

ENCIT-2018-XXXX REVIEW ON MARKET TRENDS AND SYNGAS USABILITY IN FUEL CELLS

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Abstract. *The ever-growing demand for energy and the current need for alternative ways to generate electricity has led to the implementation of new technologies in the present scenario. In this context, fuel cells have risen as both efficient and clean technology for energy generation. Although it is desired to use pure hydrogen as fuel for fuel cells, it is difficult to obtain hydrogen in its purest form. An alternative is found in gasification and syngas product. The present work aims to review latest research on gasification gas product, or syngas, quality, and understand what contaminants would affect the fuel cell performance addressing the its requirements when running using syngas. It is shown that coal and biomass feedstocks can be very attractive for hydrogen production, showing a growing trend for applications for renewable energy generation. Finally, it is crucial to invest in research and development to make possible to use syngas affordably and efficiently, improving fuel cell performance and the sustainability of the processes involved.*

Keywords: *coal gasification, biomass gasification, syngas, fuel cells, market trends.*

1. INTRODUCTION

The integration of the fuel cells as a promising technology in the renewable energy market is extremely important to assure reliability and efficiency at very low emission. This new scenario has shown gradual growth in the last years, specially in Europe, North America and Asia, as for example applications in heat and power generation, more commonly known as CHP systems, such as the 1.4 MW FuelCell Energy system installed at the UC Irvine medical center in California and the backup power system at the Verizon's Garden city, providing reliable, clean and efficient energy. A huge effort has been made in transport and vehicle applications as well, represented by great names such GM, Honda and Nissan (Wilberforce, et al, 2016).

The necessity for a cleaner and more efficient way to produce energy is very well suited by the fuel cell technology, for both portable and stationary applications. Despite all the significant features, such as, reliability, low carbon emissions, and efficiency, there is still quite to do regarding to materials and energy storage for hydrogen. Added to these challenges, the cost and competitiveness are essentially a responsibility not only for the market but also for the research field, in order to make the technology more attractive in the near future (Wilberforce, et al, 2016).

Even though facing technological and scientific challenges, great advantage regarding to fuel cell technology relies on its flexibility to use other fuels such as methanol, ethanol, natural gas, biodiesel, carbon monoxide, ammonia

and syngas for example, rather than pure hydrogen, which can be difficult to obtain and store. In those cases, the fuel is processed through reformation to obtain a good fraction of hydrogen. However, fuel poisoning is a big challenge when using reformed fuel. Usually high operating temperature fuel cells can deal easily with poison constituents, such as carbon monoxide and sulfur, providing fuel flexibility (NFCRC, 2017). Solid Oxide Fuel Cell and Molten Carbonate Fuel Cell systems, for example, can run on hydrogen, simple, and simple alcohols, and even carbon monoxide. Proton Exchange Membrane Fuel Cell systems also operate at high temperatures and are very flexible, but they usually run on liquid fuels. Some fuel cells employ electrodes, catalysts and electrolytes which are very susceptible. Platinum catalyst in Phosphoric Acid Fuel Cell systems, for instance, cannot tolerate the presence of carbon monoxide, seemingly the anode regarding to sulfur poisoning. Another fuel cell type that requires only pure hydrogen is Alkaline Fuel Cell (O'Hayre et al, 2016).

1.1 Principles and perspectives

As we make our transition to a cleaner and more reliable energy solution based on renewable sources, hydrogen plays an important role, already seen as an energy carrier. Additionally, hydrogen is finding its applications in several sectors and it is deemed to create a significant impact in the energy sector, especially important for power and heat generation using fuel cells, as previously discussed. Unfortunately, hydrogen is almost rare on earth, which makes things a little harder, which bring the need to create and improve our ways to build this cleaner path. That is where gasification processes come to play. Gasification of carbonaceous, hydrogen-containing fuels is an effective method of thermal hydrogen production and is a key technology in the transition to a hydrogen economy (Parthasarathy, P. and Narayanan, K.S, 2014).

