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D4.3 Public (PU) Report on the results of the validation test runs in REDIFUEL pilot

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Executive Summary

The overall objective in the REDIFUEL project is to develop and validate a novel and cost-competitive process for sustainable production of renewable diesel that is compatible with the EN590 fuel standard. The proposed drop-in biofuel is composed of high-cetane C_{11+} bio-hydrocarbons and C_6-C_{11} bio-alcohols resulting in improved combustion performance and reduced emissions - owing to the share of alcohols in the diesel blend. One of the core activities in the project was the pilot-scale validation of the entire process chain to reach TRL5. The know-how gained in laboratory-scale development of Fischer-Tropsch catalyst and optimization of the hydroformylation step was transferred to pilot plant level during the second year of the project. The thermochemical conversion route starting from biomass gasification and gas clean up to Fischer-Tropsch synthesis was validated at VTT's Piloting Centre Bioruukki in Espoo (Finland) and hydroformylation of the C_5-C_{10} olefin fraction at Max Planck Institute in Mülheim (Germany), respectively.

In the time period of April-June 2020, a series of week-long gasification test campaigns were carried out at VTT's Piloting Centre Bioruukki where the entire process from gasification up to Fischer-Tropsch synthesis was operated using crushed bark pellets and crushed wood pellets as feedstocks. One of the main objectives in the pilot test campaigns was to validate the performance of the novel FT catalyst developed by CSIC using real bio-based syngas. Although the catalyst was capable of producing high shares of olefins in the C_5-C_{10} hydrocarbon range, it also had a low specific activity and consequently low productivity. Due to these challenges, the target production volumes of more than 300 litres of FT products could not be achieved in the validation test campaigns. During the pilot experiments, the REDIFUEL catalyst was operated with real bio-syngas for over 300 hours and with bottled gases for over 400 hours, respectively. Roughly 11 kg of FT oil and over 6 kg of solid FT wax was produced during the testing period. The FT oil collected during the experiments contained 23-35 wt-% of C_5 - C_{10} hydrocarbons of which 13-35% were olefins. However, it should be noted that some of the lighter hydrocarbons (particularly in the C_5 - C_7 hydrocarbon range) were not fully retrieved in the product condensation steps and ended up in the gas phase, leading to lower shares of C_5 - C_{10} olefins in the FT oil fraction. The specific activity of the REDIFUEL catalyst was appr. 10-15 mmol CO/g_{cat}h.

Since direct coupling of the hydroformylation pilot with the gasification and FT synthesis process was not possible, the hydroformylation pilot plant was constructed at MPI's premises in Mülheim. The two-step catalytic system, where the first step generates aldehydes from olefins and the aldehydes are further converted to alcohols in the second step by the addition of hydrogen, was validated in the pilot-scale experiments. Due to the low amount of FT product available from the REDIFUEL gasification test campaigns, the hydroformylation reaction system was first optimized using a surrogate mixture of 1-octene and n-heptane, while the real substrate was primarily used for investigating the catalyst stability. The FT oil batch produced in the gasification test campaigns was first fractionated at Neste through distillation and the resulting C₅-C₁₀ hydrocarbon cut (approx. 3 litres) was shipped to MPI for hydroformylation experiments in autumn 2020. In the 37-hour hydroformylation experiment with the real substrate, the catalyst was proven to be stable against potential impurities. Moreover, full hydrogenation of aldehydes to alcohols was achieved along with full conversion of leftover olefins to the corresponding paraffins in the second reaction step using a commercial Raney-Nickel type catalyst.



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1 Introduction

This deliverable is related to Task 4.2 - "Upscaling and pilot testing of FT process" and Task 4.3 "Upscaling hydroformylation". The objective of these tasks was to validate the REDIFUEL technologies over the course of pilot-scale test campaigns with the following sub targets:

- Study the performance of the entire process train from gasification to Fischer-Tropsch synthesis in week-long test campaigns using woody residues as gasifier feedstock
- Validate the novel Fischer-Tropsch catalyst developed by CSIC and INERATEC's FT reactor with real woodderived synthesis gas
- Produce pilot quantities of Fischer-Tropsch hydrocarbons for subsequent hydroformylation experiments and product trials of WP3
- Operate the hydroformylation pilot plant for appr. 100-300 hours with the complex olefin mixture obtained from gasification test campaigns and prove the long-term stability of the homogeneous catalyst system and the recycling approach applied for hydroformylation and hydrogenation
- Examine the possible accumulation of side-products in the hydroformylation process
- Create data for the overall process design and assessments conducted in Task 4.4 and WP5

This deliverable summarises the results obtained in the pilot experiments and also gives a short introduction to the REDIFUEL process and its key unit operations (Chapter 2). In the timeframe of April-June 2020, a series of week-long gasification test campaigns were carried out at VTT's Piloting Centre Bioruukki in Finland where the entire process from gasification up to Fischer-Tropsch synthesis was operated using crushed bark pellets and crushed wood pellets as feedstocks. The FT oil batch (appr. 11 kg) produced in the gasification experiments was distilled at Neste and the resulting C₅-C₁₀ hydrocarbon cut was delivered to MPI for hydroformylation tests. The pilot-scale hydroformylation experiments took place in Mülheim in November 2020. The two-step catalytic system, where olefins are first converted to aldehydes and further to alcohols in two separate reactors, was validated both with surrogate mixtures and real substrate derived from the gasification experiments.



2 REDIFUEL process

The overall objective in the REDIFUEL project was to develop and validate a novel and cost-competitive process for sustainable production of renewable diesel that is fully compatible with the EN590 fuel standard. The REDIFUEL process scheme is depicted in Figure 1. The proposed drop-in biofuel is composed of high-cetane C_{11+} bio-hydrocarbons and C_{6-} C_{11} bio-alcohols resulting in improved combustion performance and reduced emissions - owing to the share of alcohols in the diesel blend. The target scale of the process is 20-50 MW (feedstock input), corresponding to a feed rate of roughly 900 m³ straw or 400 m³ wood chips per day.

The REDIFUEL process combines gasification of biomass with Fischer-Tropsch (FT) synthesis, hydroformylation and other upgrading steps. This chapter provides a brief introduction to the REDIFUEL concept and its key processing steps.



Figure 1. REDIFUEL process concept

2.1 GASIFICATION, FILTRATION AND REFORMING

Biomass conversion to bio-syngas starts with pre-processing of the feedstock e.g. by chopping or milling and drying. Dried biomass is then converted to raw syngas in a dual fluidised-bed gasification process that comprises of a circulating fluidised-bed (CFB) gasifier and a circulating fluidised-bed (CFB) oxidiser. The gasifier typically operates at 750-800 °C with steam as fluidising agent. A mixture of silica sand and dolomite is employed as bed material. Upon exiting the gasifier, entrained char and bed material are separated from the raw gas in a cyclone. These solids are transported to a circulating fluidised-bed oxidiser where char is combusted with air at 850-900 °C, and bed material - that serves as the heat carrier between the two reactors - is returned to the gasifier through the recycle loop. As the heat demand in gasification is often not satisfied by char combustion alone, off-gases produced in FT synthesis are used as supplementary feedstock in the oxidiser. Flue gases generated in combustion are filtered, cooled down to 150 °C and vented through the stack.

The raw gas formed in steam gasification comprises mainly of CO, H₂, CO₂, CH₄, H₂O and light hydrocarbons but also impurities originating from the feedstock. Typical impurities formed in biomass gasification include tars, sulphur (H₂S, COS) and nitrogen compounds (NH₃, HCN), solid particulates as well as alkali and heavy metals. These contaminants cause fouling of downstream equipment but also catalyst deactivation and therefore need to be separated from the gas stream prior to its application in synthesis processes.

The gas clean-up process involves multiple steps that starts with filtration. After cyclone separation, the raw gasification gas is filtered to remove fine particulates, alkali and heavy metals as well as most of chlorine from the gas. The solid particulates accumulate on the filter surface thereby forming a dust cake. Accumulation of dust is perceived as an increasing differential pressure over the filter. The filter elements are periodically regenerated by applying a reverse nitrogen pulse that detaches the accumulated fly ash. The detached fly ash is collected from the bottom and further combusted in the oxidiser along with char and off-gases. The filter is preferably operated at gasifier outlet temperature to eliminate the intermediate cooling and reheating steps before and after filtration and to enable tar decomposition in the filter dust cake [1].

Filtration is followed by catalytic reforming of tars and light hydrocarbons where these undesired species are converted to H₂ and CO in the presence of nickel catalyst. Nickel-based catalysts not only catalyse tar reforming reactions but are also effective in ammonia decomposition. The reformer is operated autothermally using either air or a mixture of oxygen and steam. The oxidant feed to the reformer is adjusted to maintain the reformer outlet temperature at around 900 °C. A separate water-gas shift reaction step is usually required post-reforming to adjust the syngas molar H₂/CO ratio suitable for Fischer-Tropsch synthesis (about 2). In the REDIFUEL concept, however, the desired H₂/CO ratio can already be achieved after steam gasification and subsequent reforming, and a dedicated water-gas shift unit can be omitted.

2.2 FINAL GAS CLEANING (ULTRACLEANING)

After reforming, the syngas still contains minor contaminants that need to be removed to meet the strict gas purity requirements of the subsequent Fischer-Tropsch synthesis process. The main purpose of the final gas cleaning steps is to remove sulphur compounds (H₂S, COS), trace halides, nitrogen species (NH₃, HCN) as well as residual tars, benzene and syngas moisture before feeding the gas to FT synthesis. Purification to ppb-level is required for these minor impurities to prevent catalyst poisoning. Also, CO₂ is typically removed to lower the inert gas content prior to synthesis. Table 1 shows the FT catalyst tolerance levels against syngas impurities that have been reported in the literature.



Creation	Source:	Source:	Source:	
species	Turk et al. [2], Newby et al. [3]	Tijmensen et al. [4]	Boerrigter et al. [5]	
H ₂ S	Total sulphur < 0.06 ppm	H S + COS < 0.01 ppm	$H_2S + COS + CS_2 < 1 \text{ ppm}$	
COS	Total sulphul < 0.06 ppm	1120 · 000 · 0101 ppm		
HCN	< 0.01 ppm	HCN + NH < 0.02 npm	HCN + NH < 1 ppm	
NH ₃	< 10 ppm	11014 - 1111 ₃ < 0.02 ppm		
NOx	< 0.1 ppm	-	-	
Halides	Total halides < 0.01 ppm	HCl < 0.01 ppm	HF + HCl + HBr < 0.01 ppm	
Alkalis	-	< 0.01 ppm	< 0.01 ppm	

Table 1. FT catalyst tolerance levels against syngas impurities

The final gas clean-up concept employed in REDIFUEL is based on a simplified, low CAPEX approach where conventional wet scrubbing technologies (e.g. Rectisol[®] or Selexol[®]) are replaced with sorbent-based removal of sulphur and only partial removal of CO₂. It comprises the following unit operations:

- Removal of syngas moisture, chlorine, and ammonia in a water scrubber/condenser unit
- Two-stage dry sulphur removal using activated carbon and ZnO sorbents
- Partial removal of CO₂ in a pressurised water scrubber
- Guard beds as the final polishing step

This ultracleaning scheme was developed and validated at VTT in the EU-funded project "COMSYN".

