The utilization of participating gases and long-wave thermal radiation in a passive cooling skylight

Martin Fält

Doctor of Technology Thesis

Thermal and Flow Engineering Laboratory
Faculty of Science and Engineering
Åbo Akademi University

Åbo, Finland, 2016

The utilization of participating gases and long-wave thermal radiation in a passive cooling skylight

Martin Fält

Doctor of Technology Thesis
Thermal and Flow Engineering Laboratory
Faculty of Science and Engineering
Åbo Akademi University

Turku, Finland, 2016

Martin Fält

b. 1983

M. Sc. (2009) in chemical engineering, the area of specialization: process engineering and computer technology. From 2009 to 2013, researcher/Ph.D. candidate at the Laboratory of Thermal and Flow Engineering Laboratory at Åbo Akademi University. Since 2014, as a Senior Consultant Engineering at Elomatic.

Supervisor

Professor Ron Zevenhoven

Åbo Akademi University

Opponent and reviewer

Associate Professor Mika Järvinen

Department of Energy Technology

Aalto University

Reviewer

Dr. Eero Immonen

Turku University of Applied Sciences

ISBN 978-952-12-3431-6 (Printed edition)
ISBN 978-952-12-3432-3 (Digital edition)
Painosalama - Turku 2016

Preface

This work has been conducted at the Thermal and Flow Engineering Laboratory at Åbo Akademi University. The work has mainly been funded by the Foundation of Maj and Tor Nessling 2009-2012. Funding has also been provided by Erkki Paasikivi Foundation, the Åbo Akademi University Foundation, and by a scholarship awarded by the Rector at Åbo Akademi University.

The first idea to aim for a Ph.D. came out of initial discussions regarding my M.Sc. topic with my then future supervisor Professor Ron Zevenhoven. While my M.Sc. thesis was being finalized, during the spring of 2009, we started to think about the next step and discussed possible topics for my Ph.D. thesis. Before this, in 2007, Professor Ron Zevenhoven had given a lecture at the Keenan Symposium at Massachusetts Institute of Technology. The lecture discussed utilizing long-wave thermal radiation for power production. This lecture was followed by an M.Sc. thesis (by Motolani Sakeye) and articles on the subject were presented at the ECOS 2008 and 2009 conferences. These introduced the greenhouse gas CO_2 into the process of long-wave power production. This prior work secured sufficient funding for 2009-2012 to start a Ph.D. thesis work that studies the trapping and release of long-wave thermal radiation with greenhouse gases and the transformation of this effect into passive cooling or improved insulation.

The thesis is a continuation of the above-mentioned work. The idea of focusing on radiative cooling was introduced at the beginning of the work (noting that much more can be gained from passive cooling, avoiding the use of power for air conditioning and cooling, than from producing power) after which this was developed further. This development first took place in the form of theoretical studies where the cooling availability was evaluated using weather data and mathematical models. The evaluations went further on to computational fluid dynamics simulations and experiments (including several night-time tests of many hours) in an iterative process. The work consists of developing and analyzing different designs and material combinations.

Finally, I want to thank my Professor Ron Zevenhoven for his guidance in life, science, and this thesis. My co-authors Dr. Frank Pettersson, whom I wish to thank for opening the world of optimization, and Luis Pedro Gomes for a fresh point of view and his eagerness to tackle complicated ideas. Moreover, I have a big appreciation for the people at the Laboratory of Thermal and Flow Engineering where Alf Hermanson was always there to assist and teach about constructing rigs, measuring systems etc.; Professor Henrik Saxén and Vivéca Sundberg for "running the lab"; and then the rest of my colleagues and friends at the laboratory, Johan, Inês, HP, Hamid, Calle, XP, Martin and many others who transformed work into an adventure. I also want to thank my family and friends who have helped me along the way. And then lastly my wife Petra, and our son, with you life is.

Svensk sammanfattning

Motiveringen för denna avhandling var att studera hur växthuseffekten, som idag kontrollerar temperaturen på vår planet, kan komma till användning som ett redskap för framtida energibehov. Huvudsyftet med detta arbete var att identifiera och kvantifiera möjligheter att utnyttja en kontrollerad växthuseffekt i ett flerglasfönster.

Det sätt som så kallade deltagandegaser påverkar värmeöverföringen mellan rymden och jorden utnyttjas i detta arbete för att generera konsumentenergi eller för att sänka behovet av energi användningen. Avsikten är att styra värmestrålningsflödet från byggnader eller andra föremål på marknivå, mot himlen, med hjälp av gaser som absorberar och avger värmestrålning. Gasen är innesluten i ett takfönster där den verkar som en arbetsvätska i en värmeväxlare som "kopplar" rummet med himlen. Detta förutsätter att takfönstret är tillverkat av specialmaterial och att takfönstrets design lämpar sig för att användas i byggnader. Med hjälp av detta kan en kylning eller en isolerande effekt produceras för utrymmen belägna under takfönster. Detta innebär att himlen inte bara skall ses som en potentiell källa för energi i form av direkt solljus, men också som en reservoar för kylning. Denna kyleffekt erhålls genom värmestrålning mellan en radiator, som ligger på markytan, och kalla luftmassor som är belägna ovanför radiatorn.

Då det normala kylbehovet för småhus i Finland är ca 2 W/m^2, kan ett strålningskylt takfönster, så som testats i detta arbete, uppfylla kylbehovet för ett 50 m^2 rum. Då behovet av kylning växer i Finland, ger således strålningskylning ett användbart alternativ för att minska kylbehovet i en byggnad.

De årliga variationerna och den kumulativa frekvensfördelningen för olika radiatortemperaturer undersöktes. Dessa baserades på vädermätningar som anskaffats från det meteorologiska institutet. Från vädermätningar i Helsingfors, beräknades att en radiator som emitterar värmestrålning vid rumstemperatur kan avge ett värmeflöde på 100 W/m^2 under 70 % av tiden.

Strålningskylning och isoleringsprestanda för det föreslagna takfönstret utvärderades först för typiska sommar- och vinterförhållanden i Finland med hjälp av resistansnätverk och senare med simuleringar. Anledningen var att de radiativa och konvektiva värmeöverföringsnäten beskrevs som fysiskt mycket skilda processer och därför var resultaten otillräckliga. Avhandlingen presenterar resultat från simuleringar med programvaran COMSOL. Resultat från de första simuleringarna visade att en kylning på 117 W/m^2 kan uppnås med det föreslagna systemet vid vanliga Helsingfors sommarförhållanden med CO_2 som gasen i takfönster (jämfört med 15 W/m^2 vid användning av luft). Samma takfönster i isoleringsläge visade en överföring av endast 88 W/m^2 värme under samma förhållanden med CO_2. Detta kan jämföras med 19 W/m^2 vid användning av luft. Polyeten användes som fönstermaterial för att innesluta gasen i takfönstret.

En utveckling av takfönstrets strålnings resistansnätverksmodell presenterades. Denna modell tillät att våglängden delades in i fyra olika intervall. Med detta var det möjligt att jämföra strålningskylnings möjligheter för olika gaser. I de första resistansnätverken och simuleringarna hade gasernas absorptance inget våglängdsberoende. Därför utökades beräkningarna att vara våglängdsberoende. Den initiala gasen, CO_2, bekräftades att ge begränsade resultat under normalt omgivningstryck och en ökning av trycket ansågs olämpligt då detta skulle öka materialkostnaderna och minska transmittansen av fönstret. Ett alternativ för CO_2 behövdes. Gasen bör ha en hög transparens i det synliga våglängdsområdet och en hög absorptans i spektralområdet av det atmosfäriska fönstret (8-13 pm). Dessutom bedömdes gasernas hälso-, säkerhets- och miljöpåverkan.

Nya material infördes i en utvecklad version av takfönstret. Dessa material var pentafluoretan en fluorkolvätegas som blev ett alternativ för CO_2, och zinksulfid, som blev ett fönstermaterial som användes istället för polyeten. Zinksulfid som är transparent för både synligt ljus och långvågig värmestrålning. Utvecklingar av den mekaniska konstruktionen gjorde det möjligt för takfönstret att byggas i olika dimensioner. Detta uppnåddes genom att återdimensionera fönstret till en optimerad storlek och genom att sedan modularisera fönstret till ett persienntyps takfönster. Denna uppdaterade design optimerades för att producera för sommarbruk en maximerad kylning, vilket motsvarar en så stor som möjlig värmeöverföring genom fönstret; för vinterbruk maximeras isoleringen, vilket motsvarar att en så liten om möjlig värmeöverföring går genom fönstret. För gasen i ett radiativt kylt takfönster, krävs att strålningsbanan i fönstret är tillräckligt lång för att gasen skall kunna avge tillräckligt med värmestrålning. Gasens tjocklek måste också vara tillräckligt stor för att det å ena sidan avsedda konvektiva kylflödet skall äga rum medan å andra sidan för isolering tillräckligt liten för att hindra en märkbar konvektiv värmeöverföring.

Effekterna av luft, CO_2, och pentafluoretan studerades i en uppsättning av utomhus experiment. Dessa experiment visar att faktiska temperaturer som ligger under omgivningens temperatur kan nås med takfönstret. Beräkningsströmningsdynamiska simuleringar baserade på temperaturmätningar från dessa experiment påvisade att en styrbar kyleffekt 100 W/m^2 kan uppnås. Kyleffekten är i den nuvarande anordningen begränsad till natten på grund av tillströmningen av solljus under dagen.

Eftersom mängden av kylning som behövs för nedfrysning och luftkonditionering förväntas öka markant inom en snar framtid, kommer också mängden energi som krävs för dess produktion att öka. Med hjälp av strålningskylning behövs det mindre eller ingen extern energitillförsel.

Denna avhandling visar att takfönster som hittills har tillfört ljus och givit en känsla av rymd även kan användas för att aktivt minska byggnadens energianvändning för uppvärmning eller kylning. Under en klar natt kan den passiva kyleffekten 100 W/m^2 verkligen uppnås, men denna mängd är naturligtvis väderberoende.

Abstract

The motivation for this thesis was to study how the greenhouse effect, which controls the temperature of our planet, could be put to use for future energy needs. The main objective of this work was to identify and quantify the possibilities of utilizing a controlled greenhouse effect inside a multiple-glass window.

The way so-called participating gases influence the heat transfer between space and earth is here harnessed to generate consumer energy or lower the need for energy use. The intention is to control the radiative heat flow from ground level buildings or other objects to the sky by using a gas that absorb and emit thermal radiation. The gas is contained in a skylight where it acts as the working fluid in a heat exchanger that "connects" the room with the sky. This requires that the skylight is constructed from special materials and that the skylight design is suitable for building applications. Therefore, a cooling or an insulating effect can be produced to the space located below the skylight. This implies that the sky should not only be seen as a potential source of energy in the form of the direct sunlight but also as a low-temperature reservoir of cooling. The cooling effect is obtained through radiative heat exchange between a radiator, located on the surface of the earth, and cold air masses situated above this radiator.

As the cooling demand for residential houses in Finland is around 5 W/m^2, a radiative cooling skylight as tested in this work could fulfill the cooling demand of a 20 m^2 room. Moreover, the need for cooling is growing. Thus, radiative cooling provides a viable option to decrease the cooling demand of a building.

The annual variations and the cumulative frequency distribution for varying radiator temperatures were investigated. These were based on weather measurements procured by the Finnish Meteorological Institute. Based on the weather measurements in Helsinki, a radiator working at room temperature can emit a heat flow of 100 W/m^2 during 70% of the time.

The radiative cooling and insulating performance for the proposed skylight was first assessed for typical summer and winter conditions in Finland using resistance networks and, later, with simulations. The reason for this was that the radiative and convective heat transfer networks described physically very different processes, and therefore results were inadequate. The thesis presents results from simulation work done with the modeling software COMSOL. Results from the first simulations showed that 117 W/m^2 of cooling can be achieved with the proposed system at average summer conditions in Helsinki using CO_2 as the gas in the skylight (compared to 15 W/m^2 when using air). The same skylight in insulation mode showed transfers of only 88 W/m^2 heat under the same conditions with CO_2 (compared to 19 W/m^2 when using air). Polyethylene was used as the window material for containing the gas inside the skylight.

A further evolvement of the skylights radiative resistance network model was presented. This updated model allowed the wavelength to be divided into four different band sections. By this, it was possible to compare the radiative cooling possibilities of various gases. In the first resistance networks and simulations, the gases' absorptance had no wavelength dependency. Therefore, the calculations were expanded to include wavelength dependency. The initial gas, CO_2, was confirmed to give limited results at ambient pressures, and an increase in pressure would increase material costs and decrease the transmittance of the window used. The gas should have a high transparency in the visible wavelength range, and a high absorptance in the atmospheric window spectral range (8 – 13 μm). Furthermore the gases' health, safety, and environmental impact were assessed.

New materials studied were pentafluoroethane, a hydrofluorocarbon gas, and Zinc sulfide as window material. Zinc sulfide is transparent to both visible light and long-wave heat radiation. Changes to the mechanical design enable the skylight to be built to different dimensions by re-dimensioning the window to an optimal size, and then modularizing it to a shutter-type skylight. This new design was optimized for both summer and winter use. When in summer mode, the skylight's cooling capacity is maximized, corresponding to as large a heat transfer through the skylight as possible. While for winter use, the insulation property is maximized, corresponding to a minimal amount of heat transferred through the skylight. For the radiatively cooled skylight, the gas thickness between the enclosing windows must be long enough so that the gas can emit enough heat radiation. The gas thickness must also be long enough so that the designed convective cooling will take place while, on the other hand, when in insulating mode small enough to prevent a significant convective heat transfer.

