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Life Cycle Assessment of Bio-methanol Derived from Various Raw-materials

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Bio-methanol production from biomass or from carbon dioxide and hydrogen, generated using renewable electricity, are considered to be sustainable routes nowadays. The aim of the present study consists on the environmental evaluation of bio-methanol production using Life Cycle Assessment (LCA) methodology. Two different bio-methanol production processes such as bio-methanol production from an external CO_2 stream and H_2 from water electrolysis, electricity being produced using various sources (i.e. biomass, solar, wind, and hydro or mix electricity) as well as woody biomass gasification for syngas production, syngas being further transformed into bio-methanol, are considered in the current study. The processes were simulated using computer aided design tools (i.e. ChemCAD and Aspen Plus process simulators). The environmental assessment is carried out using GaBi software. The LCA is a cradle-to-gate study with the following system boundaries: *a)* upstream processes (i.e. biomass, solvent and electricity supply chains, H_2 production, catalysts production and transportation); *b)* main processes: bio-methanol production through direct gasification and from CO_2 hydrogenation and *c)* downstream processes: solvent degradation and disposal of wastes. The production of one ton of bio-methanol was considered as functional unit in the present investigation. ReCIPe method was chosen as life cycle impact assessment method. Purities higher than 99% are obtained for the main product. Significant environmental impact categories (i.e. Global Warming Potential, Human Toxicity Potential, Fossil Depletion Potential) are discussed and the influence of various sub-processes is investigated. For instance, the best result in terms of Human Toxicity Potential, 12.30 kg 1,4-DB eq./t_{MeOH}, was obtained in the case of hydroelectric sources, while the same indicator was at least two times higher for other scenarios. From the environmental point of view, the scenario which relies on hydroelectric power performed better in six out of nine environmental impact categories as compared to other scenarios, being succeeded by the one considering wind power as electricity source.

1. Introduction

Population growth, together with the advances in technology, has caused a sharp increase in total energy consumption (Gautam et al., 2020). Fossil fuels, in particular natural gas and petroleum fuels, are the leading source when referred to electricity for either household work or industrial activities (Kumar et al., 2020). As a consequence of the above-mentioned grounds, nowadays, one of the main challenges is represented by the electricity price surge among with the environmental effects brought by the use of fossil fuels (Guo and Zhong, 2018). Several renewable and sustainable energy sources are currently investigated by researchers to find alternative solutions designed to meet the needs of a decarbonised electric system (Wang and Chen, 2019). Biomass, wind power, solar energy, hydro power, or nuclear energy are considered perfect solutions given their general availability (Owusu and Sarkodie, 2018). Nevertheless, biomass is perceived as being the most efficient amongst the popular renewable energy sources (Shen and Yoshikawa, 2013). Bio-methanol, a biomass derived biofuel, bestows an auspicious renewable energy alternative (Sippula et al., 2019). Methanol is traditionally obtained from non-renewable sources, such as natural gas, through gasification or steam reforming (Amaral et al., 2019). On account of the environmental implications and actual restrictions, the attention of the researchers has moved towards a more sustainable process, such as bio-methanol generation either through biomass gasification or CO_2 hydrogenation (van der Ham et al., 2012). The novelty of the

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current work consists on the comparison of two different bio-methanol production processes, CO_2 hydrogenation and woody biomass gasification, using the LCA methodology in order to understand which route is the most environmentally friendly.

2. Plants configurations and models assumptions

Table 1 presents the cases investigated in the present study.

