BIOGLYCEROL REFORMING FOR HYDROGEN-BASED POWER GENERATION: PROCESS CONFIGURATION, THERMODYNAMIC SIMULATION, PROCESS INTEGRATION AND PERFORMANCE ASSESSMENTS

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ABSTRACT

This paper is evaluating the conceptual design, thermodynamic modeling and simulation and techno-economic assessments of hydrogen-based power generation using bioglycerol reforming at industrial scale with and without carbon capture. The power plant concepts generated about 500 MW net power output. The power plant designs of bioglycerol reforming were thermodynamic modeled and simulated to produce mass and energy balances for quantification of key plant performance indicators (e.g. bioglycerol consumption, energy efficiency, ancillary energy consumption, specific CO_2 emissions, capital and operational costs etc.). A particular accent is put on assessment of reforming unit operation conditions, process integration issues of bioglycerol reforming unit and the syngas conditioning line with carbon capture unit, modeling and simulation of whole plant, thermal and power integration of various plant sub-systems by pinch analysis.

INTRODUCTION

Due to the continuous increase of the world energy demand and fossil fuels depletion, new sources of renewable energy are required to be developed. A solution for renewable fuels to be used in transport sector is based on biodiesel. Biodiesel is an alternative fuel of fossil diesel with positive environmental impact, non-toxic, bio-degradable and near zero CO_2 emission. The main by-product of biodiesel production is glycerol.

In addition to above mentioned aspects, hydrogen is considered to be one clean energy carrier for the future as well as an important chemical for the petro-chemical sector [1]. Hydrogen produced from bio-glycerol is seen as an important energy carrier for the future low carbon economy in combination with renewable sources and decarbonized fossil fuels [2,3]. This makes glycerol a potentially economically viable and environmentally friendly option. To produce hydrogen or other combustible gases (e.g. syngas), the glycerol steam reforming has received considerable attention.

Hydrogen production by catalytic glycerol steam reforming can occur first through glycerol dehydrogenation onto the catalyst surface and undergo desorption, followed by water gas shift or methanation reaction. The reforming process takes place under the action of a metal catalyst capable of breaking C-C bonds into smaller molecules (e.g. CH_4, CO_2, CO, H_2O, C_2H_4O) [2]. Most studies for hydrogen production from glycerol, published in literature, were mainly focused on noble metal-based catalysts and commercially available catalysts with low cost. For the bioglycerol steam reforming for hydrogen production (which can then be used for various applications), more sustainable, a low-cost catalyst is recommended: Ni–Mg–Al, Ni–Cu–Al, Ni–Cu–Mg, Ni–Mg, Ni–Al catalysts.

The major drawback of glycerol steam reforming is carbon formation due to the cracking of some hydrocarbons including CH_4 [4]. To both minimize carbon formation and favor hydrogen production, the thermodynamic studies [5] concluded that the steam reforming of glycerol should be performed at high temperatures (700 - 900^oC) with high water to glycerol molar feed ratio. The reaction pathway for bio-glycerol steam reforming involves very complex reactions such as: steam reforming (1), glycerol decomposition (2), water gas shift (3) and methanation (4) [4]:

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \quad (1)$$

$$C_3H_8O_3 \rightarrow 3CO + 4H_2 \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad (4)$$

The evaluated thermo-chemical conversion of bioglycerol to hydrogen and then to power generation based on catalytic reforming process is presented in this paper. The power block is based on a hydrogen-fuelled Combined Cycle Gas Turbine (CCGT). Another important challenge that lay in front of the whole industrial sector (including heat and power production) is the pressing need to reduce the greenhouse gas emissions. Low carbon industrial applications needs to be developed to curb the CO_2 emissions especially in heat and power systems. This paper evaluates also a carbon capture method (based on chemical gas-liquid absorption) used in conjunction with bioglycerol reforming for power generation. Although bioglycerol can be seen as a renewable energy source with low to negligible fossil CO_2 emissions, capturing CO_2 from the process will contribute to the development of innovative energy conversion systems with negative CO_2 emissions.

