Production of Urea-based De-NO$_x$ Reduction Agents with Minimum Additional Contributions to the GHG Emissions

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The present paper is a review of the most viable, sustainable, and carbon-neutral industrial routes available for producing urea based de-NO$_x$ reduction agents (e.g., AdBlue 32%), with a negligeable contribution to the GHG emissions, in comparison with the conventional current applications. Starting from the analysis of the trend in the demand of urea-based de-NO$_x$ agents and the forecast growth of such market, the study provides a quantitative assessment of the contribution to the GHG emissions due to the common production routes of these chemicals, showing an alternative industrial process which balances and neutralizes this adverse environmental effect. Indeed, some carbon-intensive industrial processes such as cement or steel productions have, as of now, no feasible way to avoid or significantly limit CO$_2$ emissions from their flue gas waste streams. The integration schemes with such existing large CO$_2$ point emitters are investigated with the objective to produce a carbon-neutral urea-based de-NO$_x$ agent with minimum additional contributions to the GHG emissions.

1. Introduction

Nitrogen oxides are well known to be troublesome gaseous components polluting atmospheric air. Among the nitrogen oxides forms (N$_2$O, NO, N$_2$O$_3$, NO$_2$, N$_2$O$_4$, N$_2$O$_5$), the most common in atmospheric air are nitrogen oxide (NO) and nitrogen dioxide (NO$_2$), which total content is marked with a common symbol NO$_x$.

Though nitrogen oxides have also non-anthropic origin, as instance the denitrification natural process of soils (Abbasi and Adams, 2000), the predominant source is represented by all combustion processes of solid, liquid and gas fuels. Several industrial activities heavily contribute to produce NO$_x$ polluted flue gas: transport and automotive, power plants, industrial processes (mostly nitric acid and derivatives) and municipal solid waste incineration. NO$_x$ emissions can cause a series of health problems, such as eye and throat inflammation, chest tightness, nausea, and headaches, as well as environmental problems, such as ozone depletion, acid rain, haze, photochemical smog, and indirect greenhouse gas effects (Fuglestvedt et al., 1996). Therefore, NO$_x$ emissions must be reduced and controlled.

Most common NO$_x$ control methods can be categorized into following ones (Zhu and Xu, 2022):

- pre-combustion (e.g. by selecting fuel sources with less nitrogen content),
- in-combustion (e.g. low NO$_x$ burners), and
- post-combustion (via reaction with absorbents, oxidants, or reductants).

By using the first two control methods, most of the exhaust gases from industrial combustion processes cannot meet emission standards. Therefore, a post-combustion approach is usually used to achieve a higher NO$_x$ reduction. The most widely used post-combustion technique is the Selective Catalytic Reduction (SCR), which reduces NO$_x$ into molecular nitrogen (N$_2$) by heterogeneous catalytic reaction with gaseous ammonia under moderate temperature (preferably in the range 250÷350 °C). Gaseous ammonia can be introduced into the flue gas chamber either as straight ammonia, or as other ammonia precursor, that releases gaseous ammonia after thermal decomposition in contact with hot flue gas. The current orientation of the market, between the different precursors of gaseous ammonia, is in favor of the usage of urea [CO(NH$_2$)$_2$] diluted in a water solution, as it is not toxic in comparison with water-ammonia solutions, and it is produced worldwide on a large scale, which makes it widely available (Halonen et al., 2017). It is well known that the production process of urea, as well as the further thermal decomposition of the same into CO$_2$ and NH$_3$ occurring in the SCR flue gas system, have a

significant contribution to GHG emissions.The demand of de-NO_x reduction agents is expected growing quickly in the next years, due to more stringent legislation on emissions of NO_x gases (such as the Directive 2010/75/EU).Based on the data currently available of CO_2 emissions from Energy Combustion and Industrial Process (IEA, 2021), a forecast of 80 Mt/y has been estimated for the world-scale demand of urea based de-NO_x reduction agents within the year 2040, for matching the most stringent NO_x emission scenarios (see table 1). The estimate is coherent with the available forecast in cutting the worldwide NO_x emissions from current 108 Mt/y to 45 Mt/y in 2040 (IEA, 2022). Such expected demand of urea based de-NO_x reduction agents, assuming a conventional production route based on natural gas, would generate in the year 2040 an amount of GHG emissions more than 90 Mt $CO_{2\,eq}$./y.It is not sustainable that the control of NO_x emissions generates a drawback effect with detrimental effects over the environment. It is then of interest to study and develop alternative routes, aimed to produce urea based de-NO_x reduction agents, that have the advantage of negligeable GHG effects.