Scrubber/condenser:

After exiting the reformer, syngas is first cooled down to around 150-160 °C in a heat exchanger and further passed to a condenser/scrubber unit. The wet gas is cooled down to room temperature (exit temperature 25 - 30 °C) in the scrubber to condense the syngas moisture, and NH_3 is simultaneously removed by dissolving it in acidic water. The scrubber/condenser design is a countercurrent-flow packed tower where the scrubbing liquid (water and acid) is sprayed on top of the column, while the gas flows upwards. Ammonia capture in the scrubber is regulated by controlling the pH of the scrubbing liquid (acid injection). In an acidic environment, ammonia reacts as follows:

$$NH_3(aq) + H_3O^+(l) \rightleftharpoons NH_4^+(aq) + H_2O(aq)$$

Bulk sulphur removal using activated carbon:

The scrubbing step is followed by removal of the major sulphur contaminant H_2S . Desulphurisation is performed in two consecutive stages: the bulk of H_2S is removed using activated carbon, while the final polishing stage involves a ZnO-based sorbent. In this first step, the bulk of H_2S along with residual tars and benzene are adsorbed in a reactor that is filled with various activated carbons (AC). The reactor is operated at room temperature.

The first AC bed consists of carbons that are intended for residual tar and benzene adsorption. Heavy molecules have a higher affinity for physical adsorption than small molecules and, with the right carbon selection, they are relatively easy to remove. The commercial-grade AC adsorbent applied in REDIFUEL has a wide pore size range, which facilitates the physical adsorption of hydrocarbons with varying sizes.

In the second AC bed, a bulk microporous activated carbon is used for H₂S removal. Experimental results show that oxidative removal of H₂S achieves better performance due to the following reaction:



$$\mathrm{H}_{2}\mathrm{S} + \frac{1}{2}\mathrm{O}_{2} \rightarrow \frac{1}{x}\mathrm{S}_{x} + \mathrm{H}_{2}\mathrm{O}$$

Thus, a small amount of air is supplied to the AC bed to improve H₂S uptake. Moisture in the gas has shown to be necessary to facilitate oxidation at sufficient rate [6]. The activated carbon surface acts as a medium for facilitating the oxidation reaction, which would not otherwise occur. Therefore, the activated carbon can be said to have catalytic properties.

After the AC reactor, the gas is compressed to 5 bar pressure.

Pressurised water scrubber for partial CO2 removal:

Conventionally, CO₂ is fully removed from the gas prior to synthesis to maximize the FT product yield. Rectisol-type wet scrubbing processes are typically applied where CO₂ is separated along with other acid gases. In the REDIFUEL concept, CO₂ is only partially removed using a pressurised water scrubber. This approach was adopted to simplify the gas clean-up and thus reduce the overall investment of the gasification/synthesis plant. The CO₂ scrubber consists of an absorber column and a stripper column. CO₂ is absorbed into water in the countercurrent flow absorber unit. The scrubber water is regenerated in the stripper column to release the dissolved CO₂. Stripping is conducted at atmospheric pressure in a countercurrent flow packed column.

Guard beds:

The final gas cleaning process involves two guard beds: the first (warm guard bed) operates at 200 °C to facilitate catalytic reactions and the latter (cold guard bed) is maintained at room temperature and acts as the final polishing step.

The warm guard bed typically involves at least two separate beds. The first contains a ZnO-based sorbent (with Al_2O_3 support) that serves as the final H_2S removal step and allows reducing the H_2S concentration in the gas to sub-ppm level. ZnO is an efficient adsorbent for H_2S capture but requires activation (heat) and the disposal of the sulfided zinc poses a challenge. Therefore, in the final gas cleaning concept of this project, ZnO is employed only for trace H_2S removal.

Owing to the Al_2O_3 support, the ZnO adsorbent not only removes H_2S but can also be used to convert carbonyl sulfide (COS) and hydrogen cyanide (HCN) into hydrogen sulfide (H_2S) and ammonia (NH_3), respectively, via hydrolysis reaction. Complete removal of COS is not necessarily achieved in the bulk sulphur removal stage (activated carbon bed), and thus COS needs to be converted to H_2S before being separated. COS hydrolysis to H_2S proceeds on metal oxide catalysts according to the following reaction:

$$COS(g) + H_2O(g) \rightleftharpoons H_2S(g) + CO_2(g)$$

The second bed involves a deoxygenation catalyst (either a precious metal catalyst, such as Pt, or a cheaper Cu-based catalyst) that is required to remove the oxygen that was injected to the gas in the first sulphur removal stage (AC reactor). The reactions over the deoxygenation catalyst are essentially combustion reactions and can be summarised as follows:

$$O_2 + 2CO \rightleftharpoons 2CO_2$$

 $O_2 + 2H_2 \rightleftharpoons 2H_2O$

The cold guard bed acts as the final step and polishes the gas from any remaining impurities with acid/basic affinity, namely NH₃, H₂S, and HCl. High-performance activated carbons are used for this purpose. If HCN is hydrolysed in the warm guard bed, it will be captured in the form of NH₃ in the cold guard bed. Otherwise, the cold guard bed acts as a precautionary step to prevent accidental or one-off high impurity concentrations from entering the downstream FT catalyst and poisoning it.



After the cold guard bed, the resulting bio-syngas comprises primarily of H_2 and CO, has a H_2 /CO molar ratio of close to 2, and is as such applicable for FT synthesis.

2.3 FISCHER-TROPSCH SYNTHESIS AND PRODUCT UPGRADING

The first key processing step after gasification is the Fischer-Tropsch (FT) process. After ultracleaning steps, the purified syngas is compressed to synthesis pressure (20-30 bar) and fed into the FT reactor, where bio-syngas is converted into a hydrocarbon mixture via the Fischer-Tropsch reaction:

$$CO+2H_2 \leftrightarrow (CH_2)+H_2O \qquad \qquad \Delta \mathrm{H}=-165 \ \mathrm{kJ/mol}$$

A tailor-made cobalt-based catalyst developed by CSIC is applied in REDIFUEL to generate the unconventional FT product distribution that is characterised by the high share of olefins in the C_5 - C_{10} hydrocarbon fraction. Moreover, the compact microstructured FT reactor technology of INERATEC (Figure 2) is employed in the REDIFUEL process. The core of INERATEC's innovative synthesis reactors is microstructured. Consequently, a very large surface for heat and mass transport is provided, allowing catalysts to operate at maximum rate. Highly exothermic reactions, such as Fischer-Tropsch synthesis, are operated efficiently and safely in compact plants. The reactors are characterized by:

- Compact design due to the microstructure technology
- High syngas conversion per reactor pass and unique reactor productivity
- Excellent temperature control
- Short start-up and shut down times
- High load-flexibility
- Cost reduction for decentralized application.

These features are essential in the context of REDIFUEL as the presence of hot spots in the reactor is expected to severely deplete the FT products in olefins by enhancing secondary hydrogenation reactions.



Figure 2. INERATEC's compact microstructured FT reactor applied in the pilot scale campaigns in REDIFUEL.

The raw Fischer-Tropsch syncrude is recovered from the reactor effluent by condensation and further fractionated via distillation:

- The C_5-C_{10} olefin-enriched hydrocarbon fraction is delivered to the second key processing step, hydroformylation, where $C_5-C_{10} \alpha$ -olefins are hydroformylated and hydrogenated with bio-syngas into C_6-C_{11} bio-alcohols (see Section 2.4).
- The middle distillate fraction (C₁₁-C₂₁) is hydroisomerised to improve the cold flow properties.
- The wax fraction (C₂₂₊) is hydrocracked and the resulting diesel cut is hydroisomerised.
- The combination of lighter products (C₁-C₄ hydrocarbons) and unconverted syngas (i.e. off-gases) are utilised within the plant mainly as complementary feedstock for the oxidiser, while the possible surplus is combusted in an auxiliary boiler to generate heat.

Finally, the two resulting products - paraffinic diesel and alcohols - are blended together to form the final EN590 compliant fuel for diesel applications.

2.4 HYDROFORMYLATION OF THE C₅-C₁₀ OLEFIN-ENRICHED PRODUCT FRACTION

The second key process step in the REDIFUEL concept is hydroformylation where the C_5 - C_{10} product fraction that is enriched in olefins is converted to C_6 - C_{11} alcohols by combining two chemical reactions: hydroformylation and hydrogenation, which will be simply called hydroformylation (HF) in the following. The first reaction step generates aldehydes from olefins, which can be further converted to alcohols by the addition of hydrogen. These reactions can either be carried out using two functionally distinct catalysts in two separate reactors or with so called tandem catalytic systems, combining both reaction steps in a single vessel under the same process conditions (Figure 3). Tandem catalytic systems for this transformation are still under development. Both approaches have already been presented in deliverable D2.1 "Report on ready hydroformylation catalyst system".



Figure 3. Hydroformylation and hydrogenation reaction network

The first catalytic system (tandem approach) is based on rhodium as the catalyst metal, with inexpensive and readily available tertiary amines as ligands. This catalytic system is able to catalyse both reactions, the hydroformylation and the hydrogenation, in a single step and therefore directly transforms olefins to alcohols. The second catalytic system (two-step approach) is also based on rhodium as the catalyst metal in combination with water-soluble phosphine ligands. This system catalyses the first hydroformylation reaction. The resulting aldehyde products are then



hydrogenated over a solid nickel hydrogenation catalyst. Both these systems were found to be promising candidates for the production of alcohols. As the second catalytic system with sulfonated phosphine ligands allows for an easy and intrinsic catalyst recycling, it was selected as the focus of future investigations and the pilot plant experiments described in this report were conducted following this two-step approach.

In both catalyst systems, the reaction is catalysed by homogenous transition metal catalysts which include rhodium. Given the high price of this necessary catalyst metal, recovery of the catalyst from the reaction products is of high importance to achieve an economically viable process. Ideally, the catalyst is recovered or immobilized in its active form, which in this project will be achieved using so called liquid/liquid multiphase systems. Herein, the catalyst complex is water-soluble and hence can be immobilized in an aqueous phase, which is immiscible with substrates as well as reaction products (Figure 4). While this process concept is already industrially applied for short chain olefins like propene (C_3), the low solubility of higher olefins like the C_5-C_{10} fraction in the catalyst remains a challenge and limits the reaction rate.



Figure 4. Multiphasic catalyst recycling

Since both catalyst systems utilize two liquid phases for catalyst recycling, the same reactor concept can be used. Furthermore, the hydroformylation pilot plant designed in REDIFUEL can be operated with both developed catalytic systems. In order to achieve maximum interfacial area and reaction rates, the hydroformylation reactor is a continuously stirred tank reactor (CSTR) with a specifically designed stirrer and baffles.

After the reaction is carried out under intensified mixing conditions, the mixture is allowed to settle and separate in an additional, non-agitated vessel. The aqueous phase containing the catalyst accumulates at the bottom of this vessel and can be recycled to the reactor. The product phase, containing more aldehydes or alcohols, depending on the reaction system used, is transferred to a second reactor. This step removes leftover olefins and, in case of the two-step process, converts the intermediate aldehydes to the desired alcohols. The paraffinic content of the C₅-C₁₀ fraction is removed in a subsequent distillation step to match the flashpoint and density requirements of the EN590. A simplified scheme of the hydroformylation process concept is presented in Figure 5.