POWER GENERATION BASED ON GLYCEROL REFORMING PROCESS

The analysis presented in this paper is evaluating the conceptual design, thermodynamic modelling and simulation and techno-economic assessments of hydrogen-based power generation using bioglycerol reforming at industrial scale with and without carbon capture (plant concept with about 500 MW net power output). The syngas resulted from the bioglycerol reforming process would be then converted into hydrogen by water gas shift reaction [3,6] and then the hydrogen-rich gas is used for power generation. Two distinct designs of hydrogen-based power generation concepts with and without carbon capture were investigated:

Case 1: Hydrogen-based power generation by glycerol steam reforming without carbon capture (as a benchmark case);

Case 2: Hydrogen-based power generation by glycerol steam reforming with carbon capture using gas-liquid absorption (Methyl-DiEthanol-Amine - MDEA).

The conceptual design of hydrogen-based power generation plant with carbon capture using gas-liquid absorption is presented in Figure 1.

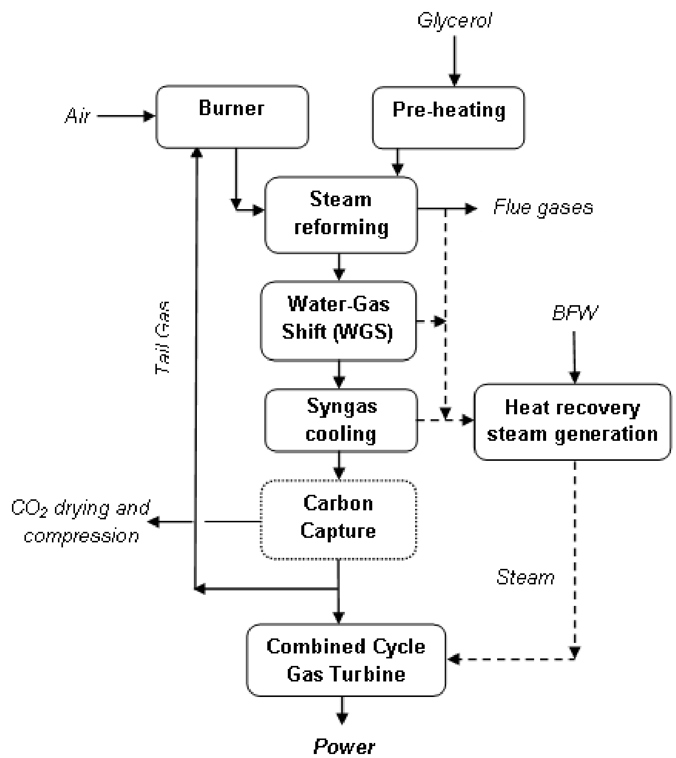

Figure 1 Bioglycerol reforming for hydrogen-based power generation concept with carbon capture unit

In the design concept proposed in this paper (see Figure 1), the preheated bioglycerol is converted into syngas using a nickel-based catalyst and which than is shifted with steam. The syngas water gas shift stage is used to transform the carbon species into CO_2 and to concentrate the syngas energy in form of hydrogen. The CO_2 stream coming from water-gas shift is captured in a gas-liquid absorption / desorption cycle using MDEA. The captured CO_2 stream is dried and compressed before being sent to storage / utilization. The hydrogen-rich gas can be used for power generation (as presented in this paper) or / and can be purified in Pressure Swing Adsorption (PSA) unit to the desired specification and sent to external customers (e.g. chemical applications, PEM fuel cells etc.). To cover the heat duty of the reforming reaction some of the hydrogen-rich gas is used in an external burner [3,7].

An important factor for the performance of any Carbon Capture and Storage (CCS) plant represents the pressure and composition of captured CO_2 stream. As CO_2 delivery pressure, 120 bar has be considered and the captured CO_2 quality specification being compatible with Enhanced Oil Recovery (EOR) applications (% vol.) :>95% CO_2,<2000 ppm CO, <250 ppm water, <100 ppm sulphur, <10 ppm oxygen, <4% other non-condensable gases (e.g. nitrogen, argon, etc.).

