Biomass-fuelled PEM Fuel Cell systems for small and medium-sized enterprises

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To my parents

致我的父母

Abstract

Biomass-fuelled proton exchange membrane fuel cells (PEMFCs) offer a solution for replacing fossil fuel for hydrogen production. Through using the biomass-derived hydrogen as fuel, PEMFCs may become an efficient and sustainable energy system for small and medium-sized enterprises. The aim of this thesis is to evaluate the performance and potential applications of biomass-fuelled PEMFC systems which are designed to convert biomass to electricity and heat. Biomass-fuelled PEMFC systems are simulated by Aspen plus® based on data collected from experiments and literature.

The impact of the quality of the hydrogen-rich gas, anode stoichiometry, CH_4 content in the biogas and CH_4 conversion rate on the performance of the PEMFC is investigated. Also, pinch technology is used to optimize the heat exchanger network to improve the power generation and thermal efficiency.

For liquid and solid biomass, anaerobic digestion (AD) and gasification (GF), respectively, are relatively viable and developed conversion technologies. For AD-PEMFC, a steam reformer is also needed to convert biogas to hydrogen-rich gas. For 100 kWe generation, the GF-PEMFC system yields a good technical performance with 20 % electrical efficiency and 57 % thermal efficiency, whereas the AD-PEMFC system only has 9 % electrical efficiency and 13 % thermal efficiency. This low efficiency is due to the low efficiency of the anaerobic digester (AD) and the high internal heat consumption of the AD and the steam reformer (SR). For the environmental aspects, the GF-PEMFC system has a high CO_2 emissions offset factor and the AD-PEMFC system has an efficient land-use.

The applications of the biomass-fuelled PEMFC systems are investigated on a dairy farm and an olive oil plant. For the dairy farm, manure is used as feedstock to generate biogas through anaerobic digestion. A PEMFC qualified for 40 % electrical efficiency may generate 360 MWh electricity and 680 MWh heat per year to make a dairy farm with 300 milked cows self-sufficient in a sustainable way. A PEMFC-CHP system designed for an olive oil plant generating annual 50 000 m^3 solid olive mill waste (SOMW) and 9 000 m^3 olive mill waste water (OMW) is simulated based on experimental data from the Biogas2PEM-FC project[1]. After the optimization of the heat exchanger network, the PEMFC-CHP

[1] Biogas2PEM-FC is an industrial research project that aims to develop the technologies for treating the olive oil mill wastes through biogas-fuelled PEM fuel cells

system can generate 194 kW electricity which corresponds to 62 % of the total electricity demand of the olive oil plant.

The economic performance of the PEMFC and biogas-fuelled PEMFC are assessed roughly including capital, operation & maintenance (O&M) costs of the biogas plant and the PEMFC-CHP, the cost of heat and electricity, and the value of the digestate as fertilizer.

Keywords: PEMFC, renewable hydrogen production, biomass, hydrogen-rich gas, biomass conversion, anaerobic digestion, steam reforming, CO removal, gasification, sustainable energy system

Sammanfattning

Biobränsleeldade bränsleceller med protonväxlings (PEMFC) erbjuder en lösning för att ersätta fossila bränslen för produktion av vätgas. Genom att använda vätgas härrörande från biomassa som bränsle, kan PEMFC bli ett effektivt och hållbart energisystem för småskalig användning, exempelvis hushåll. Syftet med denna avhandling är att utvärdera prestanda och potentiella tillämpningar av biobränsleeldade PEMFC-system utformade för att omvandla biomassa till el och värme. Biobränsleeldade PEMFC-system simuleras av Aspen plus® baserat på uppgifter som samlats in från experiment och litteratur.

Inverkan på bränslecellernas prestanda av kvaliteten på den väterika gasen, anodens stökiometri, CH_4-innehåll i biogasen och dess omvandlingshastighet undersöks. Dessutom används ”pinch technology” för att optimera nätverket av värmeväxlare för att förbättra elproduktion och termisk verkningsgrad.

För flytande och fast biomassa är rötning (AD) och förgasning (GF) relativt lönsamma och utvecklade omvandlingstekniker. För AD-PEMFC behövs också en ångreformeringsenhet för att omvandla biogas till väterik gas. För 100 kWe generation ger GF-PEMFC systemet en bra teknisk prestanda med 20 % elektrisk och 57 % termisk verkningsgrad, medan AD-PEMFC systemet endast har 9 % elektrisk och 13 % termisk verkningsgrad på grund av den låga effektiviteten hos rötkammaren (AD) och den höga interna värmeförbrukningen i AD och ångreformeringsenhet (SR). GF-PEMFC systemet har en hög kompenstations faktor för CO_2-utsläpp och AD-PEMFC systemet har en effektiv markanvändning.

Användningen av de biobränsleeldade PEMFC-systemen utreds i en mjölkgård och en olivoljefabrik, eftersom båda har biomassakällor och också är små och decentraliserade system. För mjölkgården används gödseln för att generera biogas genom rötning. En PEMFC med 40 % elektrisk verkningsgrad kan generera 360 MWh el och 680 MWh värme per år för att göra en mjölkgård med 300 mjölkade kor självförsörjande på ett hållbart sätt. Ett PEMFC-CHP system som är utformat för en olivoljefabrik kan årligen generera 50 000 m^3 SOMW och 9 000 m^3 OMW enligt simuleringar på experimentdata från Biogas2PEM-FC projektet[1]. Efter optimering av värmeväxlarnätverket kan PEMFC-CHP-systemet generera 194 kW el som motsvarar 62 % av olivoiletfabrikens totala elbehov.

Den ekonomiska utvecklingen för PEMFC och biogasdrivna PEMFC bedöms översiktligt, bland annat kapital-, drifts- och underhålls- (O & M) kostnader för biogasanläggningen och PEMFC-CHP, kostnaden för värme och el, och värdet på rötresten som gödselmedel .

Nyckelord: PEMFC, förnybar vätgas, biomassa, väterik gas, omvandling av biomassa, rötning, ångreformering, CO-borttagning, förgasning, hållbart energisystem

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Tingting Guan

Stockholm, October 2015

List of appended papers

Paper I

Tingting Guan, Per Alvfors, Göran Lindbergh. "*Investigation of the prospect of energy self-sufficiency and technical performance of an integrated PEMFC (proton exchange membrane fuel cell), dairy farm and biogas plant system"*. Applied Energy 130 (2014) 685–691.

Paper II

Tingting Guan and Per Alvfors. "*Cogeneration PEM fuel cell system fuelled by olive mill wastes for its application in an olive oil plant"*. (Manuscript)

Paper III

Tingting Guan, Bhawasut Chutichai, Per Alvfors and Amornchai Arpornwichanop. "*Biomass-fuelled PEMFC systems: evaluation of the system designs for different raw materials"*. Energy Conversion and Management 106 (2015) 1183–1191.

Paper IV

Suat Sevencan, Tingting Guan, Göran Lindbergh, Carina Lagergren, Per Alvfors and Bengt Ridell. "*Fuel cell based cogeneration: Comparison of electricity production cost for Swedish conditions"*. International Journal of Hydrogen Energy 38 (2013) 3858-3864.

Paper V

Tingting Guan, Per Alvfors. "*The economic performance of an integrated biogas plant and proton exchange membrane fuel cell combined heat and power system (PEMFC-CHP) in Sweden"*. Energy sustainability & 12th fuel cell science, engineering and technology conference (ESFUELCELL2014). Boston, Massachusetts, June 29- July 2, 2014.

Paper VI

Tingting Guan, Per Alvfors. "*An overview of biomass-fuelled proton exchange membrane fuel cell (PEMFC) systems*". The 7th international conference of Applied Energy 2015, Abu Dahbi, United Arab Emirates, March 29-31, 2015.

My contributions to the appended papers

I am the main author of Papers I, II, V and VI under the supervision of Prof. Per Alvfors. I am one of the two main authors for Paper III. I performed the simulations for AD-PEMFC systems and am also responsible for all writing except the chapter *"2.2 GF-PEMFC"* and the whole review. For Paper IV, I contributed to the data collecting.

Contents

Nomenclature and abbreviations

Abbreviations:

AD	Anaerobic digestion
AFC	Alkaline fuel cell
CHP	Combined Heat and Power
EU	European Union
GF	Gasification
GHG	Greenhouse gas
H^+ER tube	H^+ exchange resin tube
HTS	High temperature CO shift
HTSR	High temperature shift reactor
IO bed	Iron oxide bed
LTS	Low temperature CO shift
LTSR	Low temperature shift reactor
MCFC	Molten carbonate fuel cell
O	SOMW+OMW
O&M	Operation & maintenance
OMW	Olive mill waste water
P	Pig manure
PAFC	Phosphoric acid fuel cell
PEMFC	Proton exchange membrane fuel cell

PrOx	Preferential oxidation
Pt	Platinum
RGibbs	Equilibrium reactor
RStoic	Stoichiometric reactor
RWGS	Reverse water gas shift
S/C	Ratio of steam to carbon
Selox	Selective CO oxidation
SOFC	Solid oxide fuel cell
SOMW	Solid olive mill waste
SR	Steam reforming

Symbols:

P_e	Power generated by the PEMFC stack
P_h	Recovered heat
η_f	Thermal efficiency of the fuel processor
μ_{H_2}	Utilisation rate of hydrogen in the anode
$\dot{n}_{H_2}$	Mole flow rate of hydrogen from the fuel processor
$\dot{n}_{biogas}$	Mole flow rate of the biogas from the biogas plant
$\dot{n}_{CH_4}$	Molar flow rate of the CH_4 entering the SR reactor

$\dot{n}_{burned}$	Molar flow rate of the biogas burned in the burner.
$\dot{n}_{steam}$	Molar flow rate of the steam to the SR reactor
LHV_{H_2}	Lower heating value of hydrogen
LHV_{biogas}	Lower heating value of the biogas
$\dot{n}_{anode-off}$	Mole flow rate of hydrogen from the fuel processor
$\dot{n}_{CH_4}^{converted}$	Molar flow rate of the CH_4 converted in the SR reactor
$\dot{n}_{reformed}$	Molar flow rate of the reformed biogas in the SR reactor
$LHV_{anode-off}$	Lower heating value of the anode-off gas
η_{AD}	Conversion efficiency from biomass to biogas
η_{elec}	System electrical efficiency
η_{heat}	System thermal efficiency
η_{total}	Total system efficiency
Bio_{ref}/Bio_{bur}	Ratio of reformed biogas to burned biogas
$\eta_{PEMFC,el}$	Required electrical efficiency of the PEMFC
$\mu_{bio\rightarrow ele}$	Conversion rate from biomass to electricity
μ_m	CH_4 conversion rate

1 Introduction

1.1 Background

Fuel cells and PEM fuel cell in the domestic energy system

In order to limit the impact of climate change and environmental pollution, reduction of greenhouse gas (GHG) emissions has become of global importance. The European Union (EU) has committed itself to reduce CO_2 emissions by 20 % by 2020 compared to1990 levels (Böhringer et al, 2009). Fuel cells, since they have high efficiency even at part load, low emission, neat silent operation and flexibility of fuel use, are identified as a technical option for the low carbon domestic energy system (Elmer et al, 2015). Of all kinds of fuel cells, the low temperature PEMFC demonstrates the greatest promise for the early commercialization stage, attracting most attention and investment in domestic application projects (Gencoglu et al, 2009; Sammes et al, 2000; Peighambardoust et al, 2010). The short start-up time, power modulation and also useful direct hot-water output makes the PEMFC one of the best candidates for low power CHP system for residential applications. The 80 % of demonstration projects employ PEMFC technology (Hawkes et al, 2009). However, the clean nature of the PEM fuel cell is limited by the production path of the hydrogen. Presently, 50 % of the total hydrogen consumption in the world is produced from natural gas due to its abundant availability and advantageous price (Rakib et al, 2010; Chaubey et al, 2013). Nevertheless, producing hydrogen from natural gas is costly, inefficient in energy use, and due to the fossil fuel nature of natural gas, environmentally unfriendly (Shinnar, 2004; Chaubey et al, 2013). Water electrolysis is the simplest way to produce hydrogen but has a high energy cost and causes pollution if the electricity is generated by fossil fuel. According to studies by Argonne National Laboratory, 880-1026 kWh of fossil energy are used for the production of 293 kWh of hydrogen through fossil energy-based water electrolysis (Gaines et al, 2008). These facts are pressingly driving researchers and the industry to develop efficient and renewable hydrogen generation technologies to replace the conventional fossil fuel-based ones

(Sharaf et al, 2014). Systems integrating biomass/biogas with PEM fuel cells are genuinely clean energy generation and conversion systems that could potentially reach zero carbon status.

Biomass and biomass-fuelled PEMFC

Biomass possesses the characteristics of variety, abundance and CO_2-emission neutrality, which makes it a potential source for renewable hydrogen production, and likely will give the fuel cell a sustainable future (Peppley, 2006). Biomass may be divided into different groups according to its physical characteristics and the two types under study in this work are:

- Liquid biomass mainly from manure, agriculture and sludge from municipal wastes
- Solid biomass mainly as forest residues from the forest industry

In order to be usable for the PEMFC, the biomass needs to be processed to hydrogen-rich gas. Among the variety of technologies, anaerobic digestion and gasification are at present probably the most suitable and available methods for the processing of liquid and solid biomass, respectively. Anaerobic digestion is a more mature and common biological technology for biofuel generation than alcoholic digestion and fermentation which is still at the research and development stage (Chaubey et al, 2013; Ni et al, 2006). The product of the anaerobic digestion is biogas which normally contains 60 % CH_4 and may be converted to hydrogen-rich gas by steam reforming, partial oxidation or autothermal reforming. Compared with partial oxidation and autothermal reforming, steam reforming is a more commercialized and industrially available technology and has the further advantage of giving a product gas with higher hydrogen content than the alternative technologies. This will make the PEMFC system more efficient and stable (Chaubey et al, 2013; Bocci et al, 2014; Hoogers, 2003). Combined with steam reforming, anaerobic digestion is capable of generating the renewable hydrogen needed for the PEMFCs. It is suggested that integrating PEM fuel cells directly into existing natural gas infrastructure for processing biogas is a possibility for the renewable fuel cell systems (Lucia, 2014). Gasification is a thermochemical process that converts the biomass directly into hydrogen-rich gas containing 30-50 % H_2 (Holladay et al, 2009; Bocci et al, 2014). Another thermochemical process, pyrolysis, is often considered for liquid and solid fuel production, but not for hydrogen production because of the low hydrogen content in the product (Ni et al, 2006). In summary,

it may be concluded that both AD-PEMFC and GF-PEMFC are relatively viable and mature biomass-fuelled PEMFC systems.

