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A SAFER ROUTE TO MDI, An assessment of a phosgene free manufacturing process

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A SAFER ROUTE TO MDI

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 process

February 2010

Jeroen Vetter



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Jeroen Vetter
A SAFER ROUTE TO MDI
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A SAFER ROUTE TO MDI

An assessment of a phosgene free manufacturing process

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Abstract

In this research the technological and economical feasibility of a new technology for the production of methylene diphenyl diisocyanate (MDI) is assessed.

Context

The global consumption of MDI totalled 4,150 kT in 2009 and an annual growth of 4.6% is expected until 2013. MDI is almost exclusively used for the production of polyurethane (PU). Currently the growth has stagnated due to the financial crisis, but it is still expected that this downfall is temporary, and that additional capacity investments are needed in the future.

At the moment all commercial MDI production technology is based on a phosgenation process. In this process phosgene is used as a feedstock component. Phosgene is a highly toxic gas and therefore causes major safety hazards. It is also a controversial material because it can, and has been used as a chemical warfare agent. Consequently phosgene using production processes are banned from many regions, especially the Middle East.

A lot of scientific research has been conducted on phosgene free production processes of MDI, though none of these processes has been commercialized. This study assesses the technological and the economical feasibility of the most viable phosgene free route to MDI. The studied route consists of three steps:

- The synthesis of methyl phenyl carbamate (MPC) from aniline and dimethyl carbonate (DMC) feedstock.
- MPC is condensed with formaldehyde to form dimethyl methylene diphenyl dicarbamate (MDC).
- MDC is thermally decomposed to MDI. Methanol is produced as a valuable by-product.

The major advantages of a phosgene free route to MDI are: (1) the process contains less safety hazards and (2) the availability of a competitive phosgene free route to MDI does comply with the strict regulations in all regions and thus create new business opportunities.

The research was initiated by Fluor; Fluor is a "Fortune 500" company that delivers engineering, procurement, construction, maintenance (EPCM), and project management to governments and clients in diverse industries around the world, including the PU industry. The research is intended for use in business development activities.

Goal

The goal of this research is to assess the process technologies and economics of a phosgene free production process of MDI in an effort to support a Fluor strategy for further development in these markets.

This goal has led to two main research questions:

1. Is it technologically feasible to produce phosgene free MDI on a commercial scale?
2. Is it economically feasible to produce phosgene free MDI on a commercial scale?

Conclusions - Technological feasibility

The studied phosgene free production process is technologically feasible but it still contains many uncertainties. Therefore additional research is necessary before the phosgene free technology can be implemented on a commercial scale. The most important uncertainties are the following.

1. The actual reaction performance of all three synthesis reactions on a large scale.

2. The quality and functionality of the produced MDI.
3. The physical properties of all process components.
4. The separation of the DMC:methanol azeotrope.

Based on these conclusions, four steps are necessary to develop a proven process that can be up scaled to a production plant of commercial scale:

1. The physical properties and process behaviour of many components need to be investigated.
2. A reliable catalyst system for each reaction needs to be developed.
3. A separation method for the DMC:methanol azeotrope needs to be developed.
4. A pilot plant needs to be set up to prove and optimize the process.

Conclusions - Economical feasibility

The currently available phosgene free MDI production technology is economically inferior to the conventional technology. The new technology does need financial investments, but the current financial situation, with low MDI prices, is not an incentive for additional capacity investments. Moreover, the currently installed production capacity of MDI is expected to be sufficient to meet the global demand until 2013 at least. Regardless of the financial crisis, growths in the MDI markets are still expected.

Even though the phosgene free technology is not competitive today, this study indicates that it does have the potential to become cost competitive. Governments and legislative institutions could impose stricter legislation and thereby stimulate the development of the phosgene free technology and enforce a transition in this market. This is a very plausible situation since the new technology can be cost competitive in comparison to the conventional technology and it does show significant improvements concerning HSE (Health, Safety, Environment). The polycarbonate case is similar to that of MDI and does confirm this sequence of events.

The phosgene free MDI production technology may eventually become economically feasible when future circumstances change, for instance if (1) stricter legislation is imposed, (2) the performance of the phosgene free process is improved and/or (3) if the DMC cost is decreased.

Path forward – Fluor

Phosgene free production of MDI is not expected to become reality in the near future and new MDI plants will probably still be based on the conventional phosgenation production process, unless there are significant improvements in the phosgene free technology or stricter governmental legislation is imposed that would restrict the phosgene using MDI production technology and enforces alternative technologies. The latter case is not unlikely as it happened before in the similar polycarbonate technology.

For Fluor this implicates that there are multiple options possible; which range from an active to a proactive stance.

The active stance means that no immediate action is taken. The situation and developments in the MDI market will be monitored and if the business environment changes, i.e. due to technological breakthroughs or stricter governmental regulations, Fluor can act accordingly. As long as the status quo is maintained, business is continued as usual.

The proactive stance implies that Fluor will interfere in the discussion by actively promoting the development of the phosgene free MDI production technology. Promotion can be done by, for example, publishing articles that support the development of the new technology or collaborating with public or private research institutions to increase scientific progress in this field. In this way it could accelerate a transition to a new production technology in the MDI markets. By finding strategic

partners and be directly involved in new developments, this option could result in Fluor being a frontrunner in an emerging market of phosgene free MDI production.

Fluor has a very active policy concerning HSE; therefore the proactive stance would be in line with the company's strong sense of global responsibility and could even strengthen the position of Fluor in this field. However, Fluor is also a public owned company and therefore focused on profits; active involvement in the development of this new technology will consume resources and it is not certain whether it will be profitable. A trade-off has to be made between the degree of involvement and the amount of resources that Fluor is willing to dedicate to the development of a phosgene free MDI production technology.

Path forward – Scientific community

Phosgene free MDI production is not economically viable based on the current knowledge. However, this research does show that the cost of the described phosgene free process is similar to that of the conventional process. Moreover, there is definitely a cost competitive potential; especially if legislation is enforced to accelerate the development of the phosgene free MDI production technology. The major disadvantage of the technology is that the described phosgene free process is new and therefore contains many uncertainties, as opposed to the fully developed conventional production process.

As described in the 'Conclusions - Technological feasibility' paragraph above, there are four major steps necessary to develop a proven process for phosgene free MDI production. These steps serve as recommendations for further research and can be addressed by the scientific community.

However, to utilize the economical potential of the new technology, it does not only need to be proven but it does need improvement. Therefore more concrete targets for experimental research are set. These targets are derived from the economical feasibility study. Reaching these targets would significantly improve the competitive position of the phosgene free technology. The targets are the following.

- The amount of nitrobenzene needed has to be decreased by at least 50%.
- The reaction performance of the MPC synthesis reaction has to be improved; (1) the DMC:aniline ratio needs to be decreased from 7:1 to 2:1 and (2) the residence time of 8 hours needs to be decreased in order to minimize the reactor volume.

Jeroen Vetter
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Preface and acknowledgements

I started my master's thesis at Fluor in Haarlem in September 2009. At that moment in time, I did not know anything about MDI, Haarlem or Fluor. Now I have completed a solid report on phosgene free MDI production, I enjoyed living in Haarlem for six months and got to know, and like, Fluor and many of its employees. It was a great time with a satisfying result!

The research I conducted during the past six months touches many aspects of the courses that I followed in Groningen. The thesis contains a significant technical part; as it discusses several routes to MDI and a conceptual design of a phosgene free MDI production process. The technical part is directly linked to the manufacturing economics via a cost of production estimation and a NPV analysis. The strong connection between the economical and technical part is clearly demonstrated in the scenario analysis; which translates technological variations in financial results. This is very much in line with the IEM philosophy and therefore a great subject to work on.

During the research I was very well supported by Fluor; Gert Smit, as my direct supervisor, always succeeded in asking the right questions that could put things in perspective and pushed me in the right direction. The support of Hans Göebel was also of great value; Hans flawlessly picked out the weak spots in my argumentations, also he guided me through the process part of the AspenTech software that I used for the simulation models. I would also like to thank Ard Paardekooper and Martijn Koster of the estimation department; they introduced me to the world of estimation and helped me to set up my capital cost model. Last but not least, I would like to thank Daan Berends as he introduced me to all the right people and made sure I had a very good kick off at Fluor. I really enjoyed the open and international atmosphere in the Haarlem office.

At the University of Groningen I received great support from my supervisors; Francesco Picchioni was always available for high quality feedback, especially the speed at which he responds is remarkable. I would also like to thank Michel Boesten for sharing his deep knowledge of process design issues. Finally I would like to thank Wout Prins for his supervision and feedback, especially related to the research design subject.

With the experience gained in the past six months I am confidently looking forward to face the (phosgene free) future as a Master of Science!

Jeroen Vetter
February 15, 2010

Jeroen Vetter
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Abbreviations

Abbreviation	Meaning
BFD	Block Flow Diagram
CEI	Dow's Chemical Exposure Index
CO	Carbon monoxide
CoP	Cost of Production
CSR	Corporate Social Responsibility
DMC	Dimethyl carbonate
DOS	Di-n-octyl sebacate
DPU	Diphenyl urea
FAR	Field Auxiliary Room
Fdh	Formaldehyde
FEI	Dow's Fire & Explosion Index
HCl	Hydrochloride
HSE	Health, Safety, Environment
IARC	International Agency for Research on Cancer
kTa	Metric kilotonnes per year
MDA	Diaminino diphenylmethane
MDC	Dimethyl methylene diphenyl dicarbamate
MDI	Methylene diphenyl diisocyanate
MNB	Nitrobenzene
MPC	Methyl phenyl carbamate
NMA	N-methyl aniline
NPV	Net Present Value
OPWC	Organization for the Prohibition of Chemical Weapons
PC	Polycarbonate
PFD	Process Flow Diagram
PU	Polyurethane
r.t.	Residence time
TDI	Toluene diisocyanate
THF	Tetrahydrofuran
UNEP	United Nations Environmental Programme
WHO	World Health Organization

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1. Research Design

This chapter will give a brief introduction into the research subject and its origins. First the problem is analyzed from different perspectives, then the research goal, conceptual model and research questions are formulated. All the above is according to the research methodology theory as posed by Verschuren en Doorewaard¹. A more detailed introduction of MDI is given in chapter 2.

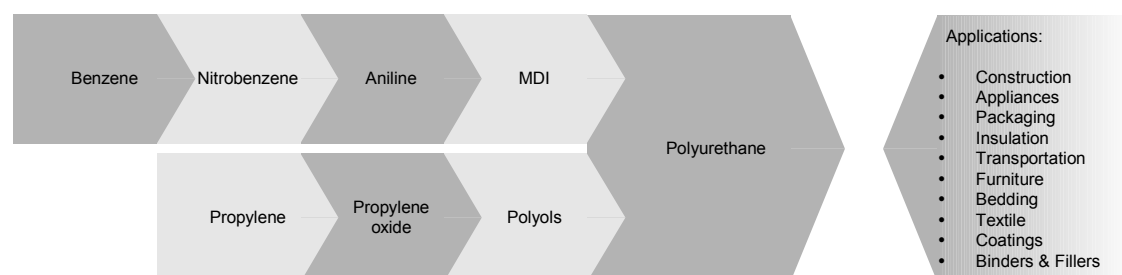
1.1. Introduction

Global safety standards and environmental regulations are getting stricter with each minute, therefore all health and environmental threats in chemical processes are to be minimized. For this reason also the use of phosgene is widely criticized. Phosgene is a highly toxic and reactive gas that was used as a chemical weapon in the First World War, therefore its use is very controversial⁵, it is under strict supervision of the OPWC (Organization for the Prohibition of Chemical Weapons). Many efforts have been made to avoid the use of phosgene in industrial production processes.

Phosgene is mainly used in the production process of diisocyanates and that of polycarbonates. Methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), which are the two main diisocyanates, accounted for 75% of the global phosgene consumption in 2006, polycarbonates are the balance. In 2006, 7% of the globally produced polycarbonates were produced without the use of phosgene and this figure is expected to have risen to 15% by 2010. For TDI, the Japanese company Mitsui Chemicals Polyurethanes is developing a phosgene free manufacturing process that is planned to be operational in 2011. For MDI, which is the largest consumer of phosgene with 46% of the total consumption in 2006, there is no commercial scale phosgene free manufacturing process, either planned or present⁵. Therefore this subject is investigated in this study.

MDI is one of the major chemical products, global consumption in 2009 was approximately 4,150 kTa³³. MDI is almost exclusively used to produce polyurethane (PU), which finds applications in a wide range of industries; a.o. construction, refrigeration, transportation. MDI is typically produced from aniline, formaldehyde and phosgene as feedstock products, in a two step production process that is described in more detail in paragraph 3.1. The value chain of MDI, including several applications, is shown in Figure 1-1 below.

Figure 1-1 Value chain of MDI based PU



A lot of private and public research has been conducted in the subject area of phosgene free production of MDI but none of the phosgene free MDI production processes has been commercialized yet. This report determines the most viable phosgene free route to MDI that is currently available, and assesses the technological and economical feasibility of a commercial sized plant that is based on that phosgene free MDI production technology.

A more detailed description of the components MDI, PU and phosgene is given in the first paragraphs of chapter 2.

1.2. Academic debate

At this moment there are several commercial ways to produce MDI but they are all based on the same reaction process; they are all using phosgene. In the two step reaction process, aniline and formaldehyde are used to produce diphenylmethanediamine (MDA). MDA is then combined with phosgene to produce MDI². The conventional reaction is described in more detail in paragraph 3.1.

The conventional reaction has two main problems. First, highly toxic phosgene is used in the second step of the production process, more details are found in paragraph 2.3; The second problem is the formation of HCl; which is highly corrosive and therefore requires special, thus expensive, equipment and maintenance for regular manufacturing; it has the T and C classification of the directive of dangerous substances set by the EC REACH program³⁵.

On industrial scale all MDI production processes are based on the phosgene reaction scheme as it is described above. Because of the safety issues of the process there is a lot of research conducted on alternative, phosgene free production processes for MDI.

Phosgene free production of MDI can be achieved by the thermal decomposition of dimethyl methylene diphenyl dicarbamate (MDC) to MDI. MDC is not commercially available but there are multiple routes to manufacture MDC, of which the two major ones are: (1) the condensation reaction between MPC (methyl phenyl carbamate) and formaldehyde and (2) the methoxycarbonylation of MDA. Both reactions can be conducted in more ways which will be discussed in chapter 3.2. The first reaction seems to be most attractive for commercialization at this moment³.

As mentioned before, none of the phosgene free production processes have been industrialized yet. The main reasons being that the alternative processes still suffer from the formation of invaluable by-products, insufficient catalyst stability, selectivity, efficiency and recovery, all these factors are rendering them economically unviable^{4, 5}. However the use of phosgene is becoming more controversial and many believe that phosgene free production of MDI on industrial scale will become reality in the near future⁶. This report describes the available techniques for phosgene free MDI manufacturing and accordingly develops a conceptual production process on industrial scale for the global MDI market. This design will show the most viable way to industrialization of phosgene free MDI that is currently available. The costs of the production process based on this design will be estimated and compared to the costs of conventionally produced MDI. The report will expose weaknesses in the currently available technology to produce phosgene free MDI and will therefore serve as a guideline for further scientific research in this specialty area, as it will show the needs of the industry. Also, it will give an update on the current status of phosgene free production of MDI.

1.3. Context of the research

The theoretical study of the technology and economics of phosgene free MDI manufacturing was initiated for business development purposes by Fluor B.V. in Haarlem, the Netherlands. This paragraph gives a brief description of the general activities of the Fluor Corporation and its interests in this research subject.

Fluor Corporation

Fluor is a company that delivers engineering, procurement, construction, maintenance (EPCM), and project management to governments and clients in diverse industries around the world. Fluor is a "Fortune 500" company⁷.

Founded as a construction company in 1912, Fluor quickly built a reputation for applying innovative methods and performing precise engineering and construction work within the emerging petroleum industry. Today, Fluor continues to develop and implement innovative solutions for complex project issues in diverse industries, including chemicals and petrochemicals, commercial and institutional (C&I), government services, life sciences, manufacturing, mining, oil and gas, power, renewable

energy, telecommunications, and transportation infrastructure. A full list of the industries that Fluor serves and the services that they offer is shown in Table 1-1.

Fluor has an international workforce of more than 40,000 employees that work either on project offices or one of Fluor's home offices. Fluor has a network of home offices in more than 25 countries across all continents. Fluor is a major player in the global building services marketplace; Engineering News Record (ENR) magazine consistently ranks Fluor Corporation among the top three on "The Top Design-Build Firms" list and "The Top 400 Contractors" list⁸.

Table 1-1 Fluors operating industries & services

Industries	Services
Biotechnology	Conceptual, Basic & Detailed Engineering
Chemicals & Petrochemicals	Procurement
Commercial & Institutional	Construction
Equipment	Operations & Maintenance
Government Services	Project Management
Gas Processing	Program Management
Manufacturing	Staffing
Microelectronics	
Mining	
Offshore Services	
Oil & Gas Production	
Petroleum Refining	
Pharmaceuticals	
Power Generation	
Telecommunications	
Transportation	

Fluor Haarlem

The Fluor Haarlem office is a "full service EPC (Engineering, Procurement & Construction) center" for the following business lines; Downstream (oil refining and petrochemicals), Chemicals and on an opportunistic basis also upstream (oil and gas exploration). Currently the office is staffed with about 600 technical and project support employees. Major clients include many international corporations such as Shell, TotalFinaElf, KNPC, BASF, DSM, ConocoPhillips and also regional players such as OMV, Ruhl Oel, Ceska, Nam, PKN and the Dutch state. The Haarlem office predominantly executes projects located in Europe, Africa, the Middle East, China and the former Soviet Union.

Fluor has always been an active contractor in the PU market and does have several clients and contacts among the major players in these markets. In the recent past the Fluor Haarlem office had contact with a major MDI producer that wanted to extent its capacity in Europe. Because of the difficult financial climate in the beginning of 2009, this project was suspended. However, from the meetings in that period it became clear that the phosgene free production of MDI on an industrial scale is getting closer to realization⁸⁵. In an effort to strengthen the position of Fluor in this market as a contractor, they want to know what technologies are available in this specialty area and what needs to be done to achieve commercialization.

Phosgene free MDI technology is also attractive for MDI production capacity in the Middle East region. Production processes using phosgene are banned from this region due to the potential use of phosgene as a chemical warfare agent; these countries do not want to be connected to hypothetical abuse of this material. A competitive phosgene free production process would open new business opportunities, in this region, for Fluor.

In general the information in this report can be used to develop a Fluor strategy for the future MDI market. Also the information in this document will improve Fluor's insight in the MDI market and will improve its position to approach manufacturers of MDI.

Other stakeholders

Besides Fluor there are also other stakeholders in this research, these are listed and briefly discussed below.

- Scientific community; this report bridges the gap between scientific research and industrial needs and points out the weak points in the current technology. Therefore it is very useful as a directive for further scientific research.
- MDI producing companies; This report gives an insight in the current status of phosgene free MDI production technology that might be the industry standard in the future, MDI producing companies will have to adapt to this possible change in the market.
- Governments and governmental institutions; this report gives an insight in the current status of phosgene free MDI production technology, this technology is safer and less controversial than the conventional technology. Therefore it might prove to be a suitable alternative which can have a serious impact on permit policy.
- Suppliers; This report gives an insight in the current status of phosgene free MDI production technology, this technology uses other supplies and especially demand in DMC might increase significantly. Suppliers will have to be ready for this new technology.
- Buyers; According to the recent emphasis on green and safe products, phosgene free MDI can be an attractive feedstock product for PU producing companies on CSR level.
- Phosgenation licensors; The market share of existing phosgenation licensors may decrease, or even disappear, if the phosgene free technology can successfully be commercialized.

The report also gives recommendations directly addressed at the scientific community. The government and its institution is also an interesting stakeholder since they are responsible for permitting. The existence of an alternative production process for MDI that avoids the use of phosgene and is competitive to the conventional process, can change regulations and therefore the entire market. This subject is discussed in more detail in paragraph 2.3.

1.4. Goal definition

In this paragraph first a brief problem statement is given, mainly based on the previous paragraphs, then a goal is formulated and the deliverables of this research are described.

Problem statement

Currently the production of isocyanates is controversial. The only commercial route to isocyanates is by reacting aniline and formaldehyde in a phosgenation reaction. This method has significant drawbacks; highly toxic and corrosive phosgene is used, and HCl is produced as a by-product. These two components make the industrial process risky and complicated. Phosgene is also controversial since it can be used as an agent in chemical weapons. To prevent accidents the safety measures are very high and therefore the process hardware and maintenance is expensive. In addition to the expenses it also poses health risks for handling personnel and it poses a threat to the environment which does make it difficult to get permits, especially in the Middle East region.

This can be broken down into two main issues that are related to the phosgene containing production process.

- Phosgene is highly toxic and therefore jeopardizes the safety of personnel and the environment.
- Phosgene is controversial since it is also an agent in chemical weapons, therefore it is banned or heavily restricted in many regions around the world, especially the Middle East.

The first issue is confirmed in the safety analysis in paragraphs 2.5 and 4.9. The second issue is quantified and confirmed in the market analysis of MDI in paragraph 2.6.

For the reasons above, this subject received a lot of scientific attention in the recent years. The conducted research yielded several phosgene free routes to isocyanates of which the routes to MDI are particularly interesting. None of the found phosgene free routes to MDI was industrialized yet and therefore the existing research didn't have any real impact yet and phosgene is still widely used in MDI manufacturing.

The two major advantages of a phosgene free route to MDI are: (1) the phosgene free process improves safety and (2) a competitive phosgene free route to MDI would be able to comply to the strict regulations concerning HSE, and create new business opportunities. Although there are clear advantages to the new MDI production technology, it still has to be technologically and economically feasible to implement it.

Fluor believes that the research of Zhao et al.³ proposes a route to MDI that can be economically feasible and Fluor wants to develop this research into a concrete method that can be taken to commercialization in the nearby future. In this report the research of Zhao et al. is evaluated and compared to other phosgene free routes to MDI. The study renders an assessment of the most viable phosgene free route to MDI that can be used for business development purposes by Fluor.

Goal definition

The goal of this research is to assess the process technologies and economics of a phosgene free production process of MDI in an effort to support a Fluor strategy for further development in these markets.

Deliverables

This report will deliver an assessment of the currently available technology and the current economics of phosgene free production of MDI that will indicate the current status of this technology in the present business environment. The deliverables are listed below, it is limited to a conceptual design, this is assumed to be sufficient at this stage of the research. Many more resources are necessary if a more detailed study has to be conducted, these are not available or necessary.

It includes:

- An assessment of all major phosgene free routes to MDI which are present in the public domain.
- The conceptual design of a phosgene free production process on commercial scale; including flow schemes, sized equipment lists, stream summaries, basis of design.
- A cost of production estimation of the phosgene free produced MDI.
- A financial analysis containing a cost of production estimation of the phosgene free MDI production process, a scenario analysis, a sensitivity analysis and a NPV analysis.
- A small HSE analysis of the new process based on Dow's Chemical Exposure Index³⁸ and Dow's Fire & Explosion Index³⁹.
- General MDI trading market information.

- Recommendations for further action for Fluor B.V. based on the assessment of the technological and economical feasibility of the phosgene free production process of MDI.
- Recommendations for further action for the scientific community based on the assessment of the technological and economical feasibility of the phosgene free production process of MDI.

It does not include:

- An empirical study of phosgene free MDI production; this would be a very valuable asset since there are several uncertain factors in the studied technologies. However, there are several hazardous substances present in the technology, which require safe lab facilities and experienced personnel, both are not available for this study.
- A production process design of phosgene free MDI that is suitable for construction of either a pilot plant or an industrial plant. This is not possible due to time and capacity restrictions. To have the documentation that is necessary for actual design much more personnel and more experience is required. This is a conceptual study and therefore these resources are not available at this stage.

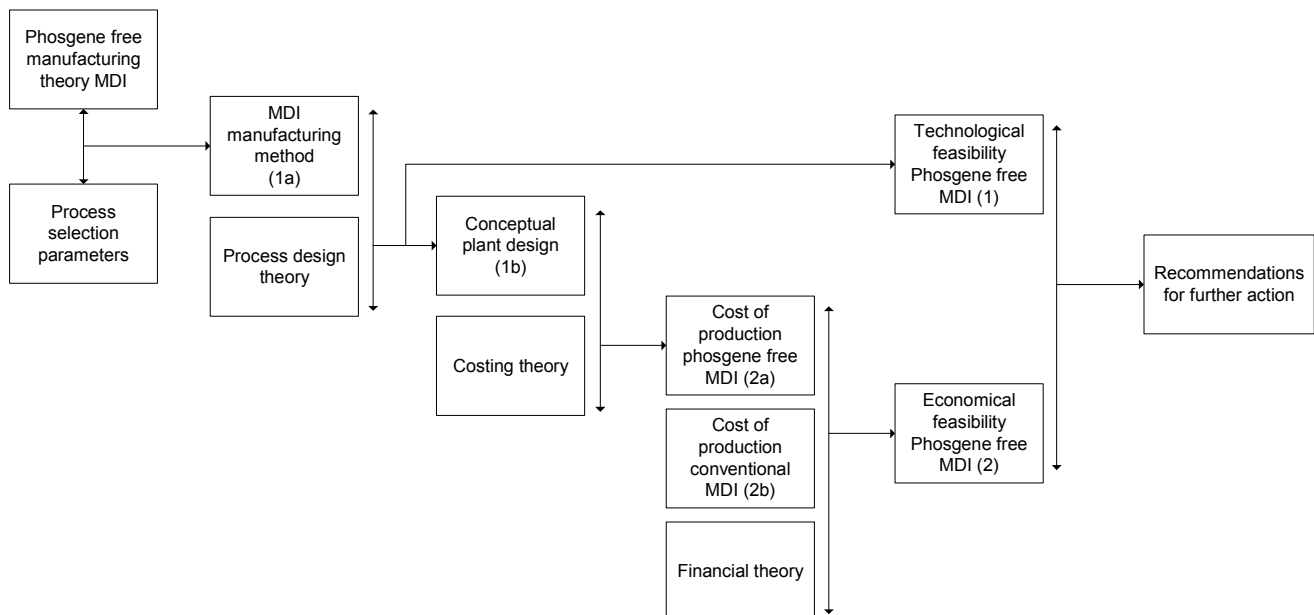
1.5. Conceptual model and research questions

This paragraph describes the conceptual model and the associated research questions. The model will serve as a guideline throughout the research. The model and the research questions will be used in an iterative way.

Conceptual model

To come to the recommendations for Fluor the technological and economical feasibility of the production method is assessed. This is done according to the model shown below.

Figure 1-2 Conceptual model



In this model, shown in Figure 1-2, all the available technologies are first reviewed based on public domain data. From these technologies the most promising one is selected based on a set of process selection parameters. With this phosgene free MDI manufacturing method and general process design theory, a conceptual plant design is made. At this point an assessment of the technological feasibility can be made.

The conceptual plant design in combination with costing theory will render a cost of production estimation of phosgene free MDI. Also a cost of production estimation of conventionally produced MDI can be derived from existing costing data on this production method. The cost of production estimations of both methods can be compared and are used for several financial analyses to assess the economical feasibility of phosgene free produced MDI.

The two feasibility assessments will lead to an assessment of phosgene free MDI as a whole and recommendations for further action for Fluor and the scientific community. Based on this conceptual model several research questions are formulated below. The research questions are directly linked to the conceptual model.

Research questions

1. Is it technologically feasible to produce phosgene free MDI on a commercial scale?
 - a. What is the most promising phosgene free manufacturing method for industrial production of MDI that is currently available?
 - b. What does the phosgene free manufacturing process of MDI look like, if designed on a commercial scale?
2. Is it economically feasible to produce phosgene free MDI on a commercial scale?
 - a. What is the cost of production for phosgene free produced MDI?
 - b. What is the cost of production for conventionally produced MDI?

The research questions will be discussed in the following chapters. Question 1a is answered in chapter 3; which gives an assessment of the major phosgene free routes to MDI based on process criteria. Question 1b is answered in chapter 4; in this chapter a base case process design is given including a basis of design, flow schemes, stream summaries, a small HSE analysis and a full sized equipment list. These deliverables will be yielded by using the most up to date software of AspenTech; Aspen Plus V7.1 and Aspen Capital Cost Estimator V7.1. AspenTech is the leading brand in this specialty area and it's process design software is used by both Fluor and the University of Groningen. If the production plant design is finished it is possible to assess the technological feasibility of the phosgene free MDI production process.

Questions 2, 2a and 2b are answered in chapter 5. In this chapter the cost of production for the base case process design is estimated and compared to several scenarios derived from the base case scenario. It is also compared to the cost of production estimation for conventionally produced MDI that is derived from existing cost data. The comparison is based on a sensitivity analysis. Chapter 5 also includes a financial analysis in which the net present value (NPV) of each scenario is calculated. This will render an assessment of the economic feasibility of phosgene free production of MDI.

Chapter 6 finally summarizes the answers on the research questions and gives recommendations for further action. A general introduction of MDI is given in chapter 2.

1.6. General sources

In this paragraph the general resources that were used in this research and are paramount in this specialty area are briefly addressed. This overview forms the framework for the conducted literature research that is mainly described in chapter 3.

The initiative to execute this research on phosgene free MDI production came forth from discussions in early 2009 between Fluor and a major MDI producer that wanted to expand its capacity in Europe⁸⁵. From these discussions it became clear that the current markets and technology do not allow cost competitive, phosgene free MDI production. Fluor decided it wanted to test this statement and issued a small literature study in which it encountered an article on the research performed by Zhao et al.³ This article describes a phosgene free production process of MDI from dimethyl carbonate (DMC) and aniline over solid catalysts. Zhao's research forms the basis of this study. Another study based on this technology was already conducted by Berends at Fluor⁷⁸.

The Japanese chemical company Asahi Kasei is currently the owner of the most promising technology for the phosgene free production of MDI. Their research group is lead by the chemist Shinsuke Fukuoka. However, his recent publications are focused on the production of aromatic carbonates. Asahi Kasei's main patents on phosgene free MDI production date back from the 1980s and 1990s^{9,10}. More recent publications on this subject are based on the research conducted by an Italian research group lead by Fabio Ragaini from the university of Milan¹¹ and several Chinese and Indian researchers^{12,13,14}. SciFinder, ScienceDirect and ISI Web of Knowledge¹⁵ were used to execute an exhaustive scientific literature search.

General information on MDI markets and production processes is found in the "Process Economics Program" and "Chemical Economics Handbook" documents provided by SRI Consulting¹⁶. News, material prices and plant and project information is provided by, Reed Business owned, ICIS.com¹⁷. Process design support is provided by Fluor, information on this subject is found in Fluor documents and experience and in the books of Coulson & Richardson's^{18,19}. Process design software of AspenTech²⁰ is used, this is the industry standard and it is also used by Fluor and the University of Groningen.

1.7. Discussion on research

In this paragraph a brief discussion on the position of this report in the public domain is given. The report handles three subjects of phosgene free MDI production; (1) a general public domain review, (2) a conceptual plant design and (3) a financial analysis.

There are more general reviews on phosgene free MDI production^{21,22}. Although it is not unique, it is the most recent review on this subject and it is focussed on the conceptual design of a commercial production process of phosgene free produced MDI.

The second subject and the third subject are seminal; in the public domain there is not such a detailed model that describes the phosgene free production process of MDI both on technological and financial level. In the reports of SRI Consulting¹⁶ and on ICIS¹⁷ several general estimations on this subject are given but none of them offers a detailed model that discusses sensitivity and different scenarios.

