CRADLE-TO-GATE LIFE CYCLE ANALYSIS OF METHYLENE DIPHENYL DIISOCYANATE (MDI)

Final Report

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Submitted by:

Franklin Associates, A Division of ERG

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PREFACE

This life cycle assessment of Methylene diphenyl diisocyanate (MDI) was commissioned and funded by the American Chemistry Council (ACC) Plastics Division to update the original data in the 2011 report, **Cradle-to-Gate Life Cycle Inventory of Nine Plastic Resins and Four Polyurethane Precursors**, as well as the U.S. LCI plastics database. The report was made possible through the cooperation of ACC member companies, who provided data for the production of olefins, chlorine/sodium hydroxide/hydrogen, nitrobenzene/aniline, and phosgene/MDA/MDI.

This report was prepared for ACC by Franklin Associates, A Division of Eastern Research Group, Inc. as an independent contractor. This project was managed by Melissa Huff, Senior LCA Analyst and Project Manager. Anne Marie Molen assisted with data collection tasks and appendix preparation. Mariya Absar aided with research and modeling. Ben Young assisted with research.

Franklin Associates gratefully acknowledges the significant contribution to this project by Mike Levy (First Environment, formerly ACC), Keith Christman, Prapti Muhuri, and Allison Chertack of ACC in leading this project. Also acknowledged are the following companies: BASF, Covestro, Dow, and Huntsman, who graciously provided primary Life Cycle Inventory data for MDI production. Their effort in collecting data has added considerably to the quality of this LCA report.

Franklin Associates makes no statements other than those presented within the report.

July, 2022

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LIST OF ACRONYMS

(Alphabetical)

ACC	AMERICAN CHEMISTRY COUNCIL
AP	ACIDIFICATION POTENTIAL
API	AMERICAN PETROLEUM INSTITUTE
BOD	BIOCHEMICAL OXYGEN DEMAND
BTEX	BENZENE, TOLUENE, ETHYLBENZENE, AND XYLENE
COD	CHEMICAL OXYGEN DEMAND
CFC	CHLOROFLUOROCARBON
EGRID	EMISSIONS & GENERATION RESOURCE INTEGRATED DATABASE
EIA	ENERGY INFORMATION ADMINISTRATION
EP	EUTROPHICATION POTENTIAL
ERG	EASTERN RESEARCH GROUP, INC
EQ	EQUIVALENTS
GHG	GREENHOUSE GAS
GHGRP	GREENHOUSE GAS REPORTING PROGRAM
GJ	GIGAJOULE
GREET	GREENHOUSE GASES, REGULATED EMISSIONS, AND ENERGY USE IN TECHNOLOGIES
GWP	GLOBAL WARMING POTENTIAL
HCFC	HYDROCHLOROFLUOROCARBON
IPCC	INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE
ISO	INTERNATIONAL ORGANIZATION FOR STANDARDIZATION
LCA	LIFE CYCLE ASSESSMENT
LCI	LIFE CYCLE INVENTORY
LCIA	LIFE CYCLE IMPACT ASSESSMENT
LPG	LIQUEFIED PETROLEUM GAS
MDA	4,4-METHYLENEDIANILINE
MDI	METHYLENE DIPHENYL DIISOCYANATE

MJ	MEGAJOULE
MM	MILLION
NAICS	NORTH AMERICAN INDUSTRY CLASSIFICATION SYSTEM
NAPAP	NATIONAL ACID PRECIPITATION ASSESSMENT PROGRAM
NGL	NATURAL GAS LIQUID
NMVOC	NON-METHANE VOLATILE ORGANIC COMPOUNDS
NREL	NATIONAL RENEWABLE ENERGY LABORATORY
ODP	OZONE DEPLETION POTENTIAL
POCP	PHOTOCHEMICAL SMOG FORMATION (HISTORICALLY PHOTOCHEMICAL OXIDANT CREATION POTENTIAL)
RCRA	RESOURCE CONSERVATION AND RECOVERY ACT
SI	INTERNATIONAL SYSTEM OF UNITS
TRACI	TOOL FOR THE REDUCTION AND ASSESSMENT OF CHEMICAL AND OTHER ENVIRONMENTAL IMPACTS
TRI	TOXIC RELEASE INVENTORY
WTE	WASTE-TO-ENERGY INCINERATION

CRADLE-TO-GATE LIFE CYCLE ASSESSMENT OF METHYLENE DIPHENYL DIISOCYANATE (MDI)

INTRODUCTION

This study provides the American Chemistry Council (ACC), their members, users of the U.S. LCI Database, and the public at large with information about the life cycle inventory and impacts for the production of methylene diphenyl diisocyanate (MDI), which is a precursor in the manufacture of flexible and rigid polyurethane foams that are used for carpet pads, furniture cushions, construction, insulation, and packaging. MDI is also used to produce polyurethanes used in elastomers, coatings and adhesives.[1] Life cycle assessment (LCA) is recognized as a scientific method for making comprehensive, quantified evaluations of the environmental benefits and tradeoffs commonly for the entire life cycle of a product system, beginning with raw material extraction and continuing through disposition at the end of its useful life as shown in Figure 1 below. This cradle-to-gate LCA includes the life cycle stages shown in the dashed box including the “Raw Materials Acquisition” and “Materials Manufacture” boxes in the figure.

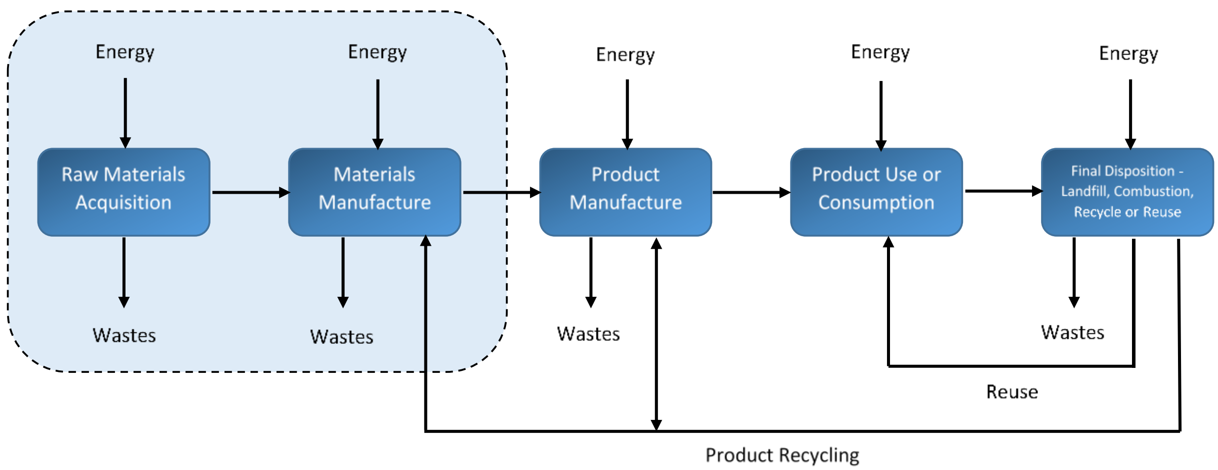

Figure 1. General materials flow for “cradle-to-grave” analysis of a product system. The dashed box indicates the boundaries of this analysis.

The results of this analysis are useful for understanding production-related impacts and are provided in a manner suitable for incorporation into full life cycle assessment studies. The information from an LCA can be used as the basis for further study of the potential improvement of resource use and environmental impacts associated with product systems. It can also pinpoint areas (e.g., material components or processes) where changes would be most beneficial in terms of reducing energy use or potential impacts.

[1] From the website: https://www.diisocyanates.org/about-institute

A life cycle assessment commonly examines the sequence of steps in the life cycle of a product system, beginning with raw material extraction and continuing through material production, product fabrication, use, reuse, or recycling where applicable, and final disposition. This cradle-to-gate life cycle inventory (LCI) and life cycle impact assessment (LCIA) quantifies the total energy requirements, energy sources, water consumption, atmospheric pollutants, waterborne pollutants, and solid waste resulting from the production of MDI. It is considered a cradle-to-gate boundary system because this analysis ends with the MDI production. The system boundaries stop at the MDI production so that the data can be linked to a fabrication process where it is an input material, and end-of-life data to create full life cycle inventories for a variety of applications, such as injection molded products, fibers, and film. The method used for this inventory has been conducted following internationally accepted standards for LCI and LCA methodology as outlined in the International Organization for Standardization (ISO) 14040 and 14044 standard documents[2].

This LCA boundary ends at material production. An LCA consists of four phases:

- Goal and scope definition
- Life cycle inventory (LCI)
- Life cycle impact assessment (LCIA)
- Interpretation of results

The LCI identifies and quantifies the material inputs, energy consumption, water consumption, and environmental emissions (atmospheric emissions, waterborne wastes, and solid wastes) over the defined scope of the study. The LCI data for the MDI unit process is shown separately in the attached Appendix. The LCI data for the pygas system is shown in the appendix of a separate report, Cradle-to-Gate Life Cycle Analysis of Olefins[3]. All unit processes will be made available to the National Renewable Energy Laboratory (NREL) who maintains the U.S. LCI Database.

In the LCIA phase, the inventory of emissions is classified into categories in which the emissions may contribute to impacts on human health or the environment. Within each impact category, the emissions are then normalized to a common reporting basis, using characterization factors that express the impact of each substance relative to a reference substance.

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[2] International Standards Organization. ISO 14040:2006 Environmental management—Life cycle assessment—Principles and framework, ISO 14044:2006, Environmental management – Life cycle assessment – Requirements and guidelines.

[3] Cradle-to-Gate Life Cycle Analysis of Olefins. Franklin Associates. Submitted to the Plastics Division of the American Chemistry Council. April, 2020.

STUDY GOAL AND SCOPE

In this section, the goal and scope of the study is defined, including information on data sources used and methodology.

STUDY GOAL AND INTENDED USE

The purpose of this LCA is to document the LCI data and then evaluate the environmental profile of MDI. The intended use of the study results is twofold:

- To provide the LCA community and other interested parties with average North American LCI data for MDI and
- To provide information about the environmental burdens associated with the production of MDI. The LCA results for MDI production can be used as a benchmark for evaluating future updated MDI results for North America.

According to ISO 14040 and 14044 standards, a critical or peer review is not required as no comparative assertions of competing materials or products are made in this study.

This report is the property of ACC acting on behalf of its Plastics Division and may be used by the trade association or members of ACC's Plastics Division or the general public at ACC's discretion.

FUNCTIONAL UNIT

The function of MDI is primarily for use as a polyurethane precursor. Industries that use polyurethanes with MDI as a precursor include automotive, construction, footwear, and adhesives/sealants. As the study boundary concludes at the MDI, a mass functional unit has been chosen. Results for this analysis are shown on a basis of both 1,000 pounds and 1,000 kilograms of MDI produced.

SCOPE AND BOUNDARIES

This LCA quantifies energy and resource use, water consumption, solid waste, and environmental impacts for the following steps in the life cycle of the MDI manufacture:

- Raw material extraction (e.g., extraction of petroleum and natural gas as feedstocks) through aniline, carbon monoxide, formaldehyde, chlorine, and sodium hydroxide production and incoming transportation for each process, and
- MDI manufacture which is aggregated with phosgene and 4,4-methylenedianiline (MDA), including incoming transportation for each material.

Pygas is a product of olefin manufacture. Because upstream olefin manufacture impacts the results for the production of MDI, some discussion of pygas data and meta-data is included throughout this report. However, the LCI data for the olefin system is provided in the appendix of a separate report, *Cradle-to-Gate Life Cycle Analysis of Olefins*[4]. Chlorine and small amounts of sodium hydroxide are intermediate chemicals used for MDI. The unit processes for these chemicals may be found in a separate report, *Cradle-to-Gate Life Cycle Analysis of Polyvinyl Chloride (PVC) Resin*[5].

This report includes LCI results, as well as LCIA results, for MDI manufacture. Figure 2 presents the flow diagram for the production of MDI. A unit process description and tables for each box shown in the flow diagram can be found in the attached appendix, or in a previously released olefins or the PVC resin report. Unit processes included within the dotted rectangle are included in an aggregated dataset.

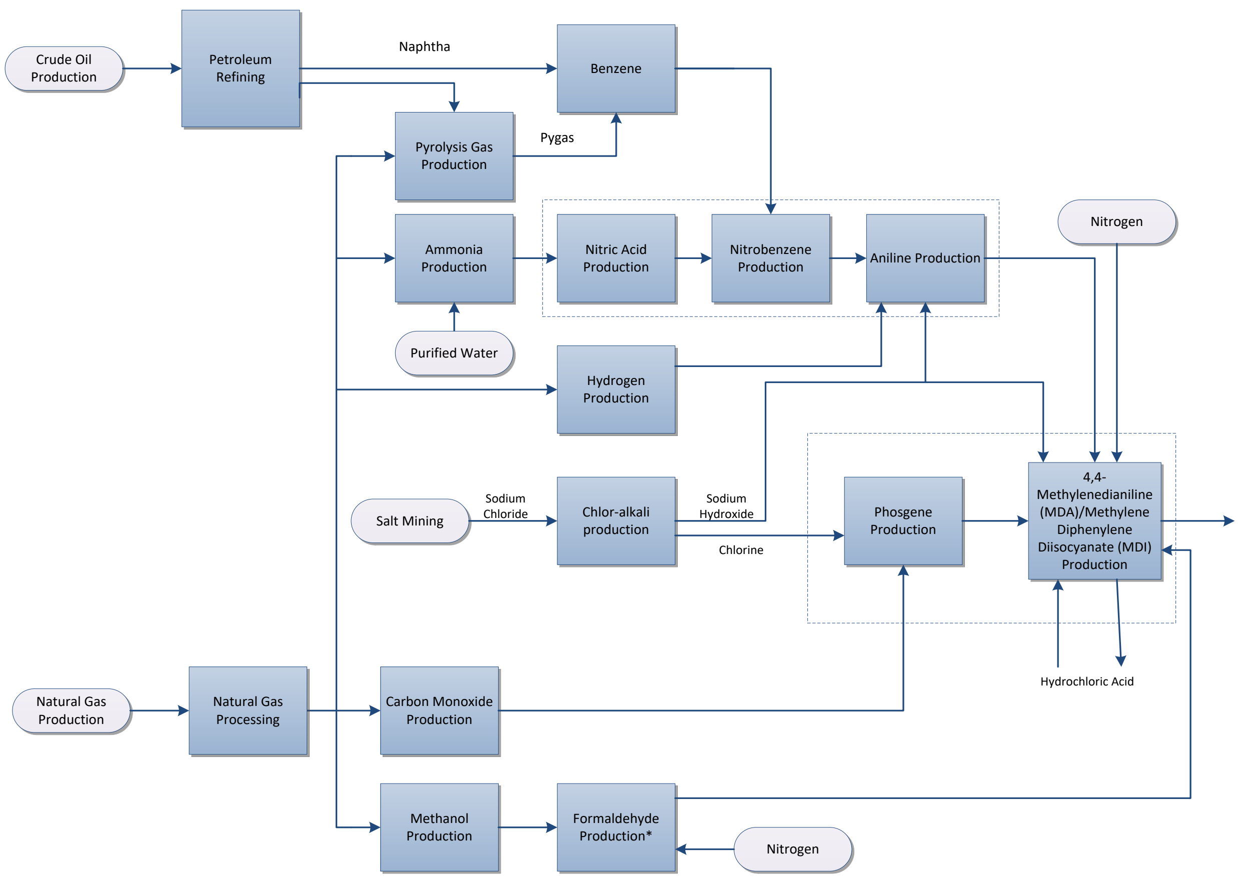

Figure 2. Flow diagram for the Production of Methylene Diphenyl Diisocyanate (MDI).

* Nitrogen and sodium chloride data are from ecoinvent and are adapted to U.S. conditions.

4 Cradle-to-Gate Life Cycle Analysis of Olefins. Franklin Associates. Submitted to the Plastics Division of the American Chemistry Council. April, 2020.

5 Cradle-to-Gate Life Cycle Analysis of Polyvinyl Chloride (PVC) Resin. Franklin Associates. Submitted to the Plastics Division of the American Chemistry Council. December, 2021.

