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HYDROGEN PRODUCTION THROUGH GASIFICATION:

FROM RAW MATERIALS TO END USERS

PhD THESIS Summary

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Keywords: Hydrogen, Gasification, Hydrogen production supply chain, Dual fluidized bed, Biomass steam gasification, Entrained flow, Biomass co-firing, Life cycle analysis

Part I - Overview and theoretical background

Chapter 1. General aspects

1.1. Thesis motivation

Hydrogen is expected to play a significant role in the future energy systems, given the global increase in energy demand which is driven by the accelerated growth of the world's population, the on-going industrial development and urbanization as well as the higher standards of living and education.

Among various alternatives, hydrogen offers the highest potential benefits in terms of diversified supply and reduced emissions of pollutants and greenhouse gases (Pant and Gupta, 2009). Hydrogen based economy is the long term view of many nations for a sustainable energy system (Saxe and Alvfors, 2007). The main goal of hydrogen economy is replacing the energy sources that are used at present (methane gas for generating heat and electric energy, liquid fuels for the transport sector) with hydrogen, but in order to achieve a hydrogen economy, developing widespread hydrogen supply systems are vitally important considering the fact that a large number of technological options exist and are still in development for hydrogen production, storage, distribution, which cause various pathways for supplying hydrogen (Qadrdan et al., 2008).

The technology of producing hydrogen is a vital aspect, for the global development and implementation of hydrogen based energy systems. Among many possible options, gasification technology presents essentials benefits like: a wide range of fuels can be used for gasification, including low-priced feedstocks, flexibility of the production capacity (from small to very high depending on a given product demand), the possibility for carbon dioxide capture and storage, the ability to produce a number of high-value products at the same time (poly-generation). Steam methane reforming is the most widely uses technology today for hydrogen production, but it is generating carbon dioxide emissions and also the natural gas reserves are expected to last less than the coal reserves, at the current rate of exploitation. Hydrogen production through water electrolysis requires electricity, which make it inefficient for large scale production capacities. Moreover, if the electricity comes from fossil fuels exploitation it has negative impact on the environment or if it comes from renewable sources like wind, geothermal, or solar energy the problem of seasonal and regional availability needs to be overcome.

1.2. Thesis objectives

Considering the facts and challenges mentioned in the previous paragraphs, the present thesis deals with investigating two different hydrogen production pathways, based on gasification technologies, from technical, economic and environmental point of view. The first hydrogen production pathway is based on biomass steam gasification process in a dual fluidized bed reactor system. Dual fluidized bed (DFB) steam gasification for biomass was developed at the Institute of Chemical Engineering, Vienna University of Technology and has been successfully demonstrated at pilot and industrial scale (Kirnbauer et al., 2012). The second hydrogen production pathway is based on coal and biomass gasification using entrained flow (EF) technology. The entrained flow and fluidized bed systems are the most promising gasification technologies for hydrogen production in terms of efficiency, carbon conversion rate, cost, flexibility of feedstock used. Thus, the main objectives of the thesis are as follows:

- The first objective of the thesis is to assess hydrogen production process based on biomass steam gasification in a dual fluidized bed (DFB) reactor system in terms of hydrogen output efficiency, overall plant heating and power duty, carbon dioxide emissions (three solvents for carbon dioxide separation from the producer gas are to be investigated).

Detailed flowsheet model of hydrogen production plant, based on the design of the biomass gasification plant in Güssing, Austria are to be developed in chemical engineering software Aspen Plus®. The producer gas composition (after the DFB system) predicted by the model will be compared with the real plant measured result.

- The second objective of the thesis is to investigate technical aspects of hydrogen production technology through co-gasification of coal and biomass based on entrained flow (EF) technology (three plant configurations based on different entrained flow reactors are to be analysed). A performance analysis regarding the energy efficiency of the process, carbon conversion rate, syngas composition and the carbon dioxide capture rate will be carried out in order to determine the most suitable plant configuration for hydrogen production. The effect of biomass co-firing on gasification based hydrogen production process will also be investigated. The simulations are made using chemical process simulation software Aspen Plus®.
- The third objective is to develop a discrete event model in order to address gasification based hydrogen production supply chains analysis under demand variability, with Arena software. Hydrogen production supply chain systems will be evaluated in terms of: hydrogen amount sold and hydrogen amount stored (MW-h), hydrogen lost sales amount (MW-h), partial sales per cent and gasification plant profit (MM Euros).
- Given the increasing concerns regarding global warming and climate change, the fourth objective of the thesis is to use the life cycle assessment (LCA) methodology to evaluate the environmental impact determined by the two gasification based hydrogen production systems, with GaBi 6 software.

1.3. Thesis structure and content

The present thesis structure is as follows: Part I – *Overview and theoretical background*, Part II – *DFB hydrogen production supply chain system*, Part III – *EF hydrogen production supply chain system*, Part IV – *Comparison and conclusions*.

Part I of the thesis includes three chapters.

In Chapter 1 entitled “General aspects”, the thesis motivation, objectives and structure are presented.

Chapter 2 entitled “Hydrogen supply chain: theoretical point of view” gives a general description of the current status of world energy demand and supply and presents the advantages and challenges of the future hydrogen based economy. Also, in Chapter 2, the entire hydrogen production pathway from raw materials to end users is presented from theoretical point of view. The most significant aspects of gasification technology are illustrated along with syngas treatment and conditioning options, raw materials characteristics and supply chain aspects. The possibilities for hydrogen delivery and storage and environmental aspects are also mentioned.

Chapter 3, which is entitled “Simulation tools”, offers a description of the simulation environments used to analyse the gasification based hydrogen production supply chain systems.

Parts II, III and IV are each divided into two chapters and represent the author’s contribution of the thesis.

Chapter 4 called “Hydrogen production through biomass steam gasification process” presents the work realized during author’s six months research internship at Vienna University of Technology. Hydrogen production process presented in this chapter is based on biomass steam gasification in a dual fluidized bed reactor system. The process also incorporates a CO water-gas shift step, a CO_2 separation step, by absorption with physical and chemical solvents (as Selexol®, MEA and potassium carbonate), a steam reformer and a PSA unit. The hydrogen production process simulation carried out in Aspen Plus®, is based on the design of the biomass gasification plant in Gussing, Austria. This part of the thesis is based on Paper I. A pilot plant for hydrogen production, which uses the producer gas from the biomass CHP Güssing, is design and used to test different steps of the process (Internet site – [w1]). The results presented in this chapter can contribute to the research work carried out for the application at industrial scale (design and operation of a 50 MW demonstration plant near a refinery in Austria).

In Chapter 5, “Biomass steam gasification – based hydrogen production supply chain analysis”, discrete event model is developed to address biomass steam gasification based hydrogen production supply chain analysis under demand variability, with Arena software. This chapter focuses on assessing the biomass steam gasification based hydrogen production supply chain, from the raw materials supply, preparation and storage stages to the hydrogen production stage, from which hydrogen is delivered to consumers by pipeline transportation. This part of the thesis is based on Paper VII.

In Chapter 6, entitled “Hydrogen production through co-gasification of coal and biomass” technical aspects of hydrogen production technology through co-gasification of coal and biomass are analysed. Three plant configurations containing entrained-flow gasifiers are studied (dry feed gasifiers: Siemens and Shell and slurry feed gasifier: GE - Texaco). This chapter also assesses the effect of biomass co-firing on gasification based hydrogen production process. Several cases consisting of various feedstocks to the gasification reactor are investigated (coal only and coal in mixture with sawdust or wheat straw). Considered plant concepts generate between 330-460 MW hydrogen of 99.99% (vol.) purity. The simulations are made using chemical process simulation software Aspen Plus®. This part of the thesis is based on Papers II, IV and V.

Chapter 7, “Effect of biomass co-firing on gasification – based hydrogen production supply chain system” focuses on assessing the implications of biomass co-firing on gasification based hydrogen production supply chain, with carbon dioxide capture and storage, from the raw materials supply, preparation and storage stages to the hydrogen production stage, from which hydrogen is delivered to consumers by pipeline transportation. The Aspen Plus® simulations and cost estimations are used to develop a discrete event simulation model with Arena software. This part of the thesis is based on Papers II and III.

Chapter 8 is called “Comparative life cycle analysis for gasification – based hydrogen production systems”. In this chapter a life cycle analysis study is carried out in order to evaluate and compare the potential environmental impact determined by the two gasification based hydrogen production pathways. The following impact categories: Global warming potential (kg CO_2 equivalent), Acidification potential (kg SO_2 equivalent), Eutrophication potential (kg phosphate equivalent), Abiotic depletion fossil (MJ), Human toxicity potential (kg DCB equivalent) are considered for the analysis. This part of the thesis is based on Paper VI.

The final chapter is Chapter 9, named “General conclusions” which emphasises the overall conclusions drawn from the thesis and also presents future work perspectives and author’s personal contribution and publications.

Part II - DFB hydrogen production supply chain system

Chapter 4. Hydrogen production through biomass steam gasification process

4.1. Introduction

Hydrogen production process presented in this chapter is based on biomass steam gasification in a dual fluidized bed reactor system. The process also incorporates a CO water-gas shift step, a CO_2 separation step, by absorption with physical and chemical solvents (as Selexol®, MEA and potassium carbonate), a steam reformer and a PSA unit. Also, the possibility for CO_2 capture with Selexol®, both from the producer gas and the flue gas, is investigated. Figure 4.1 illustrates the process flow diagram, based on the design of the biomass gasification plant in Güssing, Austria (Muller et al., 2011).