The effects of air, CO_2, and pentafluoroethane were studied in a set of outdoor experiments under different conditions, showing that indeed temperatures below the ambient can be reached in the skylight. Computational fluid dynamics simulations based on temperature measurements from these experiments imply that a controllable cooling effect of 100 W/m^2 can be attained with the designed device during summer. The cooling effect in the current setup is limited to nighttime due to the influx of sunlight during the day.

Since the amount of cooling needed for refrigeration and air conditioning is expected to increase significantly in the near future, so will the amount of energy required to produce it. However, by radiative cooling, less or no external energy input is needed for this.

This thesis concludes that skylights which have so far brought light and a sensation of space, could be used to actively decrease a building's energy use for heating or cooling. During a clear night, a passive cooling effect of 100 W/m^2 is certainly achievable, but the amount of cooling is, of course, weather dependent.

Contribution of the author and list of publications

This text functions as an introduction to the six articles presented at the end of this thesis. The introduction will place the work in a wider framework and then crystallize the initial idea, describe how it has evolved over the past years, and how it could continue into the future.

The author of this thesis is the main contributor in five of the below-listed publications and the second author in one of them.

Paper I, II: The author established the mathematical model. The author interpreted the results, wrote the first draft of the manuscript and finalized it with his supervisor.

Paper III, V: The author created the required geometries selected the specific physical models and boundary conditions for the computational fluid dynamics simulations. The author interpreted the results, wrote the first draft of the manuscript and finalized it with his supervisor.

Paper IV: The author worked together with his co-authors to establish the mathematical model, wrote parts of the paper and helped finalizing the manuscript.

Paper VI: The author planned and constructed the prototype, then planned and performed the experiments and the computational fluid dynamics simulations. The author interpreted the results, wrote the first draft of the manuscript and finalized it with his supervisor.

The list has been arranged in chronological order, and all references to these will hereafter be made by their respective Roman numerical.

I. **Radiative cooling in Northern Europe using a skylight**
M. Fält, R. Zevenhoven
Proc. of ES2010 / ASME 2010 4th International Conference on Energy Sustainability, Phoenix (AZ), May 17-22, 2010, paper (peer-reviewed) ES2010-90192
Also in: J. of Energy and Power Engineering (ISSN 1934-8975) 5 (2011) 692-702

II. **Radiative cooling in Northern Europe for the production of freezer temperatures**
M. Fält, R. Zevenhoven
Proc. of ECOS´2010, 23rd Int. Conf. on Efficiency, Cost, Optimisation, Simulation and Environmental Impact of Energy Systems, Volume III, (ISBN 1456303147), 413-419, Lausanne, Switzerland, June 14-17, 2010, paper (peer-reviewed) 208

III. **Combining the radiative, conductive and convective heat flows in and around a skylight**
M. Fält, R. Zevenhoven

Proc. of World Renewable Energy Congress 2011 (WREC 2011) 8-11 May 2011, Linköping, Sweden, paper (peer-reviewed) 0338
Also in: J. of Energy and Power Engineering (ISSN 1934-8975) 6 (2012) 1423-1428

IV. **Thermal radiation heat transfer: including wavelength dependencies into modeling**
R. Zevenhoven, M. Fält, L.P Gomes
Int. J. Therm. Sci. (ISSN 1290-0729) 86 (2014) 189-197
Also in: Proc. of CPOTE 2012 3rd International Conference on Contemporary Problems of Thermal Engineering, 18-20 Sept 2012, Gliwice, Poland, paper (peer-reviewed) 78

V. **Modified Predator-Prey Algorithm approach to designing a cooling or insulating skylight**
M. Fält, F. Pettersson R. Zevenhoven
Applied Soft Computing (ISSN 1568-4946) (2016) *Submitted*
Also in: Proc. of Clima 2013. 11th REHVA World Congress and 8th International Conference on Indoor Air Quality, Ventilation and Energy Conservation in Buildings., 16-19 June 2013, Prague, Czech Republic, paper (peer-reviewed) 1060 with title Optimizing a design for a cooling or isolating skylight

VI. **Experimentation and modeling of an active skylight**
M. Fält, R. Zevenhoven
In Proc. of ECOS´2015, 28th Int. Conf. on Efficiency, Cost, Optimisation, Simulation and Environmental Impact of Energy Systems, Pau, France, June 30-July 3, 2015, paper (peer-reviewed) 52533

Related publications

Besides the six papers listed above two unreviewed and two peer-reviewed paper were published.

VII. **Heat Flow control and energy recovery using CO_2 in double glass arrangements**
R. Zevenhoven, M. Fält
In Proc. of ES2010 / ASME 2010 4h Int. Conf. on Energy Sustainability, Phoenix (AZ), May 17-22, 2010, paper (peer-reviewed) ES2010-90189

VIII. **Modeling a cooling skylight**
M. Fält, R. Zevenhoven
In Proc. of the 2011 COMSOL Conference in Boston, October 13-15, 2011
Available: https://www.comsol.com/paper/modeling-a-cooling-skylight-12047

IX. **Passive cooling against the (night) sky**
R. Zevenhoven, M. Fält
In Proc. of the 2013 Mechanical Engineering Annual Conference on Sustainable Research and Innovation, Jomo Kenyatta Univ. of Agriculture and Technology, April 24-26, 2013, Kenya, Vol.5, p. 322-325 (peer-reviewed)
Also in: Journal of Sustainable Research in Engineering, (ISSN 2409-1243) 1, 49-54, 2014 (open source)
Available: www.jkuat-sri.com/ojs/index.php/proceedings/article /download/49/38

X. **Radiative Cooling from the sky – ongoing research points to significant energy savings**
M. Fält
Top Engineer The Elomatic Magazine 2, 24-27, 2014
Available: http://www.elomatic.com/en/assets/files/publications/Elomatic_Top _Engineer_2014-2.pdf

List of abbreviations and symbols

C_2H_4	Ethylene
C_2H_4O	Ethylene oxide
CFD	Computational Fluid Dynamics
CO_2	Carbon dioxide
EEH	Emissive Energy Harvester
EPA	Environmental Protection Agency
GA	Genetic Algorithm
GWP	Global Warming Potential
HFC	Hydrofluorocarbon
HFC-125	Pentafluoroethane
HFC-1447fz	3,3,4,4,5,5,5-Heptafluoro-1-pentene
LDPE	Low-density polyethylene
NH_3	Ammonia
PCM	Phase Conversion Material
PE	Polyethylene
PV	Photovoltaic
Q	Heat flow
R-12	Dichlorodifluoromethane
SF_6	Sulfur hexafluoride
SO_2	Sulfur dioxide
ZnS	Zinc sulfide
ZnSe	Zinc selenium
ÅAU	Åbo Akademi University
ε	Emissivity
σ	Stefan-Boltzmann constant
τ	Transmittance

Table of Contents

1. Introduction

A quest for novel energy sources is today raging stronger than ever. The goal is to satisfy the growing population of the world. Concurrently, a global environmental catastrophe has been inherited from our previous energy exploitations. A simple solution in the form of a new energy source is most likely never to be found. To ensure a cleaner future for the coming generations a renaissance must be embraced and a set of tools be discovered that can be used with small or negligible negative impact on the environment. The motivation for this thesis was to study how the greenhouse effect, which heats our planet, could be put to use as a tool for future energy needs [1].

Without greenhouse gases, the earth would be a colder place than it is today. Gases in the atmosphere are transparent to the shortwave (SW) sunlight (<4 μm) radiation that heats our planet, but these gases absorb and reradiate the heat that is emitted from the earth's surface at longer wavelengths (LW) (>4 μm). This mechanism can be compared with a greenhouse where the window glass takes the function of these gases. SW sunlight is let into the greenhouse, but the heat (as LW thermal radiation) cannot be transmitted through the windows; hence the name greenhouse effect.

Even though the energy amount emitted by the earth equals the amount of energy absorbed from the sun, is it difficult to convert the emitted heat flow into work, as the temperature difference between the emitting earth and the absorbing skies is small. The maximum conversion of heat to power is defined by the second law of thermodynamics. The second law stipulates the generated amount of entropy. This generated entropy amount is higher when the temperature differences between the objects that exchange heat are small. The temperature of the earth is around 290 K, and the figurative temperature of the sky, which the earth's surface exchanges radiative heat directly with, is around 270 K, a temperature difference relatively small when compared to the temperature difference between the sun and the earth. The challenge is that the thermal efficiency of a possible power conversion of the LW heat radiation exchanged between the sky and the earth's surface is considerably lower than that for heat radiation from the sun to earth. In other words, the possible extractable amount of work obtainable from this LW heat flow is minor. However, by creating a controlled greenhouse effect inside a skylight, a significant cooling or an effective insulation effect can be created. A variable effect is obtained through controlling the passive LW radiative heat exchange between a radiator located on the surface of the earth and cold air masses situated above it.

The need for cooling is growing [2-4]. Production of cooling power using renewable energy technology, such as photovoltaic (PV) panels and a traditional compressor cooling cycle, is possible but expensive. Passive radiative cooling could be a beneficial alternative.

The effects of radiative cooling have been known for ages, as already used in ancient Persia [5] and later in India [6] for the production of ice. Since then, various radiative cooling systems have been studied to provide cooling for buildings. Today commercial products, such as paints and roofs, already exist that utilize this cooling effect [7]. Most studied radiative cooling systems are of the radiator type, as presented in [8, 9]. In these cases, even temperatures below the ambient are obtainable by lowering the heat input from the surroundings. Convection covers that are made of materials transparent to LW heat radiation are used. Materials commonly used in studies are polyethylene (PE), PE mesh [10] and zinc sulfide (ZnS) [11]. However, further developments are needed to achieve a higher market penetration. Some studies have also been done on the radiative cooling of greenhouse gases [12-14]. However, greenhouse gases contained by windows have been limited to studies where the heat flow through the window is minimized [15-18].

The main objective of this work was to identify and quantify the possibilities of utilizing a controlled greenhouse effect inside a window.

Paper I is a continuation of the work previously done at Åbo Akademi University (ÅAU). This work presented the idea of using a double glazed window filled with carbon dioxide (CO_2) to harness power, cooling, or to recover heat from the thermal radiative flow between the sky and ground, or building. Furthermore, this work presented preliminary radiative calculations which were later developed to take into account the conductive and convective heat transfer effects. [1, 19-21].

Paper I focuses on the cooling option of buildings as assessed, as earlier stated, to be the best way further. It continues to calculate the heat transfer through a skylight window filled with (CO_2). The major difference of Paper I compared with the earlier work is the introduction of the controllable skylight concept which alters between a cooling and an insulation mode. Paper I continues to use the resistance network method for the calculation as it was also used by previous work. It presents a first estimate of the radiative cooling and insulating performance for the proposed skylight, as presented in Figure 1, during typical summer and winter conditions in Finland. Paper I offers options of what materials the skylight could be constructed of. However, improvements are needed to combine heat radiation with convective and conductive heat transfer.

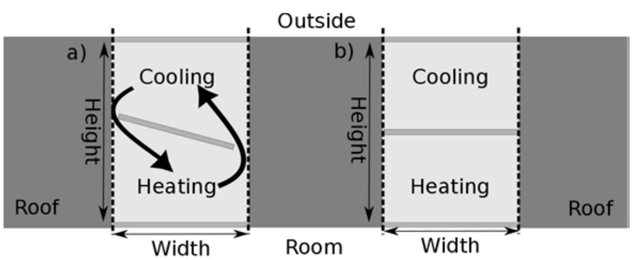

Figure 1. Initial skylight design in cooling mode a) and in insulating mode b) (Paper V)

Paper II focuses on estimating the sky's potential use as a cooling source in northern Europe. The work presents the annual variations and the cumulative frequency distribution at varying radiator temperatures. Here, measurement data procured by the Finnish Meteorological Institute was used. This paper shows that the sky not only "supplies" energy from the sun, but also presents a thermal reservoir that can be exploited for cooling.

As Paper I describes the radiative and convective heat transfer methods as separate events, there was a need to describe the heat transfer inside the skylight in a single model. The reason for this was that the coupling of the two models had been inadequate and a single model could thus better describe how the skylight functions and how its design could be improved. This was accomplished in Paper III which presents results from work done with the modeling software COMSOL 4.1. Results from the simulations showed that 117 W/m^2 of cooling can be achieved with the proposed system at average summer conditions in Helsinki using CO_2 as the gas in the skylight (compared to 15 W/m^2 when using air). The same skylight in insulation mode showed only a transfer of 88 W/m^2 heat under the same conditions with CO_2 (compared to 19 W/m^2 when using air). Paper III, therefore, showed that the skylight could be modeled using the Multiphysics tool COMSOL verifying the skylights' cooling and insulation capabilities presented in Paper I.