Technological Scope

The overall technology is similar in all plants of this analysis for producing MDI. Methylene diphenyl diisocyanate is manufactured by first producing intermediate products; diamines (MDA) and phosgene. Diamines are produced from aniline and formaldehyde reactions and phosgene is produced from carbon monoxide and chlorine gases. The intermediate products are then reacted to form a mixture of several MDI isomers. Purification of crude MDI is the final step in MDI manufacture.

Temporal and Geographic Scope

To assess the quality of the data collected for MDI, the collection method, technology, industry representation, time period, and geography were considered. The data collection methods for MDI include direct measurements, information provided by purchasing and utility records, and estimates. Data submitted for MDI represent the years 2015 and 2017 and production in U.S.

For the MDI primary data, companies were requested to provide data for the year 2015, the most recent full year of MDI production prior to the project initiation date. Companies providing data were given the option to collect data from the year preceding or following 2015 if either year would reflect more typical production conditions. Three companies provided data for the year 2015, and one company provided data for the year 2017. After reviewing individual company data in comparison to the average, each manufacturer verified data from 2015 and 2017 was representative of an average year for MDI production at their company.

The geographic scope of the analysis is the manufacture of MDI in North America. All MDI data collected were from plants in the United States and some input materials were modeled using North American databases such as the U.S. LCI database and Franklin Associates' private database, as well as ecoinvent. All datasets from ecoinvent were adapted to U.S. conditions to the extent possible (e.g., by using U.S. average grid electricity to model production of process electricity reported in the European data sets). The U.S. electricity grid from 2016 was taken from information in Emissions & Generation Resource Integrated Database (eGRID) 2016 database.

Exclusions from the Scope

The following are not included in the study:

- **Miscellaneous materials and additives.** Selected materials such as catalysts, pigments, ancillary materials, or other additives which total less than one percent by weight of the net process inputs are typically not included in assessments. Omitting miscellaneous materials and additives keeps the scope of the study focused. It is possible that production of some substances used in small amounts may be energy and resource intensive or may release toxic emissions; however, the impacts would have to be very large in proportion to their mass in order to significantly affect overall results and conclusions. For this study, no use of resource-intensive or high-toxicity chemicals or additives was identified. Therefore, the results for MDI production are not expected to be understated by any significant amount due to substances that may be used in small amounts.

- **Capital equipment, facilities, and infrastructure.** The energy and wastes associated with the manufacture of buildings, roads, pipelines, motor vehicles, industrial machinery, etc. are not included. The energy and emissions associated with production of capital equipment, facilities, and infrastructure generally become negligible when averaged over the total output of product or service provided over their useful lifetimes.
- **Space conditioning.** The fuels and power consumed to heat, cool, and light manufacturing establishments are omitted from the calculations when possible. For manufacturing plants that carry out thermal processing or otherwise consume large amounts of energy, space conditioning energy is quite low compared to process energy. The data collection forms developed for this project specifically requested that the data provider either exclude energy use for space conditioning or indicate if the reported energy requirements included space conditioning. Energy use for space conditioning, lighting, and other overhead activities is not expected to make a significant contribution to total energy use for the MDI system.
- **Support personnel requirements**. The energy and wastes associated with research and development, sales, and administrative personnel or related activities have not been included in this study. Similar to space conditioning, energy requirements and related emissions are assumed to be quite small for support personnel activities.

INVENTORY AND IMPACT ASSESSMENT RESULTS CATEGORIES

The full inventory of emissions generated in an LCA study is lengthy and diverse, making it difficult to interpret emissions profiles in a concise and meaningful manner. LCIAs helps to interpret of the emissions inventory. LCIA is defined in ISO 14044 Section 3.4 as the "phase of life cycle assessment aimed at understanding and evaluating the magnitude and significance of the potential environmental impacts for a product system throughout the life cycle of the product." In the LCIA phase, the inventory of emissions is first classified into categories in which the emissions may contribute to impacts on human health or the environment. Within each impact category, the emissions are then normalized to a common reporting basis, using characterization factors that express the impact of each substance relative to a reference substance.

The LCI and LCIA results categories and methods applied in this study are displayed in Table 1. This study addresses global, regional, and local impact categories. For most of the impact categories examined, the TRACI 2.1 method, developed by the United States Environmental Protection Agency (EPA) specific to U.S. conditions and updated in 2012, is employed.[6] For the category of Global Warming Potential (GWP), contributing elementary flows are characterized using factors reported by the Intergovernmental Panel on Climate Change

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6 Bare, J. C. Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI), Version 2.1 - User's Manual; EPA/600/R-12/554 2012.

(IPCC) in 2013 with a 100 year time horizon.[7] In addition, the following LCI results are included in the results reported in the analysis:

- Energy demand: this method is a cumulative inventory of all forms of energy used for processing energy, transportation energy, and feedstock energy. This analysis reports both total energy demand and non-renewable energy demand. Renewable and non-renewable energy demand are reported separately to assess consumption of fuel resources that can be depleted, while total energy demand is used as an indicator of overall consumption of resources with energy value. Energy is also categorized by individual fuel types, as well as by process/fuel vs. feedstock energy.
- Total solid waste is assessed as a sum of the inventory values associated with this category. This category is also broken into hazardous and non-hazardous wastes and their end-of-life (e.g., incineration, waste-to-energy, or landfill).
- Water consumption is assessed as a sum of the inventory values associated with this category and does not include any assessment of water scarcity issues.

[7] IPCC, 2013: *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013.

Table 1. Summary of LCI/LCIA Impact Categories

	Impact/Inventory Category	Description	Unit	LCIA/LCI Methodology
LCI Categories	**Total energy demand**	Measures the total energy from point of extraction; results include both renewable and non-renewable energy sources.	Million (MM) Btu and megajoule (MJ)	Cumulative energy inventory
	Non-renewable energy demand	Measures the fossil and nuclear energy from point of extraction.	MM Btu and MJ	Cumulative energy inventory
	Renewable energy demand	Measures the hydropower, solar, wind, and other renewables, including landfill gas use.	MM Btu and MJ	Cumulative energy inventory
	Solid waste by weight	Measures quantity of fuel and process waste to a specific fate (e.g., landfill, waste-to-energy (WTE)) for final disposal on a mass basis	Lb and kg	Cumulative solid waste inventory
	Water consumption	Freshwater withdrawals which are evaporated, incorporated into products and waste, transferred to different watersheds, or disposed into the land or sea after usage	Gallons and Liters	Cumulative water consumption inventory
LCIA Categories	**Global warming potential**	Represents the heat trapping capacity of the greenhouse gases. Important emissions: CO_2 fossil, CH_4, N_2O	Lb CO_2 equivalents (eq) and kg CO_2 equivalents (eq)	IPCC (2013) GWP 100a
	Acidification potential	Quantifies the acidifying effect of substances on their environment. Important emissions: SO_2, NO_x, NH_3, HCl, HF, H_2S	Lb SO_2 eq and kg SO_2 eq	TRACI v2.1
	Eutrophication potential	Assesses impacts from excessive load of macro-nutrients to the environment. Important emissions: NH_3, NO_x, chemical oxygen demand (COD) and biochemical oxygen demand (BOD), N and P compounds	Lb N eq and kg N eq	TRACI v2.1
	Ozone depletion potential	Measures stratospheric ozone depletion. Important emissions: chlorofluorocarbon (CFC) compounds and halons	Lb CFC-11 eq and kg CFC-11 eq	TRACI v2.1
	Smog formation potential	Determines the formation of reactive substances (e.g. tropospheric ozone) that cause harm to human health and vegetation. Important emissions: NO_x, benzene, toluene, ethylbenzene, xylene (BTEX), non-methane volatile organic compound (NMVOC), CH_4, C_2H_6, C_4H_{10}, C_3H_8, C_6H_{14}, acetylene, Et-OH, formaldehyde	Lb kg O_3 eq and kg O_3 eq	TRACI v2.1

DATA SOURCES

The purpose of this study is to develop a life cycle profile for MDI using the most recent data available for each process. A weighted average was calculated for the MDI data collected for this analysis from the years 2015 and 2017. Data for the manufacture of aniline was collected from two plants and two aniline producers to calculate the weighted average. One nitrobenzene/aniline producer provided data from the year 2015 and the other producer from the year 2016. To protect the confidentiality of each company providing nitrobenzene/aniline data, the dataset shown in the appendix is aggregated with nitric acid data. The pygas data was also calculated from an average of primary datasets for 2015. Secondary data was researched in 2017 for crude oil extraction and refining and natural gas production and processing. All included processes are shown in Figure 2.

LCI data for the production of MDI were collected from four producers (four plants) in North America – all in the United States. All companies provided data from the years 2015 or 2017. A weighted average was calculated from the data collected and used to develop the LCA model. Over 2.8 billion pounds of pure and polymeric MDI were produced in the U.S. in 2015[8]. The captured MDI production amount is approximately 90 percent of the MDI production in the U.S. in 2015. In 2018, of the total U.S. MDI demand, 14 percent was for pure MDI and 86 percent was for polymeric MDI[9]. Hydrochloric acid is a coproduct of MDI production, and for the results discussed in this report, a mass basis was used to allocate all inputs and outputs between the coproducts (See Coproduct Allocation for more information).

LCI data for the production of olefins were collected from three producers (ten plants) in North America – all in the United States. All companies provided data for the year 2015. A weighted average was calculated from the data collected and used to develop the LCA model. Pygas is a coproduct of olefins production, and a mass basis was used to allocate the environmental burdens among these coproducts.

DATA QUALITY ASSESSMENT

ISO 14044:2006 lists a number of data quality requirements that should be addressed for studies intended for use in public comparative assertions. The data quality goals for this analysis were to use data that are (1) geographically representative for the MDI is based on the locations where material sourcing and production take place, and (2) representative of current industry practices in these regions. As described in the previous section, four companies each provided current, geographically representative data for all primary MDI data collected for this LCA.

[8] Published by Lucía Fernández, and Jul 6. "MDI Production U.S. 2019." Statista, 6 July 2021, www.statista.com/statistics/974805/us-methylene-diphenyl-diisocyanate-production-volume/.

[9] Calculated by Franklin Associates from the website, https://www.americanchemistry.com/industry-groups/diisocyanates-dii/fast-facts-and-frequently-asked-questions. Original information taken from **2018 End-Use Market Survey on the Polyurethanes Industry,** Center for the Polyurethanes Industry, ACC.

The incoming material and fuel datasets for MDI manufacture were either updated using geographical and technologically relevant data from government or privately available statistics/studies within the US or drawn from either The Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies (GREET) Model or ecoinvent[10,11]. Datasets from ecoinvent were adapted to U.S. conditions to the extent possible (e.g., by using U.S. average grid electricity to model production of process electricity reported in the European data sets). The nitrogen input for MDI is the only process from secondary sources. The data sets used were the most current and most geographically and technologically relevant data sets available during the data collection phase of the project.

Consistency, Completeness, Precision: Data evaluation procedures and criteria were applied consistently to all primary data provided by the participating producers for all data collected. All primary data obtained specifically for this study were considered the most representative available for the systems studied. Data sets were reviewed for completeness and material balances, and follow-up was conducted as needed to resolve any questions about the input and output flows, process technology, etc. The aggregated averaged datasets were also reviewed by the providing companies as compared to the provided dataset. Companies were requested to review whether their data were complete and to comment about their or the average dataset.

Representativeness: MDI manufactured in North America is representative of the majority of MDI producers within the United States. The four companies provided data from their facilities using technology ranging from average to state-of-the-art. The captured MDI production amount is approximately 90 percent of the MDI production in the U.S. in 2015. After reviewing individual company data in comparison to the average, each manufacturer verified the average data from 2015/2017 was a representative for MDI production in North America.

The LCI data for the pygas system is shown in the appendix of a separate report, *Cradle-to-Gate Life Cycle Analysis of Olefins*[12]. Primary data were collected from propylene manufacturers from the year 2015. Companies providing data were given the option to collect data from the year preceding or following 2015 if either year would reflect more typical production conditions. After reviewing individual company data in comparison to the average, each manufacturer verified data from 2015 was a representative year for olefins production in North America.

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[10] Argonne National Laboratory, Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies Model; Energy Systems Division, https://greet.es.anl.gov/, 2017, accessed August 1, 2018.

[11] Wernet, G., Bauer, C., Steubing, B., Reinhard, J., Moreno-Ruiz, E., and Weidema, B., 2016. The ecoinvent database version 3 (part I): overview and methodology. The International Journal of Life Cycle Assessment, [online] 21(9), pp.1218–1230. Available at: <http://link.springer.com/10.1007/s11367-016-1087-8> [Accessed Sept, 2018].

[12] Cradle-to-Gate Life Cycle Analysis of Olefins. Franklin Associates. Submitted to the Plastics Division of the American Chemistry Council. April, 2020.

LCI data from the sources of input materials specific to each company providing data was not available for this analysis. Average U.S. statistics were used for refined petroleum products and processed natural gas to develop the average pygas unit process data. As impacts from crude oil and natural gas may vary depending on transportation requirements some variability in data and impact on LCA results should be expected.

The average MDI unit process data was based on the best available data at the time the study was conducted. As in all LCA studies, the ability to develop a representative average is determined by the number of companies willing to participate. Data from this analysis was used to develop the most representative average for MDI production in the 2015/2017 time frame as was possible.

Reproducibility: To maximize transparency and reproducibility, the report identifies specific data sources, assumptions, and approaches used in the analysis to the extent possible; however, reproducibility of study results is limited to some extent by the need to protect certain data sets that were judged to be high quality and representative data sets for modeling purposes but could not be shown due to confidentiality.

Order of Magnitude: In some cases, emissions data were reported by fewer than three companies. To indicate known emissions while protecting the confidentiality of individual company responses, the emission is reported only as an order of magnitude. An order of magnitude of a number is the smallest power of 10 used to represent that number. For example, if the average of two data points for a particular emission is 2.5E-4, the amount would be shown as 1.0E-4 to ensure confidentiality of the data providers but allow the impact assessment tool to include a close estimate of the amount within any pertinent impact categories. When order of magnitude is used in the LCI data shown in the Appendix of this report, it is clearly noted by an asterisk next to the amount.

Uncertainty: Uncertainty issues and uncertainty thresholds applied in interpreting study results are described in the following section.

DATA ACCURACY AND UNCERTAINTY

In LCA studies with thousands of numeric data points used in the calculations, the accuracy of the data and how it affects conclusions is truly a complex subject, and one that does not lend itself to standard error analysis techniques. Techniques such as Monte Carlo analysis can be used to assess study uncertainty, but the greatest challenge is the lack of uncertainty data or probability distributions for key parameters, which are often only available as single point estimates. However, steps are taken to ensure the reliability of data and results, as previously described.

The accuracy of the environmental results depends on the accuracy of the numbers that are combined to arrive at that conclusion. For some processes, the data sets are based on actual plant data reported by plant personnel, while other data sets may be based on engineering estimates or secondary data sources. Primary data collected from actual facilities are considered the best available data for representing industry operations. In this study, primary data were used to model the MDI, MDA, aniline, chlor-alkali, and steam cracking of the olefins. All data received were carefully evaluated before compiling the production-weighted average data sets used to generate results. Supporting background data were drawn from credible, widely used databases including the US LCI database, GREET, and ecoinvent.

A report from the International Energy Agency (IEA) that at this time has not been subject to validation through a scientific peer review suggests that unwanted methane emissions during oil and gas extraction, processing and transport are higher than assumed in current LCA databases. The IEA has created a methane tracker website reporting these additional methane emissions[13]. As a base case, the present U.S. cradle-to-gate reports use oil and gas extraction information published by the National Energy Technology Laboratory (NETL), Argonne National Laboratory (ANL), and the Energy Information Administration (EIA), which currently do not include these increased methane losses.

METHOD

The LCA has been conducted following internationally accepted standards for LCA as outlined in the ISO 14040 and 14044 standards, which provide guidance and requirements for conducting LCA studies. However, for some specific aspects of LCA, the ISO standards have some flexibility and allow for choices to be made. The following sections describe the approach to each issue used in this study. Many of these issues are specific to the olefins produced at the steam crackers.

Raw Materials Use for Internal Energy in Steam Crackers

Some of the raw material inputs to the steam cracker create gases that are combusted to provide energy for the steam cracker, decreasing the amount of purchased energy required for the reaction. Data providers listed this energy as fuel gas or off-gas and, in many cases, supplied the heating value of this gas. Using this information, Franklin Associates calculated the amount of raw material combusted within the steam cracker to produce this utilized energy source.