1.2 Previous studies (Paper VI)

1.2.1 Anaerobic digestion, biogas steam reforming and PEMFC

For the biogas-fuelled PEMFC system, the main issues are related to the determination of the parameters for fuel processor including steam reforming, CO water shift and preferential oxidation, the integration of subsystems, and the perspectives for the system applications.

Parameter determination and testing of the integrated systems

There is a series of experiments from a research group working on modeled biogas for parameters testing of the fuel processor (Xu et al, 2004; Zhang et al, 2004; Effendi et al, 2002; Effendi et al, 2005). The modeled biogas consists of 60 % CH_4, 40 % CO_2 and no H_2S. As the first step, the performances of fluidized- and fixed-bed reactors were tested at 750 ^{0}C to choose the right reactor type for the biogas steam reforming (Effendi et al, 2002). It was observed that in the fluidized-bed, the conversion of CH_4 (and CO_2) was higher than that in the fixed bed reactor by 7-15 %. Fast carbon formation was observed in the fixed-bed with high feed gas to steam ratio (1.5). For the fluidized-bed reactor, increasing temperature from 650 ^{0}C to 850 ^{0}C increased the overall conversion and reduced carbon deposits. Also, for the fluidized bed reactor, decreasing the feed gas to steam ratio gave a higher H_2 selectivity and lower CO selectivity, as well as reduced the carbon deposition significantly.

In the second step, the hydrogen yield was maximized by high temperature and low temperature CO shift reactions (HTS and LTS) following the steam reforming (Effendi et al, 2005). Based on the results in (Effendi et al, 2002), biogas steam reforming using the fluidized bed reactor was operated at temperatures between 923 and 1123 K, 1 atm. Increasing the temperature and steam to biogas ratio increased the CH_4 and CO_2 conversion and the hydrogen yield while decreasing the carbon deposition. The CO shift used the fixed bed reactors. The optimal condition for the HTS was a space velocity of 14 mg_{cat}/ml min, a temperature of 573 K, and a ratio of 1.5 steam to dry gas. For the LTS, the optimal temperature was 473K. The final product from the optimized system was composed of 68 % H_2 and 0.2 % CO (equivalent to a CO conversion of > 99 %.)

For producing the hydrogen-rich gas at the PEMFC standard (with CO less than 10 ppm), selective oxidation was included after the LTS (Zhang et al, 2004). In this step, the CO in the gas after the LTS was oxidized by oxygen. The optimal ratio of O to CO was 3 and the temperature was between 383 and 428 K. With the selective oxidation reactor, a complete fuel processor was built up, which consisted of the steam reformer, HT and LT CO water-gas shift reactors, and the selective oxidation reactor. The final product gas consisted of 69-70 % H_2, 28-29 % CO_2, 1.0-1.3 % CH_4, < 2 ppm CO. The stabilities of the commercial catalysts were proven by running the four successive reactions continuously for 7 hours.

After the fuel processor was built up, a 50 W PEMFC was integrated with it (Xu et al, 2004). As mentioned in the previous experiments, the fuel processor ran with a model biogas without the presence of H_2S. The composition of the hydrogen-rich gas was about 70 vol. % H_2, 30 vol. % CO_2, and residual CH_4 (1.0 vol. %). During the 7 hours running, it was observed that the PEMFC can work at a stable voltage and power. However, compared with pure hydrogen, the hydrogen-rich gas leaded to a lower voltage and lower power output at a given current, limiting the hydrogen utilization to only 44 %.

Another group in Germany conducted experiments on a biogas-fueled PEMFC system, which contributed valuable information about the system behavior with native biogas (Schmersahl et al, 2011). The biogas was produced by a small-scale anaerobic digester. After removing the H_2S completely using copper-impregnated activated-carbon filters, the biogas was fed to the fuel processor for hydrogen production. It was observed that the PEMFC can work stably using the hydrogen-rich gas containing more than 60 vol. % hydrogen. However, the electrical efficiency of the stack was only 22.9 % which was due to the lower hydrogen content compared with pure hydrogen. Also, the thermal efficiency of the fuel processor was only 47 % which was far away from the rated 68 %. This group later released another study also for a biogas-fueled PEMFC, which showed that the H_2S concentration ranges from 42 to 2576 ppm in the biogas depending on the digestion mode, the operation temperature and the substrate type of the digestion (Scholz et al, 2011). In contrast to continuous fermentation, the batch process was characterized by large temporal variations in the gas composition. Higher concentrations of H_2S were measured in thermophilic fermenters than in the mesophilic fermenters because of the more efficient degradation of sulphurous compounds at higher process temperatures. Pure

maize silage caused a lower H_2S concentration as substrate than mixing with cattle or pig manure due to the lower sulphur content in the maize silage.

System applications

PEMFC-CHP is an ideal system for individual homes or small-scale applications because of the high efficiency, power density, flexible size and low operation temperature. Using hydrogen from biogas as fuel will enhance the environmental contribution of the PEMFC. This system is most suitable for decentralized energy systems which are far away from the electricity grid but have the raw material for the biogas production such as a livestock farm or an olive oil plant. For a case study on a Japanese dairy farm, it is estimated that the hydrogen yield capacity from 1000 milk cows will be 400 Nm^3/day from which it is possible to generate 480 kWh/day of power with a PEMFC using this hydrogen (Ohkubo et al, 2010). Until now, there is no demonstration shown in the literature for a biogas-fueled PEMFC system, but there is one related to AFC which is also low temperature fuel cell (Duerr et al, 2007). It is recognized that for a biogas-fueled low temperature fuel cell system, this unit leads to extensive capital costs compared with other units, however, the outcome of this system will be socially, environmentally and economically effective (Duerr et al, 2007). When biogas is getting more interest due to the environmental benefit, the production cost of biogas also needs to be considered for system application. Based on the Swedish case, the economic conditions for farm-scale production of biogas and CHP are markedly influenced by the scale of production. It is found that compared with a single large dairy farm it may be more profitable for farmers to cooperate and invest in larger biogas plants in order to increase the production of biogas and electricity. However, it is not clear whether a large, centralized biogas plant, collecting manure from numerous farms, is the better choice compared to a large, farm-scale plant utilizing manure from a few neighboring farms (Lantz, 2012).

1.2.2 Gasification and PEMFC

For the PEMFC system combined with gasification, until now there is no experimental work carried out. However, some simulation work has emerged on system level investigation. For biomass gasification, wood waste is seen as the favored substrate. As mentioned, gasification converts the biomass to gaseous fuels by thermochemical methods in the presence of air/oxygen, and/or steam as

gasifying agent. Using steam as gasifying agent is an effective method for hydrogen-rich gas production; however, steam gasification is an extremely endothermic process. Thus, the addition of air to gasifiers seems to be more practical; this enhances the biomass combustion reaction and supplies additional heat to the steam gasification process (Hosseini et al, 2013). Utilization of both air and steam as gasifying media may make the gasification process achieve a self-sustainable operation (Chutichai et al, 2013). Simulation results of a biomass gasification and PEMFC integrated system utilizing wooden waste as biomass sample while choosing steam and air as gasifying agents showed that the thermal and electrical efficiencies of the gasifier could reach 51 % and 22 %, respectively (Chutichai et al, 2013). The hydrogen content in the hydrogen-rich gas was around 33 vol. % (Chutichai et al, 2013). A decentralized power production system based on biomass gasification and PEMFC using wood waste, water and air as substrates could reach 35 % total efficiency after considering the different methods of recovering the useful heat (Toonssen et al, 2009).

1.3 Aim and scope of thesis

The aim of this thesis is to evaluate potential applications of biomass-fuelled PEMFC systems which are designed to convert the biomass to electricity and heat in a small or medium-sized energy system. Based on the previous studies mentioned before, biomass-fuelled PEMFC systems show positive results in system integration, but there are few publications dealing with system performance and system design for the potential applications. These are therefore investigated in the following studies of this thesis:

- A biomass-fuelled PEMFC system is designed and modelled using Aspen Plus®. The input data comes from publications, reports, books and personal communications. Compositions of the reformate gas and the impact of the CH_4 conversion rate and the CH_4 content in the biogas on the system performance is analysed. The energy balance of the whole system is illustrated in a Sankey diagram on the basis of system performance. The fuel cell system is placed in a dairy farm, so the possibility of energy self-sufficiency of an integrated PEMFC, dairy farm and biogas plant and also the performance of the whole system is investigated. The manure production and the energy demand of the dairy farm are modelled as well as the biogas production and the energy demand of the biogas plant. In addition, the

avoided fossil fuel consumption and the CO_2 emission are discussed. ***(Paper I)***

- According to the experimental results of the EU project Biogas2PEM-FC, the performance of the PEM fuel cell stack fuelled by the biogas produced from olive oil mill waste is evaluated and then scaled-up and optimized by system simulation. The scaling-up and optimization are performed to understand the further application of the experimental system in the olive oil plant. In order to improve the performance of the scaled-up system, the anode stoichiometry and heat exchange network is optimized. The pinch technology is used for the redesign of the heat exchange network. ***(Paper II)***

- A comprehensive evaluation of biomass-fuelled PEMFC systems is made by using different system designs and raw materials from both technical and environmental perspectives. This is to initiate suggestions for future development, choice and application of these systems. AD-PEMFC and GF-PEMFC are designed for liquid and solid biomass, respectively, and both of them are intended for small and medium-sized enterprises. For the technical perspective, the biomass consumption, AD and GF performances, hydrogen-rich gas quality, electrical and thermal system performances were analyzed and evaluated. For the environmental perspective, CO_2 emission reduction of biomass-fuelled PEMFCs compared with hydrogen production via steam methane reforming and power generation of a coal-fired power plant, fossil fuel-savings and land-use efficiencies are discussed. ***(Paper III)***

- The electricity production cost of fuel-cells based cogeneration systems are calculated based on Swedish conditions such as the heat crediting system and domestic fuel prices. Also, the economic performance of a PEMFC-CHP system utilizing biogas from a manure-based biogas plant in Sweden is evaluated taking into account the heat and electricity prices, the investment and operating cost of the biogas plant, the PEMFC-CHP system, the value of the digestate as fertilizer and the different subsidies. ***(Papers IV+V)***

- An overview of the biomass-fuelled PEMFC system, focusing on the anaerobic digestion and gasification for biomass-derived hydrogen production is made. Anaerobic digestion is combined with steam reforming. These conversion systems are analyzed from various perspectives including the impact of the contaminants in the product gas generated from the steam reformer and gasification on the performance of the PEM fuel cells, experiments and simulation for biomass-fuelled PEMFC systems. ***(Paper VI)***

1.4 Methods for system simulation and evaluation

Mass and energy balance

The first law of thermodynamics is the basic principle for the study in this thesis. Achieving the mass and energy balance is the necessary requirement for system simulation. Especially, the energy balance is presented by Sankey diagram which is typically used to visualize energy or material or cost transfers between processes. Through the Sankey diagram, on the one hand, the energy balance can be checked easily; on the other hand, the system efficiencies can be calculated by the energy flows which are clearly presented.

System simulation

The technical design and simulation of the biomass-fueled PEM fuel cell system is made by Aspen Plus® which is the market-leading chemical process design and optimization software (http://www.aspentech.com, accessed on July 30, 2015). The system design and the input data refer to experimental data, the literature data, industrial reports and personal communications.

Pinch technology

In Paper II, in order to understand the conditions of the heat exchanger network of the experiment and scaled-up system, pinch technology is used. Pinch technology is a method for identifying the minimum hot and cold utility as target of the heat recovery, and then generate the optimum solution for the network of heat exchangers and energy and capital cost (Linnhoff, 2006). The composite curve and the grand composite curve are used to understand and optimize the heat exchanger network.

Environmental evaluation

Environmental impact of the biomass-fuelled PEMFC systems are evaluated by CO_2 emission reduction, fossil-fuel saving and land-use efficiency. The hydrogen and electricity generated from the biomass-fuelled PEMFC systems are both seen as CO_2-neutral and the CO_2 emissions from the upstream processes, i.e. biomass cultivation, collection, and transportation are not included in the scope of this study. The CO_2 emission reduction of hydrogen production refers to the typical hydrogen production via steam methane reforming and the CO_2 emission reduction of power generation refers to a typical coal-fired power plant. The fossil-fuel saving includes the natural-gas saving and coal saving. The land-use efficiency is evaluated for electricity generation and CO_2 reduction per hectare.

Economic evaluation

In Paper IV and V, electricity production costs for biogas-fuelled PEM fuel cell cogeneration systems are investigated for Swedish conditions. The costs include capital cost, operation & maintenance cost, and fuel cost. The calculations of PEM fuel cell systems are made using a model provided by Grontmij AB, a consultancy company (Hansson, 2007; Nyström, 2011) in Paper IV, but the fuel cost is the cost of hydrogen production. In Paper V, the cost of biogas production is included in the electricity production cost of the PEM fuel cell systems. The capital cost for PEM fuel cell systems and biogas plant use the annuity method.

1.5 Thesis outline

Chapter 1 introduces the background, previous studies, the aim and scope, and the methodology of the thesis.

Chapter 2 provides the background information of each subsystem including anaerobic digestion, fuel processing, PEM fuel cell, dairy farm and olive oil plant.

Chapter 3 shows the system simulation for steam reformer, CO removal reactors, PEM fuel cell, biomass gasifier and heat exchanger network design. Also, the environmental and economic evaluation is included.

Chapter 4 presents the results and discussion including composition of the reformate gas, impact of anode stoichiometry, CH_4 conversion rate and CH_4 content of the biogas on system performance, heat exchanger network optimization for the scaled-up system by using pinch technology; System performance, application of a biomass-fuelled PEMFC system, environmental impact of biomass-fuelled PEM fuel cell systems and economic analysis are also taken up.

Chapter 5 highlights major conclusions of the thesis.

