BioTheRoS

Collaborative actions to bring novel **BIO**fuels **THE**rmochemical **RO**utes into industrial **S**cale

DELIVERABLE 4.1

Report on constraints and opportunities for scale-up of gasification process

Date: 30/09/2024
Dissemination level: Public

Deliverable info

Deliverable Version	Final
Title	Report on constraints and opportunities for scale-up of gasification process
Due date	30/09/2024
Delivery Date	30/09/2024
Nature of Deliverable	Document, Report
Document status	Final
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Dissemination level	PU - Public

Project General Information

Grant Agreement n.	101122212
Project acronym	BioTheRoS
Project title	Collaborative actions to bring novel BIOfuels THErmochemical ROutes into industrial Scale
Starting date	1st October 2023
Duration in months	36
Call identifier	HORIZON-CL5-2022-D3-03-02
Topic	Best international practice for scaling up sustainable biofuels
Coordinator	Centre for Research and Technology Hellas (CERTH)
Partners	Centre for Research and Technology Hellas (CERTH) Biomass Technology Group BV (BTG) Centro de Investigación de Recursos y Consumos Energéticos (CIRCE) Wirtschaft & Infrastruktur GmbH & Co Planungs-KG (WIP) BEST - Bioenergy and Sustainable Technologies GmbH (BEST) Motor Oil Hellas (MOH)
Website	www.biotheros.eu

Changelog

Version	Date	Status	Authors	Reviewer	Comments
0.1	30/06/2024	Concept	BEST		
0.2	31/07/2024	Preliminary version	BEST		

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0.3	09/08/2024	Draft version	BEST	BEST internally	
0.4	30/08/2024	Final version	BEST	Consortium	
0.5	27/09/2024	Final version	BEST		

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Executive Summary

At the Syngas Platform Vienna, advanced technologies are being utilized to establish a scalable gasification route using the advanced dual fluidized bed (aDFB) technology. This process generates raw synthesis gas, which undergoes several cleaning steps to achieve the quality required for synthesis gas applications. The process concludes with an FT pilot-scale system based on slurry technology (SBCR – Slurry Bubble Column Reactor) to produce FT-syncrude, which can be further refined into products like Sustainable Aviation Fuel (SAF). These technologies enable economic scaling to sizes between 100-150 MW, where feedstock logistics become crucial in determining the growth limit. The gas production and conversion technologies are based on fluidized bed systems, including gas/solid contact in the gasification process (using a bubbling fluidized bed reactor) and gas/liquid/solid contact in the FT synthesis process (using a slurry bubble column). These systems offer good scalability and potential for cost reduction but present certain risks due to the complexity of fluidized bed conversions, such as fluid dynamics and abrasion of catalysts. Both technologies have the potential to be upscaled to hundreds of MW or even GW (e.g. slurry beds of Sasol based on gas and coal gasification). A significant market challenge is the gas cleaning section, which is highly influenced by the feedstock used. Existing systems for cleaning coal-based synthesis gas are only economically feasible at scales beyond the practical limits of bio-based syncrude plants due to feedstock supply and logistics constraints (several hundreds of MW). To address this, BEST aims to combine filters, liquid scrubbers and fixed bed adsorbers to produce synthesis gas suitable for downstream synthesis applications. The key findings of this report highlight both the bottlenecks and opportunities for scaling up this technology. Critical factors affecting output, system performance, and technology scalability include the impact on:

- product gas composition,
- the efficiency of the counter-current column,
- the performance of liquid scrubbers and fixed-bed systems for gas cleaning,
- CO conversion rates,
- and the composition of FT-syncrude.

These key points are addressed in a test and analytical plan for the activities in Task 4.2 and 4.3 to create a data basis for further project activities. This comprehensive approach aims to demonstrate the entire value chain from biogenic residue materials to high-quality fuel.

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List of abbreviations

ACG	Activated carbon guards
aDFB	Advanced dual fluidized bed
BTL	Biomass-to-Liquid process
BTX	Benzene, toluene, xylene
CAPEX	Capital expenditure
CFPP	Cold filter plugging point
CTL	Coal to Liquid
DFB	Dual fluidized bed
DoW	Description of Work
EWF	European wax federation
FID	Flame ionization detector
FPD	Flame photometric detector
FT	Fischer Tropsch
FTS	Fischer–Tropsch synthesis
GC	Gas chromatography or gas chromatograph
GC/MS	Gas chromatography-mass spectroscopy
GCS	Gas cleaning section
GTL	Gas to Liquid
HPFT	Hydro-processed Fischer-Tropsch diesel
HTFT	High temperature Fischer Tropsch
IBC	Intermediate bulk container
LCA	Life cycle assessment
LTFT	Low temperature Fischer Tropsch
N-compounds	Nitrogen compounds as NH3 and HCN
OPEX	Operational Expenditure
SAF	Sustainable aviation fuel
SBCR	Slurry bubble column reactor
SCD	Sulfur chemiluminescence detector
S-compounds	Sulfur compounds as H_2S and COS
Sim-Dist GC	Gas chromatograph for simulated distillation
RME	Rape seed methyl ester
PAH	Polycyclic aromatic hydrocarbons
PFD	Process flow diagram
PTL	Power-to-Liquid process
TCD	Thermal conductivity detector
TEA	Techno economic assessment
TSA	Temperature swing adsorption
WGS	Water gas shift reaction
WTL	Waste-to-liquid process
XTL	X (Carbon source) to Liquid

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1. Introduction

This deliverable provides a summary of the work conducted under Task 4.1, with a primary focus on identifying the constraints and opportunities for scaling up biomass gasification. In the framework of this task technical challenges for scaling up the DFB gasification technology will be identified. These challenges encompass among others technical parts of the reactor system, such as the counter-current flow column of the gasification reactor, which is currently available only in the scale of 1 MW. Furthermore, the set-up of the process chain will be evaluated regarding the use of residues as feedstock. Thus, the gas cleaning set-up consisting of hot gas filtration and a two-stage liquid scrubbing will be examined regarding its performance using product gas from gasification of residues. Once the technical challenges for scaling-up the technology are identified, these topics will be included in the measurement and analytic plan of T4.2.

To address these DoW following points are included in this deliverable:

I. Comprehensive overview on the Syngas Platform Vienna including the installed and used technologies (DFB and aDFB gasification, coarse and fine gas cleaning and Fischer-Tropsch synthesis).

II. Overview on the process chain and the technical details on the different unit operations.

III. Investigation on constraints and opportunities for scale-up of gasification process including gasification, gas cleaning and Fischer-Tropsch synthesis.

IV. Derived test and analytical plan for Task 4.2 and 4.3 activities based on observed constraints and opportunities

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2. Syngas Platform Vienna: a demonstration-scale research hub

The Syngas Platform Vienna was built for long-term operation campaigns of multiple days up to 3-4 weeks of dual fluidized bed (DFB) gasification, coarse gas cleaning, fine gas cleaning and downstream Fischer-Tropsch (FT) synthesis in demonstration- and pilot-scale. The location of the Syngas Platform Vienna is at the 11. Haidequerstraße 6, 1110 Vienna, which is the industrial site of Wien Energie. Wien Energie dedicated a defined area on their industrial waste incineration site to the development of gasification and downstream upgrading of the syngas as a rented research location to BEST GmbH and is thus a long-term collaboration partner of BEST GmbH.

Figure 1 shows an overview of the infrastructure installed at the Syngas Platform Vienna. The main infrastructure consists of walking floor containers for fuel delivery, the 1 MW DFB gasification demonstration plant, the 250 kW FT pilot plant, a laboratory / technical center with bench-scale apparatuses (such as a temperature swing adsorption unit and a bench-scale FT unit, amongst others), a measurement laboratory with gas chromatographs and a chemical storage unit.

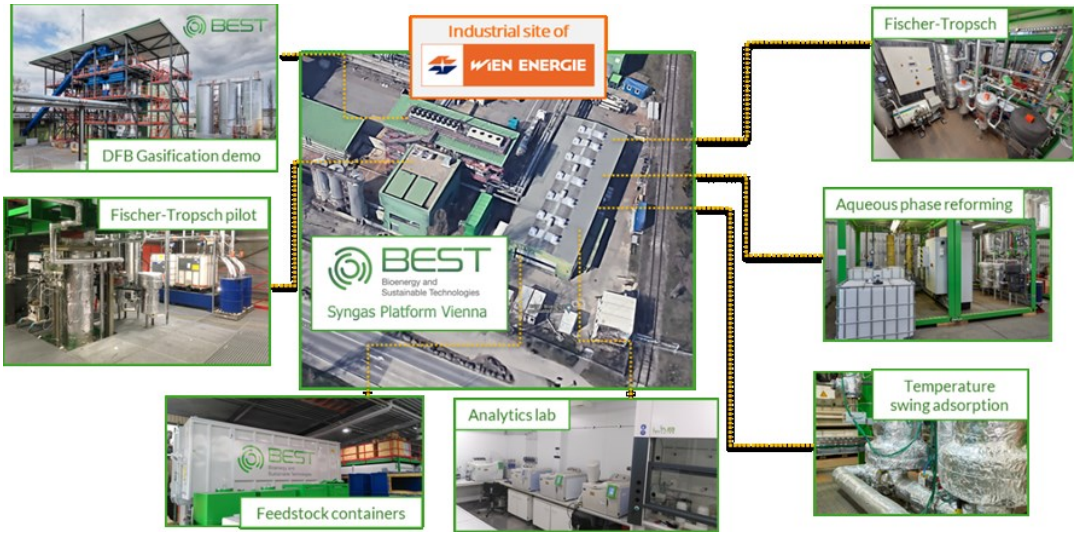

Figure 1: Overview of the Syngas Platform Vienna

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3. Dual fluidized bed (DFB) steam gasification and coarse gas cleaning

In Section 3, a comprehensive overview of the dual fluidized bed (DFB) gasification technology, including the reactor technology and the configuration of the employed gasification plant, is provided. For data support, literature values and results from past experiments (all referenced and presented in the reference section) are utilized. No outcomes from trials within the BioTheRos project are incorporated.

3.1 Fundamentals of DFB gasification

Gasification using DFB systems is a highly promising technology for the production of high-value syngas from solid feedstock such as biomass. This technology was first developed between 1992 and 2000 at the TU Wien. The DFB system consists of two fluidized beds, the first part is the gasifier itself, a bubbling fluidized bed that uses steam for gasification. The use of steam results in the production of a H_2-rich syngas that is free from nitrogen. H_2 contents of up to 50 % or more can be achieved. This factor is contributing to the growing interest in this technology. The residual coke produced after the gasification process is used as fuel in the second part of the DFB, which is a combustion chamber in the form of a fast-fluidized bed. The generated heat serves as energy supply for the gasifier. If necessary, additional fuel can be added to the process.

Figure 2 shows the basic concept of the DFB steam gasification technology. Feedstock enters the gasification reactor via a screw conveyor, where the biomass is transported into the gasification reactor. Thus, gases released from the biomass are immediately in contact with the catalytically active olivine bed material. The circulation of the bed material between the gasification and the combustion reactor works as follows: Bed material is transported together with char from the gasifier into the combustion reactor via a chute. There, fast fluidization with air as fluidizing medium transports the bed material upwards while simultaneously combusting the char in the oxidizing atmosphere. As a result, heat is released and the temperature of the bed material is increased. In a cyclone, bed material is separated from the flue gas and brought back to the gasification reactor via a loop seal, which is also operated as a bubbling bed. The bed material has a temperature of approximately 930°C when re-entering the gasification reactor, thus providing the energy needed for the drying, devolatilization and gasification reactions to proceed.

