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Chapter 6

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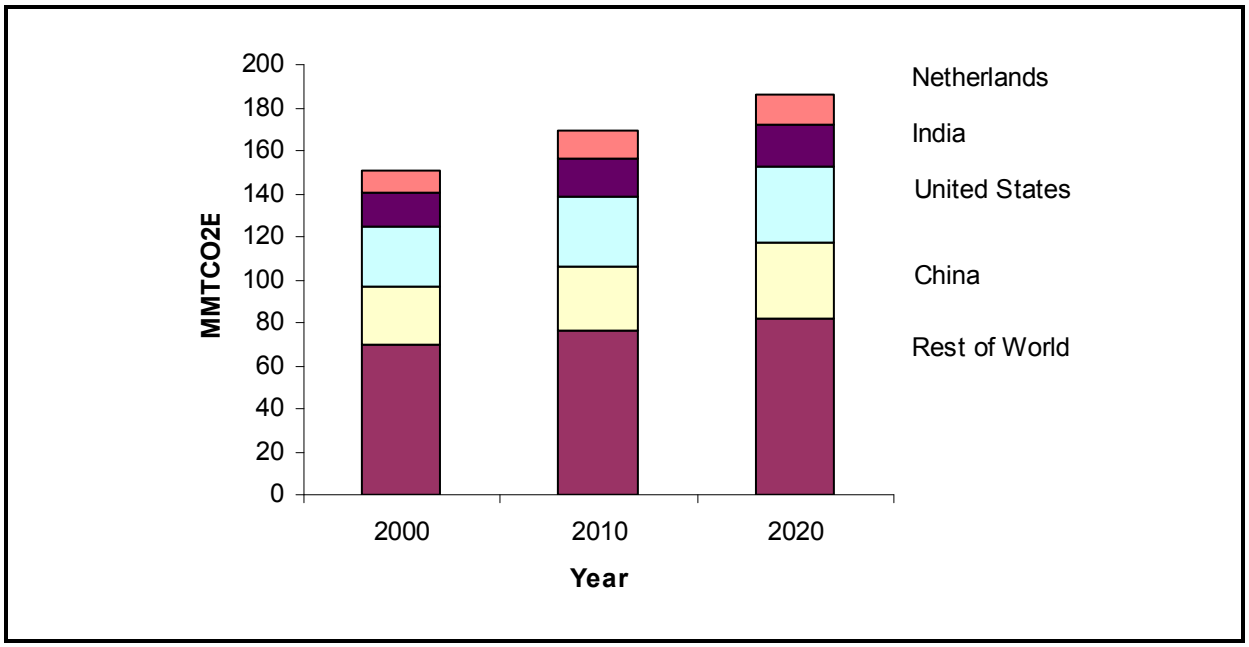
6. Industrial Process Sector (Nitric and Adipic Acid Production)

Worldwide nitrous oxide (N_2O) emissions from industrial sources account for more than 150 million metric tons of carbon dioxide equivalent (MMTCO2E) (EPA, 2005). The U.S. Environmental Protection Agency (EPA) estimates that emissions from nitric and adipic acid production together contributed approximately 5 percent of total global N_2O emissions in 2000 (EPA, 2003). Nitric acid production accounts for 67 percent of N_2O emissions from industrial production, and adipic acid accounts for the remaining 33 percent (EPA, 2003).

The United States, China, India, and the Netherlands combined account for 40 percent of total N_2O emission from industrial production (see Exhibit 6-1). The Intergovernmental Panel on Climate Change (IPCC) reports that the number of nitric acid production plants worldwide is estimated at 250 to 600. The United States is the primary producer of adipic acid, with four production sites alone, accounting for approximately 40 percent of total adipic acid production worldwide (EPA, 2001). Other countries have at most one adipic acid plant (IPCC, 2000).

Exhibit 6-1. N_2O Emissions from Industrial Production by Country: 2000–2020



Source: EPA, 2005.

Global N_2O emissions from industrial productions sources are expected to grow by approximately 16 percent between 2005 and 2020 (EPA, 2005), although the percentage distribution of emissions across countries is projected to remain relatively unchanged.