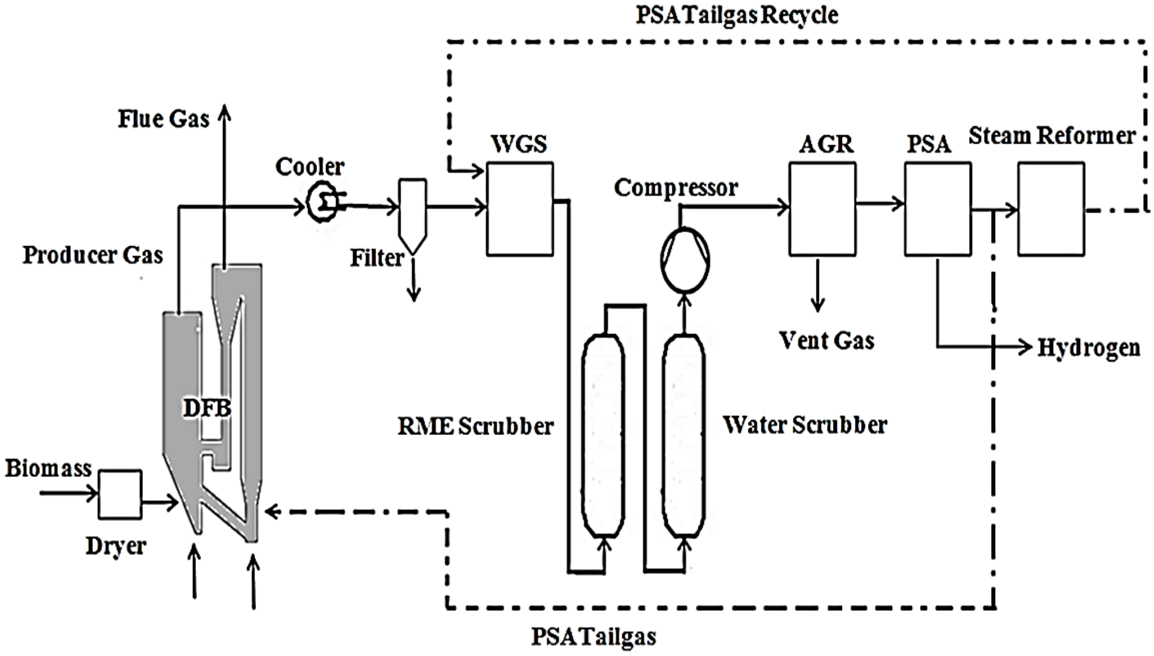


Figure 4.1. Biomass steam gasification plant design (Muller et al., 2011)

Dual fluidized bed (DFB) steam gasification for biomass was developed at the Institute of Chemical Engineering, Vienna University of Technology and has been successfully demonstrated at pilot and industrial scale (Kirnbauer et al., 2012).

4.2. Process description

The steam gasification takes places in the gasification reactor at temperatures between 850 and 900°C. The gasification part, a bubbling fluidized bed reactor is continuously fed with the feedstock and a high temperature bed material is coming from the riser (combustor). Along with the bed material from the gasifier, residual char is transported to the riser (Koppatz et al., 2008). The DFB steam gasification is depicted in the Figure 4.2.

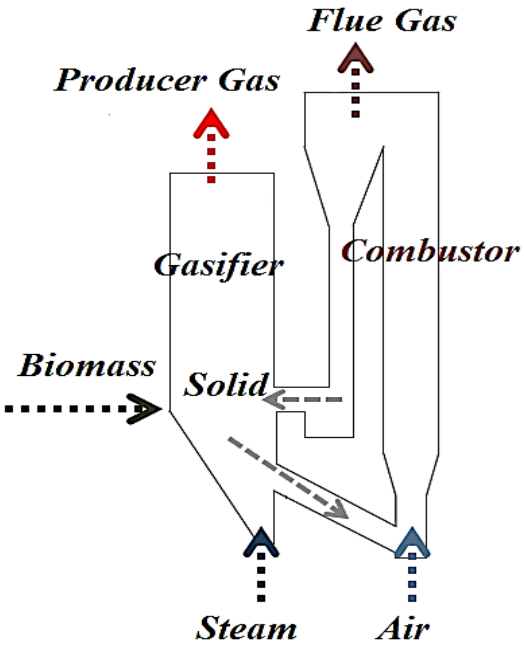


Figure 4.2. DFB steam gasification system (adapted from Koppatz et al., 2008)

The fuel into the gasifier consists of wood chips with a moisture content of 40 wt%. Before being fed to the gasifier reactor, the wood chips are dried with hot air to a moisture content of 20 wt%.

After exiting the gasifier the producer gas is cooled, then the dust is removed using a bag filter. Next the producer gas is mixed with PSA recycled tail gas and sent to the water-gas shift (WGS) stage. The water–gas shift conversion is an exothermal reaction used to produce hydrogen and carbon dioxide by reacting the carbon monoxide in the producer gas with superheated steam (Eq. 4.4) (Cormos et al., 2008). A sour shift cobalt–molybdenum sulphur tolerant catalyst is used, since this does not require any purification of the raw gas (Muller-Langer et al., 2007; Chiesa et al., 2005), and the operating temperature is around 300°C.

The tars are removed and the water is condensed in a scrubber operated with rape seed oil methyl ester (RME) and one operated with water. The required scrubber fluids cooling temperature, in order to ensure the necessary separation efficiency, is around 5°C (Muller et al., 2011).

The following step is the separation of CO_2 from the producer gas, which is achieved through a process of gas liquid absorption. Three different solvents are investigated: MEA, potassium carbonate and Selexol®.

Hydrogen purification takes place through pressure swing adsorption (PSA) technique. PSA operates on an isothermal cycle, adsorbing at high pressure (around 23 bar) and desorbing at low pressure. The delivered hydrogen purity is 99.99 vol. %. The remaining PSA tail gas has a high content of methane and C2/C3 hydrocarbons, consequently, in order to increase the overall hydrogen output of the plant, main part of the gas is fed to a steam reformer and then recycled back to the water-gas shift stage of the process. The rest of the tail gas from the PSA unit is used as additional fuel for the combustion reactor of the gasification system.

4.3. Results and discussion

4.3.1. Gasification, gas cooling and de-dusting

The model predictions for the DFB producer gas output are compared with the measurements obtained at the biomass CHP plant in Güssing, Austria. The results are illustrated in Figure 4.3.

After exiting the gasifier the producer gas contains mainly hydrogen, carbon monoxide, carbon dioxide, water, methane and small amounts of C_2/C_3 hydrocarbons and tars and has a temperature of about 850°C. As can be noticed from Figure 4.3, the producer gas composition predicted by the model corresponds well to the measured results. The main DFB performance parameters are presented in Table 4.1.

After exiting the gasifier, the producer gas is cooled to 150°C and the dust is removed in a bag filter.

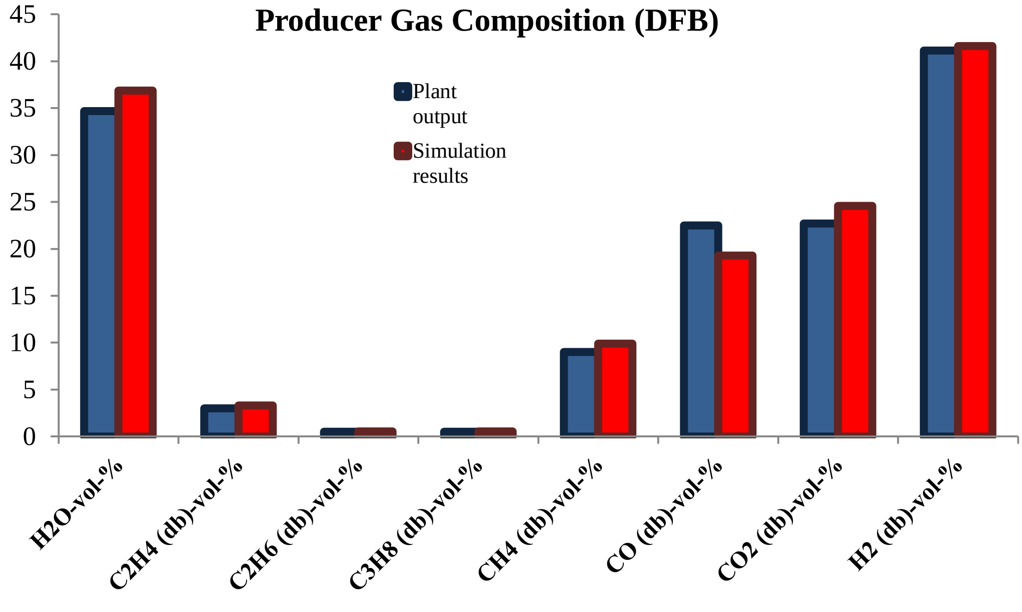


Figure 4.3. *Producer gas composition after the gasifier*

Table 4.1. *DFB performance parameters*

Parameter	Units	Value
Biomass input (after dryer)	kg/h	14070
Biomass (LHV)	MJ/kg	13.61
Biomass input to DFB	MW	53.19
Total producer gas yield	Nm^3/h	21587
Water content in producer gas	Vol.%	36.88
Producer gas yield (db)	Nm^3/h	13626
Specific producer gas yield	Nm^3_{db}/kg fuel	0.97
Producer gas LHV	MJ/Nm^3_{db}	12.30
Product gas output	MW	46.57
Tail gas recycle (combustor)	MW	10.91
Specific hydrogen yield	Nm^3_{H2}/kg fuel	0.40
Cold gas efficiency	$MW_{gasoutput}/MW_{fuelinput}$	0.67

4.3.2. Acid gas removal

For the CO_2 separation process two chemical solvents (MEA, potassium carbonate) and one physical solvent (Selexol®) are investigated. Also the possibility of CO_2 capture with Selexol® both from the producer gas and flue gas is evaluated. In all cases analysed the CO_2 capture rate is set to over 90%, as design specification in the model. Also, all three solvents absorb H_2S along with the CO_2. The capture rate is calculated by reporting the final molar flow of captured CO_2/H_2S to the initial molar flow of CO_2/H_2S from the producer gas.

4.3.2.1. Comparison between solvents

As can be seen from Figure 4.4, even though the power duty is smaller in the cases of CO_2 absorption with chemical solvents, there is extra energy required for regenerating the solvents. Comparing the Selexol® system (CO_2 removal from producer gas at 23 bar) with the MEA (10 bar) and potassium carbonate systems (23 bar) it can be noted that the specific power duty is 99.44% smaller for MEA system, respectively 6.29% smaller for potassium carbonate system. But the MEA system has the highest specific heating duty: 3.954 MJ/kg CO_2, compared with 2.66 MJ/kg for potassium carbonate system and 0.12 MJ/kg CO_2 for Selexol® system. Also the specific cooling duty is higher in the case of CO_2 absorption by MEA (3.76 MJ/kg CO_2, compared with 2.55 MJ/kg CO_2 for PC and 1.35 MJ/kg CO_2 for Selexol®).