This internally-created energy is included in the analysis by including the production of the raw materials combusted to produce the energy as well as the energy amount attributed to the combustion of those raw materials. Unlike the raw materials that become part of the product output mass, no material feedstock energy is assigned to the raw materials inputs that are combusted within the process.

Coproduct Allocation

An important feature of life cycle inventories is that the quantification of inputs and outputs are related to a specific amount of useful output from a process. However, it is sometimes difficult or impossible to identify which inputs and outputs are associated with individual

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[13] IEA (2020), Methane Tracker 2020, IEA, Paris https://www.iea.org/reports/methane-tracker-2020

products of interest resulting from a single process (or process sequence) that produces multiple useful products. The practice of allocating inputs and outputs among multiple products from a process is often referred to as coproduct allocation.

Environmental burdens are allocated among the coproducts when raw materials and emissions cannot be directly attributed to one of several product outputs from a system. It has long been recognized that the practice of allocating the environmental burdens among the coproducts is less desirable than being able to identify which inputs lead to specific outputs. In this study, co-product allocations are necessary because of multiple useful outputs from the "upstream" chemical process involved in producing MDI, chlor-alkali, and olefins.

Franklin Associates follows the guidelines for allocating the environmental burdens among the coproducts as shown in the ISO 14044:2006 standard on life cycle assessment requirements and guidelines[14]. In this standard, the preferred hierarchy for handling allocation is (1) avoid allocation where possible, (2) allocate flows based on direct physical relationships to product outputs, (3) use some other relationship between elementary flows and product output. No single allocation method is suitable for every scenario. As described in ISO 14044 section 4.3.4.2, when allocation cannot be avoided, the preferred partitioning approach should reflect the underlying physical relationships between the different products or functions.

Rationale for Choice of Allocation Method for MDI/HCl Coproducts in North America

In the case of North American isocyanate (MDI and TDI) production, Franklin Associates used a mass allocation for the original isocyanates/HCl coproduct allocation as discussed in the 2011 report. For this MDI report, results using mass allocation for MDI/HCl are provided in the results section. Recently, the European Diisocyanate and Polyol Producers Association (ISOPA) released a new dataset for MDI and TDI for European manufacturers that uses a combined elemental and mass allocation[15]. At the release of this report in July 2022 , the ISOPA report is final and uses this new method. A sensitivity analysis was provided in the ISOPA report showing results for both mass and the combined allocation methods. Thus, to be consistent, a sensitivity analysis providing both allocation methods is presented in this North American report. The results using a mass allocation allow the reader to compare to the original 2011 MDI results; while the results using combined elemental and mass allocation allow the reader to compare the current North American MDI results to the current EU MDI results. The most recent round of discussions on the product environmental footprint of isocyanates have been concluded in Europe and led to mutual acceptance of this allocation method by EU producers of MDI/TDI and ISOPA. Moving forward, the ACC will continue to work in partnership with the producers of MDI/TDI and engage with ISOPA to

[14] International Standards Organization. ISO 14044:2006, Environmental management – Life cycle assessment – Requirements and guidelines.

[15] ISOPA Eco-profile of toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI). April 2021.

discuss any further decisions made by ISOPA in collaboration with the EU government concerning LCA methodologies and approaches to ensure consistency as much as possible.

Material Coproducts

Some processes lend themselves to physical allocation because they have physical parameters that provide a good representation of the environmental burdens of each co-product. Examples of various allocation methods are mass, stoichiometric, elemental, reaction enthalpy, and economic allocation. If system expansion is not possible, simple mass and enthalpy allocation have been chosen as the common forms of allocation in this analysis. However, these allocation methods were not chosen as a default choice but made on a case-by-case basis after due consideration of the chemistry and basis for production.

Material coproducts were created in all the intermediate chemical process steps collected for this analysis, as well as the primary MDI production. The material coproducts from pyrolysis gasoline production for all plants included propylene, ethylene, butadiene, ethane, hydrogen, acetylene, crude benzene, and small amounts of various heavy end products. In the chlor-alkali plant, allocations have been made to focus on which product the inputs or outputs associate within the process. The specifics of the allocations given in the chlor-alkali plants are detailed in the report, *Cradle-to-gate Life Cycle Analysis of Polyvinyl Chloride (PVC) Resin*.[16] The material coproduct from MDI production includes a sizable amount of hydrochloric acid. The results discussed in this report are based on the MDI unit processing using a mass allocation. However, a sensitivity analysis using the elemental and mass allocation has been included. An explanation of this allocation is provided in the sensitivity analysis section.

A portion of the inputs and outputs calculated for the coproducts were removed from the total inputs and outputs, so that the remaining inputs and outputs only represented the main product in each unit process. The ratio of the mass of the coproduct over the total mass output was removed from the total inputs and outputs of the process, and the remaining inputs and outputs are allocated over the material products (Equation 1).

$$[IO] \times \left(1 - \frac{M_{CP}}{M_{Total}}\right) = [IO]_{attributed\ to\ remaining\ \ products} \qquad \text{(Equation 1)}$$

where
IO = Input/Output Matrix to produce all products/coproducts
M_{CP} = Mass of Coproduct
M_{Total} = Mass of all Products and Coproducts

Energy Coproducts Exported from System Boundaries

Some of the unit processes produce energy either as a fuel coproduct or as steam created from the process that is sent to another plant for use. To the extent possible, system

[16] Cradle-to-Gate Life Cycle Analysis of Polyvinyl Chloride (PVC) Resin. Franklin Associates. Submitted to the Plastics Division of the American Chemistry Council. December, 2021.

expansion to avoid allocation was used as the preferred approach in the ISO 14044:2006 standard. Fuels or steam exported from the boundaries of the system would replace purchased fuels for another process outside the system. System expansion credits were given for avoiding the energy-equivalent quantity of fuel production and combustion displaced by the exported coproduct energy.

Elemental/Mass Coproduct Allocation in Sensitivity Analysis

In 2021, ISOPA released their updated TDI/MDI Ecoprofile, which used an allocation method combining elemental and mass allocation. For this analysis, the elemental + mass allocation method has been applied to both the current MDI and original MDI data in a sensitivity analysis. For this allocation, the following allocations are given using the elemental + mass allocation:

- The chlorine input is fully allocated to the production of HCl.
- The inputs used to create MDA and Phosgene only are allocated fully to MDI.
- Chlorine or Hydrochloric acid atmospheric emissions or waterborne releases are fully allocated to the HCl.
- All other inputs/outputs have been given mass allocation.

Electricity Grid Fuel Profile

Electricity production and distribution systems in North America are interlinked. Users of electricity, in general, cannot specify the fuels used to produce their share of the electric power grid. Data for this analysis was collected from plants in the United States. The U.S. average fuel consumption by electrical utilities was used for the electricity within this analysis. This electricity data set uses the Emissions & Generation Resource Integrated Database (eGRID) 2016 database[17].

Electricity generated on-site at a manufacturing facility is represented in the process data by the fuels used to produce it. If a portion of on-site generated electricity is sold to the electricity grid, credits for sold on-site electricity are accounted for in the calculations for the fuel mix.

Electricity/Heat Cogeneration

Cogeneration is the use of steam for generation of both electricity and heat. The most common configuration is to generate high temperature steam in a cogeneration boiler and use that steam to generate electricity. The steam exiting the electricity turbines is then used as a process heat source for other operations. Significant energy savings occur because in a conventional operation, the steam exiting the electricity generation process is condensed, and the heat is dissipated to the environment.

[17] Online database found at: https://www.epa.gov/energy/emissions-generation-resource-integrated-database-egrid

For LCI purposes, the fuel consumed and the emissions generated by the cogeneration boiler need to be allocated to the two energy-consuming processes: electricity generation and subsequent process steam. An energy basis was used for allocation in this analysis.

In order to allocate fuel consumption and environmental emissions to both electricity and steam generation, the share of the two forms of energy (electrical and thermal) produced must be correlated to the quantity of fuel consumed by the boiler. Data on the quantity of fuel consumed and the associated environmental emissions from the combustion of the fuel, the amount of electricity generated, and the thermal output of the steam exiting electricity generation must be known in order to allocate fuel consumption and environmental emissions accordingly. These three types of data are discussed below.

1. **Fuels consumed and emissions generated by the boiler:** The majority of data providers for this study reported natural gas as the fuel used for cogeneration. According to 2016 industry statistics, natural gas accounted for 75 percent of industrial cogeneration, while coal and biomass accounted for the largest portion of the remaining fuels used[18].

2. **Kilowatt-Hours of Electricity Generated:** In this analysis, the data providers reported the kilowatt-hours of electricity from cogeneration. The Btu of fuel required for this electricity generation was calculated by multiplying the kilowatt-hours of electricity by 6,826 Btu/kWh (which utilizes a thermal to electrical conversion efficiency of 50 percent). This Btu value was then divided by the Btu value of fuel consumed in the cogeneration boiler to determine the electricity allocation factor.

   The 50 percent conversion efficiency was an estimate after reviewing EIA fuel consumption and electricity net generation data from cogeneration plants in 2016.[19] The straight average conversion efficiency for 2016 for electricity production in cogeneration plants within this database is a little more than 55 percent; however, the range of efficiency calculated per individual cogeneration plant was 23% to 87%. The 50 percent estimate of conversion efficiency was used previously in the 2011 database and so was estimated for continued use within this analysis, due to the variability of the individual cogeneration plants. Unit process data for cogeneration of electricity is provided by kWh, so that a change of efficiency could easily be applied during modeling.

3. **Thermal Output of Steam Exiting Electricity Generation:** In this analysis, the data providers stated the pounds and pressure of steam from cogeneration. The thermal output (in Btu) of this steam was calculated from

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[18] U.S. Department of Energy. *Combined Heat and Power (CHP) Technical Potential in the United States.* March 2016.
[19] U.S. Department of Energy, The Energy Information Administration (EIA). *EIA-923 Monthly Generation and Fuel Consumption Time Series File, 2016 Final Revision*

enthalpy tables (in most cases steam ranged from 1,000 to 1,200 Btu/lb). An efficiency of 80 percent was used for the industrial boiler to calculate the amount of fuel used. This Btu value was then divided by the Btu value of fuel consumed in the cogeneration boiler to determine the steam allocation factor. The 80 percent efficiency used is common for a conventional natural gas boiler, which should not change when considering the steam portion of the cogeneration system. Pounds of steam, temperature and pressure were provided by participating plants. Steam tables were used to calculate energy amounts, which was divided by the efficiency and converted to natural gas amounts in cubic feet.

LIFE CYCLE INVENTORY AND IMPACT ASSESSMENT RESULTS

This section presents baseline results for the following LCI and LCIA results for both 1,000 pounds and 1,000 kilograms of MDI:

Life cycle inventory results:

- Cumulative energy demand
- Non-renewable energy demand
- Renewable energy demand
- Total energy by fuel type
- Solid waste by weight
- Water consumption

Life cycle impact assessment results:

- Global warming potential
- Acidification potential
- Eutrophication potential
- Ozone depletion potential
- Smog formation potential

Throughout the results sections, the tables and figures break out system results into the following unit processes, for MDI:

- Cradle-to-incoming materials – includes the raw materials through the production of carbon monoxide, aniline, formaldehyde, chlorine, and sodium hydroxide (inputs to the phosgene/MDA/MDI processes)
- MDI production – is the gate-to-gate unit process and includes the production of fuels & nitrogen used in the processes to create phosgene/MDA/MDI.

Tables and figures are provided for MDI in each inventory and impact category section in this report. The phrases “cradle-to- “and “system” are defined as including all of the raw and intermediate chemicals required for the production of the chemical stated in the term (e.g., cradle-to-MDI and MDI system are interchangeable). The phrase “gate-to-gate” is defined as including only the onsite process/fuels/nitrogen for the unit process.

ENERGY DEMAND

Cumulative Energy Demand

Cumulative energy demand results include all renewable and non-renewable energy sources used for process and transportation energy, as well as material feedstock energy. Process energy includes direct use of fuels, including the use of fossil fuels, hydropower, nuclear, wind, solar, and other energy sources to generate electricity used by processes. Fuel energy is the energy necessary to create and transport the fuels to the processes. The feedstock energy is the energy content of the resources removed from nature and used as material feedstocks for most of the incoming chemicals (e.g., the energy content of oil and gas used as material feedstocks) to the phosgene/MDA/MDI.

The average total energy required to produce MDI is 24.1 million Btu per 1,000 pounds of MDI or 56.0 GJ per 1,000 kilograms of MDI. Table 2 shows total energy demand for the life cycle of MDI production. The phosgene/MDA/MDI production energy has been split out from the energy required for incoming materials. Only 8 percent of the total energy is required to produce the phosgene/MDA/MDI. The remaining 92 percent is used to create the incoming materials and their raw materials.

Table 2. Total Energy Demand for MDI

	Basis: 1,000 pounds		
	Total Energy	**Non-Renewable Energy**	**Renewable Energy**
	MM Btu	***MM Btu***	***MM Btu***
Cradle-to-Incoming Materials	22.1	21.9	0.15
Phosgene/MDA/MDI Production	2.00	1.95	0.050
Total	**24.1**	**23.9**	**0.20**
	Basis: 1,000 kilograms		
	Total Energy	**Non-Renewable Energy**	**Renewable Energy**
	GJ	***GJ***	***GJ***
Cradle-to-Incoming Materials	51.3	51.0	0.36
Phosgene/MDA/MDI Production	4.65	4.53	0.12
Total	**56.0**	**55.5**	**0.47**
	Percentage		
	Total Energy	**Non-Renewable Energy**	**Renewable Energy**
	%	***%***	***%***
Cradle-to-Incoming Materials	91.7%	91.1%	0.6%
Phosgene/MDA/MDI Production	8.3%	8.1%	0.2%
Total	**100%**	**99.2%**	**0.8%**

Non-renewable energy demand includes the use of fossil fuels (petroleum, natural gas, and coal) for process energy, transportation energy, and as material feedstocks (e.g., oil and gas used as feedstocks), as well as use of uranium to generate the share of nuclear energy in the average U.S. kWh. For MDI, 99.2 percent of the total energy comes from non-renewable sources. The renewable energy demand consists of landfill gas used for process energy in pygas production and electricity derived from renewable energy sources (primarily hydropower, as well as wind, solar, and other sources). The renewable energy (0.12 GJ/1000 kg) used at the MDI plant comes solely from nuclear, hydropower and other renewable sources (geothermal, solar, etc.) from electricity production.

The energy representing natural gas and petroleum used as raw material inputs for the production of incoming chemicals used to produce MDI are included in the cradle-to-incoming material amounts in Table 2. The energy inherent in these raw materials are called material feedstock energy. Of the total energy (56.0 GJ) for 1,000 kg of MDI, 36.7 GJ is material feedstock energy. Figure 3 provides the breakdown of the percentage of total energy required for material feedstock energy versus the process and fuel energy amounts needed to produce the MDI. Approximately 66 percent of the total energy is inherent energy in the natural gas and petroleum used as a feedstock to create chemicals such as pyrolysis gasoline, ammonia, and benzene, which in turn are used to create MDI. Of the feedstock sources for MDI, 61 percent come from natural gas, while 39 percent of the feedstock sources come from oil.

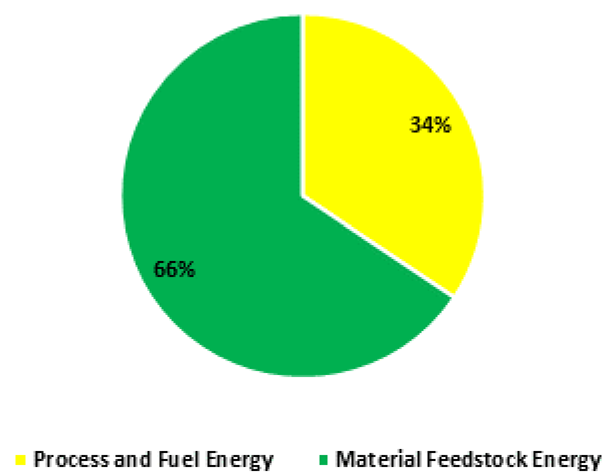

Figure 3. Process/Fuel and Material Feedstock Percentages for MDI

Energy Demand by Fuel Type

The total energy demand by fuel type for MDI is shown in Table 3 and the percentage mix is shown in Figure 4. Natural gas and petroleum together make up 91 percent of the total energy used. As shown in Figure 3, this is partially due to the material feedstock energy used to create the incoming chemicals to MDI. These material feedstock fuels are part of the energy shown in the natural gas and petroleum split out in the following table and figure. The gate-to-gate production energy for phosgene/MDA/MDI in the following table and figure represents the energy required for transportation of raw materials to the plant, the energy required to produce the output, and the production of the fuels and nitrogen needed to manufacture the phosgene/MDA/MDI.

