

Biomass based sustainable Ammonia production: Digestion vs Gasification

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Abstract

The synthesis of ammonia is one of the most important chemical process in the world. The Haber Bosch process has predominantly been used to synthesize ammonia in the last decades. However, it uses coal or natural gas as raw materials. In this work, the path to produce ammonia from biomass has been evaluated and optimized. The thermochemical and the biochemical routes have been compared. Three alternative gasification technologies have been considered together with anaerobic digestion. For the reforming stage, two alternatives have been compared: autothermal and steam reforming. Finally, ammonia is synthesised in a multibed reactor with two different configurations: direct or indirect cooling. The problem is formulated as an MINLP but solved as a set of 14 NLPs. The indirect gasifier with the steam methane reforming and direct cooling ammonia reactor presents the best performance with an ammonia production cost of about 380 €/t. The biochemical route shows worse results to ammonia due to the low yield to biogas and, therefore, to ammonia.

Keywords: Ammonia, Biomass, Digestion, Gasification, Process Design.

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Introduction

Ammonia is one of the most important chemicals worldwide with a production of about 200 million tons per year, the second largest production for any chemical.¹ Around 85% of the ammonia production is devoted to synthesizing a wide range of fertilizers: urea, ammonium nitrate, ammonium sulphate, etc. The demand of fertilizers is expected to increase following the growth in global population and, therefore, in food demand². The forecasts foresee that the global ammonia production capacity could reach 237 million tons by 2020³. Ammonia production is gaining attention due to the possibility of using it as a means to store energy itself or as a hydrogen carrier. Different alternatives are being studied to convert ammonia into energy with high efficiency such as: internal combustion engines, PEM fuel cells after ammonia cracking or solid oxide fuel cells¹.

The current production processes use, mainly, natural gas or coal, as raw material⁴. However, these production schemes present high levels of greenhouse gases emissions. Coal based ammonia releases 3.4 ton of greenhouse carbon dioxide per ton of ammonia, meanwhile in the production of natural gas based ammonia, the levels of emissions are in the order of 2.7 ton of greenhouse carbon dioxide per ton⁵. A "Decarbonization" in the chemical industry is necessary to mitigate the effects of climate change and to meet the goals of international agreements. For example, the Paris agreement establishes that the increase in global temperature must be below 2 degrees Celsius during this century⁶. Another characteristic of the actual processes is the high energy requirements. Around 1-2% of the global energy is consumed in the ammonia synthesis⁷.

Alternative ammonia production processes are being developed following three pathways. The first one consists of producing hydrogen from water via electrolysis, separating air components to obtain nitrogen and synthesizing ammonia following the well-established Haber-Bosh process^{8,9}. Different air separation technologies have been studied depending on the production capacity¹⁰. The power needed for the entire process can be supplied using renewable resources or combining it with the electrical grid¹¹. A pilot plant using a wind turbine to generate power, electrolysis to produce hydrogen and pressure swing adsorption to produce nitrogen is being operated in Minnesota, U.S.¹². Another method to produce ammonia from renewable sources is its direct electrochemical formation. In this case, ammonia is synthesized in an

electrolytic cell using nitrogen and hydrogen (or directly water). This method allows a better integration with variable renewable energies such as wind or solar¹³. However, it is still under development and further research is required¹. The last alternative to produce renewable ammonia uses biomass as raw material. In this alternative, two main processes have been proposed: ammonia production from biomass digestion or from biomass gasification¹⁴. The production of ammonia from biomass via gasification has been reported in the literature presenting competitive costs and environmental performances¹⁵⁻¹⁹. For example, Tock et al.¹⁸ carried out an economic and environmental evaluation of the process. Arora et al.¹⁹ simulated the process at small scale in ASPEN Plus. In both cases, indirect gasification was considered. So far, no systematic analysis of biomass to ammonia following different transformation paths has been presented in the literature.

In this work, a systematic process level framework has been developed to optimize and evaluate the different paths of ammonia production from biomass. In the gasification section, three different gasifier configurations have been evaluated: indirect gasification, direct gasification with O₂/steam and direct gasification with air (or enriched air) and steam. The biochemical route via anaerobic digestion has also been analysed. In the hydrocarbons reforming stage, autothermal reforming and steam methane reforming have been compared. Finally, for the synthesis of ammonia, two types of reactors have been considered: multitubed reactor with direct or indirect cooling. The rest of the paper is organized as follows: Section 2 describes the process flowsheet and the alternatives to produce ammonia from biomass. Section 3 shows the modelling approach for each unit of the flowsheet. Section 4 presents the objective function, the solution and the cost estimation procedure. Section 5 comments on the results. First, the main operating variables for the different processes and a simplified environmental index computing the carbon dioxide emissions associated with the process, next the economic analysis for each alternative. A sensitivity analysis for the biomass price is also presented. Subsequently, a scale up/down study is shown for the most promising alternatives selected in the economic analysis. Finally, in Section 6, some conclusions are drawn.

Process description

The biomass selected for this work is switchgrass, with a large potential as a bioenergy crop²⁰. The switchgrass composition (in dry and ash free basis) used in this work can be seen in Table 1. The biomass flow rate for all cases of study presented in this work is fixed to 18 kg/s (0.6 MMt/year).

Table 1: Ultimate Analysis for the Switchgrass²¹

Ultimate Analysis	% Dry and Ash free
C	49.12
H	6.13
N	0.6
S	0.11
O	43.51

In the case of gasification, a dry switchgrass is used with a moisture content of 8.16% (% biomass as received) and an ash content of 4.59% (% dry biomass). For the digestion, wet switchgrass is employed. The features of the switchgrass for digestion are shown in the supporting information.

In Figure 1, a block flow diagram for the proposed superstructure is shown. Three gasifier designs have been evaluated for the gasification stage. Indirect gasification uses one chamber for the gasification where the biomass and the steam are fed. The char is burnt in a combustor to obtain the heat necessary for the gasification step. Direct gasification uses one single unit. Oxygen and steam are fed together with biomass. Finally, direct gasification with air and steam is also evaluated. The gasifier receives air or enriched air instead of oxygen as gasifying agent.

The raw syngas generated in the gasifiers is cleaned up to remove particles and hydrogen sulphide mainly. To remove the fine particles dragged with the raw syngas, a filter is set up just after the gasification section. The H₂S is removed using a bed of ZnO. After that, the gases are fed to the reformer. In this unit, the methane and other high hydrocarbons are transformed into hydrogen, carbon monoxide or dioxide and water. Two different reformer technologies have been evaluated: steam methane reforming (SMR) and autothermal reforming (ATR). In the first one, only steam is fed to the reformer, and the heat is supplied burning a fuel gas in a separated chamber. In the second one, together with the steam, air is

supplied. A fraction of the inlet hydrocarbons is combusted inside with the oxygen delivering the heat necessary for the process.

