Gasified residual/waste biomass as solid oxide fuel cell feed for renewable electricity production

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Abstract

Gasification of waste biomass, a renewable feedstock, is considered as a sustainable technology for producing environmentally friendly feed (biosyngas) for fuel cells. This work examines the contaminants contents (i.e. sulphur and halogens) of typical waste biomass sources and evaluates their nuisance to Solid Oxide Fuel Cells (SOFC) performance for the two most considered types of anodes: metal-ceramic composites (cermets) and composite oxides. The necessity and the extent of physico-chemical purification of the bio-syngas and its cost depend upon the chemical stability of the anode material. These needs as well as their associated costs are evaluated and a first assessment of the sustainability of such solutions is undertaken and commented.

Keywords: waste, biomass, gasification, sulphur, halogens, SOFC, syngas, gas purification, anode, cermet, composite oxide ceramics.

1 Introduction

As world energy consumption increases (currently $\approx 2\%$ per annum [1]), the analysis [2] of energy scenarios concluded that it is possible to address simultaneously various sustainable development objectives, using available resources and technical options. The foreseen solutions are based on some combination of better exploitation of renewable resources, higher energy conversion efficiencies, and advanced energy conversion technologies. The latter includes the development of a variety of fuel cells, now widely identified [2] as a long term solution for higher than conventional energy conversion to electricity,
co-generation (combined heat and power or CHP), motive power and transport. Some important characteristics of the studied fuel cell technologies are presented in Table 1.

The high operating temperatures of molten carbonate (MCFC) and solid oxide fuel cells (SOFC) make them well suited for co-generation [4]. Moreover, SOFC technology offers considerably higher CHP efficiencies, potentially longer operating lifetimes [5], safer operation due to the absence of a molten solid phase and lower capital and operational costs than MCFC.

The typical «sandwich» type SOFC assemblies are composed of three, functionally distinct, layers (anode – electrolyte – cathode) where the anode is designed for electrochemical oxidation of the fuel associated with the charge transfer to a conducting contact. The most critical characteristics of materials considered as potential candidates for SOFC anodes are: electronic conductivity; oxygen diffusivity (ionic conductivity); oxygen surface exchange (reactivity); chemical stability and compatibility; thermal expansion; mechanical strength and dimensional stability under redox cycling.

The particular advantage of the SOFC concept over all other types of fuel cells, is its ability to operate with a variety of fuels, both gaseous – such as methane, biogas, biosyngas, and liquids – such as gasoline, jet fuel, diesel fuels and oxygenates, e.g. methanol, ethanol (and bio-ethanol) and “green diesel”. However such a variety of fuels with their inherent contaminants make more stringent the requirements of anode’s chemical stability and compatibility.

This capacity of solid oxide fuel cells to work with fuels originating from renewable resources like biomass is of particular interest.

Table 1: Comparison of fuel cell technologies [3].

<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Operating Temperature [°C]</th>
<th>System Output [kW]</th>
<th>Electrical Efficiency [%]</th>
<th>CHP Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Electrolyte Membrane (PEM)</td>
<td>50 – 100</td>
<td>&lt; 1 – 250</td>
<td>53 – 58 (transportation) 25-35 (stationary)</td>
<td>70 – 90 (low grade waste heat)</td>
</tr>
<tr>
<td>Alkaline (AFC)</td>
<td>90 – 100</td>
<td>10 – 100</td>
<td>60</td>
<td>&lt; 80 (low grade waste heat)</td>
</tr>
<tr>
<td>Phosphoric Acid (PAFC)</td>
<td>150 – 200</td>
<td>50 – 1000</td>
<td>&gt; 40</td>
<td>&lt; 85</td>
</tr>
<tr>
<td>Molten Carbonate (MCFC)</td>
<td>600 – 700</td>
<td>&lt; 1 – 1000</td>
<td>45-47</td>
<td>&lt; 80</td>
</tr>
<tr>
<td>Solid Oxide (SOFC)</td>
<td>600 – 1000</td>
<td>&lt; 1 – 3000</td>
<td>35-43</td>
<td>&lt; 90</td>
</tr>
</tbody>
</table>
The aim of this work is to detail the constraints imposed in order to render compatible the use of syngas originating from residual and waste biomass gasification with the SOFC anodes.

