Catalytic Partial Oxidation of Bio Gas and Reforming of Pyrolysis Oil (Bio Oil) for an Autothermal Synthesis Gas Production and Conversion into Fuels

Executive Summary:
The BIOGO-for-Production project “Catalytic Partial Oxidation of Bio Gas and Reforming of Pyrolysis Oil (Bio Oil) for an Autothermal Synthesis Gas Production and Conversion into Fuels” aimed to create a fully...
integrated and comprehensive process for the production of biofuels using novel heterogeneous nanocatalysts and sustainable resources. This process was integrated with the enabling functions of innovative micro reactor technology developed in the project.

To improve process efficiency through intensification and thereby targeting some of the challenges Europe's petro-chemical industry is facing today, BIOGO exploited the special properties of nanocatalysts, underpinned by modelling, kinetic and in-situ studies. This 48 month long project combined the expertise of at the end 13 project partner organisations to design, develop and prepare highly advanced nanoscale catalysts at an industrially relevant scale, to develop and demonstrate a process that converts renewable bio-oils from waste, e.g. forest residues, and bio-gas to synthesis gas for subsequent catalytic transformation into biofuels and chemical platform products. The developed integrated process consists of the following consecutive steps: reforming of pyrolysis oil and biogas, further treatment of the generated syngas to adjust the carbon to hydrogen ratio, the synthesis of methanol from the adjusted syngas and finally the conversion of methanol to gasoline via dimethyl ether. For all these process steps, respective catalytic reactors were developed and scaled up to the dimensions required for the miniplant.

Key output of all this work has therefore been the engineering, construction and operation of the miniplant, which is installed in a so-called Ecotrainer®. This is a transportable, standardized modular infrastructure for the realization of chemical processes. Accompanying, a cost analysis, life cycle assessment, safety and REACH analyses were carried out to support the development and operation of the miniplant as well as to get the respective figures for the exploitation of the developed BIOGO process.

In addition to technical objectives, the project has placed a strong emphasis on dissemination of project results and the broad promotion of the benefits which can be derived from adoption of the developed novel nanocatalysts and processes. Thus, the list of about 137 dissemination activities comprises 30 scientific papers and 76 oral presentations at conferences and similar. Several PhD and undergraduate students have participated in the BIOGO project, gaining a high level of knowledge in the applied techniques and training for their careers as future researchers.

Exploitation of project results is essential and key outputs include four patent applications to protect the knowledge generated in the project. Six Key Exploitable Results (KER) were determined, under the following: The generation of detailed data by operating the miniplant builds the basis for further commercial exploitation of the novel process for gasoline production from renewable feedstock. The successful demonstration of the scaled-up gas-phase nano-cluster synthesis as well as of the continuously operated nano-particle synthesis process in the liquid phase offer further exploitation potential.

Project Context and Objectives:

The petro-chemical market in Europe faces a multitude of challenges at present: increasing competition and dependency from external sources; considerable cost and ecological pressures; supply of raw materials, their relative increase in cost; consumer demands; societal demands to reduce environmental impacts, improve sustainability and industrial safety. Industrial production of fuels must respond to these changing needs in order to satisfy its environmental, economic and societal responsibilities.

The petro-chemical industry, as one of the biggest global players in the energy sector, is especially called upon to discover innovative ways of providing novel, sustainable solutions. ‘Clean’ technologies are top of the agenda in order to combat pollution levels and the consumption of exhaustible resources. The radical improvements that ‘clean’ technologies would bring can only be achieved by a complete rethinking of production processes.
The BIOGO project contributes to this transformation of the production process that is required to realise these radical improvements. BIOGO focused on biofuels from sustainable sources. Specifically, the advancement of the nanocatalysts used in the synthesis of biofuels and innovating the reactor technology itself. BIOGO aimed at the development and demonstration of a miniplant including all reaction, separation and purification steps from bio-feedstock to hydrocarbon fuel. These activities supported the progress of the European Commission’s goal of maximising the contribution of nanotechnology to sustainable development in the energy sector.

The project incorporated seven technical work packages (WPs), each clearly structured to enable the project objectives to be achieved. These work packages are related to the single steps of the BIOGO process to produce bio fuels from pyrolysis oil and bio gas or to alternative routes (WP4, WP5). In these work packages, several aspects were investigated, i.e. development of new preparation routes and methods of incorporating nanocatalysts into innovative micro-structured reactor designs, enabling compact, integrated catalytic reactor systems that exploit fully the unique properties of nanocatalysts to improve process efficiency through intensification. Catalyst development was underpinned by modelling, kinetic and in-situ studies.

A sub-set of project partners was involved in each WP in order to fulfill its special tasks. Each WP was led by a project beneficiary with extensive experience within the specific technical area. This beneficiary assumed the responsibility of ensuring effective delivery of the WP tasks.

Work Package 1; Autothermal conversion of bio gas and bio oils to synthesis gas
The key objectives of WP1 were the development of coking resistant catalysts for reforming of both bio-oil and of bio-gas to syngas, the development of the respective reactors, fundamental investigation on molecular factors governing the activity and coking stability of catalysts in the reforming of bio fuels, and the development of poison insensitive catalysts for the adjustment of the gas composition.

Work Package 2; Conversion of syngas to methanol and DME
Within WP2, improved catalysts for methanol and DME production from syngas should be developed, which work at lower reaction pressure and which have higher tolerance to poisoning by impurities by following different catalyst design routes. Furthermore it was aimed to carry out catalyst poisoning studies with dedicated catalyst and to perform kinetic studies for providing scale up data for the reactor design.

Work Package 3; Conversion of methanol to hydrocarbons
Here, main objectives were exploring new methods of catalyst preparation in an effort to develop much more stable and active catalysts for the conversion of methanol to hydrocarbons, developing innovative zeolitic catalytic systems in the form of stable coatings on structured reactors and understanding the mechanism of coke formation over different catalytic systems in order to select efficient ways to extend overall catalyst lifetime.

Work Package 4; Conversion of syngas to higher linear alcohols
The objective of this work package was to provide another option for syngas utilization and possible contingency to WP2 and WP3 activities. Thus, it was aimed to develop nanocatalysts for improved conversion of syngas to higher alcohols and to determine catalyst formulations and process conditions for controlling the chain length aiming at a narrow length range which should allow direct use of the product as fuel additive.

Work Package 5; Direct upgrading of biooil into higher alcohols and hydrocarbon fuels with minimal hydrogen consumption
WP5 was aimed at developments in two directions: The design of advanced thermochemical processes for the conversion of a selected bio-feedstock to bio-oil and the development of suited catalysts and
reactors for the direct upgrading of bio-oil into higher alcohols and hydrocarbon fuels including kinetic investigations for scale up assessment.

Work Package 6; System Integration and life cycle assessment (LCA)

Also WP6 was concerned with two different main objectives. On the one hand, the integrated BIOGO process should be designed, followed by the engineering, set-up and operation of the miniplant. On the other hand, accompanying a cost analysis, life cycle assessment, safety and REACH analyses should be carried out to support the development and operation of the miniplant as well as to get the respective figures for the exploitation of the developed BIOGO process.

Work Package 7; Scaling up and optimised production

The objective of WP7 was the scale up of selected catalyst preparation and deposition processes, based on the findings from WP1-5. This concerns both the development of gas-phase nano-cluster synthesis and deposition processes and of the development of a continuously operated nano-particle synthesis process in the liquid phase.

The technical work packages are supplemented by two work packages dealing with the dissemination and exploitation of the project results and managing the project.

The final two BIOGO WPs involved supporting activities rather than technical activities. WP8 'Impact, dissemination, exploitation' was concerned with communicating the BIOGO results to a broad audience; both technical and non-technical. Activities encompassed both a wide range of presentations and publications to the scientific community but also making project information available in a publicly accessible format. Project partners also contributed to eight Workshops on different aspects related to the BIOGO project to assist with training future scientists. WP9 was concerned with overall Project Management.

Project Results:

WP1: Catalysts for the conversion of bio gas and bio oils to synthesis gas

Granulated catalysts using Ni as active phase on doped Mg-Al mixed oxides, Ca-Ti perovskite and Mn-Cr spinel type supports and doped Ni-Ru type active entities were prepared and tested in model reactions relevant for the reforming of BioGO feedstock (The University of Warwick (UOW) and Boreskov Institute of Catalysis (BIC)) and characterized in detail (BIC and UOW). Ethanol, acetone and glycerol steam reforming were deemed suitable model reaction with most of the required catalytic functionality (C-H and C-C bond cleavage, carbon removal upon carbon oxide release and hydrogen release) being probed by these reactions. Key objectives like avoidance of rare earth constituents and decreasing use of noble metals were met by catalyst candidates issued from the initial development process. The most promising reforming catalysts formulations were retained for further testing in membrane reactors (reported below) and development of structured catalysts, e.g. reforming catalysts supported on foam substrates.