MODELING, SIMULATION, PROCESS INTEGRATION AND TECHNICAL EVALUATIONS

The power plant designs of bioglycerol reforming were thermodynamic modelled and simulated in ChemCAD using the design characteristics presented in Table 1 [3]. The mass and energy balances were used for quantification of key techno-economic and environmental plant performance indicators (e.g. bioglycerol consumption, energy efficiency, ancillary energy consumption, carbon capture rate, specific CO_2 emissions, capital and operational costs etc.).

Table 1 Main design characteristics

Bioglycerol fed and preheating	Fuel composition: 52.5% glycerol; 10% methanol; 14.5% methyl oleate Bio-fuel preheating: 400-500°C
Reformer	Catalyst: Ni - based Pressure: 30 bar Temperature: 850°C
Heat recovery steam generation (HRSG)	Pressure levels: 120 bar / 34 bar / 3 bar One medium pressure (MP) steam reheat Steam turbine isentropic efficiency: 85%
Tail gas expander	Gas preheating before expansion: 230°C Outlet pressure: 1.5 bar Expander efficiency: 70%
CO_2 compression and drying	Delivery pressure: 120 bar Compressor efficiency: 85% Drying solvent: TEG (Tri-ethylene-glycol) CO_2 quality (vol. %): >95% CO_2; <2000 ppm CO; <250 ppm H_2O; <100 ppm H_2S
Carbon capture unit	Absorption - desorption cycle Solvent: Methyl-diethanol-amine (MDEA) Solvent regeneration: thermal
Gas turbine	One turbine: M701G2 (MHPS) Net power output: 334 MW Net electrical efficiency: 39.5% Pressure ratio: 21
Heat exchangers	$\Delta T_{min.}$ = 10°C; Pressure drop: 3 - 5% of inlet pressure

As thermodynamic model used in the simulations, thermodynamic equilibrium has being assumed for calculations (e.g. glycerol reforming, gas-liquid absorption etc.). The choice of thermodynamic equilibrium was considered taking into account the high operating temperatures for the reforming unit.

Soave-Redlich-Kwong (SRK) equation of state with Boston-Mathias modifications was used as thermodynamic package. Since all carbon capture designs were equipped with a CO_2 drying unit, TEG Dehydration thermodynamic package was considered. Regarding the glycerol reforming, Gibbs free energy minimization reactor was used. The developed models and simulation results were validated against experimental data.

The plant concept of hydrogen-based power generation by glycerol steam reforming process was designed in a totally thermally integrated mode. Pinch analysis (with a conservative value of 10°C as minimum temperature difference) was used as main heat and power integration analysis tool [8]. The only energy input of the plant is the glycerol feedstock. The all heating duties needed for various processes (e.g. steam reforming, carbon capture unit etc.) are recovered from available hot streams within the plant (e.g. the hot flue gases, steam flow generated in the water gas shift stage and syngas conditioning, tail gas burner etc.). The hot and cold composite curves for bioglycerol steam reforming (without carbon capture) and for power generation in case of thermally integrated designs are presented in Figure 2 and Figure 3.