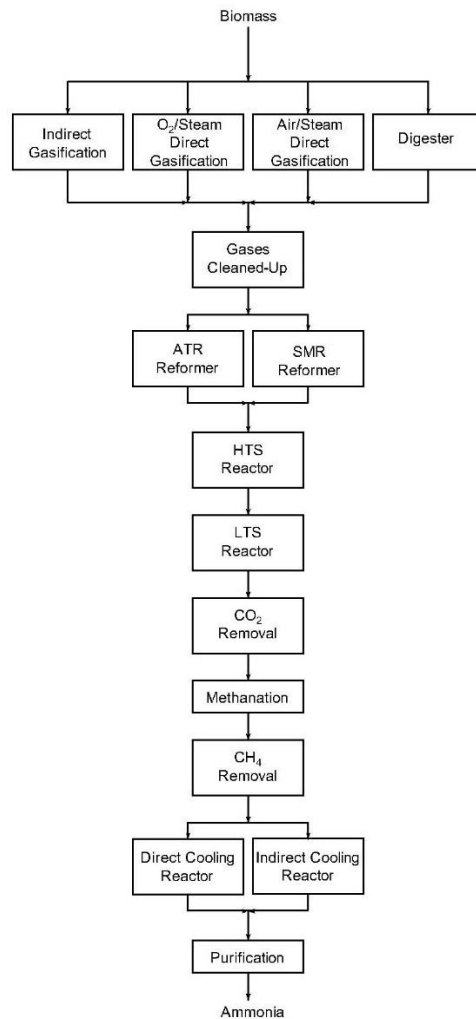


Figure 1: Simplified process superstructure for ammonia production from biomass

To reach the hydrogen concentration in the gas stream needed for ammonia synthesis, the water gas shift conversion technology is selected. A two temperature level shift is proposed. The first one operates at high temperature (high temperature shift, HTS) while the second one operates at low temperature (low temperature shift, LTS). After that, the CO₂, and other components present in smaller amounts in the stream are removed in an adsorption bed of activated carbon. CO₂ can be a raw material, for example, to produce and additional renewable methane via hydrogenation²².

Carbon monoxide poisons the catalyst used in ammonia synthesis. For this reason, its concentration must be reduced considerably. A methanation reactor is used where the traces of CO and CO₂ are transformed into methane. Next, another activated carbon bed is used to remove it. After this treatment, the gas stream is ready for synthesis²³.

The ammonia synthesis loop starts by compressing the inlet stream up to the reaction pressure. Then, the inlet and recycled gases are mixed. Two different reactor configurations have been studied: direct and indirect cooling. In the first one, the inlet stream is used to directly cool down the outlet stream from the reactor beds. In the second one, the heat generated at each catalytic bed is withdrawn generating steam in external heat exchangers. The ammonia synthesis is limited by the equilibrium. After the reactor, ammonia is condensed from the unreacted gases. A fraction of these unreacted gases is purged to avoid impurities build-up. The hydrogen in the purge stream is recovered to reduce the ammonia production costs using a membrane.

In the case of using digestion technology, a few differences have been introduced in the flowsheet. The biogas from the digester is not filtered, because no particles are expected to be present. Furthermore, its lower temperature compared to the raw syngas, makes cooling down before compression not needed. And finally, the heat exchanger before the reformer (HX7) is replaced by a furnace because it is not possible to heat up the gases to about 800-900K with steam or with other stream of the facility. The further processing of the digestate is out of the scope of this work, as it has been previously studied²⁴, and no additional revenue or credit is assumed from it.

Process model

The entire flowsheet has been modelled using an equation based approach. Here, only a brief description is presented. More information about the models has been provided in the supporting information.

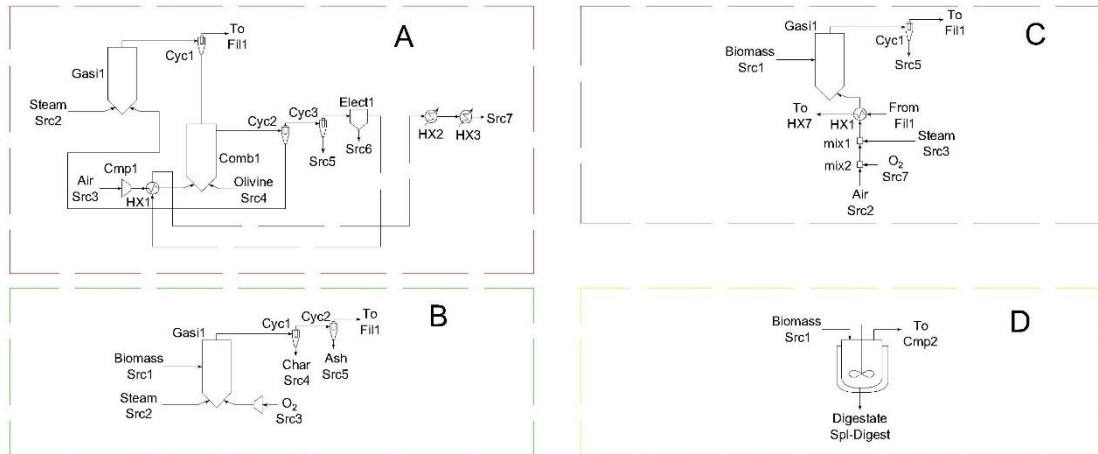


Figure 2: Process flow diagram for gasification/digestion section in the facility: A: indirect gasification, B: O₂/steam direct gasification C: air/steam direct gasification, D: anaerobic digestion.

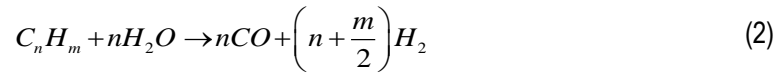
The indirect gasification (Figure 2-A) consists in two chambers. The raw syngas composition obtained in the gasifier is computed using the correlations taken from Phillips et al.²⁵. In the combustion chamber, a total combustion is considered and, therefore, it is possible to determine the outlet temperature and composition by performing mass and energy balances. The performance of the O₂/steam direct gasification (Figure 2-B) is computed using the correlations from Dutta & Phillips²⁶. Finally, for the air/steam direct gasifier (Figure 2-C), empirical correlations were developed to predict the gas composition, based on data from a pilot plant^{27,28} as a function of the gasifier temperature, the steam to biomass ratio, the oxygen percentage and the equivalent ratio. The model for the air/steam gasifier includes the yield correlations, the mass and energy balances and some empirical parameters.

The digester has been modelled according to León & Martín²⁹. The biomass experimental data required for the model are presented in the supporting information.

The next step is the gas clean up. The particles from the gasification section are separated using a cyclone while the hydrogen sulphide presented is removed using a bed of ZnO, eq. (1). Complete removal is considered.



Two kinds of reformer reactors have been considered: autothermal reforming (ATR) and steam methane reforming (SMR). Both reformers are modelled as equilibrium and adiabatic systems. Two main equilibrium reactions take place: the decomposition of methane and the water gas shift reaction (WGSR). Furthermore, all high hydrocarbons are transformed to carbon dioxide and hydrogen inside the reformers³⁰.



After the reforming stage, a two-step shift conversion is chosen to increase the amount of hydrogen in the stream. Both steps are modelled as equilibrium and adiabatic reactors. The final temperatures are in the range of 573-773K for the first one (high temperature) and 453-533K for the second one (low temperature). After the WGSR reactors, the carbon dioxide is removed from the stream using a bed of activated carbon. Because of the high poisoning effect of the CO to the ammonia catalyst, its concentration must be reduced below 10 ppm. CO and CO₂ methanation is carried out. The methanation reactor is adiabatic. Finally, the traces of methane are removed using an adsorption bed. The yields of the adsorption bed are taken based on experimental results and they can be found in the supporting information.