Table 1: Cases investigated in the present research

Case name	Final product	Technology for methanol production	Raw-material for methanol production	Electricity source for H_2 generation through water electrolysis
Case 1	Bio-Methanol	Hydrogenation	CO_2 and H_2	Sweden grid mix
Case 2	Bio-Methanol	Hydrogenation	CO_2 and H_2	EU grid mix
Case 3	Bio-Methanol	Hydrogenation	CO_2 and H_2	Solar power
Case 4	Bio-Methanol	Hydrogenation	CO_2 and H_2	Wind power
Case 5	Bio-Methanol	Hydrogenation	CO_2 and H_2	Hydroelectric power
Case 6	Bio-Methanol	Hydrogenation	CO_2 and H_2	Biomass
Case 7	Bio-Methanol	Hydrogenation	CO_2 and H_2	Nuclear power
Case 8	Bio-Methanol	Gasification	Woody biomass	-

Cases 1 - 7 describe the bio-methanol production through hydrogenation, hence starting from CO_2 and H_2, with the electricity required for water electrolysis process coming from different sources. Case 1 and Case 2 describe the bio-methanol generation through hydrogenation using electricity grid mix (for Sweden in Case 1, respectively the average grid mix value for Europe in Case 2). Solar power is used to generate the electricity for Case 3, while wind power was assumed as electric power source in Case 4. Case 5 follows the same route as the previously presented cases, using hydroelectric power. Biomass, respectively nuclear power, were used for Case 6 and Case 7 as power sources. The last case takes into consideration the analysis of bio-methanol generation through woody biomass gasification. The block flow diagram for bio-methanol production process through CO_2 hydrogenation is illustrated in Figure 1.

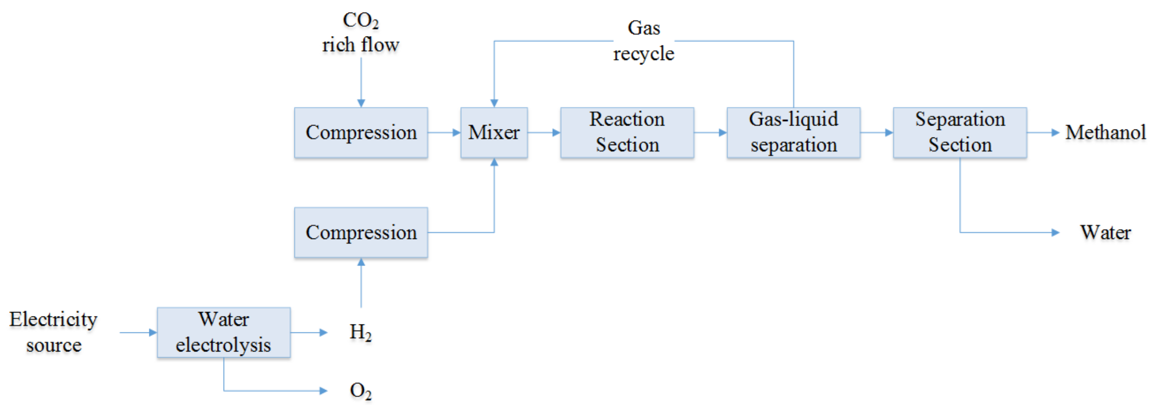


Figure 1: CO_2 hydrogenation for bio-methanol production derived from various sources

The amount of CO_2 required for synthesis is brought by a CO_2 rich flow, which may be an output from a carbon capture system. With the purpose of considering a green technology, water electrolysis was employed to produce the needful quantity of H_2, with a wide variety of electricity sources being considered. Both feed streams, H_2 and CO_2, follow a compression stage before being mixed with a gas recycle stream and further sent to the reaction section. The reactor outlet is sent to a gas-liquid separation system. The gas stream is sent to a mixer and mixed with a recycle stream, while the liquid phase moves forward to the separation section, where, finally, liquid methanol is obtained.

