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A New Nano Insulation Material for Applications in Zero Emission Buildings

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Nanotechnology	
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Preface

This master thesis was designed in collaboration with the Research Centre on Zero Emission Buildings (ZEB). It was tailored for a student that combines a degree in nanotechnology with a specialization in industrial ecology. I will be the second student to graduate with this combination from NTNU, and the first one to write the master thesis at NTNU within the field. It has been challenging to go outside of the standard list of master thesis topics. However, it has also been very rewarding to work out from ideas that are my own. I was happy to see that the zero emission building research found interest in these ideas, and invited me to apply them to a part of their work.

I would like to give special thanks to my main advisor Tor. I would also like to thank my co-advisors Edgar and Arild.

I would like to give thanks to the other people who have taken time off their busy schedule to sit down with me to explain something or to share a point of view. Thanks to Gao, Bjørn Petter, Bente and the other ZEB and SINTEF people that have supported me. Thanks to Christian and Carine from MiSA. Special thanks to Agneta.

Last but not least I would like to thank my family the friends that have helped me with proof-reading. I would especially like to thank my sister, Mari, for taking time from her own master thesis to help me.

Abstract

New materials with extremely low thermal conductivities are interesting because they can have architectonic, technical and possibly economic benefits in buildings. A new nano insulation material (NIM) is under development at the Research Centre on Zero Emission Buildings (ZEB). Both the environmental impact of the material and its thermal conductivity are crucial design perspectives for the new material. The objective in this report was to investigate the mechanisms behind these two parameters, and how they can be optimized.

The first part of the report addressed the insulation performance. In order to lower the thermal conductivity through, inter alia, the Knudsen effect, the NIM is based on the idea of creating a porous material with extremely small pores. Hollow silica nanospheres (HSN) are produced bottom-up through a template-assisted sol-gel synthesis. To date, there have been no concrete suggestions on how to assemble the spheres to form a porous insulation material – the NIM. The effective thermal conductivity of the NIM, which is already known to be dependent on multiple parameters and advanced physical effects, was found to be dependent also on macroscopic effects in the assembled insulation unit.

The second part of the report addressed the environmental performance of the NIM. Life cycle assessment was used to calculate green house gas emissions and energy consumption for the production scenarios close to the current synthesis procedure of the NIM. The life cycle assessment model was constructed with flexibility and can be used for further research. The results are in the order of 60 kg CO_2 equivalents and 1400 MJ cumulated energy demand per kg of material, for the scenario where ethanol consumption is reduced by 50% relative to the laboratory consumption. The indirect energy and emission intensity of the raw materials consumed in the NIM production were found to be the main drivers for the environmental impact of the NIM. Especially the chemicals in the sol-gel synthesis.

The two parts of the report are connected: Higher environmental costs can be tolerated per unit material thickness, if the thickness can be kept small. The results from the LCA indicate that the environmental impact of the NIM risks being relatively high, even if very low thermal conductivities can be obtained. Hence strict optimization of both insulating and environmental performance is necessary. It was concluded that the most important recommendations for this optimization include avoiding introducing phases with higher thermal conductivities than the HSN in the assembly step and reviewing the consumption of chemicals the silica synthesis procedure.

Sammendrag

Nye materialer med ekstremt lav termisk ledningsevne er interessante fordi de kan ha arkitektoniske, tekniske og økonomiske fordeler når de brukes til å isolere bygg. Et nytt nanoisolasjonsmateriale er under utvikling på det Research Centre on Zero Emission Buildings (ZEB). Både materialets miljøregnskap og dets isolasjonsegenskaper er avgjørende designperspektiver. Målet med denne oppgaven var å undersøke disse to ytelsene og hvordan de kan optimaliseres.

Den første delen av rapporten tok for seg isolasjonsytelsen. Nanoisolasjonsmaterialet er basert på idéen om å skape et porøst materiale med ekstremt små porer, med mål om å senke den termiske ledningsevnen gjennom blant annet *Knudsen-effekten*. Hule silika nanokuler har blitt produsert ”bottom-up” gjennom sol-gel syntese over nanoskopiske, sfæriske templater. Til dags dato har det ikke vært noen konkrete forslag på hvordan kulene skal bli satt sammen til et sammenhengende materiale. Det har tidligere blitt funnet at den termiske ledningsevnen til nanokulene er påvirket av mange parametere og avanserte fysiske fenomener. I denne rapporten ble det funnet at den effektive termiske ledningsevnen i materialet i tillegg også kan bli sterkt påvirket av sammenføyningen.

Den andre delen av rapporten tok for seg materialet miljøpåvirkning. Livssyklusanalyse ble brukt til å regne ut klimagassutslippet og energibruken ved produksjonen av nanoisolasjonsmaterialet. Modellen ble konstruert for å være fleksibel og robust nok til bruk i videre forskning. Den indirekte energibruken og de indirekte utslippene knyttet til råmaterialene ble funnet å være de viktigste årsakene til den betydelige miljøpåvirkningen. Kjemikaliene i sol-gel syntesen ble funnet å ha spesielt stor påvirkning på miljøregnskapet.

De to delene av rapporten henger sammen: Høyere miljøkostnader kan bli tolerert per enhet materialtykkelse, hvis materialet kan holdes smalt. Resultatene fra livsyssklusanalysen indikerer at klimagassutlippet fra nanoisolasjonmaterialet riskerer å bli høyt, selv for et materiale med svært god isoleringsevne. Dette betyr at både isoleringsevnen og miljøytelsen bør optimaliseres til det maksimale. Det ble konkludert med designanbefalinger for denne optimaliseringen. De viktigste anbefalingene ble funnet å være: unngå å introdusere faser som har høyere termisk ledningsevne enn nanokulene i sammenføyningsfasen og revurder bruken av kjemikalier i sol-gel prosessen.

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Abbreviations

CC	Climate Change impact
CED	Cumulated Energy Demand
EPD	Environmental Product Declaration
Eq.	Equation
Equiv.	Equivalents
FU	Functional Unit
GHG	Green House Gas
GWP	Global Warming Potential
HSN	Hollow Silica Nanosphere
HTP	Human Toxicity Potential
IPCC	International Panel of Climate Change (United Nations)
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
NIM	Nano Insulation Material
PCR	Product Category Rules (For EPDs)
PVP	Polyvinyl pyrrolidone
PAA	Polyacrylic acid
Rpm	Rounds per minute
TEOS	Tetraethyl Orthosilicate
Tkm	Ton kilometers
VIP	Vacuum Insulation Panel
ZEB	Research Centre on Zero Emission Buildings

Glossary

Life cycle phases:	See Figure 18 in appendix A.
Nanotechnology:	The manipulation and manufacture of materials and devices on the scale of atoms or small groups of atoms. The “nanoscale” is typically measured in nanometres, or billionths of a metre (*nanos*, the Greek word for “dwarf,” being the source of the prefix), and materials built at this scale often exhibit distinctive physical and chemical properties due to quantum mechanical effects [1].
Cradle-to-gate LCA:	LCA with system borders ending at the gate of the factory where the product is produced. In other words, operation and end-of-life is not taken into account.
Cradle-to-grave LCA:	LCA over the entire life-cycle of a product or service.
Sol-gel processing:	Stable dispersions, or sols, of small particles are formed from precursor chemicals such as metal alkoxides or other metalorganics. By partial evaporation of the liquid or addition of a suitable initiator, a polymer-like, three-dimensional bonding takes place within the sol to form a gelatinous network. The gel can then be dehydrated and calcined to obtain a fine ceramic powder [2].
Problem shifting:	The displacement or transfer of problems between different environmental pressures, product groups, regions or over time.
Packing factor:	The density of an arrangement of non-overlapping spheres.
Zero emission building:	See appendix A.

1 Introduction

The object of study in this master thesis is a new insulation material for application in zero emission buildings. This report is written at an early stage of the development of the material. The work addressing two aspects that will determine the material's design: The thermal and the environmental performance.

The building sector is accountable for a significant part of global energy consumption, greenhouse gas (GHG) emissions and waste generation. The United Nations Intergovernmental Panel on Climate Change (IPCC) is reporting that close to a quarter of the global total energy-related carbon dioxide (CO_2) emissions are stemming from the building sector [3]. Much attention is therefore focused on energy efficiency and emission abatements in this sector. As a part of this, the Research Centre on Zero Emission Buildings (ZEB) is developing buildings with zero net GHG balance throughout the life cycle. The buildings life cycle include raw material extraction and processing of construction materials, building construction, operative life and finally demolition and construction waste managent. A presentation of the zero emission building concept was presented in the candidates' project thesis [2], and a summary is given in appendix A.

Addressing energy demand for heating and cooling is assumed to have the largest and most cost-effective energy and GHG reduction potential in buildings [4]. This has lead to a growing demand of increasingly thicker insulation. However, this comes at the expense of floor space, which is a problem from architectonic and economic perspectives. Also, thick walls steal daylight from windows. In addition, material requirements and transport volumes increase, which again affect the total amount of GHGs emitted.

By nanostructure manipulation, new materials can be fabricated with very good insulating properties. Nanotechnology insulation material (NIM) can therefore be applied in considerable smaller thicknesses than conventional insulation materials. Application of NIMs to limit the wall thickness, while still achieving a satisfactory thermal resistance, is an important strategy on the pathway to sustainable buildings [5]. However, high-tech materials can be energy intensive and chemically demanding to produce, so it is important to avoid problem-shifting in the building's life cycle. Energy consumption in the operation phase of the building's life cycle traditionally dominates total life-cycle energy consumption. However, recent studies show that, in state-of-the art low energy buildings, the embodied energy of the construction risks to balance the operation energy because of the extended use of active components and advanced materials [6].

ZEB is developing a tool to calculate the contribution from the building materials to the environmental impact of the building [7] . In order for the tool to be useful, transparent environmental data of the different materials must be accessible [7]. Currently, the availability of such data is low. ZEB is therefore interested in taking in the environmental perspective when developing a new nano insulation material based on hollow silica nanospheres (HSN). This new material is the object of study in this master thesis.

The new nano insulation material is founded on the principle of confining air in extremely small pores within the structure. This is in order to lower the overall thermal conductivity of the material through, inter alia, the Knudsen effect. The idea of the hollow silica nanosphere type NIM is to try to create a super-insulating nanoporous material bottom-up from the spheres [8]. The intention is to make a high performance insulation material with interesting properties compared to conventional insulation. However, the product is at an early stage of development. The spheres are currently being produced with an average output in the order of 1 gram per synthesis. More research is needed on the final form of the material, e.g. how to make use of the spheres to create a building element with the desired properties. The production of the spheres are optimized for a successful lab experiment, and not yet optimized for a successful product. The material understudy is far from being optimized and may change considerably. This was the greatest challenge in this work: Trying to draw conclusions from a material of which almost all parameters still are variables.

What properties must the material have in order to be an interesting investment? What form should the product take in order to be a useful, practical and robust building element? One requirement is that the insulation performance is good enough to off-set the economic investment costs due to room space saving. Other requirements include robustness, flexibility and safety with regard to nanoparticle issues, fire and moisture. Finally, the energy and GHG intensity of the material should not be too high, in order to compete with other technologies in the zero emission setting. At present, most of these challenges remain unanswered within ZEB. The goal of this work is not to answer all these questions, but to make advancement in the following two areas: The estimation of the effective thermal conductivity of the NIM and the environmental impact of its production. These two areas are of course connected: **Higher environmental costs can be tolerated per unit material thickness, if the thickness can be kept small**. This is applicable whether the economic or ecologic investments costs are considered.

Environmental system analysis is needed to quantify the environmental costs of the material. Life cycle assessment (LCA) is becoming an important tool for improving the environmental performance of materials, technology and construction in the building sector[7]. LCA is a data-intensive tool in which the accuracy of the results depends primarily on the accuracy of the data input. The accuracy is problematic in cases like the one presented here, where the material is not yet finalized.

However, the LCA method is well suited to search for and detect the most important environmental loads in the supply chain of a product, as to provide understanding on how the environmental performance can be improved. Hence, there are reasons to argue for LCAs to be performed at the earliest stage possible in the product development. Even if data accuracy is low at this stage, the LCA should be performed earlier rather than later, when the process is set and it is too late for improvements. A screening-LCA of the NIM is therefore useful in order to optimize the material design.

1.1 Objective

The objective of this thesis is to investigate the basis for the effective thermal conductivity of the NIM and the causes of energy demand and green house gases from its production. This is in order to understand how the material's insulating and environmental performance can be optimized.

This work will investigate the basis for the effective thermal conductivity of the NIM by:

- Reviewing the most important microscopic mechanisms that decide the thermal conductivity of the NIM.
- Investigating additional boundary conditions for the effective thermal conductivity which may arise when the material is assembled into forming a macroscopic object.

And it will investigate the causes of energy demand and green house gas emissions from the NIM by:

- Constructing a cradle-to-gate LCA model for the NIM.
- Calculating the accumulated energy demand and the climate change impact of the NIM by using scenarios.
- Investigating the causes for the energy demand and climate change impact.
- Developing recommendations for a greener production based on those causes.

The final goal is to push the development of the NIM in a pragmatic direction. The insulating and environmental characteristics are of crucial importance for an insulation material applicable to zero emission buildings.

1.2 Outline of Report

After the introduction, the report is divided into two main parts: The Nano Insulation part (chapter 2) and the Environmental Assessment part (chapter 3).

In the first part, the material under study is outlined. First, the hollow silica nanospheres on which the material is to be based is presented, and then the future NIM is described based on the current level of knowledge. Necessary theory for thermal insulation is presented. The estimation of the thermal conductivity of hollow silica nanospheres is presented through some analytical expressions studied by the scientists working with the material. Subsequently, some other analytical expressions will be tried in order to make a contribution to the research on the NIM thermal conductivity, from another perspective.

The second of the two main sections is the most comprehensive. The LCA methodological framework is presented in order for readers unfamiliar with environmental system analysis to follow. These readers may also find some of the footnotes in chapter 3 helpful. Subsequently, a cradle-to-gate LCA, based on a constructed model for the production of the material is performed. The model is thoroughly presented because it is interesting for further research. The assessment will be performed according to the classical LCA outline including goal and scope, inventory analysis, impact assessment and interpretation. Conclusions will be drawn in form of recommendations for a greener production.

In chapter 4.1, the findings are discussed. In this chapter, the two parts coincide and cast light on each other’s results. Conclusions are summarized in chapter 5.

2 Part 1: Nano Insulation

The product assessed in this thesis is a nano insulation material (NIM). It will be referred to as the NIM, or as the silica nanosphere material, as it is based on hollow, nanoscopic spheres of silica (SiO_2). In brief, this is a new high performance insulating material founded on the principle of confining air in extremely small pores. This is in order to lower the overall thermal conductivity of the material through, inter alia, the Knudsen effect [9]. The theory on which this technology is based on is presented in chapter 2.2.

The NIM could be the new member of the family of state-of-the art insulation materials that have emerged the recent years. Among the most promising are aerogels and vacuum insulation panels (VIP). These materials will very briefly be presented here. More information can be found in, for instance, Jelle et al. 2010 [9].

Aerogel insulation is based on sol-gel technology of silica. The fluid in the silica gel is replaced by a gas in order to fabricate a solid material with a cross-linked internal structure of SiO_2-chains with a large number of nanoscopic pores filled with air (up to 99.8% air) [10]. Aerogels have very low densities and thermal conductivities.

Aerogels have a wide range of applications. Its applications as insulation material is widely studied, see for instance Schultz et al. [11], Hostler et al. 2008 or Baetens et al. 2011 [5]. Aerogel insulation was also studied in the candidate’s project thesis [2]. Commercial available areogel insulation are mostly made up of granular aerogel in fiber composites and have been reported to have thermal conductivities down to 0.013 W/mK [9]. However, aerogel insulation is expensive compared to conventional insulation materials.

No environmental product declarations[1] or life cycle assessments have been reported for commercial aerogel insulation products. One of the main producers, Aspen aerogels, are reporting some environtmental data, but will not share any of the calculation methods behind the numbers [2, 12]. A publication from Dowson et al. 2011 reports conservative estimates for the environmental impact of one cubic meter of aerogel based on laboratory experiments [13]. These results are not adapted for application in comparative analysis because of the non-compliance in the functional unit and boundary conditions.

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[1] An Environmental Product Declaration (EPD) is a standardized, LCA based tool to communicate the environmental performance of a product. The tool is based on the benchmarking of LCA results through predefined rules called Product Category Rules. In Norway, the EPD system is managed by the Norwegian EPD Association [40].

Vacuum insulation panels (VIP) are achieved by applying a vacuum to an encapsulated micro-porous material [10]. VIPs represent state-of-the-art insulation with very low thermal conductivity, but it is associated with a degradation over time [14]. The thermal conductivities range from 0.003 to 0.004 W/mK in fresh conditions to typically 0.008 W/mK after 25 years aging, due to water vapor and air diffusion into the core. Puncturing the VIP envelope causes an increase to about 0.02W/mK. The time-dependent degradation is a serious drawback, and more research is needed before a commercial break-through of VIP [8]. A review on VIPs for building applications has been written by Baetens et al. 2010 [10].

A comprehensive LCA report for two types of vacuum insulation panels were published by Schönhardt et al. 2003 [15]. Industry data from this report were obtained through Agneta Ghose who wrote a comparative LCA report on wall elements VIP and other insulation materials [16]. The data were used to calculate the cradle-to-gate climate change impact of a typical VIP, for subsequent use in the work presented here. Information about the calculation is given in appendix D.

2.1 System Description

2.1.1 Description of Hollow Silica Nanospheres

The hollow silica nanospheres are produced at the Research Center on Zero Emission Buildings at NTNU and SINTEF Buildings & Infrastructure, in collaboration with SINTEF Materials and Chemistry. To the eye, the material looks like white powder. A picture of the spheres produced in a transmission electronic microscope is presented in Figure 1. Diameters and shell thicknesses can be varied. It is desirable to optimize the pore sizes to the point where the Knudsen effect is fully exploited [10]. If this can be achieved, it is theoretically possible to achieve thermal conductivities equal to VIP, without applying vacuum [10]. At the moment, spheres in the size range of 50-200 have been fabricated with success. The procedure of achieving hollow silica nanospheres is shown in Figure 2 and detailed below the figure. The chemistry of this process was presented in the candidates' project thesis [2]. More comprehensive descriptions of the science and synthesis of hollow silica nanospheres can be found in , for instance, Gao et al. 2013 [17] and Du et al. 2010 [18].

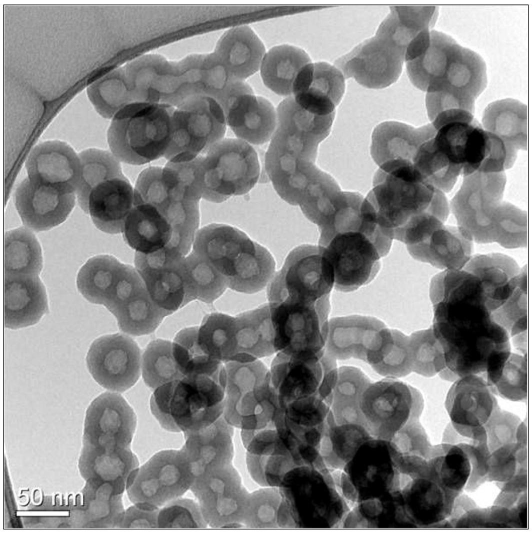

Figure 1: Transmission Electron Microscope image from of a sample of hollow silica nanospheres produced for ZEB. The image is provided by SINTEF Materials and Chemistry [19].

The following description is rewritten from an article to be submitted by Gao et al. 2013 [17]. This synthesis route has resulted in monodisperse spheres. These samples have a measured thermal conductivity of 0.02 W/mK and a density of 0.2 g/cm^3 [20].

Monodisperse polystyrene (PS) nanospheres were prepared and served as template for the subsequent growth of silica. For a typical synthesis, 1.5 g polyvinylpyrrolidone (PVP) was dissolved in 100 mL water under ultrasonic irradiation, and to this a solution 10 g styrene *solution was added. The obtained styrene/PVP solution was then heated up to 70°C under constant stirring at 500 rounds per minute (rpm). Afterwards, 10 mL potassium persulfate (KPS) solution (0.15 gram KPS in 10 mL water) was added dropwise into the PVP/styrene solution to initiate the polymerization reaction. The polymerization reaction was kept at 70°C for 24 h. After the reaction, the obtained PS nanosphere suspension was cooled naturally to room temperature for further use. 6 g of as-prepared PS suspension and 4 mL ammonium hydroxide (NH_4OH) solution were added into 120 mL ethanol under constant stirring at 500 rpm. Then, 10 mL tetraethyl orthosilicate (TEOS) ethanol solution (50 vol% TEOS in ethanol) were slowly added. The system was stirred for 10–24 h to prepare core-shell typed nanospheres. After the reaction, the solid product was separated from the mother solution by centrifugation at 10000 rpm, and the obtained sediments were washed with ethanol twice and finally dried at room temperature. Hollow silica nanospheres were readily obtained by annealing the core-shell typed nanospheres at 500°C for 3 h as to combust the core.*

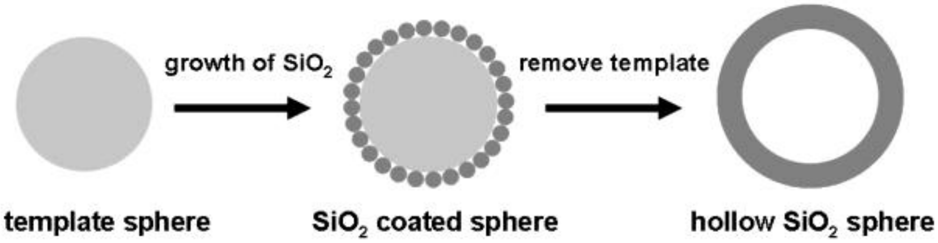

Figure 2: A schematic drawing of the template assisted synthesis procedure of the hollow silica nanospheres. The drawing is provided by ZEB [17].