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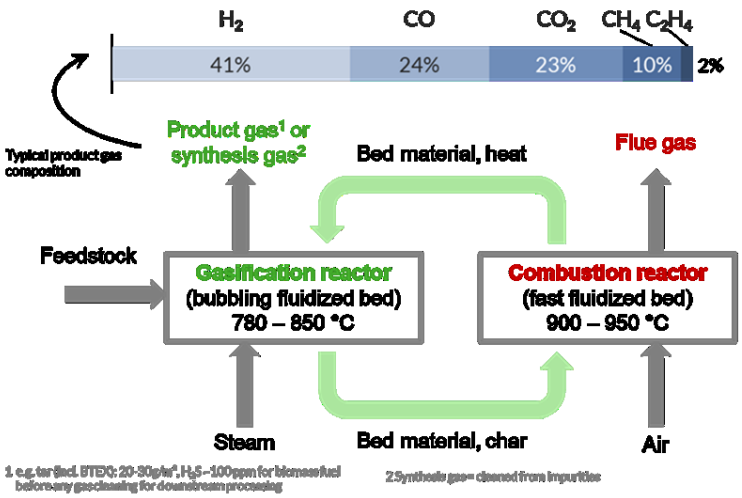

Figure 2: Basic concept and main product gas composition

As a result of the DFB reactor system, two separated gas streams leave the reactors. Product gas leaving the gasification reactor is a high-grade secondary energy carrier of main gas components H_2, CO, CO_2 and CH_4. This gas stream is almost free of nitrogen and can be further used after cleaning and upgrading downstream of the reactor. Typically, it is cooled down in heat exchangers, filtered, and washed in a product gas scrubber which uses rape seed methyl ester (RME) as scrubbing liquid. The product gas cooler is one of the critical units in the operation of the power plant as heavier hydrocarbons, also referred to as higher tars, can condense there, leading to plugging of the cooler. Thus, reducing the higher tars in the product gas is of great importance in the long-term operation of the power plant. Therefore, small particles, which are mainly unburnt char particles, are separated from the gas stream in the product gas filter. They are recirculated to the combustion reactor and act as additional fuel in the combustion reactor. Tars separated from the gas in the product gas scrubber are also brought to the combustion reactor as additional fuel, minimizing waste streams.

The second gas stream leaving the combustion reactor is referred to as flue gas, and contains mainly CO_2, H_2O, N_2 and a residual amount of O_2 from the access combustion air. A post-combustion chamber serves for optimal burn-out of the flue gas. After leaving the post-combustion chamber, the flue gas is filtered and also cooled down in heat exchangers before leaving through a chimney. Fine ash from the flue gas filter is discharged from the system and finally disposed.

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3.2 The industrial experience of first-generation DFB steam gasification

The DFB technology was developed from lab- to pilot-scale and further to a demonstration-scale power plant in Güssing, Austria, which started operation in 2002. Through the experience gathered at this demonstration plant further up-scaling of the DFB process could be realized and the first industrially operated power plants in Oberwart and Villach, Austria, started their operation. The power plant in Güssing gathered more than 100,000 operating hours over the course of 15 years and delivered the proof of technological functionality. Güssing also switched to commercial operation after an initial phase of demonstration.

Later industrial-scale power plants using the design of the Güssing plant were the HGA Senden plant in Germany and the GoBiGas plant in Gothenburg, Sweden. Furthermore, DFB plants of the same design are currently operated in Asia. In total, approx. 200,000 hours of operational experience in industrial-scale were gathered. TU Wien and BEST – Bioenergy and Sustainable Technologies GmbH scientifically accompanied the plants in Güssing, Oberwart, Villach and Senden. The GoBiGas plant was scientifically accompanied by Chalmers University.

3.3 Advanced DFB gasification (aDFB) at the Syngas Platform Vienna

The key infrastructure at the Syngas Platform Vienna is the advanced 2nd generation reactor design, which will be explained in more detail later on in section 5.2, for DFB gasification, which has been implemented at a capacity of 1 MW thermal fuel input for long-term operation (>10 days continuous operation). Figure 3 shows the 1 MW demonstration-scale DFB gasification plant.

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Figure 3: The 1 MW DFB steam gasification demonstration plant at the Syngas Platform Vienna

The reactor design was based on a 100 kW pilot plant at TU Wien, where experimental investigations have shown increased fuel conversion, reduced tar amounts in the product gas and subsequently an overall better performance especially for converting biogenic residues and waste. In addition to the new reactor design, the 1 MW gasification plant is also equipped with a novel gas cleaning concept. Product gas cleaning is performed using a product gas cyclone, a hot gas filtration unit (ceramic filter operated at 400 – 450°C) and a two-stage liquid scrubber unit. This gas cleaning set-up was also designed to be able to handle biogenic residues and waste with either higher volatile content or higher ash content.

In addition, a slip stream of the product gas is used in a connected laboratory for research in the fields of advanced gas cleaning, and lab-/bench-scale synthesis research.

In the following, the main parts of the gasification demonstration plant are explained in more detail.

3.3.1 Fuel feeding

The fuel feeding system is designed in such a way that different dry and solid wastes can be used. The feedstock is delivered to the fuel storage hall in walking-floor containers. These containers also serve as fuel storage and have to be exchanged at appropriate intervals. A double fuel transfer system ensures equalization and continuous transfer to a belt conveyor (wave-edge conveyor), which transports the fuel to the gasifier. After discharge from the belt conveyor to a distribution system, it is possible to fill two symmetrically arranged fuel supply tanks alternately. While one container is being filled, the other fuel

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supply container is used to feed the gasifier. Shut-off devices are provided both upstream and downstream of the feed tanks. During shut-off, the feed tanks are always inerted before and after being filled with nitrogen. The metered solid fuel from the fuel feed tank is fed via a feed screw to a sluice system with two cellular wheels in series. The sluice system prevents combustible gases from flowing back from the gasification reactor into the feed screw and into the fuel storage tanks. For this purpose, a continuously monitored nitrogen flow is introduced between the two cell wheels as a purge/barrier gas. Following the lock system, the fuel is fed into the gasification reactor via a drop chute.

3.3.2 Gasification

The setup of the used gasifier is based on the 2nd generation design. The solid fuel is converted into a combustible and H_2-rich product gas in the lower part of the gasification reactor, which is fluidized with steam at approx. 750 to 850°C. The typical product gas composition for the gasification of wood chips is shown in Table 1:

Table 1: Typical gas composition from DFB gasifiers (Example from Güssing [1])

Main components		
H_2	35-45	$vol\%_{dry}$
CO	19-23	$vol\%_{dry}$
CO_2	20-25	$vol\%_{dry}$
CH_4	9-11	$vol\%_{dry}$
Minor components		
C_2H_4	2-3	$vol\%_{dry}$
C_2H_6	~ 0.5	$vol\%_{dry}$
C_3H_8	~ 0.5	$vol\%_{dry}$
O_2	< 0.1	$vol\%_{dry}$
N_2	~ 1	$vol\%_{dry}$
Particles	30-100 (after gasifier)	g/Nm^3
Tars	1-5 (after gasifier)	g/Nm^3
BTX	~ 10	g/Nm^3
Catalyst poisons		
H_2S	~ 150	ppm_V
COS	~ 5	ppm_V
Mercaptans	~ 30	ppm_V
Thiophene	~ 7	ppm_V
HCl	~ 3	ppm_V
NH_3	500-1,500	ppm_V
HCN	~ 100	ppm_V

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After the fuel input from the lock system into the lower gasification reactor, the product gas contains a high fuel-dependent proportion of undesirable tars. The upper part of the gasification reactor is therefore designed as a counterflow column and serves as a tar cracker and reformer. Hot bed material flows towards the tar-laden rising product gas. The product gas leaves the gasification reactor at the upper end. The bed material leaves the lower part of the gasification reactor via a chute towards the combustion reactor. Gasification of the fuel requires energy/heat, which is supplied via the circulating bed material. The combustion reactor takes over the bed material from the gasification reactor at the lower end. The remaining residual coke, which is produced during the gasification of the fuel, is transported together with this bed material flow via a chute into the combustion reactor. Steam is introduced into the chute as a sealing and fluidizing gas. The combustion reactor is designed as a fast-fluidized bed fluidized with air. Bed material is transported upwards and discharged by the high gas velocities. In the combustion reactor, combustion of the residual coke and any auxiliary fuel (such as product gas) takes place. Light fuel oil is provided as the standard auxiliary fuel. In the combustion reactor, the cooled circulating bed material is reheated. The now heated bed material is separated via a cyclone and fed to the upper gasification reactor. During the combustion process in the combustion reactor at approx. 900 to 950°C, flue gas is produced which leaves the combustion reactor via the cyclone at the upper end. The separated bed material is fed back into the gasification reactor from above via a siphon. Steam is also introduced into this siphon as a sealing and fluidizing gas. Thus, although the two reactors are connected to each other via the circulating bed material flow, they remain separated from each other as reaction chambers where gas flows. At the lowest point of the fluidized bed system, the coarse ash is extracted and filled into drums.

3.3.3 Coarse gas cleaning section

The product gas leaving the gasification reactor typically has a temperature of approx. 800 to 850 °C and contains solids (e.g. fine bed material particles, fly ash- and coke). In a first step the gas temperature is reduced to 350-450°C by a radiant heat exchanger (it can be assumed that the tar remaining in the product gas does not yet condense). Downstream the heat exchanger a hot gas cyclone separates the coarse solid fraction. Subsequently, the product gas stream is freed from the solid fines still present via a ceramic cartridge filter. The separated solids (flue coke) are returned to the reactor system and burnt in the combustion reactor. The product gas, which is now almost dust-free, is fed into a quench with a subsequent rape seed methyl ester scrubber (referred to as RME scrubber in the following). There, the

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water vapor and the tar are specifically condensed and washed out. The condensate from the quench and the scrubber are fed into phase separators. The combustible emulsion is used energetically as support fuel in the combustion reactor. Waste water is pumped to the waste water tank. The quench water and RME circuit are cooled with heat exchangers. The purified product gas is passed on to the gas utilization system via a product gas blower. After the gas purification described above, the product gas can be fed to the afterburner chamber or the FT synthesis plant. Via a recirculation blower, it is also optionally possible to use the purified product gas as support fuel in the combustion reactor.

The exhaust gas from the combustion reactor is feed into a radiant heat exchanger before it is fed into a hot gas cyclone for the separation of solid particles. This is followed by a flue gas-air heat exchanger, which is used for combustion air preheating. A redundant cooler directly downstream ensures that the flue gas stream is cooled to below 160°C. The flue gas, which is still partially contaminated with fine dust or particulate matter, is fed firstly into a hot gas cyclone and further on into a fabric filter. The exhaust gas from the combustion reactor is fed into the flue gas pipe of a rotary kiln (downstream of its electrostatic precipitator) and cleaned together in the existing flue gas cleaning system of rotary kiln.

3.3.4 Gas utilization

It is always possible to feed the total amount of product gas produced into the afterburner chamber. The afterburner chamber required for this, is equipped with a support burner and combustion chamber monitoring. Downstream the afterburner chamber, an exhaust gas cooler is situated which dissipates the heat. In full-load operation of the gasifier, approx. 30 % of the product gas produced is required for the downstream FT synthesis plant. Any combustible off-gas to be recycled from the FT synthesis plant can also be fed into the afterburner chamber. The purified exhaust gas from the combustion reactor can also be fed into the afterburner chamber for cooling purposes. After the exhaust gas cooler, the exhaust gas from the afterburner chamber is introduced together with the exhaust gas from the combustion reactor into the flue gas line of rotary kiln (see 3.3.3).

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4. Fischer-Tropsch synthesis

In Section 4, a comprehensive introduction to the Fischer-Tropsch (FT) synthesis, the employed reactor technology and the configuration of the utilized FT pilot plant is provided. For data support, literature values and results from past experiments (all referenced and presented in the reference section) are utilized, which exclusively relied on wood chips as the feedstock. To date, there are no results concerning the application of residues for gas cleaning and FT synthesis. No outcomes from trails within the BioTheRos project are incorporated.

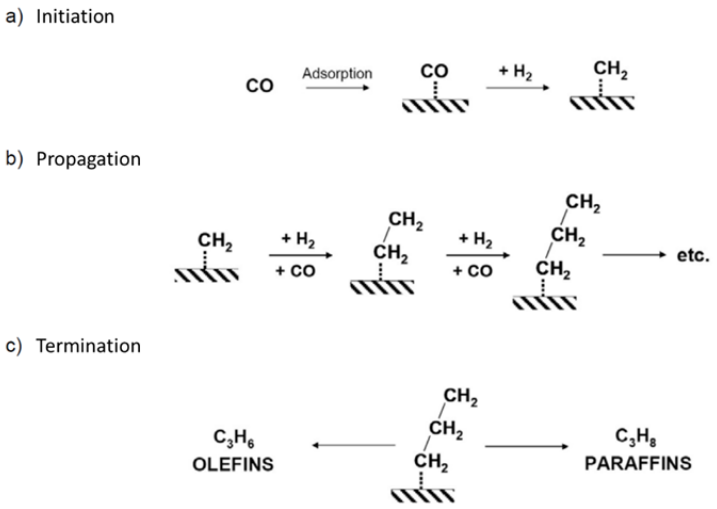
4.1 Fundamentals of Fischer-Tropsch synthesis

The FT synthesis is a chain growth reaction in which long-chain hydrocarbons (e.g. diesel, waxes) are produced from a mixture of H_2 and CO. The reactions involved are highly exothermic and preferably take place on metal catalysts (iron, cobalt, nickel, ruthenium).

