**Effect of internal hydrocarbon reforming during coupled operation of a biomass gasifier with hot gas cleaning and SOFC stacks**

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**Abstract**
In the context of energy transition and climate change, a combination of highly efficient modern solid oxide fuel cells (SOFC) and thermo-chemical conversion of biogenic residues could complement other intermittent renewable sources such as wind and solar. In order to reduce required gas cleaning efforts and to increase the process efficiency, the influence of hydrocarbons on SOFC performance is experimentally investigated in this study. For the first time, the operation of Ni/YSZ anode-supported cells in Jülich F10 stacks is performed with pre-reformed and with bio-syngas containing full hydrocarbon content at realistic current densities. Sulfur and other impurities were removed in both cases. No degradation could be observed within normal operation on clean gas. With the tar reformer bypassed, the pressure drop over the stack increased due to severe carbon deposition on the anode substrate and the nickel current collector mesh inside the SOFC stack, so that operation had to be terminated after five hours. This behavior is different from single-cell tests, where electrochemical degradation is the limiting factor. The results show that improvements are not only necessary for cell materials and that future research must also consider other stack components.

**KEYWORDS**
biomass gasification, bio-syngas, solid oxide fuel cells, tar reforming

1 | INTRODUCTION

Energetic utilization of biomass and biogenic residues will play an important role in future energy systems based on renewable sources. In contrast to solar and wind energy, biomass-based power generation is less intermittent and better controllable and can contribute to grid balancing. Besides combustion, one of the most discussed processes is the gasification of biomass. Depending on the feedstock and technology used, the produced gas (bio-syngas) can be used either for electricity generation, or for chemical synthesis as feedstock. Hence, it could help to replace conventional, fossil energy carriers for transportation, or base chemicals in industry.\textsuperscript{1,2}

Several different gasification technologies exist, which can convert biogenic residues or even municipal solid waste...
into syngas. These not only vary in reactor type, but also vary in oxidizing agent (e.g., air, oxygen, steam). Up- or down-draft fixed-bed gasifiers are mostly used in combination with internal combustion engines in small-scale applications. Entrained flow gasification is less established for biogenic feedstocks and currently under research. For special applications, even thermal plasma gasification with temperatures of up to 8000 K could be used.

Fluidized-bed gasification with steam has reached a high technology readiness level (TRL), and several plants in the range 5-20 MW have been operating in Europe. When using steam as oxidizing agent and temperatures of ~800°C, the produced gas is nitrogen-free and consists mainly of H₂O, H₂, CO, and CO₂. Contaminants (e.g., char, higher hydrocarbons, alkalis, sulfur, chlorine) have to be removed, due to the requirements of downstream equipment.

The amount and type of contaminants are also influenced by the feedstock itself. Different levels of ash, sulfur, chlorine, phosphorus, and heavy metals can occur in biomass. Hence, gas cleaning needs to be adapted to the chosen input as well as to downstream processes. Requirements and gas cleaning technologies for operation of solid oxide fuel cells (SOFC) are summarized by Gaderer et al.

State of the art in syngas cleaning involves the utilization of scrubbing liquids or solvents at temperatures below 80°C. This process is suitable for syngas utilization in combustion engines, but less attractive for downstream high-temperature processes, as discussed in this paper. Hot gas cleaning methods are not yet state-of-the-art and still under research by several groups and institutes for feedstocks like woody biomass or residues from paper industry (low in ash, sulfur, chlorine). The first cleaning step is usually represented by a filtration or separation of solids, such as unconverted char and ash compounds. Removal of higher hydrocarbons (more than two carbon atoms) and tars ((poly)aromatic hydrocarbons) in the presence of chlorine and sulfur compounds is more difficult. So far, many different catalytic systems have been investigated. These include fixed-bed, fluidized-bed, or monolithic reactors using different active materials (e.g., Ni, Fe, noble metals, dolomite). The studies are mostly based on model tar compounds (e.g., benzene, naphthalene), but results from test campaigns with real syngas can also be found in literature. Ni appears to be the catalyst with the highest conversion rates, but is prone to sulfur deactivation and carbon formation if not operated under proper conditions. Many of the gasification processes for energetic biomass utilization would be technologically feasible, but still lack economic viability and suffer from low conversion efficiencies, among others because of the required gas cleaning steps.

In order to improve the conversion efficiencies from raw product to electricity, the produced bio-syngas could be used in high-temperature fuel cells like SOFCs. Several research institutes have been working on coupled biomass gasification and SOFC systems. Still, this is a relatively young field of research and many different setups, configurations, and materials are under investigation and are outlined in the following. In the context of the European research project “BioCellus,” an innovative heat integration between gasifier and SOFC and the influence of impurities (tars from 150 to 250 mg/Nm³) on SOFC degradation (at 850°C) were analyzed. Oudhuis et al used a two-stage wood gasifier together with an electrolyte-supported HEXIS fuel cell stack. Due to the oxygen-blown second stage of the gasifier, the bio-syngas was almost tar-free, and the stack showed no significant degradation. Similarly, Gadsbøll et al successfully operated a stack with anode-supported nickel/yttria-stabilized zirconia (Ni/YSZ) anode cells at 700°C on gas from an air-blown, two-stage Viking gasifier, which, due to its special design, also produces gas with tar loads as small as 5 mg/Nm³. However, these gasifier designs have several drawbacks and limitations compared to steam-blown fluidized-bed gasifiers when it comes to the combination of biomass gasification and SOFCs, for example, dilution of the bio-syngas with nitrogen and severe efficiency losses due to the necessary gas cooling in between gasifier and SOFC. All tar-cleaning options, however, require additional equipment, which is expensive and thwarts the commercial application of SOFC gasifier systems, and should thus be reduced to a minimum. Therefore, research on the effect of tars on SOFCs and the respective degradation mechanisms is crucial.