An alternative route is suggested by Stephan Kubowicz at SINTEF Materials and Chemistry[2]. That route is presented in the candidates' project thesis [2]. However, Kubowics approach does not differ significantly from the one described by Gao. The most important difference is that the polyacrylic acid (PAA) is used as a template instead of styrene. PAA does not have to be combusted, it can simply be removed by diffusion, when washing the nanospheres in water.

It is important to recognize that this process is not fully optimized yet. As will be described in the following sections, several parameters of the spheres are affecting the thermal conductivity. These parameters need to be optimized in order to minimize the thermal conductivity of the material. Much experimental research remains in order to achieve the desired properties. Furthermore, the process is not optimized by means of an industrial scale production. An industrial production system may require substantial modifications on the fabrication route presented above.

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[2] ZEB collaborates with a group at SINTEF Material and Chemistry for the development of the NIM.

2.1.2 Description of the NIM

As mentioned in the introduction chapter, more research is needed on the final form of the material, e.g. how to make use of the spheres to create a building element with the desired properties. Nothing has yet been published on this step. It is partly unknown, partly restricted by intellectual property issues at this point. Referring to personal communication with Bente Tilset at SINTEF Materials and Chemistry [19], the intension is to create a lightweight and flexible insulating mat. The mat will be superporous because it constitutes a high packing fraction of hollow silica nanospheres. Surface modification and binders will make the spheres stick together and add flexibility. Referring to personal communication with Bjørn Petter Jelle [8], responsible for the advanced material group at ZEB, it might also be possible to fabricate the spheres in the connected form directly, but this approach has not been studied yet. In any case, the spheres will be stuck inside the mat and cannot escape into the air, unlike aerogel particles in commercial aerogel fibremats. The locking of the nanoparticles in the material is important from a health perspective. The time dependent degradation caused by air diffusion of VIPs will not be a problem with the NIM, because it does not contain vacuum. However, moisture might cause problems, so the mat must be hydrophobic and durable. A flexible, rubberlike texture is desirable. It was not possible to get any details about the modifications or the substances required to obtain this.

In conclusion, little information is available on the final properties, characteristics and production method for the NIM. A drawing of the future material, freely imagined by the candidate and realized in SolidWorks by design student Tori Klakegg Mæhlum [21], is presented in Figure 3.

Figure 3: A projection of what the NIM might look like as a complete, ready-to-use insulation material, as imagined by the candidate in cooperation with design student Tori Klakegg Mæhlum [21]. The image is realized in SolidWorks.

2.2 Thermal Conductivity

Heat spontaneously flow from a body at a higher temperature to a body with lower temperature by conduction, convection and radiation. The concepts of thermal conductivity can be derived from the phenomenological Fourier's law of heat. This law states that the time rate of heat transfer through a material is proportional to the negative temperature gradient and to the area, at right angles to that gradient, though which heat is flowing (Ws) [22]. Fourier's law of heat is given by

$$dQ = -k\frac{\partial \mathrm{T}}{\partial \mathrm{x}} \times \mathrm{dA} \times \mathrm{dt}$$

Eq. 1

where Q [Ws] is the heat flux, $\frac{\partial \mathrm{T}}{\partial \mathrm{x}}$ is the temperature gradient in the x direction, A [m] is the area and t [s] is the temperature. *k* [W/mK] is the coefficient which is referred to as the thermal conductivity. It can sometimes be referred to as the k-value or the λ-value. It is a material specific property.

The thermal resistance, *R* [m^{2}K/W], of a material is the measure of a temperature difference by which an object or material resists the heat flow. In terms of the thermal conductivity, the thermal resistance can be expressed as

$$R = \frac{d}{k}$$

Eq. 2

where *d* [m] is the thickness of the object. A building wall can be modeled as a construction composed of different, parallel, homogenous planes. Then, the total thermal resistance of the wall is equal to sum of the thermal resistances of each plane plus the transition resistances on the two surfaces, $R_{si,j}$. For a wall construction with n planes with thermal resistances R_1, R_2, …, R_n and air temperatures T_i and T_j on the two surfaces, the heat flux is expressed as

$$q = \frac{1}{R_{si} + R_1 + \cdots + R_n + R_{sj}}(T_i - T_i).$$

Eq. 3

The thermal conductance, also referred to as the U-value [W/m^{2}K], can then be defined as

$$U = \frac{1}{R_{si} + R_1 + \cdots + R_n + R_{sj}}.$$

Eq. 4

The U-value is often used to quantify how well a complete wall system insulates, in technical and environmental benchmarking.

Thermal insulation is a material that, when properly applied, retard the rate of heat flow into or out of a building. The retardation can be explained by the material having a good ability to resist heat, e.g. it has a low thermal conductivity [23]. The total thermal conductivity of a material is in principle made up from solid, gaseous, radiative and coupling contributions. For a homogeneous material, the effective thermal conductivity can be expressed as [23]

$$k_{eff}(T,P) = k_s(T) + k_g(T,P) + k_r(T) + k_c(T)$$

Eq. 5

where k_s is the solid state thermal conductivity which is connected to the lattice vibration at the atomic scale. k_g is the gas thermal conductivity that arises from gas molecules colliding with each other and thus transferring thermal energy from one molecule to the next. k_r is the radiation thermal conductivity connected to the emittance of electromagnetic radiation in the infrared wavelength region from a material surface. k_c is the term accounting for second order effects between the various other terms. Convection due to thermal mass transport, or movement of air and moisture, is normally not taken into account when dealing with building insulation, because it is assumed that there are no holes in the materials through which a pressure difference could make air and moisture leak [23, 24].

2.2.1 Knudsen effect

Research on heat transfer in nanostructured materials continue to reveal new ways for engineers to manipulate the nanostructure in order to reduce or increase thermal conductivity [25]. Nano scale effects can significantly reduce the heat transfer caused by conduction. Heat transfer by conduction is the transport of heat by microscopic diffusion and collision of particles or quasi-particles (molecule, phonon, electron etc.) within a body due to a temperature gradient. When the linear dimensions of the medium are comparable to the mean free path of the particles, the heat transport from particle to particle is inhibited. The particle will collide with the pore wall with increasing probability and the heat conduction due to intermolecular collision will be less and less probable as the pore size become smaller. This is often referred to as the Knudsen effect, or Knudsen diffusion, after the Danish physicist Martin Knudsen (1871–1949).

2.3 Thermal conductivity of the NIM

A schematic drawing of the NIM idea is depicted in Figure 4. The figure shows packed spheres of the size order of the mean free path of the gas molecules inside the spheres, thereby exploiting the Knudsen effect to considerably decrease the overall thermal conductivity of the material.

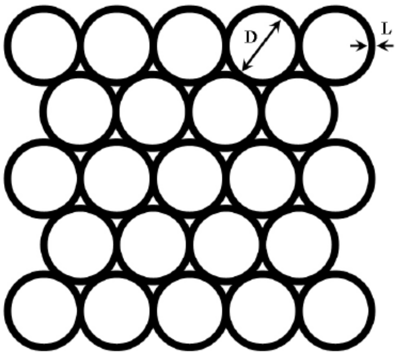

Figure 4: A schematic drawing of the NIM, in form of packed hollow silica nanospheres. Important variables are marked in the drawing. D is sphere diameter and L is shell thickness. The drawing is provided by ZEB [17].

From the figure, it is clear that the thermal conductivity of this powder depend on several parameters, like the packing factor of the spheres, the sphere diameter, the shell thickness and the intrinsic properties of the shell material. In addition, this report suggests that the surface treatment and binding chemicals will affect the properties when the final material is designed. In conclusion, both micro and macroscopic effects will have a say in the final effective thermal resistance in the new thermal insulation product.

Many numerical and analytical models have been developed to estimate thermal conductivity in materials. Some of the most fundamental analytical models originate from Maxwell's "A treatise of electricity and magnetism" 1881 [26]. Numerical models based on finite element or lattice Monte Carlo methods have been found to have good coherence with experimental data for a range of structures. However, the theoretical assessment of the thermal properties of hollow silica nanospheres has proven to be very difficult [17, 27] . Existing models are too simple to describe the complexity of the hollow silica nanospheres.

In the two following sections, some analytical expressions will be studied. In the first section, which is based on existing literature, a microscopic perspective is taken. It shows how a scientist can tune the thermal conductivity of the hollow silica spheres through nano scale manipulation. In the second section, the material will be addressed as a composite by applying an analytical model for the macroscopic effective thermal conductivity. The macroscopic contributions to the effective thermal conductivity that will come in addition when the material is completed through integration step (section 2.1.2), is not yet considered by ZEB.

Neither the microscopic nor the macroscopic approach describes the heat transfer in the NIM perfectly. This work will not go in to detail of the various physical phenomena that take place in the heat transfer. It is out of the scope of this report to find a satisfying model for the thermal conductivity of the new NIM, but both the microscopic and the macroscopic approaches presented here should be a part of the big picture.

2.3.1 Microscopic approach

All the terms in Eq. 5 should be minimized in order to minimize the effective thermal conductivity. Analytical expressions for the terms reveal how reductions can be tailored at the micro/nanoscale. Simplified analytical expressions for the conduction and the radiation term can be found in Liao et al. (2011) [28], where theory interpreting areogels was introduced to describe the thermal conductivity of hollow silica nanospheres, based on the similarities in the structures of the respective materials. Derivations of the expressions based on a simple model of infinite layers of alternating gas and solid planes can be found in Holvik et al. (2013) [27] (to be submitted).

Conduction

According to Liao et al. (2011) [28] the gaseous conduction is the most substantial contributor to the total thermal conductivity in these systems. The solid contribution, k_s, is according to that paper relatively low because of the low bulk densities in the material. The gaseous thermal conductivity is given as [27, 28]

$$k_g = \frac{\rho k_{g,0}}{1 + 2\beta K_n}$$

Eq. 6

where ρ is the porosity[3] and $k_{g,0}$ = 0.0026 W/mK is the thermal conductivity of bulk air at ambient conditions. The Knudsen effect is included in this model though the Knudsen number, $K_n = \frac{l}{d}$, with l being the gas molecule mean free path and d being the dimension where the gaseous transport takes place, i.e., the pores of the hollow nanospheres and the vacancy among adjacent spheres (capital D in Figure 4). β is a dimensionless constant accounting for the coupling effects of gaseous and solid heat transport arising from the Knudsen diffusion[4].

From Eq. 6 it is evident that reducing the diameter d of hollow nanospheres is a method to suppress the gaseous thermal conductivity k_g. Eq. 6 is presented graphically for different sphere diameters in Figure 5. β = 0.2 for air, and l is set to be 68 nm at ambient conditions[17]. A porosity of 0.80 is assumed in the figure [20]. The figure shows that k_g is decreasing with pore size reduction.

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[3] The porosity is given by the ratio V_v/V_T, where V_v is the volume of the void space and V_T is the total volume.

[4] The heat transfer arising from the particles colliding with the pore wall.

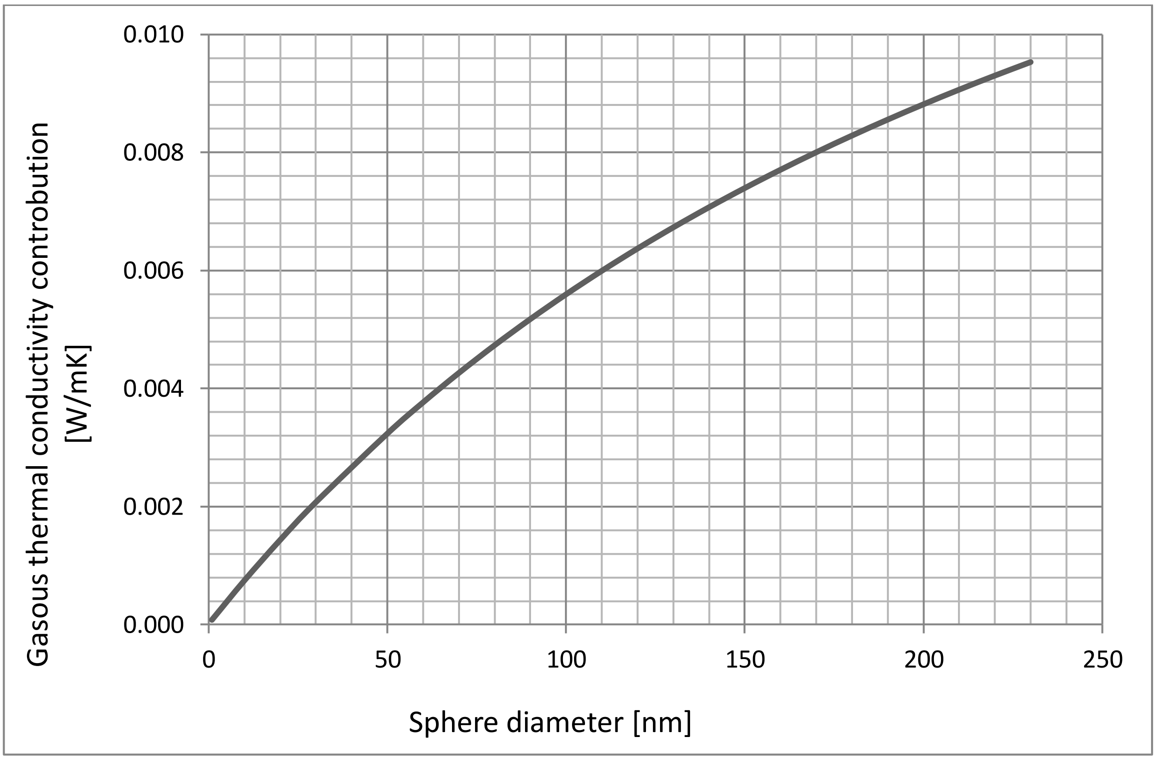

Figure 5: Graph representing Eq. 6, showing the relation between the gaseous thermal conductivity contribution on the y-axis, and the sphere diameter on the x-axis

Radiation

The radiative heat transfer is due to the emittance of electromagnetic radiation in the infrared wavelength region from a material surface. It can be manipulated by the addition of an opacifier or reflective agent. In silica aerogels, it has been shown that the radiative heat transfer can be suppressed by adding carbon black [10]. The overall thermal conductivity at ambient pressure could then be decreased to a value of 0.0135 W/mK. The opacifier will lower the conductivity by increasing the absorption coefficient, according to the Stefan-Boltzmann equation [28],

$$k_r = \frac{16n^2\sigma T^3}{3\alpha_R}$$

Eq. 7

where *n* is the dimensionless refractive index, σ [W/m^{2}K^4] is the Stefan-Boltzmann constant, *T* [K] is the mean temperature of the materials anf α_R is the Rosseland mean absorption coefficient. The Stefan Boltzmann equation does not consider near-field radiation effects.

In the publication by Liao et al. (2011) [28], where these expressions, taken from aerogel theory, are applied, also experimental values for the thermal conductivity were measured for HSN samples. The calculated values were larger than the experimental values. The deviations were explained by "the structural differences between hollow spheres and aerogels". Dr. Tao Gao at ZEB emphasizes that this simplified theory must be applied with precaution [20].

In the work done for ZEB by Holvik et al. 2013 (to be submitted) [27], a more comprehensive and advanced model is developed. It is used for the calculation of the overall bulk heat transfer with its various components through a porous material. The porous material is modeled as a structure of alterning layers of voids and solid material of thickness d_v and d_s. Contributions from the conduction in the solid and gas states, thermal radiation and also near field radiation effects are included. Near field effects stem from the part of the electromagnetic field that is very close to a body. It will not be treated in this report, since comprehensive physical explanations of heat transport is out its scope. A figure from the work by Holvik et al 2013 is shown in Figure 6. The figure shows total thermal conductivity (here denominated λ_{tot}) as a function of the d_{v+s}[5]. The gas in the pores is air and the solid material is SiO_2. The figure shows that thermal conductivities down to, and even below 0.004 W/mK is theoretically achievable according to this model.

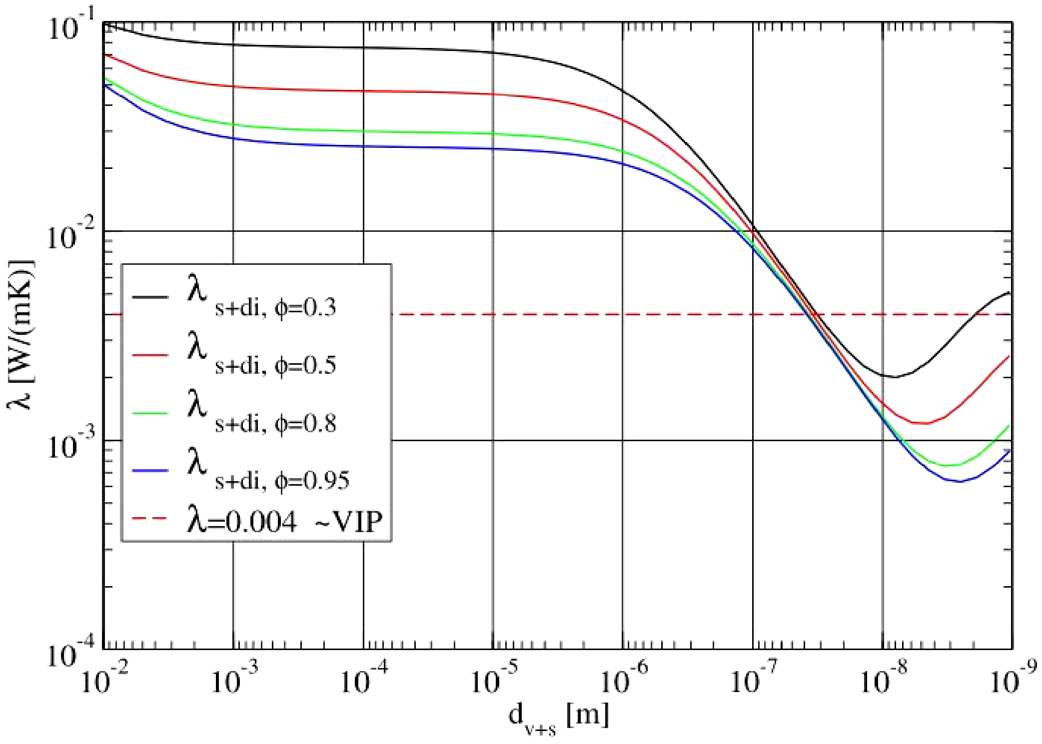

Figure 6: Total thermal conductivity λ_{tot} as a function of d_{v+s} for varying porosities[6]. Heat transfer by solid and gaseous conduction and far and near field radiation is included. The gas is the void is air under standard conditions. The solid matrix is made of silicon dioxide.

---

[5] d_{v+s} is the length of the repeated unit of void and solid layers in the model, e.g the period length.

[6] For the 1D model, the porosity simplifies to $\emptyset = \frac{d_v}{d_s+d_v}$

Figure 6 shows that, for pore sizes close to 1 nm or smaller, the thermal conductivity can increase rapidly. This is because near field radiation effects invalidate the theory in this size range.

In Figure 6, the total thermal conductivity is graphed for different porosities. It can be seen that the higher porosities, e.g. lower volume fractions of solid, gives lower thermal conductivities. For more in-dept explanations of Figure 6 and of the physical background for thermal conductivity, it is referred to the article [27].

In this chapter, literature on heat transfer in nanostructured material models has been reviewed. The conclusions from literature can be summarized as follows

- Pore sizes should be minimized within the size order where the Knudsen effect makes the thermal conductivity size dependent.
- The radiation absorption coefficient can be increased by the addition of an opacifier of reflective agent.
- Porosity should be maximized in the NIM.
- It has been calculated theoretically that thermal conductivities equal to or even lower than the thermal conductivities of VIPs are obtainable for optimal NIMs.

Modifications of these conclusions can appear as a consequence of trade-offs with other effects, yet to be discovered.

2.3.2 Macroscopic approach

As described in chapter 2.1 and illustrated in Figure 3, the material will not keep the powder form in the final product, but take the form of an integrated mat through various surface modification and binding technologies [19]. In the future product, the spheres will somehow be packed together and most probably treated with surface modifications and binding chemicals to constitute a flexible mat [19]. The exact behavior of the heat flow through the system is not known. A focus biased towards the microscopic optimization of the spheres may therefore overlook the effects from the integration step on the effective thermal conductivity of the material.

From a macroscopic perspective, it is here suggested to treat the NIM as a two-component composite of spheres and binding matrix. This approach treats the material top-down as a two component system, ignoring phenomena of structures at size level of the mean free path of phonons. It might seem incorrect to consider the material as a two-component system, since the binding probably will be a result of surface modification of the spheres rather than the introduction of an additional polymer. Nevertheless, the macroscopic approach provides interesting perspectives on what impact from the integration step can have on the effective thermal conductivity. This is a pragmatic engineering approach, simplified but useful for getting closer to an understanding of the boundary conditions for the final material design.

Effective thermal conductivity of a composite porous material is known to depend on many factors including phase composition, porosity, and microstructure. Numerous theoretical and empirical correlations have been proposed to predicate the effective thermal conductivity of composite and porous materials. However, no single approach can accurately predict the thermal conductivity of all types of composites [29, 30]. Most of the models are based on one or more of five basic structural models; the Series, Parallel, Maxwell-Eucken [31] and Effective Medium Theory (EMT) [26]. The models are described by Wang et al. 2006 [32]. A schematic of the material structures assumed by each model is shown in Figure 7. The physical structures assumed in the derivations of the Series and Parallel models are of layers of components aligned either perpendicular or parallel to the heat flow, as their names indicate. The Maxwell-Eucken model assumes a dispersion of small spheres within a continuous matrix of a different component. The EMT model assumes a completely random distribution of the components.