Figure 5. Simplified hydroformylation process concept



3 Pilot-scale validation of the gasification, gas clean-up and Fischer-Tropsch synthesis process

3.1 DESCRIPTION OF THE PILOT FACILITY AT VTT'S BIORUUKKI PILOTING CENTRE

3.1.1 GASIFICATION, FILTRATION AND REFORMING

The REDIFUEL concept is based on converting the biomass feedstock to raw syngas in a steam-blown dual fluidised-bed gasifier and the original plan was to use VTT's dual fluidised-bed (DFB) gasification pilot with a biomass feedstock capacity of 50-80 kg/h for the validation test campaigns. However, as the downstream final gas clean-up and synthesis units have been designed for a far lower syngas throughput of appr. 5 m³n/h, it was concluded at the outset of the project that the DFB gasification facility should be substituted with a slightly smaller scale PDU (Process Development Unit) unit that would offer a better match with the downstream steps. VTT's existing gasification facility BFB100 (Figure 6 and Figure 7) that consists of a bubbling fluidised-bed gasifier, a filter unit and a reformer was considered to best fit this purpose and was selected as the experimental unit for the REDIFUEL test campaigns. The BFB100 gasification facility enables the production of similar type of gas for the synthesis step as the DFB unit. Therefore, the results concerning the performance of the downstream gas cleaning and synthesis processes (downstream the gasifier) presented in this report can be considered to be representative for REDIFUEL.



Figure 6. VTT's gasification test facility in Bioruukki, Espoo





Figure 7. Schematic diagram of the BFB100 test rig

Gasifier:

The BFB100 gasification set-up comprises of a bubbling fluidised-bed gasifier, with a maximum fuel feeding capacity of ca. 5 kg/h, followed by a hot gas filter and a catalytic reformer. The gasifier (inner diameter of the bed section: 0.10 m, inner diameter of the freeboard section: 0.15 m) is equipped with electrically heated ovens, which compensate thermal losses and supply the heat for the endothermic gasification reactions in steam-blown gasification mode. Fluidising gases (steam mixed with a small amount of oxygen in this case) are introduced from the bottom of the reactor through a gas distributor plate. The fuel feeding system consists of two subsequent fuel tanks and the fuel is conveyed to the reactor with feeding screws. The fuel enters the reactor at approximately 0.08 m above the gas distributor plate. Make-up bed material is continuously supplied to the gasifier to compensate for the bed material losses caused by carry-over to the filter unit and bottom ash removal. A mixture of silica sand and dolomite was used as bed material in the REDIFUEL test campaigns.

Hot gas filter:

The filter unit contains two sintered metallic filter elements (outer diameter: 0.06 m, length: 1.1 m) that were supplied by GKN Sinter Metals Filters GmbH. These novel filter elements are manufactured from modified iron-chromiumaluminium alloy and can withstand high mechanical loads and temperatures. They also offer high resistance towards corrosive conditions. The filter unit is electrically heated and the maximum attainable filter temperature is around 850 °C. Fly ash is removed from the filter surface by periodic pulse cleaning with nitrogen and the detached filter dust is collected from the bottom of the filter into a container. The filter pulse is typically in 30-60 min intervals depending on the particulate concentration in the raw gas. The pulse pressure was maintained at approximately 3 bar(g).

Catalytic reformer:

The catalytic reformer with an inner diameter of 0.10 m is mounted inside electric ovens and equipped with gas supplies (a mixture of oxygen and nitrogen or CO₂). In the REDIFUEL test campaigns, the reformer was operated autothermally, i.e. oxidation reactions were used to provide the heat required for endothermic reforming reactions. Reformer feed gases were introduced on top of the catalyst bed to achieve the target reforming temperature and reduce soot formation/coking tendency on the catalyst. Electrical ovens were used for compensating the heat losses. Prior to the



REDIFUEL test campaigns, the one-stage reformer was packed with commercial, granular-type nickel catalysts. A mixture of oxygen and CO_2 was supplied on top of the catalyst bed. CO_2 , instead of N_2 , was selected to reduce the inert gas content in the syngas and thus, maximise the production FT hydrocarbons, which was already known to be challenging due to the low specific activity of the REDIFUEL FT catalyst (as described in deliverable D2.2).

Sampling and analysis in the front-end gasification process:

The product gas composition was continuously monitored from two sampling points, after the filter unit and after the reformer (see Figure 7), using both online gas analyzers and micro gas chromatographs. The main gas components (CO, H₂, CO₂, CH₄, and O₂) were analyzed by online gas analyzers that were mainly used for real time process control during the experiments. Micro gas chromatographs equipped with a TC detector were employed for more accurate measuring of permanent gases as well as light hydrocarbons (C₁-C₄). Tars and benzene were measured by an extractive sampling system (offline sampling) according to the standard European Tar Protocol method. The samples were quantified for tar compounds up to coronene using a gas chromatograph with a FID detector and for water content using a TC detector.

3.1.2 FINAL GAS CLEANING

The final gas cleaning process (also called the ultracleaning process, "UC5") employed in the project is illustrated in Figure 8. The process is designed for a nominal feed gas flow rate of 5 m³n/h. The raw gas is supplied to the final gas cleaning unit after reforming. Prior to entering the final gas cleaning unit, the gas is cooled down to around 150-160 °C. The final gas cleaning process is divided into two sections in terms of operating pressure. In the atmospheric section first a condenser with acid injection condenses the steam and removes ammonia, which is followed by an activated carbon (AC) reactor that is designed for bulk sulphur and residual tar+benzene removal. The pressurised 5 bar section involves two guard beds and a water scrubber. The purification steps are located inside the gasification test hall in Bioruukki (Espoo, Finland), while the gas compressors are placed in a container outside the building (Figure 9).



Figure 8. Final gas cleaning steps (post-reforming) prior to Fischer-Tropsch synthesis





Figure 9. VTT's ultracleaning unit "UC5" (left) and gas compressors (right)

Scrubber/condenser with acid injection:

The scrubber/condenser is the first unit operation in the final gas cleaning process and consists of a counter-current column (inner diameter: 0.164 m) filled with Pall rings (bed height: 1.3 m). Since acidic water improves NH₃ dissociation, the pH of the circulating water was set at pH 3 using formic acid injection. The syngas temperature at scrubber outlet was maintained at 25-30 °C.

Activated carbon (AC) reactor for bulk sulphur removal:

The activated carbon reactor (inner diameter: 0.25 cm) involved two separate beds in the REDIFUEL test campaigns. The first contained non-impregnated carbon that was intended for adsorption of residual tars and benzene. The second bed included both non-impregnated and impregnated activated carbon that were used for H₂S removal. The small bed of highly efficient caustic impregnated carbon was employed as a final precautionary step to ensure complete H₂S removal. The relative humidity of the gas was adjusted to be around 55 - 70 % in the REDIFUEL test campaigns, and the reactor temperature was kept at around 25 °C. A constant air feed of 0.2 Ndm³/min was supplied to the reactor during testing.

Pressurised water scrubber for partial CO₂ removal:

The pressurised water scrubber consists of a pressurised counter-current absorption column (inner diameter: 0.16 m) and an atmospheric desorption column (inner diameter: 0.16 m). The scrubber is based on a closed-loop system where the water (ca. 19 dm³/min) circulates between the two columns. A heat exchanger is used to cool the water loop since lower temperatures improve CO_2 solubility in water. The saturated water is led to the atmospheric pressure desorption column where the CO_2 is stripped from the water using N₂.

Guard beds:

The warm guard bed (Guard bed 1) is a pressurised reactor with an inner diameter of 0.085 m. The reactor is mounted inside a furnace and is equipped with a preheater. The two uppermost beds were packed with commercial ZnO adsorbent with Al_2O_3 support in the REDIFUEL test campaigns. A Cu-based catalyst was used for deoxygenation. The deoxygenation step was operated at slightly higher temperature, at ca. 220 - 230 °C, to maintain the ZnO beds at the target temperature of 200 °C.

The cold guard bed (Guard Bed 2) with an inner diameter of 0.08 m was operated at room temperature and involved three types of high-performance activated carbons. The cold guard bed was intended to act primarily as a precautionary step rather than actively removing syngas impurities.



Summary of sorbent/catalyst materials used in the final gas cleaning process:

Table 2 summarises the sorbent and catalyst materials that were applied in the final gas cleaning process and their respective bed masses. The beds were fresh-packed before the first REDIFUEL gasification test campaign (RED-1). They were not changed, weighed, or analyzed until after the third test campaign RED-3.

Sorbent/catalyst	Position	Mass, kg			
Activated Carbon (AC) Reactor					
Non-impregnated AC 1	Bed 1	1.4			
Non-impregnated AC 2	Bed 2: Top	6.6			
Impregnated AC 1	Bed 2: Bottom	1.6			
Guard Bed 1 (warm guard bed)					
ZnO adsorbent*	Bed 1 and 2	2.6			
Cu/Zn catalyst	Bed 3	1.8			
Guard Bed 2 (cold guard bed)					
Impregnated AC 2	Bed 1	1.3			
Doped AC	Bed 2: Bottom	0.3			
Impregnated AC 1	Bed 2: Bottom	0.3			

Table 2. Sorbent/catalyst loadings employed in the final gas cleaning unit in gasification test campaigns RED-1, RED-2 and RED-3

*Exchanged in RED-3 for another ZnO adsorbent and alumina-based COS catalyst.

Gas compression and process control:

The gas is compressed to synthesis pressure in two stages in the final gas cleaning set-up. In the REDIFUEL test campaigns, the gas was compressed to 4-5 bar in the first step (compressor KO1-3500) and further to 30 bar in the second compression step (compressor KO2-3510). The two metal diaphragm compressors are also the driving force for the unit. The compressor output is the limiting factor in the process, and thus a purge (UC5 Purge 1) was devised to allow for flexible integrated operation of the front-end gasification process and the final gas cleaning unit. A second gas purge (MOBSU Purge 1) was placed before feeding the gas to FT synthesis to match the scales between the FT synthesis unit and the final gas cleaning unit. After the second compressor, the purified syngas was directed to a small buffer tank (TA-3500) and finally fed to the FT process using a mass flow controller (MFC). Simplified flowsheets of the final gas cleaning the gas compressors and purge flows are displayed in Figure 10.





Sampling and analysis in the final gas cleaning process:

An extensive analytical setup was used for measuring trace impurities from syngas after the final gas cleaning process (prior to feeding the gas to the FT synthesis unit). Continuous analysis of permanent gases was carried out using an online gas analyser and a micro-GC. FTIR (Fourier Transform Infrared Spectroscopy) was employed for the analysis of



water vapor, benzene, toluene, and ammonia. FPD-GC (Flame Photometric Detector Gas Chromatography) was used for continuous analysis of H₂S and COS. With this set-up, sulphur compound detection was possible at sub-ppm level. In addition to continuous analysis methods, colorimetric gas detection tubes (Dräger H₂S, HCN, and HCl) were occasionally used. Analysis was primarily performed after the final gas cleaning process as the main purpose was to verify that the syngas was properly cleaned before being fed to the FT synthesis process. At times, measurements were also performed in other parts of the final gas cleaning train to gain further insight on the performance of the final gas cleaning units. The quantitative analytical methods employed for measuring syngas impurities are summarised in Table 3 along with the detection limits.

Species	Analytical method	Continuous measurement	Limit of detection (LoD)
H ₂ S	FPD-GC	FPD-GC Yes	
COS	FPD-GC	Yes	<0.1 ppm
HCN	Colorimetric tubes	No	0.1 ppm
NH ₃	FPD-GC	Yes	Unknown in syngas (estimate: low ppm level)
HCI	Colorimetric tubes	No	0.1 ppm
Benzene	FTIR	Yes	Unknown in syngas (estimate: low ppm level)

Table 3. Quantitative analytical methods employed for the major syngas impurities and the limits of detection

3.1.3 FISCHER-TROPSCH SYNTHESIS UNIT (MOBSU)

VTT's Mobile Synthesis Unit (MOBSU) was used in the REDIFUEL test campaigns (Figure 11). MOBSU is a transportable experimental laboratory unit that functions as a small-scale Power-to-X (PtX) or a Biomass-to-X (BtX) unit - depending on the gas source. The unit scale is 5 - 6 m³n/h of syngas input. The unit incorporates INERATEC's microstructured FT reactor (one-stage, once-through) and the related hardware, including water cooling cycle, hot and cold traps for product recovery and supplies for bottled gases that are required in start-up and shutdown phases and in verification runs (Figure 12).