Catalyst formulations origination from initial screening gave guidance on the focus of the theory assisted further catalyst development (Tyndall National Institute, University College Cork (Tyndall-UCC)). Goal of the related first principles simulations (catalyst properties and prevailing mechanisms in biogas to synthesis gas conversion) was in-silico screening of potential new catalyst compositions, based on metal-modified metal oxides, for C-H bond activation and methane oxidation. Density functional theory (DFT) studies covered metal oxides modified with Pt, Ni and Cu metal, ranging from single dispersed metal atoms to sub-nm clusters of the metals, and examined (1) the structure of the metal-modified oxides, (2) the thermodynamics of methane molecular and dissociative adsorption, (3) energy barriers for C-H bond breaking and (4) energies and barriers of the oxygen vacancy and spillover processes. Simulations reveal
reducible metal oxides as suitable supports for small (sub-nm) metal clusters decorating the support in a dispersed form. The adsorption energy of dissociated methane on metal-support systems served as descriptor for the C-H bond activation. Oxygen vacancy formation was used as descriptor for spillover on small metal clusters (above 10 atoms the enthalpy of metal oxide formation appears to also correlate). Results suggested Ni-Cr2O3, Cu-Cr2O3, Ni-TiO2 or Ni-CeO2 as candidate catalysts for the activation of C-H bond in methane that also being able to promote oxygen spillover. Theoretical guidance impacted directly on UOW catalyst choice for mechanistic studies in task 1.5.

A joint activity concerned the optimization of catalysts using cluster beam deposition of Ni (Teer Coatings Ltd (TCL)) on custom supports (UOW) tailored to limit handling issues during vacuum deposition. Unfortunately, Ni loadings remained low until commissioning the new cluster source design at late stage in the project and the MgO-Al2O3 custom support turned out to stabilize effectively large Ni aggregates, but being especially unfavorable in combination with small Ni clusters specifically made by the cluster beam techniques. Therefore, low the activity established in dry reforming tests at atmospheric pressure (UOW) is explained by special circumstances. Performance of structured catalysts in reforming bio-fuels to syngas was explored at lab and pilot-scale using specially designed reactors and installations allowing broad tuning of operational parameters (BIC). Effects of the nature of nanocomposite active component comprised of Ru+Ni nanoparticles on bulk/alumina-supported perovskite or Mn-Cr-O spinel, type of substrate (Ni-Al alloy and SiC(Al2O3))/Al-Si-O, Ni-Al/C foam substrates, Fecralloy microchannel plates or gauzes protected by thin corundum layer, type of fuel (natural gas, ethanol, acetone, ethyl acetate, glycerol), feed composition and temperature on yield of syngas/byproducts and performance stability are considered. The best performance in real feeds lets syngas yield approach equilibrium at short contact times without any heat/mass transfer effects. High thermochemical stability of the catalyst on heat-conducting microchannel substrates is demonstrated. Oxygen addition to the feed in optimized amounts suppresses coking and stable performance is achieved even for the case of such reactive fuel as glycerol or turpentine oil only slightly affecting syngas yield.

Self-supported mixed ionic-electronic conductive BSCFO perovskite-type membranes (UOW) and Ni-Al foam supported membranes (BIC) with three layers (perovskite-fluorite nanocomposites layer, thin dense layer: Ce0.9Gd0.1O1.95 + MnFe2O4, porous layers: LaNi0.9Pt0.1O3/Pr0.3Ce0.35Zr0.35O2-x) were prepared, characterized and examined in oxygen permeation and oxidative reforming of methane as a representative of biogas. Enhanced oxygen permeation influx was achieved over BSCFO perovskite-type membrane based on flow synthesis. Ni-Al foam supported membrane exhibited stable performance in partial oxidation of methane. The mathematical modelling of the methane partial oxidation process in the catalytic membrane reactor find the process (temperature, gas flow rates, etc.) and membrane (pore diameter of porous layer, thickness of porous layer) parameters corresponding to highest methane conversion and syngas selectivity.

Coupling exothermal partial oxidation of bio-gas to endothermic steam reforming of bio-oil was also studied. Catalysts with uniform dispersion being resistant to sintering and coke formation were developed. Laboratory reactors were developed and manufactured (Fraunhofer ICT-IMM). Gained information served in the development of reactors for the miniplant which will comprise the whole BIOGO process. SPI identified task 1.4 in the most suitable biomass type for the advanced thermochemical conversion process in BIOGO suggesting suitable lignocellulosic biomass sources for bio-oil production either by pyrolysis or hydrothermal liquefaction (HTL). Bio-oil yields, carbon recovery and energy recovery from several feedstocks were compared for HTL and pyrolysis processes with data gathered from a literature.
DFT calculations served to investigate the activation of methane and dissociation to surface bound CH3 and H on a range of metal oxide based catalysts (MgO, Al2O3 La2O3 as non-reducible, cation doped CeO2 as reducible and TiO2, CeO2, Cr2O3 carrying metal clusters as modified metal oxides). Activation barriers for the breaking of the first C-H bond in doped CeO2 show that the barrier can be reduced to as low as 0.85 eV compared to 1.45 eV on CeO2 (111). The origins of this lie partly in surface distortions due to the dopant and charge compensating oxygen vacancies. These allow for substantial surface relaxations during C-H activation as well as enhancing reducibility. However, there is no clear correlation between reducibility and C-H activation. Reduction energies and C-H activation barriers are much larger on metal-modified non-reducible metal oxides compared to reducible oxides making the latter more favorable.

Exploring 1 to 11 atoms metal cluster models on the reducible oxide supports shows reducibility to depend on the metal and the support in addition to the size of the metal cluster. Reducibility is at best slightly enhanced over the bare support while activation barriers for C-H dissociation as low as 0.34 eV are found. Key point in lowering the activation barrier is the ability of the metal-oxide system to stabilize the transition state at the metal. Partial oxidation of methane to syngas on metal cluster modified CeO2 (111) surfaces was also investigated. Metal clusters lower the activation energies for methane dissociation compared to unmodified CeO2, thus promoting methane dissociation. The dissociation products will migrate to the oxide supports where the dehydrogenation of the CHx species to syngas will take place, although our results suggest that this may shift the limiting step to the dehydrogenation of the CH2 intermediate which, for the example of Zn-CeO2, can actually desorb as formaldehyde. This indicates that the purpose of the metal clusters and doping is to enhance the initial activation of methane while the reducible oxide support will carry out the catalysis from CHx to CO + H2. UOW performed in task 1.5.1 mechanistic studies with TAP approach to complement predictions from theory. Reducibility and activity in the reduction of CO2 to CO were studied to monitor the steps closing the catalytic cycle. Good qualitative agreement was observed for the catalyst suggested according to theory predictions. Mechanistic work at BIC involved among other techniques SSITKA and showed largely good agreement with expectations according to theory results.

Three material systems were designed and explored as candidates for sulphur-tolerant WGS catalysts, namely Ni (and Ni+Ru) on reducible supports (CeO2, fluorite Pr-Ce-Zr-O and spinel Mn-Cr-O oxides) (BIC), alumina–supported Mo carbides (UOW) and core-shell CuAl on CuAlO catalysts prepared mechnochemical alloying followed by hydrothermal treatment (BIC). Thoroughly characterization (XRD, SEM, partly, also NMR and XPS) and tests in WGS using realistic feeds allowed optimization of composition and preparation methodology for high activity and stability. The Mo carbide system was found to require noble metal doping and was the active phase subject of facile oxidation, thus, the option was not followed further. The catalytic activity for the Cu/Al/AlO catalyst was proportional to the content of the Cu4Al9 phase Al-leaching under mild conditions increased the catalytic activity and observed reaction rates were close to those over a CuZnAl reference catalyst. Experiments using Ni/CeO2 and Cu/Al/AlO as two potential active components were carried out with two types of reactors (microchannel and fixed bed configuration). Methanation was shown to be absent even for realistic feeds. WGS performance data was subject of mathematical modelling based on a formal kinetic approach with a proper regard for the thermodynamic limitations. Good description of experimental results and estimation of kinetic parameters were achieved. However, the chemical proximity of the Cu/Al/AlO catalyst to the present sulphur-sensitive reference catalyst may limit the suitability in the intended use. On the other hand, the Ni-ceria system made use ceria as model for a reducible support and a direct use of rare earth material is outside the
scope of the project. Thus a substitution by other reducible supports was carried out. Ni/(Ni+Ru) loaded on fluorite Pr-Ce-Zr-O and spinel Mn-Cr-O oxides with a high oxygen mobility and reactivity operating via redox type mechanism were finally developed for water gas shift (WGS) applications.

ICT-IMM was leading in task 1.6.3 on the investigation of two alternative processes for the purification of raw syngas produced by the reforming of pyrolysis oil. A catalytic syngas purification process was selected for integration into the miniplant compiling the whole process developed within the BIOGO project. Detailed Engineering was carried out by a subcontractor and the respective documents were provided to ICT-IMM. The syngas purification unit will be realised and installed as part of the miniplant.

WP2: Catalysts for the conversion of syngas to methanol and DME

Catalysts developed in WP2 were prepared by various routes such as the formation of ZnO/Cr2O3 based catalysts by using either co-precipitation (RUB) or alternatively the hydrotalcite route (UOW), the formation of nanocrystalline Cu/ZnO formulations by co-precipitation (Brunel), the formation of Ni-, Co-, and Cr-doped Zn-containing magnetic oxide nanoparticles stabilized by polyphenylquinoxaline and hyperbranched pyridylphenylene polymer, and the synthesis of Zn- and Zn-Cr-containing catalysts based on magnetic silica (Fe3O4-SiO2) as support (INEOS).