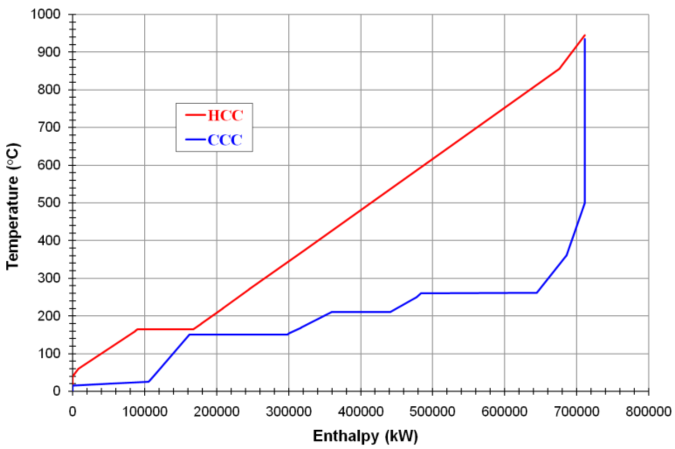

Figure 2 Hot and cold composite curves for bioglycerol steam reforming

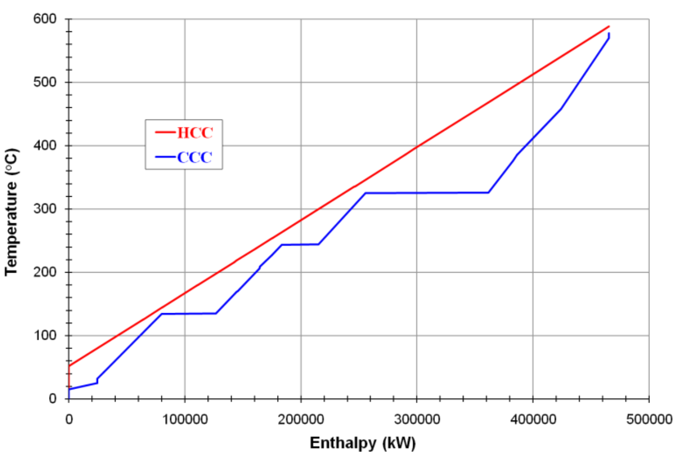

Figure 3 Hot and cold composite curves for power block (combined cycle)

Both Figures 2 and 3 show the heat duty (expressed as energy flow in kW) recovered as steam from the process hot streams (e.g. gas turbine hot gases, reformer flue gases etc.). The hot composite curves show the available heat duty of hot streams (heat sources) since the cold composite curves show the heat duty of cold streams (heat sinks).

To assess the overall techno-economic and environmental performance of the hydrogen-based power generation by glycerol steam reforming process the simulation's results: mass flows, compositions, temperatures, pressures, gross and net power were used. To compare the two power plant cases proposed in this work, the following key performance indicators [10] were used:

- Gross electrical efficiency is the ratio of the gross power output [MW_e] and bioglycerol thermal energy [MW_{th}];
- Net electrical efficiency is the ratio of the net power output [MW_e] and bioglycerol thermal energy [MW_{th}];
- Carbon capture rate (CCR) is the ratio of the molar flow of captured carbon dioxide and carbon molar flow from the bioglycerol);
- Specific CO_2 emission is calculated considering the emitted CO_2 mass flow for each MW net power output.

The key performance indicators for all evaluated cases with/without carbon capture are presented in Table 2.

Table 2 Bioglycerol reforming without CCS (Case 1) / with CCS (Case 2)

Main Plant Data	Units	Case 1	Case 2
Bioglycerol flowrate	t/h	275.56	275.56
Glycerol calorific value (LHV)	MJ/kg	15.26	
Feed thermal energy LHV (A)	MW_{th}	1168.06	1168.06
Gas turbine output	MW_e	334.00	334.00
Steam turbine output	MW_e	209.47	192.59
Expander power output	MW_e	5.22	3.77
Gross electric power output (B)	MW_e	548.69	530.36
Reformer island power consumption	MW_e	0.80	0.80
CO_2 capture, drying and compression	MW_e	0.00	20.15
Power island power consumption	MW_e	10.63	11.05
Total ancillary power consumption (C)	MW_e	11.43	32.00
Net electric power output (D = B – C)	MW_e	537.26	498.36
Gross electrical efficiency (B/A * 100)	%	46.97	45.40
Net electrical efficiency (D/A * 100)	%	45.99	42.66
Carbon capture rate	%	0.00	80.00
CO_2 specific emissions	kg/MWh	668.49	151.57

As can be noticed from Table 2, both investigated bioglycerol reforming cases generate about 500 – 538 MW net power. The net power efficiency of carbon capture case is around 42 - 43%. The energy penalty for pre-combustion CO_2 capture concept analysed in this paper is about 3.33 net electricity percentage points. This energy penalty is rather low in comparison to post-combustion CO_2 capture concepts using the same solvent (MDEA) were the energy penalty is about 10 net percentage points. The energy duty for pre-combustion CO_2 capture for Case 2 is 0.65 MJ / kg CO_2 (for the comparison reason, for post-combustion CO_2 capture the energy duty is about 3 MJ / kg).