6.1 Introduction

The two major sources of anthropogenic N_2O emissions from industry are the production of nitric and adipic acid. The production of these dicarboxylic acids produces N_2O as a by-product in the production process, which is emitted in the waste gas stream (EPA, 2001).

6.1.1 Nitric Acid

Nitric acid is an inorganic compound, typically used to make synthetic commercial fertilizer. Nitric acid is also used in the production of adipic acid, explosives, and metal etching and in the processing of ferrous metals. Nitric acid is produced through catalytic oxidation of ammonia at high temperatures, which creates N_2O as a reactionary by-product released from reactor vents into the atmosphere (Mainhardt and Kruger, 2000). IPCC believes that nitric acid production now represents the majority of N_2O emissions from industrial process as a result of implementing abatement technologies at adipic acid plants.

In the United States, the nitric acid industry controls for nitrogen oxides (NO_x) gases using a combination of nonselective catalytic reduction (NSCR) and selective catalytic reduction (SCR) technologies (EPA, 2004). The NSCR units destroy NO_x, but they also destroy N_2O. However, NSCR is considered costly and obsolete at modern plants. NSCR units were commonly installed in production facilities built between 1971 and 1977 (EPA, 2004). EPA reports that NSCR is currently used by approximately 20 percent of the U.S. nitric acid production plants, whereas the majority of the industry uses SCR or extended absorption, neither of which is known to reduce N_2O (EPA, 2004).

6.1.2 Adipic Acid

Adipic acid is a white crystalline solid used primarily as a component in the production of nylon (nylon 6/6). Adipic acid is also used in the manufacturing of low-temperature synthetic lubricants, coatings, plastics, polyurethane resins, and plasticizers and to give some imitation foods a “tangy” flavor. Industrial sources report that by 2000 all major adipic acid production plants had implemented abatement technologies and consequently have dramatically reduced N_2O emission from this source (Mainhardt and Kruger, 2000).

Adipic acid is produced through a two-stage process during which N_2O is generated in the second stage. The first stage of manufacturing usually involves the oxidation of cyclohexane to form cyclohexanone/cyclohexanol mixture. The second stage entails oxidizing this mixture with nitric acid to produce adipic acid. N_2O is produced as a by-product during the nitric acid oxidation stage and

potentially is emitted in the waste gas stream (EPA, 2004). Emissions from this source vary depending on the type of technologies and level of emission controls employed by a specific facility.

6.2 Baseline Emission Estimates

N_2O emissions correlate closely with the production of nitric and adipic acid. This section discusses production activity, suggested emission factors, and the resulting baseline emissions estimates based on publicly available reports.

6.2.1 Activity Factors

Activity factors characterize the intensity of production in these industries, which, when combined with emission factors, result in an estimated baseline emission.

Historic Activity Data

Nitric Acid. Nitric acid production levels closely follow trends in fertilizer consumption, because of nitric acid's role as a major component in fertilizer production (Mainhardt and Kruger, 2000). Trends in fertilizer production vary widely across different regions of the world. For example, in Western Europe, because of concerns over nutrient runoff, nitrogen-based fertilizer use has been scaled back. However, in regions in which agriculture accounts for a larger share of GDP, such as Asia, South America, and the Middle East, nitrogen-based fertilizer production capacity is increasing (Mainhardt and Kruger, 2000).

The actual number of nitric acid production plants globally is unknown. Previous reports cited by the IPCC have suggested the number to be between 250 and 600. This uncertainty is caused by many nitric acid plants often being part of larger facilities that manufacture products using nitric acid, such as fertilizer and explosives facilities (Mainhardt and Kruger, 2000).

Adipic Acid. Adipic acid is used primarily in the production of nylon. As a result, production of adipic acid is closely correlated with the world's nylon production. Global demand for engineering plastics has increased over time, resulting in major expansion in production capacity in North America and Western Europe and new facilities in the Asia Pacific region. In the United States, adipic acid production increased by approximately 50 percent between 1990 and 2000 (EPA, 2004).