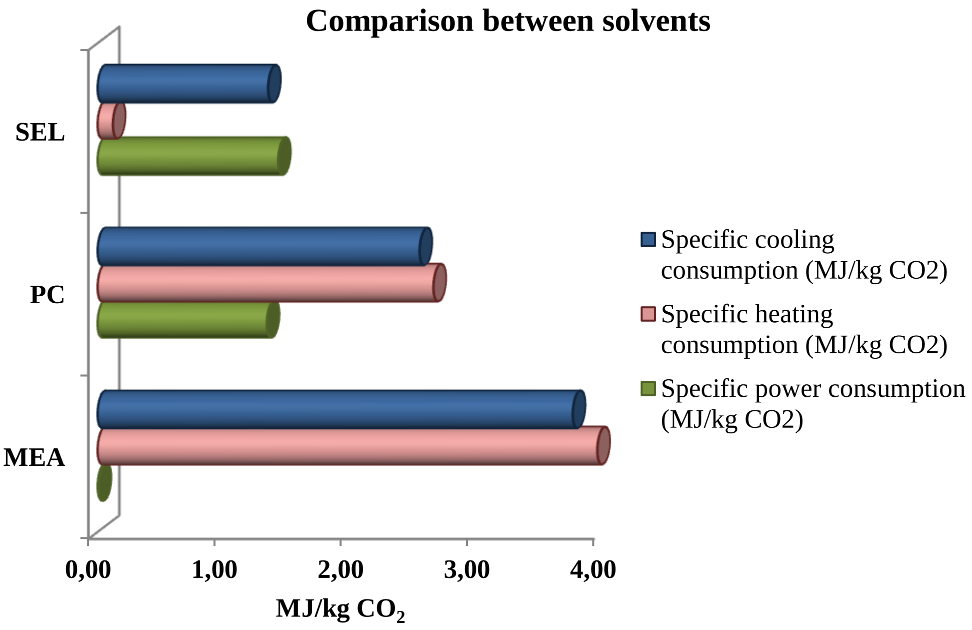


Figure 4.4. *Comparison between solvents*

4.3.3. Overall plant performance

The overall hydrogen production plant, based on biomass steam gasification, simulation results are presented in Table 4.2. The results show that from 50 MW of biomass 35.39 MW of pure hydrogen (99.99% vol.) can be generated (based on lower heating value), with a pressure of approximately 22.5 bar. The Aspen Plus® simulation results of the biomass steam gasification based hydrogen production plant match the results obtained from the IPSEpro simulation work carried out at Vienna University of Technology, Institute of Chemical Engineering, which are reported by Muller et al., (2011).

Table 4.2. *Overall plant performance parameters*

Parameter		Units	Value
Biomass input (40% wet, wf)		tonnes/h	18.76
Biomass (LHV)		MJ/kg	9.59
Biomass input		MW	50
Hydrogen output		Nm^3/h	11807
Hydrogen (LHV)		MJ/Nm^3	10.79
Hydrogen output		MW	35.39
$\eta_{hydrogen}$		%	70.78
	PD (MW)	HD (MW)	HC (MW)
MEA	3.45	8.026	3.25
PC	4.09	6.26	3.60
Selexol®	4.23	1.196	3.80
Selexol®	12.31	1.75	16.98
Plant efficiency (MEA)		%	57.57
Plant efficiency (PC)		%	58.64
Plant efficiency (Selexol®)		%	63.85
Plant efficiency (Selexol®)		%	55.24

4.4. Conclusions

For the dual fluidised bed reactor system a simplified model is created based on mass and energy balances. The producer gas composition predicted by the model is in accordance with the real plant measured result.

The overall plant simulation results show that 35.39 MW of pure hydrogen can be generated from 50 MW of biomass with a water content of 40% (wf). Also, depending on the solvent used for CO_2 separation from the producer gas, between 3.45 MW and 4.23 MW of electricity are needed and along with additional utilities. For the case of CO_2 capture from producer gas and the flue gas with Selexol® the plant power duty and cooling duty are significantly higher. The overall plant efficiency is slightly higher in the case of CO_2 separation with Selexol® (63%), compared with the cases of CO_2 separation with chemical solvents (57% - MEA, 58% -PC).

As mentioned in Section 4.1 a pilot plant for hydrogen production, which uses the producer gas from the biomass CHP Güssing, is design and used to test different steps of the process (Internet site – [w1]). The results presented in this chapter can contribute to the research work carried out for the application at industrial scale (design and operation of a 50 MW demonstration plant near a refinery in Austria).

Chapter 5. Biomass steam gasification – based hydrogen production supply chain analysis

5.1. Introduction

Using the simulations results presented in Chapter 4, a discrete event model is developed to address biomass steam gasification based hydrogen production supply chain analysis under demand variability, with Arena software. Hydrogen production supply chain system is evaluated in terms of: hydrogen amount sold and hydrogen amount stored (MW-h), hydrogen lost sales amount (MW-h), partial sales per cent and gasification plant profit (MM Euros).

This chapter focuses on assessing the biomass steam gasification based hydrogen production supply chain, from the raw material supply, preparation and storage stages to the hydrogen production stage, from which hydrogen is delivered to consumers by pipeline transportation, as depicted in Figure 5.1.

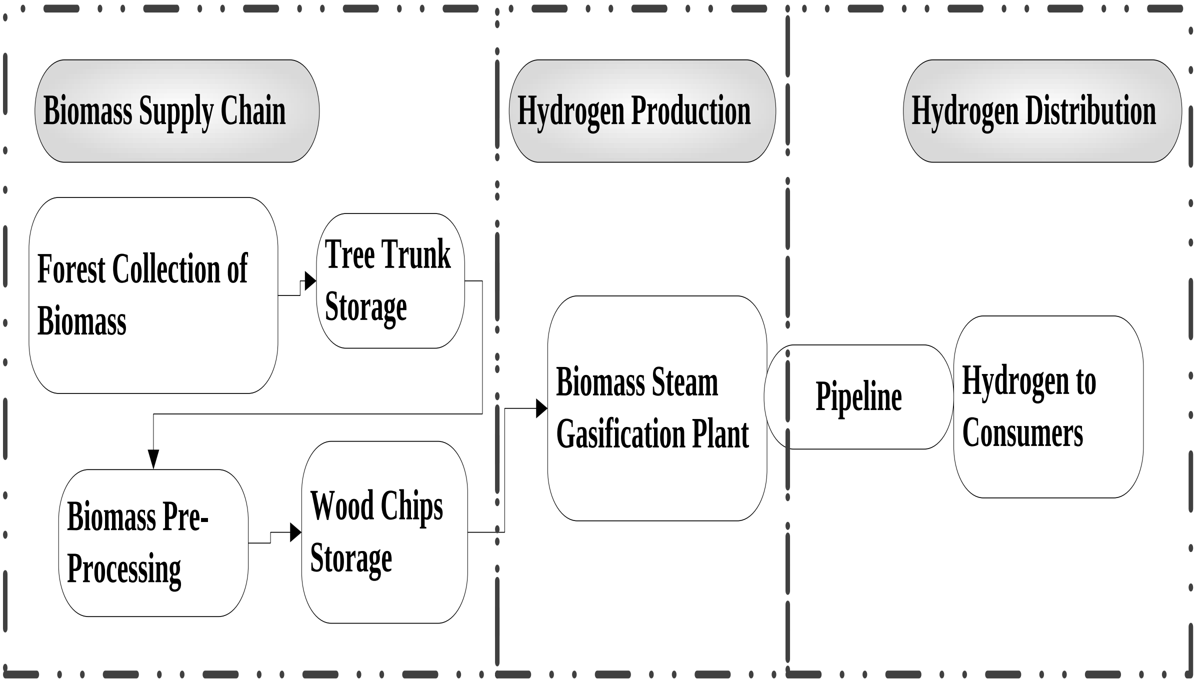


Figure 5.1. *Hydrogen production supply chain*

5.2. Biomass supply chain and hydrogen distribution

Biomass represents a renewable resource that is CO_2 neutral, making it suitable for hydrogen production as the concern of global warming increases (Nikooa and Mahinpey, 2008

The following activities are required to supply biomass from its production point to the gasification plant in order to be used as raw material for hydrogen production: collection of biomass in the forest, loading and unloading operations, transportation through the supply chain nodes, storage, pre-processing operations (Rentizelas et al., 2009). For the present study it is assumed that the wood is supplied from the surrounding area of hydrogen production plant, from within a radius of 25 kilometres. The wood trunks are dried naturally by open air storage of about 1-2 years (Internet site - [w8]), then they are pre-processed at the biomass pre-processing plant. Biomass pre-processing in this case involves chipping operations.

Storage throughout the biomass chain is necessary to adequately match biomass supply and hydrogen production plant demand (Gold and Seuring, 2011). Storage options depend on the climate, storage period, biomass processing stage and may vary from open air, roof covered and air fan (Gold and Seuring, 2011). Wood chips storage type for the present case is assumed to be roof covered.

Hydrogen can be stored as liquid hydrogen, main advantage being its high density at low pressure, making it efficient for truck delivery (Aceves et al., 2006) or as compressed gas in high pressure vessels, method preferred for fuel cell vehicle use, because of the affordable cost and the possibility of indefinite time storage (Ananthachar and Duffy, 2005; Balat, 2008).

As mentioned in Chapter 2 there are several ways of hydrogen delivery: compressed gas truck delivery, cryogenic liquid truck delivery and delivery by pipeline, the latter being the cheapest option with the highest capacity of hydrogen delivery (Balat, 2008). For the present study it is assumed that hydrogen is delivered to consumers by pipeline transportation.

High pressure is needed to ensure the transportation from production sites to end-users with low energy consumption (pressure drop along pipes network).

5.3. Arena model

The simulation results presented in Chapter 4 are used for developing a discrete event model in order to address hydrogen production supply chain analysis under demand variability, during one year time period (8000 working hours). The model is developed using Arena software and it is based on the methodology described by Tayfur and Melamed, (2007).

The biomass steam gasification-based hydrogen production supply chain consist of the following stages: biomass supplier, biomass pre-processing plant, wood chips warehouse, biomass steam gasification plant where the hydrogen demand arrives, as depicted schematically in Figure 5.2.

