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A New LCA Methodology of Technology Evolution (TE-LCA) and its Application to the Production of Ammonia (1950–2000)

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Abstract

Goal, Scope and Background. This paper presents a new LCA method of technology evolution (TE-LCA), and its application to the production of ammonia, the second largest chemical product in the world, over the last fifty years. The TE-LCA of a chemical process is the procedure in which historical information on a process, mainly the evolution of technical parameters, is translated by simulation to mass and energy balances as a function of time. These mass and energy balances are then transformed into environmental impact indicators using common LCA approaches. Finally, the evolution of environmental impact resulting from the investigated process can be related to its technical and other, i.e. legislative, developments.

Methods. The technological evolution of the production of ammonia was compiled according to three basic sources of information: patents, publications and industry data. From these sources in a first step, the major technological advances of the process were identified as a function of time delivering different process variants that were modelled using the simulation software Aspen Plus®. In a second step, the evolution of environmental regulations is studied. For those energy related emissions that were regulated, e.g. SO_x and NO_x, it was assumed that threshold values defined in legislation were realized immediately. The aggregation of both steps allows the calculation of the emissions resulting from the production (cradle to gate view) of the investigated chemical as a function of time.

Results and Discussion. The application of the TE-LCA to the production of ammonia revealed when and to which extent technological and legislative developments resulted in the reduction of energy related emissions in the production of this chemical compound. Overall, the reduction of emissions from ammonia production was highly influenced by the technological development and only to a lower extent by environmental regulations.

Conclusion. The results obtained from the TE-LCA method is useful to reveal how the environmental performance of a process developed in the past and to identify the reasons for this development. The investigated case study of ammonia production shows that investment in technological development also paid off in terms of being ahead of tightened environmental legislation that might bear potential cost consequences such as carbon dioxide tax.

Outlook. The presented method can be easily extended by including an economic analysis, which provides additional information on why certain technological developments were enforced and which the economic consequences of changes in environmental legislation were. The new methodology has to be applied to additional case studies, i.e. to other chemical sectors than basic chemicals and to other branches than chemicals. In other chemical sectors, toxic emissions from the production process might have to be considered and trade-offs between these and the overall energy consumption might result.

Keywords: Ammonia production; environmental impact as a function of time; life cycle assessment methodology; regulation impact; technology evolution (TE-LCA)

Introduction

LCA methodologies were originally developed to create decision support tools for distinguishing between products, product systems, or services on environmental grounds. In chemical process design, LCA is used as a tool to compare different process alternatives [1–4].

The performance of a chemical process is influenced by many variables during its lifetime. The introduction of new technologies, changes of the market situation and new environmental regulations among others are continually affecting environmental and economic performance. In order to identify the ecological drivers and barriers in the long term evolution of a technology, tools have to be developed to monitor the long term dynamics of the ecological process performance [5–8]. Here, inventories are needed that display the temporal development of the system under investigation. Dynamic models in LCA have been used by [9,10].

2 Methodology

The TE-LCA will be presented using the production of ammonia as a case study. The TE-LCA methodology is divided into four steps following the LCA framework [11]: goal and scope definition, inventory analysis, impact assessment, and interpretation (**Fig. 1**).

2.1 Goal and Scope Definition

The goal of the study is to obtain the TE-LCA of the production of ammonia for the last fifty years. Thus, the TE-LCA represents an environmental learning curve that com-
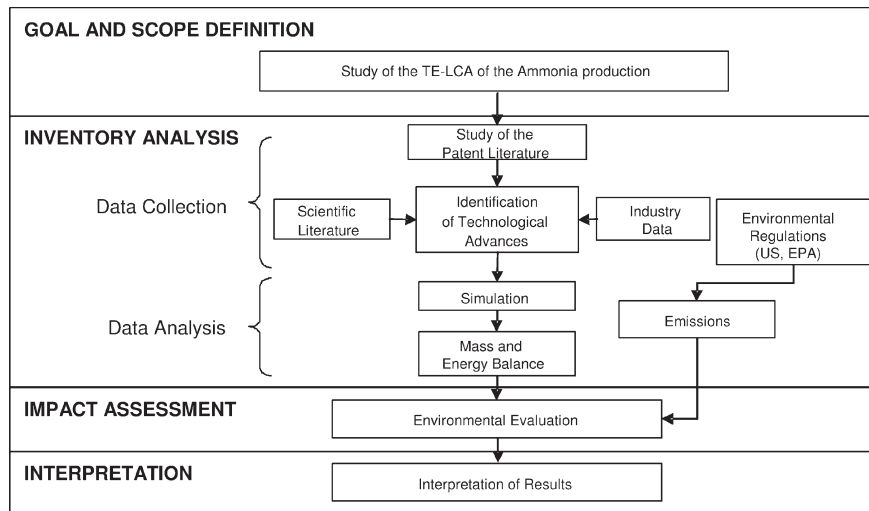
Fig. 1: Methodology of the LCA of technology evolution (TE-LCA)

plements the economic perspective on the performance of a chemical process over time. By this in particular, technology managers in industry obtain valuable information on the performance of certain technologies, which they might use for process improvements. TE-LCAs also contribute to the definition of benchmarks and Best Available Technologies (BAT).