2 Studied systems

As shown in Figure 1, biomass-fuelled PEMFC systems include different subsystems and each of them are characterised by their reactions such as anaerobic digestion, biogas purification, steam reforming, biomass gasification, high temperature water-CO shift, low temperature water-CO shift, preferential oxidation of CO, methanation and electrochemical reactions of the PEM fuel cell. Thus, a brief description of each reaction is presented in this chapter. Also, a dairy farm and an olive oil plant are described since then they are the biomass sources and beneficiaries of the biomass-fuelled PEM fuel cell system.

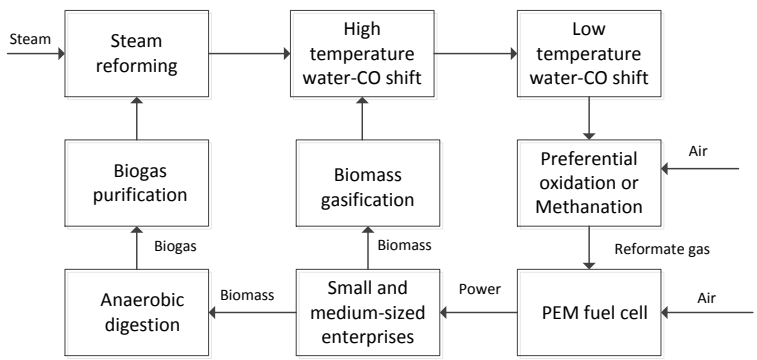


Figure 1. General process of a biomass-fueled PEMFC system

2.1 Anaerobic digestion

Anaerobic digestion is a biological process that occurs naturally when organic material (biomass) decomposes in a humid atmosphere in the absence of air but in the presence of a group of natural microorganisms which are metabolically active, i.e. methano-bacteria (Deublein et al., 2003). The product of the anaerobic digestion is biogas, which mainly consists of methane and carbon dioxide. Attributed to the high content of CH_4, the biogas can be used to produce hydrogen-rich gas for fuelling the PEMFC, by using steam reforming. The substrate for the anaerobic digestion may be sewage sludge, agricultural waste and land fill. In this thesis, agricultural waste such as cow manure from a dairy farm and olive oil mill waste from an olive oil plant are the main sources of substrate for the anaerobic digester. The anaerobic digester is operated at mesophilic conditions (36 °C). Table 1 shows the typical components and characteristics of biogas produced from agricultural waste.

Table 1 Typical components and character of biogas produced from the agricultural waste (Deublein et al., 2003)

Component	Unit	Content
CH_4	% by vol.	45-75
CO_2	% by vol.	25-55
N_2	% by vol.	0.01-5.00
H_2S	mg/Nm^3	10-30 000
NH_3	mg/Nm^3	0.01-2.50
Water vapour	% by vol.	1-5
LHV	kWh/Nm^3	5.0-7.5
Temperature	°C	35

2.2 Fuel processing

The integration of biogas purification, steam reforming or biomass gasification, water-CO shift, preferential oxidation of CO or methanation as fuel processing unit is essential for a biomass-fuelled PEM fuel cell system.

2.2.1 Biogas purification

As shown in Table 1, for biogas from anaerobic digestion, the main contaminants are hydrogen sulphide (H_2S) and ammonia (NH_3). H_2S is the most common contaminant significantly poisoning the catalyst in the reformer and the anode (Larminie and Dicks, 2003; Lopes et al, 2011; Shi et al, 2007). The ammonia can poison both the proton exchange membrane (PEM) and the catalyst layers of the anode (Zhang et al, 2009). Both are detrimental to the performance of the PEMFC. Therefore, the removal of H_2S and NH_3 from the biogas is essential for the system performance.

Physicochemical methods, chemical absorption and adsorption processes, are the most commercial methods for H_2S and NH_3 removal. For a small system such as biomass-PEM fuel cell system, adsorption is more suitable since liquid chemical absorption systems are designed for larger systems such as the oil industry. Metal oxides such as iron oxides and activated carbon are good options for H_2S removal, respectively (Abatzoglou et al., 2009). The chemical reactions involved are shown in the following equations (Crynes, 1978):

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \quad (1)$$

$$Fe_2S_3 + 3/2O_2 \rightarrow Fe_2O_3 + 3S \qquad \Delta H^{o}_{298} = -198 \text{ kJ/mole} H_2S \quad (2)$$

There is not much research on NH_3 removal for small systems, but an H^+ exchange resin tube may be a good solution (Uribe et al., 2002). The reaction is shown by equation (3). Also, as a general adsorbent, activated carbon may be used for NH_3 removal.

$$NH_3 + H_2O \leftrightarrow NH_4OH + R-H \leftrightarrow R-NH_4 + H_2O \quad (3)$$

2.2.2 Steam reforming

Steam reforming (SR) is used to convert energy carriers in the gas phase, such as hydrocarbons and alcohols, described by the general formula $C_xH_yO_z$, using steam, into a mixture of carbon monoxide and hydrogen, according to the formula provided below (Kolb, 2008):

$$C_xH_yO_z + (x-z)H_2O \rightarrow xCO + (x-z+\frac{y}{2})H_2 \quad (4)$$

The product, known as the reformate, is a mixture of gases including carbon monoxide, hydrogen, unreacted steam and fuel. Steam reforming favours the high temperature and low pressure (Sasaki et al., 2003).

Carbon monoxide and significant unreacted steam undergo the water-gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H^o_{298} = +40kJ/mole \quad (5)$$

With the presence of carbon dioxide, dry reforming takes place as shown in reaction (6) but it is much slower than the steam reforming in the presence of adequate amounts of steam (Avci et al., 2001).

$$C_xH_yO_z + (x-z)CO_2 \rightarrow (2x-z)CO + \frac{y}{2}H_2 \quad (6)$$

2.2.3 Biomass gasification

Biomass gasification is the conversion of solid or liquid biomass into useful and convenient gaseous fuel or chemical feedstock that may be burned to release energy or used for production of value-added chemicals (Basu, 2013). The gasification process may be broken down into four steps: preheating and drying, pyrolysis and /or combustion, char gasification.

The typical moisture content of freshly cut woods ranges from 30 % to 60 %, and for some biomass, it may exceed 90 % (Klass, 1998). Thus, the biomass will be preheated to remove the extra moisture. For the production of a fuel gas with a reasonably high heating value, most gasification systems use dry biomass with a moisture content of 10 to 20 % (Basu, 2013). Also, the low-molecular-weight hydrocarbons start to decompose in this step. Pyrolysis involves the thermal breakdown of larger hydrocarbon molecules of biomass into smaller gas molecules with no involvement of air, gas, or any other gasifying medium. The gasification step involves chemical reactions taking place between the hydrocarbons, steam, carbon dioxide, oxygen and hydrogen. Since the gasification reactions are endothermic, part of the char is combusted to supply the heat for the gasification reactions.

2.2.4 Water-CO shift

As mentioned before, after the steam reforming, the water-gas shift reaction (5) takes place consecutively to convert carbon monoxide and the unreacted steam to hydrogen and carbon dioxide. The water-gas shift reaction increases the hydrogen concentration of the reformate. For the fuel cell systems, in order to minimize the CO concentration, there are normally two steps of water-gas shift reaction. One is called high temperature water-CO shift and the other is low temperature water-CO shift. The high temperature increases the reaction rate but gives incomplete CO conversion. A low temperature shift following the high temperature one is used to achieve further CO conversion.

2.2.5 Preferential oxidation of CO

After the water-gas shifts steps, there are still small amounts of carbon monoxide present in the reformate beyond the tolerant level (< 10 ppm) of the PEM fuel cell to CO. Preferential oxidation of CO (PrOx) is used to remove these small amounts of CO with air (Kolb, 2008):

$$CO + 0.5O_2 \rightarrow CO_2 \qquad \Delta H^{o}_{298} = -283 \text{ kJ/mole} \qquad (7)$$

Meanwhile, the preferential oxidation is accompanied by an undesired side reaction (8) with the presence of hydrogen in the reformate.

$$H_2 + 0.5O_2 \rightarrow H_2O \qquad \Delta H^{o}_{298} = -242 \text{ kJ/mole} \qquad (8)$$

2.2.6 Methanation

Methanation, shown in equation (9), normally is the final step in carbon monoxide removal (Kolb, 2008). Compared with PrOx, since there is no air requirement for methanation, less complication and fewer safety problems are involved in this system. However, methanation consumes three moles of hydrogen per mole of CO, which will reduce the hydrogen amount in the reformate. Moreover, the undesired side reaction (10) competes with methanation of CO, and consumes more hydrogen. Therefore, it is suggested to use methanation when the concentration of CO is at ppm level but not percent level (Hoogers et al, 2002).

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta H^{o}_{298} = -254 kJ / mole \qquad (9)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \Delta H^o_{298} = -165kJ / mole \tag{10}$$

2.3 PEM fuel cell

A fuel cell is a device that converts chemical energy into electricity through electrochemical reactions. There are different fuel cell types: proton exchange membrane fuel cell (PEMFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC). The major differences between fuel cell types are summarized in Table 2.

Table 2 Major differences between fuel cell types (EG&G Technical Services, Inc., 2004; Larminie et al, 2003)

	PEMFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Solid polymer membrane	Potassium Hydroxide	Liquid Phosphoric Acid	Liquid Molten Carbonate	Ceramics
Mobile ion	H^+	OH^-	H^+	CO_3^{2-}	O^{2-}
Operating temperature (°C)	30-100	50-200	~220	~650	500-1000
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material
External reformer for hydrocarbon fuels	Yes	Yes	Yes	No, for some fuels	No, for some fuels and cell designs
External shift conversion of CO to hydrogen	Yes, plus purification to remove trace CO	Yes, plus purification to remove CO and CO_2	Yes	No	No

Normally, fuel cells are distinguished by the electrolyte they use. For the PEMFC, the electrolyte is a solid polymer, which makes this type of fuel cell inherently very simple (Larminie et al, 2003). The reactions are shown in equations (11)-(13):

Anode: $2H_2 \rightarrow 4H^+ + 4e^-$ (11)

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (12)

Overall reaction: $H_2 + O_2 \rightarrow H_2O$ ΔH°_{298}=-242 kJ/mole (13)

PEMFC contains a polymer membrane as electrolyte sandwiched between two electrodes. The membrane has a special property that allows positive ions (proton) to pass through while blocking electrons and gases. These electrodes are typically made out of carbon cloth or carbon fiber paper whereas the typical catalyst is platinum (Pt) supported on carbon.

The reactions of the PEM fuel cell take place at 30-100 °C. This low operating temperature is another characteristic of the PEM fuel cell which makes it to start up quickly and be able to meet changing demand. Thus the PEM fuel cell is suited to vehicles and mobile application and for small-scale CHP systems. One of the disadvantages of the PEMFC fuel cell is that it is extremely sensitive to CO as the fuel cell will be poisoned by > 10 ppm CO (Larminie et al, 2003), so CO removal is essential for a PEM fuel system fuelled by reformate, which makes the fuel cell systems more complicated and less efficient.

2.4 Biomass sources: Dairy farm and olive oil plant

Following oil, coal and natural gas, biomass is the fourth most used primary energy resource worldwide (Bocci et al, 2014). Different from fossil fuel, biomass does not take millions of years to form, so it is considered renewable. Moreover, although CO_2 is also released when biomass burns, since biomass is produced through photosynthesis by absorbing CO_2 from the atmosphere, so the CO_2 impact from the biomass is negligible (Holladay et al, 2009). For this reason, biomass is considered carbon-neutral.

For the studies in this thesis, the biomass mainly comes from a dairy farm and an olive oil plant which is also involved in the system studied. Thus, the description of the dairy farm and the olive oil plant are presented.

2.4.1 Dairy farm (Papers I, III and V)

In a biomass-fuelled PEM fuel cell system, the dairy farm has dual roles: as supplier of the biomass for the power production and as end user of the heat and power. On the one hand, the manure produced from the farm may be used as feedstock for the biogas generation which then may be used as fuel for PEM fuel cell system; on the other hand, the electricity and heat demand of the dairy farm

may be satisfied by the biogas-fuelled PEM fuel cell. It seems the dairy farm may be self-sufficient.

Manure production

A dairy farm is a good source for the manure for anaerobic digestion. The manure production of a milked cow is 25 tonnes/year and, for heifers and calves, it is 8 and 3 tonnes/year, respectively (ASAE, 2005). Typical biogas production from wet manure is 25 Nm^3/tonne (Edström et al, 2008). It is assumed that the content of CH_4 in the biogas is 60 %, and that the CH_4 production from wet manure is 15 Nm^3/tonne. 1 Nm^3 of biogas was set to have a heating value of 6 kWh (LHV).

Energy consumption of a dairy farm

On Swedish dairy farms, the energy use is 0.154 kWh for 1 kg milk, divided into 0.122 kWh electricity and 0.032 kWh diesel (Neuman, 2008). Milk production is estimated to be 8000 kg milk/milked cow per year, so the annual energy use of one milked cow is calculated and distributed among the different functions on a dairy farm as shown in Table 3.

Table 3 Annual energy use of a single milked cow in a Swedish dairy farm distributed among different functions (Neuman, 2008; Hörndahl, 2008)

	Wh/kg milk	kWh/milked cow, year
Feeding	40	330
Milking	45	360
Lighting	25	210
Ventilation	20	170
Manure handling	15	100
Miscellaneous	10	70
Total (diesel)	155(30)	1240(250)

Table 1 shows that, on a Swedish dairy farm, most of the energy is used for feeding, milking, lighting, ventilation and manure handling. Milking consumes most energy, almost 30 % of the total energy. This energy is used for cooling of the milk tank, heating of the water needed for the milk tank cleaning and for running vacuum pumps essential for the actual milking. On a dairy farm as a whole, about 80 % of the energy use is in the form of electricity and 20 % is in the form of diesel. In this study, the diesel consumption is excluded from the energy balance, which means that the total energy needed for a single milked

cow during a year is 1000 kWh electricity. On a Swedish dairy farm there is no heating demand for the barn because the body heat of the cows is sufficient to keep the barns at an adequate temperature.

2.4.2 Olive oil plant (Paper II)

Just as the dairy farm, an olive oil plant also plays dual roles: one is as the end user of the heat and power and the other one is as supplier of the biomass.