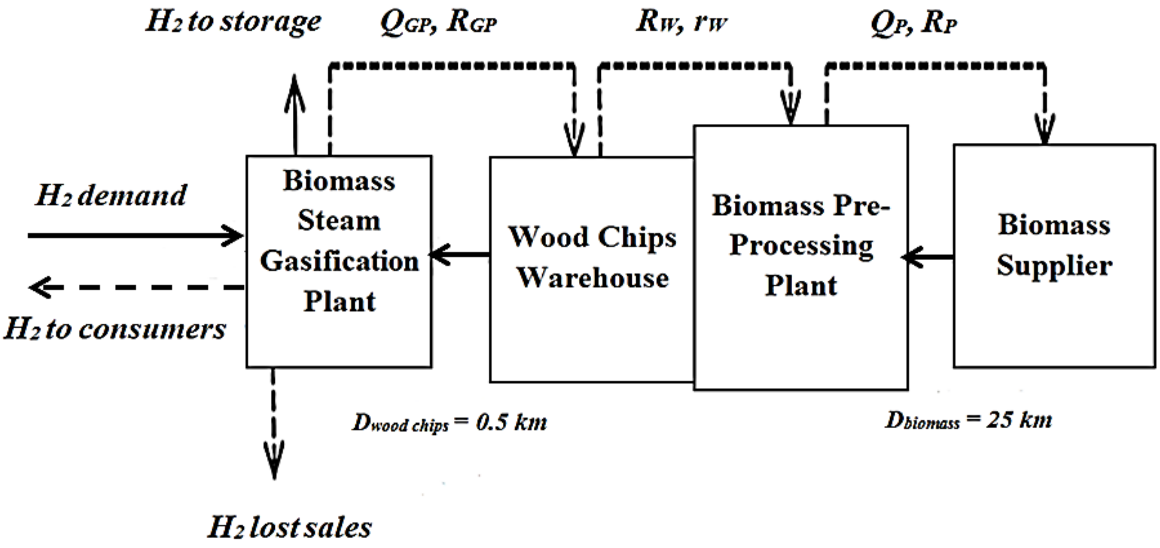


Figure 5.2. *Gasification based hydrogen production supply chain structure*

5.4. Results and discussions

As mentioned in Section 5.3 the following assumptions are made for the Base case: hydrogen demand variation is equal to hydrogen production rate, hydrogen delivery distance is 50 km and hydrogen production cost is 120 €/MW. 100 replications with 8000 hours length and 240 hours warm-up period are simulated.

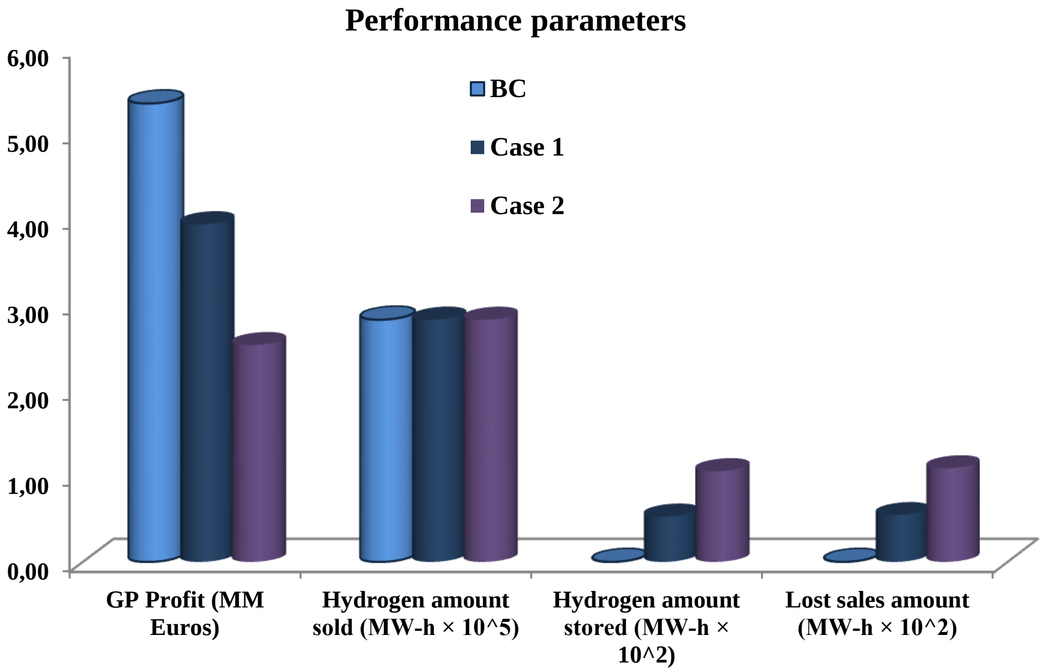


Figure 5.3. *Hydrogen demand variation ($D_{hydrogen\ delivery}$ = 50 km, $H_{2production\ cost}$ = 120 €/MW)*

Figure 5.3 illustrates the performance parameters considered for biomass steam gasification based hydrogen production supply chain analysis under demand variation. The gasification plant profit decreases by 26.3% for Case 1, respectively by 52.6% for Case 2, compared with the Base case. As hydrogen demand variation increases, hydrogen amount stored and hydrogen lost sales amount increase from zero at Base case to 53 MW-h and 55 MW-h for Case 1 and 106 MW-h and 110 MW-h for Case 2.

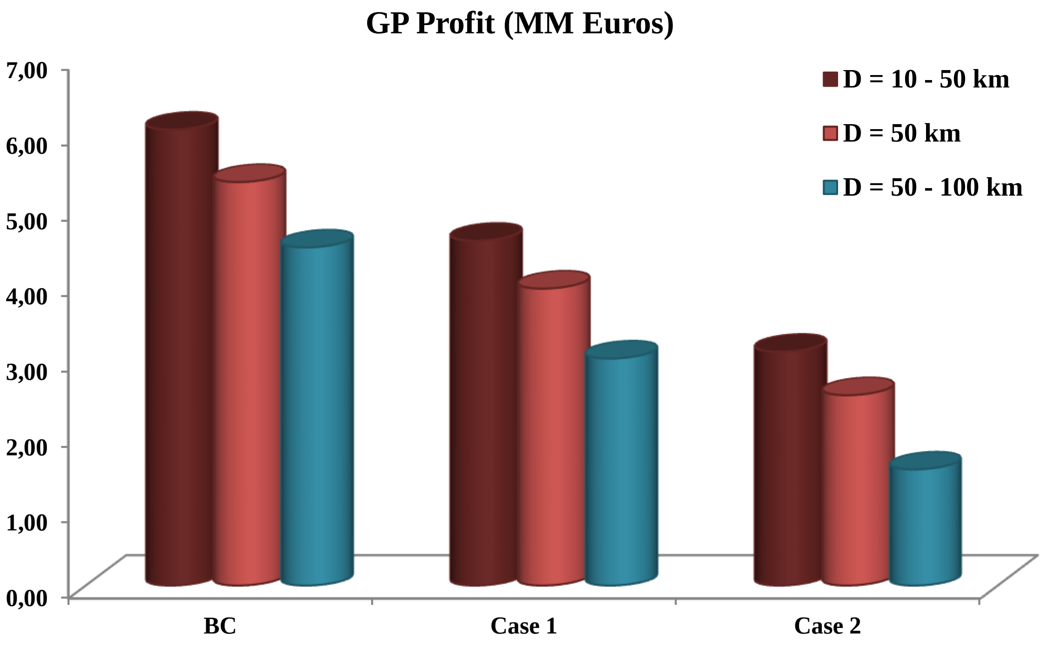


Figure 5.4. *Hydrogen delivery distance variation (*$H_{2production\ cost}$ *= 120 €/MW)*

For each of the three cases considered, hydrogen delivery distance is varied from 50 km to 10-50 km and 50-100 km. The gasification plant profit variation with hydrogen delivery distance is represented in Figure 5.4. For the Base case hydrogen production plant profit increases by 13% if hydrogen delivery distance is varied from 50 km to an interval of 10-50 km and decreases by 16% if hydrogen delivery distance is varied from 50 km to an interval of 50-100 km. For Case 1 hydrogen production plant profit increases by 16% if hydrogen delivery distance is varied from 50 km to an interval of 10-50 km and decreases by 23% if hydrogen delivery distance is varied from 50 km to an interval of 50-100 km and for Case 2 the profit increases by 23% if hydrogen delivery distance is varied from 50 km to an interval of 10-50 km and decreases by 39% if hydrogen delivery distance is varied from 50 km to an interval of 50-100 km. Hydrogen delivery distance influence on gasification plant profit is more pronounced when hydrogen demand variation is higher.

5.5. Conclusions

Hydrogen production supply chain assessment under demand variability provide a "what if" analysis and help foresee how hydrogen demand variability, hydrogen delivery distance variation and hydrogen production cost variation would affect the entire biomass steam gasification based hydrogen production supply chain, especially the gasification plant, during one year time frame (8000 working hours).

In order to reduce the wood chips quality degradation and dry matter losses risks over the storage period and to meet the gasification reactor requirements in terms of raw material properties a stock optimisation is performed in Arena OptQuest resulting in a decrease of wood chips stock at the gasification plant and at the warehouse.

Biomass steam gasification based hydrogen production supply chain system is evaluated in terms of: hydrogen amount sold and hydrogen amount stored (MW-h), hydrogen lost sales amount (MW-h), partial sales per cent and gasification plant profit (MM Euros). Hydrogen demand variation result is a decrease of gasification plant profit. Also, hydrogen delivery distance influence on gasification plant profit is more pronounced when hydrogen demand variation is higher.

Part III - EF hydrogen production supply chain system

Chapter 6. Hydrogen production through co-gasification of coal and biomass

6.1. Introduction

This chapter presents technical aspects of hydrogen production technology through co-gasification of coal and biomass based on modelling and simulation of the process. Three plant configurations containing entrained-flow gasifiers are studied (dry feed gasifiers: Siemens and Shell and slurry feed gasifier: GE - Texaco). A performance analysis regarding the energy efficiency of the process, carbon conversion rate, syngas composition and the carbon dioxide capture rate is carried out in order to determine the most suitable plant configuration for hydrogen production. Gasification technology presents a series of advantages in comparison to other hydrogen production processes (e.g. water electrolysis, steam reforming). Most important, through gasification the energy of a liquid or solid fuel (fossil fuels, biomass of different sorts or industrial wastes) is transformed into syngas with an useable heating value that can be processed to generate hydrogen as well as a large variety of chemical compounds (i.e. methanol, ammonia, urea, synthetic fuels, etc.) (Fermoso et al., 2009). Other significant advantage of gasification process described in this chapter is the limitations of greenhouse gas emissions through acid gas removal unit (carbon dioxide capture, hydrogen sulphide processing).

The gasification based hydrogen production technology assessed in this chapter has the following major components: Air separation unit (ASU), Gasification unit, Water-gas shift unit (WGS), Acid gas removal unit (AGR), Hydrogen purification unit (PSA).