Global capacity for adipic acid was approximately 2.8 million metric tons in 2003. Exhibit 6-2 lists estimated adipic acid production capacity in 2003 by country. Demand for adipic acid was estimated at 2.21 million metric tons for the same year (*Chemical Week* [*CW*], 2003). As a result of this oversupply in the global market, many adipic acid facilities have been operating at an average rate of 85 percent of capacity.

Projected Activity Data

Nitric Acid. Nitric acid production is expected to increase over time (Mainhardt and Kruger, 2000). The Global Emission Report, from which the emission projections came, used country data that did not report specific country activity data. Projected production data for nitric acid production was not available at the time of publication of this report.

Adipic Acid. Industrial demand for adipic acid is expected to continue to increase by approximately 2 percent per year between 2003 and 2008 (*CW*, 2003). Nylon 6,6 accounts for approximately 70 percent of demand for adipic acid. The demand for fiber-grade nylon 6,6 is projected to grow by 1 percent per year, whereas engineering-grade nylon 6,6 is projected to grow by 4.5 percent per year. The dramatic growth in engineering-grade nylon is a result of its increased use as a substitute for metal in "under-the-hood" automotive applications (*CW*, 2003).

Exhibit 6-2. 2003 Adipic Acid Production Capacity (Thousands of Metric Tons/Year)

Country	Adipic Acid Capacity
United States	1,002.0
Germany	408.0
France	320.0
United Kingdom	220.0
Canada	170.0
South Korea	135.0
China	127.0
Japan	122.0
Singapore	114.0
Brazil	80.0
Italy	70.0
Ukraine	56.0
World Total	**2,824.0**

Source: *Chemical Week*, 2003.

6.2.2 Emission Factors and Related Assumptions

Nitric Acid

The IPCC reports that N_2O emission factors for nitric acid production remain relatively uncertain, because of a lack of information on manufacturing processes and emission controls. The emission factor is estimated based on the average amount of N_2O generated per unit of nitric acid produced combined with the type of technology employed at a plant. The IPCC uses a default range of 2 to 9 kg N_2O per ton of nitric acid produced. As a result emission factors for nitric acid production plants may vary

significantly based on the type of technology employed at the plant. For example, NSCR is very effective at destroying N_2O, whereas alternative technologies such as SCR and extended absorption do not reduce N_2O emissions.

In the United States, a weighted average of 2 kg N_2O/ton nitric acid is used for plants using NSCR systems, and 9.5 kg N_2O/ton nitric acid is used for plants not equipped with NSCR. Exhibit 6-3 lists the reported emission factors from the IPCC in the *Revised 1996 Reference Manual.*

Exhibit 6-3. IPCC Emission Factors for Nitric Acid Production in Select Countries

Country	Nitric Acid EF
United States	2–9[a]
Norway—modern, integrated plant	<2
Norway—atmospheric pressure plant	4–5
Norway—medium pressure plant	6–7.5
Japan	2.2–5.7

[a]Emission factors up to 19 kg/ton nitric acid have been reported for plants not equipped with NSCR technology.
Source: IPCC, 1996.

The IPCC points out that potential emission factors as high as 19.5 kg N_2O/ ton of nitric acid have been estimated in previous reports. In addition, estimates of 80 percent of the nitric acid plants worldwide do not employ NSCR technology, which makes it more likely that the default range of potential emission factors provided by the IPCC greatly underestimates the true emission baselines (Mainhardt and Kruger, 2000).

Adipic Acid

The IPCC provides countries with a default emission factor of 300 kg N_2O/ ton of adipic acid produced. This emission factor assumes that no N_2O control system is in place. This factor was developed using laboratory experiments measuring the reactionary stoichiometry for N_2O generation during the production of adipic acid (Mainhardt and Kruger, 2000). This emission factor has been supported by some selected measurement at industrial plants. IPCC recommends using plant-specific data for those plants with abatement controls already in place (IPCC, 1996).

6.2.3 Emission Estimates and Related Assumptions

This section discusses the historical and projected baseline emissions from the industrial process sector for the production of nitric and adipic acid.

Historical Emission Estimates

Exhibit 6-4 lists historical N_2O emissions by country. Worldwide N_2O baseline emissions from nitric and adipic acid production decreased by 28 percent between 1990 and 2000. The United Kingdom, Germany, and Canada experienced the largest declines in baselines emission, with 88, 84, and 77 percent declines, respectively, over the same 10-year period. However, countries such as China, Japan, South Korea, and India saw baseline increases of 54, 29, 25, and 29 percent, respectively.