Ammonia, after sulfuric acid, is the second largest chemical produced worldwide [12]. It is the main raw material for fertilizer production (about 80% of ammonia is used for fertilizers) [13] and is the basic building block of most of the large tonnage chemicals that contain nitrogen. The ammonia process is known since 1913. A number of technological changes in the ammonia production occurred which render this process an excellent case study for the new method presented here.

The process boundaries considered are shown in **Fig. 2**. No impact due to service processes such as transportation or storage will be considered. The functional unit considered is the production of one kilogramme of ammonia in a cradle to gate perspective, i.e. besides the ammonia process also the feedstock processes and energy conversion is taken into account. An average production technology was assumed and technological advances were considered in the year of their publication. Each technological advance resulted in a new process layout, for which updated mass and energy balances were obtained by simulation. For those energy related emissions that were regulated, e.g. SO_x and NO_x, it was assumed that threshold values defined in legislation were realized immediately. Therefore, these emissions are obtained from the evolution of environmental regulations, i.e. the development of emission limits in the US.

The environmental impact as considered in this work only stems from energy supply and raw material production which again requires energy services. Production of energy also requires certain energy consumption. It is assumed that this energy will come from the respective energy source produced. This means that for the production of natural gas the source of energy will be natural gas and the emissions from natural gas production will be considered to come from natural gas combustion. To illustrate the principle of TE-LCA and to cover a time frame of 50 years for the ammonia process, only air emissions are considered in the case study presented here.
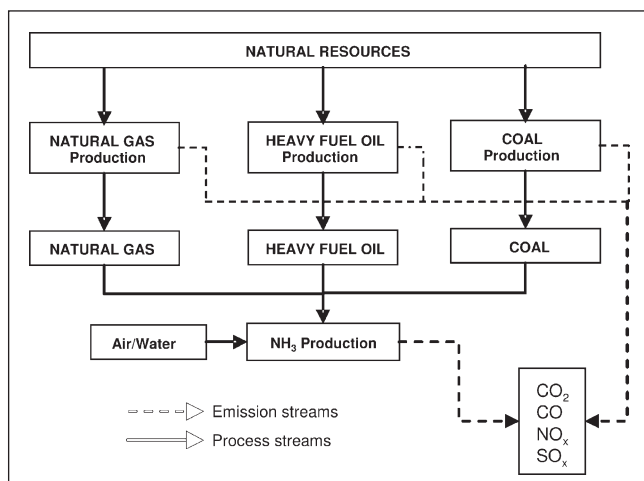
2.2 Inventory Analysis

The inventory analysis within the TE-LCA method consists of two major steps, data collection and data analysis (see Fig. 1).

2.2.1 Data collection

The data collection step for the ammonia case study and the period from 1950 to 2000 is based on three basic sources of information: patents, publications and industry data. The average ammonia technology considered is depicted in **Fig. 3**.