Petroleum-based fuels (e.g., diesel fuel) are the dominant energy source for transportation. Natural gas, coal, and other fuel types, such as hydropower, nuclear and other (geothermal, wind, etc.) are used to generate purchased electricity. Other renewables include a small amount of landfill gas used for process energy in pygas production.

Of the results for MDI production shown in Table 3 and Figure 4, 63 percent of the energy used (35 GJ/56 GJ) is from natural gas. At the MDI plant, 72 percent of the energy used (3.34 GJ/4.65 GJ) comes from natural gas. Of that natural gas used at the MDI plant, 63 percent is combusted on-site, while 35 percent is required to create electricity either through the grid or through a nearby cogeneration plant. Petroleum comprises approximately 28 percent (15.8 GJ/56 GJ) of the fuel types used for the MDI production system. The largest portion of petroleum is used for the production of benzene as a material input. The petroleum for the MDI plant is mostly used to create electricity, with the remainder used to produce the nitrogen used in the process and for transport. The coal use shown is combusted for electricity use. The 2016 U.S. electricity grid is used for this study. In this grid, approximately 30 percent of the electricity production in the US uses coal as a fuel source, while a third of the grid comes from natural gas and 20 percent from uranium. The hydropower, nuclear, and other energy are all used to create electricity, with the exception of a small amount of landfill gas used in the olefins production shown within other renewables.

Table 3. Energy Demand by Fuel Type for MDI

	Total Energy	Natural Gas	Petroleum	Coal	Nuclear	Hydropower	Other Renewable
	Basis: 1,000 pounds						
	MM Btu	*MM Btu*	*MM Btu*	*MM Btu*	*MM Btu*	*MM Btu*	*MM Btu*
Cradle-to-Incoming Materials	22.1	13.6	6.78	0.91	0.61	0.065	0.089
Phosgene/MDA/MDI Production	2.00	1.43	0.021	0.29	0.20	0.021	0.030
Total	**24.1**	**15.0**	**6.80**	**1.20**	**0.81**	**0.086**	**0.12**
	Basis: 1,000 kilograms						
	Total Energy	Natural Gas	Petroleum	Coal	Nuclear	Hydropower	Other Renewable
	GJ	*GJ*	*GJ*	*GJ*	*GJ*	*GJ*	*GJ*
Cradle-to-Incoming Materials	51.3	31.7	15.8	2.12	1.43	0.15	0.21
Phosgene/MDA/MDI Production	4.65	3.34	0.050	0.68	0.46	0.049	0.069
Total	**56.0**	**35.0**	**15.8**	**2.80**	**1.88**	**0.20**	**0.28**
	Percentage of Total						
	Total Energy	Natural Gas	Petroleum	Coal	Nuclear	Hydropower	Other Renewable
	%	*%*	*%*	*%*	*%*	*%*	*%*
Cradle-to-Incoming Materials	91.7%	56.6%	28.2%	3.8%	2.5%	0.27%	0.37%
Phosgene/MDA/MDI Production	8.3%	6.0%	0.1%	1.2%	0.8%	0.09%	0.12%
Total	**100%**	**63%**	**28.3%**	**5.0%**	**3.4%**	**0.36%**	**0.49%**

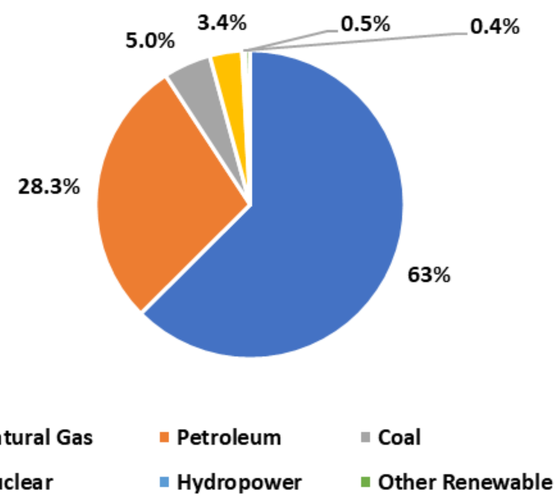

Figure 4. Percentage of Energy Separated by Fuel Type for MDI

SOLID WASTE

Solid waste results include the following types of wastes:

- **Process wastes** that are generated by the various processes from raw material acquisition through production of the olefins (e.g., sludges and residues from chemical reactions and material processing steps)
- **Fuel-related wastes** from the production and combustion of fuels used for process energy and transportation energy (e.g., refinery wastes, coal combustion ash)

No postconsumer wastes of the MDI are included in this analysis as no product is made from the material in the analysis boundaries.

The process solid waste, those wastes produced directly from the production of materials, includes wastes that are incinerated both for disposal and for waste-to-energy, as well as landfilled. Some wastes that are recycled/reused or land applied are not included as solid wastes, and no credit is given. The categories of disposal type have been provided separately where possible. Solid wastes from fuel combustion (e.g., ash) are assumed to be landfilled.

Results for solid waste by weight for the MDI system are shown in Table 4 and Figure 5. The solid wastes have been separated into hazardous and non-hazardous waste categories, as well as by the cradle-to-incoming materials and the MDI plant. Overall, the solid wastes associated with coal extraction and combustion to create electricity make up almost 60 percent of the total solid wastes. The extraction and processing of oil and gas used as a material and as a fuel create over 35 percent of the total solid wastes. A little more than one percent of the total solid waste comes from olefins production (pygas) for use in aniline production

As shown in Figure 5, only 16 percent of the total solid waste is created during the phosgene/MDA/MDI unit process. More than three-quarters of this amount comes from fuels combusted for the electricity used in the plant, while only 2 percent of the gate-to-gate MDI plant amount is process solid waste. The majority of solid waste, 84 percent, comes from the production of incoming materials used to produce phosgene/MDA/MDI. More than 50 percent of the incoming materials solid wastes come from the cradle-to-aniline production with another 25 percent coming from the cradle-to-chlorine production.

Solid wastes are shown separated by hazardous and non-hazardous wastes in Table 4. This separation was done only where primary data was collected, or if a secondary data source was clear that the solid waste was of a hazardous nature. The process solid wastes from oil and natural gas were classified as non-hazardous due to exclusions found in RCRA hazardous wastes regulations or other EPA hazardous wastes regulations. No solid wastes were stated as hazardous in the data sources for oil and gas. Only 1.2 percent of the total solid wastes were considered hazardous wastes. Of that percentage, about half comes from the aniline plant, while a quarter comes from the MDI plant and 22 percent from the olefins plant.

Table 4 also provides a breakout of the total solid wastes by the disposal fate. Of the hazardous waste, 90 percent is incinerated without energy capture, while the remainder is sent to landfill. Focusing specifically on the non-hazardous solid waste produced, 99 percent of the non-hazardous solid waste is landfilled, while much of the remainder is incinerated without energy capture.

Table 4. Total Solid Wastes for MDI

	Basis: 1,000 pounds								
		Hazardous Wastes				Non-Hazardous Wastes			
	Total Solid Waste	Waste-to-Energy	Incineration	Landfill	Hazardous Waste Total	Waste-to-Energy	Incineration	Landfill	Non-Hazardous Waste Total
	lb	*lb*	*lb*	*lb*	*lb*	*lb*	*lb*	*lb*	*lb*
Cradle-to-Incoming Materials	68.2	0	0.75	4.5E-04	0.75	9.9E-05	0.99	66.4	67.4
Phosgene/MDA/MDI Production	13.4	0	0.11	0.10	0.21	0	0	13.2	13.2
Total	**81.6**	**0**	**0.86**	**0.10**	**0.96**	**9.9E-05**	**0.99**	**79.7**	**80.6**
	Basis: 1,000 kilograms								
		Hazardous Wastes				Non-Hazardous Wastes			
	Total Solid Waste	Waste-to-Energy	Incineration	Landfill	Hazardous Waste Total	Waste-to-Energy	Incineration	Landfill	Non-Hazardous Waste Total
	kg	*kg*	*kg*	*kg*	*kg*	*kg*	*kg*	*kg*	*kg*
Cradle-to-Incoming Materials	68.2	0	0.75	4.5E-04	0.75	9.9E-05	0.99	66.4	67.4
Phosgene/MDA/MDI Production	13.4	0	0.11	0.10	0.21	0	0	13.2	13.2
Total	**81.6**	**0**	**0.86**	**0.10**	**0.96**	**9.9E-05**	**0.99**	**79.7**	**80.6**
	Percentage of Total								
		Hazardous Wastes				Non-Hazardous Wastes			
	Total Solid Waste	Waste-to-Energy	Incineration	Landfill	Hazardous Waste Total	Waste-to-Energy	Incineration	Landfill	Non-Hazardous Waste Total
	%	*%*	*%*	*%*	*%*	*%*	*%*	*%*	*%*
Cradle-to-Incoming Materials	84%	0%	0.92%	0.0%	0.9%	0.0%	1.2%	81%	83%
Phosgene/MDA/MDI Production	16%	0%	0.13%	0.1%	0.3%	0%	0%	16%	16%
Total	**100%**	**0%**	**1.1%**	**0.1%**	**1.2%**	**0.0%**	**1.2%**	**98%**	**98.8%**

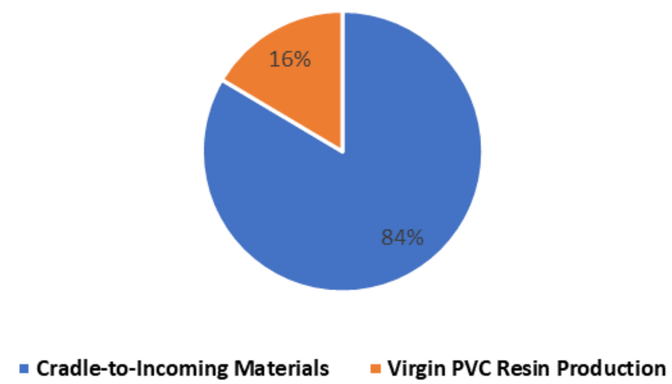

Figure 5. Percentage of Total Solid Wastes for MDI System

WATER CONSUMPTION

Consumptive use of water in this study includes freshwater that is withdrawn from a water source or watershed and not returned to that source. Consumptive water use includes water consumed in chemical reactions, water that is incorporated into a product or waste stream, water that becomes evaporative loss, and water that is discharged to a different watershed or water body than the one from which it was withdrawn. Water consumption results shown for each life cycle stage include process water consumption as well as water consumption associated with production of the electricity and fuels used in that stage. Electricity-related water consumption includes evaporative losses associated with thermal generation of electricity from fossil and nuclear fuels, as well as evaporative losses due to establishment of dams for hydropower.

Water consumption results for MDI production are shown in Table 5 and Figure 6. The greatest portion of consumption of water within the MDI comes from the cradle-to-incoming materials (71 percent). When looking at the individual input materials, about 34 percent of the total is consumed by the cradle-to-gate manufacture of the aniline. Aniline manufacture would include the production of pygas from the olefin cracker, which does include some plants that release water to a different watershed than the initial water source, which is considered consumption in the methodology used. The chlor-alkali production makes up 26 percent of the total water consumption. The MDI average data also includes some plants that release water to a different watershed. The MDI plant water consumption makes up 21 percent of the total water consumed with a large part the remaining 8 percent coming from electricity production off-site.

Throughout all the unit processes, the largest contributor to water consumption is the electricity used, which makes up approximately 29 percent of the total water consumption. This is due to evaporative losses in the use of hydropower.

Table 5. Water Consumption for MDI

	Total Water Consumption		
	Basis: 1,000 Pounds	Basis: 1,000 kilograms	Percentage of Total
	Gallons	*Liters*	*%*
Cradle-to-Incoming Materials	940	7,840	71%
Phosgene/MDA/MDI Production	379	3,165	29%
Total	**1,319**	**11,005**	**100%**

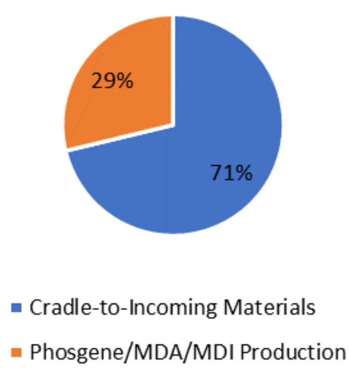

Figure 6. Water Consumption for MDI

GLOBAL WARMING POTENTIAL

The primary atmospheric emissions reported in this analysis that contribute over 99 percent of the total global warming potential for each system are fossil fuel-derived carbon dioxide, methane, and nitrous oxide. Other contributors include some HCFCs and CFCs, but these contribute less than 1 percent of the total shown. Greenhouse gas emissions are mainly from combustion. In the primary data collected for olefins, chlor-alkali, aniline and MDI, combustion emissions from flare or another type of emissions control have been included as process emissions and so their totals may be overstated by small amounts due to the inclusion of combustion of fuel used during the use of the emissions control. Data providers were asked to estimate percentages of greenhouse gases from flare from that of the combustion of fuels.

The 100-year global warming potential (GWP) factors for each of these substances as reported in the Intergovernmental Panel on Climate Change (IPCC) 2013[20] are: fossil carbon dioxide 1, fossil methane 28, and nitrous oxide 265. The GWP factor for a substance represents the relative global warming contribution of a pound of that substance compared to a pound of carbon dioxide. The weights of each greenhouse gas are multiplied by its GWP factor to arrive at the total GWP results. Although normally GWP results are closely related to the energy results, the feedstock energy is not associated with GWP due to the sequestration of the feedstock material within the plastic. It is the potential energy associated with the feedstock material, which is not combusted to create greenhouse gases.

In Table 6 and Figure 7, the life cycle GWP results for the MDI system are displayed. Of the total, 85 percent of the GWP are attributed to emissions from the incoming materials to the phosgene/MDA/MDI unit process, with the remaining associated with said unit process. The largest amount (approximately 40 percent) of the GWP is created by both industrial and utility boiler emissions created throughout the life cycle of MDI. Considering the GWP from incoming materials to MDI, the production of aniline (cradle-to-aniline) accounts for 46 percent of the total GWP. Of the total GWP, 16 percent of the total GWP are released during the production of carbon monoxide, with another 16 percent associated with the production of Chlorine.

Of the total GWP, 15 percent is associated with the phosgene/MDA/MDI unit process. Two thirds of the greenhouse gases for this unit process are released at the MDI plants; most of this is due to the use of a thermal oxidizer and/or flare, which are considered a mix of process and fuel-based emissions. Most of the remaining GWP for this unit process come from the production of electricity used at the plants.

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20 IPCC, 2013: *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013.