Also this chapter assesses the effect of biomass co-firing on gasification based hydrogen production process. Several cases consisting of various feedstocks to the gasification reactor are investigated (coal only and coal in mixture with sawdust or wheat straw). Considered plant concepts generate between 330-460 MW hydrogen of 99.99% (vol.) purity. The simulations are made using chemical process simulation software Aspen Plus®.

6.2. Results and discussion

6.2.1. Gasification plant configuration

The slurry feed based plant configuration has a lower efficiency than the dry feed ones of about 10 % mainly due to the heat requirement for vaporizing the water in the slurry. But this configuration has the advantage of producing high pressure hydrogen that can be easily transported through pipelines.

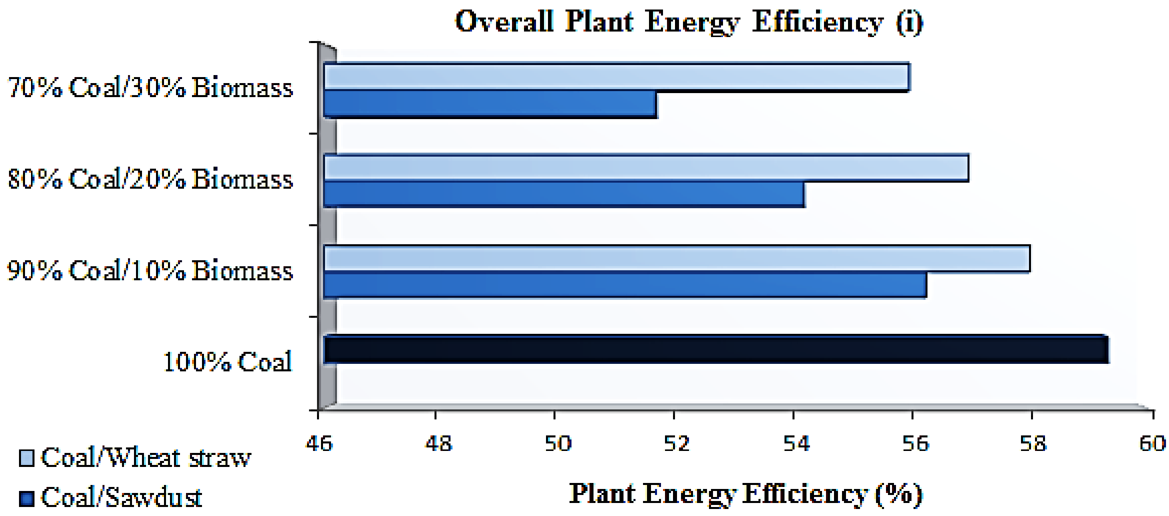
To evaluate the environmental impact determined by the hydrogen production plant carbon dioxide capture rate is calculated (% carbon content of the input fuel that was captured). As can be seen in Table 6.4, all plant configuration analysed have a carbon dioxide capture rate over 90%. The dry feed gasifier cases present a lower carbon dioxide capture rate (92%, 93%) than the slurry feed gasifier case (96%) due to the lower pressure of the AGR system (27.8 bar compared to 52.8 bar).

Based on the results, it is decided that the hydrogen production plant configuration based on dry feed gasifier with nitrogen as transport gas and water quench for cooling the gas (Siemens gasifier) will be considered for the following analysis. All three plant configurations have a carbon dioxide capture rate over 90%, but the plant configuration based on Siemens dry feed gasifier has the highest efficiency (54.15%) and the highest hydrogen output (389 MW).

6.2.2. Effect of biomass co-firing

Regarding the energy efficiency of the gasification-based hydrogen production process evaluated, it is assumed that the power needed to run the gasification plant is generated on-site. The energy balances for all cases analysed are presented in Table 6.7. The thermal energy of the fuel input and the hydrogen output are expressed taking into consideration the lower heating values (10,795 MJ/Nm^3 - for hydrogen, 27.8 MJ/kg - for coal, 18.11 MJ/kg - for sawdust and 14.94 MJ/kg - for wheat straw). The overall efficiency of the plant is calculated considering the thermal energy of the hydrogen output divided by the thermal energy of the raw materials used as feedstock. As can be seen from Table 6.7, all the electricity that is generated is consumed by the ancillaries, resulting in zero net power output of the gasification plant.

Figure 6.1 illustrates the overall gasification plant efficiency variation (i) and carbon dioxide capture rate variation (ii) with the variation of the feedstock composition.



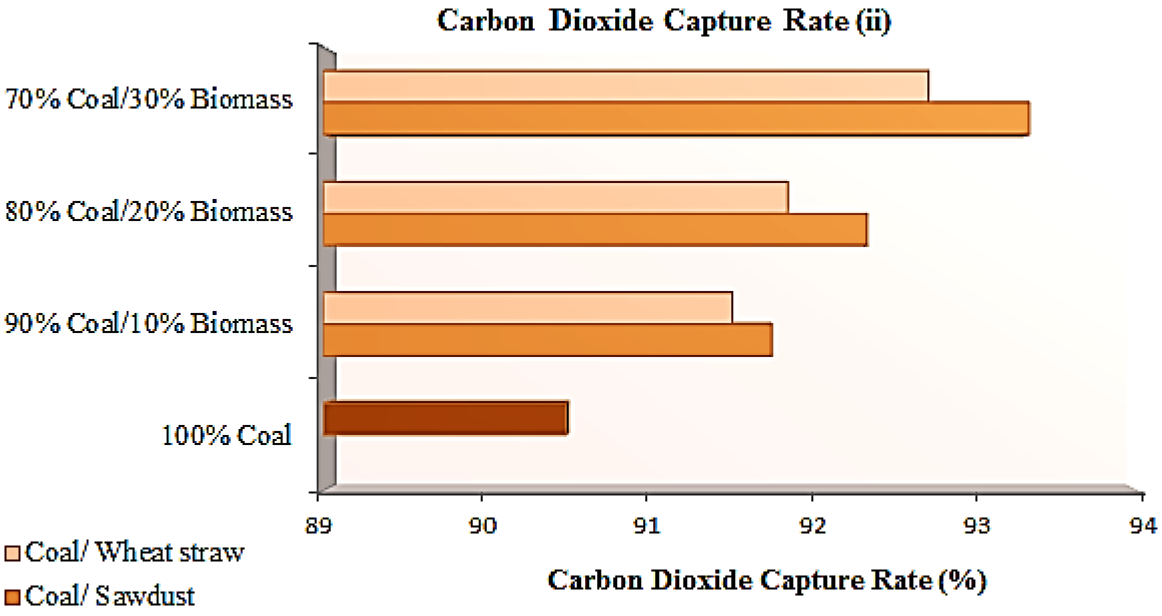


Figure 6.1. *Gasification plant efficiency (i) and carbon dioxide capture rate (ii)*

As the biomass (sawdust, respectively wheat straw) quantity in the feedstock increases from 0% to 10%, 20% and 30% the overall plant energy efficiency decreases by 5%, 9% and 13% for sawdust, respectively by 3%, 4% and 6% for wheat straw and the carbon dioxide capture rate increases by 1%, 2% and 3% for sawdust, respectively by 1%, 1.5% and 2.5% for wheat straw. From environmental point of view, biomass co-firing has a positive effect due to a decrease in specific total emissions by 10%, 12.6% and 19.7% for sawdust, respectively by 8.2%, 8.4% and 13.8% for wheat straw.

6.3. Conclusions

For evaluating the most suitable plant configuration for hydrogen production three case studies are analysed: i) dry feed gasifier with nitrogen as transport gas and water quench for cooling the gas (Case I - Siemens); ii) dry feed gasifier with nitrogen as transport gas and gas quench for cooling the syngas (Case II - Shell); iii) high pressure slurry feed gasifier with water quench (Case III – GE -Texaco). Based on the results, it is decided that the hydrogen production plant configuration based on dry feed gasifier with nitrogen as transport gas and water quench for cooling the gas (Siemens gasifier) will be considered for the following analysis. All three plant configurations have a carbon dioxide capture rate over 90%, but the plant configuration based on Siemens dry feed gasifier has the highest efficiency (54.15%) and the highest hydrogen output (389 MW).

In order to investigate the effect of different parameters on the system, a sensitivity analysis is carried out for the gasification unit. The oxygen to fuel ratio and steam to fuel ratio are varied so that the gasification temperature fit into the range of 1250- 1600°C, above the ash melting point and a carbon conversion rate over 99.99%. The maximum hydrogen output (kmol/h) for the gasification unit is obtained at high steam to fuel ratio (0.25) and small oxygen to fuel ratio (0.59). Basically, the less oxygen it is used, the more steam is needed.

Regarding the effect of biomass co-firing, the results show that as biomass quantity in the feedstock increase from 0% to 10%, 20% and 30% hydrogen production rate decreases by 8.5%, 15% and 22% for sawdust, respectively by 7%, 13% and 19% for wheat straw, the energy efficiency of the process decreases by 5%, 9% and 13% for sawdust, respectively by 3%, 4% and 6% for wheat straw, but carbon dioxide capture rate increases, therefore, from environmental point of view, co-gasification of coal and biomass represent a more suitable solution for producing hydrogen, than coal gasification alone. The CO_2 specific total emissions decrease by 10%, 12.6% and 19.7% for the cases of sawdust co-firing, respectively by 8.2%, 8.4% and 13.8% for the cases of wheat straw co-firing.

Chapter 7. Effect of biomass co-firing on gasification – based hydrogen production supply chain system

7.1. Introduction

Using the results from Aspen Plus® simulations and the cost estimations, a discrete event model is developed, to address hydrogen production supply chain analysis under demand variability, with Arena software. The implications of biomass co-firing on the system are evaluated in terms of: hydrogen amount sold and hydrogen amount stored (MW-h), hydrogen lost sales amount (MW-h), partial sales per cent and gasification plant profit (MM Euros).

7.2. Arena model

The results from Aspen Plus® simulation and the cost estimations are used for developing a discrete event model in order to address hydrogen production supply chain analysis under demand variability, during one year time period (7500 working hours). The model is developed using Arena software and it is based on the methodology described by Tayfur and Melamed, (2007).

The gasification-based hydrogen production supply chain consist of the following stages: raw materials supplier, raw materials pre-processing plant, processed raw materials warehouse, gasification plant where the hydrogen demand arrives, as depicted schematically in Figure 7.1.