Life cycle assessment (LCA) is an effective instrument used to determine the environmental burden of a product or process (ISO). Generally, as according to the International Organization of Standardization (ISO), an LCA study comprises four different stages, *Goal and Scope definition*, *Life Cycle Inventory (LCI)*, *Life Cycle Impact Assessment (LCIA)* and finally, *Interpretation*. The scope and objectives of the study, together with the definition of the functional unit and system boundaries must be clearly defined during the first phase. In the second phase, LCI, all the emissions to air, water and soil are appraised, after which, during the third phase, LCIA, all the emissions are linked with the corresponding environmental impact categories. As a final step, throughout the interpretation stage, the full results are explained, while taking into account all uncertainties (ISO, 2006). The goal of the current research is to ascertain the most sustainable route for bio-methanol production by taking into consideration several different electric power sources. Considering that all the inputs and outputs of the process are linked with a standard, the functional unit must be the same for all investigated cases. The proposed functional unit of the present study is one ton of bio-methanol. With regard to the system boundary definition, depending on the desired complexity of the study, but also on the assessed stages of the process, there are four various alternatives. *Cradle-to-grave* is the first alternative and it is used when the study covers all process' stages, from the extraction of raw materials up to the treatment of the used product. As second alternative, *Cradle-to-gate* option might be considered when only the steps from the raw materials extraction and production phase are evaluated. In order to assess the production phase, a *Gate-to-gate* approach shall be followed, while *Gate-to-grave* option allows the evaluation of the impact of a product after its distribution. The current work is a *Cradle-to-gate* study as it considers processes from raw-materials extraction (i.e. limestone extraction) up to the finished product, bio-methanol. ReCIPe impact assessment method was chosen for the current study as it is seen as an updated version of both, CML and Eco-indicator 99, due to the fact that the impact categories can be determined either at midpoint or endpoint level. Midpoint impact categories provide a better understanding, since the impact is linked with a single environmental issue (Foteinis et al., 2020). The following midpoint impact categories will be further assessed and discussed: global warming potential (GWP), freshwater eutrophication potential (FEP), ozone depletion potential (ODP), fossil depletion potential (FDP), freshwater ecotoxicity potential (FETP), human toxicity potential (HTP), metal depletion potential (MDP), photochemical oxidant formation potential (POFP) and terrestrial ecotoxicity potential (TETP).

Table 2 illustrates the main design assumptions considered for the modelling and simulation of the involved cases.

Table 2: Main modelling and LCA design assumptions

	Assumptions
Modelling and simulation assumptions for CO_2 hydrogenation	Raw materials: CO_2, Water, Air. Main product: bio-methanol; By-product: Exhaust gases, Water. Thermodynamic package used: UNIFAC. Reactor thermal mode for methanol production: isothermal 210°C. Distillation column for methanol separation and purification: 57 stages, condenser mode: distillate component recovery 99.75% CH_3OH; reboiler mode: bottom component recovery 99.75% H_2O. Compressors and pump efficiencies: 75%. HE min ΔT: 10˚C.
LCA assumptions regarding electricity generation	Sweden electricity mix consists in: 42.22% nuclear power; 41.57% coal gases, 7.31% natural gas, 5.86% biomass, 1.86% waste and the rest accounts for peat, oil, biogas, hydro, wind and photovoltaic. EU electricity mix consists in: 27.63% nuclear power, 14.74% hard coal, 14.47% natural gas, 12.83% coal gases, 10.16% lignite, 7.98% wind power, 2.67% biomass, 2.01% biogas and the rest accounts for peat, oil, hydro, wind, photovoltaic, geothermal and waste. Solar power: mix of different photovoltaic technologies; operational life time of the panels: 20 years. Wind power: operational life time of the wind turbine and cables: 20 years. Hydro power: includes the following stages: run-of-river, storage and pump storage; operational life time of the hydro power models are 60 years. Biomass electricity: electricity produced in a biomass specific power plant and/or combined heat and power plant; considers the following: firing technology, de-dusting and flue gas desulfurization technologies. Nuclear power: consists in a mixture of pressure water and boiling water reactors; include the following: mining, milling, conversion, enrichment, fuel fabrication, uranium use, end of life treatment for spent fuel, end of life treatment for low level waste and intermediate level waste.