Exhibit 6-4. N_2O Emissions from Nitric and Adipic Acid Production: 1990–2000 (MMTN2OE)

Country	1990	1995	2000
China	18.7	26.3	28.7
United States	31.4	36.1	26.6
India	12.5	14.3	15.4
Netherlands	9.3	9.4	10.7
France	26.5	24.2	10.6
Japan	7.4	7.4	9.5
Italy	6.4	6.8	6.4
Brazil	5.0	5.3	6.2
South Korea (ROK)	4.7	5.0	5.8
Belgium	3.4	4.1	3.9
Germany	24.3	24.3	3.8
Poland	4.7	4.7	3.6
United Kingdom	28.0	18.1	3.5
Canada	11.0	11.0	2.6
Spain	2.8	2.2	2.3

Source: EPA, 2005.

Projected Emissions Estimates

Exhibit 6-5 lists combined projected N_2O baseline emissions from nitric and adipic acid by country. Worldwide total N_2O emissions from nitric and adipic acid are projected to increase by approximately 16 percent between 2005 and 2020. The United States, South Korea, and Brazil are expected to experience the largest increase in baseline emissions, with 28, 22, and 22 percent, respectively, between 2005 and 2020.

Exhibit 6-5. Projected N_2O Baseline Emissions from Nitric and Adipic Acid Production: 2005–2020 (MMTCO2E)

Country	2005	2010	2015	2020
China	30.6	32.5	33.9	35.3
United States	28.0	30.3	32.9	35.8
India	16.4	17.4	18.5	19.6
Netherlands	11.2	11.5	12.1	12.4
France	11.9	13.3	13.3	13.4
Japan	10.2	10.2	10.6	11.0
Italy	6.7	7.1	7.4	7.8
Brazil	6.8	7.5	7.8	8.2
South Korea (ROK)	6.4	7.1	7.5	7.8
Belgium	4.1	4.2	4.4	4.5
Germany	4.0	4.1	4.2	4.3
Poland	3.6	3.6	3.6	3.6
United Kingdom	3.5	3.5	3.5	3.5
Canada	2.7	2.9	2.9	2.9
Spain	2.2	2.2	2.2	2.2

Source: EPA, 2005.

Nitric Acid. Emissions from nitric acid production are expected to increase by 18 percent between 2000 and 2020, because of an expanding market for synthetic fertilizer (see explanatory note 1). Mexico, India, and Brazil are projected to increase their N_2O baseline emissions by 29, 27, and 24 percent, respectively, from nitric acid production (EPA, 2003). Exhibit 6-6 provides a list of N_2O baseline emissions from nitric acid production for selected countries in MMTCO2E.

Adipic Acid. Emissions from adipic acid production are projected to increase by approximately 40 percent between 2000 and 2020, reflecting increased demand for engineering nylon (see explanatory note 1). The United States, Brazil, South Korea, and Southeast Asia are projected to experience 68, 35, 35, and 35 percent increases, respectively, in baseline emissions of N_2O respectively. Exhibit 6-7 provides a list of N_2O baseline emissions from adipic acid production for selected countries in MMTCO2E.

6.3 Emission Reductions from Industrial Processes

Abatement options for the nitric and adipic acid sectors are relatively limited. Nitric acid production plants have technologies that indirectly destroy N_2O, but enhanced flaring and improved operation and maintenance (O&M) of production equipment could reduce emissions further. Exhibit 6-8 summarizes cost and emission reductions for several opportunities for emissions reductions beyond existing baseline practices.

Exhibit 6-6. Projected N_2O Emission From Nitric Acid by Country: 2000–2020 (MMTCO2E)

Country	2000	2010	2020
EU-15	32.3	35.6	37.2
United States	18.9	20.7	22.9
China	17.2	18.4	19.8
India	15.4	17.4	19.6
Japan	6.7	7.3	7.9
Eastern Europe	4.4	4.9	5.2
Canada	1.8	2.0	2.1
Mexico	1.4	1.6	1.8
Non-EU Europe	1.4	1.4	1.4
Brazil	0.6	0.7	0.7
Australia & New Zealand	0.5	0.4	0.4
Africa	0.0	0.0	0.0
CIS	0.0	0.0	0.0
Latin America	0.0	0.0	0.0
Middle East	0.0	0.0	0.0
World Total	**100.7**	**110.3**	**118.9**

Source: EPA, 2003.