Ammonia Process. The classical Haber-Bosch plant used coal as a source of hydrogen [14] and the first plant was built in 1940 in Oppau, Germany. To avoid the expensive coking step, direct gasification of coal was explored [12]. Around 1940, natural gas became cheap in huge quantities in North America [15] and ten years later in Europe [16]. During this
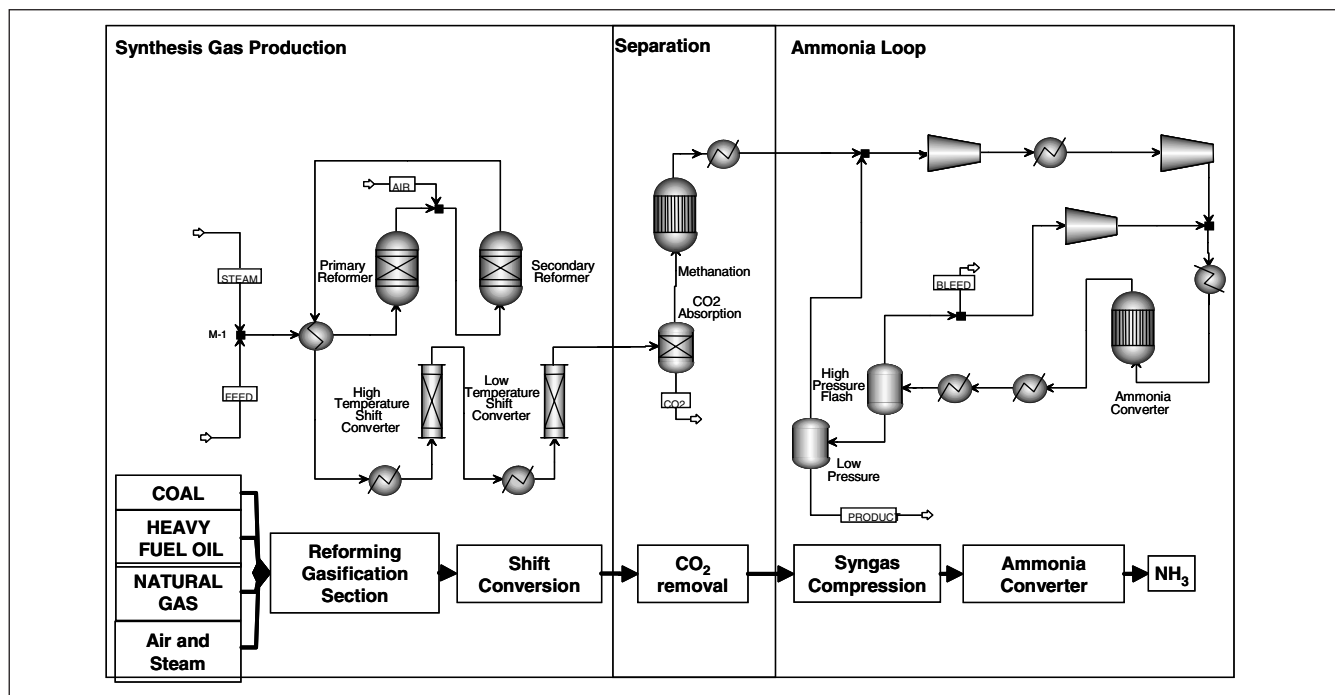

Fig. 2: Processes considered within the TE-LCA of ammonia

Fig. 3: Scheme of the average ammonia production process

period of European delay, ICI (Imperial Chemical Industries) succeeded with steam-reforming of light naphtha. The first plant went on stream in 1959 [17]. By 1952, about 80% of the synthetic ammonia in the USA was produced by plants using the methane-steam reaction. All these plants operated at essentially atmospheric pressure [18].

At the same time, oil producers (Texaco and Shell) developed partial oxidation processes. They are used for the gasification of heavy feedstock such as residual oils and coal. Extremely viscous hydrocarbons and plastic wastes may also be used as fractions of the feed [19]. An air separation unit is required for the production of oxygen for the partial oxidation step. The nitrogen is added in the liquid nitrogen wash to remove impurities from the synthesis gas and to obtain the required hydrogen/nitrogen ratio. As compared to steam reforming of natural gas, partial oxidation of fuel oil consumes 20% more energy. **Fig. 4** shows the evolution of the different raw materials used in the ammonia production. Due to its superior energy performance and based on the
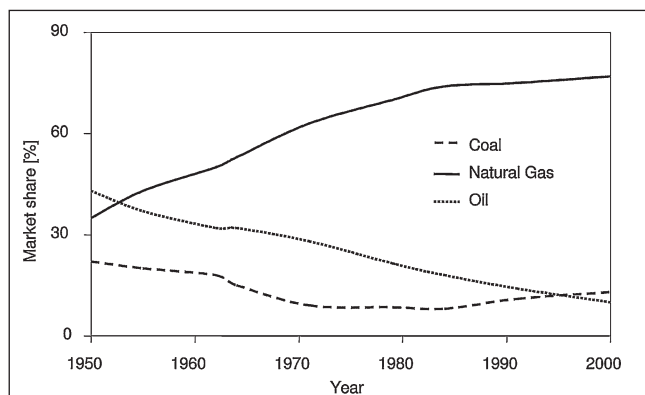

Fig. 4: Evolution of the feedstock in the world ammonia production

known resources of fossil raw materials, natural gas dominated and will dominate as the feedstock for ammonia for the next 50 years at least. In the long term, one might expect coal to take over, based on world reserves and consumption rates. Fig. 4 shows how coal is slowly increasing its market share, which is due to the fact that China is basing its ammonia production on this feedstock. Heavy oil may be attractive under special environmental concerns, when natural gas is not available and the partial oxidation process could solve a waste problem (heavy residues, plastic recycling).