The basic reaction of the FT synthesis is shown below:

$$n\,CO + \frac{n+m}{2} H_2 \longrightarrow C_nH_m + n\,H_2O$$

The exact reaction mechanism is complex, but in simplified terms it can be said that individual -CH_2- building blocks are formed from CO and H_2, which then combine via chain growth to form longer-chain hydrocarbons. The chain growth reaction is shown graphically below.



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At present, a distinction can be made between two basic processes for the production of FT fuels and chemicals that are used on an industrial scale:

- High-temperature synthesis (HTFT) and
- Low temperature synthesis (LTFT).

In high-temperature synthesis, the conversion takes place at 300 to 350°C and pressures of 20 to 40 bar. High-temperature synthesis is mainly used to produce petrochemical base materials such as ethylene, propylene and various butenes as well as gasoline. In low-temperature synthesis, the reaction takes place at low temperatures of 200 to 250°C and a pressure of around 20 to 30 bar.

Low-temperature synthesis is better suited to the production of diesel and other higher-boiling hydrocarbons. Fixed-bed reactors and slurry reactors are used for low-temperature synthesis on an industrial scale. The FT pilot plant in Vienna uses such a FT slurry reactor (SBCR: Slurry Bubble Column Reactor). LTFT mainly produces kerosenes (85-90 %), olefins (5-10 %) and oxygen compounds such as alcohols, carboxylic acids,...(~5 %). Due to the high proportion of n-paraffins and the absence of aromatic compounds, diesel with excellent combustion properties (high cetane number, almost no soot formation) can be produced, which can be used as a blending component for fossil diesel without further processing. Due to its n-paraffinic character, the diesel has poorer cold behavior than fossil diesel (higher CFPP than fossil diesel - cold filter plugging point).

Figure 4 shows the FT product spectrum: Between a chain length of the hydrocarbon compounds between C9 and C19 one speaks of diesel. Above C19, the long-chain compounds are referred to as waxes.

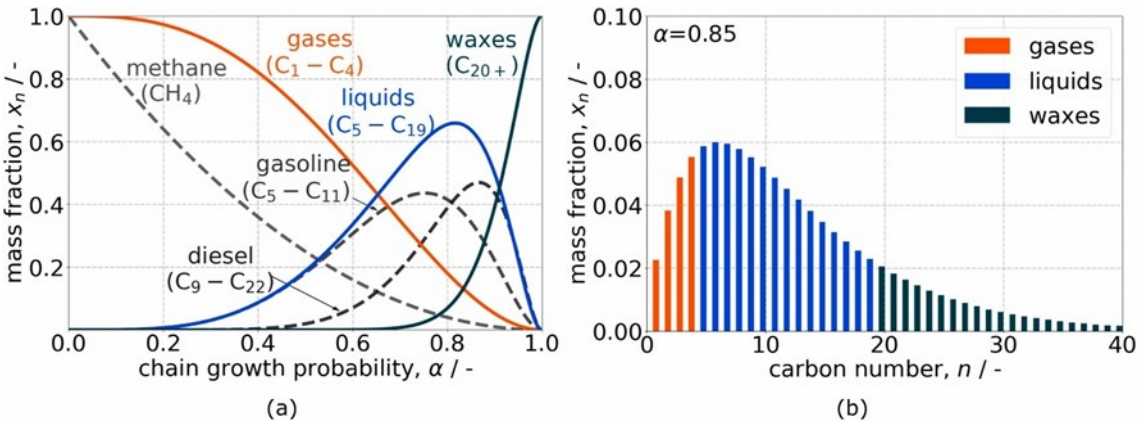

Figure 4: Chain growth probability and the FT product spectrum [2]

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In LTFT, cobalt-based catalysts are mainly used, with an average chain growth probability of between 0.85 and 0.91 (see Figure 5, i.e. in the area with a high proportion of hydrocarbons in the chain length range of FT diesel).

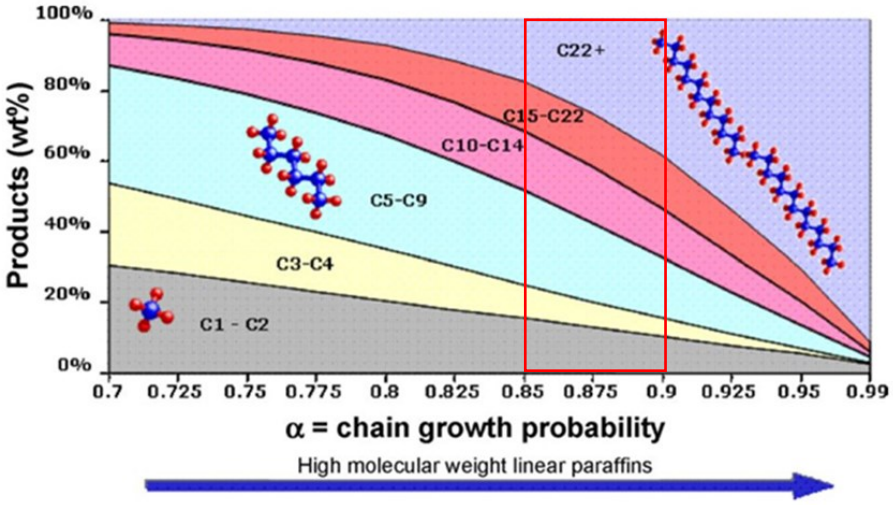

Figure 5: Products in dependence of the chain growth probability [3]

These long-chain waxes can be subjected to hydrogenation, whereby fully saturated high-quality kerosene waxes are obtained as a product. By using hydro-processing (hydro-cracking and hydro-isomerization - long-chain waxes are broken into shorter chains and saturated with H_2), further diesel can be provided from the wax, which has a very good cetane number and at the same time outstanding low-temperature behavior. The range between C10 and C14 is known as kerosene and this HPFT diesel/kerosene (Hydro-processed Fischer-Tropsch) can be used as synthetic kerosene (SAF). When using a cobalt catalyst at around 200-230°C and 20 bar synthesis pressure as well as recycling the residual gas from the synthesis reactor, a conversion of the carbon monoxide of up to 90 % can be expected. It can be assumed that between 25 % and 40 % of FT diesel can be extracted directly from the FT raw products via distillative separation (based on previous experimental results).

4.2 FT Slurry reactor for FTS

The FT fixed bed reactors (i.e., multi-tubular reactors), fluidized bed reactors and slurry bubble column reactors are available at different commercializing levels. For the design of the reactor and the heterogeneous gas phase catalysis, it is very important to discharge the heat of the strong exothermic

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reaction in a sufficient way. Normally fixed bed reactors are designed as multi-tubular reactors, which contain a large number of catalyst-filled tubes. Thereby smaller tubes improve the cooling abilities and smaller catalyst particles improve the conversion rate. High gas velocities lead to high pressure drops over the reactor and therefore a compromise has to be found to ensure smooth and stable operation. In an axial plane, a temperature gradient can occur along the reactor pipes due to different reaction zones and slow heat transfer [4], [5]. In SBCR, see Figure 6, diffusion limitations of the reaction are minimized by using a small catalyst particle size. In previous investigations, this reactor type has also shown its suitability for PtL applications [8]. Slurry reactors are three-phase reactors that consist of a liquid phase, a solid phase and a gaseous phase. The solid catalyst is suspended in the liquid FT products. The synthesis gas is blown from the bottom into the column and the mass transfer and the heat transfer is improved by swirling of the catalyst. The solid phase consists of particles with a grain size of < 100 µm. A suspension is produced by the gas flow which, in the ideal case, causes an even gas distribution over the whole column.

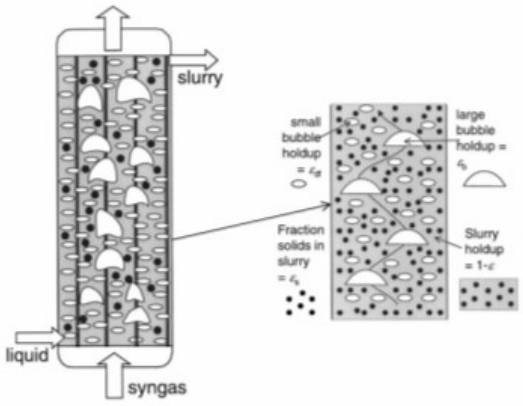

Figure 6: Three-phase slurry reactor [6]

The main advantage of this reactor type is the excellent mixing of the catalyst and thus the uniform isothermal temperature control. For the optimum operation, it is essential that the heat is dissipated immediately. Therefore, all developments of FT reactors aim for a good heat dissipation or thermal management. Fixed bed reactors are limited, thus the diameter is reduced (principle of micro-structured reactors) or the synthesis gas is diluted with recycle gas. In comparison to micro-structured reactors the economy of scale for SBCR is significantly better. There is only linear upscaling in a micro-structured reactor, whereas a slurry operates with a "one-pipe" approach, where the reactor throughput is adjusted via diameter of the SBCR. The three-phase slurry-reactor has gained attention due to several promising advantages, which are: [7]

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- Simple way of construction;
- Very good heat conduction and fast transfer of the heat;
- Addition and removal of the catalyst possible during operation;
- Reaching of a high mass-transfer coefficient;
- Optimal exploitation of the contact surface between gas, liquid and solid matter;
- Constant temperature range and therefore high operating temperatures in the reactor possible.

4.3 Fischer-Tropsch synthesis at the Syngas Platform Vienna

The key infrastructure at the Syngas Platform Vienna for the conversion of the synthesis gas to FT-syncrude is the FT SBCR, which has been implemented at a capacity of 250 kW thermal syngas input for long-term operation (>5 days continuous operation). Figure 7 shows the 250-kW pilot-scale FT pilot unit.

Figure 7: The FT pilot plant at the Syngas Platform Vienna

The reactor design was based on a 15-kW pilot plant, which was developed by BEST GmbH and TU Wien. The lab scale plant was operated at the former location of BEST GmbH in Güssing, Austria for several thousand hours of operation coupled with the first-generation 8 MW DFB gasifier. Knowledge in the field of fine gas cleaning as well as FT synthesis was gained. The obtained knowledge established the basis for the development of the FT pilot unit in Vienna [8], [9], [10].

Fine gas cleaning is performed using two-stage liquid scrubber unit, fixed bed activated carbon adsorber, gas conditioning via compression and pre-heating and final cleaning using a fixed bed metal oxide filter (zinc oxide – ZnO).

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A thermal oil cycle is used to cool the FT reactor and utilize the thermal energy of the FT reaction to pre-heat the tail gas in the recycle part.

In the following, the main parts of the FT pilot unit are explained in more detail.

4.3.1 Setup of fine gas cleaning

Figure 8 shows the fine gas cleaning section of the pilot unit as built in Vienna.

Figure 8: Fine gas cleaning (left: Fixed-bed reactors, right: Liquid based scrubber systems)

Gas scrubbing: RME scrubber, stripper and acidic scrubber

In the first step, aromatic compounds as tar (mainly naphthalene) and large proportions of the light weight aromatic compounds (BTX – benzene, toluene, xylene) contained in the gas stream are separated from the synthesis gas with the aid of an atmospheric gas scrubber (washing medium RME). The scrubber operates at a temperature of about 5°C, the water vapor contained in the gas stream is also condensed at this stage. A stripper unit is used to test the separation of naphthalene and BTX from the RME. Therefore, the RME is heated up to app. 230°C and stripped with N_2 in counterflow. The loaded N_2 can be discharged via the tail gas line into the afterburner chamber of the DFB pilot plant, where the hydrocarbon compounds are burned. The RME is reused (recycled) in the gas scrubber, where a partial stream is added as make-up stream. In the subsequent acidic scrubber, mainly the NH_3 contained in the gas stream is separated.