Exhibit 6-7. Projected N_2O Emission From Adipic Acid by Country: 2000–2020 (MMTCO2E)

Country	2000	2010	2020
China	11.6	14.1	15.6
EU-15	13.1	14.5	15.1
United States	7.7	9.6	12.9
South Korea	5.8	7.1	7.8
Brazil	5.6	6.8	7.5
Japan	2.7	3.0	3.2
Eastern Europe	1.8	2.0	2.1
South-SE Asia	0.7	0.8	0.9
Canada	0.7	0.8	0.9
Non-EU Europe	0.6	0.5	0.5
Australia & New Zealand	0.2	0.2	0.2
Africa	0.0	0.0	0.0
CIS	0.0	0.0	0.0
India	0.0	0.0	0.0
Latin America	0.0	0.0	0.0
World Total	**50.4**	**59.3**	**66.7**

Source: EPA, 2003.

Exhibit 6-8. Cost of Reducing N_2O Emissions from Industrial Processes

Abatement Technology	Year	Capital Cost ($/TCE)	Annual Cost ($/TCE)	US Emissions Available for Reduction (MMTCO2E)	Reduction Efficiency	US Emission Reductions (MMTCO2E)	Breakeven Price ($/TCE)
Nitric acid	***High-Temperature Catalytic Reduction Method***						
	2010	$8.51	$0.59	20.7	90%	18.6	$2.28[a]
	2020	$8.51	$0.59	22.9	90%	20.6	$2.28[a]
Nitric acid	***Low-Temperature Catalytic Reduction Method***						
	2010	$12.63	$0.73	20.7	95%	19.7	$3.32[a]
	2020	$12.63	$0.73	22.9	95%	21.7	$3.32[a]
Nitric acid	***Nonselective Catalytic Reduction (NSCR)***						
	2010	$23.08	$0.60	20.7	85%	17.6	$4.35[b]
	2020	$23.08	$0.60	22.9	85%	19.5	$4.35[b]
Adipic acid	***Thermal Destruction***						
	2010	$1.39	$0.58	9.6	96%	9.2	$0.81[b]
	2020	$1.39	$0.58	12.9	96%	12.4	$0.81[b]

[a]Based on 10-year lifetime.
[b]Based on 20-year lifetime.

6.3.1 Nitric Acid: N_2O Abatement Option Opportunities

High-Temperature Catalytic Reduction Method

This N_2O abatement option has several variations developed by different companies, all involving the decomposition of N_2O into nitrogen and oxygen using various catalysts. The average estimated reduction efficiency is approximately 90 percent. Total capital costs for these abatement technologies range from $8 to $12 per tons of carbon equivalent (TCE). O&M costs vary by country. In the United States, O&M costs can range from $0.50 to $0.80 per TCE. This abatement option has an average technical lifetime of 10 years, yielding a breakeven price of approximate $3/TCE.

Low-Temperature Catalytic Reduction Method

Low-temperature catalytic reduction systems work similarly to high-temperature counterparts but do not require heat to decompose the N_2O. This abatement option has a reduction efficiency of 95 percent. Some versions of this abatement option require propane to be added to the gas stream before undergoing the reaction process. Total capital cost for this option ranges from $12 to $13 per TCE. In the United States, O&M costs range from $1 to $7 per TCE. This option has a technical lifetime of 10 years, yielding a breakeven price of approximate $3/TCE.

Nonselective Catalytic Reduction (NSCR)

NSCR uses a fuel and a catalyst to consume free oxygen in the tail gas, converting NO_x to elemental nitrogen. The gas from the NO_x abatement is passed through a gas expander for energy recovery, resulting in a reduction efficiency of 85 percent. The process requires additional fuel and emits CO_2. The total capital cost for this option is $23 per TCE. In the United States, the O&M cost is estimated at $0.60 per TCE. NSCR has a technical lifetime of 20 years, yielding a breakeven price of approximately $4/TCE.