The final stage is the ammonia synthesis (Figure 3). Before being introduced in the reactor, the inlet gases are compressed up to the synthesis pressure. Two reactor configurations have been considered: direct and indirect cooling. The detailed model for these reactors is presented in Sánchez & Martín⁸. In both cases a rigorous model is solved in MATLAB to provide accurate bounds to a simple model based on non-equilibrium mass balances and adiabatic energy balances used in the flowsheet optimization. The

ammonia separation is carried out through condensation. Surrogate models were created to compute the amount of ammonia and other gases separated in the condensation. In the ammonia loop, a membrane is set up in the recycle stream to recover the hydrogen. Industrial data describe the membrane operation^{31,32}.

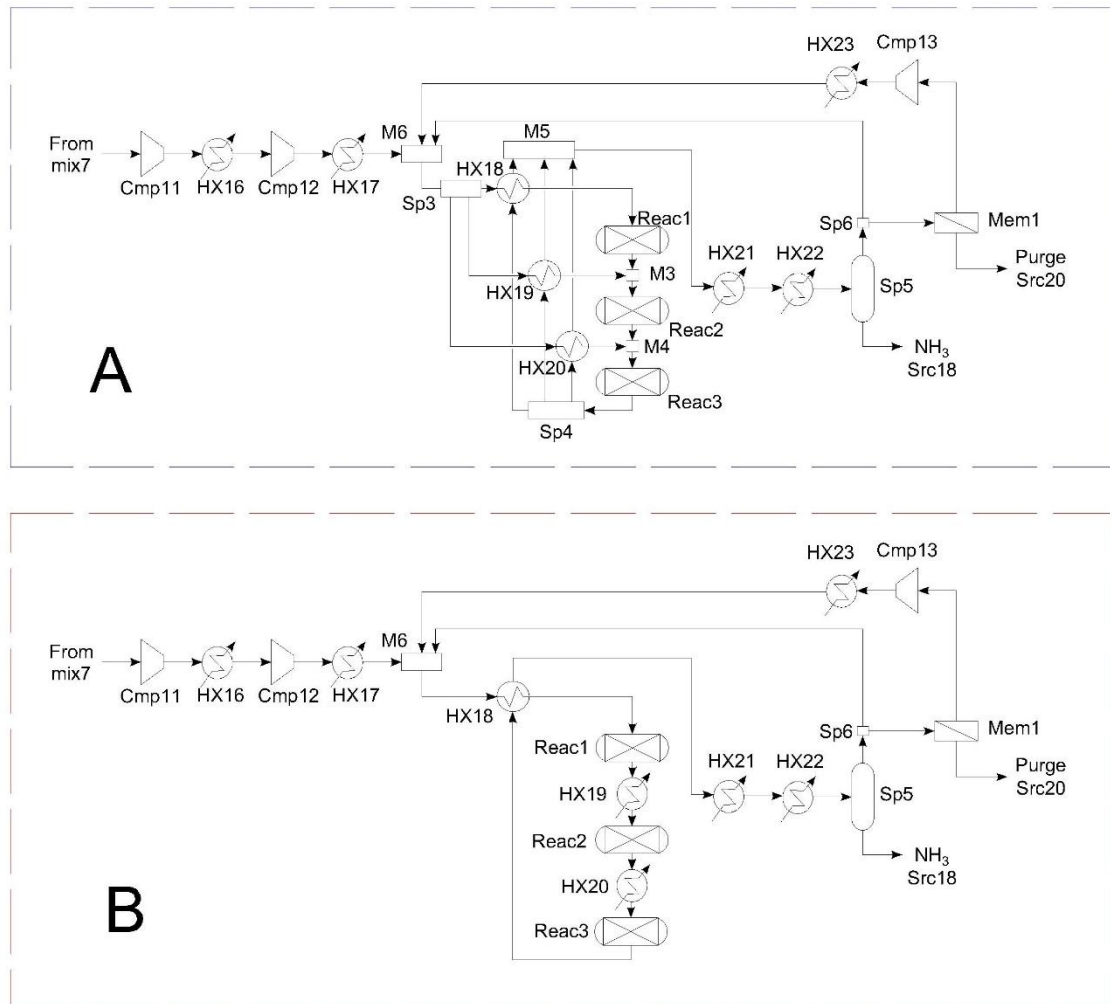


Figure 3: Process flow diagram for ammonia synthesis section: A: direct cooling reactor, B: indirect cooling reactor.

Solution Procedure

The problem is formulated as a mixed integer nonlinear problem (MINLP) with 8 binary variables to select the gasification/digestion technology (indirect gasification, direct gasification with oxygen/steam, direct gasification with air/steam or digestion), the reformer alternative (autothermal reforming or steam methane reforming) and the ammonia reactor configuration (direct or indirect cooling). The problem is relaxed to solve 14 nonlinear problems (NLP's) for the different combinations between the technologies. In the case of direct gasification with air/steam only autothermal reforming has been considered.

A simplified profit equation is used as objective function (eq.(5)). Since each of the problems solved corresponds to an NLP where the flowsheet is fixed, the capital costs do not have influence on the operating conditions and therefore, they are not included in the objective function.

$$obj = F_{NH_3} C_{NH_3} - W_{total} C_{elect} - C_{steam} F_{steam} - C_{cooling\ water} F_{cooling\ water} - C_{O_2} F_{O_2} - C_{N_2} F_{N_2} - C_{biomass} F_{biomass} - C_{olivine} F_{olivine} \quad (5)$$

Where the meaning of the different variables and the values of the cost for the different term involved are presented in Table 2.

Table 2: Symbols and costs for the objective function

Symbol	Variable	Value	Source
F_{NH_3}	Ammonia production		
C_{NH_3}	Ammonia cost	0.5€/kg	(33)
W_{total}	Total power		
C_{elect}	Electricity price	7.87 cent€/kWh	(34)
F_{steam}	Steam needed		
C_{steam}	Steam cost	2.2€/GJ	(35)
$F_{cooling\ water}$	Cooling Water needs		
$C_{cooling\ water}$	Cooling Water cost	4.58€/kt	(35)
F_{O_2}	Oxygen demand		
C_{O_2}	Oxygen price	0.021€/kg	(36)
F_{N_2}	Nitrogen demand		
C_{N_2}	Nitrogen price	0.037€/kg	(37)
$F_{biomass}$	Inlet biomass		
$C_{biomass}$	Biomass cost	58.75€/dry tonne	(38)
$F_{olivine}$	Inlet Olivine		
$C_{olivine}$	Olivine cost	275€/kg	(39)

The problem formulated in the modelling section consists of 2200-3500 equations and 2400-4000 variables depending of the technology combination. It is solved in GAMS using a multistart optimization approach with CONOPT 3.0 as the preferred solver. The decision variables in the optimization problem are the operating conditions of the units involved in the flowsheet, for instance, the amount of

oxygen/steam fed to the gasifier, the temperature in the gasifier units, the pressure in the different reactors, the amount of air/steam fed to the reformers, the pressure in the ammonia synthesis loop, as well as the feed temperature and split ratio to each bed.