One important aspect of partial oxidation is gasification at elevated pressures, which takes advantage of the volume expansion from feedstock to product gas. This constitutes considerable savings in compression energy. It is even more effective if the feedstock is available at an elevated pressure, as is the case for natural gas. For this reason, in 1953, reforming process designers began to raise the operating pressure. The extent to which this could be done, however, was limited by the tube material. For equilibrium reasons, the residual methane content in the product gas increases with raising pressure, which can be compensated by higher temperature or, less economically, by a higher steam-on-carbon ratio [12,20].

The steam/air reforming concepts (conventional, unconventional and autothermal reforming) [21,22] based on natural gas and other light hydrocarbons are considered to be the dominating technologies. The performance of the three alternatives is similar. In this study, only the evolution of conventional steam reforming was investigated. For heavy feedstocks, partial oxidation is considered as the best production process. The heat for the reforming process is supplied by burning natural gas or other gaseous fuel, the flue-gas is one of the main sources of emissions from the plant. These emissions are mainly CO_2, NO_x, with small amounts of SO_2 and CO, depending on the energy source.

The outlet from the reforming/partial oxidation section leads to the shift converter zone where carbon monoxide is reacted with water to carbon dioxide, producing hydrogen. The CO_2 is removed in a chemical or a physical absorption process. The small amounts of CO and CO_2 remaining in the synthesised gas are poisonous for the ammonia synthesis catalyst and must be removed by conversion to CH_4 in the methanator. Dried synthesis gas consists of nitrogen and hydrogen in stoichiometric proportions (1:3). Inert gases, argon and methane are also introduced into the ammonia loop. The equilibrium reaction that takes place in the loop converter yields 20% to 28% in ammonia. The ammonia is then liquefied and separated from the non-reacted synthesised gas. Since inert gases are introduced into the loop, a purge is required.

The growing demand of fertilizers due to an increase of world population generated a necessity for ammonia that together with the economy of scale resulted in an increase in the size of ammonia plants [12]. This increase reached a critical point when radial converters [21] and centrifugal compressors [23,24] appeared during the mid-sixties. During this period, improvements in the construction technology resulted in the large ammonia plant concept propagated by Kellogg. **Fig. 5** shows the evolution of the ammonia plant capacity over time.

The technological advances achieved in the reformer section focused on reducing the overall energy consumption of the plant [16,25–28]. For this reason, an increment in the operating pressure of the reformer took place to reduce the operating costs of the loop compressors. The development of centrifugal compressors [23,29] allowed working at higher pressures with lower costs (see Fig. 5). This change forced an increase in the temperature of the reforming section to obtain an equivalent conversion.

From the very beginning, only one stage of high temperature shift converter (HTSC) was used [18]. Beginning in 1962, two stages of HTSC were used [14,19,20,30,31]. In 1963, the low temperature shift converter (LTSC) appeared. In 1966, 47% of the plants used LTSC. In 1971, the Selectoxo process appeared. In this study, a conversion of 90% of carbon monoxide in one stage of HTSC [32] was assumed, while 96% of the conversion was assumed for an LTSC.

The energy consumption for solvent regeneration has always been the major driving force of technology improvement in
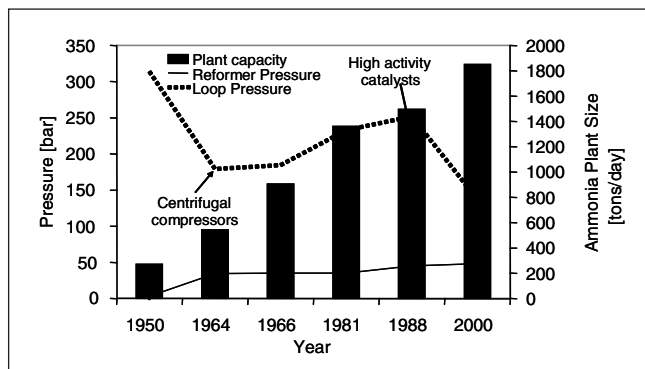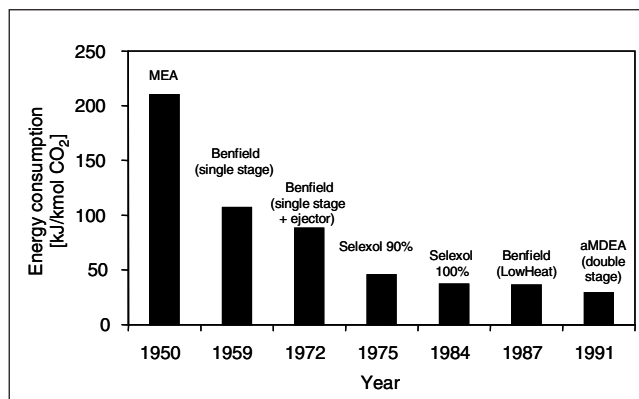
Fig. 6: Evolution of energy consumption for the CO_2 absorption process in ammonia production