In the case of the ZnO/Cr2O3 catalyst obtained by co-precipitation (RUB), the catalyst with a Zn/Cr ratio of 65:35 exhibits the highest methanol productivity. At ratios from 65:35 to 50:50, characterization results showed a lower amount of bulk ZnO phase than expected suggesting the existence of a non-stoichiometric Zn-Cr spinel. Further investigation based on DFT calculations (Tyndall UCC) identified the oxygen vacancies prevailing in the non-stoichiometric Zn/Cr spinel as the active sites for CO hydrogenation. A high degree of non-stoichiometry caused by dissolution of Zn2+ into the Zn/Cr spinel lattice (Fehler! Ungültiger Eigenverweis auf Textmarke.(a)) reduces the energy required for the formation of oxygen vacancies and therefore, improves the performance of the catalyst. This amorphous ZnO layer is the active region of the catalyst, which adsorbs CO and H2 (Fehler! Ungültiger Eigenverweis auf Textmarke.(b)). Furthermore, thermal pre-treatment in a reducing or inert gas atmosphere can also significantly improve the activity of ZnO/Cr2O3 catalyst, due to the beneficial effect for the formation of oxygen vacancies (RUB).

Fig. 2 (a): Proposed structure of the active ZnO/CrOx spinel methanol synthesis catalyst (b): Atomic structure of H and CO adsorption at (left) stoichiometric spinel ZnCr2O4 and (right) the active catalyst.

At UOW a flow synthesis route for ZnO/Cr2O3 based catalysts via hydrotalcites was developed. Various parameters such as the development of the pH, washing and drying steps, and the temperature treatment were optimized with the aim to improve the catalytic performance and to increase the production rate. Catalysts prepared with this setup were used for kinetic studies and for the miniplant. In the latter case 1.7 kg of a doped ZnO/Cr2O3 were handed over to ICT-IMM. With the aim to push the thermodynamic equilibrium of the methanol synthesis from syngas to the product side by the formation of DME, copper/zinc catalysts were incorporated into an alumina matrix (BRUNEL). In micro-structured reactors, these catalysts showed a better productivity compared to the corresponding MeOH catalysts (ICT-IMM). By DRIFTS studies various species such as carbonate, bicarbonate, formate, and methoxy were identified on the catalyst under reaction conditions (BRUNEL). It was concluded that the formation of the formate species is the key step. At higher temperatures, the formation of carbonate species is favored explaining the experimentally observed selectivity towards CO2 under these conditions. Selectivity towards MeOH and DME were explained by the presence of a methoxy species.
At INEOS the catalysts stabilised by polymer matrices were synthesized by thermal decomposition of Zn and doping metal acetylacetonates in the reaction solution of preformed magnetite NPs. It was demonstrated that Zn and a doping metal are incorporated in the magnetite NP structure. The catalyst testing carried out by TTU, demonstrated the dependence of the catalytic activity on the doping metal content and on the stabilizing polymer. Repeat experiments carried out after magnetic separation of catalysts from the reaction mixture showed excellent catalyst stability even after five consecutive catalytic runs.

Further catalysts developed by INEOS were based on doped magnetic silica. In this case, iron oxide NPs were located in mesoporous silica pores and the magnetite structure remained virtually unchanged despite the incorporation of Zn and Cr. It was found that the Zn and Cr species were intermixed within the magnetite structure as shown in Fig. 3. The catalytic experiments at TTU showed an improved catalytic performance of these catalysts compared to catalysts stabilised by polymeric matrix. The best catalytic activity was obtained for the Zn-Cr-containing magnetic catalyst prepared with 1 wt.% of Zn and Cr each. This activity surpassed that of the commercial catalyst by a factor of 79. The easy magnetic recovery, robust synthetic procedure allowing easy scaling up, and high catalytic activity make these catalysts promising for practical applications.

Fig. 3 EDS maps of Si (a), Fe (b), Si and Fe superposition (c), Zn (d), Cr (e), and superposition of all maps (except for oxygen) (f) for Zn-Cr-Fe3O4-SiO2.

Complementary to the catalyst development, Tyndall-UCC undertook DFT simulations of catalysts based on ZnO and Cr2O3, focusing on CO and H2 adsorption, CO hydrogenation and H2S adsorption as model reactions for methanol synthesis and catalyst poisoning. As a result, the formation of oxygen vacancies in Cr2O3 and ZnO was found to be more favourable in the presence of dopants such as Ni, La, Fe and Zr, i.e. these dopants facilitated the reduction process to take place at lower temperatures. The adsorption of CO was favoured on doped surfaces. The stability of CO/HCO and H2CO intermediates was also important. Finally, Tyndall-UCC used H2S as a model molecule for catalyst poisoning. Generally, sulphur binds to a surface Cr site, except for Fe doping which forms a Fe-S bond. Dissociation of H2S to HS and then to S has low barriers and is favourable, except for Fe which promotes formation of S that can be removed. The dopants also promote loss of H2O rather than H2.

WP3: Catalysts for the conversion of methanol to Hydrocarbons

Several catalysts prepared by C-Tech, INEOS, TTU, and UoW were compared in MTH reaction at the optimal reaction conditions for each catalyst.

C-Tech has prepared a series of supported catalysts from titanium isopropoxide by a reverse micelle phase sol gel method. The synthesis sol was doped with Co and Fe precursors to get different metal/Ti ratios in the catalysts. INEOS developed hierarchical H-ZSM-5 zeolites containing both iron oxide and nickel oxide nanoparticles (NPs). Modifying the iron oxide (magnetite, Fe3O4) amounts, INEOS was able to control the catalyst activity and the product distribution in the MTH process. At the medium Fe3O4 loading, the major fraction was C9-C11 hydrocarbons (gasoline fraction). At the higher Fe3O4 loading, the C1-C4 hydrocarbons prevail in the reaction mixture, while at the lowest magnetite loading the major component was the C5-C8 hydrocarbons. Addition of Ni species to Fe3O4-ZSM-5 leads to the formation of mixed Ni oxides (NiO/Ni2O3) positioned either on top or next to Fe3O4 NPs (Fig. 4).

Fig. 4 High resolution TEM image (left), superposition of Ni and Fe EDS maps (center) and a schematic representation of MTH for Fe3O4-ZSM-5-Ni.
The catalyst properties have been studied by TTU. It was demonstrated that the above modification leads to a significant improvement of the catalyst stability due to diminishing coke formation and disordering of the coke formed. The incorporation of Ni oxide species also leads to a higher catalyst activity (9.3 g-methanol/g-catalyst/h) and an improved selectivity to the C5-C8 (11.3%) and C9-C11 hydrocarbons (23.6%), making these zeolites highly promising for industrial applications.

UoW developed a series of H-ZSM-5 coatings with different Si/Al ratios (20-60) and the mean crystal size ranging from 0.8 to 2.6 μm on AISI-304 stainless steel substrates. The coatings obtained have MFI structure without the presence of other phases. A higher Si/Al ratio in the initial sol gives larger mean crystal size. A higher H2O/Si ratio gave larger crystal sizes with a wide crystal size distribution. Continuous coatings were obtained with an average coating thickness of 14 μm. SEM study confirmed that the coating is highly uniform and contains no uncoated areas (Fig. 5). An increased catalyst loading up to 0.09 kg·m-2 was achieved by repeated synthesis resulting in a coating thickness of 60 μm.

The H-ZSM-5 coating with a Si/Al ratio of 50 provided the maximum yield of gasoline range hydrocarbons. The C8-11 selectivity increases to 18.6% at a pressure of 4 bar and a residence time of 3 s. Any further increase in residence time does not change the selectivity pattern. While the C8-C11 selectivity over the H-ZSM-5 coatings is slightly lower than over the powder sample with the same composition, the amount of undesired aromatic fraction was considerably reduced to 9.6% over the coatings as compared to 19.2% over the pellets. This illustrates that the application of thin zeolitic layers gives considerable potential for tailoring and optimizing the catalytic performance in the MTH reaction.

It has been found that ion-exchange with Ca provides controllable Ca exchange ratio in Ca-H-ZSM-5 catalyst. The resulting catalysts exhibited similar structural and morphological patterns to the parent H-ZSM-5. By increasing the Ca content, the catalyst lifetime and selectivity to C8-C11 hydrocarbons were considerably improved. Ca-ZSM-5 catalysts with an exchange ratio in the range of 0.15-0.20 was found to be the most stable in the MTH reaction, maintaining an initial conversion level for over 7 h and having the highest selectivity of ca. 46% to C8-C11 gasoline fraction due to the presence of weak Brønsted acidity.