For the optimal operation of the different alternatives, capital and operating costs have been estimated using the factorial method⁴⁰. To estimate the equipment cost, correlations⁴¹ and literature data have been employed. For details of specific units and costs, we refer the reader to the supplementary material.

Results

Main Operating Variables

The main operating conditions for the facility are summarized in Tables 3 - 5. In Tables 3 - 4, a brief overview of the conditions for all gasification based processes is shown. The main components of the gas flow exiting the gasifier are carbon monoxide, carbon dioxide, hydrogen and methane. The concentrations for these species are presented in Table 3. In the SMR reformer, it is necessary to burn a fraction of the raw syngas from the gasifier to supply the heat necessary in the reformer. A trade-off is presented between the reformer conversion and the yield. To increase the conversion, a larger supply of heat is needed resulting in the consumption of a larger fraction of the inlet gas and reducing the yield to hydrogen. For this reason, a low methane conversion in the SMR reformer is recommended compared to the ATR. In Table 4, the percent of combusted stream is presented together with the methane reformer conversion.

Table 3: Main Operating Conditions for the Gasifier Section.

		Gasifier	Combustor	Gasifier out (molar % dry N ₂ free)			
		T out (K)	T out (K)	% H ₂	% CH ₄	% CO	% CO ₂
1	Ind+ATR+Dir	1287.04	1358.55	33.92	12.38	41.37	9.28
2	Ind+ATR+Ind	1287.04	1358.55	33.92	12.38	41.37	9.28
3	Ind+SMR+Dir	1287.04	1358.55	33.92	12.38	41.37	9.28
4	Ind+SMR+Ind	1287.04	1358.55	33.92	12.38	41.37	9.28
5	Dir+ATR+Dir	1236.60	-	29.13	14.87	23.23	29.87
6	Dir+ATR+Ind	1236.60	-	29.13	14.87	23.23	29.87
7	Dir+SMR+Dir	1241.66	-	27.84	14.75	25.43	28.73
8	Dir+SMR+Ind	1255.22	-	21.31	14.01	35.92	23.40
9	Air+ATR+Dir	1038.29	-	34.37	10.59	36.11	13.49

10	Air+ATR+Ind	1038.49	-	34.81	10.30	38.72	11.02
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For the indirect processes (processes 1-4), the gasifier presents the same conditions independently of the reformer technology or the reactor configuration, see Table 3. Up to 13% of the gas from the gasifier is burned to supply heat when using SMR. The final ammonia production is higher in the indirect gasifier processes due to the larger yield to hydrogen in the gasification step as it is shown in Table 3. The reformer performance is better in the SMR with more hydrogen production. However, after the WGS reactors, the hydrogen concentration is higher in the autothermal reforming processes and, therefore, the final ammonia production is also larger (see Table 4). Note that the operating pressure is fixed to the bound since there is a trade-off between the cost for compression and the experimental operating limits.

Table 4: Operating Variables in Gasification based Processes.

		Combustor	Reformer			Ammonia	
		% split	P (bar)	T out (K)	X _{CH₄} (%)	P (bar)	F NH ₃ (kg/s)
1	Ind+ATR+Dir	-	20.0	1265.22	99.2	125.0	9.95
2	Ind+ATR+Ind	-	20.0	1265.04	99.2	125.0	9.93
3	Ind+SMR+Dir	13.8	20.0	1137.99	71.7	125.0	9.69
4	Ind+SMR+Ind	13.8	20.0	1137.96	71.7	125.0	9.69
5	Dir+ATR+Dir	-	20.0	1160.08	98.2	125.0	8.65
6	Dir+ATR+Ind	-	20.0	1159.26	98.2	125.0	8.65
7	Dir+SMR+Dir	6.2	20.0	1073.00	62.4	125.0	8.48
8	Dir+SMR+Ind	11.0	20.0	1116.87	71.8	125.0	8.12
9	Air+ATR+Dir	-	20.0	1122.59	75.5	126.3	8.70
10	Air+ATR+Ind	-	20.0	1200.45	96.5	155.2	7.72

In the oxygen/steam direct gasification processes (processes 5-8), a significant increase in the percent of carbon dioxide is shown with respect to the indirect gasification. Therefore, a reduction in the ammonia production capacity takes place when direct gasification is employed.

Finally, the air/steam gasification (processes 9-10) shows an ammonia production in the same levels than oxygen/steam direct gasifier (see Table 4) because the flows of the stream in air/steam processes are quite similar to the oxygen/steam ones. In the gasifier, a steam to biomass ratio (S/B) of 0.334, an oxygen percentage of the enriched air (OP) of 0.4 and an equivalent ratio (ER) of 0.207 are selected.

Table 5: Main Operating Conditions for Digestion Processes.

		Digester out (molar %)			Combustor	Reformer			Ammonia	
		%CH ₄	%CO ₂	%H ₂ O	% split	P (bar)	T out (K)	X _{CH₄} (%)	P (bar)	F NH ₃ (kg/s)
11	Dig+ATR+Dir	55.94	25.28	15.74	5.01	20.0	1093.54	90.4	154.8	1.58
12	Dig+ATR+Ind	55.94	25.28	15.74	5.01	20.0	1093.12	90.3	152.3	1.58
13	Dig+SMR+Dir	56.87	25.27	15.73	40.16	20.0	1133.76	89.8	125.0	1.92
14	Dig+SMR+Ind	56.87	25.27	15.73	40.16	20.0	1133.65	89.8	125.0	1.81

In the digester based processes, the main conditions are shown in Table 5. In this case, the outlet gases from the digester present a high content of methane, followed by carbon dioxide and water. Hydrogen is not directly produced in the digester. The biogas must be reformed to syngas. In this flowsheet, there is no heat source to heat up the feed to the reformer. Therefore, the heat is supplied by burning a fraction of the biogas. In the case of ATR, only a small fraction is required (about 5%). However, in the SMR based processes, a larger fraction of 40% is needed to operate the heat exchanger and the reactor itself.

Comparing Tables 4 and 5, it is possible to see that for the same biomass flowrate, the amount of ammonia is significant lower in the case of digestion than in the gasification. This fact is due to the high amount of water or other components in the inlet biomass that cannot be transformed into biogas. For this case of study, around 80% of the inlet mass goes to the digestate and only 20% forms the biogas.

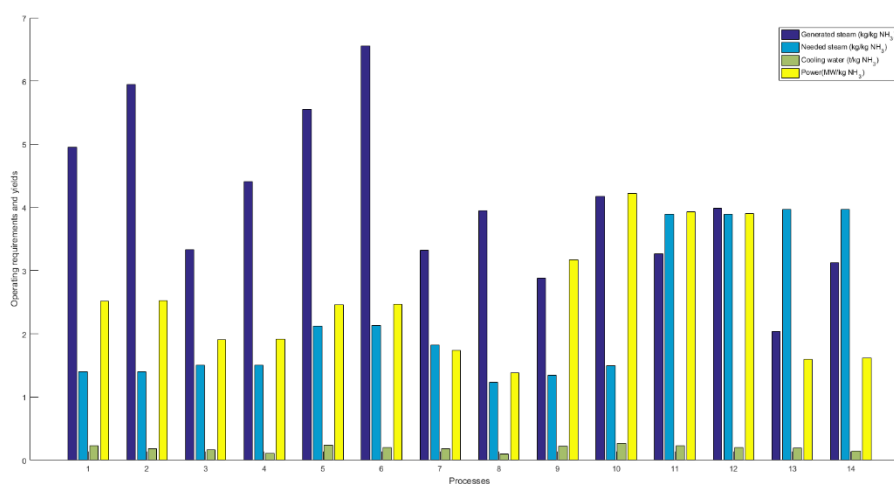


Figure 4: Steam, cooling water and power consumption for different alternatives.

