Introduction

Since the beginning of the 1990s cogeneration of heat and power based on biomass gasification has gained momentum due to enhanced climate change awareness [1]. Decentralized small-scale systems make use of the produced heat and hence permit overall efficiencies up to 90%. In common CHP systems, power is generated by an internal combustion engine. With such a configuration, electrical efficiencies are limited to 25–30%. By substituting the gas engine with a high temperature fuel cell, it is possible to boost the electrical output significantly while maintaining overall efficiency [2, 3].

High temperature fuel cells like the SOFC can utilize most gaseous fuel species found in producer gas of biomass gasification [4, 5]. Even higher hydrocarbons may in principle serve as a direct fuel for the cell due to its catalyzing effect on reforming reactions. Those endothermic reforming reactions can directly benefit from the produced heat in the cell and increase system performance [6]. As a main benefit however, complex and extensive gas cleaning can be omitted and the production of noxious wastes is avoided [7]. The approach to utilize all carbonaceous species of the wood gas is rather new, for a long time, researches treated higher hydrocarbons as contaminants [8–10] to be removed. Nevertheless, the fuel gas must fulfill certain quality demands to inhibit degradation of fuel anodes of solid oxide cells. However, for example, sulfur compounds are clearly poisonous for nickel anodes, the exact effect of higher hydrocarbons and tars, respectively is more complex [7, 11, 12].

Several studies have demonstrated the use of higher unsaturated and aromatic hydrocarbons as fuel for solid oxide fuel cells [13]. In recent years, some key issues and
appropriate operation conditions for higher hydrocarbons have been identified [14]. A major concern regarding the use of hydrocarbons is the formation of solid carbon within the Nickel catalyst structure, which can cause the degradation of the active anode material [15]. The risk for carbon deposition rises with increasing fuel gas content of methane and tars. By adjusting the steam fraction carbon formation can be prevented. More steam is, however, disadvantageous for the performance of the cell as it increases the oxygen partial pressure at the anode [16, 17].

In addition, it has been demonstrated that certain tar components (e.g., naphthalene, C_{x}H_{y}) inhibit the reforming capacity of lighter hydrocarbons such as methane [18]. This leads to a reduction in directly available fuel components (H_{2}, CO) for electrochemical oxidation on the anode material and thus causes an increase in fuel utilization. High fuel utilizations furthermore cause an important risk to local fuel starvation and Nickel oxidation on the fuel cells anode, leading to strong degradation effects and performance drops [18].

In summary, for effective and safe operation of SOFCs with tar-loaded syngas from biomass gasification it is crucial to get a detailed understanding on the behavior of hydrocarbon at typical anodes. Therefore, this work describes an evaluation approach to access hydrocarbon conversion kinetics based on cell voltage measurements. The obtained global kinetics can be used in numerical stack simulations and system designs.

Literature Review of Experimental Investigations of Tar Conversion

Tar species from biomass gasification

Hydrocarbons are inevitable components of the producer gas from decentralized gasification of biomass or coal [19]. Various heavier compounds are summarized as “tars”, with partly differing definitions however. According to Neeft, the term describes “all organic molecules with molecular weights greater than benzene” [20].

Depending on the gasification method, different amounts of tars are expected. Table 1 depicts typical concentrations and the nature of produced tars related to common biomass gasification technologies.

Besides the reactor design, gasification temperature, residence time, gasification agent and, less important, the feedstock are responsible for the nature of the formed tars. The increasing complexity of the tar molecules is the basis for the classification in primary, secondary and tertiary tars. Primary tars are mixed oxygenated pyrolysis products, also called wood oils and wood syrups. Secondary tars are olefins and phenolic compounds. The most complex molecules are polycyclic aromatic hydrocarbons (PAHs), which are called tertiary tars [24]. Air gasification creates tars with low reactivity and low viscosity, whereas steam gasification facilitates liquid tar with low molecule weight. High gasification temperatures, as seen in updraft gasifiers, promote hydrocarbons with low oxygen content, that is PAHs [26].

Figure 1 shows SPA tar measurements from the steam gasification of lignite and wood pellets. The allothermal 100 kW Heatpipe Reformer at the Chair of Energy process engineering (University of Erlangen-Nuremberg) [27] produced a hydrogen-rich gas with total tar loading ranging from 8.5 g/Nm³ (biomass) to 11.8 g/Nm³ (lignite).