2 Residual biomass availability

While renewable, so called “Green Power”, resources (hydro, wind, solar thermal and photovoltaic, geothermal, marine and biomass) are geographically more evenly distributed than fossil and nuclear resources, and energy flows from renewable resources are several thousand times higher than current total global energy use, the statistics [2] indicate that only 13.7% of worldwide primary energy use comes from renewable resources. The observed [6] most recent increase of global trade of woody biomass, primarily for energy, from 5.6 million tons in 2003 to over 11 million tons in 2007, witnesses the interest in such source of green energy. The economic potential of renewable sources is affected by many constrains including competing land use, the amount and timing of solar irradiation and wind patterns, as well as some other environmental factors. The land use is to be given priority for both human and animal feeding and, in most cases where the soil allows it, even the residuals from crop and forest harvesting are preferably to be left to replenish land’s nutrients [7]. However it is proposed [6] to periodically harvest for long-lived wood products which results in substantially greater carbon storage than when forests are left in an unmanaged state. The US Energy Information Administration, which forecasts US energy production, considers four components to the biomass supply schedule: agricultural residues, energy crops, forestry residues and urban wood waste/mill residues. The analysis [8] of their price and availability reveals that the less costly (1.42 $/GJ) is almost exclusively post-consumer urban wood waste/mill residue. Next (at 1.90 $/GJ and higher) come the agricultural residues followed by energy crops and forestry residues (at 2.18 $/GJ or higher). Such results confirmed similar projections obtained earlier [9].

The post consumer urban wood waste/mill residues include:
- wood materials (like slabs, edgings, trimmings, sawdust, veneer clippings and cores, and pulp screening) and bark generated at primary (lumber) manufacturing plant;
- similar wood scraps and sawdust from woodworking shops, furniture factories, wood container and pallet mills;
- wood residues from Municipal Solid Waste (wood chips and pallets), utility tree trimmings and construction and demolition sites.

At the European market [10] the post consumer wood is classified as:
- A - quality wood: clean wood;
- B - quality wood: slightly contaminated, e.g. with paints, glues and coatings;
- C - quality wood: hazardous wood waste contaminated with heavy metals, fire retardants and wood preservatives.
The analysis [11] of markets for recovered wood in Europe indicates, that in Germany only in year 2003 up to 6,531 million tonnes of post consumer wood were available for the price of 20-30 euro/ton air dry of A – quality wood and 7-17 euro/ton air dry for B – quality wood.

Such variety of wood residue feedstock is usually mechanically homogenized and converted into commercially available product - wood pellets.

3 Wood pellets as a fuel

Wood pellets as heating fuel originated in the US during the 1970s in response to high energy prices [12] but became recently a significant form of biomass consumption for energetic purposes with world market trades exceeding 3 000 000 tonnes per year [13]. Quite thorough analyses of global wood pellets markets and industry including policy drivers, market status and raw materials have been published recently [14]. Sweden, Canada and USA are world leading pellets producers with an annual production capacity exceeding 3 500 000 tonnes [14].

The production of wood pellets is based on several mechanical operations of milling interlaced with drying. This sequence is ending up with pressing through a mould with simultaneous plasticizing (due to lignin and resin content) of the wood. The latter operation may require some additives (like starch) for sawdust originating from hardwood (less rich in lignin) feedstock for preservation of the final shape of the pellet.

The chemical elemental composition of such biomass-derived fuels depends upon the biomass type [15], the origin of the residue and its pre-processing prior to its final destination (use). The fuel components, once consumed, will all end up transformed preferably to element’s oxides either in the gaseous (i.e. CO₂) or in solid form (ashes) and will be released to environment. While carbon dioxide and water are neutral, the release of all other compounds to the environment is regulated by norms; namely by standardization of the biomass fuels initial composition. Table 2 presents the acceptable limits of sulphur and chlorine, both

Table 2: Tolerated limits of sulphur and chlorine according to prevailing worldwide legislation.

<table>
<thead>
<tr>
<th></th>
<th>Sulphur</th>
<th>Chlorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austrian ÖNORME M7135</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood pellets:</td>
<td>≤ 0,04%*</td>
<td>≤ 0,02%</td>
</tr>
<tr>
<td>Bark pellets:</td>
<td>≤ 0,08%*</td>
<td>≤ 0,04%</td>
</tr>
<tr>
<td>German DIN51731 / DIN plus</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Group 1:</td>
<td>≤ 0,08%</td>
<td>≤ 0,03%</td>
</tr>
<tr>
<td>Group 2:</td>
<td>≤ 0,08%</td>
<td>≤ 0,03%</td>
</tr>
<tr>
<td>Group 3:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Swedish SS 187120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Group 1:</td>
<td>≤ 0,08%</td>
<td>≤ 0,03%</td>
</tr>
<tr>
<td>Group 2:</td>
<td>≤ 0,08%</td>
<td>≤ 0,03%</td>
</tr>
<tr>
<td>CEN (draft)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEN/TS 14961: 2005 Annex A</td>
<td>≤ 0,05%</td>
<td>**</td>
</tr>
</tbody>
</table>