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Activated carbon TSA

The S-compounds and the aromatics still present in the synthesis gas are separated with activated carbon. The activated carbon guards (ACG) are operated batch wise, one batch is regenerated from aromatic hydrocarbon compounds by heating and counter-flushing with N_2 (in principle a TSA) while the second batch is loaded. The gas stream is again fed into the afterburner chamber via the tail gas.

Compression

The two scrubbers and the ACG are operated at pressures between 80 (synthesis gas) and 150 (N_2) mbar(g) The synthesis gas is compressed downstream the AC beds to pressures of around 18 to 24 bar(g) using a 3-stage piston compressor. The compressor is equipped with a bypass valve and a frequency converter. The compressor controls the gas flow through the complete system. The gas flow is measured with a mass flow measurement (Coreolis-Measuring Principle) in the gas cleaning section (downstream ZnO). During N_2 operation, the pressure is controlled by a bypass valve, which recirculates the N_2 upstream of the ACG. In system operation, the system pressure is adjusted by a control valve at the end of the FT pilot unit.

Sulphur purification with ZnO

After compression, the gas is passed through two fixed-bed metal oxide reactors filled with ZnO. The ZnO adsorbs the S-compounds still present in the gas. After this final fine gas cleaning step, the synthesis gas is almost completely purified of impurities or catalyst poisons. The fine gas cleaning unit is equipped with a variety of temperature and pressure measurements to prevent overtemperature as well as overpressure.

4.3.2 Pilot-scale FT reactor

The pilot-scale FT plant, just like the fine gas cleaning, is located in an adjacent building to the 1 MW aDFB pilot gasifier at Simmering, Vienna. In this section, FT product is produced from the cleaned and conditioned synthesis gas, from which FT diesel can be produced by further subsequent upgrading steps. The pilot-scale FT reactor, the product separation as well as the tail gas compressor can be seen in Figure 9.

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Figure 9: Left: Tail gas compressor; Right: FT pilot reactor and product separation

In Figure 10 the setup of the pilot reactor is displayed. The reactor has a height of around 3.3 m. In the inlet is carried out conical to support the setting of heterogenous flow regime. The reactor consists of a tube 3.3 m high, with a diameter of DN300. The reactor contains a mixture of cobalt catalyst (particle size distribution in the range of about 50-100 µm) and paraffin waxes with chain lengths up to C100. The paraffin wax behaves like naphtha under operating conditions in terms of its fluidic properties. At the bottom of the reactor there is a conical part with diameter of DN150, in which an intermediate flange plate is inserted. This plate, made of sintered metal, is surrounded by a gas-tight sealing surface and serves as a gas distributor for introducing synthesis gas into the reactor. The conical inlet design promotes the establishment of a heterogeneous flow regime.

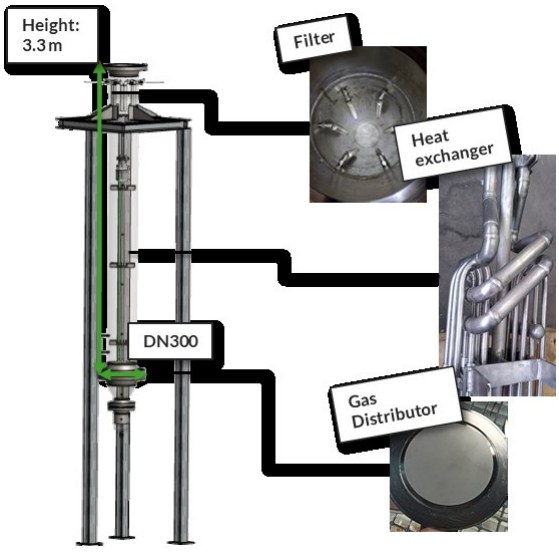

Figure 10: Setup of the FT pilot reactor

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Under ideal operating conditions, the catalyst is evenly distributed over the reactor due to the gas bubbles. The reaction between H_2 and CO then takes place on the catalyst surface. In addition to paraffines, olefins and alcohols, water of reaction and heat of reaction are also released or formed during the chemical reaction. To cool the reaction, a heat exchanger is installed in the FT reactor. It consists of a guide tube with interconnected circular bends, forming a tube bundle. These heat exchanger tubes are flushed with thermal oil, ensuring continuous removal of the reaction heat. Located in the upper part of the reactor, there are metal mesh-based filter elements.

At temperatures between 200-230°C and pressures from 18-24 bar(g), the FT synthesis reaction takes place in the SBC reactor. On the surface of the catalyst, the reaction between H_2 and CO takes place. Hydrocarbons (mainly n-alkanes) and water are formed, and heat is released during the reaction. In the top of the reactor, the unconverted syngas together with the FT product is continuously withdrawn via internal filter cartridges – the catalyst remains in the reactor. The temperature of the reactor is controlled via an internal heat exchanger, that transfers the heat of reaction to the thermal oil to ensure isothermal conditions.

4.3.3 Fractional separation of FT products

Downstream the FT reactor, a 3-stage separation of the FT product from the present tail gas is performed by incrementally cooling the reactor outlet stream to temperatures between 150 and 5°C. The setup is similar as for FT lab scale plant, but prior to the separation vessels heat exchangers are used for the condensation step.

1. In the first condensation step, the gas is cooled to about 150°C with a shell-and-tube heat exchanger using air as the cooling medium to separate the long-chain fraction (wax) of the product. In condenser 1, the condensed product is collected and filled into 220 l drums via a product outlet system.

2. The second condensation step is structured in the same way as the first, with the air being pre-heated in the same way for the first shell-and-tube heat exchanger in condensation step 1. In this part of the plant, the gas is cooled down to about 50°C and the middle distillate and the water produced during synthesis are separated. The emulsion of water and hydrocarbons is introduced into a 1000 l IBC for further separation.

3. In the third condensation step, the tail gas is cooled to approx. 5°C using a shell-and-tube heat exchanger with a glycol/water mixture. The last separable hydrocarbon fraction is then collected in condenser 3. The product outlet system is the same as downstream condensation step 2.

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4.3.4 Tail gas recycling

After the condensable products have been separated, most of the tail gas is recycled via a tail gas recycling loop. In the tail gas recycling loop a metal diaphragm compressor is used to compensate the pressure loss over the FT reactor and the product separation section. The gas flow is controlled via the speed control of the compressor and the actual flow is measured with a Coriolis flow meter (measurement of the mass flow). After compression, the tail gas is reheated to 200-230°C via two heat exchangers connected in series and then fed into the FT reactor. The pressure of the complete system (GCS and FTS) is controlled with a control valve in the tail gas stream after product separation.

4.3.5 Thermal oil cycle

A thermal circuit is used to remove the reaction heat from the FT reactor, whereby the thermal energy is used for the regeneration of the RME (heat exchanger with connection to the GCS) and for heating the tail gas (via two serial heat exchangers). In addition to the heat exchangers used, a start-up heater, a feed pump, a re-cooler and an expansion vessel are further components of the thermal oil system.

Figure 11 shows a simplified flowchart of the FT part of the pilot unit.

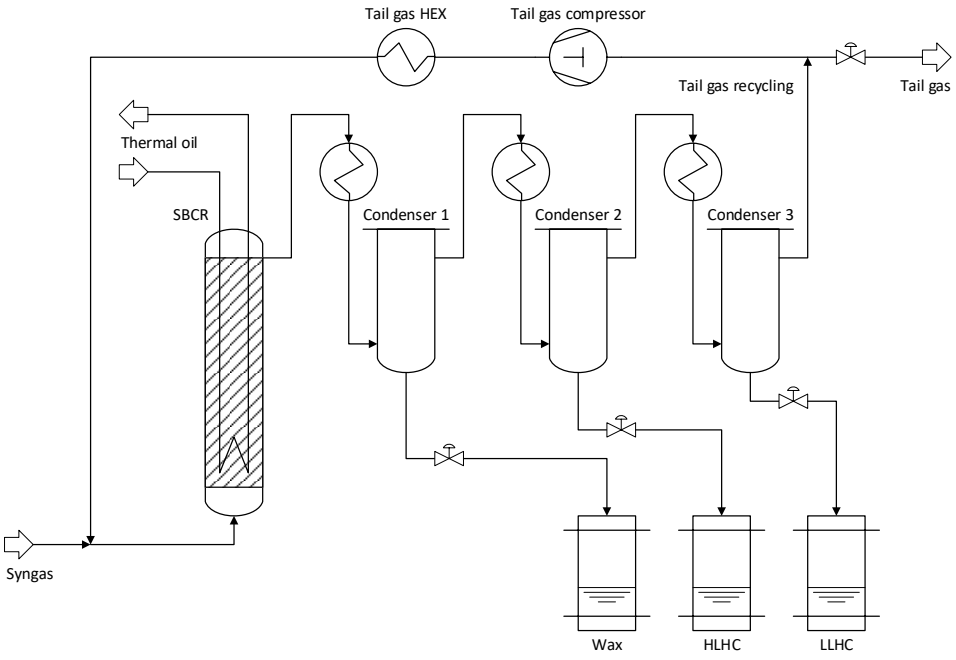

Figure 11: Process flow diagram (PFD) of the pilot-scale FT plant

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5. Full process chain - Constraints and opportunities for scale-up of gasification process

In Section 5, a comprehensive overview of the entire process chain is provided, along with specifics on the employed technologies and the interconnected limitations and possibilities. Detailed discussions focus on the advanced DFB gasification, the FT synthesis based on SBCR, and the gas cleaning process. For data support, literature values and results from past experiments (all referenced and presented in the reference section) are utilized. No outcomes from trails within the BioTheRos project are incorporated. Using the analyzed state of the technologies, potential advantages and constraints are deduced, which serve as the foundation for elaborating the framework for planned activities in Task 4.2 and Task 4.3.in Section 6.

5.1 Overview on the process chain

As already described in the previous chapters the full process, coming from residue-based feedstocks to FT syncrude involves several unit operations and inhibits a non-neglectable complexity. For this reason, some process simplifications were foreseen (e.g. only partial heat integration and recycling loops, no CO_2 separation process, no steam reforming of FT tail gas, …) to level down the complexity to an acceptable level. Furthermore, most of the unit operations of our demo site are designed to allow a certain degree of flexibility in operation to have the possibility to use different feedstocks in mixtures. The setup of the process chain as it is erected in Vienna Simmering is visible in Figure 12.

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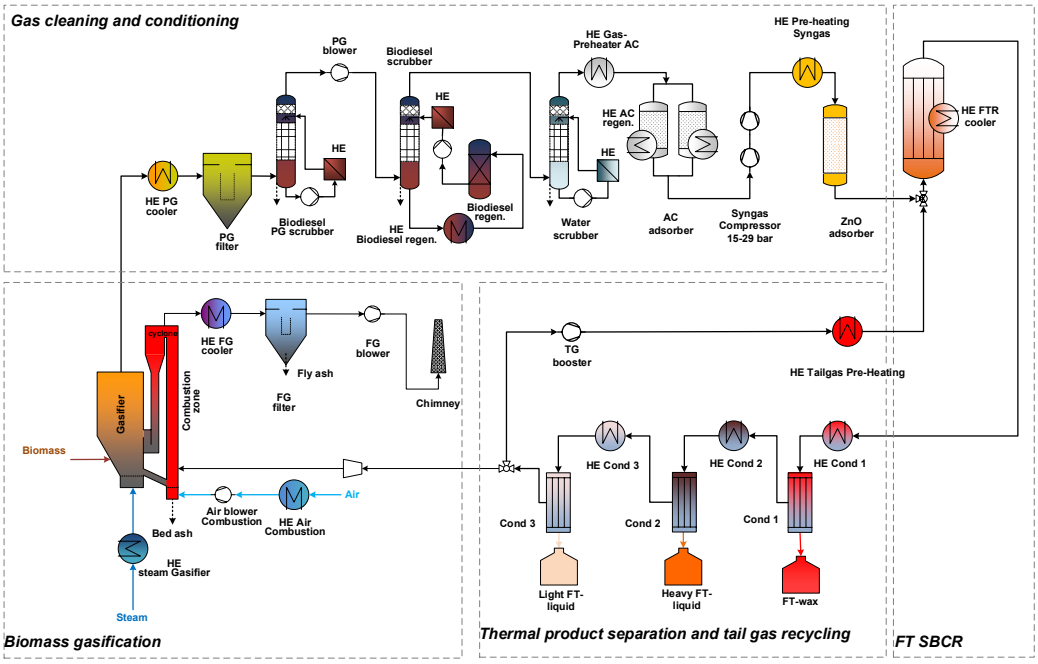

Figure 12: PFD of the full process chain

The biomass and waste-to-liquid process (BTL/WTL) in Vienna Simmering represents an integrated setup to assess different feedstocks, to study their influence on fuel feeding, gasification, gas cleaning and synthesis. The study of different feedstocks allows the assessment of the used gas cleaning strategies and answers the question if a long-term operation is possible or adaptions are necessary to establish a possible industrial scaled plant with a dedicated residue-based feedstock.