2. Mechanism of NO_x Reduction Reactions

As discussed by Halonen et al. (2017), one of the most widespread de-NO_x reduction agents for SCR systems is urea diluted in a water solution. The trade name for the urea-water solution is AdBlue in Europe and DEF (Diesel Exhaust Fluid) in the US. In the automotive industry, urea with a concentration of 32.5 wt% is typically used. This concentration was chosen because it is the concentration with the lowest crystallization point of – 11 °C even though higher concentrations of up to 50 wt% can be used (marine grade).

A simplified scheme of the thermal decomposition of urea in flue gas and NO_x reduction reactions with ammonia in SCR systems is given below (Maizak et al., 2020):

$$CO(NH_2)_2 \rightarrow NH_3 + HCNO \tag{1}$$
$$H_2O + HCNO \rightarrow NH_3 + CO_2 \tag{2}$$
$$NO + NH_3 + \tfrac{1}{4}\,O_2 \rightarrow N_2 + \tfrac{3}{2}\,H_2O \tag{3}$$
$$NO + NO_2 + 2\,NH_3 \rightarrow 2\,N_2 + 3\,H_2O \tag{4}$$
$$4\,NH_3 + 3\,O_2 \rightarrow 2\,N_2 + 6\,H_2O \tag{5}$$
$$2\,NH_3 + 2\,O_2 \rightarrow N_2O + 3\,H_2O \tag{6}$$
$$2\,NH3 + 2\,NO_2 + 2\,H_2O \rightarrow NH_4NO_3 + NH_4NO_2 \tag{7}$$

In the preferred temperature range of SCR systems (i.e. 250÷350 °C), reactions (1) to (4) are sufficient to represent adequately the thermodynamic of the system.

As per stoichiometry, every 1 mol of NO_x being reduced into N_2 is balanced by 1 mol of NH_3 being depleted.

Assuming the ammonia slip is negligeable for our considerations, based on reactions (1) and (2), 1 mol of urea is then sufficient for reducing 2 mols of NO_x into N_2.

3. Forecast of the Demand of De-NO_x Reduction Agents and Relevant GHG Impact

Though the current market of urea based de-NO_x reduction agents is only 6 Mt/y in comparison with the world urea production of 170 Mt/y (Argus and Fertecon, 2021), the demand is expected to increase quickly, motivated by the growing stringency of legislation on emissions of NO_x gases (Directive 2010/75/EU and following 2017 LCP BREF). The forecast is that the industrial sector with dominating demand of de-NO_x systems will be the massive coal and natural gas fired power generation sector, which alone represents half of the current world Total Energy Supply (IEA, 2021).
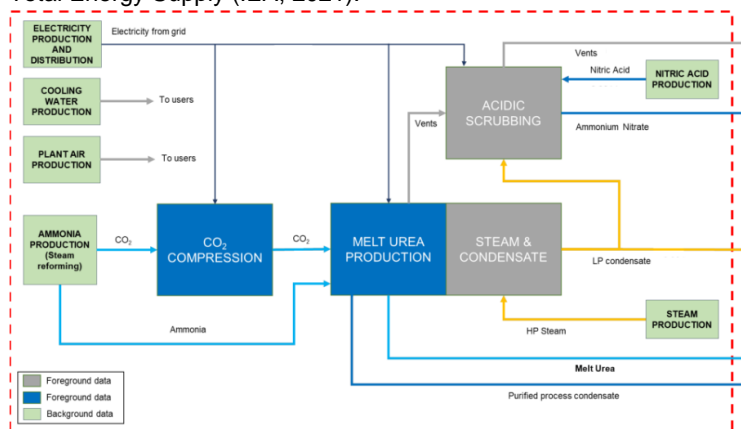

Figure 1: block diagram and main GHG sources of the conventional urea process.