The olive oil plant is the source of the olive oil waste for anaerobic digestion. The extraction of olive oil generates huge quantities of wastes that have great impact on land and water environments because of their high phytotoxicity (Roig et al., 2006). These wastes include solid olive mill waste (SOMW), a mixture of liquid and solid wastes with 55-60 % water content. Additionally, the olive mill waste water (OMW) from the olive cleaning and olive oil centrifugation has high pollution impact because of its acidity, high salinity and organic load. After analysing the SOMW and OMW characteristics it was found that biogas production through anaerobic digestion may be a viable solution for the olive mill waste (Tekin et al, 2000; Borja et al, 2003; Marques et al, 2001).

The process of olive oil extraction includes olive washing, olive grinding, oil extraction and oil washing. Olive grinding and oil extraction are mainly supported by electrical power; these are the most electricity-consuming steps in olive oil extraction. For the washing step, the water is needed at around 55 °C, which consumes heat.

3 Simulation and calculation of studied systems

This chapter presents the details of the simulation and calculation of the studied systems which includes the simulation of each subsystem of the biomass-fuelled PEM fuel cell system, simulation of the integrated system, design of the heat exchanger network, calculation of the energy balance of the dairy farm, evaluation of the CO_2 offset factor and so on. The simulation work was done using Aspen plus®.

3.1 Simulation of each subsystem

This part explains the details of the simulation. Most of the system simulation work is presented in Papers I, II and III. In Papers I and III, the input data and parameters are specified based on a literature review, reports and books. In Paper II, the simulation is made based on the data from the experimental system of project Biogas2PEM-FC.

Subsystem of the biomass-fuelled PEM fuel cell system includes a steam reformer, water-CO shift reactor, PrOx reactor or methanation reactor, PEM fuel cell, biogas purifier, gasifier and anaerobic digestor.

3.1.1 Steam reformer

The reactions taking place in the steam reformer include reactions (4), (5) and (6). As the hydrocarbon is chosen to be CH_4, reactions (4) and (6) become reactions (14) and (15).

$$CH_4 + 2H_2O \rightarrow CO + 3H_2 \quad \Delta H^{o}_{298} = -206 \text{ kJ/mole} \tag{14}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H^{o}_{298} = -247 \text{ kJ/mole} \tag{15}$$

Besides the reactions, the steam reformer is also simulated by parameters including the CH_4 conversion rate (μ_m), the ratio of steam to carbon (S/C), the ratio of reformed biogas to burned biogas (Bio_{ref}/Bio_{bur}) and physical conditions (pressure and temperature). These parameters are defined as follows:

$$\mu_m = \frac{\dot{n}_{CH_4}^{converted}}{\dot{n}_{CH_4}} \times 100\% \quad (16)$$

$$\frac{S}{C} = \frac{\dot{n}_{steam}}{\dot{n}_{CH_4}} \quad (17)$$

$$\frac{Bio_{reformed}}{Bio_{burned}} = \frac{\dot{n}_{reformed}}{\dot{n}_{burned}} \quad (18)$$

where $\dot{n}_{CH_4}^{converted}$ is the molar flow rate of the CH_4 converted in the SR reactor, $\dot{n}_{CH_4}$ is the molar flow rate of the CH_4 entering the SR reactor, $\dot{n}_{steam}$ is the molar flow rate of the steam to the SR reactor, $\dot{n}_{reformed}$ is the molar flow rate of the reformed biogas in the SR reactor, and $\dot{n}_{burned}$ is the molar flow rate of the biogas burned in the burner.

For the steam reformer simulation, in Papers I and III, the steam reforming reaction (14) and the water-CO shift reaction (5) are involved in the reformer simulation. The reactor model used is the stoichiometric reactor (RStoic) of Aspen which is specified by known stoichiometry and reaction extent or conversion. Based on the literature review, the operation temperature of the steam reformer is set to 750 °C (Larminie et al, 2003; Schmersahl et al., 2007; Hubert et al, 2006; EG&G Technical Services, 2004). The ratio of the CO_2 to CO in the product of the reformer is taken from a figure in (Larminie et al, 2003) which shows the equilibrium concentrations of steam reformation reactant gases as function of temperature. When the temperature of the steam reformer is 750 °C, the ratio of CO_2 to CO is 2/3 (Larminie et al, 2003). The conversion rate of CH_4 in the reformer is 98 % (Schmersahl et al, 2007; Hubert et al, 2006). The S/C is 3.5 (Larminie et al, 2003; Hubert et al, 2006). For the operation pressure, since the steam reforming favours the low pressure, the operation pressure is set to atmospheric or around 2 bar.

In Paper II, the simulation of the steam reformer is made based on the experimental results, so the method of simulation is different from that in Papers I and III. The composition of the product gas of the steam reformer is known, but no other parameters, so the equilibrium reactor (RGibbs) of Aspen is used to simulate the reformer under the known operating temperature and pressure, i.e.

740 °C and 1.9 bars. The RGibbs reaches chemical and phase equilibrium by Gibbs energy minimization. The S/C is 4 and all reactions (5), (7) and (8) are involved in the reformer simulation.

Since steam reforming is highly endothermic and requires a heat supply, a burner is normally used for heating the reformer. Part of the biogas is combusted by the burner and the biogas combustion reaction is shown in equation (19). The $Bio_{reformed}/Bio_{burned}$ in equation (18) is specified by the simulation.

$$CH_4+2O_2 \leftrightarrow CO_2+2H_2O \quad \Delta H^0_{298} = -804 \text{ kJ mol}^{-1} \tag{19}$$

3.1.2 CO removal reactors

Water-CO shift reactor

A high temperature and low temperature water-CO shift reactors follow the steam reformer. The reaction taking place in the reactors is reaction (5). For the high temperature shift reactor (HTSR) the operation temperature is 285 °C in Paper II and 400 °C in Papers I and III and the CO concentration after the HTSR is 2.5 vol.% in Papers I and III and 3 vol.% in Paper II (Larminie et al, 2003; Schmersahl et al, 2007; Hubert et al, 2006; EG&G Technical Services, 2004). For the low temperature shift reactor (LTSR) the operation temperature is 200 °C in Papers I and III and 250 °C in Paper II and the CO concentration after the LTSR is 0.25 vol.% in Paper I and III and 1 vol.% in Paper II (Larminie et al, 2003; Schmersahl et al., 2007; Hubert et al, 2006; EG&G Technical Services, 2004).

PrOx reactor (Papers I and III)

The operation temperature of the PrOx reactor is 120 °C. Since the preferential oxidation of CO is the last step for CO removal in Papers I and III, the CO content is reduced to less than < 10 ppm. For this step, extra oxygen is injected to the PrOx reactor, which is specified by the ratio of $\dot{n}_{O_2}$ to $\dot{n}_{CO}$. $\dot{n}_{O_2}$ is the molar flow rate of oxygen input to the PrOx reactor, and $\dot{n}_{CO}$ is the flow rate of the carbon monoxide after the low-temperature CO shift reactor. $\dot{n}_{O_2}/\dot{n}_{CO}$ is set to 1.5 (Xu et al, 2004; Zhang et al, 2004).

Methanation reactor (Paper II)

Reaction (11) is involved in the reactor simulation and the operating temperature is 220 °C. The CO content after the methanation reactor is less than 20 ppm.

3.1.3 PEM fuel cell

The PEM fuel cell stack model is built rather macroscopically and basically on the basis of mass and energy balance, since the aim of this study is not to simulate the stack in detail. The PEMFC stack model is based on the anode reaction (11) and the cathode reaction (12). In Papers I and III, the stack works at 80 °C and atmospheric conditions. In Paper II, the stack works at 72 °C and 1.34 bar.

H_2 utilisation rate and O_2 utilization rate, as important parameters for the anode and cathode, are defined in Eqs. (20) and (21).

$$\mu_{H_2} = \frac{\dot{n}_{H_2}^{utilized}}{\dot{n}_{H_2}} \times 100\% \tag{20}$$

$$\mu_{O_2} = \frac{\dot{n}_{O_2}^{utilized}}{\dot{n}_{O_2}} \times 100\% \tag{21}$$

where $\dot{n}_{H_2}^{utilized}$ is the molar flow rate of the hydrogen utilised in the anode and $\dot{n}_{H_2}$ is the mole flow rate of hydrogen from the fuel processor. $\dot{n}_{O_2}^{utilized}$ is the molar flow rate of the oxygen utilized in the cathode and $\dot{n}_{O_2}$ is the mole flow rate of oxygen inlet to the cathode. In Papers I and III, μ_{H_2} is set to 80 % and μ_{O_2} is set to 50 % (Schmersahl et al., 2007; Hubert et al, 2006; EG&G Technical Services, 2004). In Paper II, μ_{H_2} is set to 85 %. The H_2 stoichiometry is set to 1.5 and the cathode stoichiometry is set to 2 based on the results of stack testing.

3.1.4 Biogas purifier

Since there is no strong mass transportation and energy conversion for the purification processes, the purifier is not simulated and involved in the mass and energy balance but still included in the system flowsheet to show the complete whole system.

3.1.5 Gasifier

The reactions taking place in the gasifier are listed in Table 4. This is very complicated, so the equilibrium reactor (RGibbs) is chosen to simulate the gasifier. The gasifier temperature is set at 700 ^{o}C which is the hydrogen production optimal temperature (Chutichai et al, 2013). The main parameters of the gasifier are listed in Table 5.

Table 4. Biomass gasification reactions

Char partial combustion	$C + 0.5O_2 \leftrightarrow CO$	ΔH°_{298} = -111 kJ/mol
Boudouard	$C + CO_2 \leftrightarrow 2CO$	ΔH°_{298} = +172 kJ/mol
Water-gas	$C + H_2O \leftrightarrow CO + H_2$	ΔH°_{298} = +131 kJ/mol
Methanation	$C + 2H_2 \leftrightarrow CH_4$	ΔH°_{298} = -75 kJ/mol
CO partial combustion	$CO + O_2 \leftrightarrow CO_2$	ΔH°_{298} = -283 kJ/mol
H_2 partial combustion	$H_2 + 0.5O_2 \leftrightarrow H_2O$	ΔH°_{298} = -242 kJ/mol
Water shift	$CO + H_2O \leftrightarrow CO_2 + H_2$	ΔH°_{298} = -41 kJ/mol
Steam reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	ΔH°_{298} = +206 kJ/mol

Table 5. Input parameters of the gasifier

Pressure	1 bar
Gasifying agent	Steam and air
Steam temperature	200 °C
Steam to biomass ratio (S/B)	0.8
Air temperature	65 °C
Equivalence ratio (ER)	0.19

3.2 Optimization of heat exchanger network

The thermal performance of the PEMFCs systems may be improved by the optimization of the heat exchanger network. In Paper II, the experimental system is scaled up. Figure 2 shows the experimental system and scaled-up system before the optimization of the heat exchanger network in a) and b), respectively.

All of the air-cooled heat exchangers in the experimental system are replaced by counter-counter flow heat exchangers. The motivation for this replacement is

that in the scaled-up system the excess heat in the process streams and fuel cell stack is more substantial than that of the experimental system, thus this excess heat may be recovered for heating the cold streams of the system instead of being released to the atmosphere.

The hot and cold composite curves of the process streams for the scaled-up system in Figure 3 show the heating potential of the excess heat of the scaled-up system. The blue streams are the streams that need to be heated (cold streams) and the red streams are the steams that need to be cooled (hot streams). The black streams in Figure 2 are the process streams that are not involved in the heat exchange. The reactors are not involved in the heat exchange, so they are not included in the curves.

It may be seen from Figure 3 that the excess heat of the process streams and fuel cell stack totally 365 kW which will increase the thermal performance of the whole system significantly if this excess heat could be used elsewhere in the system. By analyzing the temperatures and heat capacities of the process streams and the cooling water of the fuel cell stack, solutions to utilize the excess heat are figured out. The process streams of the fuel processing may be used to preheat and vaporize the water used for the reforming and water gas shift. This steam stream could, together with the biogas for the inlet to the reformer, be further heated with the flue gas from the burner that subsequently is used to preheat the inlet stream to the burner itself, see figure 10. The heat in the PEM fuel cell stack cooling circuit may be extracted to heat the digester. As mentioned in the section on the experimental system, in order to maintain the operation temperature of digester at 36 °C, the electrical heaters are needed to produce the hot water for heating the digestor, consuming the electricity generated by the fuel cell. When the digester is heated by excess heat, the net electrical efficiency of the whole system is improved and also the thermal efficiency.