Table 6. Global Warming Potential for MDI

	Global Warming Potential		
	Basis: 1,000 Pounds	Basis: 1,000 kilograms	Percentage of Total
	lb CO2 eq	*kg CO2 eq*	*%*
Cradle-to-Incoming Materials	1,817	1,817	85%
Phosgene/MDA/MDI Production	315	315	15%
Total	**2,131**	**2,131**	**100%**

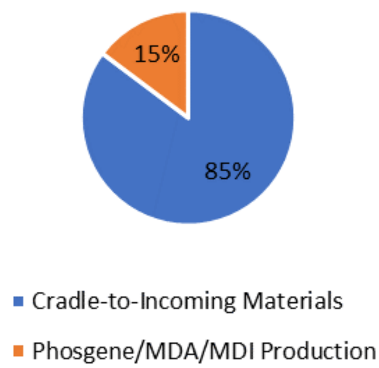

Figure 7. Global Warming Potential for MDI

ACIDIFICATION POTENTIAL

Acidification assesses the potential of emissions to contribute to the formation and deposit of acid rain on soil and water, which can cause serious harm to plant and animal life as well as damage to infrastructure. Acidification potential (AP) modeling in TRACI incorporates the results of an atmospheric chemistry and transport model, developed by the U.S. National Acid Precipitation Assessment Program (NAPAP), to estimate total North American terrestrial deposition due to atmospheric emissions of NO_x and SO_2, as a function of the emissions location.[21,22]

Acidification impacts are typically dominated by fossil fuel combustion emissions, particularly sulfur dioxide (SO_2) and nitrogen oxides (NO_x). Emissions from combustion of fossil fuels, especially coal, to generate grid electricity is a significant contributor to acidification impacts for the system at 45 percent of the total AP. Also, emissions from the

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21 Bare JC, Norris GA, Pennington DW, McKone T. (2003). TRACI: The Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts, *Journal of Industrial Ecology,* **6**(3–4): 49–78. Available at URL: http://mitpress.mit.edu/journals/pdf/jiec_6_3_49_0.pdf.

22 Bare JC. (2002). Developing a consistent decision-making framework by using the US EPA's TRACI, AICHE. Available at URL: http://www.epa.gov/nrmrl/std/sab/traci/aiche2002paper.pdf.

extraction and processing of natural gas impact the AP category at almost 30 percent of the total AP.

Table 7 shows total acidification potential results for the MDI system. Results are shown graphically in Figure 8. In the AP category, 14 percent of the AP is coming from MDI production and about 86 percent comes from the raw and intermediate material unit processes. Of the total AP, a little more than 50 percent is coming from the cradle-to-aniline input. As stated previously, much of this comes from the natural gas extraction/processing and the combustion of fuels in the industrial and utility boilers. The chlorine production makes up 17 percent of the total AP amount, with the other incoming chemicals each accounting for lesser amounts of the total AP.

Looking specifically at the phosgene/MDA/MDI, which is 14 percent of the total AP, only 0.1 percent of the total AP comes directly from the associated process emissions of the MDI unit process. The greatest part of the 14 percent AP shown in Table 7 for MDI production comes from the utility boilers used to create electricity, with smaller amounts from the production of nitrogen and the on-site industrial boilers.

Table 7. Acidification Potential for MDI

	Acidification Potential		
	Basis: 1,000 Pounds	Basis: 1,000 kilograms	Percentage of Total
	lb SO2 eq	*kg SO2 eq*	*%*
Cradle-to-Incoming Materials	5.39	5.39	86%
Phosgene/MDA/MDI Production	0.88	0.88	14%
Total	**6.27**	**6.27**	**100%**

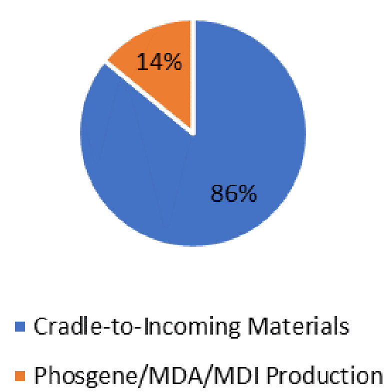

Figure 8. Acidification Potential for MDI

EUTROPHICATION POTENTIAL

Eutrophication occurs when excess nutrients (nitrates, phosphates) are introduced to surface water causing the rapid growth of aquatic plants. Excess releases of these substances may provide undesired effects on the waterways.[23] The TRACI characterization factors for eutrophication are the product of a nutrient factor and a transport factor.[24] The nutrient factor is based on the amount of plant growth caused by each pollutant, while the transport factor accounts for the probability that the pollutant will reach a body of water. Atmospheric emissions of nitrogen oxides (NO_x) as well as waterborne emissions of nitrogen, phosphorus, ammonia, biochemical oxygen demand (BOD), and chemical oxygen demand (COD) are the main contributors to eutrophication impacts.

Eutrophication potential (EP) results for MDI are shown in Table 8 and illustrated in Figure 9. The largest portion, 95 percent, of the EP results come from the incoming materials to the phosgene/MDA/MDI production. The cradle-to-aniline extraction comprises almost 80 percent of the total EP amount. This is due to 1) process emissions released in the manufacture of aniline and from many of the intermediate chemicals created to produce aniline, 2) fuel emissions from combustion of fuels in both utility and industrial boilers, and 3) emissions from the extraction of natural gas used for materials and fuels. The largest portion of this cradle-to-aniline EP amount comes from nitrate compounds and nitrogen oxides released from the nitric acid/nitrobenzene/aniline processes.

The emissions from the phosgene/MDA/MDI unit process comprise 5 percent of the total EP impact results. Less than 0.5 percent of the total EP impact comes from process emissions released at the MDI plant. When considering only the 5 percent associated with the Phosgene/MDA/MDI shown in Table 8, the process itself generates only approximately 5 percent of the 0.26 lb N_{eq}. Half of the remaining percentage represents the combustion of fuels for electricity and half represents the combustion of natural gas in boilers.

Table 8. Eutrophication Potential for MDI

	Eutrophication Potential		
	Basis: 1,000 Pounds	**Basis: 1,000 kilograms**	**Percentage of Total**
	lb N eq	***kg N eq***	***%***
Cradle-to-Incoming Materials	0.45	0.45	95%
Phosgene/MDA/MDI Production	0.026	0.026	5%
Total	**0.48**	**0.48**	**100%**

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23 Bare, J. C. Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI), Version 2.1 - User's Manual; EPA/600/R-12/554 2012.

24 Bare JC, Norris GA, Pennington DW, McKone T. (2003). TRACI: The Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts, *Journal of Industrial Ecology,* **6**(3–4): 49–78. Available at URL: http://mitpress.mit.edu/journals/pdf/jiec_6_3_49_0.pdf.

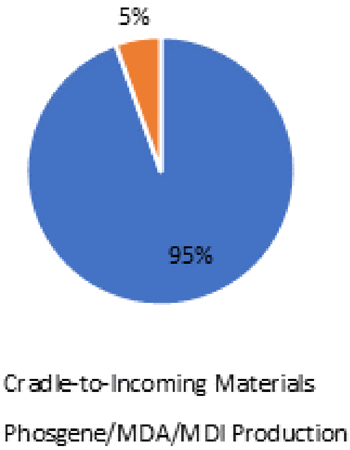

Figure 9. Eutrophication Potential for MDI

OZONE DEPLETION POTENTIAL

Stratospheric ozone depletion (ODP) is the reduction of the protective ozone within the stratosphere caused by emissions of ozone-depleting substance (e.g., CFCs and halons). The ozone depletion impact category characterizes the potential to destroy ozone based on a chemical's reactivity and lifetime. Effects related to ozone depletion can include skin cancer, cataracts, material damage, immune system suppression, crop damage, and other plant and animal effects. For the MDI system, the main sources of emissions contributing to ODP are minute amounts of tetrachloromethane, HCFCs, and halons are emitted during the extraction of petroleum, which is used as fuel and material in the production of benzene and olefins.

Table 9 shows total ODP results for the MDI system, which are also shown graphically in Figure 10. Ozone depletion results for the MDI system are dominated by the crude oil extraction and refining used to create many of the incoming materials, contributing 98 percent of the total ozone depletion impacts. The amount of the ODP shown as MDI production is mostly from the small releases of tetrachloromethane from the process. The remaining impact coming from MDI production is for the production of the petroleum fuels used in electricity and transport.

Table 9. Ozone Depletion Potential for MDI

	Ozone Depletion Potential		
	Basis: 1,000 Pounds	**Basis: 1,000 kilograms**	**Percentage of Total**
	lb CFC-11 eq	***kg CFC-11 eq***	***%***
Cradle-to-Incoming Materials	4.1E-06	4.1E-06	98.0%
Phosgene/MDA/MDI Production	8.6E-08	8.6E-08	2.0%
Total	**4.2E-06**	**4.2E-06**	**100%**

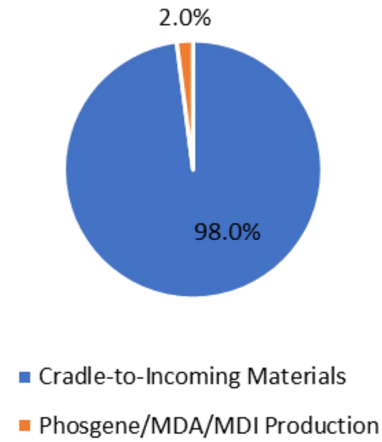

Figure 10. Ozone Depletion Potential for MDI

PHOTOCHEMICAL SMOG FORMATION

The photochemical ozone creation potential (POCP) impact category, also referred to as smog formation potential, characterizes the potential of airborne emissions to cause photochemical smog. The creation of photochemical smog occurs when sunlight reacts with NO_x and volatile organic compounds (VOCs), resulting in tropospheric (ground-level) ozone and particulate matter. Endpoints of such smog creation can include increased human mortality, asthma, and deleterious effects on plant growth.[25] Smog formation impact are generally dominated by emissions associated with fuel combustion, so that impacts are higher for life cycle stages and components that have higher process fuel and transportation fuel requirements. In this case, NO_x makes up 94 percent of the smog formation emissions, with VOCs consisting of over 5 percent.

Smog formation potential results for MDI are displayed in Table 10 and illustrated in Figure 11. Approximately 89% of the POCP impact results comes from the cradle-to-incoming materials. The cradle-to-aniline releases 57 percent of the total impact resulting the POCP. Within the production of aniline, the cradle-to-benzene produces more than half of that amount due to the POCP associated with the extraction of natural gas and oil. The POCP impact from the chlor-alkali process, which produces chlorine and sodium hydroxide used, comprises 13 percent of the total.

The remaining 11 percent of the POCP impact results is released from the MDI production process. Of that percentage, a little more than half of the POCP for the MDI plant comes from the use of electricity in the plant, which includes the combustion of natural gas and coal at power plants and cogeneration plants. Only 2 percent of the total emissions resulting in the POCP impact results are released at the MDI plant as process emissions. The remaining

[25] Bare, J. C. Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI), Version 2.1 - User's Manual; EPA/600/R-12/554 2012.

approximately 40 percent in the MDI production comes from combustion of natural gas, production of nitrogen, or transport of incoming materials.

Table 10. Photochemical Smog Formation Potential for MDI

	Photochemical Smog Potential		
	Basis: 1,000 Pounds	Basis: 1,000 kilograms	Percentage of Total
	lb O3 eq	*kg O3 eq*	*%*
Cradle-to-Incoming Materials	113	113	89%
Phosgene/MDA/MDI Production	13.8	13.8	11%
Total	**126**	**126**	**100%**

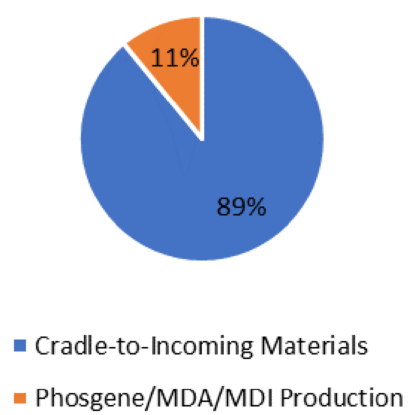

Figure 11. Photochemical Smog Formation Potential for MDI

COMPARISON OF 2022 AND 2011 LCI AND LCIA MDI RESULTS

This section provides a comparison of life cycle inventory and impact assessment category results that were included in the original cradle-to-gate MDI system[26] with the current update. These categories include total energy, non-renewable energy, renewable energy, total solid waste, and global warming potential. No comparisons are available for water consumption, solid waste broken out as hazardous and non-hazardous categories, acidification potential, eutrophication potential, photochemical smog formation, or ozone depletion potential. These categories were not included in the original study.

Table 11 shows the comparable LCI and LCIA categories for the 2011 and 2022 MDI results in both English and SI units and includes the percent change from the 2011 value for each category. Percent change between systems is defined as the difference between the 2022 and 2011 totals divided by the 2011 totals. The results in Table 11 show a decrease in all categories. Comparisons of these results have been analyzed in this section focusing on the main differences causing the change in each category. It should be noted that all figures in this section provide a percent increase or decrease above the comparable bars.

It is noteworthy that all 4 plants that provided MDI data for the updated average also provided data for the original study. This allowed for an easier comparison of the weighted average of MDI production. However, results differences between the two averaged datasets are predominantly due to the use of additional companies and manufacturing plants when updating the pygas and chlor-alkali primary data. Each plant producing the same chemical varies by the amounts of input materials used, fuel types and amounts used, amounts of emissions released, etc. The amalgamation of these changes lead to differences affecting the results for pygas and chlor-alkali. In the updated data, additional plants participated in the data collection for this update for the pygas. The Chlor-alkali data represents the years 2015 (2 plants) and 2017 (1 plant). One chlor-alkali plant was included in the previous analysis, while the other two chlor-alkali data providers had not previously provided data and replaced data from chlor-alkali plant datasets from the 1990s, which improved the data quality of the analysis.

[26] American Chemistry Council, Plastics Division, Cradle-to-Gate Life Cycle Inventory of Nine Plastic Resins and Four Polyurethane Precursors. Prepared by Franklin Associates, A Division of ERG. August, 2011.

Table 11. Comparison of 2011 and 2022 LCI and LCIA Results for MDI

	1000 pounds of Methylene Diphenyl Diisocyanate				
	LCI Results				*LCIA Results*
	Total Energy	Non-Renewable Energy	Renewable Energy	Total Solid Waste*	Global Warming
	MM Btu	*MM Btu*	*MM Btu*	*lb*	*lb CO_2 eq*
MDI 2022	24.1	23.9	0.20	80.6	2,131
MDI 2011	25.7	25.5	0.20	103	2,377
	1000 kilograms of Methylene Diphenyl Diisocyanate				
	LCI Results				*LCIA Results*
	Total Energy	Non-Renewable Energy	Renewable Energy	Total Solid Waste*	Global Warming
	GJ	*GJ*	*GJ*	*kg*	*kg CO_2 eq*
MDI 2022	56.0	55.5	0.47	80.6	2,131
MDI 2011	59.8	59.3	0.48	103	2,377
Percent Change	-6%	-6%	-1%	-22%	-10%

*Total Solid Waste excludes hazardous solid waste for 2022 as this category was not included as Solid Waste in 2011.

ENERGY COMPARISON

Overall, the total energy for the MDI system has decreased 3.8 GJ on a 1,000 kg basis (1.6 MMBtu/1,000 lb). There is a 6 percent decrease in total energy as compared to the original study's results. This percentage is due to differences mostly in the incoming materials, although the MDI plant average does play a moderate part in the decrease as well. When comparing the phosgene/MDA/MDI unit process average total energy data from the original study and this 2022 update, there is a 23 percent decrease overall. This decrease is a third of the difference between the total energy for original and current analyses. The MDI plants in this analysis were identical to the original plants included; therefore we can conclude that the MDA plants have increased the efficiencies within their plants. Figure 12 provides a graphical perspective of the unit processes associated with this energy decrease from the original energy amounts.

The energy of material resource, which pertains to the amount of inherent energy from the raw materials increased by approximately 12 percent for MDI due to the changes in the amount of raw material inputs compared to the data in the 2011 report. As the amount of material resource energy increased, but the total energy still decreased, it can be concluded that the difference in process energy decreased by a slightly greater percentage than the 6 percent shown in the total. Besides the decrease in MDI production, this decrease is also due to the energy decreases in the energy requirements for the olefins plants, as well as the oil and natural gas extraction and processing/refining, which are used to produce the carbon monoxide, methanol and ammonia as well. Updated data for some of these intermediate chemicals unit processes were not found during the research stage of the analysis, and so these chemicals were not reviewed closely in the comparison analysis.