<u>Key points with high influence on the output, the system itself, its performance and upscaling of the technology:</u>

- **Product gas composition:**
  - H_2:CO ratio in syngas: To produce a syngas with a H_2:CO ratio suitable for the synthesis process and to control its stability over time
  - Influencing factors on the composition of the product gas (process vs. fuel related topics)

- **Counter-current column:**
  - Influence of counter-current column (as tar cracker) on amount and composition of aromatic compounds (tar) in the product gas
  - Influence of counter-current column on downstream coarse and fine gas cleaning steps

- **Liquid scrubber systems (biodiesel and acidic water):**
  - Further removal of aromatic compounds downstream in coarse (focus on heavy molecules) and fine gas cleaning (focus on light weight molecules)

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  - Challenging regeneration of washing media
  - Removal of N-compounds and separation of water via liquid scrubbers

- **Fixed bed adsorber systems:**
  - Removal of possible catalyst poisons (S- and N-compounds) and gas polishing in terms of aromatic compounds in fine gas cleaning

- **FT-Product composition:**
  - Influence of H_2:CO ratio in the syngas on the product spectrum in the FT syncrude
  - Influence of other process parameters on composition and output

- **CO conversion:**
  - Overall and one-through conversion of CO to FT syncrude
  - Influence of inerts on the performance

- **Selectivities:**
  - Selectivity to gaseous and liquid FT products and influence of recycling

The mentioned key points will be further addressed in the next chapters for their influence on the full process chain and if they represent either an opportunity or a challenge in the upscaling of the technology.

5.2 Technical description of the advanced DFB gasification

The comparison between the first and the second generation of the DFB gasification reactor is illustrated in Figure 13. On the left side, the first-generation reactor design is displayed. On the right side the second generation is shown. This system is also based on two interconnected fluidized beds. As previously mentioned, any unconverted coke and additional fuel are burned in the combustion chamber and the resulting heat is returned to the gasifier through circulating bed material to provide the heat for gasification reactions. The 2nd generation DFB features a counter-current column (upper gasification reactor) that is located above the bubbling fluidized bed (lower gasification reactor), which significantly improves the product gas quality and process efficiently by increasing turbulence and contact time between the bed material and product gas. The content of unconverted hydrocarbons is reduced and the H_2 content in the product gas is increased. The unique design of the gasifier facilitates enhanced gasification of low-grade materials, including sewage sludge and other waste materials.

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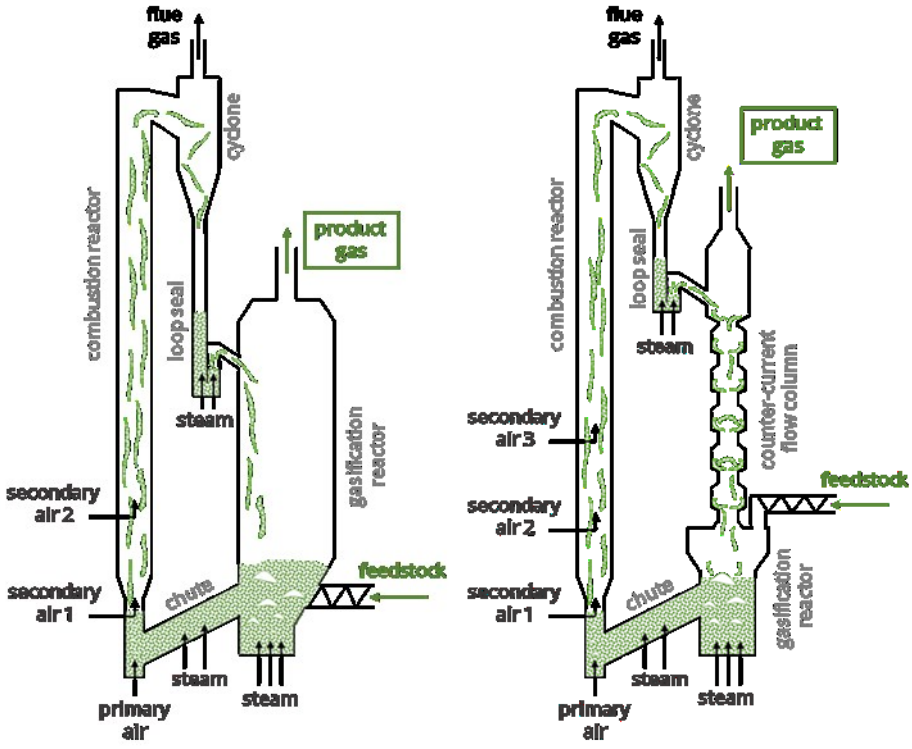

Figure 13: Left: First generation DFB design; Right: Second generation DFB design

Comparison 1st and 2nd generation design

1st generation gasification reactor: bubbling fluidized bed with freeboard above

- Light material and volatiles are not in close contact with bed material and cannot be intermixed in the fluidized bed.
- Low conversion, high amounts of undesired tars in the product gas.

2nd generation gasification (aDFB): Bubbling fluidized bed with counter-current flow column above

- Light material and volatiles are now in better contact with bed material as they are forced to be in contact in the counter-current flow column.
- Higher conversion, lower amounts of undesired tars in the product gas.

To further enhance gasification reactions and particle-solid interactions, Schmid et al. [11] developed an advanced gasification reactor design. This design features an upper gasification reactor configured as a counter-current column installed above the freeboard section of the bubbling bed. In this setup, the gas phase moves upward through the upper gasification reactor while interacting with bed material that descends, leading to improved mixing and gas-solid interactions. This enhanced interaction makes it easier to process complex feedstocks, such as biogenic or industrial waste streams. The reactor design is referred

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to as advanced dual fluidized bed (aDFB) technology. The first aDFB plant, a 100-kW pilot plant, was installed at TU Wien in 2014 [12]. Building on the pilot plant's success, a 1 MW demonstration-scale aDFB plant was installed at Syngas Platform Vienna in 2022. Figure 14 shows a sketch of the advanced DFB gasification system in Vienna Simmering.

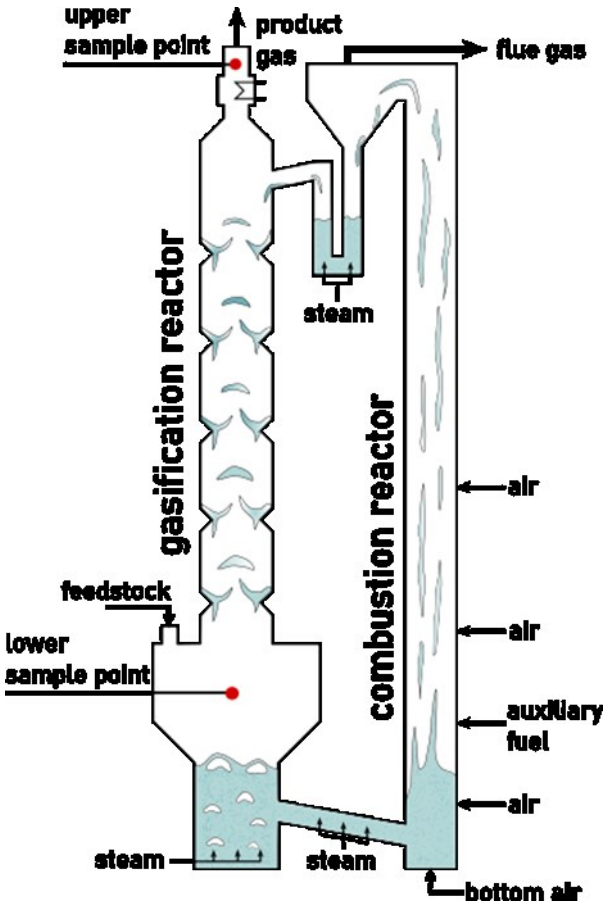

Figure 14: Sketch advanced DFB gasifier

Tar formation is largely influenced by temperature and exposure to catalysts [13], [14], meaning that the temperature profile within the gasification reactor plays a crucial role in the types of tar species that are produced. While Class II, Class III, and Class IV tars predominantly form at temperatures below 800 °C, the key reactions responsible for producing polycyclic aromatic hydrocarbons (PAHs) - such as dehydrogenation, condensation, aromatization, deoxygenation and dealkylation - occur above 800 °C [15]. A parametric study on tar formation in a DFB steam gasifier [16] identified gasification temperature as a major influencing factor, noting that tar species with a molecular mass lower than naphthalene (e.g.,

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benzofuran, styrene, and 1H-indene) increased as gasification temperature decreased. Consequently, the temperature profile of the gasification reactor shown in Figure 15 corresponds to the tar species detected at the respective sample points.

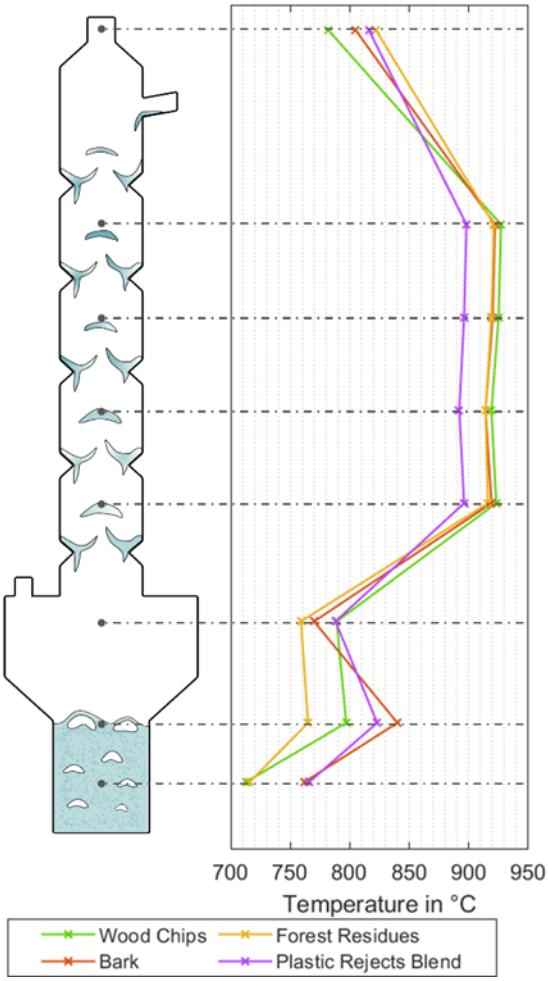

Figure 15: Temperature profile over advanced DFB gasifier

Initial experiments using biogenic residues and plastic-rich rejects were already conducted on the 1 MW demonstration-scale DFB steam gasification plant, with a particular focus on tar conversion and recombination. The results showed a significant reduction in both gravimetric tar and the sum of GC/MS tar for all feedstocks after passing through the counter-current column. When examining the tar concentrations for individual feedstocks, it was evident that lignocellulosic feedstocks produced consistently similar tar concentrations at the same sample points. While the total tar content decreased notably after the counter-current column, the behavior of individual tar species varied. The concentration of oxygen-containing Class II tars and mono-aromatic Class III tars declined significantly or became

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undetectable for certain species like phenol. Class IV tars, which can be divided into condensed light-aromatics and uncondensed aromatics, exhibited different patterns in the counter-current column. Specifically, the concentration of uncondensed 1H-indene decreased in each experiment, whereas an increase in naphthalene was observed. This increase was also noted for all Class V PAH species. [17]

5.2.1 Constraints and opportunities

The aDFB gasification technology is well suited for the conversion of a variety of different biogenic feedstocks and biogenic residues. Suitable scales for the gasification reactor and subsequently for the full process chains are well-aligned with the aim of decentralized production of synthesis gas and intermediate products, such as FT syncrude. It is expected that the scale of the technology will be set from 20 to 100 (up to 150) MW thermal fuel input. This is a scale, which is still manageable for local and regional biogenic feedstock supply.