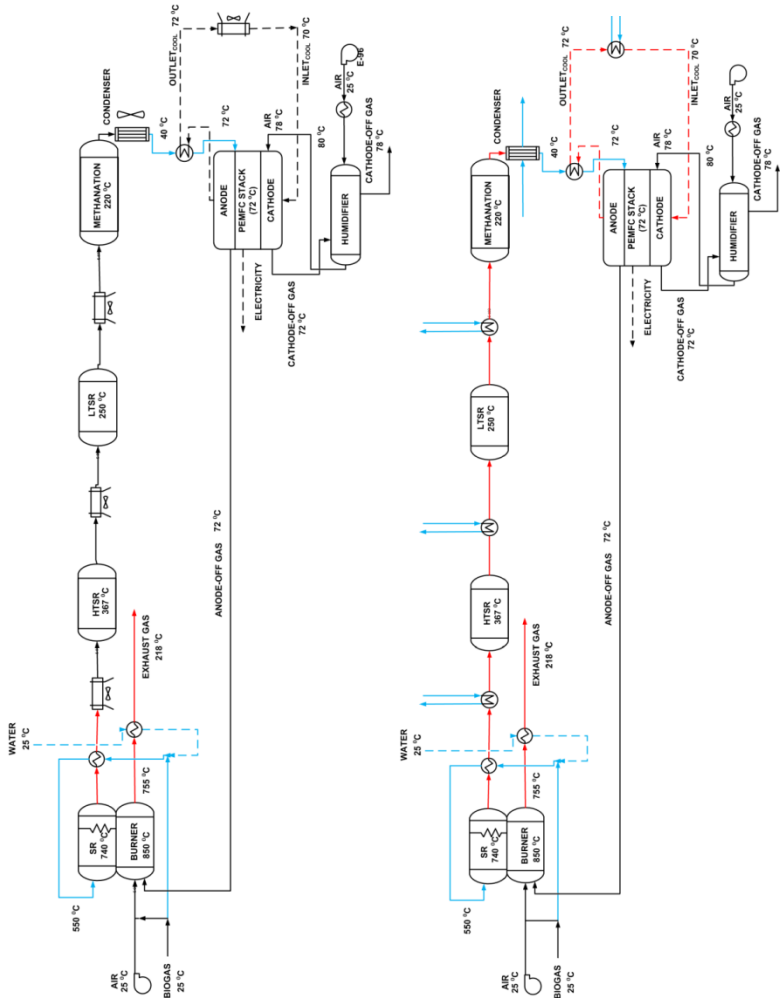


Figure 2. a) Experimental systems in detail [12]

b) Scaled-up system before the optimization of the heat exchanger network

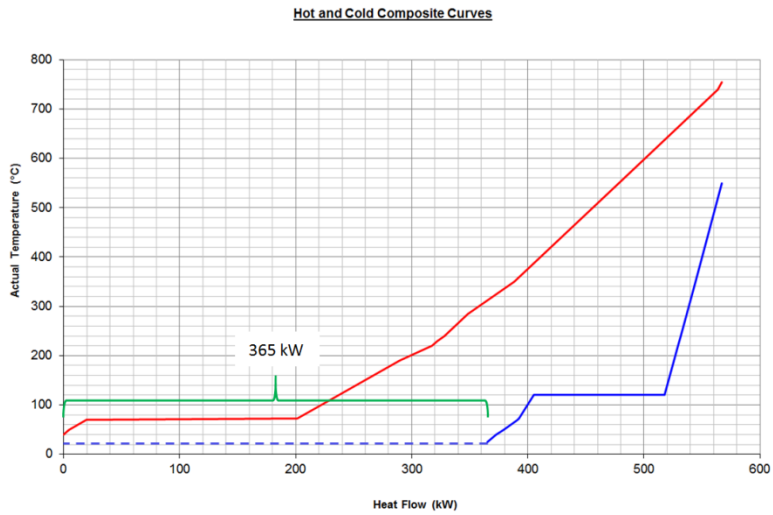


Figure 3. Hot and cold composite curves for the process streams of the scaled-up system before optimization

For the composite curves, it is found that the hot utility is constant at 0 kW, as long as the minimum temperature difference between the curves is 184 °C or less, which implies that it is possible to extract more heat from the high-temperature hot stream, see Figure 3. In the experimental system, the inlets of the steam reformer are heated to 550 °C. Figure 4 shows the Grand composite curve of the scaled-up system if the minimum temperature difference is 30 °C. It may be seen that there is surplus heat in the hot streams above 550 ^{0}C. These high temperature hot streams may heat the inlets of the steam reformer further to approach the operation temperature of the steam reformer, i.e. 740 °C. Hence, the amount of biogas burned to support the reforming reactions may be reduced. In this way, the output power of the stack would be increased.

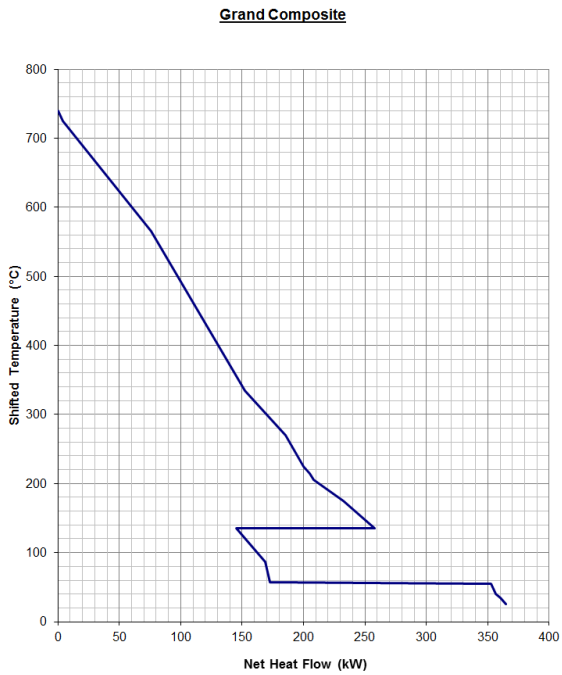


Figure 4. Grand composite curve for the scaled-up system

3.3 Environmental evaluation

The environmental performance of the biomass-fuelled PEMFC is evaluated by the CO_2 offset factor and land-use efficiency. The CO_2 emissions offset of biomass consists of two parts: the CO_2 emissions offset for hydrogen production and CO_2 emissions offset for power generation.

The CO_2 emitted from the hydrogen production via natural gas steam reforming is 10.6 kg/kg H_2 (Spath and Mann, 2001; Bonaquist, 2010). This emission is only the local emission from the hydrogen production plant, not including the upstream such as natural gas production, transportation, and distribution and electricity consumption. Every MJ natural gas consumed produces 0.66 MJ of H_2 (Spath and Mann, 2001).

For a coal-fired plant, the CO_2 emission derives from the combustion of coal. The coal-fired power plant is assumed to have 35 % efficiency from coal to electricity, which is a typical efficiency throughout the world including the Nordic countries (Nuorkivi, 2010; Yu et al, 2014). 1 tonne coal used in a coal-fired power plant emits about 2.6 tonnes CO_2 (IPCC, 2006).

All biomass originates from land but the land area is limited, so it is necessary to evaluate the efficiency of the two systems for land use. The forest residues come from woods while wet manure needs arable land to produce fodder for cows. In Sweden, the arable land area for fodder production is 1 ha/cow livestock unit on the average. One livestock unit corresponds to one dairy cow including one calf, or six calves, or 3 heifers. Based on a previous study (Guan et al, 2014), for 100 kWe, 670 cows, 400 heifers and 270 calves are needed for the manure production for the studied process unit. In the Swedish forestry industry, 9.3 % of the raw wood material will become forest residues corresponding to 270 kg/ha yearly (http://www.forestindustries.se/, accessed on Sep 26, 2013; Cederberg et al., 2004).

3.4 Economic evaluation

In Paper IV, the capital cost for PEM fuel cell systems use the annuity method with an interest rate of 6 % (Hansson, 2007; Nyström, 2011). The system lifetime is assumed to be 20,000 h. The fuel cost, i.e. the cost of hydrogen and biogas, is assumed to have the same price per MWh energy as natural gas. For natural gas the average price of the previous years is used (SCB, 2011). The data used in the calculations are collected from literature (Goddard, 2012; Fuel Cell Bull., 2009; Roads2HyCom, 2011; Millett, 2005; NREL, 2010; Tashima, 2011; Tadashi, 2012), personal interviews (Van der Meer, 2011; Rolf, 2011; Honselaar, 2011), technical reports (Remick, 2010; Vogel, 2009; Vogel, 2010) and product brochures (FuelCell Energy, 2011; ENE-FARM, 2011; Panasonic, 2011). In Paper V, for the biogas plant, the capital cost is calculated using the annuity method with an interest of 5 % and 20 years depreciation (Lantz, 2012). The investment of the biogas plant depends on the size of the reactor, which corresponds to 450-600 €/m^3 **(**Lantz, 2012**)**.

4 Results and discussion

4.1 Composition of the reformate gas

Based on the system design in Paper I, the gas compositions of the main streams throughout the system are shown in Figure 5. After the SR reactor, biogas is converted to a H_2-rich gas diluted by CO_2, unreacted CH_4 and undesirable CO. Since the PEMFC will be extremely poisoned by CO, the HTS, LTS and PrOx are used to decrease the CO to less than 10 ppm. After the PrOx step, the prepared reformate gas is fed to the anode of the PEMFC with the composition of 69 % H_2, 29 % CO_2 and a small amount of CH_4. Because of the presence of CO_2, the reformate gas will decrease the performance of the fuel cell as compared to pure hydrogen. However, it has been proven that reformate gas with a hydrogen content of 60 % is sufficient for efficient and stable operation of a PEMFC stack (Schmersahl et al, 2007). The presence of CO_2 will lead to a small voltage drop because of the reverse water gas shift (RWGS) reaction, but it will not decrease the electrical efficiency very much (Hedström et al, 2009; Nachiappan et al, 2013). Therefore, the quality of the reformate gas is good enough to support normal operation of the PEMFC-CHP. Most of the hydrogen in the reformate gas is consumed by the electrochemical reactions in the anode, but there is still around 8 % H_2 left in the anode-off gas. In order to increase the thermal efficiency of the system, the anode-off gas is recirculated to the burner for supporting the steam reformer.

For the biomass-based PEM fuel cell systems, the reformate gas composition varies for the different biomass conversion methods when using different kinds of biomass. AD-PEMFC combines anaerobic digestion and steam reforming to convert liquid biomass such as manure to the reformate gas. GF-PEMFC converts the solid biomass such as wood to reformate gas by gasification. Table 6 shows the composition of the reformate from the two systems.

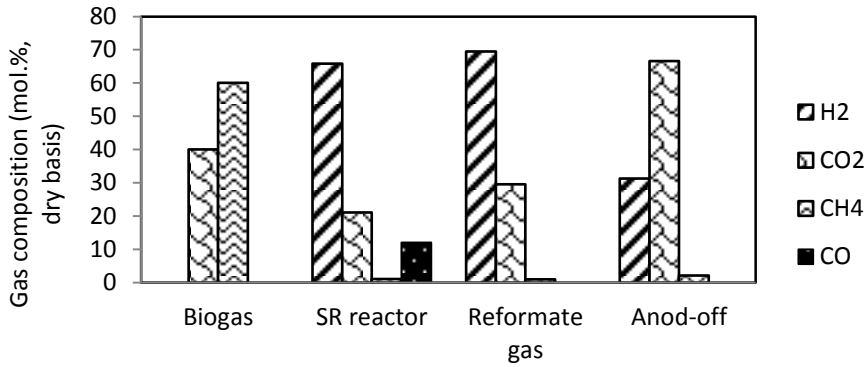


Figure 5. Composition of the biogas, the gas after the SR reactor, the reformate gas, the gas after the anode (Paper I)

As can be seen, the reformate gases of AD-PEMFC and GF-PEMFC contain 70 % and 39 % H_2, respectively. The reformate gas of the AD-PEMFC is diluted by CO_2 from the biogas, the steam-reforming and CO removal reactions. The reformate gas of the GF-PEMFC is diluted by CO_2 and N_2. The CO_2 comes from the gasification and CO removal reactions. The N_2 is derived from air as gasifying agent. The H_2 content in the reformate gas from the GF-PEMFC is much less than that of the AD-PEMFC, but it has been proven that stable operations of a PEMFC stack could be achieved when fuelled with reformate gas containing around 30 to 60 mol. % H_2 (Schmersahl et al, 2007; Cutillo et al, 2006).

Table 6. Composition of the reformate to the anode (dry basis) (Paper III)

Component	AD-PEMFC (mol. %)	GF-PEMFC (mol. %)
H_2	70	39
CO_2	29	27
N_2	0.29	34
CO	<10 ppm	<10 ppm
CH_4	0.36	0

There is much CO_2 present in both of the reformates. As discussed previously, the presence of CO_2 in the fuel will lead to a slight voltage drop due to the dilution of H_2 as well as the CO reformation from the reverse water gas shift (RWGS) reaction (Nachiappan et al, 2013). Moreover, experimental results

indicate that even when the CO_2 content is doubled from 23 % to 50 %, the stack performance just drops by less than 2 % (Hedström et al, 2009). Besides CO_2, the reformate of the GF-PEMFC is also diluted by N_2 which has a smaller negative effect on the stack performance than CO_2 (Nachiappan et al, 2013). Therefore, although the impurities in the reformate gas of both AD-PEMFC and GF-PEMFC decrease the performance, these reformate gases are employable for PEMFCs and can make the operation stable.

4.2 Impact of anode stoichiometry, CH_4 conversion rate and CH_4 content of the biogas on the system performance

4.2.1 Anode stoichiometry

Anode stoichiometry is an essential parameter, since it impacts significantly on the stability and efficiency of PEM fuel cell system. In Paper II, anode voltage was tested with increasing anode stoichiometry by the company Powercell and 1.5 is suggested by Powercell as the standard figure. However, it was observed from the results of the anode sweep experiment that when the anode stoichiometry was 1.3, the cell voltage was still stable (Biogas2PEM-FC, 2015). Therefore, in order to increase the performance of the PEM fuel cell stack, the experimental system is simulated in Paper II to check the electricity generation and system performance while the anode stoichiometry is chosen as 1.3, 1.35, 1.4, 1.45 and 1.5, respectively. The results are shown in Figures 6 and 7.

As shown in Figure 6, since the hydrogen consumption of the stack is consistent, when the hydrogen input to the anode is reduced, the hydrogen utilization rate becomes higher while the hydrogen content in the anode-off gas is decreased significantly. Because of the less energy contained in the anode-off gas, the burner requires more combusted biogas to sustain the energy balance between the steam reformer and burner. For a fixed amount of biogas input, more combusted biogas means less reformed biogas. Eventually the hydrogen production is reduced by 1000 mole/ h and then the power output, as shown in Figure 7, is just increased slightly by 5 kW although the anode stoichiometry has dropped from 1.5 to 1.3. The electrical efficiency is likewise increased slightly. The system net electrical efficiency and fuel processor efficiency are almost unchanged. Therefore, for this scaled-up system, decreasing the anode surplus would not improve the electricity generation greatly, so an anode stoichiometry of 1.5 is still appropriate for stable system performance.