Figure 11. Mobile synthesis unit MOBSU at VTT's premises in Bioruukki, Espoo



Figure 12. Schematic diagram of the MOBSU unit

The purified syngas is fed to the Mobile Synthesis Unit using a mass flow controller that allows maintaining a uniform feed flowrate. The gas is first pre-heated in a heat exchanger before feeding to the reactor. The FT synthesis is based on INERATEC's intensified one-stage reactor that is capable of achieving high conversion efficiency even in the presence of a high fraction of inert species (i.e. N₂, CO₂ and CH₄) in the gas. The reactor is equipped with an evaporative water cooling cycle. Within the REDIFUEL project, INERATEC's FT reactor design was adapted to the requirements of the newly developed catalyst by CSIC. By redesigning the outer shell and the sealing of the microstructured FT reactor, a reduction of the catalyst at temperatures of up to 400 °C was enabled to ensure catalytic activity.



The reactor effluent is cooled downstream the FT reactor to condense the FT products in two consecutive steps. The heavy hydrocarbon fraction (wax) is condensed in the hot trap that is maintained slightly below the reaction temperature. The lighter hydrocarbon fraction (oil) and the water phase are condensed in the second cooling step in the cold trap that is kept below room temperature. The gases entering the FT unit and exiting the cold trap were analyzed for permanent gases and hydrocarbons using a Shimadzu gas chromatograph with a TCD and flame ionization detector (FID). The liquid and solid FT product samples collected during the test campaigns were analysed using a gas chromatograph FID (Flame Ionization Detector) and compound-specific response factors were used to determine the mass distribution for olefin, paraffin and alcohol components.

3.2 RESULTS OBTAINED IN THE PILOT-SCALE TEST CAMPAIGNS

Prior to the piloting, the redesigned FT reactor constructed by INERATEC was packed with the FT catalyst developed in WP2 (CAO02) and then shipped to VTT, where it was mounted inside the Mobile Synthesis Unit (MOBSU). The commissioning of the new FT reactor set-up took place at VTT in late March 2020, after which the first gasification test campaign was launched. In the time period of April-June 2020, a series of week-long gasification test campaigns were carried out at VTT's Piloting Centre Bioruukki (Espoo, Finland) where the entire process from gasification up to Fischer-Tropsch synthesis was operated in parallel using woody feedstocks as raw material. VTT's staff was responsible for the real-time monitoring and operation of the gasification and gas cleaning process as well as for the peripheral equipment, while INERATEC took part in running the MOBSU unit. Due to the emergence of the global COVID-19 pandemic in March 2020 and the travel restrictions that were soon put in place, INERATEC's operators were not able to physically participate in the test campaigns in Finland. This issue was resolved by operating the MOBSU unit mostly remotely from Germany (by INERATEC), while VTT's personnel took care of the required preparations related to the FT synthesis unit prior to the experiments and the on-site operations that were necessary during testing, e.g. emptying the product traps or switching the MOBSU to run on bottled gases if the gas supply from the gasification process was for some reason interrupted.

One of the main objectives in the pilot test campaigns was to validate the performance of the novel FT catalyst developed by CSIC using bio-based syngas. The preceding lab-scale experiments had however revealed that, although the catalyst was capable of producing high shares of olefins in the C₅-C₁₀ hydrocarbon range, it also had a low specific activity and consequently low productivity. Since the production of real biomass-based FT hydrocarbons was critical for the subsequent hydroformylation experiments, the gasification test campaigns were complemented with dedicated bottled gas runs where the FT synthesis unit was operated using an artificial syngas mixture. This allowed producing enough FT product for the catalyst stability tests in hydroformylation. Since direct coupling of the hydroformylation pilot with the gasification and FT synthesis process was not possible, the hydroformylation pilot plant was constructed at MPI's premises in Mülheim, Germany. The hydroformylation pilot plant and the experiments conducted with the real substrate derived from the pilot experiments at VTT are discussed in Chapter 4.

3.2.1 FEEDSTOCKS AND BED MATERIALS USED IN THE GASIFICATION TEST CAMPAIGNS

Two types of woody feedstocks were used in the REDIFUEL test campaigns: crushed bark pellets and crushed wood pellets. Photographs of the original pellets are shown in Figure 13. Both feedstocks were crushed and sieved to the target size fraction prior to the experiments. The proximate and ultimate analyses of the two feedstocks are presented in Table 4. The base bed material employed for heat transfer in the gasifier was a mixture of silica sand and dolomite (trade name: Myanit D).





Figure 13. Photographs of Finnish wood pellets (left) and bark pellets (right) used in the REDIFUEL test campaigns

Table 4. The composition a	nd properties of feedstocks u	used in REDIFUEL test campaigns
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FEEDSTOCK	Crushed bark pellet	Crushed wood pellet		
Particle size, mm	0.4 - 0.98	0.4 - 1.89		
Moisture, m-%	8.4	7.2		
LHV, MJ/kg (dry basis)	19.4	18.4		
Proximate analysis, wt-% (dry	basis)			
Volatile matter	77.8	83.2		
Fixed carbon	18.5	16.4		
Ash	3.7	0.5		
Ultimate analysis, wt-% (dry basis)				
С	51.5	50.7		
Н	5.8	5.9		
Ν	0.3	0.1		
O (calculated as difference)	38.6	42.8		
S	0.06	0.01		
Ash	3.7	0.5		

3.2.2 PERFORMANCE OF THE FRONT-END PROCESS: GASIFICATION, FILTRATION AND REFORMING

Table 5 summarises the operation conditions and the main results concerning the performance of the front-end gasification process that involves the bubbling fluidised-bed gasifier, the hot gas filter and the reformer. The results are shown for the first three gasification test campaigns RED-1, RED-2 and RED-3. Overall, the gasification test campaigns were considered technically successful as only short-term process interruptions occurred. Only one full gasification process shutdown took place due to a sudden disturbance in the fuel feeding, but even in this case, the gasifier was revived and the original operation conditions were restored within 30 minutes. Typically, over 100 hours of operation under gasification conditions were achieved in the week-long REDIFUEL test campaigns. This allowed operating the FT synthesis unit with real bio-syngas for extended periods of time with up to 96 hours of total runtime per test campaign (see



Table 11). The first test campaign RED-1 was shorter due to the national holiday in Finland that shortened the test run to 4 days.

Gasification:

The gasification process was typically run at fixed operation conditions throughout the test campaign as the primary target was to guarantee non-interrupted supply of syngas for the FT synthesis unit. Some adjustments were required at times mostly to match the gasifier throughput with the gas demand in the downstream processing steps. In order to generate a gas similar to that obtained in a steam-blown dual fluidised-bed gasifier, steam mixed with a small amount of oxygen (appr. 10 wt-%) was used as fluidising gases in the gasifier. The gasification temperature in the bed section was kept at around 810-820 °C both with bark pellet and clean wood pellet feedstocks. A continuous make-up bed material feed consisting of a mixture of sand and dolomite was supplied to the reactor throughout the test campaigns. Bottom ash was removed typically at 30 min to 1 hour intervals to prevent char and ash from accumulating in the gasifier bed. This is particularly critical in steam gasification conditions where the carbon conversion achieved in gasification is lower and consequently more unreacted carbon remains in the reactor. It was even more critical in the bubbling fluidised-bed reactor set-up used in the project where the char is not naturally recycled to combustion, as is done in dual fluidised-bed gasification systems. An example of the raw gas composition measured after the filter unit is presented in Figure 14. More detailed gas compositions are given in







Figure 14. Dry gas composition measured after filtration (online gas analyser) in test campaign RED-3



	RED-1, Week 15/2020	RED-2, Week 17/2020	RED-3, Week 22/2020
Feedstock	Crushed bark pellet	Crushed bark pellet	Crushed wood pellet
Bed material	40%/60% sand/dolomite	40%/60% sand/dolomite	60%/40% sand/dolomite
Operation under gasification conditions, h	74	103	104
GASIFIER	1		
Fuel feed rate, g/h	3760	3760	4420
Steam-to-fuel feed ratio, kg/kg-daf	1.06	1.08	0.85
O ₂ feed, % of stoich. combustion	7.6	8.6	8.2
Bed / freeboard temperature, °C	815 / 791	810 / 792	821 / 792
Pressure in freeboard, bar (abs)	1.09	1.09	1.09
Fluidising velocity, m/s	0.59	0.56	0.60
Wet gas flow rate, m ³ n/h (raw gas)	9.6	9.7	10.1
FILTER		1	1
Filter temperature, °C (inlet/outlet)	525 / 519	522 / 516	521 / 514
Face velocity on the filter, cm/s	1.9	1.9	1.9
Particulate concentration at filter inlet, g/m ³ n	35.9	40.1	18.6
DRY GAS COMPOSITION AFTER FILTER, vol-%	1	Γ	Γ
со	15.1	16.6	18.9
CO ₂	23.7	23.7	23.2
H ₂	39.0	36.6	33.8
N ₂	14.5	14.3	15.2
CH ₄	5.5	6.0	6.4
C ₂ H ₂	0.0	0.1	0.1
C ₂ H ₄	1.8	2.3	2.0
C ₂ H ₆	0.3	0.4	0.3
C ₃ -C ₅ hydrocarbons	0.0	0.1	0.1
H ₂ O content after filter, vol-%	37.0	37.1	43.1
Tar / benzene concentration after filter, g/m ³ n (in dry gas)	9.6 / 9.2	9.6 / 9.2	11.6 / 9.9
CATALYTIC REFORMER	I	Γ	Γ
Oxygen and CO ₂ feed to reformer, g/s	0.12 / 0.22	0.13 / 0.22	0.14 / 0.22
Temperature at reformer outlet, °C	894	896	890
Pressure difference over catalyst bed, mbar	4.6	4.6	5.8
Wet gas flow rate, m ³ n/h (clean gas)	11.1	11.4	11.9
Space velocity GHSV, 1/h (STP)	1361	1400	1455
Tar / benzene conversion, %	100 / 99.4	100 / 99.3	100/ 100
Methane conversion, %	86.0	83.8	98.2
DRY GAS COMPOSITION AFTER CATALYTIC REFORMER, vol-9	6		
со	23.2	23.0	23.1
CO ₂	23.2	24.3	25.1
H ₂	40.9	40.6	40.1
N ₂	12.2	11.6	11.6
CH₄	0.5	0.6	0.1
C2-Cs hydrocarbons	0	0	0
H ₂ O content after reformer vol-%	25.5	22.0	27.1
Tars / henzene at reformer outlet a/m³n (in day apc)	33.5 0 / 0 0F	33.8 0 / 0 0F	57.1
rais, benzene acteronner outlet, g/mm (mury gas)	0/0.05	070.05	0/0

Table 5. Operation conditions and selected process parameters concerning the front-end gasification process in the first three gasification test runs.



Filtration:

The sintered metallic filter elements used in piloting had already been exposed to biomass gasification conditions for several hundreds of hours prior to the REDIFUEL test campaigns. They had been oxidised after the preceding test run to burn off any residual carbon-containing matter from the filter surface. During the REDIFUEL test campaigns, the filter temperature was maintained at approximately 520 °C, which is typically low enough to condense most of the alkali and heavy metal species from the gas. Alkali and heavy metals were not, however, measured after the filter unit to verify this argument. The face velocity on the filter, i.e. the gas flow rate divided by the filter surface area, was 1.9 cm/s, which is typical for filtration of gasification gas.