A problem with the three first papers is that the wavelength dependence of radiative heat transfer was not included in the models. The calculations of thermal radiation in the first three papers were done as gray calculations; that is the wavelength dependent properties, such as emittance and absorptance, were constant for all wavelengths. Therefore, Paper IV expands the calculations to include wavelength dependency. This reliance was obtained by further developing the resistance network created in Paper I by distinguishing between SW radiation and three "bands" of LW radiation.

Paper V improves the design of the skylight presented in Paper I by introducing new materials and a new mechanical design. These new materials are pentafluoroethane (HFC-125), a hydrofluorocarbon (HFC) gas, and ZnS, a window material. The changes to the mechanical design enable the skylight to be built to different dimensions by re-dimensioning the window to an optimal size, and then modularizing it to a shutter-type skylight, as presented in Figure 2. This new design also allows the assembly of different sized skylights without a loss in either cooling or insulating properties. This new design was optimized to produce: for summer use a cooling that is maximized, corresponding to as large heat transfer as possible through the window, and for winter use, the insulation property is maximized, corresponding to a minimal amount of heat transfer.

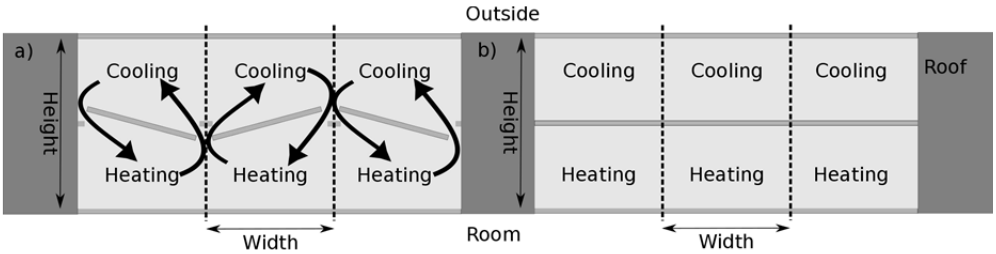

Figure 2. Developed skylight design in cooling mode a) and in insulating mode b) (Paper V)

Paper VI describes the experimental work and reports results that validate the previous modeling work on the cooling and insulation possibilities of a skylight. The top and bottom window of the skylight were built using two ZnS windows. In the center of the skylight model, a third adjustable window of acrylic plastic can be placed to control the flow. This skylight was then mounted on top of a temperature controlled box, simulating a room. The effects of air, CO_2, and HFC-125 were studied in a set of outdoor experiments under different conditions, showing that indeed temperatures below the ambient can be reached in the skylight.

2. Cooling options using heat radiation

Today 10-15% of the world's electricity is used for cooling, and this percentage is increasing; for instance, the cooling market in Europe (EU27) is today around 330 TWh per year, by 2030 this market is expected to grow to a cooling demand of 490 TWh per year [2-4]. This electricity is mainly generated from carbon-based fuels and thus contributes to climate change via the greenhouse effect. Alternative cooling methods exist, and the development of technology that is based on passive cooling is presented in this thesis.

2.1. Radiative cooling

Radiative cooling is the mechanism that, in fact, cools our planet. All the solar radiation that is absorbed by our globe is eventually re-emitted by heat radiation to space. If this were not the case, the globe would heat indefinitely. Figure 3 shows average heat flows in the earth-atmosphere energy balance. Of the incoming 341 W/m², 78 W/m² is absorbed by the atmosphere and 161 W/m² is absorbed by the surface. All this heat is later radiated away from earth by radiative cooling, as shown in Figure 3. The LW radiative cooling is independent of SW heat radiation from the sun. However, as the heat flow from the sun during daytime is significantly larger than the radiative cooling effect, radiative cooling will be significant especially during the night.

Radiative cooling is obtained by a radiator emitting its heat to the cold skies above. The heat transfer from the radiator to the sky can be estimated by calculating the radiative heat transfer between two parallel plates where the opening in between is filled with air.

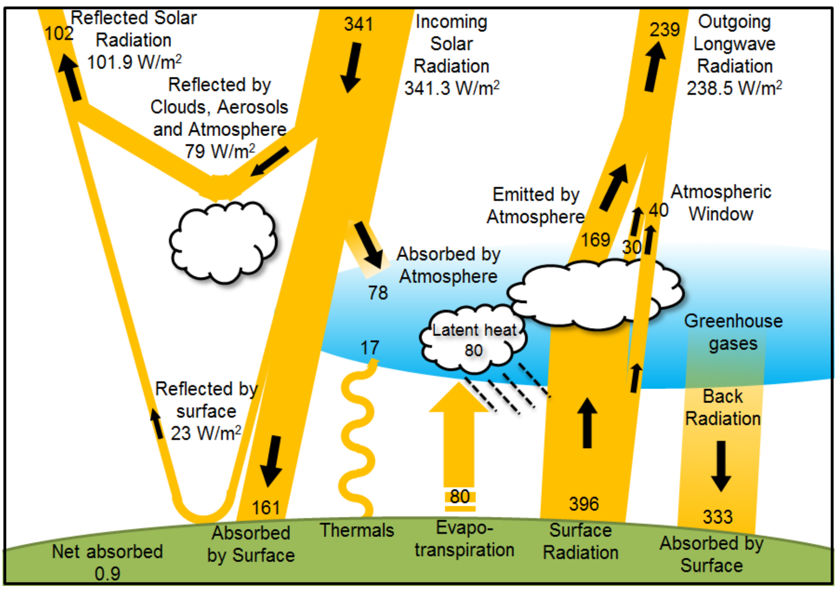

Figure 3. Earth-atmosphere energy balance based on [22]

A simple estimation is presented in Figure 4. In the equation, ε_{rad} and ε_{sky} are the emittances of the radiator and the sky, respectively. The transmittance of the atmosphere is given by τ_{atm}, and σ is the Stefan-Boltzmann constant, and T gives temperatures in K.

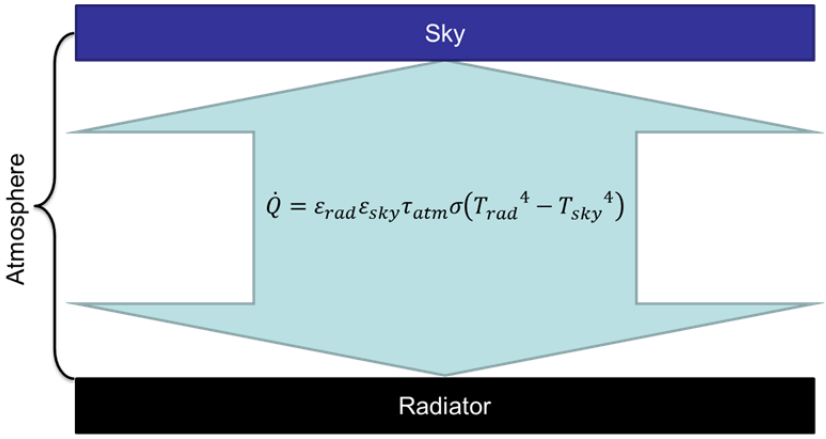

Figure 4. Radiative cooling – gray gas assumption

This radiative cooling, is thus, dependent on the temperature of the radiator and the sky. The temperature of a radiator can be easily measured. However, the emitting temperature of the sky is more difficult to measure. Figure 5 shows how the temperature of the sky varies with altitude, thus, with what height is the heat radiative exchange or at what altitude should the temperature be measured? An important factor is also the weather and the changes it brings to the water vapor content, not to mention cloud formation [23], which brings down the height of the "sky" with which heat is exchanged.

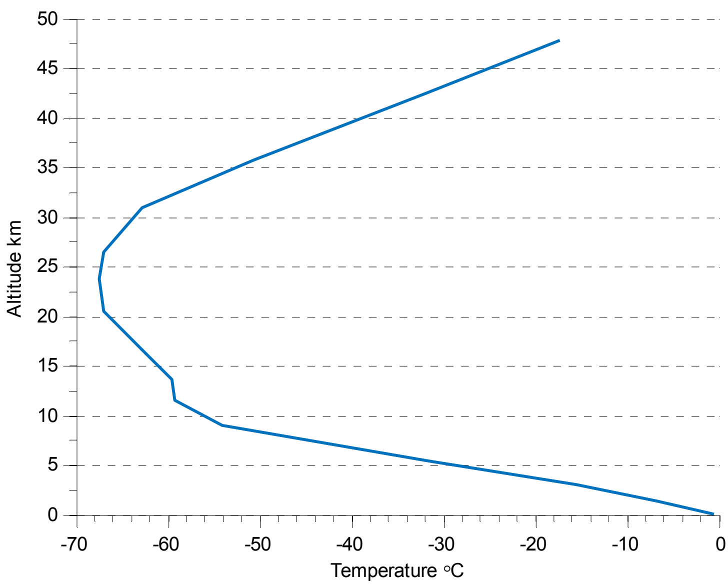

Figure 5. January average temperature profile above Iceland. Data from 0 to about 24 km height based on radiosonde measurements at Keflavik station, from 1965 to 1992. Data between 24 and about 48 km are extrapolated measurements from National Meteorological Center for a location at 64.48N and 208W, from 1979 to 1995 [24]

Different methods have been developed to derive the sky temperature from easily measured weather data such as ambient temperature and relative humidity. [25] However, an advanced alternative is to measure the downward atmospheric long-wave radiation within the 4.5-42 μm range using a pyrgeometer, as presented in Figure 6, and from there calculate the heat transfer between a radiator and the sky.

Figure 6. Picture of used pyrgeometer

Different gases absorb and emit heat radiation in various parts of the spectrum. The absorption spectrums of the main atmospheric gases are presented in the sub-pictures of Figure 7. These different spectrums do, however, leave a gap for the upgoing thermal radiation in the 8-13 μm wavelength range, as presented in Figure 3 and Figure 7. This interval is also called the "atmospheric window", and it can be used for radiative cooling purposes. [26]

Radiative cooling is a passive cooling method that thermally "connects" a hot object located e.g. on top of a building to cold sky temperature through heat radiation. Different technologies have been developed to bring as much heat to the radiator as possible and then to cool it by radiating the heat to the sky. Radiative cooling studies in general have been aimed at cooling buildings where the final medium to be cooled is the air inside the building. Most of the radiative coolers use a solid radiator that is to be cooled. This radiator can then directly cool the ingoing air to the building or indirectly by cooling a water flow that, in turn, cools the air inside the building. [27] Radiative cooling works best during the night when not overwhelmed by the incoming heat radiation from the sun [8]. However, recent studies have also shown that radiative cooling can be used during the day. The problem for daytime cooling is the influx of sunlight that must be reflected from the radiator. This reflection can be created by different films [11, 28]. Recent studies on radiative cooling have focused on optimizing the properties of the radiator using photonic planar and microstructured photonic devices to engineer maximal emissive spectrums in the atmospheric window and a maximal reflectance spectrum elsewhere. A planar photonic device has demonstrated radiative cooling 2°C below the ambient under an SW influx of 1060 W/m^2. [29, 30]

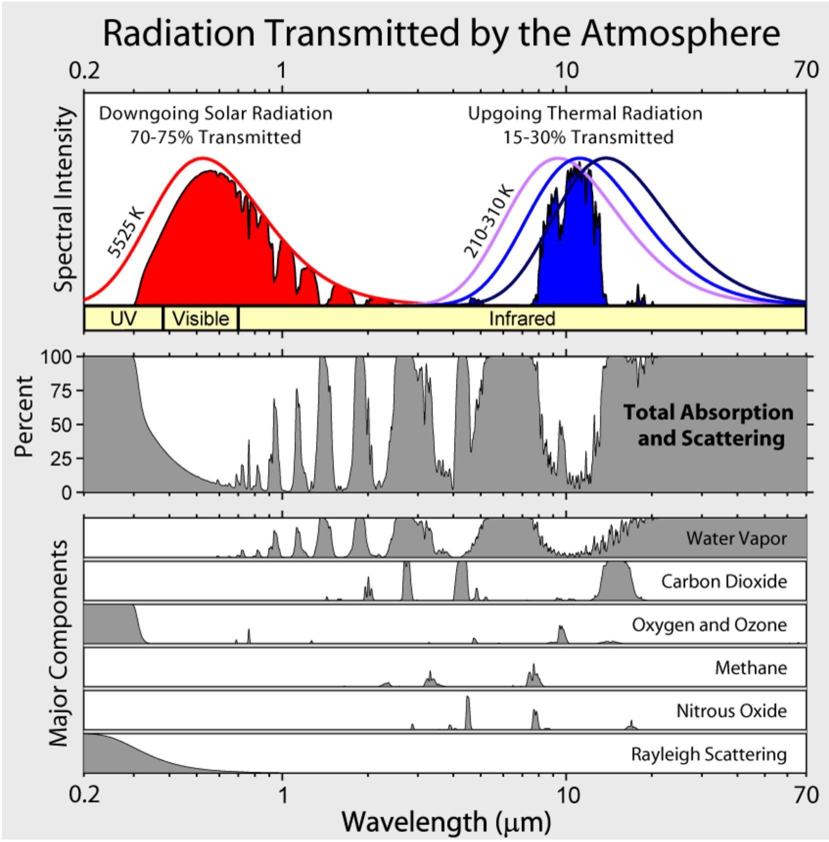

Figure 7. Radiation transmitted by the atmosphere [26]

The possibility of using long-wave heat radiation for power production has also been theoretically assessed. Work (electricity) can be obtained from a radiator that emits thermal radiation, thus called the Emissive Energy Harvester (EEH). There are two ways to produce power from an EEH where the first method works as a thermal power plant and the second type as a PV-cell. The conclusion was that a few W/m^2 could be attainable under normal weather conditions. [31]

2.2. Absorbing gases for thermal insulation and cooling

Studies of gases other than air, in the enclosed space between the double-glazing of windows, have shown to lower the heat transfer through windows. The main idea is to insert gases with lower conductive and convective properties than air and, thus, decrease heat conduction through the window. Windows containing gases like argon and krypton or a mixture of these are already commonly found on the market. However, since heat transfer through conduction is not the only way of heat transfer through windows, other gases could also be taken into account. Gases that absorb and emit thermal radiation, here called participating gases, could be considered. One of the first notions of this option was made in 1982 [32], but no calculations were made as it was stated as being too complicated. The gases that were then considered had lower thermal conductive properties than air. The gases mentioned were CO_2, sulfur dioxide (SO_2), dichlorodifluoromethane (R-12), and sulfur hexafluoride (SF_6).