Hierarchical structures were introduced to H-ZSM-5 with Si/Al ratio at 50 by a desilication treatment. Experimental evidences showed that the performance of mesoporous H-ZSM-5 catalysts was improved by regulating porous network. The presence of mesopores introduced by desilication with an alkaline solution enhanced effective diffusivity for larger hydrocarbons. The average mesopore diameter and volume as well as the surface area increased with increasing the concentration of the alkaline solution. Low desilication efficiency was observed from a very concentrated alkaline solution due to a massive dissolution of ZSM-5 catalyst and the formation of larger macropores. While the selectivity to C8-C11 hydrocarbons did not change, a higher turnover number for C8-C11 fraction was observed over the desilicated samples. The presence of the structural template in the alkaline solution reduced the mesopore diameter and preserved the microporous ZSM-5 structure. The longest lifetime and the highest TON for C8-C11 were found with a mean mesopore size of 3.1 nm and a crystal size of 2.4 μm. Meso-microporous H-ZSM-5 coating is observed to have similar textual properties as the corresponding H-ZSM-5 pelleted catalyst. The selectivity to gasoline fraction and the catalyst lifetime improved over H-ZSM-5 coatings as compared to pelleted catalysts. The meso-microporous H-ZSM-5 coatings with a thickness of 30 μm show a 5-fold increase in catalyst lifetime and two times higher selectivity to C8-C11 fraction compared to the microporous coating with the same thickness and composition. The highest selectivity to gasoline range hydrocarbons of 18.5% with a minimum formation of aromatics by-products was obtained in the MTH reaction at a temperature of 370 oC at a pressure of 4 bar and a WHSV of 10 h-1.

WP4: Catalysts for the conversion of syngas to higher linear alcohols (RUB)
Alkali-modified ZnO/Cr2O3 catalysts are of great interest for higher alcohol synthesis (HAS) from biomass-derived syngas because of the relatively high tolerance against sulphur poisoning compared to the conventional Cu-based catalysts.

Within this work package RUB aimed at optimizing the preparation procedures and the reaction conditions for modified ZnO/Cr2O3 catalysts. Initially, alkali metals were found to have a promising potential to promote the ZnO/Cr2O3 catalysts for HAS. Evidently, the promoting effect of alkali metals stems from the decrease of the surface acidity and the stabilization of the key intermediates for HAS. Alkali-doped ZnO/Cr2O3 catalysts contain ZnO and ZnCr2O4 as the dominating phases. A high alkali loading leads to an increased amount of adverse chromate species. Alkali-doped catalysts exhibit a decrease in specific surface area with increasing alkali loading. For the same loading the specific surface area of the alkali-doped catalysts follows the trend Cs>K>Na. Moreover, the alkali precursor used for wet chemical impregnation also influences the performance of the catalyst in HAS. Here, the impregnation with alkali carbonates showed a promising potential in higher alcohol synthesis.

Additionally, the morphology and the phase composition are closely related to the thermal treatment after the preparation by means of impregnation. Thermal post-treatment of the alkali-doped catalysts in air leads to a higher selectivity towards higher alcohols by suppressing methanol formation and enhancing the formation of higher alcohols. The reaction conditions are also considered to have a significant influence on the performance of the modified catalysts. Indeed, for alkali-doped catalysts, the overall CO conversion increases with increasing temperature from 280 °C to 320 °C indicating that the main reactions during HAS are still under kinetic control. With increasing temperature, hydrocarbon selectivity increases at the expense of methanol selectivity. Selectivity to higher alcohol does not change significantly. Higher temperature favours the formation of higher alcohols and hydrocarbons with short carbon chain length. It needs to be noted that the presence of K or Na leads to a decrease in CO conversion compared to the unpromoted catalyst, while doping with Cs seems to improve the overall activity of the catalyst. The highest productivity of higher alcohols was achieved with the Cs-doped catalyst with a nominal loading of 7 wt%. A high H2:CO ratio was found to favor the formation of methanol, while a low H2:CO ratio is more beneficial for higher alcohol synthesis. With increasing pressure, hydrocarbon selectivity decreases, while the selectivity to methanol and higher alcohol increases. In contrast to temperature, high pressure favors the formation of higher alcohols with a long carbon chain. Yields of higher alcohols exhibit an exponential increase with contact time indicating that the formation of higher alcohols is via a chain-growth mechanism. However, the formation rate of hydrocarbons is larger than that of methanol and higher alcohols. Therefore, a longer contact time cannot improve the selectivity to higher alcohols.

Tyndall-UCC undertook DFT simulations of catalysts for synthesis of higher alcohols. The main question to understand is the role of the alkali metal promoters on production of C2 and higher alcohols. Fig. 6 summarises the results obtained from this study. We first examined the stability of intermediates along the pathway for hydrogenation of CO and for ZnO and Zr-doped ZnO (as model catalysts), we find that the methoxy intermediate is the most stable (Fig. 6 (a), (b)).

Fig. 6 (a): Atomic structure of stable intermediates of CO hydrogenation on ZnO-based model catalysts. (b): Atomic structure of stable intermediates of CO hydrogenation on Cr-ZnO-based model catalysts. (c): Atomic structure of adsorbed formaldehyde species and glycolaldehyde on alkali doped ZnO based model catalysts (d): Atomic structure of H2S adsorbed on ZnO, Cr-ZnO and alkali metal-Cr-ZnO model catalysts.

By incorporating alkali metals, through the examples of Na and K, which tend to migrate out of the surface
layer due to their large ionic radius compared to Zn, we find that the formaldehyde-like OCH2 intermediate is the most stable, as shown in Fig. 6 (a), (b). The condensation of two formaldehyde molecules to glycolaldehyde then permits formation of both a C-C and an O-H bond and we find that two OCH2 species are stable on alkali-doped (Cr)ZnO, by ca. 1.50 eV, Fig. 6 (c). There is a further gain of ca. 1 eV when these condense to form glycolaldehyde. Subsequent reactions are more complex to unravel but these results indicate the effect of the alkali on promoting the stability of OCH2 species which further condense. Finally, in Fig. 6 (d) we show atomic structures for H2S adsorbed on ZnO, Cr-ZnO and alkali doped Cr-ZnO. They key finding here is that while ZnO and Cr-ZnO promote adsorption and dissociation of H2S to HS and H, this process turns out to be endothermic on alkali-doped Cr-ZnO which means that the adsorption and dissociation (surface poisoning) of H2S is inhibited which appears to be a further promoting effect of alkali doping.

WP5: Catalysts for the direct upgrading of bio oil into higher alcohols and hydrocarbon fuels

Concerns about the depletion of fossil fuel reserves, the impact of anthropogenic CO2 emissions, and increasing energy demands have encouraged the exploration of new catalytic procedures for converting cellulose biomass into valuable platform chemicals and renewable fuel components. The development of these sustainable catalytic transformations could potentially provide a long-term solution to the industrial dependence on fossil carbon. Cellulose is the world’s largest organic raw material resource. It has been estimated that 1011–1012 tons of cellulose are photosynthesized annually. Its quickly renewable resources can provide continuous production of chemicals and second-generation biofuels on a large scale.

Being rich in hydroxyl groups, cellulose conversion to polyols is one of the most favored routes to cellulose utilization. Cellulose is hydrolyzed into glucose which is then hydrogenated in the presence of catalysts to form sorbitol, mannitol and other C5 - C2 polyols. The cellulose conversion process was carried out under the following conditions: temperature of 245 0C, hydrogen partial pressure of 60 bar, propeller stirrer speed of 600 rpm, reaction time of 5 min. In a typical experiment 30 ml distilled water, microcrystalline cellulose and catalyst (0.042 mmol Ru, 1 g cellulose) were loaded in a steel reactor (50 cm3, Parr Instrument, USA). Then the reactor was thrice flushed with H2 to remove air. The mixture was heated and stirred at 100 rpm. After achieving 245 0C stirrer speed was increased up to 600 rpm. This moment was chosen as the reaction starting time. At the end of the experiment the catalyst and non-hydrolyzed cellulose were filtered. The conversion of cellulose (X) was calculated as the ratio of the non-hydrolyzed cellulose mass to its initial amount. The concentrations of the main products were determined by HPLC. The selectivity and yield of the reaction products were calculated on the basis of the values obtained.

The catalysts were prepared by impregnation of MN-100 with Ru(OH)Cl3, H2[PtCl6], Na2[PdCl4], H[AuCl4], Fe(Ac)3, Ni(Ac) in a solutions containing THF, methanol and distilled water. The use of 1.0 % Ru/HPS MN 270 catalyst in hydrolytic hydrogenation of cellulose can increase the total yield of sorbitol and mannitol in an average of two times compared with the commercial carbon-supported catalyst. Also the increase of cellulose conversion and selectivity to polyols C5-C4 is observed. At the almost equal X values the hexitol yield increased by 10%. At the same time, for all catalysts, the yields of lower polyols and methane are high. In the experiments without a catalyst, the brown solutions containing the products of glucose caramelization were also obtained. The yield value in such experiments decreased to 55%. This fact proves that in the presence of the catalyst both hydrolysis and hydrogenolysis of cellulose take place, which is not the case, when the catalyst is absent. The best results were obtained for 1% Ru/MN-270. This catalyst demonstrates the highest hexitol yield and the lowest yield of other products. Most likely the high efficiency of this catalyst is due to combination of the high specific surface area, narrow pore size
distribution, and small, monodisperse Ru nanoparticles.