The carbon capture rate is about 80 % (lower than in standard CCS studies which consider 90% as a minimum value) due to the residual methane and carbon monoxide in the syngas. These species are not captured by the carbon capture unit and get burned in the gas turbine. As mentioned in Table 1, the quality specification of captured CO_2 stream is important for any CCS design. The investigated carbon capture option (MDEA-based gas-liquid absorption) evaluated in this paper complies with the proposed specification of captured CO_2.

The major issues, generally speaking, of energy conversion systems with carbon capture are the energy and cost penalties compared to the similar systems without carbon capture. The lower energy and cost penalties for CO_2 capture, the more attractive the energy conversion systems with CCS are. Accordingly, reducing both energy and cost penalties for CO_2 capture is a major issue for CCS deployment at large scale.

The technical results of glycerol-based power plants show that the pre-combustion carbon capture design (Case 2) has promising high energy efficiency compared to other energy conversion systems (e.g. combustion) with post-combustion CO_2 capture where the energy penalty is much higher (in the range of 10 net power efficiency percentage points) than for the evaluated system presented here.

ECONOMIC EVALUATIONS

The economic assessment of evaluated power plants based on bioglycerol reforming cases took into consideration estimation of capital costs (total investment costs and specific investment costs per kW net power), operational and maintenance (O&M) costs and power generation costs. The followed economic assessment procedures are described in details in the literature [9,10].

Total investment costs were evaluated based on main plant subsystems using the cost correlation method. The plant subsystems considered in the evaluation were the following: reformer island, syngas processing unit, CO_2 capture plant (MDEA-based gas-liquid absorption), CO_2 processing and drying, power island and utilities and offsite units). The mass and energy balances, available after process simulation, by each specific plant subsystem were used as scaling parameter for the production capacity. The parameters of the cost correlation method used to estimate the capital costs of evaluated plant concepts are presented in [10,11]. The specific capital investments are calculated considering the capital cost and gross/net generated power for each power plant (see Figure 4).

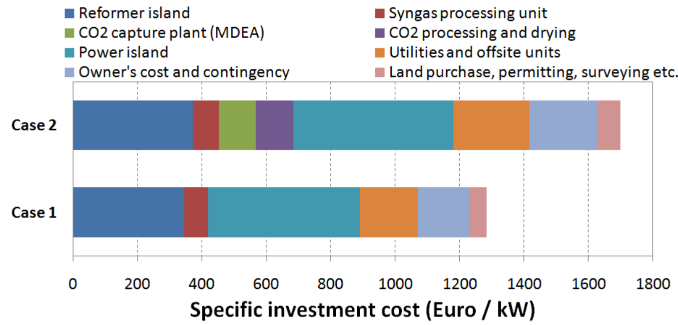

Figure 4 Specific investment cost estimation for hydrogen-based power generation by glycerol steam reforming process

As can be noticed from Figure 4, the specific investment costs per kW net power are in the range of 1283 and 1700 € / kW net. The introduction of pre-combustion CO_2 capture stage implies a 32.5% increase of specific investment cost. For comparison reason, when consider the coal-based power plants with carbon capture the specific investment costs are significantly higher than 2500 € / kW net [12,13]. This evaluation shows the potential benefits of bioglycerol-based power plants to deliver low investments solutions.

The operational and maintenance (O&M) costs have two components: fixed and variable costs. The methodology to assess the O&M costs is based on the Peter's and Timmerhaus method presented in [9]. The distribution of O&M costs (between fixed and variable components) is presented in Figure 5, expressed in €/MWh.

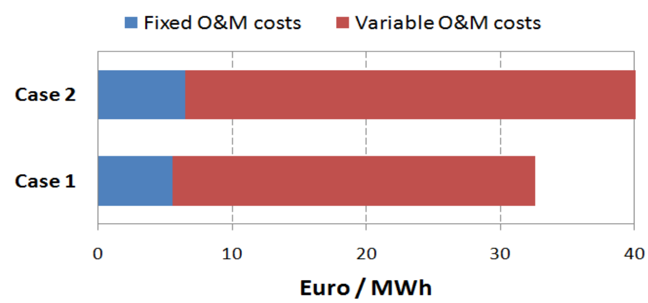

Figure 5 Distribution of O&M costs.