Participating gases have also been considered for passive cooling purposes. The gases that were studied were ethylene (C_2H_4), ethylene oxide (C_2H_4O), ammonia (NH_3) and mixtures of hydrocarbons. During experimentations, the gases were circulated through a test rig that enclosed the gas. The rig consisted of a polystyrene box laminated with an aluminum foil and polyethylene films that covered the experimental panel. The films transmitted heat radiation in the band of the atmospheric window, and the gas in turn was selected to have high emitting properties in this same band. The radiative heat transfer calculations were made as a function of the angle of incidence and wavelength. NH_3 was reported to give the highest cooling power at small gas paths ("thicknesses"), and a 50% − 50% mixture of C_2H_4 and C_2H_4O was found to give best results at higher gas thicknesses. It was concluded that no "best gas" exists and that the gas selection is determined by the needed cooling power and required decrease in temperature. It was found that an absorbing gas could diminish the radiative heat transfer taking place in a double glassed window. A conceptual model was presented that took the spectrum dependency into account but did not calculate the conductive or the convective heat transfer. Around sixteen individual gases were tested and calculated through; including mixed gases to obtain a wider coverage of the spectrum required. CO_2 was considered to be transparent for the intended purpose. A combination of gases was regarded as a result of an optimization, but no discussion was made of the optimization. [14, 33, 34]

Participating gases between double windows for increased thermal insulation is also discussed in [16]. The article provides a theoretical model that allows for calculating both the radiative and the conductive heat transfer; however, it did not take into account convection inside the window. The calculated results are then compared to earlier experimental work and to results from a simulation program called WINDOW 3.1. The model is in agreement with both the experimental results and the results from the simulation results. The conclusion of the article was that participating gases should only be used in cases where low-emissivity coatings cannot be used and where the length ("path") of the gas enclosure is small enough to prevent convective heat transfer. Since low-emitting coatings are much more efficient at decreasing radiative heat transfer and a combination of an infrared (IR) absorbing gas, and low-emitting coatings counteract with each other, the heat exchange is greater for the case with an IR-absorbing gas than with air. Convection was not taken into account in the conceptual model (although it is important for greater gas lengths where convective heat transfer becomes dominant) because most of the considered IR-absorbing gases have lower kinematic viscosity than air. (An exception to this is NH_3 that has about the same viscosity as air.) Another point made in [16] is that CO_2 lacks noticeable radiative properties.

The last work that needs mentioning here is by a research group from Brazil that wrote three articles on this subject. The first article [35] presents a model for radiative, conductive, and convective heat transfer where the radiation is wavelength dependent. The studied gases are HFCs-SF6, CFCs-SF6 and air. The following two articles compare the performance of an IR-absorbing gas filled window to a Phase Conversion Material (PCM) filled window [18] and a naturally ventilated window [15], respectively. In both articles three gas mixtures were used, the first consisting of HFC-32, HFC-134a, HFC-143a, and SF6, the second consisting of CFC-12,CFC-13, CFC-14 and SF6 the final mixture consisting of air. All of the mixed refrigerants are today forbidden, being phased out or flammable, thus inaduaquate for use in windows.

3. Radiative cooling using the window concept

Studies demonstrating radiative cooling with participating gases have been done since the 1980s. [13, 17, 33] The possibilities of using participating gases for increasing the insulating properties of a window were also studied. [17] The idea of Paper I was to develop a triple window skylight that could both cool and insulate the space below it. The author is not aware of previous work that has investigated or exploited the cooling effect of a skylight filled with a participating gas.

By using a double-glazed window with a greenhouse gas filling the inter-glazing space, it is possible to control the radiative heat flux from a building to the sky and ambient surroundings. This control between insulation and cooling is created by a gas and a third middle window. The middle window divides the skylight into two sections, an upper and a lower. The upper section is cooled by radiative cooling, and the lower window section receives heat from the room located below it. A suitable gas needs to have a high emittance in the wavelength interval of the atmospheric window. As a result, the gas radiates heat to air masses situated above the skylight at temperatures well below the ambient. The gas then acts as the working fluid in a heat exchanger that "connects" the room with the sky. This connection can be controlled by moving the center window, thus connecting or separating the radiatively cooled upper compartment with/from the lower compartment heated by the room depending on the need for either cooling or insulation.

In the following three subchapters, the cooling skylight material selection and function are discussed.

3.1. Effect of window material

The proposed skylight window properties can be divided into two distinct groups. Firstly, the proposed skylight should fulfill the same task as a normal skylight. Secondly, the material should enable radiative cooling via the skylight.

The window material's primary purpose is to separate the outside weather from affecting the inside climate. A skylight should operate and last for decades, which limits what material the skylight could be built of. The window material should be mechanically strong enough to withstand strong winds, and debris blown by the wind. Furthermore, the skylight should be robust enough to sustain mechanical stress from for example birds, snow, and even people. Other weather phenomena that should be assessed are sunlight and rain. The skylight´s window material should not be soluble in rainwater nor should it react, or deteriorate, when exposed to sunlight.

During the process of this thesis work, different window materials have been evaluated. Initially, an experimental rig was designed that would have used zinc selenium (ZnSe) as the window material. However, as the price was considered too high, it was decided that other possibilities should be studied. After a small literature search, it was found that a thin sheet of PE could be used at a much lower cost. A PE-film is introduced in Paper I for which calculations were made with the assumption that a PE would be used as the window material. As an increase in gas pressure increases the absorptance of the gas, it was studied in Paper I. An increase in pressure requires an increase in window thickness to contain the gas; however this, in turn, decreases the transmittance of the window according to Figure 8. As shown in Figure 8, the problem with the PE-film is that it needs to be thin to be transparent while very little pressurization is allowed. This became evident during preliminary experiments, for Paper VIII, where the PE-sheet was found to be prone to fracture.

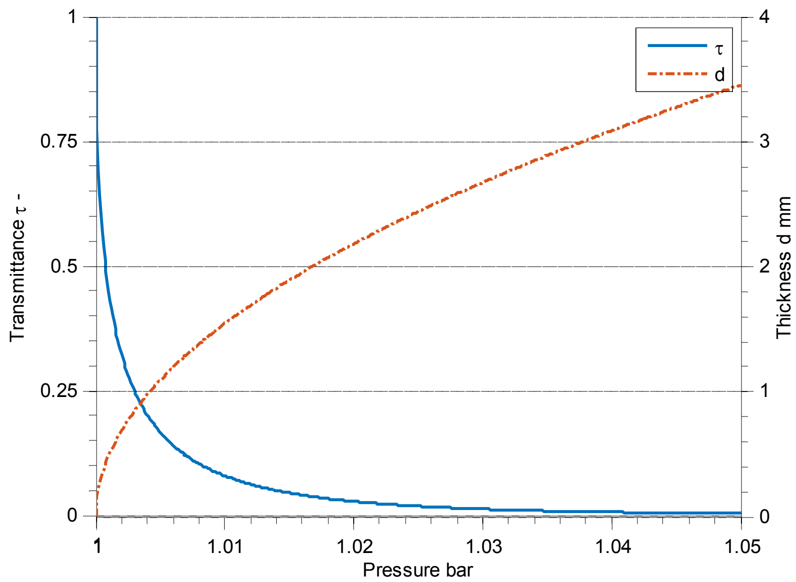

Figure 8. Transmittance τ and thickness d of an HDPE window at increasing pressures (Paper I)

Further studies indicated [36] that ZnS would be a suitable window material, despite its higher cost. Thus, the skylight simulated in Paper V and the experimental rig constructed for Paper VI consist of two windows made of ZnS, which is transparent to both visible light and long-wave heat radiation, as illustrated in Figure 9.

In the simulations in Paper V and in the experiments and simulations presented in Paper VI both the upper and lower windows were made of ZnS, transparent for LW heat radiation. Furthermore, the material should be mechanically strong to contain the gas inside the intended cooling skylight. This also implies that the window material should be strong enough to sustain pressure variations due to temperature changes. The primary purpose of a skylight is to bring in light to a space. Thus, the window material should be transparent to SW heat radiation. To accomplish the proposed radiative cooling of the greenhouse gas the outer windows must be transparent in the range of the atmospheric window. The third, middle window is only transparent to visible light and thus works as an LW radiative shield that prevents the room from being directly cooled by radiative cooling.

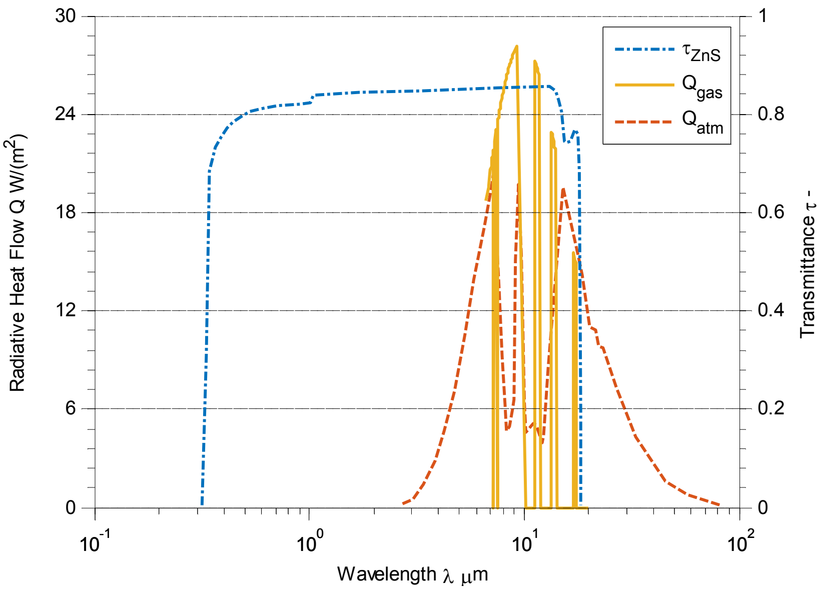

Figure 9. Transmittance τ and thickness d of a ZnS window (Paper VI)

As radiative cooling is not always needed or attainable, the skylight has been designed to make the heat flow through it controllable. This control is accomplished by the middle window. This middle window in conjunction with the greenhouse gas prevents the direct radiative cooling via the skylight. Therefore, the middle window must be opaque for LW radiation while being transparent in the visible light range. As the central window controls the convective heat flow inside the skylight, its dimensions have an impact on its heat transfer properties. The dimensions of the middle window and the height of the skylight were studied and optimized for different cooling and insulation requirements, as reported in Paper V. The middle window used in the experiments presented in Paper VI was made of an easily worked material, namely acrylic glass.

3.2. Effect of gas

The gas functions as the heart of the process that controls the heat flow. Thus, its properties play a central role for the cooling skylight. When selecting a gas, three different sets of material properties should be considered. The first set of properties affects the function of the skylight; the second set considers the health and safety regulations regarding possible leakages to the immediate vicinity of the window, and the final set considers the effect of the gas effect on the environment in general.

Of the first set material properties, the most critical are the radiative heat transfer and the convective properties of the gas. The gas should have a high transparency in the visible wavelength range, and a high absorptance in the atmospheric window spectral range. For the radiatively cooled skylight gas, it is necessary that the radiative path in the gas is long enough for it to be able to emit enough heat radiation. The gas thickness must also be large enough for the designed convective cooling flow to take place, while on the other hand, for insulation it must be small enough to hinder convective heat transfer. The viscosity of the gas should be as low as possible, so the gas can flow as easily as possible between the different sections, and therefore, the (radiative) natural convective heat transfer is maximized. The viscosity should, however, be optimized so that the gas length in the upper compartment is long enough so that it can be cooled by radiative cooling but small enough so that the convective heat transfer will not take place when the skylight is in insulating mode, while convective heat transfer will occur when in cooling mode. The gas should have low heat conductivity, as the conductive properties of the gas affect the insulating properties of the skylight. The gas should, moreover, have a high thermal capacity since the skylight is designed to function as the fluid in a heat exchanger, as the heat transfer medium. The gases boiling point should also be well below the minimal temperature that can occur.

The second set: the health and safety regulations regarding possible leakages to the immediate vicinity. As the gas is intended to be used in a window, it matters that the window will not put the building's inhabitants at a risk. The gas cannot be toxic or flammable. It should also be considered, whether many skylights would be installed at the same location, as the gas could escape into the air in the room below it and, thus, risk causing suffocation (asphyxiation) or nausea.