Most of the experimental research in this field is done with simulated syngas. In these tests, model tars are added to bottled gas and fed to SOFCs, either to isolate the effect of the respective tar species or else to facilitate the experiment compared with operation using a gasifier. Benzene at levels of 15 g/Nm³ was found to cause carbon deposits on Ni/YSZ anodes at 765°C operation temperature even with high steam content and current density, where solid carbon formation is not predicted by thermodynamics. Another relatively light tar, toluene, can be utilized as fuel at low concentrations around 3.8 ppm (15.4 mg/Nm³), but at higher levels causes degradation and metal dusting, which is the disintegration of Ni-containing structures. Cavalli et al also reported extensive carbon deposits in the fuel supply when they used acetic acid as a tar substitute in their experiments. Heavier tars like naphthalene, however, adsorb onto the anode surface even at low concentrations, where they hinder reforming reactions and block active sites. Geis et al studied the effect of phenol at concentrations from 1 to 8 g/Nm³ on Ni/YSZ anode-supported cells at 700°C. Phenol was used as model tar due to the fact that, together with benzene and toluene, it is the predominant tar species in typical bio-syngases, while at the same time, only little experimental data regarding its influence on SOFCs are available. Results showed that the addition of phenol led to an initial increase in voltage but caused subsequent voltage degradation. Noise in the voltage...
signal could be noticed as soon as tars were introduced into the gas, indicating the formation of carbon deposits.\textsuperscript{28} Postmortem analysis confirmed this assumption, and metal dusting was observed even for the lowest concentrations of phenol. Model tars, however, do not necessarily represent the properties of real gasification tars, which are a mixture of various tar species. A comparison of toluene and tars from a real gasifier showed that model tars can cause more carbon deposits and degradation, and thus that this kind of experiment might overestimate the issue of carbon deposits in the presence of tars.\textsuperscript{29} Hence, experiments with realistic syngas compositions are an important addition to single-compound tests.

For electrolyte-supported cells (ESC) with Ni/GDC (nickel/gadolinium-doped ceria) anodes, researchers have already demonstrated successful operation on tar-containing gas from a fluidized-bed gasifier.\textsuperscript{30} Typical state-of-the-art anode-supported cells however have Ni/YSZ anodes, which are known to be far less tar-tolerant than the Ni/GDC type.\textsuperscript{31} To our knowledge, only few experiments with tar-containing syngas and SOFCs with Ni/YSZ anodes have been reported in literature. Nagel used an updraft gasifier to feed a HEXIS stack similar to Ouidhuis et al.\textsuperscript{32,33} In contrast to most other literature, an operation of the stack without significant degradation for several dozen hours under tar loads of 85 g/Nm\textsuperscript{3} was proven, with the only effect being a slight increase in the fuel-side pressure drop over time. Switching to hydrogen for a short period reportedly lowered the pressure loss back to normal levels. The reason for this very tar-resistant behavior was probably the stack operating temperature of 950°C, which is much higher than the operating temperatures of modern SOFCs. Tar reforming is improved at higher temperatures, and thus, carbon deposition is avoided. However, such high temperatures contradict the goal of low-cost and long-living SOFCs. Due to the difference in temperature, the results of Nagel cannot be transferred to modern stacks.\textsuperscript{33} Hackett et al operated Ni/YSZ anode-supported single cells at 800°C with syngas from a coal gasifier.\textsuperscript{34} The gas was cleaned from particles and most of the sulfur, but tars, the remaining sulfur, and other contaminants (e.g., phosphor) present in the gas caused severe degradation in the range of 9.1 and 18.9%/1000 hours, depending on the current density applied. The tars caused a significant amount of carbon deposition; however, it is not possible to define how much of the degradation can be attributed to them.

In this paper, the influence of real bio-syngas on Ni/YSZ anode-supported cells, which are integrated in customary stacks, is investigated for the first time. For this purpose, a two-cell and a four-cell stack were operated using the bio-syngas of an alithermal biomass gasifier fed with wood pellets. The operating temperature of the stacks was 715°C, and a realistic current density of 0.5 or 0.25 A/cm\textsuperscript{2} was applied. Tar, sulfur, and chlorine species were removed by hot gas cleaning upstream of the stack. In order to evaluate a potential complexity reduction of the coupled system and to prove the applicability of the stacks for this process design, the influence of unsaturated hydrocarbons on the SOFCs was investigated by bypassing the respective cleaning reformer.

2 | EXPERIMENTAL INVESTIGATION AND METHODOLOGY

The test rig at the Chair of Energy Systems (LES) consists of three parts, which can be used separately or combined: a gasifier, catalytic hot gas cleaning, and an SOFC stack. The schematic P&ID of the setup can be found in Figure 1. Gasifier and gas cleaning have been designed for long-term operation of up to 100 hours and operating pressures up to 500 kPa. Gas sampling can be done after each of the three parts (gasifier: “G”, inlet “S\textsubscript{in}”, and outlet of SOFC “S\textsubscript{out}”).

2.1 | Biomass feedstock and gasifier setup

The bubbling fluidized-bed gasifier (stainless steel, 1.3 m height in total, DN80/DN200) can be supplied with biomass via a vibrating feeding system from the top and superheated steam as oxidizing agent from the bottom. The feed stream can be quantified using an optical camera and a Matlab video vision tool for pellet detection. The gasifier can be heated electrically with two separate heating zones for the fluidized bed and the freeboard. The temperature distribution inside the bed and differential pressure over the bed can be measured online. Before each test run, 2 L of fresh silica sand and 0.25 L of biomass char (from previous runs) were filled inside the reactor as bed material.

Conventional wood pellets (Scandbio, Sweden, pure sawdust without additives, \(d = 8\) mm, \(L \approx 12\) mm) with low moisture (6\%) and ash content (0.3\%) and a high energy density of 17.7 MJ/kg\textsubscript{ar} were used as biogenic feedstock. The proximate and elemental analyses can be found in Table 1.

Compared to other gasification feedstocks (e.g., straw, sewage sludge, municipal solid waste), the amounts of sulfur and chlorine were also quite low, which simplifies the gas cleaning steps required.