In Figure 4, the steam (generated and consumed), cooling water and power consumption for the different process alternatives are shown. In the processes that use indirect cooling reactors (odd numbers in Figure 4), the amount of steam generated is higher because it is possible to produce it between reactor beds. However, when using direct cooling configurations, no steam is generated but heat exchangers are not needed either. When using digestion, this trend also holds. For the steam requirements, the processes that use biogas digestion present higher consumption than the gasifier ones. Around 1-2 kg of steam per kg of ammonia are needed in the gasification processes versus about 4 kg of steam per kg of ammonia in the digestion ones. The cooling water consumption in all processes is around 0.2 t cooling water per kg of ammonia. As a general trend, indirect cooling processes present a lower cooling water consumption. In addition, processes using SMR also consume less water than the ATR alternatives. Finally, power consumption is a key parameter for the process profitability. Figure 4 shows that the processing using ATR are more energy intense than the correspondent SMR processes. The reason behind is that in spite of burning a fraction of the feed stream to provide energy for the SMR, the amount of ammonia produced is approximately the same than the ATR designs (a bit lower in the gasifier processes and a bit higher in the digester processes). For example, in the indirect gasifier and direct cooling ammonia reactor, the change from ATR to SMR reduces the ammonia production by 2.6% percent. However, a fraction of the raw syngas is split, sending 13.8% to the combustor. It is possible to achieve almost the same production capacity processing a smaller flow of gases. Thus, the power consumption at the compressors is lower resulting in lower total energy consumption per kilogram of ammonia. This fact is especially clear when using digestion. In the SMR about 40% of the stream is sent to the combustor. Due to this, mainly, the energy requirements per kg of ammonia decrease by 60%.

Environmental Evaluation

Using the mass and energy balances, a simplified environmental evaluation of each process has been performed following the methodology proposed by Martín⁴². In this metric, REPSIM, the operating parameters are computed as CO₂ emissions generated or mitigated.

For the purpose of this work, the inlet biomass is assumed to generate CO₂ emissions of due to collection, transportation, etc of 87.5 kg CO₂ per ton of dry switchgrass⁴³. The other two raw materials, oxygen and

nitrogen, present carbon dioxide emissions values of 556 g CO₂/Nm³ and 171 g CO₂/Nm³ respectively⁴⁴. The emissions related to the power involved in the processes are taken into account using a factor of 0.832 kg of CO₂ per kWh⁴². The cooling water for the process is computed using the energy requirement for water supply and distribution. Then, the carbon footprint is calculated using the energy to CO₂ factor. The energy requirement for the cooling water is fixed to 7775 kWh/Mgal⁴⁵. Finally, the contribution of the use of steam to CO₂ emissions is according to the energy required to produce it. Then, the carbon emissions are calculated using the same energy to CO₂ factor as in the case of the power.

Apart from these contributions, the carbon dioxide generated in processing the switchgrass is released because in the synthesis of ammonia no carbon source is necessary. Therefore, the carbon dioxide from biomass must be also added to the previous one. However, this carbon dioxide is biogenic, namely, it comes from biomass and it is later consumed by the growing biomass and no additional CO₂ is released to the atmosphere¹⁹. In general, in the literature, this CO₂ contribution is neglected in the environmental analysis. In this study, two different values for the released CO₂ are computed, one considering the biogenic carbon dioxide emissions and another one without it. As it is said previously, the carbon dioxide generated in the process could be integrated with other technologies to produce other interesting chemicals or fuels, for example methanol⁴⁶ or methane²².

In Figure 5, the results for this environmental index are shown. These results show the amount of carbon dioxide generated per kg of ammonia produced. The blue columns represent the total CO₂ emissions and the yellow ones the emissions without the biogenic carbon dioxide. If the biogenic carbon dioxide is not neglected, the level of emissions are quite similar to the actual processes (about 3-4 kg CO₂/kg NH₃)⁵. However, discounting this contribution, a reduction up to 80% can be obtained.

In terms of the comparison among process alternatives, the indirect gasifier based processes have the lowest level of emissions. As it is shown before, these processes present low cooling water consumption, high levels of generated steam and also no pure oxygen or nitrogen are required. These facts result in a better environmental performance for the indirect gasifier based processes.

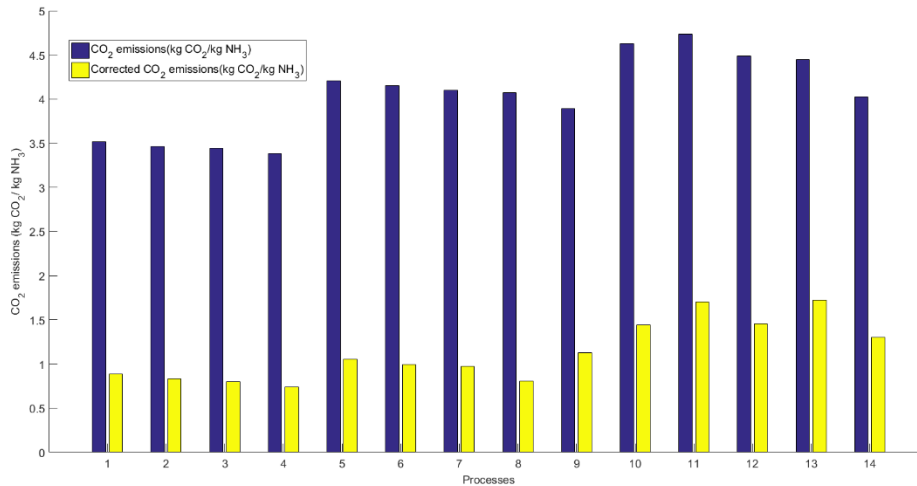


Figure 5: Carbon dioxide emissions for different alternatives.

At the other end, digestion based processes show the higher level of carbon dioxide generation. These processes are highly energy intensive and, in general, the steam generated in the facility cannot provide for its needs. For this reason, the environmental index is worse.

Investment and Production Costs

In Figure 6, a summary of the capital costs for the process alternatives can be seen. The production capacity for each facility is also shown (red line). The investment is higher for the gasification based processes than in the case of the digestion based ones. However, the ammonia production capacity is higher using gasification, for the same biomass feed. As a general trend, the configurations using indirect cooling reactor present a higher investment than the direct ones. The main reason is that in indirect cooling it is necessary to invest in heat exchangers for the reactor operation. These heat exchangers generate steam at a cost. Comparing the two reformer alternatives, the investment costs in SMR are lower than in the ATR. The explanation is that when the SMR reformer is used, a fraction of the inlet stream is burnt to produce the heat necessary. For this reason, the downstream units are smaller as well as their cost. In the gasifier alternatives, the indirect gasifier shows a small investment that the direct ones (steam/air or steam/oxygen).