the CO_2 absorption process. Chemical absorption processes have periodically decreased their steam requirements. Physical absorption processes resulted in a large technology jump when higher overall operating pressures were achieved, although hybrid processes can nowadays be considered as the process with lower energy requirements [27,33–44].

Fig. 6 shows the energy consumption per kmol of CO_2 absorbed for the different separation processes. The major barrier for the further development of these processes was the high investment cost of switching to a different technology. For example, at a certain point in time it may have been cheaper to change the additives of a chemical absorption process instead of switching to a physical absorption. The carbon dioxide produced can be sold after purification.

Changes in the technological development of the ammonia loop focused on obtaining catalysts with higher activity and converters with lower pressure drop and higher conversion [17,30,45,46] (see Fig. 5). The development of new compressors highly influenced the operating pressure of the ammonia loop. It is evident how centrifugal compressors influenced the ammonia loop pressure operation, because the economic optimum of centrifugal compressors was at 150 bar [29,47].

Pressure increased slowly to obtain higher yields until the introduction of new, highly active catalysts at the end of the 1980s allowed a pressure reduction [48]. The development of low pressure converters with a smaller pressure drop during the 1980s also justified a lower working pressure in the ammonia loop [49,50].

In a typical ammonia plant, the purge of inert gases represents 4–6% of the total synthesised gas [22]. Before 1950, the purge exited the process without any treatment. In 1952, the purge was used as combustion gas in the reformer because of its high hydrogen content. In 1964, cryogenic separators for the recovery of hydrogen became available. In 1971, a new technology based on semi-permeable membranes competed with the cryogenic separators. Efficiencies in hydrogen recovery are 85–95% in membrane recovery and 90–95% in cryogenic recovery [51]. Both technologies are improving and it is difficult to consider one better than the other.

Fig. 5: Technical parameters of ammonia plants as a function of time

In energy terms, a cryogenic purification represents an energy saving of up to 0.7 GJ per ton ammonia [52], as compared to having a purge. Nowadays, membrane purge technology has similar energy consumption.

In 1965, surplus heat from a reformer produced 1.2 tons of steam at a pressure higher than 100 bar per ton of ammonia produced [47]. This heat could be used in different parts of the ammonia plant. As an effect of the oil crisis, a higher integration (integrated auxiliary boilers) of the different parts of an ammonia plant was conducted. In 1976, about 85% of the total energy demand of the plant was supplied by waste heat [12]. The steam generated in the reformer step provides most of the power required for synthesis gas compression (85% in 1976) [12]. During the early 80s, waste heat recovery was conducted in a way that the generated surplus of energy was exported outside the ammonia plant [53].

Natural Gas, Oil and Coal Production and Combustion Processes. During the past two decades, the technological evolution of the oil and gas industry focused on improving exploration and production technology [54–56]. This led to significant levels of commercial production from a new class of natural gas collectively called unconventional natural gases.

Efficiency improvements in oil refineries are limited mainly by the lack of competitive financial conditions [56]. Due to the low price of oil, capital investments in refinery upgrades often would not provide a competitive economic return. The same is true for coal processing upgrades. Low prices of fossil fuels are consequences of many traditional policies like direct and indirect subsidies, non-inclusion of external costs associated with their production and use (environmental and social costs), large scale of consumption and long time presence in the market. These factors allowed the creation of an optimized production, transportation and commercialization structure.

Later regulations on methane emissions forced the coal, oil and gas industries to reduce such emissions. Due to the STAR programme, the natural gas industry has been reducing methane emissions over the last 10 years. Similar efforts have been made in the coal and oil production [57].

These small changes and the low impact of the production technology of natural gas itself have led to discard an in-depth study of its technology evolution. A similar situation was assumed for the oil and coal sectors where the production itself did not undergo dramatic changes over the last fifty years [58,59].

Evolution of Environmental Legislation. In this section, the evolution of the environmental regulations relevant to the case study [60] is summarized. In 1955, the US federal government decided that the air pollution problem needed to be dealt with on a national level and created the Air Pollution Control Act [61]. Eight years later, Congress passed the nation's Clean Air Act of 1963 [62]. This act dealt with reducing air pollution by setting emission standards for stationary sources such as power plants and steel mills. Amendments to the Clean Air Act were passed in 1965, 1966, 1967, and 1970 [63–66].

