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Biomass Gasifier–SOFC Systems: From Electrode Studies to the Development of Integrated Systems and New Applications

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An overview of the research activities and on-going multiple projects at Delft University of Technology aimed at the development of Gasifier–Solid Oxide Fuel Cell (SOFC) based power plants are presented. Biosyngas generated in gasifiers consists of a mixture of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), hydrogen (H_2), nitrogen (N_2), water vapor (H_2O), and minor impurities. Biosyngas can be a good fuel for SOFCs provided that the gas is sufficiently cleaned. Influence of biosyngas compositions and biomass-derived contaminants on SOFCs is presented and the removal of potential contaminants such as tar, particulates, H_2S, HCl, and alkali compounds from biosyngas is discussed. It appears that the gasification product gas can be cleaned to meet the requirements of SOFCs using currently known gas cleaning methods. Additionally, a brief discussion on the achievable system efficiencies with gasifier–SOFC systems is presented. Innovative applications of the gasifier-SOFC systems being developed at Delft, such as advanced gasifier–SOFC systems for toilet development, are also presented.

Introduction

Importance of biomass as a sustainable primary energy source is widely acknowledged. Solid oxide fuel cell–gas turbine systems (SOFC–GT systems) operating on fuels such as hydrogen and methane are expected to have electrical efficiencies of the order of 60–80%. Gasification offers a technology for converting solid biomass into a gaseous fuel known as biosyngas. The main components in the biosyngas such as hydrogen, carbon monoxide, and methane are fuels for both SOFCs and gas turbines. However, the contaminants in biosyngas such as particulates, tar, H_2S, HCl and others are widely suggested to be detrimental to the smooth operation of SOFCs and gas turbines. If the gas can be cleaned to have the contaminant levels low enough for both SOFCs and gas turbines, this introduces an excellent opportunity for generating electricity using SOFC–GT systems at high efficiencies.

Extensive studies are required for developing such systems operating at high efficiencies. As the topics being studied spread over a wide range of subjects, this becomes a multi-disciplinary research activity. The results from such studies are expected to lead to the development of clearer concepts for achieving high efficiencies with gasifier–SOFC–GT systems, employing system components which are expected to be technically and economically viable in the future. This paper reviews the multi-disciplinary research activities being taken up at Delft University of Technology (TU Delft) to evaluate the technical feasibility of biomass gasifier–SOFC–GT systems.

The research work presented in this paper can be broadly divided into two categories, i.e., 1) Electrochemical and fluid dynamic studies with synthetic and real gas mixtures at electrode and cell level, and 2) Studies on issues related to system integration such as gas cleaning, thermodynamic system modeling and integrated experiments in which SOFCs are connected to real gasifiers.

Preliminary evaluations have indicated that SOFCs with nickel/gadolinia doped ceria (Ni/GDC) anodes potentially have advantages over conventional nickel/yttria stabilized zirconia (Ni/YSZ) anodes due to the fact that ceria is a fine catalyst for carbonaceous fuels. For that reason most of the studies presented here are focused on SOFCs with Ni/GDC anodes. However, a limited number of studies have also been conducted using SOFCs with Ni/YSZ anodes. A detailed literature review carried out focusing on the influence of biomass-derived contaminants on SOFCs also revealed that the Ni/GDC anodes most likely have better contaminant tolerance when compared to Ni/YSZ anodes (1). However, detailed experimental studies are still required to confirm this.

Electrochemical Studies with Synthetic Gas Mixtures

Electrochemical Impedance Spectroscopy (EIS) for studying fuel oxidation on SOFCs with Ni/GDC anodes was presented by TU Delft jointly with the SOFC group at the Energy Research Center of the Netherlands (ECN). Symmetrical test cells under single gas atmosphere were employed for the experiments. Theoretical understanding of the impedance spectra recorded on Ni/GDC anodes was developed (2, 3). A model for DC diffusion resistance (gas phase) was developed and the results from model calculations were validated using experimental results. Impedance due to gas phase processes was separated from processes at the surface or in the bulk of the anode. The knowledge thus generated was used for planning the experiments for studying the influence of biomass-derived contaminants on Ni/GDC anodes. Experimentally observed anodic impedances with various biosyngas compositions were comparable with the impedance obtained with humidified hydrogen. The impedance measurements were carried out on Ni/GDC anodes with three contaminants, namely H_2S, HCl, and naphthalene, at 1123 and 1023 K and the results are presented in (4). Chemical equilibrium calculations were carried out to analyze the possible interactions between these contaminants and anode materials (5). The results obtained from the experiments and chemical equilibrium calculations indicated that, at the levels at which the contaminants were added (H_2S and HCl up to 9 ppm and naphthalene at 110 ppm), these contaminants had no significant impact on the anodic performance. It is also observed that tars might get reformed at SOFC anodes.