The operating set-point parameters of the gasifier (\(p = 120\) kPa, \(T = 800^\circ\text{C}\), steam/biomass \((S/B) = 2\)) were kept constant during all test runs. A constant flow of nitrogen was used as purge gas inside the feeding system.

2.2 | Gas cleaning

A substream of the bio-syngas was used within the second part of the test rig. As can be seen from the P&ID, Figure 1,
the syngas was cleaned in several steps before it was introduced into the stack. The first part of the gas cleaning was a sintered porous metal filter (Inconel 600) for volatile particles. Since its operating temperature (450°C) was lower than the reformer temperature, it can be assumed that in the filter components with high boiling points (e.g., alkalis) condensed at the particles and were removed in this step.35,36 Afterward, the gas was fed into a double-jacket fixed-bed tar reforming reactor at up to 850°C, where hydrocarbons were converted, using 150 mL of an α-Al2O3-supported Ni catalyst. According to performed measurements in previous test runs of the gasifier, it can be assumed that the tar cleaning step is operating correctly, as long as no methane is detected behind the reactor. A bypass around this tar reformer allowed an SOFC operation with hydrocarbons in the syngas. In the last two reactors, chlorine and sulfur species adsorbed on 2 L of Na2O/ZnO/Al2O3 (Clariant, ActiSorb Cl2) and 2 L of ZnO (Clariant, ActiSorb S2) packed beds, respectively. Both reactors were heated to 350°C during operation in order to avoid condensation of tars in these cleaning steps.

### 2.3 | SOFC stacks and test rig

With the main purpose of the tests being the operation of an SOFC stack with tar-containing syngas, the tar reformer can easily be bypassed using two needle valves. In order to prevent oxidation of the reformer catalyst or the SOFC anode and to maintain safe operation, a forming gas supply has been installed for both the tar reformer and the SOFC stacks.

For the experiments, F10-design stacks from Forschungszentrum Jülich (FZJ) were used.37 They consist of two (Stack A) or four (Stack B) cells of commercially available anode-supported SOFCs from CeramTec with a size of 10 × 10 cm². These cells have a NiO/3YSZ anode support, NiO/8YSZ anode, 8YSZ electrolyte, 20GDC barrier layer, and a La0.58Sr0.4Co0.2Fe0.8O3-δ (LSCF) cathode. The area of the cathode is 9 × 9 cm², determining the electrochemically active area. All interconnects, cell frames, and top and bottom plates are based on Crofer 22 APU.38 The metallic parts are sealed by glass sealant (Type 87 ZYBF-2).37 A MnCo1.9Fe0.1O4 (MCF) coating is applied via atmospheric plasma spraying (APS) on all exposed parts of the interconnector on the air side to prevent chromium poisoning.39

### TABLE 1 Proximate and elemental analyses of the wood pellets

|                  | ar   | wf  | waf |
|------------------|------|-----|-----|
| H2O w-%          | 6.22 | -   | -   |
| Volatiles w-%    | 79.79| 85.08| 85.36|
| Ash w-%          | 0.31 | 0.33| -   |
| Fixed C w-%      | 13.68| 14.59| 14.64|
| C w-%            | 46.73| 49.83| 50.00|
| H w-%            | 5.52 | 5.88| 5.90|
| N w-%            | 0.05 | 0.06| 0.06|
| S w-%            | 0.40 | 0.42| 0.42|
| O w-%            | 40.78| 43.48| 43.62|
| Cl w-%           | 0.025| 0.027| 0.027|

ar, as received; wf, water free; waf, water and ash free.

FIGURE 1 Schematic P&ID of the bench-scale test rig used at the Chair of Energy Systems with gas measurement locations depicted. Gas analysis: water content (W), permanent gas composition (PG), tar content with solid-phase adsorption (SPA).
fine and a coarse nickel mesh is used for contacting at the anode side, and a LaMn_{0.45}Co_{0.35}Cu_{0.2}O_{3} (LCC10) coating is applied for the cathode via screen printing directly onto the sintered cathode.

For operation of the SOFCs with bio-syngas, a test stand was built downstream of the described gasifier in which short stacks can be tested. The central piece of the test rig is an 8.4 kW electric furnace, in which the stack can be kept at 715°C. Fuel gas and air were supplied from the bottom via an adapter plate and flowed through the stack in countercurrent direction. During the tests, all connecting pipes between gasifier and stack were heated to 350°C with heating cords to prevent condensation of tar. The air flow was also preheated. Between the adapter plate and the stack, mica seals were used, which were compressed by 70 kg of steel plates on top of the stack.

The maximum allowable overpressure for the stacks was 10 kPa. Therefore, a pressure relief valve was installed at the fuel inlet, which nominally opens at 8 kPa and thus protects the stack in case of pressure oscillations in the gasifier or blockage of gas pipes. During heating-up, forming gas flowed through the fuel gas side. In emergency shutdown situations, for example, if the pellet dosing of the gasifier failed, a safety valve opened and the stack was flushed with forming gas. For the gas supply during the recording of the reference I-V characteristics, the stack was operated with cylinder gases, which were mixed and dosed with a mobile gas mixing unit.

Using an electrical load (Höcherl & Hackl GmbH, PLI 2106), the galvanostatic operation and the load ramps during the I-V characteristics were realized. The load was connected to the stack via two Inconel rods and two sense cables for measurement of the stack voltage. The load device also has an undervoltage protection function, which reduces the electrical current during bio-syngas operation as soon as the fuel gas flow was not sufficient. The lower limit for the stack voltage was set in a way that no single-cell voltage may fall below 0.65 V, thus minimizing the risk of nickel oxidation. In emergency shutdown situations, the load automatically switched into open clamp conditions (OCC).