Development of up-scaled catalyst production:

Two approaches for the development of up-scaled catalyst production were followed:
1) making catalysts in vacuum via magnetron sputtering technique, and deposit on to powders or directly on to micro-channel plates
2) making catalysts with wet-chemistry technique, and screen-printing onto micro-channel plates

Magnetron sputtering method (TCL)

Nanoparticles that are produced by a gas-condensation process in vacuum, have many advantages compared to those prepared via a conventional wet-chemistry route. Inherently these gas phase nanoparticles are very clean and pure, because there is no contamination from ligands, for example, which are often essential in other catalyst preparation methods, like precipitation or impregnation. As such, there is no need to carry out calcination processes afterwards to remove such organic materials, which could be a critical issue for some nanoparticle materials that are sensitive to high temperature.

The majority of the nanoparticles produced by magnetron sputtering are electrically charged, and this has made it convenient to employ a Time-of-Flight mass filter to select the particle size. Another important advantage is that nanoparticles of almost any alloy composition can be made by magnetron sputtering. For example, the alloy PtₓY is known to be active and stable for the oxygen reduction reaction in low-temperature fuel cells, but its synthesis in nano-particulate form has proved challenging. A research group in Denmark has demonstrated the synthesis, characterization and catalyst testing of model PtₓY nanoparticles prepared through the gas-aggregation technique, and showed enhanced activity of PtₓY over elemental platinum.

The equipment that can produce nanoparticles (or clusters) is called ‘Cluster-beam Deposition system’, which was originally developed at a research group in Birmingham University. It had a very limited cluster production rate, and was only used for research purpose. In 2006, TCL made a decision to make an investment, and build a team to develop this technology in order to improve its production throughput and make it suitable for industrial applications. Ever since, TCL has involved in a series of collaboration projects either funded by UK government or by EU, to investigate and develop this cluster-beam technology. By the time that BioGO project started, TCL had already increased the production rate of clusters by a factor of 10 ~ 50 times, and became a leading group in this field.

However, even with this improved production rate at 20 nA (or ~ 0.1 mg/hr), it would take at least 5 minutes to finish the deposition of clusters on a small 60 mm X 15 mm micro-channel plate, and it’s estimated the cost would be around €10 per plate. In a single mini-plant thousands of micro-channel plates will be needed, and it would take very long time to finish deposition for all of these plates, and the cost would run up to tens of thousands euros for coating alone. This is not economically viable. Therefore the key task for TCL in the BioGO project is to improve the production rate further, by 10 to 100 times; and reduce the catalyst deposition cost to a level of below €0.1 per plate.

We have identified two ways to improve the production rate significantly. One way is to study the physics inside the cluster source, and create the conditions for much more efficient cluster growth. And the other is to design an automated micro-plate handling system to greatly minimise the time wasted to transfer the parts in and out of the vacuum system.

Using a commercial Computational Fluid Dynamics (CFD) software package, we carried out the aerodynamic modelling inside the condensation chamber where the clusters have been formed. The vacuum pressure is 50 Pa, which is just in the transition regime from a continuous flow to a molecular flow. Only sputtering gas argon is considered in the simulation. The simulation results has indicated that a
conical narrow chamber with rounded edge is much more favourable for gas velocity distribution spatially and for the temperature distribution. Our assumption is that such favourable conditions would encourage more of the growth of the clusters and transportation of clusters out of the condensation chamber.

Fig. 7 a) Simulation results; (b) the upgraded Cluster-beam system.

Based on the modelling results, we completely re-designed the condensation chamber, and all the parts surrounded it. The layout of the whole system has also been changed, in order to integrate the new automated substrate handling system. The electrical wiring, and the control software have been upgraded. The majority of the upgrade was finished in the early 2017, and then we started working on the system and investigate the performance of the new cluster source.

The initial testing results was very encouraging, when the argon flow rate is 150 sccm, the mass flux produced by the upgraded system is about 20 mg/hr, while it was 0.1 mg/hr before upgrade. To the number into context, it means it would take only a few seconds to finish deposition clusters on a small micro-channel plate (60 mm X 15 mm), and the cost would be well below the target of €0.1 per plate. This has successfully demonstrated scaled-up production of catalyst for a mini-plant.

Although a much higher mass flux has been achieved, we also encountered a problem that the portion of cluster ionised is very little. The majority of the clusters produced in this way are electrically neutral, which made it impossible to focus the cluster beam using ion optics, and carry out mass filtering to control the cluster size. To overcome this issue, we have tried both electron gun and UV lamp to ionise the clusters with a hope to create enough amount of cluster ions. However, both methods didn’t make a positive change to the number of electrically charged clusters.

The current system was designed and built around the presumption that a substantial amount of the clusters are positively charged. For the next step, beyond the scope of this BioGO project, we think we have to accept the fact that the clusters are electrically neutral for high-throughput cluster-beam system, and we have to modify the system layout further so that the high flux of neutral clusters can be deposited onto micro-channel plates.

Scale-up of nano-particle synthesis in continuous flow (ICT-IMM)

Based on the experience for catalytic materials for the conversion of syngas to methanol, gained in the other work packages in this project, Cu/ZnO was chosen as the most suitable system for a scaled up production with a cost efficient realization.

In contrast to the common way to synthesize this type of catalyst, were copper and zinc are co precipitated, the developed process should be able to produce both components individually in the nano scale, binding them together afterwards. In this way it is possible to tune the material properties of catalyst (copper) and co catalyst (zinc) separately.

To increase the number of active sides on a catalytic substrate, it is necessary to increase the surface of this material. Thus it is beneficial to produce the catalytic components in a defined size, in the nano scale. Wet-chemistry offers promising methods to be able produce solid materials of sizes way below 20 nm and a narrow size distribution. Because of that Fraunhofer ICT-IMM chose to develop wet-chemical syntheses for both components of the aspired catalyst.

Process description

The main catalytic ingredient in the Cu/ZnO system is the metallic copper. To produce copper nanoparticles of evanescent size, the two-phase reduction method is the most suitable. Fraunhofer ICT-IMM was able to utilize this method to produce copper particles as small as 3 nm. Due to the usage of
micromixers and flow chemical devices, we were able to transfer the forecited synthesis into a continuous approach.

Zinc oxide, as co catalyst material, was aimed at in an individual process. Because of above-mentioned reasons, this ingredient was achieved in a wet-chemical approach as well. Other than for copper, it showed to be advantageous to not produce the final ZnO in one step, but to produce a precursor first. For the developed process a zinc oxalate gel was said interstage product, since it shows some properties which make it feasible for uses in a flow system. The gel is capable of flowing and thus pumpable and show little to none separation from solvent.

Both particle solutions can be mixed together directly after synthesis, without further purification. No transformation of one of the materials occurs, when brought together, so that the two particles species can be blended completely homogeneous. Only by addition of a precipitating agent for both particle species a breakup of the reaction media can be induced. This implies that the process could be upgraded further, to introduce even more compounds of beneficial effects into the catalyst system. After precipitating, the copper nanoparticles and the zinc precursor can as solids easily be separated from the liquid phase. This step removes all unwanted side products, excess reactants, surfactants and solvents. A following heat treatment for drying and calcining leads to the final catalyst.

Throughput and costs
The transfer of the synthesis in a micro flow system involves a couple of advantages. On the chemical side it results in a more reproducible process outcome and less deviations of the aimed particle size. From the perspective of process development, a continuous flow system offer the possibility to ramp up the throughput more easily and to achieve a wider process window, which lets more room for optimization. In the beginning of development the typical outcome of one synthesis were 10 g of catalyst per hour. Due to transfer into flow and scaling up of the set up equipment an output of 50 g/h could be achieved. The system was further optimized by using the better heat and mass transfer in micro fluidics. So the reaction time could be drastic reduced compared to batch. Thus, the throughput of the upscaled plant was increased further to 200 g/h of Cu/ZnO. At the same time the product concentration and the chemical economy could be raised. In the early phase of development the process yielded in lower than 1 %-wt of catalyst in the reaction media. This could be maximized to 4%-wt. The usage of reactants was reduced and only recommended solvents are used in the final process. This also reduced the price per kg of catalyst made by means of this process from 1.500 € to 340 €, based on typical prices for laboratory chemicals.

Performance
The synthesized catalyst was coated onto a microplate reactor and tested for its performance to convert syngas to methanol. The results are very promising. The productivity reached 190 g_MeOH/(kg_Cu*h) and the catalyst lasted over 100 h without a major decrease of it activity. These conditions make it very comparable to other Cu/ZnO systems.

Fig. 8 Conversion X of syngas (CO) and selectivity S for methanol (MeOH), dimethylether (DME), carbon dioxide (CO2) and methane (CH4) of the developed Cu/ZnO catalyst at different temperatures. Fig. 9 Conversion X of syngas (CO) and selectivity S for methanol (MeOH), dimethylether (DME), carbon dioxide (CO2) and methane (CH4) of the developed Cu/ZnO catalyst at 275 °C for a long time period.

Scale-up of wet chemistry method for catalyst coating (ICT-IMM)
At Fraunhofer ICT-IMM, an automated coating procedure for the deposition of catalyst slurries into microchannels was successfully implemented by using the screen printing technique. For this purpose, the catalytic material was suspended into solvent/binder systems to achieve catalyst slurries. For an optimisation study, various slurries were prepared containing ZSM5 and alumina. The composition of these slurries was optimised with regard to rheological properties, adhesion, and printability. Printing tests were carried out with singularised plates at first. In view of an economic process for the deposition of the catalyst, the singularised plates were replaced by big panels (Fig. 10) comprising a larger number of plates. It was confirmed that the catalyst slurries could be uniformly deposited into all microchannels of the large panel.