Nickel catalyzed tar reforming

Generally, tars can decompose due to reforming reactions, cracking and solid carbon formation. Following overall reactions are important for the conversion of tar species [28, 29]:

Steam reforming:

\[ C_{n}H_{m} + nH_{2}O \rightarrow C_{n'}H_{m'} + \left( n + \frac{m}{2} \right)H_{2} + nCO \]  

(1)

Dry reforming: \[ C_{n}H_{m} + nCO_{2} \rightarrow \left( \frac{m}{2} \right)H_{2} + 2nCO \]  

(2)

Hydro cracking: \[ C_{n}H_{m} + H_{2} \rightarrow C_{n'}H_{m'} \]  

(3)

Table 1. Tar content of different gasifiers.

| Gasification technology | Gasification temperature (°C) | Nature of tars | Tar content in raw producer gas (g/Nm³) | Source |
|-------------------------|-------------------------------|----------------|----------------------------------------|--------|
| Fluidized bed gasifier  | 800–900 750–850              | Secondary and tertiary tars | 10–40                                  | [21, 22] |
| Circulating fluidized bed (CFB) gasifier | Bed: 900–1050 gas exit: 700 | Tertiary tars | 0.015–0.5                              | [24, 25] |
| Downdraft (coflow) gasifier | Bed: 950–1150 gas exit: 150–400 | Mostly primary and some secondary tars | 30–150                                 | [24]    |
Reactions (1–5) depict the various ways how tars may undergo conversion in a hot gas environment. The steam-reforming reaction (1) accounts for both, complete reforming to $\text{H}_2$ and $\text{CO}$ as well as for incomplete dealkylation, where relatively stable light hydrocarbons can persist. Besides in decomposition reactions, the water–gas shift (WGS) reaction (6) plays an important role in adjusting the gas composition and driving selectivity toward specific reforming reactions [29].

As thermal cracking requires very high temperatures (e.g., $>1100^\circ\text{C}$ for naphthalene), reforming catalysts are widely used and investigated. Apart from dolomites, limestones, or ferric oxides, nickel-based catalysts have shown very good reactivity for tar reforming. Several researchers have investigated the decomposition of model tars on various catalysts. An overview is for example given by Devi [28], Aravind [12] or Shen [30].

According to Garcia [31] and Claude [32], the nickel catalyzed reforming of hydrocarbons can be described by the following mechanism, which is illustrated in Figure 2:

1. Hydrocarbons are dissociatively adsorbed on the nickel sites; 2. Steam and carbon dioxide adsorbs on the ceramic support, dissociates and form active species $\text{H}^*$, $\text{HO}^*$ and $\text{O}^*$; 3. Nickel-catalyzed dehydrogenation, thermal cracking, and hydrodealkylation creates adsorbed hydrocarbon-derived fragments $\text{C}_n\text{H}_{m*}$, carbon $\text{C}^*$, and hydrogen $\text{H}^*$; 4. The active species on the support surface migrate to the nickel and eventually react with the activated carbon $\text{C}^*$ and the tar fragments $\text{C}_n\text{H}_{m*}$ to $\text{CO(g)}$ and $\text{H}_2(\text{g})$. Finally, the gaseous molecules desorb from the metallic active sites [31, 32].

At typical SOFC operation conditions, reactions 1–5 are strongly limited by kinetics. The evaluation of a reforming kinetic for just one decomposition phenomena is difficult, as many reactions are simultaneously and consecutively occurring. Therefore, it is common to address kinetics by stating an overall rate of tar disappearance, where all reactions are lumped together (in the overall partial pressure of tars $p_{\text{tar}}$). This apparent tar conversion rate is usually expressed by a simple single first-order kinetic reaction, which can be calculated by assuming isothermal, plug flow behavior [33]:

$$-r_{\text{tar}} = k_{\text{app}} p_{\text{tar}}$$

with

$$k_{\text{app}} = -\ln \left(1-X_{\text{tar}}\right) = k_0,\text{app} \cdot e^{-\frac{E_{\text{app}}}{RT}}$$

Here, $k_{\text{pp}}$ expresses the apparent kinetic rate constants, with $k_0,\text{app}$ the frequency factor and $E_{\text{app}}$ the activation energy of the typical Arrhenius approach.

Due to its simplicity this approach has been widely accepted in catalytic hot gas cleaning research. The pseudo reaction order of $n = 1$ is commonly chosen, but several authors report concerns about the validity of such a simplified kinetic evaluation [33–36]. For the conversion of lighter molecules, for example, benzene and toluene, the first approach might deliver plausible results, but other kinetic models are also investigated [32, 37]. Higher hydrocarbons like naphthalene are more strongly adsorbed on the nickel catalyst. The catalyst active surface is covered by naphthalene and hydrocarbon fragments. Hence, the
reaction rate is proportional to the fraction of the covered surface. In that case, a kinetic approach like the Langmuir–Hinshelwood type can describe the conversion rate of tars [38]:

$$r_{tar} = \frac{k'_{tar} p_{tar}}{1 + k'_{tar} p_{tar}}$$  \hspace{1cm} (8)

Here, $K_{tar}$ accounts for the adsorption and desorption equilibrium. For low tar partial pressures, the reaction order is close to 1 and for high partial pressures the limit is a reaction order of 0.

The described approach to state a rate of tar disappearance is flawed, because the influence of the gas composition is neglected. As seen in reactions 1–6 H$_2$O, CO$_2$, CO and H$_2$ are reactants and their concentration and their adsorption/desorption behavior, respectively, will influence the conversion. In most studies however, it is assumed that if reactants are available in excess, the influence on the conversion rate is limited. Regarding real tar from gasification, it should be further considered that tars are an amalgamation of different species. Some of them will convert more easily than others. In that case a simple “rate of disappearance” might be very limited in its significance. Corella addressed this by proposing two alternative more sophisticated kinetic models [36].