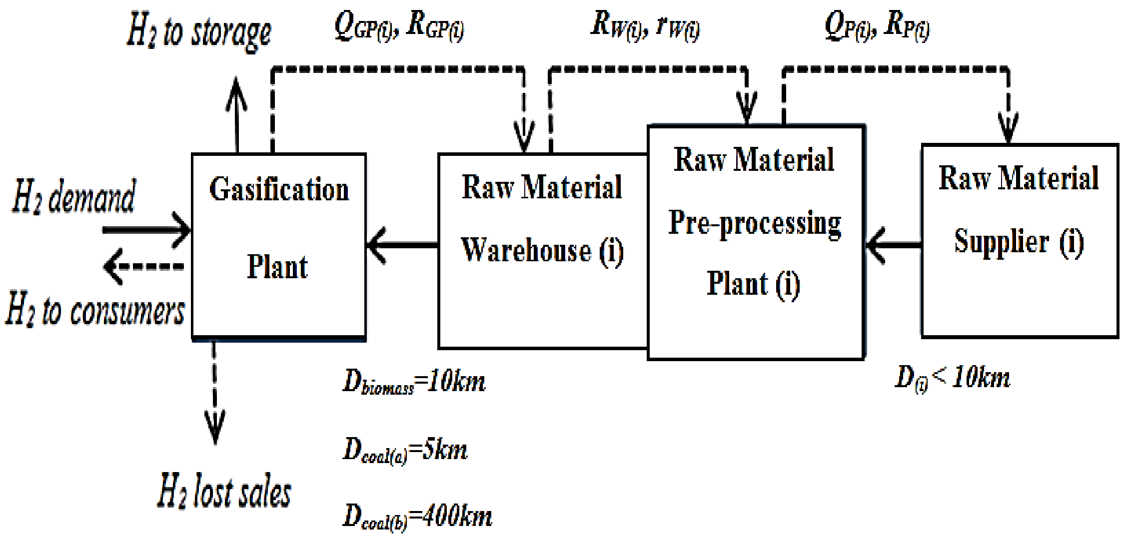


Figure 7.1. *Gasification based hydrogen production supply chain structure*

7.3. Results and discussion

7.3.1. Economical evaluation

The effect of biomass co-firing on capital and operating costs of hydrogen production is illustrated in Figure 7.2. An increase in hydrogen production capital and operating costs, express in €/MW-h, is registered when biomass quantity in the gasifier feedstock increases from 0% to 10%, 20% and 30%, due to the decrease of hydrogen production rate (e. g. 458 MW H_2 for Case 1/ 399 MW H_2 for Case 6).

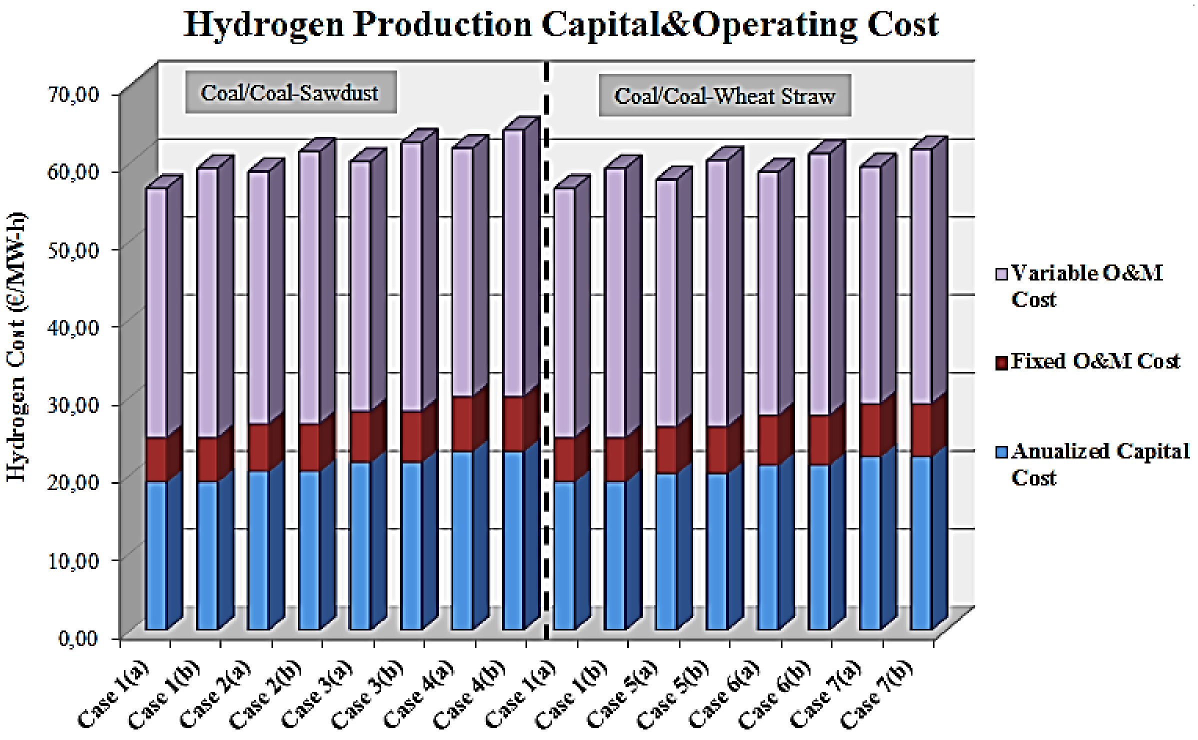


Figure 7.2. *Hydrogen production cost*

7.3.2. Supply chain aspects

The Arena model consists of four parts, corresponding to the system’s four stages, each incorporating the events: raw materials order arrival, raw materials inventory updating, replenishment order triggering and raw materials order delivery. In addition, at the gasification plant stage hydrogen demand is processed. The effect of biomass co-firing on the system performance is evaluated in terms of: hydrogen amount sold and hydrogen amount stored (MW-h), hydrogen lost sales amount (MW-h), partial sales per cent, gasification plant profit.

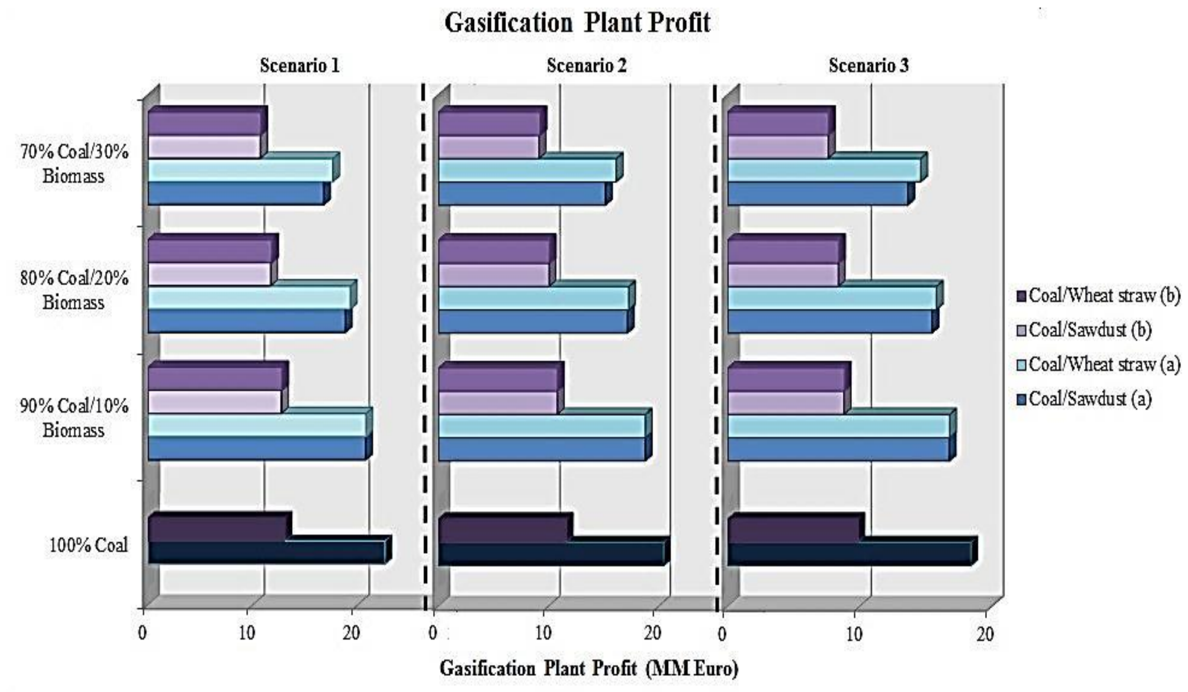


Figure 7.3. *Gasification plant profit*

The effect of biomass co-firing on gasification plant profit is illustrated in Figure 7.3. For each of the three scenarios, as biomass quantity in the feedstock composition increases from 0% to 10%, 20% and 30% gasification plant profit decreases by 8%, 17% and 26% for sawdust co-firing (coal transportation distance 5 km) and by 8%, 15% and 22% for wheat straw co-firing (coal transportation distance 5 km). When coal transportation distance is 400 km, the profit varies between case studies and between scenarios as follows: as biomass quantity in feedstock composition increases the gasification plant profit decreases by an average of 3%, 10% and 18%- Scenario 1, respectively by an average of 7%, 13%, 21% - Scenario 2 and by an average of 10%, 14%, 22%- Scenario 3. The decrease registered in plant profit is mainly due to the decrease of hydrogen production rate for the cases of biomass co-firing (e. g. 458 MW H_2 for Case 1/ 399 MW H_2 for Case 6). The decrease of hydrogen production rate, as biomass quantity in the feedstock composition increases, leads to an increase of hydrogen specific production capital and operating cost, consequently to an increase of hydrogen market price. Basically, for the cases of biomass co-firing a smaller hydrogen quantity of higher price is sold, therefore the gasification plant profit, over a year time period is smaller.