The electrochemical performance of planar SOFC cell with Ni/GDC anode with synthetic biosyngas compositions was assessed by TU Delft and ECN jointly (6). I–V and electrochemical impedance measurements were carried out. At 80% fuel utilization, stable electrochemical performance was obtained, with a power density of 2600 W/m^2 at 1123 K, and 3000 W/m^2 at 1193 K. Sulfur deactivated the Ni/GDC anode for methane reforming significantly, but not for the oxidation of hydrogen and carbon monoxide up to

9 ppm H_2S. The cell resistance (excluding gas phase resistance) amounted to 0.6 $ohm{\cdot}cm^2$ at 1123 K and 0.3 $ohm{\cdot}cm^2$ at 1193 K. At low AC frequencies, an additional polarization arc was seen in the impedance spectra, which has been attributed to gas phase processes.

Jointly with Imperial College London, the influence of operating conditions including steam levels, current density and exposure time on the performance of SOFCs with Ni/YSZ anodes fuelled by tar-containing biosyngas was studied in a different set of experiments (7). The biosyngas composition and the tar concentration used in these measurements were identical to those measured from a commercial air-blown biomass gasifier that is to be connected to an SOFC system. Operating this type of SOFC under the tar concentrations used in this work could result in severe damage of the cell due to carbon formation on the anodes. Carbon deposition was observed by Scanning Electron Microscopy (SEM) and affected the performance of the SOFC, as shown by the impedance spectra and anode polarization curves of the cells after exposure to tars. However, the risk of carbon deposition can be reduced by increasing steam levels and current loads.

An experimental study on the effects of tar on the performance of SOFCs with Ni/GDC anodes carried out at TU Delft is also reported (8). Various operating temperature levels (973, 1073 and 1173 K) under both dry and wet conditions were employed in this study. Polarization behavior, electrochemical impedance spectroscopy, and cell voltage degradation were analyzed to evaluate the cell performance. It is most likely that the cells with Ni/GDC anodes did not suffer from carbon deposition under the wet conditions studied. Dry tar-containing syngas for SOFCs is unlikely to cause carbon formation under a mild current load; however, it may induce carbon formation at open circuit. The effect of carbon dioxide that is capable of suppressing carbon deposition was experimentally investigated, and an enhanced performance was observed under the conditions studied. Under carbon risk-free operating conditions, the cell voltage increases when raising the feeding tar concentration, indicating that tar performs as fuel for SOFCs.

Biosyngas from Delft CFBG was used for feeding electrolyte supported SOFCs with Ni/GDC anodes (9). Biosyngas was cleaned using a medium temperature gas cleaning system developed by TU Graz before feeding to SOFCs. Experiments of several hours of duration were carried out with clean tar free biosyngas (after tar reforming) as well as with tar rich biosyngas (tar reformer bypassed). The tar load in the gas with no tar reforming was few thousand mg/Nm^3. No significant degradation in the SOFC performance was observed during this operation period.

In addition to the experimental and theoretical studies, we have carried out an extensive review of the available literature on the influence of biomass-derived contaminants on SOFCs. An analysis of high temperature gas cleaning systems for cleaning biosyngas for fueling SOFCs is presented in Ref. (1). It appears that the gasification product gas can be cleaned to meet the requirements of SOFCs based on Ni/GDC anodes at high temperatures (typically in the range of 1023–1223 K) by using currently known gas cleaning methods. Although information from literature, results from chemical equilibrium studies and preliminary experiments were sufficient to put forward a conceptual design for a high temperature gas cleaning system, it is observed that detailed experimental investigations are still required. This is needed to obtain detailed information on contaminant tolerance of SOFCs, and to arrive at detailed designs of gas cleaning units that are economically viable for biomass gasifier–SOFC systems.

Detailed literature review of the CFD modeling of SOFCs can be found in the previous papers from our group(10-13). CFD calculations have been employed to study the performance of SOFCs with different gas compositions including biosyngas. Calculations were carried out to evaluate the safety of SOFC operation considering carbon deposition and nickel oxidation. The biosyngas fueled cells show reasonable performance when compared with the hydrogen-fueled cells. It also shows that the methane steam reforming kinetics has an influence on the performance even with a small amount of methane in the biosyngas. The simulation results can be useful for planning useful future SOFC experiments. As the anode materials and microstructure influence the reaction kinetics, the CFD studies also can lead to the development of new materials and structures to enhance the performance of SOFC when operating with biosyngas.