**SOFC tar experiments with model components**

Investigations concerning the tar tolerance of SOFCs came into focus when the integration of gasification and solid oxide fuel cells gained more attention. Most studies of tar operation and conversion focus on individual components like toluene [17, 39–41], benzene [42, 43], and naphthalene [8, 44]. Lorente et al. [39] evaluated carbon deposition from toluene as well as from real tar. The outcome from his studies suggests that substituting real tar with a model component will not be sufficient to get comprehensive results. He focused his work on carbon deposition phenomena, but indicates that tar reforming might be affected in a similar manner. Studies which take only model compounds into consideration should be treated carefully and real tar experiments are necessary for validation purposes [19]. Furthermore, Boldrin et al. [45] stressed the importance of the gas being used in tar experiments. As carbon monoxide and tar components may compete for the same catalytically active sites, it is probably unwise to conclude from hydrogen only operation to syngas operation. Observations from the BioCellus project support the assumption that cross-interaction effects have to be considered carefully. In particular, heavier tars like naphthalene show severe inhibition tendencies for methane reforming [46].

Doyle studied the impact of tars on Ni/GDC anodes at different temperatures and with different steam to carbon ratios. Toluene as a model component was operated at 850°C on low fuel utilization. Up to 20 g/Nm$^3$ was injected without problems in a synthetic syngas mixture (26% H$_2$, 24% CO, 12% CO$_2$, 7% CH$_4$, 25% H$_2$O, balance N$_2$). A small increase in OCV due to toluene was identified (3 mV). Toluene was partly reformed, as it was still measurable at the anode outlet [47]. Mermelstein [42, 43] showed that at SOFC temperatures of 765°C load operation with tar-laden syngas is feasible. He used benzene in concentrations from 2 to 15 g/m$^3$ and did not experience carbon deposition up to 5 g/m$^3$ (15% H$_2$, 10% CO$_2$, 25% CO, 2% CH$_4$, 5% H$_2$O, balance N$_2$).

Synthetic hydrocarbon-syngas mixtures were investigated by Dekker et al. in 2007 [48]. The gas composition was set to 16% CO, 14% CO$_2$, 14% H$_2$, 13% H$_2$O, 4% CH$_4$ and 36% N$_2$. On the hydrocarbon side, 1.4% ethylene, 0.1% acetylene, 0.4% toluene, 525 ppm naphthalene, 126 ppm phenanthrene and 22 ppm pyrene were injected. However, toluene, ethylene, and acetylene contributed to the cells performance, naphthalene and pyrene caused a rapid power loss. The researcher attributed the adverse behavior of those two components to an inhibiting
character regarding other hydrocarbon reforming [48]. Methane contains – even in low concentrations that is 4% – a large proportion of the fuels heating value. In its unreformed state methane is relatively unavailable for the electrochemical conversion and fuel utilization can readily rise into ranges where safe operation of the cell cannot longer sustain [48].

Hauth et al. confirmed the inhibiting properties of naphthalene regarding methane conversion. In his simulated wood gas experiments, cell voltage dropped by 15 mV and H₂ fuel utilization quickly rose after adding 2032 ppm naphthalene. The UI Curves from these experiments are shown in Figure 3 (left). He concluded that adsorption and desorption of naphthalene decreases the reactive surface for methane reforming. However, it remains unclear if a reduced amount of naphthalene occupies less active surface or if it is just a matter of time until active sites are blocked. Papurello concluded from his tar experiments (synthetic biosyngas contaminated with naphthalene up to 10 ppm fed on an Ni-YSZ ASC at 750°C) that not only the inhibition of methane plays a role, but that there is also a strong inhibition for the water–gas shift reaction [49].

Furthermore, Hauth et al. conducted tar experiments with a simplified gas flow of hydrogen and water. Conversion rates of tar species were calculated from inlet and outlet FID measurements. At temperatures of 900°C, toluene and xylene were completely reformed, naphthalene almost. The calculated conversion rate for naphthalene decreased slightly from 100% to 97% with increasing concentration. (483–3606 ppm C₁₀ H₈).

Figure 4 shows the measured voltage increase and the maximal theoretical voltage increase from equilibrium calculations. Hauth concludes that the voltage increases should be identical if naphthalene is consumed almost completely. However, at this point, the author did not take a kinetic limitation of the naphthalene reforming

![Figure 3](image_url)

**Figure 3.** Measured increase of Open Circuit Voltage resulting from almost complete conversion of naphthalene compared to voltage increase from equilibrium calculations (adapted from [4]).