2. General Information

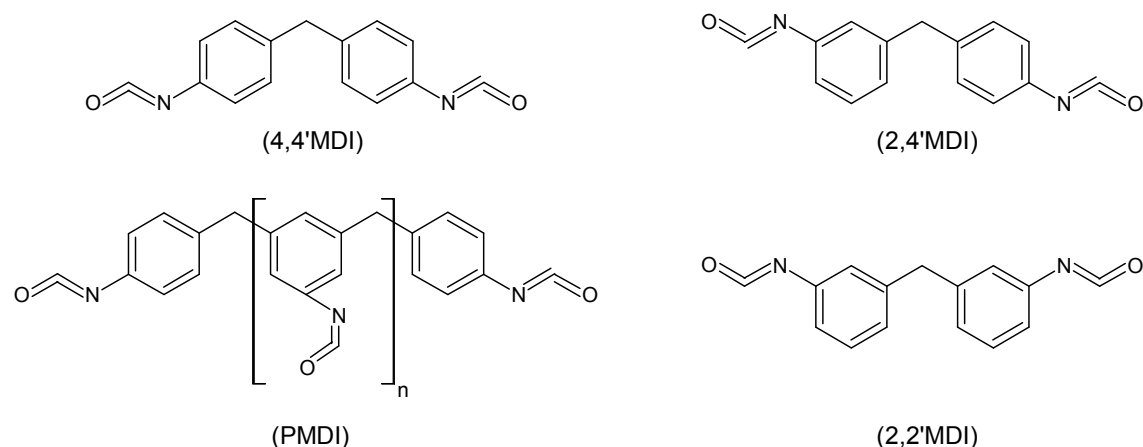
In the first paragraphs of this chapter the components MDI, polyurethane (PU) and phosgene are discussed in more detail. In the final paragraphs applications and trading markets of MDI are discussed in more detail. In paragraph 2.5 the HSE issues of MDI production are discussed and a brief HSE analysis of the conventional MDI production process with phosgene is given.

2.1. MDI

MDI is a diisocyanate; diisocyanates and polyisocyanates are reactive intermediates that are characterized by terminal isocyanate ($-N=C=O$) groups. MDI, and other isocyanates as well, are usually reacted with the hydroxyl ($-OH$) group of polyols to form polyurethanes. Crude MDI is usually derived from aniline and is a mixture of polymethylene polyphenylene isocyanate (polymeric MDI or PMDI) and p,p'-methylene diphenyl diisocyanate (MDI). Pure MDI consists only of the latter mentioned, monomeric, form of MDI.

The main variable of MDI is its functionality; functionality is the average number of reactive groups ($-N=C=O$ for isocyanates) per molecular unit. MDI is supplied in various forms, the bulk is PMDI which has a functionality between 2.3 and 3.0. Pure, monomeric MDI, logically has a functionality of 2. The grades that are used in the production of rigid foams have a functionality of 2.6 - 2.7 and typically contain 30 - 40% pure MDI; the balance is dimers and polymers, other isomers of MDI (2,2'MDI or 2,4'MDI) and their dimer, trimer and polymeric species³³. The structures of all abovementioned molecules are shown in Figure 2-1.

Figure 2-1 MDI molecules



Pure MDI is a monomer and at atmospheric conditions it is in solid form, PMDI is a low viscosity liquid at atmospheric conditions. In this report, the general term MDI refers to crude MDI or another unspecified form of MDI, pure MDI refers specifically to the pure form of the product.

2.2. Polyurethane

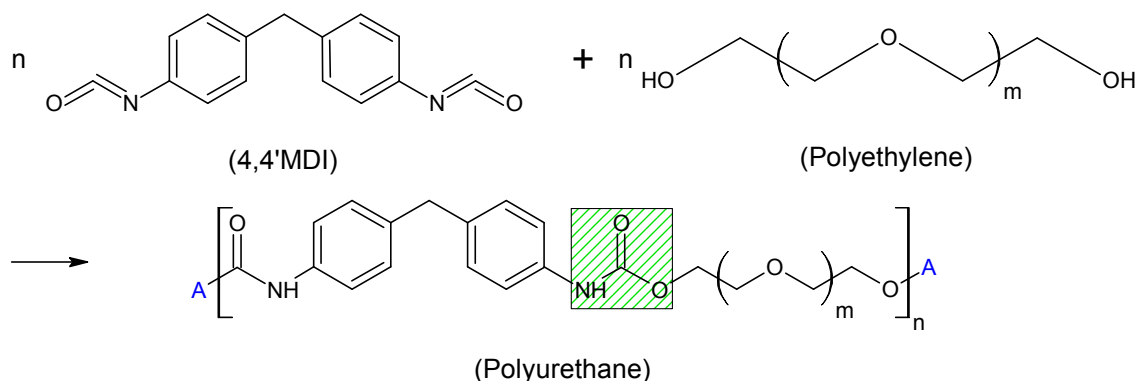
Polyurethane (PU or PUR) was discovered and reported by Bayer in 1937²³, nowadays it is a widely used plastic and more than 11 million metric tonnes are produced annually. PU occurs in two main forms; PU foams and PU elastomers. With a global production of 8.9 million metric tonnes in 2009²⁴ the PU foams market is well ahead of the PU elastomers market that has a global production of approximately 1.9 million metric tonnes in 2009²⁵.

Globally the PU foams market is almost equally divided between rigid and flexible foams. Flexible PU foams are used mainly as a cushioning material in furniture, transportation and bedding. Rigid PU foams are used primarily as an insulation material in construction and refrigeration applications. The PU elastomers global market can also be divided in two main parts; thermosetting elastomers and thermoplastic elastomers of which the thermosets have the largest market share of 75%²⁵.

There are several different methods to produce PUs which depend on the end-use of the final product. In each method there are two main raw materials; polyols and di- or polyisocyanates. Polyols are prepared from a propylene feedstock and isocyanates are prepared from a benzene feedstock. In Figure 1-1 the upstream supply chain of PU is shown, including applications. In this supply chain MDI is used as the isocyanate feedstock, typically MDI or TDI (toluene diisocyanate) are used as feedstock products for the production of PUs. This polyaddition process of diisocyanates is the only technically reasonable production method for PU plastics today. Therefore the manufacturing methods and properties of diisocyanate feedstocks make the deciding factor for PU production; the largest PU producers have their captive isocyanate raw materials production capacity in the same location as their isocyanate and PU production facilities²⁶.

A PU molecule is a polymer that consists of organic units which are connected by urethane links. The urethane link is highlighted in Figure 2-2. The urethane link is the connection between the -OH group of the polyol and the -NCO group of the isocyanate. Figure 2-2 shows the condensation of 4,4'-MDI and polyethylene glycol to a polyurethane.

Figure 2-2 Condensation of polyurethane



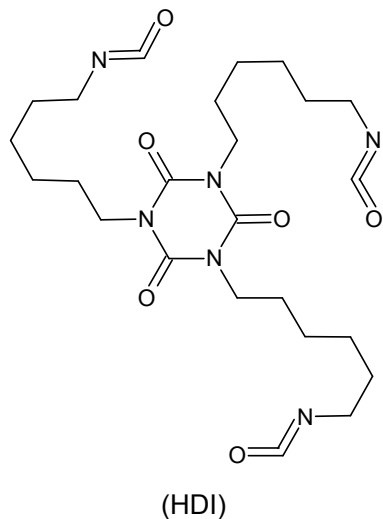
PUs may be widely used; there also are some controversial environmental and safety issues with this plastic. A blowing agent is used for the production of PU foams, this blowing agent used to be conventional chlorofluorocarbon (CFC) but the use of this ozone depleting compound and its derivatives was restricted by the Montreal Protocol that took effect in 1989²⁷. Since then there are several alternative blowing agents in use such as methylene chloride (MC) and acetone, however these two substitutes are also toxic and therefore controversial as well²⁴.

Another safety issue of PU is the use of isocyanates, especially the more volatile compounds are very dangerous. This has become painfully clear in the Bhopal disaster in India, 1984. In this tragic industrial accident 42 tonnes of methyl isocyanate escaped from a pesticide factory killing more than 8,000 people in the surrounding area²⁸. In the production of PUs, typically heavier compounds are used which are not as volatile as methyl isocyanate. But there are still issues with this feed material; isocyanates are the largest cause for occupational asthma. This is true especially in the car industry.

In the car industry usually the trimer hexamethylene diisocyanate (HDI), shown in Figure 2-3, is used for forming PU coating. This coating is dried chemically; the polyol and diisocyanate react to form polymer network. Since HDI is used, which has three -NCO groups, a strong network polymer is formed which is much more resilient than a regular chain polymer coating. The PU coating is is

synthesized directly on the car surface and therefore personnel exposure is much higher than in closed chemical production of most other PUs²⁹.

Figure 2-3 Hexamethylene diisocyanate (HDI)



The second feedstock product of PUs are polyols; typically polyether polyols, which account for 90% of the total consumed amount, the balance is polyester polyols³⁰. Polyols are usually produced internally by isocyanate manufacturers, or by a related company³³. Since, besides some niche applications like HDI, there are only two different diisocyanate feedstock products for PU, TDI and MDI, the large variety of PUs is mainly caused by the variation in polyols. The choice of polyol, especially the size and functionality of the molecule, determines the degree of cross-linking in the PU molecule. If there is more cross-linking within the PU molecule it is typically stiffer, if the degree of cross-linking is low it will be more flexible.

Also with polyols there is an opportunity to make the process greener; a recent development is the use of bio-based polyols. These are not based on the petrochemical industry but can be obtained from renewable sources such as soybeans. This results in supply chain shift: from the petrochemical industry to the food industry, with players like i.e. Cargill³¹.

In the commercial production processes of TDI and MDI phosgene is used as a reactant. Phosgene is controversial and causes safety hazards, a more detailed description of phosgene is given in the paragraph below.

A lot of research has been conducted on alternative routes to PU without the use of either phosgene or isocyanates. The production of PU without the use of isocyanates seems to be farfetched at the moment. Especially in the car industry, where it poses the largest health risks due to on-site polymerization, it is difficult to abandon isocyanates because it has the unique capability to bind with three polymer chains at once and thereby forming a strong polymer network coating. This is only possible if isocyanates with 3 or more isocyanate groups are used; i.e. PMDI or HDI³².

The prospects of phosgene free manufacturing of isocyanates in the nearby future are much better; especially the recent developments in phosgene free production of MDI, or 4,4'-methylene diphenyl diisocyanate and polymeric MDI (PMDI), are very promising. The global production of MDI in 2008 was approximately 3.9 million metric tons³³ and is therefore the most produced isocyanate. However, none of this MDI was produced without the use of phosgene.

2.3. Phosgene

Phosgene (carbonyl chloride), shown in Figure 2-4, is an extremely poisonous and toxic gas that was discovered by John Davy in 1812. Phosgene was used as chemical warfare agent during the First World War and is therefore a very controversial substance in many regions around the globe. Currently it is used to produce diisocyanates, polycarbonates (PCs), acid chlorides, chloroformates, chlorocarbamates, and organic carbonates. Phosgene is not a very efficient intermediate; yields are usually high but on average only 30% of it's weight ends up in the derivative⁵. In this paragraph first the toxicity and controversy issues are discussed and then the commercial and legislative subjects are elaborated.

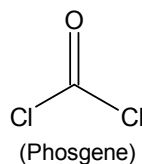
Toxicity and controversy

As said, phosgene is controversial because it can be used as an agent in chemical warfare. Phosgene is under strict supervision of the OPCW and every production facility exceeding 30 tonnes per year must be declared and can be inspected at any time. This is determined by the Chemical Weapons Convention (CWC) that was approved in 1992 and is signed and ratified by 188 countries³⁴.

Phosgene is highly toxic, therefore it requires rigorous process design standards to protect the health and safety of handling personnel, it has a T+ classification of the directive of dangerous substances set by the EC REACH program³⁵. It has an IDLH (Immediately dangerous to life of health) level of 2 ppm⁵.

The effects of phosgene on inhaling; hydrochloric acid is produced in the alveoli (the air-containing cells of the lungs), which reacts with the capillary wall of the lung and produces an Oedemal fluid. This eventually floods the lungs and causes suffocation. After initial exposure, phosgene in which produces coughing, nausea, vomiting and headache, the effects often seem to disappear. But after a period of perhaps 24 hours, the condition is worsened by exertion. In other words, the affected person is killed by drowning in their own body fluid, which worsens as their body tries to fight its effects.

Figure 2-4 Molecular structure phosgene



Production, trade and developments

Phosgene is mainly produced and consumed in the United States, Europe and Asia. It is primarily used to produce MDI, TDI and polycarbonate (PC) resins. Phosgene is typically produced and consumed on site and therefore the 7 million metric tonnes consumption in 2006 is almost equal to the annual production. Very little trade of phosgene takes place because of this reason and also because of legislative difficulties. Because of the high toxicity, very small or zero inventories are usually maintained. It is estimated that the growth in consumption of phosgene will be 4.3% globally between 2006 and 2011 and it is expected to be greatest in China. Key findings and future implications for the phosgene market include the following⁵:

- Markets and capacity is shifting towards China and other Asian countries; like TDI, MDI and polycarbonate markets to which it is closely related.
- The phosgene free production technology for polycarbonates has moderated growth prospects for this application; phosgene free capacity is 7% in 2006 and 15% in 2010 of total PC capacity.

- Toxicity concerns drive the industry to find alternative technologies.

The latter two findings clearly indicate the market trend towards phosgene free technologies. The polycarbonate market is already in a transition from phosgene using production processes to phosgene free production processes. This transition was caused by the enforcement of stricter governmental regulations concerning the use of phosgene in the PC manufacturing process³⁶. The mentioned restrictions however, can only be enforced if there is a suitable alternative production process.

A competitive phosgene free production process of MDI would find wide recognition among environmental movements and governments because of its HSE advantages. Just as with PC, this competitive alternative would make it possible to enforce stricter regulations for new MDI production facilities that exclude the use of phosgene. This would be a major incentive for further development of the phosgene free MDI production process.

Table 2-1 Consumption of MDI per major region (%)

	Flexible PU Foams	Rigid PU Foams	Nonfoam Uses
1988			
United States	3	77	20
Western Europe	5	69.5	25.5
Japan	0	50	50
1996			
United States	9	52	39
Western Europe	4	68	28
Japan	2.5	61.5	36
2004			
United States	12	54	34
Western Europe	3	68	29
Japan	3	41	56
China	5	61	34
2008			
United States	11	58	31
Western Europe	6	68	26
Japan	5	39	56
China	5	60	35
2013			
United States	11	58	31
Western Europe	6	70	24
Japan	4.5	37.5	55
China	5	61	34

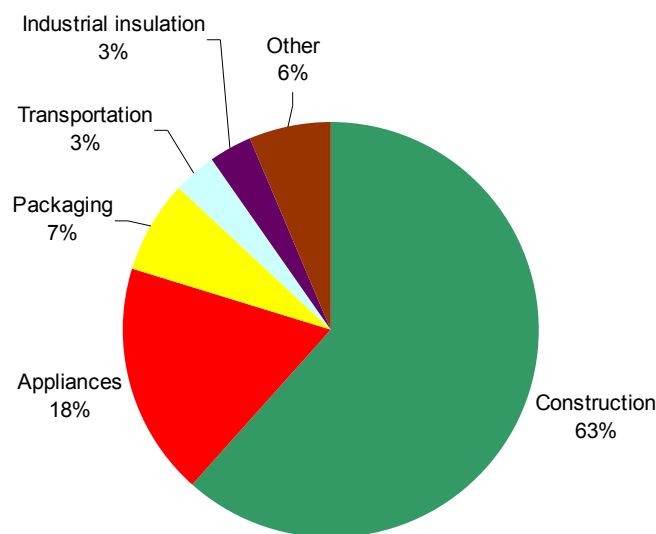
2.4. MDI Applications

MDI is used almost exclusively for the production of polyurethanes (PUs). Polyurethanes are produced by a reaction of isocyanates with polyols. PUs exist in several forms; flexible and rigid foams and non-

foam uses like in binders, coatings, adhesives and elastomers. As can be seen in Table 2-1 MDI is mostly used for rigid foams. The market share of MDI foam applications is significantly larger than the MDI non-foam applications market share.

PU rigid foams are the largest application for MDI, Figure 2-5 gives an overview of the PU rigid foam end-use pattern as it was in the US in 2008, this pattern is similar for other regions. These foams are mostly used in construction applications. Currently the housing market is collapsing due to the financial crisis and logically this also has serious consequences for the MDI market, in paragraph 2.6 this subject will be addressed in more depth. The mentioned foam and non-foam applications of MDI are briefly discussed below.

Figure 2-5 US PU rigid foam end use pattern 2008



Foams

Foams are by far the largest application for isocyanates, in 2008 this application accounted for 69% of global MDI consumption as can be seen in Table 2-1³³. Foams can be categorized into rigid and flexible foams. Typically TDI is used for flexible foams and MDI is mainly used for rigid foams. The hard- and stiffness of PU foams can be determined by varying the isocyanate, polyol and additive concentrations in the PU manufacturing process. PU foams are particularly popular in industry because they can either be premanufactured in all sizes and shapes and they can also be polymerized in situ without premanufacturing. Therefore PU foams offer great flexibility in manufacturing.

Rigid foams usually contain a polymeric isocyanate (PMDI), a polyol, a blowing agent, amine catalysts, silicone stabilizers and optionally a flame retardant. Rigid foams are mostly designed to withstand temperatures of up to 95 °C. Construction applications are by far the largest consumer for rigid foams, this application accounts for 61.6% of global MDI usage³⁷. Other applications are in refrigeration, furniture and floating devices. Substitute products for PU rigid foams are phenolic foams and expanded and blown polystyrene.

Flexible PU foams are mostly produced with TDI and is used as cushioning materials in transportation and furniture applications, mainly beds and car seats. Especially in Europe it is popular in automotive industry.

Elastomers

PU elastomers are manufactured by reacting MDI with dihydroxyalcohols or glycols to form linear polymers. The formed elastomers can either be thermosetting or thermoplastic. The formed polymer can be mixed with fillers, additives or reinforcers. The thermosets can be cured in to useful products and the thermoplastic urethane elastomers (TPUs) are especially formulated to prevent crosslinking so they are suitable for melting in molding and extrusion applications. TPUs share their rigidity and easy processing characteristics with other thermoplastic elastomers and have the toughness of thermoset rubbers. PU elastomers are used in automotive applications, flexible seating, pressure sensitive adhesives, diapers, wire and cables, footwear and other sports applications.

Coatings, sealants and adhesives

The fastest growing application for MDI is in binders for woods. The major segment is oriented strandboard (OSB) where wood chips and flakes are binded to form panels. OSB panels are a replacement for traditional plywood in construction jobs³⁷. MDI is also used as a binder for foundry cores and for use in recycling agricultural and municipal waste. These binders can be hot or cold cured and can handle relatively high moisture levels.

In coatings MDI has taken the marketshare of TDI because TDI has poor UV light resistance. An interesting application of polyurethane coatings is in automotive industry. The polymerization reaction between the polyol and isocyanate is conducted on site; the components are mixed on the coating surface and form a polyurethane network by chemical drying on the spot. This method poses health risks because the reaction, including toxic isocyanates, is conducted in the presence of employees³².

Reaction Injection Moldings (RIM)

This is also an application that shows strong growth. Pure MDI is reaction molded into lightweight, plastic parts. This is mostly used in automotive industry for the production of bumpers, body panels, spoilers and exterior trims.

The RIM foaming process comprises two stages instead of one; First polyol is reacted with an excess of MDI, this mixture is stored as prepolymer. The prepolymer is then mixed with additional polyol, additives and foaming agents in the injection molding equipment to form the final foam product. It is also possible to create a thermoset by not using the foaming agent.

2.5. HSE of MDI production

In this paragraph first the general HSE issues of MDI production are discussed. In the end a brief assessment of the Dow Chemical Exposure Index (CEI)³⁸ and the Dow Fire & Explosion Index (FEI)³⁹ of conventional MDI production with phosgene is given.

2.5.1. General HSE issues

The production and usage of MDI, and other isocyanates, comprises some safety hazards and especially the conventional process for MDI manufacturing. This paragraph discusses all hazards that are present throughout the MDI value chain.

Production and transportation safety of diisocyanates has always been a major issue for manufacturers; especially the use of phosgene and the high reactivity of diisocyanates that is potentially hazardous to humans.

Phosgene is used in the conventional method to produce MDI. Phosgene is a highly toxic material; the EU classifies it as "very toxic" (T+)³⁵ and it has the highest NFPA 704 health rating of 4, "very short exposure could cause death or major residual injury"⁴⁰. Therefore all conventional MDI production

facilities need extensive phosgene-containment safety measures. All producers use phosgene monitoring systems and standard safety practices. More detailed information on phosgene is given in paragraph 2.3 above.

All diisocyanates are very reactive chemicals that are potentially hazardous to humans. MDI can react violently with hydrogen donors, in combination with water it produces carbon dioxide which can burst containers and produce aerosols. The primary hazard is the inhalation of diisocyanate mists or vapors; therefore they must be handled with care and procedures should be designed in order to minimize exposure. The health risks of MDI in comparison with other diisocyanates are relatively low because MDI is the heaviest and least volatile diisocyanate compound.

Besides phosgene, also 4,4'-diaminodiphenylmethane (MDA), which is a precursor for MDI production, has been identified as a "Substance of Very High Concern" by REACH. This measure has been taken because MDA is a category 2 carcinogen. However, MDA is used mainly as an in situ intermediate and due to the high safety standards in the EU, the exposure of skilled workers in the chemical industry is low³³.

Diisocyanates also pose risks in its application since it can be hazardous to humans. The highest risk application of diisocyanates is in the automotive industry. In this industry PU coatings are used as a protective layer on cars, the coating's core competence is its strength caused by the network structure of the PU molecules. This structure is obtained by reacting the isocyanate and polyol directly on the car surface in the same room as the handling employee, this application is a dominant source for occupational asthma. According to estimates there are currently more than three million employees overexposed to isocyanates in Europe and 200,000 in the US. The large difference in the numbers shows that the estimations are rather uncertain but significant. It is unknown which isocyanates precisely are the main source of this problem²⁹.

Another major HSE issue that had to be addressed in the recent past was the use of CFCs (chlorofluorocarbons) blowing agents in PU foams. CFCs were a major cause of the ozone depletion problem and therefore CFC use is now heavily regulated and restricted by the Montreal Protocol of UNEP²⁷. Producers are developing substitute materials and seem to be successful with materials such as cyclopentanes, isopentane, a pentane mixture and water²⁵.

Exposure limits and handling restrictions are set by OSHA (occupational safety and health administration) in the United States and by the REACH (registration, evaluation, authorization and restriction of chemicals) program in the European Union.

2.5.2. Safety of MDI production facility using phosgene

This paragraph briefly assesses a MDI production facility that uses phosgene based on Dow's Chemical Exposure Index and Fire & Explosion Index. This is a rough calculation that is used to give a quick feel in the safety difference between the conventional and the new MDI production processes. This is not a full safety assessment.

The CEI is a simple method of rating the relative acute health hazard potential to people in neighbouring plants or communities from possible chemical release incidents. The FEI gives a similar estimation but than for risks of fire and explosions that can occur on site. The indexes can not determine if a plant is safe, but it provides a method of ranking one hazard to another. The result of the calculation is the Hazard Distance of a scenario, this is the assumed safe distance in case of the occurrence of the scenario.

Table 2-2 shows the CEI and FEI calculations of phosgene and chlorine in a MDI plant. A more detailed description of the conventional MDI production process is given in paragraph 3.1. Phosgene and chlorine are selected for the calculations because they are present in the conventional MDI production process but not in the phosgene free MDI production process. Therefore they can give insight in the difference in safety between the two processes. The information on the process comes from the SRI PerP report on TDI/MDI² and the research of Sauer et al.⁴¹

First the highest risk spots in the process are determined where chlorine and phosgene are present. Chlorine is used to produce phosgene, which is used, together with MDA, to produce MDI. Therefore the phosgene production process, the MDA phosgenation process and the phosgene storage are assessed.

In each case it is assumed that a 5 cm. hole in a 20 cm. diameter pipe is the cause of the component escape, the same leak is assumed for each scenario to make them comparable, also for the scenarios in the HSE analysis of the new technology discussed in paragraph 4.9. Further information on the components is shown in Appendix H and these are derived from Sittig⁴². Other important factors are the volume of the container, the process temperature and the outside temperature. The outside temperature is considered to be 25 °C. The other two factors differ with each scenario but are based on a 473 kTa MDI production facility.

Table 2-2 Dow CEI & FEI hazard distance of phosgene and chlorine in MDI plant

Phosgene						
	Amount			T process (°C)	T outside (°C)	CEI & FEI
	min	kg	m3			Hazard distance (m)
<i>Storage</i>	5	7212	5.30	0	25	1,123
	10	14424	10.61	0	25	1,158
	15	21636	15.91	0	25	1,158
<i>MDA Phosgenation</i>	1	1442	1.06	50	25	2,320
	2	2885	2.12	50	25	3,572
	3	4327	3.18	50	25	4,825
<i>Phosgene production</i>	1	1442	1.06	75	25	7,787
	2	2885	2.12	75	25	12,147
	3	4327	3.18	75	25	16,507

Chlorine						
	Amount			T process (°C)	T outside (°C)	CEI & FEI
	min	kg	m3			Hazard distance (m)
<i>Phosgene production</i>	1	1034	0.74	75	25	1,070
	2	2068	1.48	75	25	1,573
	3	3101	2.22	75	25	2,077

Basis						
	kTa	t/hr	MW	Mol	Feed ratio	Density (kg/m3)
MDI	473	54.7	250.3	218719	1	1230
COCl ₂	748	86.5	98.92	874876	4	1360
Chlorine	536	62.0	70.9	874876	4	1399

First the phosgene storage section is discussed, very small inventories are kept but phosgene is briefly stored in the process. Phosgene is stored at 0 °C and a 5, 10 and 15 minute buffer storage is assumed to be sufficient. This results in a hazard distance between 1,123 and 1,158 meters.

Second, the MDA phosgenation reaction is calculated, this reaction is fast and therefore an amount of 1, 2 and 3 minutes of phosgene is considered. The reaction takes place at 50 °C at a slight overpressure. Especially the elevated temperature causes a high hazard distance of between 2,320 and 4.825 meter.

Third, the production of phosgene, this occurs at a temperature of 75 °C and here it is also considered that not more than a 3 minutes buffer is present. Phosgene hazard distance is between 7.787 and

16,507 meter, chlorine is also present in this step and has a hazard distance of between 1,070 and 2,077 meter.

These figures will be used for comparison with the phosgene free MDI production process. Compared to general industry standards the hazard range of this chemicals production process is relatively high, this confirms the fact that permitting is difficult for the conventional MDI production process using phosgene. The figures of the phosgene free MDI production process are calculated and compared in paragraph 4.9.

Table 2-3 World supply/demand for MDI in 2008 (in kTa)

	Annual capacity (year-end)	Production	Imports	Exports	Consumption		Average annual growth rate 2008-2013 (%)
					2008	2013	
North America							
United States	1,280	1,019	46	309	755	875	3.0
Canada	0	0	110	0	100	117	3.2
Mexico	0	0	60	0	60	74	4.3
Total	1,280	1,019	216	309	915	1,066	3.1
Central and South America							
	40	40	94	7	127	165	5.4
EMEA							
Western Europe	1,823	1,400	0	235	1,165	1,389	3.6
Central and Eastern Europe	190	135	197	125	205	275	6.1
Africa and Middle East	0	0	180	0	180	244	6.3
Total	2,013	1,535	377	360	1,550	1,908	4.2
Asia							
China	1,090	610	344	84	871	1,280	8.0
Japan	572	414	33	238	167	170	0.4
Republic of Korea	265	260	71	167	164	181	2.0
Taiwan	0	0	65	4	61	64	1.0
Other	0	0	135	0	135	172	5.0
Total	1,927	1,284	648	493	1,398	1,867	6.0
Oceania							
	0	0	7	0	7	9	4.0
Total	5,260	3,878	1,342	1,169	3,997	5,015	4.6

2.6. MDI market

MDI is a globally produced and consumed product. Currently the highest consumption is in the EMEA area (Europe, Middle East and Africa) with 1.550 KTa but the Asia is growing rapidly and will be equally sized to EMEA around 2013. Table 2-3 gives an overview of the global supply and demand figures in 2008 as well as a forecast of the consumption in 2013.

Active worldwide trade takes place in MDI and other isocyanates. Commercial MDI is available in various forms of which the bulk is PMDI with a functionality of between 2.3 and 3.0. Major MDI exports go to the Pacific Rim countries, Central and South Americas, the Middle East and Central and Eastern Europe, as production in these regions is minimal.

Another remarkable statistic in Table 2-3 is that there is no production capacity of MDI in the Middle East and Africa region. The major reason for this is that phosgene was used in chemical warfare during the First World War and that countries in these region, especially the Middle East, don't want to be linked to this material. According to industry sources several major producers have unsuccessfully attempted to get permits for a MDI production facility, especially in the Middle East region. Also other phosgene using production facilities; i.e. of TDI and polycarbonate, are kept out of this region. The MDI demand in this region however, is relatively low; in 2008 the demand was 145 kTa in the Middle East and 35 kTa in Africa³³.

Table 2-4 Global MDI production plants (capacity in metric tons per year)

Company	Region	Country	Location	Capacity
BASF		Belgium	Antwerp	560
BASF	Chonnam	South Korea	Yosu	200
BASF	Louisiana	US	Geismar	290
Bayer		Germany	Brunsbüttel	160
Bayer		Germany	Krefeld	200
Bayer	Texas	US	Baytown	300
Bayer		Spain	Tarragona	150
Bayer	Shandong	China	Caojing	350
Bayer	Rio de Janeiro	Brazil	Belford Roxo	45
BorsodChem		Hungary	Kazincbarcika	60
BorsodChem		Hungary	Kazincbarcika	130
China National Blue Star	Shanxi	China	Taiyuan	1
Dow Chemicals	Niedersachsen	Germany	Stade	200
Dow Chemicals		Portugal	Estarreja	200
Huntsman	Louisiana	US	Geismar	390
Huntsman		Netherlands	Rozenburg	400
Mitsui Chemicals	Chonnam	South Korea	Yosu	75
Mitsui Chemicals	Fukuoka Pref	Japan	Omuta	60
Nippon	Zhejiang	China	Ruian	50
Nippon	Yamaguchi Pref	Japan	Nanyo	200
Nippon	Yamaguchi Pref	Japan	Nanyo	200
Shanghai Lianheng	Shanghai	China	Caojing	240
Bayer	Ehime Pref	Japan	Niihama	110
Dow Chemicals	Texas	US	Freeport	225
Yantai Wanhua	Zhejiang	China	Ningbo	300
Yantai Wanhua	Shandong	China	Yantai	200

Future growth of MDI is expected to be slightly higher than GDP growth. In most recent years, and especially during the recent financial crisis, the domestic demand of MDI slowed and some of the major producers have shutdown older facilities, sometimes in conjunction with new plant capacity, and increased export to the abovementioned regions. The slowdown of the global economy in 2008-2009 also led to temporary closures of production capacity in North America and Europe.

The major producers in the MDI markets have a global presence. The four largest producers of MDI are BASF, Bayer, Dow Chemical U.S.A. and Huntsman LLC, they account for 67% of worldwide production in the beginning of 2009³³. Despite it is such a difficult market to enter because of technology and high capital barriers, there are relatively new, upcoming players. For example in the rapidly growing Chinese market, where all established players are investing in new capacity, the Chinese manufacturer Yantai Wanhua is currently present with a capacity of 500 KTa. and investing in additional capacity¹⁷. The plant capacity of the major MDI manufacturers is shown per region in Table 2-4 below. Currently there is a shift of production capacity to China besides Yantai Wanhua, BASF is also planning to invest in production capacity in China¹⁷.