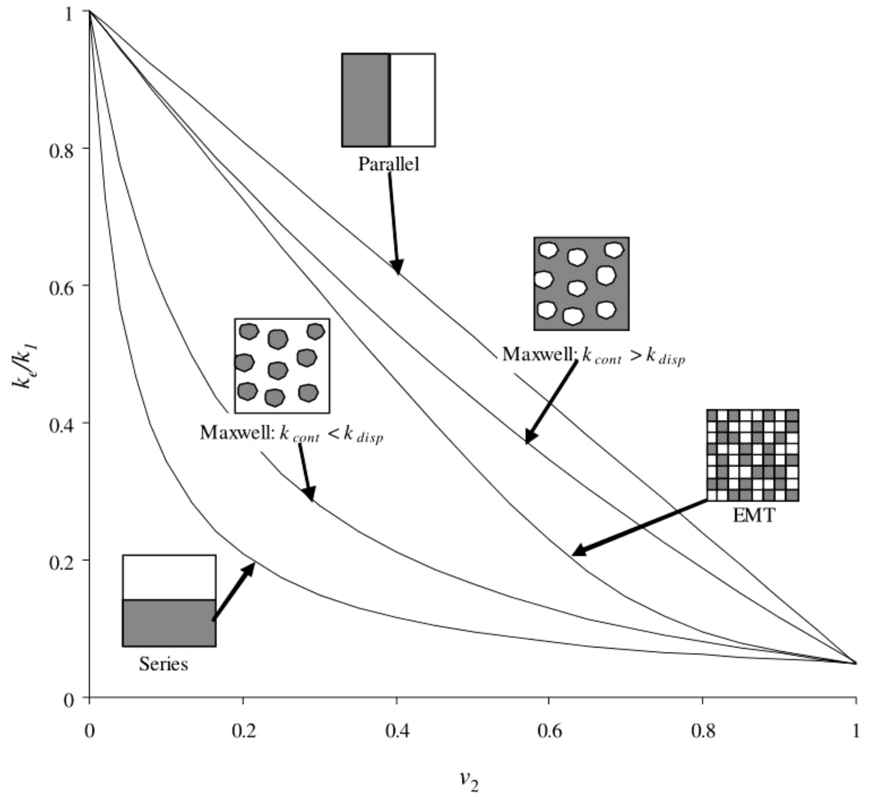

Figure 7: Plots of the Series, Parallel, Maxwell-Eucken's and EMT models with schematic representations of the structure assumed by each model. The plots show the relation between the relative thermal conductivities and the volume fractions of the two-composite material. The image is taken from Carson et. al. 2005 [33].

Carson et al. (2005) [33] plotted the relative effective thermal conductivities (effective *k-value* divided by intrinsic *k-value* of one of the components) for the Series, Parallel, Maxwell-Eucken and EMT models for a material of two components, component *1* and *2* with $k_1/k_2 = 20$, over the full range of composition. This plot is shown in Figure 7 with relative effective thermal conductivity along the y axis and the volume fraction of component 2 along the x-axis. The figure shows that the series and parallel models serve as lower and upper bounds respectively for the effective thermal conductivity of heterogeneous materials, provided that conduction is the only mechanism of heat transfer involved (macroscopic approach).

Carson proposes a distinction between internal and external porosities [33]. Internal porosity materials have bubbles/pores suspended within a continuous condensed phase, while external porosity materials include granular/particulate materials which have space between the particles. The NIM is made up of hollow spheres. The spheres have an internal porosity because they are hollow, but there is also an external porosity of voids between the spheres in the material. Heat conduction is possible both through the spheres and between them. The region between the Maxwell-bounds may be divided into an ''internal porosity region'' and an ''external porosity region'' [33], as illustrated by Figure 8.

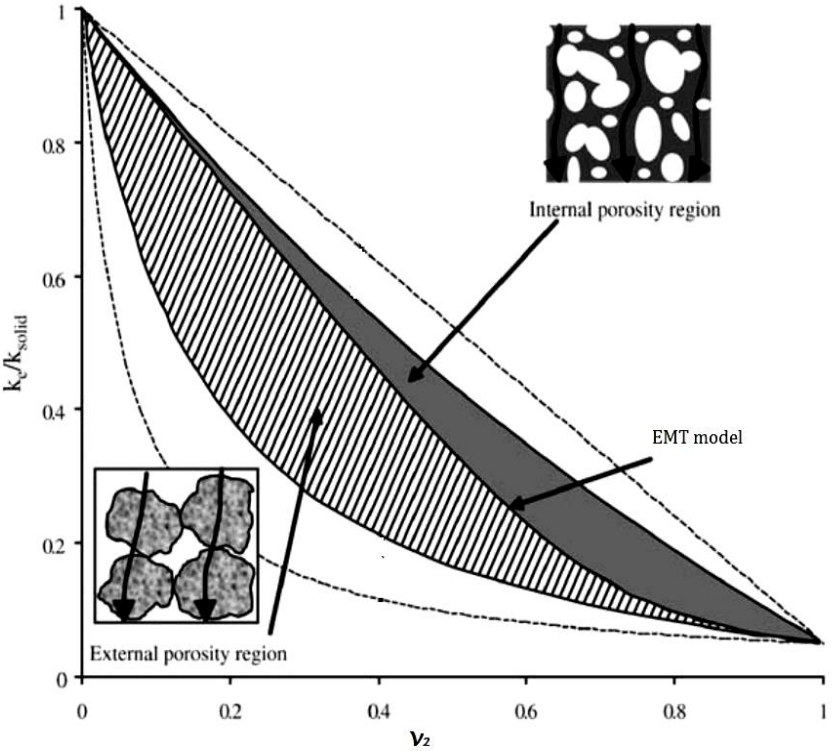

Figure 8: “Internal porosity” region bounded above by the Maxwell-Eucken model and below by the EMT model. “External porosity” region bounded above by the EMT model and below by Maxwell-Eucken. The axes are the same as in Figure 7. The image is taken from Carson et al. 2005 [33].

Effective Medium Theory modeling

Based Figure 8, the EMT model, which falls between the internal and external porosity region, is suggested as a tool to study the macroscopic thermal conductivity of the NIM. A schematic diagram of the type of structure the EMT model represents is to be found in Figure 7. It is a heterogeneous material in which the two components are distributed randomly and therefore this structure is “unbiased” towards its components.

The effective thermal conductivity of this type of structure is modeled by the EMT equation [32]:

$$(1 - v_2) = \frac{k_1 - k_e}{k_1 + 2k_e} + v_2 \frac{k_2 - k_e}{k_2 - 2k_e} = 0$$

Eq. 8

Which may be rewritten to be explicit for k_e [33],

$$k_e = \frac{1}{4}((3v_2 - 1)k_2 + [3(1 - v_2) - 1]k_1 + \sqrt{[(3v_2 - 1)k_2 + (3\{1 - v_2\} - 1)k_1]^2 + 8k_1k_2})$$

Eq. 9

where *k* is thermal conductivity and *v* is volume fraction. Subscript *e* means effective and subscript *1* and *2* means substance 1 and 2 respectively.

In other words, the variables are the volume fraction and the intrinsic thermal conductivity of the components. Once more, the case under study offers too many unknown parameters. The k-value of the “binder matrix” is unknown. The packing factor of spheres as well as the spheres intrinsic k-value is a matter under study. However, this can be solved by constructing a model based on certain assumptions. Assuming an optimistic effective thermal conductivity of the spheres of 0.004 W/mK (see end of section 2.3.1) and assuming a volume fraction of spheres ($1-v_2$) equal to the maximum random packing factor for spheres, η= 0.634 [34], the EMT model can be applied to show how the effective thermal conductivity is related to the k-value of the binding matrix. The relation is explored by graphing Eq. 9 against different values for k_2. The graph is shown in Figure 9.

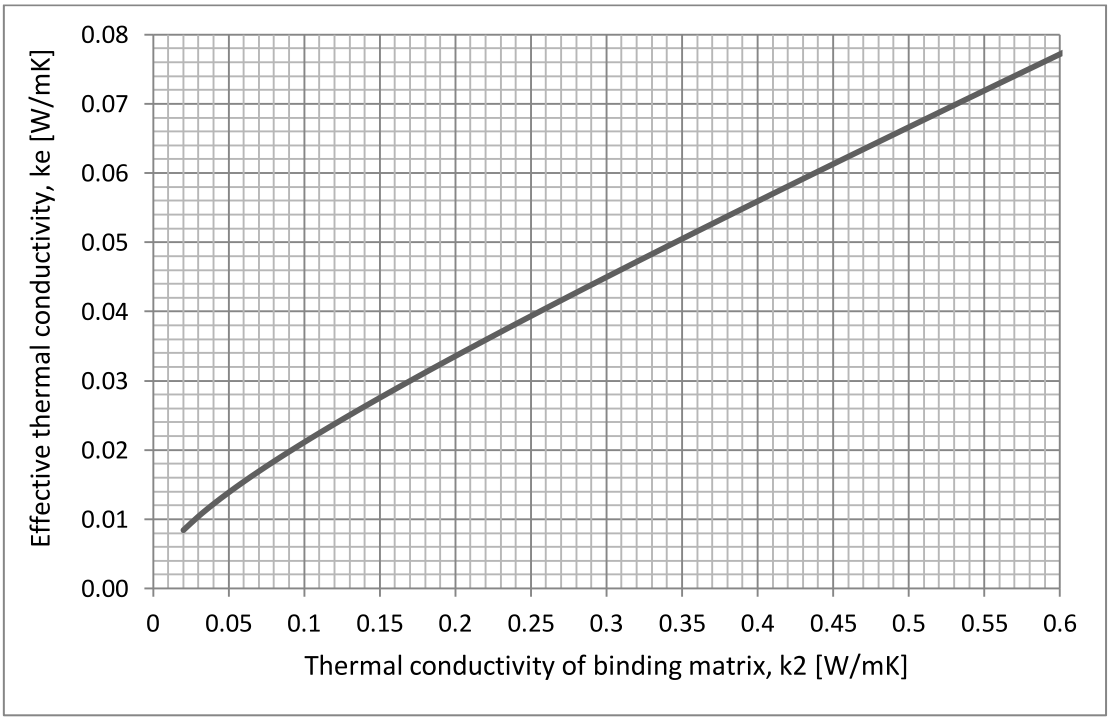

Figure 9: Eq. 9 plotted for a k_1-value of 0.004W/mK and varying k_2-values, showing how the effective thermal conductivity of the NIM will depend on not only the thermal conductivity of the hollow silica nanospheres, but also the binding matrix by which the spheres will be integrated.

Figure 9 shows a material with two phases randomly mixed. The phase with the dominating volume fraction is hollow silica nanospheres, the other phase is an arbitrary binding matrix. The figure demonstrates that the thermal properties of the latter phase are quite important for the effective thermal properties of the material as a total. The effective thermal conductivity increases fast with the increasing thermal conductivity of the binding matrix. Even when setting the intrinsic thermal conductivity of HSN to be 0.004W/mK, the effective thermal conductivity reaches undesirable high values if the binder is not very heat resistant too. This shows that it is crucial, but possibly quite difficult, to find an integration method to connect the sphere which conserves the low thermal conductivity.

In conclusion, the results obtained from applying the EMT model emphasize the importance of the impact from the integration step on the effective thermal conductivity. It is known from the microscopic model that smaller dimensions and the addition of an opacifier can lower the thermal conductivity of the hollow silica nanospheres. The effect of the packing factor and of the thermal conductivity between the spheres, arising from the EMT model, provides an additional boundary condition for the material design:

- The integration step must avoid introducing a phase with high thermal conductivity.

Vacuum insulation panels have the lowest measured thermal conductivities of all state-of-the-art insulation materials, with k-values down to 0.004 W/mK when new. It is the NIM researchers goal to obtain an equally low thermal conductivity for the new material [8]. Theoretical calculations based on advanced modeling of the microscopic heat transfer in NIMs indicate that equally low values can be achievable (section 2.3.1) However, the current samples have been measured to have k-values of 0.02 W/mK. In Liao et al. 2011 research, the experimental values for the effective k-value of hollow silica nanospheres went no lower than 0.015 W/mK [28]. For silica aerogels, lower conductivities than around 0.01 W/mK have only been achieved at low pressures (50 mbar and below), which is of little help in a real building. In addition, Figure 9 has shown that the engineering of the spheres by means of fabricating a continuous insulation material, can significantly increase the effective thermal conductivity. From a pragmatic point of view, it is therefore reasons to question the 0.004 W/mK goal, but more research is needed in order to draw a conclusion.

In addition to the insulation properties, economic, structural, safety and environmental conditions will play a role in the product design of the new NIM. In the next part, the environmental perspective will be assessed.

3 Part 2: Environmental Assessment

3.1 The Life Cycle Assessment method

Life cycle assessment (LCA) is a method for the quantification and evaluation of potential environmental impacts from a given industrial system. LCA addresses potential environmental impacts (e.g. use of resources and the environmental consequences of releases) throughout the entire life cycle. The product life cycle spans from from raw material acquisition through production, use, end-of-life treatment, recycling and final disposal (i.e. cradle-to-grave) [35]. One of the main advantages of LCAs is its robustness towards problem shifting and narrow outlooks on sustainable development. The procedures of LCA are part of the ISO 14000 environmental management standards (ISO 14040:2006 and 14044:2006) [35, 36]. Comprehensive presentations of the life cycle assessment methodology can be found in for instance Curran 2006 [37], Baumann & Tiller 2004 [38] or Strømman 2008 [39]. A summary will be presented here.

A LCA can be divided into four main steps:

- goal and scope definition
- inventory analysis
- impact assessment
- Interpretation

Goal and scope definition

An LCA starts with an explicit statement of the goal and scope of the study, which sets out the context and explains how and to whom the results are to be communicated. Main assumptions and limitations of the study, allocation methods, and the choice of environmental impact indicators are covered in the goal and scope definition [2].

Furthermore, the goal and scope definition includes a definition of the functional unit (FU) which quantifies the service delivered by the product system, providing a reference to which the inputs and outputs can be related. The FU is an important basis that enables alternative goods, or services, to be compared and analyzed[7].

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[7] For instance, in the case of a low energy light bulb compared to a normal light bulb, it would be unfair to compare the two on a unit product level, when one has twice as long lifetime as the other. A FU reflecting the function of the product, for instance, “100 h of 60 W lightening”, would make more sense.

An industrial production system is a complex, intertwined system of processes which are connected to the global economy through monetary and physical flows. It is therefore important that the system boundaries are defined. An important distinction is drawn between a cradle-to-grave and a cradle-to-gate LCA, where the latter leaves out the user phase and end-of-life phase for the product. Two LCA reports with different system boundaries do not have comparable results, as one would have ignored more environmental loads than the other. The boundary conditions are often illustrated with a simplified flowchart. The flowchart mainly includes inputs and outputs of the main manufacturing process, transport and energy use, maintenance of products and disposal of waste [39].

When two or more products share the same process(es), and the environmental load is to be expressed in relation to only one function, there is an allocation problem [38]. The environmental load must be distributed correctly over the processes. Allocation problems occur for multi-output products, i.e. chemicals that produce byproducts, for waste-treatment processes with several different inputs and for open-loop recycling systems[8]. Sometimes, but not always, the allocation problem can be avoided by increasing the level of detail in the system. This is in order to understand the environmental load of each process more correctly. If this can't be done, there are generally two methods for solving an allocation problem: Allocation through partitioning and system expansion.

Partitioning of environmental loads between the products can be based on physical relationships. Alternatively, an economic allocation can be applied based on the relative prices of the two products. For instance, a chemical byproduct, which can be sold back into the marked, is allocated with a part of the environmental load that reflects its price relative to the main product.

System expansion means that the industrial system which produces the byproduct is credited with the environmental load from the production of that product elsewhere. For instance, a process that produces heat as a byproduct, and makes use of that heat for another process which would otherwise require heat from district heating, less heat is needed from district heating. The ISO standard ranks the system borders expansion higher than partitioning allocation, and of the partitioning allocation methods [38]. This is because partitioning, regardless of which type, often is more arbitrary than the system expansion modeling.

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[88] In open loop recycling systems, the product is recycled into another product, like plastic bottles becoming office furniture. Closed loop recycling is recycling where the product is recycled to fulfill the same function as before.

Inventory analysis

The Life Cycle Inventory (LCI) analysis involves creating an inventory of flows to and from nature for a product system. Inventory flows include inputs of water, energy and raw materials, and releases to air, land, and water. The input and output data needed for the construction of the model are collected for all activities within the system boundary. It is important to understand that the LCA method accounts for not only the direct environmental impact of an industrial system, but also for all indirect impacts from the supply chain. The life cycle inventory analysis is therefore time-consuming and difficult. Typically, the LCA practitioner will not have access to data concerning indirect inputs and outputs upstream the supply chain. Generic data from databases like the Ecoinvent v.2 database [40] is then used to account for the missing information. Care must then be taken to ensure that the secondary data source properly reflects regional conditions.

The mathematical framework for LCA calculations is based on Wassily Leontief's Input Output model which analyzes inter-industry flows [41]. Only the most essential basics will be presented here. The model is based on linear algebra, where the system studied is described as a matrix, called the *A* matrix, where the a_{ij} is the requirement coefficient which suggests the input requirement of process *i* for a unit process *j*. The *A* matrix is divided in four different sections. The foreground system, A_{ff}, is where the main system components of the study are gathered. The borders of the foreground system are decided by the practitioner, often as a function of data availability. A_{bb} is the background system which essentially contains database-data. A_{bf} are the amounts going from the background to the foreground. A_{fb} are the amounts from the foreground going to the background (typically used to model recycling) [39]. Eq. 10 is the general A-matrix:

$$A = \begin{bmatrix} A_{ff} & A_{fb} \\ A_{bf} & A_{bb} \end{bmatrix}.$$

Eq. 10

For a functional unit, y (called the final demand in the economic theory), the total outputs, x, from the different processes in the system can be calculated. The total production equals the internal production plus the final demand,

$$x = Ax + y$$

Eq. 11

which can be rewritten as

$$x = (I - A)^{-1}y = Ly,$$

Eq. 12

where the term $(I\text{-}A)^{-1}$ is the Leontief Inverse matrix, of the L-matrix. The L-matrix gathers the output per process *i* per unit external demand of product *j* [41].

Environmental impact assessment

The goal of an LCA is to be able to calculate total emissions and environmental loads for a given external demand. The stressor matrix S contains the vector of environmental stressors (emitted substances, land use etc.) associated with the output for each process. Stressor data must be collected analogously to the requirements coefficients in the A matrix. The number of stressors can range from a handful and up to thousands, depending on the scope of the study. The S matrix is applied to find the stressors associated with a given final demand as follows:

$$e = Sx$$

Eq. 13

The environmental stressors, connected to the flows in the inventory, are classified into impact categories. This is according to the type of environmental impact they contribute to, generally within the three broad categories resource *use, human health* and *ecological consequences*. For example, CO_2 and methane (CH_4) contribute to *climate change* which is a hazard to human health and nature.

Impact categories that express environmental effects in units that are measurable with scientific instruments are called midpoint categories. Examples of midpoint categories are "climate change" (CC) and "Human Toxicity Potential" (HTP). CC impact is measured in *CO_2* equivalents and HTP is measured in *1,4-dichlorobenzene*[9] equivalents. Characterization factors are used to turn the effects from the stressors into midpoint impact categories (see chapter 3.1.1). Many substances contribute to more than one category, for example chlorinated hydrocarbons which will impact both HTP and CC impact categories. The characterization matrix, C, distributes the stressors to the different impact categories. Hence, Eq. 14 calculates the total impact potential of the system as a whole

$$d = Ce = CSx = CSLy = CS(I - A)^{-1}y$$

Eq. 14

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[9] An organic molecule with known toxic effects.

A set of quantified environmental indicators give a picture of the environmental performance of the product which then can be compared with the performance of alternative products. The research is however dependent on finding the causalities, driving forces and relations behind these numbers. In order to reveal the extent to which each process in the system is contributing to the various indicators (contribution analysis), the x matrix can be diagonalized. If the x-matrix is diagonalized, Eq. 14 show ($e = S\hat{x}$) how each stressor contributes to the various impact categories. Eq. 10 to Eq. 14 constitutes the basis for any life cycle assessment calculation.

In many LCAs, characterization concludes the LCI analysis; this is also the last compulsory stage according to ISO 14044:2006 [36]. Normalization, grouping, and weighting may be conducted depending on the goal and scope of the LCA study. Results are then expressed in endpoint indicators, which can be "sea level rise" or "years of life lost". Midpoint categories are considered to be links in the cause-effect chain (environmental mechanism) of an impact category, prior to the endpoints, at which characterization factors or indicators can be derived to reflect the relative importance of emissions or extractions. End point indicators are easier to communicate, however, the more the results are aggregated and weighted, the less transparent and more subjective the LCA becomes.