Final set: the gases' effect on the environment in general. Gas properties regarding the final set consider the gases' properties regarding the global warming potential (GWP) and ozone depletion. Gases that are considered harmful to the ozone are forbidden or are being phased out; the same holds for gases such as sulfur hexafluoride (SF_6) that possess a high GWP. Therefore, the gas considered for the skylight should have a low GWP and no effect on the ozone layer.

The first gas that was studied was CO_2. The effect of increasing gas pressure of CO_2 to widen and consequently enhance the absorptance of the gas was studied in Paper I. The problem was that an increase in pressure leads to a decrease in the transmittance of the window due to the need of a thicker window to contain the pressurized gas. Thus, this was abandoned in further studies. The performance of CO_2 was studied further in Papers III, IV and VI. As CO_2 was not performing as expected, an alternative gas was considered necessary. To address this, the list kept by the Agency of Environmental Protection (EPA) of gases that possess a significant GWP was used. [37] The gas preferred for the skylight should have the strongest GWP per year (which means the fastest loss of GWP per year when subjected to the ambient environment). From this, HFC-125 stood out as being the most suitable for use in the cooling skylight concept.

More details are given in Paper I-VI

3.3. Experiments and simulations

During the progress of the thesis, different materials, calculation models and experiments have been considered and performed. The starting point of the thesis leaned on prior studies at ÅAU that had studied the possibility of using the greenhouse gas CO_2. These studies evaluated the radiative heat transfer through windows with calculations made with the resistance network method [19]. Therefore, it was decided that the calculations in Paper I would continue to use the heat transfer network models and CO_2 as the gas.

The resistance networks presented in Figure 10 show the networks that were used in Paper I to assess the cooling and insulating potential of a controllable skylight filled with a participating gas. The radiation calculations were performed with the assumption that the gases' absorptance had no wavelength dependency. The difference to prior studies was that the paper introduced the radiative cooling evaluation of skylight and that two different network models were combined to evaluate the convective and conductive influence.

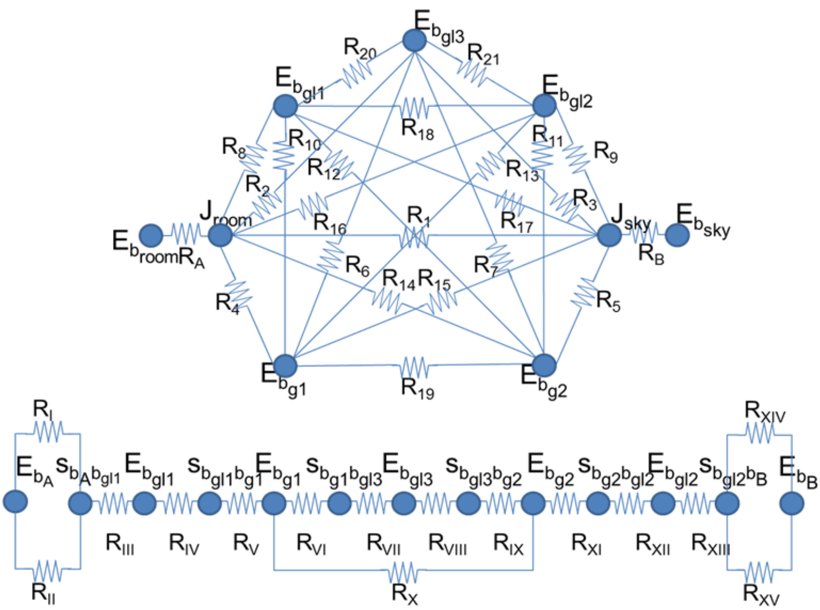

Figure 10. Resistance network (Paper I)

In Paper I, the radiative cooling effect was studied for one summer and winter month location in Helsinki for which weather data was procured. For Paper II it was deemed interesting to evaluate the annual variations of radiative cooling for two Finnish locations. For Paper II, weather data was procured by the Finnish Meteorological Institute for the two locations where pyrgeometers are installed, Helsinki, and Sodankylä in Lapland. The temperature of the sky and the ambient is plotted for a two-year period in Figure 11; the measurements were done in Helsinki during 2008-2010.

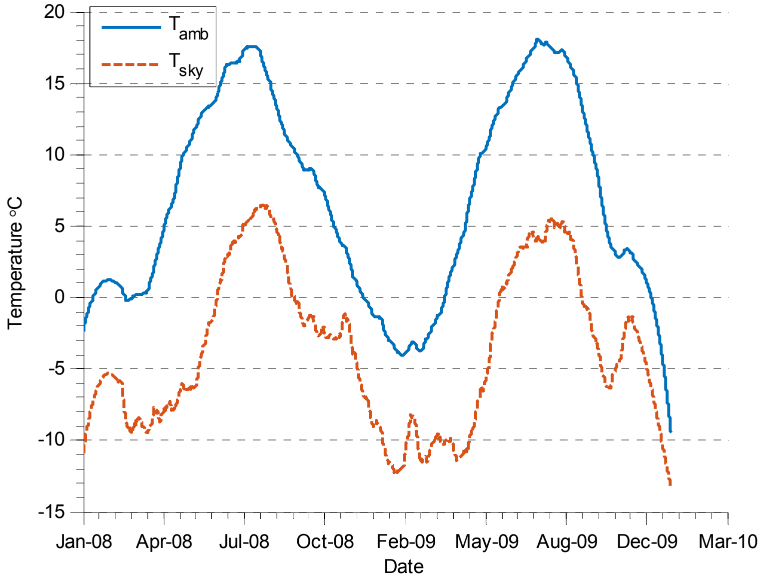

Figure 11. Ambient and sky temperatures measured at Helsinki by the Finnish Meteorological Institute (Paper II)

From these measurements, the availability of cooling at varying radiator temperatures can be assessed for a radiator with a gray surface emittance of 0.9. The results of this assessment are presented by the cumulative frequency distribution lines in Figure 12. Here six colored lines show at what frequency, and at what radiator temperature the radiative heat flow marked by the lines could be achieved during the measurement period. For example, a radiator at 0°C could have emitted 80W/m² of heat radiation during 70% of the measurement period.

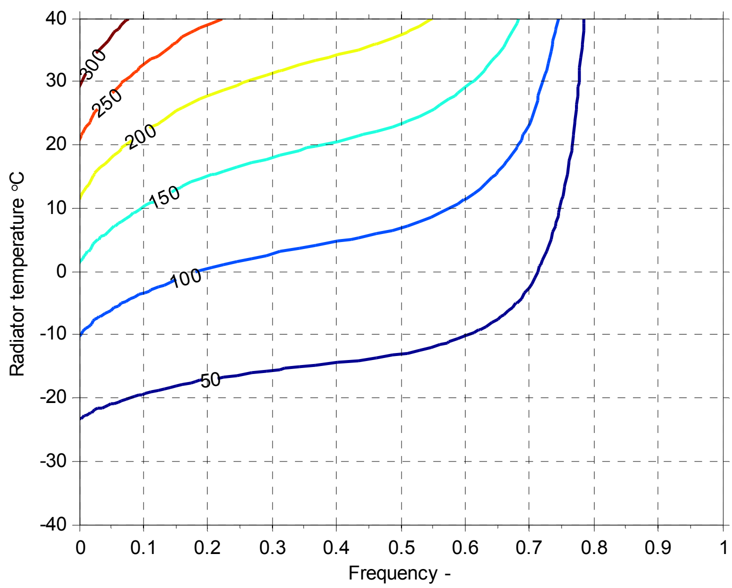

Figure 12. Cumulative frequency distribution of radiative heat exchange in W/m² at different radiator temperatures in Helsinki (Paper II)

The resistance network calculations made it difficult to combine the radiative and the convective heat flows into one single model. It was therefore evaluated that CFD simulations would give more reliable results faster. Therefore, work began to find suitable software. As COMSOL had recently released a new version (4.0) which enabled radiative heat exchange simulations with participating media, it was decided to use it in further studies. The ability of COMSOL to simulate natural convective flows has been demonstrated in a 3D enclosure [38] and also in tall 2D cavities [39]. It is, however, essential to state that to achieve precise simulation results, these simulations must be tuned carefully using feedback from experimental measurements.

COMSOL 4.1 was first used in Paper III where the same weather data was used as input in the simulations as were used for the calculations in Paper I. The velocity profile from these simulations is presented for the cooling case in Figure 13 and the insulating case in Figure 14

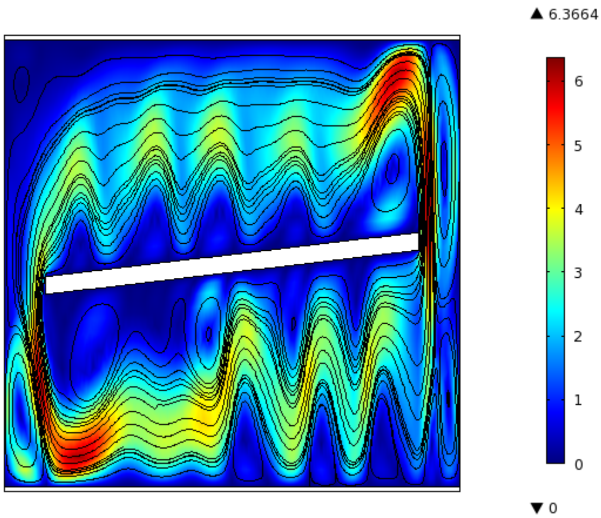

Figure 13. Velocity profile in (cm/s) for cooling mode during summer (Paper III)

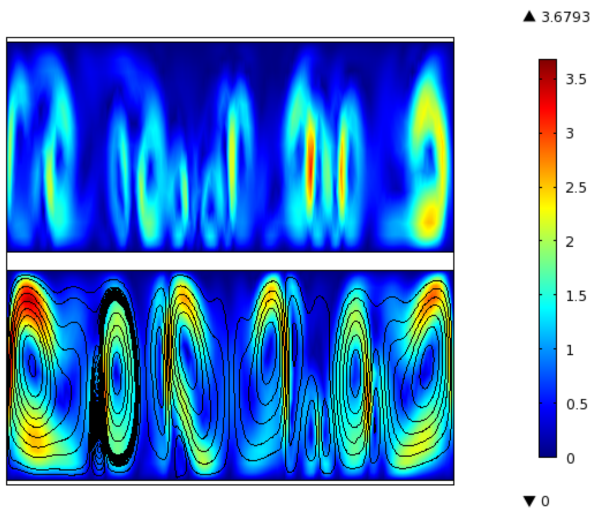

Figure 14. Velocity profile in (cm/s) for insulating mode during winter (Paper III)

The total heat flows for the results of Paper III are presented in Table 1. The results differ significantly from those reported in Paper I. The reason for the poor agreement was that the resistive network was not able to simulate the convective heat transfer inside the skylight and connect the radiative heat transfer to conductive and convective heat transfer models. The results presented in Table 1 show that a cooling effect can be created both in summer and winter conditions by using CO_2 in the skylight instead of air. When the skylight is set in the insulating mode, the insulative properties for the winter case do not differ significantly from each other and for the summer case, the skylight filled with CO_2 is outperformed by the window filled with air. A change in the windows' dimensions would increase the insulative properties of the skylight as the cooling convective flow is decreased.

Table 1. Average heat transfer simulation results for average conditions for two months in 2008 for Helsinki, Finland (Paper III)

(W/m^2)	Summer cooling	Winter insulating	Summer insulating	Winter cooling
CO_2	117	966	88	883
Air	15	983	19	655

CO_2 had been the working fluid in the calculations and simulations of Papers I and III. As the results were promising, practical experimentation started with the objective of evaluating different gases and window materials. In the paper, two identical boxes ($0.5 \times 0.5 \times 0.5$ m^3) were built to allow for comparative studies; see Figure 15. In the experiments, a thin PE sheet was used as the window material, and air was compared to CO_2 and NH_3.

Figure 15. Parallel set-ups for passive cooling experiments (Paper VIII)

Meanwhile, literature research suggested that gases other than CO_2 could potentially fulfill the requirements set for the skylight better. The results showed that temperatures below ambient are indeed achievable; however, no significant differences were observed for the various gases that were studied. (The gases that were compared were air, CO_2, and NH_3.) Also, the PE sheet window material used in the experiment was deemed to be too fragile for further use. As the gases were, as such, found not to give a significant cooling effect, they have to be pressurized if they were to achieve cooling to well below ambient temperature (Paper VIII). Pressurization is, however, not attractive as this would require thick windows that would become too expensive (and presumably heavy). As the PE window was found to be too fragile, and the gases' effect was limited, a new material was introduced for the work reported in the conference version of Paper V and further studied in the journal version of Paper IV where the wavelength dependency of CO_2 was considered. In Paper VI, the materials introduced were investigated experimentally.