* Dry basis;
** Recommended to be stated in category: Cl 0,03 ; Cl 0,07 ; Cl 0,10 ; Cl 0,10+ (if Cl > 0,10% the actual value to be stated)
elements being considered as hindering the long term operation of SOFC devices.

The comparison of the sulphur limits, as imposed by different legislations, with residual sulphur contents in a variety of clean (pristine – without any man-made additives) biomass [16] indicates, that pure bark pellets, as well as many herbaceous fuels, could not be accepted – their residual sulphur content being above the imposed limits.

The combustion of contaminated (B - quality) wood pellets for heating purposes bears some environmental consequences like increase of particulate emissions [17] beyond the current EU emission limit for dust as well as formation of dioxins [18].

4 Wood pellets from Canadian sources and their life cycle analysis

Canada has substantial Green Power resources and the natural potential to generate about half of its current electricity needs (~590 TWh) using Green Power [19]. While current installed, biomass based technologies, count for 1 935 MW (just above 1% of its total generation capacity) percentage substantial rise might be expected when co-generation technologies will be used [19].

The Canadian wood pellet industry is predominantly located in 3 provinces: British Columbia (33% of production), Quebec (28% of production) and Ontario (20% of production) [20]. Its production capacity, as well as different market sales, are presented in Fig. 1.

The origins of the raw materials for wood pellets production are the following:

![Figure 1: Evolution of Canadian wood pellet industry and different markets](image-url)
Saw mills; where harvested wood (pine, Douglas fir, spruce, birch and Western Red Cedar) is converted into lumber (construction wood) and remaining saw dust, bark and other residues like shavings, standing for about 15% [3] of the total volume of the harvested wood, are transformed into pellets.

Standing dead wood either after a forest fire or as a result of infestation (e.g. infestation of pine forest by Mountain Pine Beetle). Both reasons are making remaining wood unsuitable for usual application in timber or paper industries. Such raw material (whole tree trunk) requires more energy to convert it into the shavings size needed by pellet industry.

Such sources might be extended significantly by harvesting forest thinning, which are considered not only unnecessary to replenish forest nutrients but also the main reason for rapid spreading of forest fires. According to Canadian Forest Service [22] between 2,5 to 3 million hectares of forests are lost to about 10 000 forest fires every year.

Canada is the world’s most prominent exporter of wood pellets and its main partner is Europe. Such long haul transport, means an energy consumption (mainly fossil) estimated [23] at 2,40 $/GJ for a 35000 ton vessel travelling a distance of 18000 km [24]. Moreover, it represents a high environmental nuisance because of the Green-House-effect Gases (GHG) generated during the overseas transport [25]. The life-cycle assessments of Canadian wood pellets exported from province of British Columbia (Prince George) to Sweden (port of Stockholm) are presented in Table 3.

Table 3: Energy consumed for each stage of the wood pellet production and transport (adapted from [26]).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Process stage</th>
<th>Production</th>
<th>Harvesting of lumber</th>
<th>Transport*</th>
<th>Sawdust as fuel</th>
<th>Natural Gas as fuel</th>
<th>Transport by train (750 km)</th>
<th>Transport by ocean vessel (1500 km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy consumed [GJ/ton]</td>
<td>0,52</td>
<td>0,07</td>
<td>3,78</td>
<td>2,97</td>
<td>0,26</td>
<td>2,60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy consumed if sawdust as fuel [%]</td>
<td>7</td>
<td>1</td>
<td>52</td>
<td>-</td>
<td>4</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy consumed if Natural Gas as fuel [%]</td>
<td>8</td>
<td>1</td>
<td>-</td>
<td>46</td>
<td>4</td>
<td>40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The analysis of above data suggests, that while half of the energy is consumed for actual pellets production, their post-production transport requires between 40 and 44% of total energy.
Gasified biomass as a feed for SOFC devices