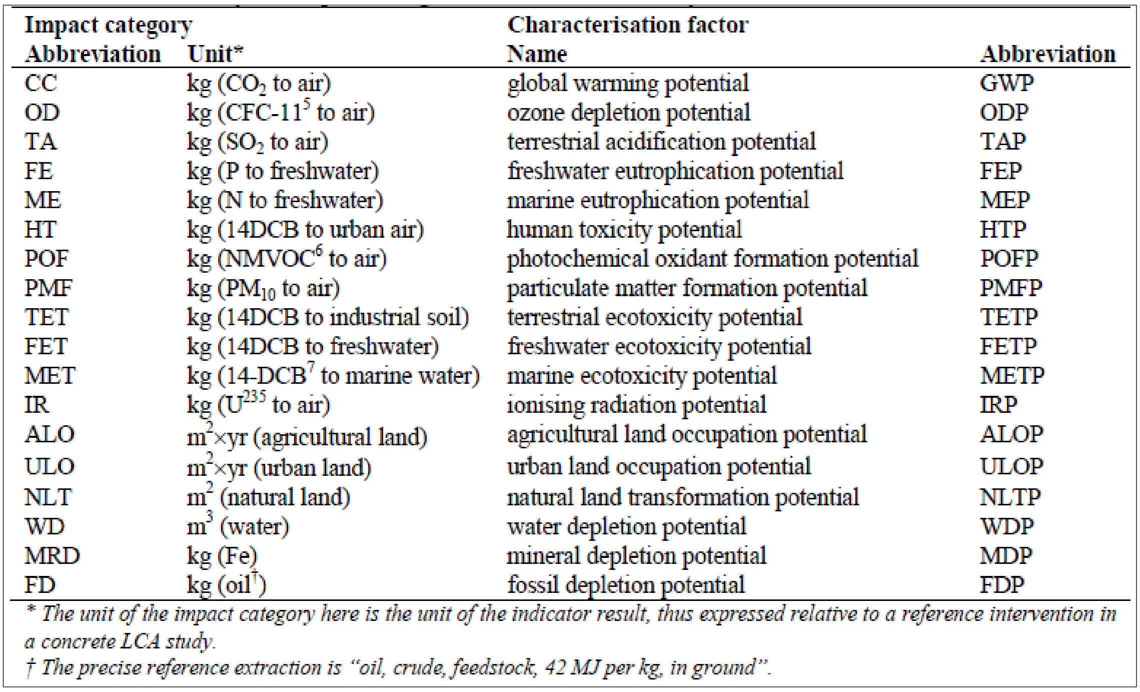
Interpretation

The results from the inventory analysis and impact assessment are summarized during the interpretation phase. The results from the life cycle inventory assessment are interpreted and analyzed. The outcome of the interpretation phase is often a set of conclusions and recommendations for the study. Limitations and data sensitivity of the study should also be discussed.

3.1.1 Environmental indicators

This work will be based on the ReCiPe 2008 midpoint method, hierarchist version [42]. The version determines the perspective of the method in terms of assumptions and timeframes. There are three versions, the optimistic and short term-interest based individualist version (I), the very precautionary egalitarian (E) version and the hierarchist (H) which is somewhere in between and the most widely applied. A comprehensive report on the method [42] can be downloaded from the ReCiPe website[10]. Table 1 shows the 18 ReCiPe midpoint categories and their characterization factors.

Table 1: ReCiPe 2008 impact categories and characterization factors [42].



Impact category		Characterisation factor	
Abbreviation	**Unit***	**Name**	**Abbreviation**
CC	kg (CO_2 to air)	global warming potential	GWP
OD	kg (CFC-11[5] to air)	ozone depletion potential	ODP
TA	kg (SO_2 to air)	terrestrial acidification potential	TAP
FE	kg (P to freshwater)	freshwater eutrophication potential	FEP
ME	kg (N to freshwater)	marine eutrophication potential	MEP
HT	kg (14DCB to urban air)	human toxicity potential	HTP
POF	kg (NMVOC[6] to air)	photochemical oxidant formation potential	POFP
PMF	kg (PM_{10} to air)	particulate matter formation potential	PMFP
TET	kg (14DCB to industrial soil)	terrestrial ecotoxicity potential	TETP
FET	kg (14DCB to freshwater)	freshwater ecotoxicity potential	FETP
MET	kg (14-DCB[7] to marine water)	marine ecotoxicity potential	METP
IR	kg (U^{235} to air)	ionising radiation potential	IRP
ALO	$m^2 \times yr$ (agricultural land)	agricultural land occupation potential	ALOP
ULO	$m^2 \times yr$ (urban land)	urban land occupation potential	ULOP
NLT	m^2 (natural land)	natural land transformation potential	NLTP
WD	m^3 (water)	water depletion potential	WDP
MRD	kg (Fe)	mineral depletion potential	MDP
FD	kg (oil[†])	fossil depletion potential	FDP

** The unit of the impact category here is the unit of the indicator result, thus expressed relative to a reference intervention in a concrete LCA study.*

[†] The precise reference extraction is "oil, crude, feedstock, 42 MJ per kg, in ground".

The methodology is here explained through the best known of the categories, the climate change. Radiative forcing, from gas molecules in the atmosphere that have the ability to absorb waves in the infrared spectrum, contributes to the green house effect. The green house gas effect is an essential criterion for the life on earth. However, when emitted to the atmosphere in large amounts, through anthropological activities, these gases contribute to global warming through an increase of the green house effect. Global warming is representing a serious threat to human development and ecological systems [3]. In the ReCiPe 2008 method [42], radiative forcing of GHG emissions are expressed through the midpoint category called climate change.

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[10] http://www.lcia-recipe.net

The characterization factor for climate change (CC) is global warming potential (GWP) [42]. The GWP of any substance expresses the integrated forcing of a pulse (of a given small mass) of that substance relative to the integrated forcing of a pulse (of the same mass) of CO_2 over some time horizon [42]:

$$GWP_{x,T} = \frac{\int_0^T a_x \times [x(t)]\, dt}{\int_0^T a_{CO2} \times [x_{co2}(t)] dt}$$

Eq. 15

T is the time horizon[11], a_x is the radiative efficiency due to a unit increase of GHG, $x(t)$ is the time dependent abundance of GHG (atmospheric decay function). The next equation shows how the classification and characterization of GHG emissions are done:

$$Climate\ Change(kgCO_2eqv) = Quantity\ of\ substance(kg) x\ GWP\ characterization\ factor(\frac{kgCO_2}{kg})$$

Eq. 16

Only those impact categories that are practically relevant for the goal and scope of the study should be included in each LCA. The LCA presented in this report apply the ReCiPe 2008 Climate Change indicator, because this is the most relevant indicator for the zero emission building theory. The Cumulated Energy Demand (CED) is also included. The CED is a not a part of the ReCiPe methodology, it is a method published by Ecoinvent v.2.0 [43]. The CED is an indicator which aggregates the total cumulative energy demand for the system under study, including losses due to transformation and transport [44]. It is therefore relevant for energy-saving products like insulation.

Hence, in this work, the term “environmental impact” refers to the cumulated energy demand and the climate change impact.

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[11] The ReCiPe 2008 (H) method has a time horizon of 100 years.

3.2 Life Cycle Assessment of the NIM

Having presented the LCA method, an approach to how it can be used to assess the NIM must be found. As presented in the introduction, research on the optimization of the NIMs characteristics and fabrication method is still going on. Neither the production method nor the final characteristics and properties of the NIM are constant. This makes it difficult to assess the NIM with LCA. The most critical information gaps are the exact effective thermal conductivity of the NIM, and the exact recipe for the inputs and outputs of its production. A comparative LCA of the NIM and other insulation materials cannot be conducted without this essential information. Nor can a cradle-to-grave analysis considering energy and GHG pay-back times for the material when applied to the building be done. Such analysis require a benchmarking of the materials overall performance, physical properties and industrial production. Such analyses are done for products that are already in commercial production. This work represents another type of challenge; its objective is to assess the production of the NIM at an early stage so as to provide understanding of how its environmental impact can be minimized.

The challenge here is therefore, as presented in the introduction, to construct a model for a screening of the cradle-to-gate environmental impact of a NIM based on the current fabrication method presented in chapter 2.1.1. The modeling of this production system is detailed step by step in the goal and scope section and the inventory analysis section below.

All LCAs are simplifications of reality. The model suggested here is constructed in order to calculate the environmental impact of a material for which only a limited dataset is available. It fills data gaps according to a suggested procedure, inspired by literature on LCA for chemicals. The model can be gradually improved as more knowledge of the NIM becomes available. A large amount of work is put down in modeling the inventory. When filling data gaps, a choice was made to keep the data constructions modest. This is because it was decided that a minimum scenario is more useful to work with than a worst-case scenario in this case. Part one in the report, assessing the thermal conductivity of the NIM, also worked out from a minimum value staring point.

The results of the impact assessment of this LCA are not constants, simply because the data inputs are not constants. Emphasis is therefore put on making the LCA model as flexible as possible. This work provides scenarios, ranging from optimistic to pessimistic, for the NIMs performance. The results are applied in an interpretive framework based on scenarios as to provide useful information. Scenarios are used in the impact assessment section as to extract trustworthy result trends and causalities in the results.

Scenarios are also used in the interpretation part of the LCA. Scenarios for the NIM performance are constructed on the basis of the LCA findings and the range of possible effective thermal conductivities. This is in order to visualize the results of the environmental assessment set in association with the thermal conductivity.

Calculation Methods and Impact Categories

The calculation methods applied for the resulting scores in this study is the ReCiPe 2008 method for the calculation of the embodied GHG emissions [42], and the Cumulative Energy Demand method for the embodied energy [44], see section 3.1.1. The results will be presented through two impact categories: The cumulative energy demand (CED) expressed in mega joules (MJ), and the climate change impact (CC) expressed in CO_2 – equivalents.

The calculations are done according to the method presented in chapter in 3.1, by use of **Microsoft Excel (2007)** and in **SimaPro 7.3.1 classroom version [45].**

Allocation problems are solved by system expansion. For example, hydrochloric acid (HCl) is produced as a byproduct of tetraethyl orthosilicate (TEOS), the main precursor for the silica nanospheres. HCL is therefore modeled as an avoided product. The avoided product is HCL produced by reaction of hydrogen with chloride. System expansion was found to a better choice than partitioning in this case. System expansion reflects the industry because HCL is an important industrial good that can be sold back into the marked. Economic allocation was found to be less applicable because the prices do not depend linearly on mass [46].

3.2.1 Goal and Scope

A screening cradle-to-gate life cycle assessment of the NIM, as it was presented in the previous chapters, will be performed here. It will sketch the main activities in industrial production of the NIM, and estimate amounts of raw materials, energy, infrastructure and transport which these activities require in order to analyze the materials environmental impact.

The goal of this analysis is to understand how the different activities in the production of the NIM contribute to global warming and demand of energy, in order to find how the environmental impacts can be minimized.

The report will be used by the scientists at ZEB to optimize the production process and choice of raw materials with regard to the environment. The main outcome of the LCA are therefore recommendations for a greener production.

Functional Unit

One of the strengths of the LCA method is that it relates the environmental impact to the *function* of a product system (see Functional Unit section in chapter 3.1). A practical functional unit for insulation systems should therefore be based on the thermal resistance under external and internal conditions that are considered typical for the performance of the system when incorporated in a building. The Product Category Rules (PCR) for Insulation materials [47], published by the Association for Environmental Product Declarations (EPD) Norway [48], suggests a functional unit for insulation materials as follows:

1 m^2 of insulation material with a thickness that give a design thermal resistance $R=1m^2K/W$ and with an expected average service life of 60 years.

This functional unit is operational for comparative cradle-to-grave studies of insulation technologies installed in buildings. For cradle-to-gate analysis, the product category rules states that "*a declared unit should be defined based on an expected (declared) value of thermal property of the insulation material assessed from measured data at reference conditions of temperature and humidity. Information provided using a declared unit should not be used for comparison*" [47].

If this study decided to follow those guidelines, a simplified model could have been constructed based on the scarce information that exist. Assuming a thermal conductivity and setting the thermal resistance to R = 1 W/m, a corresponding thickness could be calculated using Eq. 2. If, for instance, a thermal conductivity of 0.02 W/mK were assumed, it would mean an insulation mat of area $1m^2$ and of 2 cm thickness, in terms of the declared unit. The amounts of hollow silica nanospheres needed for that square meter remains unknown. So does the amounts of other chemicals and energy required. A very optimistic assumption of no added raw materials or energy for the integration step of the spheres could be tried. Then, assuming a density of 200 kg/m^3 [20], the declared unit would be equal to 4 kg of hollow silica nanospheres.

At this point, the argumentation becomes quite hypothetical, so in this case, it is therefore more transparent to use ***1 kg of hollow silica nanospheres at factory gate*** as the functional or declared unit (this work will stick to the term functional unit (FU). This unit is the only rational choice, because applying a functional unit based on the model above, would lead to a blinding mesh of approximations. A declared unit of 1 kg material allows for a transparent analysis and reflects the goal of the study.

Table 2: Functional unit for the analysis.

Functional unit:	1 kg of hollow silica nanospheres at factory gate

With this functional unit, the simplified model presented in the previous section can be applied along with scenarios for the thermal conductivity in the discussion chapter. This allows for considerations of the required thermal properties as function of environmental load, but gives at the same time a transparent analysis, which reflects the goal of the study.

System Boundaries

Figure 10 illustrates the system boundaries of the study. This figure also gives a good overview of the model that is suggested here for the NIM production. The production system of the new NIM can be summed up in two stages: The manufacturing of the hollow silica nanospheres (red box) and the assembly of the spheres into an insulation material (orange box). With reference to the Inventory Analysis section in chapter 3.1, the red and the orange boxes constitute the foreground system. This is basically a chemical production plant, where the NIM is produced. It is assumed that this plant is placed in a central part of Western Europe. The properties of the plant are assumed to be representative for the average chemical plants in that geographical area[12].

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[12] The choice of location is especially important when energy and transport is assessed. LCA results are especially sensitive to the choice of electricity mix chosen. Because this study is assuming a European production site, the UCTE-mix (Union for the Coordination of the Transmission of Electricity) is applied.

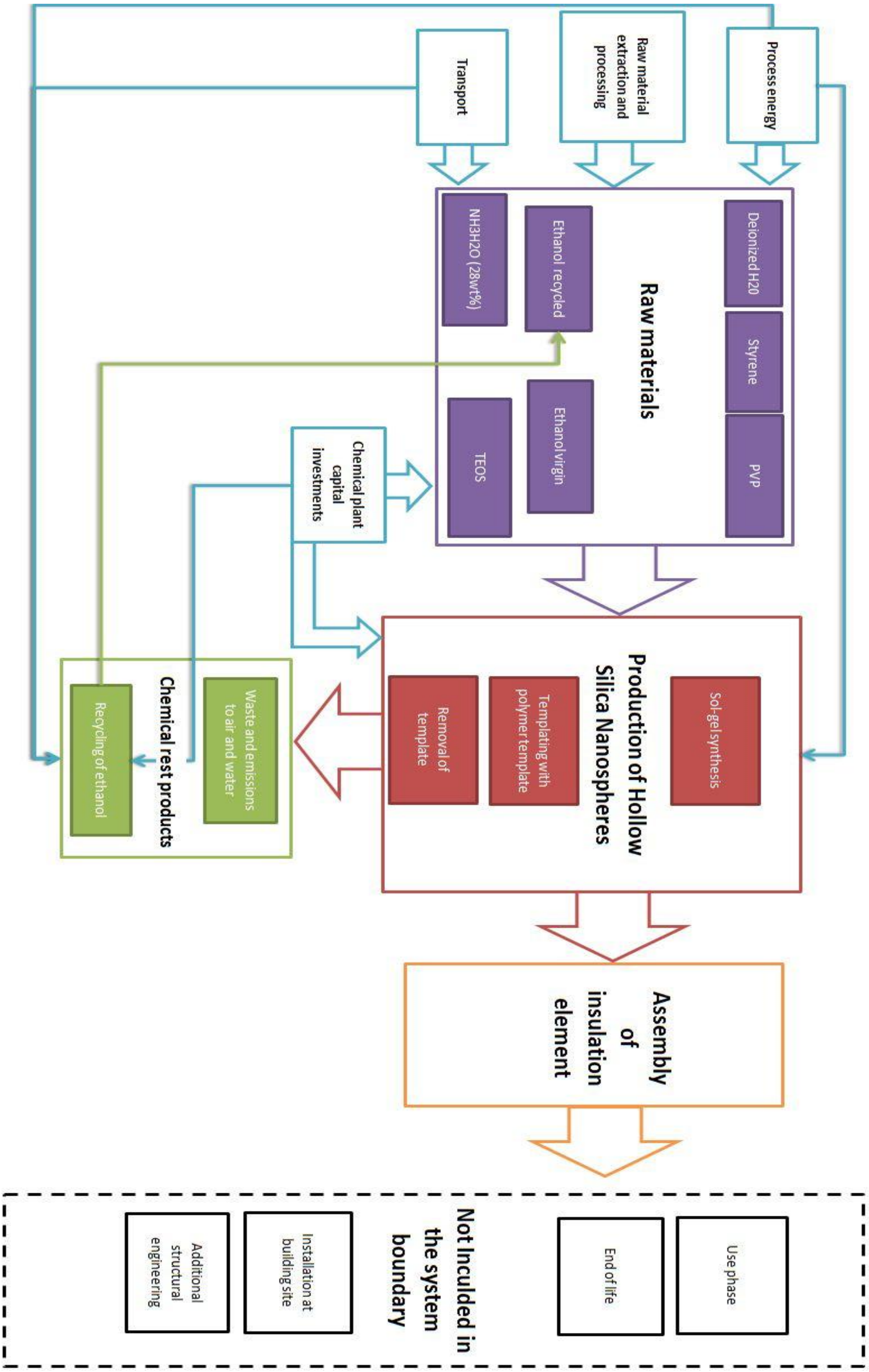

Figure 10: Flow diagram showing the system boarder of the model suggested here for the NIM production.

In Figure 10, a violet box represents the raw materials. A violet arrow is representing the flow from the background to the foreground system. Direct material inputs accounting for less than 1% of the total weight of raw materials are cut off. The raw material required for the hollow silica nanospheres are basically industrial chemicals. These chemicals have embodied energy, capital investments, transport and raw materials from upstream their production, all the way from mining or extraction to the end producer[13]. They require additional transport from their respective producers to the NIM production site.

All inflows and outflows are marked with arrows. All elements require inputs from the technosphere[14] in the form of raw materials, capital investments or infrastructure, energy and transport. Inputs from technosphere are depicted as light blue boxes. The production system turns the inputs into products, but it also generates wastes and emissions, which is depicted in green. Only direct waste and emissions from the foreground system is depicted, indirect outflows are not shown in the figure.

By reference to the synthesis route described in section 2.1.1 and Figure 2, the manufacturing of the hollow silica nanospheres (red box), can be partitioned into three main activities: The formation of a polymer template, the formation of the silica spheres on the template and finally, the removal of the template. These activities require raw materials, a certain amount of processing energy and capital investments. There is assumed to be no solid waste flow from the foreground system, only emissions to air and emissions to water, stemming from rest products of the chemical processes. It is assumed that ethanol is recycled internally with a recycling rate of 80% [20]. It can be seen that the recycling process also requires energy and capital investments (green box).

The orange box of the assembly stage is placed inside the system boundaries despite the lack of information about it. It is assumed that this stage will not cost any additional raw materials or energy. This optimistic model is eventually the same as placing the assembly step outside the system borders. The rest of the system is modeled at a quite high level of detail, which will be elaborated in the inventory analysis in the following chapter. The black dotted box to the right shows the point where the system boundaries end. This is a cradle-to-gate LCA so the use phase and end-of-life phase are placed outside the system boundaries. Any additional engineering of the material required for its structural functioning in the building is also excluded, due to lack of information.

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[13] All the embodied, indirect factors from all processes are included in the calculations through the plug-in of the Ecoinvent database, as explained in section 3.1.

[14] The word technosphere belongs to the LCA vocabulary. It refers to the part of the environment that is created or modified by humans. “Inputs from technosphere” includes industrially modified resources and products as opposed to natural resources. See glossary.

3.2.2 Inventory Analysis

Life cycle assessment of materials is a challenging task as the data availability of chemicals and chemical production systems is very low [49-51]. Very few LCI data for chemicals are published, despite the immense importance of chemicals in modern society, and the ever increasing exposure of chemicals to human life and nature.

Several research groups within the LCA area have addressed this problem. Some suggested solutions are presented in the Ecoinvent report on Life Cycle Inventories of Chemicals [49]. Hischier et al. from the Swiss Federal Laboratories for Materials Testing and Research (EMPA) suggested a choice of three methods in a publication from 2005 [51], based on the data availability of the chemical system to be studied. In the case of very weak data availability, stoichiometric equations from technical literature in combination with the Ecoinvent report solutions and other simplifications are applied to model missing data. Wernet, also from the Swiss research environment, is addressing the LCI data gaps on chemicals in several papers from 2009 to 2012 [50, 52].

This assessment encounters low data availability, not only because it is not a real industrial system, but also because of a lack of published data on chemical and nanotechnology systems. The inventory collected and modeled for this inventory is based on the laboratory data given from ZEB. Raw material data are collected from industry wherever possible. Data gaps are filled through modeling assumptions influenced by the most recent paper from Wernet et al. [50] and the paper Hischier et al. 2005 [51]. The method of how to model a system under development suggested here, can be of interest for future assessments of high-technology products.

Inventory flow diagram

Figure 11 shows an overview of the inventory. The reader will recognize the synthesis procedure described in chapter 2.1.1, page 7, when looking at Figure 11. In brief, the model consists of a three step production system of template-assisted sol-gel synthesis of silica nanospheres, and the subsequent removal of the template in a furnace. The fabrication of the template requires water, styrene and PVP. The Sol-gel process requires ethanol, TEOS and ammonia hydroxide. The ethanol is not consumed in the process, so 80% can be reused. In LCA, the term processes is used for the in- and output activities of raw materials, energy, transport and infrastructure. The removal of the template requires a furnace. All steps require energy and capital investments.