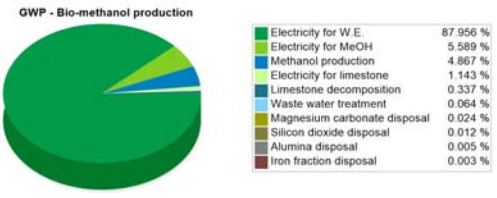
3. Results and discussions

The environmental results for the investigated cases are presented in Table 3.

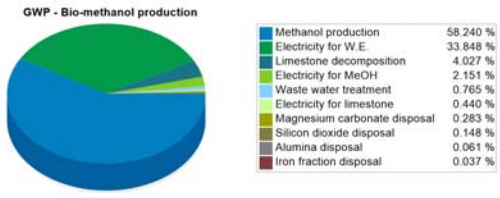
Table 3: Environmental results for the investigated cases

Scenario	Environmental impact categories								
	GWP	FEP×10^3	ODP×10^9	FDP	FETP	HTP	MDP	POFP	TETP×10^3
Case 1	1,117.23	13.40	38.04	144.35	2.39	72.40	39.52	2.37	52.55
Case 2	6,253.08	15.36	264.25	1,509.54	2.08	153.54	42.14	10.40	101.96
Case 3	1,383.42	3.58	24.20	290.90	0.55	338.50	491.75	3.60	1,743.79
Case 4	435.13	1.13	1.81	31.47	0.13	24.98	132.41	0.82	7.71
Case 5	522.57	0.93	1.05	6.48	0.10	12.30	51.27	0.67	2.44
Case 6	848.77	174.51	3.78	126.65	1.80	231.55	10.39	11.74	90.85
Case 7	392.71	1.32	83.79	26.65	4.92	82.80	28.99	0.92	90.20
Case 8	1,311.25	4.32	5.87	25.74	0.51	37.78	2.66	0.14	9.57

Nine impact categories were investigated with the highest values corresponding to the GWP and FDP, as it can be noticed from Table 3. In terms of GWP, the lowest value is obtained in the case when the electricity is produced from nuclear power, Case 7, with a GWP value of 392.71 kg CO_2 eq./t_{MeOH}, being followed by Case 4 (wind power) and Case 5 (hydro power) with 435.13 kg CO_2 eq./t_{MeOH}, respectively 522.57 kg CO_2 eq./t_{MeOH}. Case 2, electricity produced from EU electricity grid mix, records the highest value in terms of GWP (e.g. 6,253.08 kg CO_2 eq./t_{MeOH}), approximately 16 times higher as compared to the best case scenario, Case 7. Concerning the FEP indicator, Case 5 registers the smallest value, 0.93 kg P eq./t_{MeOH}, while similar values are obtained also in Case 4 and Case 7, with 1.13 kg P eq./t_{MeOH} and 1.32 kg P eq./t_{MeOH}. With regard to ODP, hydroelectric sources, Case 5, presents the smallest impact, 1.05 kg CFC-11 eq./t_{MeOH}, while at the opposite end, the case considering the electricity from EU grid mix, Case 2, has a 250 times higher impact. Similar to the GWP and FEP indicators, Case 4, with wind power electricity, has the second smallest value in terms of ODP, 1.81 kg CFC-11 eq./t_{MeOH}. With respect to FDP indicator, Case 2 shows the highest value (e.g. 1,509.54 kg oil eq./t_{MeOH}) while the lowest contribution is brought when considering Case 5 (e.g. 6.48 kg oil eq./t_{MeOH}). In the case of FETP and HTP, as well as TETP, the most environmentally friendly scenario is described by Case 5, with 0.10 and 12.30 kg 1,4-DB eq./t_{MeOH}, respectively 2.44 kg 1,4-DB eq./t_{MeOH}. Considering MDP and POFP impact categories, the lowest values, 2.66 kg Fe eq./t_{MeOH} and 0.14 kg NMVOC/t_{MeOH}, are obtained when the bio-methanol is produced through woody biomass gasification, Case 8. Considering the results of the environmental impact indicators reported in Table 3, Case 5, with electric power produced from hydroelectric sources, exhibits the best performance in six out of nine categories, hence it is considered as the most interesting route, from environmental perspective, for green methanol generation. At the opposite end, Case 2, bio-methanol production related to electricity generation from EU grid mix, registers the highest values in four out of nine impact categories, GWP, FEP, ODP and FDP. Details regarding to the most important sub-processes that have the highest influence on the main environmental impact categories, as previously mentioned GWP, FDP and HTP, are further detailed.
The GWP impact indicator for Case 2 and Case 5 is illustrated in Figure 2