As can be noticed, the CCS design exhibits a 23% increase of O&M costs compared to the case without carbon capture (40.11 € / MWh vs. 32.60 € / MWh). The next evaluated economic parameters are cost of electricity and CO_2 capture costs. The net present value (NPV) method was used for calculation of levelised cost of electricity (LCOE) [9].

The CO_2 capture costs (CO_2 removal and avoidance costs) are important parameters when assess various carbon capture technologies (e.g. pre-combustion, post-combustion, oxy-combustion) [12]. CO_2 capture costs are calculated using the levelised cost of electricity in the power plant with carbon capture (Case 2) compared with cost of electricity without carbon capture (Case 1) as well as specific CO_2 emissions in both cases, see equations (5) and (6).

$$CO_2\ removal\ cost = \frac{LCOE_{with\,CCS} - LCOE_{without\,CCS}}{CO_2\ removed} \quad (5)$$

$$CO_2\ avoided\ cost = \frac{LCOE_{with\,CCS} - LCOE_{without\,CCS}}{CO_2\ emissions_{without\,CCS} - CO_2\ emissions_{with\,CCS}} \quad (6)$$

Table 3 presents the levelised cost of electricity and CO_2 capture costs for both evaluated cases.

Table 3 Levelised cost of electricity and CO_2 capture costs

Parameter	Units	Case 1	Case 2
Levelised cost of electricity	€ / MWh	49.85	65.86
CO_2 removal cost	€ / t	-	26.75
CO_2 avoided cost	€ / t	-	31.00

For the bioglycerol-based power plant, the introduction of carbon capture implies an increase of electricity cost with about 32%. In order to evaluate the dependence of electricity cost on various factors (e.g. capital cost, fuel cost, O&M cost etc.) sensitivity analysis were performed. Figures 6 and 7 presents the variation of electricity cost and CO_2 avoided costs with capital cost (-/+ 10%), fuel cost (-/+ 10%), operation and maintenance cost (-/+ 10%), interest rate (-/+ 1%) and availability factor (+/- 5%) for bioglycerol-based power plant with carbon capture (Case 2).

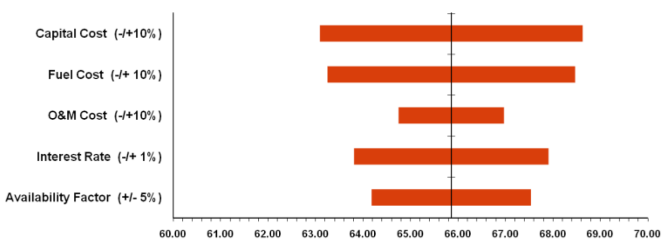

Figure 6 Levelised cost of electricity sensitivity analysis

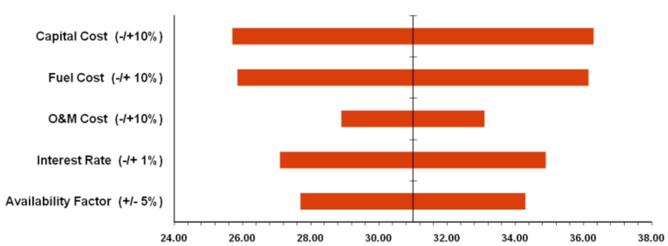

Figure 7 CO_2 avoidance cost sensitivity analysis

The capital costs and the fuel costs have the most pronounced influence on electricity and CO_2 avoidance costs, followed by the interest rate and the availability factor. For any power plant concept with carbon capture (as the situation of Case 2), the influence of CO_2 storage on electricity cost is an important aspect. Figure 8 presents the variation of electricity cost vs. CO_2 storage cost.