Gas Cleaning System Development

A Low Temperature Gas Cleaning System

Experimental and theoretical studies and the detailed review carried out on the influence of biomass-derived contaminants on SOFCs provided the required information for developing gas cleaning units for gasifier–SOFC integration. Gas cleaning at lower temperatures is more mature when compared to high temperature gas cleaning devices. However, in gasifier–SOFC systems, high temperature gas cleaning assists increasing the system efficiencies as the sensible heat is often lost when the gas is cooled down from gasifier exit temperatures.

A relatively low temperature gas cleaning system (Figure 1) is jointly developed by TU Delft and Federal University of Itajuba, Brazil (14) for cleaning the biosyngas from a two stage downdraft air blown gasifier for fuelling SOFCs primarily with Ni/GDC anodes, and then with Ni/YSZ anodes (5 kW CHP unit from Fuel Cell Technologies).

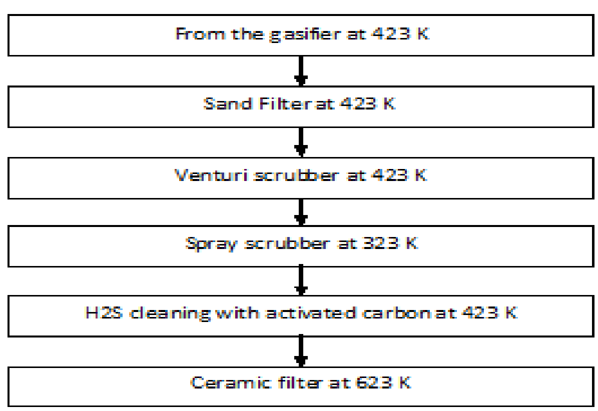

Figure 1. Flow scheme for the tested low temperature gas-cleaning system.

Experiments with selected trace species have been carried out with the gas cleaning system designed and the results are summarized in Table I. Table I shows that the gas cleaning system is able to achieve a removal efficiency of 95% for tar, 96% for particulates, 91% for H_2S, and 68% for HCl.

TABLE I. Results from the Operation of Low Temperature Gas Cleaning Unit

Impuritie	**Unit**	**Befor**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Max(%**
Tar	mg/Nm^3	321.9	22.5	64.5	14.9	49.2	31.9	30.4	26.5	12.5	95
Particulate		178.5	24.4	37.4	15.1	17.0	10.8	6.0	13.5	16.9	96
H_2S		37.8	6.5	11.6	5.8	10.2	8.9	3.6	2.9	6.2	91
HCl		318.9	136	–	102.6	169.5	138.3	167.7	116.6	134.8	68

<u>High Temperature Gas Cleaning Systems</u>

In addition to the relatively lower temperature gas cleaning system mentioned above, two higher temperature gas cleaning systems were also developed based on the research activities involving TU Delft. High temperature gas cleaning systems are expected to help obtain energy-efficient systems. The flow schemes of the two higher temperature gas cleaning systems are shown in Figure 2 and Figure 3, and they have been briefly tested during the Biocellus project.

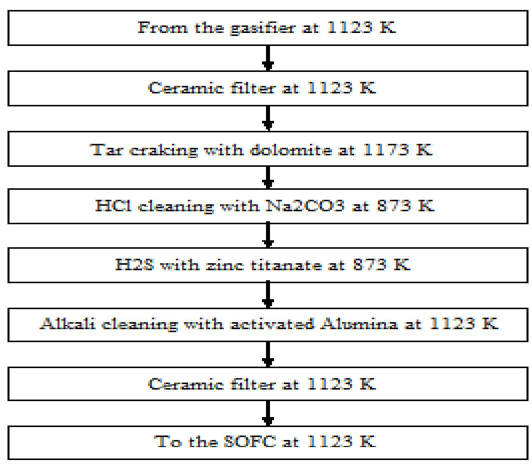

Figure 2. Flow scheme for the high temperature gas-cleaning system.