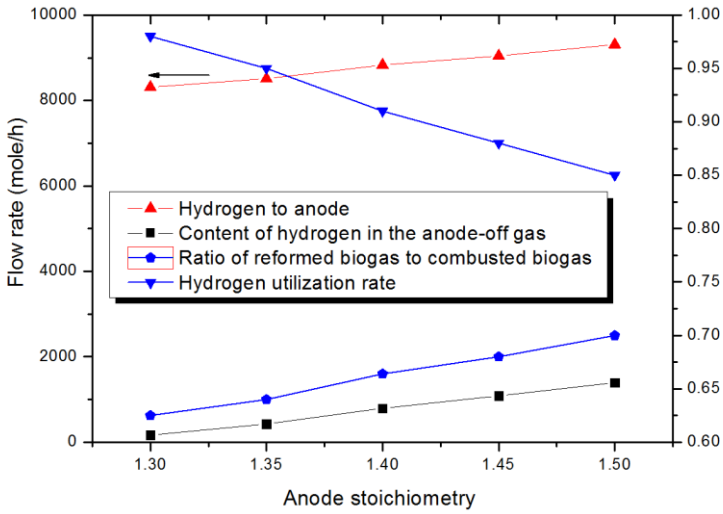


Figure 6. Impact of the anode stoichiometry on the system mass flowrate

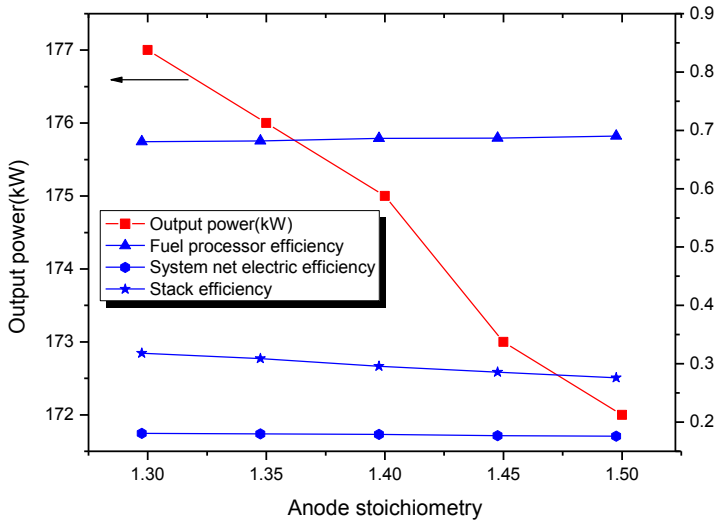


Figure 7. Impact of the anode stoichiometry on the system performance

4.2.2 CH_4 conversion rate and its content in the biogas

The CH_4 conversion rate (μ_m) and the CH_4 content in the biogas play key roles in the system performance. The CH_4 conversion rate of biogas in the SR reactor assumed in this study could vary from 90 % to the 98 %; for the biogas from agricultural waste, the CH_4 content could vary from 60 % to 75 % (Scholz et al, 2011;Schmersahl et al, 2007). In order to investigate the effect of these variations on the system performance, a sensitivity analysis was made and the results are shown in Table 7. Three scenarios are discussed to compare with the conditions in Paper I.

Comparing the conditions in Paper I with scenario 1, it is found that when the CH_4 conversion rate is fixed, the higher the CH_4 content in the biogas, the higher the hydrogen production and the lower the required electrical efficiency. The same result holds when scenario 2 is compared with scenario 3. Moreover, comparing the conditions in Paper I with scenario 2, when the CH_4 content is fixed at 60 %, the increased CH_4 conversion rate also contributes to a better system performance. However, the increased CH_4 conversion rate does not always have a positive effect on the system performance. Comparing scenarios 1 and 3, when the CH_4 content is set to 75 % and CH_4 conversion rate increased from 90 % to 98 %, the system performance is consistent and not improved. Although the higher CH_4 content and the increased CH_4 conversion rate raises the hydrogen content in the reformate gas after the SR reactor, they also reduce the energy content of the anode-off gas. The reformed biogas in the SR reactor is reduced because more biogas is burned in the burner to support the SR reactor. Therefore, the higher CH_4 content and CH_4 conversion rate may not always lead to a better performance.

Table **7** Effect of the CH_4 conversion rate and CH_4 content in the biogas on the system performance (Paper I)

The parameters	This study	Scenario 1	Scenario 2	Scenario 3
μ_m, %	98	98	90	90
CH_4 content in the biogas(%)	60	75	60	75
Bio_{ref}/Bio_{bur}	0.75:0.25	0.73:0.27	0.73:0.27	0.8:0.2
The power of the biogas (kWh)	160	201	160	201
$\dot{n}_{H_2}$	2.09	2.574	1.891	2.59
η_f	74	73	64	70
$\eta_{PEMFC,el}$	40	32.5	44	32
Heat availability (kWh)	86	103	88	102

4.3 Heat exchanger network optimization for the scaled-up system by using pinch technology

In Paper II, based on the analysis of the composite curves and the grand composite curve in Figures 3 and 4, the optimization of the heat exchanger network of the scaled-up system is implemented by simulation. The scaled-up system after optimizations is shown in Figure 8.

The process streams of the fuel processor are used to preheat the water for steam generation. The flue gas of the burner is a high-temperature hot stream which is used to heat the mixture of biogas and steam to 724 °C before they are fed into the steam reformer. The remaining heat in the flue gas is used to preheat the inlets of the burner to 145 °C. The cooling water of the PEM fuel cell stack is used to heat the digester. This will have a significant impact on the system performance, since the heat demand of the digester corresponds one fourth of the energy contained in the produced biogas. For the scaled-up system the biogas production is 783 kW and then the heat demand in the digester is equal to 196 kW. The temperature of the cooling water before and after the fuel cell stack is 70 °C and 72 °C, respectively, a this temperature difference which may supply the 196 kWh heat for the digester.

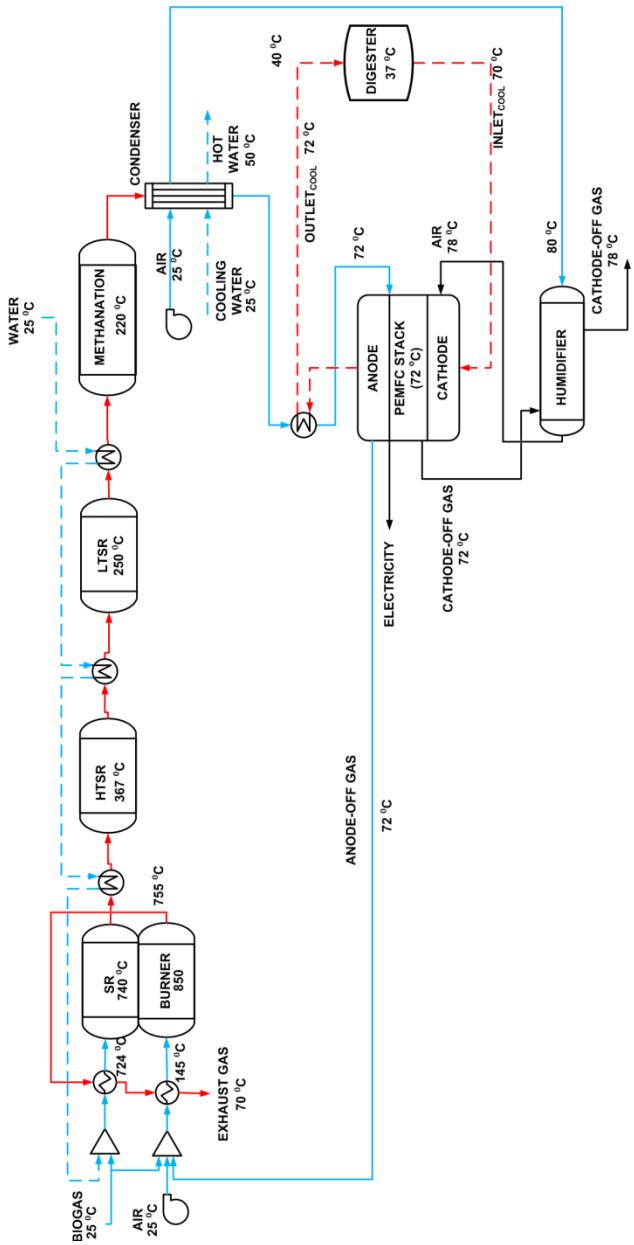


Figure 8. Scaled-up system after the optimizations of the heat exchanger network

4.4 System performance

Since the aims and applications are different, there are three kinds of system design in Papers I, II and III. Here, the performance of each system design is briefly presented. The details can be found in the papers.

4.4.1 System performance from Paper I

The system in Paper I which is shown in Figure 9 is designed to figure out the appropriate electrical efficiency of the PEM fuel stack to satisfy electrical and thermal power demand of a dairy farm. The main operating conditions and results are presented in Table 8.

Biogas flowrate is identified based on the biogas production of the biogas plant which utilizes the manure from the milk cows in the dairy farm for biogas production. Since steam reforming is highly endothermic, 25 % of the biogas is burned to supply the heat needed for this reaction. P_e is the power generated by the PEMFC stack, which includes the power demand of the dairy farm, the biogas plant and the balance of plant. P_h is the heat recovered from the flue gas of the burner, the cathode-off gas and the cooling water of the stack. The required electrical efficiency of the PEMFC stack ($\eta_{PEMFC,el}$), the system electrical efficiency (η_{elec}), the thermal efficiency of the fuel processor (η_f), the system thermal efficiency (η_{ther}) and the total system efficiency (η_{total}) are calculated according to Eqs. 22-26:

$$\eta_{PEMFC,el} = \frac{P_e}{\dot{n}_{H_2} \times LHV_{H_2} \times \mu_{H_2}} \times 100\% \quad (22)$$

$$\eta_f = \frac{\dot{n}_{H_2} \times LHV_{H_2}}{\dot{n}_{biogas} \times LHV_{biogas} + \dot{n}_{anode-off} \times LHV_{anode-off}} \times 100\% \quad (23)$$

$$\eta_{elec} = \frac{P_e}{\dot{n}_{biogas} \times LHV_{biogas}} \times 100\% \quad (24)$$

$$\eta_{ther} = \frac{P_h}{\dot{n}_{biogas} \times LHV_{biogas}} \times 100\% \quad (25)$$

$$\eta_{total} = \eta_{ther} + \eta_{elec} \quad (26)$$

where $\dot{n}_{H_2}$ is the mole flow rate of hydrogen from the fuel processor, LHV_{H_2} is the lower heating value of hydrogen and μ_{H_2} is the utilisation rate of hydrogen

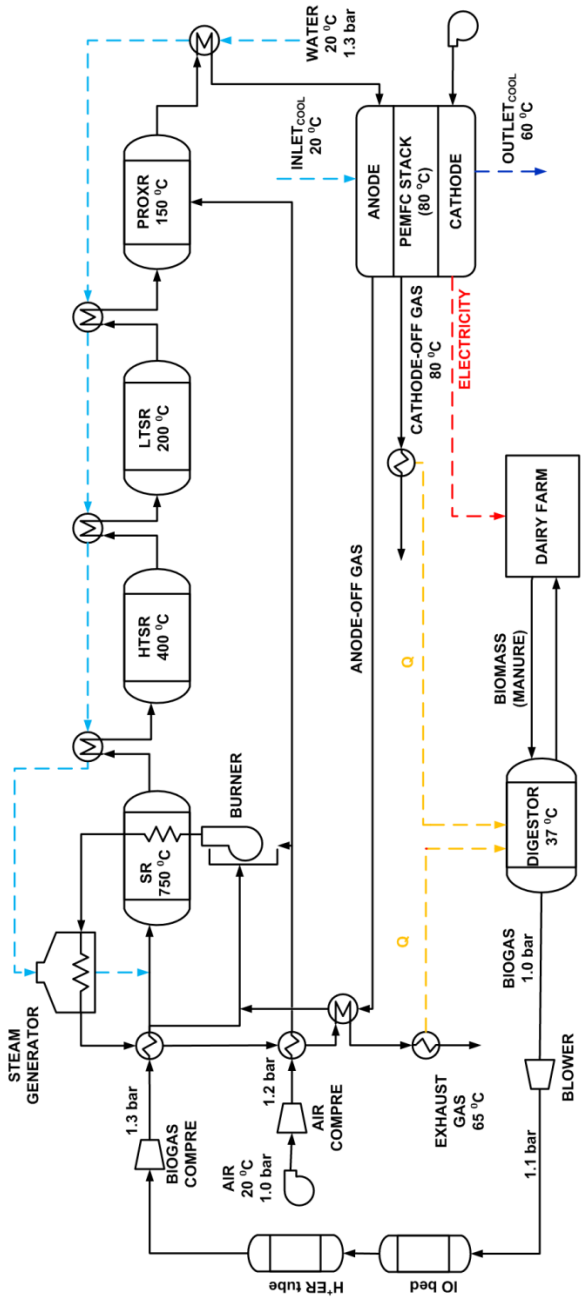


Figure 9. Flow sheet of the integrated system (Paper I)

Table 8 Main operating conditions and results of the PEMFC-CHP

Characteristics	Value
Biogas/ CH_4, kmol/h	1.20/0.72
kW	160
Bio_{ref}/Bio_{bur}	3: 1
Water, kg/hr	45
$\dot{n}_{H_2}$, kmol/hr	2.1
P_e , kW	45
P_h , kW	86
$\eta_{PEMFC,el}$	40
η_f	74
η_{ther}	54
η_{elec}	28
η_{total}	82

in the anode. The product of $\dot{n}_{anode-off}$ and $LHV_{anode-off}$ represents the lower heating value of the anode-off gas which includes H_2 and CH_4; $\dot{n}_{biogas}$ is the mole flow rate of biogas from the biogas plant, and LHV_{biogas} is the lower heating value of the biogas.

The results indicate that with an electrical efficiency of 40 % the PEMFC stack can generate the amount of electricity required by the dairy farm, biogas plant and the balance of plant. This figure may be seen as the boundary condition of the system's self-sufficiency. Although for a PEMFC fed with pure hydrogen, the electrical efficiency is in the range of 40 %-60 %, this electrical efficiency is not so easy to achieve when fed with reformate from biogas. However, taking into account future improvements in reforming and stack technology 40 % electrical efficiency may be achieved with proper design of the system (Schmersahl et al, 2007; Office of Energy Efficiency & Renewable Efficiency, 2007). The calculations of efficiencies and the energy balance of the whole system are obtained straightforwardly from the Sankey diagram in Figure10.