Five thermocouples (TC Direct, Typ K, 0-1100°C) measured the temperature of the stacks. They were inserted into drillings in the interconnector plates. Contact between thermocouples in different cell layers was prevented by insulating their sleeves with glass fabric. Four other thermocouples were fixed to the pipes of fuel and air inlets and outlets with pipe clamps. Furthermore, one thermocouple was introduced into the oven near the fuel inlet outside the stack; this was for the purpose of logging the oven temperature and monitoring leaks and thus combusting fuel, which would generate heat. Pressure difference gauges measured the difference between ambient and fuel inlet pressure, the pressure loss over the stack, and the pressure difference between ambient and air outlet pressure. The sampling point at the air outlet was chosen with the consideration that the differential pressure between air- and fuel-side should be monitored and that the difference is largest between air outlet and fuel inlet. Furthermore, the absolute pressure downstream of fuel-side was measured. The cell voltage of each cell was measured and recorded individually using a 4-channel data logger (Onset, HOBO®). Inside the oven, the connections between the cells and the logger were electrically insulated by glass fabric, in order to avoid short circuits.

### 2.4 Preparation and initial testing

Prior to the tests with bio-syngas, both stacks were joined at 850°C for 100 hours by Forschungszentrum Jülich to ensure crystallization of the glass sealant. After subsequent reduction of the anodes with a mixture of hydrogen and argon, the stacks were operated at 700°C with H₂ plus 20% H₂O at 0.5 A/cm², in order to check their proper operation. During this operation, I-V curves were recorded. These are shown in Figure 2. The gas flows were set to 1.125 Nl/min/cell of H₂, plus 20% H₂O and 4 Nl/min/cell of air.

After shipping the stacks to LES, I-V curves were recorded under comparable conditions (see Figure 2). A gas mixing station was used to provide bottle gases (Bronkhorst EL-Flow MFCs) and steam (Bronkhorst, Cori-Flow LFC with electrically heated direct evaporation). The noise in these measurements was caused by oscillating water content in the fuel gas, resulting from issues with the direct evaporation. The temperature at the fuel inlet was set to 707°C in case of Stack B. Its performance was a bit lower than during the original characterization tests, due to two effects: a decreased voltage of the bottom cell (Cell 1), which is known to deteriorate each time a stack is removed from its furnace after testing, and a lower temperature near the air inlet compared to the test in Jülich, caused by insufficient air preheating. This was addressed by improving the air preheater prior to testing Stack A, which was tested at a higher stack temperature of 712°C at the fuel inlet. The higher temperature led to better cell performance, which shifted the I-V curve of Stack A upward, and counterbalanced the deterioration of Cell 1. The results show that, while the bottom cell had deteriorated, overall stack performance was as expected and no fuel leakage was detected, since we did not measure a temperature increase inside the oven.

### 2.5 Conduction of experiments

The start-up of the test rig took place gradually. At first, the gasifier was heated and run to reach steady state. Gas cleaning was only operated after a few hours of gasifier operation. The last step was the coupling with the SOFC stack, which was preheated to 715°C at 4 K/min. During start-up, 0.5 Nl/min/cell of forming gas was supplied to the anode. Before
operation on syngas, I-V curves were recorded. Besides the aforementioned tests with humidified hydrogen for comparability with the initial performance characterization at Jülich, a mixture of 45% H\textsubscript{2} and 55% N\textsubscript{2} was chosen to serve as a reference for the degradation of the stack.\textsuperscript{41} The reference mixture was chosen to avoid the removal of deposited carbon while measuring I-V curves.

During operation on syngas, the cathode was supplied with 2 Nl/min/cell of air. For Stack A, the anode gas flow was initially set to 1.8 Nl/min/cell of syngas, but this caused fuel starvation problems due to fluctuations in the gasifier. Therefore, it was later increased to 2.2 Nl/min/cell. For Stack B, anode flow was approx. 1.1 Nl/min/cell, while cathode air flow was maintained at 2 Nl/min/cell. The anode bio-syngas flow is an estimate rather than an exact measurement, as the flow control was based on the dry gas flow behind the condenser downstream of the stack. The estimate is based on an analysis of the measured gas before the stack and on AspenPlus\textsuperscript{TM} simulations, which had shown to be reliable in earlier tests, of the change in gas composition inside the SOFC. The steam content in the simulation was adjusted until measured OCV and calculated OCV were the same. Based on this procedure, also the gas flows and fuel utilization under load were determined.

After some time of stabilization, the electrical load was increased and kept galvanostatically at 0.5 A/cm\textsuperscript{2} (Stack A) and 0.25 A/cm\textsuperscript{2} (Stack B). The lower flow rate and current density of Stack B compared to Stack A were necessary because the pressure drop over the exhaust tubing did not allow higher fuel flow rates. For Stack B, the tar reactor was bypassed after two hours of operation, whereupon tar-containing gas entered the stack. During operation, the main gas composition and the tar concentrations at the points marked in the PID (see Figure 1) were recorded. In addition, cell voltages, temperatures, pressures, differential pressures, and the volume flow of dry gas of the anode outlet were all recorded.

After the experiments were terminated, the furnace was cooled down with a maximum rate of 4 K/min, while the anode was again flushed with 0.5 Nl/min/cell of forming gas. Overall, the aim was an operation of the coupled gasifier and SOFC for at least 10 hours. The operating parameters of both stacks are listed in Table 2.

### Table 2: Tested SOFC stacks and operation conditions

| Stack | Stack A | Stack B |
|-------|---------|---------|
| Stack cells | 2 | 4 |
| Current density | 0.5 A/cm\textsuperscript{2} | 0.25 A/cm\textsuperscript{2} |
| Operation on cleaned bio-syngas under load | 15.4 h | 2 h |
| Operation on tar-containing bio-syngas under load | - | 5 h |
| Steam/biomass ratio [kg/kg] | 1.92 ± 0.5\textsuperscript{a} | |
| Temperature gasifier [°C] | 792 ± 6 | |
| Pressure gasifier [kPa] | 118 ± 5 | |
| Avg. temperature in stack [°C] | 715 | |
| Avg. fuel utilization under load | 43-53% | 43% |

\textsuperscript{a}std deviation.