6.3.2 Adipic Acid: N_2O Abatement Option Opportunities

Thermal Destruction

Thermal destruction is the destruction of off-gases in boilers using reducing flame burners with premixed methane (or natural gas). The system eliminates between 98 and 99 percent of N_2O and operates from 95 to 99 percent of the time. Total capital costs for thermal destruction are $1.40 per TCE. In the United States, O&M costs are estimated to be approximately $0.60 per TCE. This abatement option has a technical lifetime of 20 years, yielding a breakeven price of approximately $1/TCE.

6.4 MAC Curves for Selected Countries

Exhibits 6-9 and 6-10 present percentage reductions for different carbon prices ($/TCE) from the report to the Economic Modeling Forum (EMF) provided by EPA (EPA, 2003). Significant abatement potential is estimated to exist at $10/TCE. It is estimated that there are no "no-regret" options for N_2O nitric or adipic acid production. At a breakeven price of $10/TCE, the percentage abatement is 89 percent for nitric acid and 96 percent for adipic acid, reflecting the relatively high technical potential and low abatement cost for options in these industrial processes. Technology changes have not been incorporated into the abatement potential for N_2O emissions from industrial processes.

Exhibit 6-9. Percentage Abatement for Nitric Acid for Selected Breakeven Prices ($/TCE): 2000

Country	–$20	–$10	$0	$10	$20	$30	$40	$50
China	0.0%	0.0%	0.0%	88.9%	88.9%	88.9%	88.9%	88.9%
United States	0.0%	0.0%	0.0%	88.9%	88.9%	88.9%	88.9%	88.9%
EU-15	0.0%	0.0%	0.0%	88.9%	88.9%	88.9%	88.9%	88.9%
Japan	0.0%	0.0%	0.0%	88.9%	88.9%	88.9%	88.9%	88.9%

Source: EPA, 2003.

Exhibit 6-10. Percentage Abatement for Adipic Acid for Selected Breakeven Prices ($/TCE): 2000

Country	–$20	–$10	$0	$10	$20	$30	$40	$50
China	0.0%	0.0%	0.0%	96.0%	96.0%	96.0%	96.0%	96.0%
United States	0.0%	0.0%	0.0%	96.0%	96.0%	96.0%	96.0%	96.0%
EU-15	0.0%	0.0%	0.0%	96.0%	96.0%	96.0%	96.0%	96.0%
Japan	0.0%	0.0%	0.0%	96.0%	96.0%	96.0%	96.0%	96.0%

Source: EPA, 2003.

6.5 Uncertainties and Limitations

Uncertainty and limitations persist despite attempts to incorporate all publicly available information on international sectors. Limited information on the systems of developing countries increases this uncertainty. Additional information would improve the accuracy of baseline emission projections.

- *Improved Cost Data*: Improved documentation of N_2O abatement options and their cost components would improve the analyst's ability to estimate baseline reductions given some estimate of market penetration.
- *Improved Manufacturing Data for Nitric Acid*: Currently, nitric acid production worldwide is very uncertain because of a lack of good production estimates. In addition, improved data on the types of equipment generally employed by industries and trends in technology adoption in each country would improve the analyst's ability to estimate baseline emissions over time.
- *Improved Emission Factor Estimates*: Current emission factors are the result of laboratory experiments and only a few on-site facility measurements. Additional facility measurements would greatly improve the accuracy of each country's baseline emissions.

6.6 Summary

Adipic acid producers in the United States have already adopted options to mitigate emission of N_2O. Nitric and adipic acid production will continue to increase, correlating closely with the world's demand for synthetic fertilizers and nylon. However, certain abatement options may mitigate significant portions of a country's baseline if adopted by producers.

6.7 References

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Explanatory Notes

1. Separate emission estimates for nitric and adipic acid were not available for 2005, thus projected percent changes are presented for from 2000 to 2020. Note that these individual percent changes for nitric and adipic acid are not comparable with the total percent change of 16 percent which is for 2005 to 2020.