![Figure 4](image_url)

**Figure 4.** (left) Measured CV Curve from tar-free synthetic wood gas (20.8% H₂, 13.3% CO, 13.3% CO₂, 6.3% CH₄, 26.8% H₂O, balance N₂) at 900°C shows higher voltages than the same wood gas containing 2032 ppm naphthalene (adapted from [4]). (right) Below temperatures of 700°C carbon deposition causes a voltage drop of the naphthalene enriched gas (1500 ppm C₁₀H₈ in 36.4 H₂, 3% H₂O, balance N₂) (adapted from [44]).
Conversion of Tars on SOFC Anodes

T. Herrmann et al.

into account. The measured voltage is the averaged voltage across the cell. Thus, the assumption that the perceptible voltage increase equals the increase expected from equilibrium calculations is only valid if the reforming reactions take place instantly. The kinetic limitation is less distinct for the smaller investigated tar molecules. Here, equilibrium conditions are established in a very short period of time – resulting in a voltage increase close to the maximal theoretical possible increase [8, 18].

Similar experiments were conducted by Frank. She investigated the effect of 1500 ppm naphthalene on Nernst voltages depending on different temperatures. The gas stream consisted of H2 (36.4%), H2O (3%) and balance N2. Figure 3 (right) shows the results from her investigations. The graph can be divided into two regions. In the left region below 700°C the measured voltage increase was negative. This indicates that reforming did not take place and moreover the tar component had a negative effect on the voltage. Because of the minor amount of steam, conditions were favorable for solid carbon formation. Postanalysis confirmed carbon deposition for the lower investigated temperatures. Above a certain temperature, however, naphthalene is converted and the measured voltage rose [50].

**SOFC tar experiments with real producer gas**

Hofmann et al. coupled a commercial Ni-GDC anode with a circulating fluidized bed (CFB) wood gasifier. Short-term operation (7 h) with tar-laden producer gas (>10 g/Nm³) was possible without (visible) degradation. The gas had a very high steam content (73%) and fuel utilization was kept low in the range of 20%. It remains unclear to what extent tars were reformed. An increase in the Nernst potential could not be determined, as the tar-free reference gas was not suitable for comparison [51].

Investigations at the TU Graz with a fixed bed down-draft gasifier showed that the operation of an SOFC linked to a fixed bed gasifier is possible. The tar loading was up to 338 mg/Nm³ and did not contribute to further cell degradation. However, it was shown that excessive fuel utilization can be promoted by tar utilization and has to be monitored closely.

Within the BioCellus (Biomass fuel Cell Utility System) project producer gas from an allothermal fluidized bed gasifier (Heat pipe reformer: [27]) was fed to planar and tubular SOFCs (Table 2). The gas contained 3% methane and a tar loading of approx. 3 g/Nm³. The voltage was increased with respect to hydrocarbon addition, yet the

| Tar component | Gas stream | Anode operating conditions | Effect of tars on Nernst voltage and current densities | Source |
|---------------|------------|----------------------------|------------------------------------------------------|--------|
| C6H6 (570–4300 ppm) | Simulated syngas | Ni-CGO @ 765°C J = 300 mA/cm² | Unknown | [43] |
| C6H6 (1530 and 4870 ppm) | Wet simulated syngas | Ni-GDC @ 800°C J = 100 mA/cm² | Increase of Nernst Voltage by 2–6 mV; ASR remains unaffected | [41] |
| C6H6 (1300–3945 ppm) | H2, H2O | Ni-GDC (ESC) @ 800°C J = 0 mA/cm² | Increase of Nernst Voltage by 6.5–15.6 mV | [18] |
| C2H4 (1.4%), C3H6 (0.4%) | Simulated syngas | Ni-CGO (ESC) @ 850°C J = 160 mA/cm² | Increase of Nernst voltage by ~5 mV | [48] |
| C10H8 (50–525 ppm) | Simulated syngas | Ni-CGO (ESC) @ 850°C J = 140 mA/cm² | Severe decrease of Nernst voltage resulting due to an inhibition of CH4 reforming → fuel starvation | [48] |
| C10H8 (1050 ppm) | H2, H2O | Ni-GDC (ESC) @ 850°C J = 140 mA/cm² | Decrease of Nernst voltage <20 mV | [48] |
| C10H8 (1500 ppm) | H2, H2O | Ni-GDC (ESC) @ 650–850°C J = 0 mA/cm² | Decrease of Nernst Voltage because of carbon deposition (T < 700°C) Increase of Nernst Voltage up to 21 mV (T > 800°C) | [50] |
| C10H8 (483–3606 ppm) | H2, H2O | Ni-GDC (ESC) @ 800–900°C J <= 190 mA/cm² FU (H2) < 15% | Increase of Nernst voltage up to 17 mV, ASR remains unaffected | [18] |
| C10H8 (2032 ppm) | Simulated wood gas | Ni-GDC (ESC) @ 900°C J <= 190 mA/cm² FU (H2) < 8% | Decrease of Nernst Voltage by ~15 mV resulting from inhibition of CH4, ASR remains unaffected | [8] |
| Real wood gas tars (>10 g/Nm³) | Wood gas from CFB gasifier | Ni-GDC (ESC) @ 850°C J = 130 mA/cm² FU = 23% | Influence on Nernst voltage unclear, ASR decreases by 10% | [5] |
amount of reformed tar species could not be assessed exactly. Degradation was not promoted either. A 1200-h long-term experiment was conducted at the Paul Scherrer Institute. An updraft gasifier produced a tar-laden gas which was fed into a Siemens SOFC, which was operated at 950°C. The addition of 60% steam ensured a safe operation without the hazard of carbon formation. The resulting S/C ratio of 2 is commonly chosen. With a limited fuel utilization of 30% (60 mA/cm²), degradation remained below 1%/kh [52].