Paper V introduces a new design of the skylight given in Figure 2, the dimensions of which have been optimized, as unwanted Rayleigh-Bénard cells were observed in both the cooling and heating simulations of the model presented in the results from Paper III, as shown in Figure 13 and Figure 14. A cluster of Rayleigh-Bénard cells is the convective flow pattern a thin layer of fluid exhibits when it is trapped between two parallel plates of which the lower is warmer than the upper. This temperature gradient causes the fluid to rise and fall due to the fluid's buoyancy effect caused by the temperature change. [40] These unwanted swirls decrease both the cooling and insulating capacity, and their formation should, therefore, be avoided or minimized. Moreover, this new design allows the skylight to be constructed to different sizes due to its modular setup. The skylight is optimized so that it will produce an optimal amount of cooling and insulation when needed; this multiobjective optimization problem produces a set of optimal results that show the tradeoffs between cooling and insulation. This set of optimal results is also called a Pareto front that is presented by the connected circles in Figure 16.

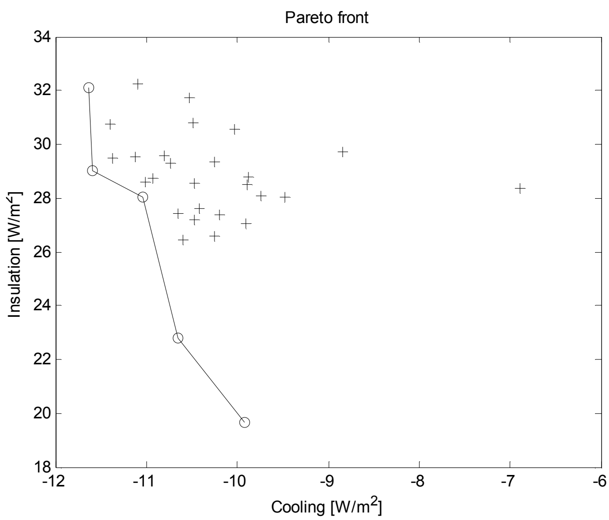

Figure 16. Results from optimization: a) The Pareto front is noted with "ɵ" and the inferior solutions are marked with "+" (Paper V)

The optimization process was done by coupling the simulation tool COMSOL 4.3a to the numerical computing program Matlab 2012b where a genetic algorithm (GA) was used for the optimization problem. Since the optimization process requires repeated simulations runs, there was a need to simplify the simulation process to limit the computation time. This was done by optimizing the skylight dimensions for only conductive and convective heat transfer and then assessing the total heat transfer including radiation for the optimized the optimal design. The results from this optimization are presented in Table 2 where the dimensions are shown in the first two columns, the optimized heat flows in the following two, and the final two present the optimized total heat flows.

Table 2. Optimal results and the effect of radiation (Paper V)

Point	Height	Width	Cooling Conduction + Convection	Insulation Conduction + Convection	Cooling + also Radiation	Insulation + also Radiation
	m	m	W/m²	W/m²	W/m²	W/m²
1	0.69	0.44	11.6	32	52.8	21.8
2	0.73	0.42	11.6	29	53.2	23.2
3	0.78	0.41	11.0	28	47.7	27,3
4	0.79	0.40	10.7	22	49.8	24,4
5	0.81	0.40	9.9	19	49.4	31,9

It can be noted that the total heat flows, containing the radiative heat flow, are at a lower level than the results reported in Papers III and VI, while simultaneously the height of the skylight is larger than that used in Paper II and VI. Therefore, it can be concluded that to reach truly optimal results the effect of heat radiation must be taken into account.

The resistance network presented in Figure 18 from Paper IV, is based on the resistance network presented in Paper VII. The developments made in Paper IV produced a resistance network which was used for wavelength dependent calculations. The data that was used in these calculations was the temperature of the ambient and that measured by a pyrgeometer. This data was then used in the resistance network shown in Figure 18. In this network, different known parameters have been used for the atmosphere, for instance, the transmittance at various wavelengths. The final parameters that the resistance network model requires are the radiative properties of the radiator that are wavelength dependent. If the radiator in Figure 17 absorbs and emits heat radiation in the whole 4.5-42 μm (LW) interval, it exchanges heat radiation with both the relatively warm ambient air and cold sky temperatures (presumably at different heights). If a radiator is selected so that it only emits and absorbs heat radiation in the atmospheric window range, it exchanges heat radiation with only the cold sky. This enables the radiator to cool to lower temperatures.

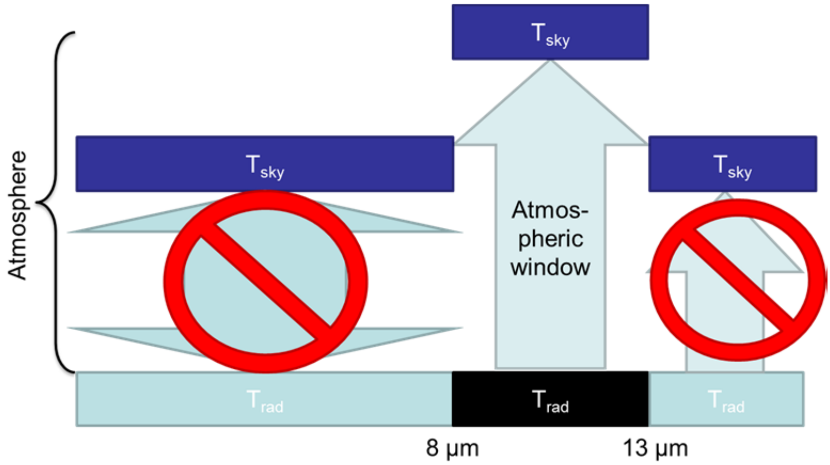

Figure 17. Possibility of the wavelength dependency

By the use of the resistance network shown in Figure 18 was it possible to compare how different gases are affected by radiative cooling. It was concluded that by comparing HFC-125, air, and CO_2, HFC-125 was found to affect the heat exchange in the 8 - 13 µm spectral range the most.

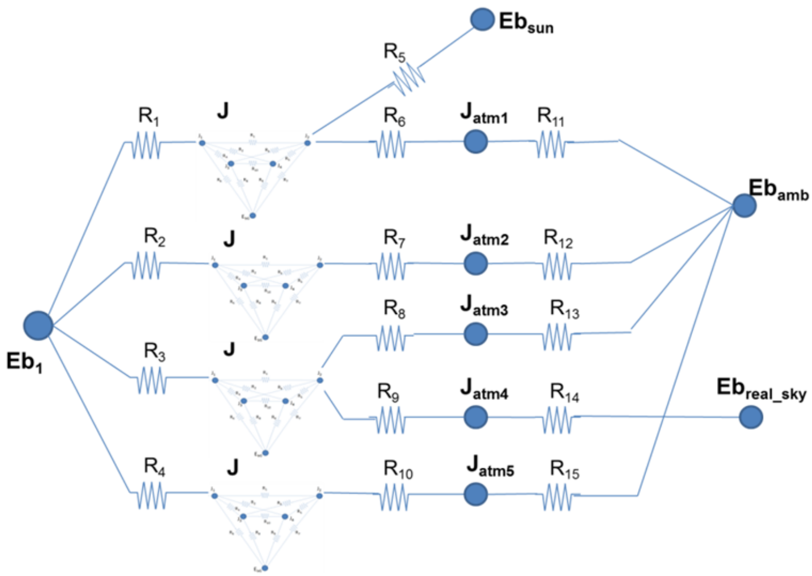

Figure 18. Resistance network for wavelength radiation model (Paper IV)

For the final article (Paper VI) enclosed in this thesis, a model skylight (10 x 10 x 10 cm^3) was constructed, see Figure 19 with two ZnS windows and a regular (non-transparent for LW radiation) window according to Figure 1. The article was divided into four different sections. In the first section, a thermal imager (Fluke Ti9) was used to assess the ZnS window's transparency and to compare the performance difference between air, CO_2, and HFC-125. The thermal imager was used as it can "see" in a wavelength range (7.5 - 14 µm) close to that of the atmospheric window (8 - 14 µm). The experiment was set up as presented in Figure 20 after which a picture of a heated water beaker was taken through the skylight (without the middle window) while filled with the studied gases. Future work requires the CFD simulations to be wavelength dependent.

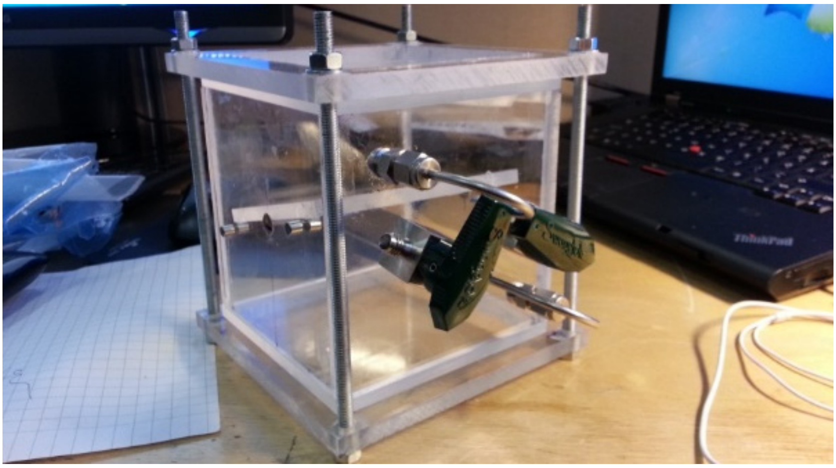

Figure 19. Constructed skylight model (Paper VI)

The thermal images for the different gases can be seen in Figure 21 where the difference between CO_2 and air is minimal, while HFC-125 lowers the observed temperatures.

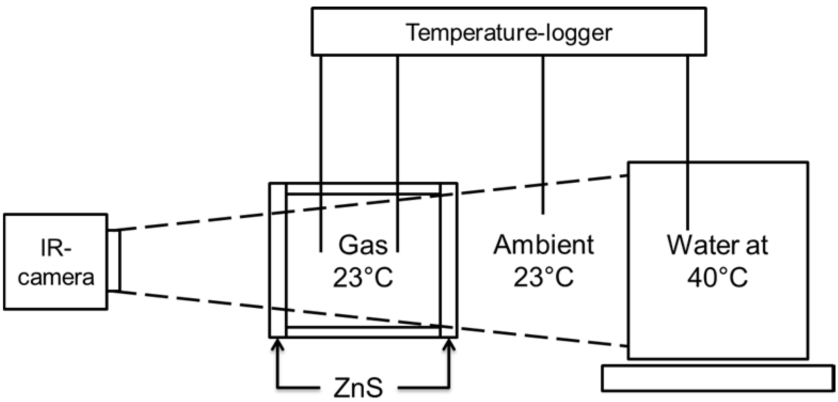

Figure 20. Experimental setup for material suitability testing (Paper VI)

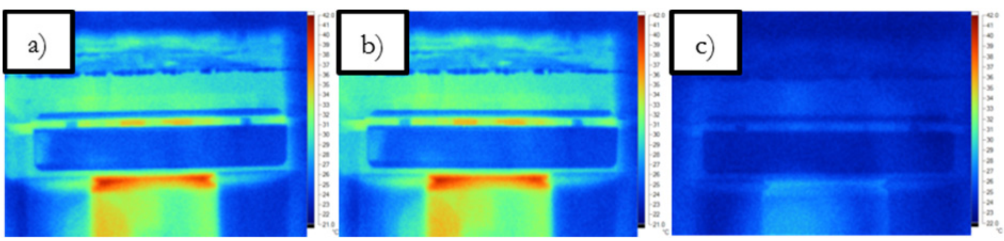

Figure 21. Thermal images of the skylight filled with a) air; b) CO_2; c) HFC-125 (Paper VI)

These results are presented in an alternative way in Figure 22 where the numbers of pixels at a certain temperature are reported. The effect of HFC-125 stands out from the other gases. The reason is that the HFC-125 absorbs and re-emits the thermal radiation to all directions, thus acting as a shield for temperature variations.

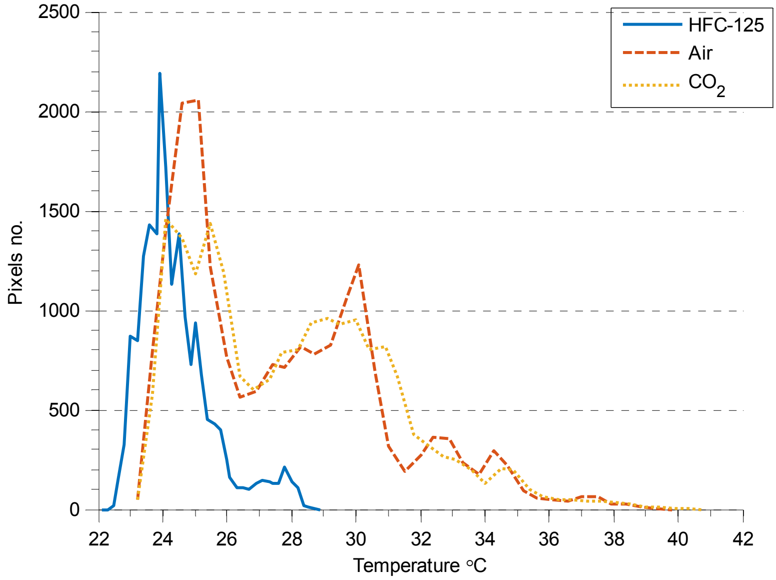

Figure 22. The number of pixels in the pictures in Fig. 6 taken with the thermal imager at a particular temperature (Paper VI)

In the second section of paper VI, the radiative properties of different gases was compared in a set-up where the middle window was left out, thus reaching a maximal gas emittance as the gas thickness was maximized. During these experiments, the skylight was mounted on top of the unheated box shown in Figure 23.