Fig. 10 Large panel with 33 single plates per panel deposited with catalyst slurry.

Process development:
A key goal of the BIOGO project was to design a process that is technically, economically as well as environmentally feasible. Thus, the BIOGO process must be scalable, while ensuring that energy and resource consumption was optimal, with minimum environmental impact. Here, the BIOGO process is developed and scaled up to match a medium to large-scale plant, by simulating three different plant sizes – 100, 500 and 1000 BPD of gasoline.

The initial BIOGO process proposed to generate gasoline starting from a mixture of biogas and pyrolysis oil. The steps that were followed are as given under:

Essentially, two main routes were proposed. These are:
- Autothermal reforming of biogas and pyrolysis oil (ATR)
- Separate, but thermally-connected steam reforming of pyrolysis oil and catalytic partial oxidation of biogas (CR)

Both routes mentioned above were simulated in Aspen Plus, assuming the raw material to be forest residue.

The carbon efficiency of the process (which is defined as the ratio of the carbon atoms in the product to the carbon atoms in the feed), was calculated. The ATR process had a carbon-efficiency of 45%, while that of the CR process was 30%. Thus, the ATR process was chosen over the CR case.

However, the calculated raw material requirement for the two routes (particularly for the 1000 BPD case) was found to be high, which might be practically infeasible. Further, it was seen that the forest residue requirement to produce biogas was 6 times higher than to produce pyrolysis oil. This increases the transport requirement and costs, as well as the environmental impact of the transport. Thus, it was suggested that the process be modified in the future large-scale plant, to carry out autothermal reforming of only pyrolysis oil, and exclude biogas from the analysis. The process description is elaborated hereafter.

The first step is the synthesis of syngas from pyrolysis oil. It is important to adjust the syngas composition to have the ratio of (H2-CO2)/(CO+CO2) slightly greater than 2. This is the ideal ratio to produce methanol from syngas. To avoid loss of carbon, and increase the conversion of CO2 to CO, a Reverse Water-gas Shift (RWGS) reactor was added after the syngas generation, and the temperature is adjusted for optimum results. After the syngas generation step, the syngas is cooled, and excess water is removed in a flash column. The feed is then heated and sent to the RWGS reactor. However, it was observed that even after the addition of the RWGS reactor, CO2 removal is still required. Hence, CO2 removal is achieved by using K2CO3, and the removal is determined by the required syngas composition. The next step is the
synthesis of methanol from the adjusted syngas. The adjusted syngas is cooled, compressed to 40 bar, and then heated once again to 230°C before sending it into the reactor. The product stream is cooled and sent to a separator, after which the unreacted feed is recycled and sent back to the methanol reactor. The final methanol stream is then heated and sent to the gasoline reactor, which operates at 20 bar and 360°C. Lastly, two distillation columns are designed – one to remove ethane, and the other to remove LPG (propane + butane). Next, a pinch analysis was done, which optimises the consumption of utilities and tries to reduce overall utility costs. The modified ATR process was found to have a carbon efficiency of 50%, which was the original target of the project. The process flow diagram is shown below (Fig. 11).

Fig. 11 Process simulation with ASPEN Plus: Process Flow Diagram.

After the BIOGO process was fixed, Fraunhofer ICT-IMM transferred the process developed at TU/e by using ASPEN Plus to the process simulation software ProSim used at IMM (Fig. 12). This enables fast adaptations of the process simulation to changes in the plant design as results of plant operation, comparison of predicted with experimental results and further detailing of the process simulation. For example, for the pyrolysis oil (PO) reformer IMM developed a detailed Excel model for PO reforming, deviated from ProSim and based on the model composition of pyrolysis oil. This allows simulation calculations directly on site of the miniplant. Similarly, for the biogas (BG) reformer a detailed Excel model for the reforming of biogas together with reformate from the PO reformer was developed, which uses the surrogate composition based on the ProSim model for the complete process. In addition, also for the methane combustion on the heating side of the BG reformer such an Excel model was developed.

Fig. 12 Transfer of the ASPEN process simulation to ProSim: Detailed Process Flow Diagram.

Reactor development:
For each of the above described process steps of the BIOGO process, i.e. reforming of pyrolysis oil and biogas, further treatment of the generated syngas to adjust the carbon to hydrogen ratio, the synthesis of methanol from the adjusted syngas and finally the conversion of methanol to gasoline via DME, the respective reactors had to be developed and scaled up to the dimensions required for the miniplant (see 1.3.5). In addition, also reactors for the investigation of alternative routes had to be developed and realised, e.g. for the direct upgrading of bio oil into higher alcohols (Fig. 13).

Fig. 13 Two-stage reactor for the hydrogenation of bio oil. Fig. 14 Microstructured test device for contacting pyrolysis oil and steam in laboratory scale.

In most cases, first these reactors were developed and realised in the laboratory scale to test their performance and to gain data for the upscaled versions. An example is shown in Fig. 14. When the activity of the deployed catalysts for the miniplant was known, all reactors were dimensioned for the miniplant, designed and manufactured. In detail this concerns the autothermal pyrolysis oil reforming reactor (PO-ATR), the biogas reformer (BG-REF), the reverse watergas-shift reactor (RWGS), the methanol synthesis reactor, the DME synthesis reactor and the methanol to gasoline (MTG) reactor. In addition, all heat exchanger were designed and manufactured which were needed for heating-up or cooling-down reactants and products, respectively.

For the reactors in the miniplant scale, different design approaches and manufacturing techniques were applied according to process requirement, i.e. operating conditions (pressure, temperature), heat release or heat demand and necessary catalyst loadings. Both the biogas reformer and the reverse watergas-shift
reactor were carried out as catalytic plate heat-exchanger reactors, but whereas the BG-REF is heated by catalytic biogas combustion (Fig. 15) the RWGS is heated by electric heating cables (Fig. 16).

Fig. 15 Biogas reformer (BG-REF).
Fig. 16 Reverse watergas-shift reactor (RWGS).

In case of the PO-ATR, one of the main challenges was the atomising of pyrolysis oil with steam in such a way, that clogging could be avoided and good equal distribution over the cylindrical cross section could be achieved. For this purpose, a two substance nozzle was integrated in the inlet section and a microstructured monolith was applied as catalyst carrier (Fig. 17).

Fig. 17 Autothermal pyrolysis oil reforming reactor (PO-ATR), first version. Fig. 18 Autothermal pyrolysis oil reforming reactor (PO-ATR), improved version for increased operating temperature.

Since experimental tests revealed that only an incomplete conversion of pyrolysis oil was achieved and higher operation temperature would be necessary, an improved second version shown in Fig. 18 had been designed and realised.

Due to the required relatively high catalyst loadings, the methanol synthesis reactor, the DME synthesis reactor and the methanol to gasoline (MTG) reactors were designed as thermally controlled fixed-bed reactors (Fig. 19). In a technically and economically viable manner, this was realised by using an additive manufacturing technique, namely selective laser melting. The same manufacturing technique was used to realise the electrically heated or with two fluidic sides equipped cylindrical heat exchangers shown in Fig. 20.

Fig. 19 Methanol synthesis reactor (3 modules), installed in an insulation box. Fig. 20 Heat exchangers with electrical heating (above) and with two fluidic sides (below).

Design, realisation and operation of the miniplant:
The aim of the miniplant is demonstrating the integrated processes for fuel production from the renewable feedstocks bio-oil and biogas. After the BIOGO process had been fixed, the engineering of the plant was done and the respective P&ID (Piping and instrumentation diagrams) were elaborated by Microinnova.

The whole BIOGO process comprises three consecutive steps (names in brackets):
Reforming of bio oil (pyrolysis oil) and bio gas and further treatment resulting in the provision of synthesis gas (“SYN – Synthesis Gas Generation”)
Conversion of syngas to methanol (“MET – Methanol Synthesis”)
Synthesis of gasoline from methanol (“BIO – Biofuel Synthesis”)

As containment for the miniplant, Fraunhofer ICT-IMM provided a so-called Ecotrainer®, purchased from Evonik Industries AG. This is a standardized modular infrastructure for the realization of chemical processes in a container of the 12 feet size (see Fig. 21). The container’s infrastructure (electrical installation, electric lighting, air conditioning and exhaust system) is based on labour, safety and environmental standards.

Fig. 21 Principal structure of the Ecotrainer® (source: Evonik). Fig. 22 Planned arrangement of the 3 modules of the miniplant inside the process room.
According to the consecutive process steps, the miniplant was split up into three modules. The modular design allows an easier transportation and an independent basic testing of the functionality of the three process steps. Each of the modules was installed in a separately exhausted compartment. All three compartments were arranged side by side in the process room of the containment (see Fig. 22). The three-dimensional design of the modules (Fig. 23) was carried out by Microinnova.

Fig. 23 3D models of the reforming and synthesis gas module (SYN, left), the methanol synthesis module (MET, middle) and the bio fuel synthesis module (BIO, right); CAD design by Microinnova.

The construction of the framework and the equipment of the modules with the main components purchased by Microinnova (Fig. 24) as well as the installation of the control cabinets were carried out by and on site of Microinnova.

Fig. 24 Partial view of the SYN module (left) and the compressor unit of the MET module as delivered by Microinnova.