Gasification appears to be the dominant biomass conversion technology. The gaseous products (syngas or biosyngas) from gasification processes are considered as vectors of high-efficiency power production or of the synthesis of chemicals and fuels. Each application requires specific syngas composition and the existing gasification technologies offer this possibility because this composition depends upon the gasification process, the gasification agent (air, oxygen, oxygen-enriched air and their mixtures with steam) and the processing temperature. Generally [27], for gasification processes carried-out at high temperatures (above 1200°C) the biomass is completely converted into CO and H₂ (besides H₂O and CO₂) with an absence of tars which makes this technology interesting for a variety of chemical synthesis routes leading to high-end products. For processing temperatures between 800-1000°C the as-produced gas composition is characterized by a larger variety of chemical species including (besides CO₂ and H₂O) CO, H₂, CH₄, aliphatic hydrocarbons, benzene, toluene, and heavier compounds under the generic name “tars”. A thorough review on tar is available in the literature [28]. The energy contained in typical syngas components (CO, H₂) stands for about 50% of the total, the remaining 50% being carried by CH₄ and higher (aliphatic and aromatic) hydrocarbons making such gas useful for power generation purposes or for production of synthetic natural gas (SNG) [27]. Such as-obtained gas requires important post-gasification treatment like thermal cracking or reforming to match the quality of the gas produced during gasification at higher temperatures.

Among the variety of gasification technologies classified as direct (auto-thermal) and indirect (or allo-thermal) processes the latter group is of particular interest as it offers nitrogen-free product gas as no oxygen is required for the gasification as well as carbon-free ashes. Another advantage of this technology is the possibility of operating it at smaller scale (less then 5 MWth) making it interesting candidate for distributed generation devices where the produced gas is fed into solid oxide fuel cells unit. During the analysis of such an option it is important, among others, to compare the produced gas composition with that required by SOFC unit. The composition of the gas produced from wood by three different indirect gasification technologies is presented in Table 4.

An analysis of the gas composition reveals that all combustibles contained in the produced gas are “consumable” at typical, Ni-based cermet type SOFC’s anode:

- Both hydrogen and carbon monoxide are desired SOFC fuels;
- Methane, C₂⁺ hydrocarbons and benzene are being reformed to CO and H₂ at high temperature over such anodes with catalytic reforming activity in the presence of steam originating from hydrogen consumption over anode’s surface;
- Ammonia is considered [29–31] as very interesting SOFC fuel;
- Carbon deposition over anode’s surface due to tar presence may be avoided under specific current density [32];
Solid particles are filtered [33] from the gaseous fuel prior to SOFC unit.

The only component of biomass gasification product, which is undesired, is the hydrogen sulphide. At very low concentrations of 0.05; 0.5 and 2 ppm, tested at 1023, 1173 and 1273 K respectively, the anode activity losses are reported [34] to be reversible once the fuel no longer contains H₂S. At temperatures below 1073 K the sulphur poisoning was found [35] to be irreversible. The cell voltage drop increases significantly with H₂S concentration in the fuel from 1 to 3 ppm and saturates at 5 ppm [36]. The reforming of methane on catalytically active sites is affected [37] as well.

Table 4: Typical gas composition of three indirect gasification processes [27].

<table>
<thead>
<tr>
<th>Gas component, dry basis</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Hydrogen H₂ [vol%]</td>
<td>30 – 45</td>
</tr>
<tr>
<td>Carbon monoxide CO [vol%]</td>
<td>20 – 30</td>
</tr>
<tr>
<td>Carbon dioxide CO₂ [vol%]</td>
<td>15 – 25</td>
</tr>
<tr>
<td>Methane CH₄ [vol%]</td>
<td>8 – 12</td>
</tr>
<tr>
<td>C₂⁺ hydrocarbons [vol%]</td>
<td>1 – 3</td>
</tr>
<tr>
<td>Benzene C₆H₆ [vol%]</td>
<td>1</td>
</tr>
<tr>
<td>Nitrogen N₂ [vol%]</td>
<td>1 – 3</td>
</tr>
<tr>
<td>Ammonia NH₃ [ppmV]</td>
<td>500 – 1000</td>
</tr>
<tr>
<td>Hydrogen sulphide H₂S [ppmV]</td>
<td>50 – 120</td>
</tr>
<tr>
<td>Tar [g/m³]</td>
<td>0.5 – 1.5</td>
</tr>
<tr>
<td>Particles [g/m³]</td>
<td>10 – 20</td>
</tr>
</tbody>
</table>

1 – Fast Internal Circulation Fluidised Bed (FCIB) process;  
2 – SilvaGas process;  
3 – MILENA process