**Effect of current densities on tar conversion**

When a current is drawn from the cell, oxygen ions migrate to the anode and react with hydrogen to steam. The electrochemical produced steam is a reactant in the reforming reaction (eq. 9) and shifts equilibrium conditions to the product side. However, investigations from methane steam reforming suggest that the influence of steam is not straightforward. For high S/C ratios, the reaction order is supposed to be slightly negative, hence the reforming reaction rate could actually decreases with increasing current density. For low S/C ratios, the opposite is seen, steam might increase the reaction rate slightly [53].

The additional oxygen ions can promote the catalytic activity of the anode. With an applied current density of 60–100 mA/cm² on Ni-GDC anodes, Fan et al. reported decreased activation energies for methane steam reforming [54].

The naphthalene experiments from Hauth, however, showed no influence of current density neither on Nernst Voltages nor on FID outlet gas analysis. As seen in Figure 5, the measured voltage increases due to naphthalene reforming do not significantly differ between open circuit voltage (OCV) and load operation. Hauth concludes that the conversion of naphthalene is not affected by current density [18].

**Carbon deposition**

Solid carbon can emerge from different reaction mechanisms and can be stable in different forms. Depending on the surrounding environment, encapsulating polymers, pyrolytic, or fibrous carbon can be formed [15]. Under SOFC conditions, the two latter species are dominant. The deposited carbon blocks pores, has high mechanical strength, and can effectively degrade nickel catalysts [55].

Regarding thermodynamics, it is possible to predict the onset of graphitic carbon formation, as it is the simplest form of solid carbon. However, at the SOFC anode, different growth mechanisms are occurring and especially heterogeneously formed carbon nanofibers (whiskers) are difficult to predict [14]. Thermodynamic considerations suggest that the addition of carbon dioxide as well as the addition of steam will have a beneficiary effect in terms of carbon deposition. Liu et al. demonstrated both under dry and wet conditions that a toluene-laden gas (10 g/Nm³) can be operated without visible degradation in Ni/GDC anodes [41]. Similarly, Mermelstein et al. showed that adding 10% CO₂ to a benzene containing H₂/N₂ stream significantly decreases carbon deposits [43]. The increase in current density is another effective way for the suppression of carbon deposition. Load operation can promote direct oxidation of hydrocarbons and deposited carbon, as local oxygen partial pressure is increased. Another viable possibility to boost the tolerance for carbon deposition can be achieved by raising the operating temperature. However, this is not true for all gas mixtures. For a methane-rich gas, temperature has rather an opposite effect on carbon formation because methane pyrolysis is favored at higher temperatures [15].

Thermodynamic trends can be evaluated with the help of ternary diagrams, but several authors came to the conclusion that this is not necessarily sufficient for correctly predicting carbon deposition. Boldrin et al. experienced carbon formation with toluene, though under comparable pure syngas operation he did not [45]. Kim (2006) evaluated carbon deposition of n-butane, n-decane, and naphta on Ce-YSZ anodes. He conducted his experiments in the thermodynamically safe domain, but this did not prevent carbon formation. Other investigations implied that the amount of carbon formed from benzene and toluene is

![Figure 5. Measured voltage increases due to naphthalene reforming at open circuit conditions and with an applied load of 160 mA/cm² (adapted from [13]).](image-url)
several magnitudes higher than from carbon monoxide [56].

Liu et al. explained those phenomena with differences between the actual conditions at the TPB and those conditions which can be measured. But more important, the equilibrium assumptions might not be justified if higher hydrocarbons are present. The rate of tar deposition most likely exceeds the rate of carbon removal reactions [57, 58].

Even if the estimation of carbon formation from tars is flawed, experiments have shown that tars can be handled in SOFCs.

**Blocking of reforming activity**

For a nickel-based fuel cell, safe operating state is not only characterized by the solid carbon boundary line, but also by the nickel oxide boundary.

Nickel oxide diminishes the performance of the SOFC. It is catalytically inactive and electrical isolating. Moreover, oxidized nickel occupies a larger volume than metallic nickel. This alteration induces mechanical stresses and cracks as the surrounding ceramic structure remains unaffected. At elevated temperatures, subsequent RedOx cycles are irreversible and will ultimately destroy the cell [50, 59].

Reoxidation of Nickel is linked to excessive (local) oxygen partial pressures. High fuel utilization, respectively, high load can produce a gas containing almost exclusively steam and CO₂. Such gas compositions or air leaks from the cathode can be the reason for critical values of \( p(O_2) \).