Full removal of particulates is generally achieved with these candle-type metal filter elements. Dedicated particulate measurements were not performed during testing, but no dust deposits were found in the reformer catalyst bed nor in the tar samples extracted downstream the filter unit. This indicates that particulates had not penetrated through the filter media, and filter leakages or breakages had not taken place. Consequently, the same set of filters were used in all experiments.

Stable filter operation was achieved in all REDIFUEL test campaigns. The cleaning pulse was applied in 30 min intervals, which was effective in detaching the filter dust cake that was formed on top of the filter elements. The baseline pressure drop across the filter remained constant throughout testing and the small variations were only due to slight changes in the raw syngas flow rate. As an example of the filter performance, the filter pressure drop and filter temperatures measured during test campaign RED-2 are presented in Figure 15.



Figure 15. Filter temperature (inlet/outlet) and pressure difference over the filter unit during test campaign RED-1

Catalytic reforming:

The one-stage reformer packed with nickel catalysts was employed in the REDIFUEL test campaigns to convert tars and hydrocarbon gases to H_2 and CO. The nickel catalyst bed was somewhat oversized, which led to lower space velocities (in the order of 1400 1/h, STP) than typically applied in reforming of biomass-based gasification gas. This was done in an effort to guarantee trouble-free operation in the downstream processing steps and prevent jeopardizing the FT catalyst. A mixture of oxygen and CO₂ was supplied on top of the catalyst bed and the oxidant feed was adjusted to maintain the gas temperature at reformer outlet around 890-900 °C.



Full conversion of C_2 - C_5 hydrocarbons and tars was achieved in the reformer. Also benzene was reformed very effectively, leading to benzene concentrations of below 60 mg/m³n (in dry gas) at reformer outlet. Sulphur species, particularly H₂S, are known catalyst poisons causing deactivation of reformer catalysts. Although both feedstocks applied in the gasification tests were relative low in sulphur, the effect of sulphur poisoning and somewhat reduced catalyst activity can be observed when comparing the results obtained with bark pellets with those of clean wood pellets. With clean wood pellet feedstock with a sulphur content of only 0.01 wt-% in dry matter, benzene and methane were reformed even more effectively than in the case of bark pellets. In test campaign RED-3, benzene and methane conversions of 100% and 98% were achieved, leaving only 0.1 vol-% of methane (in dry gas) at reformer outlet. With bark pellet feedstock with a sulphur content of 0.06 wt-% in dry matter (test campaigns RED-1 and RED-2), the corresponding figures were 99% and 84-86%, respectively.

The pressure difference across the reformer bed was continuously monitored during testing. No indications of soot nor coke formation in the reformer could be detected as the pressure drop over the catalyst bed remained constant throughout the test campaigns. This judgement was later confirmed after visual inspection of the reformer bed that was performed after the REDIFUEL test campaigns. Based on the visual inspection, the catalysts were intact and there were no signs of carbon formation on the granular catalysts even after being exposed to several hundreds of hours to biomass gasification gas. As an example of the stability obtained in the catalytic reformer, the reformer temperatures and the pressure drop are shown in Figure 16 and the dry gas composition measured downstream the reformer in Figure 17, respectively, for test campaign RED-2.



Figure 16. Reformer temperatures measured from the catalyst bed and pressure drop across the reformer in test campaign RED-2





Figure 17. Dry gas composition measured after the reformer in test campaign RED-2 (using a continuous gas analyser). Methane content is displayed on the secondary y-axis

3.2.3 PERFORMANCE OF THE FINAL GAS CLEANING PROCESS

The final gas cleaning unit "UC5" was coupled with the gasification process, which supplied reformed syngas for further conditioning. In the start-up phase, the UC5 process was first pressurised and stabilised under nitrogen flow. Once the upstream gasification process had reached steady-state conditions, the two processes were coupled and the nitrogen feed to the system was closed. Table 6 shows the total runtime achieved with the final gas cleaning unit using bio-based syngas.

Table 6. UC5 operation hours under gasification conditions in the REDIFUEL test campaigns

Test campaign	RED-1	RED-2	RED-3	Total
UC5 runtime with bio-based syngas, h	67.5	99	97.5	264

Removal of sulphur species (H₂S, COS):

Sulphur compounds were analysed from multiple points in the final gas cleaning process to investigate in which step they were removed. The results are shown only for test campaigns RED-1 and RED-2 where bark pellets with a higher sulphur content were used as feedstock (Figure 18). In test campaign RED-1, the average concentrations of H₂S and COS in the reformed syngas were 110 ppm and 14 ppm, respectively (three measurements). The concentrations increased to some extent as the test campaign progressed. In test campaign RED-2, the corresponding concentrations were 119 ppm and 19 ppm (eight measurements), and they were steady throughout the test campaign. Qualitative analysis by FPD-GC indicated that no other sulphur compounds were present in the reformed syngas, though the organic sulphur limit of detection has not been tested for this particular FPD-GC. Nevertheless, knowledge of previous tests with similar gasification facilities have shown that H₂S and COS are the only sulphur species present in post-reformer syngas.





Figure 18. Multiple sampling point analysis of sulphur compounds. Left: Concentrations in RED-1 at time 35 h. Right: Concentrations in RED-2 at time 80 h. "UC5" refers to the final cleaning unit and "AC reactor" to the activated carbon reactor

As indicated in Figure 18, the small bed packed with non-impregnated activated carbon (bed 1) that was primarily intended for removing residual hydrocarbons was also very effective in capturing sulphur species, particularly H₂S. In test campaign RED-2, the first AC bed became saturated with H₂S. The residual H₂S and also most of the COS were removed in the second bed of the AC reactor (large bottom bed) with only a trace breakthrough of COS occurring (< 1 ppm). Generally, COS does not have a very good affinity for adsorption, but apparently, the residence time on the activated carbon surface was sufficient for it to occur. It is also possible that an oxidative reaction takes place, which in turn improves COS removal over activated carbons. Neither H₂S nor COS were detected after the final gas cleaning process. Thus, the trace COS was likely removed in Guard bed 2 (cold guard bed).

The sorbent loadings were not exchanged in between test campaigns and thus, the same activated carbon beds were employed in the following test campaign RED-3. The size of the activated carbon beds was sufficient in capturing the sulphur species also in test campaign RED-3, as no breakthrough was detected. However, the sulphur concentration in the gas was much lower due to the low sulphur content of the clean wood pellet feedstock: the average concentrations of H₂S and COS in the reformed gas were only 12 ppm and 5 ppm, respectively.

Removal of ammonia and benzene:

Removal of ammonia and benzene was investigated by FTIR analysis from multiple points in the final gas cleaning train. Full removal of ammonia was targeted already in the scrubber/condenser step, while residual benzene and tars were to be removed with activated carbons in the first bed of the AC reactor. Table 7 summarises the concentrations of water vapour, ammonia and benzene measured along the final gas cleaning process.

Table 7. Concentrations of H₂O, NH₃ and benzene measured from multiple locations in the final gas cleaning process (FTIR analysis). Results are derived from test campaigns RED-1, RED-2 and RED-3

Measurement location	H ₂ O, vol-%	NH₃, ppm	Benzene, %
After scrubber/condenser	2.0	0*	0*
After AC reactor (bed 1)	2.0	Unchanged	Unchanged
After AC reactor	2.0	Unchanged	Unchanged
After UC5 (ultracleaning)	0.07	Unchanged	Unchanged

*ppm-level base concentration detected, interpreted as noise.

Ammonia was removed effectively in the water scrubber/condenser stage, as intended. The water vapour concentration measured after the scrubbing step was 2 vol-%, which corresponds to a dew point of approximately 20 °C. The gas is



further dried in the compressor stages, and the clean syngas that was fed to the FT synthesis unit exhibited a moisture content of around 0.07 vol-%.

The gas supplied from the gasification facility to the final gas cleaning process contained very little benzene (below 20 ppmv in dry gas) and virtually no tars, as they were converted efficiently already in the catalytic reformer. Therefore, FTIR could not detect benzene in any of the measurement points. It is known that benzene is not removed in the water scrubbing step at least very efficiently. Trace amounts of benzene, if any, are expected to be removed in the activated carbon bed.

Removal of oxygen:

Oxygen removal in the warm guard bed was continuously monitored using a micro-GC (estimated detection limit for O₂: 10 - 100 ppmv). No oxygen breakthrough was detected after the final gas cleaning unit indicating that complete removal of oxygen was achieved in the deoxygenation step using the copper catalyst.

Removal of HCN and HCI:

Colorimetric analysis using Dräger test tubes was performed for HCN and HCl to examine to which extent they are removed in the various gas clean-up steps. The results are summarised in Table 8. As expected, the sour water scrubbing step does not remove the acidic HCN nor HCl species, at least not very effectively. Therefore, the reported concentrations after the scrubber/condenser unit were close to those measured at reformer outlet. HCN was present in low concentrations after the condenser unit and was fully removed after the final gas cleaning process. HCl could be detected by Dräger tubes neither in the feed gas nor after the final gas cleaning process.

Table 8. Concentrations of HCN and HCl analysed with Dräger tubes in test campaigns RED-1 and RED-2.

Measurement location	HCN, ppm (dry basis)	HCl, ppm (dry basis)		
After condenser	RED-1 and RED-2 test campaigns: 1.5-2.5	0		
	RED-3 test campaign: < 0.5			
After UC5 (ultracleaning)	0	0		

Partial removal of CO2:

The CO₂ removal rate in the water scrubber depends on several factors. High water flowrate equals favorable vaporliquid equilibrium for gas absorption. Other factors affecting performance are the gas flowrate: lower flowrate equals lower CO₂ mass flow and improved removal rate. Higher CO₂ content in the inlet gas, higher operating pressure and lower temperature in the absorption column also improve the removal efficiency. The main limiting factor in the water scrubber used in the REDIFUEL test campaigns is the water flow rate. To maximize the CO₂ capture in the scrubbing step, the water scrubber was run with maximum water flowrate that the equipment could supply and using as cool water as possible.

As an example of the water scrubber performance, the results obtained during test campaign RED-2 are displayed in Figure 19. The water pump frequency was kept stable and the circulating water flowrate was $18 \text{ dm}^3/\text{min}$. The N₂ feed rate to the stripper column was kept at 20 Ndm³/min. Even though the syngas pressure varied between 3.5 to 4 bar(g), CO₂ removal rates were relatively stable at 50 %. Higher removal rates could not be achieved with the current set-up due to limitations in water supply.





Figure 19. Water scrubber performance in campaign RED-2. Red vertical line: shutdown. Green vertical line: start-up

Syngas composition after final gas cleaning:

The final gas cleaning process was successful in removing the harmful contaminants from syngas to a level acceptable for FT synthesis (according to literature sources) in all REDIFUEL test campaigns. The experiences gained from FT synthesis performance with real bio-syngas further confirmed this conclusions, as there were no indications of catalyst deactivation during the gasification experiments (as explained in more detail in Section 3.2.5).

Table 9 shows the measured impurity concentrations before and after final gas cleaning in test campaigns RED-1 and RED-2 (bark pellets as feedstock). The measured concentrations are compared against the target values and the locations in which each impurity is removed are concluded.