During the 70s [67], the issue was addressed again because the existing laws were deemed inadequate. Although technically an amendment, the Clean Air Act of 1970 established new primary and secondary standards for ambient air quality, set new limits on emissions from stationary and mobile sources, and increased funds for air pollution research.

In 1990 [68], the federal government revised the Clean Air Act due to growing environmental concerns. The Clean Air Act of 1990 addressed five main areas: air-quality standards, motor vehicle emissions and alternative fuels, toxic air pollutants, acid rain, and stratospheric ozone depletion. In many ways, this law set out to strengthen and improve existing regulations. The 1990 Clean Air Amendment authorized the EPA to establish standards for a number of atmospheric pollutants, including SO_2 and NO_x.

2.2.2 Data Analysis

In this step, the results obtained in the data collection step are converted into mass and energy balances for the production of ammonia. For this purpose, the process simulation software Aspen Plus® was used to model different variants of the ammonia process representing different points in time. **Fig. 7** shows the evolution of the average feedstock for the production of one kilogramme of ammonia. These values include the amounts of natural gas, coal and oil required for the reaction and the amount of these materials required as an energy source.

SimaPro 5.0 data for oil [69], coal [70] and natural gas [71] combustion were used as a basis for calculating the emissions per amount of energy carrier over time. Restrictions produced by environmental regulations were applied to these emissions to obtain an evolution of the emission levels per GJ over time. According to the SimaPro 5.0 database, 54MJ [71] of energy are obtained from the combustion of one kg of natural gas assuming 100% efficiency. Simple natural gas combustion produces low SO_x and NO_x emissions.

Information about emissions for the production of natural gas, coal, and oil can be found in the literature [69–75]. As an assumption, all the emissions from the production of these sources of energy will be considered to come from the combustion of the respective energy sources. As a result, 2.7 MJ, 1.465 MJ, and 5.41 MJ of energy are required for the pro-
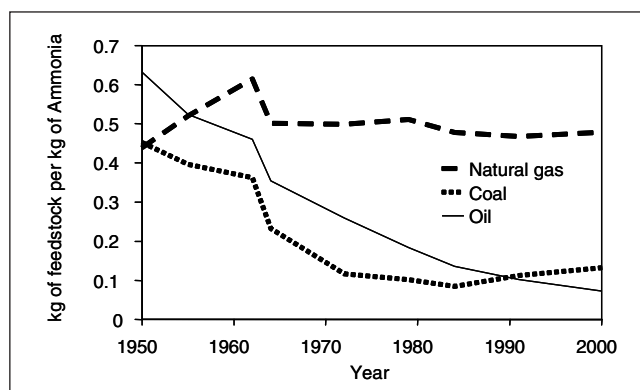

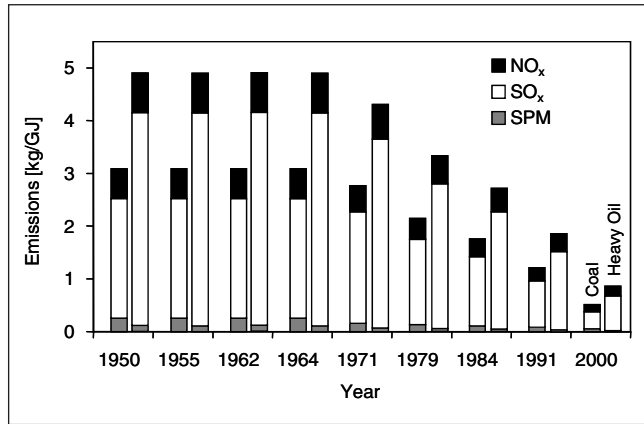**Fig. 7:** Calculated feedstock requirements per kilogramme of ammonia as a function of time

Fig. 8: Evolution of coal and heavy oil combustion emissions over time as function of environmental regulations

Fig. 9: Calculated energy requirements in ammonia production as a function of time

duction of one kg of natural gas, coal and oil, respectively. A major criticism of coal as a fuel source for energy generation is that it produces large amounts of pollutants, primarily sulfur dioxide (SO_2), nitrogen oxides (NO_x), and small particulate matter (SPM), as well as carbon dioxide (CO_2), which is implicated in global climate change.