A



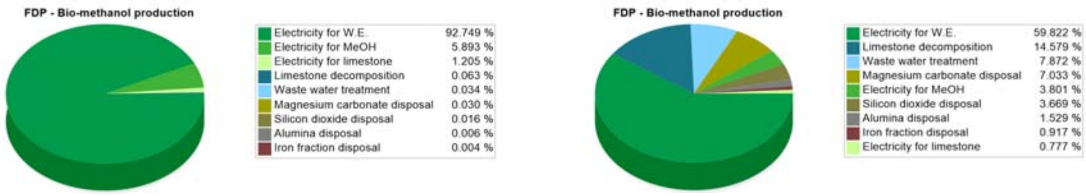
B

Figure 2: A) GWP indicator for bio-methanol production through CO_2 hydrogenation with electricity from EU-grid mix (Case 2)

B) GWP indicator for bio-methanol production through CO_2 hydrogenation with electricity from hydropower electric sources (Case 5)

Figure 2A presents the GWP distribution for Case 2, thus with the electricity coming from the EU grid mix. As noticed from Figure 2, from the total of 6,253.08 kg CO_2/t_{MeOH}, approximately 88% is due to the electricity generation required for water electrolysis process. Electricity generation for methanol production is placed as second contributor, with around 5.59% from the total GWP value, being followed by methanol production with a contribution of about 4.87% from the total share. Nevertheless, a substantial reduction on the impact of the electricity generation for both water electrolysis and methanol production occurs when hydroelectric sources

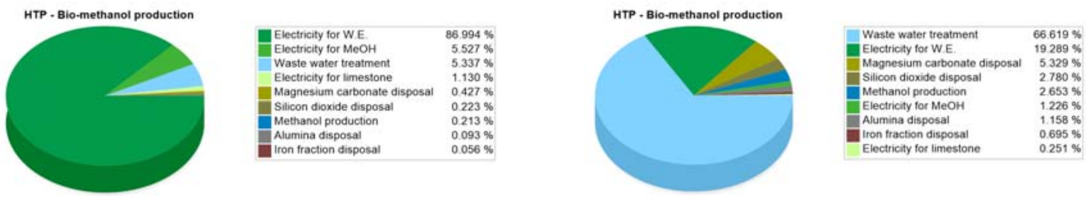
are used, Case 5. GWP distribution for Case 5 is presented in Figure 2B. As outlined, methanol production process exhibits the highest contribution to the total GWP value, more than half, more exactly 58.24%, from the total of 522.57 kg CO_2/t_{MeOH}. Electricity generation process for water electrolysis followed by limestone decomposition with 33.85%, respectively 4.03% from the total share are placed amongst the most influential sub-processes. As compared to Case 2, smaller contributions are brought by electricity generation for both, limestone extraction and decomposition and methanol production, processes.
The FDP distribution for Case 2 and Case 5 is shown in Figure 3.