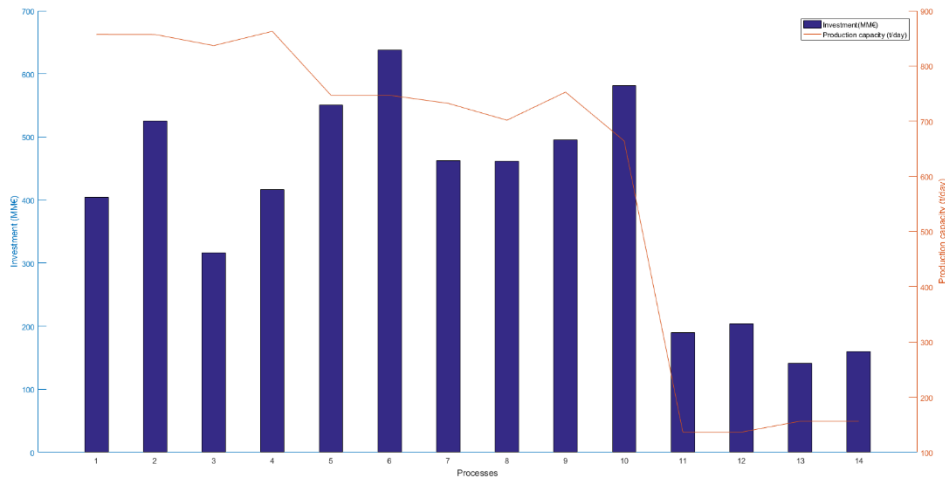


Figure 6: Investment cost for different alternatives.

In Figure 7, the production cost for the different alternatives are shown. The ammonia production capacities for the different alternatives are also in the figure (red line). The range of production cost for the ammonia from biomass is between 390 €/t (Process 3, Indirect gasifier with SMR and Direct cooling reaction) and 1284 €/t (Process 12, digester with ATR and Indirect cooling reactor). The indirect gasifier alternatives show lower costs than the direct ones. In general, the indirect gasifier presents a high ammonia production and the indirect gasifier has a lower capital cost than the direct one (see supporting information). Between SMR and ATR, SMR processes show higher yield than those using ATR. In SMR, the ammonia production capacity is similar to the ATR processes but the investment is significantly lower than for ATR. For the direct versus indirect cooling configurations, the trade-off between steam production and heat exchangers investment, it is resolved in favor of the direct cooling alternatives. The decrease in the need for steam due to the internal production does not mitigate the increase in the amortization due to the additional heat exchangers capital cost. The production costs for the digestion processes are higher than the gasification ones. As it is explained before, a large amount of inlet biomass is not converted in biogas and forms the digestate. The digestate in this work is not treated and for this reason no economical profit has been computed. A commercial use of the digestate could reduce the production cost for the ammonia, but further investigation is required to evaluate the necessary investment for these new treatments, the impact in the production cost and the market of the fertilizer. Therefore, the most promising

alternative, in economic terms, is the combination of indirect gasifier with SMR reformer and direct cooling ammonia reactor.

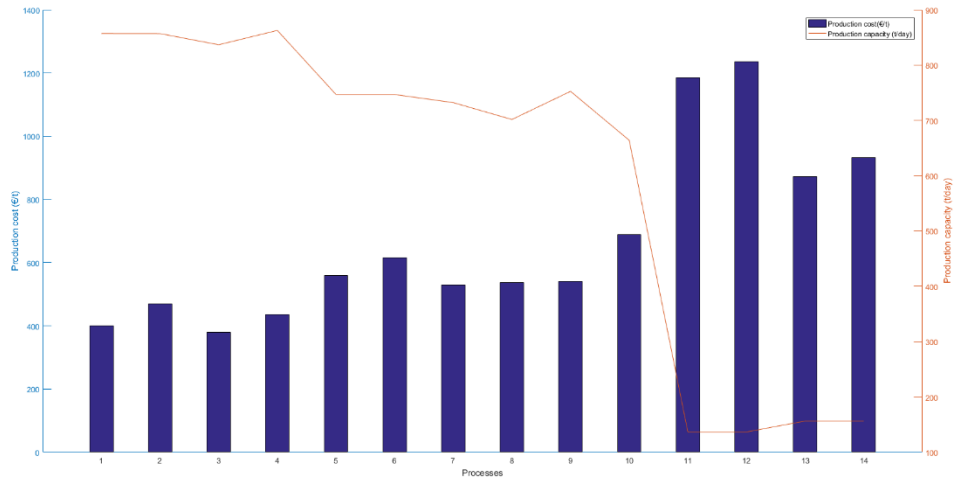


Figure 7: Production cost for different alternatives.

In Figure 8, a sample of the distribution of the equipment cost has been presented. Only ATR and direct cooling reactor are shown for the three gasifiers and the digester for comparison. The main contributors in the investment are heat exchangers, gasifier, compressors and the ammonia synthesis reactor. The heat exchangers can represent more than 50% of the total investment in the facility. Direct alternatives present a lower heat exchanger contribution as it is expected according with the reasoning presented above.

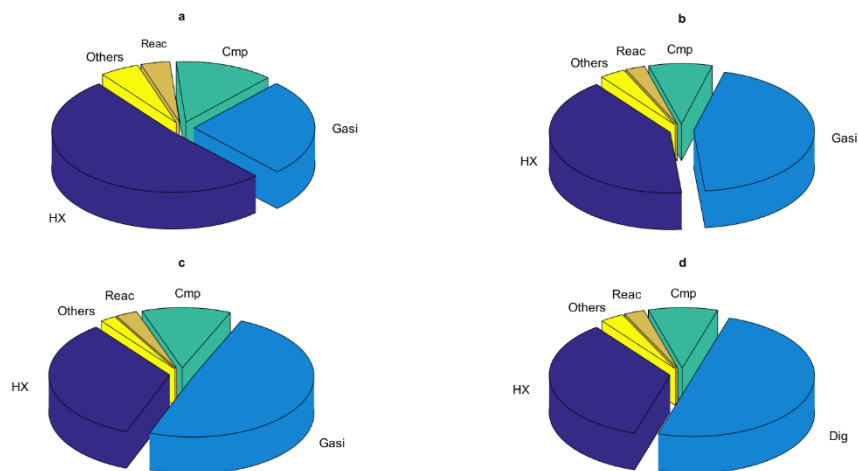


Figure 8: Equipment investment breakdown for some of the proposed alternatives (a: Indirect gasifier + ATR reforming + direct cooling; b: O₂/steam direct gasifier+ ATR reforming+ Direct cooling; c: Air/steam direct gasifier + ATR reforming+ direct cooling; d: Digester+ ATR reforming + direct cooling).

In the indirect gasifier based processes, the heat exchangers show the larger contribution. In the other gasifier technologies, is the gasifier itself which presents the principal percent in the capital cost. As it was explained before (See supporting information), the indirect gasifier presents a lower investment cost, and this is reflected in the capital cost distribution. In the digester, about 50% of the total investment is represented by the digester. Figure 9 shows the cost distribution.