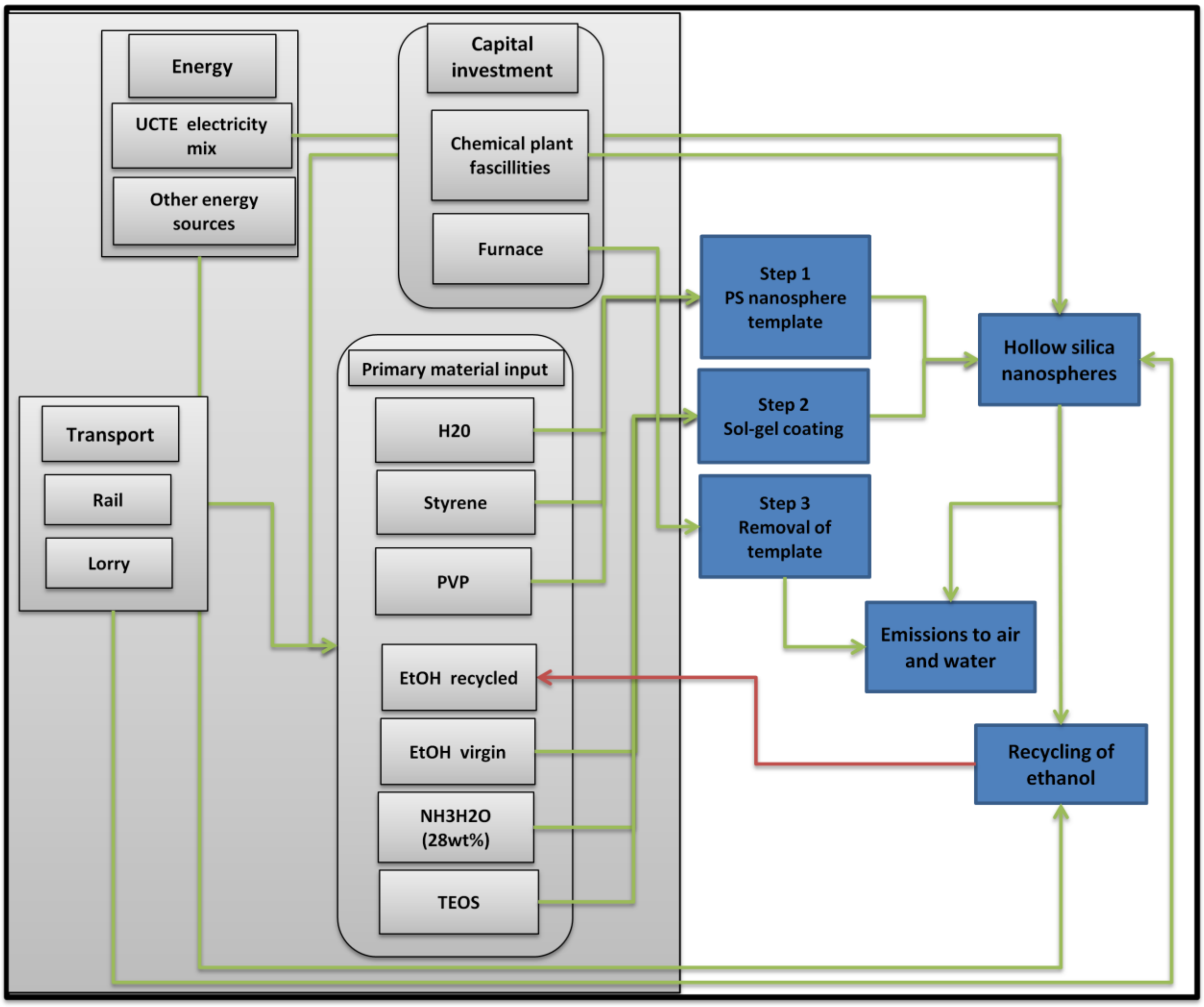

Figure 11: An overview of how the inventory analysis of the NIM is constructed. For inventory tables, see appendix B.

In Figure 11, the foreground processes are marked in blue while background processes are colored grey. It can be seen that arrows from the capital investments, transport and energy goes both directly to the foreground but also to the raw materials as indirect input. Indirect raw material requirements, e.g. materials needed for the production of TEOS, styrene, Polyvinylpyrrolidone, Ammonia and ethanol, are not depicted in the figure. Inventory tables with more details can be found in appendix B.

Raw materials

Direct raw material consumption is scaled linearly from the laboratory data. This is an acceptable assumption because of the relatively straight forward and simple nature of the sol-gel process that produces the hollow nanospheres. Industry data for the embodied energy and emissions of the raw materials where collected whenever possible, but for most of the inventory, Ecoinvent unit processes [40] were applied to replace missing industry data. Processes that could not be found in the Ecoinvent v.2 database [40] were modeled according to the procedure published in Hischier et al. 2005 [51]. This procedure consists of using stoichiometric equations from technical literature along with a set of assumptions and estimations. An extract from the article is reprinted in appendix C.

Process modeling based on technical literature was done, for instance, in the case of tetraethyl orthosilicate (TEOS), $SiC_8H_{20}O_4$. TEOS is synthesized by alcoholysis of silicon tetrachloride [53]:

$$SiCl_4 + 4ROH \rightarrow Si(OR)_4 + 4\,HCl$$

Eq. 17

Industry data where obtained for silicon tetrachloride [15]. An ethanol process from Ecoinvent v.2 database [40] was applied as the alcohol (Ethanol, 95% in H_2O, from sugar beet molasses, at distillery/ CH U). This process has a CC impact 0.54 kg CO_2-equivalents per kg. Eq. 17 shows that hydrochloric acid is the main product of this chemical reaction. As announced in section 3.2.1, system expansion was therefore applied to credit the TEOS with the avoided HCL from a hydrogen chlorination industry process.

Stoichiometric equation balancing was also used for the direct CO2 emissions arising from the combustion of styrene, C_8H_5:

$$C_8H_5 + 10O_2 \rightarrow 8CO_2 + 4H_2O$$

Eq. 18

Eq. 18 shows that 8 units of carbon dioxide are produced per unit of styrene combusted.

The risk of using basic stoichiometric and thermodynamic calculations is that these might underestimate the energy requirement as the real systems are less efficient than theory. This was to some extent corrected with assumed efficiencies of 0.95 over the stoichiometric reaction as described in Hischier 2005 [51].

Energy

Direct raw material consumption could be scaled up linearly from the ZEB laboratory data, but to model the direct energy consumption is not that straight forward. Data from measurements of direct energy consumption in the lab were available from Dr. Tao Gao, measured in a ZEB laboratory [20], and from the Dr Mathieu Grandcolas measured at SINTEF Material and Chemistry laboratory [54]. However, when upscaled linearly, those data would lead to serious overestimations of the energy consumption in the full-scale production system.

On the other hand, it was not possible to find any industry data that could replace the laboratory data, neither from companies nor process design literature. A process design modeling software could have provided reliable estimates, but to use such tools was out of the scope of this report. The software approach could be applied for this and other similar cases in the future.

An easier solution is suggested by Hischier 2005 [51]. It applies default values from an environmental report from Werk Gendorf in Germany for every process that lacks energy consumption data. However, at this point, the study presented here disagrees with Hischier's approach, because of the large variability of energy consumption for chemical processes. In case of the NIM, the foreground system is based on a synthesis with modest direct energy requirements. It is therefore expected that the embodied energy from raw materials will be much more important than the direct energy consumption at the production plant. Therefore, a simple three step-method is suggested here to establish values for the direct energy consumption of a process:

1. The process must be characterized as energy intensive or not energy intensive based on basic thermodynamic considerations: All processes that are strongly exothermic or take place at room temperature are characterized as not energy intensive, all other processes are characterized as energy intensive.
2. For processes characterized as energy intensive, basic thermodynamic data according to the nature of the process (heat of vaporization, enthalpy of formation, enthalpy of combustion etc…) are applied.
3. For processes that are characterized as not energy intensive, energy consumption should not be ignored because there is always some energy needed for stirring, centrifugation or other industrial equipment. The energy data should then be substituted with default values from the Werk Gendorf Environmental report (one of the largest chemical production sites in Germany) in accordance with Hischier 2005 [51].

While the linear upscaling of the laboratory energy data will overestimate the direct energy consumption of the NIM, it is probable that the method suggested above will underestimate it. This is because the real efficiencies are lower than efficiencies calculated from theoretical thermodynamic equations and data. The default values from the report are also quite modest.

Table 3 compares the estimated *direct energy consumption*[15] in the production of 1 kg of hollow silica nanospheres resulting from the respective approaches.

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[15] The direct energy consumption must not be confused with the cumulated energy demand which cumulates direct and indirect energy consumption.

Table 3: Comparison of the direct energy consumption in the production of the functional unit by using two different modeling approaches.

Direct energy consumption in the production of 1 kg hollow silica nanospheres (FU)		
Linear upscaling of laboratory energy monitoring, ZEB laboratory	1629	kWh
Linear upscaling of laboratory energy monitoring, SINTEF laboratory	2604	kWh
Estimations based on the rules of thumb suggested by the candidate[16]	0.9	kWh

There is difference of three orders of magnitude. The linear upscaling of the laboratory energy data can therefore be seen as a maximum value for the direct energy consumption for the production of the NIM, while the method suggested above can be seen as the minimum value. The minimum value is applied in this life cycle assessment.

Transport

All raw materials have to be transported from the supplier to the production site. Because all the raw materials can be found in the portfolio of European suppliers, it is assumed that these are preferred over Asian brands and transport distances are therefore accordingly short. Standard distances according to Frischknecht et al. [55] are applied.

Other data

Capital investments, waste and stressors are modeled according to the method suggested by Hischier et al. 2005, which essentially implement generic data. Inventory tables can be found in appendix B. According to the method, it is assumed that there is no solid waste directly from the production of hollow silica nanospheres. All chemicals that are not bound up in the product or reused (ethanol) are liquid wastes going to nature. This is mainly ethanol and ammonium hydroxide in this case. It is assumed that 2% of the liquid waste stream is evaporated as emissions to air.

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[16] This is the direct energy consumption without counting the energy requirement for the recycling of ethanol, in order for the number to be comparable to the laboratory data in which no recycling process takes place. The number is considerably higher when recycling of ethanol is included. This will be discussed in the Impact Assessment.

3.2.3 Impact Assessment

Total LCA results

The total climate change and cumulated energy demand scores for the functional unit, 1 kg hollow silica nanospheres at factory gate, are given in Table 4. The results are rounded to the nearest ten kg of CO_2 equivalents and MJ. The numbers and relationships in the following discussion will be featured at the level of accuracy that is appropriate.

Table 4: Total LCA results.

Total Climate Change Impact (CC)	100	kg CO2 equiv.
Cumulative Energy Demand (CED)	2350	MJ

1 kg of hollow silica nanospheres produced according to the current recipe, has a total embodied energy of 2350 MJ when assumption and boundary conditions stated in the previous chapters is applied. Its impact on climate change is 100 kg of CO_2 equivalents. These numbers are high, for instance, the CC impact is one order of magnitude larger than the CC per kg crude oil production [56], and two orders of magnitude higher than the production of one kg of rockwool material [57]. It is therefore necessary to make a halt already at this point. The main underlying reasons for this result must be checked before going any further.

The main reason for the high values is the huge demand on ethanol the projected production process requires for the sol-gel synthesis. Ethanol is contributing with more than 90% of the energy and GHG emissions of hollow silica nanospheres, even when reuse is considered. Reuse does reduce the emissions, which would otherwise be even larger, but it is the amounts of ethanol consumed that matters in this case: 162 kg of ethanol required per kg of hollow silica nanospheres produced. To spend 162 grams of ethanol in a laboratory experiment may not seem much, but scaled up, the ethanol consumption comes out of proportions.

Ethanol production is a very large industry worldwide, producing some billions of liters each year, although most of that goes to biofuel purposes and not to chemical industry. Ethanol can be produced synthetically as a petrochemical, by the hydration of ethylene, or via biological processes, by fermenting sugars. The latter is the most common [58]. A large variety of crops can be used, like grass, grains, potatoes, sugarcanes or sugar beets. Competition with food crops and the consequences for human development is a well known discussion from the biofuel business, but will not be reflected upon here. As to the GHG intensity of ethanol production, it does not vary very much over the different crop types. Climate change impacts about 0.45 to 2.15 kg CO_2 equivalents per kg ethanol were observed from the studies in the Ecoinvent v.2 database [40]. The synthetic production of ethanol is slightly more energy and emission intensive than the biological.

Following the calculations backwards, it can be seen that there are mainly two factors that drive the energy and emission intensity of bio ethanol production: The diesel required for the harvesting of the crops and the ammonia required for the ammonia nitrate for the fertilization of the crops. The yeast that participates in the fermentation of the sugars cannot withstand high concentrations of ethanol. All bio ethanol must therefore be distilled to obtain the desired grade. The energy required for distillation is also a significant contributor to the final emission intensity of ethanol production[17].

In the production of hollow silica nanospheres, ethanol is used for cleaning and as a solvent. When tetraethyl orthosilicate (TEOS) hydrolyses as to form the silica shell, it is necessary to use ethanol as the solvent in order to control this process and create well-defined spheres. As long as TEOS is used as the precursor, ethanol is therefore essential [20]. However, it is obvious that the usage of energy intensive solvents is not minimized in the process. It is quite probable that the ethanol consumption can and must be reduced in the future production process of hollow silica nanospheres. It is therefore necessary to run the analysis with reduced amounts of ethanol to get a clearer picture of the LCA results. The analysis was therefore run with a 25%, 50% and 75% reduction in ethanol consumption to investigate the sensitivity of the ethanol impact on the CED result. Figure 12 shows the CC results for this analysis, which indicates a clear reduction of GHG as the ethanol amounts are reduced. Figure 13 shows the same trend for the CED.

In conclusion, the important effect of the overconsumption of ethanol in the system is the first and foremost result in this impact assessment. In fact, the contribution of ethanol on the results is so large that any other contribution is small in comparison. The ZEB scientists confirm that the consumption of ethanol can be reduced without significant changes in the overall chemistry of the process [20, 59]. It makes sense to apply the 50% reduction scenario when drilling further into the impact assessment because probably more correct from an industrial point of view. The 50% ethanol reduction scenario **(CC impact: 60kg CO_2 equiv., CED: 1400 MJ)** will be applied as the baseline scenario in the following analysis, if not otherwise is stated.

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[17] Due to an update of the Ecoinvent database close to the submission date of this master thesis, some data where modified. Some ethanol processes were affected by these updates. Consequently, reproducing the results may lead to slight modifications in the discussion on the green house gas emissions related to ethanol production.

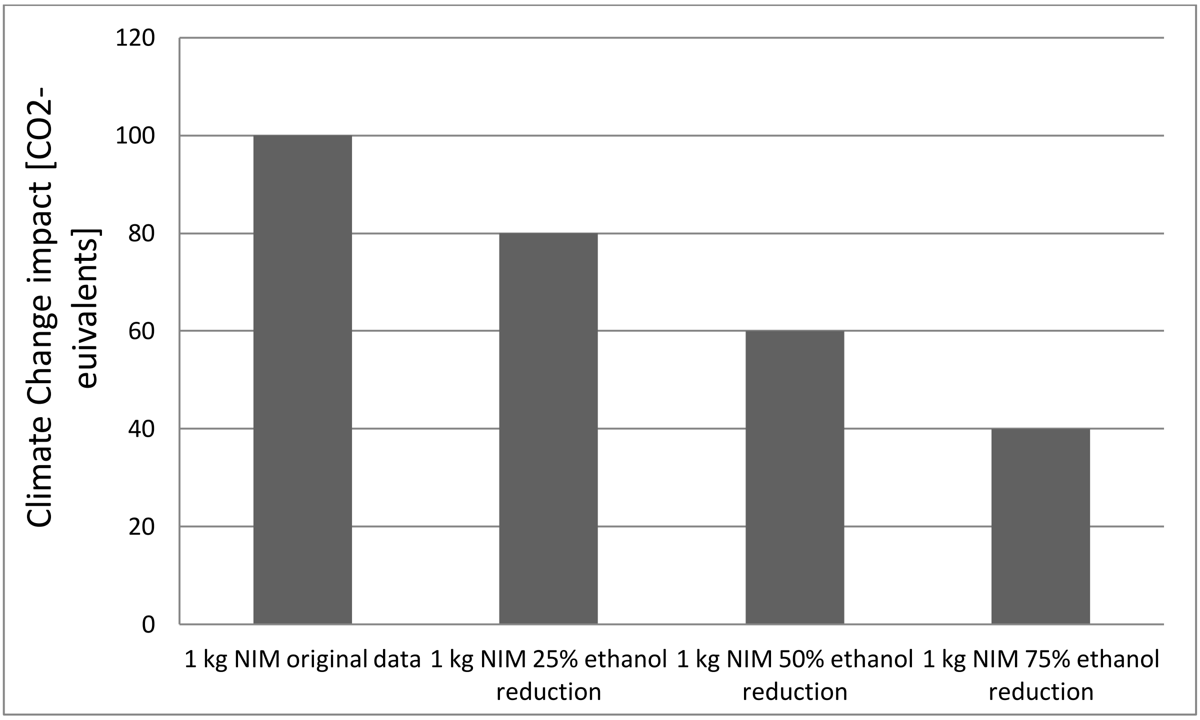


Figure 12: Climate Change Impact for four scenarios of hollow silica nanosphere production. The original scenario based on original laboratory data, and three scenarios with reduced ethanol consumption. The ethanol data is “Ethanol, at plant, from sugar beet molasses/CH U” from the Ecoinvent v.2 database [40]. The results are rounded to the nearest ten.

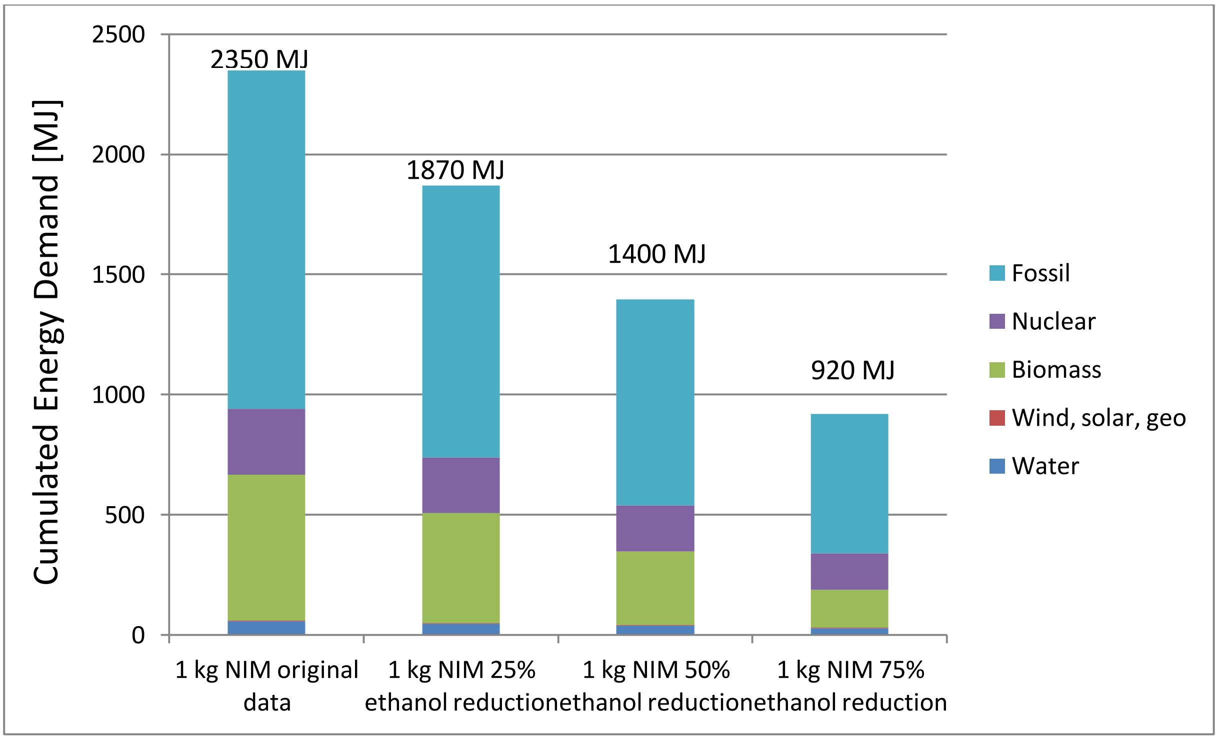
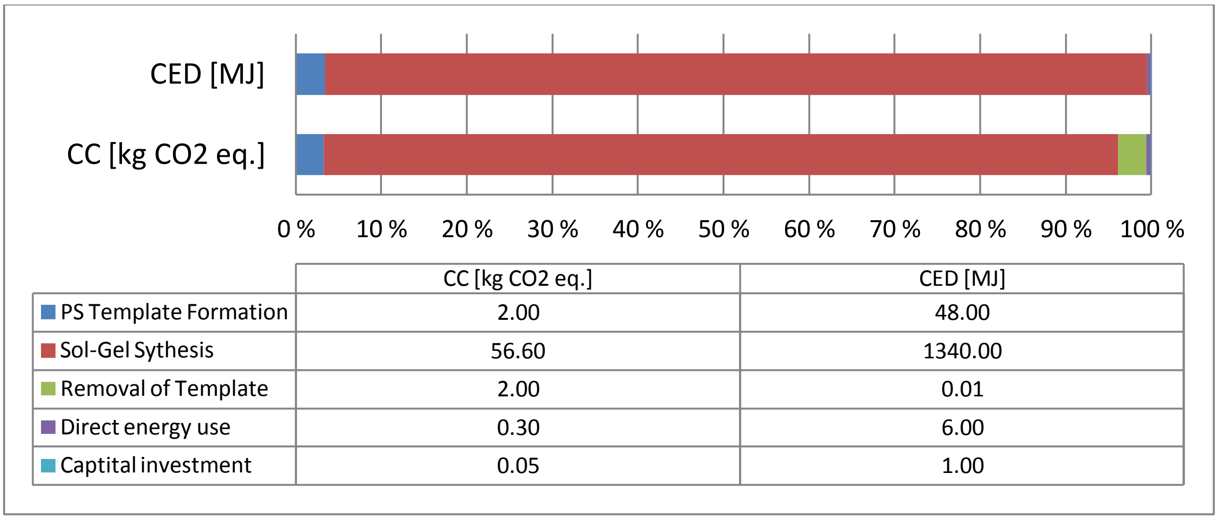


Figure 13: Cumulated Energy Demand for four scenarios of hollow silica nanosphere production. The original scenario based on original laboratory data, and three scenarios with reduced ethanol consumption. The relative contribution from each type of energy source, fossil, nuclear, biomass, water and other renewable are represented by the colors in each pillar. The ethanol data is “Ethanol, at plant, from sugar beet molasses/CH U” from the Ecoinvent v.2 database [40]. The results are rounded to the nearest ten.

