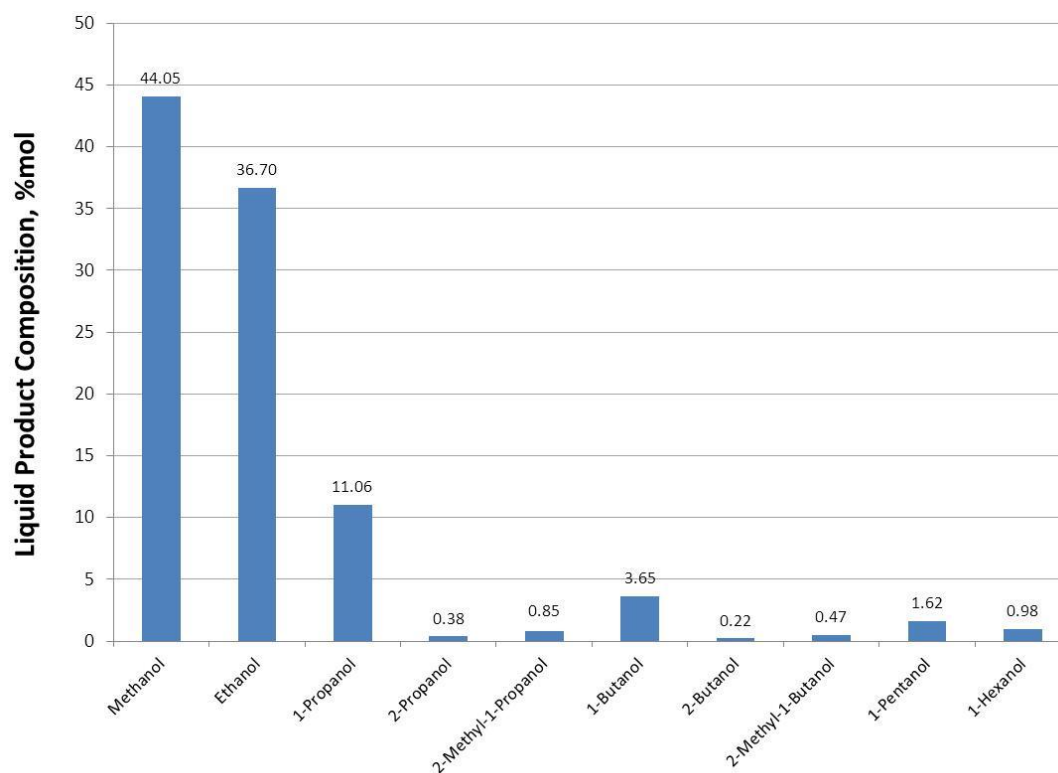


Figure 7. Composition of liquid product



Figure 8. Production of 3.5 kg of higher alcohols from CERTH test unit

Conclusions

CO hydrogenation to higher alcohols appears as a promising process for the production of jet fuel components. The long-term testing of a K/Ni/Mo₂C catalyst developed in CERTH for the production of higher alcohols from syngas on pilot scale showed that the process can be up-scaled without any significant hurdles. The testing was performed for 17 consecutive days and led to the production of 3.5 kg of product. The product attained is less than the 5kg initially anticipated due to catalyst deactivation with time-on-stream. Still, as indicated in the DoW, a lower limit of about 30% less than expected is still acceptable.

Concerning the catalytic material, deactivation problems occurred, leading to a reduction of catalyst activity with time-on-stream. Relatively fast deactivation was observed for the first 6 days, while the deactivation rate was much less in the next days with a stabilizing trend. Characterization of the used sample with BET and XRD showed that deactivation is probably due to sintering, as great reduction of the catalyst surface area was recorded. The crystal structure of the catalyst was however retained, indicating that the conversion loss is not due to an alteration of the catalytic active sites.