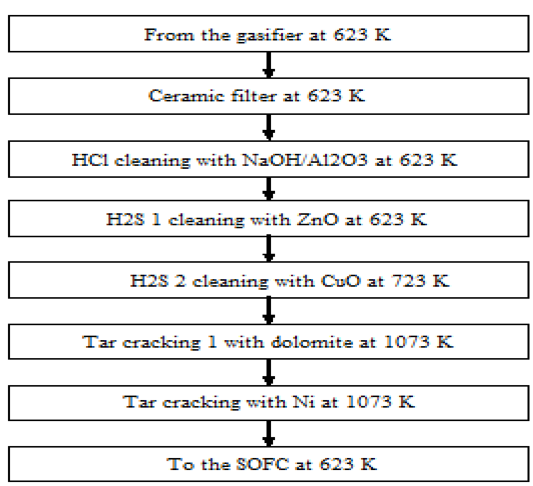

Figure 3. Flow scheme for the intermediate temperature gas-cleaning system.

Details of the high temperature gas cleaning unit are given elsewhere (1). The intermediate temperature gas cleaning unit constructed by TU Delft was based on the design of the one from TU Graz; however, TU Delft design could deliver higher flow rates which are convenient for fuel cell stacks. Details of this system are also available elsewhere (15).

Apart from the gasifier–SOFC single cell experiments mentioned before, TU Delft has involved in several other gasifier–SOFC system integration activities. This involves working with different types of gasifiers, gas cleaning systems and SOFC stacks.

As a part of the Biocellus project (15), an SOFC stack was connected to the biomass gasifier at TU Munich with TU Delft providing the gas cleaning unit and involving in the integrated experiments. The intermediate temperature gas cleaning unit mentioned above was employed. A planar stack, able to produce 1 kW power output, was constructed by Prototech for the same. A short tubular stack constructed by TU Munich was tested in parallel, as well as single planar fuel cells with improved anode configurations. The test-rigs were installed at the Biomass Heat Pipe Reformer from TU Munich. It was possible to deliver real wood gas to all the test-rigs. The planar stack was operated for approximately 7 hours on wood gas and had a very stable performance. The average power output was 300 W, the maximum power output reached while increasing the wood gas flow to the stack was 700 W.

A biomass gasifier–SOFC system is being integrated in Itajuba, Brazil as mentioned before. The system is based on a fixed bed biomass gasifier and a 5 kW SOFC CHP unit from Fuel Cell Technologies (16). The SOFC stack in the system was from Siemens Westinghouse. Apart from the development of the gas cleaning unit, modifying the SOFC unit for biosyngas operation offered significant challenges. A particularly challenging problem was the management of the flows through the system. The recirculation of electrode off-gas, particularly of anode off-gas to a pre-reformer for methane steam reforming, is employed in many SOFC systems that operate with natural gas. This recirculation simplifies the overall system configuration because the electrochemically produced steam together with the heat in the anode off-gas can be used through this process for methane steam reforming. When adopting biosyngas to the existing SOFC system which deploys ejector-driven recirculation for steam reforming, detailed studies indicated that the recirculation is not a necessity for the biosyngas (17) . It is found that the performance was improved when not implementing the recirculation (17). The net electrical efficiency increased from 14% to 36% when the recirculation is avoided. The integrated system is expected to be tested in the near future

TU Delft has been selected to participate in the 'Reinvent The Toilet Challenge' (RTTC) funded by the Bill and Melinda Gates Foundation. Aim is to develop tools and technologies that can lead to radical and sustainable improvements in sanitation in the developing world. To serve this purpose, the system should operate as a stand-alone unit i.e. it will not be connected to any existing sewerage nor should it rely on external electricity supply. The system is built on a new microwave-assisted plasma gasification unit being developed by the process intensification team at the Process and Energy Department of TU Delft for processing the fecal matter and electric power required for operating the microwave-assisted plasma gasification unit. A TU Delft team is designing and building a demonstration toilet system which employs a 3.8 kW SOFC stack with Ni/GDC anodes for electricity generation fuelled with syngas produced via a microwave plasma discharge. Due to high gasification temperatures, this gasification technique allows fast processing of large quantities of biomass, with low emissions and waste streams whilst ensuring effective pathogen removal. In addition, it is expected that the tar load of the syngas produced will be low. However, in addition to typical biomass impurities such as alkalis and sulphur compounds as mentioned earlier, also other contaminants such as phosphorous compounds and heavy metals e.g. Cu, Pb, and Cd are present (18, 19). Up till now, the effects of such compounds on SOFC performance are scarcely available. Therefore, TUD plans to carry out experimental evaluations on such contamination at electrode, fuel cell and stack levels, utilizing both simulated and real syngas from fecal matter and sewage sludge. The integrated toilet–gasifier–SOFC system will be demonstrated in the spring of 2014.