An estimate for the potential demand of urea de-NO_x reduction agents has been carried out considering the mechanism of reaction explained in paragraph 2, together with the flue gas emission database available for combustion sources in the energy and industrial process, and the NO_x emission scenarios outlined by the IEA study (2022) for the next two decades. Data available from the European IPPC Bureau (2007) have been used to appraise the GHG emissions correlated to the increased demand of urea; the Figure 1 provides a summary of main GHG contributors of the conventional urea process.

The biggest CO_2 contributor is the production of the ammonia via Steam Methane Reformer (SMR), which is equivalent to 0.97 t $CO_{2\ eq.}$/t of urea and represents almost the 85% of GHG generation. The contribution factors due to process heat (steam) and electric energy (required by the transformation and finishing process) represent roughly the 10% and 5% respectively.

To sum up, the overall carbon footprint of conventional urea production process is 1.17 t CO2 eq./t (in liquid solution form), or 1.22 kg CO2 eq./t (in solid granulated form).

The GHG generation due to the expected demand of urea de-NO_x agents is outlined in Table 1.

Table 1: urea de-NOx worldwide carbon footprint, for future scenarios of reduced NOx emissions, using the urea conventional production process.

Pollutant or Product	Coal (Mt/y)	Natural Gas (Mt/y)	Oil (Mt/y)
Current CO_2 emissions	15,300	7,500	10,700
Forecast NO_x emissions (2040)	9.8	13.7	21.5
Forecast Urea de-NO_x demand	23.7	33.1	23.3
CO_2 eq. GHG	27.8	38.8	27.3

It can be concluded that the increased demand of urea de-NO_x reduction agents awaited in the next decades, assuming a conventional urea production route based on natural gas, would generate within the year 2040 an amount of GHG emissions more than 90 Mt $CO_{2\ eq.}$/y.

4. Carbon Capture Technologies Integrated with Existing Industrial Processes

Power plants and other important industrial activities, such as cement and steel productions, release relatively high amounts of anthropogenic carbon dioxide. Integrating the recovery process of these large point source emitters with new urea plants, expected to be in operation for balancing the increasing demand of de-NO_x reduction agents, is seen as a key task to achieve the target of minimizing the GHG effects that otherwise would arise. To date, most research and development has centered on capturing CO_2 emitted from coal power plants, as these are the largest emitters; however also the CO_2 concentration plays a crucial role in selecting the most suitable and attractive source. In fact, the separation efficiency of every technology is strongly dependent on CO_2 partial pressure, hence the the cost of capture is more beneficial at higher concentrations.

As can be evaluated from table 2, comparing CO_2 emissions from power and large industrial point sources, cement and iron productions look the most attractive industrial processes for the integration with urea production process, for the higher concentration and larger emitter size.

Table 2: Large CO₂ emissions from power and industrial point sources worldwide [Baker et al., 2018].

Source	No of sources	Total CO_2 emissions Mt/y	Average source size Mt/y	CO_2 concentration (% vol.)
Electric power plant	5,840	14,600	2.5	5÷15
Cement production	1,180	930	0.8	20÷30
Refineries	640	800	1.3	30÷40
Iron and steel	270	650	2.4	20÷30
Petrochemical	470	380	0.8	5÷10