As the conversion of tars is unknown, fuel utilization is difficult to predict and might exceed safe values. Furthermore, a biomass gasifier will not produce a constant output. Syngas composition and tar content fluctuate and so does the fuel utilization.

**Modeling the Tar Conversion on SOFC Anodes**

**General considerations**

Higher hydrocarbons can follow different reaction pathways. Solid carbon formation, steam reforming, dry reforming, inert behavior, and even direct oxidation are possible reaction mechanisms on SOFC anodes. However, solid carbon formation has to be avoided, reforming reactions can increase the cell’s performance.

The way tars behave depends on the amount and nature of the hydrocarbons as well as heavily on the operating conditions of the SOFC. Temperature, gas composition, moisture, current density, and anodic material are important parameters in this context.

From a thermodynamical point of view, it is possible to assess whether safe SOFC operation is possible for a given gas mixture. Aside from obvious contaminants (i.e., sulfur) carbonaceous and oxygen-rich components are problematic, as they promote the emergence of solid carbon and/or nickel oxide. In Figure 6, a C-H-O ternary diagram illustrates the issue. Ternary diagrams constitute a possibility for an intuitive illustration of several different processes, that is, SNG production or fuel cell operation [60]. A producer gas composition from wood gasification was added to give an example how the ternary diagram can be used to predict safe operation domains. The black dot represents the gas from a 100 kW Heatpipe reformer, operated at an excess steam ratio of 3, gasification pressure ranging from 1.3 to 4 bar, and gasification temperatures from 800 to 830°C [21]. In this gasification case, the risk for solid carbon formation rises, if the temperature decreases and if hydrocarbons are added to the gas. The small unfilled dot directly above the original gas composition depicts the addition of 0.5% naphthalene to the gas. The gas composition moves toward the tar area, which is composed of different tar species (black diamonds). Steam, carbon dioxide, and applying a load reduces this risk, but increases simultaneously the risk for nickel oxidation [5, 61].

**Tar-induced voltage increase**

In a hot gas environment, the conditions at the nickel anode facilitate the conversion of hydrocarbons. Various parallel and consecutive reactions are taking place and are decomposing tar molecules. The addition of a tar component to a gas stream results in an instantaneous increase in measured cell voltage of an Ni-based SOFC [8, 18, 50]. Theoretically, hydrocarbons can directly electro-oxidize in a single-step reaction [14]. However, the nickel anode acts also as a strong catalyst for reforming and decomposition reactions (See Chapter 2.2). The products of the reactions (1–6) are the electrochemical active species H₂, CO, C*, and \( C_{\text{m}}^{\text{n}} \). The electro-oxidation of H₂ is assumed to be the most rapid electrochemical reaction [14], but the voltage increase could also be the result of different electrochemical reactions, for example, direct oxidation of hydrocarbon fragments. Hence, it is not possible to deduce a specific decomposition kinetic from a voltage increase. Instead, the measurable voltage increase can be regarded as a macroscopic evidence for the conversion of tars to electrochemical species. In this work, it is assumed, that if the decomposition of tars occurs, all products of this process contribute to the cell’s electrochemical potential. This assumption is supported by the comparison of modeled anode outlet tar concentrations and actual FID measurements from Hauth [18] (See Results).
For a hydrocarbon $j$, the effluent concentration can be used to calculate a total observable conversion $X_j$:

$$X_j = \frac{n_{c_{H_m}, in}}{n_{c_{H_m}, in}} - \frac{n_{c_{H_m}, out}}{n_{c_{H_m}, in}}$$

(9)

This conversion yield is linked to the increase in the cell voltage. However, it is often neglected that the measured cell voltage differs from the (local) Nernst voltages. As the fuel flows across the cell, the gas mixture changes and hence the local driving force in terms of the Nernst voltage. Even if no current is applied the gas composition may vary across the cell. This is especially true if nickel catalyzed-reforming reactions are taking place along the cell. The produced electrochemical species will increase the Nernst voltage and thus to some degree the cell voltage. The correlation between those two voltages is modeled by a kinetic approach. The kinetics is necessary to develop the evolution of tar species along the cell. The resulting local tar conversion is then used to model the increase in local Nernst Voltage.

The local potential may additionally be influenced by temperature deviations. A lower operating temperature leads to an increased electromotive force. Since reforming reactions are endothermic, a possible increase in Nernst potential has to be considered.