The MDI industry and markets are complex, however it is expected that the current capacity, in combination with announced capacity investments, shown in Table 2-5, is sufficient to meet the global demand in 2013. Especially China is a fast growing market and will probably be the country with highest consumption in 2013. It is expected that MDI markets continue to expand in the developing countries in Asia and especially India and Southeast Asia, also after 2013³³. The mentioned capacity figures can lower in the current period because of a very bad investment climate with a low MDI selling price as is discussed in paragraph 2.7 below.

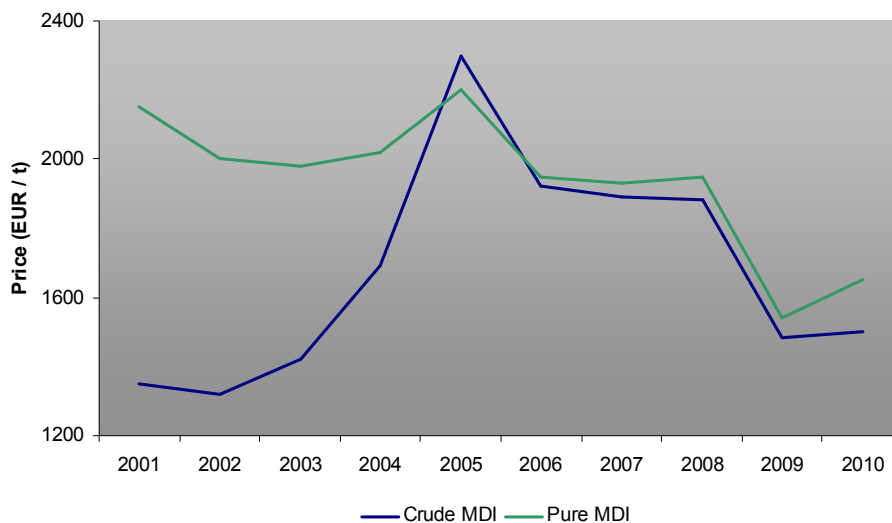
Table 2-5 Global MDI projects (capacity in metric tons per year)

Company	Region	Country	Capacity Type	Capacity	On Stream Date	Status
BASF	Chongqing	China	Total	400	Post-2010	study
BASF	Chongqing	China	Total	400	2014	study
BASF	Chongqing	China	Total	400	2011-12	study
Bayer		Germany	Expansion	400		study
Bayer			Total	400	2012-13	study
China National Blue Star	Tianjin	China	Total	200	2011	study
Chongqing Pharma-Chemical	Chongqing	China	Total	400		engineering underway
Gujarat Narmada Valley	Gujarat	India	Total	50	2010-11	study
House of Invention		Saudi Arabia	Total	100	2012-13	planned
Huntsman	Shanghai	China		0		study
Karun Petrochemical	Khuzestan	Iran	Total	40	H2 2009	construction underway
Mitsui Chemical		South Korea	Total	75	Q1 2009	construction underway
Dow Chemicals	Texas	US	Expansion	340	Post-2007	planned
Tianji Coal Chemical Industry	Shanxi	China	Total	180	By 2010	study
Yantai Wanhua	Zhejiang	China	Total	300	Q4 2010	engineering underway
Yantai Wanhua	Shandong	China	Total	600		planned

2.7. MDI price

In this paragraph the recent price history of crude MDI in Europe is briefly discussed. The prices of crude and pure MDI are shown in Figure 2-6 below. In this graph it is shown that the price of crude MDI made its way up to a peak of approximately € 2,300 per ton in 2005 and stabilized at € 1,800 until 2008. In 2008 and 2009 the financial crisis hit and the price collapsed to a bottom of € 1,500^{33,43}.

Figure 2-6 Crude MDI and pure MDI European price history



Currently (February, 2010) the price of crude MDI is still at approximately € 1,500 per ton. This price does not leave any profit margin and is therefore not sustainable. Producers are determined to increase prices by € 200 per ton on the short term to recover their margins. These low prices have a short term impact on profits but, more seriously, they also affect capacity investment decisions; this MDI price crunch due to the financial crisis can cause a lack of capacity in the future⁴³.

3. Phosgene Free Routes to MDI

Diisocyanates, like MDI, are of great commercial importance in the manufacture of polyurethanes as is elaborated in chapter 2. The conventional production of diisocyanates consists of two reaction steps of which the second one is a phosgenation step. In this phosgenation step the highly toxic phosgene is used and a large amount of corrosive HCl is formed. Therefore many efforts have been made to develop an isocyanate production process without the use of phosgene. The first successful reported attempt was made by Hardy and Bennett in 1967; the invention comprised a conversion of aromatic nitro compounds to isocyanates by CO⁴⁴. Several other methods followed; all major routes to MDI are shown in Figure 3-1 below.

Figure 3-1 Routes to MDI

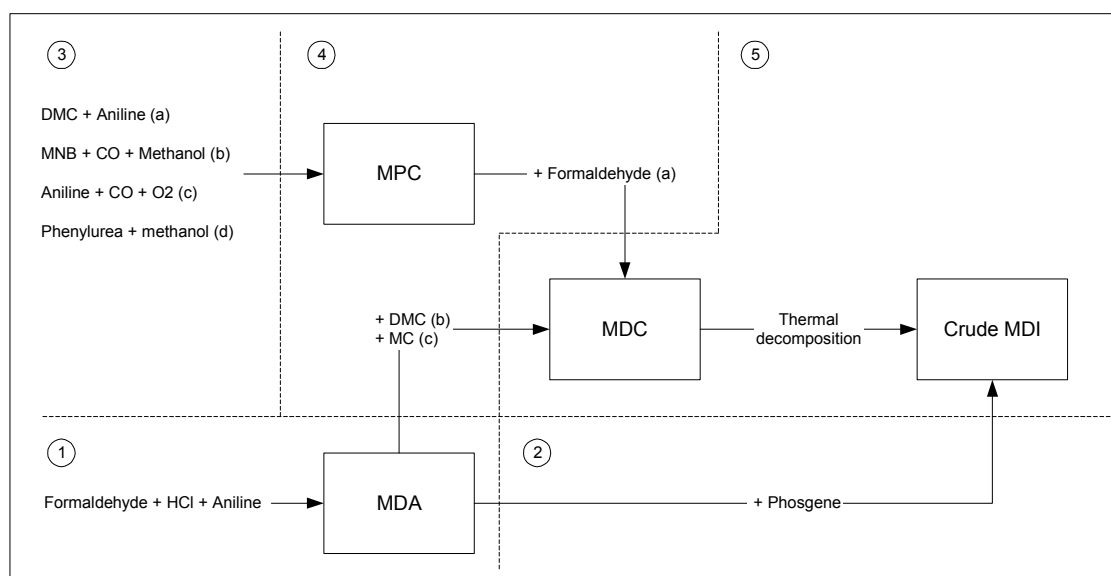


Figure 3-1 gives a schematic description of all major the routes to MDI; (1) is the synthesis step of MDA, (2) is the conventional, phosgenation route from MDA to MDI, (3) are the four different routes to form MPC, (4) are the three different routes to form MDC and (5) is the thermal decomposition step from MDC to MDI.

Steps 1 and 2 are discussed in paragraph 3.1.1 and 3.1.2 respectively. Step 3 is discussed in paragraph 3.2.1, step 4 is discussed in paragraph 3.2.2 and step 5 is discussed in paragraph 3.2.3.

This chapter reviews the available technology for the phosgene free production of MDI, as is schematically described in Figure 3-1. First the conventional route to MDI is discussed, next the phosgene free alternatives for MDI production are elaborated, finally the methods are compared and the optimal phosgene free route to MDI is selected for further use in this research.

There have also been phosgene free routes to MDI reported that instead of MPC and MDC, respectively methyl phenyl carbamate and dimethyl methylene diphenyl 4,4'-dicarbamate, use EPC and MDU, respectively ethyl phenyl carbamate and diethyl methylene diphenyl 4,4'-dicarbamate. In these routes the methyl group in –NHCOOCH₃ is an ethyl group, and thus has the following structure –NHCOOC₂H₅. MDU can also be thermally decomposed to MDI and is very similar to the thermal decomposition of MDC to MDI⁴⁵. EPC can be synthesized by using ethanol instead of methanol in the carbonylation reactions discussed in paragraphs 3.2.1.3 and 3.2.1.4 below⁴⁶. These reactions are comparable to the routes mentioned in this chapter and will therefore not be discussed separately.

3.1. Conventional route to MDI

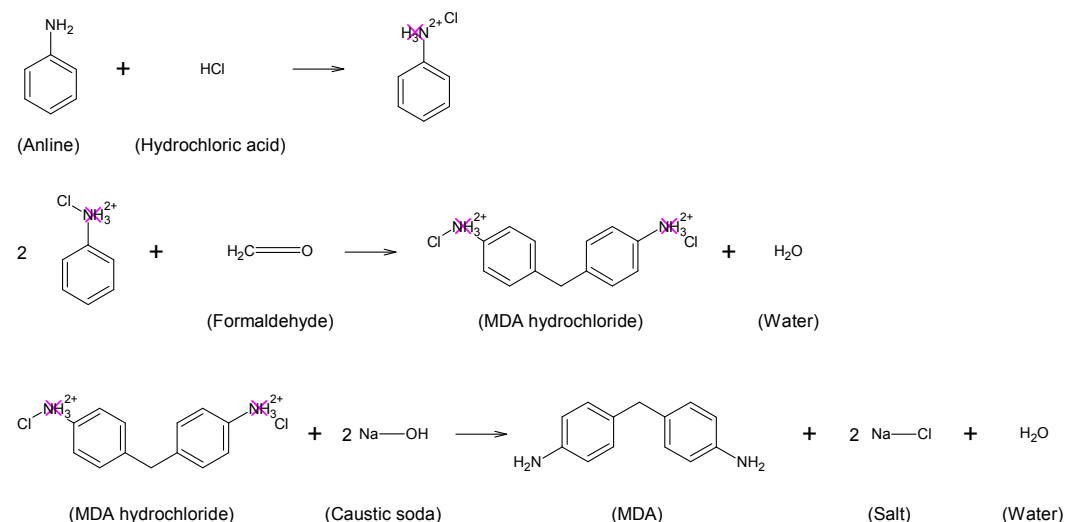
The commercial manufacturing routes for the synthesis of MDI are all based on similar designs and are all using phosgene (Figure 3-1, 1 and 2). MDI is synthesized from aniline, formaldehyde and phosgene in two reaction steps. In the first step diphenylmethanediamine (MDA) hydrochloride is synthesized from aniline, which is typically in hydrochloride form, and formaldehyde. The MDA hydrochloride is then neutralized to obtain normal MDA. In the second step MDI is produced by reacting MDA with phosgene. Both steps are described below.

3.1.1. MDA synthesis

The typical reaction sequence of the MDA synthesis is shown in Figure 3-2. Firstly aniline is treated with a stoichiometric amount of hydrochloric acid (HCl) to obtain MDA hydrochloride. This is then treated with formalin (37w% formaldehyde in water) for approximately 5 minutes at a temperature of 60-80 °C. The water content should be equal in weight to the aniline. After the formalin treatment the reactants are maintained at 100-160 °C for approximately one hour to complete the condensation reaction. By adding an excess of caustic soda the reaction mixture is separated in an aqueous and an organic layer. The organic layer is separated and further distilled to remove remaining aniline and yield crude MDA.

Crude MDA is a mixture of 4,4'-MDA, 2,4'-MDA, 2,2'-MDA and polymeric amines (PMDA). By adjusting the reaction conditions the composition of this mixture can be steered. However, PMDA is useful reactant since it forms PMDI. The reaction conditions that can be adjusted are mainly temperature, aniline:formaldehyde feed ratio and HCl feed ratio. This crude MDA can be transformed to MDI by phosgenation².

Figure 3-2 MDA synthesis reaction sequence



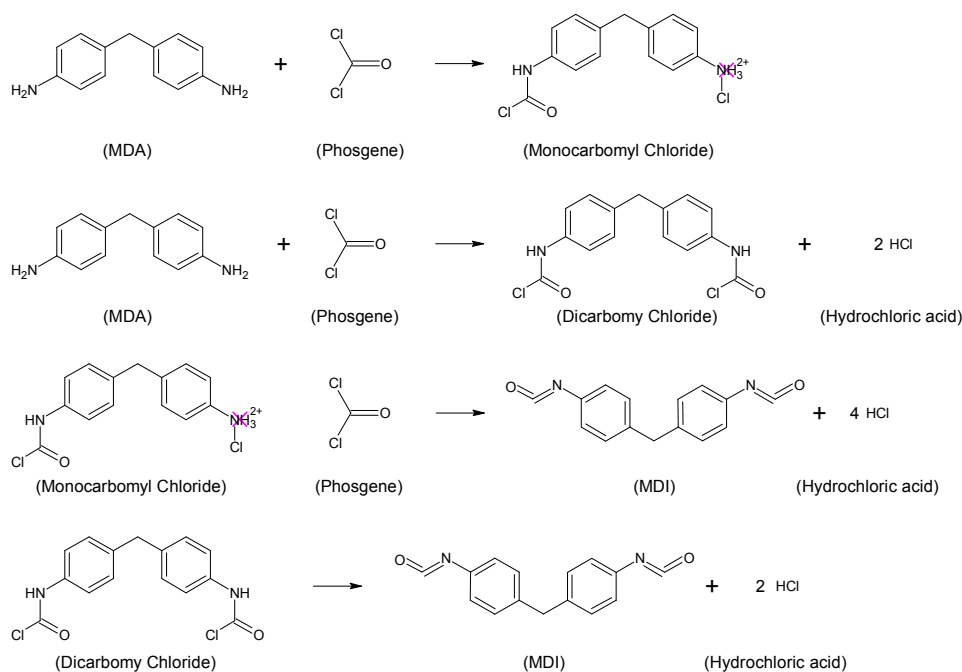
3.1.2. MDI synthesis

MDI is produced by phosgenation of MDA in a suitable solvent at a pressure of 3-4 bar and a temperature of 120 °C. Typically used solvents are 1-chlorobenzene or dichlorobenzene. The phosgenation reaction comprises two steps with at least two intermediate products. In these steps

phosgene (COCl₂) is used, this is a very toxic compound that requires high safety standards. The phosgenation process step is described below.

Crude MDA as obtained in the previous step is first dissolved in a solvent and then phosgenated in several stages to produce MDI. The initial reaction renders carbamoyl chlorides at 50-70 °C in a short time. Then the material is further heated to decompose the carbamoyls. The heating continues until no more HCl is produced. The crude MDI has to be separated and then distilled to obtain a composition of 97-98% of the 4,4'-isomer and 2-3% of the 2,4'-isomer. If necessary this can be further purified. The 4,4'-isomer contains the pure MDI, monomers, and polymers, PMDI. PMDI comprises dimers, trimers and tetramers of MDI. PMDI is a low-viscosity liquid at atmospheric conditions and pure MDI is a solid at normal conditions. Usually both MDI and PMDI are manufactured and sold by producers so the operating conditions are flexible and dependent on the demand. The polymer:monomer ratio can be steered by adjusting the aniline:formaldehyde ratio or by adjusting the distilling procedure of the MDI mixture². The MDI synthesis reaction sequence is shown in Figure 3-3.

Figure 3-3 MDI synthesis reaction sequence



3.2. Phosgene free routes to MDI

There are several scientifically proven phosgene free methods for MDI synthesis. None of these methods has been commercialized though. The basis of all available alternatives is the formation of MDC (dimethyl diphenylmethane-4,4'-dicarbamate) (Figure 3-1, 4) which can be thermally decomposed to MDI (Figure 3-1, 5). The formation of MDC can be performed in multiple ways. Most common in scientific literature is the formation of MDC by the condensation reaction between MPC (methyl phenyl carbamate) and formaldehyde (Figure 3-1, 4a). For the production of MPC there are four important routes mentioned in literature; reductive carbonylation of nitrobenzene (Figure 3-1, 3b), oxidative carbonylation of amines (Figure 3-1, 3c), the reaction between phenylurea and methanol (Figure 3-1, 3d) and the reaction between aniline and DMC (Figure 3-1, 3a). It is also possible to produce MDC with MDA as a feedstock product (Figure 3-1, 4b, 4c).

In this paragraph the synthesis of MPC is reviewed first. Hereafter the synthesis routes of MDC are discussed and finally the thermal decomposition of MDC to MDI is elaborated. The MDA formation is already described in paragraph 3.1.1. Also the options for specific reaction conditions and performance are described for the most promising routes. Based on the selection parameters given below the best set of reaction conditions, solvent and catalyst is selected for further use in this research.

Process selection parameters

Each reaction has to be conducted under different reaction conditions and with a different catalyst system. To select the right set of conditions, solvents and catalyst system, general selection parameters are introduced. These parameters describe the key aspects that determine the performance of a reaction and will be used in this chapter. The set of parameters has been developed in collaboration with Fluor experts.

Reaction information has been derived from public domain literature and not all parameters are known for each reaction, especially data on the catalyst system is often missing. The selection will therefore also be based on the amount of information that is available.

Selection parameters:

- Feedstock molar ratio; this is the molar ratio of the feedstock components of the reaction. If a component is fed in a large excess, as compared to the stoichiometric amount, it means it has to be separated and recycled afterwards so it can be used again. If the excess is really large it means that the recycle streams will be large and a lot of equipment is necessary for recovery. This will result in high capital and utility costs.
- Catalyst properties; there are several catalyst properties that are of importance for the feasibility of the reaction:
 - Type of the catalyst system; basically there are two types of catalyst systems, heterogeneous and homogeneous systems. For both types there are many different applications and ways to install or use them in a reactor⁸³. In this study the homogeneous catalysts are mixed in the liquid phase reactions and are assumed to come out of the reactor together with the product. The heterogeneous catalyst systems are all fixed bed systems, the system is packed in the reactor and might show leaking. Leaking means that the catalyst partly dissolves in the reaction mixture and is also removed from the reactor together with the product, generally this is a very slow process. If the catalyst comes out of the reactor together with the product this is considered to be disadvantage because it has to be removed from the product to (1) purify the product and (2) recover the catalyst for reuse. Catalyst removal is assumed to be costly since it is an extra step in the separation process.
 - Cost; the cost of the catalytic system is an important parameter. The cost is determined by the cost per mass unit of catalyst, the amount of catalyst that is needed per mass unit of reactants present in the reactor and the frequency that the system needs to be replaced. This factor is very complex and it is difficult to assess the systems in this report based on information coming from public domain data. In most cases empirical research is needed to properly assess this parameter.
 - Deactivation time; this is the time that the catalyst has an acceptable activity. Typically the catalyst activity decreases over time, this also causes a decrease in the reaction effectiveness, in some cases this can temporarily be corrected by i.e. increasing temperature. The deactivation time determines the frequency that the catalyst needs replacement. Not much is known about this parameter for most catalyst systems discussed in this report.

- Reaction conditions; temperature, pressure. The combination of temperature and pressure determine the phase of the reaction components, if the components are continually in the gaseous phase because of high temperature, low pressure or both, the process equipment will be large and therefore more expensive compared with liquid or solid components.
- Residence time (r.t.); the residence time determines the size of the reactor, if the residence time is high; the reactor needs to be large. A large reactor is more expensive and harder to control.
- Conversion; the conversion of the reaction is the relative amount of the smallest feedstock stream that is converted into another product. The smallest feedstock stream is determined by comparing the molar ratio of the feedstock components. This is an important parameter because it affects the size of the recycle streams; if conversion is very low, the amount feedstock products that have to be recycled for reuse is very large. This will cause large recycle streams and these require large equipment. If conversion is higher it means that smaller equipment is necessary.
- Selectivity; the selectivity is the ratio of the amount of the smallest feedstock stream that is converted into final product divided by the total amount of the smallest feedstock stream that is converted. This parameter tells something about the amount of by-product that is formed in the reaction. If the selectivity is high, it means that relatively little amounts of by-product are formed. If it is low, relatively large amounts of by-product are formed. By-products can usually not be turned into final product and have to be separated and disposed. This can be costly due to the need for separation equipment and the waste of feedstock material.

3.2.1. MPC synthesis

In the phosgene free route to MDI, MPC is the predecessor of MDC. In this research the reaction of aniline with DMC (Figure 3-1, 3a) is deemed to be the most attractive option to produce MPC, mainly because it can be conducted over a heterogeneous, solid catalyst with good performance. Besides this reaction there are three other options for MPC synthesis; reductive carbonylation of nitrobenzene (Figure 3-1, 3b), oxidative carbonylation of amines (Figure 3-1, 3c) and the reaction between phenylurea and methanol (Figure 3-1, 3d). All options are discussed in this paragraph.

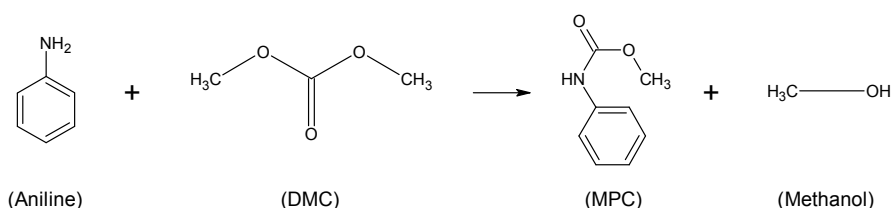
3.2.1.1 Reaction of aniline with DMC

This reaction has not been studied widely in comparison to the other MPC synthesis methods, except for the recent past. The reason is that DMC has long been synthesized from phosgene and methanol and therefore didn't pose an advantage over the conventional route. Now DMC is synthesized by oxidative carbonylation of methanol with CO₂ on a large scale which lowered the costs and made this MPC synthesis reaction more attractive⁴⁷.

This paragraph first gives a broad description of the reaction and then discusses a set of scientifically proven reaction conditions based on the abovementioned selection parameters.

The endothermic reaction of aniline with DMC to produce MPC is shown in Figure 3-4. The speed of this reaction is very low at mild temperature and pressures so a catalyst is necessary to make this reaction practically usable. One of the first reported catalytic processes for MPC synthesis describes a process using a Lewis acid as catalyst. The results are acceptable but a large amount of expensive uranium and antimony catalyst was used, making it economically unviable⁴⁸.

Figure 3-4 MPC synthesis reaction of aniline and DMC



More research followed and better results were achieved; Table 3-1 shows some promising catalytic systems for MPC synthesis by reaction of aniline and DMC. For each method the catalyst, catalyst type (either a homogeneous (H) or a supported (S) system), feed streams and reaction conditions are described.

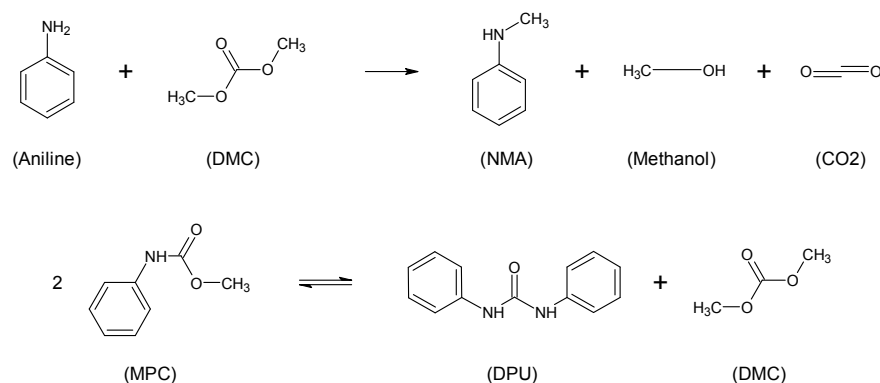
Table 3-1 Catalytic systems for MPC synthesis by reaction of aniline and DMC

Entry	Catalyst	Catalyst type	Ani:DMC (molar ratio)	Reaction time (h)	Reaction temp (°C)	Pressure P (bar)	Reaction phase	Aniline conversion	MPC selectivity	Source
1	ZnO-TiO ₂	H	1:20	7	170	>1	Liquid	97%	67%	49
2	AlSBA-15	H	1:10	3	100		Liquid	99%	71%	12
3	PbOSiO ₂	H	1:5	4	160				100%	50
4	ZrO/SiO ₂	S	1:20	7	170			99%	80%	51
5	Pb catalysts	H	1:5,4	1	160	>1	Liquid	96%	95%	52
6	Zn acetate	H	1:5	6	140	8-15	Liquid	90%	88%	53
7	Zn(OAc) ₂ /Ac	S	1:7	8	150		Liquid	80%	98%	3

The supported Zn(OAc)₂/Ac catalyst method in entry 7 of Table 3-1 is deemed to be the most suitable option for commercial production of MPC. This system is described in the research of Zhao et al.³ and it is promising for industrial applications. The system uses an affordable solid catalyst. It does have a very high aniline:DMC feed ratio but in comparison to the other systems this seems acceptable. The yield of the reaction is relatively low but higher yields for this system, up to 97%, have been confirmed⁵⁴. The selectivity of 98% is very good. The major drawback of this system is the 8 hour reaction time; this is comparable with the other systems available for this reaction except for the lead catalyst systems. Lead catalysts however are controversial because of their toxicity and environmental hazards, especially since this is a homogeneous system¹². Another drawback is that the catalyst system is leaking. The desired phase of the reactants is the liquid phase, in order to achieve this at 150 °C, a pressure above atmospheric pressure is needed i.e. 10 bar.

In the process described by Zhao et al. there are also two by-products formed during the reaction. These are DPU and NMA, they are both formed in very small amounts but they do need to be separated from the process to prevent build-ups. The reactions to DPU and NMA are shown in Figure 3-5.

Figure 3-5 By-products of MPC synthesis reaction

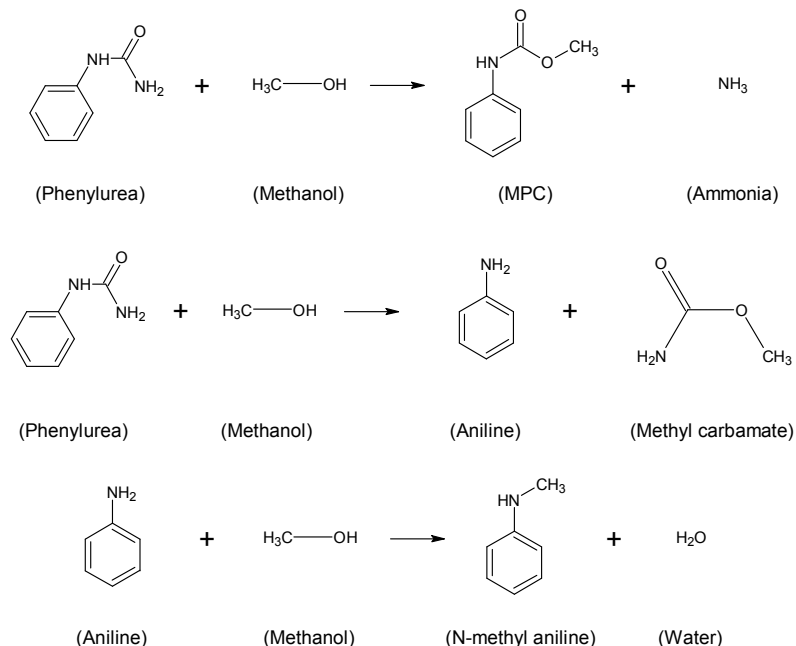


In comparison with the other MPC synthesis options this route shows the best results and is therefore selected for further use in this report. The main disadvantages being the large reaction time and aniline:DMC feed ratio.

3.2.1.2 MPC by phenylurea and methanol

Another route to MPC is by the reaction of phenylurea and methanol. This route was first reported in the research of Hwang et al.⁵⁵ In the reaction MPC and the by-products aniline, methyl carbamate and N-methyl aniline are formed in the reactions shown in Figure 3-6.

Figure 3-6 Main and side reaction of MPC synthesis by phenylurea and methanol



The research of Wang et al.⁵⁶ compares a set of catalysts suitable for this reaction and it also researches the effects of temperature and feed ratio's. A phenylurea to MPC selectivity of 85% is achieved over P-PbO catalyst at a temperature of 140 °C in an autoclave at an unknown pressure. The phenylurea:methanol molar ratio is 40:1. An advantage of this reaction is that the separation

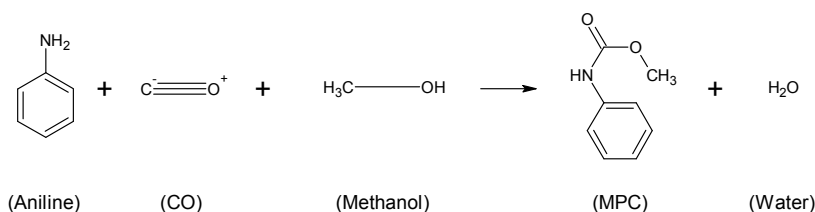
process is simple as compared to the reaction of aniline and DMC because of the absence of the DMC:methanol azeotrope.

In this reaction a homogeneous catalyst is used which will have to be recovered for reuse to make it economically viable. There is no method mentioned in the literature for a recovery process of this catalyst system. Also, there hasn't been a lot of scientific support for this technology. Therefore this process is relatively unknown, more research might prove it viable for industrialization in the future.

3.2.1.3 Oxidative carbonylation of aniline

In this method the synthesis of MPC is achieved by oxidative carbonylation of aniline. The reaction is shown in Figure 3-7 below. In this reaction aniline, CO and methanol are reacted in the presence of oxygen and thereby MPC and water are formed. This oxidative carbonylation reaction has been widely researched⁵⁷ and can be performed over noble metal catalysts.

Figure 3-7 Oxidative carbonylation of aniline

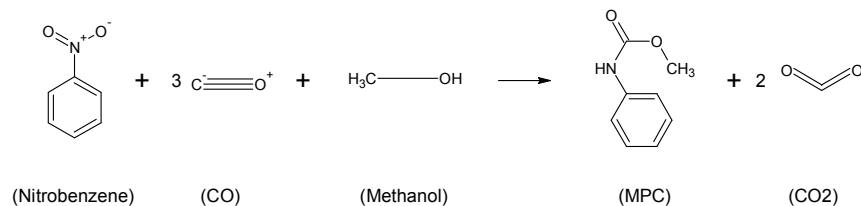


This method has been performed over a heterogeneous palladium-manganese bimetallic catalyst with reasonable results in the research of Wan et al.⁵⁸ Good results were also obtained in the research of Kim et al.⁵⁹ over a homogeneous selenium catalyst. The main disadvantages of this method are the use of expensive noble catalysts and the presence of oxygen in the reaction. The presence of oxygen causes explosion danger and therefore safety issues during operation. Because of these two disadvantages the MPC synthesis by oxidative carbonylation of aniline is not the best available method.

3.2.1.4 Reductive carbonylation of nitrobenzene

In the synthesis of MPC by reductive carbonylation of nitrobenzene, nitrobenzene is reacted with methanol and CO to form MPC and CO₂. This reaction, just as the oxidative carbonylation of aniline, is conducted over noble metal catalysts like palladium or ruthenium^{46,60}. The reaction is shown in Figure 3-8.

Figure 3-8 Reductive carbonylation of nitrobenzene



This reaction has similar disadvantages as the oxidative carbonylation reaction above, the noble metal catalysts are expensive and roughly one third of the CO is used in the reaction and afterwards the mixture of CO and CO₂ has to be separated which is an expensive process⁵⁶. Therefore the synthesis of MPC by reductive carbonylation is not as attractive as other methods like the reaction between DMC and aniline.