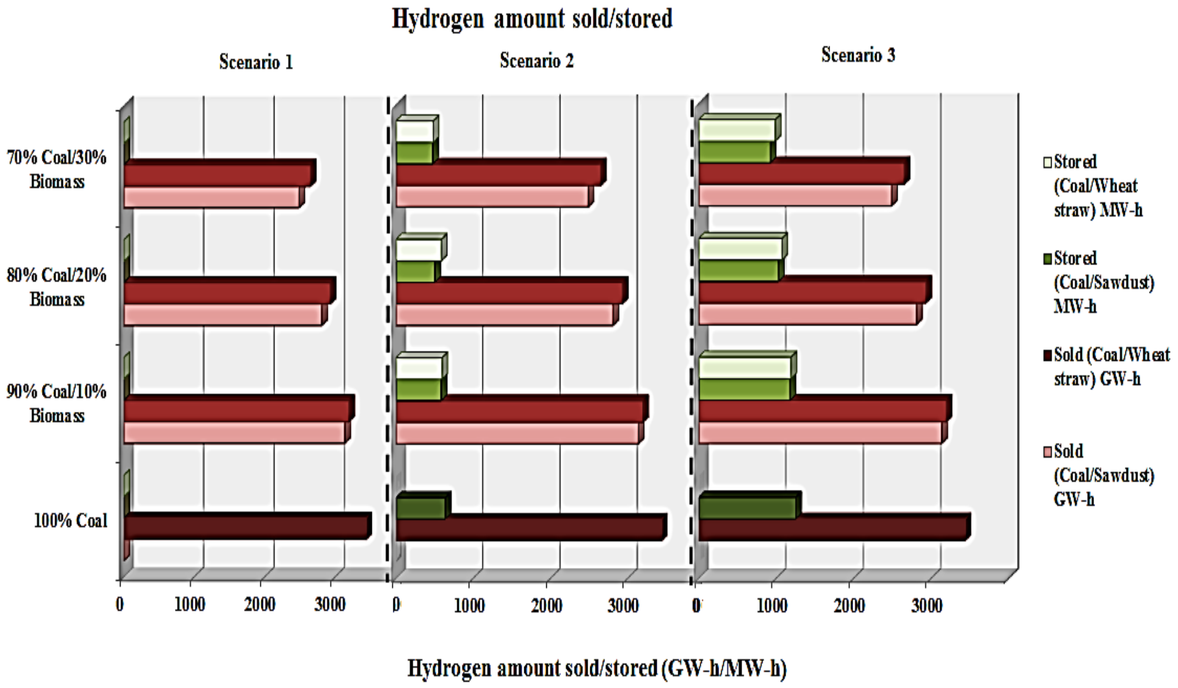


Figure 7.4. *Hydrogen amount sold/stored*

Figure 7.4 presents the variation of hydrogen amount sold and hydrogen amount stored, between case studies and between scenarios. As in the case of gasification plant profit, hydrogen amount sold and stored are related to hydrogen production rate. Therefore as the biomass quantity in feedstock composition increases from 0% to 10%, 20% and 30% hydrogen amount sold decreases by 9%, 18% and 28% for sawdust co-firing, respectively by 7%, 14% and 23% for wheat straw co-firing (Scenario1). Similar hydrogen amount sold decrease is registered for Scenarios 2 and Scenario 3. Hydrogen amount stored for Scenario 1 is equal to zero, because, for this scenario it is assumed that hydrogen demand is equal to hydrogen production rate. A decrease in hydrogen amount stored by 9%, 21% and 26% for sawdust co-firing and by 7%, 8%, 25% for wheat straw co-firing is registered for Scenario 2 and by 7%, 18% and 26% for sawdust co-firing, respectively by 5%, 14% and 21% for wheat straw co-firing for Scenario 3.

7.4. Conclusions

Regarding the economical evaluation the highest capital and operating cost are obtained for the case of coal gasification alone, and the costs decrease as biomass quantity in feedstock composition increases. The variable operating costs are higher if the coal transportation distance is 400 km due to the increase in coal price with the increase of transportation distance. If analysing the specific capital and operating costs, an increase is registered when biomass quantity in the gasifier feedstock increases, due to the decrease of hydrogen production rate (e. g. 458 MW H_2 for Case 1/ 399 MW H_2 for Case 6).

For each of the scenarios considered for the supply chain assessment, when coal transportation distance increases from 5 km to 400 km the gasification plant profit decreases (due to coal price increase with the transportation distance increase) by an average of 40%- Scenario 1, 42%- Scenario 2, 47%- Scenario 3. If analysing the effect of biomass co-firing, for all three scenarios, it can be noticed that gasification plant profit, hydrogen amount sold and stored decrease as the biomass quantity in the feedstock composition increase. The variations in gasification plant profit, hydrogen amount sold, stored and lost sales amount occur due to the fact that different hydrogen productions rates are obtained when feedstock composition varies from coal only to mixtures of coal and biomass.

By comparing the two types of biomass, used in mixture with coal, as feedstock to the gasification reactor, wheat straw offers better results than sawdust, both from the technical and the economic analysis.

The overall hydrogen production process configuration and the results for biomass co-firing effect on the system that are reported in this chapter can be used as a starting point for the basic engineering of a real plant. Also the study regarding the biomass co-firing implications from technical, economic and environmental point of view can be used for the transition of a hydrogen production plant from coal to coal/biomass co-firing.

Part IV - Comparison and conclusions

Chapter 8. Comparative life cycle analysis for gasification – based hydrogen production systems

8.1. Introduction

Life cycle assessment (LCA) is a powerful and internationally accepted system analysis tool for studying the environmental aspects and potential impacts of a product or service system throughout its life cycle (Koroneos et al., 2004). As known, LCA methodology has some advantages in comparison with other methods for evaluation of environmental impacts such as: systematic estimation of the environmental changes related to the examined product or process, quantification of consumptions and emissions and their effects on human health and eco-systems and allocation of impacts in one or more items of environmental interest (Moreno and Dufour, 2012).

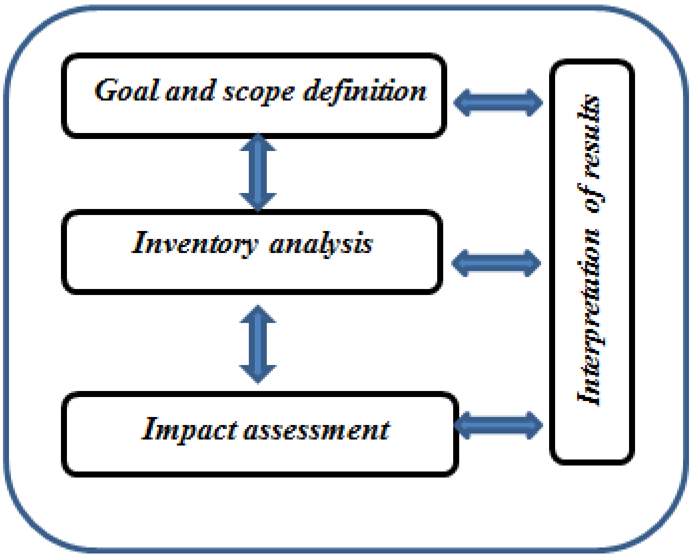


Figure 8.1. *Steps of a Life Cycle Assessment (Internet site – [w15])*

In the present study, the life cycle assessment (LCA) methodology is used to evaluate the environmental impact of two different hydrogen production technologies based on gasification of coal and biomass with GaBi 6 software. The LCA is based on the ISO 14040 (International Organization for Standardization, 1997) and ISO 14044 (International Organization for Standardization, 2006) which foresee four steps: definition of goal and scope, inventory analysis (LCI), impact assessment (LCIA) and interpretation of the results (Ochs et al., 2010; Solli et al., 2006).

8.2. Results and discussions

8.2.1. DFB system GWP results

The results for the greenhouse gas emissions for the biomass steam gasification based hydrogen production pathway in kilogram CO_2 equivalents per megawatt H_2 are displayed in Figure 8.2.

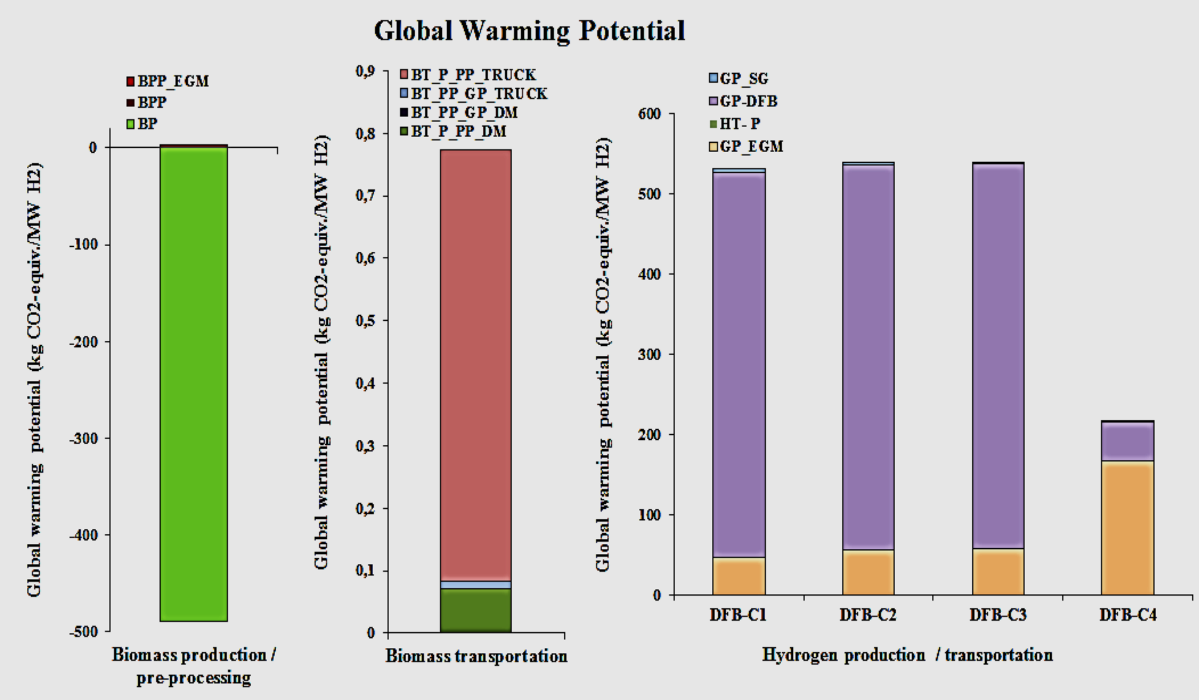


Figure 8.2. *DBF system GWP*

The environmental impact determined by the gasification plant is influenced by the solvent used for carbon dioxide absorption from the producer gas. Depending on the solvent, the overall plant power and heating duties are different as it was reported in Chapter 4. The CO_2 emissions at the gasification plant derive from the gasification process and also from the electricity and steam production. The highest CO_2 emissions are registered for the DFB-C2 (gasification plant configuration with potassium carbonate as solvent for CO_2 separation), followed by the DFB-C3 (gasification plant configuration with Selexol$^{®}$ as solvent for CO_2 separation). The lowest environmental impact is determined by the DFB-C4 (CO_2 capture with Selexol$^{®}$ both from the producer gas and the flue gas).