As stated by Minchaner (2015), gasification consists to convert fossil fuels, biomass and wastes into either a combustible gas or a synthesis gas for subsequent utilization, offering the potential both for clean power and chemicals production. In this transformation process, coal, natural gas, refinery residues, and biomass/wastes are usually included as feedstocks (Minchener, 2005). The most common gasifiers implemented on these processes are the entrained flow gasifiers, fluidized bed gasifiers, and moving bed gasifiers. Entrained flow gasifiers are commonly applied for coal gasification, where the pulverized coal particles and gases flow concurrently at high speed. In fluidized bed gasifiers the coal feed particles are mixed with the particles undergoing gasification. Finally, in moving bed gasifiers, the gases flow relatively slowly upward through the bed of coal feed. Considering biomass gasification technologies, the steam gasification is considered one of the most effective and efficient techniques of generating hydrogen from biomass. The vital process parameters that influence the yield of hydrogen generated in steam gasification would include the biomass types and properties, the biomass feed particle size, temperature, steam to biomass ratio, addition of catalysts, sorbent to biomass ratio. Steam critical water gasification and fast pyrolysis followed by steam reforming of char or char and bio-oil mixture, are other processing options for biomass to hydrogen conversion. (Parthasarathy, P. and Narayanan, K.S, 2014).

Many examples and industry applications have shown already that gasification-based systems can be the most efficient and environmentally friendly technologies to produce low-cost electricity, offering the opportunity to develop unique combinations of advanced technologies that offer low cost, reliable, and highly efficient options for meeting a whole host of market applications (Stiegel, G. and Ramezan, M. 2006). Therefore, when considering gasification, it is crucial to keep track of important variables affecting their competitiveness, such suitability and availability of the feedstock, efficiency of the catalysis, scale of production, required hydrogen purity, and economics of feedstock production. Even though these technological approaches to obtain hydrogen provide a more economical path towards alternative processes, they need to be economical, environmentally friendly, and competitive (Luque, R. and Speight, J. 2015).

2. GASIFICATION AND SYNGAS

One of the many products of gasification is the syngas or synthesis gas, which is a combustible gas mixture that typically contains carbon monoxide, hydrogen, nitrogen, carbon dioxide, and methane. The process for producing syngas involves three individual components: first, the synthesis gas generation, followed by the waste heat recovery, and finally the gas processing. The synthesis gas generated has a relatively low calorific value, ranging from 100 to 300 Btu/ft³ (Luque, R. and Speight, J. 2015).

Depending on the gasification technology employed, significant quantities of water, carbon monoxide, and methane can be present in the synthesis gas as well as several minor and trace components (Stiegel, G. and Ramezan, M. 2006). This information is very important, once it determines the applicability to different fuel cell applications, based on their sensitiveness to these components.

When considering biomass for gasification, important factors should be considered. The inherent composition of the feedstock, particle size, temperature, and steam to biomass ratio have great influence on the yield of hydrogen. Decrease in particle size increases hydrogen yield providing larger surface areas facilitating faster heat and gasification

rates. Reduction in particle size also increases dry syngas yield and carbon conversion efficiency. Another parameter that influences considerably the yield of hydrogen is the temperature. An increase in temperature increases the efficiency of gasification reactions, promoting further gas yield. Steam to biomass ratio similarly to temperature strongly affects on both product gas composition and energy input. (Parthasarathy, P. and Narayanan, K.S, 2014).

The main impurities present in the biomass gasification product gas such as particulate matter, tar, sulfur compounds, HCl, alkali metal species and ammonia can affect considerably the performance of fuel cells. High purity can be achieved by selecting proper gasification process and operational parameters, a considerable downstream syngas cleaning is essential to meet fuel cell equipment requirements to function properly (Aravind et al, 2012).