2.6 | Gas sampling and analysis

Gas sampling was performed at three locations: “G”, “S\textsubscript{in}”, and “S\textsubscript{out}” (Figure 1). Permanent gas composition was measured online using two analyzers (Sick AG, S710, Germany, each with NDIR (CO, CO\textsubscript{2}, CH\textsubscript{4}), TCD (H\textsubscript{2}), and PMA (O\textsubscript{2}) sensors). The manufacturer’s accuracy of the S710 is given with 0.5% (H\textsubscript{2}), 0.8% (CH\textsubscript{4}) and 2.0% (CO, CO\textsubscript{2}). N\textsubscript{2} was calculated as the difference to 100%. One of the permanent gas analyzers was constantly analyzing the exhaust of the SOFC (“S\textsubscript{out}”), while the second one was used alternatingly after the gasifier (“G”) and after gas cleaning (“S\textsubscript{in}”). H\textsubscript{2}S was measured with a Sick Monocolor down to 1 ppmv (lower limit of detection—LOD). Additionally, the steam content was measured after the gasifier (Bartec GmbH, Hygrophil H4230) and after the SOFC (E+E Elektronik, EE31-D). The moisture content of the uncleaned syngas has an error of 0.5 percentage points, while the accuracy of the EE31 is given with 1.3%. In earlier gasifier test runs under similar conditions, higher hydrocarbons (C\textsubscript{2}-C\textsubscript{5}), NH\textsubscript{3}, HCN, and NO were also measured. These compounds were not analyzed during the experiments performed for this paper.

The measurement of tars followed the SPA method, which was proposed by Brage et al.\textsuperscript{42} and is used by many research groups.\textsuperscript{43} This method is less complex than the “tar protocol” (DIN/CEN TS 15439) and has been proven.
At the Chair of Energy Systems, 100 mL of gas was sampled from the gas stream with a syringe pump (Cole-Parmer, Model 74905-54). Adsorbable components were captured in a precooled fixed bed of 500 mg amino phase (Sigma-Aldrich Co. LLC, Supelclean LC-NH2) and stored for max. 10 hours in a cooled box until they were eluted with 2 mL of dichloromethane (DCM). The tar concentration of polyaromatic hydrocarbons (PAH) and benzene-toluene-xylene (BTEX) compounds was then analyzed with two different methods in a GC-FID (Agilent, 7890 A, column HP-5). In total, 16 substances were calibrated and all other occurring peaks were summarized with an averaged integration factor as “unknowns”. SPA sampling of tar compounds is always associated with several error sources, with the most important typically being: moisture content of the gas sampled, temperature at the sampling location, and gas composition during short-term sampling. Hence, at least two samples were pulled and analyzed for each measurement point. The values given in Table 3 are averaged and still only approximate values.

3 | RESULTS AND DISCUSSION

In the following, relevant results from the two test runs (Stack A and Stack B) are displayed and discussed.

### 3.1 | Gasification and gas cleaning

The gasifier was operated at constant conditions ($p = 120$ kPa $\pm 5$ kPa, $T = 792^\circ C \pm 5^\circ C$, $S/B = 1.9 \pm 0.5$) in order to produce realistic syngas, which allows investigating the gas cleaning and operation of the SOFC coupled for electricity generation. While temperature and pressure inside the gasifier can be controlled easily, the feeding system was not as constant, and fluctuations in the gas composition and produced volume flow can occur. Remaining char in the fluidized bed reduced these oscillations, but they can be measured in the gas analysis and electrochemically detected in the coupled SOFC.

In Table 3, the gas composition measured is averaged for each test run and all three measurement locations (see Figure 1). No measurement of C$_2$-C$_5$ compounds was performed during these two test runs, although this was done during earlier runs under similar gasification conditions. Especially unsaturated compounds like ethylene (~0.4 v-%$_{db}$) need to be considered due to their tendency to form solid carbon on Ni surfaces. The amount of tars is displayed for the five molecules with the highest concentration and the sum of all others. The given values are related to the dry gas (dry base or “db”) with nitrogen dilution.

The main gas composition of the syngas was similar for both test runs. Only the amount of nitrogen that was used to purge the feeding system differed slightly.

| Table 3 | Averaged gas analysis (standard deviation in brackets) for both test runs at three different measurement locations |
|---------|---------------------------------------------------|
|         | Stack A                                            | Stack B                                                                 |
|         | G  | $S_{in}$ | $S_{out}$ | G  | $S_{in}$ | $S_{in}^{e}$ | $S_{out}^{e}$ |
| H$_2$   | 21.8 (1.4) | 36.3 (2.8) | 24.5 (2.9) | 23.9 (1.2) | 37.0 (2.6) | 26.9 (1.6) | 29.2 (3.6) |
| CO$_2$  | 9.8 (0.8) | 12.4 (0.7) | 18.1 (0.6) | 11.3 (0.8) | 11.6 (0.6) | 14.1 (1.0) | 21.3 (0.7) |
| CO      | 6.6 (0.7) | 7.2 (1.0) | 3.8 (0.5) | 8.7 (1.0) | 9.8 (1.1) | 7.3 (1.1) | 4.6 (0.8) |
| CH$_4$  | 3.0 (0.3) | 0.1 (0.1) | 0 (0) | 3.6 (0.5) | 0.2 (0.1) | 3.7 (0.6) | 0.1 (0.02) |
| C$_2$-C$_5$ | 0.8 | 0 (0) | 0 (0) | 0.9 | 0 (0) | 0.9 | - |
| N$_2$   | 58.0 (2.8) | 44.1 (3.9) | 53.6 (3.7) | 51.6 (2.6) | 41.4 (4.0) | 47.1 (3.6) | 45.0 (5.1) |
| H$_2$S  | 9.7 (1.2) | 0 (0) | 0 (0) | 12.2 (1.4) | 0 (0) | 0 (0) | 0 (0) |
| H$_2$O  | 40.6 | 0 (0) | 0 (0) | 42.0 (0) | 0 (0) | 0 (0) | 0 (0) |
| Benzene | 0.9 | 0 (0) | 0 (0) | 0.9 | 0 (0) | 0.8 | 0 (0) |
| Toluene | 0.6 | 0 (0) | 0 (0) | 0.6 | 0 (0) | 0.5 | 0 (0) |
| Phenol | 0.9 | 0 (0) | 0 (0) | 0.9 | 0 (0) | 0.5 | 0 (0) |
| m-Cresol | 0.6 | 0 (0) | 0 (0) | 0.6 | 0 (0) | 0.2 | 0 (0) |
| Naphthalene | 0.3 | 0 (0) | 0 (0) | 0.2 | 0 (0) | 0.2 | 0 (0) |
| Other tars | 1.8 | 0 (0) | 0 (0) | 1.8 | 0 (0) | 1.3 | 0 (0) |