Species	Measured concentration after reforming	Target concentration after ultracleaning	Measured concentration after ultracleaning	Removal location	
H ₂ S*	100-120 ppmv	< 0.1 ppmv	0 ppmv	AC reactor	
COS*	5- 15 ppmv	< 0.1 ppmv	0 ppmv	AC reactor	
NH ₃ *	325 ppmv	< 0.1 ppmv	0 ppmv	Scrubber/condenser	
HCN [*]	1.5 - 2.5 ppmv	< 0.1 ppmv	0 ppmv	Unknown	
HCI*	na	< 0.1 ppm	0 ppm		
O2 [*]	0 vol-%	< 1 ppm	0.00 vol-%	Warm guard bed	
Water vapour	35 vol-%	Dewpoint < 15 °C	Dewpoint 19 °C	Multiple	
Benzene	11-17 ppmv	< 1 ppm	0 ppm	AC reactor	
Organic S [*]	nd	-	nd		
CO ₂	20 - 25 vol-%	80% removal	45- 55 % removal	Water scrubber	

Table 9. Syngas impurities measured befo	re and after final gas cleaning ir	test campaigns RED-1 and RED-2

na = not analysed

nd = not detected

* = known catalyst poison



Owing to the stable operation achieved in both the front-end gasification process and the final gas cleaning unit, a steady supply of clean syngas could be delivered to the MOBSU unit during testing. The gas composition measured with an online gas analyser in test campaign RED-2 is shown as an example (Figure 20). During this run, only short process interruptions occurred due to a sudden hick-up in fuel feeding and a gas compressor failure, which were quickly resolved. The average composition of the clean syngas (dry basis) achieved in REDIFUEL test campaigns is presented in Table 10. The water vapour content was below 0.1 vol-%.



Figure 20. Dry gas composition measured (online gas analyser) after the final gas cleaning unit in test campaign RED-2. Methane content is displayed on the secondary y-axis.

Table 10. Dry gas composition	measured after final	gas cleaning	(microGC) in	REDIFUEL te	est campaigns
Tuble 10. Dry gus composition	measured arter mai	Bas cicaring	(111101000)	NEDITOLE (20t campaigns

Dry gas composition after final gas cleaning, vol-%	RED-1	RED-2	RED-3
СО	25.5	25.2	25.6
CO ₂	13.7	15.2	17.0
H ₂	45.0	44.6	44.3
N ₂ *	15.2	14.3	13.0
CH ₄	0.54	0.65	0.01
C ₂ H ₂	0	0	0
C ₂ H ₄	0	0	0
C ₂ H ₆	0	0	0
C ₃ -C ₅ hydrocarbons	0	0	0
02	0	0	0
H ₂ /CO ratio in syngas (mol/mol)	1.8	1.8	1.7

* Originates from purge N₂



3.2.4 FT CATALYST SELECTED FOR PILOTING

The overall objective of FT catalyst development in Task 2.1 was to identify the optimal catalyst recipe that would allow producing a nonconventional FT hydrocarbon product characterised by a particularly high share of C_5 - C_{10} olefins. Based on the screening of alternative catalyst formulations in Task 2.1, Co-Ru/Al₂O₃ catalyst prepared on a commercial support (later denoted as CAO02) was shown to possess the desired properties and was selected for piloting in real biomass syngas environment in WP4.

When selecting the FT catalyst for validation tests, the REDIFUEL consortium put specific emphasis on the production of a biofuel blend that would be highly enriched in C₆₋₁₁ alcohols. The goal was to reach even higher fraction of alcohols than originally planned (>40 vol-%) due to the EN590 fuel density considerations. However, the lab-scale catalyst studies in Task 2.1 had revealed a trade-off between the overall biosyngas conversion rate and the selectivity to olefins in the C₅-C₁₀ hydrocarbon product fraction. Catalysts that were more selective to the given fraction showed to be less active per unit mass/volume than catalysts less selective to that product slate. Given its highest selecticity to C₅-C₁₀ olefins, the catalyst CAO02 showed the lowest biosyngas overall conversion rate within the series of FT catalysts developed by CSIC. The selected catalyst also had a markedly lower density than commercial FT catalysts typically applied in MOBSU, which led to a far lower catalyst mass that could be packed into the MOBSU FT reactor for the validation tests.

Due to the low specific activity and density of the FT catalyst, the target production volumes of more than 300 litres of FT products (as stated in the GA) could not be achieved in the validation test campaigns. During the pilot experiments at VTT, the REDIFUEL catalyst was operated under syngas conditions (using real bio-syngas or syngas mixed from bottled gases) for over 750 hours. Over this time period, roughly 11 kg or FT oil and over 6 kg of solid FT wax product was produced. Although the production volumes were far from the target values, the REDIFUEL test campaigns generated valuable information on the performance of the non-conventional FT catalyst with real bio-based syngas and could be used to validate the results observed in lab conditions also in pilot scale.

Acknowledging the fact that the investment cost of the FT synthesis unit and the overall process economics are highly influenced by the specific activity and productivity of the FT catalyst, the REDIFUEL consortium put further efforts into testing and investigating alternative FT catalyst that would exhibit higher specific activity than the one selected for piloting. FT catalysts CAO01 and CAO03 that were already available at CSIC were selected for benchmarking studies and lab-scale testing was launched straight after the validation test campaigns. The test results with these alternative FT catalyst are reported separately in deliverable D2.5 "FT catalyst benchmarking results and optimal FT process specifications". These results were also used as input for the techno-economic assessment of the overall REDIFUEL process in Task 4.4 and WP5.

3.2.5 PERFORMANCE OF THE FT SYNTHESIS UNIT WITH REDIFUEL CATALYST

The FT catalyst performance was first evaluated with bottled gases (RED-0) and afterwards in a series of week-long gasification test campaigns with both bark and wood-derived syngas (RED-1, RED-2, RED-3 and RED-4) where the FT synthesis unit (MOBSU) was coupled with the gasification and gas clean-up process. A total of over 300 hours of operation with real gasification syngas was achieved over the course of the test campaigns. After test campaign RED-2, a bottled gas test campaign BG-1 was conducted to examine the REDIFUEL catalyst performance over a longer test period and also to generate more FT product for MPI's hydroformylation experiments (described in Chapter 4). During this test campaign, non-interrupted operation of over 250 hours was achieved with bottled gases. If the transition and gasification shut down phases are included, the bottled gas runtime with the REDIFUEL catalyst reduction are summarised in



Table 11.

Test campaign	RED-0	RED-1	RED-2	BG-1	RED-3	RED-4	Total
FT catalyst reduced before	Y		v		v	×	
test campaign	х		X		X	X	
Runtime with biomass-based		64	06		01	74	225
syngas, h		04	90		91	74	525
Runtime with bottled gases,	20	0	7	255	10	100	121
h	29	ð	/	255	15	102	434

Table 11. MOBSU operation hours with biomass-based syngas and bottled gases in REDIFUEL test campaigns.

Reduction of the REDIFUEL catalyst:

Before the test campaigns, the REDIFUEL catalyst CAO02 was reduced in-situ at a target temperature of 400 °C under hydrogen flow (60 Ndm³/min) for up to 5 h. Figure 21 shows a typical temperature profile in the MOBSU reactor during catalyst reduction.



• FT10 TOP 🔺 FT11 TOP = FT12 MIDDLE × FT13 MIDDLE × FT14 MIDDLE • FT15 MIDDLE • FT16 BOTTOM + FT17 BOTTOM - FT2 heater % • FT7 heater %



Test campaign RED-0 with bottled gases:

The main purpose of the bottled gas run RED-0 was firstly to commission the MOBSU set-up with INERATEC's FT reactor (that was now partly redesigned to fit the needs of the REDIFUEL project) but also to examine the catalyst performance, particularly the catalyst activity, and identify optimal operation conditions prior to the dedicated gasification test campaigns. Test campaign RED-0 comprised of four different set points (SP1-SP4) with varying space velocities and reaction temperatures. The operation pressure was 20 bar. The molar H_2 /CO ratio in the feed gas was maintained at either 1.86 (roughly matching the typical ratio achieved in pilot gasification runs) or 2.0 (stoichiometric ratio for FT synthesis).



Table 12 summarises the test conditions and the feed gas flow rates used in testing.



Set	Temperature*,	Pressure,	GHSV,	H ₂ feed,	CO feed,	N₂ feed,	Total
point	°C	bar	Ndm ³ /g _{cat} h	Ndm ³ /min	Ndm ³ /min	Ndm ³ /min	Ndm ³ /min
SP1	212-222	20	21.33	39	21	20	80
SP2	218	20	17.33	39	21	5	65
SP3	216	20	9.33	20	10	5	35
SP4	207-229	20	5.33	10	5	5	20

Table 12.	Operation	conditions	and feed	gas flow	rates a	pplied in	MOBSU in	test campaign	RED-0	(bottled	gas run).
						P. P				()))))))))))))))))))	0

*Measured maximum temperature in the FT reactor.

Set point SP1 was used as a reference point in VTT's earlier test campaigns with the MOBSU unit and was therefore chosen as the first to be tested with the REDIFUEL catalyst as well. The catalyst activity was assessed with respect to specific activity (SA), which in this report is the amount of CO converted per grams of catalyst per unit time (h). This is thus expressed as mmol CO/g_{cat}h. The outlet gases were measured after the cold trap with an online TCD/FID-GC to determine the CO conversion level achieved during testing. The results concerning the catalyst specific activity and the measured reactor temperatures in test campaign RED-0 are shown in Figure 22. The feed gas flowrates, CO and H₂ conversions as well as methane selectivity over the course of the test campaign are presented in Figure 23.



Figure 22. FT reactor temperatures, specific activity and methane selectivity obtained in test campaign RED-0 (bottled gas run)



Figure 23. Feed gas flow rates, conversions of CO and H_2 and methane selectivity in test campaign RED-0 (bottled gas run)

During the first test campaign RED-0, it became apparent that the catalyst activity is not sufficient to sustain the desired reaction temperature, i.e. the FT reactor was not autothermal. This was evident at the beginning of set point SP4, where the temperature dropped significantly during the tested period (Figure 22). The specific activity also decreased in proportion to the temperature. To retain isothermal conditions in the reactor, it was thus necessary to heat the reactor externally using electrical heaters.

As indicated in Figure 23, set points SP1 and SP2 achieved very low conversion levels (CO conversion below 5%). In the attempt to increase the CO conversion and yield more FT product, the syngas flowrate was reduced in the following set points and the temperature was increased towards the end of set point SP4 (by taking the electrical heaters into use). The maximum CO conversion of 28% and specific activity of over 15 mmol CO/g_{cat}h were achieved in set point SP4 at a temperature of approximately 230 °C. Although the higher operation temperature led to higher conversion rates, it has likely reduced the olefin selectivity to some degree.

The solid and liquid FT products formed at the end of set point SP4 were collected and analysed. Sampling was performed during the stage where the reactor temperature was increased. Figure 24 shows the product distribution of the collected oil phase (which was separated from the water phase) and the total outflow of FT products calculated from the mass balance. A time-averaged specific activity was assumed for the sampling duration in the mass balance calculation.





Figure 24. FT product analysis results in test campaign RED-0. Left: Composition of FT oil in SP4. Right: Product mass flow rates calculated for SP4 based on the mass balance

The product mass flowrates depicted in Figure 24 (right) show that the maximum density of paraffinic hydrocarbons occurs in the C_{12} - C_{16} range and olefins in the C_8 - C_{10} range. The FT chain growth probability ASF- $\alpha_{C40-C60}$ that was derived from the wax analysis was 0.895. The oil phase consisted mainly of paraffins with 17 % by mass of olefins and some alcohols. A detailed breakdown of the olefins in the oil phase is given in Table 13. The results show that the olefins are distributed more heavily towards the C₈-C₁₀ hydrocarbon range. However, it should be noted that part of the C₅-C₇ hydrocarbons are not captured in the product condensation steps and end up in the gas phase. Although the cold trap was maintained at 5 - 7 °C temperature during testing, the partial pressures of some of these species were too low in the gas to sufficiently condense them.