After the delivery to Fraunhofer ICT-IMM, the three modules were installed inside the Ecotrainer® (Fig. 25), equipped with the home-made components and the other parts provided by Fraunhofer ICT-IMM, and then interconnected by piping and wiring.

Fig. 25 Modules of the miniplant, installed inside of the Ecotrainer®. From left: syngas generation (SYN), methanol synthesis (MET), biofuel synthesis (BIO).

The automation system of the miniplant, provided by Microinnova, is composed of Wago Hardware and of control software based on Codesys. It enables full control of the modules. For flexibility reasons, and to keep the cost at a sensible value, the miniplant is not fully automated. Thus, a qualified human operator has to be physically present next to the running plant at all times. The control software is very easy and intuitive to use; no special training is needed for the user. Fig. 26 exemplarily shows the graphical user interface of the syngas generation (SYN) module. The control software comprises the plant control, a system overview with the possibility of setting main control values, a detailed interface for each module, the visualization of current values and the graphical data representation of process values, alarm, logging, reporting and alert functions.

Fig. 26 Process graphic of the syngas generation (SYN) module. After initial experiments in the technical centre at Fraunhofer ICT-IMM, the special set-up for testing the pyrolysis oil reactor and the related own control module were installed and directly operated in the Ecotrainer® (Fig. 27).

Fig. 27 Miniplant and special test rigs, installed inside of the Ecotrainer®. From left: syngas generation (SYN), test rig with PO reactor (temporarily), control module for PO reactor (temporarily), methanol synthesis (MET), biofuel synthesis (BIO).

The experiments revealed that pyrolysis oil was effectively converted, but at the achievable temperature only an incomplete conversion of pyrolysis oil was achieved. For this reason, an improved reactor version which can be operated at the necessary higher temperature was developed and manufactured (see Fig. 18). In addition, the biogas reforming process was successfully tested. In total more than 120 h stable
performance of the reformer could be achieved so far. The comparison of the experimentally achieved composition with the calculated reformate composition from the process model (using a surrogate composition) shows only minor deviations.

Cost analysis and life cycle assessment:

Cost analysis
The cost analysis is carried out for the ATR of pyrolysis oil, for 3 plant capacities – 100, 500 and 1000 BPD of gasoline – over a 20-year period. The aim is to find the capacity at which the modified BIOGO case is most profitable. Three parameters are calculated and compared for each plant size – the payback period, the Net Present Value (NPV) and the Minimum Selling Price (MSP) of gasoline.

The payback period calculation showed that the 100 BPD case does not achieve a positive cash flow at all in the 20-year period. On the other hand, the 500 and 1000 BPD cases achieve positive cash flows in year 8 and year 6, respectively. Thus, the 500 and 1000 BPD cases can be viable in terms of recovering the money invested.

Since it takes into account the time value of money, the NPV gives a better idea of the long-term viability of the project profitability. If the project has a positive annual cash flow at the end of the 20-year period, the project is said to be viable. Assuming the current gasoline selling price of 1.36 €/litre, the 100 BPD case does not reach a positive NPV at all. The 500 BPD case has a positive NPV of 8 M€ at the end of the 20 years, while the 1000 BPD is most profitable with an NPV of 81 M€. Thus, once again, the smallest size does not show profitability, while the largest size is the most viable.

Next, we find the Minimum Selling Price (MSP) at which the gasoline produced must be sold, to make NPV=0. This gives us the minimum price at which we need to sell the gasoline to avoid losses at the end of the period. We find here that the fuel from the 100 BPD case needs to be sold at a price of 2.2 €/litre, the 500 BPD fuel at 1.31 €/litre, while the 1000 BPD needs to be sold at 1.10 €/litre. Thus, the 1000 BPD has the lowest selling price, compared to the other cases.

The following table summarises the key results of the cost analysis:

<table>
<thead>
<tr>
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<th>100 BPD</th>
<th>500 BPD</th>
<th>1000 BPD</th>
</tr>
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<tbody>
<tr>
<td>Total capital investment (M€)</td>
<td>20</td>
<td>55</td>
<td>110</td>
</tr>
<tr>
<td>Operating cost (M€/yr)</td>
<td>7.9</td>
<td>22</td>
<td>33</td>
</tr>
<tr>
<td>Unit cost of production(€/litre)</td>
<td>1.49</td>
<td>0.79</td>
<td>0.64</td>
</tr>
<tr>
<td>Payback (years) @ selling price of 1.36 €/litre</td>
<td>8</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>NPV (M€/yr) @ selling price of 1.36 €/litre</td>
<td>-31</td>
<td>8.3</td>
<td>81</td>
</tr>
<tr>
<td>Minimum Selling Price (€/litre) at NPV=0</td>
<td>2.22</td>
<td>1.31</td>
<td>1.10</td>
</tr>
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In summary, we can conclude that any size larger than 500 BPD of gasoline would be profitable eventually. The larger the plant size, the more profitable the plant, and cheaper the final fuel. However, the availability of forest residue would then be the limiting factor.

Life-cycle assessment
The goal of a Life-cycle Assessment (LCA) study is to evaluate the impacts generated and resources consumed in a particular process. In this case, we investigate the environmental impacts of producing gasoline from forest residues, and compare it with the conventional production of gasoline (from crude oil). The functional unit is specified as 1 kg of gasoline and LPG produced. Thus, all impacts are assessed per
1 kg of product. It must be noted that the LCA does not include the manufacturing of the equipment in the plant such as reactors and heat exchangers. Also, the inventory associated with the manufacture of catalysts and their use has not been included in this study.

The LCA study presented here is a ‘cradle-to-factory gate’ analysis, which starts with the raw material required for the process, and stops at the production step. The process starts the collection and transport of forest residues, followed by production of pyrolysis oil. Also, since steam is generated within the process, we can obtain credits for this, since we avoid producing steam from natural gas.

The plant has a high electricity consumption per unit of gasoline produced (due to compressors as well as the Air Separation Unit, which is used for oxygen). Using the regular electricity mix results in undesirable impacts, since the Germany mix has some ‘unclean’ sources, such as coal, lignite and oil. It also has some renewable energy in the mix, but this changes constantly due to economic and technical reasons. Thus, we must choose the source of electricity correctly, to reduce the footprint of our process. Apart from electricity, the pyrolysis oil production and potassium carbonate (used for CO2 removal) are the next biggest contributors.

Other source of electricity – that is, electricity from natural gas, solar PV, wind, and hydropower are studied. It is seen that using these sources reduces the environmental impact significantly, as against the regular electricity mix. Thus, the ATR process now presents a much cleaner profile, compared to the conventional method of producing gasoline from oil. Considerable reductions are seen in the Global Warming Potential (GWP), Ozone Layer Depletion Potential (ODP) and Primary Energy Demand. Wind power and hydpo-power have almost comparable environmental footprints (better than natural gas). Still, all options (electricity from natural gas, hydro-power as well as wind power) perform better against the conventional gasoline production, with the hydro-power being the cleanest.

The figure below shows the comparison of the ATR of pyrolysis oil (including different sources of electricity) against the conventional gasoline production. The different ATR scenarios are normalised against the conventional gasoline production process; thus the impacts of the ATR scenarios are relative to the conventional gasoline production from oil.

Thus, the ATR process can be said to be environmentally more favourable, in all impact categories, than the conventional gasoline production, provided we use a cleaner source of electricity, like wind or hydropower, or even natural gas.

REACH analysis
The Registration, Evaluation, Authorisation and restriction of Chemicals (REACH) (EC 1907/2006) or the REACH regulation applies to the manufacture, import, sell or use of chemical substances within European Union; all chemical substances that are either produced or imported into the EU in quantities above 1 t/year are covered by this regulation.

In order to have a basis for where to apply the REACH regulation, a BIOGO scenario was assumed, in order to establish specific production routes, rates & locations. Therefore, the analysis was based on the final scenario selected in the Life Cycle Analysis and Cost Assessment: an industrial plant of autothermal reforming of pyrolysis oil synthesis route, with a capacity of 1000 BPD (barrel per day) and located within European Union boundaries. Bearing in mind that scenario, the main concerns that BIOGO process may have regarding REACH regulation were analysed. The focus has been on identifying the roles under REACH that a company applying BIOGO technology would have, consequently assessing the obligations
that company would have based on the identity and quantity of substances it is dealing with.