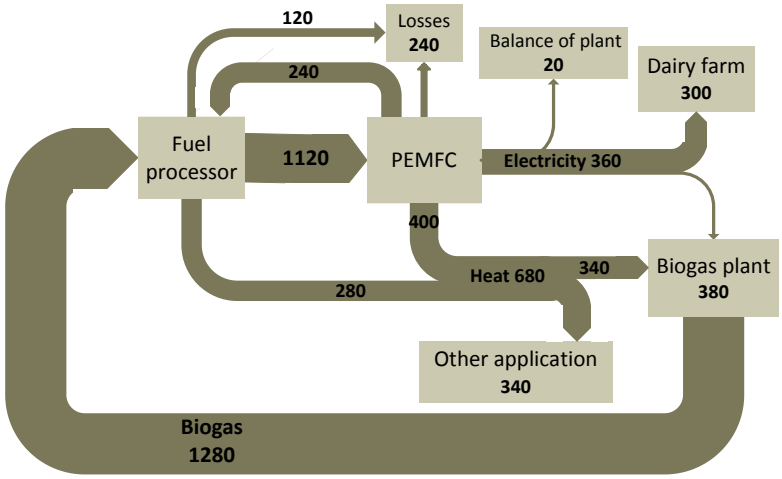


Figure 10. Sankey diagram of the integrated system

As shown in Figure 10, the gross biogas production is 1280 MWh/year and that is the total energy supply from the integrated system. The biogas is converted to hydrogen-rich gas by the fuel processor which is heated by the burned biogas and 240 MWh of heat from the anode-off gas. Using the hydrogen-rich gas, the PEMFC generates 360 MWh electricity and 80 % of this electricity is consumed by the dairy farm. The heat extracted from the flue gas of the burner, the cathode-off gas and the cooling water of the stack amount to 680 MWh which is twice the heat demand of the biogas plant. It is assumed that 50 % of the heat in the cooling water evacuated from the stack is recovered (Larminie et al, 2003). The surplus heat may be used by other applications such as heating the drinking water for the cows in the winter and the farmer's house. The overall energy from the integrated system is 1040 MWh which is enough to make this whole system self-sufficient. The losses are mostly in the form of the heat from the fuel cell stack and the fuel processor.

4.4.2 System *performance from Paper II*

In Paper II, a scaled-up system is simulated based on the experimental parameters and results of the project Biogas2PEM-FC which built an experimental system for a 1kW PEMFC system using the biogas produced from olive oil residues as fuel. The heat exchanger network of the scaled-up system is

optimized by using pinch technology. The scaled-up system after this optimization has been shown in Figure 8.

Table 9 lists the parameters for describing and comparing the system performance before and after the optimizations. Attributable to utilizing the process streams of the fuel processor for the steam generation, the power generation of the scaled-up is increased as well as the hydrogen production. After the optimization of the heat exchange network, the electricity generation is increased from 172 kW to 194 kW, whereas the net electrical efficiency is increased from 17.58 % to 19.82 %. The ratio of the reformed biogas to the total biogas is increased, which contributes to increasing of the flowrate of H_2 by 1000 mole/h. The thermal efficiency of the fuel processor is improved by 7 % because of the higher H_2 production.

Table 9 Comparison of the scaled-up system performance before and after optimizations

Parameters	Before	After
Anode stoichiometry,	1.5	1.5
Biogas, mole/h/kWh	5400/783	5400/783
The ratio of reformer biogas to total biogas inlet, mole/h	0.7	0.788
The flowrate of the H_2 to anode, mole/h	9309	10479
Anode-off gas, CH_4, mole/h	130	146
H_2, mole/h	1396	1572
Hydrogen utilization	0.85	0.85
Output electricity, P_{el}, kW	**172**	**194**
Output heat, P_{heat}, kW	**0**	**269**
η_{FP}, %	69.01	76.23
η_{PEMFC}, %	27.58	27.64
$\eta_{gross-el}$, %	21.97	24.78
η_{net-el}, %	17.58	19.82
$\eta_{thermal}$	0	34.36
η_{total}	21.97	54.18

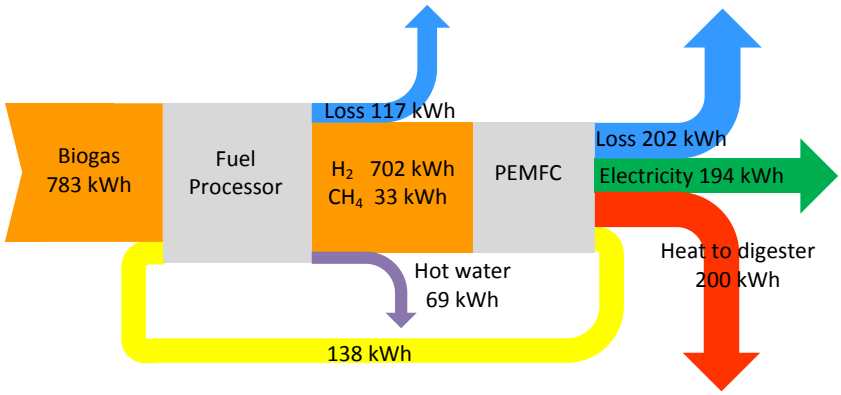


Figure 11. Sankey diagram of the optimized system

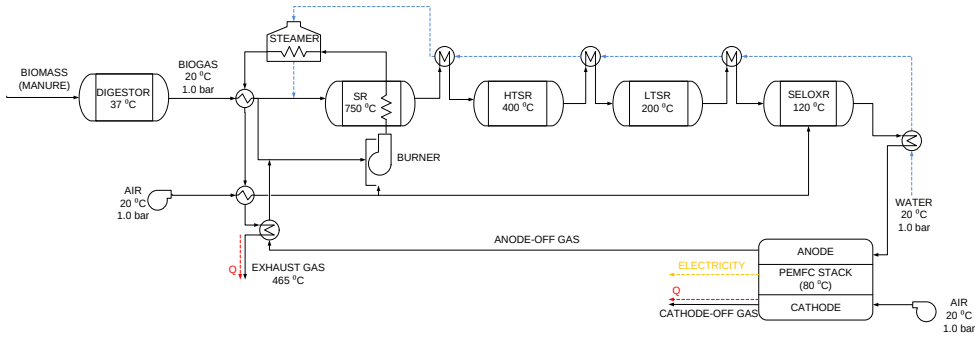
Figure 11 shows the Sankey diagram of the scaled-up system after optimization, which illustrates the energy balance explicitly. The heat supplied to the digester from the cooling water of the stack is around 200 kW, which is considered the external application of the recovered heat. The 69 kW of the heat released from the condenser is used to produce 50 ℃ hot water, 2600 kg/h, which may be used for an external application such as the olive processing in the olive oil plant. Based on the definition of the thermal efficiency, this excess heat corresponds to 34.36 % of the system thermal efficiency. Taking into account the electricity production, the total system efficiency is 54.18 %. The total system loss is 319 kW, 60 % of which is released from the stack in the form of heat.

4.4.3 System performance from Paper III

Paper III aims to summarize the performance of the biomass-fueled PEM fuel cell systems which includes the AD-PEMFC and GF-PEMFC shown in Figure 12. The AD-PEMFC converts biomass to reformate gas, so the conversion efficiency of anaerobic digestion is involved in the system performance. Both of the systems are designed for 100 kWe generation.

Performance of the anaerobic digestion (AD)

AD generates the biogas for the steam reforming (SR) for hydrogen generation. η_{AD} indicates the conversion efficiency from biomass to biogas, which is defined in Equation (27). In order to evaluate the performance of the AD, its energy balance is presented in Table 10.



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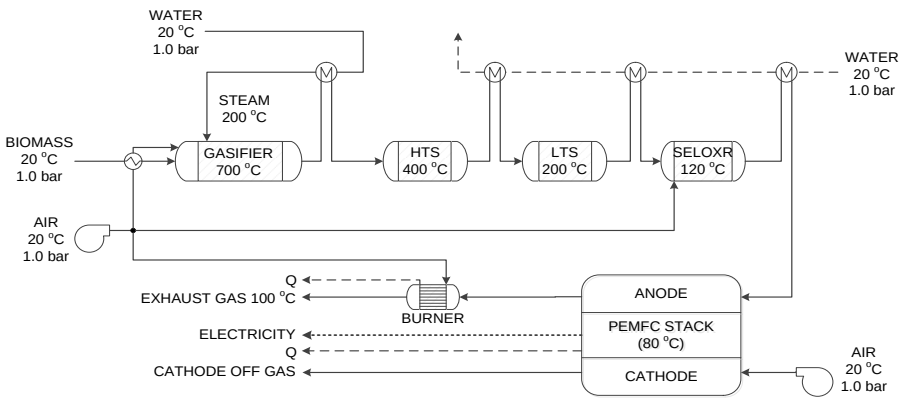


b)

Figure 12. a) Schematic diagram of an AD-PEMFC

b) Schematic diagram of a GF-PEMFC

Table 10. Energy balance of the AD

Biomass consumption, MWh/year	8587
Biogas production, MWh/year	2688
Heat demand, MWh/year	672
Electricity demand, MWh/year	81
Efficiency of AD (η_{AD}), %	29

$$\eta_{AD} = \frac{\text{Biogas production (LHV)}}{\text{Biomass (LHV)+Heat demand+Electricity demand}} \quad (27)$$

Cow manure is used as the feedstock for the AD. The operation of the anaerobic digestor needs heat for maintaining the temperature and electricity for mixing the feedstock. The calculated η_{AD} is 29 %.

Performance of fuel processor (FP)

The performance of the FP is evaluated by its thermal efficiency. The general definition of the fuel processor efficiency is given by equation (28). For the AD-PEMFC system, the energy output is the LHV of the produced hydrogen and the energy input includes the LHV of the manure, the heat and electricity demand of digester and the anode-off gases. For the GF-PEMFC system, the output includes the LHV of the produced hydrogen and also the heat recovered from the purification steps for the external application. The energy input is the LHV of the wood residues.

$$\eta_{\mathrm{f}} = \frac{\text{Energy output (LHV)}}{\text{Energy input (LHV)}} \times 100\% \quad (28)$$

The fuel processor efficiency for the AD-PEMFC system is 25 % but for the GF-PEMFC it is 75%. The AD-PEMFC has low efficiency because, on the one hand, the η_{AD} is relatively low, and, on the other hand, the recovered heat and fuel from the processes are used internally to maitain the temperature of the digestor and the SR, respectively.

System performances of AD-PEMFC and GF-PEMFC

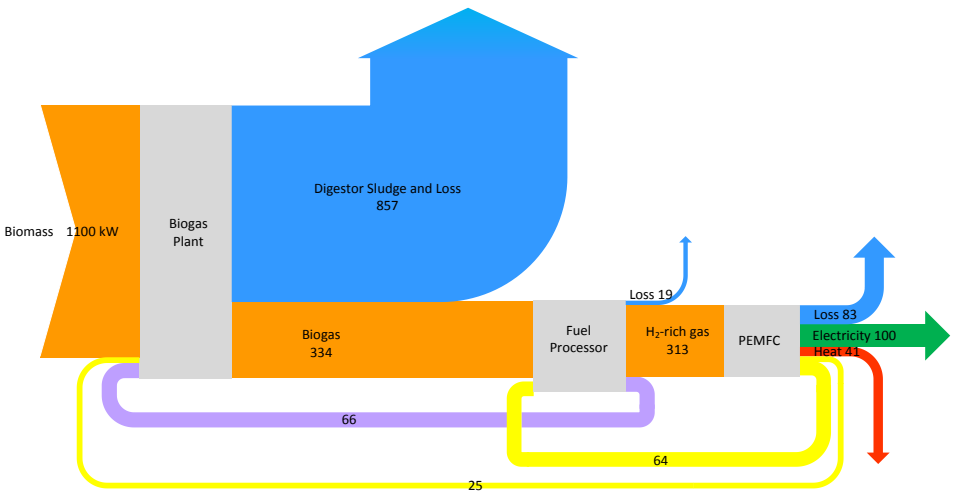
The performance of the two systems is evaluated by the conversion rate from biomass to electricity, the system electrical efficiency, the system thermal efficiency, the total system efficiency. The efficiencies are defined by equations (29)-(32) which may be calculated using the Sankey diagram shown in Figure 13.

$$\mu_{bio\rightarrow ele} = \frac{\text{Electricity generation(MWh)}}{\text{Biomass (LHV)}} \tag{29}$$

$$\eta_{\text{elec}} = \frac{\text{Net electricity produced from the system}}{\text{Input biomass (LHV)}} \tag{30}$$

$$\eta_{\text{heat}} = \frac{\text{Net heat produced from the system}}{\text{Input biomass (LHV)}} \tag{31}$$

$$\eta_{\text{total}} = \eta_{\text{heat}} + \eta_{\text{elec}} \tag{32}$$



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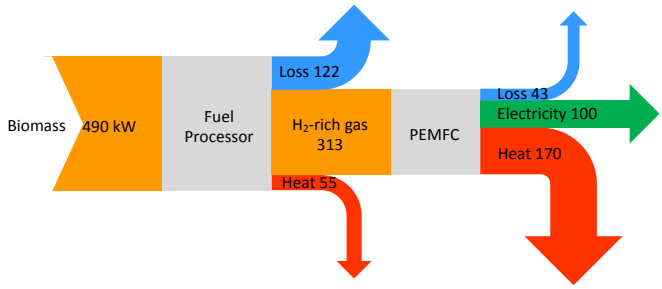

b)

Figure 13. Sankey diagrams for a) AD-PEMFC and b) GF-PEMFC

The calculated results are listed in Table 11. Clearly, the AD-PEMFC is less efficient than the GF-PEMFC which is mainly attributed to the poor η_{AD}. It can be seen from the Sankey diagram of the AD-PEMFC that after the anaerobic digestion a large part of the energy of the manure remains in the digestate. Moreover, the larger internal heat demand of the AD-PEMFC is another reason for the poor η_{heat}. The recovered heat and fuel from the fuel processing and PEMFC of the AD-PEMFC are mainly consumed by the AD and SR, not supplied for external use. For the GF-PEMFC, the heat is recovered from the FP streams, the anode-off gas and stack cooling. A burner is used to convert the anode-off gas to heat for external use. The heat to power ratio, an important parameter of a CHP system, is also presented here for suitable application.

Table 11. Energy efficiency results of an AD-PEMFC and a GF-PEMFC

	AD-PEMFC	GF-PEMFC
Conversion rate from biomass to electricity [a], kWh/tonne	362	1220
System electrical efficiency (η_{elec}), %	9	20
System thermal efficiency (η_{heat}), %	4	57
Total system efficiency (η_{total}), %	13	77
Heat to power ratio	0.44	2.85

[a] Dry basis.