**Modeling the kinetics of hydrocarbon decomposition on SOFC anodes**

Operation temperatures of 800–900°C enable the catalytic conversion of hydrocarbons at the SOFC anode. The nickel catalyst is crucial, as thermal cracking does not occur below temperatures of 1100°C [62]. Nickel catalyzed re-forming on SOFC anodes is a complex mechanism. SOFC anodes are a porous cermet, consisting of Nickel and Yttria-stabilized zirconia (YSZ). Nickel acts as catalyst and electronic conductor, whereas YSZ is the conductor for the oxygen ions. Hydrogen adsorbs on the surface of either Nickel or YSZ and diffuses to the triple phase boundary (TPB), where it reacts under the release of two electrons with the oxygen ion. For state-of-the-art anode supported cells (ASC) this electrochemical reaction is taking place in an active area close to the electrolyte. Reforming reactions are instead occurring anywhere on the anode, where Nickel is present. This includes the current collector, which is commonly a Nickel mesh.
Even within anode supported cells, geometry and composition (i.e., active layer thickness, pore size, pore distribution, Nickel content) can vary significantly. Hence, important properties for the evaluation of global reaction kinetics like gas diffusion or available active catalyst area may deviate for different anodes. However, the establishment of macroscopic kinetics is still reasonable because it can be done very conveniently in a technical-relevant setting.

The molar change in a hydrocarbon, in consequence of the decomposition reactions can be expressed according to equation (7). The rate is an equation of tar concentration and temperature. The most applied way to describe global reaction kinetics is the Arrhenius power law. It can be modeled as follows:

$$ r = k_0 e^{\frac{-\Delta H}{R_T}} \cdot P_{C_{H_m}} $$

(10)

The degree of concentration dependency is fitted by the exponent $\alpha$ of the partial pressure.

The exponent $\alpha = 1$ was chosen in reference to the nickel catalyzed tar reforming (See Chapter 2.2) and the well investigated methane reforming on Nickel anodes [63, 64]. Hence, the rate equation for tar reforming may be expressed in such way:

$$ r = k \cdot P_{C_{H_m}} = k_0 e^{\frac{-\Delta H}{R_T}} \cdot P_{C_{H_m}} $$

(11)

$k_0$ is the frequency factor, $E_A$ the activation energy and $R$ the universal gas constant.

To establish the global rate constant $k$, a model and measurements are necessary. For the analysis performed in this work, a simple 1-D discretization of the anode with steady-state plug flow conditions is assumed. Additionally, time and gas velocity, respectively, are modeled as constant. This is justified for small tar concentrations, where the volume increase in gaseous species due to reforming reactions can be neglected. In the model, a local Nernst potential can be calculated for every control volume (CV), which results from the equilibrium conditions at the volume inlet and from the increase in the electrochemical species due to ongoing tar reforming. Local temperature may deviate, for example, due to endothermic reforming, and this influences the Nernst voltage. Regarding moderate tar amounts, local temperature will vary only by very few Kelvins. A thermodynamic calculation suggests that for 3600 ppm naphthalene diluted in $H_2$ and $H_2O$, a temperature decrease of five Kelvin results only in a voltage increase of about 1.5 mV. Hence, local temperature deviations are not considered in the model. Equilibrium conditions for the calculation of the Nernst potential are based on the minimization of Gibbs energy. The equilibrium is first evaluated without tars and subsequently with full tar loading. For example, the Nernst voltage at 900°C without tars for a wet $H_2/N_2$ mixture (23.3% $H_2$, 19.5% $H_2O$, balance N2) is computed as 0.9176 V, whereas the voltage of the same gas mixture with 12.5 g/Nm³ Naphthalene is 0.9430 V. This Nernst voltage increase of 25.4 mV is the maximum increase, for the case that Naphthalene enters the cell completely converted.

However, this theoretical voltage increase does not correspond to the measured cell voltage, since conversion is not instantaneous.

Figure 7 clarifies the difference between local Nernst Voltage and cell voltage. The constant line is based on the experiments from Hauth [18]. This voltage is constant, as the cell is contacted through one continuous current collector mesh and ohmic losses therein are neglected. The Nernst Voltage is driven by the concentration difference of the electrochemical reactants between anode and cathode. In the presence of tars, the concentration difference of electrochemical reactants is increasing as more fuel from reforming reactions becomes available. In the figure, it is also shown that the absolute voltage is increased for lower temperatures, whereas the reforming is faster for higher temperatures. The implemented model uses 40 control volumes with constant area, derived from a 100 cm² square cell.

At OCV conditions, overall cell current is 0. Therefore, cell areas with fuel cell operation, that is, cell voltage below local Nernst voltage, and areas with electrolysis operation, that is, cell voltage above local Nernst voltage, balance to 0. Assuming a constant linear cell behavior represented by an area-specific resistance (ASR) this leads to the following:

$$ i_{cell} = \int \text{ASR} (V_{cell} - V_N (x)) \, dx = 0 $$

(12)

In consequence, for equally sized control volumes i and constant ASR (isothermal), cell voltage results as the arithmetic average of local Nernst voltages.

$$ V_{cell} = \frac{1}{m} \sum_{i=1}^{m} V_{Nernst,i} $$

(13)

With

$$ V_{Nernst,i} = V_{Nernst,0} + \frac{\sum_i c_{i}}{n_{i}} \cdot (V_{Nernst,\infty} - V_{Nernst,0}) $$

(14)

$V_{Nernst,0}$ is the Nernst voltage at the anode inlet, calculated from the tar-free equilibrium conditions. $V_{Nernst, \infty}$ is the Nernst voltage from tar-laden equilibrium calculations. The locally converted tar $r_i$ is modeled by first-order
kinetics (See eq. 11) and linearly contributes to the local increase in Nernst voltage according to equation (14).