To prevent such decrease in Nickel cermet based SOFC performances the removal of sulphur bearing compounds from the feed gas to acceptable level is required. A recent thorough review on H₂S removal technologies is available in the literature [38]. Although this review covers the biogas purification most of the reviewed technologies can be used as well in the case of the syngases. The extrapolation of the permissible sulphur concentration in the natural gas feed, considering a deactivation rate of Ni-based planar SOFC of 0.75% per 1000 h (6.4% per year) has indicated the value of 18 ppb [35]. Such “deep” cleaning is very difficult to reach; only zinc-based sorbents operating at 673-823 K are reported [39] to be effective in removing of H₂S to 1 ppm levels at elevated temperatures but not high enough to match typical operating temperatures of gasifier/SOFC tandem. The known deep gas cleaning technologies offers the possibility to lower the residual sulphur content but with excessive cost making such operation much less profitable from the economic stand point. The reported [40] cost of fuel processing module (sulphur removal unit, catalyst, fuel preheater and ejector) accounts for 33% of the total (without stack) balance of power (BOP) investment for 5 kW unit for building applications. The model for
250 kW planar SOFC unit for CHP application specifies [41] the cost of fuel system as 8% where the stack counts for 31% of total cost.

It is clear that high sensitivity of Ni-cermet based anodes to sulphur bearing compounds inherently present even in pristine biomass makes the gas conditioning circuit more complex and increase overall investment and operational costs of BOP. The possible Nickel-free, sulphur-tolerant replacement for SOFC anode materials like fluorite, rutile, tungsten bronze, pyrochlore, perovskite and spinel structures were identified [42] and reviewed [43–45]. The direct oxidation of methane [46, 47] or diesel fuel [48] over substituted perovskites anodes are reported as well. The all-perovskite (anode, electrolyte and cathode) SOFC may be of particular interest due to structural similarity of layers. Such fuel cell [49], based on the “sandwich” of the \((\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}\) (LSCM) as the anode, \(\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_{3-\delta}\) (LSGMCo) as the electrolyte and \(\text{Gd}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}\) (GSC) as the cathode, can minimize the polarization losses between electrolyte and electrodes, where the slight inter-diffusion between the perovskite components observed results in better contact at the interface, allowing for smoother transfer of oxygen ions between the electrodes and electrolyte.

However the actual performances of composite oxide anodes do not match these obtained for Ni-based cermet anodes. More research efforts have to be carried out for optimization of both their composition and performances. For such complex structures the application of the combinatorial chemistry approach in their synthesis is of particular interest.

Another concern for more widespread SOFC usage is the cost of their fabrication. The thermal plasma spraying, which is industrially proven and widely accepted technology, offers both rapid prototyping through combinatorial chemistry method as well as less-costly industrial mass-production allowing integrated deposition of all subsequent layers (anode, electrolyte and cathode) in one operation.

6 Conclusion

The possibility of the significant increase of biomass energy conversion efficiency for SOFC based Combined Heat and Power generation cycle is of special interest especially for colder climate regions like northern Canada.

The export of Canadian biomass as far as to Europe makes overall energy balance (energy contained in biomass vs. energy consumed for its transport) less favourable – up to 40% of energy is lost to transport.

The gasification process, compared to simple combustion or incineration, offers a better control of the release to environment of undesired conversion products, like manmade impurities contained in lesser quality wood’s residues, while still allowing for the full usage of their energy content.

The direct gasification of as-obtained biomass (without drying, size reduction and pelletizing stages) may preserve both energy spent for pellets formation and that contained in the volatiles (mainly terpenes) usually lost [50] during drying process.
The sulphur content represents a technological challenge for the gas conditioning technologies because Nickel-based SOFCs are ultra sensitive to sulphur bearing compounds. Consequently, the cleaning is usually complex and costly.

The SOFC based on composite oxide anodes are sulphur tolerant and are considered as a replacement to Ni cermet anodes; however their actual electrochemical performances are still inferior to the Nickel based ones.

The variety of the possible structures of composite oxides (perovskite-related like titanates, chromites, vanadates, gallates, niobates and ferrites; cubic fluorite related like zirconia-based and ceria-based as well as pyrochlores and spinels) makes combinatorial chemistry useful promising tool towards optimizing SOFC anode’s elemental composition and structure.

The thermal plasma deposition technology allows for rapid SOFC prototyping using combinatorial chemistry approach as well as further industrial mass production of entire multi-layered fuel cells.

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