Roles under REACH
It was assumed that the necessary substances for undertaking the product and by-products manufacture
would be obtained from market; the hypothetical case that they come from outside EU, the company would
be considered as an importer within REACH regulation. As consequence, the inputs were revised.
Equally, manufactured substances will be put on the market. Since the location of the industrial plant is
assumed to be within the EU, any substance put on the market would be susceptible of being registered.
Therefore, outputs of the manufacturing process were studied under REACH scope.
Substances subject to registration on BIOGO case

Inputs
Substance Measures in the BIOGO case Status of registration
Pyrolysis oil If imported from outside EU, there would exist the obligation of registering it in accordance
with the description of importer role under REACH, as its quantity would exceed ≧ 1 tonne per annum
threshold, and it is not one of the substances included in the Exceptions for REACH regulation. 5
substances registered with pyrolysis oil public or trade name

Potassium carbonate 1 substance registered with that name

Outputs
Substance Measures in the BIOGO case Status of registration
Ethane In accordance with manufacturer role under REACH description, the non-inclusion of this
substance within the Exceptions for REACH regulation and in view of exceeding ≧ 1 tonne per annum
threshold, there would exist the obligation of registering it. 1 substance registered with that name
LPG 1 substance registered with liquefied petroleum gas
IUPAC name (2 with
liquefied petroleum gas trade name)
Gasoline 1 substance registered with gasoline EC name
(24 with gasoline trade or public name)

Potential Impact:
1.4.1 Potential impact
The development of biofuels is widely recognised as a research priority, in line with the wider goal of
reducing the dependence on fossil fuels. The idea of BIOGO is to utilise non-food organic waste material,
such as wood residue, which is widely available across Europe. BIOGO aims to use this feedstock to
create synthetic fuels of gasoline grade. Thus, BIOGO is opening the door to little-used resources. As the
shift from crude oil to cheaper sources of natural gas, biogas (from e.g. non-crop biomass) and light
alkanes becomes economically driven, these processes will enable the industry to utilise little-used
resources by allowing their conversion to useful high-value raw materials. More selective catalysts will lead
to reduced material consumption, higher efficiencies and improved manufacturing processes. This in turn
will create less waste with lower emissions, resulting in enhanced public health and sustainable use of
resources based on environmentally sound industrial product. The product purification costs are a major
cost fraction for bio based GTL-plants using the Fischer–Tropsch technology. Here BIOGO aimed on
reducing these costs through the chosen technology itself but also further by the development of improved
catalysts being more poison resistant, which will relax purity constraints for feeds.
The aim of the planned and realised miniplant was to demonstrate the feasibility of the developed BIOGO process, comprising the reforming of pyrolysis oil and biogas to syngas, its further treatment and conversion to methanol and finally the conversion to gasoline via dimethyl ether. The minplant represents all the needed process steps, newly developed apparatuses and catalysts which are necessary to produce biofuels from pyrolysis oil and biogas as feedstocks. Also the development of the first step, the conversion of the wood residues to bio oil in a HTL plant, was part of the project, but not of the miniplant. Accompanying, a cost analysis and life cycle assessment was carried out to determine the economic framework and environmental impact of commercial plants based on the developed BIOGO process. The cost analysis was carried out for the autothermal reforming of pyrolysis oil for 3 different plant capacities. Under the assumptions made, it was concluded that any size larger than 500 BPD of gasoline should be profitable. The larger the plant size, the more profitable is the plant.

When the processes of conventional gasoline production and the autothermal reforming of pyrolysis oil were compared with respect to their environmental impact, it can be said that in all investigated impact categories the new developed BIOGO process is environmentally more favourable than the conventional gasoline production, provided clean sources of electricity, like wind or hydro-power are used, or even when natural gas serves as power source.

1.4.2 Main dissemination activities

The dissemination and communication plan (see figure below) was set up in the early stages of the project, in order to assure an efficient dissemination of the project activities and key results among relevant players.

BIOGO specific talks and posters have been presented at conferences, workshops and trade fairs by partners within the BIOGO consortium. These dissemination activities were being undertaken while controlling confidentiality to protect the IP interests of the partners. Partners have maintained a good level of presenting the project at national and international conferences, as well as a good level of scientific publication.

Overall, there are about 137 dissemination activities (a complete list is given in the A1 and A2 in Chapter 2.1). An insight in the main activities is provided in the following

Naturally the main dissemination routes from academics and the R&D institutes in the project have been to publish project results in peer-reviewed journals and to contribute to scientific conferences. These include the following major activities to disseminate the results to the scientific community:

- 30 peer reviewed scientific papers
- 75 oral presentations at scientific conferences
- 1 oral presentations at a workshop for an audience from industry
- 20 posters at scientific conferences
- 3 articles in the popular press
- 8 contributions or organisation or workshops

These activities have encompassed the full multidisciplinary aspects of the project and have included activities relating to all main technical areas. For example dissemination covers novel catalysts, novel microreactors.

Some of the more prominent dissemination activities are highlighted below.

- 10th World Congress of Chemical Engineering (WCCE-10), Barcelona, Spain

2 oral presentation and 3 posters gave an insight about achieved results near to the end of the project, reaching a broad international audience. The project coordinator reported about the conversion of bio gas
and pyrolysis oil to synthetic fuels through reforming, methanol synthesis and MTG processes operated in a miniplant in a modular containerised environment, i.e. about the project’s main demonstration activity involving and merging research results from all project partners.

• ACS National Meetings
  6 oral presentations and 4 posters about progress made in the development of improved catalysts for the single steps of the BIOGO process as well as findings gained about factors which influence their activity, selectivity and stability.
• IMRET13 and CHISA 14/16
  The 6 oral presentations given at these events are i.a. concern Europe’s future chemical manufacturing and aspects of catalyst, reactor and system design for microreactors in distributed energy related applications.

For a wider public, within external communication activities, “A step towards sustainable biofuels” article was published in EU Research magazine, spring 2017 edition (pages 74-75).
https://issuu.com/euresearcher/docs/eur12_digital_magazine_spring_2017

Similarly, “Decreasing fossil fuel dependency” article was published in Science Impact Publication.

In addition, from the public part of the BIOGO project website (www.biogo.eu), the two leaflets can be downloaded by everyone.

1.4.3 Exploitation of results
To protect the Intellectual Property of knowledge generated during the project, in total four patent applications were filed by four project partners.

In detail, the following exploitation strategies will be pursued:

Exploitation of the plant design concept and the new developed BIOGO process

The process realized in the BIOGO miniplant demonstrates a higher eco-efficiency and its conversion routes are atom-economical. Such an improved catalytic selectivity reduces waste and emissions and leads to higher resource efficiency, which has a positive impact on potential business models. This process enables the utilization of novel sustainable resources which are currently considered as waste. Therefore waste could be transformed into fuel. The process uses raw materials which avoid a competition with food production.

Operation on the miniplant level has generated and will generate detailed data for the design of an enhanced pilot plant with higher capacity and to convince a funder and/or an investor. Such a pilot plant should be realised in the framework of either a public funded follow-up project or of a research project with a potential end user.

The economic scenario depends strongly on governmental strategies, namely the prioritization of fossil free transportation fuel supply.

There are other potential additional application fields to explore, which might have an interesting economic scenario. For example:

1. Military applications: A mobile plant could eliminate the need of fuel logistics, which generate a significant strategic advantage to tactic options for any operation.
2. Outskirts of civilization: Areas, where people live far away from logistic networks. This concept benefits
from the reduction of logistic costs.

Fraunhofer ICT-IMM (from January 1, 2018 on “Fraunhofer IMM”) is currently building up a new infrastructure, which will allow building pilot plants or small production plants for customers from industry in the standardized modular infrastructure provided by the Ecotrainer®. This is based on the good experiences made with the use of such a containerized infrastructure in the BIOGO project and in the former European research projects CoPIRIDE, POLYCAT (also coordinated by Fraunhofer ICT-IMM) and MAPSYN. For this purpose, Fraunhofer ICT-IMM and Evonik Industries signed a licensing contract which enables Fraunhofer IMM to offer the development and realisation of such plants in the Ecotrainer® containment to industrial customers. Furthermore, the currently erected extension building at Fraunhofer IMM offers the possibility to bring in these containers into the technical centre and to equip the Ecotrainer® in-house with a plant, which prior to this can be operated and tested in a big walk-in fume hood of a size which is comparable with the dimensions of the process room inside the Ecotrainer®.

Figure 1: Extension building for Fraunhofer IMM at Mainz.

Teer Coatings Ltd offers the design and manufacture of coating deposition systems as well as a coating service. Here, the newly developed gas aggregation nano-cluster source with high throughput lets to expect a significant improvement of the production rate which opens new application fields. This project result is protected by a British Patent Application.

The University of Warwick has recently founded the Spin-out company Stoli Catalysts which amongst other activities provides a service for catalyst development, optimisation and characterization. Here it should be evaluated if and how this company could support the commercialisation of catalysts developed by the University of Warwick during the BIOGO project.

Microinnova Engineering GmbH has developed a new automatization concept which was for the first time applied for the process control system of the miniplant. In future, it will be commercially applied for other plants of comparable scale and complexity which will be developed and realised for mainly industrial customers. Microinnova focuses on two strategies for exploitation and has a potential for a third one.

Strategy 1:
Microinnova will use the automation concept for their own process development department to automate all lab plant setups. First level will be with operator-based operation and later on the automation will run the plant without operator. Recipe-driven operation of the lab plant will be the final step.

Strategy 2:
The second application will the automation of plant construction projects in the field of lab-, pilot and miniplant construction setups. Attractive pricing for lab and pilot plant setups is expected, since the new developed automation has very low hardware and licensing costs. This will lead to a specific USP in terms of cost leadership for this type of plants. The cost leadership is expected to push these kind of plant setups.

Potential Strategy 3:
The third strategy would be a ready to use toolkit. Potential customers could automate lab plant setups on their own. Microinnova would sell a set of building blocks of hardware and software. Additional Microinnova could sell programming of new drivers and building blocks.

List of Websites:
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Last update: 15 May 2018
Record number: 228225