According to the SimaPro 5.0 database from the combustion of one kg of coal and oil, 29.3 MJ and 41 MJ of energy are obtained respectively assuming 100% efficiency [73,74]. Over the last fifty years, advanced technologies have dramatically improved the environmental performance of flue gas desulphurization systems for SO_2 control and NO_x reduction technologies [76]. The evolution of the resulting emissions of NO_x, SO_x and SPM due to changes in environmental regulations is shown in **Fig. 8**.

2.3 Impact Assessment

For this study, the environmental indicators considered comprise nitrogen oxides (NO_x including N2O), carbon monoxide (CO), carbon dioxide (CO_2), volatile organic compounds (VOCs, including CH_4), sulfur dioxide (SO_2), and small particulate matter (SPM) [69–72].

Amounts of energy and raw materials required in the ammonia process are used to obtain the resulting emissions and were finally added up to obtain the overall emissions of ammonia production. Emissions of CO_2, NO_x and VOC were aggregated into one single impact category, the global warming potential (GWP).

2.4 Interpretation

The results of the TE-LCA method represent the environmental impact of the process as a function of time. For the case study on ammonia production, these findings reflect the influence of the technological development and environmental regulations on the environmental performance of the process.

3 Results and Discussion

In this study, the environmental assessment of ammonia production has been based on the total energy and raw material consumption of the production process and the upstream
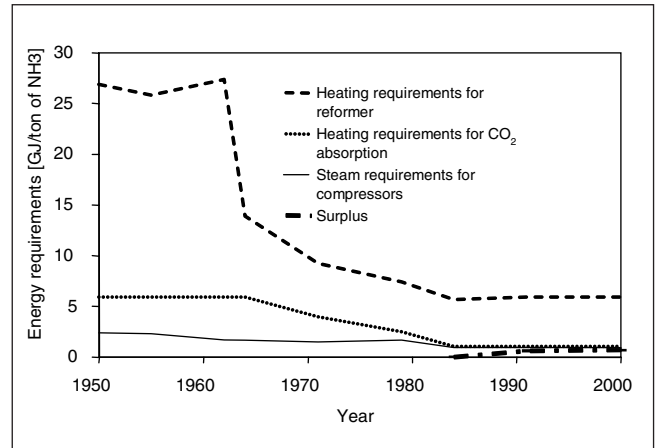
processes. Combustion of natural gas, coal and oil has been considered as a direct source of emissions. **Fig. 9** shows four major aspects of the energy consumption in the ammonia production: The heating required for running the plant, mainly the reformer section, the requirements for carbon dioxide absorption, the requirements for running the compressors before the loop and the surplus generated from the beginning of the early nineties on. These results show that ammonia production has dramatically changed over the last fifty years. Changes in feedstock, but most importantly changes in technology, have led to a more efficient process in which energy consumption has been reduced to about 25% of the requirements in 1950.

Ammonia production had a fast technological improvement as displayed in Figs. 5 and 6. Reasons for this are based on the importance of ammonia. Another reason is the ownership of the technology. There are several companies that license ammonia technology such as ICI, Kellog, Topsoe, Uhde, Ammonia Casale and competition increased efforts for further development of the ammonia process.

The emissions from the ammonia production (**Fig. 10**) are influenced by two factors, the evolution of its technology and the feedstock production. During the first ten years studied, the most important factor that affected the emissions was just the feedstock mix used. During this period, a slight descent in the emissions can be observed due to the intro-
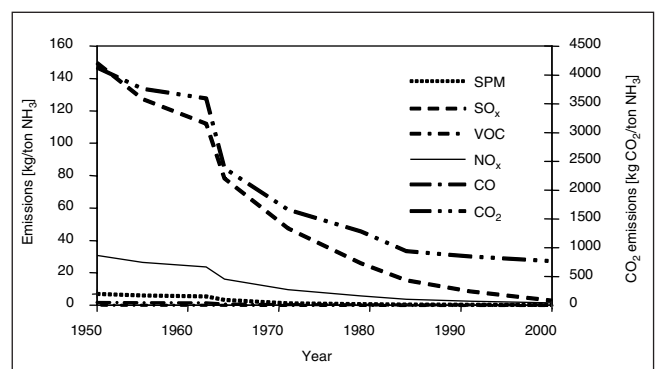

Fig. 10: Evolution of emissions from ammonia production

duction of natural gas as the main raw material. The trend to raise the reformer working pressure during the following years increased the overall energy demand due to a higher steam to carbon ratio. Emissions did not increase during this period due to the continuous introduction of natural gas as a main feedstock. The development of centrifugal compressors around 1960 allowed the increase of loop and reformer working pressures at lower energy cost and decreased the overall energy consumption of the plant significantly.