A B

Figure 3: A) FDP indicator for bio-methanol production through CO_2 hydrogenation with electricity from EU-grid mix (Case 2)
B) FDP indicator for bio-methanol production through CO_2 hydrogenation with electricity from hydropower electric sources (Case 5)

Similar to the GWP impact indicator, for Case 5 (Figure 3A), the process with the most substantial influence is represented by the electricity generation for water electrolysis process with a share of nearly 93% out of the total 1,509.54 kg oil eq./t_{MeOH}. As previously mentioned, the EU electricity mix considers the electricity produced from hard coal, natural gas, lignite, biomass and others, therefore this considerable influence on the FDP impact indicator. As expected, electricity generation for methanol production process, but also for limestone extraction and decomposition with a share of 5.90%, respectively 1.20% are placed as second and third contributors, whilst limestone decomposition process, waste water treatment process and disposal of wastes have brought minor contributions. Figure 3B illustrates the FDP distribution for Case 5, thus the electricity is produced from hydropower electric sources. More than half of the overall contribution, approximately 60%, comes, as in Case 2, from the electricity generation required for water electrolysis process. On the other side, limestone extraction and decomposition and waste water treatment process stand out as second and third contributors with a contribution of 14.58% in the case of limestone extraction and decomposition and 7.67% for waste water treatment. An important reduction in the contribution of the electricity generation for methanol production as well as limestone decomposition can be observed. As a broad conclusion, the most important sub-process with the highest influence on the FDP impact indicator is the electricity generation for water electrolysis process.
The distribution for the HTP impact indicator for Case 2 and Case 4 is presented in Figure 4.



A B

Figure 4: A) HTP indicator for bio-methanol production through CO_2 hydrogenation with electricity from EU-grid mix (Case 2)
B) HTP indicator for bio-methanol production through CO_2 hydrogenation with electricity from hydropower electric sources (Case 5)

In regard to the bio-methanol production with the needed electricity related to the EU grid mix, Case 2, Figure 4A depicts that the production of electricity for water electrolysis process has the highest influence on the HTP, close to 87% from the total of 153.54 kg 1,4-DB eq./t_{MeOH}. As second contributor, similar to GWP and FDP indicator, is the electricity generation for methanol production process with a share of nearly 5.53%, being followed closely by the waste water treatment process with close to 5.34% out of the overall value. It may be observed that the power generation for water electrolysis stands out as the primary contributor to

GWP, FDP and HTP when the electricity is produced from the EU grid mix, being followed in each instance by the electricity generation for methanol production process. On the contrary, Figure 4B reveals that, in the case of using hydroelectric sources for power generation, Case 5, the main contributor to the overall HTP value is the waste water treatment process with a percentage of 66.63% out of the overall amount of 12.30 kg 1,4-DB eq./t_{MeOH}. A substantially reduced contribution on behalf of power generation for water electrolysis process may be observed, but it is still placed as second contributor with a share of 19.29%. The disposal of both, magnesium carbonate and silicon dioxide, have reduced, but considerable contributions with a percentage of 5.33%, respectively 2.78%, positioning them as third and fourth contributors.

Conclusions

The current study evaluates, from the environmental perspective, two different routes for bio-methanol production. On one hand, bio-methanol is produced through CO_2 hydrogenation, with the H_2 coming from water electrolysis using various different energy sources, while on the other hand, woody biomass gasification was employed. Several different environmental impact indicators together with the influence of various sub-processes are presented and discussed for the evaluated cases. As pointed out, the slightest value in terms of GWP, 392.71 kg CO_2 eq./t_{MeOH}, was obtained when using nuclear power, while with regards to FDP and HTP, the lowest values, 6.48 kg oil eq./t_{MeOH}, respectively 12.30 kg 1,4-DB eq./t_{MeOH}, are obtained in the case when bio-methanol was produced through CO_2 hydrogenation, with the electricity needed coming from hydroelectric power sources, Case 5. Therefore, the most attractive route for bio-methanol production, from the environmental point of view, proved to be the CO_2 hydrogenation with hydroelectric energy used as electric source.

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