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Combined Heat and Power Cogeneration from Bioethanol and Fuel Cells: A Brief Overview on Demonstrative Units and Process Design

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Different strategies have been proposed for the co-generation of heat and power (CHP) from renewable raw materials. Bioethanol was proposed by many authors as a promising biomass derived compound, being easy to handle, non toxic, with sufficiently high power density [1-3]. Innovative routes for its production as second generation biofuel are becoming available, leading to environmentally, ethically and economically sustainable bioethanol. The economical plan proposed by Biochemtex, for instance, is based on 0.3 euro/L for the production of lignocellulosic anhydrous bioethanol [4] and a brief overview of the bioethanol production costs has been very recently proposed [5]. Thus, bioethanol can be effectively suggested as a feedstock for fuel cell based systems.

Ethanol can be used as substrate for steam reforming and the reformate can feed various types of fuel cells. For instance, Solid Oxide Fuel Cells (SOFCs) are currently under study both for stationary and automotive power generation, the latter application with very short commercialisation perspective, according to the latest news [6].

A 250 W system based on authothermal reformer and a fuel cell stack has been studied [7]. A minimum amount of process controls and little internal heat integration kept the system architecture simple, as required for portable applications, at difference with bigger power systems, where heat integration represents the core for the sustainability of the process [8,9]. Indeed, for stationary applications the increase of efficiency is seen as a predominant factor with respect to simplification.

Typically, CHP units based on fuel cells fed with bioethanol should consist of a fuel reforming system (e.g., a steam reformer), followed by a hydrogen purification section, which should be more or less sophisticated depending on the types of fuel cells in use. The main issue is represented by the tolerance of the fuel cells catalysts to the presence of CO. Normally the catalysts are more tolerant at higher working temperature. Thus for instance low temperature Polymer Electrolyte Membrane Fuel Cells (PEMFCs) operating at *ca.* 80°C are poorly tolerant to CO, with a maximum allowed value around 20 ppm. A new generation of membranes has been more recently developed, allowing operation at 160-170°C (High Temperature, HT-PEMFC) and thus increasing very much the tolerance to CO (ca. 0.5-1 vol%). Fuel cells intrinsically operating at higher temperature, such as SOFCs can stand reformate compositions almost without any CO concentration adjustment, with consequent simplification of the process layout and ultimately a decrease of cost.

Different power systems system have been proposed, with reformate purification from CO based on preferential oxidation and attention to the control logic and heat integration [10-12]. The technical feasibility of using existing steam reforming and hydrogen separation technologies to produce hydrogen from bioethanol at industrial level (100,000 Nm^3/h) has been also explored [13]. The oxidative reforming of ethanol [14] and n-hexadecane [15] has been investigated in microreactors to feed micro-fuel cell systems and computational fluid dynamics simulation of ethanol steam reforming in catalytic wall microchannels has been performed on a Co_3O_4–ZnO catalyst [16]. The application of membrane reactors was additionally proposed for CHP, in order to improve the hydrogen purification section [17-19].

A CHP system fed with bioethanol should consist of a fuel processor including an ethanol steam reforming catalyst. Various materials have been proposed recently as active for the present reaction. Two keypoints should be kept in mind. i) The highest hydrogen productivity at the lowest possible temperature: the reaction is endothermal, but much less energy demanding than rival processes, such as the steam reforming of methane. Therefore, materials can be designed to operate as low as 400-500°C with full substrate conversion. ii) Enhanced stability towards coking is compulsory when operating at relatively low temperature where possible carbon gasification reactions are not effective. Some examples can be found in the literature [20-26].

To improve the energy efficiency of the systems heat should be efficiently supplied by burning part of the fuel. Efficient reactor configurations are represented e.g., by multitubular reactors [26,27]. A possible alternative, especially required when diluted ethanol mixtures are used, is product split to use part of the reformate as fuel [9,28,29]. The most innovative designs provide a catalytic burner, the catalysts for the catalytic combustion of C_2H_5OH being coated on the outer surface of the reformer tubes, in very efficient thermal contact with the reforming catalyst which is coated on the internal skin of the same tubes [30].

Reformate purification from CO can be then accomplished by coupling in series different processes, such as Water Gas Shift (WGS) reactors in variable number, followed by a preferential oxidation (PROX) reactor, or, alternatively, a selective methanation (METH) reactor, needed when LT-PEMFCs are used. Alternatively, CO separation by Pressure Swing Adsorption (PSA) is possible, but uneasy to handle for small applications.

Demonstrative systems have been proposed for CHP from bioethanol. The key for efficiency improvement should be a better thermal integration of the system, with the reformate production at the lowest possible temperature (taking the advantage of the relatively high reactivity of the substrate), keeping in mind catalyst resistance towards deactivation by coking. At the same time, an increase of the operating temperature of the fuel cell is envisaged. The latter would ensure a better tolerance to CO, with consequent lower need of hydrogen purification and a decrease of process complexity. The use of diluted bioethanol

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streams has been further proposed in order to cope with a much less expensive and energy intensive feedstock for CHP.

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