Several studies have been presented in describing the recent development of cost-effective technologies to capture the CO_2 produced in power plants and industrial processes and utilize or sequester it underground (Figueroa et al., 2008). The main capture technology currently demonstrated at large scale is the chemical absorption, which makes use of amine based aqueous solvents, such as solutions of methyl-diethanolamine (MDEA) and mono-ethanolamine (MEA), or blend of MDEA and tri-ethylene tetramine (TETA), as discussed by Amann and Bouallou (2009).The amine solution, once enriched of CO_2 in the Absorber, is then regenerated by stripping at lower pressure and by means of steam. Capacity up to 2.0 Mt/y of captured CO_2 can be commonly achieved.The use of membranes has emerged as a promising second-generation capture technology for flue gas of power plants (Merkel et al., 2013). Membrane technology is at the development stage with several small pilot plants having been built and operated up to 100 kt/y of CO_2. Membranes are expected to have competitive capture costs, as well as operational advantages such as simple flow scheme and no other power source other than electricity, so that no changes to the power plant steam cycle are needed. (Font-Palma et al., 2021).
Ramírez-Santos et al. (2017) have estimated operation costs of less than € 33/t CO_2 for capture from steel plants. Membranes for CO_2 recovery from flue gas of both steel (Lie et al., 2007) and cement plants (Hägg et al., 2017) have been proven with pilot demonstration.
As example of practical applications of membrane separation process, the figure 2 provides a schematic diagram of a cement plant fitted with a membrane CO_2 capture system. Flue gas is available at 25% of CO_2 from kiln furnace. The system captures 80% of the CO_2 emitted (800 t/d) at an energy cost of 286 kW$_e$/t of CO_2 (Baker et al., 2018).
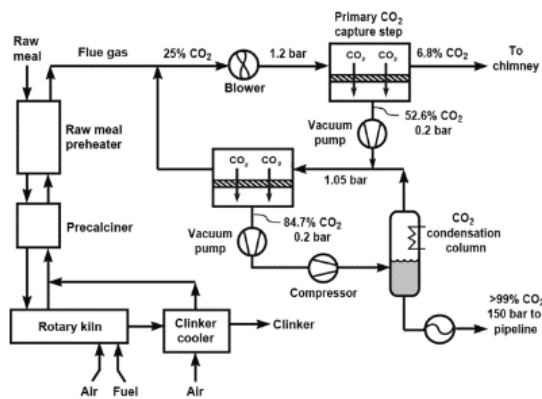

Figure 2: CO_2 membrane capture process applied to a cement plant.

Another promising application for integrated process is shown in Figure 3, which provides a simplified block diagram of a steel production process. Total CO_2 emissions are about 1.8 t CO_2/t of steel produced. Exhaust gas from blast furnace (BF) stoves are 28.5% rich in CO_2. Emissions are shown with the CO_2 concentration in the gas and the mass of CO_2 in kg/t of steel produced.
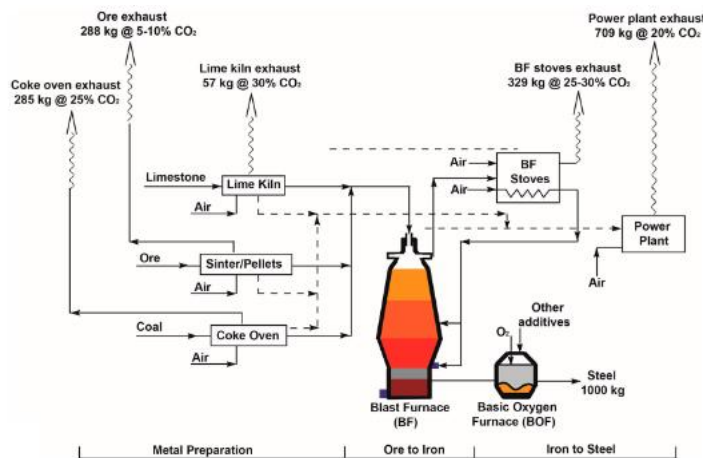

Figure 3: CO_2 emission sources for a blast furnace and BOF steel production process (Global CCS Institute, 2015).

5. Production of Urea-based De-NO$_x$ Reduction Agents with Minimum GHG Emissions

Here it is presented a case study showing how the GHG contribution of AdBlue urea solution can be minimized with an improved configuration.

5.1 Case Study for the Improved Process

Main assumptions of the case study for the carbon neutral AdBlue plant are:

- Urea is produced in liquid form (AdBlue solution 32%) with a capacity of 500 kt/y via a Total Recycle CO_2 Stripping process;
- Ammonia consumption is assumed 567 kg/t of urea and is supplied from a mix (50%/50%) of blue and green ammonia sources, assuming the relevant carbon contribution is equal to 0.17 and zero t CO_2 eq./t of NH_3 respectively (Mielke and Noelker, 2023);
- The carbon contribution due to transportation of liquid ammonia to the urea plant is assumed 0.3 t CO_2 eq./t of NH_3 (Al-Breiki and Bicer, 2020), assuming ocean tankers fuelled by Heavy Fuel Oil;
- CO_2 feedstock is assumed 740 kg/ton of urea and is sourced from a nearby existing cement plant, captured by means of double stage membrane system;
- Net consumption of process steam is zero by ensuring the recovery of the waste steam generated in the urea reactor to the pressure level required by the Stripping process (see figure 4);
- Both CO_2 and low-pressure steam compressors are driven by electromotor;
- Electricity (for both process and utilities) is produced by a NG fired generator with 40% efficiency.
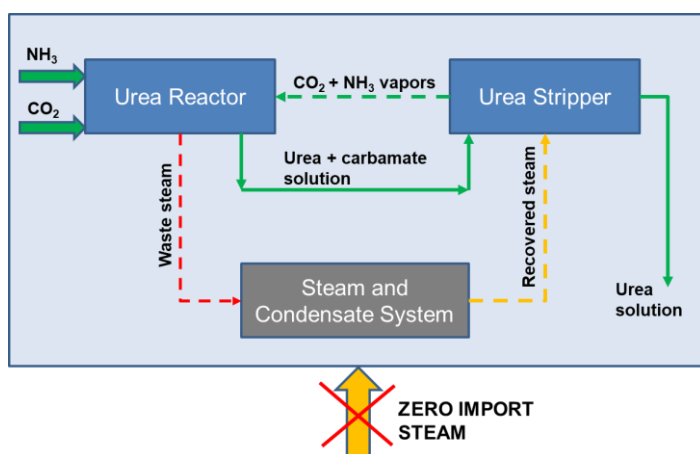

Figure 4: conceptual scheme of the urea melt section with zero import of process steam; the waste steam generated in the urea Reactor is recovered to the pressure level required by the Stripper.

A comparative quantitative analysis of the improved process has been performed against a conventional urea scheme, where the ammonia is produced via SMR, and the excess CO_2 is vented to the atmosphere after separation in the amine recovery section. The assumptions of GHG generation due to the production of the ammonia feedstock are the same ones used for the analysis previously summarized in table 1. In the conventional urea CO_2 Stripping process, the heat for Stripping is provided by medium pressure steam at 2.2 MPa, supplied from a NG fired boiler.
The results of the comparative quantitative analysis in terms of GHG emissions are summarized in Table 3.

Table 3: Comparative analysis of GHG emissions between a conventional and improved AdBlue urea plant.

Urea plant	GHG for NH$_3$ product. t CO_2 eq./t urea	GHG for NH$_3$ transport t CO_2 eq./t urea	GHG for Process steam t CO_2 eq./t urea	GHG for Electric power t CO_2 eq./t urea	Overall GHG emissions t CO_2 eq./t urea	Absolute GHG emissions Mt CO_2 eq./y
Conventional	0.97	0	0.13	0.07	1.17	93.9
Improved	0.05	0.17	0	0.17	0.39	31.3
Δ	-0.92	+0.17	-0.13	+0.10	-0.78	-62.6

To sum up, the improved AdBlue process can lower the overall GHG emissions (including the contribution of liquid ammonia transportation) of 0.78 t $CO_{2\,eq.}$/t urea, compared with the conventional route. Which means, in terms of absolute emissions, a saving of more than 60 Mt $CO_{2\,eq.}$/y.

6. Conclusions

In the next two decades, the demand of urea based de-NO_x reduction agents is expected to increase very fast, motivated by the growing stringency of legislation on emissions of NO_x gases. The forecast for the worldwide urea consumption as de-NO_x reduction agents is 80 Mt/y within the year 2040. The adverse effect of GHG emissions, caused by the conventional industrial production of urea, can be significantly limited by the integration with existing large point emitters, such as cement and steel plants. This work is presenting an improved AdBlue urea process, where the CO_2 is recovered from the flue gas of a typical cement plant, the ammonia is supplied by a mix (50%/50%) of blue and green sources, and the import of process steam is avoided by recovering the waste steam generated in the urea Reactor; within the year 2040, the improved process, despite the incremental demand of urea based de-NO_x reduction agents, can lower the expected GHG emissions from 94 down to about 31 Mt $CO_{2\,eq.}$/y, even including the carbon footprint due to ammonia transportation and assuming the required electric energy is fully generated by fossil fuels.

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