*Not measured during these test runs, indicative values from runs at similar conditions.*

*Not measured, balance to 100%.

*Reading of instruments (limits of detection: CH$_4$ ~ 0.1%, C$_2$-C$_5$ ~ 0.005%, tars ~ 10-15 mg/Nm$^3$, H$_2$S ~ 1 ppmv).*

*Measurement of $S_{in}$ and $S_{out}$ not available due to erroneous values.*

*With bypassed tar reforming reactor.*
As can be seen for both stacks, the steam reforming reactor of the gas cleaning (operated at 800°C) worked properly and all hydrocarbons were reformed to a value near or below LOD. The steam reforming increased the concentration of hydrogen and carbon dioxide. The overall gas yield was also increased, which can be seen from the reduced nitrogen dilution of the gas. This operation could be demonstrated for 100 hours during previous tests without detectable carbon deposits or obvious degradation. While ~10 ppmv of H2S can be detected at the gasifier outlet, it was also reduced to below 1 ppmv after the hot gas cleaning, both with and without tar reformer. In the case of the bypassed tar reformer, the first rows of ActiSorb Cl2 pellets in the chlorine reactor were covered with a very thin layer of solid carbon particles. They might either result from condensation of heavy polycyclic hydrocarbons or from very fine char molecules, which might have passed the filter candle. In a future application, those deposits would need to be prevented. Additionally, small amounts of chlorine were found in an elemental analysis. In the second reactor, neither carbon nor relevant amounts of sulfur could be detected in the elemental analysis of the pellets. Due to the large amount of adsorbents in the reactors, the separation efficiency was still sufficient during the tests, but modifications in the existing setup would be necessary to conduct long-term experiments of more than 50 hours.

Figure 3 shows the solid carbon (graphite, not valid for amorphous carbon or carbon nanotubes) formation region in a ternary C-O-H diagram for different temperatures. While 715°C was the nominal stack temperature, 680 and 650°C have been chosen, in order to investigate the effect of temperature drops due to internal reforming. The temperature variation actually measured during operation on bio-syngas was much smaller—in the range of less than 10 K. Therefore, these values were chosen as worst-case analysis. Other parts of the system, for example, the Inconel filter or the tubing, are well below these temperatures, but since neither the steel nor the Inconel are catalytically active, thermodynamic equilibrium is not reached, and no carbon deposits. The boundaries were calculated with the software FactSage™. The bio-syngas composition is also marked in the diagram. The location is valid for operation both with and without tar removal, as the reformer does not change the elemental ratios. Additionally, the effect of varying S/B ratios in the gasifier was investigated using equilibrium simulations in AspenPlus™. The bottom left end of the line represents an S/B ratio of 5, while it is 0.5 at the top right end. The measured syngas composition does not lie on the dotted line calculated with AspenPlus™, which can be explained by measurement uncertainties and an incomplete carbon conversion, while volatiles like hydrogen are all found in the bio-syngas. The results confirm that, from a thermodynamic point of view, no graphite formation was expected in the stack, even with certain fluctuations in gas composition and stack temperature. During SOFC operation under load, part of the bio-syngas was oxidized, and hence, the gas composition was shifted to the lower right corner in the ternary diagram, making carbon formation downstream of the inlet even less feasible.

Other researchers observed carbon deposits even though SOFCs were operated within thermodynamic carbon-free conditions, especially when tars were present. Furthermore, not only graphite, which was used for the calculation, but also other forms of carbon (nanotubes, amorphous carbon) with differing thermodynamic properties are reported in literature. For tar-free operation however, the calculations with graphite give a good initial estimate on whether or not carbon deposits will occur.

### 3.2 Stack A: 2 cells, operated on fully cleaned bio-syngas

Figure 4 shows the single-cell voltages and the electrical current during the experimental period for Stack A. For better readability, only the time frames with coupled operation are shown. After initial difficulties in adjusting the correct anode gas flow (up to around hour 1), the fuel supply was set to 1.8 Nl/min/cell of bio-syngas and the current to 40 A (0.5 A/cm²). Due to the fluctuations in gas composition and quantity, the voltage signals were noisy, especially during the first 7 hours of operation. The undervoltage protection of the electrical load had to reduce the current several times due to fuel starvation, especially around hour 5 to 7. As a
countermeasure, the fuel flow was increased to 2.2 Nl/min/cell of bio-syngas. After that, far less current and voltage drops occurred. As mentioned above, the bottom cell (Cell 1) provided a lower performance. Around hour 9, the voltage measurement for Cell 2 failed for an unknown reason, but resumed working after 1.5 hours, while Cell 1 was measured without interruption. For this reason, no data for Cell 2 are shown in the respective time slot.