As described above, the DFB technology has already been operated in industrial-scale (from 8 MW to 32 MW thermal fuel input) with woody chips as input material. The novel aDFB reactor design however, is currently being tested in demonstration-scale and has yet to be upscaled to industrial scales. The main constraint currently lies with the upscaling of the countercurrent column. Since this reactor part has only been experimentally tested in 100 kW at the TU Wien and now at 1 MW at BEST's Syngas Platform Vienna, a further upscaling has yet to be performed.

Counter-current column:

To be able to successfully upscale the reactor design further data on the conversion of tars over the height of the countercurrent column has to be derived. At the current stage, only the overall conversion (before/after) of the countercurrent column has been investigated at the 1 MW demonstration plant, while it is still necessary to gain deeper information about the tar conversion in each single chamber of the countercurrent column. It would therefore be necessary to measure tars before and after each constriction of the column.

Influence of residue-based feedstocks on the product gas:

In terms of the influence of residue-based feedstocks on the product gas composition and finally on the FT-product quality has to be differentiated between two key points:

- Influence on H_2:CO ratio due to main gas components
- and influence on gas cleaning efforts necessary due to the amount of minor components.

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The usage of biogenic residue-based feedstock for the gasification process (compared to e.g. woodchips from softwood) is accompanied with higher shares of undesired minor fuel compounds (e.g. aromatic-, S- and N-compounds), which mainly influences the necessary effort for the gas-cleanup. The main components carbon and hydrogen are quite similar for a wide range of biogenic feedstocks. Differences in hydrogen and carbon content can lead to deviations in the H_2:CO ratio. Therefore, strategies can be undertaken in gasification (e.g. amount of steam, adaption of process parameters) and synthesis (adaption of recycling stream) to adjust the H_2:CO ratio again to a suitable range. In terms of the pilot/demo setup large deviation in H_2:CO ratio coming from the gasification of waste feedstocks, which cannot be addressed by changes in operation, cannot be used in the setup. Non-biogenic residues as sewage sludge or plastics are deviating in terms of hydrogen and carbon content more profound (also in terms of minor components). Therefore, additional measures for gas upgrading (e.g. CO shift, reformer) are necessary in terms of upscaling this technology.

Table 2 gives an overview on constraints and opportunities for the aDFB gasification. Crucial factors such as scalability, the impact of the counter-current column on the gasification reactor, and the effect on syngas quality are both constraints and potential benefits for the scale-up process.

Table 2: Constraints and opportunities for aDFB gasification

Aspect	**Constraint**	**Opportunity**
Scalability of fluidized bed technology in terms of throughput	Complexity in upscaling of fluidized bed technology	aDFB technology comprises a high level of scalability (economy of scale) with regard to throughput and thermal power
Counter-current column in the gasification reactor	Complexity in engineering and manufacturing, less experience in demo scale	Improves tar conversion which allows the usage of residue feedstocks with high content of volatiles
Operation of aDFB without further gas upgrading step	Challenging operation to obtain H_2:CO ratio of 2 for FT synthesis in connection with FT tail gas loop	Levels down the complexity and uses the benefit of the steam gasification as WGS/rWGS reactor and saves costs
Usage of residues with low quality	Challenging feedstocks have to be addressed with adapted operation strategy as well as the usage of additives to the gasification process	Reduced costs for feedstock supply

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5.3 Technical description of gas cleaning section

5.3.1 Coarse gas cleaning

The aim of the coarse gas cleaning lies in the supply of a particle free syngas, with significantly reduced amounts of water, aromatics and N-compounds. The flow sheet of the investigated coarse gas cleaning is depicted in Figure 16.

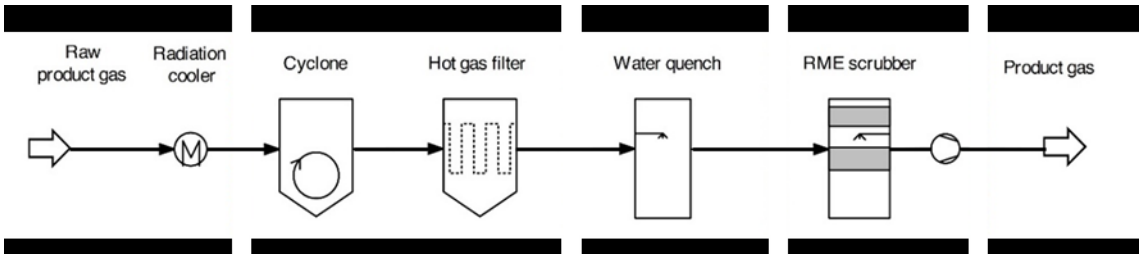

Figure 16: Simplified flowchart of the coarse gas cleaning at the 1 MW DFB gasification plant

To obtain the target on syngas purity several steps are necessary. The coarse gas cleaning starts with several steps of particle removal. The first step is a radiation cooler to remove entrained bed material which is transported back to the gasification reactor. Additionally, the gas is cooled down to below 450°C. Smaller particles (fly char, dust, coke) are removed in the following cyclone and a ceramic cartridge filter. The ceramic cartridge filter is designed as a hot gas filter so that the condensable tars are still in the gas phase at that point. In the next step the product gas is quenched down with water to around 80°C. At this step most of the steam in the gas is condensed, as well as several condensable tar. Water soluble impurities like NH_3 are also removed at this step. The last step of the coarse gas cleaning is the RME scrubber. It further removes tars and cools down the gas to around 40°C.

5.3.2 Fine gas cleaning

Downstream the coarse gas cleaning light molecular weight aromatic compounds as benzene, toluene and xylene (BTX) are still in the syngas; furthermore N-compounds and nearly the complete number of S-compounds. To obtain a syngas for the conversion in the FT reactor additional cleaning steps are necessary. The flow sheet of the investigated coarse gas cleaning is depicted in Figure 17.

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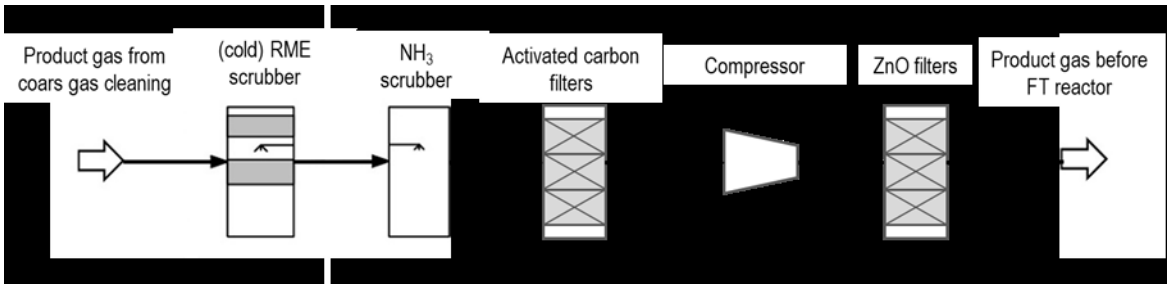

Figure 17: Simplified flow chart of the fine gas cleaning upstream of the 250kW FT pilot plant

The fine gas cleaning is operated with the coarsely cleaned product gas from the demonstration plant, using a partial stream of around 50-55 Nm^3/h. The first step is a cold RME scrubber with an operating temperature of 5°C to remove aromatic tars. The biodiesel scrubber is followed by an acidic scrubber to remove NH_3 as ammonium sulphate. After the acidic scrubber the product gas is heated up to 30°C and led into an activated carbon bed to remove S-compounds. After the AC guard bed, the product gas is compressed. The last cleaning steps are ZnO guard beds to ensure the removal of all impurities before entering the FT reactor.

5.3.3 Constraints and opportunities in terms of gas cleaning

The efforts for gas cleaning have a significant influence on the successful operation of a BTL/WTL plant. During the gasification process beside the main gas compounds also side compounds (e.g. C_2H_4) as well as possible catalyst poisons are produced (e.g. S-compounds). In Table 3, an overview on the requirements for different applications of syngas is presented.

Table 3: Requirement of gas purity for different syngas applications [18]

Parameter	Gas engine	Gas turbine	Synthesis	Fuel cell (SOFC)
Particle content	< 50 mg/m^3	< 30 mg/m^3	< 0.1 mg/m^3	-
Particle size	< 3 µm	< 5 µm	-	-
Tar content	< 100 mg/m^3	-	< 0.1 mg/m^3	< 100 mg/m^3
Alkali content	< 50 mg/m^3	< 0.25 mg/m^3	< 10 ppb	-
Ammonia content	< 55 mg/m^3	-	< 1 ppm	< 0.1 mg/m^3
Sulfur content	< 1150 mg/m^3	-.	< 0.1 ppm	< 200 ppm
Chlorine content	< 500 mg/m^3	-	< 0.1 ppm	< 1 ppm

The efforts to clean up the syngas for downstream chemical synthesis steps are significantly more demanding as for the utilization in gas engines or turbines. In [19] requirements for sulphur/alkali/chlorine of 10 ppbv and for nitrogen compounds (HCN and NH_3) of 20 ppbv are discussed for FT synthesis. These

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strict requirements are coming from e.g. catalyst suppliers to assure a long operation time of the used catalysts.

The use of more challenging biogenic and non-biogenic residue materials in the gasification process raises the question of whether all these strict standards can still be met and if achieving them is economically viable. For example, N-compounds are not catalyst poisons but can negatively affect the synthesis process and, for instance, shift selectivity or diminish the CO conversion rate per pass. S-compounds lead to the deactivation of the catalyst in any concentration present in the syngas. This means S-compounds must be reduced to the lowest possible amount, while higher concentrations of N-compounds remain questionable.

Operating the entire process chain with more challenging fuels significantly impacts the efforts required in gas cleanup. A balance must be struck between the necessary efforts for gas cleanup, resulting in higher operating expenses (OPEX) and capital expenditures (CAPEX) and the impact of higher amounts of harmful compounds on catalyst activity (which in the worst case leads to higher catalyst consumption and increased OPEX). The regeneration of used media for the separation process can significantly influence the economics of the process. Regeneration and reuse are relevant topics for scaling up the process to an industrial level.

The assessment of the cleaning capacity of the unit operations along the gas cleaning section is important to allow a further scale-up.

Table 2 gives an overview on constraints and opportunities for the gas cleaning section. Crucial factors such as the use of low-quality feedstocks, costly operating materials, setup of gas cleaning, and given requirements represent both limitations and potential opportunities for scaling up the process.

Table 4: Constraints and opportunities for gas cleaning section

Aspect	Constraint	Opportunity
Usage of residues of low quality	Challenge for gas cleaning due to higher content of impurities	Reduced costs for feedstock supply
Operating materials in gas cleaning (RME, activated carbon)	Expensive operating material	Usage of thermal waste energy from the gasification process for regeneration of operating materials in the gas cleaning section
Setup of gas cleaning section	Complex setup with several unit operations in coarse and fine gas cleaning	Unit operations modular adaptable to different feedstocks (e.g. usage of fresh

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		RME, makeup for water quench or acidic scrubber, …)
Strict requirements for syngas quality based on specifications from catalyst suppliers	High effort for gas cleaning (in terms of CAPEX and OPEX)	Optimal operating conditions for FT catalyst (No influence of impurities on the used synthesis catalyst)

5.4 Technical description of FT SBCR technology

The FT synthesis has been established for decades to produce hydrocarbons from biomass, coal, or natural gas at 200-350°C. An outstanding advantage of FT synthesis is its versatility in feedstocks and products, distinguishing it into CTL (Coal-to-Liquids), GTL (Gas-to-Liquids), BTL (Biomass-to-Liquids), WTL (Waste-to-Liquids) and PTL (Power-to-Liquids). All commercial FT plants in operation to date are based on a fossil feedstock of either coal or natural gas. In recent decades, FTS gained in interest as a way of producing renewable fuels via BTL, WTL and PTL. However, many ventures are abandoned before construction even begins and those that have been realized are demonstration plants that are not comparable in scale to their fossil counterparts.