The fact that the CC results follow the CED results as closely as they do in Figure 12and Figure 13 is a well-known result for LCA practitioners. It indicates that, finally, the transition from fossil to renewable energy sources very often is the bottom line for climate mitigation in any industrial system. More about reduction potentials will be discussed in the interpretation and interpretation chapter (chapter 3.2.4).

Analysis of total results

The bar chart in Figure 14 is showing the relative contribution template formation, template removal, silica synthesis, direct energy consumption and capital investments on the cumulated energy demand and the climate change impact of 1 kg hollow silica nanospheres (with 50% ethanol reduction scenario). This is the foreground system in Figure 11. The table underneath the bar chart gives the total values.



	CC [kg CO2 eq.]	CED [MJ]
🟦 PS Template Formation	2.00	48.00
🟥 Sol-Gel Sythesis	56.60	1340.00
🟩 Removal of Template	2.00	0.01
🟪 Direct energy use	0.30	6.00
🟦 Captital investment	0.05	1.00

Figure 14: Bar chart displaying the contribution analysis results for the NIM.

From Figure 14, it can be seen that the processing, which include raw material consumption and the according indirect energy, transport and infrastructure requirement, is much more important than the direct energy consumption in the production process. It should be recalled that the direct energy consumption is estimated based on very simplified assumptions (see page 39). The capital investment data are entirely generic. It is the indirect energy consumption which is dominating in this case, and, from Figure 14, especially the consumption of the silica sol-gel synthesis. This was expected (see chapter 3.2.2): the sol-gel synthesis is in itself an energy-modest process, but consumes chemicals with high embodied energy and emissions.

Adding the green and the blue section in Figure 14, less than 4 % of the CC impact stem from the polystyrene template. The reason why it has a relatively much higher impact on the CC than the CED is the CO_2- emissions from the combustion. The combustion is very exothermic and does not require a large energy input. The furnace needed for the combustion is allocated to the "removal of template" process. Styrene is a relatively energy intensive material to produce, and its combustion produces 3.38 kg CO_2 per kg combusted styrene (see Eq. 18, section 3.2.2). However, with the small amounts of styrene which is required here, its climate change impact is not very important for the environmental impact of the NIM.

A question raised by the ZEB and SINTEF scientist was whether it would be preferable to use the alternative template, PAA, described in chapter 2.1.1, under the pretext that it might be more environmentally friendly because it is washed out instead of combusted. From a life cycle point of view, this is incorrect, because the polymer rest product that is washed out eventually also will be incinerated or landfilled at its end-of life phase. Although a recycling scenario for PAA is theoretically possible, there is no reason to believe that there is a significant emission reduction potential in changing the template material, considering the numbers in Figure 14.

Disaggregated results, sol-gel synthesis process

The silica sol-gel synthesis contributes with more than 90% of the energy and climate change impact. The most important reason is that use of ethanol takes place in the sol-gel synthesis. A contribution analysis of the silica sol-gel synthesis is projected in Figure 15.

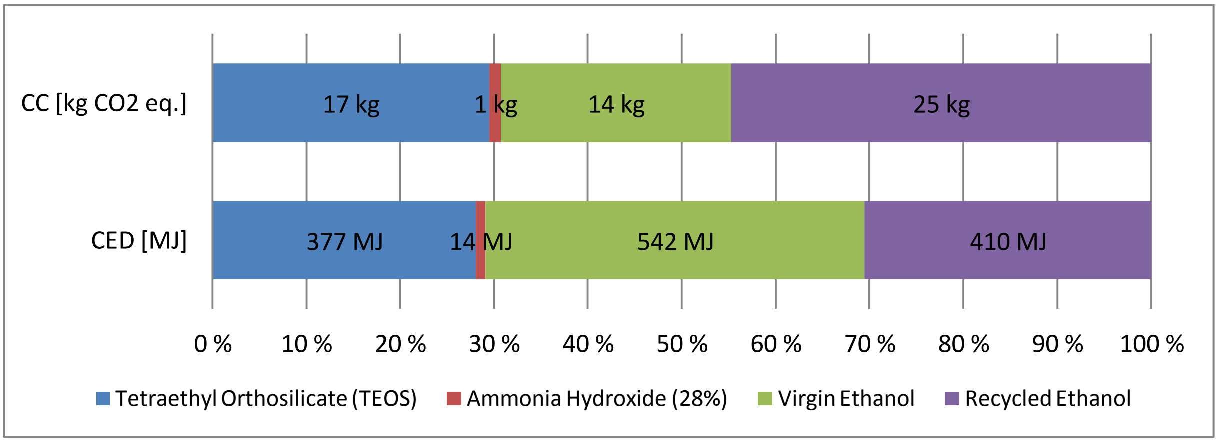


Figure 15: Bar chart displaying the disaggregated contribution from the sol-gel synthesis process step.

Figure 15 is clearly showing the dominance of the ethanol on the results. This is in spite of the 50% reduction relative to the original data. In total, virgin and recycled ethanol is counting for almost 80% of the energy consumption and GHG emissions in this scenario. Knowing that the recycling rate is set to 80%, it is obvious that the production of virgin ethanol must be very energy intensive, since it has such large impact despite the 20 to 80 ratio. It is worth noticing that the total relative contribution of ethanol is almost the same for the CC and the CED result, but while the recycled part is more important for CC, the virgin ethanol has a higher relative contribution to the CED. Calculation shows that the virgin ethanol chosen here has an embodied energy of 34 MJ per kg. When recycled, only 6 MJ is required[18]. However, the difference in embodied GHG emissions is not that large; 0.54 kg CO_2 equivalents for virgin ethanol and 0.36 kg CO_2-equivalents for recycled ethanol. To answer the question of why this is so, one more level of transparency is required. The internal recycling process at the factory is a process model constructed by the candidate. The liquid waste flow from the production is a mix of ethanol, water and Ammonia Hydroxide. Hence, in order to reuse the ethanol, it must be purified. Distillation is the most common way of purifying ethanol. Based on that, the recycling process model is basically a distillation process assuming that 1 kg steam per liter ethanol [58]. The vapor production is modeled based on data from Boustead et al. [60] in which it was used an arithmetic average of 215 European steam plants. A detailed description of the fuel mix of this production can be found in the appendix E. The considerable emission intensity of that fuel mix explains the relatively large CC contribution from the recycled ethanol.

Figure 15 shows that the material precursor, tetraethyl orthosilicate (TEOS), is relatively important. It contributes with 28% of the embodied energy and 30% of the embodied emissions of the sol-gel process in the 50% reduced ethanol scenario. TEOS is a silica alkoxide commonly used as a precursor in sol-gel processing. It is prepared by alcoholysis of silicon tetrachloride (see Eq. 17, section 3.2.2), a compound which is associated with ultrapure silicon production. In the widely applied Siemens process, silicon is reacted with hydrochloric acid to form electronic grade polysilicon [61]. Silicon tetrachloride is the main product of this process. The main driver for the environmental impacts of TEOS is therefore the embodied energy of silicon tetrachloride, which stem mainly from the high direct energy requirement of the Siemens process. It must be recalled that the LCA data for TEOS was constructed based on a mass balance consideration (Eq. 17), and that, consequently, it is associated with a high degree of uncertainty.

The contribution from Ammonia Hydroxide is relatively small because only small amounts are needed in the synthesis.

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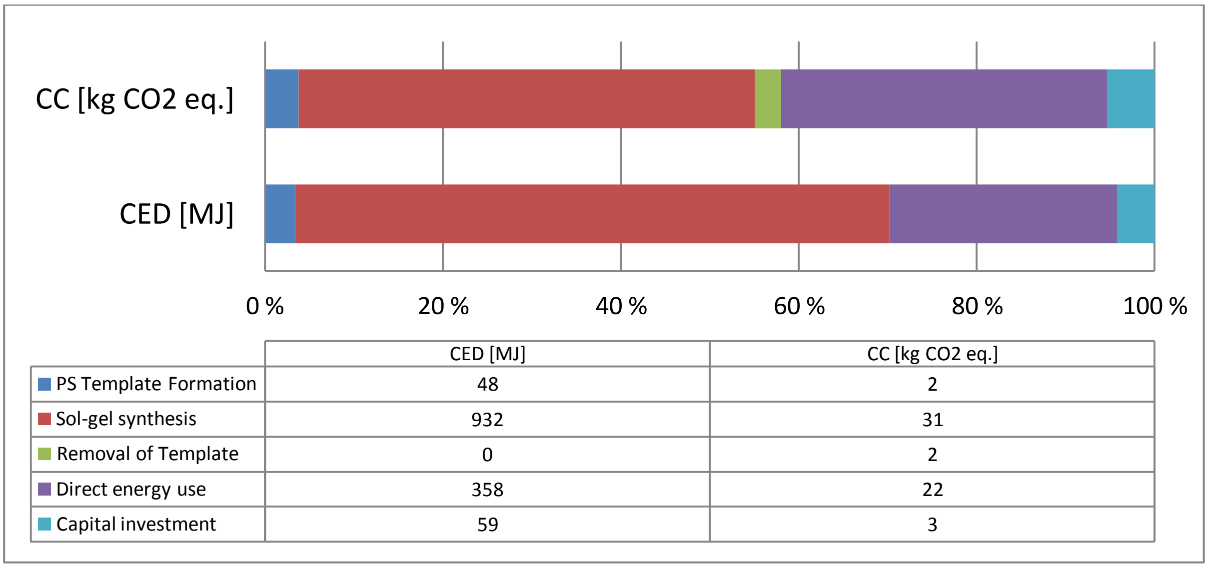
[18] The calculation is based on a simplistic estimation. Consult the inventory table in the appendix for details on how the energy demand on the recycling process or other processes were modeled and calculated.

Analysis of total results with reallocated energy consumption

In the light of Figure 15, an important comment to Figure 14 has to be added. The contribution from recycled ethanol in Figure 15 was elaborated in the previous section. The recycling process is broken down in Inventory table 7 in appendix B. The table shows that the process requires only heat and chemical infrastructure. There is no transport added to this process, because it is assumed that the ethanol is purified on the site. One way to look at it is therefore that a part of the direct energy required at the production site is allocated to the recycled ethanol. Alternatively, it could have been allocated to the foreground system and be a part of the violet sections in Figure 14. The same goes for the infrastructure related to the recycling process. If this is broken out of the recycled ethanol and rather allocated to the primary energy requirement of the functional unit, Figure 14 would look different. Of course, the total result would remain unchanged. The recalculated contribution analysis is shown in **Feil! Fant ikke referansekilden.**.



	CED [MJ]	CC [kg CO2 eq.]
🟦 PS Template Formation	48	2
🟥 Sol-gel synthesis	932	31
🟩 Removal of Template	0	2
🟪 Direct energy use	358	22
🟦 Capital investment	59	3

Figure 16: Bar chart displaying the contribution analysis results when direct energy consumption and capital investments for the recycling of ethanol and the removal of the template are reallocated to the foreground system. Note that the total MJ and CO_2 equiv. are the same as in Figure 14.

Blue, red and green are energy and emissions stemming from raw material consumption, while violet is direct energy consumption and light blue is required capital investments for the production at site. The raw material consumption is still the largest contributor. Adding the energy required for purification of ethanol, the violet bar section grew significantly as compared to Figure 14. The recycled ethanol is the largest mass flow in the system, and it is therefore expected that a energy intensive process associated with this flow will affect the results.

Sensitivity analysis

A sensitivity analysis is provided to show additional scenarios and to investigate how the system reacts on changes in different input parameters. The baseline is the total impact of the functional unit with a 50% ethanol reduction, like the analysis presented above.

Effects of some ethanol related processes

The first three tables check sensitivities of parameters related to ethanol.

Table 5: Sensitivity to choice of ethanol type on the total results for the fuctional unit. Results are rounded to the nearest five kg CO_2 equivalents.

Scenario	Final CC [Kg CO_2 equiv.]	Change of CC impact
Ethanol from grass	50	-9%
Ethanol from potatoes	75	+36 %
Ethanol from wood	50	-9%
Baseline Ethanol (sugar beet molasses)	**55**	

All the chosen ethanol types are produced in Switzerland. Table 5 shows that a different choice of ethanol could have changed the results positively or negatively. To apply wood-based ethanol or grass-based ethanol would not have changed the results significantly, but applying ethanol from potatoes would significantly have increased the CC impact of the hollow silica nanospheres. There is no reason to believe that the choice of ethanol from sugar beet molasses was an especially bad choice, or that another choice could significantly reduce the CC impact of the material.

Table 6: Sensitivity to ethanol recycling rate on the functional unit. The numbers are here rounded off to the nearest five kg CO_2 equivalents and the nearest ten MJ.

Sensitivity to recycling rate for ethanol on the total results				
Scenario	**Final CED [MJ]**	**Final CC [Kg CO_2 equiv.]**	**Change of CED impact**	**Change of CC impact**
70% recycling rate	1620	65	+16%	+8%
Baseline 80 % recycling rate	**1400**	**60**		
90% recycling rate	1180	55	-16%	-8%

Table 6 shows the sensitivity to a 10% change in the internal recycling rate for ethanol in the system. The change is measurable, but not enormous, which is in accordance with the findings in the previous chapters. It is important to consider that reuse is not only for the sake of reducing energy consumption. Ethanol can have several harmfull effects if emitted directly to nature in large amounts.

Table 7: Sensitivity to the choice of energy mix, or the composition of energy and fuel types for the direct energy consumption in the system

Sensitivity to energy requirement of the recycling process on the total results				
Scenario	**Final CED [MJ]**	**Final CC [kg CO_2 equiv.]**	**Change of CED impact**	**Change of CC impact**
Halved energy consumption in the ethanol recycling process	1220	50	-12%	-17%
Baseline	1400	60		
Double energy consumption in the ethanol recycling process	1750	85	+25%	+42%

Table 7 displays the sensitivity to the energy requirement for the recycling process. The table shows that the sensitivity is strong. This was expected because the recycled ethanol is the most important raw material in terms of mass. The recycling energy was included in the sensitivity analysis because it was modeled on the basis of simplistic assumptions (see chapter 3.2.3 and Inventory table 7 in appendix B. It is therefore quite important to notice the significant effect of these simplifications on the final results. It was assumed that the ethanol is purified through distillation. An energy requirement of 1 kg water vapor (2.75 MJ) per liter ethanol was assumed for that. This is an optimistic choice, because the energy requirement can increase up to 4 kg of vapor per liter ethanol depending on the desired level or purity [58]. In addition, nothing else is known about this recycling process, which means that its overall impact most probably is underestimated in the analysis presented here. In section 3.2.4 it was suggested to use a more energy-friendly purification process, which might lower the impacts. In conclusion, the input from the recycling process is very uncertain. It is therefore very important to notice the important effect of this uncertainty on the final results, as presented in Table 7.

Impact from TEOS

TEOS, the silica precursor, is also a process which had to be modeled by the candidate and at the same time proved to have an important contribution to both CED and CC impact. Process model of the TEOS also contain an allocation problem which was solved by system expansion. To investigate the systems sensitivity to the TEOS process model, the results are recalculated with the application of economic allocation for the partitioning of loads between TEOS and its co-product hydrochloric acid. The comparison is shown in Table 8: Sensitivity to the choice of allocation strategy in the TEOS process model.The table shows that such a change in the assumptions for the process modeling of TEOS lead to an overall change of the total CC result of 8%.

Table 8: Sensitivity to the choice of allocation strategy in the TEOS process model.

Sensitivity to the choice of allocation strategy in the TEOS process model		
Scenario	**Final CC [kg CO_2 equiv.]**	**Change of CC impact**
Baseline system expansion.	**60**	
Economic allocation based on a price estimate from Sigma-Aldrich [46].	55	-8%

Impacts based on choice of energy sources an electricity mixture

Because the production system under study is assumed to be situated in Europe, the choices of energy sources for the direct energy consumption have been picked according to European standards. The direct energy requirement for the FU includes 0.333 kWh of medium voltage electricity, represented by the electricity mix from the Union of Co-ordination of Transmission of Electricity (UCTE). In addition, 2 MJ of heat from natural gas is required, and the heat for the ethanol recycling generated from the generic fuel mix given in Boustead et al.

At a hypothetical Norwegian production site, it is probable that the total of the energy needed would be provided from the electricity grid. The carbon emissions of the Nordic electricity mix is 0,21kg CO2/kWh, while the Norwegian mix has 0,017kg CO2/kWh [16]. The appropriate electricity mix to use in LCAs of Norwegian productions is an object of discussion. Norway is a part of the Scandinavian and the European electricity mix via international electricity grid [62], and hence uses electricity imports which are not necessarily from renewable sources. It is therefore common to apply the Nordic mix. Table 9 shows the total results for the Nordic mix compared to the baseline results. It is a significant reduction in the overall results when changing to energy sources associated with lower carbon emissions.

Table 9: Sensitivity to the choice of energy sources and electricity mixture.

Sensitivity to the choice of energy sources and electricity mixture		
Scenario	**Final CC [kg CO_2-equiv.]**	**Change of CC impact**
Baseline energy mix composed of Medium voltage UCTE electricity, heat from natural gas and heat for steam from a generic production mixture given in Boustead et al. [60].	**60**	
Nordic energy mix applying electricity from the Nordic (NORDEL) electricity mix only.	75	-25%

3.2.4 Recommendations for a greener production

The main results from the environmental assessment may be summed up as follows: The NIM is quite energy and emission intensive due almost entirely to the indirect energy and emission intensity of the raw materials consumed. The sol-gel process is the most energy and emission intensive step, due to the indirect impact from ethanol and TEOS. Direct energy consumption and CO_2 emissions from the combustion of the template is less important, and the fabrication of the template is insignificant. The ethanol consumption, in the sol-gel synthesis stage of the production, is exaggerated, and therefore accountable for the majority of the emissions. The large ethanol requirement makes all processes associated with ethanol important.

Recommendations for a greener production can be developed by analyzing the mechanisms behind these results. First of all, in order to reduce the energy consumption of the NIM, it is the indirect rather than the direct energy input that should be addressed. The most important recommendation is to reduce the amounts of ethanol. Figure 12 illustrated the importance of the ethanol reduction.

When significant cuts in the ethanol requirements are done, the recycling rate should be as high as possible as to minimize liquid waste, nature hazards, transport and use of agricultural resources. However, as shown in the sensitivity analysis, as long as the recycling is based on purification by distillation, it will not reduce the overall CC impact as much as one could wish. It is can therefore be recommended to look for another purification technology, for instance based on membrane separation. The alternative purification technology will of course have to be assessed by environmental system analysis as to avoid any problem shifting.

TEOS has an almost 100% conversion rate to SiO_2 [20]. Consequently, it does not make sense to reduce the consumption of TEOS in the system. It is therefore recommended to look for substitutes that avoid the energy and emission intensive silicon tetrachloride in its formation. Aerogels, and most probably also hollow silica nanospheres, can be produced by sol-gel synthesis with water glass (Na_2SiO_3) as the precursor. Water glass is cheaper than TEOS and it has no harmful byproducts (unlike the TEOS production where acidifying and corrosive hydrochloric acid is produced). However, the production of water glass is not necessarily greener. The classical way of forming water glass is by reacting sodium carbonate with silicon dioxide, (basically soda ash and sand) [63]. These substances require high temperatures to melt and the process gives off carbon dioxide. The amorphous glass produced in the melt requires additional mixing in hot steam reactors to convert into water glass, so the overall process is quite energy intensive. An alternative production route is to directly prepare the water glass by dissolving silica sand under pressure in a heated aqueous solution of caustic soda (*NaOH)* which only forms water as a byproduct but still is a very energy intensive process [63]. A comparative life cycle assessment of hollow silica nanosphere production with respectively TEOS and water glass as precursors was not performed here. The reason is that it would require a substantial amount of practical and theoretical work to find a synthesis route for hollow silica nanosphere with the alternative precursor, as it is understood that a simple substitution would not be realistic. TEOS was chosen as the preferred precursor, by the ZEB scientists, for technical reasons. The changes in the overall production route from TEOS to water glass could have positive or negative impacts on the LCA results. The LCA results would also be sensitive towards water glass grade, e.g. the SiO_2/Na_2O ratio. A comparative assessment was therefore left out of the thesis, but should be considered as further work.