In agreement with expectations and in accordance with former single-cell tests using similar gas compositions, no detectable degradation could be observed during the 15 hours of operation with the gasifier. Nevertheless, the H₂/N₂-I-V curves that were recorded in between revealed that a slight degradation occurred at some point during the first 7 hours of operation, which is depicted in Figure 5. The degradation was more severe for Cell 1, which had been offering lower performance than Cell 2 from the start. During these first seven hours, the stack was operated with 1.8 Nl/min/cell of bio-syngas and fuel starvation caused frequent drops in current and voltage. While both cells experienced voltage drops, Cell 1 had a lower performance from beginning and therefore dropped to values even below 0.6 V. The I-V curve, which was recorded at the end of the experiment after 15 hours of operation on bio-syngas, showed that no more degradation was detected after the fuel flow was increased to 2.2 Nl/min/cell and stable operation was achieved.

Gas analysis (incl. SPA sampling) proved that the tar reforming worked flawlessly throughout the whole experiment, reducing the tar content in the bio-syngas from roughly 5 g/Nm³db (with nitrogen dilution) to values below detection limits (see Table 3). The reason for the slight initial degradation is not completely clear. It might be attributed to the insufficient bio-syngas supply and the subsequent voltage drops; however, previous experiments with similar stacks showed that their performance tends to fluctuate to a certain degree. No signs of anode re-oxidation have been found in the postmortem analysis, and there are no indications for a malfunctioning gas cleaning. Due to the short test duration, evaluation of degradation rates is not feasible. Since we observed that the performance was stable from hour 7 onward, we conclude that coupled operation of the SOFC stack and the gasifier with hot gas cleaning is feasible at reasonable current densities.

### 3.3 Stack B: 4 cells, operated on clean and tar-containing bio-syngas

Stack B was first operated on humidified bottled gas to simulate clean syngas. The gas composition was 50 vol.% steam, 25 vol.% H₂, 10 vol.% CO, 10 vol.% CO₂, and 5 vol.% CH₄, representing an idealized bio-syngas without impurities and nitrogen dilution. The data of these tests are not shown in this paper. Similar to Stack A, the performance was stable during the characterization tests at Jülich due to deterioration of Cell 1, which is shown in Figure 2. Besides that, performance was stable and showed no signs of accelerated degradation.
After this test, the stack was removed from the test rig, and later on reinstalled and used for experiments with cleaned and tar-containing bio-syngas. The results of these tests are shown in Figure 6. All four cells showed almost the same OCV. Under load, however, the voltage of Cell 1 was considerably lower than the ones of Cells 2-4. This behavior is similar to Stack A, although it is more pronounced due to the repeated removal from the test rig.

During the 2 hours of clean syngas operation, the stack performance was stable, and even showed a slight increase. After that, a reference I-V curve with nitrogen-diluted hydrogen was recorded. For better readability, this period was excluded from Figure 6. The stack and the gasifier were coupled again and operated with full gas cleaning until hour 2.6. The short decrease in current down to 10 A was due to insufficient gas supply from the gasifier. After hour 2.6, the tar reformer was bypassed and from then on, the stack was operated on tar-containing gas. This changed the stack inlet gas composition, as the tar reformer had also reformed CH₄ and shifted some of the CO. The new composition is described in Table 3. The mainly endothermic reforming reactions subsequently occurred inside the stack and had a cooling effect, thereby causing a temperature drop of around 6 K close to the fuel inlet. The change in main gas components did not affect the performance substantially, but the presence of tars caused degradation of all cells. From hour 2.6 until hour 6, the degradation rates for Cells 2, 3, and 4 were in between 2.2 and 3.6 mV/h, while Cell 1 degraded faster at a rate of 8.4 mV/h. From hour 6 onward, Cell 1 showed large fluctuations, with voltage drops down to below 400 mV. Therefore, no voltage degradation rates could be determined for this period. Due to the short test period, these rates should be regarded to be rather qualitative than quantitative values. Still, they show that Cell 1 is far more affected than the others.

Besides the voltage, the pressure drop across the stack also changed over time. Starting right when the tar reformer was bypassed, the pressure drop increased from 0.7 to 6 kPa at hour 8. The pressure relief valve, which was installed in the pipe between gasifier and stack, limited the overpressure at the stack inlet to 8 kPa and an increasing part of the bio-syngas flowed directly through it and into the exhaust. Therefore, the experiment had to be terminated earlier than expected, since the fuel gas flow through the stack was inhibited.

In Figure 7, the H₂/N₂-I-V curves recorded before operation on bio-syngas, after 2.6 hours of operation with cleaned gas, and after operation with tar-containing gas, are shown. Similar to Stack A, no degradation was observed during the first hours with clean syngas. The last curve, which was recorded after contact with tars, shows a significant performance degradation, especially for Cell 1 with a drop in voltage beyond 0.45 A/cm². This drop, which can only be seen for Cell 1, resembles the effect of fuel starvation. Nominal fuel utilization was only around 55 % but, due to the increased pressure drop across the stack, part of the H₂-N₂ mixture used as fuel for the I-V curve was released by the pressure relief valve, resulting in higher fuel utilization. Only Cell 1 showed such a striking effect. This leads to the hypothesis that the bottom cell was more affected than the others by the phenomenon that caused the increased pressure drop.
After recording the last I-V curve, the test with this stack was ended by cooling it down at 4 K/min, while also purging it with forming gas.

### 3.4 Follow-up examination

After removal of the cooled-down stacks, no carbon deposits or condensed tars could be found in any piece of the piping. On the other hand, in the case of Stack B, small quantities of carbon had been deposited at the junction between adapter plate and stack. Considering the large diameter at this position, these depositions could not have been responsible for the increased pressure drop. The reason for the inhibited gas flow had to be inside the stack itself.

This was confirmed when the stacks were opened (see Figure 8). While both the nickel mesh for contacting and the cells themselves of Stack A were completely clean, Stack B showed macroscopic carbon deposits at the anode substrate and the nickel mesh. Toward the gas inlet, the nickel meshes of all cells were covered with a dense layer of carbon filaments, which explains the greatly increased pressure drop in the stack. The Crofer plates showed spot-wise discoloration but no carbon deposits. No carbon particles could be found in the gas distribution between adapter plate and Ni mesh, which argues against the possibility that carbon was formed at the junction described above and then carried into the stack with the gas flow to accumulate on the Ni mesh.