Analysis results for FT oil								
C_5 - C_{10} hydrocarbons in oil fraction, wt-%	35							
Olefins in C ₅ -C ₁₀ hydrocarbons, wt-%	28							
C ₅ -C ₁₀ olefin distribution, wt-%								
C ₅	-							
C ₆	7							
C ₇	13							
C ₈	25							
C ₉	29							
C ₁₀	26							

Table 13. Analysis results for the FT oil collected in test campaign RED-0 (set point: SP4).

Gasification test campaigns (RED-1, RED-2, RED-3 and RED-4):

In the first gasification test campaign, RED-1, syngas flowrates of up to 50 Ndm³/min were fed to the FT reactor, but since the specific activity was not higher with these higher rates, the feed rate was subsequently lowered to 20 Ndm³/min for the remaining gasification campaigns. Based on the experiences gained in test campaign RED-0, the reactor temperature was fixed to around 230 °C (maximum temperature in the reactor), since the highest specific activities were achieved at this temperature (in set point SP4). During the start-up phase, the MOBSU unit was operated with bottled gases before switching to gasification syngas. Prior to coupling the MOBSU unit with the gasification



process, the feed gas composition and the flow rate were adjusted to roughly match with those of the real syngas generated in the gasification process. Set point SP4, which was already employed in the bottled gas run RED-0, was selected as the reference set point and was commonly used prior to coupling the MOBSU unit with the gasification process and also during long-term bottled gas operation. Table 14 gives further details on the operation conditions and feed gas flow rates applied in MOBSU both in gasification conditions and in bottled gas operation.

Table 14. Operation conditions and feed gas flow rates applied in MOBSU in gasification test campaigns (RED-2, RED-3, RED-4) and in bottled gas operation (transition conditions and bottled gas run BG-1)

Set point	Temperature*,	Pressure,	GHSV,	Feed gas flow rates, Ndm ³ /min				1
	°C	bar	Ndm ³ /g _{cat} h	Syngas	H ₂	со	N ₂	Total
Gasification run	227-233	20	6.67	20	-	-	5	25
Bottled gas operation (SP4)	227-230	20	5.33	-	10	5	5	20

*Measured maximum temperature in the FT reactor.

During test campaign RED-1, the startup/shutdown sequence was observed to negatively affect FT performance, since the specific activity of the catalyst at the reference set point (at the beginning of the test campaign) was lower than was detected at the end of the preceding test campaign. To mitigate this issue, it was decided that the catalyst was always to be reduced before operation if the reaction had been interrupted. The results for the gasification campaigns are exemplified in Figure 25 that shows results from test campaign RED-2.



Figure 25. FT results obtained in gasification test campaign RED-2: reactor temperature and specific activity of the catalyst

As shown in Figure 25, the variation in specific activity is high, which is due to the changes in the amount of nitrogen in the bio-syngas. Being based on nitrogen balance, any variation will have a negative effect on the accuracy of the



calculation results. However, a linear trendline shows that the specific activity settles at around 10 mmol CO/g_{cat}h. The maximum temperature was achieved in the middle section of the reactor, while in the first test campaign RED-0 also the bottom stage of the reactor achieved similar temperatures. During test campaign RED-2, there were two process disturbances in the upstream gasification process, during which the FT reactor was switched to operate on bottled gases. Only minor temperature increases were experienced during these process interruptions as a consequence of the slight difference in gas composition and feed rate between the bottled gases and the real syngas. As the trendline for specific activity shows, hardly any activity decrease is observed during the test campaign.

Long-term testing with bottled gases (BG-1):

The long-term test campaign with bottled gases, BG-1, was launched directly after the end of gasification test campaign RED-2. During this run, 255 hours of uninterrupted operation was achieved. The results are presented in Figure 26. At the beginning of the test campaign, the catalyst activity exceeded the activity that was observed during the preceding gasification test campaign RED-2. The different mole flow of CO and lower inert content of the bottled gases were the likely causes of this discrepancy.

As shown in Figure 26, the catalyst activity decreased over the course of the bottled gas operation. While there is a slight decrease in the reaction temperature over this time period, it cannot fully explain the trend towards lower CO conversion rates. It is suspected that the bottled gases, which were of industrial quality (99.0 or 99.5 % purity), contained impurities that caused this type of deactivation (most probably sulphur compounds).



Figure 26. FT results obtained in test campaign BG-1 (bottled gas run): reactor temperatures and specific activity of the REDIFUEL catalyst

Productivity in REDIFUEL test campaigns:

Productivity, i.e. product formation rate expressed as mass per unit time, was measured by sampling the wax and oil+water phases and weighing them. Product sampling was particularly challenging in the REDIFUEL test campaigns due to the relatively low productivities achieved with the REDIFUEL catalyst (CAO02). Long sampling intervals were required



to gain reliable productivity rates. Table 15 shows the product amounts and the estimated productivities in the REDIFUEL test campaigns.

Test campaign	RED-1	RED-2	BG-1	RED-3	RED-4	Total
Type of test run	Gasification	Gasification	Bottled gas	Gasification	Gasification	
Wax production, g	400	1000	3000	1100	1100	6600
Wax productivity, g/h	5	10	12	11	7	10
Oil + water production, g	3300	5200	15000	7300	9400	40200
Oil + water productivity, g/h	45	51	64	71	54	59

Table 15. Product quantities and productivities in REDIFUEL test campaigns (products generated in transition phases excluded)

In total, over 6 kg of solid wax product and 40 kg of liquid product, containing both oil and water phases, was produced. Of this, an estimated 11 kg was oil. The productivities varied somewhat between the test campaigns due to small differences in the operating conditions but also due to the aforementioned difficulties in sampling small product quantities accurately. The longer test campaigns, e.g. BG-1, are more reliable in this regard. The average wax productivity was approximately 10 g/h and that of oil+water roughly 60 g/h. Further details on the concentration of C₅-C₁₀ hydrocarbons and olefins in the FT oil product are given in Table 16.

Test campaign	RED-0	RED-1	RED-2	BG-1	RED-3	RED-4
Setpoint	SP4	Gasification	Gasification	SP4	Gasification	SP4
GHSV, Ndm³/g _{cat} h	5.3	10.6	6.7	5.3	6.7	5.3
Temperature, °C	215-229	233	229	229	227	228
TOS* total, h	28	105	131	277	503	755
TOS* since cat. reduction, h	28	105	25	170	57	168
C_5 - C_{10} in oil fraction, m-%	35	30	23	33	33	32
Olefins in C ₅ -C ₁₀ hydrocarbon fraction, m-%	29	13	35	20	21	28

Table 16. FT oil analysis from REDIFUEL test campaigns and operating conditions during product sampling

* TOS = time-on-stream

As indicated in Table 16, the share of C_5 - C_{10} hydrocarbons in the oil product remained unchanged by the total time-onstream (TOS). However, the reaction conditions likely affects the share of olefins versus paraffins: for example the gasification campaigns with higher space velocities and inert concentrations leading to lower olefin share in the oil. Similar olefin concentrations in oil were obtained with the REDIFUEL catalyst after 700 hours of exposure to real biosyngas or bottled gases (test campaign RED-4) as in the first test campaign RED-0.

3.2.6 UNLOADING THE USED REDIFUEL CATALYSTS FROM THE FT REACTOR

One part of the REDIFUEL project was the development of a suitable catalyst loading and unloading technique for the microstructured FT reactors developed by INERATEC. Due to the comparably small openings that are available for the filling of the catalyst, this is more complicated for microstructured reactors than for example for conventional tube reactors, which also holds true for the unloading of the reactors. The large inner surface adds another layer of complexity especially to the unloading of the reactors.



While possible issues with filling of the reactors can relatively easily be counteracted by choosing the right type of catalyst and catalyst preparation technique, the unloading of the spent catalyst is more complicated. During the project, INERATEC developed a multistage process for the unloading. This includes heating, washing with selected washing agents at pre-defined temperatures and variations of resting times for the washing agents. The more defined the reactions conditions during the synthesis process were, the easier the catalyst could be removed from the reactor.

After the REDIFUEL test campaigns were finished in June 2020, INERATEC's FT reactor was dismantled from the MOBSU unit and shipped to INERATEC where the spent REDIFUEL catalyst was to be discharged from the reactor. As it is the nature of a research project like REDIFUEL, the optimum reaction conditions may not always be applied to the reactor and the subsequent removal of the catalyst may thus turn out to be rather complex. The standard procedure that was developed for catalyst removal soon proved to be unsuccessful in removing the REDIFUEL catalyst and recovering the reactor. Therefore, several very intense cleaning options were followed. These included long and high-temperature washing with washing agents, washing with acids and bases and finally even mechanical drilling. Those reactors operated under normal conditions, which includes a load flexible operation, could be successfully cleaned via the developed standard procedure described above. Those reactors that were operated off-normal, could in parts not even be restored by mechanical drilling and had to be considered broken. This was the case with the FT reactor that was operated with the REDIFUEL catalyst in MOBSU.

Based on the analyses made afterwards, it was suggested that the challenge in discharging the catalyst was induced by the larger pore volume, the lower mechanical stability and the particle shape of the REDIFUEL catalyst compared to commercial FT catalysts that were typically applied in INERATEC's FT reactors. Due to the unconventionally high pore volume, a higher amount of hydrocarbon products could have retained in the pore structure causing this issue.



4 Pilot-scale validation of the hydroformylation process

4.1 DESCRIPTION OF THE HYDROFORMYLATION PILOT PLANT

The hydroformylation pilot plant (Figure 27) was built up in Mülheim (MPI, Germany) and designed to operate as an independent unit. The setup consists of a continuously stirred tank reactor and a phase separation vessel. Furthermore, the pilot plant is equipped with pumps for substrate feed, catalyst phase circulation and precise dosing of a make-up stream. Since the two pilot plants, the gasification/FT synthesis unit and the hydroformylation unit, could not be connected, a gas mixing assembly is needed to simulate the bio-syngas stream that is continuously supplied to hydroformylation. The gas supply is controlled by massflow controllers with high accuracy. A simplified scheme of the hydroformylation plant is displayed in Figure 27. The construction phase was finished in 09/2020 and the pilot plant was afterwards commissioned successfully using surrogate substrates and later with real substrate obtained from the gasification test campaigns.



Figure 27. Hydroformylation pilot plant scheme

Figure 28 shows photographs of the finished hydroformylation pilot. The reactor is fed by the gas supply system and pumps (HPLC substrate pump, syringe pump for catalyst make-up stream). The reaction mixture (Figure 28, left) is constantly fed to the decanter (Figure 28, right) for phase separation. After phase separation, the water phase containing the catalyst is recycled to the reactor and the product stream is collected in a bottle for further analysis. A back-pressure regulator (Figure 28, middle) controls the pressure in the system and the outflow of product.