Coal has shown great potential for gasification. Similarly, to biomass syngas, coal syngas product requires further purification so it can properly be used in fuel cells without any risks to affect the performance and equipment. Some impurities observed in the coal syngas exiting the gasification process include As, Be, Cl, Cd, Cr, Hg, Na, K, P, Pb, Sb, Se, V, and Zn. Many studies have been conducted in high temperature fuel cells such as SOFC systems, specifically. Those studies consider physical effects of impurity species on the fuel cell parts, leading to deterioration, affecting their reliability and efficiency and increasing operation and maintenance costs.

As hydrogen technologies make a way to cleaner solutions in energy it is crucial to make the path clear, promoting research and development to increase the quality and efficiency of hydrogen produced through gasification keeping the process affordable in the long way run. Among the overall benefits to adopting gasification as part of fuel cell system, is the transformation of the negative-value feedstocks into valuable products as substitute of natural gas, electricity, fuels, chemicals, and fertilizers, producing high-value products while it helps facilities offset their capital and operating costs. Similarly, gasification helps decrease company's dependence on expensive imported natural gas by using its domestic resources to produce needed products and power. Finally, gasification requires less emission control equipment, since they generate fewer emissions, further reducing a plant's operating costs (GSTC, 2017).

3. DISCUSSION: FUEL CELLS AND SYNGAS

Coal and biomass are the main fuels with potential to be used in the gasification process to obtain good quality of syngas, considering other constraints such as costs, complexity and overall efficiency. However, a very effective cleaning process is still necessary to yield even higher purity syngas product. This is due to fuel cell requirements, in which components as anode and electrolytes can be greatly affected by poisoning of the syngas components. High temperature fuel cells, MCFC, PAFC, and SOFC are the fuel cells more adequate technically and economically to be used in combination to syngas. This can be justified since these systems have fuel flexibility allowing broader possibilities for fuels, including syngas from both coal and biomass. The high operating temperature of those fuel cells allow internal reforming, some even allow impurities, not being poised or affecting its components at all. This capability of internal reforming to directly generate power without any intermediate steps can cut further costs, making it financially feasible, without many technical efforts to adapt its components as well (Aravind et al, 2008; GSTC, 2017).

As market makes place for low temperature fuel cells it grows the need of improving the level of cleanup of the syngas after reformed, yielding high-hydrogen gas product for specific requirements in downstream processes. Since low temperature fuel cells require high purity hydrogen stream, cleaning would include the removal of particulate matter, sulfur compounds, chlorine compounds, nitrogen compounds, unreacted hydrocarbons, and heavy metals. The presence of such contaminants can plug up reactors, cause corrosion, poison downstream catalysts, or prevent the plant from complying with environmental permits. SOFCs systems allow higher fuel flexibility among other high temperature technologies already mentioned, such as, PEMFC, PAFC and MCFC. This characteristic makes SOFCs often to be considered relatively tolerant to several fuel gas impurities, improving usability and reliability for syngas uses in fuel cells (GSTC, 2017).

When considering syngas from biomass, we must keep in mind that particulate matter is always present in the raw biomass and the size of the particles may be a big deal in downstream processes. What can impact the concentration and particle size then? Lots of variables involved, including the concentration of the ash in the product gas, which is dependent on the reactor design, gasifier operating parameters, mineral content of the biomass feedstock, and the temperature ranges involved. In SOFC systems for instance, the particle sizes match well with the pore sizes of SOFC anodes. This can potentially block the micro pores of the anodes and negatively affect the SOFC performance at SOFC operation temperatures. Studies about the influence of the particles in SOFC performance is scarcely available in detail in the literature. It is, therefore, not clear beforehand how such particles can influence the cell performance (Aravind et al, 2008).