Emissions kept decreasing during the following years due to the combined effect of the operating conditions and the feedstock mix. The development of centrifugal compressors also allowed the Kellog and Topsoe concept of bigger ammonia plants. This concept allowed higher energy efficiency, thus decreasing the emissions per kilogramme of ammonia produced. The 1970–1980 period was highly influenced by the energy crisis and many actions were conducted to increase energy efficiency. Heat integration and improved CO_2 absorption systems together with the continuous introduction of natural gas as preferred feedstock decreased the overall energy consumption and thus the total emissions. Finally, the development of new catalysts with a higher yield at lower pressure combined with the introduction of high capacity and low pressure drop converters during the last part of the eighties shaped ammonia processes almost to those as known nowadays.

The values of CO_2, SO_x and NO_x emissions evolved in a similar way until the beginning of the seventies (see Fig. 10). Since then, two factors affected the different behaviour of the curves, the feedstock mix and the legislation. Cleaner natural gas increased its market share in comparison to coal or oil, and highly affected the emissions of SO_x. The clean air act introduced in 1971, 1979 and 1984 controlled NO_x and SO_x emissions. The effect of legislation can be observed as a steeper descent of the SO_x and NO_x curves versus the CO_2 curve, since CO_2 was not regulated.

Fig. 11 shows the evolution of the GWP emissions, and the SO_x emissions with and without the effect of environmental regulations. The results of not having environmental regulations were obtained by using the emissions from 1950 during the whole time of study. A difference between the curves can be observed as soon as the clean air act of 1971 established first emission limits resulting in the implementation of end of pipe cleaning technologies.
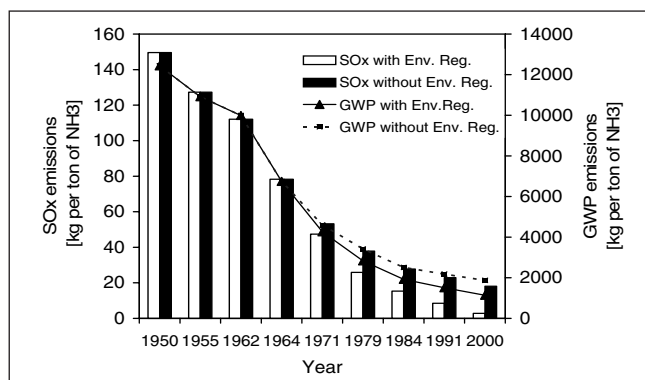

Fig. 11: Evolution of emissions of SO_x and GWP gases resulting from the ammonia production

From the environmental point of view, Fig. 11 shows that emissions have decreased as a result of the technological improvements and environmental regulations. Some of the reductions are due to the combined effect of technology and regulations, such as for NO_x, SO_x and VOC. In the case of CO_2, the reduction in emissions was only due to the effect of technological change which resulted in a more efficient use of energy. The values for SO_x emissions and GWP calculated for the year 2000 are close to the corresponding values for ammonia processes that are given in the database ecoinvent [77].

Fig. 11 shows that the emissions from ammonia production have dramatically changed over the last fifty years. The introduction of the Clean Air Act started to restrict the amounts of air pollutants released from combustion of energy carriers. Nevertheless, energy savings have been the major driving force for the reduction of emissions. Since only emissions from energy consumption were taken into account in this case study, no trade-offs between reductions in energy consumption and chemistry-specific emissions were revealed. The scenario might be different for cases in which emissions from the (chemical) production process itself have to be considered. Then, a trade-off between energy consumption and emission limits might result and the role of environmental regulations might be higher.

4 Conclusions

In this paper, a new methodology to obtain the LCA of technology evolution (TE-LCA) of the production of a chemical product was presented. The objective of the method is to obtain an overall evolution of the environmental performance of the different processes involved. The methodology was applied to the case study of ammonia production. The results revealed that the environmental performance of this process was highly influenced by the technological development and to a lower extent by the environmental regulations. Thus, it can be concluded for the case of ammonia, that not primarily legislation but technical progress led to a better environmental performance. This case study shows that investment in technological development also paid off in terms of being ahead of tightened environmental legislation, with potential cost consequences such as carbon dioxide tax.

In summary, the information obtained from this method is useful to understand how the environmental performance of a process including its precursors developed in the past. It reveals the mechanisms of technical innovation, for a specific process as well as in general, and how it is linked to and triggered by business and legislative constraints. Furthermore, the review of technological developments in a certain field identifies those technologies that hold the most promise for further improvements towards sustainability. The presented method can be extended by also including the analysis of economic performance of the system investigated.

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