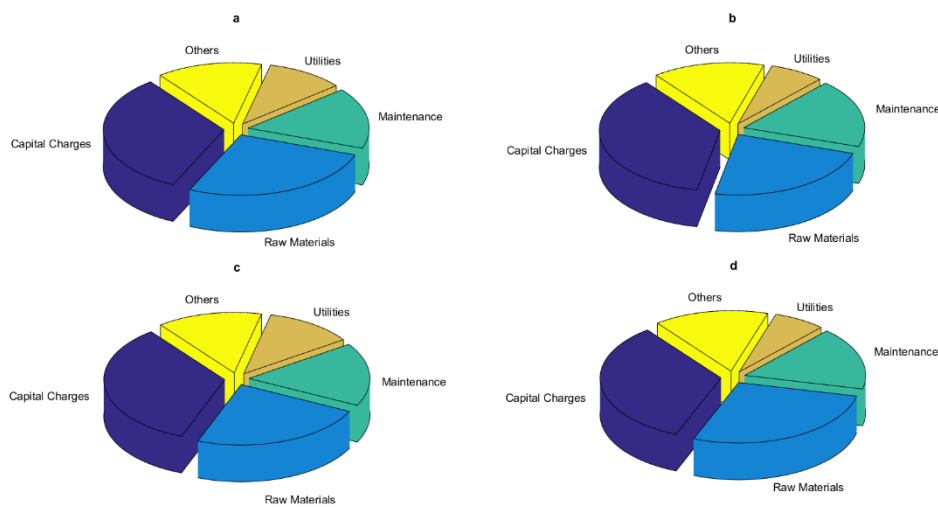


Figure 9: Operating cost breakdown for some of the proposed alternatives (a: Indirect gasifier + ATR reforming + direct cooling; b: O₂/steam direct gasifier+ ATR reforming+ direct cooling; c: Air/steam direct gasifier + ATR reforming+ direct cooling; d: Digester+ ATR reforming + direct cooling).

The most significant item in the cost analysis breakdown is the capital charges associated with the initial investment. It is followed by raw material, mainly the inlet biomass, the maintenance cost and the utilities item. The cost distribution is quite similar for all the cases presented in the figure.

Sensitivity analysis

For the previous analysis, a price of biomass equal to 58.75 €/dry tonne is taken.³⁸ However, there is large variability in the biomass price. A lot of factors affect the switchgrass production cost, for example, fertilizers prices, transportation cost, grow yield, etc.⁴⁷ Therefore, a sensitivity analysis is carried out to evaluate the influence of the biomass price in the ammonia production cost. The most promising processes for each gasification and digestion technology have been selected for the analysis. Namely,

indirect gasifier with SMR and direct cooling, oxygen/steam direct gasifier with SMR and direct cooling, air/steam direct gasifier with ATR and direct cooling and digester with SMR and direct cooling reactor.

In the sensitivity analysis, a range in the biomass prices between 30 €/dry tonne and 100 €/dry tonne has been evaluated taking into account the variability presented in the literature for the switchgrass production cost^{47,48}. The results are shown in Figure 10. For the indirect gasification with SMR and direct cooling reactor, the ammonia production cost ranges between 325 and 450 €/t. The production costs using direct gasification with either air/steam or oxygen/steam are quite similar, both in the range 470-625 €/t. The digester based processes, as it is expected, present higher production costs in the range of 725-1100 €/t. A linear trend relates the production cost with the biomass prices. The slope is higher in the digester due to the different moisture content between the switchgrass for gasification and for digestion.

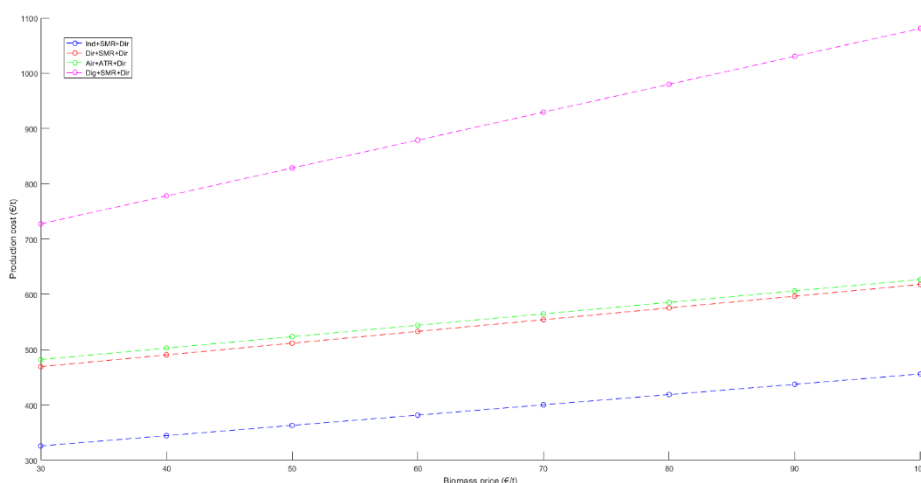


Figure 10: Sensitivity analysis for the biomass price.

The actual cost of the ammonia is in the range of \$500-600 per tonne of ammonia³³ with a strong dependency of the fossil fuels cost fluctuations⁴⁹. The calculated production cost for the ammonia from biomass can be competitive for some technologies with the current production technology.

Scale up/Scale down

The economics of scale present a high influence in the production cost and the investment in chemical plants. Traditionally, large chemicals production complexes have been installed. However, this trend is

slowly changing to new alternative processes based on resource availability⁵⁰. Distributed production in chemical facilities presents a strong link with modular design⁵¹. The methodology to scale up or down the chemical process was described in Sánchez & Martín¹⁰.

For biomass based ammonia processes, the investment and production costs have been evaluated for different biomass processing rates to assess the influence of the production capacity in these two parameters. Figure 11 shows the total investment for different production capacities for the four most promising different alternatives according to the previous analysis: indirect gasifier with SMR and direct reactor, direct gasifier with SMR and direct ammonia reactor, air/steam gasifier plus ATR and direct cooling reactor and, finally, digester combined with SMR and direct reactor. The scale index for the gasifier processes is around 0.75, a little different compared to the classical six-tenth rule. However, the power index for the case of the digestion is about 0.85. Therefore, the digestion based processes present smaller economies of scale with respect to the gasification based ones. Note that the digester represents a high share in the investment (see Figure 8), and it is an equipment without economies of scale, affecting the scale up/down behaviour of the entire process.

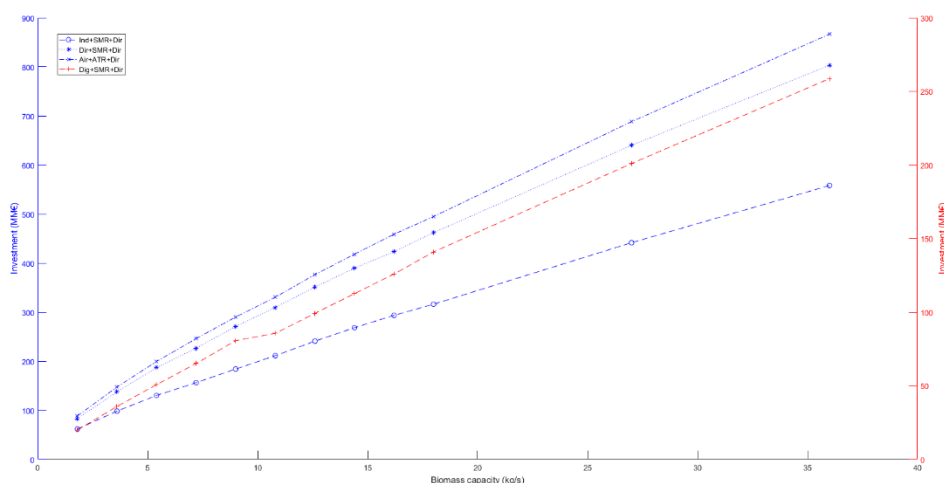


Figure 11: Scale up and down for the investment.