Reactors for FT synthesis include fixed bed (multi-tubular), fluidized bed and slurry bubble column reactors, each at different commercialization levels. Efficient heat removal is crucial due to the exothermic nature of the reaction. Fixed bed reactors typically use multiple catalyst-filled tubes; smaller tubes enhance cooling, and smaller catalyst particles improve conversion rates. High gas velocities lead to pressure drops, requiring a balance for stable operation. Temperature gradients can occur along the reactor pipes due to varying reaction zones and slow heat transfer. [20], [21]

In SBCR the catalyst particles are suspended in liquid waxes. Synthesis gas is injected into the reactor at the bottom by using a gas distributor, and gas bubbles rise up and react on the catalyst surface. At the top of the reactor the gaseous product can be withdrawn, while the liquid products remain. Liquid hydrocarbons are withdrawn at the side of the reactor. Diffusion limitations of the reaction are minimized by using a small catalyst particle size, but this results in a complex separation of liquid products and catalyst. The replacement of the catalyst during operation is advantageous. Additionally, the temperature distribution in the reactor is nearly isothermal. [22]

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5.4.1 Constraints and opportunities

Commercial plants for low temperature FT synthesis are based on coal or natural gas as feedstock and use either fixed bed (Multi-tubular - Shell technology) or slurry bed reactor technology (Sasol, SynFuels China). Beside these reactor technologies fluidized bed reactors are used in large-scale industrial plants in the field of high temperature FT synthesis (production of naphtha and olefins). In terms of upscaling the slurry technology is promising and shows high potential in terms of economy of scale. Currently main focus in the field of XTL lies on the usage of microchannel or micro-structured reactors (Velocys, Interatec, Khimod) due to their advantages in the field of scale-up risk, catalyst replacement and low mass and heat transfer limitations, but with the main disadvantage in the economy of scale due to high CAPEX for reactor construction. The production of renewable fuels for covering the future demand, e.g. in aviation sector, needs cost reduction in medium to large scale (up to 150 MW for decentralized plants) which is feasible by the usage of slurry reactors in the future prospective. That's the main reason for the choice of BEST to use slurry reactors for experimental assessments. [24], [25], [26], [27], [28], [29]

Table 5 gives an overview on the different possible FT technologies, which are currently available.

Table 5: Comparison of reactor technologies for FTS [23]

Description	Fixed bed		Slurry bed	Fluidized bed	
	Multitubular	Microchannel		Fixed fluidized	Circulating
Nature of the reactor	PFR	PFR	CSTR	CSTR	CSTR
Reaction phase	g or g+l	g or g+l	g+l	g	g
Catalyst particle size (mm)	>2	<0.1	<0.1	<0.1	<0.1
Mass transfer limitation	High	Low	Medium	Medium-low	Medium-low
Heat transfer limitation	High	Low	Low	Medium-low	Medium-low
On-line catalyst replacement	No	No	Possible	Possible	Possible
Catalyst mechanical strength	Low	Low	Medium	High	High
Catalyst–product separation	Easy	Easy	Difficult	Fairly easy	Fairly easy
Scale-up risk (lab to plant)	Low	Low	Medium	Medium	Medium
Scale-up economy of scale	Medium–Low	Low	High	Very high	High
Feed poisoning	Local	Local	Global	Global	Global
Feed turn down limitation	None	None	Catalyst settling	Defluidization	Defluidization

Upscaling of slurry technology:

The upscaling of slurry-based reactors needs the investigation of the flow regime by cold flow modelling. Therefore, the upscaling process consists of a combined process of cold flow investigations and hot

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reactor development and testing. The investigation of gas distributors, internal heat exchangers and other internals are important points in the cold flow model testing. To our current knowledge no computational fluid dynamic of a slurry-based system exists. Therefore, the cold flow modelling is the most important step in terms of upscaling the process. In experimental assessment with the hot reactor the temperature profile along the reactors gives information on the distribution of the catalyst.

Dynamic operation:

The slurry technology allows a dynamic operation due to the excellent heat management within the slurry bed. This concept was successfully demonstrated in the Austrian national project "Winddiesel". Load change tests have confirmed that slurry reactors are very well suited for use in the field of PTL, both in terms of heat management and the influence on catalyst abrasion. One of the few weak points of the slurry reactor is the abrasion of the catalyst. This produces fine particles that have to be removed from the reactor without losing the catalyst particles at the same time. A comparison between band load and load change tests carried out as part of the "Winddiesel" project has shown that catalyst abrasion is only insignificantly affected by the load change tests. [30]

Prone to catalyst deactivation:

Due to the well-mixing in the slurry reactor the used catalyst is prone to deactivation, which demands high effort in gas cleaning and constant monitoring to prevent the break-through of possible catalyst poisons. This poses a challenge in combination with residue-based feedstocks for the gasification process. Therefore, gas quality measurements on a regular basis are very important.

Influence of H_2:CO ratio on product composition:

The pilot FT unit is operated directly with the syngas from the gasifier, which means the H_2:CO ratio has a high influence on the FT product spectrum. The H_2:CO ratio is a crucial parameter in FT synthesis. High H_2:CO ratios are leading to short chain products and low H_2:CO ratios are leading to high molecular weight FT products (higher alpha value) with more unsaturated compounds (e.g. olefins). With the focus on SAF production height molecular weight products are wished, but low H_2:CO ratios can lead to coking of the catalyst. A tradeoff has to be found to achieve a suitable performance.

Table 6 gives an overview on constraints and opportunities for the FT SBCR technology. Key factors such as scale-up properties, mixing characteristics, tail gas recirculation and load variation behavior of slurry reactors are all challenges and possibilities for the scale-up process.

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Table 6: Constraints and opportunities for FT SBCR technology

Aspect	**Constraint**	**Opportunity**
Scale-up of SBCR	Higher upscaling risk from lab to pilot/demo due to complex hydrodynamics of the reactor (e.g. different flow regimes)	High potential for cost reduction in the upscaling of slurry reactors (compared to multi-tubular and microchannel reactors for LTFT)
Mixing behavior in a slurry reactor	Back mixing of impurities within slurry reactors impacts the complete catalyst bed in case of non-sufficient gas cleaning	Good mixing behavior leads to excellent mass- and heat transfer within the slurry phase
Tailgas loop	Increased complexity in operation and influence on reactor feedgas (higher share of inerts)	Increase performance due to higher overall conversion of carbon monoxide
Load change behavior of slurry reactor	Higher velocities in the reactor leads to higher catalyst abrasion	Dynamic operation allows e.g. integration of additional H_2 into the system

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6. Test and analytical plan for activities in Task 4.2 and 4.3

In light of the discussion in section 5 about defining limitations and possibilities for the scale-up of the gasification process chain, a plan for testing and analysis for the subsequent tasks (4.2 and 4.3) has been created.

6.1 Performance of advanced DFB gasification system

The performance of the advanced DFB gasification system will be evaluated based on the following key parameters:

- Temperature profile in the DFB reactor system
- Pressure profile in the DFB reactor system
- Product gas composition
    - H_2:CO ratio
    - Cold gas efficiency.

These are general indicators which are used to evaluate a steady state operation with a defined feedstock. There are, of course, additional indicators for the performance of the DFB reactor system, such as the carbon conversion efficiency, which might be included based on the available data of the experiment.

6.2 Performance of the counter-current column

As described further above, it is necessary to focus on the evaluation of the counter-current column of the aDFB reactor design. Therefore, comprehensive tar measurements, including gravimetric and GC/MS-tars, will be performed along the height of the counter-current column. In each chamber, meaning before and after each constriction of the counter-current column, additional tar measurement points need to be installed and equipped accordingly to enable the successful measurement of tars.

The tar measurements in the counter-current column will be related to the temperature measured in this part of the reactor. Additionally, the measurement results will be compared and benchmarked against existing data from the 100 kW DFB pilot plant at TU Wien of tar measurements along the height of the counter-current column.

Figure 18 shows a concept of the measurements along the reactor height in the 1 MW aDFB reactor. Certain temperature measurements in the counter-current column could be replaced with tar measurements, while keeping one or two points to measure the temperature. As shown further above, the temperature in the counter-current column is almost constant over the height of the counter-current

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column, therefore it is sufficient to keep only one or two temperature measurements. This set-up will be realized for the experiments planned in the frame of the project BioTheRos.

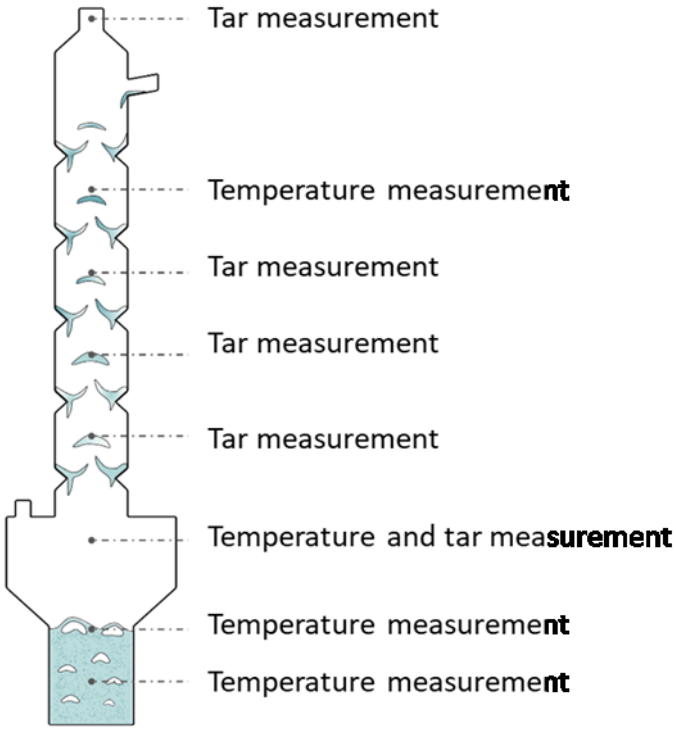

Figure 18: Concept of the measurements along the reactor height in the 1 MW aDFB reactor

6.3 Performance of gas cleaning section

The performance of coarse and fine gas cleaning section will be evaluated based on the separation efficiency of the unit operations along the process chain. Following separation efficiencies are evaluated:

- Separation of heavy (height molecular - tar) aromatic compounds along the coarse gas cleaning section
- Light weight aromatic compounds (BTX) along the fine gas cleaning section
- S-compounds along the fine gas cleaning section
- N-compounds (NH_3+HCN) along coarse and fine gas cleaning section.

6.3.1 Wet chemical measurements:

Tar:

Tars are analyzed gravimetrically and by means of gas chromatography-mass spectroscopy (GC/MS). Therefore, a sample is taken at the respective sampling points. A partial flow of the product gas is

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extracted via a heated line consisting of a cyclone and filter sleeve. The gas is then passed through several wash bottles filled with toluene. These are located in a cooling bath with a temperature of -8°C and are used to separate tars and water. The temperature is maintained by means of cryostats. The amount of gas extracted is measured with a bellows gas meter and serves as a reference value for the tar and water content. Further processing for the determination of the tar content is carried out in the laboratory.

N-Compounds:

Analysis of NH_3 and HCN are performed using two different wet-chemical analytical methods with samples extracted at the same sampling points in the gasification pilot plant. The results of methods are expected to be interchangeable.

I. Sampling is conducted similarly to the procedure for tar measurements, but the wash bottles are filled with either 0.05 M H_2SO_4 (for NH_3) or 0.1 M NaOH (for HCN). These bottles are placed in a cooling bath maintained at +2°C using cryostats. The volume of gas suctioned is measured with a bellows gas meter, which serves as a reference for determining the NH_3 and HCN content. NH_3 concentrations are analyzed using ion chromatography, while HCN concentrations are measured via capillary electrophoresis.

II. The product gas is drawn through a heated tube and a preheated filter, both maintained at 180°C. If the expected tar concentration is high, the gas is then passed through a cooled wash bottle filled with isopropanol to reduce tar content. To prevent analyte accumulation in the tars, reagents that release the analyte by adjusting pH are added. The analyte is subsequently captured in absorption solutions contained in the first and second wash bottles. For the measurement of NH_3, a 1 M sulfuric acid solution is used as the absorption solution and for HCN, a 1 M sodium hydroxide solution. Quantitative measurement of NH_3 and HCN is performed in the absorption solvents and done photometrically. Measurement of NH_3 is performed as NH_{4+} according to DIN 38406-E5-1, HCN is measured according to DIN 38405 D13-1-3. The analysis for both species is carried out in triplicate.

Figure 19 shows the setup for the sampling of N-compounds at the DFB gasification plant.