Electricity driven pipelines are used for hydrogen transportation, and the delivery distance is assumed to be 100 km.

8.2.2. EF system GWP results

As for the cases of hydrogen production from biomass steam gasification process, the results for the hydrogen production based on coal and biomass gasification using entrained flow technology are presented for each of the processes sub-systems: raw materials production and pre-processing, raw materials transportation and hydrogen production and transportation.

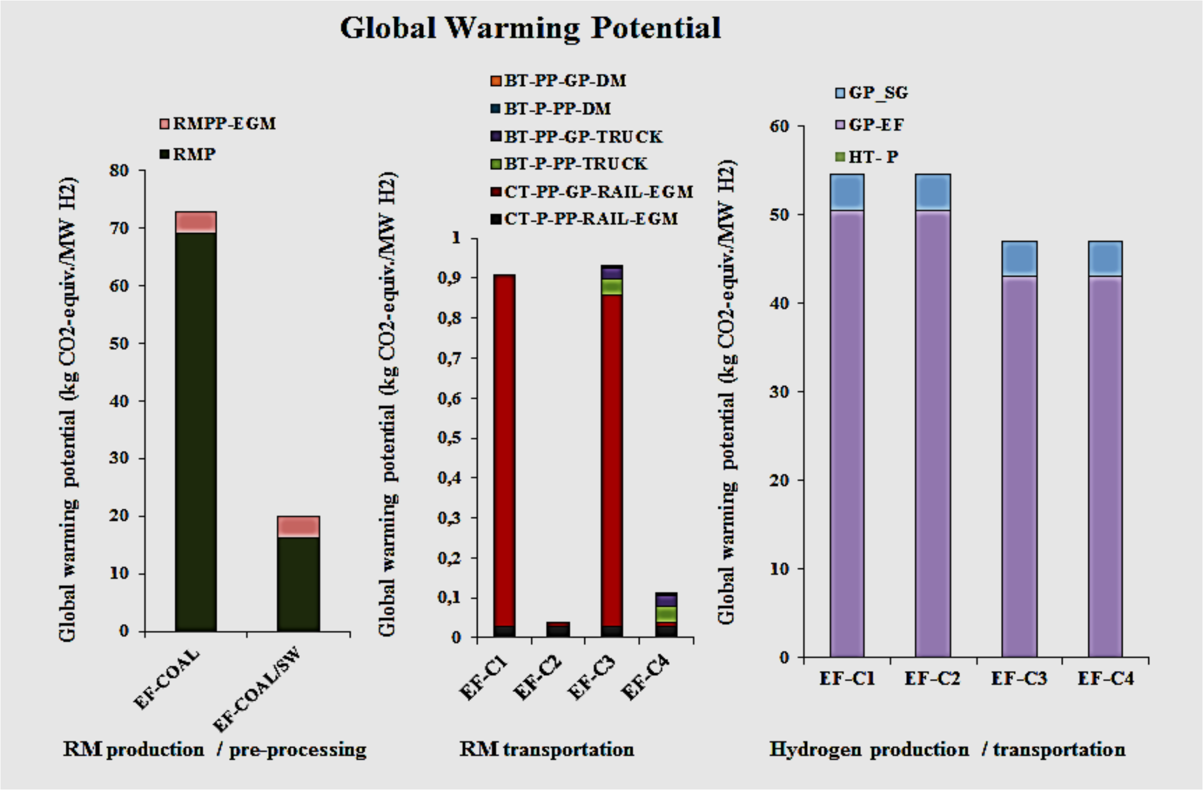


Figure 8.3. *EF system GWP*

The environmental impact determined by the gasification plant is influenced by the raw materials used. For the cases of coal gasification alone (EF-C1 and EF-C2) the CO_2 emissions are higher than for the cases of co-gasification (EF-C3 and EF-C4). The CO_2 emissions at the gasification plant derive from the gasification process and also from the steam production. As it is reported in Chapter 6, all the electricity that is generated is consumed by the ancillaries, resulting in zero net power output of the gasification plant.

Also for the cases of hydrogen production based on coal and biomass gasification, electricity driven pipelines are used for hydrogen transportation, and the delivery distance is also assumed to be 100 km.

8.3. Conclusions

The life cycle assessment (LCA) methodology is used to evaluate the environmental impact of two different hydrogen production technologies: hydrogen production by biomass steam gasification in a dual fluidised bed reactor system (DFB) and hydrogen production by gasification of coal and biomass using entrained flow technology (EF). For both hydrogen production pathways the raw materials production, pre-processing and transportation is considered and also hydrogen delivery to consumers.

The global warming potential is evaluated for each of the two hydrogen production processes sub-systems. Regarding the DBF system, the highest CO_2 emissions are registered for the DFB-C2 (gasification plant configuration with potassium carbonate as solvent for CO_2 separation), followed by the DFB-C3 (gasification plant configuration with Selexol® as solvent for CO_2 separation). The lowest environmental impact is determined by the DFB-C4 (CO_2 capture with Selexol® both from the producer gas and the flue gas). The environmental impact determined by the hydrogen production process based on gasification of coal and biomass is influenced by the raw material used. For the cases of coal gasification alone (EF-C1 and EF-C2) the CO_2 emissions are higher than for the cases of co-gasification (EF-C3 and EF-C4).

The DFB cases have smaller global warming potential than the EF cases. Also the abiotic depletion fossil potential and the human toxicity potential are smaller. The acidification and eutrophication potentials are smaller for the EF cases.

Hydrogen is a possible clean fuel of the future, however, hydrogen production should induce a lower environmental load than other energy carriers, such as gasoline, in order to gain the status of an environmentally friendly energy carrier (Ochs et al., 2010).

Chapter 9. General conclusions

9.1. Personal contributions

The author's personal contributions are detailed in the second, third and fourth part of the thesis, where two hydrogen production systems based on gasification technology are assessed form technical, economic and environmental point of view.

The hydrogen production process based on biomass steam gasification in a dual fluidized bed reactor system is analysed in terms of hydrogen output efficiency, overall plant heating and power duty, carbon dioxide emissions (three solvents for carbon dioxide separation from the producer gas are investigated). Detailed flowsheet model of hydrogen production plant, based on the design of the biomass gasification plant in Güssing, Austria are developed in chemical engineering software Aspen Plus®. The producer gas composition (after the DFB system) predicted by the model is compared with the real plant measured result.

Technical aspects of hydrogen production technology through co-gasification of coal and biomass based on entrained flow technology (three plant configurations based on different entrained flow reactors are to be analysed) are invetigated. A performance analysis regarding the energy efficiency of the process, carbon conversion rate, syngas composition and the carbon dioxide capture rate are carried out in order to determine the most suitable plant configuration for hydrogen production. The effect of biomass co-firing on gasification based hydrogen production process is also investigated. The simulations are made using chemical process simulation software Aspen Plus®.

Moreover, the results form Aspen Plus® simulations are used to develop a discrete event simulation model with Arena software in order to address gasification based hydrogen production supply chains analysis under demand variability, form the raw materials production, pre-processing and delivery stages to hydrogen production and distribution stages.

Also the two gasification based hydrogen production pathway are compared and evaluated in terms of environmental impact, following life cycle assessment methodology with GaBi software.

As mentioned in Section 4.1 a pilot plant for hydrogen production, which uses the producer gas from the biomass CHP Güssing, is design and used to test different steps of the process and the results presented in this thesis can contribute to the research work carried out for the application at industrial scale (design and operation of a 50 MW demonstration plant near a refinery in Austria). The overall hydrogen production process configuration and the results for biomass co-firing effect on the system that are reported in this thesis can be used as a starting point for the basic engineering of a real plant. Also the study regarding the biomass co-firing implications from technical, economic and environmental point of view can be used for the transition of a hydrogen production plant from coal to coal/biomass co-firing.

9.2. List of publications

I. **Mirela Muresan**, Reinhard Rauch, Hermann Hofbauer, Calin-Cristian Cormos, Paul-Serban Agachi; High purity hydrogen from biomass gasification in dual fluidized bed system: Aspen Plus® process simulation; *ICPS 13 - International Conference on Polygeneration Strategies*; Vienna University of Technology, Vienna, Austria**;** September, 3rd - 5th, 2013.

II. **Mirela Muresan**, Călin-Cristian Cormos, Paul-Serban Agachi; Techno-economical assessment of coal and biomass gasification-based hydrogen production supply chain system; *Chemical Engineering Research and Design*; 91, 8, 1527-1541, 2013; Impact factor: 1.927.

III. **Mirela Muresan**, Călin-Cristian Cormos, Paul-Serban Agachi; Multiproduct, multiechelon supply chain analysis under demand uncertainty and machine failure risk; *Proceedings of the 22nd European Symposium on Computer Aided Process Engineering* (ESCAPE 22, London, UK, 17 - 20 June 2012); 30, 462 - 466, 2012.

IV. **Mirela Badaluta**, Calin-Cristian Cormos, Paul-Serban Agachi; Hydrogen production through co-gasification of coal and biomass with carbon dioxide capture; *Studia Universitatis Babes - Bolyai, Chemia,* LVII, 1, 167-174, Cluj-Napoca, Romania, March 2012; Impact factor: 0.129.

V. **Mirela Badaluta**, Calin-Cristian Cormos, Paul-Serban Agachi; High purity, high pressure hydrogen production through co-gasification of coal and biomass; *CAPE*

Forum 2012 – Computer Aided Process Engineering, University of Pannonia, Veszprem, Hungary; 26 - 28 March 2012.

VI. **Mirela Muresan**, Călin-Cristian Cormos, Paul-Serban Agachi; Comparative life cycle analysis for gasification - based hydrogen production systems; Article under review; Submitted to *Journal of Renewable and Sustainable Energy*; August 2013; Impact factor: 1.51.

VII. **Mirela Muresan**, Călin-Cristian Cormos, Paul-Serban Agachi; Biomass gasification – based hydrogen production supply chain analysis under demand variability; Article under review; Submitted to *Journal of Renewable and Sustainable Energy*; September 2013; Impact factor: 1.51.

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