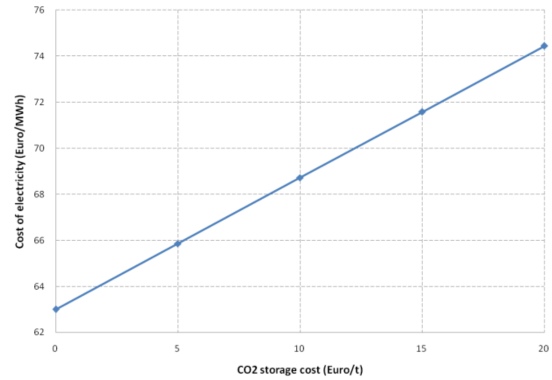

Figure 8 Cost of electricity vs. CO_2 storage cost

Evaluations of other in-depth techno-economic parameters on electricity and CO_2 capture costs are equally important [14,15]. For instance, cumulative cash flow analysis is an important economic parameter to be considered when evaluating the whole project life. In the current analysis, 29 years was considered as whole project life divided as follow: 3 years for plant construction, 25 years for plant operation and 1 year for recovering the working capital [16]. The cumulative cash flows for evaluated power plants are presented in Figure 9.

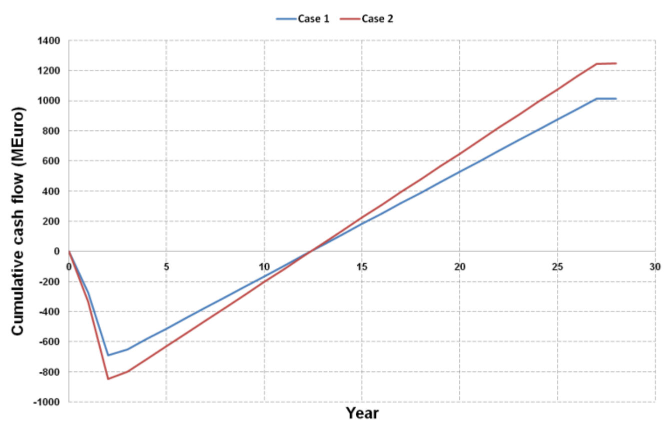

Figure 9 Cumulative cash flow analysis for different case studies with and without carbon capture

As can be noticed from Figure 9, the payback period for both bioglycerol reforming-based power plant cases are about 12.5 years. The reason for the same payback period in both cases is that the interest rate was the same (8%). The cumulative cash flow for the CCS design (Case 2) is about 22% higher than for the corresponding design without carbon capture mainly because the higher electricity cost (which implies higher revenues).

CONCLUSIONS

Two distinct conceptual designs of hydrogen-based power generation using bioglycerol reforming at industrial scale (plant concept with about 500 MW net power output) were investigated, one without carbon capture (considered as a benchmark case) and one with carbon capture. In the design with carbon capture, the shifted syngas is treated for removing CO_2 with a chemical solvent (MDEA) in gas-liquid absorption process. The carbon capture rate is higher than 80% considering the total feedstock carbon. Considering that the fuel used (bioglycerol) has a low or negligible fossil carbon footprint (being a byproduct from the biodiesel production from vegetable fats), the reforming process with CCS has a negative CO_2 emissions contributing to decreasing atmospheric CO_2.

The plant designs were thermodynamic modeled and simulated to produce the mass and energy balances for quantification of key plant performance indicators (e.g. bioglycerol consumption, gross and net electrical efficiencies, ancillary energy consumption, specific CO_2 emissions, capital and operational costs, electricity cost etc.). A particular accent is put on assessment of reforming unit operation conditions, process integration issues of bioglycerol reforming unit and the syngas conditioning line with carbon capture unit, modelling and simulation of whole plant, thermal and power integration of various plant sub-systems by pinch analysis.

The results showed a clear advantage of the pre-combustion MDEA-based carbon capture design over the benchmark design without carbon capture in term of reduced energy and cost penalty for CO_2 capture. Technical and economic indicators showed that the net electrical efficiency for benchmark case is 45.99%, and about 3 net electricity percentage points as the energy penalty was observed in case of carbon capture concept plant for an 80% CO_2 capture rate. The total capital investment costs, for studied cases, are around 1300 Euro/kW net (for the benchmark case) and 1700 Euro/kW net for carbon capture concept. As a main conclusion, the study's results show that hydrogen-based power generation using bioglycerol reforming is a promising technology for the development of future low-carbon economy.

ACKNOWLEDGMENTS

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