3.2.2. MDC synthesis

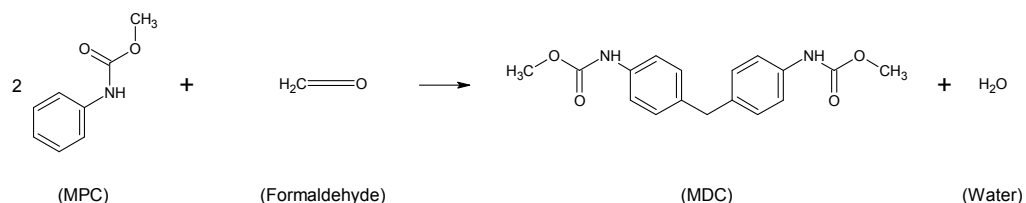
There are several methods available for the synthesis of MDC; the most common methods are discussed here. The discussion is based on scientific literature and from this literature it quickly becomes clear that MDC synthesis by the condensation reaction of MPC (methyl phenyl carbamate) with formaldehyde (Figure 3-1, 4a) shows the best performances and is the most widely researched technology at this moment. Therefore this technology will be discussed in more detail. There are some alternative routes to MDC which will also be discussed briefly.

3.2.2.1 Condensation of MPC with formaldehyde

The condensation reaction of MPC with formaldehyde is the route that shows the best performance in MDC synthesis. It is a one step, exothermic reaction that is usually conducted over an acid catalyst and MDC is usually dissolved in a suitable solvent. This paragraph first gives a broad description of the reaction and then discusses a set of scientifically proven reaction conditions. From this set a proven method will be selected for further development, the selection will be based on certain parameters that are described above.

The research of Fukuoka et al.^{9,10} was one of the first to report a viable way to produce MDC from MPC and formaldehyde. Earlier research had already proven the condensation reaction but did not obtain reasonable purities of the 4,4'-isomer of MDI^{61,62}. By now many different combinations of solvents and catalysts have been reported which render yields from approximately 40% up to 99% under varying reaction conditions. Table 3-2 summarizes proven combinations. The condensation reaction of MDC synthesis is shown in Figure 3-9.

Figure 3-9 MPC condensation reaction with formaldehyde



The reaction in Figure 3-9 shows the condensation reaction of MPC with formaldehyde to MDC and water. Usually also trimer and poly nuclear polymethylenepolyphenyl carbamates are produced as shown in the general formula in Figure 3-11. These polymers of MDC, PMDC, can be converted to PMDI in the thermal decomposition reaction. A problem that occurs in this reaction is the large amount of compounds containing a methylene-amino bond, Figure 3-10, that remain in the reaction solution if water is used as a catalyst solvent and the reaction rate decreases. These compounds are a precursor of MDC and also disturb effective MDI synthesis in the next process step if they are not converted in MDC and remain in the solution, they are difficult to separate from MDC⁶³. Other methods that should solve the two abovementioned problems were proposed^{64,65} but none seemed to be practically or economically viable¹⁰.

Figure 3-10 Precursor compound MDC

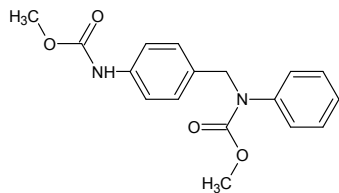
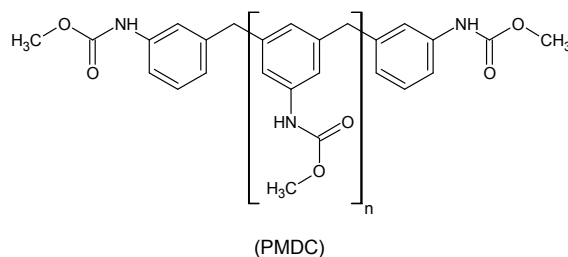


Figure 3-11 PMDC



Currently much more research has been conducted on this subject and now there are methods that seem to be economically viable and result in the right products. These methods are summarized in Table 3-2 below.

Table 3-2 MDC synthesis catalysts

Entry	Catalyst	Catalyst type ^a	Solvent	MPC:Fdh (m.r.)	MPC:cat (m.r.)	Reaction time (h)	Reaction temp (°C)	Reaction P (bar)	Phase	MDC yield	Source
1	ZnCl ₂	II				5	100	1	Liquid	81%	ixvi
2	ZnCl ₂	II	Nitrobenzene	8	2	5	120		Liquid	87%	iii
3	ZnCl ₂ /Ac	S	Nitrobenzene	4	10	3	140		Liquid	43%	iii
4	ZnCl ₂ /Ac	S	Nitrobenzene						Liquid	99%	liv
5	ZnCl ₂	H	Nitrobenzene						Liquid	87%	lviii
6	ZnCl ₂ /Ac	S	Nitrobenzene						Liquid	87%+	lviii
7	Resin catalyst	S	Calix-corch resins								lviii
8	H ₂ SO ₄	H	Composite solvent								
9	H ₂ SO ₄	II		2	0.2	3.5	95		Liquid	74%	lix
10	Mixed Acid	II	Water	1		2	100		Liquid	89%	lxx
11	H ₂ SO ₄	II	Inorganic Salt	1	0.25	4	100			77%	lxi
12	H ₂ SO ₄	H					86			92%	lxii
13	[H ₂ SO ₄ bpy]/CF ₃ SO ₃	H		12	0.25	1	70		Liquid	92%	lviii
14	[emim]PF ₆	II		4	0.25	1.5	70		Liquid	72%	lviii
15	Silicotungstic acid	S		8	40	4.5	100			83%	lviii

^a II = homogeneous catalyst system, S = supported catalyst system

Table 3-2 shows catalysts, solvents, reaction conditions and performance parameters that are available and scientifically proven for the condensation reaction of MPC with formaldehyde to MDC. Not all conditions of each reaction are known, mainly due to a lingual barrier, much literature was in Chinese or Japanese. In the selection process there is a complex set of considerations that should be taken into account that is elaborated in paragraph 3.2 above.

Based on the set of parameters the ZnCl₂/Ac system³ that is described in entry 3 and 4 of Table 3-2 is mostly suitable for commercial synthesis of MDC. This method uses a supported catalyst and has a promising confirmed yield of 99%⁵⁴. The ZnCl₂/Ac catalyst that is used in the research still demonstrates serious leakage though³. The MPC:formaldehyde feed ratio is rather high but acceptable when compared to the other systems in Table 3-2. Nitrobenzene is used as the solvent for MPC in a 1:1 ratio by weight. Selectivity of the reaction and catalyst activity are not widely discussed in the literature, this applies to all systems and therefore these factors are not considered in the selection of the MDC synthesis process. The pressure of the system is not clear in most cases, it is clear however that the reactants must be in the liquid phase.

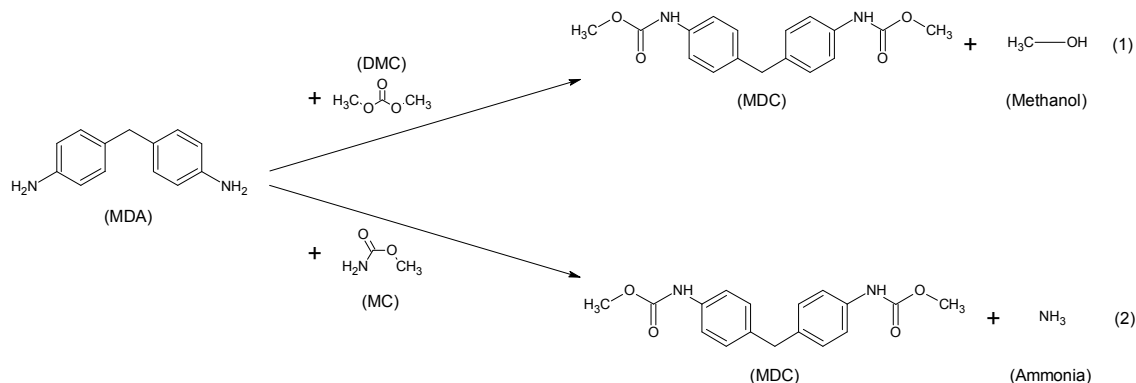
The separation process of MDC poses some difficulties. In the most widely used method first nitrobenzene is separated by steam distillation and then MDC is separated by a crystallization process in which methanol is used to dissolve MPC and by-products^{3,66,67,68,69}. This is however an extensive separation process and It is also possible to remove MDC directly by crystallization. If necessary it can be further purified by extra crystallization steps and washing with methanol¹⁰.

3.2.2.2 Methoxycarbonylation of MDA

Another feasible route to MDC is methoxycarbonylation of MDA (methylene dianiline) (Figure 3-1, 4b,c). In this reaction MDA is reacted with a methoxycarbonylation agent⁷⁰, like DMC, and thereby forming MDC. The advantage of this route is the use of MDA. As described in chapter 3.1, MDA is also used in the conventional process of MDI production. Therefore the equipment for manufacturing this material is already present and the process is well developed and optimized.

In this paragraph two methods for methoxycarbonylation of MDA are discussed. First methoxycarbonylation with DMC as agent is discussed, then the reaction with MC (methylene carbamate) is reviewed. Both reactions are shown in Figure 3-12 below.

Figure 3-12 Two methoxycarbonylation options of MDA



MDC from MDA and DMC

Methoxycarbonylation of MDA with DMC (Figure 3-1, 4b) is currently the most developed methoxycarbonylation reaction to form MDC. The reaction is shown in Figure 3-12, reaction 1. It has been performed over several catalysts, mainly Zn and Pb based catalysts^{71,3,72}. The best catalyst option that has been reported is ZC/SBA-15 by Guo et al.⁷³ In this research a MDA conversion of nearly 100% and a MDC selectivity of about 87% has been achieved. The reaction conditions are a temperature of 170-180 °C and a reaction time of 4 hours. The MDA:DMC molar ratio is 1:21.

The performance results of this research appear to be very good. However, a large excess of DMC is present during the reaction which results in very large recycle streams of DMC in the process. There is also an issue in the separation process because methanol is used for the crystallization of MDC and methanol and DMC are azeotropes. Therefore the separation requires a large amount of energy. For these reasons this method is not yet suitable for industrialization.

MDC from MDA and MC

In this methoxycarbonylation method of MDA, MDC is synthesized and MC (methyl carbamate) is used as a reactant^{70,56} (Figure 3-1, 4c). The reaction is shown in Figure 3-12 equation 2. The advantage of this methoxycarbonylation reaction over MDA with DMC is that it avoids the presence of the methanol-DMC azeotrope in the reaction solution. This makes separation by distillation easier.

In the research of Pei et al.⁷⁴ the effects on MDC yield and MDA conversion of several catalysts, reaction temperature, reaction time and molar ratio of feedstreams were investigated. The majority of catalysts tested were Zn and Pb compounds. Finally a P-PbO (C₂H₆O₂Pb) catalyst showed the best performance. A MDA conversion rate of approximately 100% and a MDC selectivity rate of approximately 83% was obtained by conducting the reaction at a temperature of 160 °C for 3 hours with a MC:MDA molar ratio of 8:1.

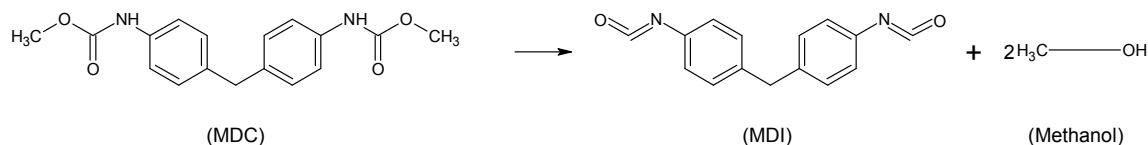
The results of this research are very promising. However, the technology is not very widely researched and performance of MDC synthesis by MPC condensation is still better. Therefore carbonylation of MDA with MC is not the preferred option for MDC synthesis at this moment.

3.2.3. MDI synthesis

The synthesis of MDI by thermal or catalytic decomposition of MDC is the third and final step in the phosgene free production process of MDI (Figure 3-1, 5). This is an endothermic and highly reversible reaction and because of the reactive –NCO group in the MDI molecule, the occurrence of several side reactions is almost inevitable. Therefore this is a very delicate reaction in which reaction conditions have to be well controlled to obtain maximum performance.

First the main and possible side reactions are discussed and then an overview of several MDI synthesis methods by MDC decomposition is given. In Figure 3-13 the thermal decomposition step of MDC to MDI is displayed. From one MDC molecule one MDI molecule and two methanol molecules are formed.

Figure 3-13 MDC decomposition to MDI



As already mentioned above, the formation of several by-products is very likely to occur during this reaction. The most common by-products to be found in the reaction mixture are the 2,4'-isomer of MDI and dimethylenetriphenyl isocyanate. Besides these two isocyanate by-products there is also the formation of MDI derivatives, usually carbodiimide compounds. These are present in much smaller quantities than the first two by-products¹⁰. Although the 4,4'MDI isomer is the best form, the 2,4'MDI and 2,2'MDI isomers are also useful products. In this reaction crude MDI is produced that consists of all MDI isomers including PMDI. These are shown in Figure 2-1.

The formation of these by-products does not only effect the yield of the reaction it also effects the purity of the resulting MDI. Pure MDI manufactured in the conventional way has a 4,4'-isomer content of 97-98% which can be further purified. Crude MDI however, has a much smaller content of the 4,4'-isomer and can be distilled to obtain a higher purity mixture.² Since the by-products in both the phosgene free and the conventionally produced MDI seem to be similar it should also be possible to purify the crude MDI, obtained by phosgene free MDI production, by distillation in the same way as in the conventional production process.

MDC decomposition methods

MDC decomposition to MDI can be conducted in multiple ways with different results. There is a general method though; in most cases MDC is first dissolved in a solvent, this is necessary because MDC is an inprocessable liquid-solid slurry, since the reaction is conducted under high temperatures the boiling point of this solvent has to be at least 150 °C. The solution is then introduced in the top section of a reactor, temperature in this reactor is above 150 °C and pressure can be vacuum, atmospheric or above atmospheric. The thermal decomposition reaction between MDC and MDI takes

place in the reactor. To push the equilibrium of the reaction to the presence of MDI, the reactants are usually contacted with a stripping agent and heat carrier, to remove the methanol and at extra heat to the endothermic reaction, often a catalyst is used as well. The methanol is taken by the stripping agent and will exit the reactor from the top section, the MDI solution will be withdrawn from the bottom section. Then the solvent will be stripped from the solution and the MDI can be further purified in a distillation process^{10,3}.

The methods differ in performance, catalyst, preferred solvent, preferred heat carrier and reaction conditions; temperature, pressure, reaction time. The selection parameters as given in the beginning of this chapter are used. Since MDC conversion is high in all systems there will be an emphasis on the yield of 4,4'MDI because of the possible occurrence of large amounts of by-products in this reaction, also the reactor volume is very important since methanol needs to be removed during the reaction to push the equilibrium to MDC conversion. The removal is easiest if the reaction is performed in falling films. For these reasons the factors that influence reactor volume are significant, these are; reaction time, reaction pressure, solvent ratio and heat carrier ratio.

Table 3-3 MDC decomposition to MDI

	1	2	Combination
Catalyst	Zn/Ac	None	Zn/Ac
Solvent	Nitrobenzene	Dichlorobenzene	Nitrobenzene
Heat carrier	DOS	N2	N2
MDC:Heat carrier (mass)		1:1.5	1:1.5
MDI selectivity	90%	90%	90%
MDC conversion	100%	100%	100%
MDC:solvent (mass)	1:8	1:9	1:4
Reactor	CSTR	Counter Current	Counter Current
Temp (°C)	280	280	280
Pressure (bar)	0.03	8-15	15
Phase	Gas	Liquid	Liquid
Reaction time (min)	1-10	1	1
Source	3, 54	10	

There are several methods to perform the thermal decomposition reaction, a complete selection is shown in Appendix A. The two best methods from this selection are shown in Table 3-3 above. According to experts these two methods can be combined with an emphasis on the second method by Fukoaka et al.¹⁰ Here the method will be discussed based on the selection parameters and the considerations for the combination are given.

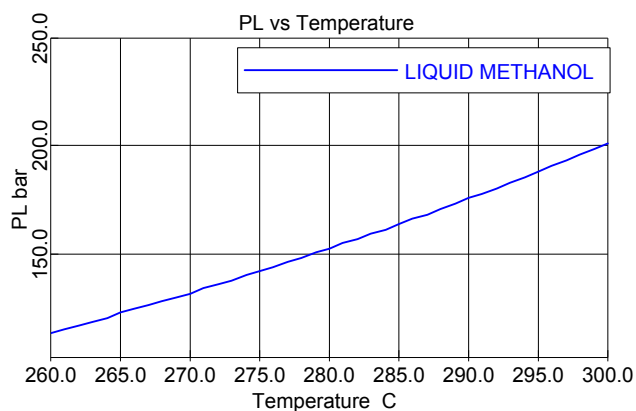
Both technologies have a 100% conversion and a high MDI selectivity of 90%. The first method uses a supported Zn/Ac catalyst system, the second method does not use any catalyst. The catalyst will improve the reaction performance and therefore the Zn/Ac catalyst system is used in the combination method.

In this reaction there is also an in situ heat carrier present, this is because the reaction is highly endothermic and therefore a constant heat flow needs to be fed into the reactor to keep the reaction going, besides regular jacketed heating. In the first system DOS (di-n-octyl sebacate) is used as a heat carrier, DOS is a heavy hydrocarbon oil, the second method uses nitrogen which is highly volatile and will be in the gaseous phase at these conditions. The nitrogen heat carrier is deemed to be more attractive, especially in a counter current (CC) reactor where it is fed into the bottom section. In such a reactor the nitrogen will quickly rise to the top section, thereby feeding heat to the reaction and also carrying methanol. The gaseous nitrogen mixture is removed from the top section of the reaction. The reaction balance is positively affected by the removal of the methanol. Therefore nitrogen is selected as the heat carrier. The amount of nitrogen that is necessary is 1.5 times by weight the amount of MDC, this can however be tested and optimized in the Aspen simulation model later on.

Because the temperature is high in the reaction the solvent with the highest boiling point is most suitable, in this case that is nitrobenzene, as opposed to dichlorobenzene. Nitrobenzene is selected as the most suitable solvent for the combination. Besides this reason, dichlorobenzene is also a suspected carcinogen according to the WHO⁷⁵. The necessary amount of nitrobenzene, according to the first method, is eight times the weight of MDC. Though the research of Feng et al.⁷⁹ claims that a ratio of 1:4 is also possible. This ratio is used for the combination of the two methods.

The last significant difference between the two reaction is the operating pressure. This is 0.03 bar in the first method, with a pressure this low, all components are in the gas phase. In the second method the pressure is between 8 and 15 bar, in this case more components stay in the liquid phase. The major driver for this decision is the vaporization of methanol, methanol has to be removed from the reaction to improve the reaction balance. Figure 3-14 shows a graph of the vapour pressure of methanol at 280 °C, a pressure of more than 150 bar is necessary to liquefy methanol, therefore a pressure of 15 bar is no problem for methanol removal in this reaction.

Figure 3-14 Vapour pressure of methanol



The main difference is the type of reactor that is used, the first method uses a CSTR and the second reaction uses a counter current (CC) reactor. The advantage of the CC reactor is that this is better for the equilibrium since methanol is removed faster from the reactor, even with the higher pressure. Therefore a CC type reactor is used for the combination method.

3.3. Phosgene free produced MDI, based on public domain data

This paragraph summarizes the phosgene free production process of MDI as it is currently available according to scientific literature. In paragraph 3.2 all phosgene free routes to MDI were discussed and MDI production from aniline, DMC and formaldehyde feedstocks is currently the most promising route. This route comprises three steps and for each step the best method was identified based on currently available public domain data. The complete route is shown in Figure 3-15 below.

The research was conducted at laboratory scale and is not intended to be directly translated into a plant on commercial scale. However, to get an insight in the process, this public domain data has been scaled up to design a process scheme for a 280 kTa MDI plant including a mass balance as is shown in Figure 3-16. The mass balance was obtained by the AspenTech software; Aspen Plus V7.1. This paragraph briefly discusses the scaled up production process and addresses major issues.

The process design used for the mass balance is based on the data that is provided by public domain literature as it is described in paragraph 3.2. The process is divided into three steps; each step

contains a feed preparation stage, a reaction stage and a product separation stage including recycle streams.

In the first section aniline is reacted with DMC over a supported $\text{Zn}(\text{OAc})_2/\text{Ac}$ catalyst to produce MPC. The mass balance shows a very large recycle stream of DMC, this will pose an issue at industrial scale since it will require very large size equipment in the process. Another issue in this step is the 8 hour reaction time and $150\text{ }^\circ\text{C}$ reaction temperature. At $150\text{ }^\circ\text{C}$, DMC, which is the major component of the reactor feed stream, is in the gas phase. This reaction time together with the large feed stream volume requires a total reactor volume of approximately $0.9 \cdot 10^6\text{ m}^3$ at atmospheric pressure. It would be impossible to build a set of reactors with this volume in reality.

Figure 3-15 Phosgene free route to MDI

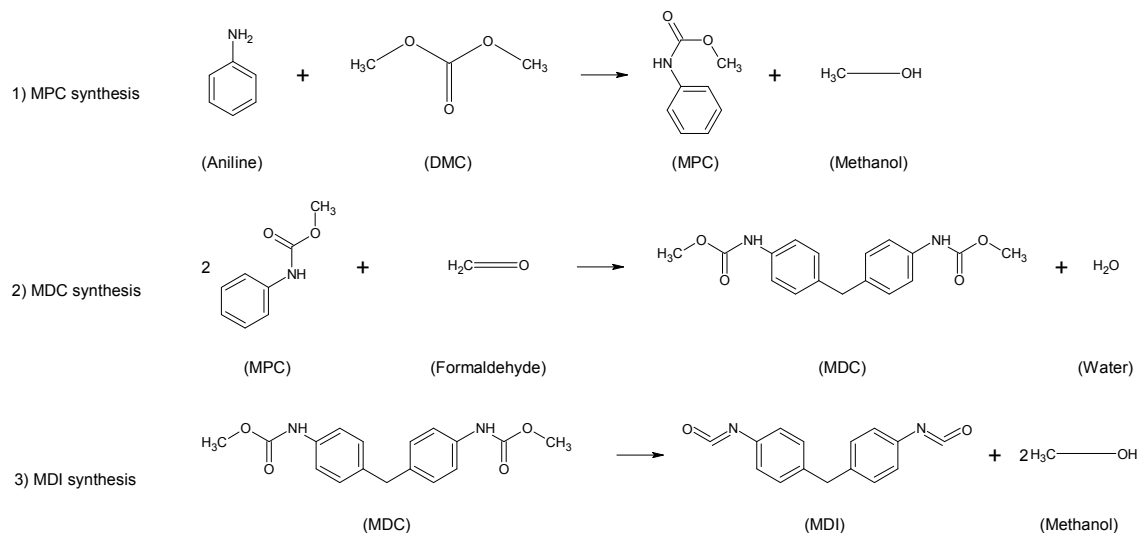
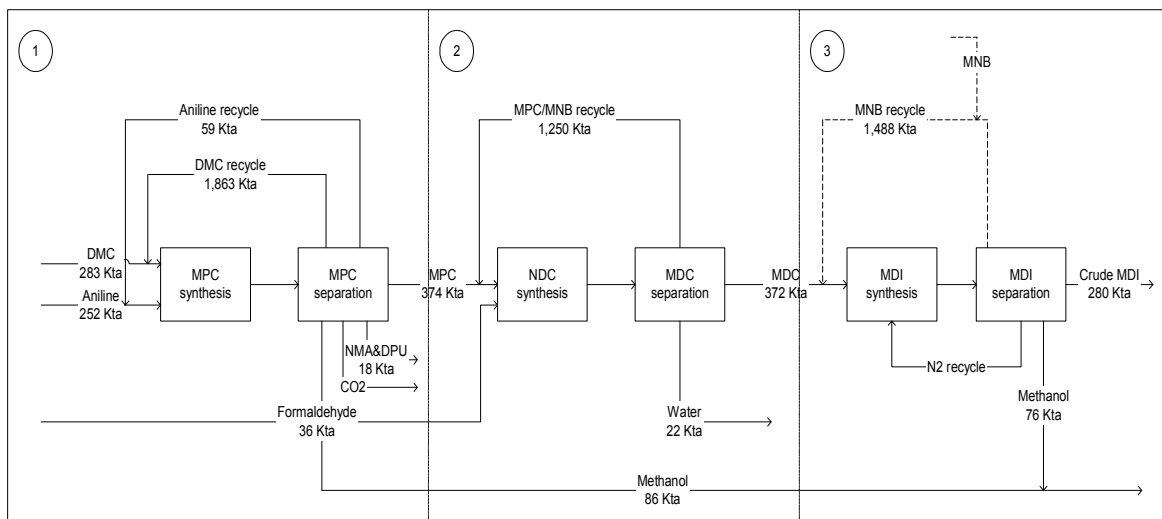


Figure 3-16 Mass balance of phosgene free production process of MDI based on public domain data



In the second step a condensation reaction between MPC and formaldehyde takes place over a supported ZnCl₂/Ac catalyst to form MDC. Also in this step there are very large volumes present, especially the MPC/MNB recycle, that is linked to the amount of MPC. The large MPC/MNB recycle is present due to the molar feed stream ratio of MPC:formaldehyde is 4:1 which equals a weight ratio of 20:1. Also this process assumes the supply of pure formaldehyde, in reality it will be supplied in a 37w% mixture with water. The water is removed after the reaction, the formalin mixture can easily be added to the liquid reaction mixture, and will even increase the waste water stream.

The thermal decomposition reaction of MDC is conducted over a supported Zn/Ac catalyst system as shown in the combination method in Table 3-3. The major issue in this process is the large recycle stream of nitrobenzene due to the high feed ratio of 1:4 of MDC:MNB.

From the brief process description above it can be concluded that there are some serious issues that occur if the process is scaled up directly based on the public domain data. In chapter 4 each step will be discussed in more extend and a base case will be formulated for further process design. Large scale advantages will be taken into account.

Alternative route

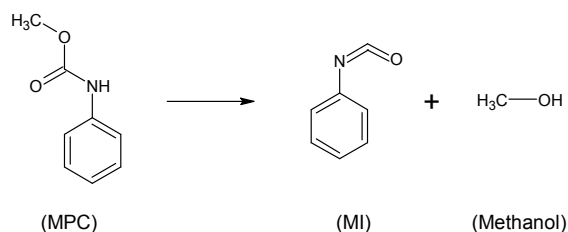
This is an alternative route that skips the separation section after MDC synthesis and MDC is directly decomposed to MDI. This route is rarely discussed in scientific literature, however it seems logical if all synthesis steps are combined as in this report.

The resulting output stream from the condensation reaction in step 2 where MDC is produced can be separated from the water by a decanter, there are two liquid phases. The organic liquid containing MDC and the MPC surplus from the reaction in a nitrobenzene solution can directly be transported to the thermal decomposition reactor in step 3. Here the thermal decomposition takes place; the MDC is converted into MDI and methanol, the MPC is converted into phenyl isocyanate (PI) and methanol. The MDI is extracted from the bottom of the reactor the PI is in the top stream of the reactor, together with the nitrobenzene. This PI can be seized with methanol and MPC can be recovered for reuse in the condensation step to MDC¹⁰.

The PI reaction route however, is only briefly mentioned in the research of Fukuoka et al.¹⁰ and is not further elaborated. Especially the reaction conditions and performance of the thermal decomposition of MPC to PI is not mentioned anywhere else, the reaction between PI and methanol to MPC is described by Sivakamasundari et al.⁷⁶ The advantage of this route is obvious; the largest part of the separation process after the condensation reaction of MPC and formaldehyde to MDC is avoided by this route since the reaction mixture can almost be directly inserted into the reactor for thermal decomposition.

On the other hand, there are some clear drawbacks; this route has not been researched and therefore the effects on the performance of the thermal decomposition of MDC to MDI are unknown and it is also unknown if MPC can be converted into PI and can then be recovered as MPC again. The R-NHCOOCH₃ group of MPC is the same as the two carbamate groups in the MDC molecule which are converted to the isocyanate, R-NCO, group in the thermal decomposition reaction. This makes it seem logical that MPC can also be thermally decomposed to PI. To obtain a high MPC recovery rate the conversion rate of the decomposition reaction is not of importance, though the selectivity is. Large amounts of by products would increase the difficulty of reversion. The described reaction sequence is shown in Figure 3-17.

Figure 3-17 The reversible reaction sequence of MPC to PI



4. Phosgene Free MDI Production Process Design

This chapter describes and determines a base case scenario and an associated process design of the phosgene free production process of MDI that is distinguished in chapter 3. The process steps and streams are already very briefly described in paragraph 3.3 in which the public domain data is directly scaled up to a full size plant. The public domain data comes from scientific research that only has been conducted on laboratory scale. A laboratory setup is usually designed to test certain reaction hypotheses and is often limited by equipment that can be used for multiple processes. It is not designed to optimize one single process. A production facility on industrial scale is fully optimized for a single process and therefore it usually shows a better performance than the same process on lab scale.

The base case, on which the process will be designed, is based on assumptions that are made with the above consideration in mind. In this chapter the process design is described including the base case assumptions.

The setup of the process design is based on the “Basis of Design” document of the University of Groningen⁷⁷. A simulation model of the base case process has been designed in Aspen Plus V7.1 and Aspen Capital Cost Estimator V7.1. The first section, of MPC synthesis, is derived from the research of D. Berends⁷⁸. The mass balance, stream information and sized equipment list have been derived from the simulation models.

The base case process design that is obtained in this chapter is used for the cost of production estimation of phosgene free MDI given in chapter 5.

Table 4-1 Process assumption summary

	MPC synthesis	MDC synthesis	MDI synthesis
Phase	Liquid	Liquid	Liquid
Temperature (°C)	150	140	280
Pressure (bar)	10	5	15
Residence time (min)	480	180	1
Feedstock ratio (molar)	Ani:DMC - 1:7	MPC:Fdh - 4:1	
Catalyst	Zn(OAc) ₂ /Ac	ZnCl ₂ /Ac	Zn/Ac
Catalyst type	Heterogeneous	Heterogeneous	Heterogeneous
Conversion	80%	92%	100%
Selectivity	98%	98%	90%
Energy	Endothermic	Exothermic	Highly endothermic
Feedstock	Aniline, DMC	MPC, formaldehyde	MDC
Product	MPC	MDC	MDI
By-products	Methanol, NMA, DPU, CO ₂	H ₂ O, MDC derivatives	Methanol, MDI derivatives
Solvent		Nitrobenzene	Nitrobenzene
Solvent feed ratio (mass)		MPC:MNB - 1:1	MDC:MNB - 1:4
Heat carrier			N ₂
Heat carrier feed ratio (mass)			MDC:N ₂ - 1:1.5

4.1. Base Case process assumptions

The phosgene free MDI process on commercial scale has not been proven yet. Therefore there are many uncertainties in the process as it is presented in chapter 3. To design the phosgene free MDI production process these uncertainties are taken into account and the base case design is based on several assumptions. Most assumptions are based on public domain data but it is also expected that performance will increase if the process is designed on commercial scale, therefore some parameters

have been improved. The assumptions for each step have been summarized in Table 4-1 above. Each step, and its assumptions, is discussed in more detail in the paragraphs below.

4.1.1. MPC synthesis

In this section there are three assumptions that are not directly based on data from scientific literature. These are explained below, all the other assumptions are based on scientific literature as it is discussed in chapter 3.

Assumptions:

1. Feed preparation
 - a. DMC:aniline ratio 7:1 by weight.
2. Reaction
 - a. Aniline conversion of 80%.
 - b. MPC selectivity over aniline; 98%.
 - c. NMA selectivity over aniline; 2%.
 - d. MPC conversion of 4%, DPU selectivity of 100%.
 - e. Reaction conditions; T = 150 °C, P = 10 bar, r.t. = 8 h.
 - f. The supported Zn(OAc)₂/Ac catalyst system is non-leaking.
 - g. A low pressure steam heated reactor with a fixed solid catalyst bed is used.
 - h. Endothermic reaction.
3. Separation & recycle
 - a. DPU decomposes at temperatures above 262 °C.
 - b. DMC and methanol azeotrope can be separated by a membrane.