Addressing this matter, Aravind et al (2008) studied the impact of contaminants present in biomass syngas on the performance of SOFC anode. They found out that usually contaminants such as H₂S, HCl, and naphthalene would not impact expressively the Ni/GDC anode performance, even considering low levels of contaminants in syngas after cleaning with viable gas-cleaning technologies. The authors suggested a long-term evaluation of these contaminants on the performance. If similar results found for short term persist then there is the great possibility for

implementation of sustainable and efficient plants integrating fuel cells and gasification at the same site (Aravind et al, 2008).

Similar research was conducted by Cayana et al (2008), studying the poisoning effects of impurity in coal syngas on the SOFC performance. Experiments were performed in order to measure the degree of degradation in the presence of contaminants in the Ni-YSZ anode, affecting both catalytic activity of Ni and the mass transport by clogging pores inside the anode. Results have shown that the presence of Hg, Si, Zn and NH₃ in the coal syngas does not strongly affect the performance of the SOFCs. Cd and Se lead to the deterioration of SOFC anodes to some extent. Cl, As, Sb and P species cause severe degradation of SOFC anodes. The performance decrease due to the presence of H₂S is usually attributed to physical adsorption of H₂S at the surface of the Ni-YSZ anode thereby reducing the effective region for electrochemical reactions. The effect of trace impurity species on the performance of SOFC anodes must be measured so it can be possible to determine the required level for removal of these species from coal syngas before reaching the anode and to develop new anode materials that resist the attack of these undesired poisoning effects (Cayana et al, 2008).

Therefore, it is important study ways to make this clean path reality, with more efficient and affordable technologies for gasification and cleaning processes. Reducing contaminants prior to reformation for proper application in fuel cells meeting its requirements may be succeeded through a hot temperature clean-up process for tar removing. This well-established process technology may impact the capital cost of investment, which is an important variable to consider when making syngas reliable and applicable to fuel cells. The main cleaning process cost contributor are the two steps of compression, accounting for 35%, the removal of particulate, tars, and alkali, which represents around 30% of total cost, and the removal of halides, H₂S and CoS, representing 35% the cost. Research conducted by Iaquanuello et al (2006) on biomass syngas for MCFC systems, shows that a considerable part of the investment is due to hot gas cleaning and syngas compression, making costs even higher by using absorbents for removing H₂S and CoS. Authors suggest further analysis looking for optimal operating conditions in the gasifier for higher hydrogen syngas with less contaminants.

4. CONCLUSION

Brazil has shown a great potential for implementing biomass in the energy sector along the years. In the agribusiness sector, biomass is used in many applications, including seed drying process and heat generation in the industry sector where demand for heat and steam processes are high, such as food and ceramic industries. Even though the market for biomass in Brazil is increasing, there is still a great need for improvements and energy efficient solutions (Melo et al, 2010). This very promising scenario is crucial for the implementation of new technologies and strategies to tackle the energy issue. The integration of biomass gasification for hydrogen production for fuel cell applications in combined cycles would be a great advantage towards a cleaner and more efficient energy generation. In order to accomplish this, it is critical a lot of effort and research to make these technologies more reliable and considering the attractive scenario. Considering the large market for biomass potential, strategies must include the improvement of the gasification process for higher quality of syngas and cost reduction for fuel cell applications.

The understating of the gasification processes and technologies, either considering coal or biomass as fuels, is crucial to develop even more efficient and cleaner ways to generate energy. When considering the possibility for integration in fuel cell applications, the potential for gasification is even greater, achieving high efficiencies and low emissions. In this case, fuel cells systems seems to be a promising suit for syngas once they offer fuel flexibility. Therefore, it is important to consider the major characteristics of the hydrogen produced from the syngas to attend the fuel cell requirements and main market drivers for future technological trends. In this scenario, research and development is crucial to make the use of gasification for hydrogen purposes even more affordable and sustainable. This would include fuel cell materials capable and resistant when dealing with fuel poisoning and more efficient clean-up processes to assure fuel cell requirements without compromising system performance. The market has shown a growing potential for the integration of gasification technologies in obtaining high purity syngas for fuel cell purposes, which brings many opportunities for research projects.

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