4.5 Application of a biomass-fueled PEMFC system

In this thesis, the biomass-fueled PEM fuel cell systems are designed for the various biomass sources and energy demands and applied in different locations. Each application has specific system considerations and issues.

4.5.1 System application to a dairy farm (Paper I)

In Paper I, the PEMFC system is designed for a dairy farm, which aims to make the farm to be operated self-sufficient by utilizing the biogas and PEM fuel cell system. In order to identify the size of the fuel cell system, the energy demand of the dairy farm and the energy balance of the anaerobic digestor are specified.

On Swedish dairy farms, the annual energy use of a single milked cow is 1240 kWh (Neuman, 2008; Hörndahl, 2008). The cow manure may be delivered to a biogas plant as feedstock for biogas production. Since the digester needs to be maintained at 37 ^{0}C for about 20-40 days to complete the anaerobic digestion process, heat is needed to keep the temperature of the digester. Normally, part of the biogas is combusted to supply the heat, which is about 25 % of the gross production of biogas (Edström et al, 2008; Brown et al, 2009; Brown et al, 2010). There is a small electricity demand for the operation of the digester, which corresponds to 0.03 kWh/kWh biogas (Edström et al, 2008; Brown et al, 2009; Brown et al, 2010). Based on the above information, the calculated results concerning the dairy farm and the biogas plant are shown in Table 12 when the size of the dairy farm is set to 300 milked cows, 180 heifers and 120 calves (Agri, 2012; Lantz, 2012).

Table 12 Calculated results of the dairy farm and biogas plant

Dairy farm	
Manure production, tonne/yr	9280
Electricity consumption, MWh	300
Biogas plant	
Gross biogas production, Nm^3/yr/MWh	232000/1280
Electricity consumption, MWh	40
Heat consumption, MWh	348

The manure production of 300 milked cows with heifers and calves can yield 1280 MWh biogas. The electricity demand of the dairy farm and biogas plant is 340 MWh, which means the size of fuel cell system should at least be 42.5 kW.

The system is assumed to run for 8000 hours per year. The possibility of the PEM fuel cell system to convert the 1280 MWh biogas to 42.5 kW electricity is the question investigated by Paper I. After system simulation, analysis and discussion, it is concluded that with 40 % electrical efficiency, the PEM fuel cell system may make the dairy farm self-sufficient. The 40 % electrical efficiency is not easy to achieve currently for a reformate-fuelled PEMFC, but taking into account the improvements in reforming and stack technology this requirement may be satisfied in the near future.

4.5.2 System application in olive oil plant (Paper II)

In Paper II, the PEM fuel cell system is designed for an olive oil plant for converting the olive oil mill waste to electricity. A 1kW PEM fuel cell system fueled by the biogas produced from the olive oil mill waste had shown the positive results through a series of experiments. In order to apply this fuel cell system to the olive oil plant, the experimental system needed to be scaled up based on the olive oil mill waste of one season. The related data concerning the olive oil plant is collected in Table 13.

Table 13 Facility technical data concerning the olive oil plant (Biogas2PEM-FC, 2015)

Work period per season	Nov to May (240 days)
Olives processed per season	51000 ton
Olive oil production per season	10 000 000 L
SOMW produced per season	50 000 m^3
OMW produced per season	9 000 m^3
Electricity consumption per season	1 800 000 kWh/313 kW

Based on the production of the olive oil waste, the biogas yield can be found out. In order to increase the biogas production of the waste, pig manure was chosen as the co-substrate for the anaerobic digestion. The biogas production is determined by the experiment. The ratio of the olive mill waste (SOMW+OMW is denominated O) to pig manure (P) in the substrate is 1, and the ratio of the SOMW to OMW is 1 as well. The experimental results indicated that the average biogas production for 1P:1O for continuous mode is 18.75 m^3/m^3 substrate (Biogas2PEM-FC, 2015). Combining the information above, the biogas yield is calculated to be 675 000 per season and the biogas flow rate for the PEMFC system is 120 m^3/h when the system runs 24 hours per day. For 120 m^3/h biogas, the experimental system is scaled up to 194 kW by system simulation and

optimization. Therefore, the PEM fuel cell system can supply 62 % of the electricity demand of the olive oil plant, i.e. 313 kW.

4.6 Environmental impacts of biomass-fueled PEM fuel cell systems

In Paper III, the environmental impacts of the biomass-fuelled PEM fuel cell systems are summarized in terms of the CO_2 emission reduction, fossil-fuel saving, and land-use efficiency. The sizes of the systems are 100 kWe.

4.6.1 CO_2 emissions offset factor

The CO_2 emission offsets of biomass-fuelled PEMFC systems are shown in Table 14. For the AD-PEMFC and the GF-PEMFC, since they have equal electricity generation, their total hydrogen production, natural-gas saving, coal saving and CO_2 reduction are the same. The annual CO_2 emission reduction from the hydrogen production is 100 tonnes more than that from the power generation. For the CO_2 emissions offset for every ton biomass, the results for these two systems are significantly different. The AD-PEMFC system has a quite low CO_2 emissions offset factor compared to the GF-PEMFC, due to the low conversion rate from manure to hydrogen and electricity and also the low energy density of wet manure.

Table 14. CO_2 emissions offset of biomass-fuelled PEMFC systems

	AD-PEMFC	GF-PEMFC
Biomass consumption[a], t/year/MWh/year	18 400/8 587	820/3 955
Hydrogen production[d], tonnes/year	76	
Electricity production, MWh/year	800	
Coal-saving[b], tonnes/year	300	
Natural-gas saving[c], tonnes/year	304	
CO_2 emissions reduction for power generation, tonnes/year	700	
CO_2 emissions reduction for hydrogen production, tonnes/year	805	
CO_2 emissions offset factor for hydrogen production, kg CO_2/t biomass	43	982
CO_2 emissions offset factor for power generation, kg CO_2/t biomass	38	854
Total CO_2 emissions offset factor, kg CO_2/t biomass	81	1836

[a] the energy content of wood pellets is 4.8 kWh/kg=17 GJ/t (M Cocchi, 2012).
[b] 1 kg coal corresponds to 8.141 kWh, 29.3 MJ.
[c] 1 kg CH_4 = 45 MJ = 12.5 kWh
[d] 1 kg H_2 = 423.3 scf gas = 11.126 Nm^3 gas=120 MJ =33 kWh (Spath and Mann, 2001)

4.6.2 Land-use efficiency for electricity production and CO_2 reduction

For AD-PEMFC system, wet manure needs arable land to produce fodder for cows. In Sweden, the arable land area for fodder production is 1 ha/cow livestock unit on the average (Cederberg et al, 2004). One livestock unit corresponds to one dairy cow with one calf, or six calves, or 3 heifers (Cederberg et al, 2004). Based on a previous study, for 100 kWe generation, 670 cows, 400 heifers and 270 calves are needed for the manure production (Guan et al, 2013). For GF-PEMFC, the forest residues come from forestry industry. In the Swedish forestry industry, 9.3 % of the raw wood material will become forest residues corresponding to 270 kg/ha yearly (Skogs industrierna, 2013; SLU, 2013).

Table 15 shows the results of the calculations of the land-use efficiency for electricity production and CO_2 reduction. It indicates that the AD-PEMFC system has much better land-use efficiency than the GF-PEMFC system, which means the AD-PEMFC system generates more electricity and makes a greater contribution to CO_2 reduction per unit area of land.

Table 15. Land-use efficiency

	AD-PEMFC	GF-PEMFC
Land use, ha	900	2500
Land-use efficiency for electricity generation (kWh/ ha /year)	750	313
(W/ha)	90	40
Land-use efficiency for CO_2 reduction (kg/ha)	778	280

4.7 Economic analysis (Paper IV and V)

Excluding the fuel cost and heat credit from the final results of Paper IV, the net cost of PEM fuel cell systems for electricity generation may be obtained as 340 €/MWh_{el} for the year 2010 and 210 €/MWh_{el} for the year 2020. The biogas production cost obtained from Paper V is 39 €/MWh_{el}. The electrical efficiency of the PEMFC is assumed to be 20 % and 40 % for the years 2010 and 2020,

respectively **(**Schmersahl et al, 2007**)**. The electrical efficiency is defined by the ratio of the system electricity production to the biogas input. Based on this assumption, the cost of biogas for a 50 kW PEM fuel cell system for the years 2010 and 2020 is calculated and it is 190 and 95 €/MWh_{el}, respectively. Combing all the results of Table 16, the electricity production cost of a biogas-fuelled PEMFC-CHP for the years 2010 and 2020 are shown.

Table 16 Electricity production cost of a PEMFC-CHP

Scenarios	2010	2020
Capital Cost, €/MWh_{el}	200	120
O&M Costs, €/MWh_{el}	140	90
Biogas cost, €/MWh_{el}	190	95
Electricity cost, €/MWh_{el}	530	305

With their comparatively shorter lifetime and higher capital costs, fuel cell-based CHP systems in comparison with other semi-commercial small scale technologies such as biogas-internal combustion engine, natural gas motor, biogas organic rankine cycle, waste heat organic rankine cycle and solar cells have higher electricity costs (Nyström et al, 2011). PEM fuel cell-based cogeneration systems cannot compete, now or in 2020, with the conventional systems without governmental subsidies or a leap in the development status. However, all advantages of fuel cells, such as high electrical efficiency, no moving parts, quiet operation, modularity, should be considered if fuel cells are to be able to make it to the market on commercial grounds. The research efforts should focus in particular on lifetime and durability. Cost reduction and higher efficiencies might be achieved by using more efficient auxiliary equipment. Creation of a reasonably broad market is essential since increasing production volumes will help a great deal in reducing capital costs.

5 Conclusions

This study evaluates the potential application of biomass-fuelled PEMFC systems which convert biomass to electricity and heat for small and medium-sized enterprises.

The reformate gas produced from the fuel processor using biomass as fuel consists of 39-70 % hydrogen, ~30 % CO_2, 0-34 % N_2 and a trace amount of CO. Although the reformate gas decrease the performance to some extent compared with the pure hydrogen, it is still employable for PEMFCs and can make the operation stable. Anode stoichiometry impacts significantly on the stability and efficiencies of a PEM fuel cell system. Reducing the anode stoichiometry will increase the electricity generation while keeping the amount of input hydrogen constant. However, for the system in Paper II, when the anode stoichiometry has dropped from 1.5 to 1.3, the electrical efficiency of the fuel cell stack is increased but the system net electrical efficiency and fuel processor efficiency are almost unchanged. Thus, the l.5 of anode stoichiometry is still appropriate for the whole system performance. The higher CH_4 content in the biogas may cause a better system performance but not a higher CH_4 conversion rate. The simulation results show that with 75 % CH_4 in the biogas, the system using 98 % CH_4 conversion rate has the same performance as that using 90 % CH_4 conversion rate. Pinch technology is used to optimize the scaled-up experimental system. After analyzing the hot and cold composite curves and the grand composite curve of the process streams, the heat exchanger network of the scaled-up experiment system is rearranged and optimized. The electricity output is highly increased after the optimization.

For different kinds of biomass, biomass-fuelled PEMFC systems give different performances. The AD-PEMFC and the GF-PEMFC are designed for liquid and solid biomass, respectively. Manure is chosen as a typical liquid biomass for anaerobic digestion (AD), and forest residues are chosen as a typical solid biomass for gasification (GF). For 100 kWe generation, the GF-PEMFC yields 20 % electrical efficiency and 57 % thermal efficiency. The AD-PEMFC has muchlower efficiencies, which is mainly attributed to the low efficiency of the

AD. But both AD and SR are more mature and industrialised processes than the GF and can offer a more stable performance for the application. Moreover, under conditions when biogas is obtained externally and the AD stage can be excluded from the system evaluation, a biogas-fuelled PEMFC system may reach up to 30 % electrical efficiency. Since both AD-PEMFC and GF-PEMFC systems utilise biomass as fuel, they make considerable contributions to fossil-fuel saving and CO_2 emissions reduction compared to a coal-fired power plant and the hydrogen production plant via steam methane reforming. The GF-PEMFC system has a high CO_2 emissions offset factor and AD-PEMFC system has an efficient land-use.

Biomass-fuelled PEMFC systems are suitable for a decentralized system with abundant biomass such as livestock farm or a food plant. For a dairy farm with 300 milked cows, PEMFC-CHP systems utilizing the biogas produced from the cow manure may cover of the whole electricity and heat demand of the farm and the fuel cell system as long as the PEMFC stack yields as 40 % electrical efficiency. PEMFC-CHP systems generate 360 MWh electricity and 680 MWh heat annually, which is equivalent to 160 tonnes coal and 416 tonnes CO_2 emissions when comparing with a typical coal-fired CHP plant. The system electrical efficiency is 28 % and the system thermal efficiency is 54 %.

Based on the experimental data of the Biogas2PEM-FC project, a PEMFC-CHP system designed for an olive oil plant annually generating 50 000 m^3 SOMW and 9 000 m^3 OMW is simulated. After the optimization of the heat exchanger network, the PEMFC-CHP system may generate 194 kW electricity which corresponds to 62 % of the total electricity demand of the olive oil plant. Additionally, there is 269 kW recovered heat which could be used to heat the digester and produce hot water. Taking into account this thermal benefit, the total system efficiency is 54.18 %.

The cost of a PEMFC cannot compete with the conventional technologies even by 2020. However, all advantages of fuel cells, such as high electrical efficiency, no moving parts, quiet operation, modularity, should be considered if fuel cells are to be able to make it to the market on commercial grounds. Compared with natural gas, biogas may be an economical source of hydrogen production for household use. The break-even cost of this system is 197 €/MWh if the generated electricity could sell at 150 €/MWh and the heat at 40 €/MWh. With the current trend of the fuel cell industry development, the electricity production

cost from this integrated system may reach the break-even price or even become profitable in the near future.

Above all, although the biomass-fuelled PEMFCs are technically and environmentally promising, they are still restricted in some aspects. One is the geography-dependent nature of the biomass. The distribution of biomass will determine where these two systems may be located. Another is the technological immaturity of the biomass-fuelled PEMFC systems. More experiments and demonstrations are needed to validate these technologies further. With the improvement and development of the technologies in the future, biomass-fuelled PEMFCs will become outstanding energy systems for power generation in locations with abundant biomass supply.

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