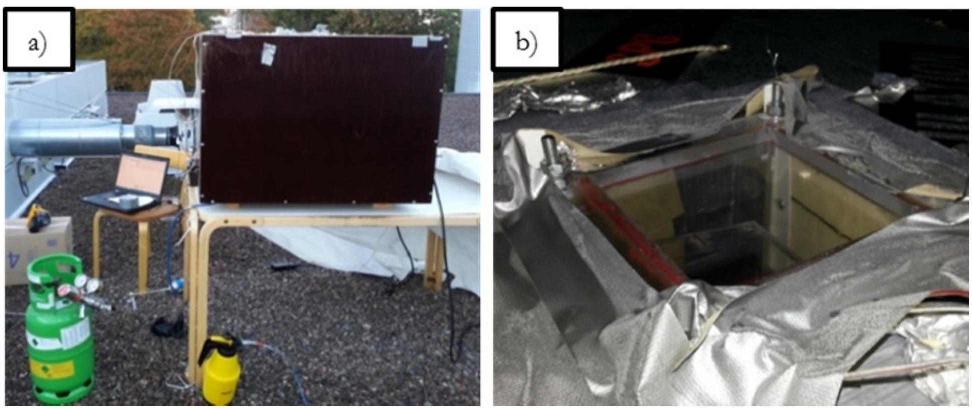

Figure 23. Experimental set-up for the second and third set of experiments: a) the total set-up, showing the dark sidewall of the "room"; b) the top of the skylight (Paper VI)

During a test, different temperatures in the rig and the weather were logged using J-type thermocouples. Two thermocouples were placed inside the skylight, one in the upper section and one in the lower section. The thermocouples were not shielded from thermal radiation. Thus the thermocouples, in fact, measured the energy balance temperature. The motivation to exclude the shields was that these could potentially disturb the convective and radiative heat flow. It was found that these thermocouples give some noise when subjected to radiative heat exchange, thus, it is better to use other thermocouples in future experiments. The logged temperatures are shown in Figure 24.

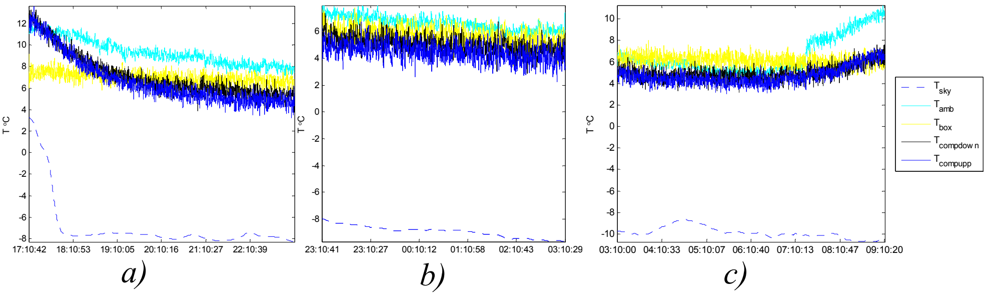

Figure 24. Temperature profiles from the experiment with: a) CO2; b) Air, c) HFC-125 (Paper VI)

Part of the logged data was then used as input data for COMSOL simulations and the rest of the measured temperatures were used to verify the simulation. The fact that the thermocouples were left unshielded was compensated by including the thermocouple into the COMSOL simulations and, thus, the results from the measured and simulated thermocouple temperature are presented with the other results in Table 3. These results concur with the experiments from the thermal camera experiments that air and CO_2 function in the same manner. However, HFC-125 stands out at decreasing the heat flow through the window, as it functions as a heat shield in the test-rig.

Table 3. Temperature measurements and simulation results for the selected time (Paper VI)

Experiment	8a	8b	8c	8c
time	22:30	2:15	3:50	6:15
T_{room} (°C)	6,79	5,36	6,17	5,85
T_{sky} (°C)	-7,42	-9,43	-10,00	-9,87
T_{amb} (°C)	7,99	6,12	6,21	5,45
v_{wind} (m/s)	2,65	2,16	1,69	1,58
gas	CO_2	Air	HFC-125	HFC-125
$T_{gas\ measure\ upp}$ (°C)	4,75	3,91	4,48	3,77
$T_{gas\ measure\ down}$ (°C)	5,75	4,65	4,08	4,61
$T_{gas\ simulation\ upp}$ (°C)	2,33	1,30	4,07	3,58
$T_{gas\ simulation\ down}$ (°C)	3,32	2,26	4,04	3,58
Q_{tot} (W/m²)	-157,95	-151,28	-148,17	-137,66

In the final section of Paper VI, the middle window was installed and the cooling skylight concept was studied for air and HFC-125 using the set-up shown in Figure 23. During the experiments the room was heated to simulate a room.

Then data from the experiments were used in COMSOL simulations. The simulations agreed well in most cases with the measured temperatures, as listed in

Table 4, with the exception of the experiments described by Fig. 9b and 10a. From the experimental and simulations results it can be noted that weather conditions affect the cooling performance significantly and that the difference between air and HFC-125 is around 50 W/m². The heat flow through the skylight varies with the weather (including cloud coverage of the sky). This can be seen clearly in the heat flow difference between the two moments simulated from Fig. 11 with significantly different sky temperatures. It can also be noted that the presence of the middle window seems not to affect the cooling capacity of the skylight. This middle window has a central role for the skylight, as it makes the change from cooling to insulating possible.

Table 4. Temperature measurements and simulation results for the selected time (Paper VI)

Experiment	9a	9b	10a	10b	11	11
time	01:00	03:10	01:40	05:45	1:20	5:00
T_{room} (°C)	32,09	17,69	18,65	17,57	17,40	14,54
T_{sky} (°C)	2,03	-7,94	0,81	0,81	-2,01	4,39
T_{amb} (°C)	14,95	9,87	12,36	9,00	13,37	-0,57
v_{wind} (m/s)	2,21	0,51	0	0	0,84	0
gas	HFC-125	HFC-125	Air	HFC-125	HFC-125	HFC-125
$T_{gas\ measure\ up}$ (°C)	20,39	9,60	12,36	11,00	13,50	10,40
$T_{gas\ measure\ down}$ (°C)	23,99	13,95	15,03	13,16	15,19	12,13
$T_{gas\ simulation\ up}$ (°C)	24,25	7,16	11,32	11,63	13,56	10,38
$T_{gas\ simulation\ down}$ (°C)	25,38	9,811	13,75	12,46	14,23	11,45
Q_{tot} (W/m²)	-131,68	278,24	-90,16	-66,85	-146,8	-8,39

During experimental work for Paper VI, initial trials of flow velocity measurements were made at Tampere University of Technology using particle image velocimetry to confirm that a convective heat flow is formed inside the window. In the experiment, the lower window was heated to 50°C with a heating plate, while the upper side was cooled with a cold water beaker. A powder was injected into the skylight using a syringe; the powder was, however, too heavy to stay in the convective stream to confirm that such had formed. Future studies could devise smoke that would be produced outside (there is no air inside the skylight and HFC-125 is used as a fire detergent) the skylight and then injected to the skylight

More details are given in Paper I-VI

4. Conclusions and suggestions for future work

During the progress of this thesis, the greenhouse effect has played a central role. It has simultaneously been a source of inspiration as it has set the limitations and opened opportunities for the concept of a cooling skylight. The thesis continued on initial studies at ÅAU that aimed at exploiting the greenhouse effect for power production. While the need for cooling is increasing, it was estimated that a controlled radiative cooling effect would offer a worthwhile alternative. Meanwhile, as a method for exploiting the heat flows in greenhouse effect for power production, it would suffer from poor efficiency.

The first controllable cooling and insulating skylight design was described at the beginning of the thesis. Though radiative cooling is a known phenomenon, it has not previously been incorporated into a skylight design. The studies of this thesis continued developing the radiative cooling skylight by calculations, simulations, and experiments. Temperatures below the ambient were achieved in the experimental setups. The experiments continued for a few hours to three days during which sufficient data, such as temperature and weather data, were collected. CFD simulations based on temperature measurements from these experiments imply that a controllable cooling effect of 100 W/m^2 can be attained with the designed device during summer. The cooling effect in the current setup is limited to nighttime due to the influx of sunlight during the day. By controlling the transparency of the window material the influx of sunlight could be limited or even cancelled. This could be accomplished with reflective coatings or a honeycomb structure that would shadow, as presented in Figure 25 a), the skylight from direct sunlight while sustaining a view of the sky, Figure 25 b). However, the main idea of this skylight is not to only cool the room located below it but also to bring light into it. Thus, blocking out all the sunlight to decrease the cooling load would turn the skylight into nothing more than a heat exchanger.

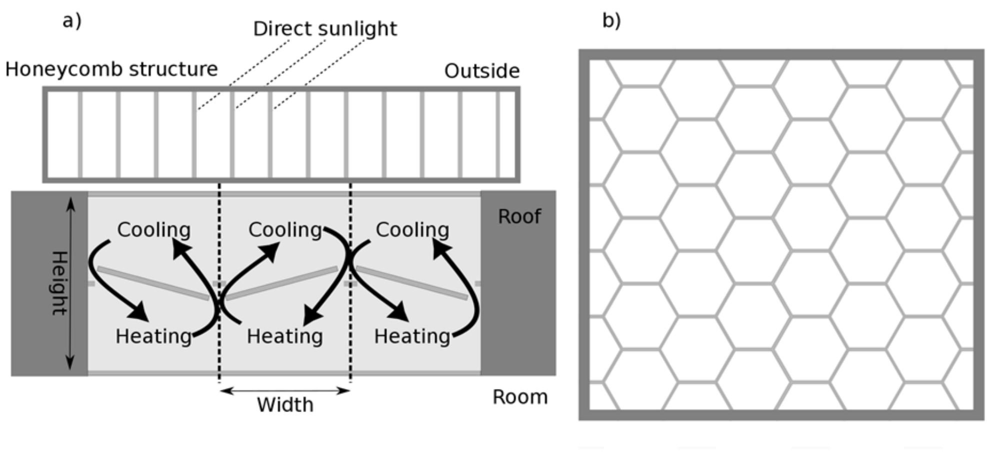

Figure 25. A schematic presentation of the intended honeycomb structure, a) side view of the skylight and the honeycomb structure, b) view from beneath the skylight

The results reported here were achieved with careful design and material selections that are durable and safe to use. The preliminary gas, CO_2, was confirmed to give limited results under ambient pressures, and an increase in pressure would increase material costs. The process of identifying suitable materials is still ongoing, but materials that are possible to be used for proof of concept were identified and studied. The most promising materials are HFC-125 acting as the gas and ZnS as the window material.

The system suggested here has low operating costs compared to high-tech systems under development that also give significant daytime cooling. The primary competing technology is solar refrigeration where the sun is used to drive a cooling cycle. The power can either be produced using PV-panels or thermal collectors. A PV panel can produce around 100W/m^2 electricity from 1000 W/m^2 of sunlight which gives 300W of cooling at a cost of 4000 €/kW cooling. Thermal collectors could in turn produce around 350-400 W/m^2 of cooling from the same amount of sunlight at a cost of 1200€/kW. [41] For the experiments ZnS windows were custom made, at an optics company, and thus, their price was high. The price of one (112 mm x 112 mm) ZnS window as used here was 794 €. Thus, the price becomes 80 000 €/m^2. Further studies should explore what the price of ZnS windows in mass production would be. If the price remains at an unprofitable level, other alternatives must be studied. In further work the price of the gas should be assessed too, as should also the price of a whole skylight.

An option to decrease the cost would be to use a normal silica window in the position of the lowest window. ZnS might give a limited increase in heat transfer to the gas as radiative heat transfer, but most likely not the dominant method of heat transfer, as heat transfer by convection and conduction from the room is probably more dominant. Future studies on the middle window should concentrate on its radiative properties. A middle window with high absorptance in the LW could further cool the greenhouse gas; it may be that the cooling effect can be accomplished with air. If insulation is needed, the middle window should be as reflective as possible in the LW range. Thus, the middle window could be flipped or its position varied when changing between cooling and insulation.

Recently it was found out that HFC-125 will be phased out in the near future. Further evaluation should be made of other gases which show a promising absorptance spectrum in the atmospheric window while simultaneously having a low GWP, with short atmospheric lifetime, and no ill effect on ozone. A candidate for this is HFC-1447fz [42] which seems to be stable for use in a skylight as it does not break down in sunlight.

Future work should also include performing long-term tests to assess the skylight's performance and to identify additional problems and solutions that long-term usage brings up. Of special concern is the accumulation of dirt on the skylight and how this affects the radiative cooling effect and puts requirements on technical maintenance.

Skylights which have previously brought light and a sensation of space, could be used to actively decrease a building's energy use for heating and cooling. As the normal cooling demand for buildings in Finland is around 2 W/m^2, a radiative cooling skylight could fulfill the cooling demand of 50 m^2. Thus, radiative cooling provides a viable option to decrease the cooling demand of a building.