Figure 28. Reactor close-up of the biphasic reaction mixture (left), HF pilot plant (middle) and phase separation vessel (right)

4.2 PILOT PLANT RESULTS WITH SURROGATE MIXTURES

Due to the low amount of FT product available from the REDIFUEL gasification test campaigns, the reaction system was first optimized using a surrogate mixture of 1-octene and n-heptane, which represent the average of the C_5 - C_{10} chain length distribution. After optimization of the pilot plant design as well as the reaction conditions, the pilot plant was operated in continuous flow for up to 50 hours (Figure 29). During this experiment, catalyst deactivation by the loss of water into the product stream was detected and avoided by the continuous addition of a pure water make-up stream of 0.5 ml/h during the whole experiment. For longer operation time, the addition of the used ligand could also be necessary since small amounts of oxygen or peroxides present in the substrate could potentially lead to the loss of catalyst. In the experiment shown in Figure 29, the rhodium content of the product mixture was detected to be below 2 ppm, which represents the feasibility of the chosen catalyst recycling approach.







The results displayed in Figure 29 show only partial conversion of the olefins to aldehydes. This is due to the reaction conditions, which were chosen to investigate catalyst deactivation phenomena, but still reached a Total Turnover Number (TTON) of 68.419, which is of industrially relevant magnitude. Additionally, time profile experiments revealed maximum aldehyde yields of up to 80% with increased reaction time, which could not be implemented in the pilot plant due to limited reactor size and operation windows of the equipment.

4.3 PILOT PLANT RESULTS WITH FT PRODUCT OBTAINED FROM GASIFICATION TEST CAMPAIGNS

Pilot plant experiments with the actual FT product (C_5 - C_{10} hydrocarbon fraction) derived from the REDIFUEL gasification test campaigns were dedicated to test the catalyst activity. The FT oil batch was first fractionated at Neste through distillation and the resulting C_5 - C_{10} hydrocarbon cut (appr. 3 litres) was delivered to MPI for hydroformylation experiments in autumn 2020. The composition of the C_5 - C_{10} hydrocarbon product is shown in Figure 30.



Figure 30. C_5 - C_{10} mixture composition (used as hydroformylation feed)

Due to the low amount of substrate available, the operation time was limited to 37 hours (Figure 31). Over this period, the catalyst was proven to be stable against the FT-derived substrate and no effect on the catalysts stability deviating from the surrogate substrate experiments. Hence, the catalyst system was not affected by any potential impurities of the FT-derived substrate. The activity of the catalyst achieved a TTON of 23.679.





Figure 31. Hydroformylation results with FT product substrate mixture

Since the desired products of the HF step are alcohols, continuous flow hydrogenation experiments were carried out using the intermediates generated in the experiments described above. As expected, a commercially available Raney-Nickel type catalyst led to full hydrogenation of all aldehydes to alcohols and also converted leftover olefins to the already present corresponding paraffins after optimization of the reaction conditions (Figure 32).



Figure 32. Hydrogenation results



5 Summary and conclusions

Front-end gasification process:

- The gasification process was coupled with the final gas cleaning unit and the FT synthesis process (MOBSU) and successfully operated in several week-long experiments using woody biomass as feedstock. Due to the stable conditions obtained in the upstream gasification process, the FT synthesis unit could be run with real bio-syngas for extended periods of time, with up to 79 hours of non-interrupted operation achieved.
- Filter: Stable operation was achieved in the filter at a temperature of 520 °C. No signs of filter blinding nor filter breakages/leakages were detected.
- Catalytic reformer: The one-stage reformer utilising commercial nickel catalysts was highly effective in converting light hydrocarbons (C₂-C₅), tars, benzene but also methane. Methane conversions were higher than typically achieved in biomass gasification conditions due to the oversized catalyst bed. No tar compounds were detected in the reformed gas and benzene concentrations were below 60 mg/m³n (in dry gas).

Final gas cleaning:

- The final gas cleaning process "UC5" was successful in supplying synthesis-quality gas to the MOBSU unit and the target levels set for syngas impurities (according to literature sources) were achieved. The gas was rather clean already prior to the final gas cleaning unit thanks to the efficient hot gas cleaning section and the relatively pure feedstocks. Therefore, bed changes in between the test campaigns were not needed and a total of 264 h operation time was achieved without a detectable breakthrough of any of the analysed impurities. The main impurities were sulphur species, H₂S and COS, especially in test campaigns RED-1 and RED-2 where bark was used as gasifier feedstock.
- Scrubber/condenser: The water vapour was condensed in the scrubbing step and the resulting gas dew point at scrubber outlet was approximately 20 °C. Scrubbing with acidic water (pH 3) was very effective in ammonia removal.
- AC reactor: The AC reactor that was packed with multiple activated carbons removed all H₂S and also most of COS, which is typically difficult to adsorb. Additional tests during the REDIFUEL experiments showed that oxygen injection has a marked effect on H₂S removal, as higher oxygen feed rates resulted in improved removal of H₂S over non-impregnated carbons. No signs of exhaustion of the larger bottom bed was detected, and thus it can be concluded that, considering the sulphur loading in the gas, the material volumes in the AC reactor were oversized for the purpose. The detection limits for H₂S and COS were < 0.1 ppm.
- Guard bed 1 (warm guard bed): COS hydrolysis could not be tested properly during the test campaigns, as COS was removed effectively already in the activated carbon step. Full removal of oxygen was obtained in the deoxygenation step using the Cu-based catalyst, as intended. This was further verified by conducting an experiment where the bed was temporarily bypassed and the effluent was analysed to contain oxygen.
- Pressurised water scrubber for CO₂ removal: CO₂ removal rate of approximately 50 % was achieved. Higher removal rates could not be attained with the current set-up due to limitations in water supply to the scrubber.
- Guard bed 2 (cold guard bed): The cold guard bed was deemed redundant in the REDIFUEL test campaigns as the impurities were removed efficiently already in the preceding clean-up steps.



Fischer-Tropsch synthesis:

- High olefin selectivity was obtained in the pilot test campaigns with real bio-syngas but due to the low specific activity of the REDIFUEL catalyst, the production volumes remained far from the target values. The specific activity was in the range of 10-15 mmol CO/g_{cat}h. Higher reaction temperature was applied in the pilot experiments (230 °C) compared to lab-scale testing (200-215 °C) in an effort to increase CO conversion over the catalyst. This has presumably lowered the olefin selectivity to some degree.
- The FT oil collected during the REDIFUEL experiments contained 23-35 wt-% of C₅-C₁₀ hydrocarbons of which 13-35% were olefins. However, it should be noted that some of the lighter hydrocarbons (particularly in the C₅-C₇ hydrocarbon range) were not fully retrieved in the product condensation steps and ended up in the gas phase, leading to lower shares of C₅-C₁₀ olefins in the FT oil fraction.
- The REDIFUEL catalyst was run with real gasification syngas for over 300 hours in total. Considering this operation time with bio-syngas, there were no direct signs of catalyst deactivation, indicating that the gas cleaning process seems to be successful in removing the critical catalyst poisons from the gas prior to synthesis. Longer runs, however, would be needed to approve this assumption.
- Due to the low specific activity of the REDIFUEL catalyst, its industrial application would require investing in considerably bigger FT reactors than needed with commercial FT catalysts. This was not considered economical and hence, the FT catalyst development and testing continued in WP2 to identify a FT catalyst that would not only have high olefin selectivity but would also be more productive than the catalyst selected for piloting.
- The REDIFUEL catalyst could not be discharged from the microchannel reactor using INERATEC's standard procedure developed for commercial catalyst unloading. The reactor could not be fully recovered even after intense solvent-based and mechanical cleaning procedures. The challenge in discharging the catalyst from the reactor was suggested to be induced by the unconventionally high pore volume of the catalyst and consequently more intense accumulation of hydrocarbon products in the pore structure. This topic requires further investigation.

Hydroformylation:

- The two-step hydroformylation process along with the catalyst recycling approach was validated successfully in pilot scale using surrogate mixtures and finally with the real substrate derived from the gasification experiments. Catalyst deactivation could be prevented by a continuous make-up water feed.
- Catalyst stability was verified in the 37-hour continuous run with the real C₅-C₁₀ hydrocarbon fraction.
- Due to the low amount of FT product available from the gasification experiments, the target operation hours or the alcohol production volumes set for the pilot-scale hydroformylation experiments were not achievable.
- Separation of the paraffins from the final alcohol/paraffin mixture via distillation might be challenging.



6 Deviations from Annex 1

Owing to the low specific activity and density of the FT catalyst that was selected for piloting, the following objectives set for the pilot experiments could not be fully achieved:

#1 Produce more than 300 litres of Fischer-Tropsch hydrocarbons for subsequent hydroformylation experiments and product trials of WP3

Due to the low productivity of the REDIFUEL catalyst, only roughly 6 kg of FT wax and 11 kg of FT oil was produced over the course of the REDIFUEL test campaigns (using both real bio-syngas and bottled gases).

2 Operate the hydroformylation pilot plant for appr. 100-300 hours with the C₅-C₁₀ hydrocarbon mixture obtained from gasification test campaigns and produce 100-200 litres of hydroformylated product with a maximum content of alcohols

Due to the shortage in product delivery from the gasification test campaigns, considerably less FT product (roughly 3 litres) was available for the subsequent hydroformylation experiments. Consequently, the original production target of 100-200 litres of hydroformylation products could not be reached. Instead, the focus in the hydroformylation experiments was to use the real FT product for catalyst stability testing to deliver the proof-of-concept, while other experiments were done mostly with surrogates. The C₅-C₁₀ hydrocarbon cut derived from the gasification experiments was enough for a 37-hour catalyst stability test.



7 References

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9 Risk register

Risk	WP	What is the risk?	Probability of	Effect	Solutions to overcome the risk
No.			risk occurrence ¹	of risk ²	
1	WP2, WP4	The novel cobalt-based FT catalyst exhibits significantly lower productivity than commercial FT catalysts, which leads to reduced production of FT hydrocarbons in pilot test campaigns	2	2	Conventional iron-based catalyst (VTT's portfolio) considered as an alternative option. Moreover, GTL and surrogate alcohols can be purchased and blended with the bio-based REDIFUEL to produce enough fuel for the truck test.
2	WP2, WP4	The novel cobalt-based FT catalyst undergoes unacceptable activity/selectivity decrease when benchmarked with a bio-syngas feed-stream with realistic composition	2	2	Deactivation reasons are identified, which guide adjustments in bio-syngas cleaning section as well as the formulation of a second generation of catalysts. Conventional iron-based catalyst (VTT's portfolio) considered as an alternative option.
3	WP2, WP4	Mechanical properties of the novel cobalt-based FT catalyst pose a challenge for the loading of microstructured reactors: reduced catalyst loading due to low density or unfit shape of the catalyst → leads to reduced production of FT hydrocarbons in pilot test campaigns	2	2	Conventional iron-based catalyst (VTT's portfolio) considered as an alternative option. Moreover, GTL and surrogate alcohols can be purchased and blended with the bio-based REDIFUEL to produce enough fuel for the truck test.
4	WP2, WP4	Low selectivity towards terminal alcohols observed upscaling development of HF process. High once-through conversion of HF necessary to minimize olefin losses.	2	1	Adjustment of the catalyst system at the expense of catalyst overall cost. Alcohol functionality on terminal or 2-carbon atom might not translate into remarkable combustion differences.
5	WP2, WP4	Real FT product and bio-syngas as hydroformylation substrate leads to catalyst deactivation (e.g. because of impurities)	2	2	Change of operating conditions or catalyst system, alternatively removal of impurities
6	WP4	Integration and testing of the entire pilot process is delayed due to technical problems	3	2	Piloting process is simplified by testing problematic units separately

¹ Probability risk will occur: 1 = high, 2 = medium, 3 = Low

² Effect when risk occurs: 1 = high, 2 = medium, 3 = Low