Indeed, it would be interesting to see if a water glass-based synthesis route would demand less ethanol. Since it was shown that TEOS and ethanol clearly are the largest CC contributors, a critical revision of the TEOS-based sol-gel synthesis procedure in general should be considered.

The effects of the waste stream are not quantified here because the effects of ethanol and ammonium emitted to water and air affects other impact categories than climate change. However, we know that, while 80% of the ethanol is reused, 20% is emitted to nature. It has already been concluded that the ethanol consumption must be reduced considerably. In addition, responsible chemical waste management should be among the recommendations. A higher recycling rate of ethanol was shown to not have a large reduction potential as far as climate change was concerned. However, serious problem shifting could be the consequences of irresponsible waste handling.

The impact assessment presented here (ch. 3.2.3) affirms a typical LCA result: It is, essentially, the indirect emissions from the final demand on non-renewable energy sources that pulls the strings in the environmental impact of the production of a good or a service. Sugar beet harvesting for ethanol, production of water vapor in the distillation process that purifies the effluents, and the Siemens process for the preparation of TEOS: All these industrial processes places a substantial demand on oil, coal and gas resources. The shift towards low carbon energy sources is therefore an important part of the recommendations, even if this in many cases is outside the control of the producers.

4 Interpretation and discussion

The objective of this master thesis was to push the discussion of the NIM in a pragmatic direction through addressing its effective thermal conductivity and its climate footprint.

The first part (chapter 2) threw light on the effect of the assembly or integration of the spheres on the thermal conductivity. It was found that the intrinsic thermal conductivity of the phase arising from the binding substances, will affect the overall thermal conductivity of the NIM. Taking an HSN thermal conductivity of $k_{HSN} = 0.004$ W/mK as the starting point, it was found that when assembled, the effective thermal conductivity of the NIM would increase due to the introduction of a new phase. A measurement of the thermal conductivity of the HSN is therefore representative only as an absolute minimum of the effective thermal conductivity of the NIM. Increment must be assumed as a consequence of the assembly step.

The effect of the intrinsic thermal conductivity of an eventual binder phase should hence be added to the list of conditions that must be taken into consideration when tailoring the NIM. This effect comes in addition to sphere diameter, opacity and other parameters which are known from micro/nano level studies. The macroscopic description ignores the microscopic description and vice versa. Both approaches should therefore be considered. To accurately predict the thermal conductivity of the NIM remains a difficult task, giving even more the reason to take note of the boundary conditions these different models provide.

The second part (chapter 3) assessed the environmental impact of the NIM, assuming a production procedure close to the current synthesis method. Indirect energy and emission intensity of the raw materials consumed in the sol-gel process resulted in a relatively important environmental impact, on a per kilogram basis. Because scientists confirm that the ethanol consumption can be significantly reduced in a full scale production, the environmental impact was calculated for scenarios with 25%, 50% and 75% reductions of ethanol. If the 75% ethanol reduction scenario is assumed, there are reasons to believe that reasonable minimum values for climate change and cumulated energy demand are found for a NIM based on the current synthesis procedure for HSN. These values are in the order of 40 kg CO_2 equivalents Climate change impact, and 900 MJ cumulated energy demand per kg spheres. Generally, these values are quite high on a per kilogram basis. To reduce them, a critical revision of the TEOS-based sol-gel synthesis is needed. First and foremost, a process with lower solvent consumption is required.

4.1 Interpretation of LCA results with respect to insulation performance

For transparency and accuracy reasons, the functional unit of this life cycle assessment was chosen to be 1 kg of hollow silica nanospheres at factory gate (see the

Functional Unit section in chapter 3.2). However, it does not generate LCA results that are comparable to LCAs of commercial insulation materials. An operational functional unit for comparative analysis insulation materials is a one square meter slab of material with a thickness corresponding to a fixed thermal resistance [47]. Such analysis of different commercial insulation materials can be found through the EPD system or in literature, for instance in Papadopoulos et al. 2007 [64] and Ghoses' report from 2011 [16].

In order to run such a comparative analysis with the NIM, at least two dimensions of knowledge is required: Knowledge of the final thermal resistance of the material and more detailed data on what inputs from the technosphere the product requires. This is the reason why this work chose to address these two aspects; they really are crucial characteristics of the NIM. The results of this work are not exact answers, but suggestions and estimates at the best possible level of accuracy with the current knowledge.

In this chapter, the analysis of the research is taken one step further. Scenarios for the NIM performance will be constructed on the basis of the LCA findings and the range of possible effective thermal conductivities by the use the model suggested in the Functional Unit section chapter 3.2. The model is repeated in the next section.

Model

Assume that the assembly step requires no additional substances or processing. Then start with an insulation unit which is a slab cut to one square meter. This slab coud look like the drawing in Figure 3. Assume a thermal conductivity. Set the thermal resistance to 1 W/m and calculate the corresponding thickness of the slab using Eq. 2. Assume that the material is only made up of hollow silica nanospheres, and that the density of these spheres is 200 kg/m^3 [20]. Calculate the corresponding mass of HSN required for the insulation unit and subsequently the environmental impact based on the LCA results.

LCA results with respect to insulation performance

The results are shown for k-values from 0.004 W/mK to 0.03 W/mK in Table 10. The 50% ethanol reduction scenario still applies.

Table 10: Environmental performance of the NIM, for varying insulation performances.

Thermal conductivity [W/mK]	Thickess [m]	Mass [kg]	CC [kg CO_2 equiv.]	CED [MJ]
0.004 (goal)	0.004	0.8	48	1120
0.013 (as aerogel)	0.013	2.6	156	3640
0.02 (as current HSN sample)	0.02	4	240	5600
0.03	0.03	6	360	8400

A graphical projection of this experiment conducted with the different ethanol scenarios can be seen in Figure 17. Figure 17 is graphing the cradle-to-gate climate change impact as a function of the thickness required for a thermal resistance of R = 1 m^2K/W. Hence, the figure is assuming a fixed thermal resistance at 1 m^2K/w and a fixed area of 1 m^2. Note that the CC impacts are normalized to the CC impacts for 1m^2 VIP (21.1 kg CO_2 equivalents).

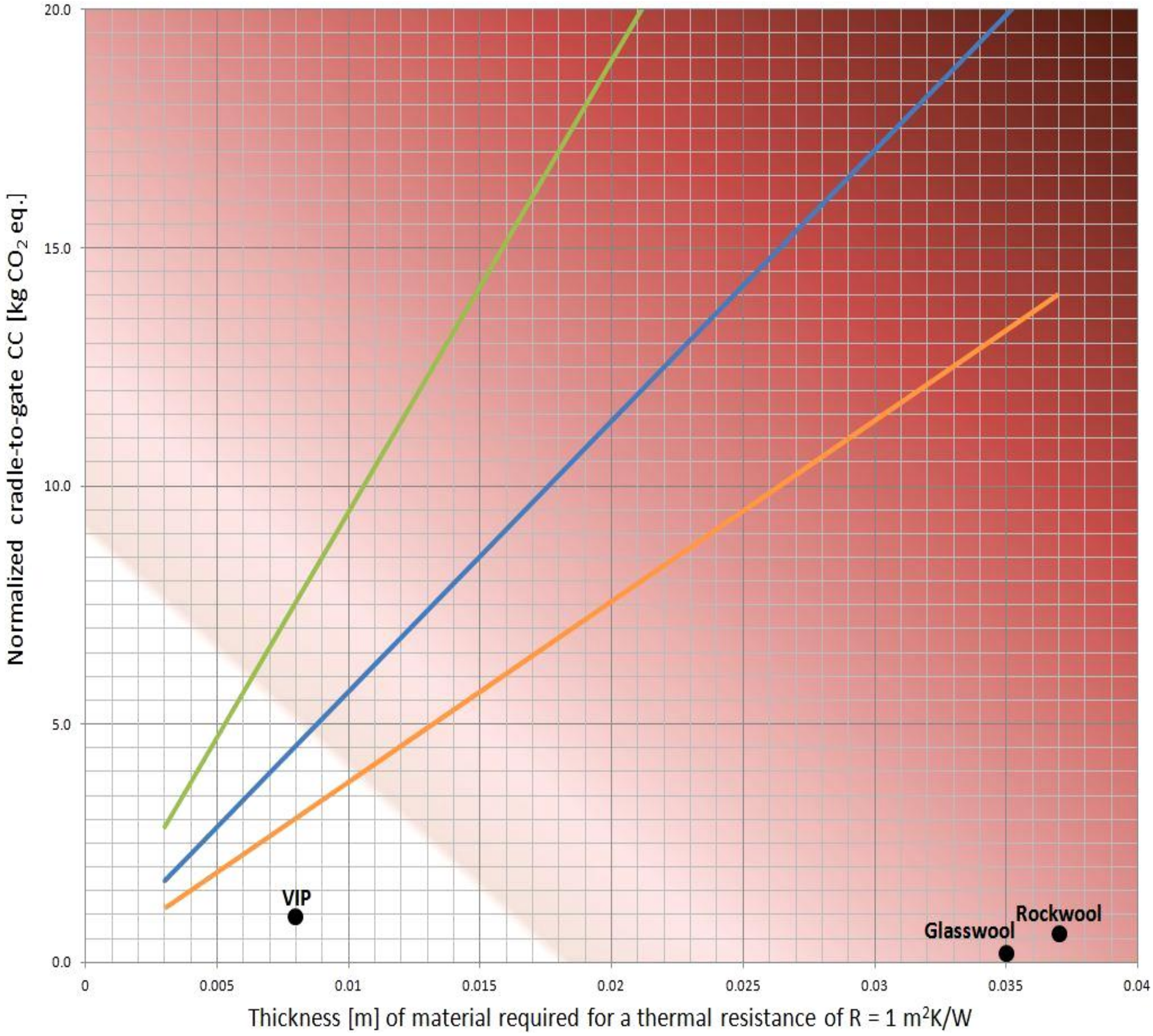


Figure 17: Map of performance for different building insulation technologies. Horizontal axis representing the thermal performance given in meter thickness of material required for a thermal resistance of R = 1 m^2K/W and vertical axis representing thermal performance given in kg CO_2 equivalents. Existing products are fixed points whereas the NIM is varying along performance scenarios.

Explaination of Figure 17

The thickness required for the fixed thermal resistance is increasing along the x-axis. The x-axis is therefore representing the insulating performance of the material: The smaller the thickness the better is the thermal resistance. The amount of CO_2 produced for the according volume of insulation material produced is increasing along the y-axis.

For rockwool, glasswool and vacuum insulation panels, the thicknesses and the corresponding CC impacts are fixed: To achieve a thermal resistance of 1 m^2K/w, 35 mm of Glava Proff 35 glasswool is needed. Correspondingly 37 mm of Rockwool is needed[19]. The thickness that should be assumed for VIP is more debatable. As presented in chapter 2, its thermal conductivity increases over time. 0.008 W/mK is assumed as the value for the thermal conductivity in this case, the corresponding thickness is therefore 0.008 m.¨

From EPD- literature, it is found that this represents 0.6 kg CO_2 equivalents for glasswool [65] and 1.449 kg CO_2 equivalents for Rockwool [57] on a cradle-to-gate basis. The CC impact for VIP is documented in Schnhardt et al. for Institut für Energie in Germany [15]. As presented in the introduction to part 1, page 6, it had to be calculated according to the model applied here. Details on the calculation can be found in appendix D. The calculation gave a cradle-to-gate CC impact of 21.1 kg CO_2-equivalents. Glasswool, rockwool and VIP are therefore fixed points in Figure 17. The reason for not including aerogel insulation in the figure is simply that satisfying data for aerogel is not available [2].

The CC impact of the NIM, which was estimated in this thesis, is graphed in Figure 17 as a function of the potential insulation performance, e.g. thickness required for the fixed thermal resistance of 1 m^2K/w. The graph was developed for the three different ethanol scenarios: Original amount (green line), 50 % reduction (blue line) and 75 % reduction (orange line). The graph was shaded by color to indicate where, in the area spanned out between the environmental and the thermal performance, an attractive material should be. The white area is the most attractive, whereas the dark red is undesirable. The shading is for illustrative purposes only; it is not based on any calculations or exact criteria.

Observations from of Figure 17

The figure spans out all possibilities by means of the current production method, from very optimistic to very pessimistic. To evaluate the future of the NIM, or to extract exact design criteria out of Table 10 and Figure 17 would be wrong. The reason is the high degree of

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[19] Rockwool and glasswool come in different qualities and products. Both wools can achieve a thermal conductivity down to 0.035 W/mK. The examples applied here are representative for the standard types.

uncertainty the green, orange and yellow line is representing. However, some useful observations can be extracted from it.

The most important observation is that, for the NIMs performance to land in the attractive lower left corner of Figure 17, strict optimization of both thermal and environmental performance is necessary. It can be seen that the environmental impact of the NIM cannot be justified unless the thermal performance is extremely good.

Looking at a combination of a minimum thermal conductivity value and a minimum environmental impact (75% ethanol reduction scenario), the NIM can be estimated to have a CC impact of 32 kg CO_2 for a thermal resistance of 1 m^2K/W. This is considerable higher than mineral wool and about the same as VIP, according to Figure 17. This gives reasons to conclude that the environmental performance of the NIM will be not better than the environmental performance of VIP. It can be argued that the overall performance of the NIM can be *comparable* to VIP, if the thermal conductivity can be optimized to VIP-level or better. However, this result is very sensitive to parameters and assumptions that are highly uncertain. Indeed, the insulation and the environmental performance are likely to be affected negatively by the assembly step. It seems to be no reason to classify the NIM, made with the current production method, as an especially green material. This material is quite GHG emission intensive, even when considering best case scenarios.

It must then be asked: What are the performance limits for an acceptable material? What are the success criteria for the environmental performance of the NIM? Such a criterion can only be developed by considering the NIM in a holistic perspective. It is known that the VIPs thermal performance degrades over time. If the NIM has a cradle-to-gate environmental impact comparable to VIP but hold a *constant U-value*, it surely has a competitive advantage. A quantitative criterion for the maximum acceptable CC impact of the NIM can only be found by looking at the building as a whole, considering net life-cycle energy and GHG balance.

4.2 Validity of models

In the first part of this report, two different approaches were taken to describe the main mechanisms for thermal conductivity in the NIM. In the microscopic approach, different models used in the ZEB literature were reviewed. In the macroscopic approach, the EMT-model for thermal conductivities in two-component porous systems was applied to investigate the effective thermal conductivity of the NIM from a top-down perspective. The validity of these models were shortly discussed in the respective chapters.

In the environmental assessment part, two models have been suggested. The first model is the model of the production of 1 kg of hollow silica nanospheres. The model of the system and system borders, for which the LCA is done, is based on a laboratory recipe. Even though modifications and modeling have been done in order to reflect a production on an industrial scale (addition of transport, reduction and reuse of ethanol and modifications of the direct energy consumption), the model is following the recipe quite closely. This is not a real industrial system, and it does not contain real industrial data. The current LCA results calculated from this model is therefore valid only for internal communication within the research. However, the model is robust, comprehensive and transparent enough for further work. When more information is available, the model can be adapted. And if real industry data become available in the future, these can replace constructed and generic data in the model. The results can then be used for external communication.

The model on which the performance scenarios, illustrated by Table 10 and Figure 17 in chapter 4.1, are based, is also valid only for internal communication. This is because the model is based on three assumptions: The assumption of no added materials or energy in the assembly or integration step, the assumption of a density of 200 kg/m^3 and the assumption of comparability with calculated cradle-to-gate CED and CC results for three other insulation materials. All of these assumptions are uncertain. Furthermore, it is probable that additional chemicals and energy is required for the integration step and therefore, the performance of the NIM is likely to be affected negatively. That is because this is likely to increase the thermal conductivity, as shown in chapter 2.3.2, and because it will require input that will increase the climate change impact. The assumed density is reflecting the current sample of the NIM. It can change when the spheres are optimized in terms of diameter and shell thickness. The comparability across the different insulation material studies is in no sense guaranteed in this comparison. Consequently, this last part of the report must be seen only as an interpretive framework for illustration purposes, not applicable for external communication.

Different applications of the NIM have not been discussed in detail in this work. The discussion in chapter 4.1 assumes that the material is in direct competition with mineral wools and VIPs, which is not necessarily the case. It might be that the NIM can find another market section than the conventional house insulation materials. For instance, aerogel is considered to be very well adapted for retrofitting of old construction because it is thinner. Other applications includes, but are not limited to, pipe insulation, insulation of translucent roof cladding, technology for food cooling etc.

4.3 Problem shifting

The CED and the ReCiPe 2008 (H) CC were chosen as indicators in this work. Environmental pressures that are not taken into account here include, but are not confined to, eutrification and acidification of surface waters, human toxicity, ozone depletion and particulate matter formation. These pressures should be included if the LCA of the NIM is to be further developed.

Toxicity to humans and the environment

The issue of toxicity is of special importance. Materials to be installed in buildings must not be harmful to touch or degrade indoor air quality. In addition, there are toxicity challenges associated with nanoparticles. More knowledge is needed on the consequences of nanoparticles on human health and environment. Intuitively, there is no reason to think that the hollow silica nanospheres are especially reactive or toxic. However, they are in a size range of particles that is worrying toxicologist around the globe [66, 67]. The bioavailability of nanoparticles are dramatically increased if the particles are dispersed in air and not locked inside a product. The many aspects of nanotoxicology are discussed elsewhere, but this absolutely must be taken into consideration for the NIM.

Narrow system boundaries

With reference to Figure 10, the system borders of the LCA presented here are narrow relative to the practical implementation of the NIM. The assembly step has been discussed and in addition comes practicalities for the installation in the buildings. What additional material, substances and processes are required for a wall element insulated by NIM? It can be glue, an additional moisture barrier, a complicated fitting etc all of which are placed outside the system boundaries in this work.

4.4 Further work

LCA of the NIM

With the current level of knowledge of the NIM, it is difficult to develop the LCA with further details than what is presented here. When key characteristics like thermal conductivity, sphere dimensioning and assembly method is decided, a cradle-to-grave LCA should be conducted as to really understand the implications, advantages and disadvantages of introducing NIM for insulation applications in zero emission buildings. A non-exclusive summary of aspects that the cradle-to-grave LCA should cover can be listed as:

- Energy pay-back times for a zero emission building applying NIM for different insulation applications.
- GHG pay-back times.
- More impact categories.
- A special regard to nanoparticle issues.
- Waste scenarios, possibilities for recycling.
- Comparative analysis of wall construction and whole buildings with different insulation solutions (wide system borders).

Effects of solid fraction

In chapter 4.1 scenarios with varying insulation and environmental parameters were shown. However, the effect of material density, which was kept at 200kg/m^3 was not discussed. This is an interesting parameter to investigate further, because it is related to both the environmental impact and the thermal conductivity.

Because climate change impact is given on a per kg basis in this work, the material density will affect this result. The density of the hollow silica nanosphere material is given by the volume fraction of solid matter, that is, the volume fraction of silica. An important result from the LCA was that the process of making the silica shell, the sol-gel process, was the most contributing step in terms of environmental impact, because of the embodied energy and the emissions associated with the chemicals involved. Consequently, from an environmental point of view, the volume fraction of solid matter should be kept as low as possible.

Porosity is the volume fraction of pores, e.g. air, divided by the total material volume, and consequently also negatively correlated with volume fraction of solid matter. Figure 6 showed that the effective thermal conductivity decreased with increasing porosity. This result harmonizes with the environmental perspective: It is desirable to keep the volume fraction of solid matter as low as possible.

Holding the sphere diamater constant the porosity can be increased by making the sphere walls thinner, that is reducing the *L* parameter in Figure 4. This is done in the calculations illustrated by Figure 6[20]. More research is needed on the effect of thinner walls. Is the thickness of the spheres easily tunable or is this difficult and resource demanding? What are the effects on the thermal conductivity? Will thinner walls have implications for the structural properties of the material? This should be considered for further research because it can have a quite important effect on the NIMs' overall performance.

Finally, research on structural and functional properties other than the effective thermal conductivity should be a priority in the future NIM research. The economical perspective is also decisive for the product; costs and benefits must be evaluated together.

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[20] According the the model applied by Holvik et al. 2013, the porosity is increased by increasind d_v while holding d_{v+s} constant.

5 Conclusions

This report has investigated thermal and environmental design perspectives of a new insulation material. The idea of this new material has arisen from the increasing focus on energy saving and emission abatements in the building sector. It is believed that better insulation have a considerable GHG reduction potential in this sector [4, 68], which currently stands for close to a quarter of the total global energy-related carbon dioxide (CO_2) emissions [3]. Hence, the Research Centre on Zero Emission Buildings is putting an emphasis on insulation improvement. Advanced new materials with extremely low thermal conductivities are part of the solution because they can have architectonic, technical and possibly economic benefits. However, the environmental cost of producing advanced new components must be accounted for in the zero emission balance. In order to proceed with this balance, transparent environmental data for the building materials must be reported. Such reports have limited availability, especially for state-of- the-art materials.

For the development of the new NIM, ZEB is not only interested in reporting the material's environmental impact, but in screening it at an early stage in order to optimize the process. In this master thesis, a model was constructed for the screening LCA of the new NIM. Because many of the characteristics of the NIM still are under development, the model was built as flexible as possible. It can therefore be used for further research and development. The model is constructed in order to calculate the environmental impact of a material for which only a limited dataset is available, because it fills data gaps according to a suggested procedure, inspired by literature on LCA for chemicals. The model can be gradually improved as more knowledge of the NIM becomes available. The weakest point in the model is that it ignores in- and outputs related to the assembly step of the material. This is because no information is available on this step yet. The functional unit of the LCA is set to 1 kg of hollow silica nanospheres. This should be updated when more knowledge of the NIM is available.