5. References

[1] R. Zevenhoven. Can the infrared radiation that causes the enhanced greenhouse effect be put to better use? Presented at Meeting the Entropy Challenge: An International Thermodynamics Symposium in Honor and Memory of Professor Joseph H. Keenan. 2008, Available: http://dx.doi.org/10.1063/1.2979059. DOI: 10.1063/1.2979059.

[2] M. Airaksinen, J. Seppälä, T. Vainio, P. Tuominen, P K. Regina, P. Peltonen-Sainio, S. Luostarinen, K. Sipilä, J. Kiviluoma, M. Tuomaala, I. Savolainen, M. Kopsakangas-Savolainen, "Rakennetun ympäristön hajautetut energiajärjestelmät," Suomen ilmastopaneeli, Espoo, Finland, Tech. Rep. 4/2013, 20.1.2013. 2013.

[3] Adato Energia Oy, "Kotitalouksien sähkönkäyttö 2011," Ministry of Employment and the Economy (in Finland), 26.02.2013. 2013.

[4] M. Airaksinen, T. Vainio, T. Vesanen and P. Ala-Kotila, "Rakennusten jäähdytysmarkkinat," VTT, Tech. Rep. VTT-CR-06168-15, Dec. 2015.

[5] M. Mahdavinejad and K. Javanrudi. Assessment of ancient fridges: A sustainable method to storage ice in hot-arid climates. *Ach 4(2),* pp. 133-139. 2012. Available: http://www.ccsenet.org/journal/index.php/ach/article/view/13822. DOI: 10.5539/ach.v4n2p133.

[6] M. W. Herold. Ice in the tropics: The export of 'Crystal blocks of yankee coldness' to india and brazil. *Revista Espaço Acadêmico. 11(126),* pp. 162-177. 2011. Available: http://eduem.uem.br/ojs/index.php/EspacoAcademico/article/view/15209/8153.

[7] S. Davidson. SkyCool-extraordinary paint on a hot tin roof. *ECOS Magazine,* pp. 12-12. 2004. Available: http://www.ecosmagazine.com/?act=view_file&file_id=EC119p12.pdf.

[8] A. Dimoudi and A. Androutsopoulos, The cooling performance of a radiator based roof component, *Sol. Energy,* vol. 80, pp. 1039-1047, August, 2006. Available: http://www.sciencedirect.com/science/article/pii/S0038092X05002616.

[9] E. Erell and Y. Etzion, Radiative cooling of buildings with flat-plate solar collectors, *Build. Environ.,* pp. 297-305, May, 2000. Available: http://www.sciencedirect.com/science/article/pii/S0360132399000190.

[10] A. Gentle, K. Dybdal and G. Smith. Polymeric mesh for durable infra-red transparent convection shields: Applications in cool roofs and sky cooling. *Solar Energy Mater. Solar Cells, 115*pp. 79-85. 2013. Available: http://www.sciencedirect.com/science/article/pii/S0927024813001141. DOI: 10.1016/j.solmat.2013.03.001.

[11] T. M. J. Nilsson and G. Niklasson A., Radiative cooling during the day: simulations and experiments on pigmented polyethylene cover foils, *Sol. Energy Mater. Sol. Cells,* pp. 93-118, April, 1995. Available: http://www.sciencedirect.com/science/article/pii/0927024894002002.

[12] E. M. Lushiku, A. Hjortsberg and C. G. Granqvist. Radiative cooling with selectively infrared-emitting ammonia gas. *J. Appl. Phys., 53(8),* pp. 5526-5530. 1982. Available: https://www.osapublishing.org/ao/viewmedia.cfm?uri=ao-23-11-1835&seq=0&html=true. DOI: 10.1364/AO.23.001835.

[13] E. M. Lushiku, T. S. Eriksson, A. Hjortsberg and C. G. Granqvist. Radiative cooling to low temperatures with selectively infrared-emitting gases. *Solar & Wind Technology, 1(2),* pp. 115-121. 1984. Available: http://www.sciencedirect.com/science/article/pii/0741983X84900134. DOI: 10.1364/AO.23.001835.

[14] E. M. Lushiku and C. Granqvist. Radiative cooling with selectively infrared-emitting gases. *Appl. Opt, 23(11),* pp. 1835-1843. 1984. Available: http://ao.osa.org/abstract.cfm?URI=ao-23-11-1835. DOI: 10.1364/AO.23.001835.

[15] K. A. R. Ismail, C. Salinas and J. R. Henriquez. A comparative study of naturally ventilated and gas filled windows for hot climates. *Energy Convers. Manage, 50(7),* pp. 1691-1703. 2009. Available: http://www.sciencedirect.com/science/article/pii/S0196890409001101. DOI: 10.1016/j.enconman.2009.03.026.

[16] S. Reilly, D. Arasteh and M. Rubin. The effects of infrared absorbing gasses on window heat transfer: A comparison of theory and experiment. *Solar Energy Materials, 20(4),* pp. 277-288. 1990. Available: http://www.sciencedirect.com/science/article/pii/016516339090060E. DOI: 10.1016/0165-1633(90)90060-E.

[17] T. S. Eriksson, C. G. Granqvist and J. Karlsson. Transparent thermal insulation with infrared-absorbing gases. *Solar Energy Materials, 16(1-3),* pp. 243-253. 1987. Available: http://www.sciencedirect.com/science/article/pii/0165163387900244. DOI: 10.1016/0165-1633(87)90024-4.

[18] K. A. R. Ismail, C. Salinas and J. R. Henriquez. Comparison between PCM filled glass windows and absorbing gas filled windows. *Energy Build., 40(5),* pp. 710-719. 2008. Available: http://www.sciencedirect.com/science/article/pii/S0378778807001636. DOI: 10.1016/j.enbuild.2007.05.005.

[19] R. Zevenhoven, Modifying and using the thermal infra-red radiation that causes the enhanced greenhouse effect, in *Proceedings of the 21rd International Conference on Efficiency, Cost Optimization, Simulation and Environmental Impact of Energy Systems,* Krakow-Gliwice, Poland, 2008, pp. 1475-1482.

[20] M. Sakeye, Heat radiation analysis of a CO_2-containing double-glass enclosure, *M. Sc Thesis, Åbo Akademi University,* pp. 72, February, 2009.

[21] R. Zevenhoven and M. Sakeye, Recovery of heat from thermal infra-red radiation; the role of heat conduction and convection, window material and system lay-out, in *Proceedings of the 22rd International Conference on Efficiency, Cost Optimization, Simulation and Environmental Impact of Energy Systems,* Foz do Iguaçu - Paraná - Brasil, 2009, pp. 223-231.

[22] K. E. Trenberth, J. T. Fasullo and J. Kiehl. Earth's global energy budget. *Bull. Amer. Meteor. Soc., 90(3),* pp. 311-323. 2009. Available: http://journals.ametsoc.org/doi/abs/10.1175/2008BAMS2634.1. DOI: 10.1175/2008BAMS2634.1.

[23] K. Fung and V. Ramaswamy. On shortwave radiation absorption in overcast atmospheres. *J. Geophys. Res. D: Atmos., 104(D18),* pp. 22233-22241. 1999. Available: http://onlinelibrary.wiley.com/doi/10.1029/1999JD900457/pdf. DOI: 10.1029/1999JD900457.

[24] C. Lacasse. Influence of climate variability on the atmospheric transport of icelandic tephra in the subpolar north atlantic. *Global Planet. Change, 29(1–2),* pp. 31-55. 2001. Available: http://www.sciencedirect.com/science/article/pii/S0921818101000996?np=y. DOI: 10.1016/S0921-8181(01)00099-6.

[25] L. Adelard, F. Pignolet-Tardan, T. Mara, P. Lauret, F. Garde and H. Boyer. Sky temperature modelisation and applications in building simulation. *Renewable Energy, 15(1-4),* pp. 418-430. 1998. Available: http://www.sciencedirect.com/science/article/pii/S0960148198001980?np=y. DOI: 10.1016/S0960-1481(98)00198-0.

[26] (6.7.2015). *Global Warming Art.* Available: www.globalwarmingart.com/wiki/File:Atmospheric_Transmission_png.

[27] E. Erell, S. Yannas and J. L. Molina. Roof cooling techniques. Presented at PLEA2006 - the 23rd Conference on Passive and Low Energy Architecture. 2006, Available: https://www.researchgate.net/profile/Evyatar_Erell/publication/267771767_Roof_Cooling_Techniques/links/54649c4e0cf2cb7e9daa87cf.pdf.

[28] A. P. Raman, M. A. Anoma, L. Zhu, E. Rephaeli and S. Fan. Passive radiative cooling below ambient air temperature under direct sunlight. *Nature, 515(7528),* pp. 540-544. 2014. Available: http://www.nature.com/nature/journal/v515/n7528/abs/nature13883.html. DOI: 10.1038/nature13883.

[29] M. M. Hossain, B. Jia and M. Gu. A metamaterial emitter for highly efficient radiative cooling. *Adv. Opt. Mater., 3(8),* pp. 1047-1051. 2015. Available: http://onlinelibrary.wiley.com/doi/10.1002/adom.201570046/abstract. DOI: 10.1002/adom.201570046.

[30] A. R. Gentle and G. B. Smith. A subambient open roof surface under the Mid‐Summer sun. *Adv. Sci., 2(9),* pp. 1-4. 2015. Available: http://onlinelibrary.wiley.com/doi/10.1002/advs.201500119/full. DOI: 10.1002/advs.201500119.

[31] S. J. Byrnes, R. Blanchard and F. Capasso. Harvesting renewable energy from earth's mid-infrared emissions. *Proc. Natl. Acad. Sci. U. S. A., 111(11),* pp. 3927-3932. 2014. Available: http://www.pnas.org/content/111/11/3927.short. DOI: 10.1073/pnas.1402036111.

[32] M. Rubin. Calculating heat transfer through windows. *Int. J. Energy Res., 6(4),* pp. 341-349. 1982. Available: http://onlinelibrary.wiley.com/doi/10.1002/er.4440060405/full. DOI: 10.1002/er.4440060405.

[33] C. G. Granqvist. Radiative cooling to low temperatures general considerations and applications to selectively emitting SiO films. *J. Appl. Phys., 52(6),* pp. 4205-4220. 1981. Available: http://scitation.aip.org/content/aip/journal/jap/52/6/10.1063/1.329270. DOI: 10.1063/1.329270.

[34] T. S. Eriksson, E. M. Lushiku and C. G. Granqvist. Materials for radiative cooling to low temperature. *Solar Energy Materials, 11(3),* pp. 149-161. 1984. Available: http://www.sciencedirect.com/science/article/pii/0165163384900674. DOI: 10.1016/0165-1633(84)90067-4.

[35] K. A. R. Ismail and C. Salinas. Non-gray radiative convective conductive modeling of a double glass window with a cavity filled with a mixture of absorbing gases. *Int. J. Heat Mass Transfer ,49 (17–18),* pp. 2972-2983. 2006. Available: http://www.sciencedirect.com/science/article/pii/S0017931006001414?np=y. DOI: 10.1016/j.ijheatmasstransfer.2006.01.051.

[36] S. N. Bathgate and S. G. Bosi. A robust convection cover material for selective radiative cooling applications. *Sol. Energy Mater. Sol. Cells, 95(10),* pp. 2778-2785. 2011. Available: http://www.sciencedirect.com/science/article/pii/S0927024811002844. DOI: 10.1016/j.solmat.2011.05.027.

[37] (March 2011). *Global Warming Potentials of ODS Substitutes.* Available: http://www.epa.gov/ozone/geninfo/gwps.html.

[38] D. W. Pepper and X. Wang. Benchmarking COMSOL multiphysics 3.5 a–CFD problems. Presented at COMSOL Conference 2009 Boston. 2009, Available: https://www.comsol.asia/paper/download/44676/Pepper_pres.pdf.

[39] H. E. Dillon, A. Emery and A. Mescher. Benchmark comparison of natural convection in a tall cavity. Presented at COMSOL User Conference 2009 Boston. 2009, Available: https://www.comsol.eu/paper/download/44496/Dillon.pdf.

[40] P. Manneville. Rayleigh-bénard convection: Thirty years of experimental, theoretical, and modeling work, in *Dynamics of Spatio-Temporal Cellular Structures* Anonymous 2006, Available: http://link.springer.com/chapter/10.1007%2F978-0-387-25111-0_3. DOI: 10.1007/978-0-387-25111-0_3.

[41] D. S. Kim and C. A. Infante Ferreira. Solar refrigeration options – a state-of-the-art review. *Int. J. Refrig. 31(1),* pp. 3-15. 2008. Available: http://www.sciencedirect.com/science/article/pii/S0140700707001478. DOI: 10.1016/j.ijrefrig.2007.07.011.

[42] E. Jiménez, S. González, M. Cazaunau, H. Chen, B. Ballesteros, V. Daele, J. Albaladejo and A. Mellouki. Atmospheric degradation initiated by OH radicals of the potential foam expansion agent, $CF_3(CF_2)_2CH=CH_2$ (HFC-1447fz): Kinetics and formation of gaseous products and secondary organic aerosols. *Environ. Sci. Technol. 0(3),* pp. 1234-1242. 2015. Available: http://pubs.acs.org/doi/abs/10.1021/acs.est.5b04379. DOI: 10.1021/acs.est.5b04379.

ISBN 978-952-12-3431-6
Painosalama - Turku 2016