For the base case a DMC:aniline ratio of 7:1 by weight is assumed. This ratio is according to scientific literature³. The DMC recycle however is very large because of the excess, therefore a decrease in this ratio is investigated in the scenario analysis in paragraph 5.3.1.

As in the research of Zhao et al.³ the conversion of aniline is 80% (2a) with a selectivity of 98% and 2% for MPC and NMA respectively (2b and 2c). 4% of the MPC is converted into DPU. In reality these reactions occur in a single reactor, in Aspen V7.1 it was modeled as two serial placed reactors for ease of programming. An increase in the conversion of aniline would decrease the recycle streams in the separation process. The largest recycle however, is caused by DMC which is dosed in a large excess, an increase of the conversion would hardly impact this recycle stream and therefore the conversion is not of major importance in this reaction.

The pressure during the reaction is 10 bar (2e); this is done to prevent the forming of gasses and thereby drastically decreasing the reactor size. Pressure is not mentioned as an important parameter for reaction performance in scientific literature³ and therefore no problems are expected. As can be seen in Table 3-1, the reaction is typically executed in the liquid phase and this requires a pressure higher than atmospheric.

It is also assumed that the catalyst system is non-leaking (2f). In the research of Zhao et al.³ this catalyst system shows serious leakage. In accordance with several experts it is assumed that additional research will be able to solve this problem. Leakage would create the necessity for additional separation equipment to clear the product streams from catalyst components.

It is assumed that the reactor is heated with low pressure steam (LPS) and that it is packed with a fixed solid catalyst bed (2g). LPS is sufficient for heating the reactor according to the simulation models used. The fixed solid catalyst bed is also used in the research of Zhao et al.³

DPU decomposes at temperatures above 262 °C (3a). This should be taken into account in the separation process; if DPU decomposes it forms a black, sticky material that is not processable⁸².

The last assumption (3b) is in the separation section; it is assumed that it is possible to use a semi permeable membrane to separate the DMC:methanol azeotrope. An azeotrope can be broken either by using an entrainer or solvent, or by using pressure, or by using a semi permeable membrane, these can be designed for specific cases¹⁸. The same trade-off was made in the research of Berends⁷⁸. A more detailed explanation of this separation step is given in paragraph 4.12.

4.1.2. MDC synthesis

In this section there are four assumptions that deviate from the scientific literature. There is also one assumption that is not mentioned in scientific literature. These are explained below, all the other assumptions are based on scientific literature as it is discussed in chapter 3.

Assumptions

1. Feed preparation
 - a. MNB:MPC weight ratio; 1:1
 - b. Fdh:MPC weight ratio; 1:20.
2. Reaction
 - a. Fdh conversion of 92%.
 - b. 4,4'MDC selectivity over Fdh; 98%.
 - c. 2,4'MDC selectivity over Fdh; 2%.
 - d. 2,4'MDC represents all possible MDC derivatives in the simulation model.
 - e. ZnCl₂/Ac is a supported, non-leaking catalyst.
 - f. Reaction conditions; T = 140 °C, P = 5 bar, r.t. = 3 h.
 - g. A cooling water cooled reactor with a fixed solid catalyst bed is used.
 - h. Exothermic reaction.
3. Separation & recycle
 - a. 4,4'MDC and 2,4'MDC are a processable slurry.
 - b. MDC does only crystallize in CR201.
 - c. The separation of MDC must be conducted at temperatures lower than 200 °C.

A formaldehyde conversion of 92% (2a) is assumed that is converted into 98% 4,4'MDC (2b) and 2% 2,4'MDC (2c). This is according to the research of Zhao et al.^{3,54} Also here the formaldehyde is not in excess and the largest recycle streams are that of MPC. Therefore an increase in conversion would not significantly impact the process design.

For ease of simulation it is assumed that 2,4'MDC represents all MDC derivatives (2d), in reality there will be more derivatives present as is discussed in paragraph 3.2.2. In scientific literature it is not mentioned that there are by products present that would disorder the process. It might only affect the quality of the final product. Several public sources claim that the resulting MDC mixture is suitable for MDI production^{3,10}.

Also here it is assumed that the solid catalyst system is non-leaking (2e). According to the research of Zhao et al.³ the catalyst system shows leakage. In accordance with several experts it is assumed that additional research will be able to solve this problem. Leakage would create the necessity for additional separation equipment to clear the product streams from catalyst components.

The reaction pressure is set at 5 bar (2f) to prevent the forming of gasses. The research of Zhao et al.³ does not mention pressure as a major influential factor on reaction performance, therefore it is assumed that his small pressure increase does not influence reaction performance. It is clear though, that the reaction needs to be performed under liquid conditions, as can be seen in Table 3-2. Therefore this pressure increase is necessary.

The reactor is cooled by cooling water and the catalyst is on a fixed solid bed (2g). According to the simulation models in the Aspen software, cooling water is suitable for cooling the reactor. The reactor heats up due to the exothermic condensation reaction. The fixed solid catalyst bed is also used in the research of Zhao et al.³

It is assumed that MDC comes as a processable slurry out of the crystallizer (3a). It is not entirely clear what the phase of the mixture is that comes out of the crystallizer unit. This depends on the composition of the exit stream. For ease of simulation it is assumed that this stream is processable. In reality it is likely that this can be achieved by adapting the reaction conditions and thereby influencing the output composition of the reaction. However, there is no specific data available on this subject in the public domain therefore this is deemed to be a just assumption.

In the public domain there is very little information available on the crystallization properties of MDC. It is assumed that MDC will only crystallize in CR201 (3b). MDC is dissolved in MNB in the entire process except for the part after the crystallizer (CR201). Therefore experts consider this is a reasonable assumption.

The crystallization properties of MDC as stated in the two abovementioned assumptions are critical for successful processing. If MDC crystallizes outside CR201 it can block the entire system and if it is not possible to separate MDC by crystallization it will change the entire separation section of this process step. In literature however, it is mentioned that, in general, crystallization is a suitable method for separating MDC from the reaction mixture^{3,10}. Therefore these assumptions seem to be viable.

It is assumed that the separation in the evaporative crystallizer cannot be conducted at temperatures above 200 °C (3c). Higher temperatures will not result in the desired condensation product¹⁰. This assumption is a rigid constraint in the base case; future empirical experiments may loosen this constraint as the process is developed in more detail.

4.1.3. MDI synthesis

In principle all assumptions are based on the research of Zhao et al.^{3,54} and Fukuoka et al.^{9,10} as is mentioned in paragraph 3.2.3 but there are some exceptions, these are discussed below.

Assumptions:

1. Feed preparation
 - a. MDC:MNB weight ratio; 1:2.
 - b. MDC:N₂ weight ratio; 1:0.5.
2. Reaction
 - a. Reaction conditions; T = 280 °C, P = 15 bar, r.t. = 1 min.
 - b. 4,4'MDC conversion of 100%.
 - c. 4,4'MDI selectivity over 4,4'MDC of 90%.
 - d. 2,4'MDI selectivity over 4,4'MDC of 10%.

- e. 2,4'MDI represents all by-products and derivatives.
- f. Zn/Ac is a supported, non leaking catalyst.
- g. Counter current, packed reactor design according to Fukuoka et al.¹⁰ It is heated by low temperature heating oil.
- h. Highly endothermic reaction.

3. Separation

- a. Temperatures in the separation of MNB and MDI should not exceed 180 °C.
- b. The reactor has a gaseous top and a liquid bottom outlet stream.

It is assumed that a MDC:MNB weight ratio of 1:2 is sufficient (1a). The research of Feng et al.⁷⁹ has proven that an MDC:MNB weight ratio of 1:4 is possible. There is very little data on the solubility of MDC available and therefore this weight ratio has been assumed. This is a very uncertain factor though, which can have significant consequences for the process design since the MNB recycle stream is very large, therefore the MDC:MNB ratio is investigated in the scenario analysis in paragraph 5.3.1.

It is also assumed that an MDC:N₂ weight ratio of 1:0.5 is sufficient to maintain the reaction temperature and effectively remove methanol (1b). This is based on the results from the process simulation model in Aspen V7.1. A larger amount would require larger volumes and would also remove more MNB from the top section of RE301 which would cause an increase in the amount of MNB necessary to dissolve MDC.

In scientific literature the reaction time (2a) is not explicitly mentioned, but it is a fast reaction; so a reaction time of 1 minute is assumed. This is based on simple calculations of falling velocity in the reactor used in the research of Fukuoka et al.¹⁰. The same research indicates the assumed temperature and pressure of 280 °C and 15 bar.

A 4,4'MDC conversion of 100% is assumed (2b) and a 90% and 10% selectivity of respectively 4,4'MDI and 2,4'MDI is assumed (2c and 2d). This is all based on the research of Zhao et al.^{3,54}

2,4'MDI represents all derivatives and by-products of the reaction (2e). This is assumed to simplify the simulation research model. In reality there will be more derivatives of MDI present in the product stream, it is very complex to determine the exact composition beforehand and this can more easily be done in a pilot plant.

It is assumed that the Zn/Ac catalyst is a non-leaking system (2f). The research of Zhao et al.³ does not indicate whether the system is leaking or non-leaking, in this research it is assumed that the catalyst system is non-leaking. More research is necessary to prove this assumption.

A counter current, packed reactor is assumed (2g). This reactor design is described in the research of Fukuoka et al.¹⁰ The MDC mixture is added in the top section and the nitrogen is added in the bottom section. The MDC mixture falls down and decomposes in MDI and methanol, since it is a strongly endothermic reaction heat is added by the nitrogen. The nitrogen also takes the methanol away from the MDI since they are both gaseous. The reactor is also jacketed and heated with low temperature heating oil, this is deemed suitable according to the Aspen V7.1 simulation models.

Temperatures in the separation of MNB and MDI should not exceed 180 °C (3a). Higher temperatures will cause secondary reactions of the isocyanate and will decrease the product quality¹⁰. This assumption does need empirical testing since there is not much known about the quality of the produced MDI in this process.

Finally it is assumed that the reactor, RE301, has a top and bottom outlet stream (3b). The top stream is gaseous and mainly contains nitrogen, methanol and nitrobenzene. The bottom stream is liquid and mainly contains nitrobenzene and MDI. This reactor is described by Fukuoka et al.¹⁰

4.2. Function of the facilities

The function of the facilities designated as the MDI plant is to produce 473 kTa of MDI from aniline, DMC and formaldehyde as a feedstock. A 473 kTa capacity is a standard capacity for this industry. The MDI plant is assumed to be built in the Netherlands, close to an existing MDI production site that uses a phosgenation process. Products will be sold in the global MDI market as it is described in Chapter 2.6. Methanol will be produced as a by-product, methanol can be used in the on site production process of DMC that is not described in this report.

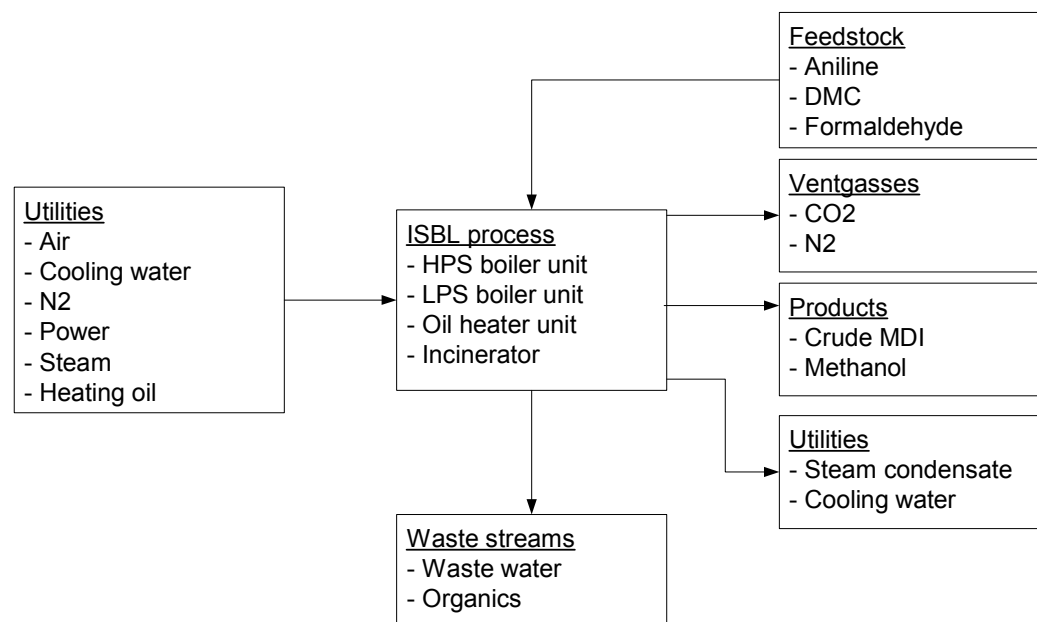
The products will either be directly stored or it will first be further purified before it is stored. Storage of MDI is OSBL and not discussed in this report. Waste water is sent to the process sewer system and will be treated in the on site waste water treatment plant. All waste streams are dealt with in agreement with governmental laws, permit requirements and corporate requirements and guidelines. Vent gasses are sent to an on site ventgas scrubber before they are sent into the atmosphere.

The utilities will be available at battery limits as is shown in Figure 4-1.

The production of 473 kTa is based on an on stream time of 360 days/year and 24 hours/day. This leads to a MDI production of 54.7 t/hr. The facilities of the MDI plant will be designed with a life time expectancy of 10 years, where possible. Due to this high on stream time a spare is present for each piece of rotating equipment except for reactors.

A block flow diagram (BFD) of all in and outgoing streams is shown in Figure 4-1 below.

Figure 4-1 Stream summary



4.3. Description of the facilities

4.3.1. Tag coding of equipment

The process is divided into three sections based on the synthesis steps described in chapter 3. The sections are:

- MDI01
- MDI02
- MDI03

Beside these three sections there is also a main area in which general supports like a control room, utility equipment a.o. are placed. Equipment is tagged by first; a two letter abbreviation of the type of equipment, the equipment abbreviations are shown in Table 4-2. Second; a three digit code; the first number represents the section, 1,2 and 3, and the other two digits are just a count. For example the fifth pump in the third section is tagged by PU305. The full equipment list of the facility is given in Appendix B.

Table 4-2 Tag coding of equipment

Code	Type of equipment
CD	Condenser
CP	Compressor
CR	Crystallizer
DC	Distillation column
DE	Decanter
FL	Flash drum
HE	Heat exchanger
IC	Incinerator
ME	Membrane unit
MI	Mixer unit
PP	Pneumatic pipe
PU	Pump
RB	Reboiler
RE	Reactor
RV	Reflux vessel
TA	(Storage) tank
VB	Vacuum booster pump
VE	Vacuum ejector package
VP	Vacuum pump

4.3.2. Production facilities

The facility is divided into three sections, the division of the sections is based on the three steps that are also described in paragraph 3.2; MPC synthesis, MDC synthesis and MDI synthesis. In the paragraphs below each section is described in detail. The process assumptions as stated in paragraph 4.1 have been taken into account in the design of these processes.

There is also a main area in which general supports are placed.

4.3.2.1 Main area

General support facilities are included in the main area. These include interconnected piping, steel structures, utility boiler units and piping. A complete list of this area is shown in appendix B.1.

The most important support facilities are briefly discussed here. The utility transport system is a pipe system that transports the utilities from either BL or the main area to each section. External piping are pipe connections with OSBL facilities that either supply feedstock products or use product streams. The heater units are for heating the oil that is used in the process, each unit delivers 10 MW. The steel structures are for supporting the larger pieces of equipment. The pipe rack carries the intersection pipe connections. The HPS and LPS boiler units are for heating the steam streams.

4.3.2.2 MPC synthesis

In this section MPC is produced by reacting DMC with aniline over a $Zn(OAc)_2/Ac$ supported catalyst system. The PFD of this section is shown in appendix Appendix D. The sized equipment list of this section is shown in Appendix B.2.

This section has two feedstock inlet streams; one is on spec DMC, the other is on spec aniline. These two feedstock products are pressurized, mixed, heated and fed into the reactor (RE101). The molar ratio DMC:aniline is 7:1. RE101 consists of 13 reactors, each reactor operates at a temperature of 150 °C, a pressure of 10 bar and is packed with $Zn(OAc)_2/Ac$ catalyst. The residence time is 8 hours, hence the large volume of the reactors. The outlet stream of RE101 consists of MPC, DPU, aniline, DMC, NMA, methanol and CO₂. This is directly fed into DC101, 2 columns, where the heavy components; MPC, aniline, NMA and DPU are separated from the light components; DMC, methanol and CO₂. A more detailed description of RE101 is given in paragraph 4.12.

The CO₂ in the top stream, containing the light components, is flashed off in FL101. The CO₂ is transported to the OSBL vent scrubber before it is released in the atmosphere. The other light components; methanol and DMC are azeotropes. They have to be separated because DMC can be recycled and methanol can be used in the on-site, but OSBL, production process of DMC. This azeotrope is separated by membrane separation that is described in more detail in paragraph 4.1.1.

The bottom stream of DC101 containing the heavy components is fed into a large column, DC104, which has 3 exit streams. The top stream contains mainly aniline and is recycled to the beginning of this section. Then there is a side stream that mainly contains the by-product NMA, this stream is fed into the incinerator, IC301, before disposal. The bottom stream contains MPC and DPU, this stream is fed into the last column, DC105. DC105 is operated at a pressure of 0.13 bar, this is to lower the temperature and prevent DPU decomposition. Decomposition occurs at temperatures above 262 °C and results in a black, unprocessable, sticky material. The bottom stream contains all DPU and is also pumped to the incinerator, IC301, before disposal. The top stream contains MPC of high purity, that is transported to the second section; MDI02. There is also a very small waste stream from the vacuum ejector package, VE101, which is transported to the incinerator, IC301.

4.3.2.3 MDC synthesis

The second step of phosgene free MDI production is the synthesis of MDC. In this section MDC is produced by the condensation reaction of formaldehyde and MPC over a supported $ZnCl_2/Ac$ catalyst system. The PFD of this section is shown in Appendix D.

There are three feedstreams in this section; the first is the inlet stream of on spec MNB, the second is the MPC stream from the first section, MDI01, the third stream is the inlet of formalin, containing formaldehyde. The MPC and MNB stream are both brought to a pressure of 5 bars and then mixed in a 1:1 weight ratio to dissolve MPC in MNB. The mixture is heated, HE201, to 140 °C and fed into the reactor, RE201. The formalin stream is pressurized and heated to a pressure of 10 bar and temperature of 140 °C. This stream is also fed into the reactor. RE201 is operated at 140 °C, 5 bar and a residence time of 3 hours.

The outlet stream of RE201 is fed into a CR201, an evaporation crystallizer. CR201 is operated at a pressure of 0.1 bar to keep the temperature below 200 °C, temperatures above 200 °C will affect MDC quality. In CR201 MDC crystallizes and is separated from the evaporated water, MNB, MPC mixture. The MDC is mixed with pure MNB. The mixture is transported to the next section, MDI03, where it is transformed into MDI. The top product is condensed in CD201 and the majority of the water is separated by two decanters, DE201 and DE202. The water is transported to the OSBL water treatment facility for further treatment and disposal. The non aqueous stream is recycled and reused.

4.3.2.4 MDI synthesis

In this section the MDC is thermally decomposed to MDI over a supported Zn/Ac catalyst. The PFD of the section is shown in Appendix D.

The section has 6 inlet streams. The bottom four; MDI02C, MDI01A, MDI01B and MDI01C are fed directly into the incinerator, IC301, for further treatment and disposal. The other two are feedstreams; MDI02A is the inlet of the MNB, MDC mixture from the previous section and N₂ is imported from OSBL. The MNB mixture is pressurized and heated to 15 bar and 280 °C, and fed into the top of reactor RE301. The N₂ is also pressurized and heated to 15 bar and 280 °C and is fed into the bottom of reactor RE301. The reactor is operated at 280 °C, 15 bar and has a residence time of approximately 1 min. The thermal decomposition reaction is a highly endothermic equilibrium reaction; therefore the N₂ is introduced from the bottom to function as a heat carrier, it also removes methanol to keep the reaction balance at the MDI side.

The N₂ mixture containing mainly N₂, methanol, and MNB coming from the top section outlet of RE301, is cooled, HE303, and fed into a flash drum, FL301. The N₂ is flashed off and recycled. The bottom product of FL301 is fed into DC301. Methanol is the top product and is condensed and transported OSBL. The bottom product of DC301, mainly MNB, is recycled, transported to section MDI02 and reused for dissolving of MDC in MI201.

From the bottom of RE301 another stream is removed, this stream mainly contains MDI and its derivatives and MNB. To prevent further reactions of MDI to unwanted products it is necessary to keep the temperature in the process below 180 °C. Therefore the separation between MDI and MNB is performed at a pressure below atmospheric pressure. MNB is separated in a column, DC302, and a flash drum, FL302. The column is operated at a pressure of 0.1 bar and the flash drum at 0.05 bar. The MDI is the bottom product and transported OSBL for further use, the MNB is the top product and is recycled and reused. Due to the vacuum ejector packages, VE301 and VE302, there are some small waste streams that are further treated in the incinerator, IC301. The incinerator, IC301, also has two exit streams, these are transported OSBL for further treatment and disposal.

4.3.3. Utility facilities

The utilities available at battery limit are specified in paragraph 4.11 below. Inside battery limits a HPS boiler unit, a LPS boiler unit and an oil heater unit are present to make OSBL recycle and reuse of utilities possible.

4.3.4. General facilities

4.3.4.1 Water treatment and sewerage

Surface water which can reasonably be expected not to be contaminated shall be collected in a clean water sewer system, which has to be connected to the existing main sewer. (Domestic sewage shall first be treated in a biological pond prior to drainage into the clean water sewer system.) Process water and contaminated surface water shall drain to a process sewer system. Then, via an OSBL API-

separator, to the biological pond. The maximum allowable temperature of waste water in sewage systems is 30 °C.

4.3.4.2 Bleed, relief and disposal systems

The relief system has to protect equipment and piping against overpressure, and shall be designed in such a way that the maximum credible relief quantity can be handled, regardless of mode of operation. The system shall be designed in such a way that a release cannot upset the operation of other sections in the plant or adjacent installations.

Gases containing combustible components which are blown off by safety valves shall be relieved to a flare system or to 'safe location'. Dispersion calculations might be required to determine 'safe location'. A risk assessment study and evaluation will have to be made before the start of the basic engineering. Gases containing non-combustible, non-poisonous or non-odorous components may be relieved to local vents. The design of these vents must prevent dangerous ground level concentrations of suffocating components (N₂, NH₃, CO₂ etc.) and liquid entrainment. Venting should always be to a safe location.

Waste gases produced continuously during normal operation and containing significant amounts of combustible, poisonous or odorous components shall be incinerated.

For draining of liquids containing combustible, poisonous or odorous components a closed piping system and/or a slop tank shall be installed. Organic liquids not miscible with water are separated and recovered.

4.3.4.3 ISBL buildings

ISBL a field auxiliary room (FAR) and a control room are included. Other rooms are assumed to be present on the existing OSBL facilities.

4.3.4.4 Outside battery limit

OSBL connections are specified in the stream summary shown in Figure 4-1.

4.4. Plant site information

It is assumed that the plant will be located in the Netherlands at an existing phosgenation MDI production site. A preliminary plot plan sketch is shown in Appendix C. The following details are shown; battery limits of the plant, access and internal roads, areas designated for construction facilities.

It is assumed that the site is flat, free of obstacles and underground cables so it doesn't need any landscaping. It is also assumed that the site is not polluted.

4.5. Plant capacity and flexibility

The phosgene free MDI plant will have a production capacity of 473 kTa with a composition as is shown in the stream summaries in Appendix D. A more detailed description of the plant capacity is given in chapter 5.

4.6. Facility mass balance

Table 4-3 shows the mass balance of the total production facility and the mass balance of each section. The mass balances are based on simulation models of each section of the production

process. The simulations were made in Aspen Plus V7.1 and they are based on the process as described in this chapter.

There is a small deviation in the mass balance. This deviation is caused by a small difference between the MPC output of MDI01 and the MPC input of MDI02; the two sections were simulated in two different simulation models. The deviation is considered negligible.

Table 4-3 Mass balance phosgene free MDI production process

	Total		MDI01		MDI02		MDI03	
	In	Out	In	Out	In	Out	In	Out
	t/hr	t/hr	t/hr	t/hr	t/hr	t/hr	t/hr	t/hr
2,4MDI		46.1						46.1
4,4MDI		5.1						5.1
Aniline	44.1	0.6	44.1	0.6				
CO2		0.5		0.5				
DMC	41.8	0.6	41.8	0.6				
DPU		1.9		1.9				
Formaldehyde	6.7	0.4			6.7	0.4		
MDC							64.4	64.4
MDC24		1.4					1.4	1.4
Methanol		28.1		15.0				13.1
MNB	6.4	6.4			1.7	1.7	4.7	4.7
MPC		2.2		66.1	65.5	2.2	2.2	2.2
N2	0.4	0.4					0.4	0.4
NMA		1.3		1.3				
Water	11.4	15.2			11.4	15.2		
	110.8	110.1	85.9	85.9	85.3	85.3	73.0	73.0

4.7. Stream specifications

The stream summary of each section is shown in Appendix D. These schemes were generated directly from the simulation models in Aspen Plus V7.1. The streams S204, S205 and S214 are in the MDI03 scheme. These streams were included in the third section for ease of simulation.

The origin of each inlet stream and the destination of each outlet stream for each section is discussed below. The inlet streams are: S101, S102, S201, S202, S204, S205, S301 and S302. The outlet streams are: S106, S113, S116, S118, S119, S120, S210, S212, S214, S308, S315 and S309, S310 and S313 together.

4.7.1. Inlet streams

S101

This is the on spec DMC inlet stream from TA101. On spec DMC is supplied to TA101 on a regular basis.

S102

This is the on spec aniline inlet stream from TA102. On spec aniline is supplied to TA102 on a regular basis.

S201

This is one of the two on spec MNB inlet streams. This stream is to compensate MNB losses in MDI02 and retain the right amount of MNB to dissolve MPC.

S202

This is the MPC inlet stream in the MDI02 section. This comes from MPC storage tank TA203 that is supplied by outlet stream S118.

S204

This is the second of the two on spec MNB inlet streams. This stream is to compensate MNB losses in MDI03 and retain the right amount of MNB to dissolve MDC.

S205

This is the MNB recycle stream from MDI03. This stream is a mixture of streams S309, S310 and S313.

S301

S301 is the inlet stream of fresh N₂ to compensate N₂ losses in section MDI03. This stream is supplied by the existing on site OSBL N₂ facility; i.e. an air liquefaction plant.

S302

This is the inlet stream of the MNB, MDC mixture from section MDI02. It is directly fed into the top section of reactor RE301.

4.7.2. Outlet streams

S106

This stream is the vent of CO₂. This stream is fed into an OSBL vent gas scrubber before it is released into the atmosphere.

S113

This stream is the methanol output stream of section MDI01. It can be stored for sale or it can be used in another on site production process i.e. DMC production.

S116

This stream mainly contains NMA. It is transported to incinerator IC301 in section MDI03 for further treatment and disposal.

S118

This stream contains MPC, the main product of section MDI01, that is transported to section MDI02 to be reacted into MDC.

S119

This stream mainly contains DPU. It is transported to incinerator IC301 in section MDI03 for further treatment and disposal.

S120

This is the condensation stream of the vacuum ejector package VE101. It is transported to incinerator IC301 for further treatment and disposal.

S210

This is the condensation stream of the vacuum ejector package VE201. It is transported to incinerator IC301 for further treatment and disposal.

S212

This is a waste water stream that is transported to the OSBL water treatment facility for further treatment and disposal.

S214

This stream is the major output of section MDI02. It is MDC dissolved in MNB that is transported to section MDI03 for the thermal decomposition step.

S308

This stream is the methanol output stream of section MDI03. It can be stored for sale or it can be used in another on site production process i.e. DMC production.

S309, S310 and S313

These are the MNB recycle stream from section MDI03 that are transported to section MDI02 for reuse as a solvent for MDC.

S315

This is the MDI product outlet stream. It can either be transported to a storage tank or to an OSBL purification process for further purification.

4.8. Component physical properties

In the discussed process model, fifteen different components are used. Table 4-4 shows all components and their physical properties. Most components are very common and do not need further elaboration. The components MPC, MDC and DPU however, are rare and not available in Aspen Plus V7.1. The properties of these components were estimated by using the property estimation tool in

Aspen Plus V7.1. This tool is capable of estimating component properties based on the molecular structure, it also uses data from the NIST database⁸⁰.

Table 4-4 Physical properties

	Formula	Molecular weight	Density at 15.6 °C (kg/m ³)	Boiling point (°C)	Freeze point (°C)	CAS number	Danger symbol(s)
2,4MDI	C15H10N2O2	250.3	1203	335.9	38.1	5873-54-1	Xn
4,4MDI	C15H10N2O2	250.3	1203	335.9	38.1	101-68-8	Xn
Aniline	C6H7N	93.1	1017	184	-6.0	62-53-3	T,N
CO2	CO2	44.0	815	-78.5	-56.6	124-38-9	None
DMC	C3H6O3	90.1	1060	90.3	0.0	616-38-6	F
DPU	C13H12N2O	212.3	1292	431.4	232.0	102-07-8	-
Formaldehyde	CH2O	30.0	732	-19.1	-92.0	50-00-0	T
MDC	C17H18N2O4	314.3	1905	595.3	179.0	7450-63-7	-
MDC24	C17H18N2O4	314.3	1905	631.9		78948-89-7	-
Methanol	CH4O	32.0	801	64.7	-97.7	67-56-1	F, T
MNB	C6H5NO2	123.1	1195	210.8	5.8	98-95-3	T, N
MPC	C6H9NO2	151.2	1241	244.5	47.0	2603-10-3	-
N2	N2	28.0	519	-195.8	-210.0	7727-37-9	None
NMA	C7H9N	107.2	983	195.9	-57.0	100-61-8	T,N
Water	H2O	18.0	1000	100	0.0	7732-18-5	None

The danger symbols for each component are based on the directive of dangerous substances⁸¹ of the European Union. They use the following labels: E, explosive; O, oxidizing agent; F, highly flammable; F+, extremely flammable; T, toxic; T+, very toxic; Xn, harmful; Xi, irritant; C, corrosive; N, dangerous for the environment. Several components are not listed in this directory; DPU, MDC, 2,4'MDC and MPC. There are no substances present that need extreme caution; it is assumed that all safety measures conform the governmental regulations. Phosgene (CAS: 75-44-5) i.e. has a danger symbol T+ and therefore special safety measures are necessary. More detailed information on component properties can be found in component databases^{82,80} and material safety datasheets (MSDS).

It should be noted that these component properties of MPC, MDC and DPU are estimations and that their behaviour may vary in reality. The production process is based on scientific research that often performed empirical experiments on lab scale, however more experimental data should be gathered to prove the behaviour of the components. Especially the behaviour of MDC might be problematical since it has a high melting point and tends to crystallize⁹, therefore the solubility of MDC in MNB is critical is mentioned above in paragraph 4.1.2. From data based on empirical research it was retrieved that DPU has a decomposition temperature of 262 °C and should not be treated at higher temperatures⁸².

The MDI outlet stream S315 will contain a mixture of MDI, PMDI and derivatives. The exact output of the reaction is unknown and can only be found by empirical research. 2,4'MDI and 2,4'MDC represent all MDI derivatives in this model. It is assumed that the output is of a standard industry quality. The mixture can always be further purified by the same vacuum distillation process as in the conventional MDI production process.