Finally, the rate \( r \) can be iteratively calculated from measured and calculated voltage increases:

\[
r = f \left( \frac{\Delta V_{\text{measured}}}{\Delta V_{\text{equilibrium}}} \right)
\]

(15)

**Results and Discussions**

The naphthalene measurements from Hauth (see Chapter 2.2) were reevaluated with the described kinetic model. The temperature-dependent decomposition rate constant \( k \) was computed for two temperatures. It can be obtained from the OCV measurements based on a least square approach:

\[
\min_k \sum (\Delta V_{\text{measured}} - \Delta V_{\text{modeled}})^2
\]

(16)

Table 3 shows the resulting conversion rate constants for exemplary OCV measurement data. The rate constants vary with the investigated tar species (naphthalene, toluene) and the operation temperature (800–900°C) in the range 0.1–1.04 mol/sec/m²/bar.

For both regarded temperatures the rate constant of toluene is approximately three times higher than the rate constant of naphthalene. The results showed good consistency within varying tar concentration levels. The standard deviation of the calculated rate constants at the concentration regime was small, except for naphthalene at 900°C, indicating that the chosen modeling approach seems to be appropriate. It must be kept in mind that only few measuring points were available for evaluation.

With the modeled kinetic constants, the effluent tar concentrations were assessed. Table 4 compares the modeled effluent concentrations and the FID measured concentrations from Hauth's investigations [18].

Even if only three measurements could be evaluated, the model seems to describe the decomposition behavior very good.

The proposed kinetic investigation method is easy applicable. It uses the potential difference as sensor and delivers rate constants without the need for extensive gas analysis. However, the outcome should be treated with some caution. As suggested in Chapter 2.2, the first-order Arrhenius approach for hydrocarbons may not be the best fit. Furthermore, the extent of the influence of the gas components \( \text{H}_2, \text{H}_2\text{O}, \text{CO}_2, \) and \( \text{CO} \) is unclear. For the methane conversion, Dicks et al. [65] reported a significant influence of the hydrogen partial pressure, whereas Nguyen observed doubled activation energies, if CO is present in the gas stream. As the adsorption energy of carbon monoxide on Nickel is larger than the adsorption energies of steam and methane, the conversion rate is inhibited [53].

In conclusion, the transferability of the derived constants may not be given in a broad application range. Therefore,

| Table 3. Apparent kinetic rate constants \( k \) as calculated by the model based on experiments from Hauth [18]. |
|---------------------------------|-----------------|-----------------|-----------------|
| Tar component                  | Gas stream      | Anode operating | Rate constant \( k \) [mol/sec/m²/bar] |
| C\(_7\)H\(_8\) (2600–4000 ppm) | \( \text{H}_2 \) (23%), \( \text{H}_2\text{O} \) (20%) | Ni-GDC (ESC)    | 0.34 ± 0.02     |
| C\(_{10}\)H\(_8\) (1113–3606 ppm) | \( \text{H}_2 \) (23%), \( \text{H}_2\text{O} \) (20%) | Ni-GDC (ESC)    | 0.11 ± 0.00     |

| Table 4. Measured and calculated outlet tar concentrations. |
|---------------------------------|-----------------|-----------------|-----------------|
| \( \text{C}_{12}\text{H}_8 \) inlet concentration [ppm] | 1000 | 2000 | 3000 |
| \( \text{C}_{12}\text{H}_8 \) outlet concentration (FID measurement) [ppm] [18] | 3   | 27  | 99  |
| \( \text{C}_{12}\text{H}_8 \) outlet concentration (modeled) [ppm] | 2   | 27  | 95  |
larger experimental campaigns are required and it should always be stated in which setting the constants are evaluated.

Conclusions

Possible benefits from using tars in SOFCs are the performance increase due to the additional fuel and the simplified upstream gas cleaning. On the other hand, tars might cause deterioration regarding the operation of the cell. The two major threads for nickel-based SOFCs operated on tar-laden gas are the oxidation of nickel due to fuel starvation and the formation of solid carbon. In order to avoid these hazards, this paper describes an investigation and modeling approach that focuses tar conversion kinetics on SOFC anodes. It permits the determination of the apparent kinetic rate constants based on simple OCV measurements. The approach was applied to measurement data from literature. Resulting conversion rate constants varied with the investigated tar species (naphthalene, toluene) and the operation temperature (800–900°C) in the range 0.1–1.04 mol/sec/m²/bar. They showed good consistency within varying tar concentration levels and with FID measurement in the off gas of the SOFC anodes. For a broader applicability, the proposed methodology should be applied to a larger range of tar species and anode compositions.

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Conflict of Interest

None declared.

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Conversion of Tars on SOFC Anodes

T. Herrmann et al.

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