System Thermodynamics

In addition to the electrochemical and fluid flow studies, gas cleaning and system integration efforts, TU Delft fuel cell systems team is involved in extensive system calculations of gasifier–SOFC based power plants. Such system calculations are done mainly for two different purposes; one is to support our system integration efforts and the other is to envisage futuristic high efficiency power plants. The system calculations done for supporting the Itajuba and the toilet projects represent the former and the system calculations being done for gasifier–SOFC–GT systems represent the latter.

In one set of calculations, thermodynamic calculations were carried out to evaluate the performance of small-scale gasifier–SOFC–GT systems of the order of 100 kW. SOFCs with Ni/GDC anodes being considered for the system. It is observed that high system electrical efficiencies above 50% are achievable with these systems. The results obtained indicate that when gas cleaning is carried out at temperatures lower than gasification temperature, additional steam need to be added to biosyngas in order to avoid carbon deposition. It is also observed that steam addition does not have significant impact on system electrical efficiency. However, generation of additional steam using heat from gas turbine outlet decreases the thermal energy and exergy available at the system outlet, thereby decreasing total system efficiency. With the gas cleaning at atmospheric temperature, there is a decrease in the electrical efficiency of the order of 4–5% when compared to the efficiency of the systems working with intermediate to high gas-cleaning temperatures (20). However at such small power levels even with low temperature gas cleaning, such systems offer significant efficiency advantages when compared to competing systems such as gasifier–micro turbine systems and gasifier–IC engine systems.

In another effort, four different systems based on integrated gasifier–SOFC–GT systems were modelled to study the influence of the gasification technology, gas cleaning technology and system scale on the overall system performance (21). The different gasification technologies evaluated were the atmospheric indirect steam gasification and pressurized direct air gasification. The gas cleaning technologies evaluated are low temperature gas cleaning and high temperature gas cleaning and the two scales are 100 kWe and 30 MWe. The results show that the large scale system based on pressurized direct air gasification and high temperature gas cleaning has the highest electrical exergy efficiency of 49.9%. Large scale systems have a higher efficiency than small scale systems, due to larger exergy losses in smaller systems mainly in the balance of plant components.

Yet another system model is developed for application of wet biomass in energy conversion systems. Drying can be very energy intensive especially when the biomass has moisture content above 50 wt.% on a wet basis (22). The combination of hydrothermal biomass gasification and SOFC–GT units could be an efficient way to convert very wet biomass into electricity. It is noted that such integrated systems have electrical exergy efficiencies around 50%, therefore, the combination of supercritical water gasification and SOFC–GT hybrid systems seems promising.

A concept for very highly efficient systems has recently been developed at Delft. Integration of the allothermal gasification process and the exothermal fuel cell done by deploying heat pipes can result in a higher system performance (23), which utilize vaporizing liquid in order to create high heat fluxes from any heat source, in this case the SOFC, to a heat user, in this case the gasifier, where the endothermic gasification reactions take place. We propose a construction using SOFCs in series with the heat pipes placed in between for intercooling. Instead of one SOFC as in Ref. (20) we now use two SOFCs. The heat is transferred to the heat pipes from first SOFC outlet pipes and after the combustion chamber. Hot product gases (1000°C) are cooled down to about 900°C before they enter the second fuel cell. The heat is transferred by the heat pipes to the gasifier. Heat pipes are also proposed to carry a part of the heat from the combustion products to the gasifier. Such systems have shown electrical efficiencies close to 70% using solid biomass as fuel.

The system calculations clearly indicate the potential with gasifier–SOFC–GT systems for electricity production from solid fuels with extremely high efficiencies. High efficiencies can be achieved at smaller power levels of few hundred kW or with large centralized power plants. This opens up a wide range of opportunities for SOFC developers and power plant builders.

Conclusions

The following important observations were made during the course of our research efforts on gasifier–SOFC systems: 1) Electrochemical measurements indicated the SOFCs can work with clean biosyngas as fuel; 2) Cleaning biosyngas to the levels required for SOFCs especially the ones with Ni/GDC anodes is most likely achievable with currently known gas cleaning systems; and 3) System efficiencies of the order of 50–70% are achievable with gasifier–SOFC–GT systems. However, construction of commercially viable power plants based on these concepts requires further research and development of the technologies involved including the fuel cells and gas cleaning systems.

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