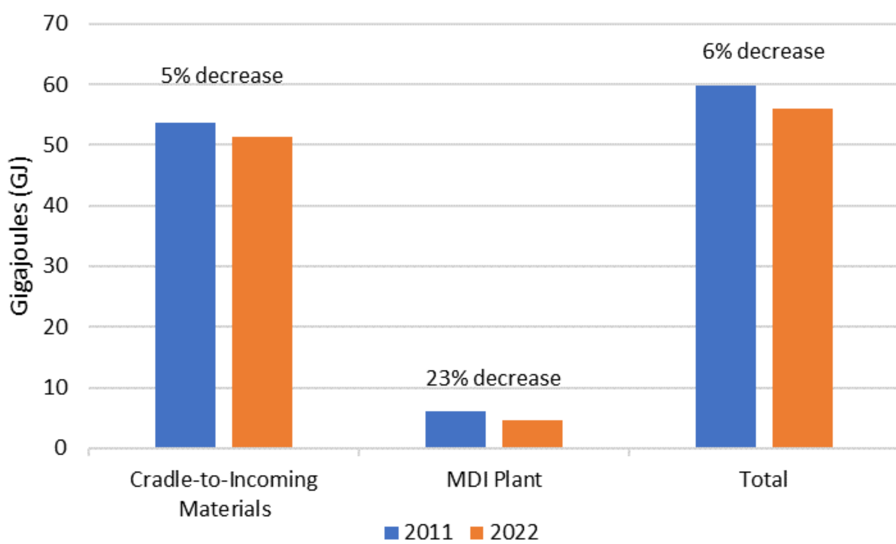

Figure 12. Change in Energy by Stage per 1,000 kg (GJ)

SOLID WASTE COMPARISON

When compared to the 2011 MDI total solid waste amount, the current MDI analysis shows 22.4 kg per 1000 kg less solid waste, which is a 22 percent decrease from the original study. Figure 13 provides a visual of the total solid waste amount split out by the MDI unit process and cradle-to-incoming materials. Most of this decrease is due to the differences in the cradle-to-intermediate chemicals data between the 2011 and 2022 reports; however, a little more than 10 percent of the difference is a decrease in the Phosgene/MDA/MDI data. A decrease occurs for both cradle-to-incoming materials and at the MDI plant. The same plants were used to create the MDI average data, so this shows a decrease in plant solid waste during production overall. This includes solid waste from the plant itself as well as those solid wastes created during the production and combustion of fuel offsite. The decrease in cradle-to-incoming materials is a mix of lower amounts of solid waste at the plants, as well as an overall decrease in the electricity use in the case of the olefins plant. The solid waste from the aniline production average decreased by a high percentage but is smaller than that of the fuel-related solid waste. Process solid wastes from the natural gas and crude oil production also decreased by small amounts.

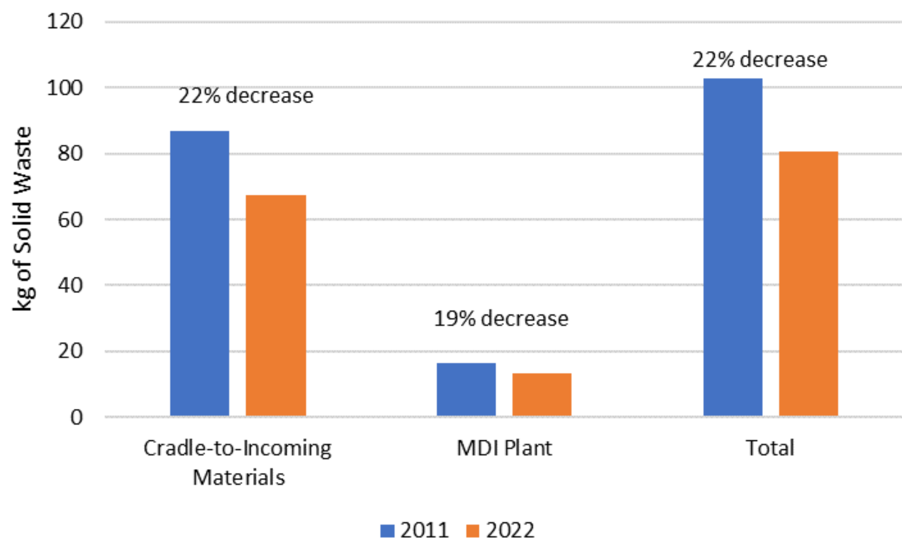

Figure 13. Change in Solid Waste Weight by Unit Process (kg Per 1,000 kg)

GLOBAL WARMING POTENTIAL COMPARISON

The total global warming potential decreased by 246 kg CO2 equivalents/1000 kg of MDI, which calculates to a 10 percent decrease. Figure 14 displays a column chart with the MDI and cradle-to-incoming materials results that makeup the decrease when comparing the 2011 and 2022 GWP results. This overall decrease follows the trend shown in total energy, since much of the greenhouse gases are created from fuel production. The total energy

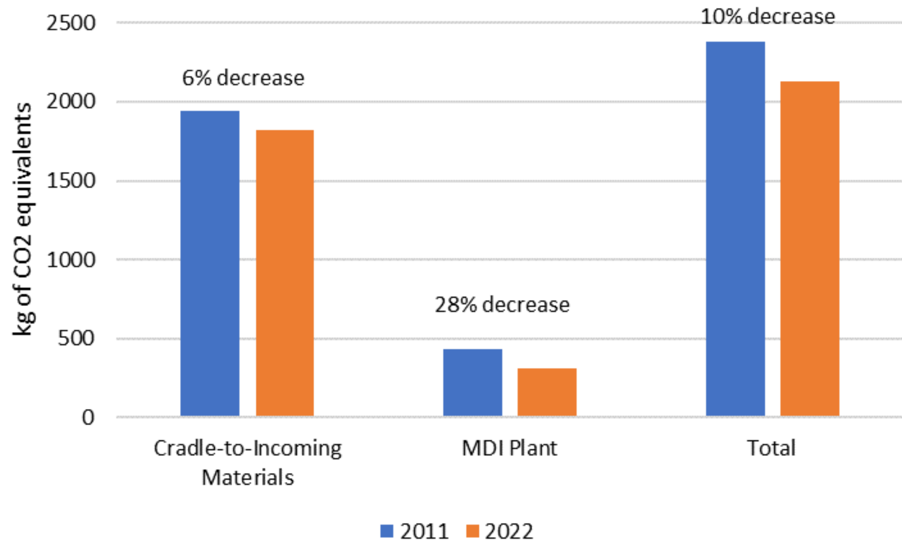

Figure 14. Change in Global Warming Potential by Unit Process (kg of CO2 eq. per 1,000 kg)

amount includes the material resource energy, which has no greenhouse gases associated with it as it is not combusted.

The GWP specific to the MDI plant decreased by 28 percent, while the energy for the plant also decreased by close to that same percentage. The MDI plant GWP amount is approximately 15 percent of the total GWP amount and does not include GWP for the energy of material resource, and so this affects the total a little more than seen in the energy comparison. The decrease in GWP for the cradle-to-incoming materials comes from decreases in energy use for the raw materials and for the olefins and aniline plant. The amount of coal combusted for the US average electricity grid has decreased over time with an increase in natural gas combustion. Coal production and combustion releases higher amounts of greenhouse gases compared to natural gas production and combustion.

It should also be noted that the characterization factors for the GWP have changed since the 2011 report. The methane amount increased from 25 to 28 lb CO2eq/1 lb methane and the nitrous oxide amount decreased from 298 to 265 lb CO2eq/1 lb. As the methane and nitrous oxide releases account for less than 5 percent of the GWP characterization, the change in results due to this characterization factor difference is small.

SENSITIVITY ANALYSIS

For this MDI report, results using mass allocation for MDI/HCl are provided in the results section. Recently, the European Diisocyanate and Polyol Producers Association (ISOPA) released a new dataset for MDI and TDI for European manufacturers that uses a combined elemental and mass allocation.[27] This sensitivity analysis is included to provide results for both allocation methods as was done in the ISOPA study. The results using a mass allocation allow the reader to compare to the original 2011 MDI results; while the results using combined elemental + mass allocation allow the reader to compare the current North American MDI results to the current EU MDI results. Also provided are results using the MDI datasets from the original 2011 report using the elemental + mass allocation as a comparison.

Table 12 provides the results using both mass and the elemental + mass allocation methods for both the 2011 LCI data as well as the 2022 LCI data. When comparing the results of the two allocation methods for either year, an increase is seen when using the elemental + mass allocation. The mass of hydrochloric acid created from the process of creating MDI is almost one third of the output by weight. When mass allocation is used, almost a third of the resulting impacts are given to the HCl, which is why there is a substantial decrease in the results when this allocation method is used. When the inputs to MDA and Phosgene are allocated to the MDI alone as done in the elemental + mass allocation, most of the resulting impacts increase. The exceptions are the renewable energy and water consumption, these are due to the removal of chlorine production.

Focusing on the 2022 total energy for both allocation methods, there is an increase of 36 percent when switching to the elemental + mass allocation method. The 2011 change in allocation method shows a similar increase. The global warming potential calculated for 2022 increases by 23 percent if the elemental + mass allocation is used. Although much of the GWP is based on the energy amount, the smaller increase is due to the inclusion of feedstock energy in the energy shown, which would all be allocated to the MDI and would carry no GWP amount as is inherent in the plastic and not combusted.

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[27] ISOPA Eco-profile of toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI). April 2021.

Table 12. Comparison of 2011 and 2022 LCI and LCIA Results for MDI Using Both Mass and Elemental + Mass Allocation Methods

	1 kilogram of MDI									
	LCI Results					*LCIA Results*				
	Total Energy	**Non-Renewable Energy**	**Renewable Energy**	**Water Consumption**	**Total Solid Waste**	**Global Warming**	**Acidification**	**Eutrophication**	**Ozone Depletion**	**Smog Formation**
	MJ	***MJ***	***MJ***	***Liters***	***kg***	***kg CO_2 eq***	***kg SO2 eq***	***kg N eq***	***kg CFC-11 eq***	***kg O3 eq***
NA MDI **2011** (Mass allocation)	59.8	59.3	0.48	NA	0.10	2.38	NA	NA	NA	NA
NA MDI **2011** (Elemental+Mass allocation)	78.0	77.7	0.38	NA	0.10	2.69	NA	NA	NA	NA
NA MDI **2022** (Mass allocation)	56.0	55.5	0.47	11.0	0.08	2.13	0.0063	4.8E-04	4.2E-09	0.13
NA MDI **2022** (Elemental+Mass allocation)	76.0	75.5	0.46	11.1	0.09	2.62	0.0076	6.8E-04	6.0E-09	0.16

APPENDIX: METHYLENE DIPHENYL DIISOCYANATE (MDI) MANUFACTURE

This appendix discusses the manufacture of MDI, which is a precursor in the manufacture of flexible and rigid polyurethane foams that are used for carpet pads, furniture cushions, construction, insulation, and packaging. The captured MDI production amount is approximately 90 percent of the MDI production in the U.S. in 2015 (Statista, 2021). The unit process for MDI includes the manufacture of both pure and polymeric MDI. The flow diagram of processes included for MDI is provided in Figure 15.

Individual unit process tables on the bases of 1,000 pounds and 1,000 kilograms are also shown within this appendix. The following processes are discussed in this appendix:

- Methanol
- Ammonia
- Benzene
- Hydrogen
- Nitric Acid
- Nitrobenzene
- Aniline
- Carbon Monoxide
- Formaldehyde
- Phosgene
- MDA/MDI

Primary LCI data for pyrolysis gasoline, chlorine, sodium hydroxide, nitrobenzene/aniline and phosgene/MDA/MDI were collected for this update to the U.S. LCI plastics database by both member and non-member companies of the American Chemistry Council. Primary LCI data from the original report released in 2011 were used for benzene and formaldehyde. Data for the production of formaldehyde is a confidential dataset and is not shown. Secondary LCI data was used for methanol, ammonia, hydrogen, carbon monoxide, crude oil extraction and refining and natural gas production and processing. LCI data for the production of pygas, crude oil, and natural gas can be found in the report, ***Cradle-to-Gate Life Cycle Analysis of Olefins*** (Franklin Associates, 2020). LCI data for the production of sodium chloride (salt) solution mining, chlor-alkali (chlorine, sodium hydroxide, and hydrogen) can be found in the report, ***Cradle-to-Gate Life Cycle Analysis of Polyvinyl Chloride (PVC) Resin*** (Franklin Associates, 2021). LCI data for salt mining and nitrogen were adapted from the ecoinvent 3 database. The adaptations included the use of the US electricity grid and US transportation.

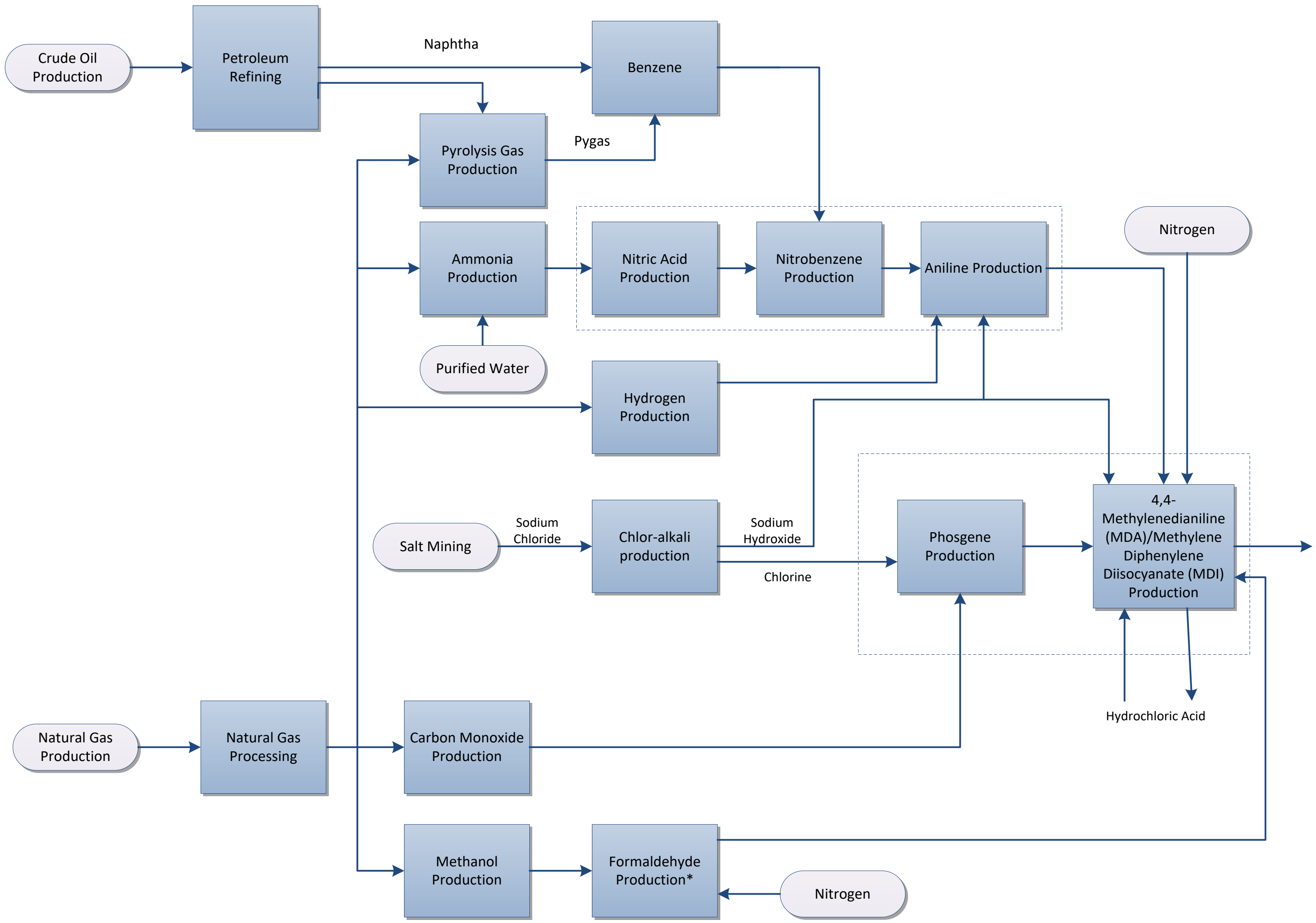

Figure 15. Flow diagram for the Production of Methylene diphenyl diisocyanate (MDI).
* Nitrogen and sodium chloride data are from ecoinvent and are adapted to U.S. conditions.

Methanol Production

Methanol is produced from light hydrocarbons derived from petroleum products. Recent research (Borisut & Nuchitprasittichai, 2019; Chakraborty et al., 2022; Samimi et al., 2017) has explored the production of methanol from the direct hydrogenation of carbon dioxide as a way to mitigate carbon dioxide emissions, however this process is 2-2.5 times more costly than the conventional process (Atsonios et al., 2016) of steam reforming and low-pressure synthesis of light hydrocarbons.