4.9. Safety analysis

In this paragraph a brief HSE analysis of the phosgene free MDI production plant is provided based on Dow's CEI and FEI, these indexes are described in more detail in paragraph 2.5. The calculations are based on the same assumptions as the calculations of the conventional MDI production process using phosgene. This is a rough calculation that is used to give a quick feel in the safety difference between the conventional and the new MDI production processes. For each scenario a 5 cm. hole in a 20 cm. diameter pipe is assumed. This is not a full safety assessment.

First the highest risk spots in the process are identified. These are the reactors, because of the relatively high pressures and temperatures, and large storage tanks, because of the large volumes present; RE101, RE201, RE301, TA102, TA201 and TA204. For each piece of equipment the relative impact of each component is taken into account and the hazard distance is calculated. The results are shown in Table 4-5. The component data is given in Appendix H.

Table 4-5 CEI & FEI hazard distance of phosgene free MDI production process

Equipment	Vessel volume	Temperature	Pressure	Components	CEI & FEI Hazard Distance
	<i>m3</i>	<i>°C</i>	<i>bar</i>		<i>m</i>
RE101	1500	150	10	DMC, MPC, Aniline	48
TA102	350	25	1	Aniline	0
TA201	1000	25	1	Nitrobenzene	1
RE201	1500	140	5	MPC, MDC, MNB	34
TA204	9500	25	1	Formalin	9
RE301	30	280	15	MNB, MDI, N2, Methanol	433

The highest risk in the phosgene free process is in RE301 in which each reactor has a hazard distance of 433 meter. This hazard distance is even lower than the lowest hazard distance in the conventional process, which is 1,070 meter. Based on these figures it can be confirmed that the phosgene free MDI production process is indeed safer than the conventional MDI production process using phosgene.

4.10. Waste stream specifications

4.10.1. Air pollution

All gaseous waste streams will be such that air pollution is kept within governmental regulations. Emissions include the total of normal and continuous vent and purge losses, normal leakage from flanges, pumps and valves and the losses during cleaning and/or repair of equipment. Losses due to blow-off of relief valves and other losses which are not normal but can be expected, i.e. start-up and shutdown losses, are not included.

4.10.2. Water pollution

The water flow to the process sewer should be as minimal as feasible. The quantity of organic and inorganic components in the water should be known for normal operating conditions as well as special cases i.e. start-up, blow-down. The temperature is typically 25 °C and shall not exceed 30 °C.

4.10.3. Soil pollution

The soil is protected to prevent possible pollution. The site is entirely paved with concrete, containing drainage trenches, an underground slop system and an underground sewer system that is connected to OSBL waste treatment facilities.

4.11. Utility specifications at battery limits

All utilities that are used in the phosgene free production process are shown in Table 4-6 below. These specifications have been used for general utility calculations and are not further specified in this research.

Table 4-6 Utility specifications at battery limits

Utility specifications at battery limits				
	Inlet temperature (°C)	Exit temperature (°C)	Operating Pressure (KPA)	Utility type
Steam @2760KPA	229.2	229.2	2760	Heat source
Steam @1135KPA	184	184	1135	Heat source
Steam @690KPA	164	164	690	Heat source
Low Temp Heating Oil	315	287	2523	Heat source
High Temp Heating Oil	385	357	2523	Heat source
Cooling Water	24	35	105	Heat sink
Air	Ambient	50	100	Heat sink
Electric Power				Power source

Steam is produced in on site ISBL boiler units. Cooling water is taken from the already existing on site OSBL cooling water supply; i.e. a closed cooling water system or a natural cooling water source like a river or sea. Electricity is tapped from the existing electricity distribution network that is already present on site. The supply of utilities will be controlled from the FAR and control room. Oil can be recycled and is heated in the ISBL heater unit. The nitrogen that is used in the process is tapped from existing on site OSBL facilities; i.e. an air liquefaction plant. Air is used in the air cooled condensers, these are deployed if the outlet temperature is not below 40 °C. The air is filtered and free of oil and dust. The plant is built in the Netherlands and it is assumed that ambient temperature will not be above 40 °C.

4.12. Equipment details

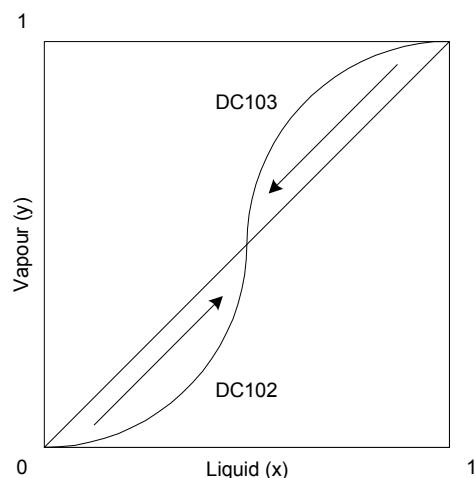
All equipment is listed in Appendix B, most pieces of equipment are standard, however there are some more exotic pieces of equipment that are explained in more detail in this paragraph.

ME101 & azeotropic separation

ME101 is a membrane unit that is used to separate the two azeotropic components DMC and methanol. It is assumed that this membrane is more permeable to one of the two components than to the other. Therefore the two output streams have different compositions, S110 into DC102 has a larger DMC fraction and S111 that is fed into DC103 has a larger methanol fraction. This causes DC103 to be on the upper side of the azeotrope and DC102 to be on the lower side of the azeotrope, as shown in Figure 4-2. This way the azeotrope is broken and methanol can be recovered in DC103 and DMC can be recovered in DC102.

This unit is simulated by a “Component separator” in the Aspen Plus V7.1 simulation model of section MDI01. It is assumed that it reaches a 90:10 molar split ratio for DMC and methanol.

Figure 4-2 Columns working at opposite sides of the azeotrope



RE101

As is shown in the equipment list of section MDI01 in Appendix B.2. RE101 consists of 13 reactor vessels with a 5 m. diameter and a 15 m. height. Each reactor is packed and jacketed. This set of reactor vessels has to be this huge due to an assumed reaction time of 8 hr. of the MPC synthesis reaction. Hence the extremely high costs for RE101.

VE101, VE201, VE301, VE302

VE101, VE201, VE301 and VE302 are the vacuum ejector packages (VEPs) that are necessary in the phosgenefree production process. The function of the vacuum is to make effective separation possible at lower temperatures to prevent further reaction and decomposition of components.

In this phase it is not clear what these VEPs should look like in detail. For this report it is assumed that each unit consists of one or more two stage ejectors with condenser (VE), one or more vacuum pumps (VP) and one or more vacuum booster pumps (VB). In the flow schemes they are modelled as one block that is tag labelled VE. In the cost estimation in chapter 5 all abovementioned units are taken into account. It is assumed, in accordance with an estimation expert, that this will cover the costs necessary for the VEPs.

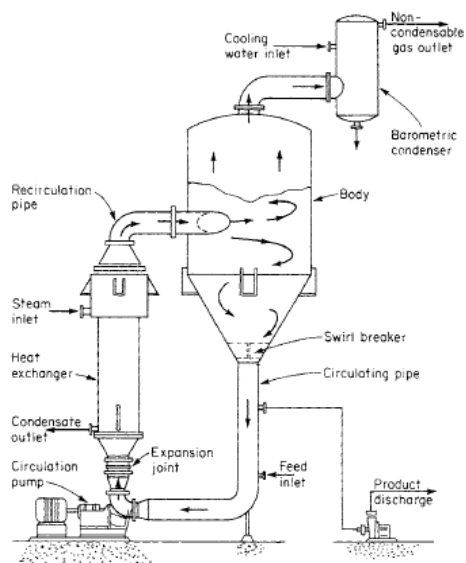
CR201

CR201 is positioned behind RE201 and separates MDC for further reaction. It is assumed that this separation can successfully be executed by an evaporative crystallizer, i.e. a forced circulation evaporative crystallizer as is shown in Figure 4-3⁸³. This unit operation is modelled by a "Flash2" unit in the Aspen Plus V7.1 simulation model of section MDI02. It obtains approximately a 95% purity MDC separation. Since the component properties of MDC and therefore its behaviour is unknown it is impossible to make a more realistic simulation without extra empirical data. It is however possible to separate MDC from this mixture by crystallization, it is also possible to obtain higher purities by washing the mixture with methanol⁹. For this research it is assumed that a single crystallization unit is sufficient for successful MDC separation.

RE301

RE301 is a jacketed, continuous, heterogeneous, packed bed, falling film reactor. In this reactor the highly endothermic thermal decomposition reaction of MDC to MDI and methanol takes place. The MDC stream, S302, enters RE301 in the top section. This mixture of MNB and MDC falls down in a film over the packed bed and the MDC decomposes into MDI and methanol, the methanol immediately vaporizes and is taken to the top section. In the bottom section the N₂ is introduced in RE301, the function of N₂ is to transport heat into the reactor and to remove the methanol. The bottom outlet contains liquid MNB and MDI, the top outlet is gaseous and contains MNB, methanol and N₂.

Figure 4-3 Forced circulation evaporative crystallizer (Swenson Process Equipment Inc.)



IC301

IC301 is the ISBL incinerator unit that is capable of handling all process waste streams that are present in this production process.

5. Financial Analysis

In this chapter the phosgene free MDI production process is analysed based on economics. It is also compared to the conventional MDI production process using phosgene. First the cost of production estimation is discussed, then the phosgene free MDI production process is compared to the conventional process in a sensitivity analysis, a scenario analysis and a NPV analysis.

5.1. Basis

The cost of production estimates discussed in this chapter are based on world-scale plants built in the Netherlands, European region. It is assumed that the plants are built instantaneously in 2010. Evaluations are made on a 2009/2010 average basis. Due to the financial crisis price fluctuations have been very unpredictable and therefore it is difficult to estimate. Sources are always mentioned and prices have been used consistently throughout the entire report.

5.1.1. Material valuation

Table 5-1 below shows the material prices that are used in the cost of production estimates.

Table 5-1 Material prices

	Cost per metric ton
	EUR
DMC	420
Aniline	1,051
Formalin	371
Methanol	127
Nitrobenzene	1,002

It is assumed that DMC is produced on site, therefore the DMC price is an internal price. DMC can be produced in high yield from methanol and urea when dimethyldimethoxytin is used as a catalyst in combination with triglyme⁸⁴. Also there is almost no trade in DMC. This price is based on an early 2009 estimation that was used by Fluor internally⁸⁵. Other prices are based on averages of ICIS.com⁸⁶ and from prices given in chemsystems PERP reports¹⁶. Methanol is a by-product and is used in an on site production process, for methanol 80% of the actual market price was used. Formalin is a 37 weight % formaldehyde solution in water. These prices are based on tank trucks, delivered materials.

5.1.2. Investment basis

A process plant can be viewed as consisting of two types of facilities. The first is the manufacturing area, containing all process equipment needed to convert the raw materials into the product. The capital costs of these facilities are commonly referred to as the inside battery limits (ISBL). The second group of facilities contains the outside battery limits (OSBL) or offsites. These include general utilities (e.g. instrument and utility air, nitrogen, fire water), administrative buildings, steam generation facilities, cooling water systems, electrical distribution systems, and waste disposal facilities. In addition to the plant capital, the owner usually incurs other project costs (OPC), such as project management and startup, which can be capitalized for tax purposes. The phosgene free MDI production project does only include ISBL and OPC costs but no OSBL costs. All installed support capital is specified only for this production facility and is therefore considered ISBL.

For all the cases considered, investment costs assume “instantaneous” construction or implementation in the designated year. This is a simplification because initiation, design, and construction can take several years to complete. In order to undertake the instantaneous analysis, phased investment costs and associated financial charges are consolidated into a single overall project cost.

5.1.3. Cost of production basis

The cost of production (CoP) gives a product cost price per ton of product, in the analysis it is broken down into variable costs, fixed costs and a depreciation and ROI factor. The costs are not exactly known beforehand and therefore it is a CoP estimation.

Capital costs are estimated by using the estimation software of aspentech; Aspen Capital Cost Estimator V7.1. Default European region settings were used except for the settings mentioned. Contingency was set at 25% because of the high uncertainty in this project. The wage rate for all crafts was set at 70 EUR/hr, an average wage rate for the Netherlands. In all equipment where the end product is handled SS304 was used as material, in all other equipment default materials were used.

Labor costs are based on typical manpower rates for the Netherlands. Direct overhead and maintenance costs are set on general industry standards; 45% of labor costs and 4% of TDM respectively. General plant overhead, Insurance and property and Environmental costs are also set at standard industry levels; 60% of direct fixed costs, 1% of TFC and 0.5% of TFC respectively.

Cash costs can be separated into two discrete categories:

- Variable costs – raw material, including catalysts and membrane; utilities and by-products.
- Fixed costs – direct operating costs and allocated costs.

Raw material costs, utility costs and by-product credits are considered variable costs since they are, to a large extent, dependent on the plant’s operating rate. Fixed operating and allocated costs are largely independent on the plant’s operating rate and are considered fixed costs. Fixed costs are largely dependent on the capital costs. The sum of the variable and the fixed costs is termed the cash cost of production. This is the “out-of-pocket” expense that an owner incurs before including capital charges such as depreciation and return on capital.

All capital is depreciated over 10 years, which is the industry standard for ISBL and OPC costs. A return on invest rate of 10% over total invested capital (TIC) is used in the cost of production estimation.

For the raw material cost estimations the mass balance from paragraph 4.6 is used.

5.1.4. NPV basis

The NPV (Net Present Value) analysis is a very common project valuation method. NPV is defined as the present value of future cash flows, discounted at the appropriate cost of capital, minus the initial net cash outlay for the project. Basically projects with a positive NPV should be accepted and projects with a negative NPV should be rejected. If the projects are mutually exclusive, as is the case for this report since multiple option for one plant are compared, the project with the highest NPV is the best option⁸⁷.

The NPV analysis is based on two parameters; the net cash flow per year and the discount rate. The discount rate is set at 10% which is industry standard. The net cash flow during the operating years is the MDI selling price minus the MDI cash cost derived from the CoP estimation. After the capital is fully depreciated, which is after 10 years, it is assumed that the production rate decreases by 25%, this is determined by the End of depreciation factor. The capital investments are made in the first three years; it is assumed that land cost are MM€ 20 for each project and the TIC costs are equally divided over these years. The working capital is assumed to be 10% of the TIC and the proceeds of the plant

sale and working capital are assumed to be 10% of the working capital. The scenarios and financial results are shown in a cumulative cash flow diagram.

5.2. Cost of production

In this paragraph the costs of production estimations for phosgene free MDI are discussed. First the build-up of the capital costs is elaborated and then the cost of production per ton MDI are discussed.

5.2.1. Capital cost

The capital cost estimation for the phosgene free MDI production process is based on the process description that is given in chapter 4. Based on the flow schemes in Appendix D and the given capacity of 473 kTa a sized equipment list has been made that is shown in Appendix B. This list was loaded into the Aspen Capital Cost Estimator V7.1 simulation program with the settings described in paragraph 5.1.3 above. With this software the project costs have been generated and these are shown in Figure 5-1.

Figure 5-1 Project capital cost summary phosgene free MDI

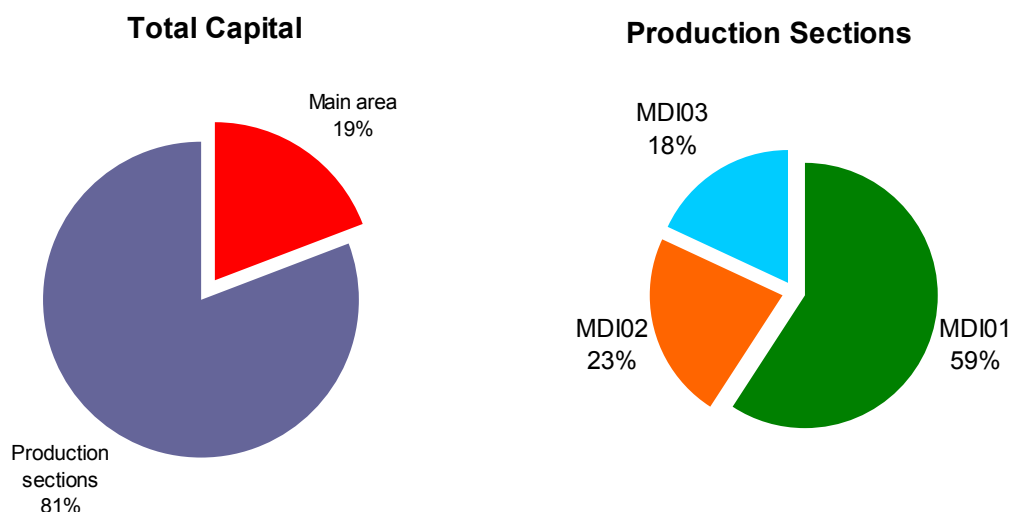
Aspen ICARUS						
Project Cost Summary						
<i>Project Title:</i> Phosgene free MDI			<i>Scenario Name:</i> KBaseCase			
<i>Project Name:</i> MDI total			<i>Job No.:</i> --			
<i>Proj. Location:</i> Rotterdam			<i>Prep. By:</i> --		<i>Currency:</i> EURO EUR	
<i>Estimate Date:</i> 14JAN10 11:53:10			<i>Est. Class:</i>			
Account	MH	Wage Rate	Labor Cost	Matl Cost	Total Cost	Percentages
(2) Equipment	27,114	70.00	1,897,990	77,516,789	79,414,780	50.8% of TDC
(3) Piping	197,032	70.00	13,792,237	15,838,560	29,630,797	19.0% of TDC
(4) Civil	86,609	70.00	6,062,636	2,740,202	8,802,838	5.6% of TDC
(5) Steel	38,224	70.00	2,675,659	6,713,885	9,389,544	6.0% of TDC
(6) Instruments	43,672	70.00	3,057,239	10,311,168	13,368,407	8.6% of TDC
(7) Electrical	26,560	70.00	1,859,214	3,168,347	5,027,561	3.2% of TDC
(8) Insulation	83,720	70.00	5,860,413	2,794,064	8,654,477	5.5% of TDC
(9) Paint	24,891	70.00	1,742,397	259,238	2,001,635	1.3% of TDC
Total Direct Field Costs	527,822		36,947,785	119,342,254	156,290,039	100.0% of TDC
	(TDMH)		(TDL)	(TDM)	(TDC)	
Indirect Field Costs	96,874				32,870,800	89.0% of TDL
	(IFMH)				(IFC)	
Total Field Costs	624,696				189,160,839	63.2% of TIC
	(TFMH)				(TFC)	
Freight		3% of TDM			3,580,268	3.0% of TDM
Owner's costs		5% of TDC			7,814,502	5.0% of TDC
Engineering and HO	145,136				11,018,600	3.7% of TIC
Other Project Costs					12,745,739	4.3% of TIC
Contingency					74,773,316	25.0% of TIC
Total Non-Field Costs	145,136				109,932,425	36.8% of TIC
	(HOMH)					
Project Total Costs					299,093,264	191.4% of TDC
					(TIC)	

Total project costs (TIC) consist of field costs (TFC) and non-field costs. Total field costs are the sum of direct (TDC) and indirect (IFC) field costs. Direct field costs are divided over 8 accounts; equipment,

pipng, civil, steel, instruments, electrical, insulation and paint. Each account is the sum of labor (TDL) and material (TDM) costs. The accounts cover all the equipment and facilities that are necessary for the production plant, these include roads, sewer systems, instrumentation and many more, a complete list is shown in Appendix B. The ratio of each account to TDC has been checked by an industry expert and the ratios are conform to industry standards. The indirect field costs consist of support expenses that are necessary for construction i.e. scaffolding, home office support costs etc. A complete overview of the IFC is given in Appendix E. The non-field costs are costs that are not directly linked to the actual construction of the facilities, these include engineering costs, contract fee and also contingency. A full overview is given in Appendix E.

The total capital investment for a 473 kTa phosgene free MDI production facility, including a contingency factor of 25%, is estimated to be € 299 million.

Figure 5-2 Capital costs per section



The division over the capital costs over the three major sections and the main area is shown in Figure 5-2 above. The main area accounts for 19% of the capital costs. The capital costs of section MDI01 are by far the largest with 59%. The main reason for this is the very large size of RE101; 13 reactors, each with a volume of 295 m³. These cost a staggering € 38.2 million, which is 24% of the total direct field costs (TDC) on it's own. The reason is the 8 hr. residence time. Also DC101, DC102 and DC104 and their associated pieces of equipment are very expensive; mainly due to the large recycle streams in this section.

In section MDI02 also the reactor RE201 is very expensive and the crystallizer CR201 as well. The large reactor size is also caused by a large residence time of 3 hr. In section MDI03 there are no clear outliers.

5.2.2. Cost of production

In Appendix A the estimated cost of production of phosgene free MDI is shown. The cash costs of MDI are estimated at € 1,582 per ton. Including a depreciation of capital of 10% of TIC and a linear ROI rate of 10% of TIC a MDI cost of € 1.709 per ton is estimated. It should be noted that the depreciation factor does not include OSBL depreciation costs since they are not within the scope of this report.

The largest component is the raw material cost, which accounts for 82.8% of total MDI costs. Within the raw materials the feedstock materials; aniline, DMC and formalin are the largest cost. What does stand out is the large amount of nitrobenzene, which is a solvent that is needed in this process.

The utilities represent 10.9% of the total MDI cost. A very large factor herein is the cost of steam that accounts for 81% of the total utility costs. An overview per section is given in Table 5-2 below.

Table 5-2 Utility cost overview phosgene free MDI production

Utility	MDI01	MDI02	MDI03
	<i>MMEUR</i>	<i>MMEUR</i>	<i>MMEUR</i>
LTHO	2.83	0.00	8.52
HTHO	0.95	0.00	0.22
CW	0.06	1.62	0.67
EL	0.57	0.76	0.60
HPS	17.41	18.68	4.67
MPS	0.00	0.00	5.55
LPS	19.17	6.11	0.00
Total	40.98	27.16	20.23

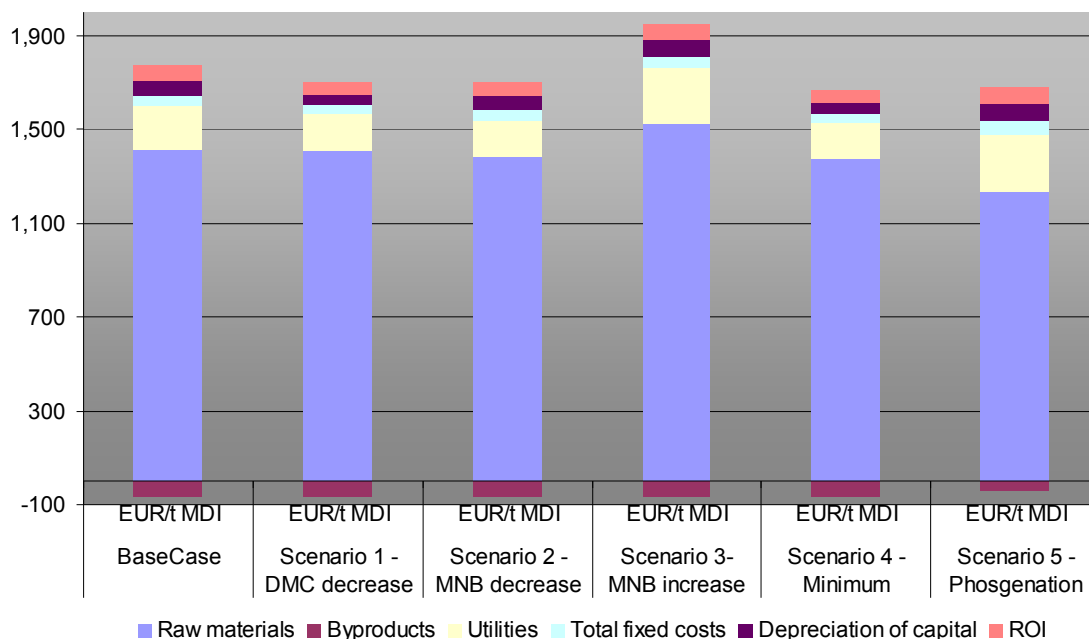
5.3. Economical analysis

In this paragraph the sensitivity of the estimated MDI cost from paragraph 5.2 is analyzed. First the technical aspects are assessed and several scenarios are set up. The phosgene free production process will also be compared to the conventional phosgenation process. Finally some sensitivity tests are conducted to find and test key differences in the cost of production estimations of both technologies.

5.3.1. Scenarios

For this scenario analysis the scenario described in paragraph 5.2 above will be taken as the base case scenario. Four scenarios have been set up based on the base case scenario; the results are shown in Figure 5-3 and Appendix G. There is also a fifth scenario that is based on the phosgenation production process of MDI². Each scenario is elaborated below.

Figure 5-3 Scenario analysis



Scenario 1 – Decrease DMC:aniline feedstock ratio

As mentioned in paragraph 5.2.2 the steam costs of phosgene free MDI production are relatively high. In Table 5-2 it can be seen that 53% of the steam is used in the first section, MDI01, of the plant. From the equipment list in Appendix B it can be seen that DC101, DC102 and HE101 consume 91% of the steam in section MDI01. An important factor for the energy usage is the size of the streams, in this section there are very large recycle streams, especially of DMC, that cause high energy usage. Therefore this scenario assumes a smaller DMC:aniline feedstock ratio of 2:1, opposed to the 7:1 ratio in the base case scenario. The smaller streams also affect the capital costs.

Due to this measure the total utility costs go down by 19% and the steam costs are down by 23%. It also affects the capital costs; DC101 and DC102 are both down to 1 column instead of 2 and have also decreased in diameter, RE101 is down from 13 reactors to 4 and also less utility hardware is necessary. The total project costs (TIC) decreased by 22%. This scenario's measure does not have a significant impact on the mass balance. In total it results in a 4.2% decrease in the MDI cost, down to € 1,637 per ton.

The decrease in the DMC:aniline ratio could be achieved if the reaction performance of the MPC synthesis reaction would improve. This can be achieved by improving the catalyst performance.

Scenario 2 – Decrease amount of MNB solvent

In this process nitrobenzene is used as a solvent for mainly MDC. Not much is known about the properties of MDC and therefore the amount of MNB solvent that is necessary is uncertain. This scenario assumes that only half the amount of MNB is necessary in comparison to the base case scenario. It is likely that this will affect the raw material costs, the utility costs and also the capital costs since it will change the stream sizes. MNB is only used in the sections MDI02 and MDI03 and will therefore only affect those sections.

Due to this measure the supply of MNB decreased by 39% and caused a decrease of 2% in the raw material costs. Utility costs in MDI02 decreased by 16% and in MDI03 by 34%. Total utility costs decreased by 16%. Several minor volume decreases caused a TIC shrink of 7%. The total MDI cost went down with 4.1%.

Scenario 3 – Increase amount of MNB solvent

This scenario is based on the same uncertainty as scenario 2, only this scenario assumes a double amount of MNB compared to the base case scenario. This will also affect raw material costs, utility costs and capital costs since it will change the stream sizes in section MDI02 and MDI03.

The supply costs of MNB increased by 125% and raw material costs increased by 8%. Utility costs in MDI02 increased by 32% and in MDI03 by 37%. Total utility costs went up by 24%. The main adjustment in the capital costs is the increase of DC302 from 2 to 3 units, together with other minor changes in hardware this increased TIC by 6%. The total MDI cost went up with 10.4%.

Scenario 4 – Phosgene free minimum

In the fourth scenario the minimum costs for MDI are estimated based on the base case material prices. Stochastic amounts of raw materials are assumed and for the other factors the minimum of the other scenarios is taken. This scenario is for referential purposes and it is highly unlikely to be achieved in reality. However, it does give an insight in the scope and possibilities of the phosgene free technology.

According to this scenario the phosgene free produced MDI cost can not go very far below the cost of conventionally produced MDI.

Scenario 5 – Phosgenation

This scenario is based on the phosgenation production process of MDI². The cost of production estimation of the 473 kTa plant as shown in Appendix A is derived from a cost of production estimation of a phosgenation plant with a capacity of 136 kTa in 1998. The same prices were used as in the base case estimations, the material prices of chlorine, caustic, CO from gas and HCl have been updated. The up scaled plant capital costs have been calculated according to the following formula¹⁹:

$$CC_1 = \left(\frac{Cap_1}{Cap_0} \right)^{2/3} CC_0$$

CC = Capital Cost

Cap = Capacity

The up scaled OSBL costs have been halved because the OSBL costs of the phosgene free plant have not been taken into account in the base case scenario. However ISBL utility costs have been taken into account in the base case scenario and these were part of the OSBL section in the original 136 kTa phosgenation plant. The capital cost estimation is also shown in Appendix A.

Appendix A shows that the MDI cost of € 1,641 per ton is 3.9% lower than the base case scenario but slightly higher than the scenarios 2 and 3. Raw material costs are significantly lower, but utility costs and capital costs are higher than the phosgene free MDI production process. Compared to the base case scenario raw material costs are 13% lower, utility costs are 31% higher and the total capital investment is 14% higher.

5.3.2. Price sensitivity

The raw material costs represent the larger part of the total costs in both phosgene free and phosgenation production of MDI; 84% and 76% respectively. The feedstock products however, are very similar. The major difference is the use of DMC in the phosgene free production process; therefore the change in MDI price compared to a change in DMC price for both processes is investigated. Also a change in all raw material prices and a change in capital costs has been investigated. The results of this sensitivity analysis are shown below.

Figure 5-4 shows the sensitivity of the MDI cost to a variation in the DMC cost, the base DMC cost is € 420 per ton. Logically it is linear relation and a DMC cost variation of 10% causes a € 33 MDI cost difference. The MDI cost of the phosgenation scenario is € 1,633 per ton MDI so the economic feasibility of phosgene free MDI production is very much dependent on the DMC cost.