Furthermore, the anode substrates of all cells of Stack B showed bright areas which preceded the carbon-covered area. The changed color indicated structural deterioration in the anode support due to metal dusting. This degradation mechanism was observed in previous experiments with phenol as model tar and is triggered by carbon deposits. It mainly affects the cell structure and is not visible in electrochemical data until the active anode layer is attacked or electrical contact quality is significantly decreased. Other authors have also reported on this degradation mechanism occurring during operation of SOFCs with carbon-rich fuel gases.

Detailed analysis of the microstructure of Stack B showed that the substrate was unaltered in areas toward the outlet of the cells. In areas with brighter color, loss of connectivity between Ni and YSZ could be observed. Ni particles were coarsened, whereas the YSZ matrix was still intact. The coarsening can be attributed to incipient metal dusting. The substrate under the deposited carbon was affected by a total loss of connectivity between Ni and YSZ due to metal dusting. The structure of carbon deposits was also analyzed. They consisted of carbon fibers with Ni particles at their tips. Such structures called carbon-whiskers are known in steam reforming catalysis. They are formed when solved carbon diffuses through nickel particles to nucleate at the rear of the crystallite, where the particle is connected to the substrate. By the continuous precipitation of carbon, the particle is lifted from the substrate. The Ni particle is still catalytically active and therefore the whisker keeps growing, whereas the carbon tail takes up more and more space which leads to the observed increase in the pressure drop.

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**Figure 8** State of the lowest cell of both stacks after performed experiments. A, Clean contacting Ni mesh Stack A. B, Clean anode support Stack A. C, Carbon deposits on contacting Ni mesh Stack B. D, Carbon deposits on anode support Stack B
Also the Ni mesh was affected by degradation. Its wires were covered with a dense layer of carbon filaments in a whisker-like form with Ni particles on the tips. Cross-sections revealed distinct detachment of wire material due to metal dusting which is remarkable, given the short operation time with tar-containing gas. This shows that even with cell materials that are tolerant to the presence of tars, like cells with GDC anode, this element of the stack will degrade and lose the electrical contact between anode and interconnector. Alternative current collector materials are therefore necessary and should be considered in future stack concepts.

It can be concluded that Ni catalyzed the formation of carbon deposits whereas the carbon depositions led to degradation of substrate and Ni mesh. The deposits have caused degradation at stack level by blocking the flow channels and leading to increased pressure drop over time. Apparently, this effect was not evenly distributed over the whole stack and was more severe for the bottom cell, where fuel starvation was observed toward the end of coupled operation (see Figure 6) as well as during the final I-V curve (see Figure 7). The slightly lower temperature at the bottom of the stack might inhibit reforming reactions and thus increase the deposition rate. Additionally, the flow path through the bottom cell is the shortest, which could result in higher gas (and tar) volume flows.

Furthermore, stable tars like naphthalene are known to decrease the performance of SOFCs. The hydrocarbons affect the performance of the cells in different ways: Since their reforming is slow, they block the catalytically active centers involved in the reforming of methane; by accumulating in the pores of the support, they also affect the diffusion of fuel to the triple-phase boundaries, thereby increasing concentration polarization; owing to incomplete conversion, they lead to carbon deposition and its consequences. It is assumed that the presence of these stable tars might have caused the voltage degradation rates observed.

4 CONCLUSION AND OUTLOOK

The performed experiments on the one hand successfully demonstrated the coupling of an allothermal biomass steam gasifier with catalytic hot gas cleaning and subsequent electricity generation using anode-supported Ni/YSZ SOFC stacks at 715°C. On the other hand, no constant operation of the SOFC was possible when the tar reformer was bypassed and hydrocarbons were internally reformed in the SOFC. Degradation of the Ni/YSZ anodes was caused by carbon deposition at the inlet of the cells and subsequent metal dusting of the anode substrate structure. Also the nickel meshes for contacting were affected by metal dusting. It can be concluded that, for the given SOFC and stack design, tars and unsaturated hydrocarbons must be removed upstream to guarantee stable operation. One optimization measure would be the replacement of the nickel-based contacting mesh with another material that is not catalyzing carbon deposition.

An increase in differential pressure over the stack was found to be a clear indicator of degradation. This parameter should therefore be monitored closely during operation. The repeated recording of standardized I-V curves proved to be beneficial to relate degradation effects with operational conditions. They also permit evaluation of the condition of the stack, as the bottom cell is deteriorating with each removal from the test rig. The application of electrochemical impedance spectroscopy (EIS) at stack level would be beneficial. Modifications in the catalytic and adsorptive hot gas cleaning must be considered if an operation without the tar reformer is to be pursued for longer time frames. Long-term operation would also be required to quantify the degradation rates of the stacks. Additionally, single-contaminant tests should be continued, in order to find the most affecting molecules and define the gas cleaning requirements. The regeneration of degraded stacks could be investigated in future test campaigns.

In the end, the blocked flow channels were revealed as the critical degradation effect of the tars or unsaturated hydrocarbons. Thus, they made further operation impossible, even though the performance of the cells themselves had not degraded much during the 5 hours of operation with tar-containing bio-syngas.

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ABBREVIATIONS

| Abbreviation | Description |
|--------------|-------------|
| DN           | diameter nominal |
| EIS          | electrochemical impedance spectroscopy |
| FZJ          | Forschungszentrum Jülich |
| GC-FID       | gas chromatography–flame ionization detector |
| GDC          | gadolinium-doped ceria |
| LCC10        | La_{0.45}Mn_{0.55}O_{1.5} |
| LES          | Chair of Energy Systems |
| LOD          | limit of detection |
| LSCF         | La_{0.5}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} |
| MCF          | MnCo_{1.0}Fe_{0.1}O_{4} |
| OCC          | open clamp conditions |
| OCV          | open circuit voltage |
| P&ID         | piping and instrumentation diagram |
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