In steam reforming, the feed gas is compressed, preheated, and desulfurized. Then, it is mixed with steam, preheated further, and fed to a copper catalytic reformer (Mäyrä & Leiviskä, 2018). The synthesis gas from the reformer, containing primarily hydrogen, carbon monoxide, and carbon dioxide, is cooled to remove condensate to the proper temperature for entry into the compressor section.

From the compressor, the pressure of the synthesis gas is raised, and the feed goes to a multi-bed inter-cooled methanol converter system. Converter effluent is sent to a cooler, and the crude methanol is removed from the gas mixture. The crude methanol is then brought to atmospheric pressure and distilled to eliminate dissolved gases and obtain the desired grade (María et al., 2013; Marlin et al., 2018).

Table 13 lists the energy requirements and environmental emissions for the manufacture of 1,000 pounds of methanol. Steam production is included in energy use for methanol production. The energy inputs for the methanol manufacture were updated using GREET 2019 (Wang et al., 2019). Water consumption and atmospheric emissions for methanol production use GREET 2017 (Wang et al., 2017). Solid waste outputs were updated using primary data from 2016 (Methanex, 2016). The transportation energy is calculated using estimated from the percentages of the different types of natural gas piped to methanol production facilities.

Ammonia Production

Ammonia is produced primarily by steam reforming natural gas. Natural gas is fed with steam into a tubular furnace where the reaction over a nickel reforming catalyst produces hydrogen and carbon oxides. The primary reformer products are then mixed with preheated air and reacted in a secondary reformer to produce the nitrogen needed in ammonia synthesis. The gas is then cooled to a lower temperature and subjected to the water shift reaction in which carbon monoxide and steam are reacted to form carbon dioxide and hydrogen. The carbon dioxide is removed from the shifted gas in an absorbent solution. Hydrogen and nitrogen are reacted in a synthesis converter to form ammonia (Pattabathula & Richardson, 2016).

Table 13. LCI Data for the Production of Methanol

	1,000 lb		1,000 kg	
Material Inputs				
Inputs from Nature				
Oxygen	380	lb	380	kg
Inputs from Technosphere				
Processed Natural Gas	620	lb	620	kg
Energy				
Process Energy				
Electricity from grid	114	kWh	252	kWh
Natural gas	118	ft^3	7.37	m^3
Transportation Energy				
Pipeline - natural gas products	150	ton·mi	483	tonne·km
Environmental Emissions				
Atmospheric Emissions				
Carbon dioxide, fossil	390	lb	390	kg
VOC, volatile organic compounds	0.50	lb	0.50	kg
Carbon monoxide	0.72	lb	0.72	kg
Nitrogen oxides	1.11	lb	1.11	kg
Particulates, < 10 um	0.26	lb	0.26	kg
Particulates, < 2.5 um	0.26	lb	0.26	kg
Sulfur oxides	0.33	lb	0.33	kg
Methane	4.59	lb	4.59	kg
Nitrogen dioxide	0.010	lb	0.010	kg
Solid Wastes				
Non-hazardous waste to landfill	0.26	lb	0.26	kg
Solid Waste Sold for Recycling or Reuse	0.21	lb	0.21	kg
Hazardous waste for disposal	0.0069	lb	0.0069	kg
Hazardous waste, recovery	0.0085	lb	0.0085	kg
Water Consumption	47.2	gal	394	l

References: Methanex, 2016; Wang et al., 2017, 2019

Table 14 presents the energy and emissions data for the production of ammonia. Since carbon dioxide from ammonia plants is commonly recovered and used for urea production, the material input amounts for this analysis are based on 90 percent of the coproduced carbon dioxide from the steam reforming/shift reaction being treated as a coproduct. The amount of nitrogen from air was updated so that all nitrogen inputs are allocated only to the ammonia output instead of mass allocation for ammonia and carbon dioxide outputs. The energy data for ammonia was calculated from secondary sources (Kent, 2003) and from stoichiometry. The transportation data was estimated from the ammonia and acrylonitrile plant sites and from the acrylonitrile data provider. The remaining carbon dioxide (10 percent) is released as an atmospheric emission (Confidential, 2008). The atmospheric emissions and solid wastes are estimates, while the waterborne emissions are from a 1970's source (U.S. EPA, 1973), which were reviewed and revised in 1994.

Table 14. LCI Data for the Production of Ammonia

	1,000 lb		1,000 kg	
Material Inputs (1)				
Natural gas	267	lb	267	kg
Water (from steam)	1.50	lb	1.50	kg
Nitrogen (in air)	824	lb	824	kg
Energy				
Process Energy				
Electricity from grid	63.5	kWh	140	kWh
Natural gas	2,243	ft^3	140	m^3
Transportation Energy				
Pipeline - gas products	134	ton·mi	430	tonne·km
Truck	1.34	ton·mi	4.30	tonne·km
Rail	1.34	ton·mi	4.30	tonne·km
Environmental Emissions				
Atmospheric Emissions				
Ammonia	1.00	lb	1.00	kg
Carbon dioxide, fossil	97.0	lb	97.0	kg
Organic substances, unspecified	1.00	lb	1.00	kg
Waterborne Releases				
Ammonia	0.060	lb	0.060	kg
BOD5, Biological Oxygen Demand	0.050	lb	0.050	kg
COD, Chemical Oxygen Demand	0.23	lb	0.23	kg
Oils, unspecified	0.050	lb	0.050	kg
Suspended solids, unspecified	0.050	lb	0.050	kg
Solid Wastes				
Solid waste, process to landfill	0.20	lb	0.20	kg

(1) The material input amounts are based on 90% of coproduced CO2 from steam reforming/shift reaction being treated as a coproduct, since CO2 from ammonia plants is commonly recovered and used for urea production.

References: Confidential, 2008; Kent, 2003; U.S. EPA, 1973

Benzene Production

Benzene is the most widely used aromatic petrochemical raw material. The two major sources of benzene are catalytic reformate and pyrolysis gasoline. Additionally, benzene is produced by the toluene disproportionate processes (Meng et al., 2017).

In the reforming process, naphtha is fed through a catalyst bed at elevated temperatures and pressures. The most common type of reforming process is platforming, in which a bi-functional catalyst is used, usually containing platinum and an acid. Products obtained from the platforming process include aromatic compounds (benzene, toluene, xylene), hydrogen, light gas, and liquefied petroleum gas (Rahimpour et al., 2013). The aromatics content of the reformate varies and is normally less than 60 percent (Gentry, 2007). The reformate from the platforming process undergoes solvent extraction and fractional distillation to produce pure benzene, toluene, and other coproducts.

Pyrolysis gasoline is a byproduct of the steam cracking of hydrocarbons for the production of ethylene and propylene. Raw pyrolysis gas is composed of a mixture of C5 to C8 hydrocarbons, including several aromatic compounds. To separate the aromatics from the pyrolysis gas, C5 and C7 hydrocarbons are separated from C6 hydrocarbons, which releases the hydrogen produced. The remaining hydrocarbons undergo a distillation process using a very polar solvent (commonly an alcohol) that dissolves the aromatic components. The aromatics can then be separated from the solvent using fractional distillation. The solvent is recovered and re-used (Intratec Solutions, 2018).

Table 15 represents the energy requirements and environmental emissions for producing benzene. Only catalytic reforming and pyrolysis gasoline are considered as the source of benzene in this analysis. These technologies account for 93 percent of the world production of benzene (Niziolek et al., 2016). It is estimated that one-third of this production is from pyrolysis gasoline and two-thirds are produced from catalytic reforming (Franklin Associates, 2005). The collected datasets were weighted using these fractions.

Numerous aromatic coproduct streams are produced during this process. Fuel gas and off-gas were two of the coproducts produced that were exported to another process for fuel use. When these fuel coproducts are exported from the aromatics separation process, they carry with them the allocated share of the inputs and outputs for their production. No energy credit is applied for the exported fuels, since both the inputs and outputs for the exported fuels have been removed from the data set.

No new benzene data was collected for this update. The benzene data from pyrolysis gas used for this module represent 1 producer and 1 plant in the U.S in 2003. While data was collected from a small sample of plants, the benzene producer who provided data for this module verified that the characteristics of their plant is representative of the extraction of benzene from pyrolysis gasoline for North American benzene production. The average dataset was reviewed and accepted by the benzene data provider.

Table 15. LCI Data for the Production of Benzene

	1,000 lb		1,000 kg	
Material Inputs				
Refined Petroleum Products- material use	667	lb	667	kg
Refined Petroleum Products- fuel use	16.0	lb	16.0	kg
Processesed Natural Gas - fuel use	22.1	lb	22.1	kg
Pygas	335	lb	335	kg
Energy				
Process Energy				
Electricity from grid	72.6	kWh	160	kWh
Electricity from cogen	4.35	kWh	9.60	kWh
Natural gas	625	ft^3	39.0	m^3
Residual fuel oil	3.83	gal	32.0	l
Diesel	0.40	gal	3.30	l
Transportation Energy				
Barge				
Diesel	11.5	ton·mi	37.0	tonne·km
Residual oil	37.3	ton·mi	120	tonne·km
Rail	46.6	ton·mi	150	tonne·km
Pipeline - petroleum products	74.6	ton·mi	240	tonne·km
Truck	9.32	ton·mi	30.0	tonne·km
Environmental Emissions				
Atmospheric Emissions				
Carbon monoxide	0.011	lb	0.011	kg
Carbon dioxide, fossil	45.0	lb	45.0	kg
Chlorine	1.0E-04	lb	1.0E-04	kg
Nitrogen oxides	0.062	lb	0.062	kg
Particulates, > 2.5 um, and < 10um	0.0010	lb	0.0010	kg
NMVOC, non-methane volatile organic compounds, unspecified origin	0.010	lb	0.010	kg
Hydrogen	1.0E-06	lb	1.0E-06	kg
Sulfur oxides	0.44	lb	0.44	kg
Waterborne Releases				
Benzene	1.0E-06	lb	1.0E-06	kg
BOD5, Biological Oxygen Demand	0.47	lb	0.47	kg
COD, Chemical Oxygen Demand	1.10	lb	1.10	kg
Suspended solids, unspecified	0.11	lb	0.11	kg
Oils, unspecified	0.018	lb	0.018	kg
Sulfide	0.0010	lb	0.0010	kg
Suspended solids, unspecified	0.0010	lb	0.0010	kg
TOC, Total Organic Carbon	1.0E-05	lb	1.0E-05	kg
Solid Wastes				
Solid waste, process to landfill	0.43	lb	0.43	kg
Solid waste process, to incineration	0.051	lb	0.051	kg
Water Consumption	0.75	gal	6.30	l

References: Primary data, 2005 and Primary data, 1992

The two steam reforming datasets were collected in 1992. The 2003 data were collected from direct measurements and engineering estimates. The collection methods by the data provider for the 1992 data are unknown.

Hydrogen Production

Hydrogen and carbon dioxide are coproducts in the production of syntheses gas. Synthesis gas is primarily produced from natural gas by steam-methane reforming. Natural gases, or other light hydrocarbons, and steam are fed into a primary reformer over a nickel catalyst at high temperatures to produce hydrogen and carbon oxides, generally referred to as synthesis gas. Most of the hydrocarbon feed is converted to synthesis gas in the primary reformer. The effluent from the reformers, mainly carbon monoxide, is fed into carbon monoxide shift converters where the carbon monoxide undergoes a water-gas shift reaction by reacting with water to form carbon dioxide and hydrogen. Pressure swing adsorption is used to separate the hydrogen and carbon dioxide from the remaining effluent as coproducts. The excess water is removed through condensation. (Energy.gov, n.d.; Hajjaji et al., 2012; Peng, 2012) Steam methane reforming has an efficiency of approximately 70 percent (Hajjaji et al., 2012).

The ratio of carbon monoxide to hydrogen in the synthesis gas differs depending on the specifications for the synthesis gas, and therefore the amounts of hydrogen and carbon dioxide coproducts differ also. Synthesis gas is a raw material for many different processes, each with specific requirements. Because of this difference in requirements, it is difficult to show a generic or widely applicable material balance for this process.

Nitric Acid Production

The raw materials necessary for nitric acid production are ammonia, air, and a platinum-rhodium catalyst. Liquid ammonia is evaporated and superheated to a gaseous for which is then mixed with air and passed over the catalyst to produce nitric oxides. Reaction water is removed as 2% nitric acid condensate. Through oxidation the nitric oxides are converted into nitrogen dioxide. (Cheremisinoff, 1995) Secondary air containing recycled nitrogen dioxide is added to the nitrous gas, which is compressed and fed into an absorption column, where acid is formed. (Speight, 2017) Nitrogen dioxide remaining in the gas is absorbed in the nitric acid and must be stripped from the acid by secondary air, which is recycled.

The energy and emissions data for nitric acid production is from a primary European source from 1990. This dataset has been included with the aniline/ nitrobenzene average dataset in Table 16 to conceal the confidential data of the provider.

Nitrobenzene Production

The energy and emissions data for nitrobenzene production are from two provider companies and are aggregated with the aniline/nitric acid dataset in Table 16 to protect the data's confidentiality.

Nitrobenzene and other nitroaromatics, such as nitrochlorobenzene and dinitrotoluene, are formed by nitrating the appropriate aromatic hydrocarbon, mainly benzene, with a mixed acid containing nitric and sulfuric acid which acts as a catalyst. (Agustriyanto et al., 2017) The nitrated aromatic is separated from the acid mixture in a centrifugal separator, neutralized and washed, and finally dried in a drying column. The recovered acid mixture containing nitric acid and nitro compounds is recycled.

Nitrobenzene data was collected with the aniline data as one dataset from 2 producers. The average dataset was reviewed and accepted by both nitrobenzene/aniline data providers. The nitrobenzene production data was shown within Table 16.

Aniline Production

Aniline is formed by the hydrogenation of nitrobenzene in the presence of a copper-chromium or copper-silica catalyst, or by vapor phase ammonolysis of phenol and ammonia.

For hydrogenation of nitrobenzene, preheated hydrogen and nitrobenzene are fed into an evaporator, and aniline is formed by vapor phase catalytic reduction. The aniline is dehydrated to remove the water produced during the reaction. Pure aniline (99.95 wt. %) is obtained after a purification step in which the dehydrated aniline goes through a distillation process. (Intratec Solutions, 2016)

In the ammonolysis process, phenol and ammonia are preheated and fed into an adiabatic, fixed abed reactor and passed over a catalyst to produce aniline and water. The effluent gas is partially condensed, and the liquid and vapor phases separated. The vapor phase containing unreacted ammonia is recycled. Ammonia is stripped from the liquid fraction, and the aniline is dried and distilled. Unreacted phenol is recovered and recycled.

Table 16 presents the data for the production of nitric acid, nitrobenzene, and aniline. Data for the production of nitrobenzene and aniline were provided by two leading producers (2 plants) in the United States to Franklin Associates. Steam/heat is produced as a coproduct during this process. System expansion was used to show this steam/heat as an avoided fuel (natural gas).

The aniline data collected represents approximately 71 percent for 2015 of the total U.S. aniline production amount (Fernandez, 2022). The aniline producers who provided data for this module verified that the characteristics of their plants are representative of a majority of U.S. aniline production. The average dataset was reviewed and accepted by both aniline data providers.

To assess the quality of the data collected for aniline, the collection methods, technology, industry representation, time period, and geography were considered. The data collection methods for aniline include direct measurements, information provided by purchasing and utility records, and engineering estimates. All data submitted for aniline ranges from 2015-2016 and represents U.S. production.