The analysis of N-compounds is performed after the test runs are completed in the laboratories. Therefore, on-site results are needed to release the cleaned synthesis gas for downstream FT synthesis.

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Dräger gas detection tubes are used to determine the amounts of NH_3 and HCN in the synthesis gas. These tubes are easy-to-use tools for detecting and measuring chemical substances in the gas phase, based on adsorption on a reactive substance applied to a carrier material within a glass tube. A hand pump is used to pass the gas through the tubes. The number of necessary strokes correlates with the amount of the substance in the gas phase. Previous results, based on comparisons between wet chemical measurements and short-term measurements with sampling tubes, showed a good correlation between the two measurement principles. [31]

Figure 19: Setup of sampling N-compounds at the DFB gasification plant

6.3.2 Gas chromatography

For the characterization of gas-, S- and BTX compounds several gas chromatographs (GCs) with different detectors are used. Figure 20 shows the used GCs for BTX and S-compound characterization. Gas samples are taken from the respective sampling points with gas sampling packs. Therefore, several measurements can be made simultaneously from the gas sampling bags.

Figure 20: Left: Clarus 500 GC with FID detector for BTX measurement; Right: Clarus 580 GC with SCD for S-compound characterization

Following detectors are used:

- FID (Flame Ionization Detector):
  - Used for the detection of organic compounds (e.g. BTX, CH_4, C_2H_6, C_3H_8…)
  - Detection is based on the ions from the components, that can be burned
  - Detection limit: ~500 ppm_v
- TCD (Thermal Conductivity Detector):
  - Used for the detection of permanent gases (e.g. O_2, N_2, CO, CO_2…)

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  - Detection is based on the change of thermal conductivity of the column effluent and to compare it with the reference flow of the carrier gas (helium)
  - Detection limit: ~500 ppm_v

- SCD (Sulfur Chemiluminescence Detector):
  - Used for the detection of S-compounds
  - The SCD is a selective, high-sensitivity detector
  - The detection is based on the chemiluminescence reaction caused by ozone oxidation
  - Detection limit: ~1 ppb_v

- FPD (Flame Photometric Detector):
  - Used for the detection of S-compounds
  - The FPD is highly selective
  - The detection is based on emitted unique light wavelengths when target compounds are burned
  - Detection limit: ~ 1 ppm_v

The characterization of gas main compounds (H_2, CO, CO_2 and CH_4) is performed with online gas measurements.

6.4 Performance of SBCR FT synthesis

The performance of the FT system is characterized by following key parameters:

- CO conversion
- Selectivities
- Product distribution

6.4.1 CO conversion

The conversion of CO over the reactor is one of the main key parameters, which represents the performance of the FT process. The used FT slurry system uses a tail gas recycling, therefore two CO conversion rates can be considered:

I. **Overall CO conversion:** The CO content of the fresh synthesis gas prior to the recycling loop is compared with the content of CO in the tail gas leaving the process.
II. **One-through CO conversion:** The CO conversion is directly measured over reactor, which means CO content in the gas at the reactor inlet is compared to the content in the tail gas leaving the reactor.

The overall CO conversion is higher due to the recycling of the tail gas, where CO is reused in a gas loop. To calculate the CO conversion rates, information on the respective mass flows and compositions are necessary. The mass flows of the inlet and outlet streams of the system are measured using Coriolis

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measurement equipment. Gas composition is characterized with an online gas measurement system that alternates sampling between the inlet and outlet. Additionally, gas samples taken are analyzed with a gas chromatograph (GC).

6.4.2 Selectivities

The CO is converted to a wide spectrum of hydrocarbons, ranging from C1 to more than C60. The selectivity to CH_4, CO_2 and C_{5+} gives information on the selectivity of the process (gaseous and liquid products, side reactions,…). Therefore, the gas composition up to C_{5+} is measured to obtain information on:

I. Selectivity to CH_4: Methane (CH_4) is an undesired but unavoidable synthesis product. Its selectivity is influenced by several parameters and the chosen catalyst, with temperature and the H_2:CO ratio having the most significant impact. The goal is to minimize the amount of CH_4 produced in the tail gas.
II. Selectivity to CO_2: Carbon dioxide (CO_2) is a byproduct of the water-gas shift (WGS) reaction, which occurs to some extent with a cobalt-based catalyst, though less than with an iron catalyst. The objective is to minimize the amount of CO_2 in the tail gas.
III. Selectivity to C_{5+}: The selectivity to C_{5+} products indicates the amount of liquid and solid hydrocarbons (e.g. wax, which is solid at ambient conditions) produced.

The calculation of selectivities is based on the obtained values from gas composition analysis and mass flow measurements, comparing the inlet and outlet streams of the reactor.

6.4.3 Product distribution

The condensed Fischer-Tropsch (FT) products are analyzed for carbon number distribution (alpha-value) and compound class distribution using a Simdist GC from Perkin-Elmer. Three GC methods are employed to analyze each condensed raw FT fraction.

I. Method 1 is used to analyze light liquid hydrocarbons with a carbon number range from C_6 to C_{15}.
II. Method 2 is applied to the heavy liquid phase ranging from C_7 to C_{24}.
III. Method 3 is used to analyze the solid hydrocarbon fraction covering C_8 and higher.

The individual hydrocarbons are identified by their retention times, and their weight percentages are calculated using FID based on the detected area. Methods 1 to 3 are derived from the European Wax Federation (EWF) standard Method 001/03 [32] with several deviations.

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7. Conclusion and outlook

Deliverable 4.1 in the frame of work package 4 of the project BiotheRos should comprise following key points:

I. Provide an overview of the setup and technologies used in the gasification pathway for obtaining FT-syncrude in section 3, 4 and 5.
II. Discuss constraints and opportunities of the technologies for further scale-up, focusing on the use of biogenic waste feedstocks in section 5.
III. Develop a test and analytical plan in section 6 for foreseen activities in Task 4.2 and 4.3 based on the discussion to guide demonstration activities for obtaining syncrude.

At the Syngas Platform Vienna promising technologies are employed to establish the basis for scaling up the gasification route using aDFB technology. This process produces raw synthesis gas, undergoes several gas cleaning steps to achieve a quality suitable for synthesis gas applications and culminates in an FT pilot-scale system to obtain FT-syncrude, which can be further processed into products such as SAF. The technologies used enable economic scale-up to sizes between 100-150 MW, where feedstock logistics play a major role in determining the limit of growth.

The technologies for gas production and conversion are based on fluidized bed systems. This includes gas/solid contact in the gasification process (using a bubbling fluidized bed reactor) and gas/liquid/solid contact in the FT synthesis process (using a slurry bubble column). These systems offer good scalability and high potential for cost reduction but also present certain risks due to the complexity of conversions in fluidized beds, such as the influence of fluid dynamics and abrasion. Both technologies have the potential to be upscaled to hundreds of MW or even GW scale (e.g. slurry beds using syngas from natural gas steam reforming and coal gasification).

A significant challenge in the market is the gas cleaning section, which is greatly influenced by the feedstock used. While there are systems for cleaning coal-based synthesis gas, these technologies are only economically feasible at scales where bio-based syncrude plants are not possible due to feedstock supply and logistics constraints (several hundreds of MW). To address this, BEST aims to combine filters, liquid scrubbers and fixed bed adsorbers to produce synthesis gas with qualities suitable for downstream synthesis applications.

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Following the discussed framework within the BioTheRos project, the key points with significant impact on the output, system performance and technology scaling are summarized as follows:

- **Product gas composition:**
  - H_2:CO ratio in syngas: To produce a syngas with a H_2:CO ratio suitable for the synthesis process and to control its stability over time
  - Influencing factors on the composition of the product gas (process vs. fuel related topics)
- **Counter-current flow column:**
  - Influence of counter-current flow column (as tar cracker) on amount and composition of aromatic compounds (tar) in the product gas
  - Influence of counter-current flow column on downstream coarse and fine gas cleaning steps
- **Liquid scrubber systems (biodiesel and acidic water):**
  - Further removal of aromatic compounds downstream in coarse (focus on heavy molecules) and fine gas cleaning (focus on light weight molecules)
  - Challenging regeneration of washing media
  - Removal of N-compounds and separation of water via liquid scrubbers
- **Fixed bed adsorber systems:**
  - Removal of possible catalyst poisons (S- and N-compounds) and gas polishing in terms of aromatic compounds in fine gas cleaning
- **FT-Product composition:**
  - Influence of H_2:CO ratio in the syngas on the product spectrum in the FT-syncrude
  - Influence of other process parameters on composition and output
- **CO conversion:**
  - Overall and one-through conversion of CO to FT-syncrude
  - Influence of inerts on the performance
- **Selectivities:**
  - Selectivity to gaseous and liquid FT-products and influence of recycling

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The constraints and opportunities derived from the analysis of various factors in the gasification process chain's different areas are summarized in Table 7.

Table 7: Constraints and opportunities of aDFB gasification pathway

	Aspect	Constraint	Opportunity
aDFB gasification	Scalability of fluidized bed technology	Complexity in upscaling	High economy of scale
aDFB gasification	Counter-current column	Complexity in engineering and manufacturing	Improved tar conversion which allows the usage of residue feedstocks
aDFB gasification	Operation of aDFB without further gas upgrading steps	Challenging operation to obtain H_2:CO ratio of 2	Levels down the complexity
aDFB gasification	Usage of residues with low quality	Adapted operation measures necessary	Reduced costs for feedstock supply
Gas cleaning	Usage of residues of low quality	Challenge for gas cleaning	Reduced costs for feedstock supply
Gas cleaning	Operating materials in gas cleaning	Expensive operating material	Usage of thermal waste energy for regeneration
Gas cleaning	Setup of gas cleaning section	Complex setup with several unit operations	Unit operations adaptable
Gas cleaning	Strict require-ments for syngas quality	High effort for gas cleaning	Optimal operating conditions for FT catalyst (No influence of impurities on the used synthesis catalyst)
FT SBCR technology	Scale-up of SBCR	Higher upscaling risk from lab to pilot/demo	High potential for cost decrease in the upscaling
FT SBCR technology	Mixing behavior in a slurry reactor	Global influence of back mixing	Good mixing behavior leads to excellent mass- and heat transfer
FT SBCR technology	Tail gas loop	Increased complexity in operation	Higher overall conversion of carbon monoxide
FT SBCR technology	Load change behavior of slurry reactor	Higher catalyst abrasion	Integration of H_2 into the system possible

A SWOT analysis was conducted for the three primary components of the gasification process: aDFB, gas cleaning and FT SBCR technology, considering the resulting limitations and possibilities for various aspects of the process chain.

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Table 8: SWOT analysis based on derived constraints and opportunities

	Threats	Opportunities	Strengths	Weaknesses
aDFB gasification	Complex upscaling	High economy of scale	Broad range of possible feedstocks	Syngas contains higher loads of tar and dust compared to other gasification technologies
Gas cleaning	Complex setup and expensive operating materials	Costs savings by regeneration, remaining impurities less severe for used FT catalyst	Unit operations modular adaptable	High influence of increased share of impurities
FT SBCR technology	Complex upscaling	High economy of scale	Load flexibility, high mass- and thermal transfer rates within slurry phase	Prone to catalyst deactivation, abrasion due to higher gas velocities

Based on the previously discussed points that significantly influence the system and the further upscaling of the technologies, the following actions will be included in the test and analytical plan for the BiotheRos project:

- Determine the performance of the aDFB gasification system with respect to temperature and pressure profiles.
- Determine the H_2:CO ratio and cold gas efficiency of the gasification system.
- Evaluate the performance of the novel counter-current column.
- Assess the separation efficiency of various unit operations along the gas cleaning section using several analytical techniques, including wet chemical, online and gas chromatograph measurements.
- Analyze the performance of the FT system based on key performance indicators such as CO conversion, selectivity to gaseous and liquid products and the obtained product spectrum.

The obtained data will serve as a basis for further activities in the project, including evaluating the potential for upscaling these technologies, conducting simulation work, performing economic (TEA) and sustainability assessments (LCA) and producing SAF from the provided FT syncrude. This comprehensive approach aims to demonstrate the entire value chain from biogenic residue materials to high-quality fuel.

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The BioTheRoS Project has received funding from the European Union's Horizon Europe research and innovation programme under Grant Agreement No. 101122212

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The BioTheRoS Project has received funding from the European Union's Horizon Europe research and innovation programme under Grant Agreement No. 101122212