Figure 5-4 MDI cost sensitivity to DMC cost variation

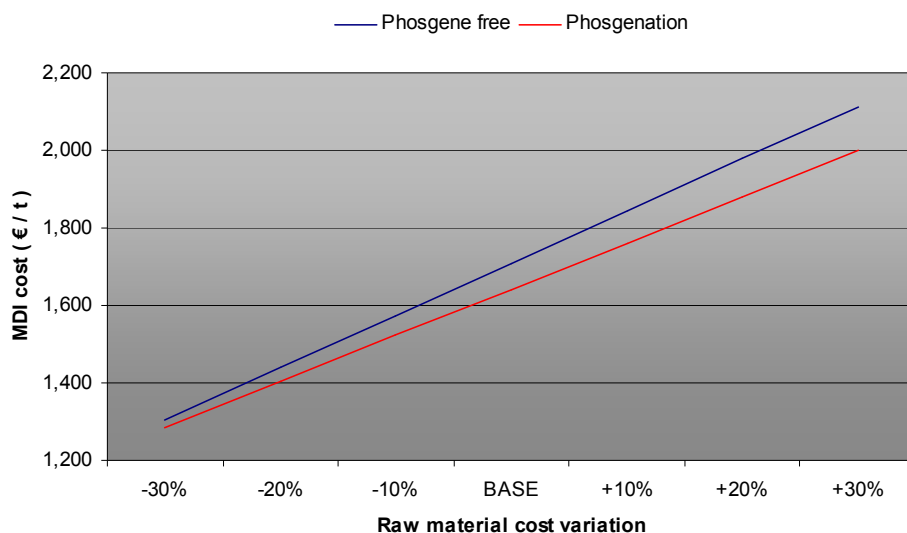
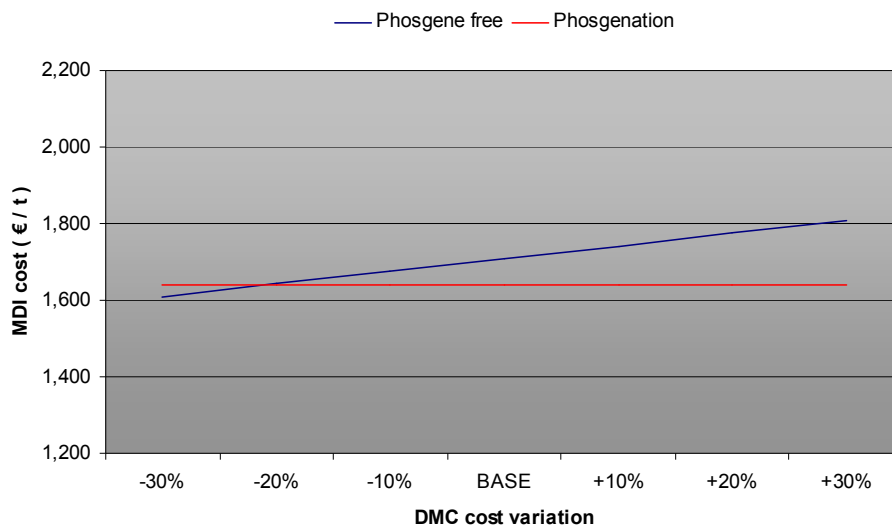


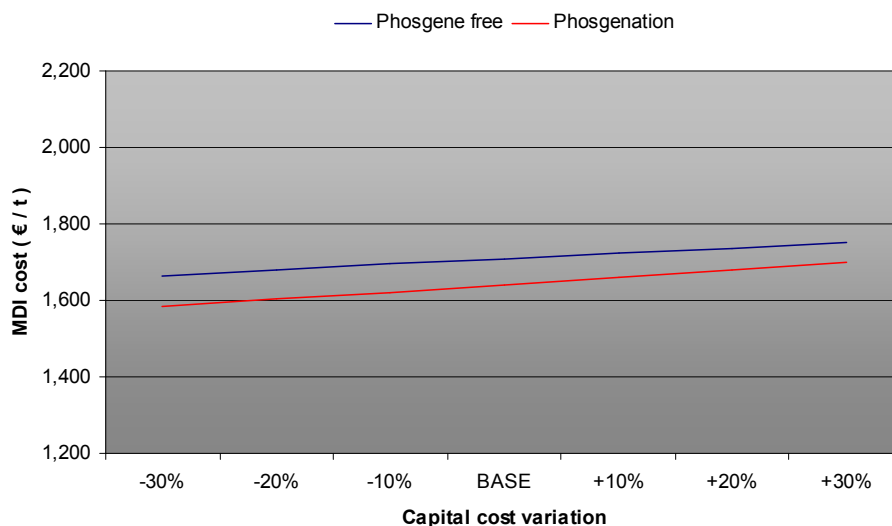
Figure 5-5 shows the sensitivity of the MDI cost to a variation in the raw material costs for both the phosgene free and the phosgenation production process of MDI. It shows that the phosgenation is slightly less sensitive to changes in the raw material costs than the phosgene free process. This is to be expected since the portion of the raw material costs of the phosgenation process is a bit smaller than in the phosgene free process.

Figure 5-5 MDI cost sensitivity to raw material cost variation



In Figure 5-6 it is shown that the MDI cost in both the phosgenation and the phosgene free production process are not very sensitive to changes in the capital cost.

Figure 5-6 MDI cost sensitivity to capital cost variation



5.4. NPV analysis

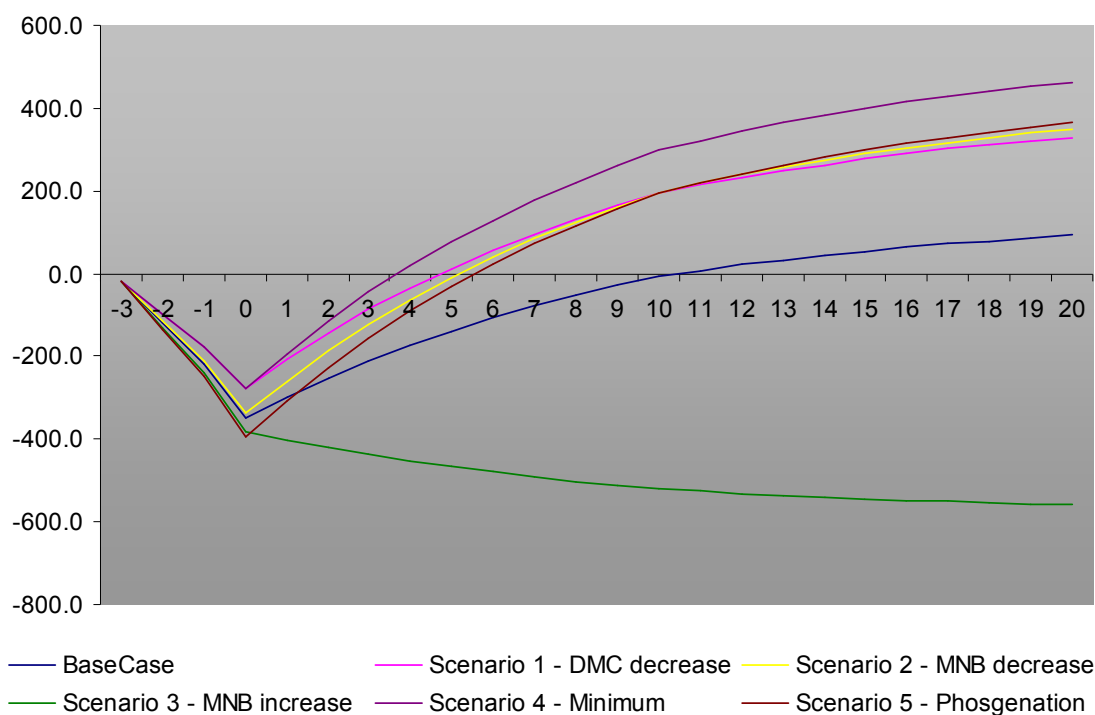
In this paragraph the scenarios are compared based on NPV analysis and also the financial performance of the scenarios, related to the MDI selling price is briefly discussed.

NPV

The basis of the NPV analysis of the scenarios is given in paragraph 5.1, the input and results are shown in Table 5-3 and Figure 5-7 below. In all scenarios a MDI selling price of € 1,700 is assumed, this is an average based on the market information in paragraph 2.7. Two aspects of the NPV are assessed, the initial investment that has to be made, which is mainly the TIC, and the final NPV value.

The analysis shows that scenario 4 has the best financial results, it has an NPV of MM€ 350 and also the lowest investment costs. However this is a hypothetical scenario that shows the potential of the phosgene free MDI production method, it does show that the phosgene free production method can be more profitable than the conventional production method.

Figure 5-7 Cumulative cash flow diagram



After the minimum scenario the scenarios 1, 2 and 5 have very similar NPVs. Scenario 5 is the conventional production process that uses phosgene, it does have the highest investment costs due to its high TIC but it also shows the largest profit over MDI. Scenario 1 and 2 are both optimistic scenarios of the phosgene free production process that assume better feedstock ratios. In theory a combination of these two methods is also possible; even larger advantages can be obtained in this way.

The base case scenario also has a positive NPV, which means it is economically feasible to use this method for MDI production. It is however far less profitable than the abovementioned scenarios.

Finally there is scenario 2, which assumes larger feedstock streams. This has a negative NPV and is therefore not economically feasible. This scenario shows the risk that the new method imposes.

In general the phosgene free processes show worse profit margins but lower investment costs than the conventional production process using phosgene.

Table 5-3 NPV basis

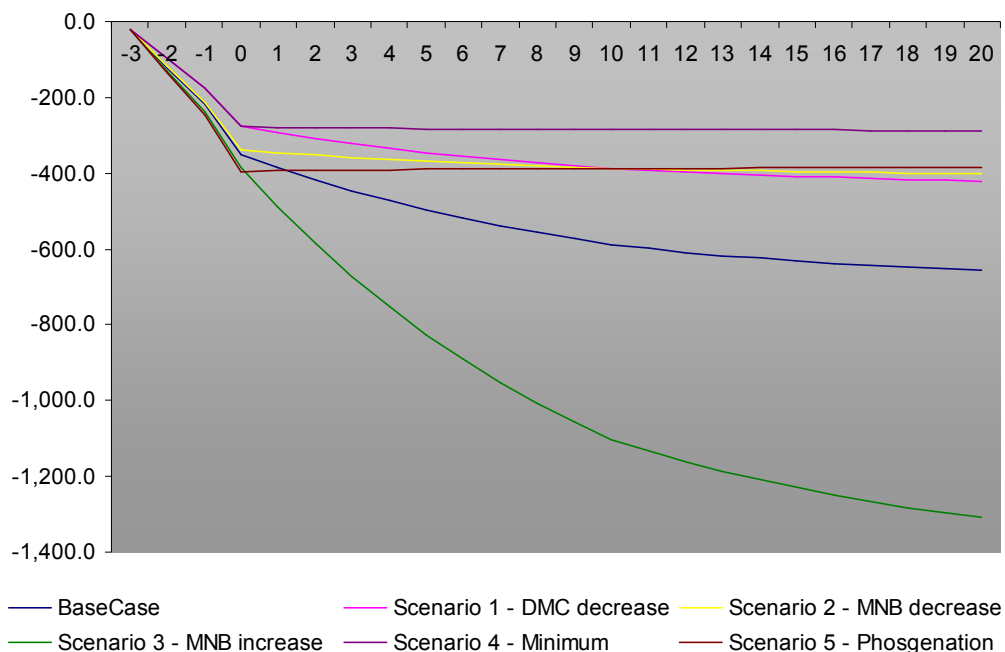
	BaseCase	Scenario 1 - DMC decrease	Scenario 2 - MNB decrease	Scenario 3 - MNB increase	Scenario 4 - Minimum	Scenario 5 - Phosgenation
Capacity (t)	473472	473472	473472	473472	473472	473472
MDI profit (MMEUR)	55.7	76.7	86.7	-22.2	93.6	96.0
MDI selling price (EUR/t)	1700	1700	1700	1700	1700	1700
MDI cash cost (EUR/t)	1,582	1,538	1,517	1,747	1,502	1,497
End of depreciation factor	0.75	0.75	0.75	0.75	0.75	0.75
Land (MMEUR)	20	20	20	20	20	20
TIC (MMEUR)	299.1	234.4	289.0	329.9	234.4	341.5
Working capital (MMEUR)	29.9	23.4	28.9	33.0	23.4	34.1
Proceeds plant sale (MMEUR)	3.0	2.3	2.9	3.3	2.3	3.4
Discount rate (%)	10%	10%	10%	10%	10%	10%
NPV (MMEUR)	92.2	329.5	349.1	-559.0	463.3	364.9

Current situation

In the NPV analysis conducted above a MDI selling price of € 1,700 is assumed. As said in paragraph 2.7, the current MDI selling price is far below that figure at € 1,500. This is mainly due to financial crisis and it is expected that the margins will be recovered. At this price level producers state that no profits are made and that this does affect capacity investment decisions⁴³.

In Figure 5-8 the NPVs of the same scenarios are shown but now with a MDI selling price of € 1,500. The graph confirms the statement above; hardly any value is gained after the initial investment is done in year 0 and none of the scenarios is profitable. This means that with the current prices capacity investments are not feasible.

Figure 5-8 Cumulative cash flow diagram (MDI selling price € 1,500 per ton)



6. Conclusions and Path Forward

In this chapter the findings of the study are summarized and recommendations for further action are formulated, both for Fluor and the scientific community.

This research was initiated by the statement that phosgene free production of MDI poses two major advantages to conventional production of MDI: (1) the phosgene free process improves safety and (2) a competitive phosgene free route to MDI would be able to comply with the strict regulations concerning HSE, and thereby create new business opportunities.

Both advantages are confirmed in this study; the safety analysis in paragraphs 2.5 and 4.9 confirms the safety improvement caused by phosgene free production of MDI. Also in paragraph 2.3 it is confirmed that a phosgene free route to MDI can create new business opportunities; especially the polycarbonate industry is a convincing example since it is a similar case.

Even though there are clear advantages to the new technology, in order to be implemented, it also has to be technologically and economically feasible. Therefore the following research goal was formulated:

Assess the process technologies and economics of a phosgene free production process of MDI in an effort to support a Fluor strategy for further development in these markets.

This research goal has resulted in the formulation of two main research questions:

1. Is it technologically feasible to produce phosgene free MDI on a commercial scale?
2. Is it economically feasible to produce phosgene free MDI on a commercial scale?

These two questions have been answered in this report; the first question is mainly discussed in chapters 3 and 4, the second question is mainly answered in chapter 5. Conclusions are given in the next paragraph. Finally a recommendation for further action is specified.

6.1. Conclusions

The conclusions of this research are summarized in this paragraph; in general it can be concluded that (1) in principle it is possible to produce phosgene free MDI on a commercial scale but more empirical research is necessary to achieve this, and (2) the currently available phosgene free produced MDI does not show a cost advantage but the technology has potential, it is not improbable that governments impose stricter regulations to enforce a transition. Further elaboration on these conclusions is given below.

Technological feasibility

This part of the study concludes that phosgene free production of MDI is technological feasible but the actual process performance is currently based on a process model that contains uncertainties.

Several assumptions have been made to overcome the uncertainties in the process model that has been used for this research. Before this process can be up scaled to an actual commercial production facility it is necessary to conduct further experimental research in order to clarify the uncertainties; these four are deemed to be the most important.

1. The actual reaction performance of all three synthesis reactions on large scale.
2. The quality, and functionality, of the produced MDI.
3. The process behaviour of all components, especially MPC and MDC.
4. The separation of the DMC:methanol azeotrope.

The third uncertainty mentioned above is relatively easy to determine on lab scale, since the most important properties for this process are solubility ratios and component behaviour related to the processability of MDC and MPC; i.e. crystallization properties of MDC and boiling points.

The other three uncertainties are more difficult to investigate. A lot of scientific research on reaction performance has been conducted but to prove performance on an industrial level the reactions have to be executed and studied on a larger process scale. An important parameter for the reaction performance is the performance of the catalyst system. The catalyst system directly affects two large cost drivers; the feedstock ratios that are necessary for the reaction and the residence time. If the catalyst is developed; a pilot plant scale reaction process needs to be set up in order to study the quality of the produced MDI and the reaction performances on a larger scale.

It is assumed that the DMC:methanol azeotrope can be separated with the use of membrane, this technology is not proven yet. A method for this separation step needs to be developed in order to successfully up scale the phosgene free MDI production process.

Based on these conclusions, four further research steps are necessary to develop a proven process that can be up scaled to a commercial scale production plant:

1. The physical properties and process behaviour of many components need to be investigated.
2. A reliable catalyst system for each reaction needs to be developed.
3. A separation method for the DMC:methanol azeotrope needs to be developed.
4. A pilot plant needs to be set up to prove and optimize the process.

Economical feasibility

The currently available phosgene free MDI production technology is economically inferior to the conventional technology. The new technology does need financial investments, but the current financial situation, with low MDI prices, is not an incentive for additional capacity investments. Moreover, the currently installed production capacity of MDI is expected to be sufficient to meet the global demand until 2013 at least. Regardless of the financial crisis, growths in the MDI markets are still expected.

Even though the phosgene free technology is not competitive today, this study indicates that it does have the potential to become cost competitive. Governments and legislative institutions could impose stricter legislation and thereby stimulate the development of the phosgene free technology and enforce a transition in this market. This is a very plausible situation since the new technology can be cost competitive in comparison to the conventional technology and it does show significant improvements concerning HSE. The polycarbonate case is similar to that of MDI and does confirm this sequence of events.

The phosgene free MDI production technology may eventually become economically feasible when future circumstances change, for instance if (1) stricter legislation is imposed, (2) the performance of the phosgene free process is improved and/or (3) if the DMC cost is decreased.

The NPV analysis indicates that the effective process improvements are (1) a decrease of the amount of nitrobenzene used in the process and (2) an increase of the MPC synthesis reaction performance.

6.2. Path forward

This paragraph gives recommendations for further action for both Fluor and the scientific community.

Fluor

From the conclusions above, it becomes clear that, in order to obtain industrial phosgene free production of MDI some serious investments in empirical research are needed; especially a pilot plant will be expensive. If these investments are made it is not certain that the phosgene free production process will offer significant cost advantages over the existing MDI production process. Moreover, the current financial climate does not allow capacity investments at all.

However, the new technology does have significant advantages concerning HSE. It is not unlikely that governments will interfere by enforcing legislation to accelerate the development of the phosgene free technology. The new technology is potentially cost competitive and it is in compliance with the trend to improve the safety and environmental hazards in the chemical industry. The example of the polycarbonate case in paragraph 2.3 emphasises this argument.

Based on these arguments, it can be expected that phosgene free production of MDI will not become reality in the near future and new MDI plants will probably still be based on the conventional phosgenation production process, unless there are significant improvements in the phosgene free technology or stricter governmental legislation is imposed that would restrict the phosgene using MDI production technology and enforces alternative technologies. The latter case is not unlikely as it happened before in the similar polycarbonate technology.

For Fluor this implicates that there are multiple options possible; which range from an active to a proactive stance.

The active stance means that no immediate action is taken. The situation and developments in the MDI market will be monitored and if the business environment changes, i.e. due to technological breakthroughs or stricter governmental regulations, Fluor can act accordingly. As long as the status quo is maintained, business is continued as usual.

The proactive stance implies that Fluor will interfere in the discussion by actively promoting the development of the phosgene free MDI production technology. Promotion can be done by, for example, publishing articles that support the development of the new technology or collaborating with public or private research institutions to increase scientific progress in this field. In this way it could accelerate a transition to a new production technology in the MDI markets. By finding strategic partners and be directly involved in new developments, this option could result in Fluor being a frontrunner in an emerging market of phosgene free MDI production.

Fluor has a very active policy concerning HSE; therefore the proactive stance would be in line with the company's strong sense of global responsibility and could even strengthen the position of Fluor in this field. However, Fluor is also a public owned company and therefore focused on profits; active involvement in the development of this new technology will consume resources and it is not certain whether it will be profitable. A trade-off has to be made between the degree of involvement and the amount of resources that Fluor is willing to dedicate to the development of a phosgene free MDI production technology.

Scientific community

It is clear that phosgene free MDI production is not economically viable based on the current knowledge. However, this research also shows that the estimated cost of the described phosgene free process is similar to that of the conventional process. In addition, there is definitely a cost competitive potential; especially if legislation is enforced to accelerate the development of the phosgene free MDI production technology. The major disadvantage of the technology is that the described phosgene free process is new and therefore contains many uncertainties, as opposed to the fully developed conventional production process.

As is described in the first part of paragraph 6.1 above, four research steps are needed to develop a proven process for phosgene free MDI production. These steps serve as recommendations for further research and can be addressed by the scientific community.

1. The physical properties and process behaviour of each component needs to be investigated.
2. A reliable catalyst system for each reaction needs to be developed.
3. A separation method for the DMC:methanol azeotrope needs to be developed.
4. A pilot plant needs to be set up to prove and optimize the process.

To utilize the economical potential of the new technology, it does not only need to be proven but it needs improvement. Therefore more concrete targets for experimental research are set. These targets are derived from the economical feasibility study. Reaching these targets would significantly improve the competitive position of the phosgene free technology. The targets are the following.

- The amount of nitrobenzene needed has to be decreased by at least 50%.
- The reaction performance of the MPC synthesis reaction has to be improved; (1) the DMC:aniline ratio needs to be decreased from 7:1 to 2:1 and (2) the residence time of 8 hours needs to be decreased in order to minimize the reactor volume.

Another, minor, subject that can be addressed is the loss of nitrobenzene, the losses are quite high in the base case; incremental improvements in the process design might decrease losses and therefore also the necessary feedstock amount of nitrobenzene, this can however result in higher utility and capital costs for extra separation equipment.

The economical part of this study also offers opportunities for further research. A more detailed investigation in the prices of the feedstock material and the connection to the DMC production process would provide a better foundation of the CoP estimation and would also give a better insight in the pricing dynamics. In this study it is assumed that the conceptual plant is build in the Netherlands, an investigation in the options of constructing of the plant in other geographical locations i.e. the Middle East, could influence the feasibility of the new technology.

Besides further research on the phosgene free route to MDI that is used for this research, that is considered to be the most viable, there might also be attractive research opportunities in other existing routes, or completely new routes, without phosgene to MDI.

7. Reflection

In this chapter first a reflection is given on the content and methodology of the research itself, next a personal reflection is given, in which this research is reviewed from the perspective of the Product and Process Technology master's of Industrial Engineering and Management (IEM).

7.1. Research

In this paragraph the research is reflected upon based on content and based on methodology.

Content

Research is always limited to the available resources; in this case the research was conducted in a six month period by a master's student in the Industrial Engineering and Management specialty area. Support has been provided by Fluor and the University of Groningen. The research broadly touches three different subjects. These three subjects are evaluated below.

The initial subject is a chemistry subject; all routes to MDI. This subject is focussed on chemical technology and requires the reading and evaluation of many pieces of scientific literature; patents, articles and books. This part of the study is deemed to be exhaustive. From the beginning the focus of Fluor was very strongly on the selected phosgene free route. Although it is easy to accept this vision right away and start the analyses, the route has been put in perspective and is compared to all other viable phosgene free routes to MDI. This method results in a clear and objective selection procedure that renders the best route to MDI that is currently available, based on a set of criteria. Besides the thorough selection that is achieved, another advantage of this method is its transparency; this makes the method transcribable for future research.

The second subject is focussed on the process design specialty area. The most viable route to MDI is up scaled to a conceptual production plant design on industrial scale. In this specialty area, experience is a key issue for success. It requires a wide knowledge of equipment and extensive routines to complete a conceptual plant design. Therefore the support of both Fluor and the University of Groningen has been mostly used in this subject area. The research renders a conceptual design including flow schemes, sized equipment lists, stream summaries and a basis of design. The level of detail and quality of these analyses is sufficient to serve as a solid foundation for a financial analysis. The result in this subject is satisfactory, especially considering the available resources.

The final subject is focussed on the financial analysis of a manufacturing process. Based on the conceptual plant design a cost of production (CoP) estimation of the phosgene free MDI production process has been made. This CoP estimation is the basis of the financial analyses that are used to compare the new technology to the existing technology. In this subject industry experience is essential to properly judge the financial results. Fluor, especially the estimation department, provided support to generate the capital investment estimation and to gain insight in the CoP comparison. The results, obtained from the financial analyses, are satisfactory; they do confirm the current market situation.

In general the results of this research, especially when considering the available resources, are very satisfying. Both the technological and the economical feasibility of the phosgene free MDI production method are studied in enough detail to pinpoint the most important weaknesses and strengths of the new technology. Therefore the recommendations for both Fluor and the scientific community are presented with confidence.

Methodology

The research has been setup based on the "regulative cycle" as it is taught in the IEM curriculum, starting already from the first course "Introduction to Industrial Engineering". Research based on the

regulative cycle should contain four phases: First, the goal definition from a vague set of demands, then the determination of the real problem, next the formulation of a solution based on parameters and finally the practical implementation and evaluation of the design.

The first two phases are described in the first two chapters. In these chapters the problem is identified and the research goal is determined. Initially Fluor had already determined a phosgene free route to MDI that had to be researched, however, the scope of the research is broader, it also includes the determination of the best phosgene free route to MDI. This did not cause any problems as Fluor proved to be very flexible and cooperative in determining the broader scope.

The third chapter contains the third phase; based on a set of parameters the most viable phosgene free route to MDI for up scaling is selected. The rest of the report discusses the practical implementation of this route. The technology is evaluated in chapter 6. The methodology of the regulative cycle fits perfectly for this report.

Besides the phases the research also involves multiple stakeholders; Fluor, the scientific community, the government, legislative institution and MDI producers. This puts the results of the study in a broad perspective that allows the formation of solid recommendations.

Another important factor is the transcribability of the research; it is important that future research is able to fall back on this report and is able to copy the used methods. The report is very transparent and every research decision has been validated. Also all assumptions are clearly stated throughout the report.

Finally the research can be applied in reality; the analyses are based on real sets of data that have been evaluated and approved by industry experts. The assumptions that are used in the research have also been discussed with industry experts.

7.2. Personal

In the previous paragraph the research has been broken down into three subject areas. These subject areas are in line with the subjects that are taught in the Product and Process Technology (PPT) master's curriculum and the philosophy of the Industrial Engineering and Management (IEM) department.

The first subject focuses on chemistry and largely is a literature study. In the courses Interfacial Engineering and Polymer Products a.o., similar issues are handled. These courses combine detailed chemistry with a practice oriented report. This subject should therefore be familiar to a student in this field.

The second subject focuses on process design issues. These issues are handled in the Process Design courses, the Special Process Equipment course and the Powder Technology course a.o. It is a broadly discussed subject in the PPT master's, however in this subject, as mentioned before, experience is a key factor. In this case there is the opportunity to fall back on the experience of Fluor and that of the University of Groningen which make it possible to obtain a design of sufficient quality. This combination of resources, the experience and the foundation of the IEM courses, make sure that this subject is a steep learning experience that provides a much broader insight into the process design specialty area.

The financial subject is also taught in several IEM courses; Process Design 1 & 2 and Applied Capital Budgeting & Finance a.o. Therefore the basis of this research subject should be present. In this study however, the link between the financial analysis and the technological design is very clear, as well as the impact that changes in technology can have on project finances. This subject is also briefly touched in the courses, but never with real time pricing data available and never in this level of detail. The support and information received from Fluor makes it possible to get a realistic financial analysis that can actually be used for strategy development purposes. This is a clear distinction from the courses in IEM that significantly increases the value of the analysis and thereby also the value for the student. This level of accuracy can hardly be achieved in a purely educational environment and

therefore the business environment in which this study was conducted added significant value to the quality of this report.

In general, the combination of subjects in this study is almost perfectly aligned with the subjects that are taught in the PPT master's. It combines a scientific foundation with a technological design which is used for a financial analysis that has a real impact on business.

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Appendix A MDI synthesis reaction comparison

Table A-1 MDI synthesis reaction comparison

Catalyst	Solvent	Heat carrier	MDI yield	MDC conversion	MDC:catalyst	MDC:solvent	Reactor	Temp (°C)	Pressure (bar)	React time (min)	Source
ZnO/Zn			67.3%	99.2%	2.5:1.6 (mass)	1:40 (mass)		250		80	Appendix A ¹
ZnO			52.1%	99.1%							Appendix A ²
Zinc Powder	Mixed solvents		87.3%				Cistr				Reference 3
Zn/Ac	MNB-THF (1:1)	DOS	81.0%			MDC:THF:MNB=0.003:0.29:0.2 (mol)	Cistr	280	0.03	120	Reference 3
Bismuth nitrate (Bi(NO ₃) ₃)			75.0%					260	0.0008	30	CN 2007-10048329
Bismuth oxide Bi ₂ O ₃			83.0%					260	0.0008	30	CN 2007-10048330
Montmorillonite	Decaline		75.0%	100.0%	4:1 (mass)	1:40 (mass)		190	Vacuum	1440	Appendix A ³
Synthetic silicates (montmorillonite)	Dichlorobenzene		96.0%	100.0%	4:1 (mass)	1:104 (mass)				300	EP 1160239
None	Dichlorobenzene	N ₂	90.0%	100.0%		1:9 (mass)	CC	280	8-15	20-30	Reference 10
		DOS	90.0%	98.0%		MDC:DOS 100:250-500 (mol)	CC	210-290	0.09	30-180	CN1850792
	Dodecylbenzene	N ₂	87.0%	98.0%			CC		atm		A14

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Appendix B Equipment list

B.1. Main area

Table B-1 Main area equipment list

ID	Component	Qty	Material	Total direct costs		Capacity	
				EUR	Unit	Unit	Amount
1	Utility transport system	3		2,218,260	m		100
2	Heat tracing	1		15,581	m		50
3	UG sewer system	6		126,228	m		50
4	UG slop system	6		65,682	m		50
5	Eyewash & Showers	3		38,124			
6	Interconn. Pipe product	6		390,879	m		200
7	External Piping	6		4,796,472	m		2000
8	Interconn. Pipe other	5		325,732	m		200
9	Drainage Trench	6		197,744	m		50
10	Control unit	1		101,351			
11	FAR	1		69,729			
12	Heater unit	6	A 214	5,151,863	MW		10
13	Steel structures	20		7,602,242			
14	Steel Piperack	1		1,576,568	m		200
15	Secondary Steel	6		124,577	m		50
16	Roads	1		133,500	m		200
17	HPS boiler unit	1	A285C	2,309,680	kg/hr		175000
18	LPS boiler unit	1	A285C	1,840,507	kg/hr		125000
Total				27,084,720			

B.2. MDI01

Table B-2 MDI01 Equipment list

ID	Tag	Equipment class	Qty	Material	Total costs	Design conditions		Size		Flow rate	Total capacity		Utility
						direct	EUR	Temperature (°C)	Pressure (bar)		Diameter (mm)	Height (mm)	
19	DC101	Towers	2	SS304	4,225,075		260	4	4200	19050	m3	2110	
20	DC102	Towers	2	A285C	2,150,202		125	4	4200	14780	m3	1637	
21	DC103	Towers	1	A 516	420,729		125	4	1220	19050	m3	89	
22	DC104	Towers	1	SS304	2,840,702		275	4	3960	24230	m3	1193	
23	DC105	Towers	1	SS304	937,665		375	4	3200	6250	m3	201	
24	RV101	Horizontal Tanks	2	A 516	749,315		125	4			m3	47	
25	RV102	Horizontal Tanks	2	A 516	424,717		125	4			m3	12	
26	RV103	Horizontal Tanks	1	A 516	124,867		125	4			m3	3	
27	RV104	Horizontal Tanks	1	A 516	278,210		214	4			m3	23	
28	RV105	Horizontal Tanks	1	SS304	359,202		205	4			m3	15	
29	RB101	Reboilers	2	A 214	2,823,871		260	30			MW	36.9	HPS
30	RB102	Reboilers	2	A 214	655,075		195	7.6			MW	27.6	LPS
31	RB103	Reboilers	1	A 214	159,306		195	7.6			MW	2.3	LPS