For the production cost, Figure 12 presents the influence of the biomass capacity in the ammonia production costs. For the smaller capacities, the ammonia cost is around 600-900 €/t for the gasification based processes, about a 60% of increase with respect to the base case. In the case of digestion, the cost

for smaller capacities surpasses the level of 1000€/t, showing an increase of around 45% with respect to the base case. Smoother trends are obtained for the gasifier processes due to the need for additional reactors as they become filled in the digester bases processes.

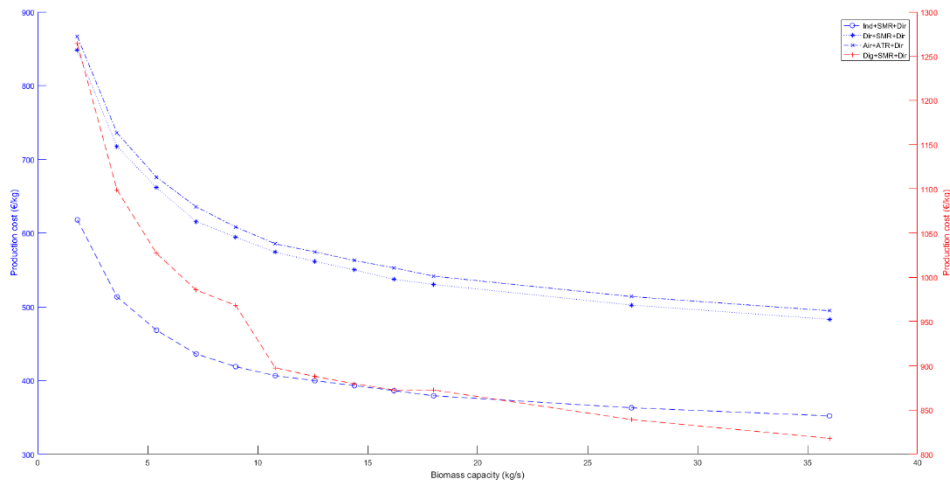


Figure 12: Operating cost for different inlet biomass capacity.

Conclusions

In this work, the synthesis of ammonia from biomass has been systematically evaluated. Different alternatives for gasification, reforming and ammonia synthesis reactors have been compared. The main decision variables for the process are determined in the optimization procedure, for example, the working temperature in the gasifier, the amount of steam fed to the reformers, the water gas shift operating conditions or the ammonia synthesis pressure. The economic results show that the combination of indirect gasifier with steam methane reforming and direct cooling reactor is recommended for the biomass to ammonia process. This alternative presents a production cost about 380 €/t, competitive with the actual production processes, and an investment of approximately 316 MM€. This process also shows a good environmental performance regarding the processes analyzed. In the digestion processes, the production cost increases up to 900-1200€/t. The high amount of digestate determines the economic performance of this way.

A sensitivity analysis of the effect of biomass price is carried out. The digestion processes are strongly affected by this price. Finally, a scale up/down study is presented to analyze the economies of scale in biomass to ammonia processes.

Acknowledgement

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Nomenclature

C_{NH_3} Ammonia cost (€/kg)

C_{elect} Electricity price (cent €/kWh)

C_{Steam} Steam Cost (€/GJ)

$C_{Cooling\ Water}$ Cooling water price (€/kt)

C_{O_2} Oxygen price (€/kg)

C_{N_2} Cost for nitrogen gas (€/kg)

$C_{biomass}$ Biomass price (€/dry t)

$C_{olivine}$ Olivine cost (€/kg)

F_{NH_3} Final ammonia production (kg/s)

F_{Steam} Total steam needed in the facility (GJ/s)

$F_{Cooling\ Water}$ Total amount of cooling water in the plant (kt/s)

F_{O_2} Oxygen total flow (kg/s)

F_{N_2} Nitrogen inlet flow (kg/s)

$F_{biomass}$ Biomass flow as raw material (dry t/s)

$F_{olivine}$ Total inlet flow of olivine (kg/s)

W_{total} Total power in the facility (kWh)

Supporting Information

Process modelling issues and cost estimation procedure can be found in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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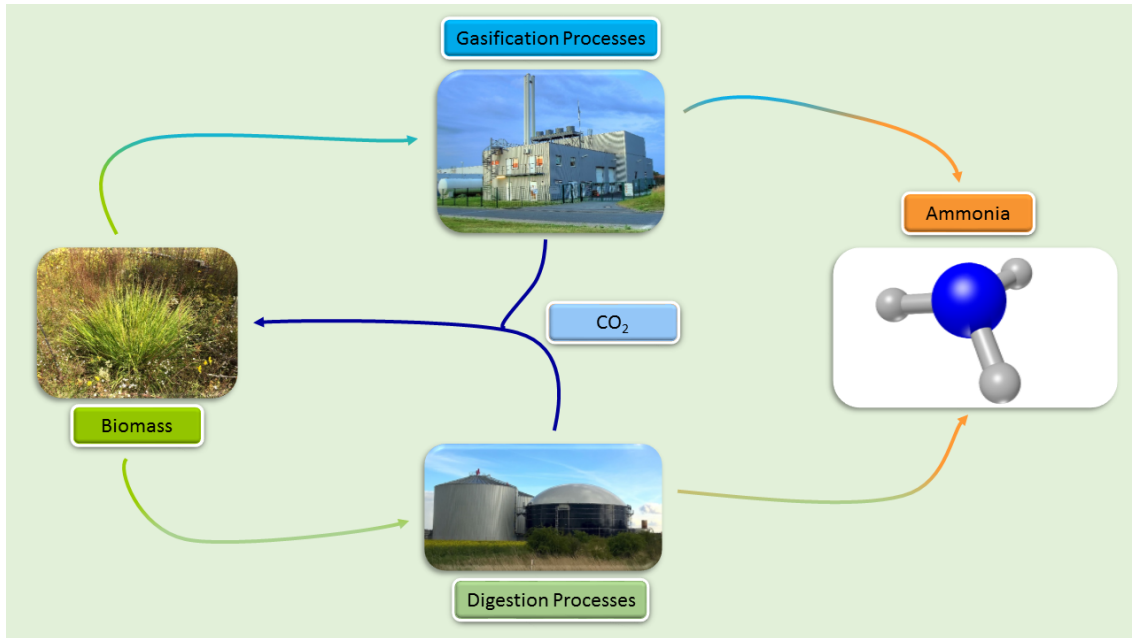
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Biomass based sustainable Ammonia production: Digestion vs Gasification

Antonio Sánchez, Mariano Martín, Pastora Vega

A systematic approach for the selection of the biomass path towards renewable ammonia production