Table 16. LCI Data for the Production of Nitric Acid/Nitrobenzene/Aniline

	1,000 lb		1,000 kg		
Material Inputs					
Hydrogen	67.0	lb	67.0	kg	
Ammonia	203	lb	203	kg	
Benzene	848	lb	848	kg	
Sodium hydroxide	10.0	lb	10.0	kg	
Energy					
Process Energy					
Electricity from grid	63.0	kWh	139	kWh	
Electricity from cogen	25.9	kWh	57.0	kWh	
Natural gas	500	ft^3	31.2	m^3	
Avoided Energy Energy					
Natural gas avoided due to export of steam	2,307	ft^3	144	m^3	
Transportation Energy					
Pipeline -refinery products	0.62	ton·mi	2.00	tonne·km	
Pipeline - gas products	0.99	ton·mi	3.20	tonne·km	
Truck	0.10	ton·mi	0.32	tonne·km	
Environmental Emissions					
Atmospheric Emissions					
Ammonia	0.0010	lb	0.0010	kg	*
Carbon monoxide	0.010	lb	0.010	kg	*
Chlorine	1.0E-05	lb	1.0E-05	kg	*
Hydrogen chloride	1.0E-05	lb	1.0E-05	kg	*
Methane, chlorodifluoro-, HCFC-22	1.0E-05	lb	1.0E-05	kg	*
Nitrogen oxides	1.40	lb	1.40	kg	
NMVOC, non-methane volatile organic compounds, unspecified origin	0.010	lb	0.010	kg	*
Organic substances, unspecified	0.0010	lb	0.0010	kg	*
Particulates, < 2.5 um	0.010	lb	0.010	kg	*
Sulfur oxides	1.0E-04	lb	1.0E-04	kg	*
Sulfuric acid	1.0E-06	lb	1.0E-06	kg	*
Methane	1.0E-04	lb	1.0E-04	kg	*
Carbon dioxide, fossil	10.0	lb	10.0	kg	*
Dinitrogen monoxide	0.32	lb	0.32	kg	
Waterborne Releases					
TOC, Total Organic Carbon	0.0010	lb	0.0010	kg	*
Suspended solids, unspecified	0.010	lb	0.010	kg	*
BOD5, Biological Oxygen Demand	0.0010	lb	0.0010	kg	*
Aniline	0.10	lb	0.10	kg	*
Nitrobenzene	0.10	lb	0.10	kg	*
Nitrate	0.10	lb	0.10	kg	*
Nitrate compounds	1.00	lb	1.00	kg	*
	1,000 lb		**1,000 kg**		
Solid Wastes					
Solid waste process, to landfill	0.0010	lb	0.0010	kg	*
Solid Waste Sold for Recycling or Reuse	0.010	lb	0.010	kg	*
Hazardous waste to incineration	1.00	lb	1.00	kg	*
Water Consumption	216	gal	1,800	l	

* To indicate known emissions while protecting the confidentiality of individual company responses, the emission is reported only by the order of magnitude of the average.

References: Primary data, 2020a, Primary data, 1990.

Carbon Monoxide Production

The raw materials necessary for the production of carbon monoxide are the gases resulting from steam reformation, as in the production of synthesis gas for ammonia manufacture, or from partial combustion of hydrocarbons. (Rydén & Lyngfelt, 2006) The feed gas must be stripped of carbon dioxide by scrubbing with ethanolamine solution and then passed through a molecular sieve to remove traces of carbon dioxide and water. Carbon monoxide and unconverted methane are condensed from the gas mixture and separated by lowering the pressure to remove entrained gases. The methane is recycled, and the carbon monoxide comes out as a product after evaporation, warming, and compression.

The energy and emissions data for carbon monoxide are from secondary sources and estimates; however, this data is kept confidential due to its use in another process where it is used with confidential data. The transportation energy was calculated from information by an acetic acid producer.

Formaldehyde Production

Formaldehyde is most commonly produced by oxidation of methanol, in the presence of either a silver or ferric molybdate catalyst. (Qian et al., 2003) Along with the silver catalyst, methanol, air, and water are preheated and fed into the reactor vessel. The heat from the reaction gas is recovered by generating steam, and the gases are then sent to an absorption tower.

The process for the metal oxide catalyst differs from the silver catalyst process in that the metal oxide reaction occurs at lower temperatures and requires a much greater excess of air in the feed. Heat recovered from the reaction gases is used to preheat the feed, and the excess steam is exported.

The formaldehyde is stripped from the reaction gases with water and then distilled. (Braun & Ritzert, 1989) A solution containing 60 percent urea can also be used during the stripping process. (Conner & Bhuiyan, 2017)

Data for the production of formaldehyde was collected from one confidential source in 2007 in the United States. Due to the confidentiality of this source, the formaldehyde unit process LCI data is not available.

Although the formaldehyde data collected represents only a small portion of the total North American formaldehyde production amount, the formaldehyde producer who provided data for this module verified that the characteristics of their plants are representative of a majority of North American formaldehyde production.

To assess the quality of the data collected for formaldehyde, the collection methods, technology, industry representation, time period, and geography were considered. The data collection methods for formaldehyde include direct measurements, information provided by purchasing and utility records, and engineering estimates. The data submitted for formaldehyde represents 2007 U.S. production.

Phosgene Production

Phosgene (also called carbonyl chloride, carbon oxychloride, or chloroformyl chloride) is produced by the reaction of carbon monoxide and chlorine in the presence of an activated charcoal catalyst. Careful production, handling, and trace recovery must be maintained because of phosgene's toxicity. Chlorine gas and carefully purified carbon monoxide are mixed with a slight excess of carbon monoxide to insure complete conversion of chlorine. The reaction is exothermic and is carried out in relatively simple tubular heat exchangers. (Rossi et al., 2021) The product gas is condensed, and the phosgene removed in an absorption column. Any non-condensed phosgene is removed in a caustic scrubber.

Phosgene data was collected with the formaldehyde, MDA and PMDI/MDI energy and emissions and is included in Table 17 and Table 18.

Methylene diphenyl diisocyanate (MDI) Production

Methylene diphenylene isocyanate (MDI) formation consists of two steps. In the first, 4,4-methylenedianiline (MDA) is created as an intermediate by the condensation of aniline and formaldehyde in the presence of an acid. In the final step, MDA is phosgenated to produce MDI. A mixture of MDI, its dimer and trimer is formed, and referred to as polymeric MDI (PMDI). Pure MDI is distilled from the reaction mixture. The market split from 2018 is approximately 86 percent polymeric MDI and 14 percent pure MDI. Polyurethanes commonly utilize the PMDI for rigid foams, while the pure MDI is more commonly used in thermoplastic and cast elastomer applications. (BASF, 2019)

Table 17 presents the LCI data for the production of phosgene, MDA, and PMDI/MDI with a mass allocation for the products MDI and HCl, while Table 18 presents the LCI data using the elemental + mass allocation. The unit process using both allocation methods have been provided here although only results for mass allocation are shown in the body of the report. The elemental + mass allocation results have been shown in a sensitivity analysis.

Data for the production of phosgene, MDA, PMDI/MDI were provided by four leading producers (4 plants) in North America to Franklin Associates. A large amount of hydrogen chloride is produced as a coproduct during this process. As stated previously, a mass basis was used to partition the credit for each product in the main results of the study. Once collected, the data for each plant is reviewed individually. At that time, coproduct allocation is performed for the individual plant. After coproduct allocation is complete, the data of all plants are averaged using yearly production amounts. This was also done using the elemental + mass allocation method for each plant with results using this allocation shown in the Sensitivity Analysis section.

Table 17. LCI Data for the Production of Methylene diphenyl diisocyanate (MDI) – Mass Allocation

	1,000 lb		1,000 kg		
Material Inputs					
Carbon monoxide	146	lb	146	kg	
Aniline	526	lb	526	kg	
Sodium hydroxide	46.0	lb	46.0	kg	
Formaldehyde	204	lb	204	kg	
Nitrogen	37.0	lb	37.0	kg	
Hydrochloric acid (from the process)	35.0	lb	35.0	kg	
Energy					
Process Energy					
Electricity from grid	79.8	kWh	176	kWh	
Electricity from cogen	29.5	kWh	65.0	kWh	
Natural gas	849	ft^3	53.0	m^3	
Hydrogen	161,237	Btu	170	MJ	
Transportation Energy					
Barge	5.90	ton·mi	19.0	tonne·km	
Rail	4.97	ton·mi	16.0	tonne·km	
Pipeline - gas products	0.53	ton·mi	1.70	tonne·km	
Environmental Emissions					
Atmospheric Emissions					
Aldehydes, unspecified	0.0010	lb	0.0010	kg	*
Ammonia	0.0013	lb	0.0013	kg	
Carbon dioxide, fossil	31.0	lb	31.0	kg	
Carbon monoxide	0.063	lb	0.063	kg	
Chlorine	1.0E-04	lb	1.0E-04	kg	*
Hydrogen chloride	0.10	lb	0.10	kg	*
Methanol	0.0010	lb	0.0010	kg	*
Nitrogen oxides	0.010	lb	0.010	kg	*
Nitrous oxide	1.0E-05	lb	1.0E-05	kg	*
NMVOC, non-methane volatile organic compounds	0.0011	lb	0.0011	kg	
Particulates, < 2.5 um	0.0037	lb	0.0037	kg	
Sulfur oxides	1.0E-04	lb	1.0E-04	kg	*
Particulates, > 2.5 um, and < 10um	0.011	lb	0.011	kg	
Organic substances, unspecified	0.010	lb	0.010	kg	*
Propene	1.0E-04	lb	1.0E-04	kg	*
Methane	0.0010	lb	0.0010	kg	*
Ethane,1,1,1,2-tetrafluoro-, HFC-134a	1.0E-08	lb	1.0E-08	kg	*
Lead	1.0E-07	lb	1.0E-07	kg	*
Mercury	1.0E-06	lb	1.0E-06	kg	*
Phenylisocyanate	1.0E-08	lb	1.0E-08	kg	*
Methylene diphenyl diisocyanate (MDI)	1.0E-07	lb	1.0E-07	kg	*
4,4'-Methylenedianiline (MDA)	1.0E-05	lb	1.0E-05	kg	*
Aniline	1.0E-04	lb	1.0E-04	kg	*
Benzene, chloro-	1.0E-04	lb	1.0E-04	kg	*
Methane, tetrachloro-, CFC-10	1.0E-07	lb	1.0E-07	kg	*
Phosgene	1.0E-05	lb	1.0E-05	kg	*
Benzene, hexachloro-	1.0E-09	lb	1.0E-09	kg	*

	1,000 lb		1,000 kg		
Waterborne Releases					
Ammonia	1.0E-04	lb	1.0E-04	kg	*
BOD5, Biological Oxygen Demand	0.0010	lb	0.0010	kg	*
COD, Chemical Oxygen Demand	0.010	lb	0.010	kg	*
Copper	1.0E-06	lb	1.0E-06	kg	*
Suspended solids, unspecified	0.0010	lb	0.0010	kg	*
Phenols, unspecified	1.0E-04	lb	1.0E-04	kg	*
Nickel	1.0E-06	lb	1.0E-06	kg	*
TOC, Total Organic Carbon	0.010	lb	0.010	kg	*
Aniline	1.0E-04	lb	1.0E-04	kg	*
Sodium chloride	10	lb	10	kg	*
Benzene, chloro-	1.0E-05	lb	1.0E-05	kg	*
Methanol	1.0E-04	lb	1.0E-04	kg	*
4,4'-Diaminodiphenylmethane	1.0E-05	lb	1.0E-05	kg	*
Solid Wastes					
Solid waste, process to landfill	0.042	lb	0.042	kg	
Hazardous waste to landfill	0.10	lb	0.10	kg	
Hazardous waste to incineration	0.11	lb	0.11	kg	
Water Consumption	279	gal	2,330	l	

* To indicate known emissions while protecting the confidentiality of individual company responses, the emission is reported only by the order of magnitude of the average.

References: Primary data, 2020b

The PMDI/MDI data collected represents a majority of the total North American PMDI/MDI production amount. The PMDI/MDI producers who provided data for this module verified that the characteristics of their plants are representative of the majority of North American PMDI/MDI production. The average dataset was reviewed and accepted by all PMDI/MDI data providers.

To assess the quality of the data collected for PMDI/MDI, the collection methods, technology, industry representation, time period, and geography were considered. The data collection methods for PMDI/MDI include direct measurements, information provided by purchasing and utility records, and engineering estimates. All data submitted for PMDI/MDI represents the years 2015 for 3 MDI producers and 2017 for 1 MDI producer.

Table 18. LCI Data for the Production of Methylene Diphenyl Diisocyanate (MDI) – Elemental + Mass Allocation

	1,000 lb		1,000 kg		
Material Inputs					
Carbon monoxide	226	lb	226	kg	
Aniline	816	lb	816	kg	
Sodium hydroxide	46.0	lb	46.0	kg	
Formaldehyde	317	lb	317	kg	
Nitrogen	37.0	lb	37.0	kg	
Hydrochloric acid (from the process)	35.0	lb	35.0	kg	
Energy					
Process Energy					
Electricity from grid	79.8	kWh	176	kWh	
Electricity from cogen	29.5	kWh	65.0	kWh	
Natural gas	849	ft^3	53.0	m^3	
Energy required for hydrogen combustion	161,426	Btu	170	MJ	
Transportation Energy					
Barge	9.32	ton·mi	30.0	tonne·km	
Rail	7.46	ton·mi	24.0	tonne·km	
Pipeline - gas products	0.53	ton·mi	1.70	tonne·km	
Environmental Emissions					
Atmospheric Emissions					
Aldehydes, unspecified	0.0010	lb	0.0010	kg	*
Ammonia	0.0013	lb	0.0013	kg	
Carbon dioxide, fossil	31.0	lb	31.0	kg	
Carbon monoxide	0.063	lb	0.063	kg	
Methanol	0.0010	lb	0.0010	kg	*
Nitrogen oxides	0.010	lb	0.010	kg	*
Nitrous oxide	1.0E-05	lb	1.0E-05	kg	*
NMVOC, non-methane volatile organic compounds	0.0011	lb	0.0011	kg	
Particulates, < 2.5 um	0.0037	lb	0.0037	kg	
Sulfur oxides	1.0E-04	lb	1.0E-04	kg	*
Particulates, > 2.5 um, and < 10um	0.011	lb	0.011	kg	
Organic substances, unspecified	0.010	lb	0.010	kg	*
Propene	1.0E-04	lb	1.0E-04	kg	*
Methane	0.0010	lb	0.0010	kg	*
Ethane,1,1,1,2-tetrafluoro-, HFC-134a	1.0E-08	lb	1.0E-08	kg	*
Lead	1.0E-07	lb	1.0E-07	kg	*
Mercury	1.0E-06	lb	1.0E-06	kg	*
Phenylisocyanate	1.0E-08	lb	1.0E-08	kg	*
Methylene diphenyl diisocyanate (MDI)	1.0E-07	lb	1.0E-07	kg	*
4,4'-Methylenedianiline (MDA)	1.0E-05	lb	1.0E-05	kg	*
Aniline	1.0E-04	lb	1.0E-04	kg	*
Benzene, chloro-	1.0E-04	lb	1.0E-04	kg	*
Methane, tetrachloro-, CFC-10	1.0E-07	lb	1.0E-07	kg	*
Phosgene	1.0E-05	lb	1.0E-05	kg	*
Benzene, hexachloro-	1.0E-09	lb	1.0E-09	kg	*

	1,000 lb		1,000 kg		
Waterborne Releases					
Ammonia	1.0E-04	lb	1.0E-04	kg	*
BOD5, Biological Oxygen Demand	0.0010	lb	0.0010	kg	*
COD, Chemical Oxygen Demand	0.010	lb	0.010	kg	*
Copper	1.0E-06	lb	1.0E-06	kg	*
Suspended solids, unspecified	0.0010	lb	0.0010	kg	*
Phenols, unspecified	1.0E-04	lb	1.0E-04	kg	*
Nickel	1.0E-06	lb	1.0E-06	kg	*
TOC, Total Organic Carbon	0.010	lb	0.010	kg	*
Aniline	1.0E-04	lb	1.0E-04	kg	*
Benzene, chloro-	1.0E-05	lb	1.0E-05	kg	*
Methanol	1.0E-04	lb	1.0E-04	kg	*
4,4'-Diaminodiphenylmethane	1.0E-05	lb	1.0E-05	kg	*
Solid Wastes					
Solid waste, process to landfill	0.042	lb	0.042	kg	
Hazardous waste to landfill	0.16	lb	0.16	kg	
Hazardous waste to incineration	0.11	lb	0.11	kg	
Water Consumption	279	gal	2,330	l	

* To indicate known emissions while protecting the confidentiality of individual company responses, the emission is reported only by the order of magnitude of the average.

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