32	RB104	Reboilers	1	A 214	760,669	345	27.7		MW	13.1	LTHO
33	RB105	Reboilers	1	A 214	524,183	415	27.7		MW	4.4	HTHO
34	PU101	Centrifugal Pumps	2	CS	337,540	125	10		110 MW	0.095	EL
35	PU102	Centrifugal Pumps	2	CS	95,785	125	10		20 MW	0.01	EL
36	PU104	Centrifugal Pumps	3	CS	541,845	125	4		126 MW	0.15	EL
37	PU105	Centrifugal Pumps	2	CS	297,591	125	4		100 MW	0.03	EL
38	PU106	Centrifugal Pumps	3	CS	222,497	125	4		35 MW	0.037	EL
39	PU107	Centrifugal Pumps	2	CS	156,298	125	4		10 MW	0.01	EL
40	PU108	Centrifugal Pumps	2	CS	156,298	125	4		10 MW	0.01	EL
41	PU109	Centrifugal Pumps	2	CS	145,302	125	4		6 MW	0.01	EL
42	PU110	Centrifugal Pumps	2	CS	78,149	125	4		10 MW	0.01	EL
43	PU111	Centrifugal Pumps	2	CS	148,795	125	4		100 MW	0.03	EL
44	PU112	Centrifugal Pumps	2	SS304	329,100	125	4		30 MW	0.01	EL
45	PU113	Centrifugal Pumps	2	CS	130,479	214	4		60 MW	0.03	EL
46	PU114	Centrifugal Pumps	2	CS	160,337	200	4		10 MW	0.01	EL
47	PU115	Centrifugal Pumps	2	SS304	281,438	260	4		10 MW	0.01	EL
48	PU116	Centrifugal Pumps	2	SS304	168,718	205	4		40 MW	0.02	EL
49	PU117	Centrifugal Pumps	2	A285C	81,924	260	4		10 MW	0.01	EL
50	HE101	Heat Exchangers	1	A 214	458,669	195	11		MW	17.2	LPS
51	HE103	Heat Exchangers	1	A 214	129,883	195	7.6		MW	1.2	LPS
52	HE104	Heat Exchangers	1	A 214	217,151	195	7.3		MW	0	CW
53	HE105	Heat Exchangers	1	CA443	108,482	195	10		MW	0	CW
54	HE106	Heat Exchangers	1	CA443	105,642	195	10		MW	0.2	CW
55	HE107	Heat Exchangers	1	CA443	105,642	195	10		MW	3.5	CW
56	TA101	Vertical Tanks	1	A285C	811,262	50	4		m3	320	
57	TA102	Vertical Tanks	1	A285C	1,050,415	50	4		m3	350	
58	TA103	Vertical Tanks	1	A285C	1,271,106	50	4		m3	10000	
59	CD101	Heat Exchangers	2	A 214	1,326,421	150	4		MW	0.2	EL
60	CD102	Heat Exchangers	2	A 214	244,841	150	4		MW	0	EL
61	CD103	Heat Exchangers	1	A 214	122,420	150	4		MW	0	EL
62	CD104	Heat Exchangers	1	A 214	122,420	150	4		MW	0	EL
63	CD105	Heat Exchangers	1	A 214	1,101,002	150	4		MW	0.2	EL
64	VE101	Ejectors	1	A285C	45,990						
65	VP101	Vacuum Pumps	2	CS	184,300				MW	0.02	EL
66	VB101	Vacuum Pumps	1	A285C	105,825				MW	0.02	EL
67	ME101	Vertical Tanks	2	A 516	717,232	125	4		m3	26	
68	RE101	Agitated Tanks	13	SS304	38,261,865	180	14		MW	0.3	EL
									MW	4.7	LPS
									m3	1500	
69	FL101	Vertical Tanks	1	A 516	175,742	125	4		m3	3.4	
Total			91		67,432,197.37						

B.3. MDI02

Table B-3 MDI02 Equipment list asdf

ID	Tag	Equipment class	Qty	Material	Total costs EUR	Design conditions		Size		Flow rate l/s	Capacity Unit	Utility Amount
						direct	Temperature (°C)	Pressure (bar)	Diameter (mm)			
70	HE201	Heat Exchangers	1	A 214	350,692		200	8			MW	13.5 LPS
71	HE202	Heat Exchangers	1	A 214	155,047		200	8			MW	3.4 LPS
72	PU201	Centrifugal Pumps	2	CS	150,624		125	4		10	MW	0.01 EL
73	PU203	Centrifugal Pumps	2	SS304	235,512		125	8		10	MW	0.01 EL
74	PU204	Centrifugal Pumps	2	CS	206,879		125	10		50	MW	0.02 EL
75	PU205	Centrifugal Pumps	2	CS	253,652		125	4		55	MW	0.06 EL
76	PU206	Centrifugal Pumps	2	CS	150,624		125	4		10	MW	0.01 EL
77	PU207	Centrifugal Pumps	2	CS	224,264		125	4		40	MW	0.04 EL
78	PU209	Centrifugal Pumps	2	CS	150,624		125	4		10	MW	0.01 EL
79	PU210	Centrifugal Pumps	2	CS	224,264		125	4		40	MW	0.04 EL
80	PU211	Centrifugal Pumps	2	CS	129,223		125	4		10	MW	0.01 EL
81	RE201	Agitated Tanks	5	SS304	8,736,817		170	8	5000	15000	MW	0.4 EL
											MW	51.2 CW
											m3	1500
82	CR201	Crystallizers	1	A285C	5,451,991		170	4			MW	39.6 HPS
83	DE201	Separation Equipment	1	A285C	336,055		125	4		28		
84	DE202	Separation Equipment	1	A285C	336,055		125	4		28		
85	CD201	Heat Exchangers	1	A 214	357,326		230	4			MW	49.7 CW
86	VE201	Ejectors	1	A285C	45,990							
87	VP201	Vacuum Pumps	5	CS	1,123,875						MW	0.55 EL
88	VB201	Vacuum Pumps	5	A285C	725,998						MW	0.4 EL
89	TA201	Vertical Tanks	1	A285C	315,992		125	4			m3	1000
90	TA202	Vertical Tanks	1	A285C	279,165		125	4			m3	3000
91	TA203	Vertical Tanks	1	SS304	2,535,918		150	4			m3	500
92	TA204	Vertical Tanks	1	A285C	1,195,570		125	4			m3	9500
93	PP201	Conveyors	5	SS304	322,239				100		m	100
94	MI201	Agitated Tanks	1	SS304	2,117,669		125	4			MW	0.06 EL
											m3	100
Total			50		26,112,061							

Appendix C Plot plan

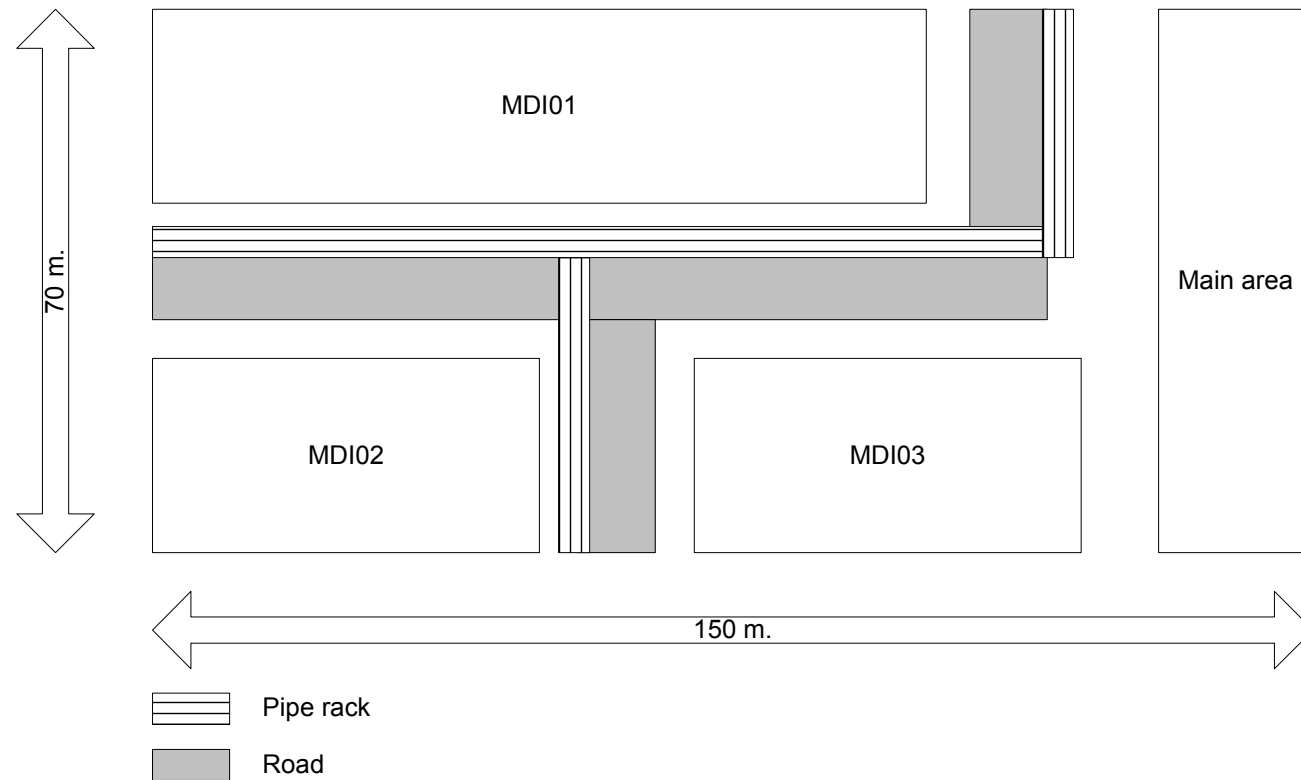
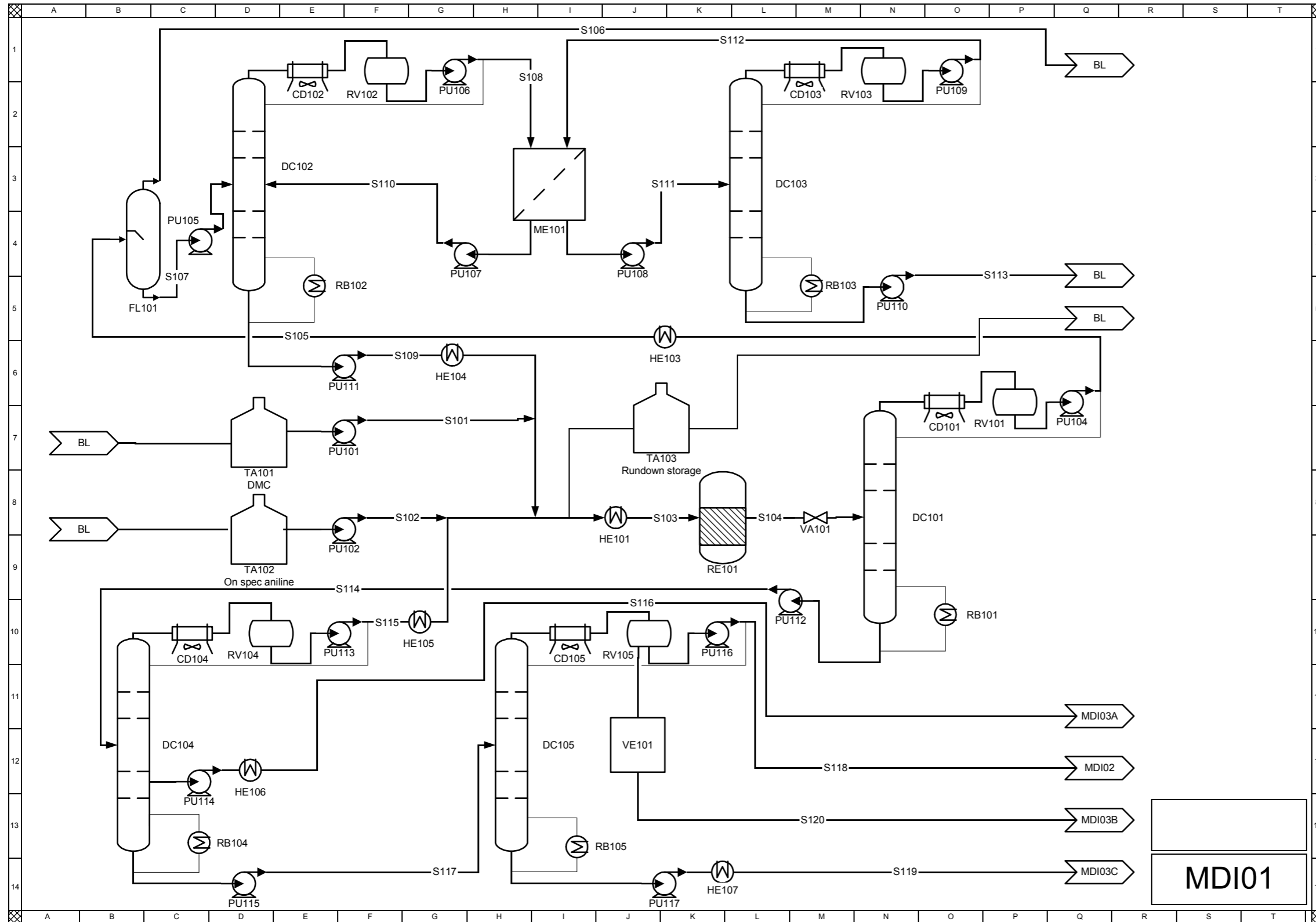
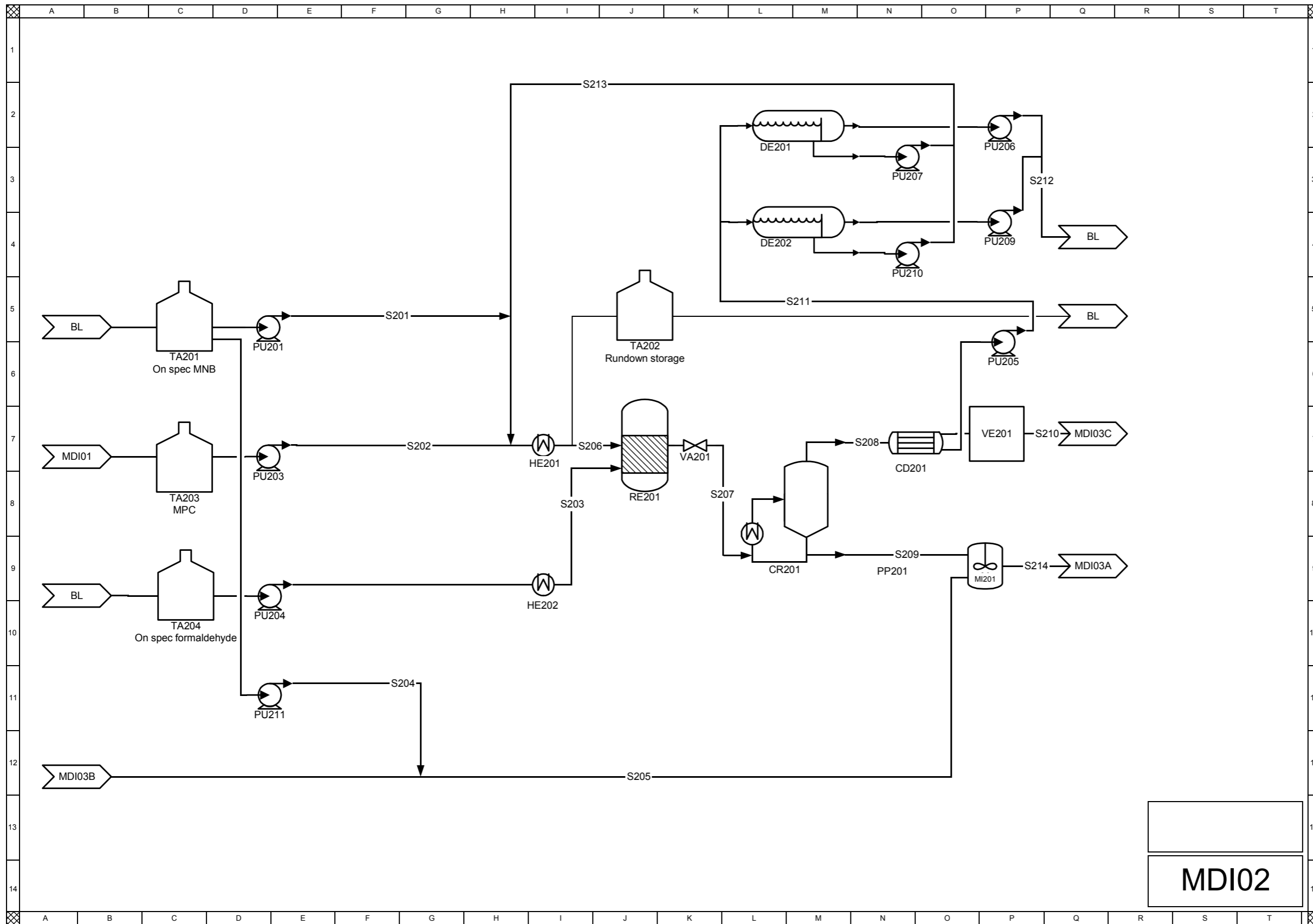


Figure C-1 Example plot plan sketch phosgene free MDI production site (Size based on 25m² per piece of equipment)

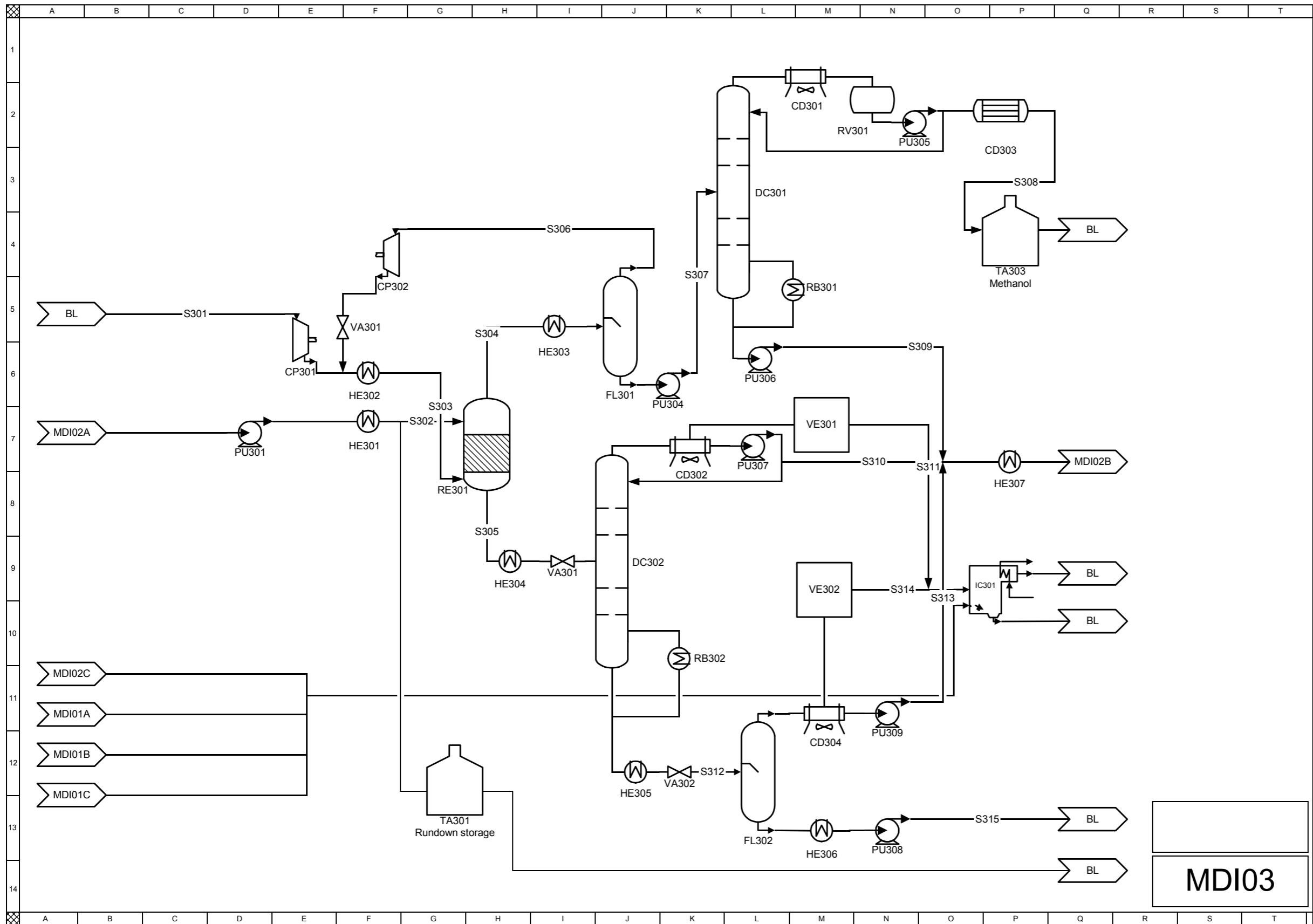
Appendix D Flow schemes and stream summaries





MDI02

MDI02



Appendix E Capital cost summary

Aspen ICARUS						
Project Cost Summary						
Project Title: --		Scenario Name: KBaseCase				
Project Name: MDI total		Job No: --		Prep. By: --		
Proj. Location: Rotterdam		Est. Class:		Currency: EURO EUR		
Estimate Date: 25JAN10 14:48:26						
Account	MH	Wage Rate	Labor Cost	Matl Cost	Total Cost	Percentages
(2) Equipment	27,114	70.00	1,897,990	77,516,789	79,414,780	50.8% of TDC
(3) Piping	197,032	70.00	13,792,237	15,838,560	29,630,797	19.0% of TDC
(4) Civil	86,609	70.00	6,062,636	2,740,202	8,802,838	5.6% of TDC
(5) Steel	38,224	70.00	2,675,659	6,713,885	9,389,544	6.0% of TDC
(6) Instruments	43,672	70.00	3,057,239	10,311,168	13,368,407	8.6% of TDC
(7) Electrical	26,560	70.00	1,859,214	3,168,347	5,027,561	3.2% of TDC
(8) Insulation	83,720	70.00	5,860,413	2,794,064	8,654,477	5.5% of TDC
(9) Paint	24,891	70.00	1,742,397	259,238	2,001,635	1.3% of TDC
Total Direct Field Costs	527,822		36,947,785	119,342,254	156,290,039	100.0% of TDC
	(TDMH)		(TDL)	(TDM)	(TDC)	
Indirect Field Costs	96,874				32,870,800	89.0% of TDL
	(IFMH)				(IFC)	
Total Field Costs	624,696				189,160,839	63.2% of TIC
	(TFMH)				(TFC)	
Freight	3%	of TDM		3,580,268		3.0% of TDM
Owner's costs	5%	of TDC		7,814,502		5.0% of TDC
Engineering and HO	145,136			11,018,600		3.7% of TIC
Other Project Costs				12,745,739		4.3% of TIC
Contingency				74,773,316		25.0% of TIC
Total Non-Field Costs	145,136				109,932,425	36.8% of TIC
	(HOMH)					
Project Total Costs					299,093,264	191.4% of TDC
					(TIC)	

Aspen ICARUS Indirect Field Cost Summary

Code	Description	Ind MH	Ind Cost
81	Home Office Const Suppt	21,120	1,774,100
85	Field Const Supv	67,278	4,447,200
86	Start-up, Commissioning	8,476	724,800
Field Office Staff		96,874	6,946,100
Code	Description	Ind MH	Ind Cost
11	Fringe Benefits		7,389,600
12	Burdens		6,281,100
13	Consumables, Small Tools		1,477,900
14	Misc (Insurance, Etc)		1,847,400
15	Scaffolding		2,586,300
16	Equipment Rental		2,660,200
18	Field Services		581,500
19	Temp Const, Utilities		144,900
22	Travel		2,955,800
Construction Indirects Total			25,924,700

Aspen ICARUS Non - Field Cost Summary

Code	Description	Ind M
Freight Total		
Code	Description	Ind M
Taxes and Permits Total		
Code	Description	Ind M
71	Basic Engineering	37,3
72	Detail Engineering	91,7
73	Material Procurement	16,0
Engineering & HO Total		145,1
Code	Description	Ind M
90	G and A Overheads	
91	Contract Fee	
Other Project Costs Total		
Code	Description	Ind M
99	Contingency	
Contingency Total		

Appendix F Cost of production estimations

Table F-1 CoP base casae

MDI Plant										
Start-up	2010									
Location	The Netherlands									
Capacity	473	kTa								
	473472	t/year								
Operating	360	days/year								
Scenario	BaseCase									
Production cost summary		Unit	Units per t product	Price EUR/unit	EUR/t product	Annual cost MMEUR	% of total			
Raw materials	Aniline	t	0.8047	1,051	845.71	400.42				
	DMC	t	0.7628	420	320.64	151.81				
	Formalin	t	0.3303	371	122.64	58.07				
	Nitrobenzene	t	0.0839	1,002	84.10	39.82				
	Nitrogen	t	0.0073	-	0.00	0.00				
	Catalyst & membrane	3%	of total raw material			41.19	19.50			
	TOTAL RAW MATERIALS					1,414.28	669.62	82.77%		
Byproduct	Methanol	t	0.5073	-127	-64.53	-30.55				
TOTAL BYPRODUCT CREDITS					-64.53	-30.55	-3.78%			
Utilities	Heating oil	GJ	3.81	6.94	26.42	12.51				
	Cooling water	t	209.45	0.02	4.96	2.35				
	Power	kWh	75.40	0.05	4.07	1.93				
	Steam	t	5.83	25.31	151.21	71.59				
TOTAL UTILITIES					186.67	88.38	10.92%			
TOTAL VARIABLE COSTS					1,536.42	727.45	89.92%			
Direct fixed	Operators	32	at EUR/yr	45000	3.04	1.44				
	Foreman	7	at EUR/yr	55000	0.81	0.39				
	Supervisor	1	at EUR/yr	75000	0.16	0.08				
	Maint., mat. And labor	4%	of TDM		13.20	6.25				
	Direct overhead	45%	of labor		7.75	3.67				
TOTAL DIRECT FIXED COSTS					24.96	11.82				
Allocated fixed	General plant overhead	60%	of direct fixed costs		14.98	7.09				
	Insurance, property	1%	of TFC		4.00	1.89				
	Environmental	0.50%	of TFC		2.00	0.95				
TOTAL ALLOCATED FIXED COSTS					20.97	9.93				
TOTAL FIXED COSTS					45.94	21.75	2.69%			
TOTAL CASH COSTS					1,582.35	749.20				
Depreciation Capital	10%	of TIC			63.17	29.91	3.70%			
COST OF PRODUCTION					1,645.52	779.11				
ROI	10%	of TIC			63.17	29.91	3.70%			
MDI COST					1,708.69	809.02	100.00%			

CoP Phosgenation

MDI Plant									
Start-up	2010								
Location	The Netherlands								
Capacity	473	kTa							
	473472	t/year							
Operating	360	days/year							
Scenario	Phosgenation								
Production summary		cost							
		Unit	Units per t product	Price EUR/unit	EUR/t product	Annual cost MMEUR	% of total		
Raw materials	Aniline	t	0.7610	1,051	799.73	378.65			
	DMC	t	0.0000	420	0.00	0.00			
	Formalin	t	0.3894	371	144.59	68.46			
	Nitrobenzene	t	0.0000	1,002	0.00	0.00			
	Nitrogen	t	0.0000	-	0.00	0.00			
	Chlorine	t	0.6101	109	66.54	31.50			
	CO Ex Gas	t	0.2621	231	60.53	28.66			
	Caustic	t	0.7048	180	126.60	59.94			
	Catalyst & membrane	3%	of total raw material		35.94	17.02			
TOTAL RAW MATERIALS					1,233.93	584.23	75.17%		
Byproduct	HCl, 32%	t	0.9557	-42.77	-40.87	-19.35			
	Methanol	t	-	-127	0.00	0.00			
TOTAL BYPRODUCT CREDITS					-40.87	-19.35	-2.49%		
Utilities	Heating oil	GJ	0.00	6.94	0.00	0.00			
	Cooling water	t	1036.26	0.02	24.55	11.62			
	Power	kWh	1213.85	0.05	65.48	31.00			
	Steam	t	6.10	25.31	154.41	73.11			
TOTAL UTILITIES					244.44	115.74	14.89%		
TOTAL VARIABLE COSTS					1,437.50	680.62	87.57%		
Direct fixed	Operators	32	at EUR/yr	45000	3.04	1.44			
	Foreman	7	at EUR/yr	55000	0.81	0.39			
	Supervisor	1	at EUR/yr	75000	0.16	0.08			
	Maint., mat. And labor	4%	of TDM		18.13	8.58			
	Direct overhead	45%	of labor		9.96	4.72			
TOTAL DIRECT FIXED COSTS					32.11	15.20			
Allocated fixed	General plant overhead	60%	of direct fixed costs		19.26	9.12			
	Insurance, property	1%	of TFC		5.56	2.63			
	Environmental	0.50%	of TFC		2.78	1.32			
TOTAL ALLOCATED FIXED COSTS					27.61	13.07			
TOTAL FIXED COSTS					59.72	28.27	3.64%		
TOTAL CASH COSTS					1,497.22	708.89			
	Depreciation Capital	10%	of TIC		72.12	34.15	4.39%		
COST OF PRODUCTION					1,569.34	743.04			
	ROI	10%	of TIC		72.12	34.15	4.39%		
MDI COST					1,641.46	777.18	100.00%		

Table F-2 Phosgenation capital costs

Phosgenation plant capital costs			
		473 kTa	136 kTa
		MMEUR	MMEUR
ISBL		214.6	93.1
OSBL		48.8	42.4
Total plant capital	(TFC)	263.4	135.5
Other project costs		78.0	33.8
Total capital investment	(TIC)	341.5	169.3
OSBL factor	0.5		
473 kTa upscaling factor	2.31		
Maintenance costs	(TDM)	8.6	3.7
Working capital		36.4	15.8

Appendix G Scenario analysis

Table G-1 Scenario analysis

	BaseCase	Scenario 1 - DMC decrease	Scenario 2 - MNB decrease	Scenario 3- MNB increase	Scenario 4 - Minimum	Scenario 5 - Phosgenation
	<i>EUR/t MDI</i>	<i>EUR/t MDI</i>	<i>EUR/t MDI</i>	<i>EUR/t MDI</i>	<i>EUR/t MDI</i>	<i>EUR/t MDI</i>
Raw materials	1,414	1,413	1,380	1,528	1,379	1,234
Byproducts	-65	-64	-66	-63	-65	-41
Utilities	187	152	158	232	152	244
Total Variable costs	1,536	1,501	1,472	1,697	1,465	1,438
Direct fixed	25	20	24	27	20	32
Allocated fixed	21	17	20	23	17	28
Total fixed costs	46	37	45	50	37	60
Total cash costs	1,582	1,538	1,517	1,747	1,502	1,497
Depreciation of capital	63	50	61	70	50	72
ROI	63	50	61	70	50	72
MDI cost	1,709	1,637	1,639	1,886	1,601	1,641
Price change	0.00%	-4.19%	-4.08%	10.39%	-6.28%	-3.93%
TIC (MMEUR)	299	234	289	329	234	341

Appendix H CEI & FEI basis

Table H-1 CEI & FEI component properties

Component	Molecular weight (MW)	Atmospheric boiling point (Tb)	Melting point (Ts)	Flash point (Tv)	Auto-ignition temperature (Tz)	Stof is zelfmeldend (ZMS)	NFPA -code Health	NFPA -code Flammability	NFPA -code Reactiviteit	Vapor pressure (at 20°C) (Po)	Accute toxicity limit (TOX)	L.E.L. value in air (LEL)	U.E.L. value in air (UEL)	Liquid density (sm)
	[kg/kmol]	[°C]	[°C]	[°C]	[°C]	[-]	[-]	[-]	[-]	[bar]	[mg/m ³]	[vol.%]	[vol.%]	[kg/m ³]
Aniline	93.13	184	-6.3	70		ZM	3	2	0	0.001	100000	1.3	11	1019
Chlorine	70.91	-34.1				ZM	3	0	0	7.8	58			1399
Dimethyl carbonate	90.08	90	2	18	458	ZM	1	3	0	0.056	5E+06			1070
Formaldehyde	30.03	-19.1	-92	50	430	ZM	3	4	0	0.024	31	7	73	812
Formalin	30.03	101	-15	60	300	ZM	3	4	0	0.0017	31	7	73	1012
Hydrogen Chloride	36.46	-85	-114			ZM	3	0	1	47.7	149			805.2
Methanol	32.04	64.7	-97	12	464	ZM	1	3	0	0.123	5E+06	6.3	36	791.8
Nitrobenzene	123.06	245	5.85	88	525	ZM	2	3	1	0.0002	2000	2	9	1199
NMA	107.15	196	-57	79	500					0.0004	276920			989
Phosgene	98.92	7.5	-118			NZM	4	0	1	1.899	4			1360
MDI	250.3	314	37	199	240	ZM	2	1	1	1E-09	380			1230