The model was used to calculate cradle-to-gate climate change impact and cumulated energy demands for production scenarios close to the current synthesis procedure of the NIM. The results are in the order of 60 kg CO_2 equivalents and 1400 MJ cumulated energy demand per kg of material for the scenario where ethanol consumption is reduced by 50% relative to the laboratory consumption. The ethanol consumption was reduced because linear upscaling from the laboratory data resulted in exaggerated amounts. An 80% reuse rate of ethanol is assumed in this scenario. Because ethanol is the largest material flow in the system, the results are very sensitive to the processes associated with it. A scenario with

75% ethanol reduction relative to the laboratory data gave 40 kg CO_2 equivalents and 920 MJ per kg nanospheres.

The LCA results gave insight on how the NIM process can be optimized for a greener production. First of all, it is the indirect emissions and embodied energy of the chemicals that must be addressed in order to reduce the environmental impact of the NIM production. The sol-gel process was found to be responsible for over 90% of the impact. This is because it requires chemicals in large amounts and because these chemicals are associated with energy and emission intensive fabrication processes. Ethanol is the largest contributor, even in scenarios with 50% and 75% reduction. Ethanol consumption must be minimized in order to significantly improve the environmental impact. In addition, reuse and responsible waste handling should be ensured to minimize direct and indirect emissions to nature. Reused ethanol must be purified, and as the flow of reused ethanol is the largest flow in the system, the energy required for the purification process is important. This energy consumption should therefore be minimized, for example by using membrane separation instead of distillation. TEOS consumption cannot be reduced in the context of the current synthesis, so research on alternative synthesis methods with other silica precursor is recommended. It could not be concluded upon whether waterglass is an advantageous alternative to TEOS, so this should be considered for further research. The impact from the template formation and subsequent combustion was found to be insignificant compared to the sol-gel chemicals.

The environmental impact of one kg of HSN does not give a meaningful prediction of the NIMs environmental performance if it is not associated with the insulating properties of the material. Indeed, these two areas are connected: Higher environmental costs can be tolerated per unit material thickness, if the thickness can be kept small. That is the reason why the first part of this thesis was dedicated to a review of theories for thermal conductivity of the NIM. Microscopic phenomena including the Knudsen effect for gaseous conduction of heat in the pores and radiation effects were briefly reviewed. Subsequently, the discussion was taken one step further by introducing a macroscopic model for the prediction of effective thermal conductivity in a composite. The model was used to investigate the effect of the assembly of the spheres on the thermal conductivity. It was found that an eventual introduction of a binder phase will have an important contribution to the thermal conductivity of the NIM.

The LCA model, the recommendations for a greener production and the contribution of the macroscopic perspective on the thermal conductivity are the main outcomes of this thesis.

When the NIM research has reached the point where an assembly method is suggested and a thermal conductivity is set, environmental impact can be calculated relative to a unit which reflects the function of the material and its thermal performance. This report laid the foundations for such analysis. As a part of the interpretation of the result, a simplified model for the assembled NIM was constructed. The environmental performance of this NIM model was plotted for different thermal conductivity scenarios and different ethanol reduction scenarios. Cradle-to-gate climate change results for Rockwool, Glava and VIP, collected from the literature, was placed as fixed point in the same coordinate system. This map added a visual dimension to the results, but must be considered as an experiment of thought and not as results for external communication. The map indicated that the NIM risks having a high climate change impact, which was expected because the results per kilogram were very high. This calls for strict optimization of both environmental and thermal performance.

However, the performance of the NIM will depend on how, where and when it is used. It is not given that the NIM will substitute VIP or mineral wool in a building; it might find another marked segment based on its properties and characteristics. Other impact categories like human toxicity should be a part of the evaluation as well. A holistic, multi-criteria approach is necessary to really evaluate the detriments and benefits of the NIM. In the meantime, based on the work done in this thesis, recommendations for the material design can be summed up as follows:

- A strict optimization of both environmental and thermal performance is necessary.

- More research is needed on the nanostructure manipulation of the NIMs thermal conductivity, but this research should keep in mind that the assembly step can significantly affect the effective thermal conductivity of the NIM through macroscopic effects. Introducing phases with higher thermal conductivity than HSN should be avoided.

- It is necessary to reduce the amount of ethanol consumed in the fabrication of the spheres, and the ethanol should be recycled by the application of a low-energy/low carbon purification technology.

- Research is needed on alternative synthesis routes that can improve the overall environmental performances of the system. Routes that can eliminate consumption of ethanol and emission intensive precursor are especially interesting.

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Appendices

Appendix A A short introduction to zero emission buildings

The UN IPCC is reporting that energy-related carbon dioxide emissions from the building sector are responsible for close to a quarter of the global total [3]. A reduction of used energy in this sector could contribute significantly to a total lower energy demand. There is a fast development towards more energy efficient buildings and concepts such as “low energy buildings”, “passive house” are applied more frequently [69] . The Norwegian Ministry of Environment (2012) states, in report 21 to the Norwegian Parliament [68], that *“the technical buildings regulations (byggteknisk forskrift) will require passive house standard in 2015 and almost zero energy standard in 2020”*.

A zero emission building is a more ambitious concept than a passive house or a zero energy standard. Conceptually, a Zero Emission Building (ZEB) is a building with greatly reduced energy demand and the ability to generate electricity (or other energy carriers) from renewable sources in order to achieve a carbon neutral balance. However, a clear and agreed definition of Zero Emission Building (ZEB) is yet to be achieved [70]. The current understanding of the zero emission building concept is a building that has a zero net value GHG emissions throughout its life cycle.

Figure 18 is showing a general, schematic drawing of a product life cycle and the associated energy demand and emissions.

The Building Life Cycle refers to the view of a building over the course of its entire life, taking the design, installation, commissioning, operation and decommissioning phases into consideration [71]. With reference to Figure 18, the life cycle of a building starts at the raw material acquisition for the construction and stops at the deposition of waste from the demolition of the building. The main phases of a building life cycle are often referred to as the construction phase, the use phase and the demolition phase. Acquisition and processing of raw materials can be included in the construction phase or be distinguished as a separate phase. Installation of insulation costs energy in the acquisition and processing of raw materials but saves energy in the operation phase.

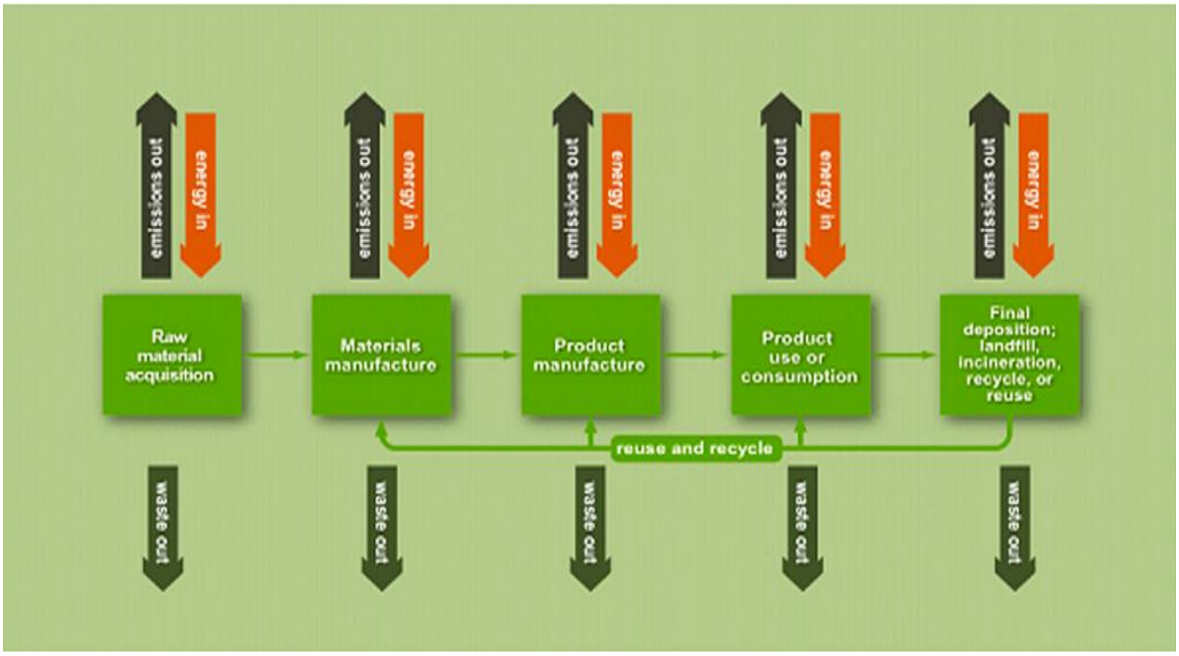

Figure 18: A schematic drawing of the phases in a product life cycle [71].

A building with a zero carbon balance throughout the total of its life cycle is in a practical sense a building in which emissions are reduced to a minimum in the construction, operation and demolition phase, in the use phase, and in the rest of the emissions are compensated by the generation of clean energy from components in the building (solar panels etc.). The calculation of the carbon balance is dependent on the system boundaries, the time-frame, crediting methods and other factors. Ongoing research is addressing the development of an unambiguous definition of the zero emission building standards.

Appendix B Inventory tables

INPUT	**DEMAND**	**UNIT**	**REFERENCE**	**DATA QUALITY**

Inventory table 1: Hollow silica nanospheres.

HOLLOW SILICA NANOSPHERES [1 KG]				
Silica by sol-gel synthesis	1	kg		Laboratory data
Polystyrene nanospheres template solution	5.7	kg		Laboratory data
Styrene combusted in furnace	0.54	kg		Laboratory data
Energy				
Heat, natural gas, at industrial furnace >100kW	2	MJ	Werk Gendorf Environmental report [72]	Generic
Electricity, medium voltage, production UCTE	0.333	kWh	Werk Gendorf Environmental report [72]	Generic
Capital investments				
Chemical plant, organics	4E-10	p	Hischier 2005 [51]	Generic
Emissions to air				
Ethanol	6.28	kg	Hischier 2005 [51]	
Ammonia	0.0588	kg	Hischier 2005 [51]	
Emissions to water				
Ethanol	31.8	kg	Hischier 2005 [51]	
Ammonia	0.28	kg	Hischier 2005 [51]	

INPUT	DEMAND	UNIT	REFERENCE	DATA QUALITY

Inventory table 2: Sol-gel synthesis.

SILICA BY SOL-GEL SYNTHESIS [1KG]				
Tetraethyl orthosilicate	4.76	kg	Process model Ullmann et al.	Mass balance calc.
Ethanol, from sugar beet molasses[21]	32.4	kg		Laboratory data
Ethanol, recycled internally	130	kg		Laboratory data Assumption: Ethanol has 80% recyclability
Ammonia Hydroxide (28%)	1.05	kg		Laboratory data Modified Ecoinvent unit process

Inventory table 3: Template.

POLYSTYRENE NANOSPHERES TEMPLATE [1 KG]				
Water, deionized	0.91	l	Laboratory data	Good
Styrene	90.91	g	Laboratory data	Good
Vinylpyrrolidone[22]	1.05E-4	g		Mass balance calc.

Inventory table 4: Styrene combusted in furnace.

STYRENE COMBUSTED IN FURNACE [1 KG]				
Capital investments				
Industrial Furnace 1MW	1.19E-7	piece		Generic. Assumption: Same as for fuel oil combusted in furnace.
Emissions to air				
Carbon dioxide	3.38	kg		Mass balance calc. Eq. 18

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[21] Ethanol 96% in H_2O from Sugar beet Molasses CH U.

[22] Modelling polyvinylpyrroliodone by mass considerations (molar mass polymer: 4000 g/mol, molar mass monomer 111.14 g/mol.

INPUT	DEMAND	UNIT	REFERENCE	DATA QUALITY

Inventory table 5: Tetraetyl orthosilicate

TETRAETYL ORTHOSILICATE (TEOS) [1 KG]				
Silicon Tetrachloride	819.4	g		Mass balance calc.
Ethanol	233.2	g		Mass balance calc.
Additional outputs to technosphere:				
Hydrochloric acid, from TEOS-production	175 x 0.38 Alloc. [46]	g		Mass balance calc.
Capital investments				
Chemical plant, organic	4E-10	piece	Hischier 2005 [51]	Generic
Transport				
Transport, lorry >16 ton, fleet average	0.105	tkm	Frischknect 2007	Generic

Inventory table 6: PVP.

VINYLPYRROLIDONE [1 KG]				
Monoethanolamine	1.23	kg	US. Patent	Conservative
Butyrolactone	1.73	kg	US. Patent	Conservative
Water, deionized	1.07	kg	US. Patent	Conservative
Capital Investments				
Chemical plant, organic	4E-10	piece	Hischier 2005 [51]	Generic
Transport				
Transport, freight, rail	1.78	tkm	Frischknect 2007	Generic
Transport, lorry >16 ton, fleet average	0.296	tkm	Frischknect 2007	Generic

Inventory table 7: Recycled ethanol.

RECYCLED ETHANOL				
Energy				
Heat, unspecific, in chemical plant	3.42	MJ	Boustead (1999) [60]	Generic
Capital investments				
Chemical plant, organic	4E-10	piece	Hischier (2005) [51]	Generic

INPUT	DEMAND	UNIT	REFERENCE	DATA QUALITY

Inventory table 8: Silicon tetrachloride.

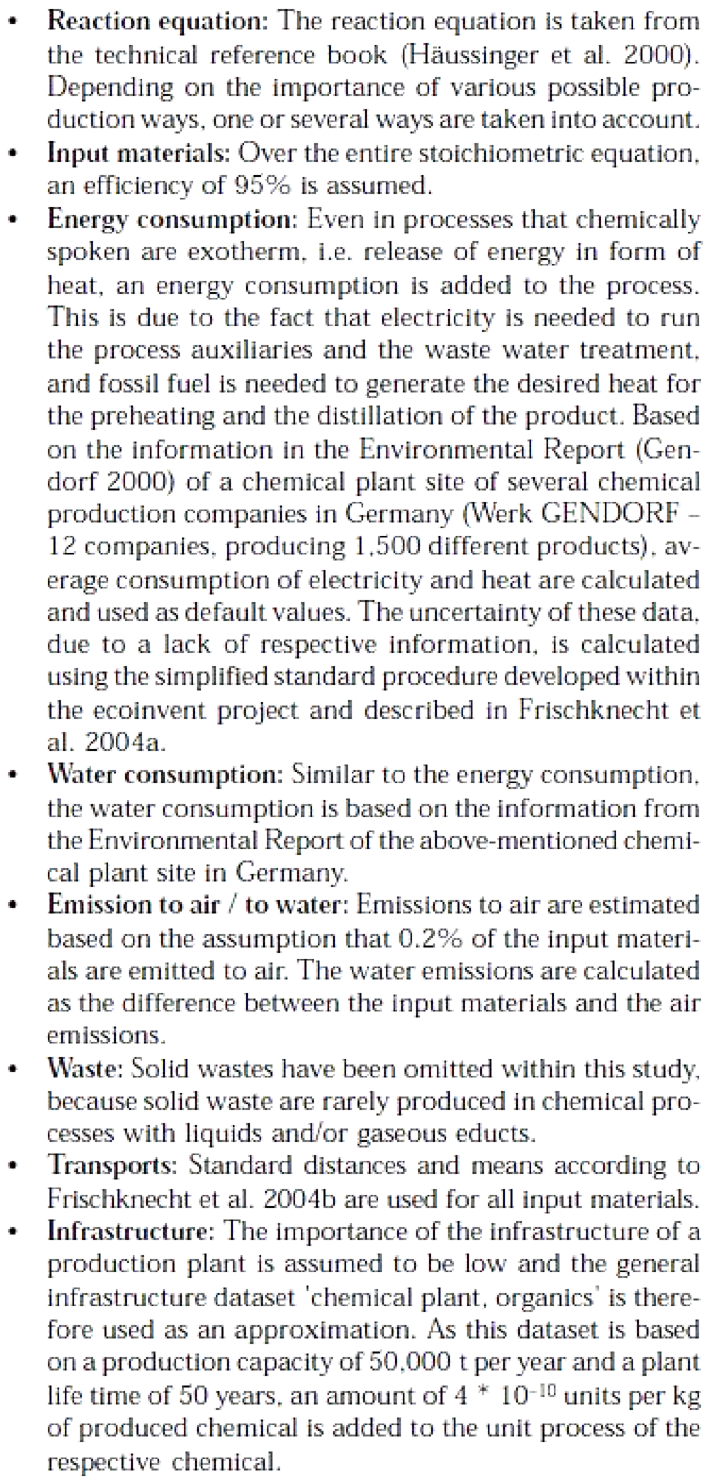
SILICON TETRACHLORIDE [1 KG]				
MG-silicon, at plant	0.0279	kg	Schönhardt (2003) [15]	Industry data
Transport, lorry >16t, fleet average	0.799	tkm	Schönhardt (2003) [15]	Industry data
Polyethylene, HDPE, granulate, at plant	0.00013377	kg	Schönhardt (2003) [15]	Industry data
Tetrafluoroethylene, at plant	0.00012786	kg	Schönhardt (2003) [15]	Industry data
Sodium hydroxide, 50% in H2O, production mix, at plant	0.041	kg	Schönhardt (2003) [15]	Industry data
Graphite, at plant	0.00014191	kg	Schönhardt (2003) [15]	Industry data
Hydrochloric acid, 30% in H2O, at plant	0.83333	kg	Schönhardt (2003) [15]	Industry data
Energy				
Electricity, medium voltage, production UCTE, at grid	0.00001869	TJ	Schönhardt (2003) [15]	Industry data
Transport				
Transport, freight, rail	0.298	tkm	Schönhardt (2003) [15]	
Capital investments				
Silicone plant	2.132E-12	p	Schönhardt (2003) [15]	

Inventory table 9: VIP.

VIP (800 nm Al) AT FACTORY GATE (1 m^2)				
Fumed silica	5.277	kg	Schönhardt (2003) [15]	Industry data
Silicon carbide	0.914	kg	Schönhardt (2003) [15]	Industry data
Polypropylene	0.00135	kg	Schönhardt (2003) [15]	Industry data
Composite film manufacture	13.31	m^2	Schönhardt (2003) [15]	Industry data

Appendix C Extract from Hischier et al. (2005)

Extract from “Establishing life cycle inventories for chemicals based on differing data availability” by Hischier et al (2005) [51].



- **Reaction equation:** The reaction equation is taken from the technical reference book (Häussinger et al. 2000). Depending on the importance of various possible production ways, one or several ways are taken into account.
- **Input materials:** Over the entire stoichiometric equation, an efficiency of 95% is assumed.
- **Energy consumption**: Even in processes that chemically spoken are exotherm, i.e. release of energy in form of heat, an energy consumption is added to the process. This is due to the fact that electricity is needed to run the process auxiliaries and the waste water treatment, and fossil fuel is needed to generate the desired heat for the preheating and the distillation of the product. Based on the information in the Environmental Report (Gendorf 2000) of a chemical plant site of several chemical production companies in Germany (Werk GENDORF – 12 companies, producing 1,500 different products), average consumption of electricity and heat are calculated and used as default values. The uncertainty of these data, due to a lack of respective information, is calculated using the simplified standard procedure developed within the ecoinvent project and described in Frischknecht et al. 2004a.
- **Water consumption:** Similar to the energy consumption, the water consumption is based on the information from the Environmental Report of the above-mentioned chemical plant site in Germany.
- **Emission to air / to water:** Emissions to air are estimated based on the assumption that 0.2% of the input materials are emitted to air. The water emissions are calculated as the difference between the input materials and the air emissions.
- **Waste:** Solid wastes have been omitted within this study, because solid waste are rarely produced in chemical processes with liquids and/or gaseous educts.
- **Transports:** Standard distances and means according to Frischknecht et al. 2004b are used for all input materials.
- **Infrastructure:** The importance of the infrastructure of a production plant is assumed to be low and the general infrastructure dataset 'chemical plant, organics' is therefore used as an approximation. As this dataset is based on a production capacity of 50,000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg of produced chemical is added to the unit process of the respective chemical.

Appendix D Cradle-to-gate CC impact of VIP

Inventory table 9 shows the inventory of a 1m^2 of typical VIP with 800 nm aluminum cover. SimaPro 7.3.1 classroom version [45] was used to calculate the cradle-to-gate Climate change impact (ReCiPe 2008 (h)) and the cumulated energy demand (Ecoinvent v.2.0 1.06). For the calculations, a material density for the VIP core of 160 kg/m^3 was applied. This and all other data needed for the calculation was taken from Scönhardt (2003)[15].

Appendix E Heat from steam

The source of heat for the production of damp to purify ethanol for internal reuse is a fuel mix for the average steam production in the European chemical industry, according to Boustead et al. 1999 [60]. The energy demand for this heat is 2.75 MJ/kg steam which corresponds to an overall efficiency of 74%. The mix of energy sources that fill this demand is shown in Inventory table 10.

Inventory table 10: Gross energy in MJ required for producing on-site steam in percentage of total [60].

Fuel type	**Energy content of delivered fuel for 1 kg of steam Boustead 1999**
Coal	14.25%
Oil	20.97%
Gas	50%
Hydro electricity	0.81%
Nuclear electricity	1.34%
Lignite	<0.01 MJ
Biomass	<0.01 MJ
Hydrogen	9.14%
Recovered energy	3.50%
Unspecified	0.27%
Peat	<0.01